Zr−Alkyl Isomerization in ansa-Zirconocene-Catalyzed Olefin Polymerizations. Contributions to Stereoerror Formation and Chain Termination[1]

Margarete K. Leclerc and Hans H. Brintzinger*

Contribution from the Fakultät für Chemie, Universität Konstanz, D-78464 Konstanz, Germany

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Abstract: In polymers made from (*E*)- or (*Z*)-[1-D]propene with methyl alumoxane (MAO)-activated ansa-zirconocene catalysts, signals of deuterium-labeled mrrm pentads document that stereoerrors arise mainly from an isomerization of the Zr-bound chain end. Reduced D-atom redistribution in poly([2-D]propene) indicates a kinetic isotope effect of $k_H/k_D \approx 3$ for the β-H/D transfer associated with the isomerization reaction. In all poly([1- and 2-D]propenes) studied, D-labeled mmmm pentads occur with a probability similar to that of D-labeled mrrm pentads; this observation requires further mechanistic clarification. Olefinic chain ends of polymers obtained with $C_2H_4(thind)_2ZrCl_2$-MAO from (*E*)- or (*Z*)-[1-D]propene deviate in their D-label distributions from the expected stereochemistry. Isomerization of the Zr-bound chain end, probably *via* a Zr-bound tertiary alkyl intermediate, thus contributes also to chain-growth termination. With the sterically hindered catalyst $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{Bu}\text{-}C_5H_2)_2ZrCl_2$-MAO, almost all chain terminations appear to occur *via* chain-end isomerization, which does not lead to stereoerrors here. With the high-performance catalyst $Me_2Si(2\text{-}Me\text{-}benz[e]indenyl)_2ZrCl_2$-MAO, finally, no D-label is found in the mrrm and mmmm pentad signals; here, Zr-alkyl isomerization can apparently not compete with the high rate of olefin insertion.

Introduction

Well-defined homogeneous ansa-zirconocene catalysts for the stereoregular polymerization of α-olefins[2] offer an opportunity to clarify the mechanisms of polymer chain growth and, in particular, the origins of its stereoselectivity. NMR studies by Zambelli and co-workers[3] on the stereochemistry of olefin insertions into metal-bound $^{13}CH_3$ and $^{13}CH_2CH_3$ groups and molecular-mechanics studies by Corradini and co-workers[4] on ansa-metallocene catalysts have led to the notion of *chain-segment-mediated catalytic-site control*: The enantiotopicity of each coordination site at the catalyst center[5] determines the orientation of the last-inserted, metal-bound $C(\alpha)-C(\beta)$ chain segment; the latter then controls the enantiofacial orientation of the following olefin insertion, such that the olefin substituent is placed trans to the $C(\alpha)-C(\beta)$ segment at the incipient C···C bond.[6]

This model of chain-segment-mediated catalytic-site stereocontrol has recently been complemented by the notion that α-*agostic interactions* control the stereochemistry of olefin-insertions by stabilizing alternative transition states.[7] This hypothesis is supported by kinetic isotope effects associated with the presence of a metal-bound α-CHD-group.[8−11] Stereocontrol by chain-segment orientation and by α-agostic interaction are entirely compatible with each other and in fact mutually supportive: Interaction of one or the other of the two H atoms of the Zr-bound α-CH_2 group with the Zr center gives two orientations of the $C(\alpha)-C(\beta)$ segment, of which one is sterically unencumbered and indeed just that predicted to yield minimal van der Waals repulsions.[4] The alternative Zr←H interaction (which would give rise to a stereoirregular olefin insertion) is sterically inaccessible for chiral ansa-zirconocene complexes, in which the coordination sites are unilaterally blocked by one β-substituent at each C_5-ring ligand. This explanation for the stereoselectivity of chiral ansa-metallocene polymerization catalysts is supported by several recent theoretical studies by ab initio and local-density methods.[12]

The rigidity of the three-membered Zr←H−C(α) ring and of the adjoining four-membered cycle of the olefin-insertion transition state would lead to the expectation that high (if not essentially complete) selectivities for stereoregular olefin inser-

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Scheme 1
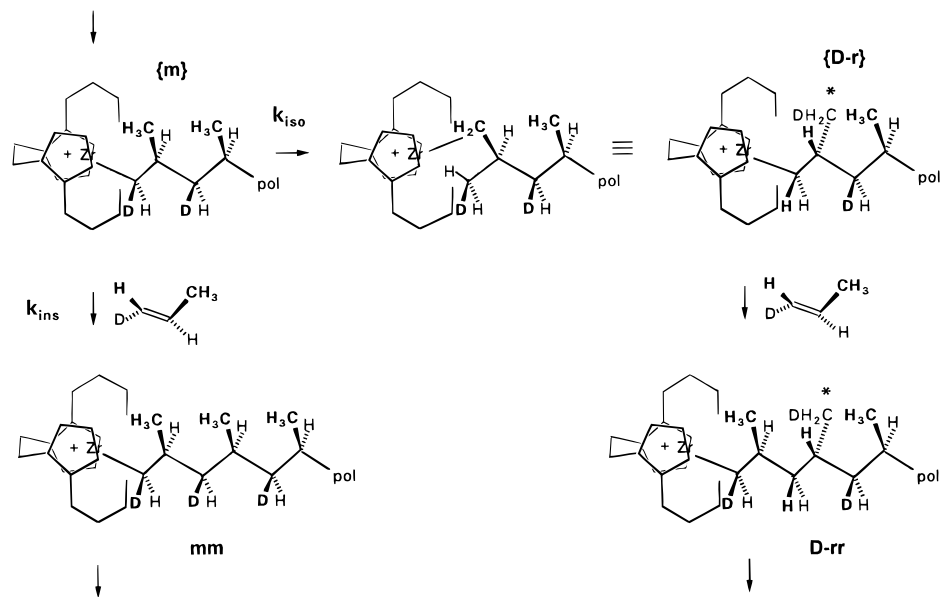
tion are found for all appropriately substituted ansa-zirconocene catalysts. Quite in contrast to this, many chiral ansa-zirconocene catalysts will give polypropene with high isotacticities (i.e. with [mmmm] values above 90%) only at temperatures around or below ambient; polymerizations at temperatures of 50 °C or higher lead to strongly decreased stereoregularities, with [mmmm] values down to ca. 50%.[14−16]

Exceptions in this regard are zirconocene catalysts with bulky β-substituents, such as *t*-butyl or 1-methylcyclohexyl groups, which produce polypropene with isotacticities of [mmmm] > 95% even at 80 °C, albeit at the expense of decreased polymer chain lengths.[16] Modern ansa-zirconocene catalysts of practical utility, such as $Me_2Si(2-Me-benz[e]indenyl)_2ZrCl_2$-MAO[17,18] or $Me_2Si(2-Me-4-arylindenyl)_2ZrCl_2$-MAO,[17] on the other hand, combine high stereoselectivities (i.e. values of [mmmm] > 95%) with high polymer chain lengths and also with very high productivities.

The strong stereoselectivity variations observed among these catalysts do not appear to be compatible, prima facie, with such a "binary" stereoselection model, which would predict that the

mere presence or absence of a β-substituent in a particular quadrant of the ansa-zirconocene complex determines the stereochemical course of each olefin insertion.[19] Important insights with regard to the origin of stereoselectivity variations among different chiral ansa-zirconocene catalysts were obtained by Cipullo and Busico[20,21] and by Resconi and co-workers:[22] Decreased monomer concentrations were found to lead to strongly diminished stereoregularities, especially at elevated reaction temperatures. Catalysts of relatively low activity appear to be distinctly more sensitive to decreased monomer concentrations than high-activity catalysts such as $Me_2Si(2-Me-benz[e]-indenyl)_2ZrCl_2$-MAO.[20] This effect of monomer concentrations on stereoselectivities was ascribed to an epimerization at the asymmetric methine center of the last-inserted, Zr-bound C_3H_6 unit. This reaction appears to compete with the insertion of another olefin whenever the insertion rates are diminished, be it by reduced monomer concentrations or by low activities of the catalyst employed.

In studying the effects of α-deuteration on polymer-chain growth[11] we have obtained independent evidence for the occurrence of such a chain-end isomerization: In the ^{13}C NMR spectra of polymers produced with chiral ansa-zirconocene catalysts from cis- or trans-α-deuterated propenes, we observed that the mrrm pentad signal, i.e. the signal due to stereoinverted CH_3 groups, is largely replaced by a triplet arising from stereoinverted CH_2D groups. The origin of these mrrm-framed CH_2D groups was tentatively ascribed to the rearrangement represented in Scheme 1. In the following, we present further evidence, from deuterium labeling patterns arising in the polymerization of deuterated monomers with a number of typical zirconocene catalysts, for the nature and the possible mechanisms of this rearrangement reaction. We also present evidence that isomerization of the Zr-bound chain end contributes not only to the formation of stereoerrors but also to chain-growth termination.

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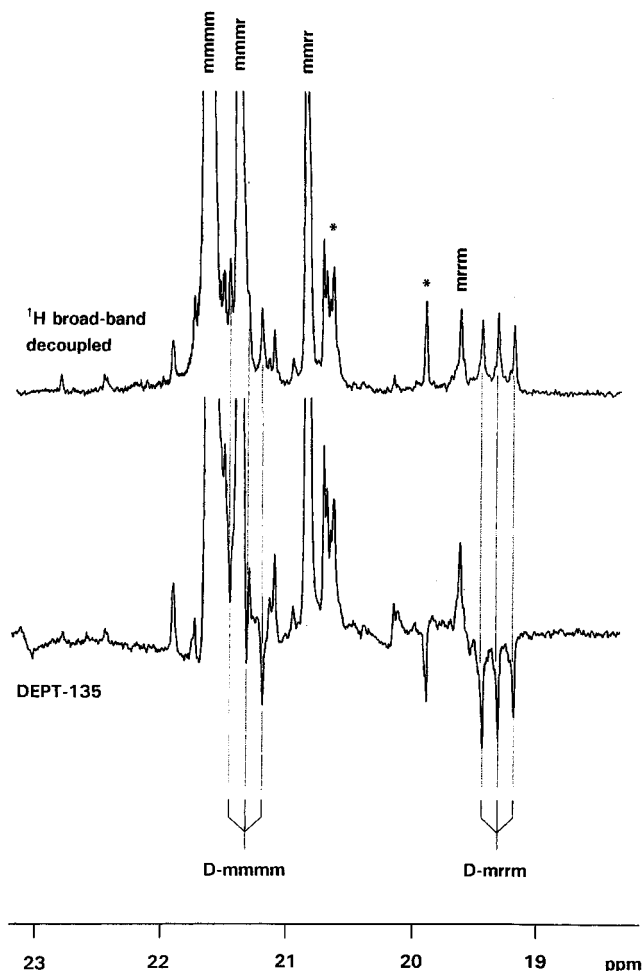
Figure 1. ^{13}C NMR spectra (pentad region) of poly((Z)-[1-D]propene) produced with C$_2$H$_4$(thind)$_2$ZrCl$_2$-MAO at 50 °C, measured at 150 MHz on a Bruker DRX 600 spectrometer in ^{1}H broad-band decoupled (top) and DEPT 135 (bottom) NMR modes. Asterisks denote CH$_2$ and CH$_3$ signals associated with *n*-propyl chain ends and 3,1-misinsertions, respectively.

Results and Discussion

1. D-Label Distribution in the Poly([1-D]propene) Chain. When (E)- or (Z)-[1-D]propene is polymerized with the catalyst system C$_2$H$_4$(thind)$_2$ZrCl$_2$-MAO, the isotactic polymer chains contain, as expected, CHD instead of CH$_2$ groups in their polymer backbone, recognizable by ^{13}C NMR triplet signals in the region of 45.4−45.8 ppm. Additional changes are apparent in the pentad region of the ^{13}C NMR spectra of these polymers: Instead of the catalytic-site controlled 2:2:1 distribution of mmmr, mmrr, and mrrm pentad signals observed with undeuterated propene, one finds a mrrm pentad signal with an intensity reduced to about one-quarter of the expected size and slightly upfield from it, a 1:1:1 triplet with $J = 19$ Hz, which signals the presence of a D atom in stereoinverted methyl groups (Figure 1).

Support for an interchange of CHD and mm-centered CH$_3$ groups for CH$_2$ and rr-centered CH$_2$D groups (cf. Scheme 1), is derived from a splitting of the mmrr signal into two barely resolved signals of equal intensity in poly((E)-[1-D]propene) and by its broadening in poly((Z)-[1-D]propene):[23] The rearrangement represented in Scheme 1 implies that the two mr-centered CH$_3$ groups adjacent to a rr-centered CH$_2$D group are inequivalent, the one closer to the metal center being flanked by a CH$_2$ and a CHD group rather than by two CHD groups.

(23) Different gauche effects caused by the unequal configurations of the flanking CHD groups are the most likely cause of this difference.

Table 1. Degree of Polymerization, P_N, and Pentad Distribution (in %) for Polypropene Obtained from (E)-[1-D]- and (Z)-[1-D]Propene (1 bar, 0.33 mol/L^a) with Catalysts **1-4**^{c}

catalyst/monomer (polym, temp °C)	P_N	mmmm	mmrr	mrrm (rr-CH$_3$)	D-mrrm (rr-CH$_2$D)
1/(E)-[1-D] (30)	134	82	7.2	1.4	2.2
1/(Z)-[1-D] (30)	101	79	8.4	1.2	3.0
1/(E)-[1-D] (53)	78	52	19.2	2.7	6.9
1/(Z)-[1-D] (53)	45	47	21.2	3.5	7.1
2/(E)-[1-D] (50)	59	87	5.2	0.8	1.8
2/(Z)-[1-D] (50)	46	86	5.6	1.0	1.8
3/(E)-[1-D] (50)	124	>98	<1	<0.5	<0.5
3/(Z)-[1-D] (50)	94	>98	<1	<0.5	<0.5
4/(E)-[1-D] (54)	b	95	2.0	1.0	0
4/(Z)-[1-D] (54)	b	95	2.0	1.0	0

^{a} Solubility data: ref 18b. ^{b} Not determinable by ^{13}C NMR; $P_N \approx$ 700 ± 50 by GPC. ^{c} Polymerization conditions: [Zr] = 1.5·10^{-5} M for catalysts **1-3**, 2.5·10^{-6} M for catalyst **4**; [Al] = 0.045 M.

Table 2. Degree of Polymerization, P_N, and Pentad Distribution (in %) for Poly((E)-[1-D]propene) Obtained with C$_2$H$_4$(thind)$_2$ZrCl$_2$/MAO (Catalyst **1**) at 30 °C at Different Monomer Pressures^a

p(C$_3$H$_5$D), bar	c(C$_3$H$_5$D), mol/L^c	P_N	mmmm	mmrr	mrrm (rr-CH$_3$)	D-mrrm (rr-CH$_2$D)
0.9^b	0.42	140	73	11	1.4	3.9
2^c	0.99	290	80	8.0	1.2	2.8
3^c	1.58	440	84	6.4	1.2	2.0

^{a} Other conditions are as in Table 1. ^{b} Total pressure, including the vapor pressure of toluene at 30 °C. ^{c} Partial pressure of C$_3$H$_5$D, added to the catalyst solution under 1 bar of Ar. ^{d} c(C$_3$H$_5$D) $\approx$ (p(C$_3$H$_5$D)/bar − 0.1)0.53 mol/L (from data in refs 18b and 22).

Additional signals are apparent in the ^{13}C-NMR spectra of poly((E)- and (Z)-[1-D]propene) close to the mmmm pentad signal. The DEPT spectrum shows three signals of equal intensity, with an equidistant spacing of 19 Hz and with inverted sign, centered 0.3 ppm upfield of the mmmm pentad signal (Figure 1). These characteristics indicate that poly((E)- and (Z)-[1-D]propene) contain also *stereoregular*, mm-centered CH$_2$D units. The intensities of these D-mmmm signals are similar to those of the D-mrrm signals discussed above. These and other analytical data of the polymers obtained from (E)- and (Z)-[1-D]propene (Table 1) will be further discussed below.

2. Effects of Monomer Concentration and Catalyst Composition. In order to ascertain the origin of the CH$_2$D groups found in these polymers, we have studied the effects of changing monomer concentrations on the D-label distribution. Polymers obtained with the catalyst system C$_2$H$_4$(thind)$_2$ZrCl$_2$-MAO (catalyst **1**) (30 °C) at (E)-[1-D]propene pressures ranging from 0.9 to 3 bar yield the data listed in Table 2.

In accord with earlier observations on undeuterated polypropenes,[20−22,24] isotacticities and chain lengths are found to increase with increasing CHD=CHCH$_3$ pressure. The increase in isotacticity with increasing monomer pressure is clearly due to a decrease of the fraction of stereoerrors associated with the rr-CH$_2$D triplet centered at 19.35 ppm. The fraction of undeuterated rr-triads, on the other hand, is found to be essentially constant at [mrrm] $\approx$ 1.2−1.4%, independent of the propene pressure. This is in accord with the view[20−22] that a relatively low fraction of "intrinsic" stereoerrors is caused by faulty enantiofacial olefin insertions and that these intrinsic errors are superimposed by increasing fractions of isomerization-induced stereoerrors when olefin insertion rates are decreased by reduced monomer concentrations.

Further insights with regard to the competition between olefin insertion and chain-end isomerization can be obtained from a

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Table 3. Degree of Polymerization, P_N, and Pentad Distribution (in %) for Undeuterated Polypropene and Poly([2-D]propene) Obtained with Catalyst **1** at 30 and 50 °C[a]

monomer (polym temp, °C)	P_N	mmmm	mmrr	mrrm (rr-CH$_3$)	D-mrrm (rr-CH$_2$D)
D$_0$-propene (30)	124	84	6.4	3.2	0
2-D-propene (30)	188	95	2.0	1.0	<0.5
D$_0$-propene (50)	73	61	15.5	8.0	0
2-D-propene (50)	110	84	6.4	1.0	2.2

[a] Other conditions are as in Table 1.

comparison of different ansa-zirconocene catalyst (Table 1): essentially analogous isotactities and D-label distributions as with catalyst **1** are found with Me$_2$Si(2,4-Me$_2$-C$_5$H$_2$)$_2$ZrCl$_2$-MAO (catalyst **2**). The catalyst system Me$_2$Si(2-Me-4-*t*Bu-C$_5$H$_2$)$_2$ZrCl$_2$-MAO (catalyst **3**), on the other hand, produces polymers which are so highly isotactic that it is barely possible to detect any error pentad signals.[16] Accordingly, no triplet signal due to mrrm-CH$_2$D groups is discernible in poly((*E*)- or (*Z*)-[1-D]propene) made with this catalyst.

Catalyst **4**, Me$_2$Si(2-Me-benz[*e*]indenyl)$_2$ZrCl$_2$-MAO, finally, yields polymers with an isotacticity of [mmmm] ≈ 95% even at higher polymerization temperatures. In poly((*E*)- or (*Z*)-[1-D]propene) prepared with this catalyst, the mrrm error pentad signals are clearly discernible, however, and in fact indistinguishable with regard to its relative intensity from that in undeuterated polypropene prepared with catalyst **4**; we can thus exclude that any significant fraction of the rr-centered CH$_3$ groups of these polymers carry a deuterium atom. In accord with the isotacity data obtained by Cipullo and Busico,[20] olefin insertion appears to occur so fast in this highly active catalyst system even at a low monomer pressure of 0.5 bar that chain-end isomerization cannot significantly compete with it.

DEPT NMR spectra of poly((*E*)- or (*Z*)-[1-D]propene), made with either catalyst **3** or catalyst **4**, do not show any D-labeled satellites of the mmmm pentad signal. We regard this as evidence that the mm-centered CH$_2$D groups of polymers made with catalyst **1** arise only in connection with the chain-end isomerization discussed above and not, for example, by an isomerization of free [1-D]propene to [3-D]propene.

3. Polymers obtained from [2-D]propene. Polymerizations of β-deuterated propene with C$_2$H$_4$(thind)$_2$ZrCl$_2$-MAO (catalyst **1**) have recently been studied by Busico and co-workers.[21] In accord with their observations, we find that poly([2-D]propene) has a substantially higher isotacity than undeuterated polypropene produced under identical conditions (Table 3). In the ^{13}C NMR spectra of poly([2-D]propene) one observes, besides the expected methine C−D signals in the range of 27.8−28.3 ppm, again the triplet at 19.35 ppm, associated with stereoinverted CH$_2$D groups. The β-D atom in a ZrCH$_2$CD(CH$_3$)-pol unit is thus obviously shifted to the newly formed methyl group during the chain-end isomerization process. As noted by Busico and co-workers, this can be taken as evidence that the isomerization reaction proceeds *via* a tertiary intermediate of the type ZrCMe$_2$-pol.[21]

In addition to these rr-centered CH$_2$D groups, however, we also observe here— as in poly((*E*)- and (*Z*)-[1-D]propene)—an additional negative DEPT triplet of similar intensity 0.3 ppm upfield of the mmmm pentad. Stereoregular, mm-centerd CH$_2$D groups are thus clearly present also in these poly([2-D]propene) samples. As discussed in more detail below, this observation is not easily explicable in terms of the reaction mechanisms commonly considered for metal−alkyl isomerizations.

As noted above (Table 4), the isotacticity of poly([2-D]propene) is substantially higher than that of undeuterated polypropene or of poly((*E*)- or (*Z*)-[1-D]propene). This appears

to be entirely due to a diminished rate of isomerization: While the relative integrals of the undeuterated mrrm pentad signals due to "intrinsic" stereoerrors in poly([2-D]propene) are, with 1.0−1.4%, quite close to those observed in poly([1-D]propene) obtained under the same conditions, a substantially reduced probability of isomerization-induced stereoerrors is apparent from the reduced fraction of D-mrrm pentads: In poly([2-D]-propene) prepared with catalyst **1** at 30 °C for instance, the triplet signal due to stereoinverted CH$_2$D groups is hardly detectable; accordingly, the isotacticity almost reaches its "intrinsic" value of [mmmm] ≈ 95% here. For poly([2-D]-propene) prepared at 50 °C, the rate of chain-end isomerization appears to be only about one-third of that for undeuterated polypropene or poly([1-D]propene) obtained with catalyst **1** at the same temperature. These data lead to the estimate that an isotope effect of k_H/k_D ≈ 3 is associated with the breakage of the β-C-H/D bond in the rate-limiting step of the isomerization process.[25]

An isotope effect is also evident with regard to the reactions which control the chain lengths of these polymers: Both at 30 and 50 °C, the mean degree of polymerization, P_N, of poly([2-D]propene) is higher by a factor of 1.5−1.6 than that of undeuterated polypropene (Table 4). This isotope effect is undoubtedly connected with the rate-determing step of the chain termination reaction (cf. section 4).

4. D-Label Distribution in the Unsaturated Chain End. The control of chain lengths is an important aspect for the practical utilization of ansa-zirconocene-based polymerization catalysts; it would thus appear useful to clarify the details of the underlying chain-termination reactions. We have thus extended our present D-label distribution study also to an investigation of the reaction paths which generate the unsaturated chain ends of these polymers.

In polypropene prepared with C$_2$H$_4$(thind)$_2$ZrCl$_2$-MAO or related catalyst systems, 2-propenyl units are the dominant end groups resulting from chain termination;[26] they arise by β-H transfer either to the metal center or to a coordinated olefin (Scheme 2).[18,27] In either case, the cis-stereochemistry of olefin insertion and β-H transfer reactions predicts that poly((*E*)-[1-D]propene) should have a [1-D]-2-propenyl end group with its D-atom trans to the polymer chain (**A**), while poly((*Z*)-[1-D]-propene) is expected to have a propenyl end group with cis-

(25) A primary KIE of k_H/k_D = 2.0 has been observed for the β-H transfer reaction Cp$_2$ZrCH$_2$CH$_2$D(NCCH$_3$) → Cp$_2$Zr(H,D)(NCCH$_3$) + CH$_2$CH-(H,D): Alelyunas, Y. W.; Guo, Z.; LaPointe, R. E.; Jordan, R. F. *Organometallics* **1993**, *12*, 544. Related isotope effects: Evans, J.; Schwartz, J.; Urquhart, P. W., *J. Organomet. Chem.* **1974**, *81*, C37. Alibrandi, G.; Scolaro, L. M.; Minniti, D.; Romeo, R. *Inorg. Chem.* **1990**, *29*, 3467. Negishi. E. I; Nguyen, T.; Maye, J. P. Choueiri, D. Suzuki, N.; Takahashi, T. *Chem. Lett.* **1992**, 2367.

(26) Not detectable in the polymers considered here are end groups derived from β-methyl transfer (Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147. Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998; Horton, A. D. *Organometallics* **1996**, *15*, 2675), from C-H activation of the monomer (Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Stevens, J.; Richardson, D. E.; Ryan, M. *Makromol. Chem. Macromol. Symp.* **1993**, *66*, 215), or from β-H transfer from a secondary unit (Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 3356; refs 18b and 22). Isopropyl signals arising from alkyl exchange between Zr and Al centers (Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489; Mogstad, A. L.; Waymouth, R. M. *Macromolecules* **1992**, *25*, 2282; refs 22, 24a) occur with an intensity of ca. 30% of *n*-propyl end groups in polymers made with catalyst **1** and about equally frequent as *n*-propyl end groups in polymers made with catalyst **3** (cf. ref 16). Occasionally, 2-propenyl end groups are observed to isomerize to 1-isobutenyl groups (presumably by traces of acid) during ^{13}C NMR measurement in C$_2$D$_4$Cl$_2$ at temperatures above 100 °C.

(27) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428. Busico, V.; Cipullo, R.; Corradini, P. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 97. Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudmeijer, O. *Macromolecules* **1994**, *27*, 7538.

Table 4. End Group Distribution (in %) in Polymers Obtained from (*E*)-[1-D]-, (*Z*)-[1-D]-, and [2-*D*]Propene with Catalysts **1** and **3**[a]

catalyst/monomer	monom pressure, ar (polym temp, °C)	integral ratios of signals at various ppm				end group ratios		
		4.72	4.70	4.64	4.62	**A**	**B**	**C**
1/(*E*)-[1-D]	1 (50)	0.99	0.28	1	0.70	36	14	50
1/(*E*)-[1-D]	2 (50)	0.98	0.31	1	0.80	38	15	47
1/(*Z*)-[1-D]	1 (50)	0.98	0.88	1	0.27	13	41	46
1/2-D	1 (30)	1	<.03	1	<.03	<3	<3	>95
1/2-D	1 (53)	1	0.1	1	0.1	8	8	84
3/(*E*)-[1-D]	0.75 (50)	0.99	0.24	1	0.35	22	15	63
3/(*Z*)-[1-D]	0.75 (50)	0.96	0.19	1	0.17	13	14	73

[a] Conditions as in Table 1.

Scheme 2
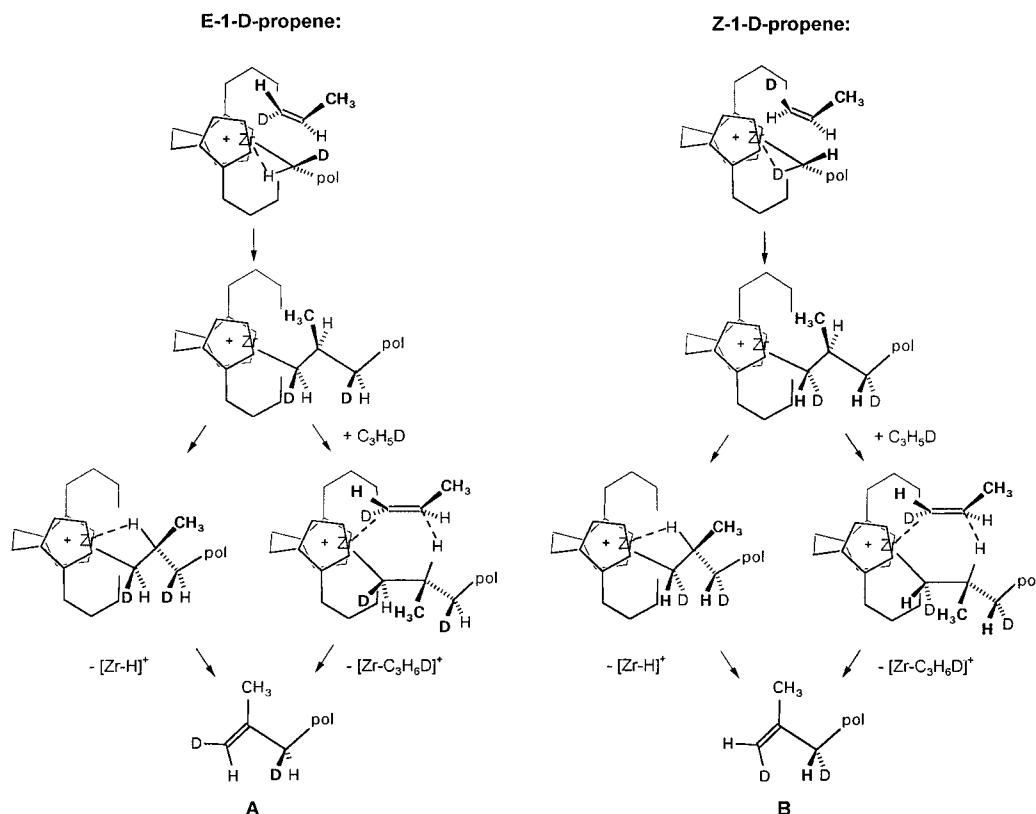
deuterated geometry (**B**). The HDC terminus of both end groups appears in the ^{13}C NMR spectra of poly((*E*)- or (*Z*)-[1-D]-propene) as a 1:1:1 triplet with $J = 19.6$ Hz at 111.0 ppm. In addition, however, the signal of the undeuterated CH_2 terminus is also apparent at 111.3 ppm. Some D-atom redistribution is thus obviously involved also in the generation of these unsaturated end groups.

In order to assign possible isotopomers, we have undertaken an analysis of the ^{1}H NMR signals associated with 2-propenyl end groups. Two-dimensional HMQC and ROESY spectra of undeuterated polypropene and of poly((*E*)- and (*Z*)-[1-D]-propene) samples, discussed in detail in the Experimental Section, lead to the assignment summarized in Figure 2. For each of the protons at the CH_2 terminus, the signal is shifted upfield by ca. 0.02 ppm, to 4.70 and 4.62 ppm, when a D atom occupies the opposite terminal position (Figure 3). The ratios of the different end group isotopomers can thus be estimated from the relative intensities of these signals: The weights of end groups **A** and **B** are measured by the integrals of the signals at 4.62 and 4.70, respectively, while that of end group **C** is obtained from the averaged integral of the signals at 4.64 and 4.72 ppm.

The ^{1}H NMR spectra of polymers obtained from either (*E*)- or (*Z*)-[1-D]propene (Figure 3) show that both polymers contain
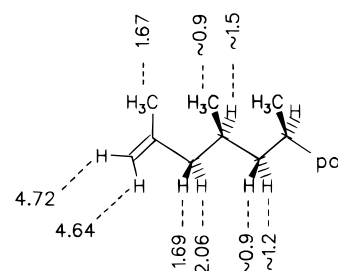
Figure 2. ^{1}H NMR signal assignments (δ in ppm) for unsaturated 2-propenyl chain ends (cf. Experimental Section).

all three types of unsaturated end groups, i.e. trans- and cis-HDC=CMe-pol (**A** and **B**) as well as H_2C=CMe-pol (**C**). Most of the D-label content missing in the terminal positions of H_2C=CMe-pol appears to be associated with the methyl group of this unit, as indicated by a partial replacement of the ^{13}C NMR signal of the 2-propenyl methyl group at 22.5 ppm by a triplet with $J \approx 19$ Hz, centered at 22.2 ppm. The D-label content of the ZrCHDCHMe unit thus appears to be mostly redistributed among its three C atoms during β-H transfer, rather than being lost from it.[28]

The proportions of the three isomeric end groups **A**, **B**, and **C** are found to be different for polymers derived from (*E*)-[1-

Scheme 3
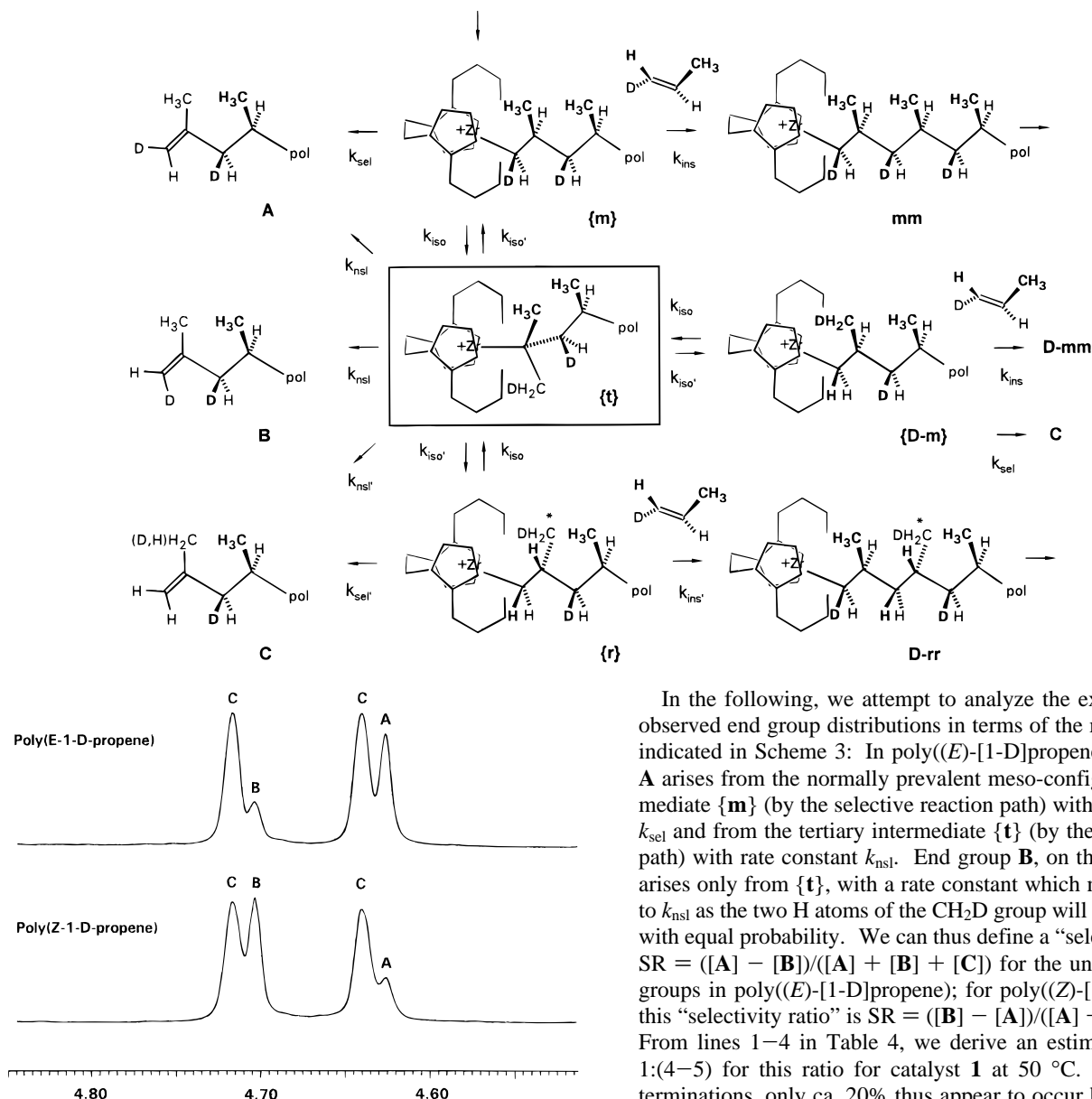
Figure 3. ¹H NMR spectra (olefin region) of poly((E)-[1-D]propene) (top) and poly((Z)-[1-D]propene) (bottom). Assignments according to Scheme 3.

D]propene and from (Z)-[1-D]propene: As expected from the reaction sequences outlined in Scheme 2, end group **A** is more frequent with poly((E)-[1-D]propene) while **B** prevails with poly((Z)-[1-D]propene) (Table 4).

Two different reaction paths for β-H transfer apparently compete with each other: One leads stereoselectively to the expected products while the other involves a scrambling of D-atoms within the last-inserted unit. At the propene pressures studied, the stereoselective β-H transfer path appears to account only for a minor part of the unsaturated end groups. The dominant D-scrambling reaction path, on the other hand, appears to be related to the isomerization which causes the formation of stereoerrors: An intermediate ZrC(CH₃)(CH₂D)-pol, arising by a migration of Zr to the tertiary C atom, would be expected to generate end groups **A**, **B**, and **C** with comparable probability (Scheme 3).

In the following, we attempt to analyze the experimentally observed end group distributions in terms of the rate constants indicated in Scheme 3: In poly((E)-[1-D]propene), end group **A** arises from the normally prevalent meso-configurated intermediate {**m**} (by the selective reaction path) with rate constant k_{sel} and from the tertiary intermediate {**t**} (by the nonselective path) with rate constant k_{nsl}. End group **B**, on the other hand, arises only from {**t**}, with a rate constant which must be equal to k_{nsl} as the two H atoms of the CH₂D group will be eliminated with equal probability. We can thus define a "selectivity ratio" SR = ([**A**] − [**B**])/([**A**] + [**B**] + [**C**]) for the unsaturated end groups in poly((E)-[1-D]propene); for poly((Z)-[1-D]propene) this "selectivity ratio" is SR = ([**B**] − [**A**])/([**A**] + [**B**] + [**C**]). From lines 1−4 in Table 4, we derive an estimate of SR ≈ 1:(4−5) for this ratio for catalyst **1** at 50 °C. Of all chain terminations, only ca. 20% thus appear to occur by direct β-H transfer. This ratio does not appear to vary substantially with propene pressure.

End group **C**, finally, arises mainly from the tertiary intermediate {**t**}, with a rate constant $k_{nsl'}$.[29] For the latter, one can estimate, from a minor secondary isotope effect of 1.05−1.1, that the reaction is likely to favor transfer of a β-H atom from a CH₃ over that from a CH₂D group[30] and, from a statistical choice of three H atoms, a ratio of $k_{nsl'}/k_{nsl} \approx 3.2$. The close accord of this estimate with the ratio of [**C**]/[**B**] ≈ (3.1−3.5) found for poly((E)-[1-D]propene) and of [**C**]/[**A**] ≈ 3.5 for poly-((Z)-[1-D]propene) (cf. Table 4) confirms the chain-termination sequence represented in Scheme 3.

The validity of this reaction sequence is further supported by end group distributions for poly([2-D]propene) (Table 4): At 30 °C, where no isomerization is apparent for poly([2-D]-propene), deuterium is not incorporated to any noticeable degree into the 2-propenyl end group either. At 50 °C, where deuterium

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(28) We find no signs that extra D atoms would be incorporated into position 2 of the *n*-propyl end group by Zr−D units arising from abstraction of β-D atoms.

(29) The low fraction of intermediates {**d-r**} and {**d-m**}, multiplied by the relatively small rate constants $k_{nsl'}$ and k_{sel} make any additional contributions to the formation of **C** negligeable.

(30) Secondary kinetic isotope effects on β-H transfer and related reactions: Schröder, D.; Schwarz, H. *Chimia* **1989**, *43*, 317. Poirier, R. A.; Wang, Y.; Westaway, K. C. *J. Am. Chem. Soc.* **1994**, *116*, 2526.

is transferred into rr-centered CH_2D groups, it also appears in the terminal positions of the 2-propenyl end group. Nonselective formation of end groups **A** and **B** can occur here only from {**t**}, with rate constant k_{nsl}. Comparison with the data for (E)- and (Z)-[1-D]propene shows that isomerization of {**m**} to {**t**} is less frequent than in poly([1-D]propene) by a factor of ca. 1.7, undoubtedly due to a retardation of β-D vs β-H transfer.[25]

A related kinetic isotope effect is probably also responsible for the increased P_N values of poly([2-D]propene) mentioned above. This increase in P_N could in principle reflect an increase in k_{ins} or a decrease in k_{sel} and/or k_{iso} for the 2-deuterated olefin. Of these, k_{ins} (the rate constant of olefin insertion) is unlikely to be influenced to any substantial degree by β-deuteration of the monomer.[30] The rate constants which control the rate of chain termination, k_{sel} and/or k_{iso}, thus appear to be associated with a kinetic isotope effect of $k_H/k_D = 1.5-2$, as one would expect if a β-H transfer limits the rates of these reactions.[25]

The increase of the mean degree of polymerization, P_N, with increasing monomer concentrations, [M], observed for catalyst **1** (Table 2, cf. refs 20, 22, and 24), is explicable by a rate of polymer growth proportional to [M], $v_P = k_{ins}$[M], and a monomer-independent rate of chain termination by the predominant route via intermediate {**t**}. This would imply that isomerization of {**m**} to {**t**} occurs by way of a species which does not contain a coordinated olefin, presumably via β-H transfer to the metal (vide infra). Because of the still unclarified significance of a higher-order dependence of the rate of polymer growth on [M] ($v_P \approx k_{ins}$[M]^n with $n \approx 1.5-2$) reported for this and related catalysts,[18,22] the numbers of olefin molecules participating in each of the competing reactions in Scheme 3 will eventually require further elaboration.

Phenomenologically, anyhow, we can delineate the fate of the preponderant intermediate {**m**}, e.g. at 50 °C, if we take the reciprocal mean degree of polymerization, $(P_N)^{-1}$, as the frequency of chain terminations and the "'nonselectivity" ratio NR = 1 − SR = ([**C**] + 2[**B**])/([**A**] + [**B**] + [**C**]) $\approx$ 0.75 as the fraction of unsaturated end groups arising via {**t**}. From the frequency of stereoselective end groups (SR$(P_N)^{-1}$) on the one hand and from the sum of the frequencies of nonstereoselective end groups (NR$(P_N)^{-1}$) and of **D-rr** and (equally frequent) **D-mm** units on the other (Tables 1 and 4), we estimate that {**m**} is channelled toward stereoselective chain termination, toward isomerization, and toward chain growth in a ratio of $k_{sel}:k_{iso}:\{k_{ins}$[M]$\} \approx (0.028 \pm 0.007):1:\{(16.7 \pm 0.5)$[M]$\}$. Isomerization to {**t**} thus appears to occur 30−40 times more frequently than chain termination by direct β-H transfer.

As for the further fate of intermediate {**t**}, alternative chain terminations via β-H transfer from the CH_3 and CH_2D groups and chain-end isomerization to intermediates {**D-r**} and {**D-m**} compete with each other. From the data in Tables 1 and 4 we can estimate for the rate constants k_{nsl}, $k_{nsl'}$, and $k_{iso'}$—which govern the distribution of {**t**} toward end groups **A** and **B**, toward **C**, and toward intermediates {**D-r**} and {**D-m**}, respectively—a ratio of $k_{nsl}:k_{nsl'}:k_{iso'} \approx 1:(3.5 \pm 0.1):(32 \pm 8)$ for catalyst **1**. The tertiary intermediate {**t**} will thus give rise to intermediates {**D-r**} and {**D-m**} 10−15 times more frequently than to an unsaturated chain end.

For $Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{Bu-}C_5H_2)_2ZrCl_2$-MAO (catalyst **3**), the difference between [**A**] and [**B**] is too small for a reliable determination of k_{sel}. For this catalyst we can assume that chain termination almost always occurs via chain-end isomerization; the data in Table 1 thus lead to the estimate that intermediate {**m**} is channelled here to {**t**} and to chain growth in a ratio of $k_{iso}:(k_{ins}$[M]$) \approx 1:\{(320 \pm 50)$[M]$\}$. In this sterically encumbered catalyst system, isomerization appears to be disfavored

relative to chain growth by a factor which is ca. 20 times larger than for catalyst **1**.

The further fate of intermediate {**t**} is also different from that in catalyst **1** where isomerization of {**t**} to {**D-r**} or {**D-m**} occurs 10−15 times more frequently than generation of chain ends **A**, **B**, or **C**: Catalyst **3** generates almost no stereoerrors at all (Table 1) but high proportions of nonstereoselective end groups (Table 4). Any intermediate {**t**} formed with catalyst **3** thus appears to undergo chain termination exclusively, rather than further isomerization to a {**D-r**}- or {**D-m**}-configured Zr-alkyl unit. Again, the bulky ligand substituents appear to impede chain-end isomerization relative to competing reaction modes.

In catalyst **4**, finally, intermediate {**m**} appears to escape from β-H transfer and chain-end isomerization, probably due to an exceptionally high rate of olefin insertion. It remains to be understood through which mechanisms different complex structures affect the relative rates of competing reaction modes of intermediates {**m**} and {**t**}.

Conclusions

As shown above, stereoerror distributions as well as polymer chain lengths of polyolefins produced by a particular ansa-zirconocene catalyst will be determined by the rate of chain-end isomerizations, relative to that of olefin insertion and of chain-termination by β-H transfer. It would thus be of substantial interest to clarify the mechanisms and rate-limiting factors of these isomerization reactions.

The mechanism most frequently considered for an isomerization of metal−alkyl units is β-H elimination to a metal−hydride−olefin complex, rotation of the olefin ligand around the metal−olefin bond, and reinsertion to form the rearranged metal−alkyl unit.[31] This mechanism has been proposed to account, for example, for the rearrangement of 2,1-regioinverted units to n,1-units, which competes with olefin insertion into the secondary Zr−alkyl bond,[15,20,32] as well as for related migrations of Ni and Pd centers along metal-bound polymer chains in the formation of 2,ω-polyolefins and branched ethene polymers.[33,34] Busico and co-workers have proposed that such a reaction sequence is operative also for the chain-end isomerizations discussed here (Scheme 4).[20,21]

This reaction sequence would plausibly explain the formation of stereoinverted **D-rr** units in poly([1- and 2-D]propene), as well as the kinetic isotope effect caused by a β-D atom at the tertiary carbon center. It is not apparent, however, how this reaction sequence could explain the occurrence of stereoregular, mm-centered CH_2D groups (**D-mm** units) observed in poly-((E)- and (Z)-[1-D]propene) as well as in poly([2-D]propene): for this rearrangement, the Zr-H fragment would have to move from one enantioface of the olefin ligand H_2C=$C(CH_2D)$-pol to the other (Scheme 4).[35] Once lost from the Zr-center,

(31) Cramer, R. *Acc. Chem. Res.* **1968**, *1*, 186. Hartley, F. R. *Chem. Rev.* **1969**, *69*, 799. Whitesides, G. M.; Gaasch, J. F. Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

(32) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 305. Grassi, A.; Ammendola, P.; Longo, P.; Albizzati, E.; Resconi, L.; Mazzocchi, R. *Gazz. Chim. Ital.* **1988**, *118*, 539. Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Makromol. Chem.* **1989**, *190*, 1177. Asakura, T.; Nakayama, N.; Demura, M.; Asano, A. *Macromolecules* **1992**, *25*, 4876.

(33) Möhring, V. M.; Fink, G. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1001.

(34) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(35) To test for the possibility that isomerization of the monomer, CHD=CHCH$_3$ → CH$_2$DCH=CH$_2$, gives rise to **D-mm** units, we have conducted a polymerization with catalyst **1**/MAO (conditions as in Table 1) in which the pressure of (Z)-[1-D]propene was allowed to fall below 1

Scheme 4
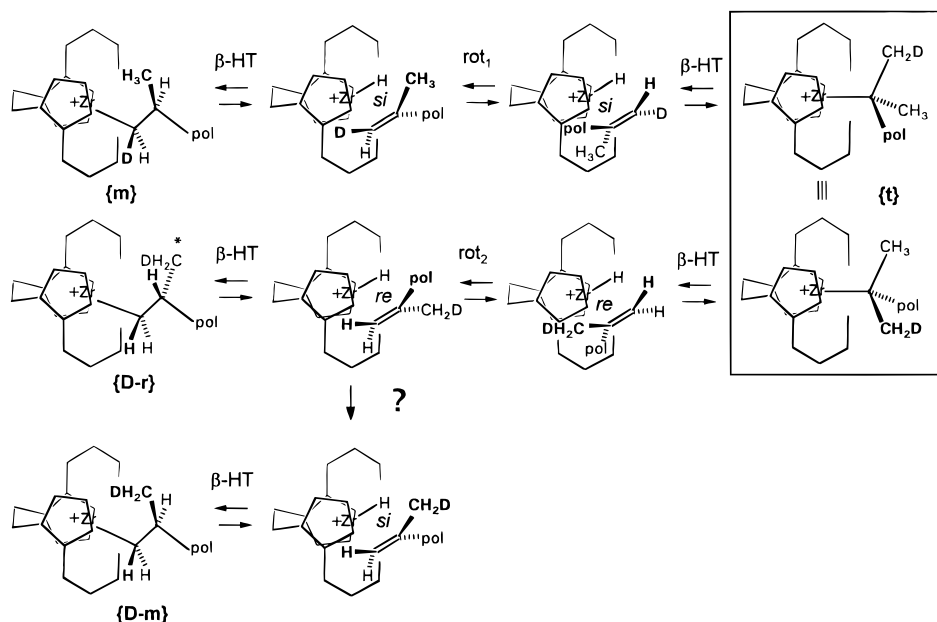
however, the disubstituted olefin $H_2C=C(CH_2D)$-pol would hardly be capable of competing with the large excess of propene present for reinsertion into the Zr—H unit.[36]

Equally puzzling is the question why isomerization of intermediate {t}, while producing equal fractions of **D-rr** and **D-mm** units, does not also lead to equal fractions of undeuterated **rr** (as well as **mm**) units. As discussed above, undeuterated **rr** units are found only in minor amounts and appear to be derived from faulty olefin insertions rather than from chain-end isomerizations. Substantial further experimental and theoretical studies are obviously required to ascertain through which reaction sequences these chain-end isomerizations do actually proceed.

Experimental Section

General. All operations were performed in an inert atmosphere with rigorous exclusion of oxygen and moisture using Schlenk, vacuum-line, or glovebox techniques. Solvents were thoroughly dried (ether and THF over Na/benzophenone, toluene over Na) and distilled prior to use. Lithium metal contained 1.3% sodium.

(Z)-[1-D]Propene. A 11.3 g (0.342 mol) sample of MeOD was added to 13.7 g (0.298 mol) of propynyllithium (from propyne and ^nBuLi); the [1-D]propyne thus generated was added to a suspension of dicyclohexylborane[37] in diethyl ether at −50 °C. The mixture was stirred for 4 h while the temperature was allowed to rise to −10 °C. After complete dissolution of the white solid, the solvent was removed in vacuum. The resulting dicyclohexyl[1-D]propen-1-ylborane was dissolved in 150 mL toluene and cooled to −20 °C. (Z)-[1-D]propene was liberated by adding 22 g (0.37 mol) of acetic acid and condensed through a cold trap (−50 °C) into a storage vessel at −196 °C to yield 7.3 g (0.17 mol, 57%). The ^{2}H NMR spectrum showed a purity of 94% for the (Z)-isomer ($\delta = 4.98$ ppm for the (E)-isomer, 5.08 ppm for the (Z)-isomer, in CHCl_3).

(E)-[1-D]Propene. (E)-1-Chloro-1-propene (54 g, 0.71 mol) was added to freshly cut lithium (15 g, 2.16 mol) in 300 mL of ether at

−10 °C. After stirring for 3 h, the mixture was filtered and the filtrate evaporated to dryness. The resulting white solid (25 g, 0.527 mol) was suspended in 150 mL of toluene. At 0 °C, 22 g (0.67 mol) of MeOD was added; the gas evolved was condensed through a cold trap (−50 °C) into a storage vessel at −196 °C to yield 12 g (0.279 mol, 39%). The ^{2}H-NMR spectrum showed that the product contained 98% (E)-[1-D]propene and 2% (Z)-[1-D]propene.

[2-D]Propene. 2-Bromopropene (62 g, 0.52 mol) was added to freshly cut lithium metal (13 g, 1.87 mol) in 600 mL of ether at 0 °C under exclusion of light. After stirring for 2 h, the mixture was filtered, the filtrate evaporated to dryness, and the solid residue suspended in 150 mL of toluene. At 0 °C, 29 g (0.88 mol) of MeOD was added; the gas evolved was collected through a cold trap at −50 °C in a storage vessel kept at −196 °C to yield 17 g (0.395 mol, 76%). The ^{1}H-NMR spectrum showed complete deuteration at C(2) ($\delta = 5.00$ ppm for *cis*-*H*CH=CDMe, 4.92 for *trans*-*H*CH=CDMe, and 1.70 for H_2C=CDC*H*_3).

Polymerizations and Polymer Analysis. For a typical experiment, 2 mL of a stock solution of the ansa-zirconocene dichloride studied ($c = 1.5 \cdot 10^{-4}$ M in toluene) was added, under an Ar atmosphere, to 17 mL of toluene containing 0.6 mL of a 10% solution of MAO (Witco, MG ≈ 900) in toluene in a 50-mL Schlenk vessel; the mixture was thermostated at 30 °C. After evacuating the vessel to the vapor pressure of toluene, (E)- or (Z)-[1-D]propene or -[2-D]propene was admitted to the specified total pressure. The pressure was monitored and held constant by further additions of monomer by way of an electronically controlled magnetic valve. After 60 min, the polymerization was quenched by addition of 50 mL of methanol and 0.5 mL of concentrated hydrochloric acid. The polymer (typical yield ca. 200 mg) was collected on a filter paper and dried overnight in the air. Polymerization at elevated pressures were carried out analogously in a 100-mL autoclave, but without evacuation of the Ar atmosphere prior to the admission of C_3H_5D; the partial pressure of the latter is indicated in these cases in Table 2.

To determine the polymer microstructure, ^{13}C and ^{1}H NMR spectra were recorded on a JEOL JNM GX400 or Bruker DRX 600 spectrometer. The more soluble polymers with shorter chain lengths, obtained at 50 °C, were measured in CDCl_3 solutions at 303 K to avoid any extraneous chain-end isomerization, e.g. by traces of acid, which is occasionally observed during NMR measurements at temperatures above 100 °C. The less soluble, long-chain polymers were measured in C_2D_2Cl_4 solution at 373 K. Chemical shifts are referenced to residual protons in deuterated solvents (tetrachloroethane-d_2, $\delta = 5.98$ ppm; CDCl_3, $\delta = 7.24$ ppm) for ^{1}H NMR and to the characteristic triplets of tetrachloroethane-d_2 at $\delta = 74.1$ ppm and of CDCl_3 at $\delta = 77.0$ ppm for ^{13}C NMR. Pentad signals were assigned according to literature

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atm. Residual propene, collected after quenching with CH_3OH by condensation into 1 mL of CHCl_3, gave a ^{2}H NMR spectrum indistinguishable from that of an unreacted sample of (Z)-[1-D]propene; no CH_2D signal is apparent above the detection limit of ca. 2−3%.

(36) That a metal can traverse between alkene enantiofaces without dissociation has been observed in chiral rhenium olefin complexes (Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174), but this isomerization requires many hours even at elevated temperatures.

(37) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988; p 422.

data,[32b,38] pentad distributions estimated from the integral ratios of the mmmm and mmrr pentad signals (which are not superimposed by end-group and misinsertion signals), assuming a catalytic-site-controlled ratio of mmmr:mmrr:mrrm ≈ 2:2:1. The relative proportions of undeuterated and deuterated mrrm pentad and chain-end signals were estimated by the cut-and-weigh method and mean degrees of polymerization, P_N, from the integral ratio of all ^{13}C NMR signals in the range of 22.5−19.0 ppm[39] to that of the *n*-propyl end group at 14.3 ppm.

The ^{1}H NMR signals associated with 2-propenyl end groups were assigned as follows: The olefinic protons appear at 4.64 and 4.72 ppm, the CH$_3$ group next to the double bond at 1.67 ppm, and the adjacent CH$_2$ group, finally, has diastereotopic protons of which one gives a signal at 2.06 ppm while the other appears at 1.68 ppm, partly coincident with the multiplet of the CH$_3$ group at 1.67 ppm.[40] This assignment is based on two-dimensional HMQC spectra which show cross peaks for the signals at 4.64 and 4.72 ppm with the ^{13}C resonance at 111.3 ppm, for the signal at 1.69 ppm with the 2-propenyl CH$_3$ ^{13}C signal at 22.5 ppm and for the signals at 2.06 and 1.69 ppm with that of the methine carbon at 45 ppm.[41]

Further assignments given in Figure 2 are derived from a ROESY spectrum of a polypropene sample: The signal at 4.72, which shows cross-relaxation with the CH$_3$ signal at 1.67, is assigned to the H atom cis to this methyl group, while the signal at 4.64 ppm, which shows cross-relaxation with the diastereotopic proton signals of the CH$_2$ group at 2.06 and 1.69 ppm, is assigned to the H atom cis to this CH$_2$ group. The assignment of the two diastereotopic CH$_2$ protons is derived from ^{1}H NMR spectra of polymers made from (*E*)- and (*Z*)-[1-D]propene: In poly((*E*)-[1-D]propene), the combined integral of the signal group at 1.67/1.69 ppm is diminished by about 1 H; in poly((*Z*)-[1-D]propene), the signal at 2.06 ppm is absent. This implies that the signal at 1.69 is due to the proton in the cis position relative to the last *m*-CH$_3$ group in the saw-horse projection shown in Scheme 3, while that at 2.06 is due to the proton trans to this CH$_3$ group.

Supporting Information Available: ^{1}H-, ROESY-, ^{13}C-, and DEPT-NMR-spectra of deuterated and undeuterated polypropene samples (olefinic and pentad regions) (13 pages). See any current masthead page for ordering and Internet access instructions.

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(38) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. Cheng, H. N.; Ewen, J. A. *Macromol. Chem.* **1989**, *190*, 1931.

(39) In this range, each C$_3$H$_6$ unit, including misinsertions and *n*-propenyl and 2-propenyl end groups, has just one CH$_3$ signal.

(40) A COSY spectrum also shows cross signals for the protons at 2.06 and 1.69 ppm with those at 4.64 and 4.72 ppm.

(41) These shift values refer to polypropene solutions in CDCl$_3$; in C$_2$D$_2$-Cl$_4$ solutions, these resonances are shifted to higher fields by ca. 0.08 ppm.