Effect of Counterion Structure on Zirconocenium Catalysis of Olefin Polymerization

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The catalytic species for olefin polymerization[1] derived from group 4 metallocene precursor is the 14-electron 3d^0 cation.[2–4] It can be obtained from a dimethylmetallocene by the abstraction of a methide ligand.[3b–g,5] Two appealing cocatalysts are triphenylcarbenium tetrakis(pentafluorophenyl)borate (**1**)[6] and tris(pentafluorophenyl)borane (**2**).[7,8] We have compared them and found the former to be superior for propylene polymerization by virtue of their difference in ion-pair interactions.

The precursors of this study are *rac*-ethylenebis(1-η^5-indenyl)zirconium dimethyl (**3**, $\mathrm{Et[Ind]_2Zr(CH_3)_2}$) and dichloride (**4**, $\mathrm{Et[Ind]_2ZrCl_2}$). Literature procedures were adopted for the synthesis of **1**,[6c,9] **2**,[7,9] **3**,[6c,10] and **4**[6c,10] in high yields and purities. All the operations were performed under argon using standard Schlenk techniques. Polymerization of propylene[6c,11] and isolation and characterization of the polypropylene followed our published methods.[10c]

The two cocatalysts were employed first to activate **3** directly.

$$\mathbf{3/1}\text{:}\ \ \mathbf{3} + \mathbf{1} \rightarrow \underset{\mathbf{5}}{\mathrm{Et[Ind]_2Zr^+(CH_3) + B^-(C_6F_5)_4}} + \mathrm{(C_6H_5)_3C(CH_3)} \qquad (1)$$

$$\mathbf{3/2}\text{:}\ \ \mathbf{3} + \mathbf{2} \rightarrow \underset{\mathbf{6}}{\mathrm{[Et[Ind]_2Zr^+(CH_3){\cdot}(CH_3)B^-(C_6F_5)_3]}} \qquad (2)$$

Propylene polymerization by **3/1** at 0 °C has only modest catalytic activity (*A*) and isospecificity[12] (Table I, run 1). The concentration of catalytic species ([C*]) was only 2.2% of [Zr] as determined by quenching polymerizations with tritiated methanol followed by radioassay.[13] The catalyst **3/2** (run 2), however, is even much inferior to **3/1**. It has only 1/37 of the *A* and produced lower molecular weight (MW) polypropylene with *ca.* half the yield of highly stereoregular polypropylene insoluble in refluxing *n*-heptane (IY). The lower *A* is not due to the inefficiency of eq 2 because [C*] was found to be 4.4% of [Zr] in this case. The main drawback in both processes is that most of **3** (>90%) was wasted to scavenge impurities.[14]

We have found that a far more effective way to generate catalysts similar to **5** or **6**, i.e., the ethyl derivatives, is by reacting **4** with the respective cocatalyst in the presence of a judicious amount of triethylaluminum (TEA) just sufficient to scavenge all the impurities and to alkylate **4**.[15] The polymerization by **4/1**/TEA (runs 3–5) has very high *A*[16] and IY,[17] both of which increase with the lowering of T_p. The catalyst **4/2**/TEA produces polypropylene with lower IY than the former and has *A* which decreases monotonically with the lowering of T_p (runs 6–8). Radiolabeling determination showed that [C*] = 94% of [Zr] for the **4/1**/TEA case, whereas it is 77% of [Zr] for the **4/2**/TEA system. The rate constants of propagation[18,19] are given in the last column of Table I.

According to eqs 1 and 2, the intermediates **5** and **6** have the same cation but dissimilar counterions. We have found that this difference is largely responsible for the observed discrepencies in *A*. For example, the catalyst **3/2** (run 9), which produces the $\mathrm{[CH_3B(C_6F_5)_3]^-}$ counterion, has *A* = 3 × 10^4 g of P/(mol of Zr·mol of $\mathrm{[C_3H_6]}$·h). When the noncoordinating $\mathrm{[B(C_6F_5)_4]^-}$ ion (*vide infra*) was added in an amount twice that of the former ion (run 10), the *A* was raised by 30-fold. When TEA is present, there is an exchange of the propagation polymer chain on Zr with an ethyl group of TEA. This exchange occurs at a much faster rate in the case of **5** than in **6**; the rate constant values are 1.15×10^{-2} and 2.53×10^{-4} s^{-1}, respectively. This difference can be explained by the better accessibility of TEA to the Zr–polymer bond when the counterion is $\mathrm{[B(C_6F_5)_4]^-}$ rather than $\mathrm{[CH_3B(C_6F_5)_3]^-}$.

Table I. Comparison of 1 and 2 as Cocatalysts for Propylene Polymerizations

run no.	catalyst[a] Zr	catalyst[a] µM	cocatalyst[b,c]	TEA (mM)	T_p (°C)	A[d] × 10^{-6}	IY[e] (%)	$\bar{M}_w$[f] × 10^{-4}	k_p[g]
1	**3**	300	**1**		0	1.85	89.2	6.1	560
2	**3**	450	**2**		0	0.05	49.2	5.6	7.5
3	**4**	10	**1**	1.0	20	82	35.6	2.6	580
4	**4**	10	**1**	1.25	0	64	89.0	6.3	450
5	**4**	5	**1**	2.0	−20	210	94.4	11.2	1480
6	**4**	25	**2**	1.5	20	6.1	0	2.6	52
7	**4**	25	**2**	2.0	0	3.6	48.9	5.6	31
8	**4**	25	**2**	2.25	−20	0.7	91.2	9.7	6
9	**3**	508	**2**		0	0.03			
10[h]	**3**	508	**2**		0	0.88			
11	**3**	820	**2**		0	0.05			
12[i]	**3**	820	**2**		0	0.54			
13	**3**	550	**1**		0	1.84			
14[i]	**3**	550	**1**		0	1.65			

[a] **3** = $\mathrm{Et[Ind]_2Zr(CH_3)_2}$, **4** = $\mathrm{Et[Ind]_2ZrCl_2}$. [b] **1** = $\mathrm{(C_6H_5)_3C^+(C_6F_5)_4B^-}$, **2** = $\mathrm{(C_6F_5)_3B}$. [c] The amount of cocatalyst is the same as that of the catalyst. [d] *A* = activity in g of polypropylene/(mol of Zr·mol of $\mathrm{[C_3H_6]}$·h). [e] IY = wt % of polypropylene insoluble in refluxing *n*-heptane and is a measure of isospecificity of the catalyst. [f] $\bar{M}_w$ by intrinsic viscosity: Chiang, R. *J. Polym. Sci.* **1956**, *28*, 235. [g] k_p is the average value for the rate constant of propagation[17] in M^{-1} s^{-1}. [h] 1.02 mM of $\mathrm{LiB(C_6F_5)_4}$ was added. [i] *o*-Dichlorobenzene was the solvent instead of toluene.

The X-ray molecular structure of $\mathrm{[1,2\text{-}(CH_3)_2\text{-}C_5H_3]_2Zr^+(C'H_3){\cdot}C''H_3B^-(C_6F_5)_3}$[7a] showed the Zr–C′ and Zr–C″ distances to be 2.253 and 2.549 Å, respectively. This result indicates a weak bonding interaction between the metal and the methyl group of the counterion. Since this interaction is partially ionic in nature, it should be significantly weakened in a polar medium. We have tested this effect by substituting *o*-dichlorobenzene (ϵ = 9.93) for toluene (ϵ = 2.38) as the medium for polymerization catalyzed by **3/2**. The *A* was 10 times higher in *o*-dichlorobenzene (run 12) than in toluene (run 11). In contradistinction, the polymerization activities catalyzed by **3/1** in both solvents (runs 13 and 14) are nearly the same, which is consistent with the common held view[3h] that $\mathrm{[B(C_6F_5)_4]^-}$ is an inert *noncoordinating* counterion.

It is interesting but contraintuitive that **6** is less stereoselective than **5** especially at 20 °C, at which T_p no refluxing heptane-insoluble polypropylene was produced by **6** (run 6). This may be rationalized by the assumption that ion-pair dissociation–reassociation causes oscillation between catalytic structures differing in stereochemical control of propylene insertion, resulting in low net stereoselectivity.[20,21] The higher k_p for **5** is not accompanied by higher MW than **6** probably because the former is likely to be more facile toward β-hydrogen chain termination by virtue of the absence of a coordinating counterion. Catalysis by compound **3** with $\mathrm{(C_6H_5)_3CB(C_6H_5)_4}$, $\mathrm{(C_6H_5)_3CBF_4}$, or $\mathrm{B(C_6H_5)_3}$ as cocatalyst produced little or no polypropylene, due to known side reactions.[22–24] In conclusion, the catalytic activity and stereoselectivity

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of alkyl zirconocenium species are strongly influenced by the nature of the counterion.

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(8) Cocatalysts **1** and **2** are soluble in hydrocarbons. The former produces the innocuous alkane 1,1-triphenylethane as a reaction product while the latter forms a weakly coordinated methyltriphenylborate without byproducts. In contrast, some of the other cocatalysts, i.e., Ag^+, Cp_2Fe^+, and $R_2NH_2^+$, form undesirable Ag^0, Cp_2Fe, and R_2NH byproducts.

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(11) The order of addition of catalyst components to toluene solution of propylene is important for maximum activity. For eqs 1 and 2, the $Et[Ind]_2Zr(CH_3)_2$ was added first followed by an equimolar amount of either **1** or **2**. In the polymerizations using $Et[Ind]_2ZrCl_2$ (**4**) as the precursor, the order of addition was TEA, **4**, and finally **1** or **2**.

(12) The catalytic activity (*A*) is given by g of PP/(mol of Zr·mol of C_3H_6·h); the isospecificity is expressed as isotactic yield (IY), which is the weight percent of refluxing *n*-heptane-insoluble polypropylene.

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(15) The optimal amount of TEA was found empirically by conducting polymerizations for a given range of [**4**] and [cocatalyst]. *A* reaches a constant and maximum value when the optimal [TEA] was used. The amount is larger for low T_p, high propylene pressure, or larger volume of solvent.

(16) The increase of *A* with the lowering of T_p has been attributed to the mechanism of a reversible Zr–olefin complex intermediate leading to olefin insertion in the forward direction and dissociation in the reverse.[14b]

(17) The decrease of IY with the raising of T_p is attributable to thermal activation of C* to conformations having reduced stereoselectivity.[14b]

(18) This is the average value, $\bar{k}_p = \sum C^*_i k_{p,i}$, for *i* number of active species with rate constant $k_{p,i}$, which produces the *i*th fraction of polypropylene separated by solvent extraction. In the case of catalysis by *rac*-ethylenebis(tetrahydroindenyl)dichlorozirconium/methylaluminoxane, the various active species were found to differ in stereoselectivity as well as $k_{p,i}$ values.[19]

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(22) Alkyl zirconocenium ions have exceedingly high electrophilic reactivity. They have been shown to extract F^- from PF^-_6[23] and $Al(CH_3)_2F$.[3e] A similar reaction is to be expected for BF^-_4 ion. Alkyl zirconocenium ions have also been found to complex with a phenyl ring of $B^-(C_6H_5)_4$ by η^3 (*m*,*p*) or η^2 (*m*,*p*) coordination[24] at low temperature and to metalate one of the phenyl rings of $[B(C_6H_5)_4]^-$ at higher temperatures.[3d] The above side reactions are the reasons for the lack of catalytic activities when $(C_6H_5)_3CBF_4$, $(C_6H_5)_3CB(C_6H_5)_4$, or $B(C_6H_5)_3$ was used as the cocatalyst with **3** in reactions 1 and 2, respectively.

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