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Distinguishing Chain Growth Mechanisms in Metal-catalyzed Olefin Oligomerization and Polymerization Systems: C₂H₄/C₂D₄ Co-oligomerization/Polymerization Experiments Using Chromium, Iron, and Cobalt Catalysts

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A series of co-oligomerization and copolymerization reactions of C₂H₄/C₂D₄ (1:1) mixtures have been carried out using various transition metal catalysts based on Cr, Co, and Fe in combination with MAO. The oligomeric α -olefin products have been analyzed by GC and GC/MS, and the experimental results have been compared with the theoretical mass spectra derived from mathematical models. Solid polymer samples have been analyzed by ¹³C{¹H} and ¹³C DEPT-135 NMR spectroscopy. C₂H₄/C₂D₄ co-oligomerization can be used as a method to differentiate between a metallacyclic or a Cossee-type chain growth mechanism in oligomerization systems. In the case of a metallacyclic mechanism, no H/D scrambling is observed, whereas for a Cossee-type mechanism, similar rates of chain propagation and chain termination (β -H elimination) result in rapid H/D scrambling of the C₂H₄/C₂D₄ feed. This method is therefore limited to oligomerization systems and cannot be applied in polymerization systems, where the rate of chain propagation is much faster than the rate of chain termination.

Introduction

The development of new catalysts for the oligomerization and polymerization of olefins continues to attract a great deal of interest both in academia and in industry.^{1–4} Ever-increasing control over the polymerization reaction has led to remarkable advances in this area, in terms of both novel polymer architectures and product selectivities. Significant developments during the last 15 years have been the discovery of highly active mid- and late-transition metal polymerization catalysts based on iron, cobalt, and nickel as well as the discovery of ultrafast chain transfer agents to give catalyzed chain growth on zinc^{5–7} and the subsequent development of chain shuttling to give block copolymers.^{8,9} Selective oligomerization reactions of ethylene, e.g., trimerization and

tetramerization to give 1-hexene and 1-octene, constitute another milestone in this area.^{10–13}

A detailed understanding of the chain growth mechanism in olefin polymerization is of immense practical importance because many polymer properties are related to the microstructure of the polymer, which in turn is controlled by the catalyst. Important elementary reaction steps in transition metal catalyzed oligomerization and polymerization reactions of olefins are propagation (k_p) and termination (k_t). In the absence of any termination reaction, living polymerization occurs, and in the event that propagation is terminated deliberately at an early stage, a Poisson distribution of polymer chains is obtained.¹⁴ However, in most transition metal catalyzed alkene polymerization systems, chain termination reactions occur, most importantly via β -H elimination, which results in a Schultz–Flory distribution of either dimers (when $k_p/k_t < 1/10$), oligomers (when $1/10 < k_p/k_t < 10/1$), or polymers (when $k_p/k_t > 10/1$). The most commonly accepted mechanism for chain propagation in alkene polymerization is the one proposed by Cossee and involves alkyl

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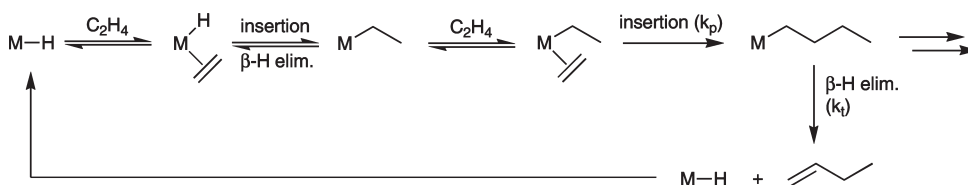
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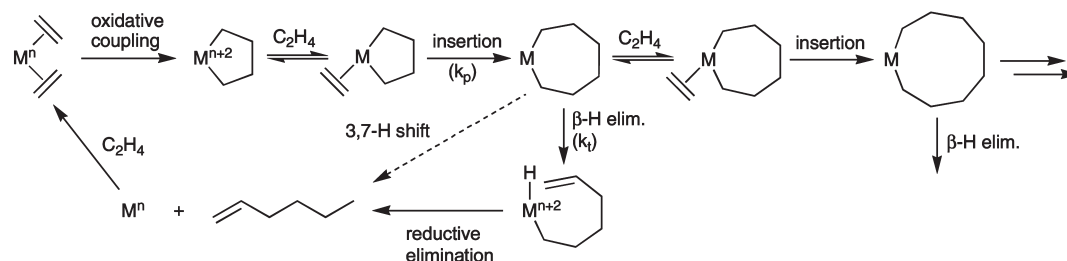
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Scheme 1. Ethylene Oligomerization/Polymerization Mechanisms

a) Cossee Mechanism



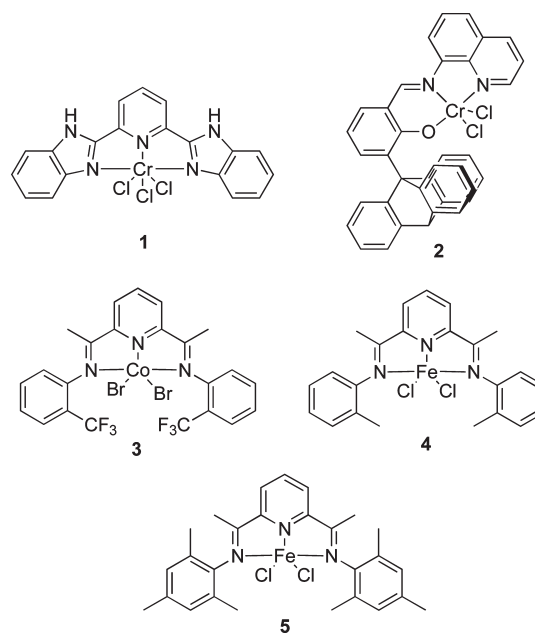
b) Metallocyclic Mechanism



migration to a coordinated olefin (Scheme 1a).¹⁵ An alternative chain propagation mechanism, originally proposed by Briggs, has been implicated in selective trimerization and tetramerization reactions and involves metallocyclic intermediates (Scheme 1b).¹⁶ Here, oxidative coupling of two coordinated ethylene molecules at a metal center forms a metallacyclopentane, which upon further insertions can grow to a metallacycloheptane and so on.^{12,13} Subsequent release of the product proceeds either via a sequential β -H elimination–reductive elimination process or alternatively through a concerted [3, ω]-hydrogen shift.¹⁷ With certain chromium catalysts higher molecular weight oligomers can be obtained via this mechanism.^{18–20}

Important information regarding the chain growth mechanism by which a particular catalyst operates can be obtained from C_2H_4/C_2D_4 co-oligomerization or copolymerization studies.^{21,22} In a metallocyclic mechanism where olefin coordination or chain propagation is the rate-determining step, only a very small kinetic isotope effect (KIE) is expected if C_2D_4 is used instead of C_2H_4 . However, a significant isotope effect on propagation would be expected in the case of reversible formation of metallocyclic intermediates. In recent years, Bercaw and co-workers have shown that, by analyzing the isotopologue distributions obtained in a C_2H_4/C_2D_4 cotrimerization reaction, the absence of H/D scrambling implies a metallocyclic mechanism for this reaction.^{23,24} Similar observations have been made

Scheme 2. Selected Ethylene Oligomerization and Polymerization Catalysts 1–5



for ethylene tetramerization reactions.²⁵ We were interested to find out whether this technique can also be applied to higher oligomers and polymers, and we have therefore carried out C_2H_4/C_2D_4 co-oligomerization or copolymerization experiments with a series of catalysts, 1–5, as shown in Figure 2.

Chromium catalysts 1 and 2 shown in Scheme 2 and related systems have been shown previously to be highly active for the oligomerization of ethylene.^{18,26–28}

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Table 1. Ethylene Oligomerization Catalyzed by Complexes 1–4/MAO

run	cat.	$m_{\text{cat.}}, \mu\text{mol}$	P, bar	$T, ^\circ\text{C}$	yield, g	act., g/mmol·h·bar	LAO, ^e wt %	α^f
1 ^a	1	1	4	32	24.8	5315	98.5	0.76
2 ^b	2	1	4	50	29.8	7450	98.9	nd
3 ^c	3	0.5	1	25	4.18	8360	100	0.75
4 ^d	4	2	5	50	20.1	2010	100	0.73

^a Reaction conditions: toluene; MAO (8 mmol); 70 min.; from ref 18. ^b Reaction conditions: toluene; MAO (2.2 mmol); 60 min.; from ref 33. ^c Reaction conditions: toluene; MAO (1 mmol); 60 min.; from ref 31. ^d Reaction conditions: isobutane; MAO (0.2 mmol); 60 min.; from ref 30. ^e LAO = linear α -olefin fraction. ^f $\alpha = k_p/(k_p + k_t)$ (see ref 30).

Preliminary co-oligomerization experiments employing $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ (1:1) with these catalysts have shown that the oligomer fraction consists of even-numbered isotopologues only, which is consistent with a metallacyclic chain growth mechanism.¹⁸ In addition, ethylene/1-nonene co-oligomerization experiments with catalyst **1** have shown no incorporation of the higher 1-alkene. Taken together, these observations indicate that higher oligomers are formed via large-ring metallacyclic intermediates for these catalysts.

Examples of another family of highly active catalysts for the oligomerization of alkenes are the cobalt and iron complexes **3** and **4** containing 2,6-bis(imino)pyridine ligands.^{29–31} Chain growth with these catalysts is believed to occur via a Cossee-type mechanism whereby $k_p \approx k_t$. Experimental evidence for the involvement of this mechanism was initially obtained from $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ co-oligomerization experiments using a bis(imino)pyridine cobalt(I) chloride catalyst similar to **3**, in combination with MAO. This catalyst gave mainly 1-butene and 1-hexene products ($k_p \ll k_t$), and the analysis of the C_6 fraction by MS showed complete H/D scrambling suggesting a Cossee-type mechanism.³²

Here we present our results obtained from $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ co-oligomerization experiments, carried out on a series of catalysts based on Cr, Co, and Fe shown in Scheme 2. The ability to distinguish between different chain growth mechanisms has been investigated using the oligomerization catalysts **1–4**, which are believed to operate via a metallacyclic (Cr) or a Cossee-type mechanism (Co, Fe). In order to determine the limits of this technique for distinguishing between different chain growth mechanisms, an iron-based polymerization catalyst **5**, where $k_p \gg k_t$, has also been investigated. The lower molecular weight oligomeric products have been analyzed by GC and GC/MS, whereas the higher molecular weight fractions have been analyzed by ^{13}C NMR spectroscopy. Statistical analyses of the isotopologue distributions and mathematical models for the calculation of the theoretical mass spectra have been included in the Supporting Information.

Results and Discussions

C_2H_4 Oligomerization. Standard ethylene oligomerization reactions using catalysts **1–4** in combination with MAO as

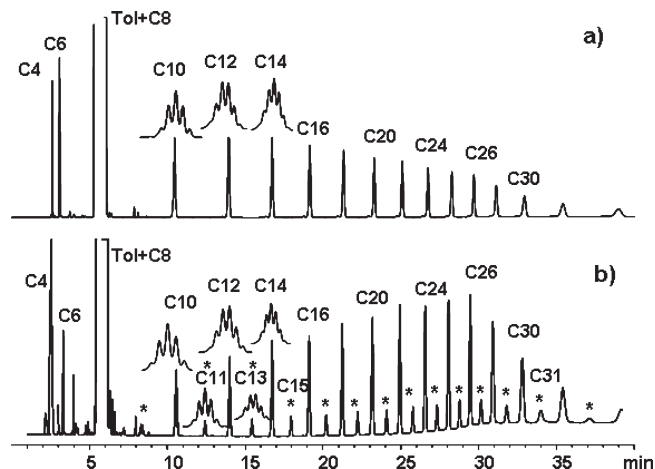


Figure 1. Gas chromatogram showing the product distribution from a co-oligomerization of a $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ mixture (1:1) with catalysts **1** (a) and **2** (b) (* = odd-numbered alkane products).

the cocatalyst have been reported previously, and the results are collected in Table 1.^{18,30,31,33} The catalysts **1**, **3**, and **4** result in a Schultz–Flory distribution of linear α -olefins (LAO), while catalyst **2** gives a slightly different product distribution due to an additional, but minor, chain transfer to aluminum process. Chain transfer to aluminum is a common termination mechanism for catalyst **2** in the presence of MAO cocatalyst.³³ For catalysts **1**, **3**, and **4**, a linear relationship between catalyst productivity and ethylene pressure has been observed, and the α values, which describe the shape of the distribution,³⁰ are invariant with ethylene concentration, which indicates that both the rate of propagation (k_p) and the rate of termination (k_t) are first order with respect to ethylene concentration.

$\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ Co-oligomerization. The co-oligomerization reactions of a $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ mixture (1:1) with catalysts **1–4**, activated by MAO, have been carried out in toluene solution (see Experimental Section for further details). The reaction products have been analyzed by GC and GC/MS, and the isotopologue distributions of the C_{10} , C_{12} , and C_{14} olefin fractions have been analyzed and compared with theoretical distributions (see Supporting Information, Figures S5–S30). The number of possible isotopologues and the variation in their relative abundance increase rapidly with the length of the oligomer chain, resulting in resolution problems for fractions higher than C_{14} . The GC traces for the co-oligomers obtained using catalysts **1–4** are shown in Figures 1 and 2.

In the case of catalysts **1** and **2**, the GC signals for the C_{10} , C_{12} , and C_{14} fractions are well resolved. In contrast, the corresponding signals obtained using catalysts **3** and **4**

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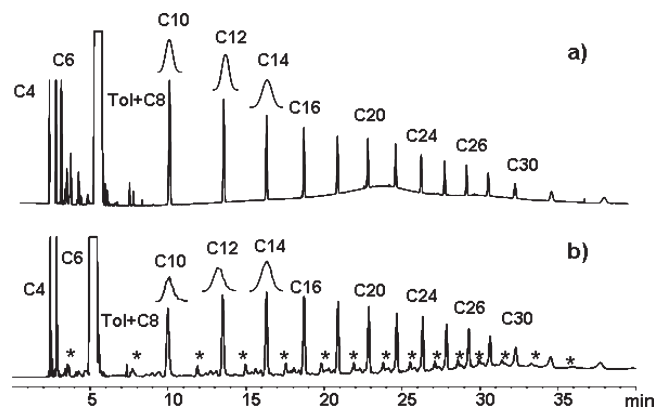


Figure 2. Gas chromatogram showing the product distribution from a co-oligomerization of a C_2H_4/C_2D_4 mixture (1:1) with catalysts **3** (a) and **4** (b) (* = odd-numbered alkane products).

Table 2. Schultz–Flory Oligomer Distribution Analysis for Catalysts 1, 3, and 4^a

cat.	C_2H_4 oligomerization		C_2H_4/C_2D_4 co-oligomerization		KIE
	α_H	β_H	$\alpha_{H/D}$	$\beta_{H/D}$	
1	0.76	0.31	0.84	0.19	5.1 ± 0.9
3	0.75	0.33	0.77	0.31	1.5 ± 0.2
4	0.73	0.36	0.80	0.25	

$$^a \alpha = k_p/(k_p + k_t); \beta = k_t/k_p = (1 - \alpha)/\alpha \text{ (see ref 30).}$$

appear as broad unresolved signals, indicating the presence of a larger number of isotopologues. The signals marked by asterisks are odd-numbered linear alkanes, which show a similar splitting pattern to the corresponding even-numbered alkenes. The odd-numbered linear C_{2n+1} alkanes are formally derived from the corresponding even-numbered C_{2n} alkenes by the addition of CH_3 (from $Al(CH_3)_3$ in MAO) and H (from H_2O upon quenching) across the double bond. Although chain transfer to aluminum is more commonly associated with a Cossee-type mechanism, it can also occur in a metallacyclic mechanism, as is shown here for catalyst **2**. The mechanism for this exchange reaction is unclear at this stage, but it is believed to involve a bimetallic Cr/Al intermediate, as suggested by McGuinness and co-workers.²⁰

Kinetic Isotope Effects. The kinetic isotope effect (KIE) on the rate of ethene insertion (k_p) for C_2H_4 versus C_2D_4 is a secondary kinetic isotope effect due to the difference in reactivity between the two monomers, and this effect is expected to be rather small.^{34,35} The rate of β -H elimination (k_t) generally has a primary KIE, and values up to 7 can be expected. Studies on β -H elimination reactions of palladium(II) alkyl complexes have shown that the KIE for *syn*- β -H elimination is typically smaller (2–3) compared to the values observed for *anti*- β -H elimination (5–7).³⁶ The α - and β -values for the Schultz–Flory distributions of α -olefins obtained with catalysts **1**, **3**, and **4** are collected in Table 2. The KIE on the rate of chain termination was determined by comparing the β -values (k_t/k_p) obtained for C_2H_4 oligomerization versus C_2H_4/C_2D_4 co-oligomerization (see Supporting Information for details).

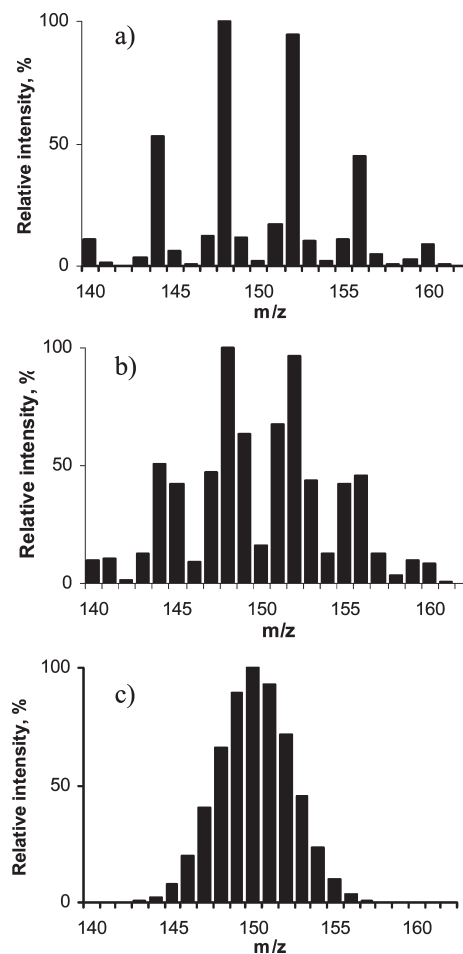


Figure 3. Theoretical mass spectrum for the 1-decene fraction from a co-oligomerization using C_2H_4/C_2D_4 (1:1): (a) for a metallacyclic mechanism, (b) for a Cossee-type mechanism with partial H/D scrambling, and (c) for a Cossee-type mechanism with complete H/D scrambling.

In general, smaller β -values are observed for the ethylene/ d_4 -ethylene co-oligomers ($\beta_{H/D}$) in comparison to the unlabeled products (β_H). These differences are caused by a change in the relative rates of termination due to the KIE on β -H versus β -D elimination. As a result, the higher oligomer fractions will become increasingly enriched in deuterium. The KIE for chain termination was determined as 5.1 ± 0.9 for catalyst **1**, whereas for catalyst **3** a KIE of 1.5 ± 0.2 was determined. KIE values could not be determined for the other catalysts due to additional chain termination to aluminum reactions. These values are in agreement with the proposed mechanisms for chain termination for catalysts **1** and **3**, whereby β -H elimination in a metallacyclic mechanism is more akin to an *anti*- β -H elimination process, whereas β -H elimination from a linear chain in a Cossee-type mechanism is more likely to occur in a *syn* fashion.

Isotopologue Distributions. The theoretical isotopologue distributions of the C_{10} , C_{12} , and C_{14} fractions have been used to calculate the expected mass spectrum for each fraction, in the case of both a metallacyclic and a Cossee-type mechanism (see Supporting Information for details). In these calculations, the natural abundances of ^{13}C and deuterium as well as the protio impurities in C_2D_4 have been taken into account (the natural abundance of ^{13}C is 1.1%, for

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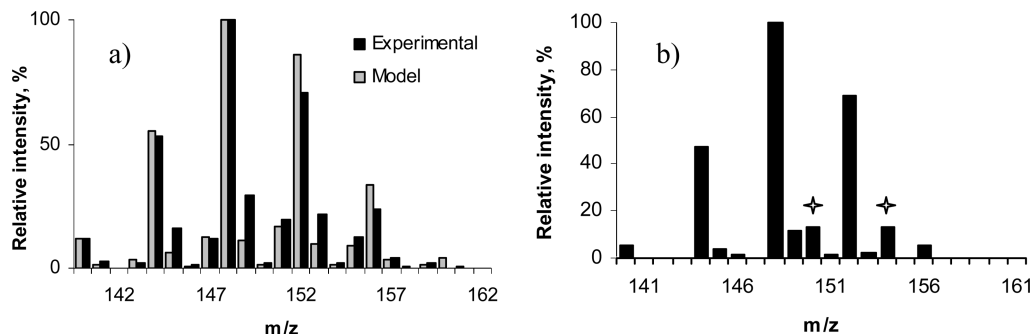


Figure 4. (a) Theoretical and experimental mass spectrum for the 1-decene fraction arising from a metallacyclic mechanism for catalyst **1**. (b) Experimental mass spectrum for the 1-decene fraction obtained with catalyst **2**. The decane products are indicated by +.

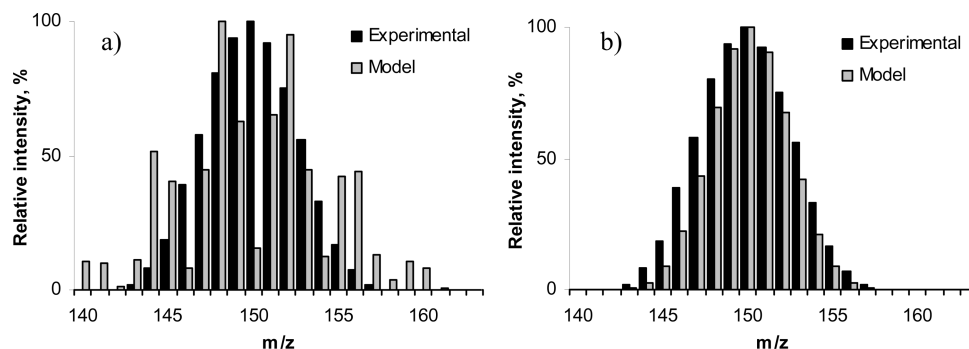


Figure 5. Theoretical and experimental mass spectrum for the 1-decene fraction arising from a Cossee-type mechanism, involving (a) partial H/D scrambling ($\text{KIE} = 1.3 \pm 0.2$) and (b) complete H/D scrambling ($\text{KIE} = 1.5 \pm 0.2$) for catalyst **3**.

deuterium 0.015%, and the isotopic purity of C_2D_4 used was 99%D). The KIE will also affect the mass spectrum, and this has also been included in the calculations of the spectra where the KIE values are known.

In the case of a metallacyclic mechanism, the theoretical mass spectrum shown in Figure 3a exhibits six major even-numbered peaks (M_e) at m/z 140, 144, 148, 152, 156, and 160. Each of these peaks is joined by less intense odd-numbered signals. The $M_e + 1$ lines are due to the natural abundance of ^{13}C and D. The $M_e - 1$ signals are caused by the presence of about 1% partially deuterated ethylene (protio impurities) in C_2D_4 . In the case of a Cossee-type mechanism, the same main peaks will be observed, but the odd-numbered peaks will be more intense, which relates to whether the chain is initiated from, or terminates to, a metal-H or metal-D. In Figure 3b, a theoretical mass spectrum is shown for the 1-decene fraction, calculated for a Cossee-type mechanism with partial scrambling, including the protio impurities in C_2D_4 and the ^{13}C and deuterium natural abundances, but excluding the KIE. However, this hypothetical mass spectrum is only of theoretical interest. In reality, before chain growth in an ethylene oligomerization reaction via a Cossee-type mechanism, many ethylene insertions into a M-H (or M-D) bond and deinsertions from a M-ethyl species will have taken place because k_p and k_t are very similar. In other words, the main product in a Schultz–Flory product distribution is in fact ethylene. As a result of this, the initial $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ mixture will be rapidly scrambled to a statistical mixture of C_2H_4 , $\text{C}_2\text{H}_3\text{D}$, $\text{C}_2\text{H}_2\text{D}_2$, C_2HD_3 , and C_2D_4 , and this will result in an isotopologue distribution described by the general formula $\text{C}_{2n}\text{H}_m\text{D}_{4n-m}$ (n is degree of polymerization and $m = 0, 1, \dots, 4n$). The theoretical mass spectrum for a Cossee-type mechanism with complete H/D

scrambling will therefore be a binomial distribution, as shown in Figure 3c.

Analysis of the 1-Decene Fraction. The experimentally determined mass spectra for the α -olefins obtained with catalyst **1** have been compared with the calculated spectra. In Figure 4a is shown the theoretical mass spectrum of the C_{10} fraction, calculated on the basis of a metallacyclic mechanism including the ^{13}C and D natural abundances, the isotopic purity of d_4 -ethylene, and a KIE on termination of 5.1, together with the experimentally determined spectrum. The close similarity between the two spectra clearly shows that 1-decene obtained with catalyst **1** is formed via a metallacyclic mechanism.

For the second chromium catalyst **2**, the C_2H_4 oligomerization and $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ co-oligomerization reactions are complicated due to the presence of the additional chain transfer to aluminum termination process. This chain transfer occurs only after the chain growth for a particular oligomer has completed and therefore does not contribute to H/D scrambling and will not affect the appearance of the isotopologue distributions. It does preclude, however, the precise calculation of the KIE for β -H elimination. The experimental mass spectrum for the 1-decene fraction obtained with catalyst **2** is shown in Figure 4b. The formation of isotopologues containing only even numbers of hydrogen and deuterium atoms clearly confirms the involvement of a metallacyclic mechanism for the oligomerization reaction using this catalyst. The signals at m/z 150 and 154 (indicated by + on the spectrum) correspond to two minor decane isotopologues, $\text{C}_{10}\text{H}_{14}\text{D}_8$ and $\text{C}_{10}\text{H}_{10}\text{D}_{12}$, respectively, which are formed via chain transfer to aluminum reactions. The α -olefin isotopologue distribution is biased toward the protio-enriched products due to the KIE on termination.

The cobalt catalyst **3** co-oligomerizes C_2H_4/C_2D_4 (1:1) to partially deuterated linear α -olefins that follow a Schultz–Flory distribution. GC/MS analysis of the 1-decene fraction reveals multiple C_{10} -isotopologues with a statistical distribution that suggests extensive H/D scrambling (compare Figure 5a and b). The theoretical spectra calculated for the two possible scenarios, with complete and partial H/D scrambling (including an appropriate KIE), are shown in gray. From these results, it is clear that catalyst **3** operates via a Cossee-type mechanism.

The analysis of the product mixture obtained from the co-oligomerization experiment of C_2H_4/C_2D_4 (1:1) with catalyst **4** has shown that besides β -H elimination, chain transfer to aluminum also operates as a termination mechanism under the conditions used, albeit to a lesser extent compared to catalyst **2**. The shape of the mass spectrum, the m/z of the formed isotopologues, and their relative abundances confirm the involvement of a Cossee-type mechanism for this catalyst. Complete H/D scrambling in the products suggests that the initial C_2H_4/C_2D_4 (1:1) mixture has been scrambled prior to or during the oligomerization reaction at a rate that is far greater than the rate of chain growth. The mass spectrum is biased toward the protio-enriched isotopologues due to the KIE and the purity of C_2D_4 and possibly also due to hydrolysis with H_2O of the alkane fraction.

Analysis of Higher α -Olefin Fractions. The same analysis as described in the previous section for the C_{10} fraction of the C_2H_4/C_2D_4 co-oligomerization experiments with catalysts **1–4** was also performed for the C_{12} and C_{14} fractions. Essentially the same conclusions can be drawn from the analyses of these fractions, and the full details can be found in the Supporting Information (Figures S1–S4). The detailed analysis of higher molecular weight fractions (C_{16+}) is prohibited by the resolution of the GC and GC/MS equipment, and we have therefore analyzed these higher molecular weight fractions separately by NMR spectroscopy. The higher molecular weight fraction for each catalyst was separated from the reaction product mixture by precipitation with methanol, and after removal of all volatiles (60 °C, 1 mmHg, 12 h), the material was analyzed by $^{13}C\{^1H\}$ and ^{13}C DEPT-135 NMR spectroscopy.

The $^{13}C\{^1H\}$ and ^{13}C DEPT-135 NMR spectra of the solid oligomers obtained with catalyst **1** are shown in the top spectra in Figure 6. The average molecular weight of the higher molecular weight fraction obtained with catalyst **1** was determined by NMR to be in the range 280–320 Da, which corresponds to an average chain length of 22 carbon atoms. The assignment of the $^{13}C\{^1H\}$ NMR spectrum was carried out according to the previously reported analysis of partially deuterated, high molecular weight polyethylene.³⁷ The signals at ca. 30 ppm correspond to the methylene carbon atoms from the ethylene-centered triads (EEE, EED, DEE, and DED), whereas the d_4 -ethylene centered triads (EDE, DDE, EDD, and DDD) are observed as a sextet at ca. 29 ppm. The CD_2 resonances are subject to ^{13}C – D coupling ($J_{C-D} = 19$ Hz), resulting in the formation of a quintet for each d_2 -methylene carbon with a 1:2:3:2:1 intensity ratio. The quintets from the four d_4 -centered triads overlap and appear as a sextet. Both the $^{13}C\{^1H\}$ and the ^{13}C DEPT-135 NMR spectra confirm that the C_2H_4/C_2D_4

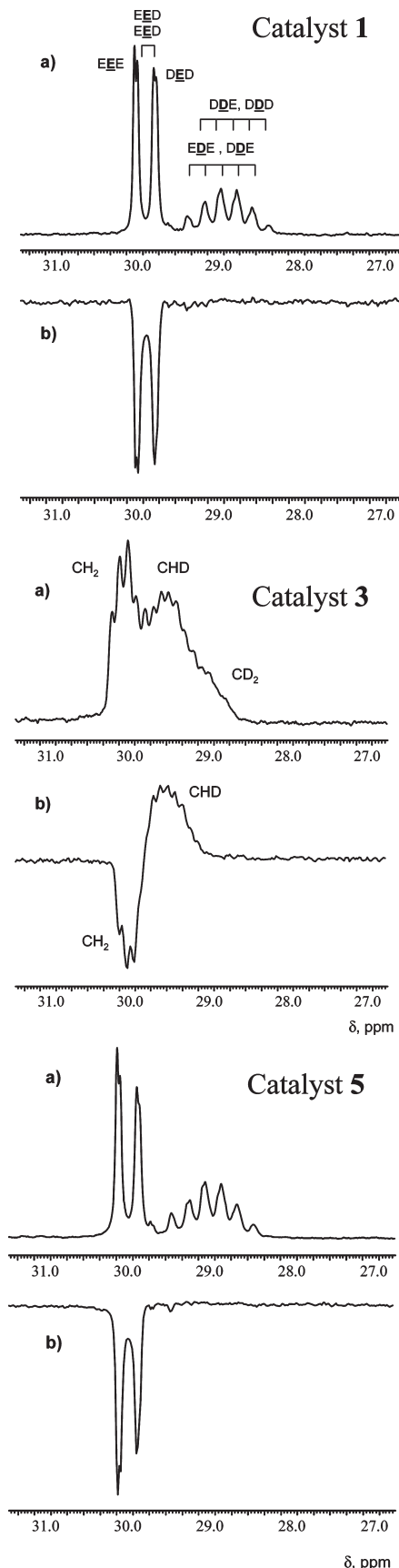


Figure 6. $^{13}C\{^1H\}$ (a) and ^{13}C DEPT-135 (b) NMR spectra of the higher C_2H_4/C_2D_4 co-oligomer fraction obtained with catalyst **1** (top), **3** (middle), and **5** (bottom) (E = C_2H_4 , D = C_2D_4).

(37) Cheng, H. N.; Dziemianowicz, T. S. *Makromol. Chem.* **1988**, *189*, 845–849.

co-oligomers, obtained using catalyst **1**, consist of discrete C_2H_4 and C_2D_4 sequences in which the CH_2 and CD_2 groups have not undergone any H/D scrambling. The C_2D_4 incorporation, obtained by integration of the ethylene and d_4 -ethylene regions in the ^{13}C NMR spectrum, was determined to be 54.3 mol %. A calibration curve to account for NOE effects was obtained by measuring the ^{13}C NMR spectra of preweighed mixtures of polyethylene and perdeuterio-polyethylene (see Supporting Information, Figure S35). The higher oligomer fractions are slightly enriched in deuterium due to the KIE, whereas the C_{10} , C_{12} , and C_{14} fractions are protio-enriched.

The cobalt complex **3**, when activated with MAO, gives C_2H_4/C_2D_4 co-oligomers with complete H/D scrambling in the C_{10} – C_{14} fractions, as was shown by the GC/MS analysis in the previous section. The higher molecular weight fraction, which has been analyzed by ^{13}C NMR, shows that, in addition to signals for the CH_2 and CD_2 units, also signals for CHD units are observed. This is particularly clear in the DEPT-135 spectrum (Figure 6, middle).

Ethylene Polymerization. In the previous sections it has been shown that C_2H_4/C_2D_4 (1:1) co-oligomerization experiments can be used to distinguish between a metallacyclic mechanism and a Cossee-type chain growth mechanisms. We were interested in establishing whether or not this method can be extended to polymerization systems, utilizing ^{13}C NMR spectroscopy as a method for analysis of the polymer. The iron polymerization catalyst **5** was employed, because this catalyst is closely related to the oligomerization catalyst **4** and therefore can be reasonably anticipated to operate via a Cossee-type chain growth mechanism, resulting in extensive H/D scrambling. However, as can be seen from the spectra at the bottom in Figure 6, no H/D scrambling is observed in the copolymer.

At first sight this observation may seem surprising. However, it is readily explained as a consequence of a high rate of chain propagation versus chain termination for polymerization catalyst systems. In the case of the oligomerization catalyst **4**, the rate of propagation k_p and the rate of termination k_t are comparable, and therefore extensive H/D scrambling is observed, both in the product and in the C_2H_4/C_2D_4 starting feed. With similar rates between insertion and deinsertion (β -H elimination), extensive H/D scrambling of the C_2H_4/C_2D_4 mixture occurs, leading to statistical distributions of H and D, both in the starting material and in the product. For the polymerization catalyst **5**, and also for other polymerization catalysts, the rate of propagation is generally much greater than the rate of termination, and therefore H/D scrambling will be minimal or not observed at all since insufficient time will be available to scramble the starting material. It is therefore not possible to use this methodology to determine whether polymerization occurs by a metallacyclic or a Cossee-type mechanism. Instead of analyzing the polymer, if the reaction time is kept very short (i.e., less than a second), it is possible to generate low molecular weight product and analyze it by GC/MS. This experiment was effectively carried out by Grubbs and co-workers,²² using a titanium-based polymerization catalyst and a reaction time of 0.7 s. No H/D scrambling was observed, despite a Cossee-type mechanism.

Conclusions

In the present study, we have investigated the ability to distinguish between chain growth mechanisms for ethylene

oligomerization catalysts using C_2H_4/C_2D_4 co-oligomerization experiments. The experimentally determined mass spectra for the C_{10} , C_{12} , and C_{14} fractions obtained with the series of oligomerization catalysts **1**–**4** have been compared with the calculated mass spectra. The theoretical calculations have taken into account the natural abundances of ^{13}C and deuterium, the isotopic purity of C_2D_4 , and the experimentally determined KIE. For chromium catalyst **1**, a metallacyclic chain growth mechanism has been clearly established. Chromium catalyst **2** also operates via a metallacyclic mechanism, but an accurate calculation of the predicted mass spectrum is precluded due to the additional chain transfer to aluminum process. For the cobalt- and iron-based oligomerization catalysts **3** and **4**, a Cossee-type mechanism has been confirmed on the basis of the complete H/D scrambling observed in the mass spectra of the oligomer fractions. Higher oligomer fractions have been analyzed by $^{13}C\{^1H\}$ and ^{13}C DEPT-135 spectroscopy, and it has been shown that these analytical techniques can be used to distinguish between a metallacyclic and a Cossee-type mechanism in oligomerization systems. However, this method is not applicable to polymerization systems, where the rate of propagation is much faster than the rate of termination.

There are two important outcomes of this study: (1) C_2H_4/C_2D_4 co-oligomerization experiments can be readily used to differentiate between metallacyclic and Cossee-type chain growth mechanisms for oligomerization catalysts in general; (2) for polymerization systems, the extent of H/D scrambling is dependent upon the ratio of the rate of propagation to the rate of termination. To achieve high molecular weight products, polymerization catalysts, by definition, will have a much higher rate of propagation relative to termination. Therefore, the products will remain unscrambled even if the chain growth process proceeds via the Cossee mechanism. Under these circumstances, determining the chain growth mechanism for polymerization catalysts is best approached by studying closely related analogues, i.e., with identical ligand donor groups and backbone connectivities, which produce products in the C_{10} – C_{14} range suitable for analysis by GC/MS.

Experimental Section

Air-sensitive reactions were performed using standard Schlenk and vacuum line techniques. Toluene was dried by passing through a cylinder filled with commercially available Q-5 catalyst (13% Cu(II) oxide on Al_2O_3). Ethylene (99.95%) was obtained from BOC. d_4 -Ethylene (99% D) was obtained from Aldrich. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (1H) and 100 MHz (^{13}C) at 293 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. GC/MS analysis was carried out using a VG Autospec-Q mass spectrometer, connected to a HP-5890 gas chromatograph (GC column: SGE BPX-5, 5% phenyl polysilphenylene-siloxane, 25 m \times 0.22 mm \times 1 μm). GC analyses of oligomers were carried out on a HP-5890 gas chromatograph (GC column: HP-5, 5% phenylmethylsiloxane, 30 m \times 0.32 mm \times 0.25 μm). MAO (10% solution in toluene, 1.6 M) was purchased from Chemtura.

Ethylene Oligomerization Procedure. A Fisher-Porter bottle, dried and flushed with N_2 , was charged with toluene (220 mL), 2,2,4,4,6,8,8-heptamethylnonane standard (~ 0.5 g), and MAO (1.6 M in toluene, 4.4 mL, 7.5 mmol). This was followed by injection of a 1–5 μmol aliquot of the preactivated catalysts, prepared *in situ* by reacting 10–50 μmol of the corresponding

precatalyst with MAO (1.6 M in toluene, 2.5 mL) in toluene (50–250 mL). The reactor was then connected to an ethylene supply and charged to the desired pressure. The polymerization reactions were carried out under mechanical stirring, at the required temperature for 60 min. Each reaction was terminated by disconnecting the reactor from the ethylene line. After withdrawing a small sample for GC analysis the reaction mixture was hydrolyzed by addition of water (10 mL).

Co-oligomerization (copolymerization) of a C_2H_4/C_2D_4 (1:1) Mixture. Complexes **1–5** ($\sim 5 \mu\text{mol}$) were placed in a 100 mL, thick-walled Schlenk tube and suspended in toluene (30 mL). After addition of MAO (1.6 M in toluene, 2.5 mL), the reaction mixture was degassed and then frozen at -196°C . The vessel was connected, via a T-connector, to a 400 mL thick-walled glass ampule charged with a mixture of C_2H_4 and C_2D_4 (1:1, mol:mol) at ~ 4 bar absolute pressure. After evacuation of the connecting line and the reaction vessel, the reaction mixture was allowed to warm to room temperature and the C_2H_4/C_2D_4 mixture was then introduced. After stirring at room temperature for 1 h, an aliquot was withdrawn, passed through a layer of

neutral silica to remove the components of the catalyst mixture, and analyzed by GC and GC/MS. Cumulative MS spectra were obtained for each GC fraction by summation of the MS spectra for all isotopologues in a given oligomer fraction.

Co-oligomerization experiments can also be conducted by condensing the C_2H_4/C_2D_4 (1:1) mixture directly onto a degassed and frozen (-196°C) catalyst/MAO/toluene mixture in a thick-walled glass ampule, followed by warming to room temperature. The product distributions obtained by the two methods were essentially the same.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.