

# Articles

## Influence of Cocatalyst on the Stereoselectivity of Unbridged 2-Phenylindenyl Metallocene Catalysts

Gregg M. Wilmes, Jennifer L. Polse, and Robert M. Waymouth\*

Department of Chemistry, Stanford University, Stanford, California 94305

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**ABSTRACT:** Unbridged 2-arylindenyl metallocene complexes, such as bis(2-phenylindenyl)zirconium dichloride, in the presence of methylaluminoxane (MAO), are catalyst precursors for the synthesis of elastomeric polypropylene. The nature of the cocatalyst is shown to have a significant influence on the productivity and stereoselectivity of these metallocenes. Propylene polymerizations in liquid propylene in the presence of bis(2-phenylindenyl)zirconium dimethyl (**5**) activated by three different types of methylaluminoxane, trityl tetrakis(pentafluorophenyl)borate (**1**), dimethylanilinium tetrakis(pentafluorophenyl)borate (**2**), or tris(pentafluorophenyl)borane (**3**), revealed a significant influence of activator on the polymerization behavior of these catalysts: both the productivity and stereoselectivity of the catalyst systems were highest with MAO and lowest with the borane **3** (MAO > **1** ≈ **2** >> **3**). Catalysts derived from the borane **3** yielded amorphous atactic polypropylenes under conditions where those from cocatalysts MAO, **1**, or **2** yielded semicrystalline, low-tacticity polypropylenes. The type of MAO also influences the stereoselectivity: MAOs containing isobutylaluminum groups yielded higher tacticity polypropylenes than those with only methylaluminum groups. Solution polymerizations in solvents of varying polarities revealed that the polarity of the solvent influenced the productivities but had little influence on the stereoselectivity.

### Introduction

The use of structurally well-defined coordination complexes as olefin polymerization catalysts has stimulated new developments in olefin polymerization, advanced our current understanding of polymerization catalysis, and led to new commercial processes for polyolefin production.<sup>1,2</sup> The ability to correlate the coordination geometry of the transition-metal precursor with the polymerization behavior of the catalyst systems has illuminated many of the mechanistic features of olefin insertion and the origins of stereo- and regiocontrol.<sup>3</sup> Typical catalyst systems are comprised of a coordination compound of group 4, group 6, or group 8 metals and methylaluminoxane. Although the nature of the coordination compound is generally well-defined, the same cannot be said for the methylaluminoxane cocatalyst, whose structure is often poorly defined and quite variable depending on its method of synthesis, storage, and use.<sup>4</sup> A number of mechanistic studies have helped to establish that one of the important roles of aluminoxanes is to generate both a reactive cationic transition-metal center and an ill-defined but presumably diffuse and poorly coordinating methylaluminoxane anion. Support for this hypothesis has come from the independent generation of cationic transition-metal complexes,<sup>5,6</sup> which were shown to be active polymerization catalysts. For metallocene-catalyzed polymerizations in the absence of MAO, typical catalyst recipes include mixtures of the metallocene dialkyls and one of

a number of well-defined activators which generate cations with poorly coordinating anions.<sup>7</sup> These include trityl tetrakis(pentafluorophenyl)borate, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>8,9</sup> (**1**), and dimethylanilinium tetrakis(pentafluorophenyl)borate, [HMe<sub>2</sub>NPh][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>10,11</sup> (**2**), both of which ultimately abstract a methyl anion and yield the B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> anion, and strong Lewis bases such as tris(pentafluorophenyl)borane, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**3**), which can abstract a methyl group to yield the methyltris(pentafluorophenyl)borate anion, MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup>. In some of these catalyst formulations, small amounts of alkylaluminum reagents are added to scavenge impurities in the reaction systems;<sup>7</sup> these alkylaluminum scavengers can also react with the perfluorophenylboranes.<sup>12</sup> These formulations do not always generate species of identical catalytic activity; for example, the nature of the counterion can have a significant effect on both the productivity of the catalyst and the molecular weight of the polymer produced. The nature of the counterion can also have an influence on the stereoselectivity of metallocene catalyst systems.<sup>7,9,13–25</sup>

That the active catalysts generated from either MAO or other activators have significant ionic character is also supported by observations that the polarity of the solvent can influence both the productivity and stereoselectivity of the catalysts and the molecular weights of the polymers produced. Effects of solvent polarity on propylene polymerizations have been investigated for a variety of stereoselective metallocenes including those which generate isotactic,<sup>26</sup> syndiotactic,<sup>27</sup> and hemiisotactic polypropylenes.<sup>28</sup>

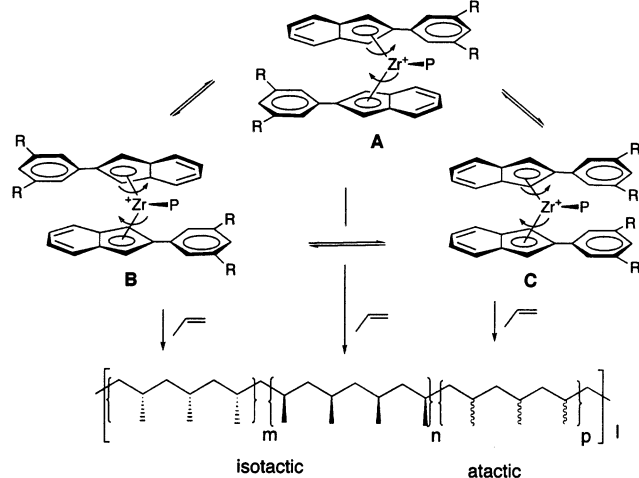
\* Corresponding author: e-mail waymouth@stanford.edu.

**Table 1. Liquid Propylene Polymerizations with (2-PhInd)<sub>2</sub>ZrX<sub>2</sub><sup>a</sup> (4, X = Cl; 5, X = CH<sub>3</sub>)**

entry	metal-locene	activator	Zr / μmol	scavenger	scavenger/ μmol	product- ivity <sup>b</sup>	[mmmm] <sup>c</sup>	M <sub>n</sub> <sup>d</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>	ΔH <sub>f</sub> (J/g) <sup>e</sup>
1	5	MMAO-I	3.5	none	N/A	2420	42	81 100	4.7	57
2	5	MAO-II	1.7	none	N/A	440	29	89 300	4.2	27
3	5	MAO-III	1.7	none	N/A	1220	23	150 000	3.2	
4	5	[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] (1)	3.5	TIBA	252	1320	26	127 000	3.5	19
5	5	[HMe <sub>2</sub> NPh][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] (2)	3.5	TIBA	252	770	26	79 700	3.4	
6	5	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (3)	30	TIBA	252	155	11	69 700	3.0	
7	5	MMAO-I	3.5	TIBA	252	2520	49	108 000	3.5	64
8	5	MAO-II	1.7	TIBA	252	1230	46	150 000	3.3	49
9	5	MAO-III	1.7	TIBA	252	1740	43	25 300	4.5	
10	5	MMAO-I	1.7	EtAl(BHT) <sub>2</sub>	256	4300	43	129 000	3.4	42
11	5	MAO-II	1.7	EtAl(BHT) <sub>2</sub>	256	1430	28	183 000	2.9	32
12	5	[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] (1)	7.0	EtAl(BHT) <sub>2</sub>	256	169	18	163 000	3.7	4
13	4	MMAO-I	1.7	none	N/A	2810	44	100 000	3.0	
14	4	MMAO-I	1.7	TIBA	252	2230	47	109 000	3.2	

<sup>a</sup> Conditions: 95 mL of propylene/5 mL of toluene, T<sub>p</sub> = 20 °C, time = 30 min, [MAO]/[Zr] = 1000, [B]/[Zr] = 1. <sup>b</sup> In kg of PP/(mol of Zr h). <sup>c</sup> By <sup>13</sup>C NMR. <sup>d</sup> By high-temperature GPC vs polypropylene standards. <sup>e</sup> By DSC.

### Scheme 1. Proposed Mechanism of Elastomeric Polypropylene Formation



In this paper, we demonstrate that the nature of the cocatalyst has a significant effect on both the productivity and stereoselectivity of metallocene catalysts based on bis(2-phenylindenyl)zirconium dichloride (4). This metallocene, when activated with MAO, generates a low-tacticity elastomeric polypropylene.<sup>29</sup> We have proposed that the low tacticity of the polypropylenes produced by these metallocenes is a consequence of the conformational dynamics of these metallocenes in competition with olefin insertion.<sup>30</sup> Isomerization of the metallocene between isospecific *rac* rotamers of opposite stereoselectivity and an aspecific *meso* rotamer at a rate slower than monomer insertion has been proposed to generate a stereoblock structure containing isotactic segments, which can cocrystallize across chains, and atactic segments, which provide flexibility (Scheme 1).<sup>29–33</sup> The polymerization behavior of these catalyst systems is very sensitive to the ligand structure, monomer concentration, metal, and polymerization temperature.<sup>29–36</sup> We now report our investigation of the effect of the nature of the cocatalyst on the polymerization productivity, molecular weight, and polymer microstructure on propylene polymerizations with bis(2-phenylindenyl)zirconium dimethyl (5) in liquid propylene and in polymerization solvents of varying polarity.<sup>33,37,38</sup>

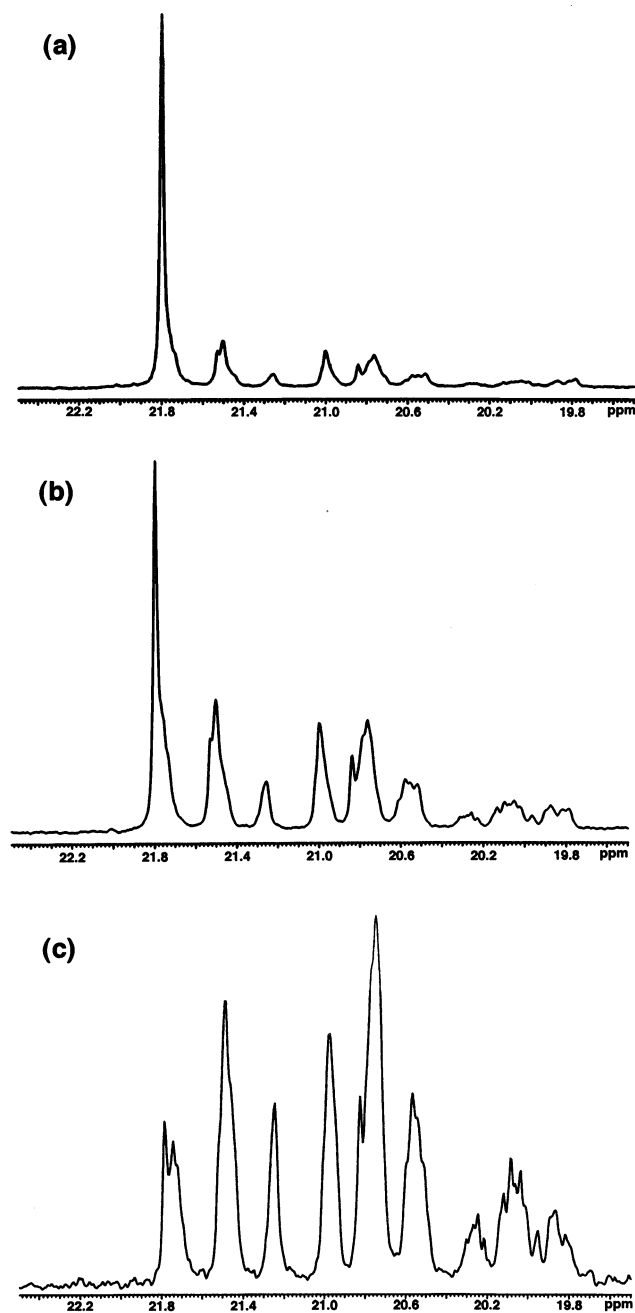
### Results

**Liquid Propylene Polymerizations.** Propylene polymerization with bis(2-phenylindenyl)zirconium dimethyl (5) was carried out in liquid propylene in the presence of three different types of methylaluminoxane (MAO): [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (1), [HMe<sub>2</sub>NPh][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (2), and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (3). The results are given in Table 1. Of the three different samples of MAO, MMAO-I was a type IV modified MAO obtained from Akzo-Nobel as a toluene solution and dried in vacuo prior to use, MAO-II was obtained from Albemarle as a toluene solution and dried similarly in vacuo, and MAO-III was from the same toluene solution from Albemarle and was used as received. For each polymerization, a 5 mL toluene solution of zirconocene, activator (and where indicated triisobutylaluminum (TIBA) or ethylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (EtAl(BHT)<sub>2</sub>), was injected with 250 psig of Ar pressure into a temperature-controlled stirred 300 mL reactor containing 95 mL of liquid propylene at 20 °C. TIBA or EtAl(BHT)<sub>2</sub> was necessary as a scavenger in the non-MAO-activated runs; in the absence of aluminum scavenger with these activators, no polymer was obtained. When B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was used as the activator, no polymer was obtained unless the concentration of metallocene and activator was greater than 200 μM. The polymers obtained were analyzed by <sup>13</sup>C NMR, DSC, and high-temperature GPC.

The nature of the counterion and scavenger had a significant effect on both the productivities and the microstructures of the polymers made, as determined by <sup>13</sup>C NMR (Figure 1). Cocatalysts 1 and 2, which contain the tetrakis(pentafluorophenyl)borate B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> anion, yielded less productive catalyst systems than those derived from MAO; catalysts generated from 2 were slightly less productive than those derived from 1. Catalysts derived from 1 and 2 also yielded polypropylenes of lower isotacticity than those derived from the Akzo MMAO-I (26% vs 49%) but similar to those derived from the Albemarle MAOs MAO-II and MAO-III (Table 1, entries 1–5). Inspection of the pentad distributions derived from the <sup>13</sup>C NMR spectra (Table 2) reveals that the major difference in the pentad distributions of polymers produced from cocatalyst 1, and MMAO-I is the larger [mmmm] pentad for polymers derived from MMAO-I. Catalyst systems derived from the borane 3 showed very low productivity and yielded a nearly atactic polypropylene ([mmmm] = 11%).

**Table 2. Complete Pentad Distributions of Representative Polymers Made in Liquid Propylene**

activator	mmmm	mmmr	rmmr	mmrr	xmrx	mrmr	rrrr	mrrr	mrrm
MMAO-I	48.60	12.94	3.44	7.82	12.60	5.87	1.58	3.53	3.62
[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] ( <b>1</b> )	26.32	15.07	4.96	10.97	18.14	9.62	3.02	6.82	5.07
B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ( <b>3</b> )	10.64	14.94	7.14	12.78	24.49	11.71	4.12	9.85	4.32



**Figure 1.** <sup>13</sup>C NMR spectra of polypropylenes synthesized with bis(2-phenylindenyl)zirconium dimethyl activated by (a) MAO-I, (b) [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], or (c) B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in the presence of TIBA.

The nature of the MAO and the type of alkylaluminum added also influence both the productivity and stereospecificity of catalysts derived from bis(2-phenylindenyl) metallocenes. Catalysts derived from the Akzo MMAO-I were both more productive and yielded polypropylenes of higher tacticity than those derived from the Albemarle MAO-II and MAO-III ([mmmm] = 42% vs 23–27%, Table 1, entries 1–3). However, when TIBA was added to the reaction mixture, the catalysts derived from MAO-II and MAO-III yielded polypropylenes of

**Table 3. Properties of Polymerization Solvents**

solvent	dielectric constant	dipole moment/D	press. for [C <sub>3</sub> H <sub>6</sub> ] = 4.34 M/psig
propylene	2.1	0.37	N/A
toluene	2.4	0.38	70
1,1,2,2-tetrachloroethane	9.2	1.32	85
1,2-dichlorobenzene	10.1	2.50	100

similar tacticity to that of MMAO-I. The addition of TIBA enhanced the productivity of catalysts derived from MAO-II (Table 1, entries 8 vs 2) but had little effect on those derived from MAO-III; nevertheless, the productivities of catalysts derived from the Albemarle MAO samples were roughly half of those derived from the Akzo-Nobel MMAO.

As a further test of the role of added alkylaluminums, we investigated the polymerization activity of catalysts generated with added ethylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (EtAl(BHT)<sub>2</sub>),<sup>39</sup> a sterically hindered alkylaluminum. The addition of EtAl(BHT)<sub>2</sub> enhanced the productivity of catalysts derived from MMAO-I and MAO-II but had little effect on the tacticity of the polymer produced. Catalysts generated from **2** in the presence of EtAl(BHT)<sub>2</sub> were both less productive and generated polypropylenes of lower tacticity than those generated in the presence of TIBA (entries 12 vs 4).

Polymerizations run with the metallocene dichloride **4**/MMAO-I and the dimethyl **5**/MMAO-I gave very similar results.

**Propylene Polymerizations in Solution.** To investigate the role of solvent on the stereoselectivity of these catalysts, solvents of varying dielectric constant and dipole moment were selected as media for polymerizations (Table 3).<sup>40</sup> Because the solubility of gases depends on the nature of the solvent, the solubility of propylene at 20 °C in the various solvents was measured using a procedure previously described.<sup>30</sup> Polymerizations were carried out with catalysts generated from **5** and MMAO-I, **1**, or **2** in the presence of TIBA at a propylene concentration of 4.34 M. Results are shown in Table 4.

At similar monomer concentrations, the nature of the solvent had a significant effect on the productivities but very little influence on the stereospecificity of the catalysts generated from a variety of cocatalysts. The productivities of catalysts generated from MMAO-I in dichlorobenzene were similar to those generated in toluene, while those generated in tetrachloroethane were much lower (Table 4, entries 1 vs 5 vs 8). In contrast, the tacticity of polypropylenes produced from catalysts generated from MMAO-I were identical in both toluene and tetrachloroethane and only slightly lower in dichlorobenzene. For the other cocatalysts, productivities are highest in DCB and lowest in TCE, and there is very little change in the microstructure of the polypropylenes produced with a given cocatalyst in the different solvents (Table 4).

The trends for the productivities and polypropylene microstructures for polymerizations done in toluene and TCE were the same as those done in neat monomer:

**Table 4. Solution Propylene Polymerizations with (2-PhInd)<sub>2</sub>ZrMe<sub>2</sub><sup>a</sup>**

entry	solvent	activator	μmol of Zr	productivity <sup>b</sup>	[mmmm] <sup>c</sup>	M <sub>n</sub> <sup>d</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>
1	toluene	MMAO-I	1.7	4430	36	94 500	4.7
2	toluene	[HMe <sub>2</sub> NPh][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	5.0	1050	25	91 400	4.2
3	toluene	[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	5.0	1530	22	91 400	4.1
4	toluene	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	30	90	9	54 600	3.9
5	TCE	MMAO-I	3.5	590	36	nd <sup>e</sup>	nd <sup>e</sup>
6	TCE	[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	5.0	50	21	nd <sup>e</sup>	nd <sup>e</sup>
7	TCE	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	30	30	12	nd <sup>e</sup>	nd <sup>e</sup>
8	DCB	MMAO-I	1.7	4160	28	132 000	5.4
9	DCB	[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	1.7	5050	25	62 800	2.5
10	DCB	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	30	610	14	180 000	3.2

<sup>a</sup> Conditions: 95 mL of solvent/5 mL of toluene, T<sub>p</sub> = 20 °C, time = 30 min, [MAO]/[Zr] = 1000, [B]/[Zr] = 1, [C<sub>3</sub>H<sub>6</sub>] = 4.34 M, 0.252 mmol of TIBA. <sup>b</sup> In kg of PP/(mol of Zr h). <sup>c</sup> By <sup>13</sup>C NMR. <sup>d</sup> By high-temperature GPC vs polypropylene standards. <sup>e</sup> Not determined.

MMAO-I > **1** >> **3**; the molecular weights of the polypropylenes appeared to be more sensitive to the cocatalyst in DCB than the other solvents. The molecular weight distributions of the polymers made in the solution phase were in the range 2.5 < M<sub>w</sub>/M<sub>n</sub> < 5.4.

## Discussion

Conformationally dynamic catalysts derived from unbridged 2-arylindene catalysts are remarkably versatile for the production of low-tacticity and elastomeric polypropylenes. While there are a number of other strategies for preparing low-tacticity polypropylenes,<sup>41–47</sup> the conformationally dynamic 2-arylindene catalyst systems can be tuned to produce a wide range of low-density, high-melting polypropylenes with properties ranging from gum elastomers to softened thermoplastics.<sup>48–50</sup> The polymerization behavior of these catalyst systems is extremely sensitive to the nature of the catalyst precursor and the polymerization conditions (ligand, metal, monomer concentration, temperature).<sup>29–32,34–36</sup> The results of this study indicate that the stereospecificity and productivity of catalysts derived from conformationally dynamic 2-arylindenylmetallocene catalysts are also very sensitive to both the nature of the cocatalysts<sup>33,38</sup> and the presence and nature of alkylaluminums added to the reaction medium. The influence of the nature of the cocatalyst on the productivity might be explained by differences in the efficiencies of generating the active catalyst, but the influence of the cocatalyst system on the stereospecificity suggests that the counterion and the nature of the alkylaluminum additives play an intimate role in modulating the behavior of the catalyst itself.

**Influence of Alkylaluminum Agents.** Early in our investigations on the polymerization behavior of 2-arylindenylmetallocenes, Coates had noted that the nature of the MAO could have an influence on the stereospecificity of these catalysts.<sup>51</sup> In this study, we have carried out a series of comparisons on the effects of MAO and added alkylaluminum agents and have illuminated at least one source of these effects—the presence of isobutylaluminum groups. As shown in Table 1, we observe higher tacticities for polypropylenes derived from catalyst systems generated from Akzo MMAO (MMAO-I) than those generated from Albemarle MAO. Akzo type IV MMAO is a modified MAO which contains isobutylaluminum groups.<sup>52</sup> In contrast, Albemarle MAO contains no isobutyl groups. The higher tacticity of the polypropylenes produced from Akzo MMAO can be attributed at least in part to the presence of isobutylaluminum groups as evidenced by the observation that addition of triisobutylaluminum to catalyst systems derived from the Albemarle MAO-II and MAO-III yields

polypropylenes with very similar microstructures to those derived from the Akzo MMAO-I (entries 8, 9 vs 1, Table 1).

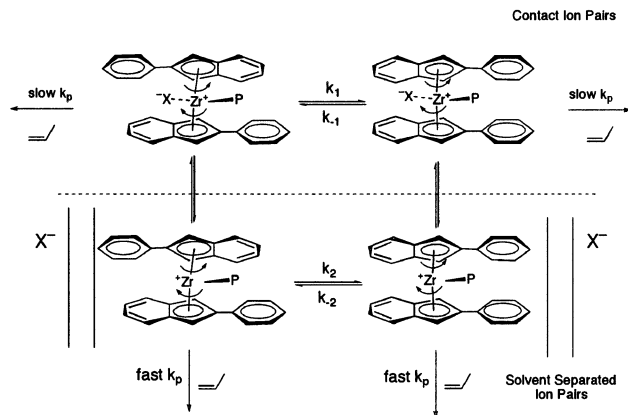
The strong influence of TIBA on the stereospecificity of these catalyst systems indicates that this additive, commonly used as a scavenger of impurities, is not an innocent spectator. A recent study reported a significant influence of the cocatalyst on the polymerization behavior but did not account for the effect of added TIBA.<sup>38</sup> Given the strong sensitivity of the stereospecificity to the added TIBA, the influence of the counterion on the polymerization can easily be masked by that of TIBA if these two factors are not independently taken into account.

The increase in stereospecificity with added TIBA could be ascribed either to an inhibition in the rate of the conformational dynamics by TIBA or to selective poisoning of conformations giving rise to atactic stereosequences. In previous studies,<sup>53</sup> we have shown that the addition of TIBA to catalyst systems derived from 2-arylindenylmetallocenes results in an increase in the tacticity of the polypropylene generated. We also observed both a decrease in the productivity and an increase in the tacticity of the average microstructure of a reactor blend prepared from a mixture of ansa-metallocenes: *rac*-Me<sub>2</sub>Si(2-PhInd)<sub>2</sub>ZrCl<sub>2</sub> and *meso*-Me<sub>2</sub>Si(2-PhInd)<sub>2</sub>ZrCl<sub>2</sub>. These effects were attributed to the selective poisoning by TIBA of the nonstereoselective *meso* conformers for both the stereorigid and conformationally dynamic 2-arylindenyl metallocenes. TIBA may also influence the rate of conformational dynamics; studies to assess this are in progress.

In contrast to TIBA, the more sterically hindered alkylaluminum EtAl(BHT)<sub>2</sub><sup>39</sup> does not appear to influence the stereospecificity of 2-arylindenyl metallocenes: The presence of EtAl(BHT)<sub>2</sub> did not affect the stereoselectivity of catalysts generated from MMAO-I or MAO-II (entries 10, 11 vs 1, 2).

**Influence of the Counterion on Stereospecificity.** The nature of the cocatalyst has a significant influence on the stereospecificity and productivity of 2-arylindenyl metallocenes (Tables 1 and 3). This is true even if the effects of TIBA are taken into account. The most significant and dramatic effect is observed with catalysts generated from the borane **3**: The stereoselectivity and productivity of catalysts generated from **3** are, under all conditions investigated, lower than those generated from any of the MAOs or the cocatalysts **1** or **2** containing the B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> anion. The polypropylene produced by **5/3**/TIBA is nearly atactic ([mmmm] = 11%) with a <sup>13</sup>C NMR spectrum reminiscent of that formed by aspecific C<sub>s</sub>-symmetric catalysts (Figure 1c).<sup>1,54</sup>

**Scheme 2. Involvement of Ion-Pairing in Formation of Elastomeric Polypropylene (Only One *rac* Isomer Shown for Clarity)**



Others have observed an influence of cocatalyst on the stereospecificity of metallocene catalysts,<sup>7,15,16,18,19</sup> but the dramatic drop in stereospecificity of **5** in the presence of the borane cocatalyst **3** relative to MAO, **1**, and **2** is noteworthy. The strong influence of the counterion on the productivities and stereospecificities could be attributed to the coupling of ion-pairing dynamics (contact ion pairs with solvent-separated ion pairs) with the conformational dynamics of the metallocene itself (Scheme 2). While there is every reason to believe that ion-pair dynamics are involved in some way with these complicated systems, our results showing that the stereospecificity is not strongly influenced by the nature of the solvent for a variety of cocatalyst systems (Tables 3 and 4) suggest that additional factors are in play for the system **5/3/TIBA**. One possibility is that the strongly coordinating anion  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  inhibits the rate of olefin insertion to the point where it becomes competitive with the conformational isomerism (Schemes 1 and 2).<sup>33</sup> If the rate of enchainment of propylene into the metallocenium cation derived from **5** is inhibited by the  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  anion to the point where it becomes competitive with or slower than the rate of conformational isomerism, then an atactic polypropylene would result. This hypothesis is supported by Landis's kinetic studies which imply that the rate of olefin insertion into metallocenium cations paired to the  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  anion is slower than the rate of insertion into those paired with the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  anion.<sup>7,55,56</sup> The much lower productivities observed in the presence of **3** (Tables 1 and 4) are also consistent with this hypothesis.<sup>33</sup>

While there are clear differences in the stereospecificities between catalysts derived from the perfluoroborate counterions and the MAOs, an even bigger difference is observed between systems derived from the borane **3** and those derived from either **1** or **2**. The higher but still intermediate stereoselectivities of catalyst systems generated from the various MAOs or cocatalysts **1** and **2** might be a consequence of either (1) the ability of the monomer to more readily displace the anions derived from MAO, **1**, or **2** or (2) the ability of these systems to access more loosely associated ion pairs which can then insert propylene at a rate competitive with but slightly faster than isomerization.

A comparison of the stereoselectivities of catalysts derived from the cocatalysts **1** and **2** relative to those derived from MAO must also account for the influence of any scavenger used, especially TIBA. The use of the more sterically hindered alkylaluminum scavenger EtAl-

(BHT)<sub>2</sub><sup>43</sup> is one way to address this issue. In contrast to TIBA, this scavenger has little effect on the stereospecificity of MAO-II-derived catalyst systems (Table 1, entries 2 vs 11). Catalysts generated from the cocatalyst **1** in the presence of EtAl(BHT)<sub>2</sub><sup>43</sup> generate polypropylenes of slightly lower tacticity and crystallinity ( $[\text{mmmm}] = 18\%$ ,  $\Delta H_f = 4 \text{ J/g}$ ) than those observed for catalysts derived either from MAO cocatalysts lacking isobutylaluminum groups (MAO-II, III  $[\text{mmmm}] = 23\text{--}28\%$ ,  $\Delta H_f = 27\text{--}32 \text{ J/g}$ , Table 1, entries 2 and 3) or those derived from **1** in the presence of TIBA ( $[\text{mmmm}] = 26$ ,  $\Delta H_f = 19 \text{ J/g}$ , entry 4, Table 1). This result suggests that the magnitude of the counterion effect when one compares MAO and cocatalyst **1** is comparable to the influence of TIBA.

**Influence of the Solvent.** The influence of the nature of the counterion on the stereoselectivity of metallocene **5** prompted us to investigate the role of solvent polarity on the stereospecificity of these metallocenes (vide supra). Several investigators have studied the role of the solvent polarity on the polymerization behavior of metallocenes,<sup>26,27,38</sup> but we were unable to find any data on the solubility of propylene in different solvents. In view of the strong dependence of the stereospecificity of these catalysts to monomer concentration, we felt it important to measure the solubility of propylene in order to compare the polymerization behavior at constant monomer concentration (Table 3). As shown in Table 3, the solubility of propylene depends sensitively on the nature of the solvent; an additional overpressure of 30 psig must be added over dichlorobenzene to relative to toluene solutions to obtain a monomer concentration of 4.34 M.

Under these conditions, we observe that the polarity of the solvent has little influence on the stereospecificity of these catalysts (Table 4). This result implies that solvent effects, while important to the productivities (see below), are not strongly stereodifferentiating, at least for the range of solvents investigated. At a monomer concentration of 4.34 M in each of the solvents, there was little change in isotacticity of the polymers produced with **1**, though there was a slight drop in isotacticity with MAO ( $[\text{mmmm}] = 28\%$  in DCB vs 36% in toluene) and a slight increase with **3** ( $[\text{mmmm}] = 14\%$  in DCB vs 9% in toluene).

Although the nature of the solvent had little effect on the stereospecificity, both the productivities and the molecular weights of the polymers were strongly influenced by the nature of the solvent. Low productivities were observed in TCE, whereas much higher productivities were observed in DCB with cocatalysts **1** and **3**. Similar effects on the productivities have been observed by Fink and co-workers.<sup>27</sup>

## Conclusion

The stereoselectivity of catalyst systems derived from unbridged bis(2-phenylindenyl)zirconocenes depend strongly on the nature of the cocatalyst and the nature of the alkylaluminum compounds present in the reaction medium, much more strongly than is the case with systems based on bridged metallocenes. The presence of isobutylaluminum groups in the reaction medium increases the stereoselectivity of these catalyst systems, implying that it is not an innocent scavenger of impurities. Catalyst systems derived from (2-phenylindenyl)-ZrMe<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> generate low-tacticity amorphous polypropylenes ( $[\text{mmmm}] = 11\%$ ) under conditions where other

activators generate intermediate tacticity polypropylenes ( $[mmmm] = 18\text{--}47\%$ ). The low stereospecificity derived from the  $B(C_6F_5)_3$  activator is attributed to the strong coordinating ability of the  $CH_3B(C_6F_5)_3^-$  anion, which inhibits the rate of propylene insertion. The polarity of the solvent influences the productivity of these catalyst systems but does not appear to have a significant influence on the stereoselectivity.

## Experimental Section

**General Considerations.** The metallocenes (2-phenylindenyl) $_2$ ZrCl $_2$  and (2-phenylindenyl) $_2$ ZrMe $_2$  were prepared as previously described;<sup>29,57</sup> tris(pentafluorophenyl)borane, dimethylanilinium tetrakis(pentafluorophenyl)borate, and trityl tetrakis(pentafluorophenyl)borate were a gift from the Albemarle Corp. and were used as received. Type IV methylaluminoxane (MAO-I) was purchased from Akzo Nobel in a toluene solution and dried in vacuo at room temperature prior to use. MAO was received from Albemarle Corp. and dried in vacuo at room temperature prior to use (MAO-II) or used as received (MAO-III). TIBA was obtained from Aldrich and used as received. Ethylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) was synthesized according to a literature procedure from triethylaluminum and 2,6-di-*tert*-butyl-4-methylphenol.<sup>58</sup> Polymerization grade propylene was received from Praxair, Matheson, or BP-Amoco and was purified through towers containing alumina and Q5 prior to use.<sup>22</sup> Toluene was purchased from Aldrich and purified through towers containing alumina and Q5 prior to use. 1,1,2,2-Tetrachloroethane and 1,2-dichlorobenzene were distilled from CaH $_2$ . Polymerizations were conducted in a 300 mL stainless steel Parr reactor with mechanical stirrer. The temperature for all polymerizations was maintained at 20 °C via an ethylene glycol/water cooling loop.

**Preparation of Activated Catalysts for Polymerization.** Toluene stock solutions of metallocenes, activators, and aluminum scavengers were prepared under a N $_2$  atmosphere in a drybox. For each polymerization, a 4 mL solution of activator and metallocene (5 mL if scavenger was not used) was stirred for 10 min, and 1 mL of scavenger solution, if used, was added immediately prior to injection.

**Propylene Polymerizations in Liquid Propylene.** The reactor was flushed six times with 70 psig of propylene, charged with 95 mL of liquid propylene, and cooled to 20 °C. The 5 mL of activated catalyst solution was placed in a single-ended injection tube, pressurized, and injected with 250 psig of Ar. After 30 min, the polymerization was quenched with 10 mL of methanol.

**Propylene Polymerizations in Toluene.** The reactor was flushed six times with 70 psig of propylene. The reactor was vented to 60 psig, and 95 mL of toluene was injected with propylene pressure. The toluene was equilibrated under 70 psig of propylene pressure with stirring at 20 °C for 1 h. The 5 mL of activated catalyst solution was placed in a double-ended injection tube, the stirrer turned off, the reactor vented to 60 psig, and the catalyst solution injected with 70 psig of propylene pressure. The stirrer was turned back on immediately after injection, and the polymerization was quenched with 10 mL of methanol after 30 min.

**Propylene Polymerization in Tetrachloroethane or Dichlorobenzene.** A 95 mL aliquot of solvent was added to the reactor via a Teflon cannula attached to a quick-connect stem. The reactor was flushed six times with propylene and then equilibrated with stirring at 20 °C at the relevant pressure. Injection was the same as for runs in toluene.

Polymers were collected and precipitated into acidified methanol (5% HCl) and stirred overnight. The polymers were then filtered and washed with methanol and dried in a vacuum oven at 40 °C.

**Polymer Characterization.** High-temperature GPC measurements of polymers were performed at BP on a Waters 150-C ALC/GPC at 139 °C in 1,2,4-trichlorobenzene using two Polymer Laboratories PL GEL mixed-B columns at a flow rate of 1 mL/min and referenced to polypropylene standards.

Solution  $^{13}C$  NMR spectra were run at 75 MHz at 100 °C on a Varian Inova-300 NMR spectrometer equipped with a 10 mm broad-band probe. Samples were prepared in 10 mm tubes in 3 mL of 1,1,2,2-tetrachloroethane containing 0.5 mL of *d* $_2$ -1,1,2,2-tetrachloroethane. Differential scanning calorimetry was performed using a Perkin-Elmer DSC 7. Polymer samples were annealed at 180 °C for 10 min, cooled to 20 °C at a rate of 10 deg/min, and allowed to rest at room temperature for 36 h. Heating curves were measured with a heating rate of 20 deg/min from 20 to 180 °C.

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## References and Notes

- Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170.
- Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, 2000; Vols. 1 and 2.
- Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1346.
- Ystenes, M.; Eilertsen, J. L.; Liu, J. K.; Ott, M.; Rytter, E.; Stovng, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3450–3450.
- Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325–387.
- Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255–70.
- Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434.
- Straus, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, *369*, C13–C17.
- Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570–8571.
- Turner, H. W. Eur. Pat. Appl. EP 0 277 004 A1, 1988 (Exxon Chemical Co.).
- Hlatky, G. G.; Upton, D. J.; Turner, H. W. PCT Int. Appl. WO 91/09882, 1991 (Exxon Chemical Co.).
- Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908–5912.
- Chen, Y. X.; Stern, C. L.; Yang, S. T.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451–12452.
- Chen, Y. X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582–2583.
- Chen, Y. X.; Metz, M. V.; Li, L. T.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287–6305.
- Chien, J. C. W.; Song, W.; Rausch, M. D. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2387–2393.
- Chien, J. C. W.; Song, W.; Rausch, M. D. *Macromolecules* **1993**, *26*, 3239–3240.
- Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3326–3327.
- Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 12114–12129.
- Jia, L.; Yang, X. M.; Ishihara, A.; Marks, T. J. *Organometallics* **1995**, *14*, 3135–3137.
- Jia, L.; Yang, X. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842–857.
- Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
- Yang, X. M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623–3625.
- Yang, X. M.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375–1377.
- Yang, X. M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015–10031.
- Vizzini, J. C.; Chien, J. C. W.; Babu, G. N.; Newmark, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2049–2056.
- Herfert, N.; Fink, G. *Makromol. Chem.* **1992**, *193*, 773–778.
- Herfert, N.; Fink, G. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 157–178.
- Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217–219.
- Lin, S.; Tagge, C. D.; Waymouth, R. M.; Nele, M.; Collins, S.; Pinto, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 11275–11285.

- (31) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586–11587.
- (32) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174–11182.
- (33) Wilmes, G. M.; Lin, S.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 5382–5387.
- (34) Petoff, J. L. M.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909–5916.
- (35) Lin, S.; Hauptman, E.; Lal, T. K.; Waymouth, R. M.; Quan, R. W.; Ernst, A. B. *J. Mol. Catal. A: Chem.* **1998**, *136*, 23–33.
- (36) Tagge, C. D.; Kravchenko, R. L.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 380–388.
- (37) Busico, V.; Cipullo, R.; Segre, A. L.; Talarico, G.; Vacatello, M.; Castelli, V. N. A. *Macromolecules* **2001**, *34*, 8412–8415.
- (38) Busico, V.; Cipullo, R.; Kretschmer, W. P.; Talarico, G.; Vacatello, M.; Van Axel Castelli, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 505–508.
- (39) Williams, V. C.; Dai, C. Y.; Li, Z. M.; Collins, S.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695–3698.
- (40) *CRC Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press LLC: Boca Raton, FL, 1999.
- (41) Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrel, J. R.; Mulhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851–3858.
- (42) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030–2031.
- (43) Bravakis, A.; Bailey, L.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000–1009.
- (44) Nele, M.; Mohammed, M.; Xin, S.; Collins, S.; Dias, M. L.; Pinto, J. C. *Macromolecules* **2001**, *34*, 3830–3841.
- (45) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelae, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348–4355.
- (46) Kuhl, O.; Koch, T.; Somoza, F. B.; Junk, P. C.; Hey-Hawkins, E.; Plat, D.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *604*, 116–125.
- (47) Dreier, T.; Erker, G.; Froehlich, R.; Wibbeling, B. *Organometallics* **2000**, *19*, 4095–4103.
- (48) Hu, Y. R.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908–6916.
- (49) Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 8100–8106.
- (50) Wiyatno, W.; Pople, J. A.; Chen, Z. R.; Gast, A. P.; Waymouth, R. M.; Fuller, G. G. *Macromolecules*, submitted for publication.
- (51) Waymouth, R. M.; Hauptman, E.; Coates, G. W. U.S. Patent US 5969070, 1999 (Stanford University).
- (52) Type IV modified methylaluminumoxane is no longer listed for sale by Akzo Nobel. According to hydrolysis gas composition results given on the product quality certificate, the alkyl substituents on the aluminum are 12% isobutyl and 88% methyl.
- (53) Petoff, J. L. M.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 7984–7989.
- (54) Petoff, J. L. M.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316–11322.
- (55) Liu, Z.; Somsook, E.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 2915–2916.
- (56) Liu, Z.; Somsook, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 11193–11207.
- (57) Waymouth, R. M.; Hauptman, E.; Coates, G. W. PCT Int. Appl. WO 95/25757, 1995 (Stanford University).
- (58) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409–416.

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