Macromolecules

Volume 28, Number 16 July 31, 1995

C_{2v}- and C_2-Symmetric *ansa*-Bis(fluorenyl)zirconocene Catalysts: Synthesis and α-Olefin Polymerization Catalysis

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Received September 19, 1994; Revised Manuscript Received May 9, 1995[®]

ABSTRACT: C_{2v}-symmetric ethylenebis(9-fluorenyl)zirconium dichloride (**1**) and its C_2-symmetric bis-[9-(1-methyl)fluorenyl] derivative (**2**) have been synthesized in good yields using a convenient synthetic route. Precursor **1** activated with triphenylcarbenium tetrakis(pentafluorophenyl)borate (**3**) catalyzes propylene polymerization with a constant activity of $(6.28 \pm 1.63) \times 10^7$ g of PP/((mol of Zr)·[C_3H_6]·h) between −20 and +70 °C. The polypropylene is ideally atactic and has the same $\bar{M}_W$ of $(6.03 \pm 1.19) \times 10^5$. The above system catalyzes ethylene polymerization with a maximum activity of 1.4×10^{10} g of PE/((mol of Zr)·[C_2H_4]·h) at −20 °C which decreases exponentially with an increase of T_p. All the polyethylenes produced between −20 and +50 °C have the same $\bar{M}_W$ of $(5.57 \pm 0.49) \times 10^5$. In contrast, precursor **2** catalyzed the formation of anisotactic polypropylene of low stereoregularity. Molecular mechanics calculations indicated that substituents on the fluorenyl rings have little effect on both diastereomeric ratios in the synthesis and stereoselectivities in the polymerization.

Introduction

The synthesis of ethylene-bridged metallocene compounds[1] and the discovery of isospecific polymerizations of α-olefins by chiral metallocenes[2] opened up new horizons for Ziegler–Natta catalysis. It is understandable that most of the research efforts have been focused on metallocene precursors which can be transformed to isospecific[3] or syndiospecific[4] polymerization catalysts. Nonbridged C_{2v}-symmetric and *meso–ansa* metallocenes are devoid of stereoselectivity and have poor catalytic activity as exemplified by Cp_2ZrCl_2[5] and *meso*-ethylenebis(tetrahydroindenyl)zirconium dichloride.[6] These complexes when activated with methyl aluminoxane (MAO) produced atactic polypropylene (*a*-PP) at ambient temperature of polymerization (T_p) with molecular weight ($\bar{M}_W$) of only about 2000[7] and at activities of *ca.* 10^5 g of PP/((mol of Zr)·[C_3H_6]·h). When the free rotation of ligand frameworks is restrained, a nonbridged metallocene catalyst can exhibit stereoselectivity at low T_p attributable to the preferential existence of chiral rotamers.[8] Furthermore, nonbridged bis(1-methylfluorenyl)zirconium dichloride catalyzed the isospecific propylene polymerization at conventional polymerization temperatures.[9] One purpose of this study is to investigate the effect of bridging of the hapto ligands on the polymerization behavior of these precursors. In the C_{2v}-symmetric case, we have synthesized ethylenebis(9-fluorenyl)zirconium dichloride (**1**) for the investigation. To compare with nonbridged bis(1-methylfluorenyl)zirconium dichloride, we have synthesized ethylenebis[9-(1-methyl)fluorenyl]zirconium dichloride (**2**). The polymerization behaviors of **1** and **2** showed pronounced influence of the rigidly held bulky and electron-donating ligands on the olefin π-complexation, migratory insertion, and β-hydride elimination processes.

After this program was completed and the manuscript had been submitted, there appeared two reports on complex **1**. Alt et al.[10a] described the synthesis of **1** with a procedure similar to ours and reported its utility in the polymerization of ethylene using MAO as cocatalyst. Resconi et al.[10b] polymerized propylene with **1**/MAO at one temperature. In our study, both MAO and triisobutylaluminum (TIBA)/**3** were employed as cocatalyst to catalyze ethylene as well as propylene polymerization from −20 to +70 °C. Complex **2** is a new compound; its synthesis and polymerization catalysis are reported for the first time.

Experimental Section

All reactions were carried out using Schlenk or glovebox techniques under an argon atmosphere. Solvents were dried over a Na/K alloy or CaH_2 (CH_2Cl_2) and distilled under argon prior to use. Routine ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer at ambient temperature; chemi-

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[®] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

cal shifts are referenced with respect to TMS. ^{13}C NMR spectra of the polymer products were measured on a Bruker AMX-500 spectrometer (125.77 MHz) in $C_2D_2Cl_4$ at 110 °C. Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst. Melting points were uncorrected.

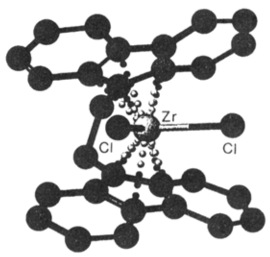
Triphenylcarbenium tetrakis(pentafluorophenyl)borate [$Ph_3CB(C_6F_5)_4$] (**3**) was prepared according to literature procedures.[11] Methylaluminoxane (MAO) was obtained from Akzo Chemicals. Ethylene and propylene were purchased from Mariam Graves and purified by passing through two Matheson Gas Purifiers (Model 6404). Unless otherwise indicated, all other chemicals were obtained from Aldrich.

Ethylenebis(9-fluorenyl)zirconium Dichloride (1). 9-Fluorenyllithium (3.62 g, 21.0 mmol) and 150 mL of hexane were placed in a 250-mL Schlenk flask, followed by the addition of 1,2-dibromoethane (0.86 mL, 1.88 g, 10.0 mmol) at room temperature. The reaction mixture was then heated at reflux with stirring for 24 h. The resulting mixture was filtered through Celite and washed with two 30-mL portions of hexane. The remaining solid was washed again with two 50-mL portions of methylene chloride, and the filtrate was collected in another flask. The solvent of the combined methylene chloride washings was removed, and the residue was rinsed with pentane and dried to produce 3.09 g (82.1%) of 1,2-di-9-fluorenylethane as a faint yellow solid. Mp: 223–225 °C (lit.[12a] mp 226 °C, 1.88%; 56.0%[12b]). ^{1}H NMR ($CDCl_3$): δ 7.76 (d, J = 7.16 Hz, 4 H, aromatic H), 7.40–7.29 (m, 12 H, aromatic H), 3.85 (br s, 2 H, H-9), 1.74 (m, 4 H, $-CH_2CH_2-$). To a solution of the above ligand (0.64 g, 1.78 mmol) in 20 mL of THF was added dropwise at room temperature 2 equiv of methyllithium in diethyl ether (2.54 mL, 1.40 M in diethyl ether, 3.56 mmol). The resulting red solution was stirred for an additional 4 h, the solvents were then removed under vacuum, and the residue was dried under high vacuum overnight. The solid was washed with pentane to give the dilithiated compound as an orange powder in quantitative yield. The powder was used for the next reaction without further purification.

The above dry dilithio salt was mixed with $ZrCl_4$ (0.41 g, 1.78 mmol) followed by the addition of 50 mL of dry pentane. The resulting suspension was stirred at room temperature overnight, the pentane was decanted, and the remaining solid was extracted with methylene chloride. The resulting red suspension was filtered through a Celite plug to remove LiCl. Cooling the filtrate at −20 °C for 1 week gave 0.59 g (total yield of 64.1%, including the second crop) of complex **1** as red crystals. Mp: 178 °C (dec). Anal. Calcd for $C_{28}H_{20}Cl_2Zr$ (518.59): C, 64.85; H, 3.89. Found: C, 64.43; H, 4.09. ^{1}H NMR (CD_2Cl_2): δ 7.83 (d, J = 8.67 Hz, 4 H, aromatic H), 7.74 (d, J = 8.67 Hz, 4 H, aromatic H), 7.29 (m, 4 H, aromatic H), 7.17 (m, 4 H, aromatic H), 4.49 (s, 4 H, $-CH_2CH_2-$).

***rac*- and *meso*-Ethylenebis[9-(1-methyl)fluorenyl]zirconium Dichloride (2).** A diastereomeric mixture of 1,2-bis[9-(1-methyl)fluorenyl]ethane was synthesized from the reaction of 1-methylfluorenyllithium and 1,2-dibromoethane in hexane according to the synthesis of 1,2-di-9-fluorenylethane as white crystals after the recrystallization from methylene chloride and hexane at −20 °C. Mp: 292–292.5 °C. Anal. Calcd for $C_{30}H_{26}$ (386.54): C, 93.22; H, 6.78. Found: C, 92.98; H, 6.75. ^{1}H NMR ($CDCl_3$): δ 7.72 (d, J = 7.16 Hz, 2 H, aromatic H), 7.57 (m, 2 H, aromatic H), 7.35–7.19 (m, 8 H, aromatic H), 7.02 (m, 2 H, aromatic H), 3.83 (br s, 2 H, H-9), 2.02 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.57–1.40 (m, 4 H, $-CH_2CH_2-$).

The above ligand, methyllithium, and $ZrCl_4$ were reacted as described above for the synthesis of complex **1**, affording a mixture of *rac* and *meso* (*rac*/*meso* ~ 1:1) diastereomers of **2** (15.7%) as a red crystalline solid. ^{1}H NMR (CD_2Cl_2): δ 8.09–6.85 (m, 28 H, *rac* + *meso*, aromatic H), 4.76 (m, 2 H, *meso*-CH_2-), 4.54 (m, 4 H, *rac*-CH_2CH_2-), 4.28 (m, 2 H, *meso*-CH_2-), 2.93 (s, 6 H, *rac*-CH_3), 2.86 (s, 6 H, *meso*-CH_3). Purification attempts failed to separate these two diastereomers, and the diastereomeric mixture was therefore used for the polymerizations directly.



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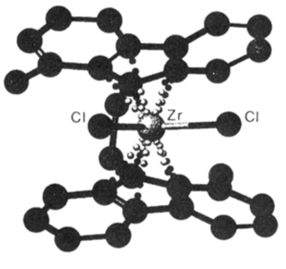
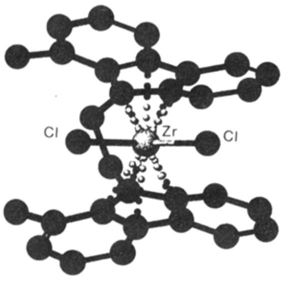


rac-**2**



meso-**2**

Polymerization. Polymerizations were carried out in a 250-mL crown-capped glass pressure reactor with a magnetic stirring bar. The system was first evacuated and flushed with argon, and 50 mL of toluene was injected. The system was evacuated again and saturated with the appropriate monomers for *ca.* 20 min. The order of addition of reagents and detailed procedures for polymerizations have been described previously.[11a,13] The polymerization mixture was quenched with acidic methanol (containing 1% HCl), filtered, washed with methanol, and dried at 70 °C to a constant weight.

The values of activity (A) were calculated using the measured solubility of propylene and ethylene.[14] Intrinsic viscosities of polyethylene and polypropylene were measured in decalin at 135 °C using a Ubbelohde viscometer, and melting temperatures were measured by differential scanning calorimetry (Perkin-Elmer DSC 4). Stereo- and regioregularities of the polymers obtained were determined by ^{13}C NMR spectroscopy and analyzed by known methods.[2b,13a,15]

Results and Discussion

Polymerization of Propylene by the C_{2v}-Symmetric Complex 1. Propylene was polymerized by zirconocenium species ($\mathbf{1}^+$) formed in situ by the reaction of **1**, TIBA, and **3**[11,13b,c] in runs 1–4 of Table 1. The results are rather unusual. The propylene polymerization activity (A_p) between −20 and +70 °C has the constant value of (6.28 ± 1.63) × 10^7 g of PP/((mol of Zr)·[C_3H_6]·h). All other catalysts studied by us[13,16] showed variation of A with T_p in the same manner or other. Even more striking is the independence of $\bar{M}_w$ of *a*-PP found in these experiments on T_p. The MW of polyethylene (PE) or PP produced by other metallocene catalysts invariably *decreases* significantly with an increase of T_p. In the present case, $\mathbf{1}^+$ produced *a*-PP having the same $\bar{M}_W$ of $(6.03 \pm 1.19) \times 10^5$ ($-20\ °C < T_p < +40\ °C$). Furthermore, no previous catalysts had been able to produce *a*-PP of such high MW. These results showed that the activation parameter is *ca.* 0 kcal/mol for A_p and for $\bar{M}_W$.

It is generally accepted that the propagation process in Ziegler–Natta catalysis involves the formation of an olefin π-complex with equilibrium constant K_π followed by migratory insertion with rate constant k_1. In the case of a "naked" cation, we can write this process

Table 1. Results of Polymerizations Catalyzed with 1[a]

run no.	M^b	T_p (°C)	[Zr] (μM)	cocat.	[Al] (mM)	time (min)	yield (g)	$A^e \times 10^{-6}$	T_m (°C)	$\bar{M}_w{}^f \times 10^{-5}$
1	P	−20	25	**3**[c]	2.0[d]	2.5	3.44	70.1		6.10
2	P	0	25	**3**[c]	1.5[d]	5	4.55	57.7		6.84
3	P	40	25	**3**[c]	1.0[d]	10	3.85	52.1		5.15
4	P	70	25	**3**[c]	0.6[d]	15	1.60	71.3		2.98
5	P	0	50	MAO	90	60	0.25	0.13		5.08
6	P	50	50	MAO	80	60	2.49	3.88		2.26
7	P	70	50	MAO	80	40	1.32	11.0		2.77
8	E	−20	2.5	**3**[c]	2.0[d]	1/12	0.98	13900	140	5.70
9	E	0	2.5	**3**[c]	1.5[d]	1/6	0.65	5120	139	5.88
10	E	25	2.5	**3**[c]	1.0[d]	1/2	0.45	1470	141	5.22
11	E	50	2.5	**3**[c]	0.8[d]	1	0.39	827	139	5.50
12	E	70	2.5	**3**[c]	0.6[d]	5	0.41	238	140	3.74
13	E	0	10	MAO	80	30	0.04	0.45	137	4.93
14	E	25	10	MAO	69	15	0.71	19.3	138	4.45
15	E	50	10	MAO	60	5	0.57	60.4	139	2.77
16	E	70	10	MAO	60	5	0.85	123	138	2.67

[a] Conditions: toluene, 50 mL; monomer pressure = 10 psig. [b] Monomers: P = propylene, E = ethylene. [c] [**3**] = [Zr]. [d] Amount of TIBA. [e] *A* in units of g of polymer/((mol of Zr)·[monomer]·h). [f] $\bar{M}_w$ by viscosity.

simply as:

$$Zr^+{-}P_n + C_3H_6 \overset{K_\pi}{\rightleftharpoons} C_3H_6{\cdot}Zr^+{-}P_n \tag{1}$$

$$C_3H_6{\cdot}Zr^+{-}P_n \xrightarrow{k_1} Zr^+{-}P_{n+1} \tag{2}$$

The rate of polymerization is

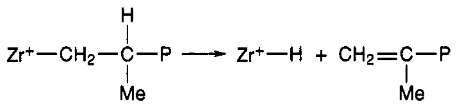
$$-d[C_3H_6]/dt = K_\pi k_1[Zr^+{-}P_n][C_3H_6] \tag{3}$$

The activation energy for propagation (ΔE_p) is

$$\Delta E_p = \Delta H_\pi + \Delta E_1 \tag{4}$$

Since $\Delta E_p \sim 0$ kcal/mol (*vide supra*), ΔH_π is approximately equal to $-\Delta E_1$ of migratory insertion. ΔE_1 is small and positive for organic cationic polymerizations. If ΔE_1 is also small and positive for **1**$^+$, then ΔH_π is small and negative for the $(C_3H_6){\cdot}$**1**$^+$ complex.

The $\bar{M}_W$ (weight-average molecular weight) is about equal to $2\bar{M}_n$ (number-average molecular weight), and $\bar{M}_n = 42\overline{DP}_n$ (number-average degree of polymerization). Since the chain-limiting process is predominantly that of β-hydride elimination, i.e.



$$Zr^+{-}CH_2{-}\underset{Me}{\overset{H}{C}}{-}P \longrightarrow Zr^+{-}H + CH_2{=}\underset{Me}{C}{-}P \tag{5}$$

then we have

$$\overline{DP}_n = \bar{M}_W/84 = R_p/R_{tr} = K_\pi k_1[Zr^+{-}P_n][C_3H_6]/k_{tr}[Zr^+{-}P_n] = K_\pi k_1[C_3H_6]/k_{tr} \tag{6}$$

where R_p represents the rate of propagation, R_{tr} represents the rate of the chain transfer process, and k_{tr} represents the rate constant of chain transfer. The temperature dependence of $\bar{M}_W$ is then

$$\Delta E\bar{M}_w = \Delta H_\pi + \Delta E_1 + \Delta H_S - \Delta E_{tr} \tag{7}$$

ΔH_S is the heat of solution of propylene, which is only −0.5 kcal/mol (−20 °C < T_p < +40 °C). Since $\Delta H_\pi \sim -\Delta E_1$, then $\Delta H_S \sim \Delta E_{tr}$ for this system. Therefore, the β-hydride elimination process (eq 5) for **1**$^+$ is entropically controlled. At high T_p, i.e., 70 °C and above, other chain-terminating processes can occur to lower the polymer MW.

From the A_p value given above, we can estimate a value of $K_\pi k_1 \approx 415$ (M s)$^{-1}$. Previously, Chien and Sugimoto[13d] had determined the $K_\pi k_1$ values for the formation of stereoirregular PP and stereoregular PP catalyzed by ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride/MAO. The former has values of 80−275 (M s)$^{-1}$, and this is comparable to the present catalyst. The latter has much greater values of 1400−2600 (M s)$^{-1}$.

The propylene polymerization activity of the **1**/MAO system (runs 5−7) is much lower than that of **1**$^+$. At T_p = 0 °C, A_p(**1**/MAO) = $^1/_{440}A_p$(**1**$^+$), and it is $^1/_{6.5}$ of A_p(**1**$^+$) at 70 °C. The activation energy for A_p obtained from an Arrhenius plot of runs 5−7 is about 11.8 kcal/mol. We have suggested previously that the lower *A* of the MAO-activated system is due to the fact that in the presence of MAO, **1**$^+$ is complexed with either MAO or MAO$^-$. These associated species are much less active than the naked **1**$^+$, i.e., essentially dormant. The addition of MAO to a polymerization catalyzed by zirconocenium ion causes a large drop of the activity.[13c] Therefore, in order for polymerization to occur in the **1**/MAO system, predissociation of this complexation is necessary. In other words, eqs 1 and 2 are preceded by

$$MAO{\cdot}Zr^+{-}P_n \overset{K_D}{\rightleftharpoons} Zr^+{-}P_n + MAO \tag{8}$$

Assuming that all the Zr precursor became catalytically active[14] and MAO is present in large excess, then eq 3 can be written as

$$-d[C_3H_6]/dt = K_D K_\pi k_1[Zr]_0 \tag{9}$$

The activation parameter is now

$$\Delta E_p = \Delta H_\pi + \Delta H_D + \Delta E_1 \tag{10}$$

The results of runs 5−7 indicate a value of 11.8 kcal/mol for ΔE_p, which is the enthalpy of dissociation of the Zr$^+$·MAO complex since $\Delta H_\pi \sim -\Delta E_1$.

The $\bar{M}_W$s of polypropylene produced by **1**/MAO and **1**$^+$ are nearly the same at T_p = 0 and 70 °C. This phenomenon is observed for nearly all the metallocenes we have investigated comparing the two types of activation.[18] It means that the catalytic species in **1**/MAO has

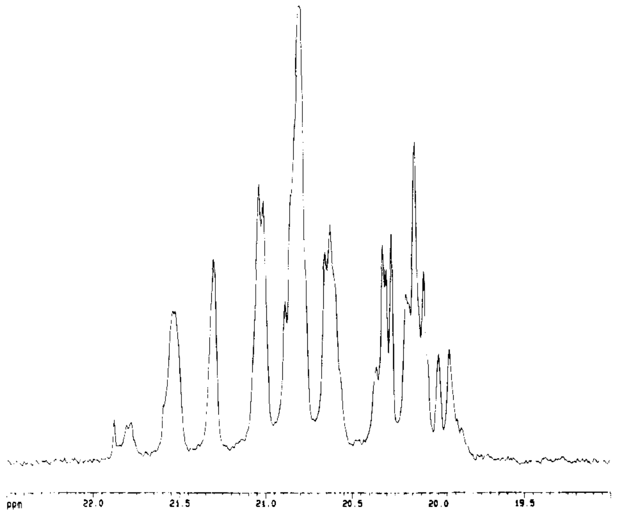


Figure 1. Typical ^{13}C NMR spectrum of the methyl pentad regions of the atactic polypropylene obtained with **1**.

the same $K_{\pi}k_1$ and k_{tr} as $\mathbf{1}^+$, which supports the hypothesis that it is the free $Zr^+—P_n$ without complexed MAO.

Polypropylenes obtained with either catalytic system at all T_p are completely stereorandom as expected (see Figure 1). Table 2 summarizes the methyl pentad distributions of polypropylenes produced. The heterotactic triad population is $[mr] = \sim 0.50$ for perfectly random statistics. With a C_{2v}-symmetric structure, the active species of the catalyst **1** cannot discriminate between the two enantiofaces of the prochiral propylene, thus resulting in the formation of a totally random microstructure. However, unlike other nonbridged C_{2v} catalysts, which can produce anisotactic polypropylene with a slight preference for *meso* insertion at low T_p,[2b] the present catalytic system is devoid of stereoselectivity over the −20 to +70 °C T_p range because there is no fluxional movement.

The $\bar{M}_W$ of *a*-PP in this study is several hundred times greater than that produced by Cp_2ZrCl_2[5] and *meso*-$Et(THID)_2ZrCl_2$[6] and 10−30 times higher than racemic *ansa*-zirconocene systems at elevated T_p.[16] The unusually high $\bar{M}_W$ of the atactic polypropylene indicates a slow rate for the reaction 5. The value of $\bar{M}_W$ corresponds to $\overline{DP}_n \sim 7 \times 10^3$ and thus a k_{tr} value of $5.9 \times 10^{-2}\ s^{-1}$. Two contributing factors can be suggested. The first is the stronger electron donation of fluorenyl-containing ligands compared to their indenyl and cyclopentadienyl counterparts. This fact can cause the zirconium center to have reduced electrophilicity and thus a lower rate of β-hydride elimination. Second, the two fluorenyl rings bridged by the $-C_2H_4-$ moiety have a small hinge angle and a large steric hindrance which make it unfavorable to form the transition state for reaction 5. Of course, there is probably another chain-limiting process which is with a monomer.[3a] The above-mentioned steric hindrance will also make this process unfavorable.

The polymerization of ethylene by $\mathbf{1}^+$ (runs 8−12) differs markedly from the propylene polymerization (runs 1−4). Instead of the temperature-independent activity observed for the propylene polymerization, the ethylene polymerization has an activity which *decreases* significantly with *increasing* T_p. The activity was 1.39×10^{10} g of PE/((mol of Zr)·[C_2H_4]·h) (run 8) at T_p of −20 °C; it was 60-fold slower at +70 °C. The Arrhenius plot (Figure 2) gave $\Delta E_p \cong -7.4$ kcal/mol. According to eq 4, $\Delta E_p = \Delta H_{\pi} + \Delta E_1 = -7.4$ kcal/mol for ethylene polymerization but ~0 for propylene polymerization. This difference may be attributable to a lower stability of the $PZr^+{\cdot}C_2H_4$ complex than $PZr^+{\cdot}C_3H_6$ and to a smaller activation energy for migratory insertion of ethylene than propylene.

It is remarkable that the polyethylene produced by $\mathbf{1}^+$ has the same $\bar{M}_W$ of $(5.57 \pm 0.49) \times 10^5$ between −20 °C < T_p < +50 °C. Equation 7 and the discussion following it apply here as well. As in propylene polymerization, the $\bar{M}_W$ of polyethylene also declines at T_p of 70 °C for a similar reason.

The polyethylenes obtained at the same T_p with **1**/MAO (runs 13−16) are comparable to those produced with $\mathbf{1}^+$. The activities of the former are again very low compared to the latter by factors of 1.1×10^4 and 2 at $T_p = 0$ and 70 °C, respectively. Figure 3 is an Arrhenius plot of log activity versus T_p^{-1} for ethylene polymerization catalyzed by **1**/MAO. According to eq 10, this plot suggests a value of about 14.6 kcal/mol for the enthalpy of dissociation of the $Zr^+{\cdot}MAO$ complex.

Polymerization Behavior of the Complex 2. A mixture of equal amounts of *rac* and *meso* diastereomers obtained directly from the synthesis was used for the polymerization. Since the chirality has no effect on ethylene polymerization,[3c] we first performed an ethylene polymerization (Table 3, run 17) using $\mathbf{2}^+$. Both the activity and $\bar{M}_W$ are about one-third of those produced by $\mathbf{1}^+$, which could be attributed to the steric effect of the methyl substituent of fluorenyl rings on the rate of propagation.

Generally speaking, bridged metallocene catalysts have higher stereoselectivities than their unbridged counterparts. Since the nonbridged compound bis(1-methylfluorenyl)zirconium dichloride was found to catalyze the isospecific propylene polymerization at conventional polymerization temperatures,[9] we expected that the bridged analog **2** would show greater isospecificity. Also for C_2-symmetric *ansa*-zirconocene complexes, the stereoselectivities are markedly higher for ligands providing more steric constraints.[3b] Therefore, one might expect **2** to be more isospecific than *rac*-ethylenebis(1-indenyl)zirconium dichloride.

The results of propylene polymerization catalyzed by $\mathbf{2}^+$ (runs 18−20) showed a drop in A_p as in the ethylene polymerization and also a very large decrease of $\bar{M}_W$ as compared with those by $\mathbf{1}^+$. The result indicates that factors in addition to the steric effect of the two methyl groups may be important. The presence of the *meso* isomer in the mixture used for the polymerization is one factor. A *meso* isomer is known to produce atactic PP and exhibit much lower activity for the propylene polymerization.[6] We fractionated the whole polymer from the product of run 18 (PP-18). There was no acetone-soluble material, but 27.5 wt % of the polymer was extracted by refluxing diethyl ether. The *a*-PP produced by **1** is also insoluble in refluxing acetone and completely soluble in refluxing diethyl ether. The ^{13}C NMR spectrum of the diethyl ether soluble fraction from PP-18, given in Figure 4, has the methyl pentad distributions $[mmmm] = 0.52_1$, $[mmmr] = 0.12_8$, $[rmmr] = 0.02_6$, $[mmrr] = 0.14_6$, $[mrmm] + [rmrr] = 0.05_6$, $[mrmr] = 0.02_4$, $[rrrr] = 0.01_8$, $[mrrr] = 0.03_4$, and $[mrrm] = 0.04_7$ and the triad population of $[mm] = 0.67_5$, $[mr] = 0.22_6$, and $[rr] = 0.09_9$. The polymer which remained after diethyl ether extraction of PP-18 is more isotactic with triad distributions of $[mm] = 0.81_3$, $[mr] = 0.15_1$, and $[rr] = 0.03_6$. The corresponding ^{13}C NMR

Table 2. Methyl Pentad Distributions of Polypropylene

sample[a]	21.8 *mmmm*	21.5 *mmmr*	21.3 *rmmr*	21.0 *mmrr*	20.8 *mrmm* *rmrr*	20.6 *mrmr*	20.3 *rrr*	20.1 *mrrr*	19.8 *mrrm*
A	0.03_1	0.08_6	0.07_4	0.13_9	0.25_2	0.11_6	0.11_2	0.14_1	0.04_9
B	0.02_2	0.07_5	0.06_6	0.12_6	0.25_1	0.13_1	0.10_9	0.15_6	0.06_3
C	0.03_9	0.10_7	0.08_8	0.15_1	0.23_3	0.11_7	0.09_4	0.11_3	0.05_5
D	0.02_8	0.08_1	0.06_8	0.13_0	0.26_7	0.12_9	0.09_1	0.14_7	0.05_9

[a] A: PP prepared with $\mathbf{1}^+$ at 0 °C, $mr = 0.50_7$. B: PP prepared with $\mathbf{1}^+$ at 40 °C, mr = 0.50_8. C: PP prepared with **1**/MAO at 0 °C, mr = 0.50_1. D: PP prepared with **1**/MAO at 50 °C, mr = 0.52_6.

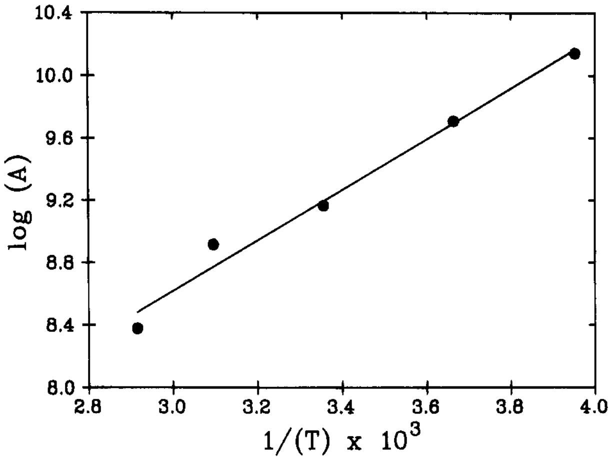


Figure 2. Variation of log activity of ethylene polymerization with T_p^{-1} catalyzed with $\mathbf{1}^+$.

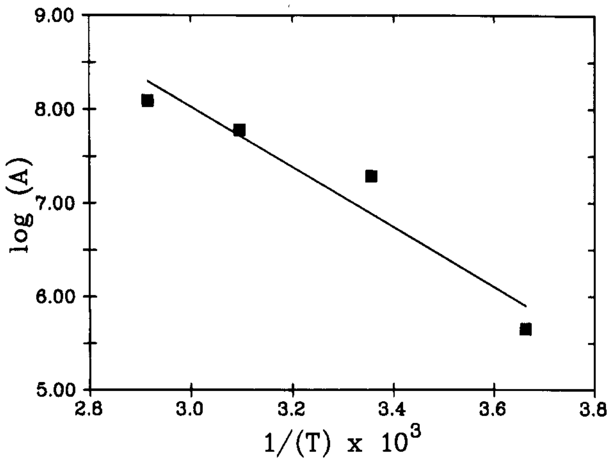


Figure 3. Variation of log activity of ethylene polymerization with T_p^{-1} catalyzed with **1**/MAO.

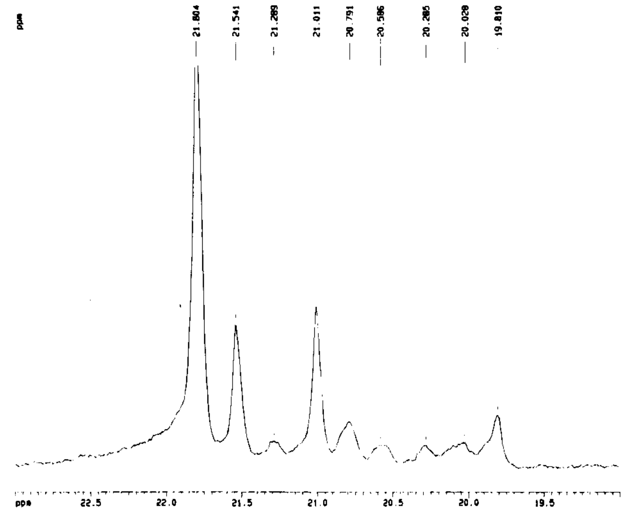


Figure 4. ^{13}C NMR spectrum of the methyl pentad regions of the polymer of a diethyl ether soluble fraction from run 18.

Table 3. Ethylene and Propylene Polymerizations Catalyzed with 2/TIBA/3[a]

run no.	monomer	T_p (°C)	[Zr] (μM)	[TIBA] (mM)	time (min)	yield (g)	$A^b \times 10^{-6}$	$\bar{M}_w{}^c \times 10^{-4}$
17	C_2H_4	50	2.5	0.8	5	0.76	322	13.0
18	C_3H_6	0	25	1.5	5	2.79	35.8	24.5
19	C_3H_6	25	25	1.0	10	2.65	25.3	9.68
20	C_3H_6	50	25	0.8	15	0.95	11.8	3.82

[a] Conditions: toluene, 50 mL; $P(C_2H_4)$ = 10 psig; $P(C_3H_6)$ = 10 psig. [b] *A* in units of g of polymer/((mol of Zr)·[monomer]·h). [c] $\bar{M}_w$ by viscosity.

methyl pentad distributions are [*mmmm*] = 0.67_9, [*mmmr*] = 0.12_6, [*rmmr*] = 0.00_8, [*mmrr*] = 0.12_9, [*mrmm*] + [*rmrr*] = 0.01_4, [*mrmr*] = 0.00_8, [*rrrr*] = 0.00_8, [*mrrr*] = 0.00_2 and [*mrmm*] = 0.02_6. Therefore, the polypropylene is less stereoregular and the catalyst $\mathbf{2}^+$ is less stereoselective than expected (*vide supra*). The polymers do not crystallize as indicated by the absence of any melting endotherm with DSC.

The lower stereoselectivity of **2** than the well-known precursors *rac*-ethylenebis(1-indenyl)zirconium dichloride (**4**) and *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**5**) is to be expected. In the latter instances, the six-membered ring of the indenyl group discriminates one prochiral face of propylene over the other. On the other hand, there are six-membered rings on both sides of the η^5-system in either fluorenyl moiety. The introduction of methyl groups on the 1-position of Flu has only a slight nonbonded interaction effect on the orientation of the incoming monomer, whereas the antistereoselective influence of the aromatic system of Flu remained. The differences are quantifiable in terms of the steric energy difference between *meso* and *racemic* insertions, ΔE_{st}.[17] The values are 4.2 and 3.5 kcal/mol for the π-complexes of **5** and **4**, respectively,[18] consistent with high isospecificity. The same calculation afforded ΔE_{st} = 1.1 kcal/mol for the present C_2-symmetric precursor **3** and estimates of [*mm*] = 0.65 and [*mmmm*] = 0.48 which are closed to observed results of 0.67 and 0.52 for polypropylene having a low melting transition temperature and crystallinity.

Summary and Conclusions

We have synthesized the ideally C_{2v}-symmetric *ansa*-bis(fluorenyl)zirconocene precursor **1**. The catalyst system **1**/TIBA/**3** produces polyethylene as well a perfectly atactic polypropylene at all T_p, both with $\bar{M}$ws of a half million over a broad T_p range and with exceedingly high activities. It is apparent from the results presented in this paper, as well as the work of others,[9,10] that the two bulky and electron-rich fluorenyl rings make chain-transfer processes sterically and electronically unfavorable whether it is via β-hydride elimination or chain transfer with monomer. C_{2v} symmetry is the necessary and sufficient condition for a catalyst to produce perfectly atactic poly(α-olefins). Formation of polymers of even slight stereoregularity most likely means that rotamers belonging to lower symmetry species are catalyzing the polymerization.

The C_2-symmetric precursor **2** we have synthesized catalyzed partially isospecific polymerization of propylene when activated with TIBA/**3**. Both the experimental and theoretical studies suggest that the relative substitution effect on either the *rac*/*meso* ratio in the synthesis or the tacticity in the polymerization follows an order of *ansa*-bis(Cp) metallocenes > *ansa*-bis(Ind) metallocenes > *ansa*-bis(Flu) metallocenes. A substituent has a relatively small effect on the *ansa*-bis(Flu) system. Whereas a C_2 symmetry is necessary for isospecificity, the degree of stereoselectivity is governed by the steric energy difference between *meso* and *racemic* insertion transition states.

Acknowledgment. This work was supported by the Materials Research Laboratories of the National Science Foundation at the University of Massachusetts, Amherst.

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MA946321A