Elastomeric Polypropylene from Unbridged 2-Arylindenyl Zirconocenes: Modeling Polymerization Behavior Using *ansa*-Metallocene Analogues

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Abstract: Bis(2-arylindenyl)zirconium dichlorides activated by methylaluminoxane (MAO) produce elastomeric polypropylene. The elastic properties of this material are proposed to arise from a stereoblock microstructure. The silyl bridged catalysts *rac*- and *meso*-dimethylsilyl(bis(2-phenylindenyl))zirconium dichloride were prepared and used to model the polymerization behavior of the unbridged catalysts. The meso isomer is approximately twice as productive as the rac isomer in propylene polymerization. Additionally, blends of isotactic and atactic polypropylene were prepared by using varying amounts of the rac and meso isomers until the IR and NMR characteristics matched polypropylenes produced from bis(2-phenylindenyl)zirconium dichloride. These studies suggest (1) that the rac isomer is favored in the isomerization equilibrium for the unbridged catalysts and (2) that the larger fraction of atactic polymer in the elastomeric polypropylene is a consequence of the higher rate of polymerization for the meso isomer.

Introduction

Elastomeric polypropylene was first discovered by Natta who interpreted its properties in terms of an isotactic−atactic stereoblock structure.[1−3] Isotactic sequences in neighboring polypropylene chains are believed to cocrystallize, forming physical cross-links in the material which account for the observed elasticity. More recently, Collette and co-workers observed that elastomeric polypropylene could also be obtained using supported tetraalkyl group IVB catalysts.[4,5] The first metallocene system to yield elastomeric polypropylene was developed by Chien and co-workers in 1990.[6−8] 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 been suggested.[9,10] Collins and co-workers have recently reported a 3-methyl substituted *ansa*-zirconocene which produces elastomeric polypropylene.[11]

We have reported that bis(2-arylindenyl)zirconium dichlorides, when activated by methylaluminoxane (MAO), produce elastomeric polypropylene.[12−19] The elastomeric properties are believed to arise from an isotactic−atactic stereoblock structure which arises from isospecific and aspecific rotamers that interconvert on the time scale of growth of a single polypropylene chain (Scheme 1).[12,13]

According to this proposed mechanism, the structure of the resulting polymer is governed by a number of interrelated rates. The simplest model invokes two active catalyst states each with differing stereospecificities. The relative amounts of each state present during polymerization will be affected by the stability of each state (K_{eq}) and the rate at which they interconvert (k_i, k_{-i}). Additionally, the different catalytic states may polymerize propylene at different rates. Because of the fluxional nature of the catalyst system, it is difficult to obtain information about any one rate independently of the other relevant rates.

An X-ray crystal structure of the parent bis(2-phenylindenyl)zirconium dichloride revealed both syn and anti rotamers in the solid state, suggesting that both rac and meso geometries are of similar stability, at least in the solid state.[12,14,20] We have been able to examine the rates of ligand rotation for the model compound bis(2-phenylindenyl)zirconium dibenzyl using variable temperature dynamic NMR.[17] The relative energies of the

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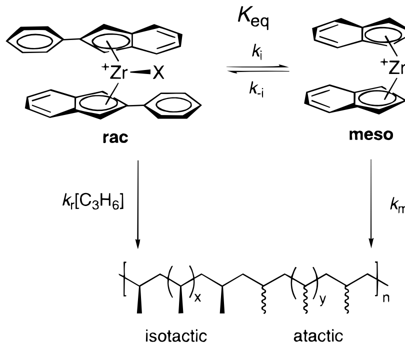
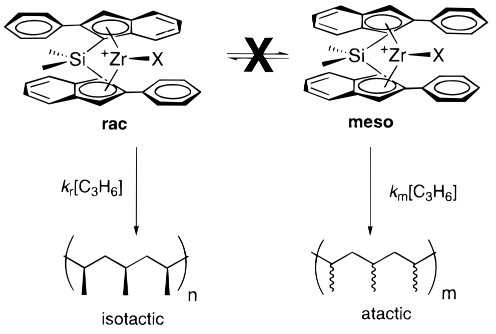
Scheme 1



Scheme 2



rac and meso rotamers have also been estimated computationally, taking into account stabilizing π-stacking interactions.[21]

In this paper, we report the propylene polymerization behavior of *rac*- and *meso*-dimethylsilyl(bis(2-phenylindenyl))zirconium dichloride as a model for the production of elastomeric polypropylene by the two rotamers of bis(2-phenylindenyl)zirconium dichloride. By conducting polymerizations with these stereorigid isomers[12b] alone and in combination, the equilibrium constant between (K_{eq}) and the relative rates of propagation for the rac and meso rotamers could be estimated for the unbridged system (Scheme 2).

Results

Bis(2-phenylindenyl)zirconium dichloride (**2**) was prepared according to a published procedure.[12,17] Bis(2-phenylindenyl)dimethylsilane was prepared by deprotonating 2-phenylindene with *n*BuLi and then reacting the corresponding lithium salt with dichlorodimethylsilane to yield the rac and meso isomers of the desired ligand. These isomers could be separated and characterized. Dimethylsilyl(bis(2-phenylindenyl))zirconium dichloride (**1**) was synthesized by a modified literature procedure originally used for the production of a stereorigid bisfluorenyl complex.[22] The silyl bridged ligand was deprotonated with *n*BuLi and reacted with a slurry of $ZrCl_4$ in a mixture of diethyl ether and pentane. The meso isomer was isolated by extraction of the crude product mixture into hot toluene and subsequent recrystallization from toluene at room temperature. A small amount of residual powdery rac isomer was washed away from the larger meso crystals with toluene or pentane. The toluene insoluble product was extracted into refluxing methylene chloride for 3 days to yield the analytically pure rac isomer upon removal of the solvent. Isomers and their mixtures were each stored in aluminum foil lined containers in an inert atmosphere drybox to avoid photoisomerization, known to occur for similar complexes.[23,24] Both isomers were characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

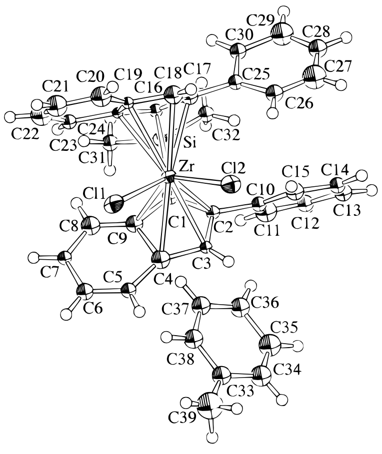


Figure 1. ORTEP diagram of complex **1-meso**.

rac-Dimethylsilyl(bisindenyl)zirconium dichloride (**3-rac**) is commercially available. To obtain a sample of the meso isomer, **3-rac** was suspended in toluene and irradiated for 3 h using a 400 W medium-pressure Hg arc lamp.[23,24] The ^{1}H NMR spectrum of the resulting bright yellow powder showed a 45/55 mixture of **3-rac**/**3-meso**.

X-ray quality crystals of *meso*-dimethylsilyl(bis(2-phenylindenyl))zirconium dichloride (**1-meso**) were obtained by dissolving the isolated meso isomer in hot toluene and then allowing the solution to stand and cool to room temperature in an inert atmosphere drybox. The solid-state structure of this complex was determined by X-ray crystallography (Figure 1). Compound **1-meso** crystallized with an equivalent of toluene. Relevant structural parameters are similar to those reported for bis(2-phenylindenyl)zirconium dichloride (**2**):[12,13] **1-meso**: Cl−Zr−Cl = 94.41°, Zr−Cl1 = 2.41 Å, Zr−Cl2 = 2.44 Å. **2**: Cl−Zr−Cl = 94.39° (*rac*-**2**), 97.03°(*meso*-**2**); and Zr−Cl = 2.43 Å. The Cp−Zr−Cp angle differs marginally for the two complexes: **1-meso** = 125°; **2** = 131°. The most significant difference between the bridged and unbridged complexes is the angle between the plane containing the phenyl substituent and that containing the indenyl framework. This angle is less than 10° for both rotameric forms of **2** but about 60° for **1-meso**.

Propylene polymerizations were carried out in the presence of **1-rac** or **1-meso** and methylaluminoxane (MAO) (Al:Zr = 1000:1) in 100 mL of liquid propylene. Catalyst solutions utilized for polymerization with individual isomers were prepared from stock solutions, as outlined in the Experimental Section. Three identical polymerizations were carried out using each isomer with high reproducibility between runs (Table 1). As expected, **1-rac** yielded isotactic polypropylene (%mmmm = 87%), while **1-meso** yielded atactic polypropylene (%mmmm = 6.5%) as determined by ^{13}C NMR, IR, and differential scanning calorimetry (DSC). The productivity of **1-meso** is approximately twice that of **1-rac** (4034 vs 2436 kg of PP/(mol Zr h)). Additionally, the molecular weight (M_w) of polypropylene produced by **1-rac** is approximately three times that obtained from **1-meso** (4.43×10^5 vs 1.55×10^5). The molecular weight distribution (M_w/M_n) is consistently larger for the polypropylene obtained from **1-rac** ($M_w/M_n = 3.3$) than for

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Table 1. Summary of Polymerization Results Using **1-rac**, **1-meso**, and **3**

catalyst	% rac	yield (g)	prodvity[a]	%mmmm[b]	%m[b]	M_w[c] ($\times10^{-3}$)	M_w/M_n	IR index	T_m (°C)	ΔH_f (J/g)
1	100	4.01	2408	86	96	425	2.6	0.9	139	68.4
1	100	3.88	2327	87	96	410	3.1	0.9	139	73.8
1	100	4.29	2573	88	96	495	4.1	0.9	138	67.9
1	0	6.82	4092	7.0	50	150	2.1	0.2		
1	0	6.59	3951	6.2	48	125	2.0	0.2		
1	0	6.76	4058	6.2	49	194	2.2	0.2		
1[d]	100	2.20	3270			1850	2.9		nd[e]	nd
1[d]	0	1.74	2610			1470	3.1		nd	nd
3	100	10.39	6234	92	98	121	2.2	nd	nd	nd
3	45	1.75	1050[f]	91	98	nd	nd	nd	nd	nd

[a] Kilograms of polypropylene per mole Zr per hour. [b] Determined by ^{13}C NMR spectroscopy. [c] Determined by gel permeation chromatography versus polypropylene standards. [d] Ethylene polymerization. [e] Not determined. [f] mol of Zr = 5×10^{-7}; 50 mg of MAO used due to catalyst exothermicity.

Table 2. Summary of Polymerization Results Using Mixtures of **1-rac** and **1-meso**

entry	% rac	yield (g)	prodvity[a]	%mmmm[b]	%m[b]	M_w[c]($\times10^{-3}$)	M_w/M_n	IR index	T_m (°C)	ΔH_f (J/g)	% isotactic polymer[d]
1	42	4.00	2400	34	64	293	3.1	0.41	139	21.3	34
2	57	5.29	3172	39	69	312	3.3	0.48	138	26.1	46
3	61	5.09	3052	45	73	345	3.4	0.56	138	28.7	50
4	75	4.47	2680	57	79	374	3.9	0.64	139	49.9	63
5	2PhInd[e] (**2**)	4.59	2756	39	73	502	3.6	0.50	138	16.9	36−42[f]

[a] Kilograms of polypropylene per mole Zr per hour. [b] Determined by ^{13}C NMR spectroscopy. [c] Determined by gel permeation chromatography versus polypropylene standards. [d] Weight percent of hexanes insoluble polymer. [e] Polymerization using the unbridged catalyst for comparison. [f] Determined by statistical analysis of the ^{13}C NMR spectrum using the method of Chujo.

polymers obtained from **1-meso** ($M_w/M_n = 2.1$) or **3-rac** ($M_w/M_n = 2.2$, vide infra).

Compounds **1-rac** and **1-meso** were also used in ethylene polymerizations ($P = 30$ psig). The productivities observed in each case were similar with **1-rac** slightly more productive that **1-meso** (3270 vs 2610 kg of PE/(mol of Zr h), Table 1). The molecular weights (M_w) obtained for polymers produced from **1-meso** and **1-rac** were similar (1.47×10^6 vs 1.85×10^6). The molecular weight distributions for polyethylene produced with each isomer were similar but broader than expected for typical single site, metallocene catalyzed polymerizations.[25]

rac-Dimethylsilyl(bisindenyl)zirconium dichloride (**3-rac**) was used to polymerize propylene under identical conditions employed for propylene polymerizations using **1** (Table 1). Compound **3-rac** proved to be approximately three times more productive than **1-rac** (6234 vs 2436 kg of PP/(mol of Zr h)). The polymerization behavior of the mixture of **3-rac** and **3-meso** prepared by photolysis was also investigated (Table 1).[26] Fractionation of the resulting polymer in refluxing hexanes indicated that **3-rac** is over 20 times more productive than **3-meso** (2217 vs 95.5 kg of PP/(mol of Zr h)). The ^{13}C NMR spectrum corroborates these data in that the spectrum of the polypropylene blend is practically indistinguishable from the spectrum obtained for polypropylene produced by **3-rac** alone.

Polymerizations were conducted with mixtures of **1-rac** and **1-meso** to give reactor blends of isotactic and atactic polypropylene. A mixture containing the desired ratio of **1-rac:1-meso** was prepared by dissolving the isomers in toluene and then removing the solvent in vacuo. The composition of the catalyst mixture was determined by ^{1}H NMR (ratio of **1-rac**:**1-meso**). The amount of catalyst mixture required for each polymerization was measured out and added to solid MAO. The catalyst components were dissolved in toluene. This activation procedure gave reproducible results (NMR, IR, DSC) between runs but exhibited some variability in measured productivties due to the difficulty in accurately weighing out milligram quantities of material for consecutive runs. The results of these experiments are summarized in Table 2. As the amount of **1-rac** in the catalyst mixture increases, the isotacticity and crystallinity of the resulting blends increase as evidenced by ^{13}C NMR (%mmmm, %m), IR (A_{998}/A_{974}), and DSC. The molecular weight of the polymer blends increases with increasing **1-rac** content. The molecular weight distribution also broadens as the %rac isomer increases. For comparison, propylene polymerizations were carried out using unbridged **2** to give elastomeric polypropylene and are reported in Table 2.

The polymer blends produced from polymerizations in the presence of a mixture of isomers appear to be homogeneous. There is no visible phase separation of the isotactic and atactic polymer in these reactor blends. In support of this, NMR, DSC, and IR data are reproducible when different samples of the same polymer are analyzed.

The polymers produced from **2** or from mixtures of **1-rac** and **1-meso** were fractionated with refluxing hexanes.[27] The components of the polypropylene blends prepared from **1** were fully separated over 24 h. The hexanes insoluble fraction was identical by ^{13}C NMR to the polymer produced from **1-rac** alone. Similarly, the hexanes soluble fraction was identical to polypropylene produced by **1-meso**. As the concentration of **1-rac** in the catalyst mixture increased, so did the fraction of hexanes insoluble material. The composition of the various blends is indicated in Table 2. Stereoblock polypropylene from **2** also separates into hexanes soluble and insoluble fractions. However, these fractions are clearly different from those obtained for mixtures of **1-rac** and **1-meso**. Polypropylene produced by **2** yields hexanes soluble and insoluble fractions with %mmmm = 25 and 67%, respectively.

The catalyst mixture containing 57% **1-rac** gives a polymer blend with %mmmm of 39% matching that of the stereoblock polymer from unbridged **2**. The molecular weight of the

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[26] A lower catalyst load was employed ([Zr] = 5×10^{-7} mol) to minimize the exothermicity of the polymerization reaction.

[27] Some of the polymer blends prepared from combinations of **1-rac** and **1-meso** were fractionated below the boiling point of hexanes using a Soxhlet extraction apparatus but gave results identical to the fractionations run at the boiling point.

stereoblock polymer is higher than that of the corresponding polypropylene blend and also has a slightly broader molecular weight distribution. Evaluation of the polypropylene blend and analogous stereoblock polypropylene indicate significant differences in ΔH_f for the two systems. The stereoblock polymer exhibits a lower ΔH_f despite having identical isotacticity to the blend (as measured by ^{13}C NMR and IR). The peak melting point and crystallization temperatures of the stereoblock polymer and polypropylene blends are similar, but the DSC transitions for the stereoblock polymer (melting range = 60−153 °C) are much broader than those observed for polypropylene blends (melting range = 118−146 °C).

To further establish the compositional similarity between stereoblock polypropylene from **2** and the polymer blend with identical %mmmm (Table 2, entry 2), the weight fraction of isotactic polypropylene contained in each sample was calculated. For the isotactic−atactic polymer blend, the weight percent of isotactic polymer was determined both by fractionation with refluxing hexanes and statistical analysis of the ^{13}C NMR pentad distribution of the unfractionated blend using the Chujo method.[28] Both methods yielded a value of 46% for the weight fraction of isotactic polypropylene in the blend. Similar statistical analysis of stereoblock polypropylene from **2** indicates an isotactic weight fraction between 36 and 42%, depending on the sample, indicating reasonable agreement between the stereoblock polymer and polymer blend.

Discussion

In this study, we sought to investigate the polymerization behavior of silyl bridged, **1**, as a model of the mechanism of polymerization operating in the case of unbridged **2** and derivatives. Preparation of **1** was straightforward and utilized procedures outlined in the literature for other *ansa*-metallocenes.[22] The large difference in solubility between **1-rac** and **1-meso** facilitated isolation of the two pure diastereomers.

The solid-state structure of **1-meso** was investigated by X-ray crystallography. The geometry and bonding of this complex are quite similar to other *ansa*-metallocenes reported in the literature[29−41] and to the meso rotamer of **2**.[12] The main difference between **1-meso** and **2-meso** is the large angle (60° vs <10°) between the planes containing the indenyl framework and the phenyl ring evidenced for the silyl bridged complex.[42] Such distortion could be a consequence of the steric interaction between the phenyl ring and the bridging Me_2Si group. There are few crystal structures reported in the literature for meso *ansa*-metallocenes.[38−40,43−45] Compound **1-meso** is similar to the other meso isomers in the literature in that the two Zr−Cl distances are different (2.41, 2.44 Å). Zr−Cl and Zr−Cp distances and Cp−Zr−Cp angle are within the range of other *ansa*-metallocenes (rac and meso).[29−40] The Cl−Zr−Cl angle is smaller than reported examples (94.41° compared to 97−100°). This is most likely due to a steric interaction with the bulky phenyl group in the 2-position. Only dimethylsilyl(bis-(2-(*N*,*N*-dimethylamino)indenyl))zirconium dichloride has a similar angle (94.9°),[29] supporting the effect of a sterically bulky substituent in the 2-position.

Polymerization in the presence of **1-rac** and **1-meso** individually indicates that the productivity of **1-meso** is nearly twice that of **1-rac**. In most cases where the relative productivities of *ansa*-metallocenes have been investigated, the rac isomer is more productive than the meso isomer.[24,43,45−47] The meso isomer was found to be more productive than the rac isomer for non-MAO activated propylene polymerizations involving *ansa*-metallocenes possessing substituted cyclopentadienyl ligands[46] and polymerizations involving higher α-olefins including pentene, hexene, and octene.[24] We compared the polymerization behavior of the individual isomers with the behavior of the catalyst systems containing mixtures of **1-rac** and **1-meso**. Analysis of the reactor blends provided further information on the relative reactivity and stereoregularity of the rac and meso isomers. A series of equations (outlined in the Supporting Information) was derived which relate measured characteristics of the polymers produced from varying combinations of **1-rac** and **1-meso**. The isotactic pentad content (%mmmm), %m, %isotactic polymer (from fractionation studies), and ΔH_f were plotted against the percentage of **1-rac** in the polymerization mixture. These expressions yield the productivity of the individual isomers upon curve-fitting (Table 3).[48] The values

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(28) Chujo's concurrent model assumes that two sites of differing stereospecificity undergo polymerization simultaneously to yield a polymer blend. Stereoblock polypropylene is a limiting case for this model, and error in the calculated isotactic weight fraction may be introduced due to the interfacial region between the isotactic and atactic blocks. The Chujo method and a method which simulates the pentad distribution of the stereoblock material calculate similar isotactic weight fractions (0.27 vs 0.3), indicating that the Chujo method gives a good approximation of the fraction of isotactic polymer contained in the stereoblock polypropylene. See: Inoue, Y.; Itabashi, I.; Chujo, R.; Doi, Y. *Polymer* **1984**, *25*, 1640−1644. Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707−2715.

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Table 3. Calculated and Experimental Productivities for **1-rac** and **1-meso**

entry	method[a]	rac productivity	meso productivity
6	%mmmm	2408 (166[b])	4037 (30)
7	%m	2471 (155)	4033 (14)
8	% isotactic polymer	2652 (253)	3977 (77)
9	ΔH_f	2545 (149)	4648 (784)
10	exptl	2436[c]	4034[d]

[a] Variable plotted against %rac. [b] Standard error. [c] Average of entries 1, 2, and 3 in Table 1. [d] Average of entries 4, 5, and 6 in Table 1.

calculated are in good agreement with experimental data obtained from polymerizations using **1-rac** and **1-meso** individually.

The higher productivity observed for **1-meso** relative to **1-rac** results from the introduction of a phenyl substituent at the 2-position of the ligand. For the nonphenyl substituted analogue, **3**, the rac isomer is much more productive than the meso isomer at 70 °C in liquid propylene.[47] Soga and co-workers also reported propylene polymerization behavior of a mixture of rac and meso isomers of **3** at 40 °C.[49] The resulting polymers exhibited %mmmm = 83.3, again indicating the dominating productivity of **3-rac**. We found under our conditions that **3-rac** is over twenty times more productive than **3-meso** and nearly three times more productive than **1-rac**. This unusual trend in productivity for **1-rac** and **1-meso** may be a consequence of the geometric placement of the bulky 2-phenyl subsituent.[50] For **1-meso**, both phenyl substituents intrude on only one active site, while in **1-rac** both active sites are congested by a phenyl group.

The differences in productivity for **1-rac** and **1-meso** are likely a consequence of different rates of propagation or different numbers of active sites for the two isomers. Similar trends in productivity would be expected for both ethylene and propylene polymerization if relative propylene polymerization productivities were a consequence of electronic differences between **1-rac** and **1-meso**. The fact that the productivities of **1-rac** and **1-meso** are similar in ethylene polymerization suggests that the differences in productivity between **1-rac** and **1-meso** in propylene polymerization arise for steric reasons; propylene is not polymerized as effectively by the more sterically hindered **1-rac**.

Unbridged **2** and various mixtures of **1-rac** and **1-meso** were employed in propylene polymerizations under identical conditions to produce stereoblock and stereoblend polypropylenes which could be compared in terms of ^{13}C NMR and IR characteristics as well as the amount of isotactic material contained in each polymer. The best match for stereoblock polypropylene from **2** was obtained from a mixture of **1-rac** and **1-meso** containing 57% **1-rac** (Table 2). To the extent that the bridged catalysts are good models for the unbridged complex **2**, this suggests that $K_{eq} = 0.7 \pm 0.1$[51] for the unbridged rotamers (Scheme 1). This would suggest that the rac and meso geometries are close in energy with the rac isomer slightly favored in the rotamer equilibrium. This result is consistent with calculations performed on **2** that indicate that the rac rotamer should be slightly more stable than the meso rotamer due to a greater degree of stabilization via π-stacking.[21]

To the extent that **1-rac** and **1-meso** are reasonable models for the rac and meso rotamers of **2**, these studies suggest that K_{eq} favors the rac rotamer but that the meso rotamer is more productive. The ratio of the atactic block length to the isotactic block length (BL_a/BL_i) can be evaluated from this information (eq 1).[18] If an equal number of active sites for **1-rac** and **1-meso** is assumed, then the productivity will be proportional to k_r and k_m (Scheme 1) and can be substituted into eq 1 (eq 2).

$$\frac{BL_a}{BL_i} = K_{eq}\frac{k_m}{k_r} \tag{1}$$

$$\frac{BL_a}{BL_i} = K_{eq}\frac{\text{productivity}_{meso}}{\text{productivity}_{rac}} \tag{2}$$

Substitution of our estimate of $K_{eq} = 0.7$ and the relative productivities into eq 2 yields an estimate of $BL_a/BL_i = 1-1.3$, suggesting an equal or slightly longer atactic sequence length relative to the isotactic sequence length. Simulations of the pentad distributions of stereoblock polypropylene derived from **2** estimate a slightly higher $BL_a/BL_i = 2$.[18] While the trends are in agreement, the absolute difference between BL_a/BL_i values obtained using chemical and computer models illustrates the limitations inherent in any model system.

Enantioface selectivity parameters,[52] α, could be determined from the pentad distribution for polypropylene produced from **1-rac** and **1-meso**. The values obtained for **1-rac** ($\alpha = 0.98$) and **1-meso** ($\alpha = 0.55$) are in good agreement with those obtained from simulations of the atactic ($\alpha_1 = 0.55-0.63$) and isotactic segments ($\alpha_2 = 0.93-0.98$) of stereoblock polypropylene chains.[18]

While ^{13}C NMR and IR characterization data as well as %isotactic material contained in polypropylene from **2** and mixtures of **1-rac** and **1-meso** are in good agreement, the elastomeric polypropylene derived from **2** and the isotactic–atactic reactor blends derived from **1** exhibit different degrees of crystallinity by DSC. Polypropylenes produced from **1** and **2** both exhibit similar peak melting temperatures, but the polymer blends from **1** exhibit much sharper melting transitions. Additionally, the ΔH_f for the reactor blend (%mmmm = 39%) is larger than that measured for polypropylene from **2**. The fractionation behavior of polypropylene from **2** and mixtures of **1** are also different. Reactor blends from **1** are completely separated into isotactic and atactic polypropylene, while polypropylene from **2** is separated into hexanes soluble and insoluble fractions which exhibit intermediate %mmmm = 25 and 67%, respectively. This indicates that while we have been able to match isotacticity characteristics (^{13}C NMR, IR index, %isotactic material) of polypropylene from **1** and **2**, we have not produced identical materials. Typically, simple physical mixtures of isotactic and atactic polypropylene are not elastomeric.[53−55]

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(49) Soga, K.; Kim, H. J.; Shiono, T. *Macromol. Chem. Phys.* **1994**, *195*, 3347−3360.

(50) This trend in reactivity is in contrast to that observed for analogous unbridged systems. Bis(2-phenylindenyl)zirconium dichloride (**2**) is more productive than bisindenylzirconium dichloride in both ethylene and propylene polymerizations. Some have attributed the higher productivity of **2** to conjugation of the phenyl ring with the indenyl framework in effect destabilizing the metal ligand bond and thereby increasing the reactivity of the metal center. See: Bravaya, N. M.; Dzhabieva, Z. M.; Maryin, V. P.; Strelets, V. V. *Polimery* **1997**, *42*, 591−594. Bruce, M. D.; Waymouth, R. M. Ph.D. Thesis, Stanford University, Stanford, CA, 1997.

(51) This value is limited by the accuracy of NMR integration for both the polymers and catalyst mixtures.

(52) Inoue, Y.; Itabashi, I.; Chujo, R.; Doi, Y. *Polymer* **1984**, *25*, 1640−1644.

(53) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. *Macromolecules* **1997**, *30*, 3447−3458.

(54) Carlson, E. D.; Krejchi, M. T.; Shah, C.; Terakawa, T.; Waymouth, R. M.; Fuller, G. G. *Macromolecules* **1998**, *31*, 5343−5351.

(55) Some recent reports have claimed elastomeric properties for reactor blends derived from isospecific and aspecific metallocenes. See: Canich, J. A. M.; Yang, H. W.; Licciardi, G. F. (Exxon) U. S. Pat. 5516848 A, 960514. Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. *Macromolecules* **1997**, *30*, 3447−3458.

These observations suggest that polypropylene produced from **2** is not just a physical mixture of isotactic and atactic polypropylene chains.

Conclusions

The proposed mechanism for the production of elastomeric polypropylene by 2-arylindenylzirconocenes involves a number of interrelated rates which cannot be individually evaluated due to ligand rotation. Model studies using stereorigid **1-meso** and **1-rac** suggest that the rac and meso rotamers of **2** are nearly equal in energy with **2-rac** favored slightly ($K_{eq} = 0.7$). These model studies also suggest that the meso rotamer is more productive than the rac rotamer, which accounts for the larger fraction of atactic polymer in the elastomeric polypropylene. This trend in productivity is in contrast to reports in the literature which indicate that *ansa*-metallocenes with a rac geometry are generally more productive than the corresponding meso isomers.[24,43,45−47]

Elastomeric polypropylene prepared from **2** and reactor blends prepared from mixtures of **1-rac** and **1-meso** exhibit different fractionation behavior and DSC profiles. This suggests that polypropylene from **2** is not simply a physical mixture of isotactic and atactic polypropylene homopolymers.

Experimental Section

Standard inert atmosphere techniques were used in handling air- and moisture-sensitive compounds.[56] Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl. Methylene chloride and pentane were distilled from calcium hydride prior to use in reactions. Toluene was dried over Q5 and alumina. Bis(2-phenylindenyl)zirconium dichloride was prepared according to a literature procedure.[12] *n*-Butyllithium (*n*BuLi) was purchased from Aldrich. Chlorotrimethylsilane and $ZrCl_4$ were obtained from Fluka. *rac*-Dimethylsilyl(bisindenyl)zirconium dichloride was provided by Witco. NMR spectra were recorded on a Varian Gemini 400 MHz or a Varian UI 300 MHz spectrometer. Molecular weight data for polypropylene samples were obtained at Amoco Chemical Co. Elemental analyses were performed by E&R Microanalytical Labs.

Bis(2-phenylindenyl)dimethylsilane. 2-Phenylindene (10 g, 0.052 mol) was weighed into a 250 mL Schlenk flask and diluted with 100 mL of toluene. THF (40 mL) was added to give a translucent, pale yellow solution. *n*BuLi (2.5 M in hexanes, 0.052 mol) was added dropwise at 0 °C. After addition was complete, the solution was allowed to warm to room temperature and stir for 1 h. The solution was then recooled to 0 °C and dichlorodimethylsilane (3.35 g, 0.026 mol) was added causing a precipitate to form. The reaction was then heated at 50 °C and stirred for 4 h. The reaction was quenched with 150 mL of distilled water. The aqueous layer was extracted with diethyl ether, and the combined organics were dried over molecular sieves, filtered, and concentrated via rotary evaporation. The resulting orange solid was washed with cold hexanes to yield a white powder. A second crop of product was collected after recrystallization of the hexanes filtrate at −20 °C. Yield: 30% (3.451 g). The ligand crystallizes as two isomers which can be distinguished by ^1H NMR. ^1H NMR (rac isomer, 400 MHz, $CDCl_3$): δ −0.94 (s, 6H), 4.42 (s, 2H), 7.06 (s, 2H), 7.13−7.26 (br m, partially obscured by solvent), 7.25−7.32 (m, 8 H), 7.46 (d, 2 H, $J = 7.4$ Hz), 7.54 (d, 2 H, $J = 7.4$ Hz) ppm. ^1H NMR (meso isomer, 400 MHz, $CDCl_3$): δ −1.02 (s, 3H), −0.81 (s, 3H), 4.24 (s, 2H), 7.06 (s, 2H), 7.18 (t, 2H, $J = 6.2$ Hz), 7.25 (m, partially obscured by solvent), 7.31−7.38 (m, 10H), 7.44 (d, 2H, $J = 7.6$ Hz), 7.52 (d, 2H, $J = 7.3$ Hz) ppm. ^{13}C NMR (both isomers combined): δ −6.63, −5.62, −5.55, 43.8, 43.9, 121.3, 121.4, 123.1, 123.2, 123.7, 123.9, 125.4, 125.5, 126.0, 126.1, 127.1, 127.3, 127.5, 128.4, 128.5, 137.0, 137.1, 144.7, 145.4, 145.5, 149.7, 149.8 ppm. C, H Anal. Found (Calcd) for $C_{32}H_{28}Si$: C, 87.08 (87.23); H, 6.33 (6.41).

Dimethylsilyl(bis(2-phenylindenyl))zirconium dichloride (1). Bis-(2-phenylindenyl)dimethylsilane (1.5 g, 3.40 mmol) was weighed into a 250 mL Schlenk flask equipped with a stir bar. Diethyl ether (75 mL) was added to give a creamy slurry. *n*BuLi (2.5 M in hexanes, 2.72 mL) was added dropwise at 0 °C to give a transparent yellow solution which was allowed to warm to room temperature and stirred for 45 min. Meanwhile, $ZrCl_4$ (0.792 g, 3.40 mmol) was weighed into a separate Schlenk flask and was diluted with 100 mL of pentane. The lithium salt was added to the zirconium slurry at −78 °C to give a yellow slurry. The reaction was allowed to warm to room temperature and stir overnight. The reaction mixture was filtered, and the dull orange residue was extracted with CH_2Cl_2. The solution was filtered, and the solvent was removed in vacuo. The resulting solid was extracted with hot toluene and recrystallized at −20 °C to give the pure meso isomer. The toluene insoluble products were continuously extracted (using a Soxhlet Apparatus) for 3 days into refluxing CH_2Cl_2 to give a turbid orange solution. The solvent was removed in vacuo to give the analytically pure rac isomer. A second batch of catalyst was made in which the diastereomers were not separated. This "reaction ratio" mixture contained 57% of the rac isomer.

Meso isomer (with 1 equiv toluene). ^1H NMR (300 MHz, C_6D_6): δ 0.207 (s, 3H), 1.09 (s, 3H), 2.10 (s, 1.65H), 6.64 (m, 2H), 6.80 (d, 2H, $J = 0.8$ Hz), 6.86−6.93 (m, 8H), 6.96−7.02 (m, 2.75H), 7.25 (dt, 2H, $J = 0.9$, 8.7 Hz), 7.48−7.54 (m, 4H), 7.55 (d, $J = 1.2$ Hz), 7.58 (d, 2 H, $J = 0.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 3.2, 7.7, 84.7, 121.0, 125.2, 125.3, 126.1, 126.7, 126.9, 127.4, 127.7, 128.2, 129.0, 150.0 ppm. C, H Anal. Found (Calcd) for $C_{39}H_{34}Cl_2SiZr$: C, 67.54 (67.76); H, 5.08 (4.95).

Rac Isomer. ^1H NMR (400 MHz, C_6D_6): δ 0.61 (s, 6H), 6.58 (t, 2H $J = 6.7$ Hz), 6.69 (d, 2H, $J = 8.8$ Hz), 6.83 (s, 2H), 7.10−7.22 (m, partially obscured by solvent), 7.31 (dd, 2H, $J = 0.86$ Hz, 8.8 Hz), 7.50 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 5.0, 83.3, 120.0, 125.6, 125.9, 126.2, 127.4, 127.6, 128.4, 131.3, 133.1, 134.9, 150.0 ppm. C, H Anal. Found (Calcd) for $C_{32}H_{26}Cl_2SiZr$: C, 63.84 (63.98); H, 4.59 (4.36).

Photoisomerization of *rac*-(Dimethylsilylbisindenyl)zirconium dichloride (3-rac). Compound **3-rac** (200 mg) was suspended in 25 mL of toluene. The mixture was sealed in a Schlenk tube under nitrogen and irradiated for 3 h using a medium-pressure 400 W Hg lamp. The mixture was shaken periodically. The bright yellow solution was decanted from the remaining starting material. The solvent was removed in vacuo to give a bright yellow solid which was found to contain 55% **3-meso** as evidenced by integration of peaks in the ^1H NMR (C_6D_6, 400 MHz) spectrum at δ 0.36 (meso), 0.52 (rac), and 0.73 (meso) ppm due to the dimethylsilyl protons.

Propylene Polymerizations. Toluene and liquid propylene[57] 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 powder. 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.

(a) Preparation of Activated Catalysts for Polymerizations Utilizing 1-rac, 1-meso, or 3. Metallocene stock solutions were prepared by dissolving 2.5×10^{-5} mol of zirconocene in 25 mL of toluene. Gentle warming was required to bring all the material into solution. After letting the stock solution cool to room temperature, a 5 mL (0.5 mL for the mixture of **3-rac** and **3-meso**) aliquot was added to 294 mg of MAO (50 mg for the mixture of **3-rac** and **3-meso**) dissolved in 20 mL of toluene (24.5 mL for the mixture of **3-rac** and **3-meso**).

(b) Preparation of Activated Catalysts for Polymerizations Utilizing Mixtures of 1-rac and 1-meso. Batches of solid mixtures (about 50 mg) with a fixed ratio of **1-rac/1-meso** were prepared by combining the catalyst "reaction ratio" mixture with either pure **1-rac** or **1-meso** in varying amounts. The **1-rac** or **1-meso** enriched mixtures were stirred in toluene, and then the solvent was removed in vacuo. The ratio of isomers was measured by integration of the $SiMe_2$ proton

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(56) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986.

(57) Caution should be exercised when running polymerizations in liquid propylene. An exotherm initiated by a particularly productive metallocene (i.e.: **3-rac**) can cause a dangerous increase in pressure in the reaction vessel.

resonances obtained by ^{1}H NMR. Only one scan was acquired for each spectrum to ensure accuracy of integral measurement. Catalyst solutions were prepared in the inert atmosphere drybox by dissolving 294 mg of MAO and 5×10^{-6} mol of metallocene in 25 mL of toluene.

(c) Typical Procedure. The reactor was flushed three times with 50 psig N_2. Liquid propylene (100 mL) was then introduced to the reactor. The catalyst solution was injected into the reactor under 200 psig N_2 to start the reaction. Polymerizations were allowed to proceed for 20 min and then were quenched with 15 mL of methanol injected under N_2 pressure. The reactor was vented, and the polymers were collected and precipitated into acidified methanol (5% HCl). After stirring overnight, the polymers were collected and dried in a vacuum oven at 40 °C.

Ethylene Polymerizations. Toluene and ethylene were passed over towers containing Q5 and alumina prior to use. Metallocene stock solutions were prepared by dissolving 8.3×10^{-6} mol of zirconocene in 25 mL of toluene. Gentle warming was required to bring all the material into solution. The reactor was flushed three times with 50 psig N_2 followed by 30 psig ethylene. MAO (100 mg) was dissolved in 44 mL of toluene and injected into the reactor. The toluene solution was allowed to equilibrate with ethylene for 30 min. The reactor was vented to 20 psig. The metallocene (6 mL) was injected into the reactor under 30 psig ethylene pressure to start the reaction. The ethylene feed was immediately reconnected to the reactor. Polymerizations were allowed to proceed for 20 min and then were quenched with 15 mL of methanol injected under N_2 pressure. The reactor was vented and the polymers were collected and precipitated into acidified methanol (5% HCl). After stirring overnight, the polymers were collected and dried in a vacuum oven at 40 °C.

Polymer Characterization. Number and weight average molecular weights (M_n and 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. The isotactic pentad contents (%mmmm) were determined via ^{13}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 on a Perkin-Elmer DSC 7. Samples were annealed at 180 °C for 10 min followed by cooling to 50 °C for polymer blends (−30 °C for block copolymers) and then reheating to 180 °C. The cycle was then repeated. All temperature scans were carried out at 10 °C/min. Two samples of each polymer were run to ensure that the measured numbers were reproducible.

Fractionation Studies. Polypropylene (100−1000 mg) produced from mixtures of **1-rac** and **1-meso** or **3-rac** and **3-meso** were measured into an extraction thimble. The material was extracted into refluxing hexanes under argon for 24 h. The hexanes soluble material was reprecipitated into methanol. Both fractions were then dried at 40 °C in a vacuum oven.

X-ray Diffraction Study. *meso*-Dimethylsilyl(bis(2-phenylindenyl))zirconium dichloride (*1-meso*). An orange-red crystal of $C_{39}H_{34}Cl_2SiZr$ (fw = 692.879 g/mol) with approximate dimensions of $0.27 \times 0.24 \times 0.22$ mm^3 grown from a solution of toluene was mounted on a glass fiber in paratone oil at −80 °C using an improvised cold stage. All measurements were made on a Siemens SMART[58] diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods[59] and expanded using Fourier techniques.[60] All non-hydrogen atoms were refined anisotropically except the carbon atoms. Hydrogen atoms were included at idealized positions, 0.95 Å from their parent atoms. One toluene molecule was found as a solvent of crystallization. All calculations were performed using the teXsan[61] crystallographic software package of Molecular Structure Corp. Crystal data and details of data collection and structure analysis are summarized in Table 4.

Table 4. Summary of Crystal Structure Parameters for **1-meso**

formula	$C_{39}H_{34}Cl_2SiZr$
fw	692.91
temp (K)	163
space group	*Pna*21 (No. 33); orthorhombic
cell constants[a,b]	
a (Å)	10.4464(2)
b (Å)	17.4269(4)
c (Å)	17.2855(4)
vol (Å^3)	3146.8(2)
Z	4
abs. coeff., μ_{calc} (cm^{-1})	5.85
F_{000}	1424
$d_{obs}{}^c$ ($^d{}_{calc}$) (g cm^{-3})	(1.46)
cryst size (mm$^{3)}$	$0.27 \times 0.24 \times 0.22$
radiation	Mo K$_\alpha$ ($\lambda = 0.710\,69$ Å)
monochromator	highly-oriented graphite
diffractometer	Siemens SMART
reflcns measd	($+h$, $+k$, $\pm l$)
2θ range	$2.34° < 2\theta < 52.2°$
scan type	ω
scan width	0.3
scan speed	10 s frame exposure
reflcns collecd	17 121
unique reflcns:	3306 ($R_{int} = 0.03$)
reflcns with ($F_o{}^2 > 3\sigma(F_o{}^2)$)	2311
no. of variables	192
param-to-variable ratio	12.04
R (R_w)[d]	0.051 (0.069)
final diff ρ_{max} (e^-/Å^3)[e]	+0.73; −0.56

[a] Unit cell parameters and their estimated standard deviations (esd's) were derived by a least-squares fitting of 8192 reflections with $I > 10\sigma(I)$ and 2θ between 4.0° and 45.5°. [b] The esd's of all parameters are given in parentheses. [c] The density of the crystal was not measured. [d] The unweighted and weighted agreement factors in the least-squares refinements were as follows: $\sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]$, where $w = 4F_o{}^2/s^2(F_o{}^2)$; $s^2(F_o{}^2) = [S^2(C + R^2B) + (pF_o{}^2)^2]/\mathrm{Lp}^2$, 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, and p = p-factor (0.00). [e] Maximum negative and positive difference peaks.

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Supporting Information Available: Text of X-ray crystallographic determination of **1-meso** and curve-fitting procedure to determine productivities from polymer blend properties, tables of crystallographic data, bond lengths and angles, and positional parameters, and figures of an ORTEP diagram of **1-meso** and components of the blends (19 pages, print/PDF) See any current masthead page for ordering information and Web access instructions.

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(58) *SMART: Area-Detector Software Package*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

(59) SHELXS-86: Sheldrich, G. Institut fur Anorganische Chemie: Gottingen, Germany, 1986.

(60) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *DIRDIF92*; The DIRDIF program system; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(61) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: Woodlands, TX, 1985 and 1992.