Organometallics **2000,** *19,* 4077−4083

New C_1 Symmetric Ziegler−Natta Type Zirconocenes for the Production of Isotactic Polypropylene

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Received March 27, 2000

As part of our continued investigation of the polymerization behavior of substituted asymmetric indenyl−fluorenyl metallocenes, three new zirconocenes bearing 2,4-disubstitution on the indenyl moiety have been synthesized and evaluated as α-olefin polymerization catalysts. For the new complex ethylene-1-(9-fluorenyl)-2-[1-(2-methyl-4-phenyl)indenyl]-zirconium dichloride (**11**), highly isotactic polypropylene with [mmmm] = 91% and M_w 1.1 × 10^5 at T_p = 40 °C was produced in very high yield. The dimethylsilylene analogue (**13**) gave similar results in terms of stereoregularity with a 2-fold increase in M_w. In addition, dimethylsilylene(9-fluorenyl)[1-(2,4-dimethyl)indenyl]zirconium dichloride (**12**) was prepared and found to be an effective catalyst precursor, although the smaller methyl substituent at the 4-position resulted in polypropylenes of lower stereoregularity.

Introduction

The production of highly isotactic polypropylene (PP) using Ziegler−Natta type homogeneous metallocenes is an area of great interest industrially and academically. The discovery that chiral C_2 symmetric metallocenes could produce stereoregular polypropylenes[1] efficiently led to many studies in order to fully optimize the polymerization behavior of this class of metallocenes.[2,3] In recent years, research has increased in the area of C_1 symmetric systems, which have been shown to polymerize propylene to PP with varying microstructures from aspecific[4] to stereoblock[5] to syndiotactic[6] to hemiisotactic[7] to isotactic,[8] depending on the nature of the hapto ligands. This behavior is due to fact that C_1 symmetric complexes have two coordination sites that are diastereotopically related to each other. As a result, monomer coordination can occur with different stereospecificity at each site and the polymer chain can prefer to occupy one site over the other due to steric interactions. For example, Razavi et al.[8a] demonstrated that placing a *tert*-butyl group at the 3-position of the cyclopentadienyl moiety of isopropylidene[cyclopentadienyl][fluorenyl]zirconium dichloride led to the production of highly isotactic polypropylene (*i*-PP). These observations were attributed to the large steric bulk of the *tert*-butyl group preventing the polymer chain from occupying one of the coordination sites. Monomer coordination thus occurred stereoselectively at that site, and a chain stationary insertion mechanism was proposed.

Rieger et al.[8b] published a study on the use of an asymmetric ethylene-bridged indenyl−fluorenyl zirconocene, ethylene-1-[-9-fluorenyl]-2-[-1-indenyl]zirconium dichloride (**1**), that produced moderately isotactic PP (Chart 1). We were interested to investigate the effects of placing substituents on the indenyl moiety of **1** on polymerization behavior and particularly PP microstructure. An alternative, versatile synthetic route to **1** was devised and applied to the preparation of a series of methyl-substituted zirconocenes which were all shown to be highly efficient catalyst precursors for both ethylene and propylene polymerization.[9] Depending on the substitution pattern on the indenyl ring and the polymerization conditions, polymers varying from aspecific to highly isotactic were obtained. We found that by placing substituents at both the 2- and 4-positions of the indenyl moiety highly isotactic PP was produced. Ethylene-1-[-9-fluorenyl]-2-[-1-(2,4,7-trimethyl)indenyl]-zirconium dichloride (**2**) (Chart 1) polymerized propylene with an activity of 1.4 × 10^7 and 4.8 × 10^7 g polymer/[(mol Zr)[C_3] h] at 20 and 70 °C, respectively. The PP had [mmmm] values of 89 and 79% for the two runs. Under liquid pool polymerization conditions at 70 °C,

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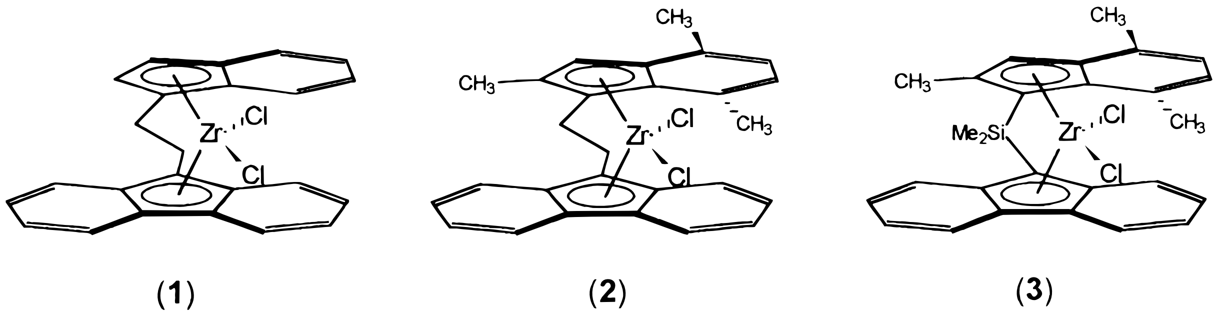
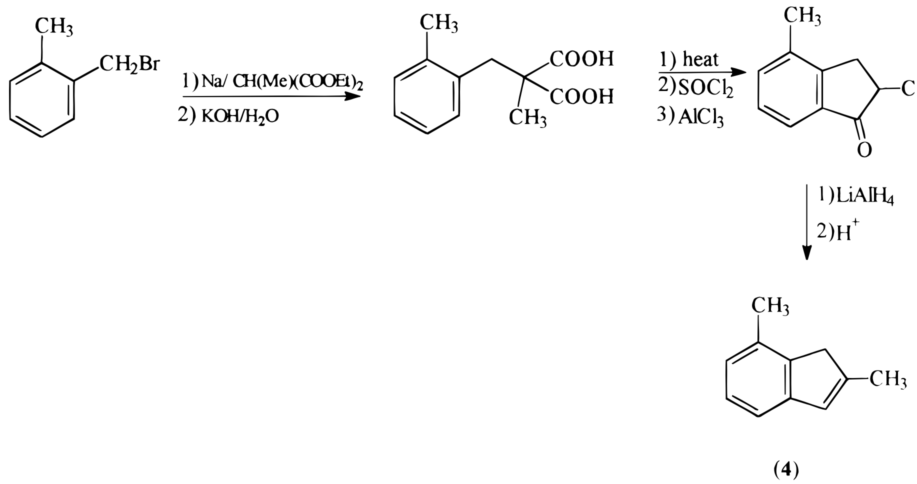
10.1021/om000256d CCC: $19.00

Chart 1



Scheme 1



the catalyst productivity was 1.3 × 10^8 g polymer/[(mol Zr) h] and the resulting polymer was 91% isotactic with a molecular weight of 27 000.[9]

In an effort to increase the molecular weight of the polymer, the silicon-bridged analogue of **2** was prepared. Surprisingly however, dimethylsilylene[9-fluorenyl][1-(2,4,7-trimethyl)indenyl]zirconium dichloride (**3**) (Chart 1) was found to be a highly unstable complex that showed lower activity and lower stereoselectivity toward propylene polymerization (0.14 and 0.23 × 10^7 g polymer/[(mol Zr)[C_3] h], at 20 and 70 °C, [mmmm] = 39 and 48%, respectively).[10] Similar trends were observed in liquid pool propylene polymerization studies, although the molecular weight of the PP was improved to 43 000. The instability of **3** was attributed to a weak Zr–fluorenyl bond and also to the presence of the 7-methyl group, which we believed interfered sterically with the methyl groups on the dimethylsilylene bridge. For this reason and also because it was thought that the 7-methyl group may be detrimental to the molecular weight of the PP, we undertook the synthesis of a series of 2,4-disubstituted indenyl–fluorenyl ethylene-bridged and dimethylsilylene-bridged zirconocenes in order to investigate their potential as catalyst precursors for the production of highly isotactic, high molecular weight PP.

Results and Discussion

Synthesis of Ligands and Zirconocene Complexes. The study of two 2,4-disubstituted indenyl moieties as hapto ligands was undertaken: the new compound 2,7-dimethylindene (**4**) and the known compound 2-methyl-7-phenylindene (**5**), the synthesis of which was published by Spaleck et al.[3a,c] Compound **4** was prepared by modification of Spaleck's procedure in an overall yield of 45% (Scheme 1). Proton NMR showed **4** to be a mixture of double-bond isomers. The two indenyl ligands **4** and **5** were then deprotonated and reacted as shown in Schemes 2 and 3 with 1 equiv of 1-(9-fluorenyl)-2-bromoethane (**6**) using a modification of a procedure previously published[9] in order to synthesize the new ethylene-bridged indenyl–fluorenyl ligands **7** and **8**. As can be seen in Scheme 2, in the case of 2,7-dimethylindene, two structural isomers **7a** and **7b** were formed in a 1:1 ratio whereby nucleophilic substitution occurred at both the 1- and 3-positions of the indenyl ligand. The two isomers could not be separated, and therefore no further studies were undertaken with **7**, since formation of the zirconocene dichloride would lead to two compounds with 2,4- and 2,7-substitution that would adversely effect polymerization behavior. In the case of **5**, however, the presence of the more sterically demanding 7-phenyl group led to the exclusive formation of the desired bridged moiety **8** in good yield (Scheme 3).

We were also interested in the synthesis of the analogous dimethylsilylene-bridged ligands **9** and **10** (Scheme 4). The two ligands were prepared in good yield by first reacting the respective indenyllithium salts with an excess of dichlorodimethylsilane to form the corresponding silyl chlorides, which were not isolated. Reaction with 1 equiv of fluorenyllithium afforded **9** and **10**. In both cases, only the desired structural isomer was formed. We also found that both dimethylsilylene

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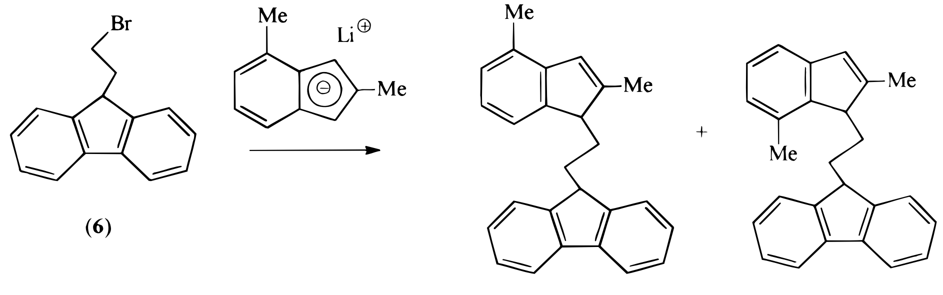
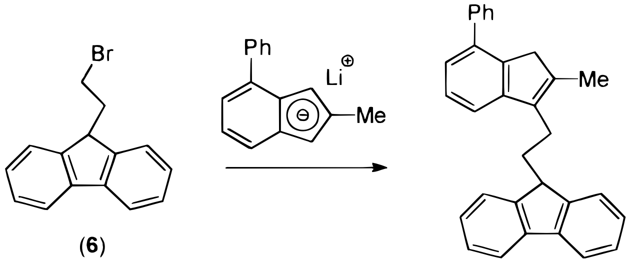
Scheme 2



(6) (7a) (7b)

Scheme 3



(6) (8)

ligands could be prepared in similar yields by reaction with the known compound 9-(chlorodimethysilyl)fluorene[11] with the corresponding 2,7-substituted indenyllithium.

The three new bridged ligands **8**, **9**, and **10** were then converted to their corresponding zirconocenes **11**, **12**, and **13** according to Scheme 5. It is noteworthy that in the case of **9** and **10**, the zirconocenes were readily prepared using this method and were isolated as stable complexes. We have previously reported the difficulties[10] encountered in the synthesis of the 2,4,7-trimethylindenyl derivative **3**, which required reaction of $ZrCl_4$ with the dianion in refluxing toluene. Furthermore, **3** was found to be highly unstable in solution, which we attributed in part to the steric interactions between the methyl groups on the bridge and the 7-methyl group of the indenyl moiety. This theory is supported by the fact that **12** and **13** are highly stable complexes and do not possess the 7-methyl group.

Polymerization Studies. The three new zirconocenes **11**, **12**, and **13** were examined as Ziegler−Natta type homogeneous polymerization catalyst precursors. In the presence of a cocatalyst (methylaluminoxane, MAO) they were found to be highly efficient catalysts for both ethylene and propylene. To compare directly with the polymerization results obtained with **3**/MAO, complexes **12** and **13** were preactivated for 10 min with 1 mL of MAO before addition to the reaction vessel. In the case of ethylene (Table 1), **11**, **12**, and **13**/MAO produced polyethylene with activities of 6.5, 8.1, and 7.9 × 10^7 g PE/[(mol Zr)[C_2] h], respectively. These results are comparable with those obtained with previously reported results for both **2**[9] and **3**.[10]

Tables 2 and 3 summarize the propylene polymerization results obtained under two different polymerization conditions, 30 psi propylene pressure and liquid pool propylene, respectively. At 30 psi propylene pressure, polymerizations were carried out at two different temperatures, 20 and 70 °C. We found that the most active catalyst precursor was the ethylene-bridged zirconocene **11**/MAO, which polymerized propylene with an activity of 2.7 × 10^6 g PP/[(mol Zr)[C_3] h] at 20 °C and 3.2 × 10^7 g PP/[(mol Zr)[C_3] h] at 70 °C. These activities are comparable with those reported for **2**/MAO.[9] In the case of the dimethylsilylene-bridged zirconocenes **12** and **13** the activities were lower at both polymerization temperatures (T_p) (ca. 10^6 g PP/[(mol Zr)[C_3] h]. We previously reported similar observations for **3**/MAO versus **2**/MAO[10] and also found reports in the literature of silicon-bridged fluorenyl complexes being less active than ethylene-bridged analogues. For example, Resconi et al.[12] reported the polymerization behavior of ethylenebis(fluorenyl)zirconium dichloride and the dimethylsilylenebis(fluorenyl)zirconium dichloride. It was found that the former complex gave slightly higher activities than the latter. We believe this trend is a consequence of the Si−fluorenyl bond, which results in a less stable zirconium complex relative to an ethylene-bridged analogue due to lower hapticity of the Zr−fluorenyl bond.[13] Studies of related systems containing partially or fully saturated fluorenyl derivatives support this theory.[14] Similar trends in activity for complexes **11**−**13** were found for polymerizations carried out in liquid pool propylene, as shown in Table 3.

The tacticities of the PP samples obtained vary depending on the catalyst and the polymerization conditions. The full pentad analysis for **11**−**13** is shown in Table 4. For complex **12** with a 2,4-dimethylindenyl moiety, the PP is more isotactic for the polymerization run at 70 °C than that at room temperature; [mmmm] = 83.8 and 42.4%, respectively (Tables 2 and 4). Under liquid pool conditions the results of triad analysis are 71 and 51% for T_p = 70 and 40 °C, respectively. Similar observations in the change in PP tacticity with T_p were reported for **3**/MAO.[10] For both **11** and **13**, where a phenyl group is placed at the 4-position of the indenyl ligand, highly isotactic polypropylene is produced under all polymerization conditions. The highest polymer tacticity was obtained with **11**/MAO at 20 °C. The PP displayed an [mmmm] pentad of 93% and polymer

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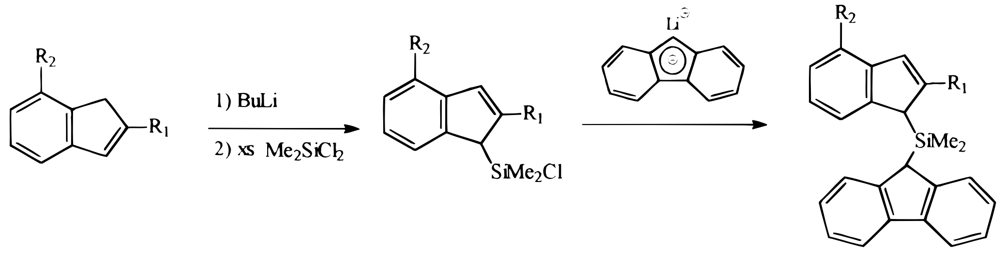
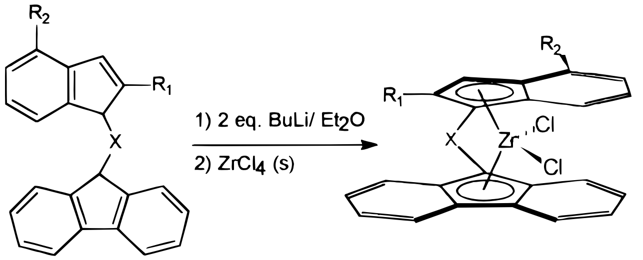
Scheme 4



(**4**) $R_1 = R_2 = Me$
(**5**) $R_1 = Me; R_2 = Ph$

(**9**) $R_1 = R_2 = Me$
(**10**) $R_1 = Me; R_2 = Ph$

Scheme 5



(**8**) $R_1 = Me; R_2 = Ph; X = C_2H_4$
(**9**) $R_1 = R_2 = Me; X = SiMe_2$
(**10**) $R_1 = Me; R_2 = Ph; X = SiMe_2$

(**11**) $R_1 = Me; R_2 = Ph; X = C_2H_4$
(**12**) $R_1 = R_2 = Me; X = SiMe_2$
(**13**) $R_1 = Me; R_2 = Ph; X = SiMe_2$

Table 1. Polymerization of Ethylene with 11−13/MAO[a]

catalyst precursor	yield (g)	activity 10^{-7} [b]
11	0.45	6.5
12	0.56	8.1
13	0.54	7.9

[a] Conditions: pressure 15 psi; time of polymerization 6 min; [Zr] = 5 μM; Al:Zr = 4000:1; temperature 50 °C, catalyst precursors **12** and **13** preactiviated with 1 mL of MAO for 10 min before injection. [b] Activity expressed as g polymer/[(mol Zr)[C_2] h].

Table 2. Polymerization of Propylene with 11−13/MAO at 30 psi[a]

catalyst precursor	temp (°C)	yield (g)	activity 10^{-6} [b]	T_m (°C)[c]	[mmmm] %[d]	M_w/ 10^{-4} [e]	PDI
11	20	3.35	2.7	144	93.5	2.5	2.3
11	70	5.6	32.0	137	89.0	0.7	1.7
12	20	1.41	1.1	72	42.4	4.4	2.0
12	70	0.32	1.8	119	83.8	0.8	1.6
13	20	0.71	0.6	137	90.5	5.6	2.0
13	70	0.76	4.3	135	88.9	0.7	1.6

[a] Conditions: Polymerization pressure = 30 psi; time of polymerization = 1 h; [Zr] = 25 μM; Al:Zr = 4000:1, catalyst precursors **12** and **13** preactiviated with 1 mL of MAO for 10 min before injection. [b] Activity expressed as g polymer/[(mol Zr)[C_3] h]. [c] Determined by DSC. [d] [mmmm] pentad analysis by ^{13}C NMR at 80 °C in trichlorobenzene. [e] M_w determined by GPC.

Table 3. Polymerization of Propylene with 11−13/MAO in Liquid Pool Propylene[a]

catalyst precursor	temp (°C)	yield (g)	productivity 10^{-7} [b]	T_m (°C)	[mm] %	M_w/ 10^{-5} [c]	PDI
11	40	131	2.62	139	91	1.1	3.1
11	70	540	10.8	142	92	0.5	2.8
12	40	85	1.70	130	51	1.2	2.2
12	70	56	1.12	87	71	0.5	2.7
13	40	45	0.9	138	92	1.9	3.7
13	70	51	1.02	138	91	0.5	2.5

[a] Conditions: liquid pool propylene, time of polymerization = 1 h, [Zr] = 5 μM, Al:Zr = 15 000 mol:mol. [b] Productivity expressed as g polymer/[(mol Zr) h]. [c] M_w determined by GPC.

melting point (T_m) of 144 °C (Table 2). Higher T_p and changing the nature of the bridge from ethylene to dimethylsilylene gave no significant change in polymer properties.

In addition to the high isotacticities obtained, it can be seen that the molecular weights of the PP increased significantly for all three complexes compared to the 2,4,7-trimethylindenyl derivatives **2** and **3**.[9,10] Particularly the M_w of the samples obtained with the dimethylsilylene complexes **12** and **13** were high. Table 3 shows that the M_w for the PP from **13**/MAO at 40 °C was 1.9×10^5. Slightly lower values of 1.1×10^5 and 1.2×10^5 were obtained for **11** and **12**, respectively, at the same T_p. As expected, the M_w values decreased with higher T_p to 0.5×10^5. It is significant that the M_w of the PP obtained from **11**/MAO at 70 °C under liquid pool conditions (0.5×10^5) is almost double that obtained for the 2,4,7-trimethylindenyl derivative **2**/MAO under the same conditions (0.27×10^5). This result supports the theory that the 7-methyl group is detrimental to M_w presumably by creating a steric environment favorable to β-hydride elimination. A comparison by Resconi et al. of the polymerization behavior of ethylenebis(indenyl)zirconium dichloride and ethylenebis(4,7-dimethylindenyl)zirconium dichloride showed the former to produce much higher M_w PP than the latter.[15] In addition, the molecular weights of PP samples produced from several 2,4-disusbtituted bis(indenyl) metallocenes[3a] are much higher than for related 4,7-[15] and 2,4,7-bis(indenyl)[16] complexes.

Mechanism of Polymerization. We have previously discussed the relationship between catalyst geometry and the microstructure of the polypropylenes obtained under various polymerization conditions.[10] For C_1 symmetric catalysts, there are two distinct coordination sites available for propagation (Figure 1, sites A and B). We discussed a *return to initial configuration* (*ric*) mechanism to account for the polymers obtained from a series of substituted asymmetric zirconocenes.[5,7,8,10] In the case of C_2 or C_s symmetric metallocenes the two coordination sites are homotopic or enantiotopic, respectively, and the mechanism of propagation occurs by chain migratory insertion. In the case of C_1 complexes, the coordination sites are diastereotopic. The growing polymer chain can prefer to occupy the more open coordination site A

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Table 4. Pentad Distributions for Polypropylenes Produced in Table 2[a]

catalyst	temp[a]	mmmm	mmmr	rmmr	mmrr	mmrm+rmrr	mrmr	rrrr	mrrr	mrrm
11	20	93.5	3.5	0	3.0	0	0	0	0	0
11	70	89.0	5.5	0	5.5	0	0	0	0	0
12	20	42.4	18.5	0.3	23.6	2.5	0	2.3	3.6	6.7
12	70	83.8	6.7	0	7.8	0	0	0	0	1.7
13	20	90.5	5.6	0	3.94	0	0	0	0	0
13	70	88.9	3.91	0	6.14	0	0	0	0	1.0

[a] Pentad distributions expressed as %.

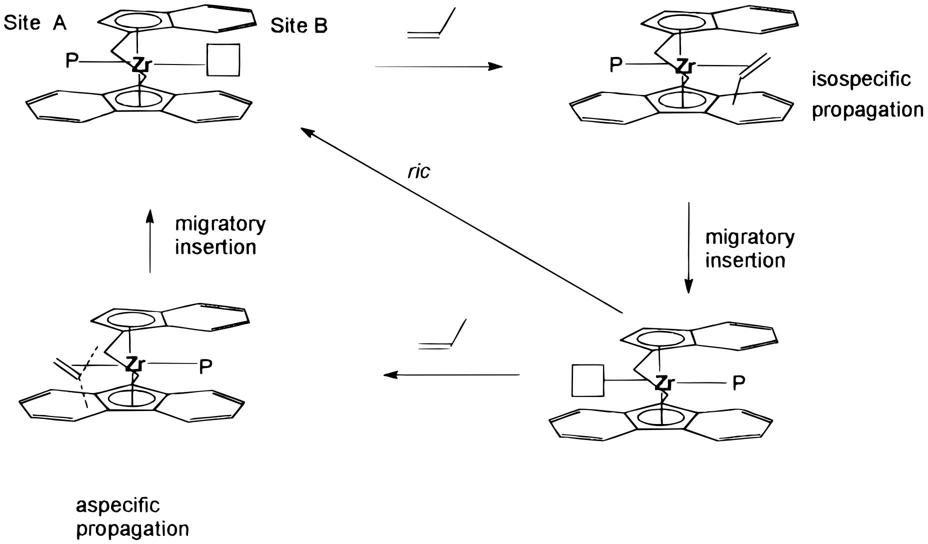

Figure 1. Schematic representation of the *return to initial configuration* mechanism for propylene polymerization by asymmetric indenyl−fluorenyl zirconocenes.

and can therefore return to that site following chain migration to B and before the next monomer inserts (Figure 1). As can be seen from Figure 1, monomer coordination at site B should be stereospecific, thus leading to isotactic PP. Furthermore, this mechanism accounts for the fact that isotacticity increases with increasing T_p, opposite of the trend observed for C_2 symmetric systems operating by a chain migratory insertion mechanism.[10,17] Recently, Rieger et al. proposed a similar mechanistic model to account for the polymerization behavior of a related but different series of asymmetric indenyl−fluorenyl systems.[18]

We proposed a *ric* mechanism in the case of **3** and believe it to also be the case for the new zirconocene **12**. The rate of *ric* increases at higher T_p, leading to more isotactic PP under those conditions. At lower T_p, the rate of *ric* competes with monomer coordination, and less stereoregular PP results. For both **3** and **12**, there is a significant increase in [mmmm] at high T_p compared to low T_p. For the previously reported ethylene-1-[-9-fluorenyl]-2-[-1-(2,4,7-trimethyl)indenyl]zirconium dichloride (**2**),[9] highly isotactic PP was obtained at both low and high T_p. In this case, [mmmm] pentad values decreased with increasing T_p from 89 to 79% at 20 and 70 °C, respectively, in a manner similar to that for C_2 symmetric systems operating by the chain migratory insertion mechanism.[19] We proposed that, in this case, due to the substitution pattern, both coordination sites are isospecific and that the complex is effectively pseudo C_2 symmetric.[10]

An alternative explanation of the high isotacticity of the polymer obtained with **2** would be to assume a chain stationary insertion mechanism similar to that proposed by Ewen et al.[2b] and Razavi et al.[8a] whereby steric hindrance prohibits the chain from occupying one coordination site during polymerization. However, in this case, isotacticity should not be affected by T_p, and in fact, Razavi reports negligible changes in [mmmm] over a 60 °C range in T_p for (η^5-C_5H_3-t-C_4H_9-CMe_2-η^5-$C_{13}H_8$)$ZrCl_2$.[8a] We therefore did not believe that such a mechanism was operating for **2**/MAO.

However, when one now studies the polymerization results for the new zirconocenes **11** and **13**, it can be seen that [mmmm] remains almost constant when T_p changes from 20 to 70 °C. Table 4 gives the full pentad distributions for all three complexes, and it can be seen that the stereoerrors for **11** and **13** are negligible. We believe in these cases that the sterically more demanding 4-phenyl substituent now makes coordination site B (Figure 2) inaccessible to the polymer chain, i.e., that the chain occupies only site A, and monomer coordination occurs stereoselectively at site B and inserts via a chain stationary insertion mechanism in the same manner proposed by Razavi et al.[8a]

Conclusions

We have developed a series of novel asymmetric ethylene- and dimethylsilylene-bridged 2,4-disubstituted indenyl−fluorenyl zirconocenes. When activiated by a cocatalyst, the complexes are highly efficient catalysts

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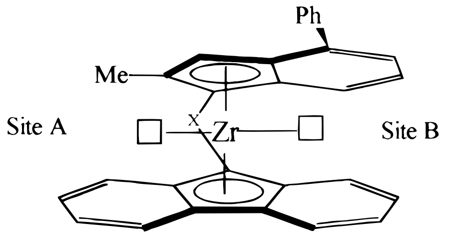

X = C_2H_4 or $SiMe_2$

Figure 2. Representation of the two coordination sites for complexes **11** and **13**.

for the Ziegler−Natta type polymerization of ethylene and propylene. In addition, the complexes polymerize propylene to stereoregular polypropylene. When the substituents are both methyl groups (**12**), the PP obtained is moderately isotactic at high T_p and slightly less stereoregular at lower T_p. This observation is accounted for by a *return to initial configuration* mechanism, whereby the polymer chain prefers to occupy the more open coordination site and returns to that site following chain migratory insertion and before the next monomer coordinates. This mechanism is faster at higher T_p, and therefore stereospecific propagation at one site prevails, leading to a more isotactic PP.

When the 4-substituent is a phenyl group (**11** and **13**), highly isotactic PP results under all polymerization conditions. We believe that in these cases the bulky phenyl group prohibits the polymer chain from occupying coordination site B, and therefore highly stereospecific propagation occurs exclusively at that site. The ethylene-bridged analogue **11** is more active than the dimethylsilylene-bridged analogue **13** for propylene polymerization, which we have previously shown to be the case for related systems. In all cases, the molecular weights of the PP samples are higher for **11-13**/MAO than when the indenyl moiety contains a 7-substituent. In fact for the dimethylsilylene-bridged zirconocenes **12** and **13**, high M_w PP is obtained (2×10^5). Further studies of related systems are in progress.

Experimental Section

General Procedures. Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) (10.69 wt % based on Al) 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. 2-Methyl-7-phenylindene (**5**)[3a] and 1-(9-fluorenyl)-2-bromoethane (**6**)[9] were synthesized according to literature procedures. ^{1}H NMR spectra were recorded on an AC-200 spectrometer. ^{13}C NMR spectra were recorded on an AMX500 spectrometer. Elemental analyses and mass spectra were recorded at the University of Massachusetts, Amherst, MA.

2,7-Dimethylindene (4). 2,7-Dimethylindene was prepared by modification of the literature procedure for the synthesis of 2-methyl-7-phenylindene.[3a] To 2.600 g (0.113 mol) of sodium in 50 mL of dry ethanol was added diethyl methylmalonate (20.00 g, 0.115 mol) followed by slow addition of 2-methylbenzyl bromide (21.80 g, 0.118 mol). The resulting white suspension was heated under reflux for 4 h. Water (60 mL) and potassium hydroxide (16.8 g, 0.29 mol) were added, and the mixture was heated under reflux for 4 h. After cooling to room temperature, the solvents were removed in vacuo and the residue was dissolved in 50 mL of water and acidified with concentrated HCl to pH = 1. The white precipitate was filtered and dried to give the diacid, which was heated for decarboxylation for 1 h at 130 °C to yield 18.2 g (90.9%) of 2-(2-methylbenzyl)propionic acid. The acid was reacted at room temperature overnight with 19.0 mL of thionyl chloride (0.26 mol). The excess thionyl chloride was removed under aspirator pressure. Dry toluene (30 mL) was added and removed in vacuo three times to remove any remaining thionyl chloride. The acid chloride was dissolved in 60 mL of dry toluene and added to $AlCl_3$ (15.2 g 0.11 mol) in 250 mL of dry toluene at 0 °C. The red solution was heated at reflux for 1 h and then cooled and poured onto ice. After acidification with concentrated HCl to pH = 1, the mixture was extracted with diethyl ether. The organic phases were collected, washed with saturated aqueous $NaHCO_3$ and then with a brine solution, dried ($MgSO_4$), and filtered, and the solvents were removed under vacuo. 2,4-Dimethyl-1-indanone (14.0 g, 87%) was characterized by ^{1}H NMR and used in the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 7.62−7.26 (m, 3 H, arom), 3.36−3.25 (m, 1 H), 2.80−2.54 (m, 2 H), 2.35 (s, 3 H, CH_3), 1.34−1.31 (d, 3 H, CH_3).

The ketone in 100 mL of dry diethyl ether was added dropwise to $LiAlH_4$ (3.30 g, 87.0 mmol) in 200 mL of dry diethyl ether and heated under reflux for 4 h. After slow hydrolysis with H_2O and a 10% HCl aqueous solution, the mixture was filtered. The organic phase was dried ($MgSO_4$) and filtered, and the solvent was removed under vacuum. The residue was dissolved in 250 mL of toluene, ca. 100 mg of *p*-toluenesulfonic acid was added, and the mixture was heated under reflux overnight. A Dean Stark apparatus was used to collect the water. The reaction mixture was hydrolyzed with a saturated aqueous solution of $NaHCO_3$, the organic layer was collected, dried ($MgSO_4$), and filtered, and the solvent was removed under vacuum. 2,7-Dimethylindene (**4**) (7.3 g, 45.0% overall) was distilled at 65−70 °C at 0.5 mmHg to give a colorless oil as a mixture of double-bond isomers. ^{1}H NMR ($CDCl_3$): δ 7.18−6.89 (m, 3 H, arom), 6.58−6.47 (m, 1 H, Ind-C_5-sp^2), 3.29 minor, 3.19 major (s, 2 H, Ind-sp^3), 2.39 minor, 2.33 major (s, 3 H, CH_3), 2.17−2.16 (d, 3 H, CH_3). Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.45; H, 8.64.

1-(9-Fluorenyl)-2-[1-(2,4-dimethyl)indenyl]ethane and 1-(9-Fluorenyl)-2-[1-(2,7-dimethyl)indenyl]ethane (7a and 7b). To a solution of 2,7-dimethylindene (**4**) (1.00 g, 6.93 mmol) in 20 mL of dry THF at 0 °C was added dropwise a 1.6 M solution of butyllithium in hexane (4.33 mL, 6.93 mmol). The solution was stirred at room temperature for 5 h and then added via cannula to a solution of 1-(9-fluorenyl)-2-bromoethane (**6**) (1.89 g, 6.93 mmol) in 20 mL of dry THF. The reaction mixture was stirred overnight at room temperature and then hydrolyzed with 50 mL of aqueous NH_4Cl. The organic phase was separated, and the aqueous layer was extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and filtered, and the solvents were removed under vacuum. The resulting yellow oil was crystallized from 100% ethanol to give **7a**,**b** as a white solid (1.05 g, 45.0%); mp 123−130 °C as a 1:1 mixture of structural isomers. ^{1}H NMR ($CDCl_3$): δ 7.77−6.83 (m, 11 H, arom), 6.56−6.44 (m, 1 H, Ind-C_5-sp^2), 3.87−3.85 (m, 1 H, Flu-C_5-sp^3), 3.14−3.07 (m, 1 H, Ind-C_5-sp^3), 2.38 (s, 1.5 H, CH_3), 2.06 (s, 1.5 H, CH_3), 1.93 (s, 1.5 H, CH_3), 1.86 (s, 1.5 H, CH_3), 1.74−1.27 (m, 4 H, bridge). Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.68; H, 7.12.

1-(9-Fluorenyl)-2-[3-(2-methyl-7-phenyl)indenyl]ethane (8). Following the procedure described for **7**, **5** (1.00 g, 4.85 mmol), 1.6 M butyllithium (3.03 mL, 4.85 mmol), and **6** (1.33 g, 4.85 mmol) gave **8** as a white solid, which was recrystallized from toluene/hexane (1:9) (1.13 g, 59%); mp125−127 °C. ^{1}H NMR ($CDCl_3$): δ 7.82−7.05 (m, 16 H, arom), 4.16−

4.10 (t, 1 H, Flu-C_5-sp^3), 3.23 (s, 2 H, Ind-C_5-sp^3), 2.43−2.12 (m, 4 H, bridge), 1.83 (s, 3 H, CH_3). Anal. Calcd for $C_{31}H_{26}$: C, 93.42; H, 6.58. Found: C, 93.46; H, 6.57.

(9-Fluorenyl)-1-[(2,4-dimethyl)indenyl]dimethylsilane (9). To a solution of 1.89 g (13.1 mmol) of **4** in 30 mL of dry diethyl ether at 0 °C was added dropwise a 1.6 M solution of butyllithium in hexane (8.20 mL, 13.1 mmol) The solution was stirred at room temperature for 5 h and then added dropwise via cannula to 3.17 mL (26.10 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 2.18 g (13.1 mmol) of fluorene and 8.20 mL (13.1 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 1:1 toluene/hexane to give 3.35 g of **9** (69%); mp 94−95 °C. ^{1}H NMR ($CDCl_3$): δ 7.90−7.00 (m, 11 H, arom), 6.71 (s, 1 H, Ind-C_5-sp^2), 4.24 (s, 1 H, Flu-C_5-sp^3), 3.75 (s, 1 H, Ind-C_5-sp^3), 2.45 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), −0.40 (s, 3 H, Si−CH_3), −0.43 (s, 3 H, Si−CH_3). Anal. Calcd for $C_{26}H_{26}Si$: C, 85.19; H, 7.15. Found: C, 85.48; H, 7.35.

(9-Fluorenyl)-1-[(2-methyl-4-phenyl)indenyl]dimethylsilane (10). Following the procedure described above, **5** (1.00 g, 4.85 mmol), 1.6 M butyllithium (3.03 mL, 4.85 mmol), dichlorodimethylsilane (1.18 mL, 9.70 mmol), and fluorene (0.80 g, 4.85 mmol) were reacted to give **10** (1.16 g, 56%) as a white solid, which was recrystallized from toluene/hexane; mp 152−155 °C. ^{1}H NMR ($CDCl_3$): δ 7.91−7.12 (m, 16 H, arom), 6.82 (s, 1 H, Ind-C_5-sp^2), 4.27 (s, 1 H, Flu-C_5-sp^3), 3.83 (s, 1 H, Ind-C_5-sp^3), 2.21 (s, 3 H, CH_3), −0.34 (s, 3 H, Si−CH_3), −0.39 (s, 3 H, Si−CH_3). Anal. Calcd for $C_{31}H_{28}Si$: C, 86.86; H, 6.58. Found: C, 86.63; H, 6.41.

Ethylene-1-(9-fluorenyl)-2-[1-(2-methyl-4-phenyl)indenyl]zirconium Dichloride (11). To a solution of **8** (1.00 g, 2.50 mmol) in 25 mL of dry diethyl ether at 0 °C was added dropwise 2 equiv of 1.6 M butyllithium in hexane (3.13 mL, 5.00 mmol). The resulting suspension was stirred for 6 h at room temperature. The solvent was removed under vacuum, and the residue was washed with 2 × 10 mL portions of dry pentane. The yellow solid was suspended in 20 mL of dry diethyl ether and cooled to 0 °C. $ZrCl_4$ (0.58 g, 2.50 mmol) was added as a solid. The orange suspension was stirred overnight at room temperature, and the solvent was removed by filtration. The residue was extracted in dry methylene chloride, concentrated, and stored at − 20 °C to give **11** (340 mg, 24.3%) as an orange solid. ^{1}H NMR ($CDCl_3$): δ 7.95−7.05 (m, 16 H, arom), 6.36 (s, 1 H, Ind-C_5), 5.30 (s, 1 H, CH_2Cl_2), 4.69−3.85 (m, 4 H, bridge), 2.21 (s, 3 H, CH_3). Anal. Calcd for $C_{31}H_{24}Cl_2Zr\cdot 0.5CH_2Cl_2$: C, 62.94; H, 4.19. Found: C, 63.23; H, 4.24. HRMS (EI) *m/z* for $C_{31}H_{24}Cl_2Zr$: calcd 556.0302; found 556.0262.

Dimethylsilylene-(9-fluorenyl)-[1-(2,4-dimethyl)indenyl]zirconium Dichloride (12). Following the procedure described for **11**, **9** (1.00 g, 2.73 mmol), 1.6 M butyllithium in hexane (3.41 mL, 5.46 mmol), and $ZrCl_4$ (0.64 g, 2.73 mmol) gave **12** (225 mg, 15.6%) as an orange/red solid. ^{1}H NMR ($CDCl_3$): δ 7.96−6.73 (m, 11 H, arom), 6.62 (s, 1 H, Ind-C_5), 5.30 (s, 0.6 H, CH_2Cl_2), 2.28 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 1.54 (s, 3 H, Si−CH_3), 1.43 (s, 3 H, Si−CH_3). Anal. Calcd for $C_{26}H_{24}Cl_2SiZr\cdot 0.3CH_2Cl_2$: C, 57.21; H, 4.49. Found: C, 57.28; H, 4.30.

Dimethylsilylene-(9-fluorenyl)-[1-(2-methyl-4-phenyl)indenyl]zirconium Dichloride (13). Following the procedure described for **11**, **10** (0.59 g, 1.38 mmol), 1.6 M butyllithium (1.73 mL, 2.76 mmol), and $ZrCl_4$ (0.32 g, 1.38 mmol) gave **13** (210 mg, 26.0%) as an orange/red solid. ^{1}H NMR ($CDCl_3$): δ 7.91−6.85 (m, 16 H, arom), 6.75 (s, 1 H, Ind-C_5), 5.30 (s, 2 H, CH_2Cl_2), 2.26 (s, 3 H, CH_3), 1.58 (s, 3 H, Si−CH_3), 1.44 (s, 3 H, Si−CH_3). Anal. Calcd for $C_{31}H_{26}Cl_2SiZr\cdot 1.0CH_2Cl_2$: C, 57.05; H, 4.18. Found: C, 57.12; H, 4.12. HRMS (EI) *m/z* for $C_{31}H_{26}Cl_2SiZr$: calcd 586.0228; found 586.0245.

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.[20] 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 **12** and **13**, 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 $C_6H_3Cl_3$ with C_6D_6 on an AMX 500 spectrometer. Molecular weights were determined by Gel Permeation Chromatography using a Waters 150C instrument (solution in 1,2,4-trichlorobenzene at 135 °C and PS standards for calibration.

Acknowledgment. We would like to thank Dr. G. Dabkowski for microanalyses, Dr. L. C Dickinson for help with ^{13}C NMR, and Dr. I. Kaltashov for mass spectra. We would also like to thank SOLVAY Polyolefins Europe−Belgium for obtaining the liquid pool polymerization results and for their financial support of this research program.

OM000256D

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(20) Monomer concentration as a function of pressure is calculated as follows: monomer concentration = [1 + (pressure/14.67 − *P*)]*S*, where *P* = vapor pressure of toluene at a given temperature and *S* = solubility of monomer in toluene at a given temperature.