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Oligomerization–transmetalation reactions of $Cp^*CrMe_2(PMe_3)$/methylaluminoxane catalysts

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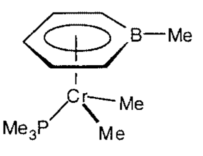
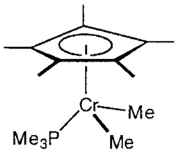
Chain growth in the reaction of ethylene with $Cp^*CrMe_2(PMe_3)$ activated with methylaluminoxane is restricted by a fast Cr/Al transmetalation process.

A range of metal ligand combinations exists for catalyzing the polymerization[1] and oligomerization[2] of olefins. The varying structures control the polymerization process to different extents and provide a means to tailor the polymer structure and the ensuing physical properties. The ‘single site’ technology is making a profound impact in the manufacture of this important class of commodity materials.[3]

Within this context, we recently reported that boratabenzene complexes of chromium(III), such as $(C_5H_5B–Me)CrMe_2(PMe_3)$ **1**, lead to active ethylene polymerization catalysts upon activation with methylaluminoxane (MAO).[4] Since the reactivity of boratabenzene catalysts differs from the performance of their isoelectronic cyclopentadienyl-based counterparts,[5] it was of interest to compare **1**/MAO against $Cp^*CrMe_2(PMe_3)$/MAO (**2**/MAO). Compound **2** has been prepared previously and investigated because complexes of this type exhibit extreme ^1H and ^2H NMR parameters,[6] however little is known on its reactivity potential. In this contribution we show that the **2**/MAO catalysts react with ethylene to produce a distribution of low molecular weight oligomers with an *odd* number of carbon atoms.



1



2

Addition of a solution of **2** to MAO in toluene (50 μmol Cr; $[Cr] = 1 \times 10^{-3}$ M; Al/Cr = 1000, 23 °C) results in a color change from dark purple to red. Fast consumption of ethylene is observed when this solution is exposed to 1 atm of the monomer.[7] An activity of 87 kg[product]/(mol Cr h)$^{-1}$ was determined by measuring the amount of ethylene incorporated into the reaction vessel over a 30 min period. No precipitate was observed under these conditions. Using the same experimental setup, the Cp_2ZrCl_2/MAO catalyst system consumed 85 kg[ethylene]/(mol Zr h)$^{-1}$ to give high molecular weight polyethylene. Thus, under these conditions the affinity of **2**/MAO toward ethylene is comparable to those that characterize group 4 metallocene catalysts.

The mixture obtained from the **2**/MAO reaction was quenched with water and worked up with aqueous base. Analysis of the organic product by GCMS [Fig. 1(a)] reveals that the major product (*ca.* 98%) is a distribution of straight chain *n*-alkanes with an *odd* number of carbon atoms. The minor component corresponds to the homologous progression of *even* numbered alkanes.

Scheme 1 provides a plausible reaction pathway for the formation of the main product. In analogy to metallocene-type catalysts,[8] and taking into consideration the known reactivity of **1**[4] and the work of Theopold and coworkers,[9] it is likely that the reaction between MAO and **2** leads to catalytic species of the type $[Cp^*(Me_3P)Cr–Me]^+$ ([Cr]–Me in Scheme 1). Insertion of ethylene leads to the propagating chain **I** in Scheme 1. Transfer to aluminium gives the aluminium alkyl **II** and regenerates $[Cp^*(Me_3P)Cr–Me]^+$. The reaction sequence shown in Scheme 1 provides odd carbon alkanes upon hydrolysis of **II**.

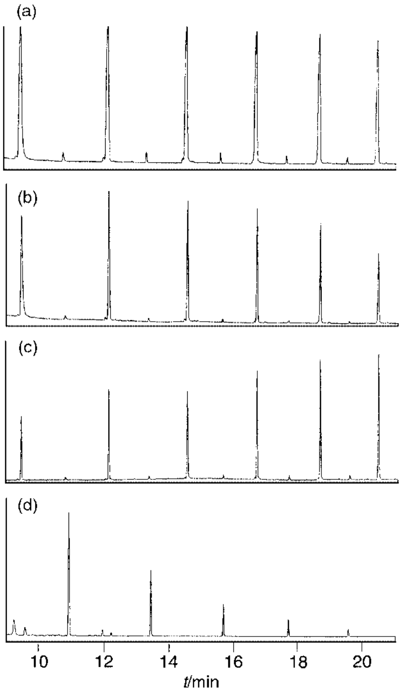
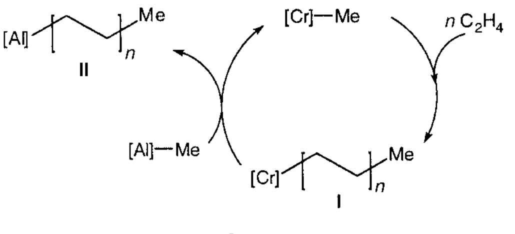


Fig. 1 GCMS analysis of C_{13} through to C_{23} products obtained from the following reactions: (a) **2**/MAO/C_2H_4; (b) **2**/MAO/C_2H_4 with 415 equiv. Al_2Me_6; (c) **2**/MAO/C_2H_4, after removal of volatiles from MAO *in vacuo*; (d) **2**/MAO/C_2H_4 with 830 equiv. ‘$AlEt_3$’. For all reactions: 50 μmol Cr; $[Cr] = 1 X 10^{-3}$ M; Al/Cr = 1000; 1 atm C_2H_4.

The chemical structure of ‘[Al]–Me’ in Scheme 1 is not precise, in part because of the complex and poorly defined structure of MAO and because commercially available MAO contains varying amounts of trimethylaluminium. To explore the effect of increasing the concentration of ‘[Al]–Me’ an additional 415 equiv. of Al_2Me_6 were added to the catalyst solution and the reactivity with ethylene measured. As shown by the GCMS chromatogram in Fig. 1(b), the additional Al_2Me_6



Scheme 1

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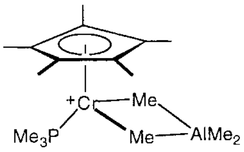
shifts the distribution in favor of the shorter alkanes, however the overall activity decreases to 34 kg[product]/(mol Cr h)$^{-1}$.

To examine the effect of reduced Al_2Me_6 concentration, the commercially available MAO solution was placed under vacuum for 16 h.[10] The resulting MAO solids were redissolved in toluene and the reaction with **2** and ethylene was carried out as before. Under these conditions, the activity was measured at 133 kg[product]/(mol Cr h)$^{-1}$ and polyethylene precipitates out of solution, accounting for *ca.* 85% of the product. The distribution of soluble alkanes gives a greater proportion of the heavier products [Fig. 1(c)]. Also relevant in this context is that only polyethylene is produced when **2** is activated by $B(C_6F_5)_3$.[4]

The overall trends illustrated in Fig. 1(a)–(c) are consistent with the mechanism proposed in Scheme 1. Additional Al_2Me_6 increases the rate of chain transfer to aluminium and gives rise to a distribution of shorter chain alkanes. The slower rate of ethylene consumption with the additional Al_2Me_6 may be due to the formation of bridging species such as **III**. It is anticipated that the coordination of $AlMe_3$ to [Cr]–Me in **III** decreases the concentration of the active species thereby decreasing overall ethylene uptake. Removing free trimethylaluminium from MAO has the opposite effects—longer chains are obtained and more ethylene is consumed. Finally, we propose that the small fraction of even alkanes observed in the product results from a small fraction of ethyl and/or hydride found in the MAO.[11] When triethylaluminium is added (830 equiv. of '$AlEt_3$') to **2**/MAO (50 μmol Cr; $[Cr] = 1 \times 10^{-3}$ M; Al/Cr = 1000, 23 °C) the product is a homologous distribution of *n*-alkanes with an *even* number of carbon atoms [Fig. 1(d), activity = 97 kg[product]/(mol Cr h)$^{-1}$].



III

In summary, the **2**/MAO combination is an active catalyst for the oligomerization of olefins. Chain growth is limited by efficient Cr/Al transmetalation reactions.[12] After aqueous workup the product is a distribution of linear alkanes. The overall cycle shown in Scheme 1 reduces to the Cr-catalyzed insertion of ethylene into the Al–C bond.[13] It is also noteworthy that the isoelectronic boratabenzene–cyclopentadienyl substitution for the chromium catalysts (**1** *vs.* **2**), has a different effect than in zirconium catalysts. Under similar reaction conditions, the combination $Cp^*_2ZrCl_2$/MAO gives high molecular weight polyethylene, while $[C_5H_5B{-}OEt]_2ZrCl_2$/MAO[2b] produces low molecular weight 1-alkenes. In the zirconium case differences in reactivity stem from faster rates of β-hydride elimination for the boratabenzene complexes. For chromium, boratabenzene complexes exhibit slower rates of transmetalation with aluminium functionalities in MAO, leading to higher molecular weight polymer.

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