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Propene Polymerization Using *ansa*-Metallocenium Ions: Excess Activator Effects on Polymerization Activity and Polymer Microstructure

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*Summary: The initial and steady-state rates of propene polymerization using the metallocene complexes $Me_2X(Cp)IndZrMe_2$ (**1**, X = C, Si) and $Me_2C(Cp)FluZrMe_2$ (**2**) activated with $B(C_6F_5)_3$ increase in the presence of excess borane; the kinetic data are consistent with two different forms of the propagating catalyst in equilibrium with each other in the presence of excess borane. The ratio k_p/k_i for the ion pair $[Me_2C(Cp)IndZrMe][MeB(C_6F_5)_3]$ (**3**) is sensitive to the presence of excess borane, while the molecular structure of **3** reveals strong ion pairing in the solid state. Variable-temperature NMR spectra of $[Me_2C(Cp)IndZr^{13}Me][^{13}MeB(C_6F_5)_3]$ in the presence of excess borane are consistent with the doubly activated intermediate $Me_2C(Cp)IndZr\{(\mu\text{-}^{13}Me)B(C_6F_5)_3\}_2$ (**4**) being present.*

The study of counterion effects in metallocene-catalyzed olefin polymerization has led to significant advances in our understanding of this process.[1] The counterion, though weakly coordinating, is known to affect catalyst stability and activity[2] as well as polymer properties such as molecular weight[1,2] and tacticity[3] in a direct manner. It is not unreasonable to state that the interaction of the counteranion with the metal center[4] is *decisive* in affecting catalyst performance. The search for more active catalysts has focused on activators in which two group 13 atoms are linked via an anionic bridge.[5] This type of activator can give rise to very active catalysts, in comparison to those formed using mononuclear activators, and it is interesting to speculate as to the possible role of such species in polymerizations involving the latter.[5a]

Recent studies on 1-hexene polymerization using $[en(Ind)_2ZrMe][MeB(C_6F_5)_3]$ indicate that excess $B(C_6F_5)_3$ has no effect on the kinetics of initiation and propagation.[2h] However, enhancement of ethylene or propene polymerization activity was noted when using 2 vs 1 equiv of $Al(C_6F_5)_3$, and metallocene or constrained-geometry catalysts.[6a] This was attributed to "double-activation" of the catalyst precursor, on the basis of the X-ray structure of $[Me_2Si(Ind)_2Zr][MeAl(C_6F_5)_3]_2$. An alternative explanation based on transient formation of $[Me_2Si(Ind)_2ZrMe][(C_6F_5)_3Al(\mu\text{-}Me)Al(C_6F_5)_3]$[6a] featuring a more weakly coordinating dinuclear anion[6b] was not excluded. It should be noted that a related dicationic complex, $[(^tBu_3P{=}N)_2Ti][MeB(C_6F_5)_3]_2$, is *inactive* in ethylene polymerization.[6c] More recently, the use of excess $[Ph_3C][B(C_6F_5)_4]$ significantly increases the rate of a number of metallocene-catalyzed propene polymerizations;[7] only a portion of this activation has been attributed to an increase in active site concentration.[2]

During the course of some mechanistic work involving the activation of $Me_2X(Cp)IndZrMe_2$ (**1**, X = C, Si) using

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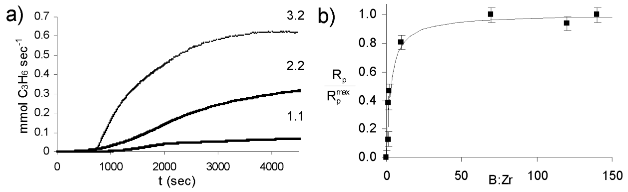


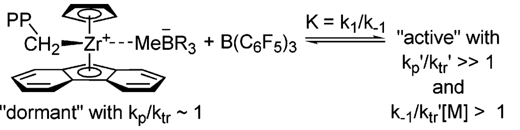
$$\frac{R_p}{R_p^{max}} = \frac{\{1+K[Zr]_o(1+r)\} - \sqrt{\{1+K[Zr]_o(1+r)\}^2 - 4K^2[Zr]_o r}}{2K[Zr]_o}, r = \frac{[BR_3]_o}{[Zr]_o}$$

Figure 1. (a) Propene uptake vs time for polymerizations initiated by complex **1** ([Zr] = 40 μM) and 1.1, 2.2, and 3.2 equiv of $B(C_6F_5)_3$. Conditions: 30 °C and 30 psig of C_3H_6. (b) Steady-state rate of polymerization, expressed as R_p/R_p^{max} vs B/Zr ratio for catalyst **2**. Conditions: 30 °C and 30 psig of C_3H_6. The solid line represents the fit of the data to the expression shown.

$B(C_6F_5)_3$,[3c] we encountered poor reproducibility in propene polymerization initiated by ion pairs that were *preformed* using a B/Zr ratio of (1.0−1.2)/1. Subsequent work has revealed that the activity of these zirconocene catalysts is very sensitive to the B/Zr stoichiometry used to form the ion pairs and that similar behavior is also observed using the more well-studied $Me_2C(Cp)FluZrMe_2$ catalyst **2**. We report here preliminary details of these *unexpected* observations.

As shown in Figure 1a, the rate of initial propene uptake using catalyst **1** (X = C) *and* the steady state rate of propene consumption are strongly increased in the presence of excess borane. Additional experiments revealed that this effect is also observed on addition of excess borane to this catalyst at steady state *after* initiation has occurred.[8] Similar behavior is also observed for catalyst **1** (X = Si) or for the C_s-symmetric catalyst **2**.[8]

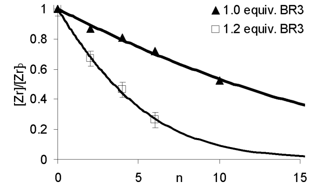
In the case of catalyst **2** where large excesses of borane relative to metallocene were systematically explored, saturation behavior on the steady-state rate of polymerization is observed (Figure 1b). The data can be accommodated by postulating two forms of the catalyst, one active and the other "dormant" (or much less active) in equilibrium with one another in the presence of excess borane, according to eq 1. The value



(1)

of K (~10^4 M^{-1} at $[Zr]_0 = 5$ μM), estimated from the fit of the data to the equation shown in Figure 1, implies *irreversible* activation of the *propagating* intermediate at sufficiently high $[Zr]_0$.

With complex **1**, the tacticity of the oligomeric PP formed was *insensitive* to changes in B/Zr stoichiometry over the range studied (1.1/1 to 70/1), while the molecular weights (M_w) of the oligomers formed, as judged by the intensity of signals due to vinylidene end groups, increased by about a factor of 2.[8] The former finding tends to suggest that the catalyst (and counterion) is the same[3]—there is simply more of it in the presence of excess borane. The change in M_w could be consistent with this hypothesis, provided excess borane *indirectly* affects the relative rates of chain transfer to propagation, through an equilibrium analogous to that shown in eq 1.



$$0 = n + \frac{k_p}{k_i}\ln\left(\frac{[Zr]}{[Zr]_o}\right) + \left(1 - \frac{k_p}{k_i}\right)\left(\frac{[Zr]}{[Zr]_o} - 1\right)$$

$$\frac{k_p}{k_i} = 9.6 \pm 0.3\ (1.0\ \text{eq.}\ BR_3)$$

$$\frac{k_p}{k_i} = 3.1 \pm 0.1\ (1.2\ \text{eq.}\ BR_3)$$

Figure 2. Unreacted ion pairs **3** as a function of n equiv of propene added. The solid lines are the fit of the equation shown[9] to the experimental data.

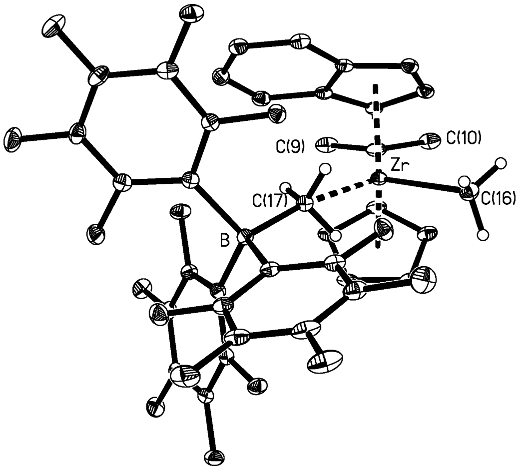


Figure 3. Molecular structure of ion pair **3b** with 30% thermal ellipsoids and selected H atoms depicted.[11]

Using complex **2** there were detectable changes in PP microstructure; the intensity of the isolated *m* and *mm* stereoerrors, as measured from the pentad distributions, decreased by about a factor of 50 and 30%, respectively, on going from 1.1 to 70 equiv of borane.[8] Since the *mm* errors are diagnostic of chain end epimerization while the *m* errors are characteristic of chain back-skip,[3] it would appear that excess borane subtly and differentially affects the rates of these processes relative to insertion.

We also examined the reaction of ion pairs **3**, prepared at ratios of 1.0 and 1.2 B/Zr from **1**, with variable amounts of propene using both ^1H and ^{19}F NMR spectroscopy in C_6D_6 at 25 °C.[10] As shown in Figure 2, it is evident that characteristic ratio of k_p/k_i[2f] decreases by about a factor of 3 on comparing 1.2 vs 1.0 equiv of borane. Since the change in this ratio is larger than the corresponding increase in R_p as a function of added borane (Figure 1a), we conclude that excess borane has a greater effect on initial insertion rates than on propagation.

Although ion pairs **3** exist as an isomeric mixture in solution (eq 2),[3c] we were able to crystallize the *minor* stereoisomer from this mixture, and the molecular structure of **3b** appears in Figure 3.[11] This complex, in which the methylborate moiety is located at the more hindered, lateral coordination site, features very strong interaction of the counteranion with the metal center. In particular, the Zr−C(17) distance, at 2.501(2) Å, is

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(8) See the Supporting Information for details.

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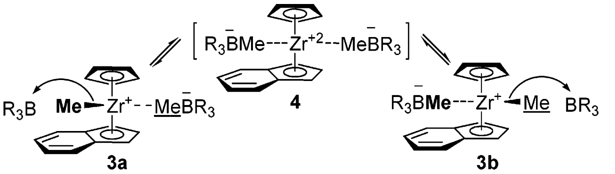


(2)

the shortest yet reported for a metallocenium ion partnered with a methylborate anion.[1b] However, this distance is less than 1% shorter than that observed for the methylborate ion pair derived from complex **2** (2.521(4) Å)[3a] or for [(Me$_2$C)$_2$Cp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$] (2.517 Å).[12] While the B−C(17)−Zr angle of 163.7(2)° approaches linearity, the parent complex [Cp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$] features a more obtuse angle of 169.1(2)°.[13] Although the close Zr−H(17A) and H(17B) distances of 2.29(3) and 2.28(3) Å are consistent with agostic interactions of these B−C−H bonds with the metal, the average C−H bond lengths (0.95(3) Å) and B−C(17)−H angles about the B−Me group (109(5)°) are not statistically different from those of C(16) (0.96(1) Å and 111(3)°), C(9) (0.98(3) Å and 111(4)°), or C(10) (1.00(7) Å and 109(4)°). To the extent that the strength of ion pairing in these complexes correlates directly with polymerization activity,[1] one might expect these otherwise sterically open *ansa*-metallocenium ions to be rather unreactive toward initial monomer coordination and insertion.

We sought spectroscopic evidence for the formation of new species using ion pairs **3** in the presence of excess borane. ^{1}H−^{1}H EXSY spectra reveal exchange correlations between BMe and ZrMe groups on *different* ion pairs (eq 2) in the presence of excess borane[8] that are consistent with a mechanism first proposed by Brintzinger and co-workers,[14] in which excess borane electrophilically attacks the remaining Zr−Me group to form the doubly activated intermediate **4**.

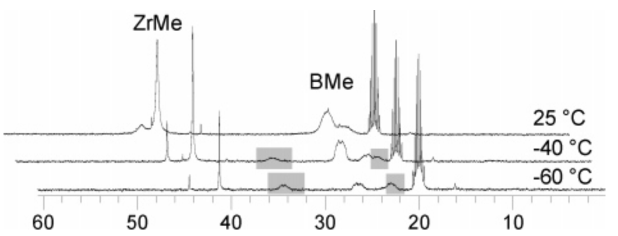
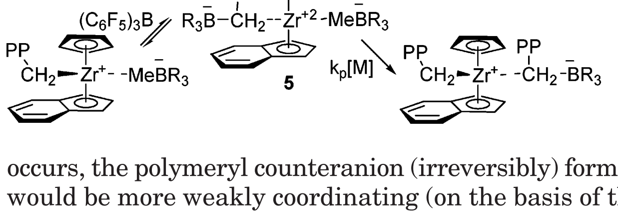


Figure 4. ^{13}C NMR spectra of a mixture of ion pairs **3** and 3.0 equiv of B(C$_6$F$_5$)$_3$ formed from **1**-$^{13}Me_2$ and 4.0 equiv of borane in toluene-d_8. Signals due to Zr−Me and B−Me resonances of ion pairs **3** are labeled, whereas new signals due to **4** are highlighted in gray.

At −20 to −60 °C, a fluxional species whose relative concentration increases at lower *T* (or higher absolute concentration) is detected. The ^{19}F NMR spectra are consistent with the intermediate **4**, provided there is an independent mechanism that averages the *o*-, *p*-, and *m*-F resonances of the inequivalent MeB(C$_6$F$_5$)$_3$ moieties in **4** at higher *T*.[8] ^{13}C NMR spectra using labeled **1**-$^{13}Me_2$ and excess borane revealed two exchange- (and quadrupole-) broadened peaks over this *T* range (Figure 4), consistent with intermediate **4** (eq 2).

Thus, the intermediacy of **4** can account for enhancement of initiation rates, by analogy to the work of Chen and co-workers.[6a] However, it is unclear if this same explanation can account for the increased propagation rates, required by the kinetic data, as it is evident that the NMR experiments ($K = [\mathbf{4}]/[\mathbf{3}][BR_3] \approx 6\ M^{-1}$ at −60 °C)[8] are not *quantitatively* consistent with the polymerization rate data (Figure 1b).

As suggested in eq 3, insertion of monomer into the Zr−C bonds of intermediate **5** could occur into either the Zr- - -CH$_2$PP or the Zr- - -Me bond. If the latter occurs, the polymeryl counteranion (irreversibly) formed would be more weakly coordinating (on the basis of the recent work of Baird and co-workers using homologues of MeB(C$_6$F$_5$)$_3$)[15] and this could account for the enhancement in propagation and relative decrease in chain transfer rates seen. However, in the experiments summarized in Figure 2, the principal Zr byproduct formed at high B/Zr ratios following chain transfer is [Me$_2$C(Cp)IndZrMe][HB(C$_6$F$_5$)$_3$] (**6**),[16] rather than [Me$_2$C(Cp)IndZrR][PP$_n$CH$_2$B(C$_6$F$_5$)$_3$], as required by the mechanism depicted in eq 3.



(3)

In situ but irreversible formation of a catalyst partnered with the weakly coordinating [(C$_6$F$_5$)$_3$B(μ-Me)B(C$_6$F$_5$)$_3$] anion[6b,17] or a related species—e.g. [(C$_6$F$_5$)$_3$B(μ-

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(10) These kinetic experiments were set up in the following manner: A solution of 2,3,5,6-tetrafluoro-*p*-xylene standard (20 mg in 4.5 mL in benzene-d_6) was prepared. Using this solution, stock solutions of metallocene **1** in benzene-d_6 (∼0.04 M) and borane (∼0.04 M) were prepared at 25 °C and NMR spectra were recorded to determine exact concentrations. Then a series of stock solutions of ion pairs **3** were prepared with Zr/B ratios of 1/1 and 1/1.2 and at four different concentrations for each ratio. A common stock solution of propylene in benzene-d_6 (ca. 0.50 M) containing mesitylene as a standard was prepared and an NMR spectrum recorded to verify concentration. Inside a glovebox, solutions of ion pairs were added to 5 mm screw-cap NMR tubes equipped with septa, and next to the NMR instrument, appropriate amounts of the propylene solution were injected into the ion pair solution via a gastight microliter syringe while stirring with a Vortex mixer. The samples were then immediately monitored via ^{19}F NMR spectroscopy to determine consumption of the ion pairs. The quantities and concentration of each ion pair stock solution were chosen so that following the addition of the required amount of propene, the final [Zr]$_0$ concentration was the same.

(11) Stock solutions of Me$_2$C(Ind)CpZrMe$_2$ (0.10 M) and B(C$_6$F$_5$)$_3$ (0.10 M) in toluene-d_8 were mixed in a 1/1 ratio at 25 °C in a glovebox. On addition of the metallocene to the B(C$_6$F$_5$)$_3$ solution, an immediate color change from colorless to orange-red indicated a rapid reaction at this temperature. The ^{1}H and ^{19}F NMR spectra[8] of the resulting solution showed two sets of signals in a roughly 1/3.5 ratio at ambient temperature due to the different stereoisomers. Orange crystals of the minor stereoisomer separated on leaving a 5 mm NMR tube standing at 25 °C for 18 h and were isolated by decanting the mother liquor. The molecular structure of complex **3b** with 30% thermal ellipsoids is depicted in Figure 3: monoclinic, $P2_1/c$, $a = 13.974(1)$ Å, $b = 14.794(1)$ Å, $c = 21.766(2)$ Å, $\beta = 107.511(1)$°, $V = 4291(1)$ Å^3, $Z = 4$, $R = 0.0422$, $R_w = 0.1117$ for 9833 unique reflections with $I > 2\sigma(I)$. See the Supporting Information for metrical data and full details of this structure.

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(17) We have been unable to detect this counteranion in a mixture of B(C$_6$F$_5$)$_3$ and [Bu$_4$N][MeB(C$_6$F$_5$)$_3$] by NMR spectroscopy. Separate and sharp signals for each component are observed in a 1/1 mixture of these two compounds in C$_6$D$_6$/CD$_2$Cl$_2$ (5/1 v/v) solution at room temperature.

$H)B(C_6F_5)_3]$ formed from **6** following initial chain transfer[16]—has to be considered as a plausible explanation. Future work will address these important issues.

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Supporting Information Available: Text, tables, and figures giving experimental procedures, selected NMR spectra, and crystallographic and metrical data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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