Polymerization of Cyclopentene Using Metallocene Catalysts: Competitive Cis- and Trans-1,3 Insertion Mechanisms

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ABSTRACT: Hydrooligomerization or polymerization of cyclopentene using racemic 1,2-ethylenebis(η^5-indenyl)zirconium dichloride (**1**) and methylaluminoxane leads to the production of poly(*cis*-1,3-cyclopentane). Analogous reactions using racemic 1,2-ethylenebis(η^5-tetrahydroindenyl)zirconium dichloride (**2**) leads to the production of oligomers in which cyclopentene is incorporated in a cis- or trans-1,3 manner. Two plausible mechanisms for trans-1,3 insertion are presented which involve reversible β-hydrogen elimination reactions of unsaturated oligomers or direct interconversion of olefin hydride complexes via the intermediacy of a σ-CH complex. Copolymerization of cyclopentene and 3-cyclopentylcyclopentene-*2-d* (**9**) reveals that the former process can occur but is not competitive with simple copolymerization; this, in combination with other observations, suggests that reversible chain transfer is unlikely to account for trans-1,3 insertion. Polymerization of cyclopentene-d_8 led to significantly different, instantaneous ratios of cis to trans trimers compared with that observed during polymerization of cyclopentene. The observed deuterium isotope effect on stereochemistry, in combination with other work, can be interpreted in terms of trans-1,3 insertion occurring predominantly via the second mechanism.

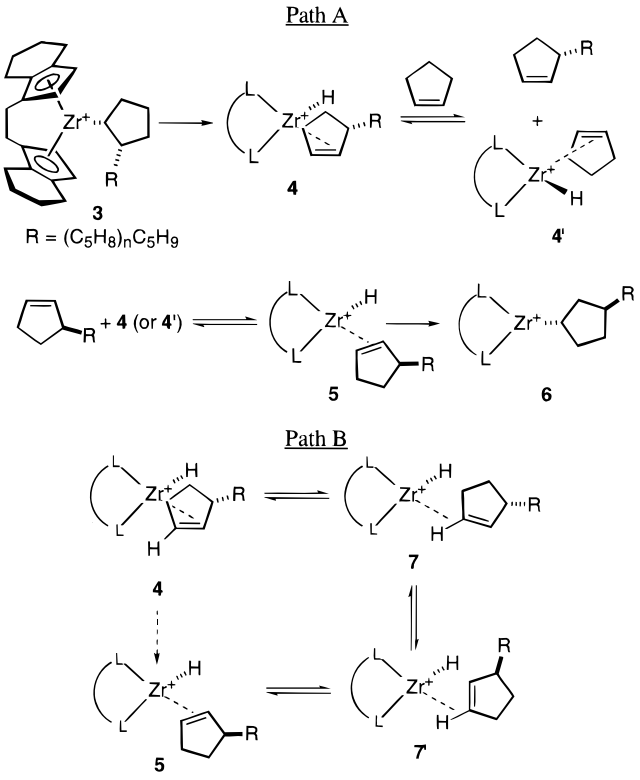
Introduction

Cyclopentene and other cyclic olefins can be polymerized using *rac*-ethylenebis(η^5-indenyl)zirconium dichloride (**1**) in the presence of methylaluminoxane (MAO) cocatalyst to give polymers without detectable ring opening.[1] Previous work involving both polymerization and hydrooligomerization has established that cyclopentene is incorporated in a cis-1,3 manner in which the stereochemical relationship between cyclopentane rings in the polymer and hydrooligomers is isotactic.[2]

When *rac*-ethylenebis(η^5-tetrahydroindenyl)zirconium dichloride (**2**) is employed in the hydrooligomerization or polymerization of cyclopentene, the hydrooligomers or polymer have cyclopentane rings that are incorporated in both a cis-1,3 and trans-1,3 manner, with the relative stereochemistry between rings being dictated by isotactic placements of monomer with respect to the penultimate cyclopentane ring.[2b] This leads to the production of two saturated trimers (cis- and trans-1,3) and four major, saturated tetramers (isotactic, cis,cis, isotactic cis,trans, syndiotactic cis,trans, and syndiotactic trans,trans) under hydrooligomerization conditions.[2b]

The fundamental processes observed in polymerization of simple olefins using metallocene catalysts are now firmly established. With α-olefins (e.g., propylene), propagation consists of repetitive cis-1,2 migratory insertion, and, to a much lesser extent, both cis-2,1 and cis-1,3 enchainments of monomer.[3] Chain-transfer reactions are dominated by β-hydride elimination so as to give terminal unsaturation (i.e., vinylidene end groups),[3b] whereas β-alkyl elimination has also been observed with sterically demanding catalysts.[4] Chain initiation processes involve cis-1,2 insertion of monomer into Zr−H (generated by β-hydride elimination) so as to give saturated *n*-propyl end groups.[3b] More recent work has established that, under starved feed conditions, metallocenes can also act as epimerization catalysts via a reversible β-H elimination/insertion mechanism.[5] Finally, remote C−H activation processes have been implicated in polymerization of 4-methylpentene using sterically hindered metallocene catalysts.[4b]

Scheme 1



The occurrence of trans-1,3 insertion in the polymerization of cyclopentene using catalyst **2** is of fundamental interest. Since concerted trans insertion of an olefin into M−C or M−H bonds is without good precedent in transition-metal chemistry, it is likely that trans-1,3 insertion occurs via an indirect route. Two plausible mechanisms (i.e., those with some literature precedent) that could account for the occurrence of trans-1,3 insertion of cyclopentene are outlined in Scheme 1.

In the first of these (path A, Scheme 1), an olefin hydride complex **4**, produced via β-hydride elimination

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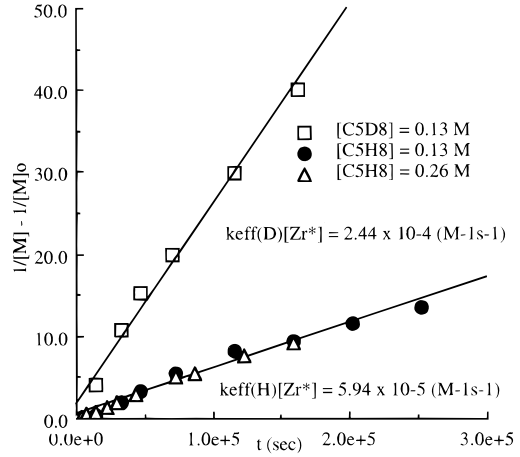


Figure 1. Reciprocal monomer concentration vs time for polymerizations of cyclopentene and cyclopentene-d_8 using catalyst **2** (conditions: toluene solution, 25 °C; $[\mathbf{2}]_0 = 2.5\ \mu$M; [Al]:[**2**] = 1000—raw data are summarized in Table 1).

from **3**, could undergo a displacement reaction by, e.g., monomer. This process would initiate a new polymer chain and produces an oligomer with terminal unsaturation. If the latter product recoordinates to another metal center via its opposite face (to give **5**) and inserts, the resulting stereochemical relationship between the metal and the penultimate cyclopentane ring is now trans-1,3 as in **6**. In essence, the process of trans-1,3 insertion would then involve reversible chain transfer, which has been postulated to occur (with low frequency) in some olefin polymerizations.[6]

An alternative mechanism (path B, Scheme 1), which does not invoke reversible chain transfer, involves indirect isomerization **4** to **5** via the intermediacy of a σ-CH complex **7**. This process has been advanced to account for the observed isomerization of diastereomeric Re—olefin complexes without prior olefin dissociation[7a] and, more recently, has been implicated in isomerization reactions of cationic, ω-(π-alkenyl)alkoxyzirconocene complexes.[7b]

This paper describes our efforts to study the mechanism of trans-1,3 (and cis-1,3) insertion in an attempt to distinguish between these two processes.

Results and Discussion: Polymerization Kinetics

The kinetics of polymerization were studied by GC analyses of quenched aliquots in the presence of an internal standard (*n*-decane). The consumption of monomer does not obey first order kinetics as is typically encountered.[3] Plots of $1/[M] - 1/[M]_0$ vs t (Figure 1) were linear, indicating a second-order dependence of the rate of polymerization on monomer concentration. Experiments at higher monomer concentrations also conformed to this behavior (Figure 1). The implication of this result is that 1,2 insertion of cyclopentene does not occur in the conventional way (i.e., rate-limiting insertion from an olefin alkyl complex) but is triggered by coordination of additional monomer (e.g., eq 1).[8] It is not immediately obvious whether this unusual 1,2 insertion mechanism impacts on the cis/trans-1,3 insertion issue; presumably, the latter two processes occur subsequent to this rate-limiting step.[2]

This mechanism does provide an attractive explanation for the stereochemical control seen in polymerizations of cyclopentene with chiral catalysts that incorporate cyclopentene in a cis-1,3 fashion.[2] As shown in

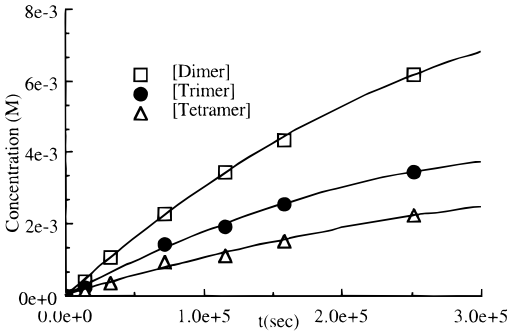
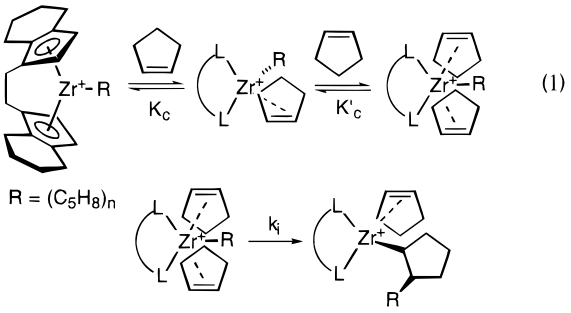


Figure 2. Production of oligomers vs time for polymerization of cyclopentene using catalyst **2** (conditions: toluene solution, 25 °C; [Cp-h_8] = 0.13 M; $[\mathbf{2}]_0 = 2.5\ \mu$M; [Al]:[**2**] = 1000—raw data from Table 1).

eq 1, two molecules of cyclopentene could coordinate to the metal center via the same enantiotopic face (by external comparison) in such a catalyst so as to favor isotactic insertion of either monomer unit.[9]

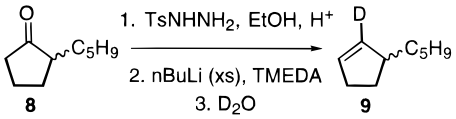


$$-d[M]/dt = K_cK'_ck_i[Zr^*][M]^2 = k_{eff}[Zr^*][M]^2$$

Reversible Chain-Transfer Mechanism. A requirement of the first mechanism for trans-1,3 insertion is that unsaturated oligomers be produced and consumed during the course of the polymerization. Previous work demonstrated that unsaturated oligomers are indeed produced during polymerization of cyclopentene, but this is expected given the low average degree of polymerization observed and the expected molecular weight distribution (i.e., $M_n \sim 620$ using catalyst **2** and $M_w/M_n \sim 2$).[2] In principle, consumption of oligomers should be readily observed by monitoring their concentration during polymerization. As shown in Figure 2, there is no evidence for significant depletion of unsaturated dimer, trimer, tetramer, etc., as a function of time. Given that the concentration of monomer is much greater at all times than any of these oligomers during the time scale of this experiment, one would not expect to observe a significant decrease in their concentration until $k_{eff}[Zr^*][M]^2 \approx k_i[Zr^*][M_n]$where $[M_n]$ is the concentration of oligomer with DP = n and k_i is the effective rate constant for coordination and insertion of this oligomer into the Zr—H bond (Scheme 1, path A). This condition is obviously not satisfied over the time scale of these polymerizations, which do not proceed to completion under these conditions, possibly due to catalyst deactivation.

Copolymerization Studies. To determine whether, e.g., unsaturated dimer is consumed and how it is incorporated in this polymerization, the specifically labeled compound (**9**: 88% d_1) was prepared as shown in eq 2. A copolymerization of this material with cyclopentene was carried out at 50 °C where the initial concentrations of these two compounds were 2.83 and 0.19 M, respectively.[10] There was clear evidence for

consumption of dimer. Based on the deuterium content of the dimer fraction that was recovered and the amount of (unlabeled) dimer normally produced from cyclopentene under these conditions, about 40% of **9** was consumed.[11]



8 **9** (2)

While consumption of labeled dimer is consistent with reversible chain transfer (Scheme 1, path A), it is also conceivable that consumption is due to direct insertion of compound **9** into a growing polymer chain.[12] Examination of the trimer fraction, formed under these conditions, should provide evidence for the latter process.

In the absence of the labeled dimer, four unsaturated trimers are produced as revealed by ^{13}C NMR spectra and GC−MS analyses of this fraction; these arise from competitive cis- and trans-1,3 insertion combined with formation of 2- and 3-cyclopentenyl end groups.[2b] In addition to these compounds, at least two other unsaturated trimers were formed in the presence of labeled dimer **9**. The major isomer had two signals at δ 125.4 (1:1:1 t, $J_{CD} = 24$ Hz) and 148.3 (4 °C) due to olefinic carbon atoms and additional signals at higher field in the ^{13}C NMR spectrum of the trimer fraction. The ^{2}H NMR spectrum of the trimer fraction exhibited a single resonance at 5.35 ppm that could be attributed to this compound (Figure 3a). The other isomer was present in lower amounts but exhibited a characteristic signal at 2.3 ppm in the ^{2}H NMR spectrum of the mixture. In addition to these resonances, several absorptions were present in the region δ 1.0−2.0.

As the ^{13}C NMR spectra of the trimer fraction were complex (i.e., all compounds were unsymmetrical and therefore difficult to identify and quantitate due to overlap of signals), a hydrooligomerization was performed using cyclopentene and compound **9** at room temperature in order to obtain saturated (i.e., symmetrical) material. As shown in Figure 3b, this approach was only partially successful; the signals at 5.35 and 2.3 ppm were reduced in intensity, and there was, at least, one new peak at 1.6 ppm and a more intense peak at 1.4 ppm. This mixture was then hydrogenated [$(Ph_3P)_3RhCl$, C_6H_6, 50 psi H_2, 25 °C] to provide the material whose ^{2}H NMR spectrum is depicted in Figure 3c. Not all of the unsaturated trimers present could be fully hydrogenated under these conditions. In particular, the signal at 5.35 ppm, although diminished in intensity, is clearly present, but the signal at 2.3 ppm is absent. In addition, there was the appearance of a new peak at 0.75 ppm.

A ^{13}C NMR spectrum of this mixture revealed the complete consumption of all unsaturated trimers with the exception of that with signals at 125.4 and 148.3 ppm. There were several resonances present, which exhibited coupling to a single deuterium atom, at δ 48.2 ($J_{CD} = 19$ Hz), 38.5 ($J_{CD} = 19$ Hz), 38.3 ($J_{CD} = 20$ Hz), and 36.5 ($J_{CD} = 19$ Hz) ppm.[13] Detailed spectroscopic studies established that the saturated trimers that were present included compounds **11t**, **11c**, **14**, and **15** (Schemes 2 and 3).[14]

The interpretation of these results is depicted in Schemes 2 and 3. Insertion of labeled dimer into Zr−H followed by further insertion of cyclopentene and chain transfer gives rise to trimers **10t** and **10c** in which the terminal ring is unsaturated, with the double bond being at the 2 (major) or 3 (minor) position (Scheme 2).[2b] Under hydrooligomerization conditions or on hydrogenation of the mixture, the corresponding saturated trimers **11t** and **11c** are formed with the indicated stereochemistry.

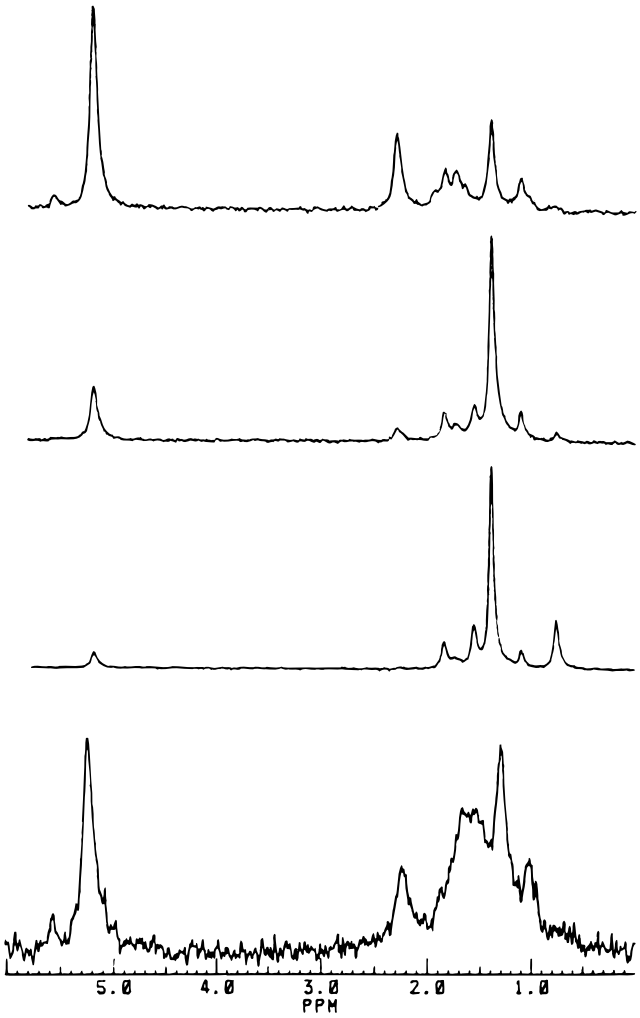
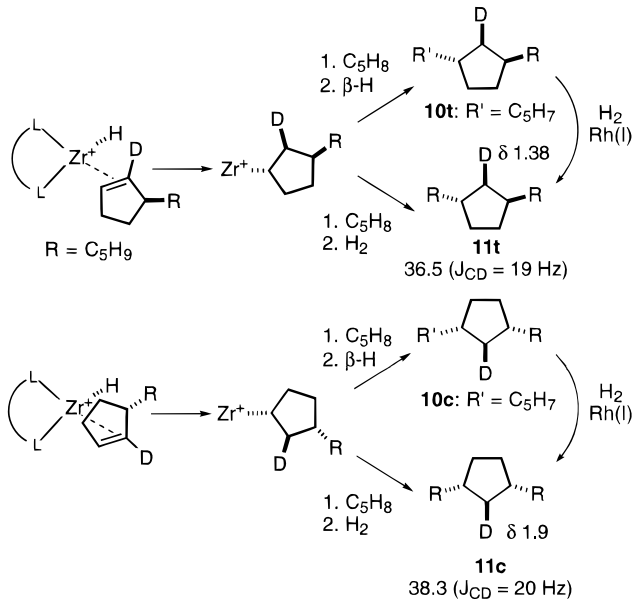


Figure 3. ^{2}H NMR spectra (30.7 MHz, $CHCl_3$) of fractions obtained from the copolymerization of cyclopentene and **9** (see text and Experimental Section for details). (a) Trimer fraction formed at 50 °C. (b) Trimer fraction obtained in the presence of H_2 at 25 °C. (c) Trimer fraction from b) following hydrogenation [$(Ph_3P)_3RhCl$, H_2, benzene]. (d) Higher MW fraction (insoluble in methanol) formed at 50 °C (conditions: 120 °C; TCB, 30.7 MHz).

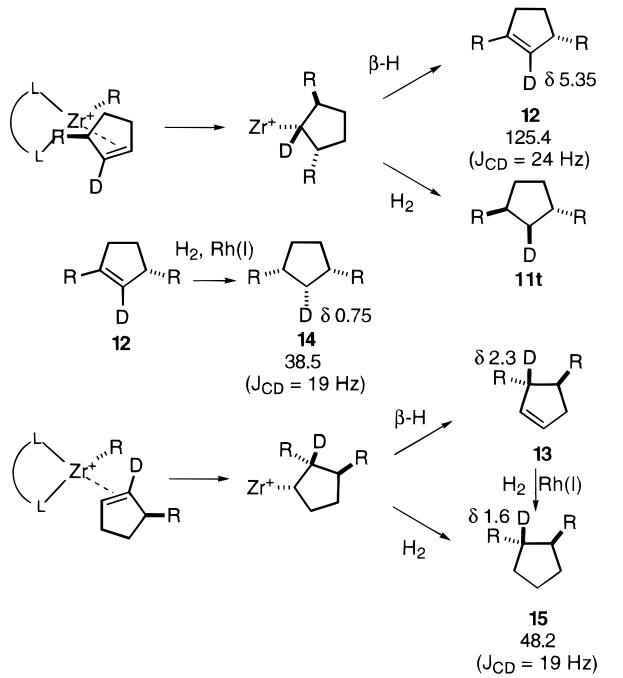
Insertion of labeled dimer into Zr−C could occur with different regiochemistry and gives rise to unsaturated trimers **12** and **13** following β-hydride elimination (Scheme 3). Under hydrooligomerization conditions, competitive hydrogenolysis of the Zr−C bond in these intermediates leads to the production of **11t** and **15**, respectively. Hydrogenation of trimer **12** using Wilkinson's catalyst is expected to be stereoselective (in the manner shown) and produces saturated trimer **14** (the epimer of **11c**), whereas isomer **13** is transformed to **15**.

Having clarified the nature of the products formed, we found that the ^{2}H NMR spectrum of the trimer fraction formed from cyclopentene and **9** at 50 °C is more readily interpreted. From Figure 3a, it is readily apparent that trimer **12** is a major component of this fraction (∼50 mol %), while isomer **13** and compounds **10t** and **10c** comprise ca. 17 and 33 mol %, respectively. Thus, nearly 70% of the incorporated dimer undergoes

Scheme 2. Insertion of Dimer 9 into Zr−H



Scheme 3. Insertion of Dimer 9 into Zr−C



insertion into Zr−C (i.e., copolymerization, Scheme 3), with the remainder inserting into Zr−H as depicted in Scheme 2. Furthermore, the stereoselectivity of the latter process is consistent with that required for trans-1,3 insertion—i.e., **10t** dominates over **10c** (ca. 3:1).

However, these results seem inconsistent with a reversible chain-transfer process being largely responsible for trans-1,3 insertion (Scheme 1, path A) as very little insertion of unsaturated oligomers into Zr−C bonds occurs under normal conditions.[15] Having said this, the product distribution in the trimer fraction obtained from copolymerization of cyclopentene and **9** is probably misleading; intermediates derived from insertion of **9** into Zr−H can undergo further insertion of monomer, whereas those arising from insertion of **9** into Zr−C (especially that involved in the formation of **12**) probably do so much less readily. Thus, trimers formed from Zr−C insertion will tend to accumulate, whereas those formed from insertion into Zr−H will not. Indeed, the ^{2}H NMR spectrum of a higher MW fraction indicated somewhat lower amounts of insertion into Zr−C vs Zr−H (ca. 50:50, Figure 3d).[16]

These experiments suggest that a reversible chain-transfer mechanism is an unlikely candidate for trans-1,3 enchainment of cyclopentene. Under normal conditions, incorporation of unsaturated oligomers by insertion into Zr−H appears to be minimal,[15] and under conditions where significant incorporation is observed, copolymerization (i.e., insertion into Zr−C) appears to dominate or is at least competitive.

Trans-1,3 Insertion via *σ*-CH Isomerization. The alternative mechanism (path B, Scheme 1) for trans-1,3 insertion is consistent with the results reported above, but direct evidence for such a nondissociative isomerization process would be desirable. Indirect evidence that a unimolecular pathway might be operative was obtained from polymerization studies employing racemic and optically pure **2**.[2b] *Identical* product distributions for the trimer and tetramer fractions were obtained. This result is compatible with the mechanism depicted in Scheme 1 (path B) but is unlikely to be observed if a reversible chain-transfer mechanism is operative (i.e., *perfect* stereoelection for the unsaturated oligomers produced would be required).

As previously mentioned, the *σ*-CH pathway has been invoked to explain unimolecular isomerization of metal−olefin complexes that occurs without olefin dissociation.[7] In the case of Re−olefin complexes, the rate of interconversion of the two complexes could be studied by standard kinetic techniques, and as might be expected for such a process, a secondary deuterium isotope effect on this rate was observed (k_H/k_D = 1.64).[7a] In the present case, this type of direct study is precluded in that the olefin−hydride complexes (i.e., **4** and **5**, Scheme 1) are unstable intermediates in what is undoubtedly a rather complicated process.

Nevertheless, if *σ*-CH isomerization is responsible for trans-1,3 insertion, there should be a kinetic isotope effect associated with this process. If the isomerization depicted in Scheme 1 is not rate-limiting, this isotope effect will manifest itself in the stereochemistry of the polymerization process (i.e., the cis:trans ratio) rather than on the overall rate of polymerization.[17] Furthermore, as is implied in Scheme 1, this isomerization process may be freely reversible. This is the worst possible case as one would then be looking for a 2° isotopic perturbation of an equilibrium. This effect is inherently small[18] and in the present case likely to be negligible; intermediates **4** and **5** are very similar in structure. In any event, a reversible chain-transfer process (Scheme 1, path A) is not expected to exhibit an appreciable isotope effect on stereochemistry.

With this in mind, the polymerization of cyclopentene-d_8 (Cp-d_8) was investigated and compared to that of cyclopentene (Cp-h_8).[19] The stereochemistry of polymerization was most conveniently monitored by GC analysis of quenched aliquots; the cis and trans trimers produced are separable by this technique. As shown in Figure 4a, the cis:trans ratio of the trimer fraction was not constant during the polymerization of cyclopentene, and significantly different, instantaneous cis:trans ratios were observed during the polymerization of Cp-d_8.

The interpretation of these results, in terms of kinetic parameters, is not straightforward. As shown in Scheme 3, cis trimer would be formed from **4** by insertion to form **6** (cis) followed by 1,2 insertion of monomer and *β*-hydride elimination; a similar sequence applies to the

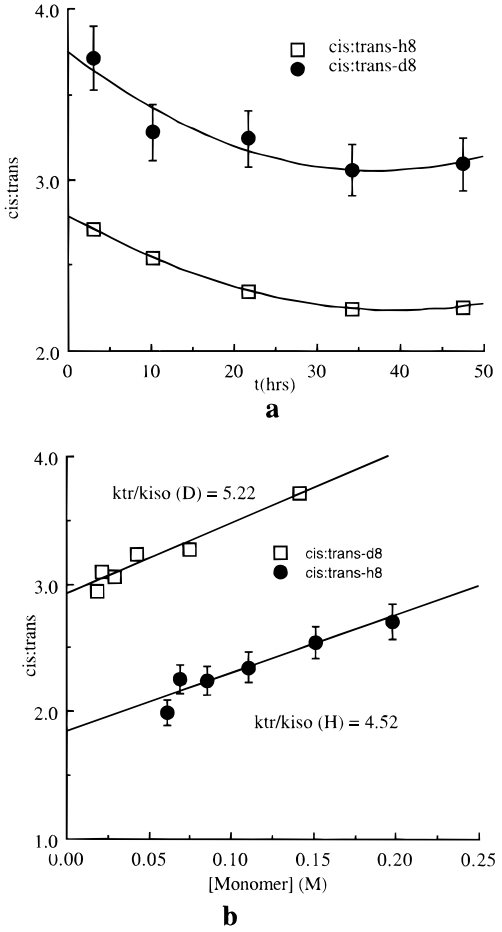
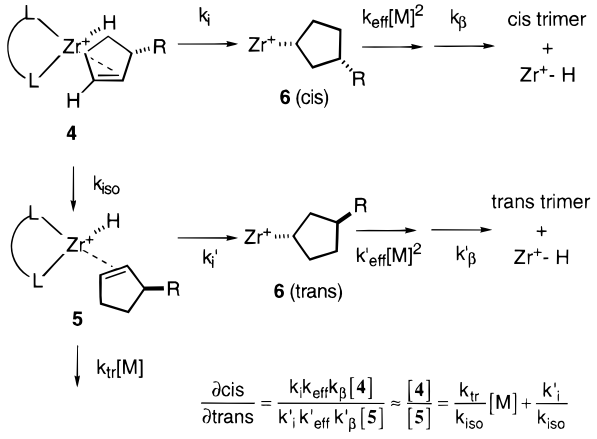


Figure 4. Cis:trans trimer ratio vs (a) time and (b) monomer concentration for cyclopentene-h_8 and -d_8 (data are summarized in Table 2).

Scheme 4



$$\frac{\partial \text{cis}}{\partial \text{trans}} = \frac{k_i k_{eff} k_\beta [4]}{k'_i k'_{eff} k'_\beta [5]} \approx \frac{[4]}{[5]} = \frac{k_{tr}}{k_{iso}}[M] + \frac{k'_i}{k_{iso}}$$

formation of trans trimer from **5**. The instantaneous cis:trans ratio of the trimer fraction should be *constant* with time if these are the only relevant pathways. The fact that the cis:trans ratio is not constant implies that there are additional competing reactions involving intermediates **4** and **5**. The simplest and most reasonable pathway that can be invoked involves displacement of the bound olefin from **5** (and **4**) by monomer (Scheme 4).

For simplicity, we will assume in this analysis that insertion from intermediates **4** and **5** and propagation from intermediates **6**(cis) and **6**(trans) occur at identical rates.[20] Application of the steady-state approximation to **5** then leads to the expression shown in Scheme 4 for the instantaneous cis:trans ratio. Thus, a plot of the cis:trans ratio vs instantaneous monomer concentration should be linear if the mechanism depicted is operative. Plots of the cis:trans ratio for both Cp-h_8 and Cp-d_8 vs [M] were linear (Figure 4b) with significantly different slopes and intercepts. As can be appreciated from Scheme 4, the slope is equal to k_{tr}/k_{iso} and the ratio of the slopes should provide an estimate for the isotope effect associated with the isomerization process, if the isotope effect associated with k_{tr} is negligible (i.e., $k_{tr}D \times k_{iso}H/k_{tr}H \times k_{iso}D \approx k_{iso}H/k_{iso}D$).[21] The computed value is 1.27 ± 0.13. This probably represents a *lower* bound for $k_{iso}H/k_{iso}D$ as any secondary isotope effect associated with displacement of the olefin from the metal center is expected to be small but normal rather than inverse.

The fact that the isotope effect observed (1.3) is smaller than that determined previously for an unambiguous example of a σ-CH isomerization process (1.64) is not too much of a concern. In the latter case, the metal complex was a d^6 system, whereas here it is d^0; presumably the lack of backbonding to the CH σ^* in the present case may lead to an increase in the force constant for CH stretching in the σ-CH complex/transition state and therefore a decreased 2° isotope effect.[17] Having said that, while all of the results obtained are consistent with σ-CH isomerization as a mechanism for trans-1,3 insertion, we cannot exclude other possible mechanisms on the basis of the evidence obtained to date.[22]

Conclusions

In summary, mechanistic evidence gathered to date does not appear to be compatible with trans-1,3 insertion occurring via a reversible chain-transfer mechanism. On the basis of the studies presented here, an alternative process involving a σ-CH complex is in agreement with the experimental results. Although such olefinic, CH complexes have not been directly observed in early-transition-metal systems of the type studied here, the propensity of these electrophilic complexes to engage in agostic CH interactions and to effect CH activation (even of simple olefins) by σ-bond metathesis reactions is well documented.[23] It would be desirable to study the isotope effect for such a process using a simpler system in which such isomerization processes could be directly observed in the absence of competing monomer polymerization.[7b]

Experimental Section

All solvents and chemicals were reagent grade and purified as required. Tetrahydrofuran, diethyl ether, and toluene were dried by distillation from sodium benzophenone ketyl. Cyclopentene (Aldrich, 97%) and TMEDA were dried by distillation from $LiAlH_4$ under nitrogen. Methylaluminoxane was obtained from Texas Alkyls as a solution in toluene and the solvent removed under high vacuum to obtain solid MAO used in the polymerizations. Metallocenes **1** and **2** were prepared by the methods described in the literature.[24] Cyclopentanone **8** was prepared from 2-cyclopentylidene−cyclopentanone (Lancaster) by hydrogenation (Pd/C, EtOH).[25] All synthetic reactions were conducted under an atmosphere of dry nitrogen in dry glassware unless otherwise noted.

^{1}H and ^{13}C NMR spectra were recorded in a $CDCl_3$ or C_6D_6 solution on either a Bruker AM-250 or AC-200 spectrometer; chemical shifts are referenced with respect to residual $CHCl_3$ or C_6D_5H. ^{2}H NMR spectra were recorded on an AC-200 spectrometer in $CHCl_3$ or TCB containing benzene-d_6 at 25 or 120 °C. Chemical shifts are referenced with respect to benzene-d_6.

Table 1. Cyclopentene Polymerization[a]

t (10^3 s)	$[C_5D_8]$ (M)	t (10^3 s)	$[C_5H_8]$ (M)	dimer (10^{-3} M)	trimer (10^{-3} M)	tetramer (10^{-3} M)
0.0	0.1292	0.0	0.1292	0.0	0.0	0.0
14.4	0.0846	14.4	0.1218	0.40	0.23	0.15
32.4	0.0538	32.4	0.1033	1.08	b	0.37
46.8	0.0436	46.8	0.0900	b	b	b
72.0	0.0362	72.0	0.0754	2.30	1.43	0.92
115.2	0.0265	115.2	0.0630	3.43	1.91	1.13
162.0	0.0209	158.4	0.0582	4.34	2.54	1.50
		201.6	0.0520	b	b	b
		252.0	0.0470	6.17	3.45	2.23

[a] The concentrations were determined by GC analysis using *n*-decane as an internal standard. [b] Not determined.

IR spectra were recorded on a Bomem MB-100 FTIR spectrometer. Mass spectra were obtained using a Kratos MS-890 instrument at the University of Guelph. Gas chromatography was performed on a Hewlett-Packard 5890 instrument equipped with FID detectors and a 0.25 mm × 50 m, Supelco SE-30 capillary column or a 0.25 mm × 25 m J&W Scientific DB1701 column. GC−MS analyses were obtained using a Hewlett-Packard 5890 Series II instrument equipped with a 5971A mass selective detector and a 0.32 mm× 25 m HP-5 column. Elemental analyses were determined by M. H. W. Laboratories of Phoenix, AZ.

Kinetic Studies. To a round-bottomed flask containing MAO (0.30 g, 5.1 mmol) dissolved in toluene (45 mL) was added cyclopentene (0.440 g, 6.46 mmol) and 0.50 mL of *n*-decane (previously dried over activated MS 4Å) as an internal standard. A solution of compound **2** (4.0 mg, 9.4 μmol) in 5 mL of toluene was then added via syringe at 25 °C. Aliquots (1.5 mL) were removed periodically over a period of 3 days at this temperature and were filtered through silica gel to remove catalyst, MAO, and polymer prior to GC analysis (conditions: 40 °C (2 min) to 250 °C (10 min) at 10 °C/min). The results are summarized in Table 1 and in Figure 1: An experiment was conducted under identical conditions, employing 6.46 mmol of cyclopentene-d_8 (99% d), and the data are also collected in Table 1 and plotted in Figure 1.

2-Cyclopentylcyclopentanone (*p*-toluenesulfonyl)hydrazone (16). The hydrazone derivative of ketone **8** was prepared following a general literature procedure.[26] To a round-bottomed flask equipped with a condenser was added *p*-toluenesulfonylhydrazide (7.0 g, 0.038 mol), methanol (80 mL), concentrated HCl (0.2 mL), and **8** (5.0 g, 0.033 mol). The mixture was refluxed under nitrogen for 3 h and allowed to cool. The white crystals were filtered, and the mother liquor was concentrated in vacuo to provide a second crop. Both fractions were combined and recrystallized from methanol, providing 9.0 g of **16** (85% yield). Mp: 152 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.82 (d, J = 5 Hz, 2 H), 7.27 (d, J = 6 Hz, 2 H), 7.2−7.1 (br, 1 H), 2.41 (s, 3 H), 2.34−0.9 (m, 16 H). ^{13}C NMR (62.85 MHz, $CDCl_3$): δ 169.78, 143.86, 135.42, 129.37 (2 C), 128.15 (2 C), 49.10, 41.58, 30.79, 29.73, 29.21, 28.25, 25.14, 24.90, 22.36, 21.57. IR (KBr, disk) 3222 (s), 2947 (s), 2865 (s), 1651 (m), 1597 (m), 1450 (m), 1400 (s), 1332 (s), 1304 (sh), 1291 (sh), 1210 (w), 1184 (sh), 1166 (s), 1092 (s), 1012 (s), 918 (s), 844 (w), 811 (s), 702 (s), 619 (m), 545 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.92; H, 7.57. Found: C, 63.60; H, 7.49.

3-Cyclopentyl-2-deuteriocyclopentene (9). Compound **9** was synthesized from hydrazone **16** using a general procedure outlined in the literature.[27] To a round-bottomed flask was added 6 g of **16** and 60 mL of TMEDA (distilled from *n*-BuLi). The slurry was cooled using a dry ice−acetone bath, and to the frozen solution was added by syringe *n*-BuLi in hexane (2.5 M, 3 mL, 7.5 mmol). The reaction flask was allowed to warm slightly to melt the TMEDA (−55 °C) and then cooled back down to −78 °C. To the cold slurry was then added *n*-BuLi (2.5 M, 27 mL, 0.068 mol) over 15 min, at which time the cold bath was removed. The red slurry, containing white crystals, slowly became homogeneous after approximately 5 min. The solution was allowed to warm to room temperature, and after a total of 6 h, it was deep red−brown in color. At this time the solution was cooled to 0 °C and D_2O (3 mL, 0.167 mol) was added. The product was extracted with pentane (100 mL) and dried over Na_2SO_4 before being purified by flash chromatography on silica gel eluting with pentane. Compound **9** was obtained as an oil (2.36 g, 85% yield). Deuterium incorporation was determined to be 88% based on GC−MS and 88% based on ^{13}C NMR. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.70 (m, 1 H), 2.6−2.4 (br, 1 H), 2.4−2.2 (br m, 2 H), 2.1−1.9 (m, 1 H), 1.85−1.4 (br m, 8 H), 1.3−1.0 (br, 2 H). ^{13}C NMR (62.85 MHz, $CDCl_3$): δ two sets of signals at 134.55 and 134.26 (t, 1:1:1, J_{CD} = 24.4 Hz) in a 1:1 ratio, two sets of signals at 130.45 and 130.32 in a 1:6.8 ratio, two sets of signals at 51.33 and 51.24 in a 1:6.8 ratio, 45.84, 32.15, 31.16, 30.80, 28.82, 25.55, 25.36. IR (NaCl, neat) 3049 (m), 2939 (s), 2863 (s), 2278 (w, ν_{CD}), 1597 (w), 1454 (m), 1363 (w), 1322 (w), 1291 (vw), 1242 (w), 1130 (vw), 1041 (vw), 1011 (w), 980 (vw), 937 (w), 898 (w), 863 (w), 831 (w), 800 (w), 751 (w), 721 (m), 655 (m) cm^{-1}. Mass spectrum (EI): m/e 137 (M^+).

Cyclopentene-d_8. Cyclopentene-d_8 was synthesized from cyclopentene following a literature procedure with some modifications.[28] To a 22 cm long × 19 mm o.d., medium-walled glass tube was added cyclopentene (0.82 mL), decalin (3.2 mL), and 1% w/v DCl/D_2O (16 mL). The mixture was degassed via three freeze/pump/thaw cycles and the tube sealed under vacuum. Three tubes, prepared in the above manner, were placed in a 1 L Parr autoclave reactor (Series 4000 Rocker type) containing 400 mL of water and agitated for 24 h at 145 °C. After cooling to room temperature, the tubes were removed and opened. The product was recovered by freezing the aqueous layer and decanting the decalin/cyclopentene solution, which was dried over K_2CO_3, distilled over CaH_2, and finally fractionally distilled over $LiAlH_4$, resulting in 1.5 mL of product (63% yield) having a deuterium content of ∼90% as determined by GC−MS.

Repetition of this procedure yielded 1.1 mL (46% yield) of product having a deuterium content of 99.2% as determined using ^{1}H NMR spectroscopy by comparing the area ratio of signals due to residual $CHCl_3$ in known amounts of $CDCl_3$ (99.8% d_1) to those of the product.

Copolymerization of Cyclopentene and Compound 9. A solution of compound **2** (4.3 mg) in toluene (5.0 mL) was added to a solution of cyclopentene (5.0 mL, 56.5 mmol), the labeled dimer (0.52 g, 88% d_1, 3.8 mmol), and MAO (0.15 g) in toluene (10.0 mL). After 12 h at 50 °C, a known aliquot of the toluene-soluble fraction was analyzed by GC using *n*-decane as an internal standard. The total amount of deuterated dimer present (after correcting for the amount of dimer formed from cyclopentene under these conditions) was 0.31 g; about 40% of compound **9** was incorporated into higher oligomers. The suspension was quenched with methanol (30.0 mL) and the insoluble fraction of the polymer was isolated by filtration (yield 2.4 g). ^{2}H NMR spectroscopy in TCB at 125 °C revealed that it contained deuterium which was found in both the aliphatic and olefinic C−D regions (see Figure 3d).

The MeOH−toluene-soluble fraction was concentrated in vacuo at 25 °C and 1.0 mmHg, and the distillate was collected in a liquid-N_2-cooled trap. The distillate was carefully distilled at atmospheric pressure using a long Vigreux column to remove the toluene−MeOH azeotrope, and additional MeOH was added until all the toluene had been removed. The residual MeOH was extracted with pentane, and the pentane extracts were concentrated in vacuo. Bulb-to-bulb distillation provided recovered dimer (0.14 g). GC−MS analysis indicated that the total deuterium content of the recovered dimer was 68.7%. The ^{13}C NMR spectrum indicated the presence of

Table 2. Polymerization of Cyclopentene and Cyclopentene-d_8

t (10^4 s)	$[C_5H_8]$ (M)	cis:trans	$[C_5D_8]$ (M)	cis:trans
0.00	0.226	n.a.	0.226	n.a.
1.08	0.197	2.71	0.142	3.71
3.69	0.151	2.54	0.074	3.28
7.83	0.110	2.35	0.042	3.24
12.30	0.085	2.24	0.029	3.06
17.10	0.069	2.26	0.022	3.09

signals at δ 130.45, 130.32, and 130.24 (2C) ppm due to 3-cyclopentylcyclopentene (**17**),[2] compound **9**, and 4-cyclopentylcyclopentene (**18**),[2] respectively, in a mole ratio of 5.4:14.4:1. In the absence of labeled dimer, but under the same conditions, the mole ratio of **17** to **18** was 4.4:1. Thus, based on the molar amount of **18** present in the mixture, the deuterium content of recovered **9** was 86.7%.

The residue remaining from the initial removal of the toluene and MeOH (ca. 0.5 g) was bulb-to-bulb distilled at 80 °C and 0.01 mmHg to provide the trimer fraction (0.040 g) which was a mixture of at least six isomers as revealed by GC and ^{13}C, ^{2}H, and ^{1}H NMR spectroscopy. Relevant spectral data for this fraction are discussed in the text and presented in Figure 3a.

Hydrocooligomerization of Cyclopentene and Dimer 9. A solution of catalyst **2** (4.3 mg, 10 μmol) in 5 mL of toluene was injected by syringe to a magnetically stirred solution of cyclopentene (10.0 mL, 113 mmol), compound **9** (1.78 g, 13 mmol), and MAO (0.15 g) in 5 mL of toluene in a 300 mL Parr reactor under 30 psi of H_2. After 72 h at 25 °C, the mixture was quenched by the addition of MeOH (1.0 mL) and the reactor vented to the atmosphere. The product was fractionated as described above to give 0.9 g of a MeOH−toluene soluble fraction.

The trimer fraction was isolated and purified as described above, and the spectroscopic data for this material (0.18 g) are presented in the text and in Figure 3b.

Hydrogenation of Deuterated Trimers Using $(Ph_3P)_3RhCl$. This procedure was adopted from a literature reference.[29] In a glovebox, $(Ph_3P)_3RhCl$ (10 mg) was added to a Parr autoclave. To this was added 10 mL of degassed, distilled (from Na and benzophenone) benzene containing 100 mg of the deuterated trimer obtained from the above experiment. The reactor was then purged with H_2 and finally pressurized to 50 psi with H_2. After 48 h the reactor was vented and the solution was filtered through Celite and the solvent removed in vacuo. Final purification was effected by filtering a pentane solution of the trimer down a small silica gel column eluting with pentane. The trimer was the first product to elute, and 85 mg of pure material was obtained. Spectral data for this material are summarized in Figure 3c and in the text.

Kinetic Studies of Cyclopentene and Cyclopentene-d_8 Polymerization. To a round-bottomed flask containing MAO (0.29 g, 5.1 mmol) was added toluene (45 mL), cyclopentene (1.0 mL, 11.3 mmol), and *n*-decane (0.5 mL). A solution of **2** (4.0 mg, 9.4 μmol) in 5 mL of toluene was then added via syringe ($[C_5H_8]_0 = 0.226$ M). Aliquots (1.5 mL) were removed periodically over a period of 4 days and filtered through silica gel to remove catalyst, MAO, and polymer prior to GC analysis (40 °C/5 min to 200 °C/5 min at 10 °C/min).

In a simultaneous experiment, cyclopentene-d_8 (0.859 g, 11.3 mmol) was polymerized under the following conditions: **2** (4.0 mg), MAO (0.29 g), *n*-decane (0.5 mL), and toluene (50 mL). Aliquots were obtained and analyzed as above. The data are summarized in Table 2 and in Figure 4.

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(8) The rate of disappearance of monomer with time is also consistent with a mechanism in which propagation is first order in monomer and catalyst concentration, but there is a catalyst deactivation process that is second order in catalyst concentration and independent of monomer concentration. However, experiments at higher monomer concentration (and the same catalyst concentration) were not consistent with this model but were consistent with second-order kinetics (Figure 1). For a discussion of triggered insertions in propylene polymerization, see: Ystenes, M. *J. Mol. Catal.* **1991**, *129*, 383.

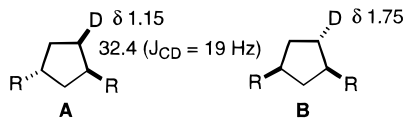
(9) The trigger mechanism proposed by Ystenes[8] argues for the approach of two monomer units to the same vacant coordination site in classical Z−N catalysts. In the present case, a consideration of both frontier molecular orbital arguments and available experimental data on ligand exchange reactions and solution structures of related 18 e^-, d_0 zirconocene complexes, the arrangement depicted in eq 1, seems more plausible. For a review, see: Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 352 and references therein.

(10) Similar results were obtained when this experiment was conducted at lower temperatures although the extent of scrambling[13] was reduced and the amount of low MW material formed is greatly diminished, making isolation and characterization of the various fractions formed experimentally demanding: Kelly, W. M. Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1994.

(11) Very little deuterium was lost from the dimer recovered from these experiments—i.e., 86% d_1 (after accounting for the production of unlabeled material produced from cyclopentene) vs 87% d_1 in the starting material.

(12) Control experiments revealed that the dimer was not homopolymerized by catalyst **2.**

(13) In addition to these compounds, a DEPT-90 pulse sequence revealed an additional signal at 32.4 ($J_{CD} = 19$ Hz) ppm. This peak was assigned to the compound **A** on the basis of detailed NMR studies.[14] The presence of the corresponding epimer, **B**, was inferred from the appearance of an additional signal at δ 1.75 in the ^{2}H NMR spectrum (Figure 3b). The formation of these isomers must arise from further isomerization of the intermediates leading to **10t** and **10c** (Scheme 2) prior to cyclopentene insertion.



(14) In particular, ^{2}D, ^{13}C, and ^{1}H chemical shift correlation studies on *unlabeled* **11c** and **11t** allowed nearly complete assignment of the 500 MHz ^{1}H NMR spectrum based on the more readily interpreted 13C NMR spectrum. This information, when coupled with both the ^{2}H and ^{13}C NMR spectrum of the trimer fraction formed in the presence of labeled dimer, allowed definitive identification of labeled **11c** and **11t** with the indicated stereochemistry. Similarly, compound **14** (the epimer of **11c**) was readily identified, whereas the presence of **15** was inferred from the appearance of additional signals at 48.7 (CH), 48.2 (CD, $J_{CD} = 19$ Hz) and 25.4 (CH_2) ppm.

For detailed studies, consult: Kelly, W. M. Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1994.
(15) Compounds **12** and **13** cannot be detected by ^{1}H or ^{13}C NMR spectroscopy under conditions where trans-1,3 insertion of cyclopentene is facile (e.g., 25 °C).
(16) When 0.5 g of an ether-soluble fraction of perdeuterated cyclopentene oligomers (prepared from cyclopentene-d_8) were copolymerized with cyclopentene (5.0 mL), the ether-soluble portion was found to contain ca. 92% of the total deuterium added; very little was incorporated into higher MW polymer, as would be expected for a reversible chain-transfer mechanism. Kelly, W. M. Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1994.
(17) For related studies involving isotopic perturbation of stereochemistry in olefin polymerization, see: (a) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377. (b) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (c) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412.
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(19) There is an unexpectedly large, inverse kinetic isotope effect on the rate of propagation (Figure 1: $k_{eff}D/k_{eff}H = 4.1 \pm 0.4$). The interpretation of this surprising result is complicated by the fact that there are, at least, two deuterium atoms bonded to carbon atoms undergoing changes in hybridization based on the mechanism shown in eq 1 and, in addition, at least six remote deuterium atoms (three proximal deuteria on each coordinated cyclopentene ring) that probably suffer some steric compression in the transition state for insertion. Using the range of values associated with these two effects, one can estimate an inverse isotope effect of ca. 3.0−4.0 for the propagation sequence depicted in eq 1. For determination and a discussion of remote deuterium isotope effects in electrophilic bromination of sterically crowded olefins, see: Slebocka-Tilk, H.; Motallebi, S.; Nagorski, R. W.; Turner, P.; Brown, R. S.; McDonald, R. *J. Am. Chem. Soc.* **1995**, *117*, 8769.
(20) This assumption does not change the overall conclusions regarding isotopic perturbation of stereochemistry. This is because the isotope effects associated with these competing insertion/propagation processes are expected to largely cancel out. However, the absolute magnitude of the observed isotope effect is probably not that meaningful from a mechanistic perspective.
(21) An estimate for k_{iso} is also available from the ratio of the two intercepts, assuming kinetic (rather than thermodynamic) control of stereochemistry applies at high monomer conversion. In addition, this would require estimation of the 1° isotope effect associated with insertion of olefin into Zr−H vs Zr−D (i.e., k_i). In our opinion, given these uncertainties, the value obtained from the slopes is more meaningful. For a study of isotope effects associated with olefin insertion into Nb−H bonds, see: Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.
(22) For example, cis−trans isomerization (and indeed 1,3 insertion) might occur via remote C−H activation processes as have been observed with other systems (we thank Dr. Luigi Resconi for bringing this concept to our attention).[4b] In our opinion, the relevant transition states would be too strained for the cis−trans isomerization process to occur easily via this mechanism.
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