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An Unprecedented α-Olefin Distribution Arising from a Homogeneous Ethylene Oligomerization Catalyst

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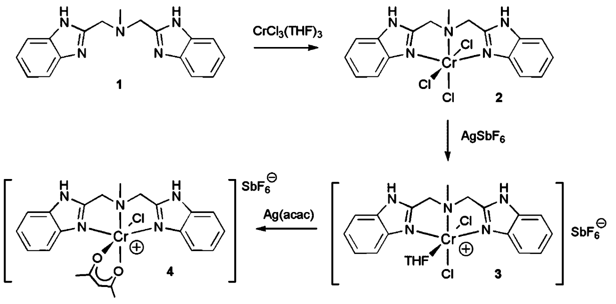
There has been much recent interest in the development of catalysts for the selective oligomerization of ethylene to α-olefins due to their use in a variety of industrial processes, ranging from comonomers for the production of polyolefins to intermediates for synthetic lubricants, plasticizers, and surfactants.[1] Presently, α-olefins are produced by the Alfen[2] or SHOP[3] processes to give a relatively wide distribution of products that have to be separated by distillation. The development of more selective catalysts has recognized potential for dramatically altering the economics of α-olefin production.

Following the commercialization of chromium-based catalysts for the selective trimerization of ethylene to 1-hexene by the Phillips Petroleum Co.,[4] there have been a number of recent reports of new highly selective chromium catalyst systems based on NNN,[5] PNP,[6,7] and SNS[8] ligands. Certain PNP ligands have also been shown to facilitate the selective formation of 1-octene.[7] Herein we report a new, and exceptionally active, homogeneous chromium ethylene oligomerization catalyst supported by a tridentate bis(benzimidazolyl)amine ligand that affords a hitherto unobserved distribution of higher α-olefin products, an observation that highlights the potential for further refinement of selective α-olefin production technology.[9]

Scheme 1. Synthesis of Bis(benzimidazolyl)methylamine Chromium Complexes



The bis(benzimidazolyl)amine **1** was readily prepared[10] by treatment of *o*-phenylenediamine with methylamino diacetic acid. Its reaction with $CrCl_3(THF)_3$ in tetrahydrofuran (THF) gave the green, octahedral Cr(III) complex **2**, which was converted to the cationic derivative **3** upon treatment with $AgSbF_6$ in THF (cationic species are purported to be the active components of these catalysts). Further reaction with Ag(acac) (acac = acetylacetonate) afforded the acac complex, **4**. Crystals of **4** suitable for an X-ray structure determination were obtained from a layered CH_2Cl_2−pentane solution. The molecular structure (Figure 1) revealed a meridional coordination mode for the bis(benzimidazolyl)methylamine ligand, with Cr−N(benzimidazole) bond distances [2.031(5), 2.013(5) Å] comparable to those in analogous Cr(III) complexes bearing chelate pyridine [2.090(6), 2.077(7) Å][11] or benzimidazole [2.062(3), 2.050(3) Å][12] ligands.

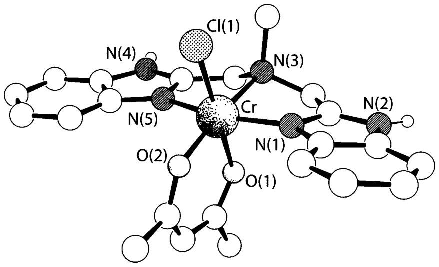


Figure 1. View of the cation in **4**.

Upon activation by MAO in toluene, **2** gave an exceptionally active ethylene oligomerization catalyst,[13] requiring nanomolar catalyst loadings to avoid excessive exotherms. At 58 psi ethylene pressure, activities in excess of 8 000 000 g/gCr·h (>400 000 gmmol^{-1} h^{-1}) are attained (Table 1). **3**/MAO and **4**/MAO resulted in catalysts with still very high activities but somewhat lower than that for **2**/MAO, most probably due to the presence of oxygen donor residues arising from the THF and acac ligands.

Table 1. Ethylene Oligomerization Using **2**−**4**[a]

run	catalyst	$P_{Eth.}$ (bar)	yield[b] (g)	activity (gmmol^{-1} h^{-1} bar^{-1})	liquid fraction[c] (wt %)	α-olefin[d] (wt %)
1	**2**	1	3.2	100000	20	99
2	**2**	3	10.3	107300	23	99
3	**2**	4	13.1	102300	21	99
4	**3**	4	2.0	15600	24	99
5	**4**	4	2.7	21100	21	99

[a] Reaction conditions: 200 mL of toluene, 0.032 μmol of catalyst, 7 mmol of MAO as cocatalyst/scavenger, 50 °C, 60 min. [b] Comprises the combined liquid and solid fractions. [c] The fraction analyzable by GC. [d] Liquid fraction.

The GC trace of the liquid fraction arising from exposure of **2**/MAO to ethylene is shown in Figure 2, which reveals a surprising and unprecedented feature. The concentrations of the C_{4n} products (C_8, C_{12}, C_{16}, etc.) are substantially greater than those for C_{4n+2} (C_{10}, C_{14}, C_{18}, etc.). To our knowledge, such a distribution of oligomers arising from a single catalyst has not previously been documented. At first sight, it is tempting to view it as a combination of two distinct distributions, one comprising the lower intensity C_{4n+2} products, the other the more prevalent C_{4n} products. However,

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these two distributions cannot be generated by two different catalysts since this would require chain extension by four carbons at a time; a catalyst with two differentiated sites could, however, account for the observed distribution (vide infra).

With a view to obtaining an understanding of the mechanism of chain propagation, a labeling experiment[14] was performed whereby **2**/MAO was treated with a 50:50 mix of C_2H_4 and C_2D_4. This afforded predominantly 1-olefins comprising even-numbered H/D isotopomers for both the major (C_{4n}) and minor (C_{4n+2}) products, consistent with a metallacyclic propagation mechanism.[15]

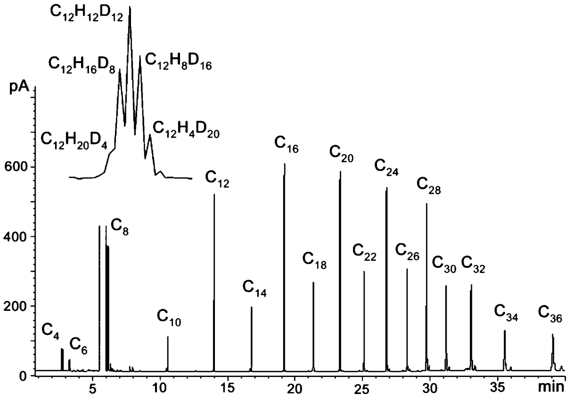
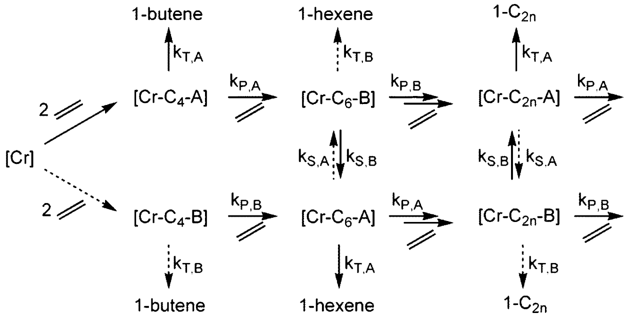


Figure 2. Molecular weight distribution of linear α-olefins obtained from the oligomerization of ethylene using catalyst **2**/MAO (expansion: GC−MS trace of the C_{12} fraction arising from treatment of **2**/MAO with a 50:50 mix of C_2H_4 and C_2D_4).

Since the C_{4n+2} metallacycle products derive directly from the C_{4n} metallacycles, and vice versa, examination of mol % versus carbon number plots for each series can provide useful mechanistic insight (Figure 3). While the major (C_{4n}) series follows a Schulz−Flory distribution, it can be seen that the minor (C_{4n+2}) series deviates substantially from Schulz−Flory behavior. The overall distribution can be modeled using a statistical treatment (see Supporting Information) in which the metallacycle occupies two distinct sites. Such differentiated sites could readily arise, and indeed might be anticipated, from the nonplanarity of the central nitrogen donor.

Scheme 2. Model Based on Two (A and B) Propagating Sites ($k_{P,A}/k_A \approx 0.87$; $k_{T,A}/k_A \approx 0.13$; $k_{S,A}/k_A \approx 0.0$; $k_{P,B}/k_B \approx 0.89$; $k_{T,B}/k_B \approx 0.0$; $k_{S,B}/k_B \approx 0.11$; $k_X = k_{P,A} + k_{T,A} + k_{S,A}$ (X = A or B); disfavored pathways are indicated by broken arrows)



A good overall fit could only be obtained when limiting constraints are applied to the model (see Scheme 2 and Figure 3). First, the initially formed metallacyclopentane must have a strong preference for one of the two sites; second, elimination preferentially occurs from one of the two sites (A as shown in Scheme 2), and third, the propagating metallacycle must be able to "swing" from one site to the other, at a rate competitive with monomer insertion. Any relaxation of these constraints leads to substantial deviations from the observed distribution.

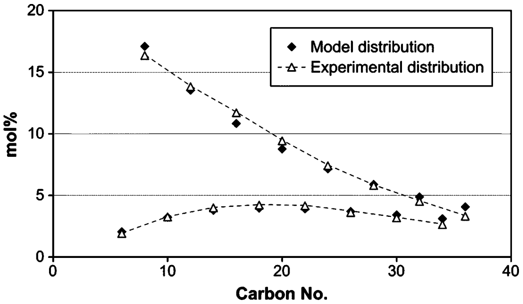


Figure 3. Experimental and modeled distributions for the C_{4n} and C_{4n+2} series of 1-olefins generated using **2**/MAO.

These observations suggest that it should be possible to further control the product distribution by judicious ligand modifications and through changes to the reaction conditions. Studies are currently in progress to refine the selectivity profiles for these catalysts.

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Supporting Information Available: Crystallographic data for **4**. Ligand and complex syntheses, procedures for ethylene oligomerization, GC and GC−MS spectra, and mechanistic model. This material is available free of charge via the Internet at http://pubs.acs.org.

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