Communication

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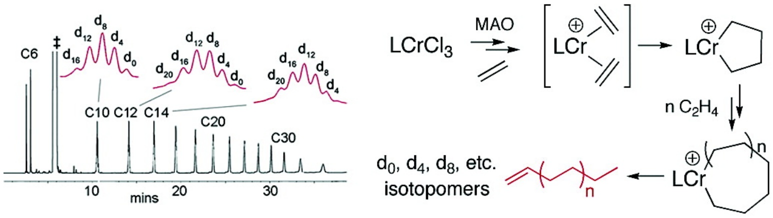

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Experimental Evidence for Large Ring Metallacycle Intermediates in Polyethylene Chain Growth Using Homogeneous Chromium Catalysts

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Chromium catalysts play a central role in the oligomerization and polymerization of ethylene,[1] as well as in the selective trimerization[2] and, more recently, tetramerization[3] of ethylene. While there has been a vigorous ongoing debate over the propagation mechanism in heterogeneous polymerization systems,[1] strong experimental evidence has been obtained for the intermediacy of metallacycles in the selective trimerization of ethylene to 1-hexene.[2b,4] A similar metallacyclic pathway has also been proposed for homogeneous titanium catalysts,[5] supported by computational studies.[6]

A challenge in the study of heterogeneous polymerization systems is the extremely rapid formation of relatively insoluble high molecular weight linear polyethylene, which yields limited information as to its mechanism of formation. With a view to learning more about the chain propagation mechanism in chromium systems, we decided to examine two homogeneous oligomerization catalysts recently discovered in our laboratories that would allow the chain-lengthened products to be examined by gas chromatography and mass spectrometry.

The procatalysts **1** and **2** (Scheme 1), upon activation with methylalumoxane (MAO), afford highly active catalysts for the linear oligomerization of ethylene. Complex **1** has previously been described[7] but not investigated for ethylene polymerization, while **2** was recently discovered as part of a screen of Schiff base ligands in homogeneous chromium-based polymerization systems.[8] Table 1 gives the polymerization results for **1** under differing conditions of temperature and pressure; results for **2** have been reported previously.[8] At 32 °C, the selectivity of **1** for α-olefins is 98.5% (entry 1), falling to 85.7% at 75 °C (entry 3). The yields obtained at 50 °C (entries 2, and 4−6) reveal a first-order dependence of the reaction rate on ethylene concentration (approximated by pressure).

Scheme 1

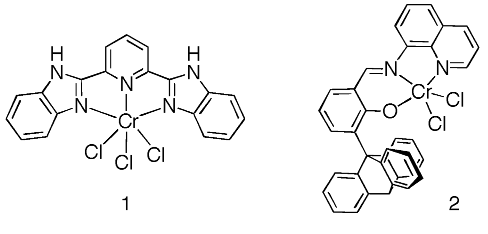

Table 1. Ethylene Oligomerizations Using **1**/MAO[a]

run	P (bar)	T (°C)	yield (g)	prod.[b]	α-olefin (wt %)	K
1	4	32	14.3	3064	98.5	0.84
2	4	50	24.8	5314	91.2	0.87
3	4	75	25.0	5357	85.7	0.86
4	1	50	5.9	5095	91.0	0.88
5	2	50	12.2	5229	93.3	0.85
6	3	50	17.4	4971	93.0	0.85
7[c]	4	50	21.4	4586	89.0	0.87

[a] Reaction conditions: toluene (220 mL), **1** (1 μmol), MAO (8 mmol), 70 min. [b] In g mmol^{-1} h^{-1} bar^{-1}. [c] In the presence of 1-nonene (8.7 g).

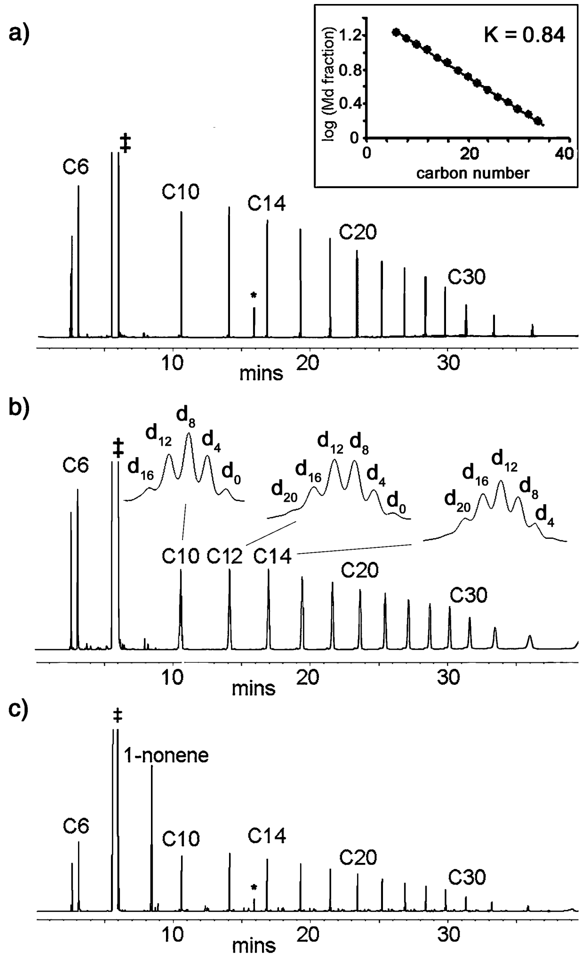

Figure 1. (a) GC trace of hydrocarbon products generated upon treatment of **1**/MAO with ethylene (insert: plot of log (mol %) versus carbon number showing Schulz−Flory distribution). (b) GC trace of the products arising from treatment of **1**/MAO with a 50:50 C_2H_4:C_2D_4 mixture with expansions and assignments (by GC−MS) of the isotopomers for C_{10}, C_{12}, and C_{14} (‡ tol/C_7/C_8 fractions; *2,2,44,6,88-heptamethylnonane standard). (c) GC trace of products obtained in the presence of 1-nonene.

A typical GC trace of the oligomers generated using **1**/MAO is shown in Figure 1a, revealing the high selectivity for linear α-olefin formation. A plot of log (mol %) versus carbon number (inset, Figure 1a) shows a Schulz−Flory distribution with a *K* value of 0.84. The experiment was then repeated using a 50:50 mixture of C_2H_4 and C_2D_4; the GC trace of the protio/deuterio oligomer products is shown in Figure 1b. Expansions of the C_{10}, C_{12}, and C_{14} fractions (Figure 1b) show that each resolves into an envelope

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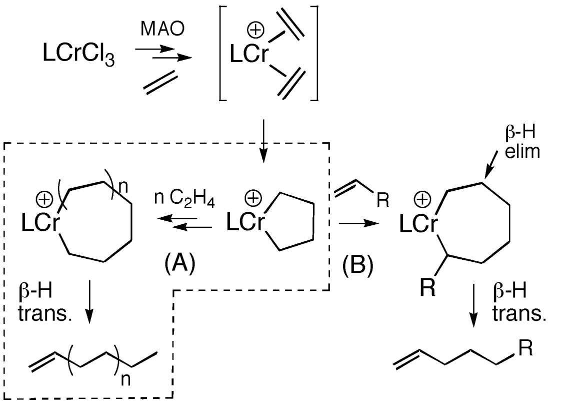
Scheme 2. Possible Mechanistic Pathways for Linear α-Olefin Chain Growth Proceeding via Large Metallacyclic Rings (A) or Incorporation of Higher α-Olefins into Smaller Rings (B)



of peaks attributable to different isotopomer products. GC−MS analyses of these peaks showed that they are comprised of even numbered isotopomers (d_0, d_4, d_8, etc.), consistent with a metallacyclic chain growth mechanism (H/D scrambling would be expected for a Cossee−Arlman or a Green−Rooney mechanism).[4] Rather than ideal binomial distributions within the isotopomer sets, a bias toward the protio-rich products is seen, consistent with a kinetic isotope effect (KIE), which can be calculated to be 1.9 ± 0.3 (see Supporting Information for details).

To establish whether the chain lengthening process proceeds via large ring metallacycles or, alternatively, by incorporation of higher α-olefins into small metallacycle ring intermediates (Scheme 2), the experiment was repeated in the presence of 1-nonene, which was chosen as an odd-numbered, nonvolatile α-olefin that would allow for ready observation (and quantification) of its incorporation into the growing polymer chains. The resulting GC trace is shown in Figure 1c, revealing that virtually no odd-numbered α-olefins are generated. It is, thus, reasonable to conclude that chain growth does not proceed via incorporation of higher α-olefins and strongly implicates a mechanism involving the growth of large ring metallacycles (path A, Scheme 2).

The GC trace for the soluble hydrocarbon products obtained using **2**/MAO is shown in Figure 2a. A key difference is the presence of a small amount of odd-numbered carbon products, which are likely to arise from a “chain transfer to aluminum” termination mechanism mediated by the Me_3Al present in MAO. To probe this, the experiment was repeated in the presence of excess Me_3Al, which led to an increase in the proportion of the odd-numbered products (see Figure S8 in Supporting Information). Analysis of the C_{10}, C_{12}, and C_{14} fractions from a 50:50 C_2H_4:C_2D_4 experiment by GC−MS revealed even-numbered isotopomers (Figure 2b), which again is consistent with a metallacycle mechanism.

When the reaction was conducted in the presence of 1-nonene, there was no significant growth in the odd-numbered products, indicating that the primary growth mechanism is again via large metallacyclic ring formation. Interestingly, analysis of the low intensity odd carbon-numbered products from the C_2H_4/C_2D_4 experiment showed that these too are comprised of even-numbered isotopomer products, indicating that the chain transfer to Al process proceeds via ring-opening of the metallacycle intermediates.

In conclusion, analyses of the isotopomer distributions arising from oligomerizations of a 50:50 C_2H_4:C_2D_4 mixture by two different homogeneous chromium catalysts show that polyethylene chain growth occurs predominantly via metallacyclic intermediates, while the nonincorporation of higher α-olefins strongly implicates the involvement of large ring metallacycles.

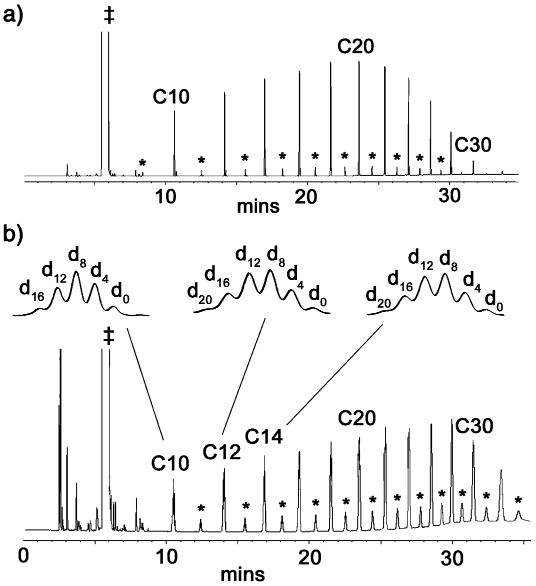


Figure 2. (a) GC trace showing hydrocarbon products generated upon treatment of **2**/MAO with ethylene. (b) GC−MS trace of the products arising from treatment of **2**/MAO with a 50:50 C_2H_4:C_2D_4 mixture with expansions and assignments of the isotopomers for C_{10}, C_{12}, and C_{14} (∗products of chain transfer to aluminum).

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Supporting Information Available: Experimental details for the oligomerization reactions, GC−MS data for the isotopomer products. This material is available free of charge via the Internet at http://pubs.acs.org.

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