

Proofs to: Dr. George Britovsek
Department of Chemistry
Imperial College London
Exhibition Road
South Kensington
London SW7 2AY
UK
Tel. +44-(0)20-75945863
Fax. +44-(0)20-75945804
e-mail: g.britovsek@imperial.ac.uk

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

Atanas K. Tomov, Vernon C. Gibson,* George J.P. Britovsek,* Richard J. Long, Martin van Meurs, David J. Jones, Kilian P. Tellmann and Juan J. Chirinos

Department of Chemistry, Imperial College London, Exhibition Road, London, SW7 2AY, UK.

Abstract

A series of co-oligomerization and co-polymerization 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 analysed 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 analysed 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.

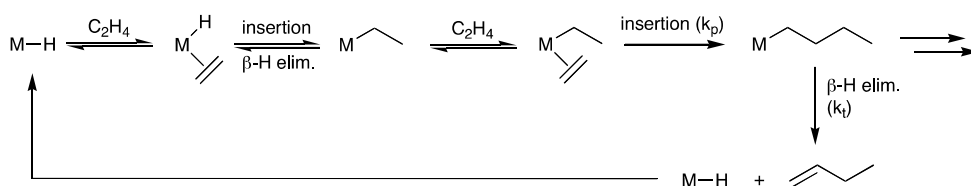
Keywords: ethene, oligomerization, polymerization, deuterium, labelling, mechanism

Introduction

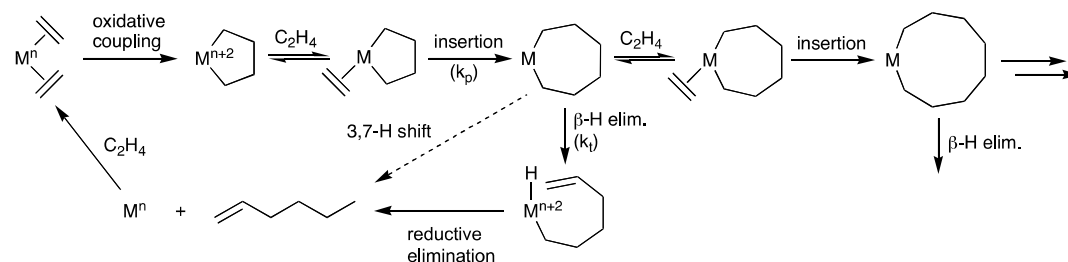
The development of new catalysts for the oligomerization and polymerization of olefins continues to attract a great deal of interest both in academia and in industry.¹⁻⁴ Ever-increasing control over the polymerization reaction has led to remarkable advances in this area, both in terms of novel polymer 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 ultra-fast chain transfer agents to give catalyzed chain growth on zinc⁵⁻⁷ and the subsequent development of chain shuttling to give block co-polymers.^{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 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 metallacyclic intermediates (Scheme 1b).¹⁶ Here, oxidative coupling of two coordinated ethylene molecules at a metal centre form 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.^{18,19,20}

a) Cossee Mechanism

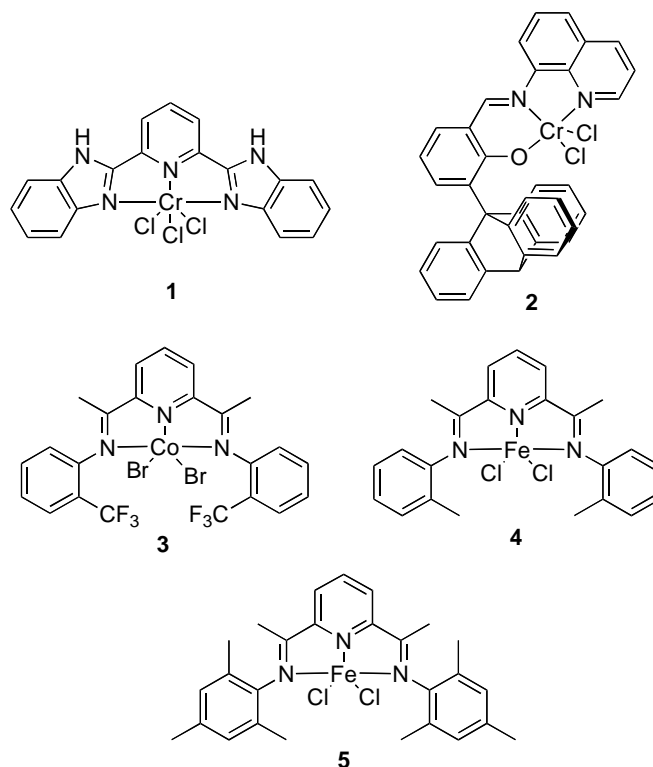


b) Metallacyclic Mechanism



Scheme 1. Ethylene oligomerization/polymerization mechanisms.

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 co-polymerization studies.^{21,22} In a metallacyclic 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 metallacyclic 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 co-trimerization reaction, the absence of H/D scrambling implies a metallacyclic mechanism for this reaction.^{23,24} Similar observations have been made for ethylene tetramerisation 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 co-polymerization experiments with a series of catalysts **1** – **5**, as shown in Figure 2.



Scheme 2. Selected ethylene oligomerization and polymerization catalysts **1** – **5**.

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} Preliminary co-oligomerization experiments employing C_2H_4/C_2D_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 C_2H_4/C_2D_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 C₂H₄/C₂D₄ 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 ¹³C 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

C₂H₄ Oligomerization

Standard ethylene oligomerization reactions using catalysts **1-4** in combination with MAO as the co-catalyst 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 co-catalyst.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.

Table 1. Ethylene oligomerization catalyzed by complexes **1-4**/MAO

Run	Cat.	m_{cat} μmol	P bar	T $^{\circ}\text{C}$	Yield g	Act. $\text{g}/\text{mmol}\cdot\text{h}\cdot\text{bar}$	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

Reaction conditions: a) Toluene; MAO (8 mmol); 70 min.; from ref. 18. b) Toluene; MAO (2.2 mmol); 60 min.; from ref. 33. c) Toluene; MAO (1 mmol); 60 min.; from ref. 31. d) 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).

C_2H_4/C_2D_4 Co-oligomerization

The co-oligomerization reactions of a C_2H_4/C_2D_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, Figs. S5-S30). The number of possible isotopologues and the variation in their relative abundance increases 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.

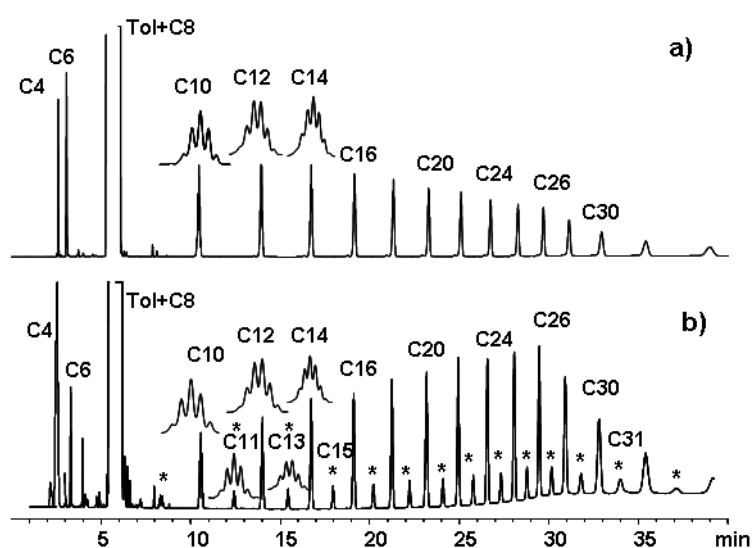


Figure 1. Gas chromatogram showing the product distribution from a co-oligomerization of a C_2H_4/C_2D_4 mixture (1:1) with catalysts **1** (a) and **2** (b) (* = odd-numbered alkane products).

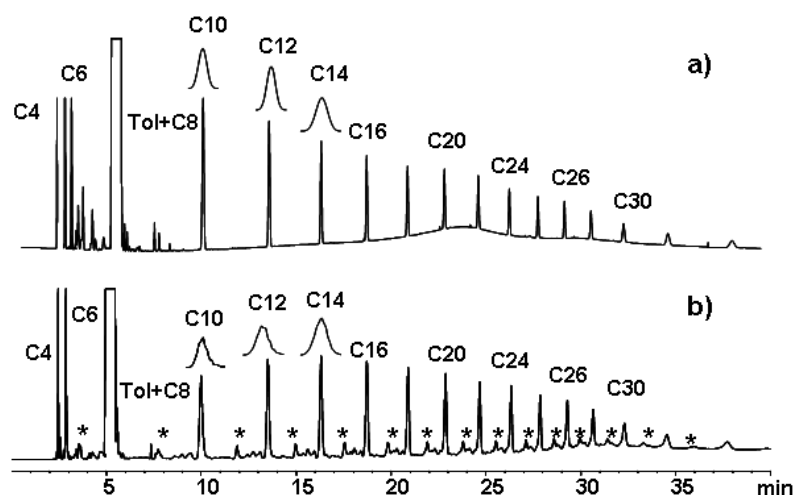


Figure 2. Gas chromatogram showing the product distribution from a co-oligomerization of a C_2H_4/C_2D_4 mixture (1:1) with catalysts **3** (a) and **4** (b) (* = odd-numbered alkane products).

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** 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 as 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 metallocyclic 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).

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.

Table 2. Schultz-Flory oligomer distribution analysis for catalysts **1**, **3** and **4**.

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	-

$\alpha = k_p/(k_p + k_t)$; $\beta = k_t/k_p = (1-\alpha)/\alpha$ (see ref. 30).

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, both in the case of 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 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 experimentally determined 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 de-insertions 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.

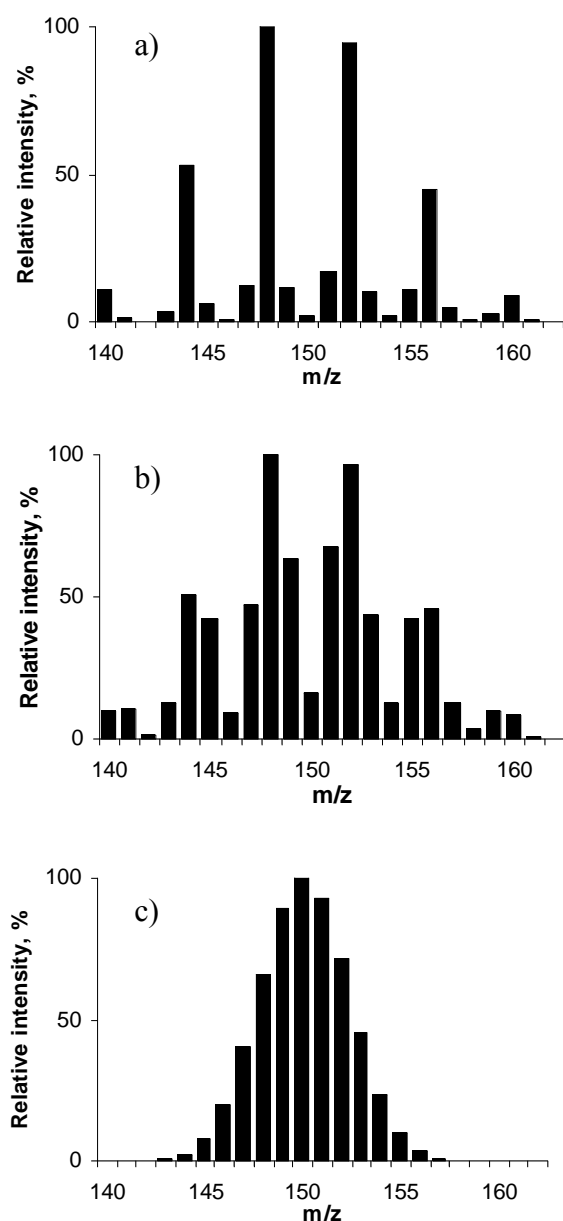


Figure 3. Theoretical mass spectrum for the 1-decene fraction from a co-oligomerization using C_2H_4/C_2D_4 (1:1); a) for a metallacyclic mechanism, b) for a Cossee-type mechanism with partial H/D scrambling and c) for a Cossee-type mechanism with complete H/D scrambling.

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 C_2H_4/C_2D_4 co-oligomerization reactions are complicated due to the presence of the additional chain transfer to aluminum termination process. This chain transfer only occurs 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 \star on the spectrum) correspond to two minor decane isotopologues $C_{10}H_{14}D_8$ and $C_{10}H_{10}D_{12}$, respectively, which are formed via chain transfer to aluminum reactions. The α -olefin isotopologue distribution is biased towards the protio-enriched products due to the KIE on termination.

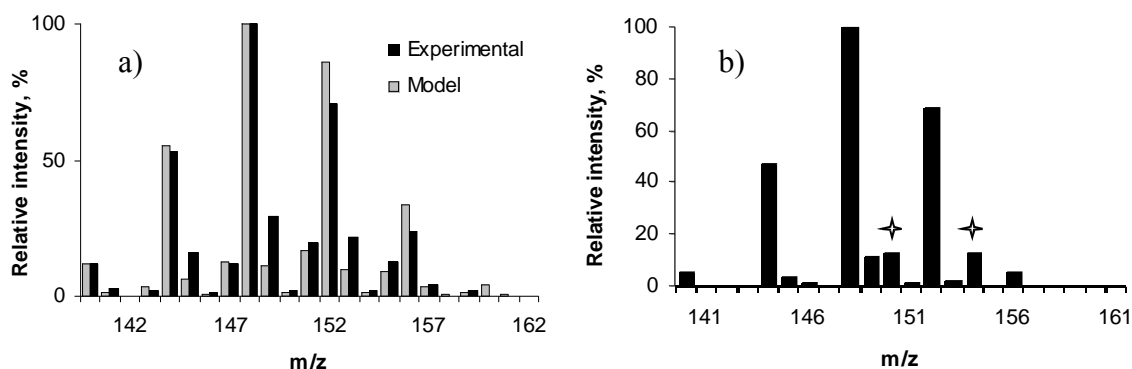


Figure 4. a) Theoretical and experimental mass spectrum for the 1-decene fraction arising from a metallacyclic mechanism for catalyst **1**; b) Experimental mass spectrum for the 1-decene fraction obtained with catalyst **2**. The decane products are indicated by \star .

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 Figs. 5a and 5b). The theoretical spectra calculated for the two possible scenarios, with complete and partial H/D scrambling (including an appropriate KIE) are shown in grey. From these results, it is clear that catalyst **3** operates *via* a Cossee-type mechanism.

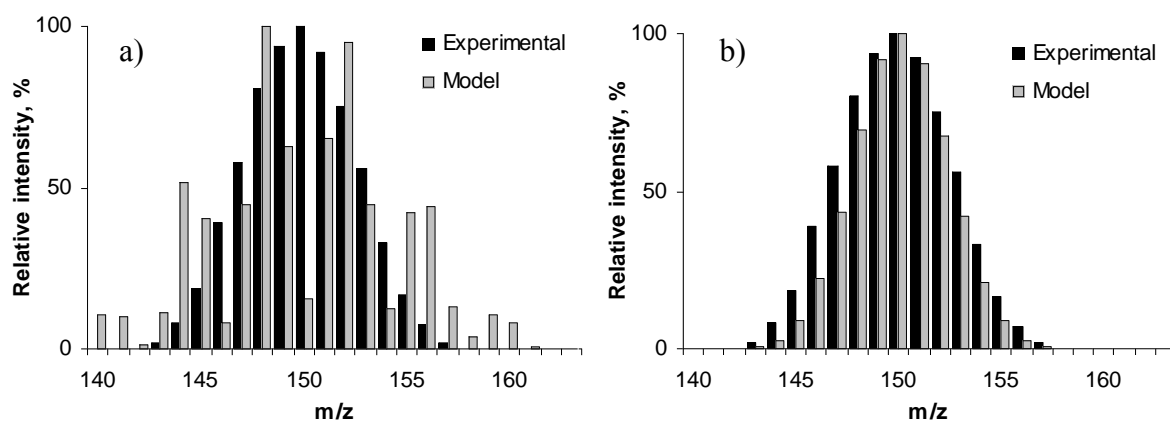


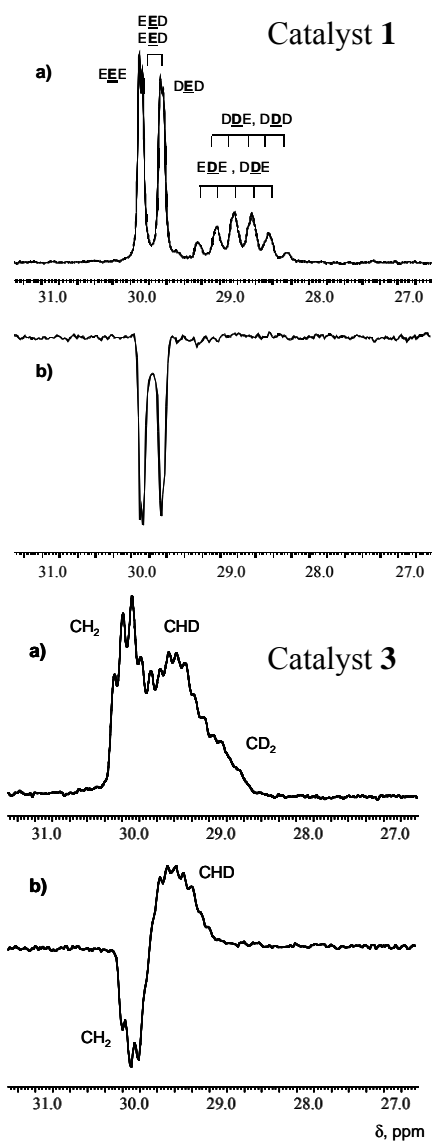
Figure 5. Theoretical and experimental mass spectrum for the 1-decene fraction arising from a Cossee-type mechanism, involving a) partial H/D scrambling ($KIE = 1.3 \pm 0.2$) and b) complete H/D scrambling ($KIE = 1.5 \pm 0.2$) for catalyst **3**.

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 towards 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 Supplementary Material (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 mm Hg, 12h), the material was analyzed by $^{13}C\{^1H\}$ and ^{13}C DEPT-135 NMR spectroscopy.



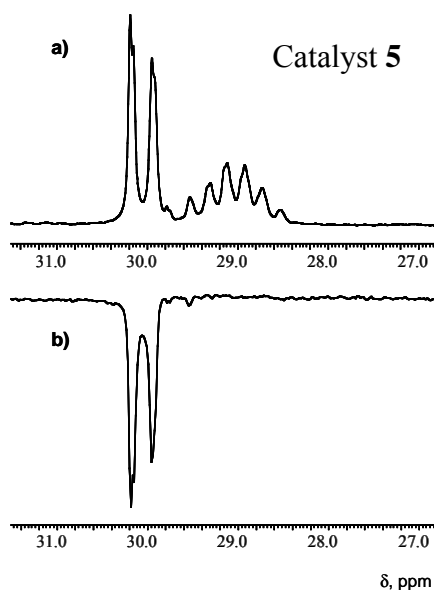


Figure 6. $^{13}\text{C}\{^1\text{H}\}$ (a) and ^{13}C DEPT-135 (b) NMR spectra of the higher $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ co-oligomer fraction obtained with catalyst **1** (top), **3** (middle) and **5** (bottom) (E = C_2H_4 , D = C_2D_4).

The $^{13}\text{C}\{^1\text{H}\}$ 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 of 280–320 Da, which corresponds to an average chain length of 22 carbon atoms. The assignment of the $^{13}\text{C}\{^1\text{H}\}$ 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 ($^1J_{\text{C-D}} = 19$ 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 $^{13}\text{C}\{^1\text{H}\}$ and the ^{13}C DEPT-135 NMR spectra confirm that the $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ 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 pre-weighed mixtures of polyethylene and perdeuterio-polyethylene (see Supporting Information, Fig. S35). The

higher oligomer fractions are slightly enriched in deuterium due to the KIE, whereas the C₁₀, C₁₂ and C₁₄ fractions are protio-enriched.

The cobalt complex **3**, when activated with MAO, gives C₂H₄/C₂D₄ co-oligomers with complete H/D scrambling in the C₁₀-C₁₄ fractions, as was shown by the GC/MS analysis in the previous section. The higher molecular weight fraction, which has been analyzed by ¹³C NMR shows that, in addition to signals for the CH₂ and CD₂ 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 C₂H₄/C₂D₄ (1:1) co-oligomerization experiments can be used to distinguish between a metallacyclic mechanism and a Cossee-type chain growth mechanisms. We were interested to establish whether or not this method can be extended to polymerization systems, utilizing ¹³C 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 C₂H₄/C₂D₄ starting feed. With similar rates between insertion and de-insertion (β -H elimination), extensive H/D scrambling of the C₂H₄/C₂D₄ 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 oligomerisation 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 a series of oligomerisation 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 oligomerisation catalysts **3** and **4**, a Cossee-type mechanism has been confirmed based on 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 product in the C_{10} – C_{14} range suitable for analysis by GC MS.

Experimental

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 Al₂O₃). Ethylene (99.95%) was obtained from BOC. d⁴-Ethylene (99 %D) was obtained from Aldrich. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (¹H) and 100 MHz (¹³C) 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 x 0.22 mm x 1 micron). GC analyses of oligomers were carried out on a HP-5890 Gas Chromatograph (GC column: HP-5, 5% phenylmethylsiloxane, 30 m x 0.32 mm x 0.25 micron). MAO (10% solution in toluene, 1.6 M) was purchased from Chemtura.

Ethylene oligomerization procedure.

A Fisher-Porter bottle, dried and flushed with N₂, was charged with toluene (220 mL), 2,2,4,4,6,8,8-heptamethylnonane standard (~0.5g) 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 pre-activated catalysts, prepared *in situ* by reacting 10 - 50 μmol of the corresponding pre-catalyst 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 minutes. 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 (co-polymerization) of a C₂H₄/C₂D₄ (1:1) mixture

Complexes **1–5** (~5 μmol) were placed in a 100 mL, thick-walled Schlenk tube and suspended in toluene (30 mL). After addition of MAO (1.6M 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 ampoule charged with a mixture of C₂H₄ and C₂D₄ (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 up to room temperature and the C₂H₄/C₂D₄ mixture was then introduced. After stirring at room temperature for 1 hour, 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 C₂H₄/C₂D₄ (1:1) mixture directly onto a degassed and frozen (-196 °C) catalyst/MAO/toluene mixture in a thick-walled glass ampoule, followed by warming to room temperature. The product distributions obtained by the two methods were essentially the same.

Acknowledgements We are grateful to Ineos for financial support. Mr. J. Barton is thanked for the collection of mass spectral data. We thank Mr R. Sheppard and Mr P. Haycock for helpful discussions regarding NMR spectroscopy.

References

- (1) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283-316.
- (2) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 428-447.
- (3) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169-1203.
- (4) *Oligomerisation of Ethylene to Higher Linear Alpha-olefins*; Vogt, D., Ed.; VCH: Weinheim, 2002.
- (5) Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; van Meurs, M. *J. Am. Chem. Soc.* **2004**, *126*, 10701-10712.
- (6) van Meurs, M.; Britovsek, G. J. P.; Gibson, V. C.; Cohen, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 9913-9923.
- (7) Kempe, R. *Chem. Eur. J.* **2007**, *13*, 2764-2773.
- (8) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714-719.
- (9) Gibson, V. C. *Science* **2006**, *312*, 703-704.
- (10) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858-859.
- (11) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712-14713.

- (12) Wass, D. F. *Dalton Trans.* **2007**, 816-819.
- (13) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641.
- (14) Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Maddox, P. J.; van Meurs, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 489-491.
- (15) Cossee, P. *J. Catal.* **1964**, *3*, 80-88.
- (16) Briggs, J. R. *J. Chem. Soc. Chem. Commun.* **1989**, 674-675.
- (17) Blok, A. N. J.; Budzelaar, P. H. M.; Gal, A. W. *Organometallics* **2003**, *22*, 2564-2570.
- (18) Tomov, A.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, *127*, 10166-10167.
- (19) McGuinness, D. S. *Organometallics* **2009**, *28*, 244-248.
- (20) McGuinness, D. S.; Suttill, J. A.; Gardiner, M. G.; Davies, N. W. *Organometallics* **2008**, *27*, 4238-4247.
- (21) Maruyama, K.; Kuroki, T.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2002.
- (22) Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479-4480.
- (23) Agapie, T.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2007**, *129*, 14281-14295.
- (24) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304-1305.
- (25) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Haasbroek, D.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 10723-10730.
- (26) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038-1039.
- (27) Tomov, A.; Chirinos, J. J.; Long, R. J.; Gibson, V. C.; Elsegood, M. R. J. *J. Am. Chem. Soc.* **2006**, *128*, 7704-7705.
- (28) Zhang, W.; Sun, W.-H.; Zhang, S.; Hou, J.; Wedeking, K.; Schultz, S.; Fröhlich, R.; Song, H. *Organometallics* **2006**, *25*, 1961-1969.
- (29) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728-8740.
- (30) Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J. *Chem. Eur. J.* **2000**, *6*, 2221-2231.

- (31) Tellmann, K. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Organometallics* **2005**, *24*, 280-286.
- (32) Humphries, M. J.; Tellmann, K. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Organometallics* **2005**, *24*, 2039-2050.
- (33) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J.; White, A. J. P.; Williams, D. *J. J. Am. Chem. Soc.* **2005**, *127*, 11037-11046.
- (34) Grigoryan, E. A.; Drachkovskii, F. S.; Shilov, A. Y. *Vysokomol. Soedin. Ser. A* **1965**, *7*, 145-149.
- (35) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85-93.
- (36) Lloyd-Jones, G. C.; Slatford, P. *J. Am. Chem. Soc.* **2004**, *126*, 2690-2691.
- (37) Cheng, H. N.; Dziemianowicz, T. S. *Makromol. Chem.* **1988**, *189*, 845-849.

For Table of Contents Use Only

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

Authors: Atanas K. Tomov, Vernon C. Gibson,* George J. P. Britovsek,* Richard J. Long, Martin van Meurs, David J. Jones, Kilian P. Tellmann and Juan J. Chirinos

For Table of Contents Use Only

Graphic for TOC:

