# **Propylene Polymerization with Unbridged Metallocenes:** Ligand Effects on the Selectivity for Elastomeric **Polypropylene**

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Bis(2-arylindenyl)zirconium dichlorides activated by methylaluminoxane produce elastomeric polypropylene with a stereoblock microstructure. In an effort to experimentally explore the importance of the 2-arylindene ligand in producing these materials, a series of catalysts was investigated that differed significantly from the parent ligand architecture. In particular, we sought to examine the influence of ligand aryl stacking on the polymerization behavior of these metallocenes. We discovered that the bis(2-arylindenyl) framework is important for the production of elastomeric polypropylene by this type of unbridged complex. Small changes in the fundamental catalyst structure upset the delicate balance between ligand rotation and monomer insertion resulting in the production of amorphous polymers.

#### Introduction

Homogeneous metallocene polymerization catalysts provide new opportunities to tailor the structure and properties of  $poly(\alpha$ -olefins) through manipulations of the catalyst ligand structure.<sup>1,2</sup> A wide variety of homoand copolymer architectures are possible using metallocene catalysts.<sup>1</sup> For polypropylene, isotactic,<sup>3–7</sup> syndiotactic,<sup>4,6,8,9</sup> heterotactic,<sup>4,6</sup> and stereoblock microstructures<sup>10-21</sup> can be prepared using metallocene catalysts.

- <sup>®</sup> Abstract published in Advance ACS Abstracts, December 1, 1997. (1) Brintzinger, H. H.; Fischer, D.; Muelhaupt, R.; Rieger, B.; Waymouth, R. M. Angew. Chem., Int. Ed. Engl. **1995**, *34*, 1143-70.
- (2) Ziegler Catalysts: Recent Scientific Innovations and Technological Improvements; Fink, G.; Muelhaupt, R.; Brintzinger, H. H., Ed.;
- Springer-Verlag: 1995. (3) Ewen, J. A. J. Am. Chem. Soc. **1984**, 106, 6355–6364.
- (4) Ewen, J. A. *Macromol. Symp.* **1995**, *89*, 181–196.
   (5) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P.
- Angew. Chem., Int. Ed. Engl. 1985, 24, 507-508. (6) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robingson, K. Makromol. Chem., Macromol. Symp.
- **1991**, 48/49, 253-295.
- (7) Ewen, J. A.; Haspeslagh, L.; Elder, M. J.; Atwood, J. L.; Zhang, H.; Cheng, H. N. In Transition Metals and Organometallics as Catalysts for Olefin Polymerization ; W. Kaminsky and H. Sinn, Ed.;
- (8) Ewen, J. A.; Jones, R. L.; Razavi, A. J. Am. Chem. Soc. 1988, 110, 6255-5256.
- (9) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Curtis, S.; Cheng, H. N. In Catalytic Olefin Polymerization (Stud. Surf. Sci. Catal.); T. Keii and
- K. Soga, Ed.; Elsevier: Tokyo, 1990; Vol. 56; pp 439–483.
   (10) Coates, G. W.; Waymouth, R. M. Science 1995, 267(5195), 217–
- 19 (11) Gauthier, W. J.; Collins, S. Macromolecules 1995, 28, 3779-
- 86. (12) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S.
- (13) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem.*
- Soc. **19**(5), 117, 11586-7. (14) Kaminsky, W.; Buschermohle, M. In Recent Advances in Mechanistic and Synthetic Aspects of Polymerization (NATO ASI Series. Series C: Mathematical and Physical Sciences); M. Fontanille and A. Guyot, Ed.; D. Reidel Publishing Company: Dordrecht, 1987;

Vol. 215; pp 503-514.
(15) Erker, G.; Aulbach, M.; Kruger, C.; Werner, S. J. Organomet. Chem. 1993, 450, 1-7.

Natta was the first to discover an elastomeric polypropylene and interpret its properties in terms of an atactic-isotactic stereoblock microstructure.<sup>22-24</sup> Collette and co-workers observed that elastomeric polypropylene could also be produced by supported tetralkyl group IVB catalysts.<sup>25,26</sup> The first metallocene system for the production of elastomeric polypropylene was introduced by Chien and co-workers in 1990.<sup>19–21</sup> Chien's catalyst precursor was a chiral, stereorigid ansa-titanocene where polymer chain growth was purported to alternate between aspecific and isospecific metallocene coordination sites, although other interpretations have recently been forwarded.<sup>11,12</sup>

We have reported that bis(2-arylindenyl)zirconium dichlorides, when activated by methylaluminoxane (MAO), produce elastomeric polypropylene. These catalysts were designed to interconvert between chiral,  $C_2$ symmetric (rac) and achiral,  $C_s$  symmetric (meso) geometries to give isotactic and atactic blocks in the same polymer chain (Scheme 1).<sup>10,13</sup> We have observed significant substituent effects for derivatives of bis(2phenylindenyl)zirconium dichloride where electron donating (CH<sub>3</sub>) and electron-withdrawing (CF<sub>3</sub>) groups

- (16) Knickmeier, M.; Erker, G.; Fox, T. J. Am. Chem. Soc. 1996, 118, 9623-9630.
- (17) Erker, G.; Nolte, R.; Tsay, Y.-H.; Kruger, C. Angew. Chem. Int. Ed. Engl. 1989, 28, 628-629.
- (18) Erker, G.; Nolte, R.; Tsay, Y. H.; Krueger, C. Angew. Chem. 1989, 101, 642-4.
- (19) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. J. Am. Chem. Soc. 1990, 112, 2030-2031.
- (20) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G.-Y.; Winter,
- (21) Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y. H., V. H., Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242– 1253
- (22) Natta, G.; Mazzanti, G.; Crespi, G.; Moraglio, G. *Chim. Ind.* (*Milan*) **1957**, *39*, 275–283.
  - (23) Natta, G. J. Polym. Sci. 1959, 34, 531-549.

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(24) Natta, G.; Crespi, G. (Montecatini) U. S. Patent 3,175,999, 1965. (25) Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.;

Su, A. C. L.; Harrell, J. R.; Mulhaupt, R.; Anderson, B. C. Macromolecules 1989, 22, 3851.

(26) Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. Macromolecules 1989. 22. 3858–3866.

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Chart 1



Scheme 1



have been introduced at the 3 and 5 positions of the phenyl ring.<sup>13</sup> These minor changes have a significant influence on the tacticity of the resulting polymers with the isotactic pentad content, percent mmmm (m<sup>4</sup>), ranging from 24 to 73%.

The design of the bis(2-arylindene) metallocene catalysts was based on a 1,3,4-substitution pattern on the cyclopentadienyl ligand such that rotation of the cyclopentadienyl ligands would lead to chiral and achiral torsional isomers.<sup>15,27–33</sup> A further consideration was that the substituents on the cyclopentadienyl ligand be sufficiently demanding such that each torsional isomer would have a lifetime sufficient to insert a sequence of propylene units prior to interconverting to the other isomer.<sup>10</sup> (Thus, for example, bis(indenyl)zirconium dichloride can interconvert between a chiral and achiral torsional isomer, but this metallocene produces atactic polypropylene<sup>34</sup>). In an effort to further study the role of the nature of the ligand on the polymerization behavior of this class of catalysts, we have prepared a series of unbridged metallocenes that retain the symmetry of the 2-arylindenyl complexes, but where we have varied the substituents at the 1, 3, and 4 positions of the cyclopentadienyl ligand. These studies reveal that the 2-arylindenes are rather specialized in being able to produce elastomeric polypropylenes.

- (27) Luke, W. D.; Streitweiser, A. J. J. Am. Chem. Soc. 1981, 103, 3241 - 3243.

- (31) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermuhle, D.; Kruger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590– 4601
- (32) Okuda, J. J. Organomet. Chem. 1988, 356, C43-C46.
- (33) Kruger, C.; Nolte, M.; Erker, G.; Thiele, S. Z. Naturforsch 1992,  $47b_{-}995-999$
- (34) Resconi, L.; Abis, L.; Franciscono, G. Macromolecules 1992, 25, 6814 - 6817

## Results

Bis(2-cyclohexylindenyl)zirconium dichloride (2), bis(2cyclohexyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (3), and bis(2-phenyl-4,5,6,7-tetrahydroindenyl)(2cyclohexylindenyl)zirconium dibromide (4) were synthesized to investigate the role of the aromaticity of the ligands on the polymerization behavior.<sup>35</sup> Bis(1-aryl-3,4-dimethylcyclopentadienyl)zirconium dichlorides 5-7 were chosen as models of a "truncated" indene ligand system where the methyl groups attached to the Cp ligand represent an altered version of the fused benzo ring present in **1**. (See Chart 1).

1-Aryl-3,4-dimethyl-1,3-cyclopentadienes and 2-phenyl-4,5,6,7-tetrahydroindene were prepared by reacting the appropriate arylmagnesium bromide with 3,4-dimethylcyclopent-2-en-1-one<sup>36</sup> and 3,3a,4,5,6,7-hexahydro-2(2H)-indenone,<sup>37</sup> respectively. 2-Cyclohexylindene was produced by a nickel-catalyzed coupling<sup>38</sup> of 2-bromoindene<sup>39</sup> and cyclohexylmagnesium chloride.

The parent metallocene, 1, was prepared by a previously reported procedure.<sup>13</sup> The fully saturated metallocene, 3, was prepared by catalytic hydrogenation of 1 with PtO<sub>2</sub> at 80 psig H<sub>2</sub> for 4 h.<sup>40</sup> Catalysts 2 and 5-7 were obtained using standard metalation procedures.<sup>13</sup> 4 was prepared by a new method developed in our laboratories.<sup>41</sup> In this procedure, the indene ligand is reacted with tetrakis(dimethylamino)zirconium to give the indenylzirconium triamide with elimination of dimethylamine.42 The triamide is then treated with bromotrimethylsilane and the resulting (2-phenyl-4,5,6,7tetrahydroindenyl)zirconium tribromide treated with (2cyclohexylindenyl)lithium to give 4 upon recrystallization from toluene.

The molecular structure of the mixed-ring compound 4 was confirmed by X-ray crystallography. The metallocene crystallizes as two independent molecules in the asymmetric unit which differ only in the orientation of the cyclohexyl substituent (Figure 1). The other bonding parameters for the mixed-ring 4 are normal and comparable to the parent bis(2-phenylindenyl)zirconium dichloride (1).

- (35) Pietsch, M. A.; Rappe, A. K. J. Am. Chem. Soc. 1996, 118, 10908-10909.
- (36) Conia, J.-M.; Leriverend, M.-L. Bull. Soc. Chim. Fr. 1970, 1981. (37) Welch, S. C.; Assercq, J.-M.; Loh, J.-P.; Glase, S. A. J. Org. Chem. 1987, 52, 1440.
- (38) Tamao, K.; Sumitani, K.; Kumada, M. J. Am. Chem. Soc 1972, 94. 4405-4407
- (39) McEwen, I.; Ronnqvist, M.; Ahlberg, P. J. Am. Chem. Soc. 1993, 115 3989-3996
- (40) Waymouth, R. M.; Bangerter, F.; Pino, P. Inorg. Chem. 1988, 27. 758-759.
- (41) Tagge, C.; Waymouth, R. M., Unpublished results.
- (42) Chandra, G.; Lappert, M. F. J. Chem. Soc. (A) 1968, 1940-1945

<b>Fable 1. Summary of Polymerization Results Using Unbridg</b>	ed Metallocenes <sup>a</sup>
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entry	catalyst	propylene press (psig)	prodvity <sup>b</sup>	% mmmm <sup>c</sup>	% <i>m</i>	$M_{ m w}{}^d$ ( $ imes$ 10 $^{-3}$ )	$M_{\rm w}/M_{\rm n}$
1	1	50 <sup>e</sup>	1380	31	69	310	3.2
2		$75^{f}$	1480	35	71	399	3.8
3		bulk <sup>g</sup>	2525	32	70	542	3.5
4	2	50	374	11	57	117	3.8
5		75	602	11	55	131	3.9
6		bulk	2340	15	62	219	3.3
7	3	50	940	3	46	20	1.9
8		75	2020	3	45	27	1.9
9		bulk	2390	5	52	40	1.9
10	4	50	531	6	49	52	2.6
11		75	957	7	51	78	2.9
12		bulk	3394	13	58	186	3.1
13	5	50	3657	10	59	146	2.0
14		75	4511	10	58	215	2.2
15		bulk	8797	10	59	392	3.2
16	6	50	2325	10	59	201	3.1
17		75	3235	10	58	290	2.9
18		bulk	7120	10	60	323	3.1
19	7	50	867	10	59	94	2.1
20		75	1027	11	59	140	2.2
21		bulk	2833	11	61	217	2.7

<sup>*a*</sup> Conditions: T = 20 °C;  $[Zr] = 5.0 \times 10^{-5}$  M; [Al]/[Zr] = 1000. <sup>*b*</sup> Kilograms of polypropylene per mole of Zr per hour. <sup>*c*</sup> Determined by 1<sup>3</sup>C NMR spectroscopy. <sup>*d*</sup> Determined by gel permeation chromatography versus polypropylene standards. <sup>*e*</sup>  $[C_3H_6] = 3.24$  M. <sup>*f*</sup>  $[C_3H_6] = 4.49$  M. <sup>*g*</sup> 100 of mL liquid propylene and 25 mL of toluene.



**Figure 1.** ORTEP diagram of complex **4**. The two independent molecules in the asymmetric unit are separated for clarity.

**4:** Cp-Zr-Cp = 130.3 (A),  $131.0^{\circ}$  (B); Br-Zr-Br = 95 (A),  $94.5^{\circ}$  (B); Zr1-Br1 = 2.60 Å; Zr1-Br2 = 2.59 Å; Zr2-Br3 = 2.59 Å; Zr2-Br4 = 2.61 Å. **1:**  $Cp-Zr-Cp = 131^{\circ}$ ;  $Cl-Zr-Cl = 94.39^{\circ}$  (*rac-1*),  $97.03^{\circ}$  (*meso-1*); Zr-Cl = 2.43 Å.<sup>10</sup> The Zr-Br bonds from **4** are somewhat longer than the Zr-Cl bonds in **1**.

Bis(1-aryl-3,4-dimethylcyclopentadienyl)zirconium dichlorides are stable to air and moisture: **5** and **6** have been stored for months in air with no decomposition. **7** does discolor in air over several months but is still pure by <sup>1</sup>H NMR. **5**–**7** may be purified using "wet" solvents. The solid-state structure of **6** was also determined by X-ray crystallography (Figure 2). Relevant structural parameters for **6** are nearly identical to those reported for **1** and related compounds:<sup>10,13</sup> **6**: Cp–Zr–Cp = 130.7°, Zr–Cl = 2.44 Å, and Zr–Cp = 2.22 Å. Cl–Zr–



Figure 2. ORTEP diagram of complex 6.

Cl differs marginally for these two complexes. This angle is 95.44°, 94.39°, and 97.03° for *rac*-1, *meso*-1, and **6**, respectively. The dihedral angle between the planes containing the phenyl and substituted cyclopentadienyl rings is less than 10° for 1 and derivatives. However, in **6**, this angle has increased to 22.5°. Compound **6** crystallizes in a  $C_2$ -symmetric conformation where the methyl groups of the cyclopentadienyl ring are staggered over the chloride ligands; a configuration that is reminiscent of the  $\delta$  conformation recognized by Brintzinger and co-workers as being easily accessible to various *ansa*-titanocenes and zirconocenes.<sup>43</sup>

Propylene (PP) polymerizations were carried out in the presence of the metallocene dichlorides and MAO (Al:Zr = 1000:1) in toluene solution under a variety of propylene pressures or in liquid propylene (Table 1). While the productivities for **1** differ somewhat from values previously reported (880 vs 1380 kg of PP/mol of Zr at 50 psig),<sup>13</sup> the degrees of isotacticity are in the same range.

<sup>(43)</sup> Burger, P.; Diebold, J.; Gutmann, S.; Hund, H.-U.; Brintzinger, H. H. Organometallics **1992**, *11*, 1319–1327.

Dimethylcyclopentadienyl derivatives were up to 3 times more productive than bis(2-phenylindenyl) **1**. Substitution of the phenyl ring tempered productivity gains somewhat, with 7 producing the least polymer. Solution polymerizations using **2**-**4** were more sluggish than those utilizing 1, but the productivities in bulk polymerizations were comparable. The weight-average molecular weights  $(M_w)$  of polypropylenes produced from the various catalysts are significantly different. Fully hydrogenated 3 gave the lowest molecular weights and narrowest molecular weight distributions  $(M_w/M_n)$  of all catalysts investigated.  $M_{\rm w}$  also increased with propylene pressure for catalysts 1-7.

Ligand effects on the stereospecificity of propylene polymerization with this class of unbridged catalysts are dramatic. For these studies, the isotacticity of the polypropylenes is reported in terms of the mole fractions of isotactic pentads ([mmmm]), as determined by <sup>13</sup>C NMR.<sup>44</sup> Substitution of the phenyl group of the phenvlindenyl complex by a cyclohexyl substituent results in a dramatic decrease in the isotacticity of the polymer produced: polypropylene produced in liquid propylene from the bis(2-cyclohexylindenyl)zirconium dichloride (2) has an isotactic pentad content [mmmm] = 15%, whereas [mmmm] = 32% for the polymer produced under similar conditions with 1. Under like conditions, the fully hydrogenated derivative 3 yields atactic polypropylene ([mmmm] = 5%). Similarly, polypropylenes obtained from the mixed ring complex and (2-aryl-3,4dimethyl)cyclopentadienyl derivatives 4-7 were amorphous with isotactic contents in the range of 10-11%. IR spectra were nearly identical for polypropylene samples prepared using catalysts 2-7. The structure of polypropylene can also be represented by the IR index  $(A_{998}/A_{974})$ , which is a measure of the helical content of the polypropylene.<sup>45</sup> Values of the IR index of polypropylenes obtained from catalysts 2-7 ranged from 0.14 to 0.22, indicative of atactic polypropylene. For comparison, the IR index of polypropylene produced by 1 ([mmmm] = 26%) is  $A_{998}/A_{974} = 0.59$ .<sup>13</sup> Highly isotactic polypropylene has an IR index approaching 1. Differential scanning calorimetry (DSC) profiles of polymer samples prepared using 2-7 provided no evidence of crystallinity. In contrast, polypropylene prepared from 1 (Table 1, Entry 3) exhibits a broad melting transition,  $T_{\rm m} = 30 - 152$  °C and  $\Delta H = 28.0$  J/g.

# Discussion

In this study, we sought to investigate the polymerization behavior of structural analogs of bis(2-arylindenyl)zirconium dihalides to gain insight into the breadth of unbridged catalyst types that can produce elastomeric polypropylene. For these studies, metallocenes with symmetries comparable to the 2-arylindene metallocenes were prepared to study electronic and steric effects of the ligands and to explore the relevance of aryl stacking<sup>46</sup> on the polymerization behavior of these unbridged metallocene complexes. Calculations by Pietsch and Rappe<sup>35</sup> have indicated that  $\pi$ -stacking interactions<sup>46,47</sup> might help stabilize the *rac* and *meso* geometries of the 2-arylindenyl metallocenes and contribute to the barrier for interconversion.

To investigate the role of the 2-arylindene ligands on the polymerization behavior of these metallocenes, we made systematic modifications of the ligand structure by replacing the aromatic substituents (phenyl and indenyl) with their saturated analogs. For 2, the phenyl ring was replaced with a saturated cyclohexyl moiety. For complex 3 both the phenyl and benzo groups of the indenyl ligand were converted to their saturated analogs. The mixed-ring complex 4 was prepared to test whether  $\pi$ -stacking interactions<sup>35</sup> might bias the torsional isomers to favor the anti conformation. The truncated ligands 5–7 were prepared to study the role of the indenyl ligand. All metallocenes prepared were dichlorides except for the mixed-ring complex 4. In this instance, the intermediate 2-phenyl-4,5,6,7-tetrahydroindenylzirconium tribromide is easier to prepare and purify than the corresponding trichloride. Polymers prepared from the metallocene dibromide 4 and metallocene dichlorides were directly compared in this work. Investigations of the parent metallocene **1** and **1**-Br<sub>2</sub> indicate that the choice of halide does not significantly affect polymerization behavior or the microstructure of the resulting polypropylene.<sup>41</sup>

The solid-state structure of 4 was investigated by X-ray crystallography. Two independent molecules were observed in the asymmetric unit each with slightly different conformations of the cyclohexyl ring.<sup>48</sup> The cyclohexyl ring adopts a chair conformation in both structures with the indenyl framework occupying an equatorial position. Steric factors appear to dictate the solid-state structure of 4 in that the catalyst adopts "meso-like" geometries in the crystal structure, placing the bulky cyclohexyl and tetrahydroindene substituents furthest apart. These steric factors appear to dominate whatever  $\pi$ -stacking interaction might exist between the indenyl and phenyl substituent. The solid-state structure of the 3,4-dimethylcyclopentadienyl derivative (6) was also investigated. This compound crystallizes in a  $C_2$ -symmetric conformation where the phenyl groups of the ligand are oriented *trans* to the Zr-Cl bonds.

The polymerization behavior of all these metallocenes reveals some important differences. Productivities in liquid propylene (20 °C) are in the range of 2300-8800 kg of PP/mol of Zr and appear to be highest for the 3,4dimethyl substituted complexes 5 and 6. Molecular weights of the polymers are in the range of 20 000-500 000 and are lowest for complexes 3 and 4 containing the tetrahydroindenyl ligands.

The increase in molecular weight with increasing monomer concentration evidenced for all catalysts investigated is not unprecedented<sup>49</sup> and implies that  $\beta$ -H elimination is an important chain-transfer process. The literature suggests that substitution of the indenyl ligand framework of ansa-metallocenes in the 2 position hinders chain transfer to monomer.49

The most striking difference in the polymerization behavior of these complexes is the stereospecificity.

<sup>(44)</sup> For random polypropylene [mmmm] = 6%, for highly isotactic polypropylene, [mmmm] = 100%

 <sup>(45)</sup> Luongo, J. P. J. Appl. Polym. Sci. 1960, 3, 302–309.
 (46) Aryl stacking is defined as an electrostatic interaction between the partially positive  $\sigma$  framework of an aromatic system and the negatively charged  $\pi$  cloud of a nearby neighbor.

<sup>(47)</sup> Hunter, C. A.; Sanders, J. K. M. J. Am. Chem. Soc. 1990, 112, 5525 - 5534.

<sup>(48)</sup> Close inspection reveals that the two structures are related via

<sup>pseudo-translational symmetry.
(49) Stehling, U.; Diebold, J.; Kirsten, R.; Roll, W.; Hans-Herbert,
B.; Jungling, S.; Muelhaupt, R.</sup> *Organometallics* 1994, *13*, 964–970.

## Propylene Polymerization with Unbridged Metallocenes

Under comparable conditions, only the 2-phenylindenyl complex **1** produced a semicrystalline elastomeric polypropylene. Whereas complex **1** in liquid propylene yielded a polymer with an an isotactic content [mmmm] = 32%, complexes **2**-7 all produce amorphous polymers with isotactic contents ranging from [mmmm] = 5 to 15%.44 Complex 2 yielded polymers with the highest isotactic content ([mmmm] = 15%), but this material was amorphous by DSC. Rappe had suggested on the basis of steric grounds (UFF force field)<sup>35</sup> that this complex should give isotactic polypropylene as he calculated that the rac isomer was more stable than the meso for this derivative.

The 2-cyclohexyltetrahydroindenyl complex 3 afforded atactic polypropylene. On the basis of steric grounds, one might argue that this ligand is even more sterically demanding than the 2-phenylindene ligand (see Figure 1) and should thus yield isotactic polypropylene. However, in this compound, we have removed all possible  $\pi$ -stacking interactions thus eliminating an electronic preference for a rac or meso conformation. To further test this aryl-stacking hypothesis,<sup>35</sup> the mixed-ring compound 4 was prepared. For this compound, the 2-phenyl substituent of one ring was envisioned to be appropriately positioned to undergo a favorable stacking interaction with the geminal indenyl ligand to favor the chiral or isospecific form. However, only the meso form is observed in the solid-state (Figure 1) and the catalyst derived from this metallocene yielded amorphous polypropylene. That 4 gives lower tacticity polymers than 2-cyclohexyl derivative 2 suggests that ligand contributions in these metallocenes are additive rather than synergistic, a result seemingly at odds with the arylstacking hypothesis. Catalysts derived from 5-7 also produce amorphous polypropylenes, indicating that the indenyl ligand also plays an important role.

The fact that compounds 2-7 all yield amorphous polypropylenes under conditions where the 2-phenylindene complex 1 yields a semicrystalline elastomeric polypropylene suggests that both the 2-aryl substituent and the indenyl ligand are important for producing elastomeric polypropylenes. We have previously proposed a mechanism (Scheme 1) that involves interconversion of the chiral and achiral torsional isomers to produce stereoblock microstructures. In order for a stereoblock microstructure to be produced by this mechanism, several factors have to be closely balanced: the two forms of the catalyst must be close in energy to be nearly equally populated and the rate of interconversion must be slower than insertion of the olefin but faster than the time it takes to construct a single polymer chain.<sup>10,13</sup> All of the complexes **1**-7 have the appropriate symmetries to interconvert between chiral and achiral forms. Solution NMR spectroscopy of complexes 1-7 at room temperature reveal time-averaged  $C_2$ symmetry, indicating that rotation of the ligands for the dichlorides is facile for 1-7. Catalysts derived from metallocenes 1–7 all produce polypropylene with roughly comparable productivities. The fact that only 1 yields an elastomeric polymer indicates that the competition among the various rates is extraordinarily subtle. For the derivatives examined here, only the 2-arylindenyl metallocenes maintain the appropriate balance between rates of catalyst isomerization and monomer insertion to give rise to thermoplastic elastomers.

In summary, our results indicate that catalysts derived from a 2-arylindenyl metallocene framework are unusual in being able to produce elastomeric stereoblock polypropylenes. The symmetry of this ligand allows it to interconvert between chiral and achiral torsional isomers, but this appears to be a necessary but not sufficient condition for producing elastomeric polypropylenes. While we have found no experimental evidence for  $\pi$ -stacking as an important influence on the behavior of these unbridged 2-arylindene metallocenes, we cannot rule out that  $\pi$ -stacking occurs in these complexes. The results of this study imply that relatively slight changes in structure are enough to disrupt the carefully balanced interplay of rates that are necessary to yield stereoblock polymers.

## **Experimental Section**

Standard inert atmosphere techniques were used in handling air- and moisture-sensitive compounds.<sup>50</sup> Diethyl ether and tetrahydrofuran (THF) were distilled from Na/benzophenone ketyl and methylene chloride was distilled from calcium hydride prior to use in reactions. Toluene was dried over Q5 and alumina. 3,4-Dimethylcyclopent-2-en-1-one,<sup>36</sup> 3,3a,4,5,6,7hexahydro-2(2H)-indenone,<sup>37</sup> 2-bromoindene,<sup>39</sup> ZrCl<sub>4</sub>(THF)<sub>2</sub>,<sup>51</sup> **1**,<sup>52</sup> and zirconium tetrakis(dimethylamide)<sup>53</sup> were prepared by reported methods. n-Butyllithium (nBuLi), phenylmagnesium bromide, p-tolylmagnesium bromide, cyclohexylmagnesium chloride, [1,2-bis(diphenylphosphino)ethane]nickel dichloride, and 2-naphthyl bromide were purchased from Aldrich. Bromotrimethylsilane and ZrCl<sub>4</sub> was obtained from Fluka and Adam's catalyst (PtO) was purchased from Strem. NMR spectra were recorded on Varian Gemini 200 and 400 MHz spectrometers.

3,4-Dimethyl-1-phenyl-1,3-cyclopentadiene. Diethyl ether (30 mL) was added to a dry 100 mL Schlenk flask under argon. Phenyl magnesium bromide (3 M in ether, 6.1 mL) was added followed by dropwise addition of 3,4-dimethyl-2-cvclopenten-1-one at 0 °C to yield a slurry which was stirred at room temperature for 1 h. The reaction was quenched with 50 mL of ether and 50 mL of saturated NH<sub>4</sub>Cl(aq). The aqueous layer was extracted with ether, and the combined organics were stirred with *p*-toluenesulfonic acid monohydrate (1 g) for 30 min. The mixture was washed twice with 50 mL of water, and then the organic solution was dried over MgSO<sub>4</sub>, filtered, and concentrated via rotovap. The resulting solid was washed with cold methanol followed by cold hexanes. A second crop of product was obtained by recrystallizing the methanol solution at -20 °C. The purified product was stored at -20 °C to prevent decomposition.<sup>54</sup> Yield: 0.93 g (30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.88 (s, 3H), 1.96 (s 3H), 3.26 (s, 2H), 6.65 (s, 1H), 7.13 (t, 1H, J = 7 Hz), 7.27 (t, 2H, J = 7 Hz), 7.44 (d, 2H, J = 7 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  12.6, 13.4, 45.2, 124.5, 126.0, 128.5, 131.7, 135.5, 136.4 ppm. C, H analysis for C<sub>13</sub>H<sub>14</sub>. Anal. Found (Calcd): C, 91.51 (91.71); H, 8.49 (8.29).

3,4-Dimethyl-1-p-tolyl-1,3-cyclopentadiene. A modified literature procedure was employed.<sup>55</sup> The preparation of 3,4dimethyl-1-p-tolyl-1,3-cyclopentadiene follows the same procedure as that used to make 3,4-dimethyl-1-phenyl-1,3-

<sup>(50)</sup> Shriver, D. F.; Drezdzon, M. A. The Manipulation of Air-(51) In Inorganic Syntheses ; J. P. J. Fackler, Ed.; John Wiley &

<sup>(52)</sup> Coates, G. W. Ph.D. Thesis, Stanford University, May 1994.
(53) Diamond, G. M.; Rodewald, S.; Jordan, R. F. Organometallics

<sup>1995, 14, 5-7.</sup> 

<sup>(54)</sup> The ligand quickly decomposes at elevated temperature to give a sticky red solid. At room temperature, decomposition occurs over several hours

<sup>(55)</sup> Jungling, S.; Muelhaupt, R. J. Organomet. Chem. 1993, 460, 191 - 195.

cyclopentadiene substituting *p*-tolylmagnesium bromide for phenylmagnesium bromide. Yield: 69%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  1.88 (s, 3H), 1.96 (s, 3H), 2.31 (s, 3H), 3.24 (s, 2H), 6.59 (s, 1H), 7.08 (d, 2H, J = 8 Hz), 7.32 (d, 2H, 8 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  12.5, 13.3, 21.0, 45.3, 124.4, 129.1, 130.8, 133.7, 135.2, 135.4, 135.6, 142.5 ppm. C, H analysis for C<sub>14</sub>H<sub>16</sub>. Anal. Found (Calcd): C, 91.04 (91.24); H, 8.54 (8.75).

3,4-Dimethyl-1-(2-naphthyl)-1,3-cyclopentadiene. A three-neck round-bottom flask equipped with a reflux condenser and dropping funnel was charged with Mg turnings (0.515 g, 20 mmol) under argon. A few crystals of I2 were added followed by 5 mL of diethyl ether. After 1 h, when the solution color faded, 2-bromonaphthalene (4.14 g, 20 mmol) in 25 mL of ether was added dropwise. The reaction was heated to reflux and stirred for 2 h. The solution was cooled in an ice bath and then transferred to a clean Schlenk flask. 3,4-Dimethylcyclopent-2-en-1-one was added dropwise at 0 °C, and the resulting solution was stirred at room temperature for 2 h. The reaction was then quenched with 75 mL of ether and 75 mL of saturated NH<sub>4</sub>Cl(aq). The aqueous layer was extracted with ether, and the combined organics were stirred with 2 g of p-toluenesulfonic acid monohydrate for 30 min. The solution was washed three times with water, and then the organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated via rotovap to a yellow/orange paste. The crude product was washed with methanol at -78 °C to give analytically pure material. The product was stored at -20 °C. Yield: 2.4 g (60.4%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  1.92 (s, 3 H), 2.01 (s, 3 H), 3.40 (s, 2 H), 6.79 (s, 1 H), 7.39-7.42 (m, 2 H,), 7.62-7.77 (m, 5 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 12.9, 13.4, 45.3, 122.3, 123.6, 125.1, 126.1, 127.6, 127.7, 127.9, 132.2, 132.5, 133.8, 133.9, 135.6, 136.2, 142.5 ppm. C, H analysis for C17H16. Anal. Found (Calcd): C, 92.59 (92.68); H, 7.56 (7.32).

2-Phenyl-4,5,6,7-tetrahydroindene. A modified literature procedure was used.<sup>56</sup> A 100 mL Schlenk flask was charged with 3,3a,4,5,6,7-hexahydro-2(2H)-indenone (1.69 g, 12.4 mmol) and 25 mL of diethyl ether. Phenylmagnesium bromide (3 M in diethyl ether, 6.2 mmol) was added dropwise under argon at 0 °C. The reaction was allowed to warm to room temperature to give a milky solution that was stirred for 24 h. The reaction was carefully quenched with 20 mL of distilled water, and the organic layer was washed with 10% HCl(aq) (25 mL). The combined aqueous layers were extracted into 50 mL of diethyl ether. The combined organics were dried over MgSO<sub>4</sub>, filtered, and concentrated via rotovap. The resulting orange solid was recrystallized from diethyl ether at -30 °C to give an analytically pure white powder upon drying in vacuo. Yield: 567 mg (23%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.72 (br s, 4 H), 2.33 (br d, 4 H), 3.24 (s, 2 H), 6.66 (s, 1 H), 7.13 (t, 1 H, J = 7 Hz), 7.29 (t, 2 H, J = 8 Hz), 7.46 (d, 2 H, J = 8 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  11.8, 23.0, 23.2, 24.4, 25.5, 43.1, 124.6, 126.0, 128.4, 129.5, 136.6, 139.2, 143.1 ppm.

**2-Cyclohexylindene.** 2-Bromoindene (2.2 g, 11 mmol) and [1,2-bis(diphenylphosphino)ethane]nickel dichloride (0.1 g, 0.02 mmol) were combined in a two-neck 100 mL round-bottom flask equipped with a reflux condenser, N<sub>2</sub> inlet, and magnetic stir bar. Anhydrous diethyl ether (40 mL) was introduced, and the mixture was cooled to 5 °C. Cyclohexylmagnesium chloride (2 M in ether, 5 mL), was added dropwise via syringe, causing an exothermic reaction that produces a heavy precipitate. The reaction was stirred at room temperature for 12 h and then was quenched with dilute HCl(aq). The ether layer was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* to give a yellow oil which was purified by fractional distillation (140 °C (0.2 mmHg)) to give analytically pure material. Yield: 1.01 g (46.5%). <sup>1</sup>H NMR (CDCl<sub>3</sub>,

200 MHz):  $\delta$  1.22–1.41 (br m, 4 H), 1.69–1.97 (br m, 4 H), 2.40 (br m, 1 H), 3.31 (s, 2 H), 6.48 (s, 1 H), 7.08 (dt, 1 H, J=1.7, 7 Hz), 7.24 (dd, 2 H, J=8, 8 Hz), 7.37 (d, 2 H, 1 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  26.3, 26.4, 33.1, 39.2, 39.9, 120.0, 123.4, 123.5, 126.2, 142.8, 145.6, 156.2 ppm. C, H analysis for C<sub>15</sub>H<sub>18</sub>. Anal. Found (Calcd): C, 90.62 (90.85); H, 8.95 (9.15).

Bis(2-cyclohexylindenyl)zirconium Dichloride (2). ZrCl<sub>4</sub> (575 mg, 2.47 mmol) and (2-cyclohexylindenyl)lithium<sup>57</sup> (1.01 g, 4.94 mmol) were placed in a 100 mL round-bottom flask and a swivel frit was attached. Toluene (50 mL) was added to the combined solids at -78 °C. The reaction was allowed to warm to room temperature and stir for 24 h. Toluene was removed from the yellow, heterogeneous mixture, and methylene chloride was introduced. The solution was filtered through Celite, which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The solution was concentrated in vacuo and washed with pentane. Analytically pure material was obtained upon solvent evaporation under reduced pressure. Yield: 793 mg (58%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  0.89–1.01 (br m, 3 H), 1.23-1.33 (br m, 2 H), 1.52-1.62 (m, 4 H), 1.72 (br d, 2 H), 2.75 (m, 1 H), 5.61 (s, 2 H), 6.93 (m, 2 H), 7.48 (m, 2 H) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz): δ 26.5, 33.7, 39.2, 103.4, 124.7, 126.0, 126.2, 127.6, 151.2 ppm. C, H analysis for C<sub>30</sub>H<sub>34</sub>Cl<sub>2</sub>Zr. Anal. Found (Calcd): C, 64.51 (64.72); H, 6.37 (6.16).

**Bis(2-cyclohexyl-4,5,6,7-tetrahydroindenyl)zirconium Dichloride (3). 1** (1.07 g, 1.97 mmol) and Adam's catalyst (60 mg) were loaded into a Fischer Porter bottle.  $CH_2Cl_2$  (100 mL) was introduced, and then the reactor was pressurized to 80 psig  $H_2$  for 4 h. During this time, the solution color changed from orange to gray. The reactor was vented and the product solution filtered. The solvent was removed *in vacuo* to give a white powder which was recrystallized from toluene at -20 °C to give analytically pure material. Yield: 847 mg (76%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.04–1.22 (m, 3 H), 1.30–1.40 (m, 4H), 1.58 (br d, 1 H), 1.66–1.73 (m, 4 H), 2.11 (d, 2 H), 2.37–2.44 (m, 2 H), 2.6–2.66 (m, 1 H), 2.83–2.9 (m, 2 H), 5.86 (s, 2 H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  22.8, 25.0, 26.4, 26.6, 34.0, 38.8, 112.0, 129.0, 137.5 ppm. C, H analysis for C<sub>30</sub>H<sub>42</sub>-Cl<sub>2</sub>Zr. Anal. Found (Calcd): C, 63.89 (63.80); H, 7.35 (7.49).

**Bis(2-phenyl-4,5,6,7-tetrahydroindenyl)(2-cyclohexylindenyl)zirconium Dibromide (4).** A Schlenk flask was charged with 2-phenyl-4,5,6,7-tetrahydroindene (236 mg, 1.2 mmol), zirconium tetrakis(dimethylamide) (321 mg, 1.2 mmol), and toluene (10 mL). The resulting solution was stirred for 1 h at room temperature. The solvent and liberated dimethylamine were then removed *in vacuo* to give (2-phenyl-4,5,6,7tetrahydroindenyl)zirconium tris(dimethylamide) which was used without further purification. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.65 (m, 4 H), 2.54 (m, 4 H), 2.82 (s, 18 H), 6.12 (s, 2 H), 7.05 (t, 1 H), 7.19 (dd, 2 H), 7.44 (d, 2 H) ppm.

The crude yellow oil was redissolved in toluene (10 mL) and was cooled to 0 °C. Bromotrimethylsilane (1.1 mL, 8.25 mmol) was slowly added to give a bright yellow solution laden with precipitate. The solution was allowed to warm to room temperature. After 30 min, the solution was filtered and the remaining yellow solids were extracted with toluene. The combined organics were concentrated *in vacuo* to to give crude (2-phenyl-4,5,6,7-tetrahydroindenyl)zirconium tribromide which was used without further purification. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.27 (m, 2 H), 1.75 (m, 2 H), 2.22 (m, 2 H), 2.74 (m, 2 H), 6.34 (s, 2 H), 7.52 (d, 2 H) ppm. (The remaining aromatic resonances are partially obscured by C<sub>6</sub>D<sub>6</sub>).

Cyclohexylindene (243 mg, 1.2 mmol) was dissolved in diethyl ether (15 mL). nBuLi (2.5 M in hexanes, 0.5 mL) was added dropwise via syringe at 0 °C to give a slightly yellow solution laden with precipitate. The reaction was allowed to warm to room temperature and stir for 30 min. The solvent was then removed *in vacuo*, and the crude product was washed

<sup>(57)</sup> See experimental preparation of  ${\bf 4}$  for details regarding lithium salt generation.

with hexanes to give a bright white solid which was then diluted with toluene (10 mL). The (2-phenyl-4,5,6,7-tetrahydroindenyl)zirconium tribromide was dissolved in toluene and was added to the lithium salt at -78 °C. The solution was allowed to warm to room temperature to give a bright yellow/ orange slurry. After 6 h, the toluene solution was filtered, and the solid residues were extracted with hot toluene. The combined organics were concentrated in vacuo and then washed with pentane. The product was redissolved in toluene and filtered through Celite. Bis(2-phenyl-4,5,6,7-tetrahydroindenyl)(2-cyclohexylindenyl)zirconium dibromide recrystallized with 0.75 equiv of toluene at -30 °C as analytically pure material. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  0.85–1.1 (br m, 3 H), 1.2-1.31 (br m, 4 H), 1.53 (m, 3 H), 1.69 (m, 2 H), 1.87 (m, 2 H), 2.15-2.25 (br m, 2 H), 2.5-2.56 (br m, 2 H), 2.66 (m, 1 H), 6.09 (s, 2 H), 6.22 (s, 2 H), 6.82 (m, 2 H), 7.1-7.2 (m, partially obscured by C<sub>6</sub>D<sub>6</sub>), 7.51 (d, 2 H) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz): δ 21.6, 22.5, 24.8, 26.6, 26.7, 33.6, 40.1, 104.4, 113.5, 125.0, 125.7, 125.9, 126.5, 127.8, 128.7, 129.2, 129.5, 131.3, 134.0 ppm. C, H analysis for C<sub>30</sub>H<sub>38</sub>Br<sub>2</sub>Zr 0.75(C<sub>7</sub>H<sub>8</sub>). Anal. Found (Calcd): C, 59.21 (59.41); H, 5.28 (5.37).

Bis(3,4-dimethyl-1-phenylcyclopentadienyl)zirconium Dichloride (5). 3,4-Dimethyl-1-phenyl-1,3-cyclopentadiene (1 g, 5.87 mmol) was dissolved in 20 mL of diethyl ether. nBuLi (1.6 M in hexanes, 3.7 mL) was added dropwise at 0 °C to give a creamy precipitate. The reaction was allowed to proceed for 30 min at room temperature, and then the lithium salt was collected via filtration. The solid was washed three times with 10 mL of hexanes and then dried in vacuo. The lithium salt (0.81 g, 4.6 mmol) was combined with ZrCl<sub>4</sub>(THF)<sub>2</sub> (0.867 g, 2.3 mmol) in the N<sub>2</sub> drybox. THF (20 mL) was slowly added at -78 °C to give a yellow solution upon warming to room temperature. The reaction was allowed to stir for 1 h, and then the solvent was removed in vacuo to give a sticky vellow solid. The product was reprecipitated from CH<sub>3</sub>CN to give an air- and moisture-stable yellow powder. The product was dissolved in CHCl<sub>3</sub> and filtered through Celite. The solvent was stripped in vacuo to give analytically pure 5. Yield: 369 mg (32%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.75 (s, 12 H), 6.25 (s, 4 H), 7.28 (t, 2 H, J = 7 Hz), 7.46 (m, 8 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 13.0, 116.1, 122.1, 125.1, 127.3, 128.2, 129.1, 133.1 ppm. C, H analysis for C<sub>26</sub>H<sub>26</sub>Cl<sub>2</sub>Zr. Anal. Found (Calcd): C, 62.12 (62.38); H, 5.30 (5.23).

Bis(3,4-dimethyl-1-p-tolylcyclopentadienyl)zirconium Dichloride (6). 3,4-Dimethyl-1-p-tolyl-1,3-cyclopentadiene (2 g, 10.8 mmol) was dissolved in 25 mL of diethyl ether in a 100 mL Schlenk flask. nBuLi (1.6 M in hexanes, 6.7 mL) was added dropwise at 0 °C to give a creamy precipitate. The mixture was allowed to stir at room temperature for 30 min. The solvent was removed in vacuo, and then ZrCl<sub>4</sub>(THF)<sub>2</sub> (2.04 g, 5.4 mmol) was added in the N<sub>2</sub> drybox. THF (25 mL) was added slowly at -78 °C under argon flow to give a bright yellow solution. The solution was stirred overnight at room temperature. The solvent was stripped in vacuo, and the resulting sticky yellow solid was washed with cold, dry hexanes. The remaining material was reprecipitated from acetone at -20 °C. The solid was dissolved in CHCl<sub>3</sub>, filtered through Celite, and layered with hexanes. Air- and moisturestable crystals that formed were analytically pure. Yield: 2.8 g (49%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.76 (s, 12 H), 2.39 (s,  $\overline{6}$ H), 6.19 (s, 4H), 7.23 (d, 4H, J = 8 Hz), 7.35 (d, 4H, J = 8Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 13.1, 21.2, 115.8, 122.6, 125.1, 127.9, 129.8, 130.5, 137.2 ppm. C, H analysis for C<sub>28</sub>H<sub>30</sub>Cl<sub>2</sub>Zr. Anal. Found (Calcd): C, 63.77 (63.61); H, 5.67 (5.72).

**Bis(3,4-dimethyl-1-(2-naphthyl)cyclopentadienyl)zirconium Dichloride (7).** 3,4-Dimethyl-1-(2-naphthyl)-1,3cyclopentadiene (1 g, 4.54 mmol) was dissolved in 25 mL of diethyl ether in a 50 mL Schlenk flask. nBuLi (1.6 M in hexanes, 2.8 mL) was added dropwise at 0 °C to give a solution laden with a yellow precipitate. The reaction was allowed to warm to room temperature and stir for 30 min. The solvent

was then stripped in vacuo to give a pale yellow solid. Meanwhile, ZrCl<sub>4</sub>(THF)<sub>2</sub> (0.856 g, 2.27 mmol) was weighed into a clean, dry Schlenk flask in the N2 drybox. The solids were individually dissolved in THF (10 mL). The solution containing the lithium salt was cooled to -78 °C, and then the ZrCl<sub>4</sub>(THF)<sub>2</sub> solution was added via cannula. The reaction was allowed to warm to room temperature and stir for 1 h. During this time, the solution color went from bright red to dull orange. The solvent was removed in vacuo to give a sticky vellow/orange solid. The product was dissolved in CH<sub>3</sub>CN, filtered, and layered with hexanes. Shaking the immiscible solutions caused a bright yellow solid to precipitate at the interface which was collected via vacuum filtration. The product was dissolved in CHCl3 to give a bright yellow solution which was filtered through Celite. The solvent was removed in vacuo to give the analytically pure metallocene. Yield: 65 mg (4.8%). <sup>1</sup>H NMR: (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.8 (s, 12 H), 6.27 (s, 4 H), 7.50–7.82 (m, 6 H), 7.86–7.93 (m, 8 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  13.3, 116.3, 122.6, 123.6, 123.7, 126.2, 126.9, 127.8, 128.0, 128.6, 129.0, 131.1, 132.5, 133.6 ppm. C, H analysis for C<sub>34</sub>H<sub>30</sub>Cl<sub>2</sub>Zr. Anal. Found (Calcd): C, 68.11 (67.98); H, 4.80 (5.03).

**Polymerizations.** Toluene, gaseous propylene, and liquid propylene were passed over towers containing Q5 and alumina prior to use. Methylaluminoxane (MMAO Type 4) was obtained from Akzo Nobel as a toluene solution and was dried *in vacuo* to give a white solid before use. Polymerizations were carried out in a 300 mL Parr reactor equipped with a mechanical stirrer. Temperature was maintained at 20 °C via an ethylene glycol/water cooling loop. Catalyst solutions were prepared in the N<sub>2</sub> drybox by dissolving 294 mg of MAO in 23 mL of toluene. A 2 mL aliquot of a  $5 \times 10^{-5}$  M metallocene solution was then added to give the activated catalyst with Al:Zr = 1000:1. Propylene concentrations were calculated for runs using gaseous propylene by utilizing a method reported by Busico (P, concentration 50 psig, 3.24 M; 75 psig, 4.49 M).<sup>58</sup>

(1) Solution Polymerizations. Toluene (75 mL) was introduced to the reactor under 50 psig argon which was then vented. The solvent was allowed to saturate with the desired amount of propylene and then the catalyst solution was injected under propylene pressure. After sufficient time had passed, 30 min for 5 (due to its high activity) and 60 min for all other catalysts, the reaction was quenched with 15 mL of methanol injected under argon pressure.

(2) Bulk Polymerizations. The catalyst solution was introduced to the reactor under argon pressure which was then vented. Liquid propylene (100 mL) was then added to start the reaction. Polymerizations were allowed to proceed for 20 min and then were quenched with 15 mL of methanol injected under argon pressure.

The polymers were collected and precipitated into acidified methanol (5% HCl). After being stirred overnight, the polymers were dried in a vacuum oven at 40  $^\circ$ C.

**Polymer Characterization.** Number- and weight-average molecular weights ( $M_n$ ,  $M_w$ ) were obtained using a Waters 150C high-temperature chromatograph. Samples were run in 1,2,4-trichlorobenzene at 139 °C using two Polymer Laboratories PL GEL Mixed-B columns at a flow rate of 1 mL/min.  $m^4$  was determined via <sup>13</sup>C NMR spectra recorded at 75.425 MHz on a Varian UI 300 spectrometer at 100 °C using 10 mm sample tubes. Samples were prepared in 1,1,2,2-tetrachloroethane containing about 0.5 mL of 1,1,2,2-tetrachloroethane  $d_2$ . IR spectra were obtained from polypropylene films on a Perkin Elmer 1600 Series FTIR. DSC traces were acquired by heating samples from -25 to 200 °C at 20 °C/min on a Perkin Elmer DSC 7.

X-ray Diffraction Studies. (1) Bis(2-phenyl-4,5,6,7tetrahydroindenyl)(2-cyclohexylindenyl)zirconium Dibromide (4). An orange block crystal of  $C_{67}H_{84}Br_4Zr_2$  (FW =

<sup>(58)</sup> Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. Macromolecules **1997**, *30*, 3971–3977.

Table 2.	Summary	of Crystal	Structure	Parameters

compound	4	6
formula	$C_{67}H_{84}Br_4Zr_2$	$C_{28}H_{30}Cl_2Zr$
FW	1391.46	528.67
temp (K)	119	156
space group	$P2_1/n$ (No. 14); monoclinic	P41212 (No. 92); tetragonal
cell constants <sup><i>a,b</i></sup>		
a (Å)	17.6826(2)	12.7602(1)
<i>b</i> (Å)	14.0689(2)	12.7602(1)
c (Å)	23.6703(1)	15.1049(2)
volume (Å <sup>3</sup> )	5738.85(9)	2459.42(4)
Z	4	4
abs coeff, $\mu_{ m calc}$ (cm $^{-1}$ )	31.98	6.77
$F_{000}$	2824	1088
$d_{\rm obs}^{c}$ ( $d_{\rm calc}$ ) (g cm <sup>-3</sup> )	1.61	1.428
crystal size (mm <sup>3</sup> )	0.29 imes 0.21 imes 0.12 .	0.16 imes 0.19 imes 0.20
radiation	Mo K $\alpha$ ( $\lambda = 0.710$ 73 Å)	Mo K $\alpha$ ( $\lambda = 0.710$ 73 Å)
monochromator	highly oriented graphite	highly oriented graphite
diffractometer	Siemens SMART	Siemens SMART
reflections measured	$+h,\pm k,\pm l$	$-14 \le h \le 13; -15 \le k \le 14; -18 \le l \le 17$
$2\theta$ range	$2.4^\circ < 2 heta < 52.0^\circ$	$4.5^\circ < 2 heta < 50.50^\circ$
scan type	ω	ω
scan width (deg)	0.3	0.3
scan speed	10-s frame exposure	10-s frame exposure
no. of reflectns colltd	27 318	11 537
no. of unique reflectns	$10568\ (R_{\rm int}=0.045)$	$2286 (R_{\rm int} = 0.035)$
reflectns with $(F_0^2 > 3\sigma(F_0^2))$	4606	1934
no. of variables	335	141
parameter-to-variable ratio	13.75	13.7
$K(R_{\rm W})^{\prime\prime}$	0.038 (0.048)	0.022 (0.028)
Intai diff $\rho_{\rm max} (e^-/A^3)^e$	+0.80; -0.6	+0.24; -0.27

<sup>a</sup> Unit cell parameters and their ESDs were derived by a least-squares fitting of 8192 reflections with  $I > 10 \sigma(I)$  and  $2\theta$  between 4.0 and 45.5°. <sup>b</sup> The ESDs of all parameters are given in parentheses. <sup>c</sup> The density of the crystal was not measured. <sup>d</sup> The unweighted and weighted agreement factors in the least-squares refinements were as follows:  $R = \sum ||F_0| - |F_c|| / \sum |F_0|; R_w = (\sum w(|F_0| - |F_c|)^2 / \sum wF_0^2)^{1/2}$ where  $w = 4F_0^2/s^2(F_0^2)$ ;  $s^2(F_0^2) = (S^2(C + R^2\dot{B}) + (pF_0^2)^2)/Lp^2$ . S, scan rate; C, total integrated peak count; R, ratio of scan time to background counting time; B, total background count; Lp, Lorentz-polarization factor; p, p-factor (0.00). e Maximum negative and positive difference peaks.

1391.46)  $^{59}$  with approximate dimensions of 0.29  $\times$  0.21  $\times$  0.12  $mm^3$  was mounted on a glass fiber in Paratone oil at -80 °C. All measurements were made on a Siemens SMART<sup>60</sup> diffractometer with graphite-monochromated Mo K $\alpha$  radiation. The structure was solved by direct methods<sup>61</sup> and expanded using Fourier techniques.<sup>62</sup> Two independent molecules were found in the Fourier map. Only Zr and Br atoms were refined anisotropically. A number of carbons were nonpositive definite so all carbon atoms were refined isotropically. Hydrogen atoms were included at idealized positions 0.95 Å from their parent atoms except for the disordered toluene molecule which was found as a solvent of recrystallization. The disordered toluene was refined as 50/50 disordered. Crystal data and details of data collection and structure analysis are summarized in Table 2.

(2) Bis(3,4-dimethyl-1-p-tolylcyclopentadienyl)zirconium Dichloride (6). A deep yellow single crystal of  $C_{28}H_{30}Cl_2Zr$  (FW = 530.12) with approximate dimensions of  $0.16~\times~0.19~\times~0.2~mm^3$  was mounted on a glass fiber in

Paratone oil at -118 °C. All measurements were made on a Siemens SMART<sup>60</sup> diffractometer with graphite-monochromated Mo K $\alpha$  radiation.

The structure was solved by direct methods<sup>61</sup> and expanded using Fourier techniques.<sup>62</sup> All non-hydrogen atoms were refined anisotropically. From the Fourier map, the hydrogen atoms were located on the cyclopentadienyl ring and its two methyl substituents, while on the benzene ring and its corresponding methyl substituent, the hydrogen atoms were positioned at an idealized geometry, 0.95 Å from their parent atoms before the last cycle of refinement. All calculations were performed using the teXsan crystallographic software package.<sup>63</sup> Crystal data and details of data collection and structure analysis are summarized in Table 2.

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Supporting Information Available: X-ray crystallographic determination of 4 and 6 (52 pages). Ordering information is given on any current masthead page.

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<sup>(59)</sup> Formula and Formula Weight values count both molecules in the asymmetric unit and the disordered toluene molecule that is present.

<sup>(60)</sup> SMART: Area-Detector Software Package; Siemens Industrial Automation, Inc.: Madison, WI, (1995).

<sup>(61)</sup> SHELXS-86: Sheldrich, G. (1986). (62) DIRDIF92: Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. and Smykalla, C. (1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

<sup>(63)</sup> teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).