Substituent Effects on the Stereospecificity of Propylene Polymerization by Novel Asymmetric Bridged Zirconocenes. A Mechanistic Discussion

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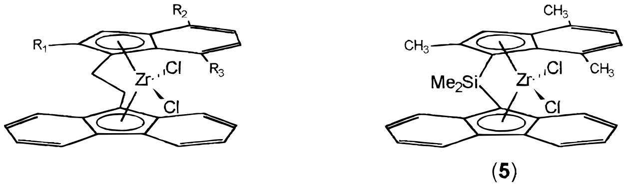
ABSTRACT: The synthesis and polymerization behavior of a new C_1-symmetric bridged indenyl−fluorenyl zirconocene dimethylsilylene [9-fluorenyl][(2,4,7-trimethyl)indenyl]zirconium dichloride (**5**) is reported. The complex when activated by MAO was found to polymerize ethylene and propylene, although the activity and stereoselectivity of **5** for propylene were found to be lower than for the previously prepared ethylene-bridged analogue **4** and several other ethylene-bridged precursors. It has been found that, depending on both the substitution patterns on the indenyl ligand and the nature of the bridge in this series of asymmetric zirconocenes, polypropylenes with varying microstructures from aspecific to highly isospecific are obtained. The propylene polymerization behavior of the new complexes has been studied in detail, and the mechanistic aspects of polymerization are discussed.

Introduction

The field of catalyst design for the stereochemical control of propylene polymerization using homogeneous Ziegler−Natta type metallocenes is a very competitive one, both academically and industrially. Following the initial discoveries by Kaminsky et al.[1] and Ewen[2] that the C_2-symmetric metallocenes *rac*-ethylenebis(tetrahydroindenyl)dichlorotitanium and -zirconium produced isotactic polypropylene (*i*-PP), many studies have been carried out concerning the relation between the geometry of the catalyst precursor and resulting polymer microstructure (tacticity).[3] Generally, it has been shown that the symmetry of the metallocene has a strong influence on the polymer tacticity. A C_2-symmetric system leads to *i*-PP, C_{2v} to atactic polypropylene (*a*-PP), and C_s to syndiotactic PP (*s*-PP). The mechanisms explaining these observations have been proposed.[2,3] These relationships are not, however, strongly exclusive, i.e., to be regarded as selection rules. In the case of asymmetric metallocenes belonging to the C_1 group, there is no fixed relationship between molecular symmetry and stereochemical control. This type of catalyst has been shown to produce polymers of varying microstructures from atactic[3,4] to elastomeric[5] to hemiisotactic[3,6] to isotactic[3,7,8] depending on the nature of the complex and in particular the substitution pattern.

In 1994, Rieger et al.[8] published a route to asymmetric ethylene-bridged zirconocenes containing indenyl and fluorenyl fragments. They also varied substitution on the ethylene bridge. The unsubstituted system ethylene-1-(η^5-9-fluorenyl)-2-(η^5-1-indenyl)zirconium dichloride (**1**) was shown to be moderately isospecific. Studies with C_2-symmetric *rac*-ethylenebis(indenyl)zirconium dichlorides by Spaleck et al.[9] have demonstrated that key substitution can lead to highly stereoregular polypropylenes. We have recently developed a different synthetic route to a series of substituted ethylene-bridged asymmetric zirconocenes.[10] Initial polymerization data showed them to be highly effective in both ethylene and propylene polymerizations, the latter with varying degrees of stereochemical control.[10] In this paper, the synthesis and polymerization behavior of the novel catalyst precursor dimethylsilylene-(η^5-9-fluorenyl)[η^5-1-(2,4,7-trimethyl)indenyl]zirconium dichloride is described, and the polymerization results have been compared with those obtained with the ethylene-bridged analogues. The central objective of this paper is to develop a mechanistic explanation for the results we obtained.

Chart 1



(**1**) = $R_{1,2,3}$ = H
(**2**) = R_1 = Me; $R_{2,3}$ = H
(**3**) = R_1 = H; $R_{2,3}$ = Me
(**4**) = $R_{1,2,3}$ = Me

Table 1. Propylene Polymerization Results for Catalyst Precursors 2−5/MAO at 30 psi[a]

catalyst precursor	temp (°C)	yield (g)	A^b	T_m (°C)	[mmmm][c]
2	20	7.9	0.63×10^7	no mp	29.3
2	70	5.3	3.02×10^7	82	47.1
3	20	8.0	0.63×10^7	no mp	6.0
3	70	2.0	1.10×10^7	no mp	13.5
4	20	17	1.40×10^7	132	89.1
4	70	8.5	4.80×10^7	124	79.5
5	20	1.8	0.14×10^7	74	39.4
5	70	0.4	0.23×10^7	125	48.1

[a] Conditions: toluene solution, polymerization pressure = 30 psi; time of polymerization = 1 h; [Zr] = 25 μM; Al:Zr = 4000:1. [b] Activity expressed as g of polymer/[(mol of Zr)·[C_3]·h]. [c] [mmmm] pentad analysis by ^{13}C NMR.

Results and Discussion

Synthesis. The asymmetric zirconocenes **2**−**5** used in this study are shown in Chart 1. The synthetic details of complexes **2**−**4** have previously been described and were all found to be highly active catalyst precursors for propylene polymerization (Table 1).[10] In particular, **4** has very high activity as well as unexpectedly high isospecificity. However, **4** as well as **2** and **3** afforded modest molecular weight polypropylenes (Table 2).

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Scheme 1

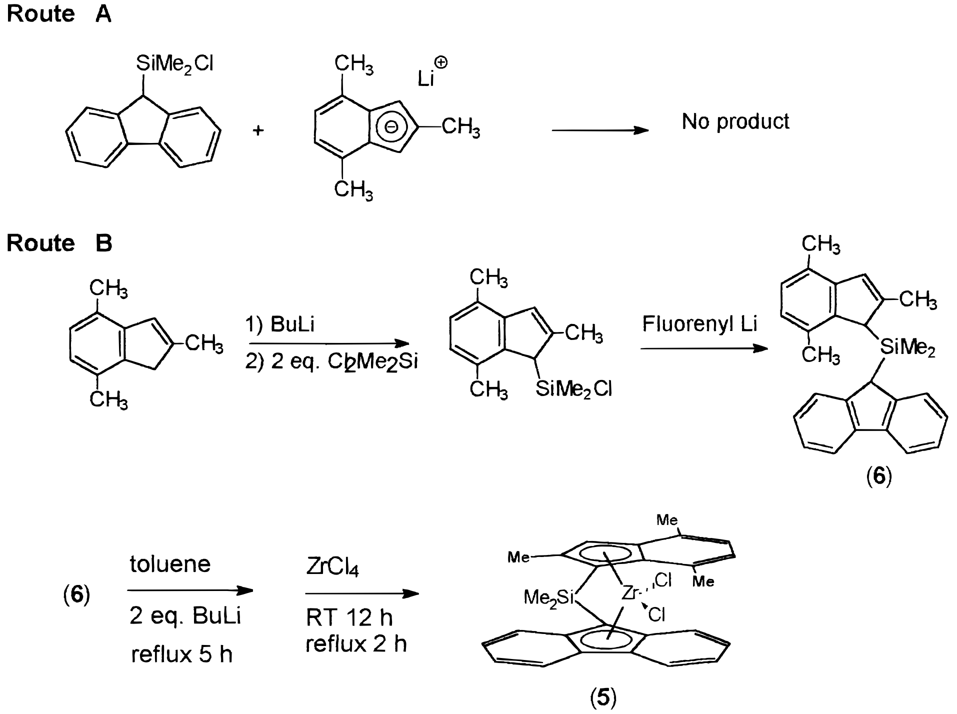

Table 2. Propylene Polymerization Results for Asymmetric Catalyst Precursors 2–5/MAO in Liquid Propylene[a]

catalyst precursor	productivity[b]	isotacticity (mm, mol %)	T_m (°C)	M_w (g/mol)[c]
2	1.500×10^8	57	114	40 000
3	1.560×10^8	25	no mp	22 000
4	1.320×10^8	91	151	27 000
5	0.074×10^8	79	95.7	43 000

[a] Conditions: liquid pool, pressure = 30 bar, temperature = 70 °C; time of polymerization = 1 h. [b] Productivity expressed as g of polymer/(mol of Zr)·h]. [c] Molecular weights determined by GPC.

Several studies have indicated that replacing an ethylene bridge with a dimethylsilylene bridge in C_2-symmetric catalysts can dramatically improve the molecular weight.[9,11] Therefore, dimethylsilylene-(η^5-9-fluorenyl)[η^5-1-(2,4,7-trimethyl)indenyl]zirconium dichloride (**5**) was synthesized (Scheme 1). The dimethylsilylene-bridged analogue of **1** had previously been prepared by Chen et al.[12] as part of another study. Initial attempts to prepare the new ligand (9-fluorenyl)-[(2,4,7-trimethyl)indenyl]dimethylsilane (**6**) via the method used by Chen et al.[12] (route A) failed, presumably due to unfavorable steric interaction between the trimethylindenyllithium and the chlorodimethylsilylfluorene. An alternate method of addition (route B), however, resulted in the desired ligand in 75% yield.

Synthesis of the zirconcocene **5** itself also proved difficult. The method used to prepare **2**–**4** involved addition of zirconium tetrachloride to the relevant dianion in diethyl ether.[10] However, in the case of **5**, a major product using this method was unreacted ligand which we attribute again to steric factors. To overcome this difficulty, the dianion and zirconium tetrachloride were refluxed in toluene (Scheme 1). Under this more vigorous condition, the desired product **5** was isolated, but there was 8% starting ligand in the reaction mixture according to ^{1}H NMR and elemental analysis which could not be eliminated by recrystallization because of the instability problems of **5** in solution. We found that **5** was much less stable than the previously prepared ethylene-bridged zirconocenes **2**–**4**. All attempts to modify the reaction to avoid this contamination were unsuccessful. Because of the very short lifetime of **5** in solution, the catalyst precursor had to be preactivated with methylaluminoxane (MAO) in order to perform polymerizations. Similar observations were made by Resconi et al.[13] concerning silicon-bridged fluorenyl zirconocenes.

Polymerization Studies. Complexes **2**–**4** all show very high activity when activated with MAO for both ethylene and propylene.[10] Activities of 10^7g/(mol of Zr·[monomer]·h) were obtained in most cases for propylene and in all cases for ethylene. Under the same conditions (i.e., no preactivation) **5**/MAO does not even polymerize ethylene due to the short lifetime of the species in solution. However, repeating with preactivation of **5** in toluene with 1 mL of MAO for 10 min resulted in the production of polyethylene with an activity of 5.3×10^7 g/(mol of Zr·[C_2]·h), which is comparable to the activities obtained with **2**–**4**/MAO.[10]

Tables 1 and 2 summarize the propylene polymerization results obtained under two different polymerization conditions, 30 psi propylene pressure and liquid pool, respectively. The activities of **5**/MAO for propylene at 30 psi and 20 °C were lower by a factor of 3 compared with those of **2**/MAO and by a factor of 10 compared to those of the ethylene-bridged analogue **4**/MAO (Table 1). The difference in activities is even greater in liquid pool polymerization (Table 2). Again, it was necessary to preactivate **5** with 1 mL of MAO in toluene for 10 min before injecting the solution into the polymerization vessel; otherwise, no polymer was produced. We were initially surprised by the large differences in activities between the ethylene-bridged and the dimethylsilylene-bridged complexes as generally changing the nature of the bridge from ethylene to dimethylsilylene in C_2-symmetric systems does not result in decreased polymerization activities. On the contrary, it often improves activity, stereospecificity, and molecular weight.[9,11]

Table 3. Comparison of Propylene Polymerization Behavior of Catalysts 1 and 2/MAO[a]

catalyst	temp/°C	activity[b]	mmmm[c]/%
1	20	0.4	*d*
1	50	2.9	53
2	20	0.6	*d*
2	50	7.3	44

[a] Conditions: toluene solution, polymerization pressure = 15 psi; time of polymerization = 20 min; [Zr] = 50 μM; Al:Zr = 4000:1. [b] Activity expressed as 10^{-6} g of polymer/[(mol of Zr)·[C_3]·h]. [c] [mmmm] pentad analysis by ^{13}C NMR. [d] Not determined.

However, there are several reports of silicon-bridged fluorenyl compounds in the literature that display a similar effect. Resconi et al.[13] reported the polymerization behavior of ethylenebis(fluorenyl)zirconium dichloride and the dimethylsilylene analogue. They found that the former compound gave higher activities than the latter. Similarly, Chen et al.[12] prepared the silicon-bridged analogue of **1** which showed less activity and stereoselectivity than that reported by Rieger et al. for **1**.[8]

Of particular interest is the great difference in stereoselectivity obtained with complexes **2**−**5** for propylene polymerization. Rieger et al. reported an [mmmm] pentad of 64% at 50 °C for **1**/MAO, indicating moderate isotacticity.[8] In our laboratory, we obtained a slightly lower (53%) but comparable value for **1**/MAO at 50 °C. For complex **2**, where a methyl substituent has been placed at the 2-position of the indenyl ligand, a similar value of 47.1% was obtained, and the polymer melted at 82 °C (Table 1). It is very significant that there was a sharp decrease in stereoselectivity at lower polymerization temperature. The polymers obtained at 20 °C for both **1** and **2** were much less stereoregular and displayed no melting points. A comparison of the polymerization behavior of these two complexes in our laboratories is given in Table 3. Rieger et al. reported no polymerization data below 50 °C. This large drop in stereoselectivity with decreased polymerization temperature (T_p) is contrary to the trend observed for C_2-symmetric metallocenes where isotacticity decreases with increased T_p.

In the case of **3** where methyl groups have been placed at the 4- and 7-positions of the indenyl ligand, a very different polymer results. Under all conditions, an oily, waxy material is obtained that displays no melting point (Tables 1 and 2). The full pentad analysis for all of the polymer samples obtained for **2**−**5** at 30 psi is shown in Table 4. Again, there appears to be a significant change in the microstructure of the polymers obtained with **3**/MAO at room temperature compared to those obtained at 70 °C. It can be seen that the polypropylene produced at 20 °C has a very low mmmm pentad (6.0%) and a relatively high rrrr pentad (28.5%). At 70 °C, this syndiotactic bias is not observed, and the microstructure appears more atactic in nature.

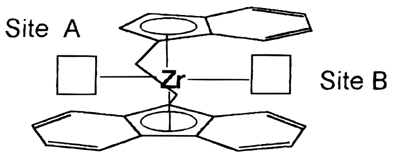

Figure 1. Representation of the two active coordination sites of the asymmetric indenyl−fluorenyl-bridged metallocenes.

Changing the substitution pattern on the indenyl ring to a 2,4,7-trimethylindenyl moiety (**4**) led to highly stereoregular polypropylene under all conditions. At 20 °C, the polymer had a melting point of 132 °C and mmmm of 89.1%. At higher temperature, the isotacticity is virtually unchanged (Table 1). Under liquid pool conditions, the resulting polypropylene melted at 151 °C, and triad analysis by ^{13}C NMR gave mm = 91% (Table 2).

In all three cases, while the complexes **2**−**4** were highly active catalyst precursors, it can be seen from Table 2 that the molecular weights of the PP were relatively low (22 000−40 000), especially for the stereoselective precursor **4**. Our goal in preparing the silicon-bridged analogue **5** was to increase the polymer molecular weight. This goal was met to a certain extent in that the MW increased from 27 000 for **4** to 43 000; however, from Tables 1, 2, and 4 it can be seen that the catalyst activity, polymer melting point, and stereospecificity all decreased dramatically. From Table 4, it can be seen that the PP had a melting point and microstructure more comparable to that obtained for **2**/MAO at 70 °C with [mmmm] = 48.1% than to the PP obtained for the ethylene-bridged analogue **4**. Also, in this case, a decrease in stereoregularity with decreasing T_p is observed.

Mechanism. The mechanism for homogeneous Ziegler−Natta isospecific polymerization with C_2-symmetric metallocenes has been intensely studied. It is widely accepted to involve enantiomorphic site control, i.e., monomer coordination followed by insertion with chain migration leading to highly isotactic polypropylene.[2,3] Similarly, such a mechanism describes the syndiospecific propagation by C_s-symmetric catalysts. The mechanism for propagation by C_1-symmetric catalysts is less clearly understood.[3,4−8] A variety of microstructures can be obtained (vide supra). It appears that a number of factors need to be considered in elucidating an accurate mechanistic description.

One of the most important differences between C_1-symmetric species and C_2 or C_s complexes is that a C_1-symmetric complex has two distinct catalytic sites diastereotopically related to each other (Figure 1). Monomer insertion can occur at either site with different stereochemistry, and generally, one site is stereospecific while the other is aspecific. Furthermore, the growing polymer chain itself can favor one site over the other energetically due to steric interaction. This can result

Table 4. Pentad Distributions for Polypropylenes Produced in Table 1

catalyst	temp[a]	mmmm	mmmr	rmmr	mmrr	mmrm + rmrr	mrmr	rrrr	mrrr	mrrm
2	20	29.3	3.2	17.9	25.9	1.7	6.6	7.7	2.6	5.1
2	70	47.1	15.6	14.7	17.6	3.2	1.7	0	0	0
3	20	6.0	4.2	4.3	18.4	17.1	4.8	28.5	11.8	4.9
3	70	13.5	2.1	12.9	24.5	16.7	6.4	8.9	6.2	8.8
4	20	89.1	4.3	0	5.3	0	0	0	0	1.2
4	70	79.5	9.4	0	8.8	0	0	0	0	2.3
5	20	39.4	18.0	13.8	16.6	3.9	3.8	0	2.2	2.6
5	70	48.1	17.5	12.1	16	3.9	2.3	0	0	0

[a] Polymerization temperature (°C); pentad distribution expressed as %.

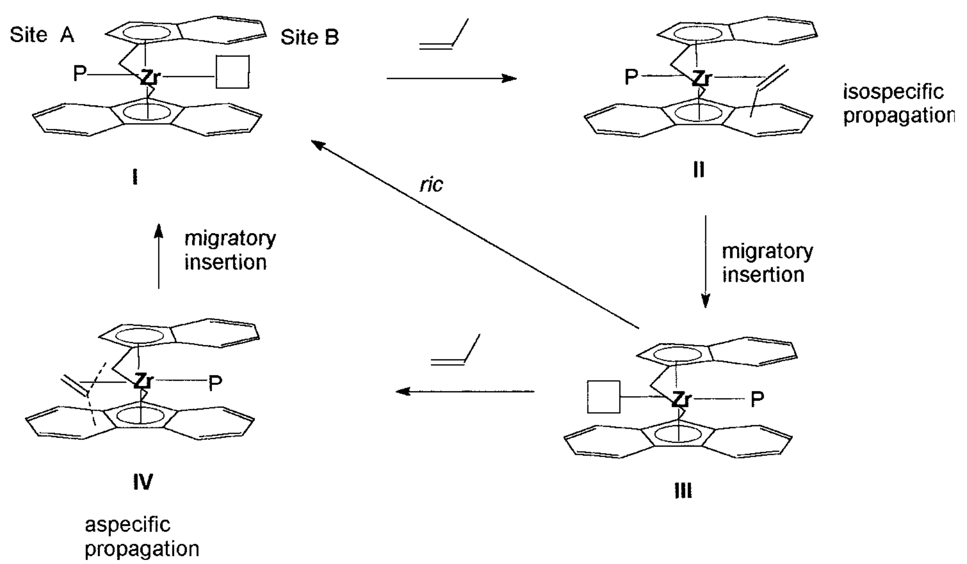

Figure 2. Schematic representation of the propylene polymerization mechanisms of asymmetric systems.

in *site switching* or *return to initial configuration* (*ric*) whereby the polymer chain returns to its initial configuration following migratory monomer insertion before the next monomer coordinates. Figure 2 depicts these mechanisms. State **I** shows the empty coordination site at site B. Monomer coordination at this site is stereoselective—**II**. Migratory insertion leads to **III,** at which time a new monomer can coordinate at site A (**IV**), or the polymer chain can return to its initial configuration to give **I**. The rate of monomer insertion can be faster than the rate of *ric* or it can be the same or slower. Of course, there is the limiting case in which only one of the two sites is accessible and participates in polymerization; i.e., a chain stationary insertion mechanism operates as proposed by Razavi et al.[7b] Depending on the catalyst structure, these factors play different roles and therefore can begin to explain the variety of stereochemical polymers that result.

There are at least three different mechanistic models to explain the production of *i*-PP from the novel asymmetric systems **2**−**5.** First, a chain migratory insertion mechanism with *ric* after each monomer insertion would lead to *i*-PP. Second, if both catalytic sites are isospecific, then a chain migratory insertion mechanism would result in *i*-PP. Third, a chain stationary mechanism with the chain exclusively occupying site A would result in *i*-PP. It seems apparent from the pentad analysis of **2**−**5** that *ric* is occurring to at least some extent. This could explain the decrease in stereospecificity with decreasing polymerization temperature as opposed to the reversed trend usually observed with an enantiomorphic site control mechanism for C_2-symmetric complexes. That *ric* is occurring in some cases is perhaps most obvious from studying the pentad data for complex **2**. In both **1** and **2**, monomer coordination at one site (site A, Figure 2) should lead to aspecific propagation while coordination at the other site (site B) should lead to isospecific propagation. Therefore, on a statistical basis assuming a chain migratory mechanism, one should expect to obtain hemiisotactic polypropylene (*hi*PP).[6,14] However, from the [mmmm] values for both **1**[8] and **2** at higher polymerization temperature, the polymer microstructure is moderately isospecific. Even at lower T_p, the pentad data for **2** does not match the statistical fingerprint for *h*iPP (mmmm:mmmr:rmmr:mmrr:rrrr:mrrr:mrrm = 3:2:1:4:3:2:1).[14] Allowing for some misinsertions, the microstructure still does not approach that of *hi*PP.

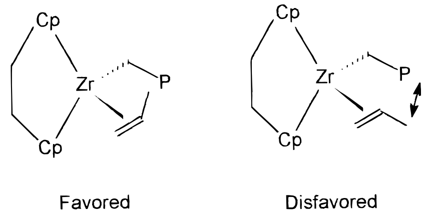

Figure 3. Representation of the "trans effect" whereby a trans relationship between the monomer methyl group and the polymer chain dominates due to favored steric interactions.

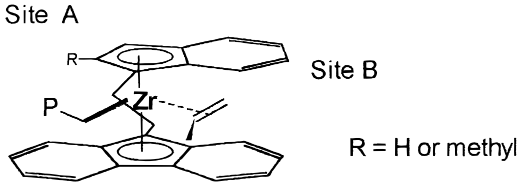

Figure 4. Schematic showing the proposed preferred polymer chain configuration and the resulting monomer coordination at site B for complexes **1** and **2**.

It has been proposed that the stereochemistry of the olefin insertion is determined by the polymer chain end configuration via nonbonded interactions. A trans relationship between the methyl group of the propylene monomer and the polymer chain extending from the carbon α to the zirconium atom dominates (Figure 3).[15] In Figure 4 (representing complexes **1** and **2**) it can be seen that at site A, which resembles a *rac*-2-substituted ethylenebis(indenyl)zirconium dichloride complex, the polymer chain can preferentially lie in a given configuration thus determining the stereochemistry of the incoming monomer at site B leading to isospecific propagation. However, when the polymer chain is at site B (resembling *meso*-ethylenebis(indenyl)zirconium dichloride), no such preference exists, and therefore monomer coordination at site A is aspecific. Sterically, the polymer chain would prefer to reside at the more open site A. Therefore, *ric* can occur leading to a dominance of the chain residing at site A and isospecific propagation at site B. A consequence of this mechanism is that at higher temperature the rate of *ric* is high because the

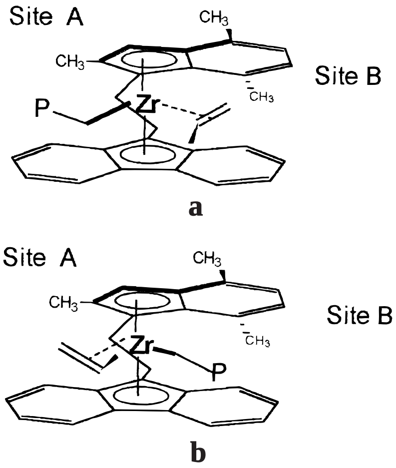

Figure 5. Representation of the isospecific propagation at both sites A and B for complex **4**.

system has more energy to overcome the energy barrier to interconversion.[16] Isospecific propagation therefore prevails at higher polymerization temperature as the rate of *ric* is faster than the rate of monomer coordination. At lower T_p, the usual migratory insertion mechanism prevails. However, although the PP obtained at 20 °C from **2**/MAO does not have a melting point, it can be seen from the ^{13}C NMR analysis that the polymer still has a slight isotactic character rather than purely atactic or hemiisotactic.

When one considers the trisubstituted complex **4**, it can now be seen that both sites A and B become isospecific (Figure 5) and may be said to be a pseudo-C_2-symmetric species. Therefore, isotactic polypropylene would result with or without chain migration. There are two possible mechanistic models to explain the high isospecificity of **4**. One could postulate that, due to the presence of the 4-methyl group, the steric constraints placed on the chain occupying site B are great. Thus, the chain only occupies site A, and monomer coordination occurs selectively at site B. That is to say that a chain stationary insertion mechanism similar to that proposed by Razavi et al.[7b] dominates, leading to highly isotactic PP. On the other hand, one could postulate that chain migratory insertion does occur, but as both sites are stereoselective, *i*-PP results in the same manner as for C_2-symmetric catalysts (Figure 5); i.e., **4** could be said to be pseudo-C_2-symmetric. That *ric* is not occurring is confirmed by the slight drop observed in the mmmm value at higher T_p as this is the usual trend for chain migratory enantiomorphic site control. Further evidence of this can be found by studying the pentad data for **4**. The pentad relationship of [mmmr]:[mmrr]:[mrrm] ≈ 2:2:1 which is characteristic of isospecific catalysts operating under enantiomorphic site control is applicable to **4**/MAO at 20 °C and is close at 70 °C.[17] The decrease in [mmmm] from 89.1 to 79.5% for T_p of 20 and 70 °C, respectively, supports the chain migratory insertion mechanism model as opposed to the chain stationary insertion mechanism model as there is generally no significant change in [mmmm] with temperature in the latter model.[7b]

As we have already discussed for the case of the silicon-bridged complex **5**, one would initially expect similar polymerization behavior to **4**. However, poor activity and stereospecificity were observed with **5**/MAO, which can be explained in several ways. First, we have discussed the instablility of **5** in solution, which may be due to a weaker Si−fluorenyl bond and in turn a weaker fluorenyl−zirconium bond. The low hapticity and instability of fluorenyl-containing metallocenes are well documented.[3e] Furthermore, on the basis of current research,[18] we also believe that the methyl group at the 7-position could interfere sterically with the methyl groups on the silicon bridge, adding to the instability. This inherent instability in the complex may result in the lower activities obtained for propylene polymerization. The lower stereoselectivity may be explained as follows. Molecular modeling studies of complexes **4** and **5** indicate that the geometry around the coordination center is actually slightly more open in **5** than it is in **4**, placing the 4-methyl group on the indenyl ligand in **5** further away from the active center than in **4**. The consequences of a more open geometry are twofold. First, the 4-methyl group could have less of a stereochemical directing effect in **5** compared to **4**. Second, any steric constraints to chain migration would be at least partially removed, and *ric* could occur as described for **1** and **2**. The overall result is a less stereoregular polymer than that obtained with **4**/MAO. Again, at higher T_p, the rate of *ric* increases, leading to a more isotactic PP at 70 °C than at 20 °C. The fact that moderately isotactic PP is obtained at 20 °C does imply that the 4-methyl group still has a signficant effect on stereoregularity compared to **1** and **2** where there is no 4-methyl group present.

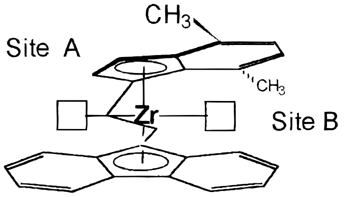

Figure 6. Representation of the twisted geometry of **3** resulting from unfavorable steric interactions of the 7-methyl group and the ethylene backbone.

The result that **3**/MAO affords only poorly stereoregular PP is unexpected as the two catalytic sites should be isospecific. Furthermore, there is a distinct syndiotactic bias in the pentad distribution for the polypropylene obtained with **3**/MAO at 20 °C ([rrrr] = 28.5%) that is not observed with any of the other polymers. A molecular modeling study of **3** and **4** suggests a different geometry for **3** compared to **4**, showing the indenyl moiety in **3** to be twisted forward, thus relieving the steric interaction between the 7-methyl group and the bridge atoms. This forward twist (Figures 6 and 7) results in the 4-methyl group being moved away from the active site at site B and over the zirconium center toward site A.

These observations are supported by similar reports in the literature. Ethylene-bridged metallocenes can exist as two conformers: δ-forward and λ-backward conformations. Rieger et al. demonstrated the effect of isolating pure conformers in asymmetric diastereomeric complexes containing bulky bridge substituents on polymerization behavior.[8] They suggested that the unsubstituted system **1** was free to adopt a sterically optimal geometry which we believe would also be the case for **2.** It has been shown that placing a methyl group at the 7-position of ethylenebis(indenyl)zirconium dichloride leads to a twisting of the geometry in order to relieve steric interaction of the methyl group with the atoms in the bridge.[19] Resconi et al.[19a] reported that ethylenebis(4,7-dimethylindenyl)zirconium dichloride

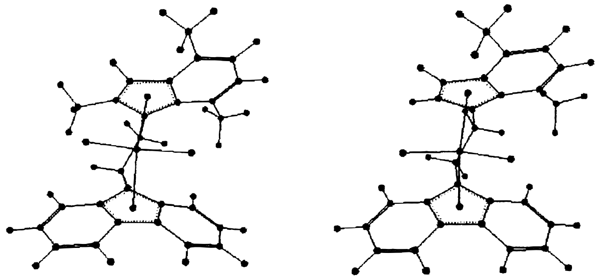

Figure 7. Molecular modeling structures of complex **4** (left) and complex **3** (right) demonstrating the twist effect of the 7-methyl group in complex **3**. Distances complex **3**: 4-methyl group C atom−Cl^A = 4.7935 Å; 4-methyl group C atom−Cl^B = 4.2004 Å. Distances complex **4**: 4-methyl group C atom−Cl^A = 5.0347 Å; 4-methyl group C atom−Cl^B = 4.0571 Å. Cl^A = chloride at site A (left-hand side); Cl^B = chloride at site B (right-hand side).

exists as mostly one conformer where the indenyl group is forward. The twisting effect for 4,7-dimethyl-substituted systems has also been discussed by Rappe et al.[19b] and Spaleck et al.[9] Such a dramatic twist in geometry is not expected in **4** and **5** because the 2-methyl group has an equal and opposite effect, giving the complexes a rigid geometry.[19c] We believe that the position of the 4-methyl group now affects monomer coordination at both catalytic sites and leads to a decrease in stereoselectivity at both compared to the other systems **1**, **2**, and **4**.

It has been shown in several studies that monomer concentration has an effect on polymer stereregularity with C_1 catalysts.[5,8] The polymerization runs reported in Table 1 were also carried out at 5 psi to study this effect of monomer concentration on stereoregularity using the new catalysts. Table 5 shows a comparison of the activity and melting points of the polypropylenes obtained for **2**/MAO and **4**/MAO at 30 and 5 psi. No large changes in activity and melting point were observed. Minimal changes in stereoregularity with C_1-symmetric catalysts were also reported by Soga et al.[20]

The molecular weights of polypropylenes obtained from C_1-symmetric catalysts are usually much lower than those obtained from C_2- and C_s-symmetric catalysts. This may be due in part to the involvement of *ric* processes, which do not contribute to monomer addition and chain growth. Finally, we wish to mention that ^{13}C NMR analyses for all of the polypropylene samples from Table 1 show no evidence of 2,1 and 1,3 mis insertions, indicating that all complexes are highly regioselective catalysts.

Conclusions

The synthesis and polymerization behavior of a new dimethylsilylene-bridged asymmetric indenyl−fluorenyl zirconocene is described. The polymerization results have been compared with a series of ethylene-bridged analogues previously prepared. A detailed study of the polymerization behavior of these catalysts shows that a wide variety of polymer microstructures result by placing substituents at different positions on the indenyl ring. Furthermore, a general trend of increasing stereoregularity with increasing polymerization temperature, opposite to that observed with C_2-symmetric catalysts, indicates that a mechanism other than chain migratory insertion is operating. We propose that a combination of mechanisms is occurring depending on the geometry of the catalyst whereby chain migration can occur freely (chain migratory insertion), is restricted and results in return to initial configuration (*ric* mechanism), or is prohibited (chain stationary insertion mechanism).

Table 5. Comparison of Propylene Polymerization Behavior of Catalyst Precursors 2 and 4/MAO at Different Monomer Concentrations[a]

catalyst	press./psi	temp/°C	activity[b]	T_m/°C
2	5	20	0.56	no mp
2	5	70	3.1	71
2	30	20	0.63	no mp
2	30	70	3	82
4	5	20	1.6	134
4	5	70	6	108
4	30	20	1.4	132
4	30	70	4.8	124

[a] Conditions: time of polymerization = 1 h; [Zr] = 25 μM; Al:Zr = 4000:1. [b] Activity expressed as 10^{-7}g of polymer/[(mol of Zr)·[C_3]·h].

We have been able to show that substitution at the 2,4,7-positions of the indenyl ligand (**4**) leads to a highly active, isospecific catalyst. We believe that placing substituents at both the 2- and 4-positions is essential for isospecific propagation as this leads to a stereorigid geometry, with both active sites being isospecific, resulting in highly isotactic polypropylene. Changing the nature of the bridge in this class of C_1-symmetric catalysts from ethylene to dimethylsilylene appears to have a negative effect on stereoregularity, which we attribute to a movement of the 4-methyl group away from the active center leading to less indirect steric control. Further studies of related novel asymmetric systems are currently in progress.

Experimental Section

General Procedures. Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo Nobel and used as received. All other reagents were purchased from Aldrich and used without further purification. Diethyl ether, THF, and pentane were distilled from Na/K alloy under argon. Dichloromethane was distilled from CaH_2 under argon. The synthesis of the zirconocenes **2**−**4** has previously been described.[10] ^1H NMR spectra were recorded on a AC-200 spectrometer. ^{13}C NMR spectra were recorded on DPX 300/AMX500 spectrometers. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. Molecular modeling studies were carried out using PC Spartan Plus PM3.

(9-Fluorenyl)-1-[(2,4,7-trimethyl)indenyl]dimethylsilane (6). To a solution of 5.00 g (31.6 mmol) of 2,4,7-trimethylindene[19c] in 30 mL of dry diethyl ether and 10 mL of dry THF at 0 °C was added dropwise a 1.6 M solution of butyllithium in hexane (19.70 mL, 31.6 mmol) The solution was stirred at room temperature for 5 h and then added dropwise via cannula to 7.67 mL (63.2 mmol) of dichlorodimethylsilane in 20 mL of dry diethyl ether at 20 °C. The addition was carried out over a 1 h period, and the suspension was then stirred for 1 h at room temperature. The solvents and excess dichlorodimethylsilane were then removed under vacuum, and the resulting oil was suspended in 30 mL of dry diethyl ether at 0 °C. To this was added dropwise by cannula 1 equiv of fluorenyllithium prepared from 5.25 g (31.6 mmol) of fluorene and 19.7 mL (31.6 mmol) of butyllithium in 30 mL of dry ether and 10 mL of dry tetrahydrofuran. The suspension was allowed to stir overnight at room temperature and hydrolyzed with aqueous NH_4Cl. The organic phase was separated, and the aqueous layer was extracted with ether. The combined organic phases were dried ($MgSO_4$) and filtered, and the solvent was removed. The residue was recrystallized from toluene/hexane 1:1 to give 9.05 g of **6** (75%); mp 121−123 °C. ^1H NMR

($CDCl_3$): δ 7.90−7.34 (m, 8 H, arom), 6.95−6.88 (d, 1 H), 6.78−6.75 (d, 1 H), 6.66−6.65 (d, 1 H, Ind sp^2), 4.17, (s, 1 H, Flu sp^3), 3.85 (s, 1 H, Ind sp^3), 2.38 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), −0.35 (s 3 H, Si−CH_3), −0.55 (s 3 H, Si−CH_3). Anal. Calcd for $C_{27}H_{28}Si$: C, 85.21; H, 7.41. Found: C, 85.47; H, 7.35.

Dimethylsilylene(9-fluorenyl)[(2,4,7-trimethyl)indenyl]-zirconium Dichloride (5). To a solution of 1.00 g (2.63 mmol) of **6** in 20 mL of dry toluene at 0 °C was added dropwise 2 equiv of a 1.6 M solution of butyllithium in hexane (3.3 mL, 5.25 mmol). The solution was heated under reflux for 5 h, giving an orange suspension. The suspension was then cooled to −25 °C, and zirconium tetrachloride (0.61 g, 2.63 mmol) was added as a solid. After stirring at room temperature overnight, the mixture was heated under reflux for an additional 4 h to ensure complete reaction. Upon cooling to room temperature, the suspension was filtered and the orange residue was extracted in dry methylene chloride. The solution was concentrated and stored at −20 °C to give 156 mg of **5** as an orange powder (11%). ^{1}H NMR ($CDCl_3$): δ 8.00−6.62 (m, 11 H, arom), 2.72 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 1.47 (s, 3 H, Si−CH_3), 1.46 (s, 3 H, Si−CH_3). Anal. Calcd for $C_{27}H_{26}SiCl_2Zr{\cdot}0.08C_{27}H_{28}Si$: C, 61.32; H, 4.98. Found: C, 61.80; H, 5.00.

Polymerizations. A 250 mL crown-capped glass pressure reactor containing 50 mL of toluene was equilibrated with the appropriate monomer and pressure at the desired temperature. The desired amount of methylaluminoxane (MAO) was added as a solution in toluene via syringe, and the solution was stirred for 5 min. One milliliter of the appropriate catalyst solution in toluene was added, and the mixture was stirred until the desired reaction time was reached. In the case of **5**, the catalyst precursor was preactivated by addition of 1 mL of MAO to the catalyst solution in toluene followed by stirring at room temperature for 10 min before addition to the polymerization vessel. The mixture was quenched with 2% HCl in methanol, filtered, and dried in a vacuum oven at an appropriate temperature for the polymer sample.

Polymer Analyses. Melting points were determined by DSC with a Perkin-Elmer DSC-4 system. ^{13}C NMR spectra were determined on a DPX300 spectrometer in $CDCl_3$ at room temperature and at 80 °C in C_6D_5Cl or $C_6D_3Cl_3$ on an AMX 500 spectrometer.

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