

Catalytic Insertion of Ethylene into Al–C Bonds with Pentamethylcyclopentadienyl–Chromium(III) Complexes

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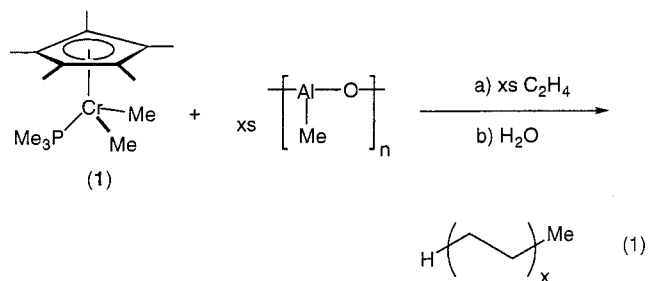
Addition of ethylene to mixtures of $\text{Cp}^*\text{CrMe}_2(\text{PMe}_3)$ (**1**) and excess methylaluminoxane (MAO), followed by aqueous workup of the resulting solutions, results in the formation of a distribution of odd-carbon alkanes. When $\text{B}(\text{C}_6\text{F}_5)_3$ is added to **1**, followed by THF, one obtains dark crystals. A single-crystal X-ray diffraction study revealed that the product of the reaction is $[\text{Cp}^*\text{CrMe}(\text{PMe}_3)(\text{THF})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**2**). Polyethylene is obtained when using **1** and 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$. The reaction of ethylene with a mixture of **1** + 2 $\text{B}(\text{C}_6\text{F}_5)_3$ + 380 "AlMe₃" produces a distribution of odd-carbon alkanes. If triethylaluminum is used, instead of trimethylaluminum, the product is a distribution of even-carbon alkanes. The product distribution shifts to lower molecular weight product, and lower activities are attained with increasing triethylaluminum concentration. Use of more dichloromethane instead of toluene or hexane increases the ethylene consumption. Triisobutylaluminum and trioctylaluminum result in considerably lower activities. A mechanism for the oligomerization of ethylene involving fast transmetalation reactions between chromium and aluminum is proposed.

Introduction

Trialkylaluminum reagents find extensive practical use in large-scale industrial processes.¹ For example, they are used for the preparation of α -olefins via a displacement reaction.¹ The oxidation with oxygen² or amine oxides³ to give linear alcohols is also practiced. Commercial processes to trialkylaluminum compounds typically begin with the reaction of triethylaluminum with ethylene under elevated temperature and pressure or in the presence of suitable transition metal reagents under moderate reaction conditions.⁴ Nickel compounds are of notable historical importance in this respect.⁵ Catalysts based on actinide metallocenes are also noteworthy for generating a product with a Poisson-type chain length distribution.⁶ The chain length distribution in these processes is determined by the rates of reaction for ethylene insertion, for direct elimination of the growing chain at the metal, and for the transmetalation exchange between the metal and aluminum.⁷

In connection to the transmetalation reactions, we recently reported that the combination of Cp^*CrMe_2 -

$(\text{PMe}_3)^8$ (**1**) with methylaluminoxane (MAO) reacts with ethylene to give an alkylaluminoxane product with the chain growth product attached to the aluminum sites.⁹ Hydrolysis of this product gives a distribution of odd-carbon, straight chain alkanes, as shown in eq 1.



In this contribution, we report on further details of the reactions of **1** with MAO, and we report on our studies of the reaction using **1** and the borane activator $\text{B}(\text{C}_6\text{F}_5)_3$. As will be shown, this combination of reagents allows for the use of well-defined homogeneous chromium reagents to create a process that catalyzes the insertion of olefins into the Al–C bond. In view of the rising interest in homogeneous organochromium catalysts for olefin polymerization reactions, these results give an additional useful handle for controlling polymer molecular weight.¹⁰

Results and Discussion

Reactions of 1/MAO/ C_2H_4 with Trialkylaluminum Reagents. A consideration of the experimental details is of importance for determining the efficiency

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of transmetalation/oligomerization processes. In our previous communication,⁹ the reactions were carried out by introducing a solution containing the appropriate ratios of **1**, MAO, and the AlR_3 into a round-bottom flask inside a glovebox. After attaching a Teflon needle valve adapter with suitable ground glass joints, the flask was attached to a double manifold line and then evacuated for a brief period of time (~ 5 s). Ethylene was then introduced over the resulting solution. To maintain a constant 1 atm of ethylene over the reaction, the ethylene was allowed to exit via an oil-filled bubbler. Under these "open" conditions, the activity was measured at 87 kg product/(mol Cr·hr), and only soluble products were obtained.

For the reactions described herein, the MAO and **1** were introduced into a flat bottom glass reactor inside the glovebox. The reactor was then connected to the ethylene line directly, by using a quick-connect adapter. Ethylene was then introduced at 15 psig. This setup, referred to as "closed" conditions, enables better stirring and a more efficient mass transfer of ethylene into the solution. These conditions lead to a higher consumption of ethylene, 278 kg product/(mol Cr·h), and the formation of a solid product (30% of total product), which precipitates as the reaction proceeds. Thus, the conditions reported in this paper, relative to our previous work, favor propagation processes on the basis of increased ethylene concentration.

Oligomerization–Transmetalation Reactions Using Well-Defined Borane Activators. On the basis of Theopold's studies on mono(cyclopentadienyl)chromium(III) catalysts for ethylene polymerization¹¹ and the reactivity of isoelectronic boratabenzene complexes,^{12,13} we postulated that **1** with $\text{B}(\text{C}_6\text{F}_5)_3$ ¹⁴ would generate a single-site catalyst for fast insertion of ethylene into the Cr–C bond, followed by Cr–C/Al–C exchange. Addition of **1** to solutions of $\text{B}(\text{C}_6\text{F}_5)_3$ results in a color change from purple to dark green. Due to the

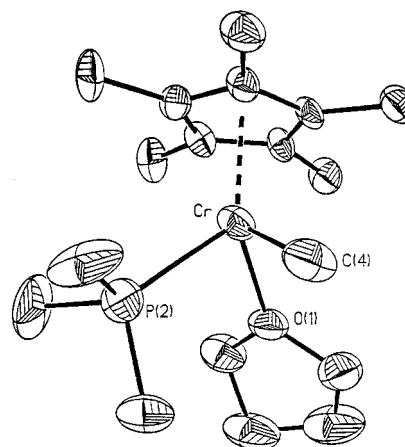
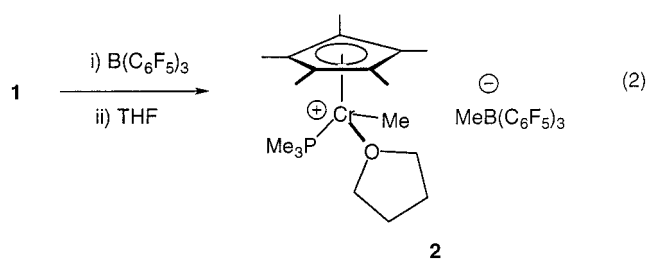


Figure 1. ORTEP view of **2**. Atoms are shown at the 30% probability level. Hydrogen atoms and the $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ anion are not shown for clarity.

paramagnetic nature of chromium(III), it is not possible to characterize the resulting products using ^1H NMR spectroscopy. Efforts to isolate crystalline material from this reaction failed in all cases. However, addition of THF followed by crystallization from $\text{Et}_2\text{O}/\text{Pr}_2\text{O}$ gives black crystals of the cation/anion pair, $[\text{Cp}^*\text{CrMe}(\text{PMe}_3)(\text{THF})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**2** in eq 2). The molecular structure of **2** was determined using single-crystal X-ray crystallography, and the results are illustrated in Figure 1. The phosphine and one methyl ligand remain bound to the metal upon reaction of **1** with $\text{B}(\text{C}_6\text{F}_5)_3$. The isolation of **2** suggests that the active species for ethylene insertion using **1** in conjunction with $\text{B}(\text{C}_6\text{F}_5)_3$ or MAO is $[\text{Cp}^*\text{CrMe}(\text{PMe}_3)]^+$ (vide infra) with a loosely bound, or solvent-separated, borate counteranion ($[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$).



Addition of trimethylaluminum (1.4 g, 19 mmol) to a solution of **1** with 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene changes the color from green to red.¹⁵ Reaction with ethylene under "open" conditions ($[\text{Cr}] = 1 \times 10^{-3}$ M; 1 atm C_2H_4 ; 30 min reaction time; 23 °C maintained by an external water bath) results in rapid monomer consumption, and no polymer precipitation is observed. When "closed" conditions were used ($[\text{Cr}] = 1 \times 10^{-3}$ M; 15 psig C_2H_4 ; 30 min reaction time; 23 °C maintained by an external water bath), the precipitation of low molecular weight polyolefin occurs. The solid material accounts for approximately 50% of the total mass of ethylene consumed. After hydrolysis and workup with aqueous base, the organic layer was analyzed by GC/MS, and the results of these reactions are summarized in Table 1. As shown in Figure 2a, the reaction product is a distribution of

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(15) When only 1 equiv of borane is added, the reactivity toward ethylene is considerably reduced.

Table 1.

entry ^a	activator	AlR ₃ , R = [Al]/[Cr] ^c	solvent	activity ^b
1	MAO		1000 toluene	278
2	2 B(C ₆ F ₅) ₃	Me	380 toluene	152
3	2 B(C ₆ F ₅) ₃	Et	380 toluene	154
4	[Ph ₃ C][B(C ₆ F ₅) ₄]	Et	380 toluene	94
5	2 B(C ₆ F ₅) ₃	isoBu	380 toluene	48
6	2 B(C ₆ F ₅) ₃	octyl	380 toluene	17
7	MAO ^b	octyl	1380 toluene	29
8	2 B(C ₆ F ₅) ₃	0	0 toluene	139 ^c

^a Reaction conditions: [Cr] = 1×10^{-3} M; 23 °C; 30 min reaction time; 15 psig C₂H₄; toluene solvent. ^b Activity reported in kg[product]/molCr·h. ^c Product is polyethylene (>95%).

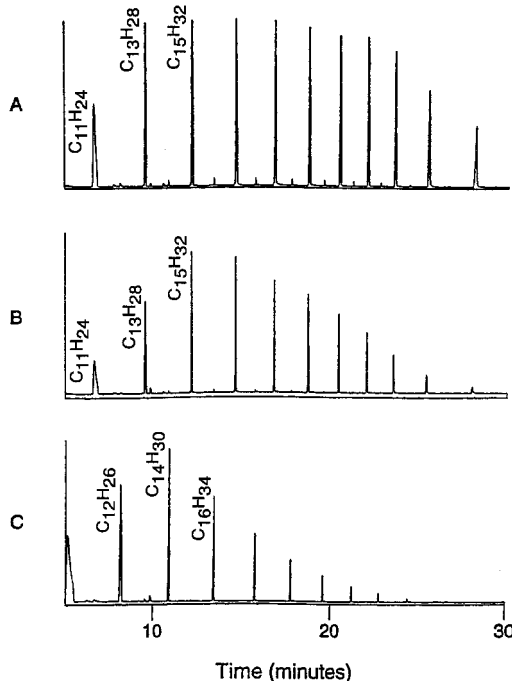
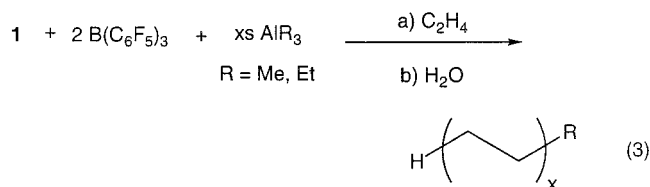


Figure 2. GC/MS traces of the alkane products obtained from the reaction of ethylene with (a) **1** + 2 B(C₆F₅)₃ with trimethylaluminum (380 Al/Cr); (b) MAO (1000 Al/Cr); and (c) 2 B(C₆F₅)₃ with triethylaluminum (380 Al/Cr). The first three peaks are labeled according to molecular weight.

(>98%)¹⁶ *odd*-carbon alkanes (Table 1, entry 2) (eq 3). For comparison, the distribution of alkanes using **1**/MAO (1000 overall Al/Cr) is provided in Figure 2b (Table 1, entry 1). Note that the activity of **1** + 2 B(C₆F₅)₃ + trimethylaluminum toward ethylene consumption is about half that obtained with **1**/MAO under similar reaction conditions (Table 1, entries 1 and 2).



Performing the reaction using **[1** + 2 B(C₆F₅)₃] in the presence of triethylaluminum under “closed” conditions results in the exclusive formation of soluble products. The total amount of ethylene consumed is similar to the

(16) The commercially available source of trimethylaluminum used in these experiments was 97% pure. It is likely that the impurities in this reagent are responsible for the minor distribution of even-number alkanes.

Table 2.

entry ^a	solvent	activity ^b	<i>K</i>
1	toluene	154	0.55
2	hexane	117	0.60
3	CH ₂ Cl ₂	210	0.49

^a Reaction conditions: [Cr] = 1×10^{-3} M; 23 °C; 30 min reaction time; 15 psig C₂H₄; [B(C₆F₅)₃]/[Cr] = 2; [AlEt₃]/[Cr] = 380.
^b Activity reported in kg[product]/mol Cr·h.

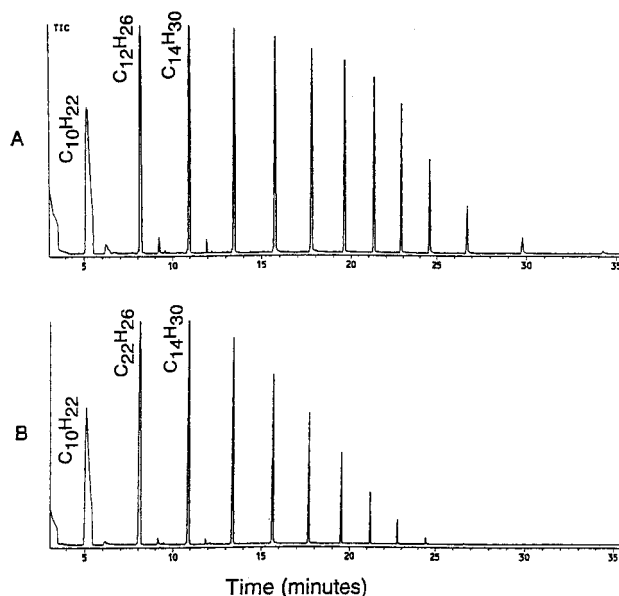


Figure 3. GC/MS traces of the alkane products obtained from the reaction of ethylene with (a) $[1 + 2 \text{ B}(\text{C}_6\text{F}_5)_3 + \text{C}_2\text{H}_4]$ with triethylaluminum (380 Al/Cr) in hexane; (b) $[1 + 2 \text{ B}(\text{C}_6\text{F}_5)_3]$ with triethylaluminum (380 Al/Cr) in $\text{CH}_2\text{-Cl}_2$. The first three peaks are labeled according to molecular weight.

reaction with trimethylaluminum (Table 1, entry 3). In this case however, only *even*-carbon alkanes are detected (Figure 2c). Other cocatalysts are suitable for activating **1**. For example, 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^{17}$ and **1** provide a catalyst (Table 1, entry 4) with slightly lower activity compared to $[\mathbf{1} + 2 \text{ B}(\text{C}_6\text{F}_5)_3]$.

The choice of solvent influences both the overall activity and the chain length distribution. Keeping the reaction variables constant (C_2H_4 pressure, temperature, and triethylaluminum concentration) and using the less polar solvent hexane reduces ethylene uptake and shifts product distribution to longer chains, as judged by the observation of product precipitate (Table 2, entry 2, and Figure 3a) and the larger K factor of the soluble fraction.¹⁸ By use of the more polar dichloromethane, one obtains a higher consumption rate and a shift to shorter chains, as shown by the smaller K factor (Table 2, entry 3, and Figure 3b).

Figure 4 shows the distribution of the mole fractions of C10 through C22 alkanes as a function of triethylaluminum concentration, as determined by using GC. At higher aluminum concentrations, a shift to lighter alkanes is observed. In the absence of triethylaluminum,

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(18) The K factor is defined by the molar ratio of the C_{n+2} and C_n products. This ratio also corresponds to the rate of propagation over the sum of the rate of propagation and the rate of chain transfer: $K = (\text{moles } C_{n+2} \text{ olefin})/(\text{moles } C_n \text{ olefin}) = R_p/(R_p + R_{CT})$.

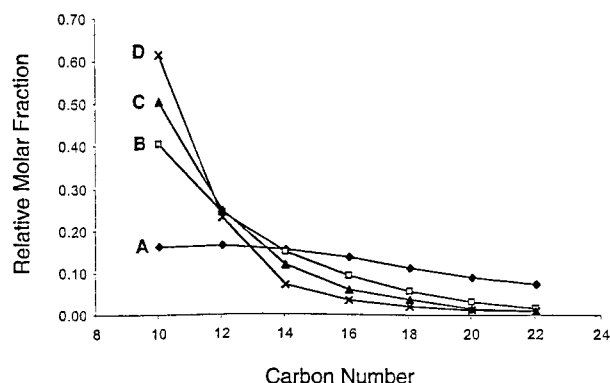


Figure 4. Graph of the mole fractions of the C10 through C22 products found using **1** + 2 $\text{B}(\text{C}_6\text{F}_5)_3$ + C_2H_4 and triethylaluminum at Al/Cr ratios of (a) 73; (b) 146; (c) 730; and (d) 1460.

Table 3.

entry ^a	$[\text{AlEt}_3]/[\text{Cr}]$	activity ^b	<i>K</i>
1	73	124	0.88
2	146	174	0.59
3	380	154	0.55
4	730	60	0.47
5	1460	2	0.34

^a Reaction conditions: $[\text{Cr}] = 1 \times 10^{-3} \text{ M}$; 23 °C; 30 min reaction time; 15 psig C_2H_4 ; $[\text{B}(\text{C}_6\text{F}_5)_3]/[\text{Cr}] = 2$; toluene. ^b Activity reported in kg[product]/mol Cr·h.

Table 4.

entry ^a	activity ^b	mixing time ^c	$C_{\text{even}}/C_{\text{odd}}^d$
1	260	15 min	10
2	255	1.5 h	5
3	259	17 h	5

^a Reaction conditions: $[\text{Cr}] = 1 \times 10^{-3} \text{ M}$; 23 °C; 30 min reaction time; 15 psig C_2H_4 ; $[\text{B}(\text{C}_6\text{F}_5)_3]/[\text{Cr}] = 2$; toluene; $[\text{Al}]/[\text{Cr}] = 380$; initial $[\text{AlMe}_3]/[\text{AlEt}_3] = 1$. ^b Activity reported in kg[product]/mol Cr·h. ^c Time between the mixing of trimethylaluminum with triethylaluminum and the reaction with **1**, $\text{B}(\text{C}_6\text{F}_5)_3$, and ethylene. ^d Determined by GC analysis.

one obtains polyethylene (Table 1, entry 8). Decreasing the triethylaluminum concentration also increases the activity toward ethylene (Table 3, entries 2–5). Entry 1 in Table 3 is an exception to this trend. Under these conditions ($[\text{Al}]/[\text{Cr}] = 73$) a substantial amount of precipitate is observed. It is likely that catalyst entrapment within the polymer and isolation from the monomer may be responsible for the activity decrease.

Mixtures of trialkylaluminum reagents were also examined. Table 4 shows the results for reactions that contained an equimolar mixture of trimethylaluminum and triethylaluminum. The oligomerization/transmetalation reactions were done after the two reagents were mixed neat for specific periods (~15 min, 1.5 h, and 17 h). There is no obvious change in the overall reactivity as a function of mixing time. However, the ratio of even-carbon alkanes to odd-carbon alkanes changes from 10:1 in entry 1 to 5:1 in entries 2 and 3. The ethyl functionality is thus more prone to transmetalation, relative to methyl.

Larger Alkyl Chains and Consumption Profile.

Two additional commercially available trialkylaluminum complexes were examined, trioctylaluminum and triisobutylaluminum. For trioctylaluminum, the total ethylene uptake is approximately an order of magnitude lower than that observed with triethylaluminum, over

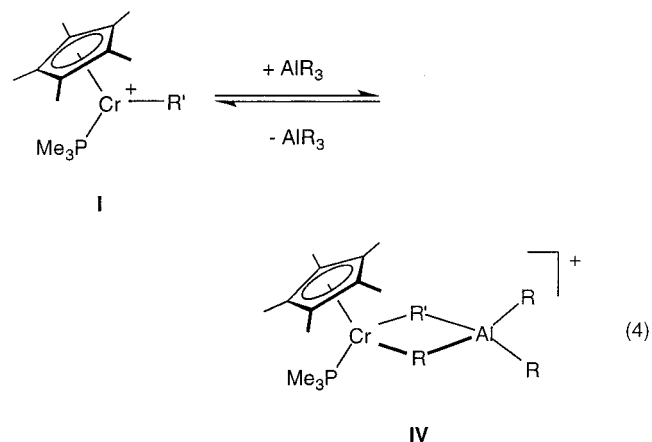
a 30 min period of time (Table 1, entry 6). The GC result shows that the majority of the product from entry 6 in Table 1 is $\text{C}_{10}\text{H}_{22}$ (72 mol %); in other words, the single insertion product is predominant. For the reactions with triisobutylaluminum, the ethylene uptake is also considerably depressed, compared to triethylaluminum (Table 1, entry 5). In the GC/MS trace of the products, one observes a distribution of 2-methylalkanes (>98%). These end groups arise from the isobutyl fragments originally on aluminum.

It is possible to measure the rate of ethylene uptake at a constant pressure by using a mass flow controller attached to the reaction flask intake. Figure 5 shows the total weight of ethylene incorporated into the reaction as a function of time for different aluminum alkyl groups. There appears to be no induction period. In the case of trimethylaluminum and triethylaluminum, the consumption is close to linear with time, indicating no decomposition of the catalytically active species within 30 min. The dependence on triisobutylaluminum is interesting. Within the first 10 min of the reaction an activity similar to those of the trimethylaluminum and the triethylaluminum reactions is observed. However, after approximately 15 min the consumption ceases. At this stage, approximately 2 equiv of ethylene, relative to aluminum, have been incorporated into the reaction. Finally, for trioctylaluminum only a sluggish uptake takes place.

Summary Discussion

Thepold's work,¹¹ the isolation of **2**, and our work with $[(\text{C}_5\text{H}_5\text{B-Me})\text{CrMe}(\text{PMe}_2)_2][\text{MeB}(\text{C}_6\text{F}_5)_3]$ ¹² suggest that the product forms as shown in Scheme 1. Ethylene insertion occurs at the cationic chromium alkyl species of type **I**, where $[\text{Cr}] = [\text{Cp}^*(\text{Me}_3\text{P})\text{Cr}]$. Chain growth at **II** is restricted by fast transmetalation reactions with Al–R. This step produces the distribution of trialkylaluminum compounds represented by **III**. Hydrolysis of **III** gives the alkane product.

The effect of triethylaluminum concentration on the chain distribution of the product and the activity of the catalytic species suggests an equilibrium between species **I** (same **I** as in Scheme 1) and **IV** in eq 4. It is



anticipated that ethylene insertion occurs at **I**, while species such as **IV** are responsible for chain transfer to aluminum. That the activity decreases with increasing triethylaluminum concentration (Table 3) suggests that

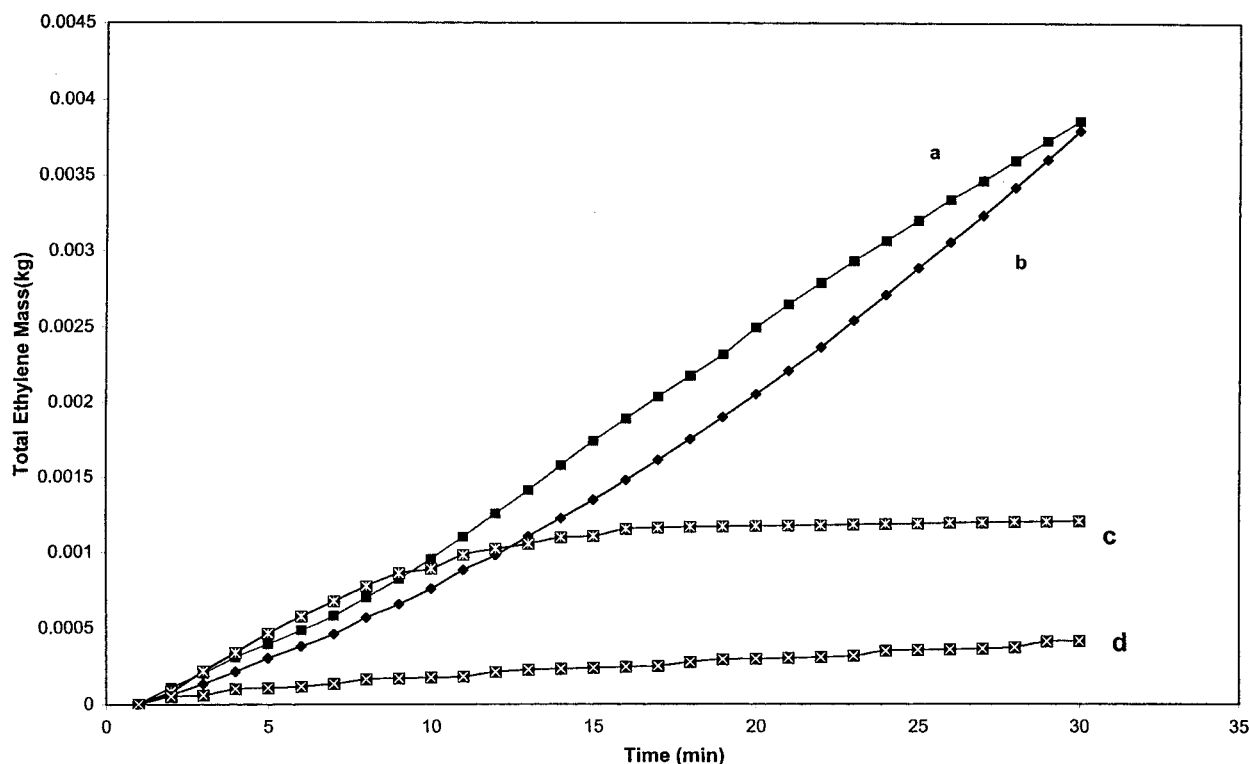
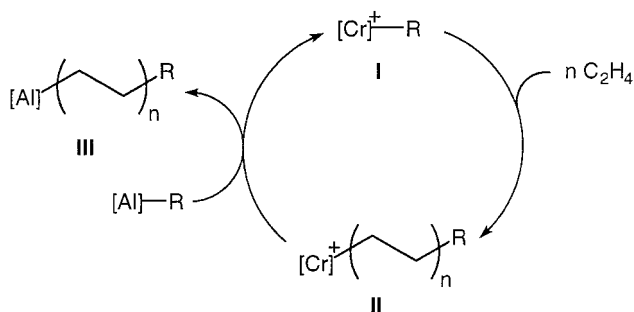


Figure 5. Graph of total ethylene mass consumption versus time with $[1 + 2 \text{ B}(\text{C}_6\text{F}_5)_3/\text{C}_2\text{H}_4]$ using (a) trimethylaluminum; (b) triethylaluminum; (c) triisobutylaluminum; and (d) trioctylaluminum.

Scheme 1



IV does not undergo ethylene insertion. Bochmann and co-workers have shown that species similar to **IV** can be found in trimethylaluminum¹⁹ and triethylaluminum²⁰ adducts of group 4 metallocene cations.²¹ In their study, a similar trend in activity and molecular weight with added trialkylaluminum was observed for the polymerization of propylene.

Several observations are interesting and warrant further study. For example, it is not clear at this stage why the even-carbon products are preferentially obtained when mixtures of triethylaluminum and trimethylaluminum are present (Table 3). In solution, these species are predominantly in the form of dimers, with the methyl species held together more tightly.^{22,23}

It may be that the effectively higher concentration of the reactive monomer for the ethyl-containing species accounts for their increased participation in transmetalation reactions. Trioctylaluminum is monomeric in solution, and despite the increased steric interference expected in species such as **IV**, these are generated more readily, accounting for the low ethylene consumption rates. There is no obvious explanation as to why the reactions with triisobutylaluminum shut down after a given time.

Experimental Section

General Remarks. All manipulations were performed under inert atmosphere using standard glovebox and vacuum line techniques.²⁴ The synthesis of **1** has been described previously.⁸ Methylaluminoxane was obtained from Akzo Chemical, and $\text{B}(\text{C}_6\text{F}_5)_3$ was purchased from Boulder Scientific Co. and used after sublimation. GC/MS analyses were done using a Shimadzu GCMS-QP5000. GC analyses were done using a Shimadzu GC-17A. Ethylene was obtained from Matheson Co and passed through an oxygen/moisture trap.

Isolation of $[\text{Cp}^*\text{CrMe}(\text{PMe}_3)(\text{THF})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (2**).** A solution of **1** (19 mg, 65 μmol) in 1 mL of toluene was added to a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (33 mg, 64 μmol), resulting in a color change from purple to dark green. Addition of THF (~1 mL) produces a color change to dark brown. The solvent was removed in vacuo, and the resulting sticky solid was dissolved in $\text{Et}_2\text{O}/\text{Pr}_2\text{O}$ (1:1). Cooling to -35°C results in brown-black crystals of **2**. This solid is unstable at room temperature for extended periods of time and is exceptionally air and moisture sensitive.

General Oligomerization Procedure. In a nitrogen-filled glovebox, 50 μmol of **1** was weighted to the nearest 0.1 mg and dissolved in toluene. This solution was combined with the

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appropriate amount of activator (MAO, 10.3 wt % Al, 1000 Al/Cr, or $\text{B}(\text{C}_6\text{F}_5)_3$, 100 μmol , or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, 50 μmol) and placed inside a 500 mL flat-bottom glass reactor with a magnetic stir bar. Sufficient toluene was added to bring the total volume to 50 mL. The glass reactor was fitted with a reactor head and removed from the glovebox. The apparatus was connected to an ethylene line and a pressure gauge via a quick-connect adapter. The glass reactor was immersed in a water bath at room temperature. Ethylene was introduced to the glass reactor for approximately 1 min before activating a mass flow controller. The ethylene pressure was maintained at 15 psig for 30 min. The total ethylene consumption was recorded every minute. After 30 min, the ethylene feed was stopped and the reaction was quenched using 5–10 mL of 2-propanol at 0 °C, followed by same amount of water. Any

alumina salts were dissolved in aqueous base. Separation of the toluene layer provides the product. The quantity of ethylene consumed was determined by use of a flow mass regulator or by weighing the entire reaction assembly before and after ethylene addition; the two techniques are in agreement to within $\pm 5\%$.

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Supporting Information Available: Complete details for the crystallographic study of **2** (PDF). The material is available free of charge via the Internet at <http://pubs.acs.org>.

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