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Chain Epimerization during Propylene Polymerization with Metallocene Catalysts: Mechanistic Studies Using a Doubly Labeled Propylene

Jeffrey C. Yoder and John E. Bercaw*

Contribution from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California, 91125

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Abstract: The mechanisms of chain epimerization during propylene polymerization with methylaluminoxane-activated *rac*-(EBTHI)$ZrCl_2$ and *rac*-(EBI)$ZrCl_2$ catalysts (EBTHI = ethylenebis(η^5-tetrahydroindenyl); EBI = ethylenebis(η^5-indenyl)) have been studied using specifically isotopically labeled propylene: $CH_2{=}CD^{13}CH_3$. These isospecific catalysts provide predominantly the expected [*mmmm*] pentads with [$-CH_2CD^{13}CH_3-$] repeating units (^{13}C NMR). Under relatively low propylene concentrations at 50 and 75 °C, where stereoerrors attributable to chain epimerization are prevalent, ^{13}C NMR spectra reveal ^{13}C-labeled methylene groups along the polymer main chain, together with [$CD^{13}CH_3$] units in [*mmmr*], [*mmrr*], and [*mrrm*] pentads and [$CH^{13}CH_3$] units in [*mmmmmm*] and [*mmmmmr*] heptads, as well as [*mrrm*] pentads. The isotopomeric regiomisplacements and stereoerrors are consistent with a mechanism involving β-D elimination, olefin rotation and enantiofacial interconversions, and insertion to a tertiary alkyl intermediate [Zr$-$C(CH_2D)($^{13}CH_3$)**P**] (**P** = polymer chain), followed by the reverse steps to yield two stereoisomers of [Zr$-$CHDCH($^{13}CH_3$)**P**] and [Zr$-^{13}CH_2$CH(CH_2D)**P**], as well as unrearranged [Zr$-CH_2$CD($^{13}CH_3$)**P**]. The absence of observable [$-CH_2CH^{13}CH_2D-$] in the [*mrrm*] pentad region of the ^{13}C NMR spectra provides evidence that an allyl/dihydrogen complex does *not* mediate chain epimerization.

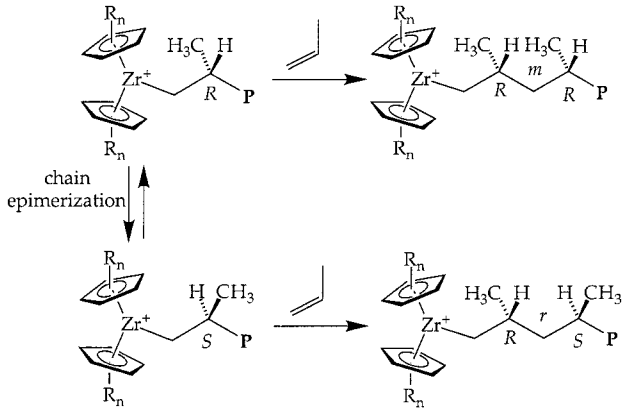
Introduction

It has been generally observed that the isotacticity of polypropylene samples obtained from C_2-symmetric metallocene catalyst systems decreases when the polymerizations are carried out at low propylene concentrations.[1] Homogeneous, isospecific, nonmetallocene catalysts can also display this behavior.[2] Busico first ascribed this phenomenon to a competition between bimolecular chain propagation and a unimolecular process involving epimerization at the β-carbon of the growing polymer (termed "chain epimerization") (Scheme 1).[1b]

Polymerization studies using isotopically labeled propylene monomers have been performed in an attempt to elucidate the mechanism of this process. Examination of the ^{13}C NMR spectra of polypropylene samples obtained from either (*E*)- or (*Z*)-[1-D]propylene revealed a reduction in the expected intensity for the [*mrrm*] pentad relative to polypropylene-d_0 samples.[3] In addition, a 1:1:1 triplet was observed slightly upfield of the [*mrrm*] resonance, assigned to a deuterium labeled methyl group in an [*mrrm*] stereochemical arrangement. If the integrations of both the triplet and singlet [*mrrm*] resonances are summed, the expected ratio of intensities (2:2:1 for [*mmmr*]:[*mmrr*]:[*mrrm*] for an isospecific polymerization operating under enantiomorphic site control) is realized.

Thus, the triplet signal reflects stereoerrors arising from chain epimerization (labeled *b* in Scheme 2), whereas the normal [*mrrm*] signal (labeled *a*) reflects stereoerrors derived from simple enantiofacial misinsertion. Consistent with these assignments, for polymerization runs performed at varying monomer concentrations, the intensity of the type *a* signal was independent

Scheme 1



* Corresponding author. E-mail: bercaw@caltech.edu.

(1) (a) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145. (b) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329. (c) Busico, V.; Cipullo, R. *J. Organomet. Chem.* **1995**, *497*, 113. (d) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667. (e) Jungling, S.; Mulhaupt, R.; Stehling, U.; Brintinger, H.-H.; Fischer, D.; Langhauser, F. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1305. (f) Schneider, M. J.; Kaji, E.; Uozumi, T.; Soga, K. *Macromol. Chem. Phys.* **1997**, *198*, 2899. (g) Moscardi, G.; Resconi, L.; Cavallo, L. *Organometallics* **2001,** *20*, 1918.

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(3) (a) Leclerc, M. K.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. (b) Leclerc, M. K.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **1996**, *118*, 9024.

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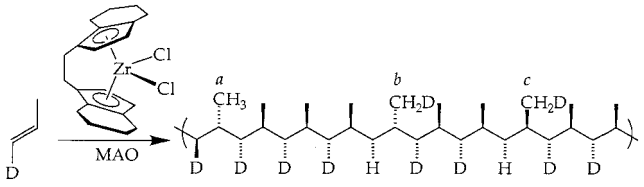
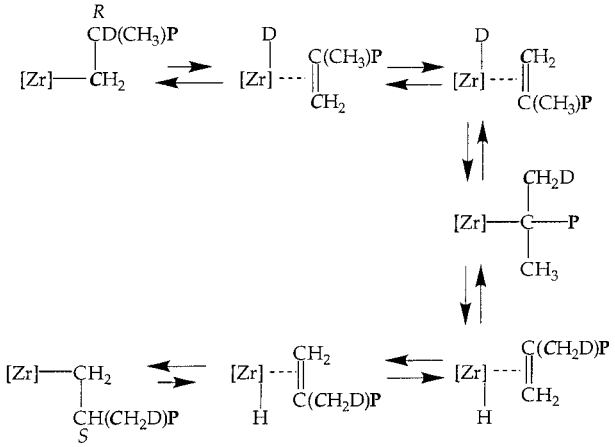
Scheme 2



(MAO = methylaluminoxane)

Scheme 3



([Zr] = Cp_2Zr^+; **P** = remaining polymer chain)

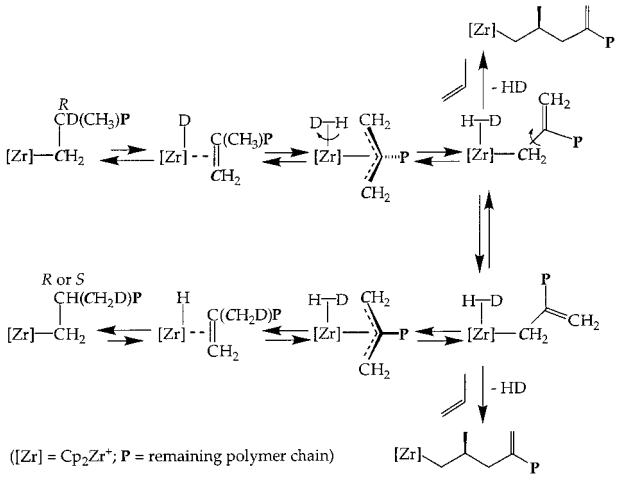
of the propylene concentration, while the intensity of the triplet resonance (type *b*) was reduced when the polymerizations were carried out at higher monomer concentration.[3b] An important additional feature of these studies was that a 1:1:1 triplet was also observed (in a DEPT experiment) slightly upfield of the [*mmmm*] methyl group pentad, indicating the presence of deuterium in methyl groups of *correct* stereochemistry (labeled *c* in Scheme 2). The signals corresponding to the deuterium labeled methyl groups for the [*mmmm*] and [*mrrm*] pentads were estimated to be of similar intensity.

Polymerization of [2-D]propylene yielded similar results in that deuterium incorporation was observed in methyl groups of both correct and inverted stereochemistry.[3b,4] However, both the isotacticity (and molecular weight) of the resultant poly([2-D]-propylene) were higher than polypropylene-d_0 generated under identical polymerization conditions. This result indicates that for chain epimerization (and for chain transfer) β-H (or β-D) elimination either precedes or constitutes the rate-determining step; an isotope effect of approximately 3 at 50 °C was estimated.[3b,5]

Two principal mechanisms have been put forward to explain these observations. The first, offered by Busico, enlists tertiary alkyl complexes formed by reversible β-H elimination and olefin rotation (Scheme 3).[1b,c]

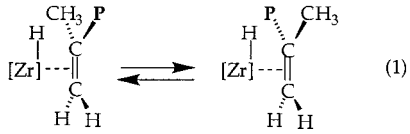
To explain the presence of deuterium atoms in methyl groups of correct stereochemistry for polymerization of both [1-D]-propylene and [2-D]propylene, the geminally disubstituted olefin resulting from β-H elimination must switch coordination to the opposite enantioface during the chain epimerization process (eq 1). Complete dissociation and recoordination to the other olefin

Scheme 4



([Zr] = Cp_2Zr^+; **P** = remaining polymer chain)

face does not seem plausible, since the large excess of propylene monomer would be expected to overwhelm the geminally substituted olefin effecting chain transfer. The presence of deuterium labeled methyl groups of the correct stereochemistry (those labeled *c* in Scheme 2) is thus somewhat problematic for this proposed mechanism. Computation methods have examined the energetics of various pathways for transformations in Scheme 3, as well as for eq 1.[6]



(1)

Another mechanistic proposal was put forward by Resconi and involves dihydrogen/η^3-allyl complex intermediates (Scheme 4).[7] The intermediacy of allyl complexes had been implicated in the production of vinylidene unsaturation along the main chains and spontaneous generation of dihydrogen during propylene polymerizations.[8] Resconi's proposal is also appealing because well-established $\eta^3 \rightleftarrows \eta^1$ allyl interconversions with rotation about the C−C single bond of an η^1-allyl intermediate[9] would provide a reasonable process for olefin enantiofacial switching required to explain the occurrence of type *c* isotopomeric rearrangements (Scheme 2). Computational studies of this mechanism[10] and the details of allyl formation[11] have been performed and support the feasibility of this mechanistic alternative.

We have devised an isotopic probe by utilizing CH_2═CD-$^{13}CH_3$ that is designed to distinguish between these two mechanistic proposals. We describe herein the results of those studies that are consistent with the tertiary alkyl mediated mechanism of Scheme 3 and inconsistent with the allyl/dihydrogen mediated process shown in Scheme 4.

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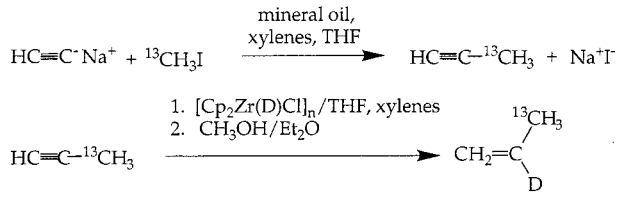
Scheme 5



Results and Discussion

Synthesis of CH_2═CD$^{13}CH_3$. A synthetic route to 2-*d*-3-^{13}*C*-propene (Scheme 5) was developed and tested several times with unlabeled methyl iodide. These test runs revealed that monodeuterioethylene (C_2H_3D) was produced along with the desired propylene product. We conclude that the sodium acetylide suspension was contaminated with acetylene, since the amount of ethylene observed was significantly reduced, if the suspension was subjected to dynamic vacuum prior to beginning the synthesis.

Thus, after removal of all volatiles from the sodium acetylide suspension in vacuo, reaction with ^{13}C-labeled methyl iodide proceeded over about 10 h to afford ^{13}C-labeled propyne. Subsequent deuterio-zirconation and quenching with CH_3OH afforded a multigram quantity of crude CH_2═CD$^{13}CH_3$. Despite rigorous evacuation of the starting sodium acetylide suspension to remove acetylene impurities, the ^{1}H NMR analysis of the crude product revealed the presence of a small amount of deuterium- (but not ^{13}C-) labeled ethylene. We assume that a small amount of acetylene is produced in the first reaction step via competitive deprotonation of the product propyne by the sodium acetylide (eq 2), generating, after deuterio-zirconation, deuterioethylene-d_1. Trap-to-trap distillation at −145 °C successfully removed essentially all deuterioethylene from the crude CH_2═CD$^{13}CH_3$, in what appeared to be a 1:1 azeotrope with propylene.

$$HC{\equiv}C^{-}Na^{+} + HC{\equiv}C{-}{}^{13}CH_3 \rightleftarrows HC{\equiv}CH + Na^{+}{}^{-}C{\equiv}C{-}{}^{13}CH_3 \quad (2)$$

At this stage NMR spectra of the CH_2═CD$^{13}CH_3$ sample displayed vinyl resonances attributable only to the desired product, but features due to a second ^{13}C- and ^{2}H-labeled species were evident. GC-MS analysis indicated that this second product was propane with a ^{13}C and multiple deuteriums, presumably arising from overreduction of propyne by the deuterated Schwartz's reagent. The absence of ethylene (as well as other heavier olefins) in the purified sample was also confirmed by GC-MS. All attempts to separate the labeled propane from the propylene product by fractional distillation on a vacuum line failed. Since propane was anticipated to be inert during propylene polymerization experiments, this mixture of CH_2═CD$^{13}CH_3$ and labeled propane was used without further attempts at purification. Shown in Figure 1 is a ^{1}H NMR spectrum of the propylene/propane mixture. By integration, the isotopic purity of the propylene is estimated to be 97% for both deuterium in the 2-position and ^{13}C in the methyl group.

Polymerization Experiments Using the Doubly Labeled Monomer. Polymerizations of CH_2═CD$^{13}CH_3$ were carried out in toluene using both *rac*-(EBTHI)$ZrCl_2$/MAO and *rac*-(EBI)-$ZrCl_2$/MAO catalyst systems. A glass apparatus was constructed to allow addition of individual toluene solutions of zirconocene dichloride and MAO to a solution of CH_2═CD$^{13}CH_3$ in toluene at the desired reaction temperature. To minimize the decrease in propylene concentration during a run, polymerizations were carried to low conversion. Five test runs using 1 atm of unlabeled propylene with *rac*-(EBTHI)$ZrCl_2$/MAO as catalyst system at 50 °C were carried out. The intensities of the resonances in the ^{13}C NMR spectra of the polymers produced in these five test reactions were essentially identical with [*mmmm*] ≈ 56%. Using these same conditions, poly(2-*d*-3-^{13}*C*-propylene) was prepared. Shown in Figure 2 is a representative ^{13}C NMR spectrum of poly(2-*d*-3-^{13}*C*-propylene) obtained with the *rac*-(EBTHI)$ZrCl_2$/MAO system. Table 1 lists the peak assignments and their intensities.

To reconcile the observed spectrum with those expected according to the two alternative mechanisms for chain epimerization, Scheme 6 summarizes the types of propylene enchainments expected for the tertiary alkyl mechanism (Scheme 3), including the provision for enantiofacial interconversions of eq 1; chain epimerization via the allyl/dihydrogen mechanism of Scheme 4 leads to enchainments shown in Scheme 7 (details of the possible rearrangements according to these two mechanisms are given in the Supporting Information).

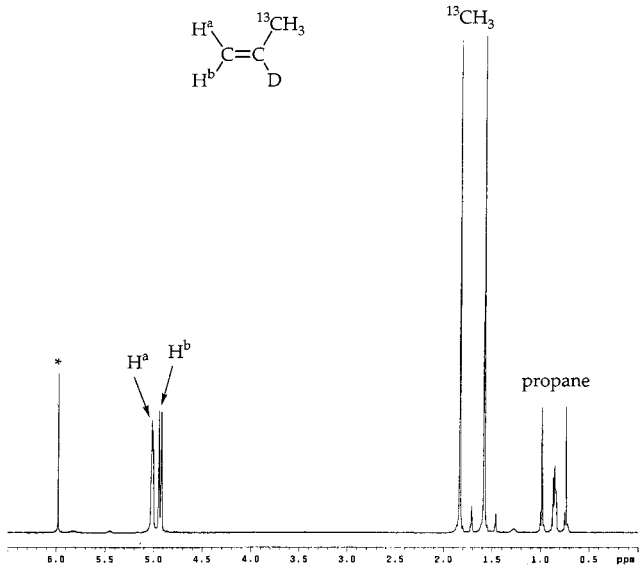


Figure 1. ^{1}H NMR spectrum of CH_2═CD$^{13}CH_3$ containing $CH_xD_{3-x}CH_yD_{2-y}{}^{13}CH_3$ impurities. The peak at 6.0 ppm marked with an asterisk indicates the protio impurity in 1,1,2,2-tetrachloroethane-d_2 solvent.

Table 1. Assignments of the Resonances and Their Intenisities in the ^{13}C NMR Spectrum of Poly(2-*d*-3-^{13}*C*-propylene) Shown in Figure 2[a,b]

signal no.	δ (ppm)[c]	group	microstructure	intensity[d]
1	46.2−45.9	$-CH_2-$		4.2
2	28.5−27.5	$-CL(CH_3)-$[e]		1.3
3	21.92	$-CH(CH_3)-$	mmmmmm	3.0
4	21.88	$-CH(CH_3)-$	mmmmmr	2.3
5	21.82	$-CD(CH_3)-$	mmmmmm	63.7
6	21.76	$-CD(CH_3)-$	mmmmmr	15.5
7	21.49	$-CD(CH_3)-$	mmmr	7.2
8	21.00	$-CD(CH_3)-$	mmrr	7.1
9	19.77	$-CH(CH_3)-$	mrrm	0.44
10	19.65	$-CD(CH_3)-$	mrrm	0.70

[a] Polymerization conditions: 0.25 mg of *rac*-(EBTHI)$ZrCl_2$, 1500 equiv of MAO, 1 atm CH_2═CD$^{13}CH_3$, 7.5 mL of toluene, 50 °C. Spectrum acquired in $C_2D_2Cl_4$ at 85 °C. [b] Assignments made according to ref 4. [c] Downfield from $Si(CH_3)_4$. [d] Total intensity of methyl groups set to 100; methine and methylene resonances scaled accordingly. [e] L = H or D.

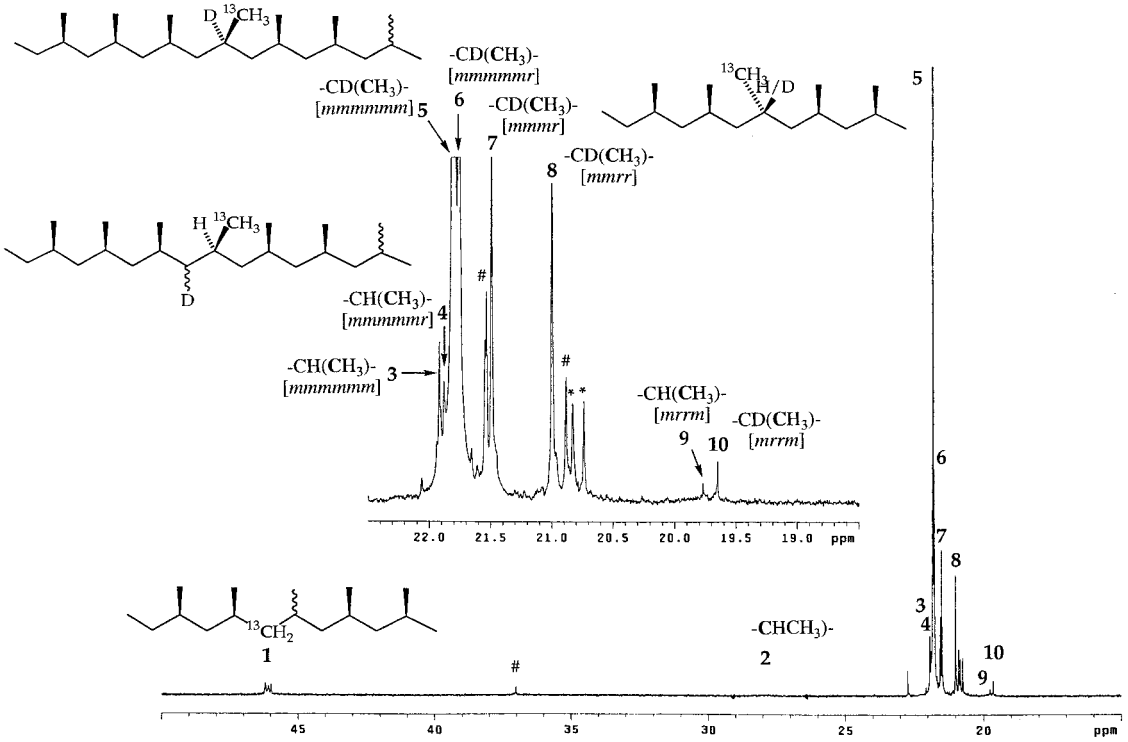
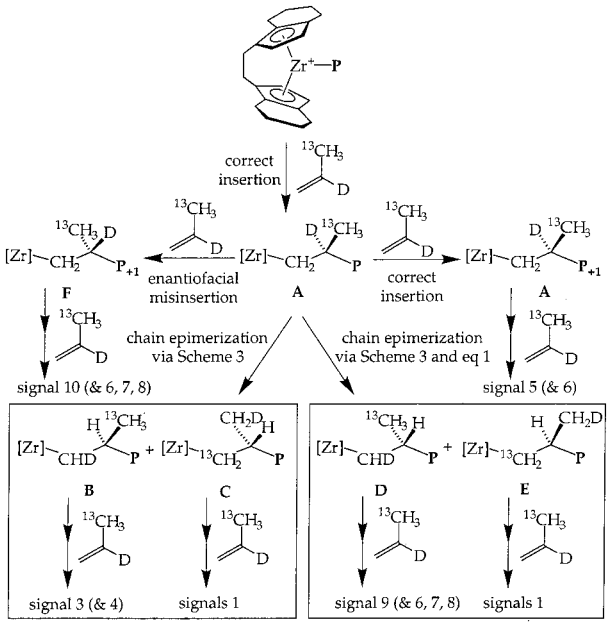


Figure 2. ^{13}C NMR spectrum of poly(2-*d*-^{13}*C*-propylene) prepared using *rac*-(EBTHI)$ZrCl_2$/MAO in toluene with 1 atm monomer at 50 °C. Peaks marked with an asterisk are assigned to chain ends, and those with a number sign, to regioerrors that result in 3,1-misinsertions.

Scheme 6



Due to the low (ca. 1%) natural abundance of ^{13}C, the most notable signals observed in Figure 2 are those derived from the highly enriched methyl group of $CH_2{=}CD^{13}CH_3$. Qualitatively, the spectrum resembles that expected for an isospecific polymerization of unlabeled propylene under conditions where considerable stereoerrors have occurred under enantiomorphic site control, with signals due to chain ends (those marked with *) and regioerrors (those marked with #) also evident.[12] On closer examination several distinctive features are apparent:

(i) As expected, the principal ^{13}C-labeled methyl signals (signals **5**−**8** and **10**) are due to [−CD(*C*H_3)−], rather than [−CH(*C*H_3)−] units, although the latter are clearly in evidence (signals **3**, **4**, and **9**). (ii) The 2:2:1 ratio of intensities for [*mmmr*]:[*mmrr*]:[*mrrm*] pentads (signals **7**:**8**:**10**) attributable to [−CD(*C*H_3)−] units, for an isospecific polymerization operating under enantiomorphic site control, is not obtained. (iii) There are multiple signals due to ^{13}C-enriched methylene units along the polymer backbone.

Significantly, *there are no detectable 1:1:1 triplets attributable to doubly labeled methyl groups (*$^{13}CH_2D$*) observed* anywhere in the spectrum, counter to the predictions of the allyl/dihydrogen mechanism of Scheme 4.[13] Specifically, there is no detectable triplet signal at ca. δ 19.3, i.e. slightly upfield of signal **10**, for a −CH(*C*H_2D)− unit of an [*mrrm*] pentad.[14] DEPT experiments are in accord with the assignments of

(12) Under these polymerization conditions the only operative chain termination pathway is β-H elimination which gives rise to equal amounts of vinyl and *n*-propyl chain end groups. Regioerror enchainments are exclusively of the 1,3-misinsertion type. Resonances were identified for those carbons expected to be ^{13}C labeled for all of these groups (see Supporting Infromation). Integrations of the resonances due to vinyl and *n*-propyl end groups are of similar intensity as required. Signals observed for the terminal carbons of both the vinyl end group (δ 110 ppm) and the *n*-propyl end group (δ 14 ppm) are not shown in Figure 2. Assignments of the resonances are according to those described in the following: (a) Rieger, B.; Reinmuth, A.; Röll, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67. (b) Busico, V.; Cipullo, R.; Talarico, G.; Caporaso, L. *Macromolecules* **1998**, *31*, 2387.

(13) Another distinguishing feature of the two mechanisms concerns rearrangements that place deuterium in the (non-^{13}C-labeled) methylene units along the main chain. Schemes 3 and 6 predict such, and Schemes 4 and 7 do not. ^{2}H NMR spectra for this polymer and the others from Table 2 do display broad resonances at chemical shifts assignable to the *anti* (δ 1.27) and *syn* (δ 0.8) methylene deuteriums. However, these signals are not sufficiently well resolved from nearby methine and *m* diad methyl deuteriums to assign them as methylene deuteriums with confidence.

(14) Observation of a 1:1:1 triplet in the ^{13}C NMR spectra of the poly(2-*d*-3-^{13}*C*-propylene) samples could also arise from crossover of the terminally unsaturated polymer chain, i.e. by interchange of *gem*-olefins between zirconium−hydride units. While olefin crossover may seem a rather unlikely scenario, given the expected very low concentration of the olefin/hydride intermediates and the much higher reactivity toward a zirconium hydride expected for propylene vs a gem-disubstituted olefin. Since there is no evidence for a doubly labeled [$^{13}CH_2D$] methyl group, this is effectively a nonissue.

Scheme 7

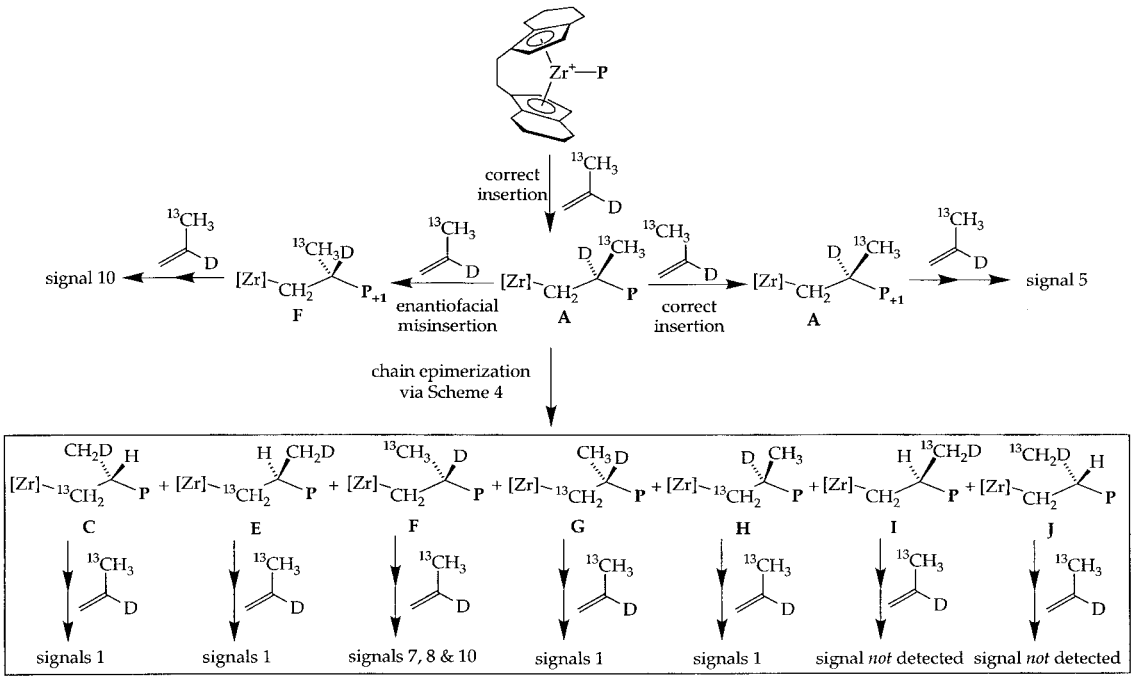
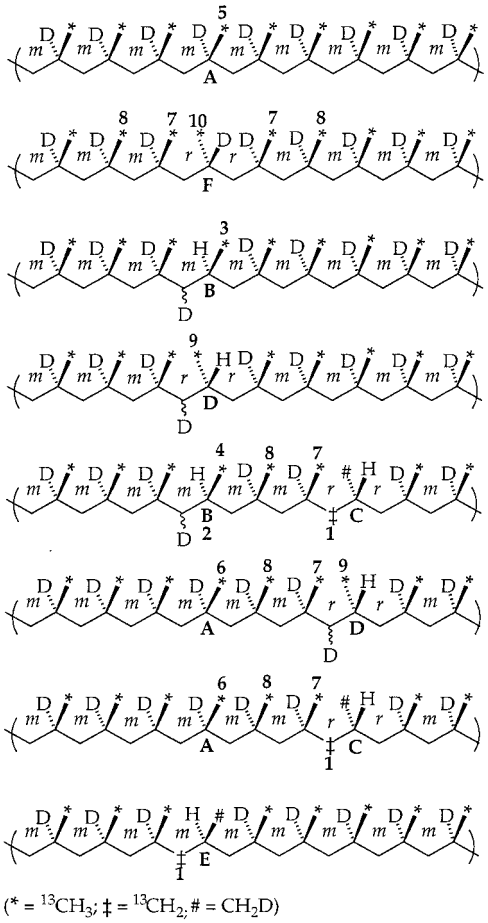


Table 1 and confirm the absence of $^{13}CH_2D$ methyl groups. Moreover, these DEPT experiments confirm that all three resonances assigned to methylene resonances are [$-^{13}CH_2-$] (not [$-^{13}CHD-$]) units. A quantitative analysis of the relative intensities (vide infra) of the various pentad and heptad assignments (Table 1) further supports the preliminary conclusion that the tertiary alkyl mediated process (Scheme 3) augmented by olefin enantiofacial switching (eq 1) is the most likely mechanism for chain epimerization under these conditions.

Chart 1 lists all possible polymer segments expected for polymerization of $CH_2{=}CD^{13}CH_3$ with chain epimerization and enantiofacial misinsertions according to Scheme 6. As can be seen, all of the signals predicted by this analysis are observed in the ^{13}C NMR spectrum of Figure 2 and Table 1. Before the relative intensities of these signals are considered, adjustments must be made for natural abundance ^{13}C in the methylene position and ^1H in the methine positions of the polypropylene. The signal intensity due to the natural abundance concentration of ^{13}C in the methylene position is measured as the (very weak) relative integration of the methine resonance at δ 27.5−28.5 (ca. 1.3), since neither enantiofacial misinsertion nor chain epimerization via Scheme 6 (nor via Scheme 7, for that matter) moves ^{13}C from the methyl position to the methine position. This amount of the three roughly equal intensity signals should be subtracted from the total methylene carbon signal integration (4.2), since it is attributable to natural abundance ^{13}C in the methylenes of correctly inserted monomers.[15] Further, a correction must be made for residual protium in the 2-position of the monomer (3% by ^1H NMR). A portion of signals **3** + **4** (methyl groups in [*mmmm*] pentad arrangement adjacent to CH methine carbon) and also signal **9** (methyl group in [*mrrm*] pentad arrangement adjacent to CH methine carbon) derive from

Chart 1



this isotopic impurity. Hence, 3.09% (=(100/97 − 1) × 100%) of the sum of integrations for the [$-CD(^{13}CH_3)-$] signals **5** + **6** should be subtracted from the sum of the [$-CH(^{13}CH_3)-$] signals **3** + **4** and the same amount added to signals **5** + **6**. Similarly, 3.09% of the integration of the [$-CD(^{13}CH_3)-$] signal

(15) It is likely that one of the three roughly equal intensity peaks in this region is due to natural abundance [$-CH_2CD^{13}CH_3-$] units with correct stereochemistry. Unfortunately, the specific assignments of resonances in the methylene carbon region have not been made. See: Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M.; Segre, A. L. *Macromolecules* **1997**, *30*, 6251.

Table 2. Normalized Methylene and Pentad Intensities of Resonances in the ^{13}C NMR Spectra for Poly(2-*d*-3-^{13}C-propylene)[a–c]

run	propylene pressure[d] (atm)	*T* (°C)	**1**[e] [CH_2]	**3** + **4**[f] [*mmmm*]	**5** + **6**[g] [*mmmm*]	**7** [*mmmr*]	**8** [*mmrr*]	**9**[h] [*mrrm*]	**10**[i] [*mrrm*]
1[j]	1	50	2.9	2.9	81.7	7.2	7.1	0.42	0.72
2[j]	≈0.66	50	4.7	4.0	74.2	10.0	10.4	0.71	0.63
3[j]	0.66[l]	50	10.1	4.8	63.8	14.8	14.6	1.4	0.80
4[j]	1	75	15.7	4.0	52.2	19.2	21.6	1.9	1.2
5[k]	1	50	0.52	2.9	83.3	5.5	5.9	0.23	2.2
6[k]	1	75	4.8	4.4	68.5	11.2	12.5	0.91	2.4

[a] Signal numbers refer to Figure 2 and Table 1. [b] Standard conditions: 0.25 mg of precatalyst, 1500 equiv of MAO, 7.5 mL of toluene, spectra acquired in $C_2D_2Cl_4$; reaction time 1.0 min. [c] Total pentad intensity data normalized to sum to100%, and all signal intensities normalized to isotopically pure $^{12}CH_2{=}^{12}CD^{13}CH_3$ monomer. [d] See text. [e] Contribution from natural abundance of ^{13}C subtracted. [f] Contribution from residual protium in 2-position of monomer (3% of the intensities of **5** + **6**) subtracted. [g] Contribution from residual protium in 2-position of monomer (3% of the intensities of **5** + **6**) added. [h] Contribution from residual protium in 2-position of monomer (3% of the intensity of **10**) subtracted. [i] Contribution from residual protium in 2-position of monomer (3% of the intensity of **10**) added. [j] Precatalyst = *rac*-(EBTHI)$ZrCl_2$. [k] Precatalyst = *rac*-(EBI)$ZrCl_2$. [l] Polymerization was allowed to proceed for 3 min, rather than 1 min, and monomer pressure decreased substantially during the run.

10 should be subtracted from that for the [$-CH(^{13}CH_3)-$] signal **9** and the same amount added to signal **10**.

Additional polymerization runs (2−6) under various conditions with both *rac*-(EBTHI)$ZrCl_2$/MAO and *rac*-(EBI)$ZrCl_2$/MAO catalyst systems were performed, and the pentad intensities, corrected for residual protium at the *2*-position of the monomer and natural abundance ^{13}C as indicated above, are listed in Table 2. In these experiments, the average pressure during the polymerizations was unknown, so that the numbers reported are the initial pressures of monomer to which the apparatus was filled at room temperature. Run 3 refers to a reaction in which a small amount of monomer was initially added (ca. 500 Torr) and the polymerization allowed to proceed for 3 min instead of the usual 1 min, resulting in depletion of a substantial amount of the monomer; consistent with this assertion, a higher than normal yield (by mass) of polymer was isolated from this run.

These ^{13}C NMR data for the test polymerizations carried out with unlabeled monomer (vide supra) and for the labeled polymer listed for run 1 (carried out under the same conditions) compare well with literature data for these standard polymerization conditions, corresponding to a monomer concentration of approximately 0.3−0.4 M and hence a propylene pressure of about 1 atm. Brintzinger reported [*mmmm*] = 61%, [*mmrr*] = 15.5%, and [*mrrm*] = 8.0% for unlabeled propylene and [*mmmm*] = 84%, [*mmrr*] = 6.4%, [*mrrm* (CH_3)] = 1.0%, and [*mrrm* (CH_2D)] = 2.2% for poly([2-D]propylene) under these conditions.[3b] Additionally, comparison of the ^{13}C NMR data for the sample obtained in run 3 with data from Busico's laboratory[5] reveals that the propylene pressure in this experiment is less than 0.6 atm, as desired.

Using the relationship that, for an isospecific polymerization which follows the enantiomorphic site control mechanism, isolated stereoerrors should result in a 2:2:1 ratio of the [*mmmr*]:[*mmrr*]:[*mrrm*] pentads,[16] we can estimate the percentages of each of the [$-^{13}CC_2DH_5-$] structures **C** and **E**. If the sum of the intensities of [*mrrm*] peaks **9** and **10** is subtracted from half of the averaged intensities of peaks **7** ([*mmrr*]) and **8** ([*mmmr*]), the result is an approximation of the integration due to structure **C**, since the "missing intensity" from the 2:2:1 pentad distribution appears in the methylene resonance, together with the enriched methylene group of structure **E** having correct stereochemistry. The approximate percentage of structure **E** is then simply the difference between this number and the integration of peak **1** (after correction for natural abundance). The percentages estimated in this manner are shown in Table 3, together with the percentages of structures **B** (adjusted intensity of signals **3** and **4**), **D** (adjusted intensity of signal **9**), **F** (adjusted intensity of signal **10**), and **A** (remainder) in the polypropylene samples for all six runs.

Table 3. Estimated Percentages of Doubly Labeled Propylene Structures for Enchainments Labeled According to Scheme 6

run[a]	A	B	C	D	E	F
1	93.1	2.9	2.5	0.42	0.42	0.72
2	90.0	4.0	3.8	0.71	0.93	0.63
3	83.0	4.8	5.3	1.3	4.9	0.80
4	77.2	4.0	7.1	1.9	8.6	1.2
5	94.1	2.9	0.38	0.23	0.14	2.2
6	87.5	4.4	2.6	0.91	2.1	2.4

[a] Run numbers correspond to those in Table 2.

Consistent with the assignment of peak **10** to stereoerrors derived through enantiofacial misinsertion (structure **F**), its intensity remains essentially constant as the propylene pressure is lowered (runs 1−3). Also consistent with their assignments, the intensities of resonances due to structures **B**− **E**, arising from unimolecular chain epimerization competing with bimolecular chain propagation, increase as the propylene pressure is lowered (runs 1−3) and as the polymerization temperature is raised (run 1 vs 4 and run 5 vs 6). We also find that the favorability of chain epimerization is lower for the *rac*-(EBI)-$ZrCl_2$ system as compared to *rac*-(EBTHI)$ZrCl_2$ (run 1 vs 5 and run 4 vs 6), consistent with earlier results.[1c] ^1H and ^2H NMR spectra of the polypropylene samples are also consistent with an increase in the occurrence of chain epimerization as propylene pressure is lowered and temperature is raised. Thus, the intensities of the methine resonances in the ^1H NMR spectrum (δ 1.6) increase as do the intensities of the methyl and methylene resonances in the ^2H NMR spectrum (δ 0.9).[17]

For a sample of poly([2-D]propylene) prepared analogously to the sample of entry 1, Brintzinger and Leclerc had estimated the monodeuterated methyl groups due to chain epimerization (labeled *b* in Scheme 2) were of roughly equal intensity to those of correct stereochemistry (labeled *c* in Scheme 2).[3b] This finding was unexpected, since it implied that olefin enantiofacial switching (eq 1) is fast relative to the slow step in Scheme 3. By contrast, for the polymerization run 1, the percentages of

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(17) As might be noted, the movement of deuterium into the methylene positions is consistent only with the tertiary alkyl mechanism (Schemes 3 and 6), and thus, the observation of an increase in these ^2H NMR signals with increasing chain epimerization also argues against the allyl/H_2 mechanism (Schemes 4 and 7). Unfortunately, the ^2H NMR spectra were not sufficiently well resolved to unambiguously distinguish the methylene from the methyl signals.

epimerized structures **B** and **C** are approximately equal and ca. 6 times higher than for *non*epimerized structures **D** and **E** (also equal). The sum **B** + **C** > sum **D** + **E** provides further support for the tertiary alkyl mechanism, since **B** and **C** arise by β-H elimination from the [Zr]−C($^{13}CH_3$)(CH_2D)**P** intermediate, whereas **D** and **E** are formed by β-H elimination from the inverted [Zr]−C(CH_2D)($^{13}CH_3$)**P** intermediate that arises from enantiofacial switching for the intermediate *gem*-olefin complex (eq 1). The fact that **B** ≈ **C** and **D** ≈ **E** for runs with *rac*-(EBTHI)$ZrCl_2$ as precatalyst (runs 1−4) is somewhat puzzling. Whereas a small secondary kinetic deuterium vs ^{13}C isotope effect difference for β-H elimination is anticipated, a simple statistical factor should favor β-H elimination from the ($^{13}CH_3$) group and, more importantly, site control by the C_2-symmetric zirconocene fragment should favor β-H elimination from one of the methyl groups of the tertiary alkyl intermediate. As can be seen from the data for runs 5 and 6, the *rac*-(EBI)$ZrCl_2$ catalyst system has more disparate fractions of **B** and **C** and fractions of **D** and **E**, but the scatter in the data raises the question of their true significance. It does, however, appear that for both catalyst systems the amounts of **D** and **E** are consistently less than the amounts of **B** and **C**. Considering that the former require the additional olefin enantiofacial switching process of eq 1, one might well expect them to arise less frequently. Since the previous estimate by Brintzinger and Leclerc of roughly equal amounts of types *b* and *c* [CH_2D] side groups rests on an extrapolation of the relative intensity of an inverted 1:1:1 triplet in the DEPT experiment which barely emerged from the large [*mmmm*] pentad for the poly([2-D]-propylene) sample, our results herein for poly(2-*d*-3-^{13}*C*-propene) are likely more reliable.

Conclusions

Polymerization of doubly labeled propylene CH_2=$CD^{13}CH_3$ has provided strong supporting evidence for the tertiary alkyl mechanism for chain epimerization. Indeed, all of the expected resonances in the ^{13}C NMR spectra for polypropylene samples, prepared under conditions where stereoerrors arising from chain epimerization are prevalent, are observed. Rearranged structural units **B** and **C** with lesser amounts of **D** and **E** are readily accommodated by the mechanism of Scheme 3 with enantiofacial switching (eq 1). The lower concentrations of the latter suggest that the eq 1 has a significantly higher barrier, but given the very fast nature of the polymerization process with these catalyst systems, no barrier can be large on an absolute scale. It is likely that this enantiofacial switching process occurs without full dissociation from zirconium; otherwise chain transfer would be expected. The very large concentration of propylene monomer would undoubtedly out-compete the more hindered *gem*-disubstituted olefin of the polymer end for the reactive zirconium hydride. There is precedent for this process: Gladysz reported that a rhenium olefin complex undergoes facial switching without dissociation, although the process requires hours at 100 °C.[18] Since the olefin binding to a cationic d^0 zirconium center is undoubtedly much weaker than that for a neutral d^6 rhenium center, a faster process might be expected. We remain somewhat puzzled about the issue of dissociative vs nondissociative enantiofacial switching, however. There is a growing body of evidence that α-olefin coordination to the active catalytic site is fast *and reversible* with these types of olefin polymerization systems.[19] Thus, one might expect the barrier for olefin dissociation to be lower than that for reinsertion, even reinsertion into a zirconium−hydride bond. Perhaps the geminally substituted olefin is held to the cationic Zr center sufficiently well to block propylene displacement, even when the π interaction has been broken. Coordination through one or two C−H σ bonds, as suggested by Gladysz and Brintzinger,[6,18] could conceivably provide the barrier to prevent chain transfer from occurring before olefin enantiofacial switching is complete.

The failure to observe 1:1:1 signals attributable to [−CH_2-$CH^{13}CH_2$D−] enchainments in the [*mrrm*] pentad region of the ^{13}C NMR spectra of poly(2-*d*-^{13}C-propylene) samples, along with the presence of structures **B**−**E** in relative amounts that might be expected according to Scheme 6, argue persuasively in favor of the tertiary alkyl mechanism for chain epimerization and against the allyl/dihydrogen alternative. On the other hand, previous observations of internal vinylidene unsaturation along polymer chains and dihydrogen evolution during propylene polymerizations[8] are readily accommodated by Scheme 4. It seems likely that the strength of the metal−dihydrogen interaction is not sufficient to prevent (effectively irreversible) dihydrogen dissociation prior to the remaining required steps to effect chain epimerization. Insertion of propylene into the resulting zirconium−allyl bond would then result in formation of an internal unsaturation (Scheme 4). We conclude therefore that although such an allyl/dihydrogen complex might well form, it does not mediate chain epimerization.

Experimental Section

General Methods. All air- and/or moisture-sensitive compounds were manipulated using standard high-vacuum line, Schlenk, or cannula techniques or in a glovebox under a nitrogen atmosphere, as described previously.[20] Argon was purified and dried by passage through columns of MnO on vermiculite and activated 4 Å molecular sieves. Solvents were stored under vacuum over titanocene[21] or sodium benzophenone ketyl. The synthesis of [(η^5-C_5H_5)ZrD(Cl)]$_n$ was carried out as previously reported.[22] Methanol (EM Science), propylene (Aldrich), sodium acetylide (Strem), (*rac*-ethylenebis(indenyl))zirconium dichloride (Aldrich), and (*rac*-ethylenebis(4,5,6,7-tetrahydroindenyl))zirconium dichloride (Strem) were purchased and used as received. ^{13}C-labeled methyl iodide was purchased (Cambridge Isotopes), purified by passage through a plug of silica, and distilled from CaH_2 before use. Methylaluminoxane (MAO) was purchased (Albemarle) and dried in vacuo to remove free trimethylaluminum before use. NMR spectra were recorded on a Varian Unity Inova 500 (499.853 MHz for ^{1}H) spectrometer. Analysis by GC-MS was carried out on an HP 5890 Series II gas chromatograph connected to an HP 5972 mass spectrometric detector. A 60 m × 0.32 μm internal diameter column was used which was coated with a 5 μm thick 100% methylsiloxane film.

Synthesis of (η^5-C_5H_5)$_2$Zr(Cl)[CH=CD($^{13}CH_3$)]. In an inert-atmosphere glovebox, a suspension of sodium acetylide (17.3 wt %)

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in a mixture of mineral oil and xylenes (85 g of suspension = 14.7 g of NaC_2H, 0.306 mol) was weighed into a 500 mL three-necked round-bottom flask. A large condenser designed for the use of dry ice/acetone as coolant and fitted with a gas inlet adapter was attached to the flask, as was a glass stopper and a rubber septum. The assembly was evacuated for 90 min, and THF (300 mL) was then added by cannula. The condenser was cooled to −78 °C, and $^{13}CH_3I$ (approximately 36 g, 0.252 mol) was injected using a syringe. The reaction was allowed to proceed for 9 h after which time the apparatus was evacuated and the volatiles transferred under dynamic vacuum into a trap cooled to 77 K. In an inert-atmosphere glovebox, $[Cp_2ZrD(Cl)]_n$ (67 g, 0.259 mol) was weighed into a 500 mL round-bottom flask. This flask was attached to a swivel frit assembly, and the apparatus was evacuated. The trap containing the crude reaction mixture was then isolated from dynamic vacuum, and the contents were transferred into the apparatus containing the Schwartz reagent. The reaction was allowed to proceed for 3 h at room temperature, after which time the solution was dark green/black. The solvent was then removed in vacuo, and diethyl ether (200 mL) was added by vacuum transfer. An orange/red precipitate was separated from the product by filtration. This precipitate was washed 4 times with diethyl ether, and the solvent was then removed from the filtrate in vacuo leaving the desired product as a sticky, dark green tar. ^{1}H NMR (THF-d_8): δ 7.48 (d, ZrC(*H*)═CD^{13}CH$_3$, 1H, $^3J_{CH}$ = 12 Hz), 6.98 (s, C_5H_5, 10H), 1.54 (d, ZrC(H)═CD^{13}CH$_3$, 3H, $^1J_{CH}$ = 124 Hz). ^{2}H NMR (THF): δ 5.72 (s (br), ZrC(H)═C*D*^{13}CH$_3$).

Synthesis of CH_2═$CD^{13}CH_3$. The dark green product of the previous reaction was dissolved in diethyl ether (200 mL), and the solution was transferred to a 500 mL three-necked round-bottom flask. A large condenser designed for the use of dry ice/acetone as coolant and fitted with a gas inlet adapter was attached to the flask, as was a glass stopper and a rubber septum. The condenser was cooled to − 78 °C, and the reaction flask was cooled to 0 °C. Methanol (10.0 mL, 7.91 g, 0.247 mol) was then added dropwise using a syringe. The reaction was allowed to proceed for 1 h at 0 °C, after which time the mixture was dark red and a tan solid had precipitated from solution. The apparatus was then evacuated, and the volatiles were transferred, under dynamic vacuum, into a trap cooled to 77 K. When finished, the trap was isolated from dynamic vacuum and the contents of the trap were transferred to a thick walled glass vessel. The vessel was cooled to −95 °C using a toluene/dry ice slush, and the portion which was volatile at this temperature was transferred, under dynamic vacuum, through one −95 °C trap into a trap cooled to 77 K. The contents of the 77 K trap were then transferred into a thick-walled glass vessel, and this process was repeated twice. After this time, all diethyl ether had been removed from the sample, as characterized by ^{1}H NMR. The reaction vessel containing the propylene was then cooled to −145 °C using a slush composed of a mixture of *n*-pentane and isopentane cooled with liquid nitrogen. The contents of the trap which were volatile at this temperature were then transferred, under dynamic vacuum, through one −145 °C trap into a trap cooled to 77 K. After this procedure, the thick-walled reaction vessel contained a mixture of CH_2═$CD^{13}CH_3$ and ^{13}C- and ^{2}H-labeled propane. This mixture was stored, perpetually cooled to −78 °C, in a thick-walled glass vessel. *Caution! Extreme care should be taken with the storage of propylene in a closed container as its vapor pressure at room temperature exceeds 12 atm.* ^{1}H NMR (benzene-d_6): δ 4.99 (m, *cis*-CH(*H*)CD^{13}CH$_3$, 1H), 4.94 (d, *trans*-C*H*(H)CD^{13}CH$_3$, 1H, $^3J_{CH}$ = 12 Hz), 1.53 (dm, $CH_2CD^{13}CH_3$, 3H, $^1J_{CH}$ = 126 Hz). ^{13}C {^{1}H} NMR (C_6D_6): δ 133.3 (d(1:1:1 t), $CH_2CD^{13}CH_3$, $^2J_{CC}$ = 42 Hz, $^1J_{CD}$ = 42 Hz), 115.7 (s, $CH_2CD^{13}CH_3$), 19.2 (1:1:1 t, $CH_2CD^{13}CH_3$, $^2J_{CD}$ = 0.7 Hz). ^{2}H {^{1}H} NMR ($C_2H_2Cl_4$): δ 5.88 (s (br), $CH_2CD^{13}CH_3$).

Polymerization Experiments. The polymerization apparatus consisted of two separate reaction chambers connected, at a 135° angle, by glass tubing with an O-ring joint. A needle valve with a ground glass joint was also present for connection to a vacuum line, and the entire apparatus was made out of thick-walled glass. In an inert-atmosphere glovebox, individual toluene solutions of the catalyst (0.25 mg in 0.25 mL) and MAO (50 mg in 7.5 mL) together with a magnetic stir bar were loaded into the reaction chambers and were not allowed to contact. The apparatus was then assembled and subsequently evacuated on a high-vacuum line. The gas manifold of the vacuum line was filled with 1 atm of the monomer, the needle valve to the vessel containing the monomer was closed, and the needle valve to the polymerization apparatus was opened. Dissolution of the monomer was monitored by the pressure drop in the manifold, and this procedure was then repeated until no further pressure decrease was observed. Four iterations of this process sufficed to completely saturate the solutions; thus low-pressure polymerizations were carried out using only one iteration. After addition of the desired amount of monomer, the apparatus was placed in an oil bath at the appropriate temperature and allowed to equilibrate for 15 min. The individual solutions of catalyst and MAO were then mixed, resulting in activation of the catalyst, and as no pressure regulation was possible in these experiments, the polymerizations were allowed to proceed for only 1 min to ensure minimal pressure drop over the course of the reaction. A 4:1 mixture of methanol and HCl was then added to quench the reaction, and the polymer was isolated by extraction from methanol/HCl. Approximately 100 mg of polymer was typically isolated.

NMR Experiments. The NMR spectra were acquired on a Varian Unity Inova 500 MHz spectrometer operating at 125.699 MHz for ^{13}C, 499.853 MHz for ^{1}H, and 76.730 MHz for ^{2}H. ^{13}C and ^{1}H NMR spectra were obtained at 85 °C using dilute solutions of polymer in 1,1,2,2-tetrachloroethane-d_2 (∼5 mg in 0.7 mL). ^{2}H spectra were acquired at 85 °C using samples of the same concentration in 1,1,2,2-tetrachloroethane with no solvent lock. For ^{13}C, a calibrated 90° pulse width was used with 4−10 s recycle delay, 2−3 s acquisition time, inverse gated ^{1}H decoupling, and 800−1000 transients. For ^{2}H, a calibrated 90° pulse width was used with 5 s recycle delay, 1 s acquisition time, and 64 transients.

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Supporting Information Available: Schemes showing how the rearrangements according to Schemes 6 and 7 give rise to the structures labeled **A**−**J** and schemes showing the predicted chain ends and ^{13}C NMR signals attributed to them and to 1,3 regioerrors. This material is available free of charge via the Internet at http://pubs.acs.org.

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