[Ethylidene(1-η5-tetramethylcyclopentadienyl)(1-η5-indenyl)]dichlorozirconium: Synthesis, Molecular Structure, and Polymerization Catalysis

Geraldo Hidalgo Llinas,[†] Roberta O. Day,[*,‡] Marvin D. Rausch,[*,‡] and
James C. W. Chien[*,†,‡]

*Department of Polymer Science and Engineering and Department of Chemistry, University of
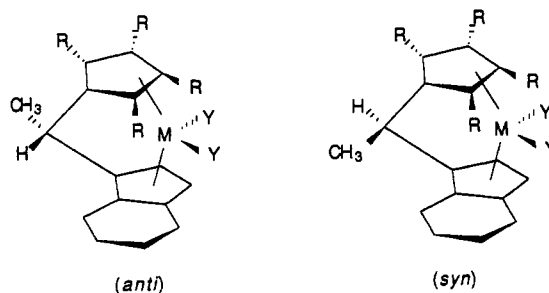Massachusetts, Amherst, Massachusetts 01003*

Anti (1) and syn (2) diastereomers of *rac*[ethylidene(1-η5-indenyl)(1-η5-2,3,4,5-tetramethyl-cyclopentadienyl)]dichlorozirconium were synthesized by the reaction of the dilithium derivative of 1-(1-indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane with zirconium tetrachloride, under different conditions. Both diastereomers were characterized by elemental analysis, ^{1}H NMR, and 2D ^{1}H NMR. Compound 1 crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.158(2)$ Å, $b = 9.752(2)$ Å, $c = 15.807(2)$ Å, $\beta = 104.26(2)°$, and $Z = 4$; the X-ray molecular structure is reported. The catalytic system 2/methylaluminoxane has exceedingly low activity for propylene polymerization, forming hemiisotactic polymer. The crystal structure of 1 showed a commodious environment at the catalytic center and a possibility for isomerization between sites with and without stereochemical control. This catalyst also has unusually low ethylene polymerization activity. The polyethylene it produces exhibits two melting endotherms, indicating the presence of two types of catalytic sites.

Introduction

There is considerable interest in the preparation of metallocenes of group 4 transition elements as precursors for ethylene polymerization catalysts.[1] *ansa*-Zirconocene type compounds are capable of producing isotactic[2-4] or syndiotactic polypropylenes.[5,6] The hafnocene analogs are less catalytically active but produce polymers of higher molecular weight than the corresponding zirconocene complex, while the titanocene derivatives are inferior to Zr and Hf complexes in both regards.

We have recently synthesized the nonsymmetric anti (3) and syn (4) diastereomers of *rac*[ethylidene(1-η5-tetramethylcyclopentadienyl)(1-η5-indenyl)]dichlorotitanium.[7,8] Catalyst 3 upon activation with methylaluminoxane (MAO) in the presence of propylene produced stereoblock polypropylene comprised of alternating crystalline and amorphous segments.[8] An X-ray molecular structure has been obtained for compound 5, which is the

(anti)   (syn)

1	R = CH3	**2**	R = CH3
	M = Zr		M = Zr
	Y = Cl		Y = Cl
3	R = CH3	**4**	R = CH3
	M = Ti		M = Ti
	Y = Cl		Y = Cl
5	R = CH3		
	M = Ti		
	Y = CH3		

dimethyl derivative of 3.[9] These titanocene catalysts, 3/MAO and 4/MAO, have very low propylene polymerization activities. Researchers to date have found zirconocene compounds to exhibit higher catalytic activity than the analogous titanocene compounds. The purpose of the present study was to synthesize both anti (1) and syn (2) diastereomers of *rac*-[ethylidene(1-η5-indenyl)(1-η5-2,3,4,5-tetramethylcyclopentadienyl)]dichloro-

† Department of Polymer Science and Engineering.
‡ Department of Chemistry.

(1) (a) Sinn, H.; Kaminsky, W.; Vollmer, H.-J.; Woldt, R. *Angew. Chem.* 1980, *92*, 396; (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* 1980, *18*, 99.

(2) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 507.

(3) (a) Ewen, J. A. *J. Am. Chem. Soc.* 1984, *106*, 6355. (b) Ewen, J. A. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1986; p 271.

(4) (a) Rieger, B.; Chien, J. C. W. *Polym. Bull.* 1989, *21*, 159. (b) Rieger, B.; Mu, X.; Mallin, D. T.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* 1990, *23*, 2559.

(5) (a) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* 1987, *109*, 6544. (b) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* 1988, *110*, 6255.

(6) Fierro, R.; Yu, Z.; Rausch, M. D.; Dong, S. H.; Alvarez, D.; Chien, J. C. W. *Macromolecules*, submitted.

(7) (a) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.-H.; Chien, J. C. W. *J. Am. Chem. Soc.* 1990, *112*, 2030. (b) Chien, J. C. W.; Rieger, B.; Sugimoto, R.; Mallin, D. T.; Rausch, M. D. In *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Elsevier Kodansha: Tokyo, 1990; p 535.

(8) Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* 1992, *25*, 1242.

(9) (a) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* 1991, *113*, 8569. (b) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Polym. Sci. Part A: Polym. Chem.* 1992, *30*, 2601.
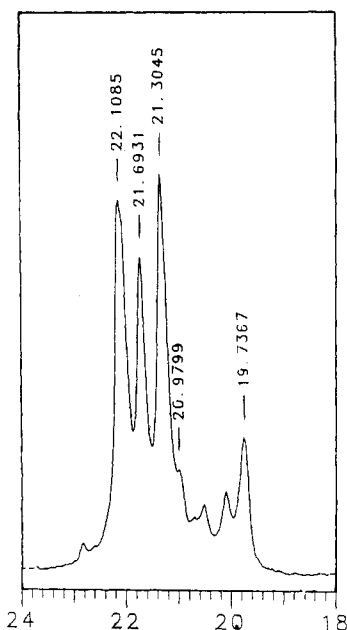
Figure 1. C-NMR (300 MHz) spectra of oligomeric polypropylene produced by 2/MAO in trichlorobenzene at 130 °C.

zirconium compounds, to determine molecular structure by X-ray diffraction (XRD) and by NMR, and to investigate their catalytic properties in ethylene and propylene polymerizations.

Results and Discussion

Synthesis. The chiral *ansa*-metallocenes, in which the ligand framework has a ethylidene bridge between the different cyclopentadienyl rings, were prepared by the reaction of $Li_2[CH_3CH(C_9H_{12})(C_9H_6)$ (**6**) with $ZrCl_4$ in different solvents. Compound **6** was obtained by the lithiation of the mixture of 1-(1-indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane isomers in diethyl ether. This salt was precipitated, washed, and isolated as a white powder. Reaction of **6** with $ZrCl_4$ at -75 °C in CH_2Cl_2 gave the diastereomer **1**. The same reaction performed in diethyl ether and at higher temperature yielded only the other diastereomer **2**. Recrystallization afforded the pure diastereomers.

Polymerization Catalysis. In the cases of the titanium complexes **3** and **4**, it is the syn diastereomer **4** which is the more active percursor for propylene polymerization.[10] Therefore, the syn diastereomer of the zirconium complex **2** was investigated for polymerizations in this study as well.

Propylene (10 psig) was polymerized at 0 °C with 0.12 mM **2** using MAO as the cocatalyst; the [Al]/[Zr] ratios employed were 440, 880, 1760, and 3400. No solid polymer was formed in all these experiments. After removal of toluene (100 mL), only milligram quantities of oligomer were isolated, Figure 1 illustrates a typical C-NMR spectrum of the oligomer. The pentad distributions are [*mmmm*] = 0.24, [*mmmr*] = 0.20, [*rmmr*] = 0.26, [*mmrr*] = 0.074, [*mrmm* + *rmrr* + *mrmr*] = 0.035, [*rrrr*] = 0.043, [*mrrr*] = 0.053, and [*mrrm*] = 0.096. This pattern is characteristic of hemiisotactic poly(propylene)[11] in which

(10) Llinas, G. H.; Chien, J. C. W. *Polym. Bull.* **1992**, *28*, 41. The polymerization behaviors of the two diastereoisomers, activated by MAO, have been compared from -20 °C to +25 °C. Precursor **4** formed about 30% more active species than **3**, which polymerizes propylene 20 to 50% faster depending on T_p and produced PP of higher molecular weight.

Table I. Ethylene Polymerization by 2/MAO[a]

run no.	[MAO] mM	[Al]/[Zr]	yield	polymerization activity × 10⁻⁴ (g of PE/(mol Zr·[C₂H₄]·h))	T_m (°C)	
182	54	400	0.023	0.19	119.1	130.4
183	108	880	0.12	1.0	118.6	130.0
184	216	1760	0.30	2.4	126.9	
185	432	3520	0.63	5.1	126.2	

[a] Polymerization conditions: [**2**] = 0.12 mM, toluene 100 mL, ethylene 10 psig, T_p = 0 °C, t_p = 60 min.

every other tertiary carbon atom tends to be isotactic while the others tend to be randomly heterotactic.

It is a well-known phenomenon of metallocene catalysis of propylene polymerizations[4,7,12-14] that the lower the temperature of polymerization (T_p), the greater both the molecular weight and stereoregularity of the polymer produced. However, this benefit was not observed for the present 2/MAO catalyst. For instance, polymerization of propylene at -78 °C by [**2**] = 0.12 mM and [Al]/[Zr] = 1760 produced also only milligram amounts of oligomer, as at higher T_p.

In our prior studies, the olefin polymerization activity of a zirconocene-type catalyst was found to increase with a decrease of [Zr] and an increase of [Al]/[Zr] ratio.[4,12-15] In the current study, propylene was polymerized with [**2**] = 2.4 μM at T_p = 0 °C for a range of [Al]/[Zr] ratios from 440 to 1.8×10^5. Still, only a trace of oligomer was formed.

The inability of the 2/MAO system to catalyze polymerization of propylene to high MW polymer prompted an investigation of its activity in ethylene polymerization. Using the conditions of [**2**] = 0.12 mM, [Al] = 48 mM (MAO), and 10 psig of ethylene in 100 mL of toluene at 0 °C, we found an extremely low activity of 1.9×10^3 g of PE (mol Zr·bar·h)⁻¹. The catalytic activity increased with an increase of the [Al]/[Zr] ratio (Table I). However, the maximum activity observed here is at least 4 orders of magnitude lower than the Cp_2ZrCl_2/MAO system.[1,12]

Polyethylene Morphology. THe morphology of the poly(ethylenes) obtained with 2/MAO depends on the [Al]/[Zr] ratio employed. At low ratio (runs 182, 183 in Table I) there are distinctly two melting endotherms (Figure 2a,b); the two peaks move closer together with the increase of [MAO] employed in the polymerization (Figure 2c,d).

One of the products, sample 183, was further characterized by extraction with refluxing *n*-heptane. The soluble fraction has a single sharp T_m at 121.8 °C (Figure 2e). The insoluble fraction melts at 134.0 °C (Figure 2f), but it still contains a good deal of lower melting polymers. Clearly, this polyethylene has a bimodal distribution.

The T_m of a polyethylene depends both upon its molecular weight and linearity. The T_m becomes significantly depressed when the degree of polymerization (DP) of the polyethylene is low or the number of short or long branches increases. The polyethylenes produced by metallocene catalysts are quite linear according to both IR and NMR. Thus, the dual DSC transitions suggests two kinds of active species differing in their k_p/k_{tr} ratios, where k_p and k_{tr} are the rate constants for propagation and transfer, respectively, (vide infra). The sites having

(11) Farina, M. *Top. Stereochem.* **1987**, *17*, 1.
(12) Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci. Part A* **1990**, *28*, 15.
(13) Chien, J. C. W.; Sugimoto, R. *J. Polym. Sci. Part A* **1991**, *29*, 459.
(14) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.
(15) Chien, J. C. W.; Razavi, A. *J. Polym. Sci. Part A* **1988**, *26*, 2369.
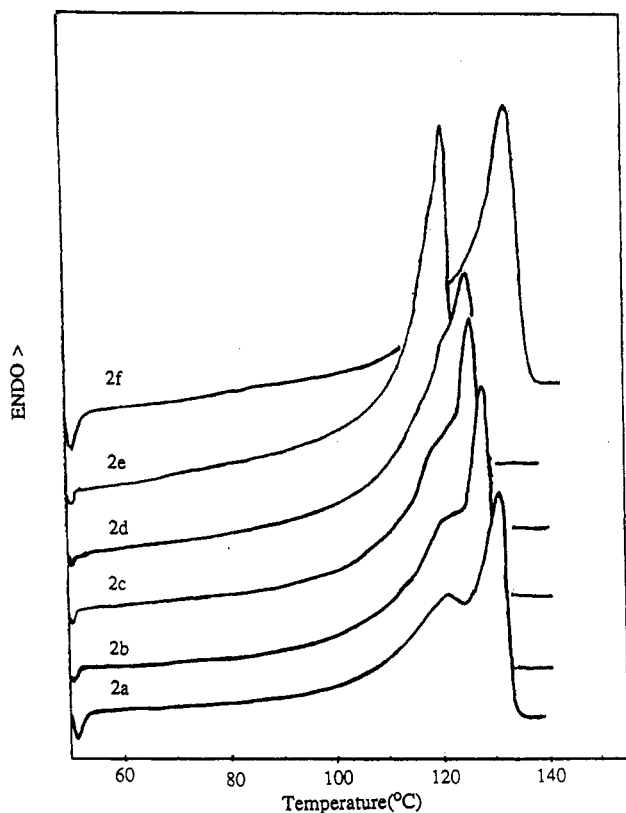
Figure 2. DSC curves on polyethylenes of Table I: (a) sample 182, (b) sample 183, (c) sample 184, (d) sample 185, (e) *n*-heptane-soluble fraction of sample 183, (f) *n*-heptane-insoluble fraction of sample 183.

large (or small) k_p/k_{tr} ratios produce polyethylenes of higher (or lower) MW which exhibit $T_m \geq 130$ °C (or $\leq$ 120 °C). Polyethylenes exhibiting bimodal GPC curves have also been produced by other *ansa*-zirconocene catalysts with molecular structure closely related to 2.[16]

The reaction of a zirconocene compound with MAO has been shown to produce the catalytically active cation.[17] For this highly electrophilic zirconocenium species,[14] its propagating chain is terminated mainly by β-H or β-methyl elimination. The resulting olefin may insert into a propagating Zr–polymer bond.[4b] The latter process is of low probability; however, its infrequent occurrence to form branched polyethylenes cannot be entirely discounted.

Molecular Structure. Diffraction-quality crystals were obtained for **1** but not **2**. Therefore, the molecular structure of **1** was determined even though the polymerizations were studied with **2**/MAO. The atomic coordinates for **1** are given in Table II. Figure 3 shows the ORTEP plot. Table III contains the selected distances and angles. The zirconium atom is in a pseudotetrahedral environment which is defined by the two chlorine atoms and by the centroids of the two five-membered rings (Table III). The plane defined by the Zr atom and the two centroids is nearly perpendicular to the plane defined by the Zr atom and the two chlorine atoms (dihedral angle = 89.80(7)°).

The five-membered rings are essentially planar (±0.015-(3) Å for the ring containing C1 and ±0.005(3) Å for the

(16) *rac*-Isopropylidene(1-η^5-cyclopentadienyl)(1-η^5-indenyl)dichlorozirconium and *rac*-isopropylidene(1-η^5-cyclopentadienyl)(3-methyl-1-η^5-indenyl)dichlorozirconium have been synthesized and used to polymerize ethylene (Fierro, R., unpublished results). The polymers exhibited bimodal GPC curves.

(17) Sishta, C.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112.

Table II. Atomic Coordinates in Crystalline *rac*-[*anti*-Ethylidene(1-η^5-tetramethylcyclopentadienyl)-(1-η^5-indenyl)]zirconium Dichloride (1)[a]

atom[b]	x	y	z	B(equiv),[c] Å^2
Zr	0.24621(2)	0.22120(3)	0.00994(2)	2.812(5)
Cl1	0.05071(6)	0.29547(9)	−0.03558(5)	4.15(2)
Cl2	0.26152(7)	0.06326(9)	−0.10710(5)	4.08(2)
C1	0.3473(3)	0.1860(3)	0.1616(2)	3.60(6)
C2	0.3568(3)	0.0610(3)	0.1175(2)	4.03(7)
C3	0.2501(3)	−0.0040(3)	0.0935(2)	4.15(7)
C4	0.0550(3)	0.0576(4)	0.1244(2)	4.57(8)
C5	0.0030(3)	0.1533(4)	0.1625(2)	4.85(8)
C6	0.0620(3)	0.2698(4)	0.2053(2)	4.52(8)
C7	0.1734(3)	0.2908(3)	0.2087(2)	3.88(7)
C8	0.2317(3)	0.1943(3)	0.1679(2)	3.46(6)
C9	0.1723(3)	0.0753(3)	0.1258(2)	3.87(7)
C10	0.4314(3)	0.3040(3)	0.1737(2)	3.66(7)
C11	0.4036(2)	0.3667(3)	0.0822(2)	3.19(6)
C12	0.4338(2)	0.3149(3)	0.0071(2)	3.36(6)
C13	0.3610(2)	0.3764(3)	−0.0685(2)	3.37(6)
C14	0.2849(2)	0.4648(3)	−0.0403(2)	3.42(6)
C15	0.3101(2)	0.4591(3)	0.0523(2)	3.22(6)
C16	0.5306(3)	0.2229(4)	0.0003(2)	4.53(8)
C17	0.3709(3)	0.3597(4)	−0.1601(2)	4.68(8)
C18	0.1977(3)	0.5565(4)	−0.0962(2)	4.85(8)
C19	0.2539(3)	0.5509(4)	0.1061(2)	4.36(7)
C20	0.5554(3)	0.2510(5)	0.2127(3)	5.7(1)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Equivalent isotropic thermal parameters are calculated as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.
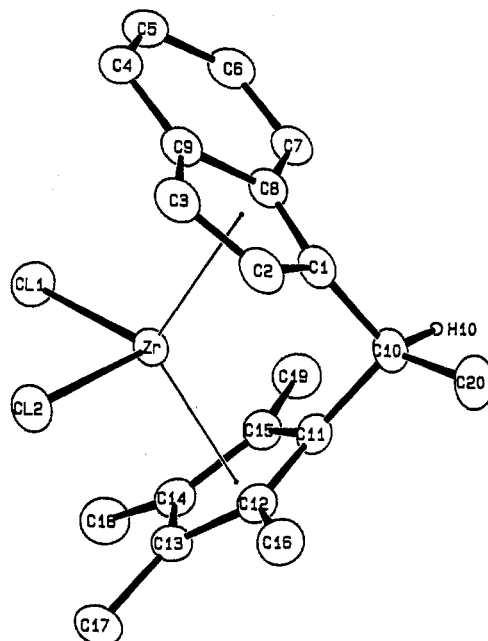

Figure 3. ORTEP plot of *rac*-[*anti*-ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)]dichlorozirconium (1), with thermal ellipsoids as the 30% probability level. Hydrogen atoms except for H10 are omitted for clarity.

ring containing C11), and the dihedral angle between these planes is 108.5(1)°. Atom C10 is displaced out of these planes by about 0.4 Å in a direction toward the Zr atom (0.401(3) Å for the ring containing C1 and 0.396(3) Å for the ring containing C11). The bond angle at the bridging C10 is somewhat smaller than the ideal tetrahedral angle (C1–C10–C11 = 101.5(2)°). The displacement of C10 from these planes as well as the compression in the angle suggests some strain in the molecule.

The planarity of the five-membered rings is consistent with the η^5 bonding mode. There is somewhat more variation in the metal to carbon distances in these rings

**Table III. Selected Distances (Å) and Angles (deg) for
rac-[*anti*-Ethylidene(1-η⁵-tetramethylcyclopentadienyl)-
(1-η⁵-indenyl)]zirconium Dichloride (1)[a]**

Zr–Cl1	2.4186(8)	Zr–CENT1[b]	2.223(3)
Zr–Cl2	2.4493(9)	Zr–CENT2[c]	2.197(3)
Zr–C1	2.434(3)	Zr–C11	2.429(3)
Zr–C2	2.452(3)	Zr–C12	2.468(3)
Zr–C3	2.557(3)	Zr–C13	2.575(3)
Zr–C8	2.560(3)	Zr–C14	2.584(3)
Zr–C9	2.645(3)	Zr–C15	2.486(3)

Cl1–Zr–Cl2	102.45(3)	CENT1–Zr–CENT2	118.2(1)
Cl1–Zr–CENT1	109.32(8)	Cl2–Zr–CENT1	108.37(8)
Cl1–Zr–CENT2	109.38(8)	Cl2–Zr–CENT2	109.70(8)

[a] Estimated standard deviations in parentheses. The atom labeling
scheme is shown in Figure 1. [b] Centroid of the five-membered ring which
contains C1. [c] Centroid of the five-membered ring which contains C11.

**Table IV. Chemical Shifts of the Aromatic Protons in
Compounds 1 and 2**

H	anti Zr diastereomer (1)		syn Zr diastereomer (2)	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
1	5.68	d, 3.20	5.38	d, 3.20
2	6.71	d, 3.20	6.71	d, 3.20
3	6.74	d, 8.25	6.73	d, 7.92
4	7.0	dd	7.02	t, 7.87
5	7.01	dd	7.37	t, 8.92
6	7.33	d, 8.74	7.40	d, 8.84

(a range of 0.211 Å for the ring containing C1 and a range
of 0.155 Å for the ring containing C11) than is found in
corresponding compounds that do not have the ethylidene
bridge. The bridge is most probably responsible for this
feature, and in both rings the shortest Zr–C bond distances
involves the atom bonded to the bridging C10 (Table III).
The variation is most apparent for the five-membered ring
of the indenyl group. The two Zr–Cl distances are not
equal; one is 0.031 Å longer than the other.

The proton NMR spectral parameters are summarized
in Table IV. The chemical shift assignments for the
aromatic protons in 1 and 2 are made with the aid of 2D
¹H NMR spectroscopy. In both diastereomers the H¹
proton is shifted to high field from the aromatics. The
anti diastereomer 1 shows a doublet at 5.68 ppm ($J = 3.20$
Hz) whereas the doublet for the syn isomer 2 is located at
5.38 ppm ($J = 3.20$ Hz). The methyl group resonance of
the ethylidene bridge is a doublet at 1.63 ppm ($J = 7.51$
Hz) for the anti diastereomer, whereas the syn doublet
signal at 1.78 ppm ($J = 7.63$ Hz) is 0.17 ppm deshielded
from anti resonance. This difference may be due to the
effect of the ring current field generated by the six-
membered ring.

Structure–Catalysis Relationships. The polymer-
ization behaviors of 2/MAO contributed two pieces of
valuable information regarding the relationships between
the metallocene structure and catalysis. The first one is
concerned with the singularity of catalytic species. There
is an increasing usage of "single-site catalysts" to describe
the metallocenium-based system, especially in industrial
pronouncements. It is well-known in polymer chemistry
that polymerization by a single initiation species produces
a polymer having unimodal molecular weight distribution
with $\bar{M}_w/\bar{M}_n \sim 2$, soluble in a single solvent, exhibiting

only one melting transition and the other characteristics
for a uniform macromolecular substance. This may be
true for polymers synthesized by some metallocene catalyst
for a narrow range of experimental conditions. In general
the polydispersity index is appreciably broadened at high
T_p, high monomer pressure, and low [Al]/[Zr] ratios.

The polyethylenes produced by 2/MAO (vide supra)
and other similar catalysts[16] have bimodal distributions,
indicating two or more active species. The kinetics of
ethylene polymerizations catalyzed by CpZrCl₃/MAO and
Cp₂ZrCl₂/MAO[12] indicate the presence of two catalytic
species. In the case of the catalysis of propylene polym-
erization by *rac*-[ethylenebis(1-η⁵-tetrahydroindenyl)]di-
chlorozirconium/MAO,[13] radioassay of solvent-separated
fractions of polypropylenes tagged with tritiated methanol
showed that there are catalytic sites differing in k_p and k_{tr}
as well as stereoselectivity. When propylene was polym-
erized with optically active [(S)-1,2-ethylenebis(tetrahy-
droindenyl)]zirconium O-acetyl (R)-mandalate/MAO,[18]
the polymer fractions separated by solvent extraction even
exhibit optical rotations opposite in signs. There are
several possible sources for the multiple active sites. The
formation of zirconocenium species having different
numbers and types of coordinated MAO[12,13,18] is one
possibility. Conformational isomerism and complexation
with dissimilar numbers of olefin or solvent molecules are
the others.

The second result relevant to structure–catalyst rela-
tionships is unexpected and perplexing. 2/MAO has
ethylene polymerization activity of about 10⁴ g of PE/
(mol Zr·[C₂H₄]·h), which is 4 orders of magnitude lower
than that of Cp₂ZrCl₂/MAO.[1] The polyethylene contains
materials melting below 120 °C, indicating very low DP.
The activity of propylene polymerization by 2/MAO is
even lower (<10⁴) and could not be determined because
of difficulty in the quantitative isolation of oily or gummy
oligomeric substances. The polypropylene has either a
hemiisotactic type of structure or is essentially atactic. In
contrast, the titanium analog of the title complex 3 does
polymerize propylene at 25 °C with an activity of 4 × 10⁵
g of PP/(mol Ti·[C₃H₆]·h) to high molecular weight
polymers having crystalline/amorphous block structure
with properties of a thermoplastic elastomer.[8] We will
discuss below the possible molecular structural basis for
these differences.

Jordan et al.[19] reported that a stereorigid bridged
metallocene cation usually has closely equivalent metal to
centroid bond lengths and angles as does its neutral
precursor. Thus, the latter structure may be relied on as
models for the former and for interpretation of the
polymerization results. Figure 4 compares those atomic
distances and angles in 2 and 5 which are likely to be of
importance for catalysis. The distances from Zr to the
carbon atoms of the η⁵-ring are 0.1–0.4 Å longer than the
corresponding distances for Ti. The centroid to centroid
distance in 2 is greater by 0.14 Å than in 5. The metal to
bridging carbon atom distance is 2.99 Å for the Ti
compound 5; it is 3.09 Å for the Zr compound 2. The
centroid–metal–centroid angles are 127.0° and 118.3° for
Ti and Zr, respectively. These parameters indicate that
the Ti atom in 5 is situated more deeply in the wedge,
closer to the bridging carbon. This commodious envi-

(18) Chien, J. C. W.; Vizzini, J.; Kaminsky, W. *Makromol. Chem. Rapid
Commun.*, in press.
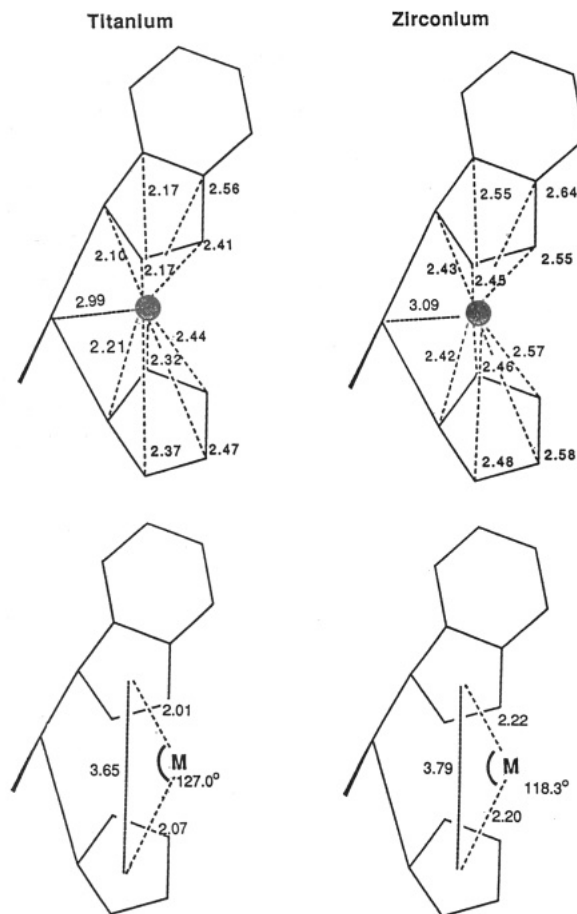(19) Jordan, R. F.; Lapointe, R. E.; Baenziger, N.; Hinch, G. D.
Organometallics **1990** *9*, 1539.

Figure 4. Comparison of relevant atomic distances and angles in Zr compound **2** and titanium compound **5**.

Experimental Section

Materials. Chemicals were purchased from Aldrich. Solvents were purified as described elsewere.[22] Solutions of *n*-butyllithium in hexane were titrated prior to use. The 1,2,3,4,6-pentamethylfulvene and 1-(1-indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane derivatives were prepared according to the methods of synthesis previously reported.[7a] All reactions were carried out under an argon atmosphere using Schlenk techniques or a DLX-00-S-G Vacuum Atmospheres glovebox.

Methods. Proton nuclear magnetic resonance spectra were recorded on a Varian XL 300-MHz spectrometer operating in the Fourier transform mode. Chemical shifts are reported in δ units referenced to tetramethylsilane using the residual solvent protons. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

Reaction between 1-(1-Indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane and *n*-Butyllithium. *n*-Butyllithium (11.28 mL, 18.06 mmol, 1.6 M *n*-hexane solution) was added dropwise to a solution of 1-(1-indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane (2.45 g, 9.03 mmol in 100 mL of diethyl ether) at 0 °C. After the reaction mixture was warmed to room temperature, stirring was continued for 4 more h at 25 °C. The solvent was removed under vacuum, and the white powder was washed three times with a total of 50 mL of hexane. The product was then dried under reduced pressure to give 2.4 g (8.58 mmol) of $Li_2[CH_3CH(C_9H_{12})(C_9H_6)]$ as a white air-sensitive solid in 95% yield.

Synthesis of 1. To the above synthesized dillithium salt was added 2.0 g (8.58 mmol) of zirconium tetrachloride. The solid mixture was cooled at −75 °C, and 50 mL of chilled methylene chloride was added very slowly via cannula. After 20 min the reaction mixture was allowed to warm gradually to room temperature, and it developed a yellow color. The mixture was vigorously stirred for 4 h and filtered through Celite. Evaporation of the methylene chloride under reduced pressure gave 3.09 g of **1** (7.3 mmol) as a yellow solid in 85% yield. Recrystallization from toluene/hexane gave pure **1** (1.67 g, 3.94 mmol, 54%). Anal. Calcd for $C_{20}H_{22}Cl_2Zr$: C, 56.58; H, 5.18. Found: C, 56.40; H, 4.98. ^1H NMR (C_6D_6): δ 1.58 (s, 3 H), 1.63 (d, $J = 7.51$ Hz, 3 H), 1.75 (s, 3 H), 1.80 (s, 3 H), 1.84 (s, 3 H), 4.37 (q, $J = 7.57$ Hz, 1 H), 5.68 (d, $J = 3.20$ Hz, 1 H), 6.71 (d, $J = 3.20$ Hz, 1 H), 6.74 (d, $J = 8.25$ Hz, 1 H), 7.0 (dd, 1 H), 7.01 (dd, 1 H), 7.33 (d, $J = 8.74$ Hz, 1 H).

Synthesis of 2. To 2.76 g (10 mmol) of **6**, suspended in 30 mL of diethyl ether, was added 2.33 g (10 mmol) of zirconium tetrachloride suspended in 20 mL of diethyl ether at room temperature. The reaction mixture developed a pale orange color. After 8 h, the solvent was evaporated and replaced by 30 mL of methylene chloride. After filtration through Celite and workup using the same procedure described above for **1**, **2** (1.9 g/4.5 mmol) was obtained as a yellow solid in 45% yield. Anal. Calcd for $C_{20}H_{22}Cl_2Zr$: C, 56.58; H, 5.18. Found: C, 56.31; H, 4.70. ^1H NMR (C_6D_6): δ 1.50 (s, 3 H), 1.78 (d, $J = 7.63$ Hz, 3 H), 1.80 (s, 3 H), 1.81 (s, 3 H), 1.86 (s, 3 H), 4.33 (q, $J = 7.82$ Hz, 1 H), 5.38 (d, $J = 3.20$ Hz, 1 H), 6.71 (d, $J = 3.20$ Hz, 1 H), 6.73 (d, $J = 7.92$ Hz, 1 H), 7.02 (t, $J = 7.87$ Hz, 1 H), 7.37 (t, $J = 8.92$ Hz, 1 H), 7.40 (d, $J = 8.84$ Hz, 1 H).

Polymerizations. The procedures used to polymerize ethylene[12] and propylene[7-10,13] have been given in detail.

X-ray Study of 1. Yellow plate-like crystals of **1**, suitable for X-ray diffraction study, were grown by the slow cooling of a toluene/hexane solution at −20 °C. A somewhat irregular crystal (approximate dimensions of 0.28 × 0.38 × 0.40 mm) was mounted in a thin-walled glass capillary which was sealed under argon. Data was collected with an Enraf-Nonius CAD4 diffractometer with graphite monochromated molybdenum radiation ($\lambda K\bar{\alpha} = 0.710\,73$ Å) at an ambient temperature of 23 ± 2 °C.

ronment of Zr is not inducive for stereochemical regulation. The exposed Zr atoms are susceptible to deactivation for instance by the formation of $Zr-CH_2-CH_2-Zr$ adducts.[20] This could contribute toward the low catalytic activities of the **2**/MAO catalyst.

Finally, we had proposed[7-9] a mechanism for the formation of polypropylene having different microstructures by the asymmetric metallocenes **1–4**. The cation of such a metallocene can exist in two conformation states **c** and **a** which catalyze the meso and random insertions of monomer, respectively. If the $\mathbf{c} \rightleftharpoons \mathbf{a}$ isomerization occurs infrequently as compared to propagation, then polypropylene chains composed of alternating stereoregular/crystallizable and stereoirregular/amorphous segments are produced. Such thermoplastic elastomer was produced by **3**/MAO at $T_p \geq 25$ °C.[7-9] If $\mathbf{c} \rightleftharpoons \mathbf{a}$ occurs at the same rate as monomer insertion, then hemiisotactic polypropylene results as in the present catalysis by **2**/MAO. Lastly, if monomer incorporation is slower than isomerization, the polymer produced would be atactic as those obtained with **3**/MAO at $T_p \leq 0$ °C.[7-9] This mechanism can be generalized to more catalytic species with different regio- and stereoselectivities.

(20) (a) Sinn, H.; Kolk, E. *J. Organomet. Chem.* **1966**, *6*, 373. (b) Sinn, H.; Patat, F. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 93.

(21) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem. Makromol. Symp.* **1991**, *48/49*, 253.

(22) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press Ltd.: Oxford, 1980.

Crystal Data. $C_{20}H_{22}Cl_2Zr$, monoclinic space group $P2_{1/n}$ (alternate setting of $P2_{1/c}$, C^5_{2h}-No.14[23]), $a = 12.158(2)$ Å, $b = 9.752(2)$ Å, $c = 15.807(2)$ Å, $\beta = 104.26(2)°$, $Z = 4$, and μ Mo K$\bar{\alpha}$ = 8.889 cm^{-1}. A total of 3198 independent reflections were measured (θ–2θ scan mode; $3° \leq 2\theta$ Mo K$\alpha \leq 50°$; $+h$, $+k$, $\pm l$). No corrections were made for absorption.

The structure was solved by use of Patterson and difference Fourier techniques and was refined by full-matrix least-squares.[24] The 23 independent non-hydrogen atoms were refined aniso-tropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers (ideal positions or regularized difference Fourier position for methyl groups). The final agreement factors[25] were $R = 0.029$ and $R_w = 0.041$ for the 2629 reflections with $I \geq 3\sigma(I)$. All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

---

(23) *International Tables for X-ray crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(24) The function minimized was $\Sigma w([F_o] - [F_c])^2$, where $w^{1/2} = 2F_oLp/\sigma_l$.

(25) $R = \Sigma([F_o] - [F_c])/\Sigma[F_o]$ and $R_w = \Sigma w([F_o] - [F_c])^2/\Sigma[F_o]^2]^{1/2}$.

DSC of Polyethylene. DSC was performed on a Perkin-Elmer Thermal System IV. A polyethylene specimen was heated to 140 °C for 5 min and cooled to 50 °C at 10 °C min, and then the DSC was recorded at a heating rate of 10 °C/min.

Supplementary Material Available: A complete listing of bond distances and angles (Table S1), anisotropic thermal parameters (Table S2), and hydrogen atom parameters (Table S3) (6 pages). Ordering information is given on any current masthead page.

OM920647V