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Variation of Poly(propylene) Microtacticity by Catalyst Selection

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The polymerization of propylene with use of soluble catalysts derived from *rac*-(1,2-ethylenebis(η^5-3-alkylcyclopentadienyl))zirconium dichlorides (*rac*-**1**) and their corresponding meso isomers (*meso*-**1**), in combination with methylaluminoxane cocatalyst, was studied. The polymerization activity of catalysts derived from compounds *rac*-**1** and *meso*-**1** was somewhat lower than that reported for the well-studied catalysts of this structural type *rac*-(ethylenebis(η^5-indenyl)))zirconium and *rac*-(ethylenebis(η^5-tetrahydroindenyl))zirconium dichlorides (**2** and **3**, respectively); however, the degree of microtacticity of the poly(propylene) produced was higher, as determined by ^{13}C NMR spectroscopy. The polymerization activity of the meso compounds (*meso*-**1**) was lower than that of their racemic counterparts. Finally, *meso*-(ethylenebis(η^5-tetrahydroindenyl))zirconium dichloride (**4**) was isolated in pure form as a minor product from the preparation of the racemic isomer. This compound is less active than its racemic diastereomer **3** and produces atactic poly(propylene). Compound **4** was characterized by a single-crystal X-ray diffraction analysis: space group $P2_1/c$; $Z = 4$; $a = 12.051$ (2) Å, $b = 15.184$ (3) Å, $c = 9.939$ (2) Å, $\beta = 92.94$ (1)°; $V = 1816.3$ (5) Å^3; $R = 0.0256$, $R_W = 0.0299$ for 2784 unique reflections with $I > 3\sigma(I)$.

Introduction

There is widespread, current interest in the use of soluble catalysts for the Ziegler–Natta polymerization of olefins following initial reports that isotactic poly(propylene) is produced with use of active catalysts derived from chiral, *ansa*-metallocene compounds of the group 4 transition elements (e.g. compound **3**, Scheme I) and methylaluminoxane (MAO) cocatalysts.[2] These catalysts produce isotactic poly(propylene) by an enantiomorphic site control mechanism[2a] wherein the ligand framework controls the orientation[2e] of insertion of the monomer into the metal–carbon bond of these quasi-cationic[3] zirconocene or titanocene catalysts, as depicted in Scheme I. It occurred to us that it should be possible to influence the difference in energy between diastereomeric transition states for this insertion process (Scheme I) by varying the degree of steric hindrance at the metal center in catalysts derived from compounds of general structure *rac*-**1** (see eq 1). We report here that the chain microtacticity of poly(propylene) can indeed be influenced in a predictable manner using catalysts derived from compounds *rac*-**1** in which the size of the substituent R is varied.

Table I. Crystallographic Data for Compound 4

formula	$C_{20}H_{24}Cl_2Zr$
mol wt	426.56
cryst syst	monoclinic
a, Å	12.051 (2)
b, Å	15.184 (3)
c, Å	9.939 (2)
β, deg	92.94 (1)
volume, Å^3	1816.3 (5)
space group	$P2_1/c$
Z	4
ρ_c, g cm^{-3}	1.56
$F(000)$	872
T, K	295
μ(Mo Kα), cm^{-1}	8.90
cryst size, mm	0.33 × 0.37 × 0.40
scan method	ω
scan speed, deg min^{-1}	2.93–29.3
scan width, deg	1.2
2θ range, deg	3.5–50.0
std reflns	080; 700
std variation, %	2
transmissn factors	0.50–0.55
unique data	3192
no. of obsd data ($I > 3\sigma(I)$)	2784
no. of variables	313
R $(=\sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert)$	0.0256
R_w $(=\lvert\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert\rvert^{1/2})$	0.0299
R (all data)	0.0302
R_w (all data)	0.0388
GOF $(=[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\mathrm{NO} - \mathrm{NV})]^{1/2}$	1.42
weighting scheme, $w^{-1} = \sigma^2(F) + aF^2$ (a)	0.0040
max residual electron density, e Å^{-3}	0.48

Results and Discussion

Compounds **1** (R = Me, *i*Pr, *t*Bu) were prepared from the corresponding ethylenebis(3-alkylcyclopentadienes)[4] and zirconium(IV) chloride in THF solution as shown in eq 1.[5] In all cases, the desired racemic isomer, *rac*-**1**, was formed along with the corresponding meso isomer, *meso*-**1**. Separation of isomers could not be accomplished by fractional crystallization or by chromatography, but relative stereochemistry was established by conversion of the

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(1) David A. Holden (born 1956) passed away April 26, 1990, after a lengthy battle with cancer. This paper is dedicated to him.

(2) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. W. R. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Kaminsky, W. *Angew. Makromol. Chem.* **1986**, *145/146*, 149. (d) Ewen, J. A. Ligand Effects on Metallocene Catalyzed Polymerizations. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1986; p 271. (e) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (f) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. (g) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 305. (h) Corradini, P.; Guerra, G.; Vacatello, M.; Villani, V. *Gazz. Chim. Ital.* **1988**, *118*, 173. (i) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (j) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzochi, R. *Macromolecules* **1988**, *21*, 617. (k) Kaminsky, W.; Ahlers, A.; Moller-Lindehof, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *101*, 1216. (l) Rieger, B.; Chien, J. W. C. *Polym. Bull.* **1989**, *21*, 159. (m) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Makromol. Chem.* **1989**, *190*, 1177. (n) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. W. C. *J. Am. Chem. Soc.* **1990**, *112*, 2030.

(3) (a) Eisch, J. J.; Piotrowski, A. M.; Browstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219 and references therein. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (d) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. (e) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148 and references therein. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

(4) These ligands and the corresponding titanium analogues of compounds **1** were prepared by a new route, which is fully described elsewhere: Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695.

(5) Compounds **1** and **4** were fully characterized by their IR, ^{1}H NMR, ^{13}C NMR, and mass spectra. All new compounds had satisfactory elemental analyses (see Experimental Section).

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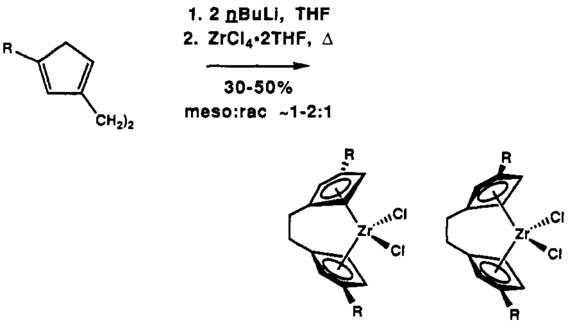

(1)

rac-1a:R=Me meso-1a:R=Me
rac-1b:R=iPr meso-1b:R=iPr
rac-1c:R=tBu meso-1c:R=tBu

dichlorides to the corresponding dimethyl derivatives. The meso dimethyl derivatives all exhibited two signals due to the nonequivalent methyl groups, whereas the racemic isomers had a single absorption in the ^{1}H NMR spectra of the mixtures (see Experimental Section).

The known *rac*-(ethylenebis(η^5-indenyl)))zirconium and *rac*-(ethylenebis(η^5-tetrahydroindenyl))zirconium dichlorides (**2** and **3**, respectively; Scheme I) were also prepared.[6] We managed to isolate small amounts of the more soluble meso diastereomer of compound **3**,[7] which was converted separately to the meso tetrahydroindenyl compound **4** (Scheme I), the structure of which was confirmed by X-ray diffraction (Figure 1, Tables I–III, and supplementary material).

As can be seen from Figure 1, thermal disorder exists within the six-membered rings of the tetrahydroindenyl ligand. Carbons C(5) and C(6′) are disordered with respect to C(55) and C(66′), respectively. A satisfactory refinement proved possible (see Experimental Section) by assigning site occupancies of 0.85 and 0.15 to C(5) and C(6′) and C(55) and C(66′), respectively. The two metal–chloride distances in this structure are significantly different (Zr–Cl(1) = 2.4203 (6) and Zr–Cl(2) = 2.4568 (7) Å, respectively; see Table III). The average Zr–Cl distance of 2.4386 (7) Å is, however, identical with that observed in racemic compound **3** (2.4386 (8) Å), as is the average metal–centroid distance (2.217 (3) and 2.214 (3) Å, respectively).[6a] The angles about zirconium (Table III and supplementary material) are quite similar in the two structures as well. Perhaps, the significant difference observed in the metal–chloride distances is due to steric compression of the Zr–Cl(1) bond by the two six-membered rings of the tetrahydroindenyl ligand, which is accompanied by lengthening of the Zr–Cl(2) bond, while other features of the geometry about the metal are unaffected. It should be noted that the titanium analogue of compound **4** has also been structurally characterized.[6c] In the latter structure, the Ti–Cl distances are the same, within experimental error, whereas the ansa ligand is severely twisted in such a way that a methylene group (corresponding to C(4′) of this structure) of one of the tetrahydroindenyl ligands almost bisects the angle subtended by the Cl–Ti–Cl moiety. A similar structural distortion is not seen in the structure reported here; both methylene groups of the tetrahydroindenyl ligands nearly eclipse Cl(1). The differences between the two structures are probably the result of the longer Zr–C distances and therefore reduced steric interaction between the tetrahydroindenyl ligands with the equatorial chlorides.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3)

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	2168.2 (2)	113.2 (1)	1849.6 (2)	36.8 (1)
Cl(1)	4004.8 (5)	−297.1 (5)	2733.0 (8)	58.3 (2)
Cl(2)	1859.4 (7)	−1095.2 (5)	229.7 (8)	69.5 (3)
C(1)	955 (2)	710 (2)	3580 (3)	47.6 (8)
C(2)	306 (2)	167 (2)	2691 (3)	51.5 (9)
C(3)	633 (2)	−707 (2)	2909 (3)	52.0 (9)
C(3A)	1497 (2)	−726 (2)	3919 (3)	49.2 (8)
C(4)	2066 (3)	−1499 (2)	4563 (4)	70 (1)
C(5)[b]	2428 (4)	−1247 (4)	6036 (5)	93 (2)
C(55)[c]	2964 (18)	−1361 (14)	5442 (22)	56 (5)
C(6)	3047 (4)	−424 (4)	6126 (4)	99 (2)
C(7)	2467 (3)	370 (3)	5522 (3)	68 (1)
C(7A)	1686 (2)	153 (2)	4334 (3)	46.9 (8)
C(8)	891 (3)	1698 (2)	3666 (4)	63 (1)
C(1′)	1667 (2)	1682 (2)	1379 (3)	49.8 (8)
C(2′)	1422 (3)	1181 (2)	207 (3)	61 (1)
C(3′)	2412 (3)	918 (2)	−315 (3)	67 (1)
C(3A′)	3307 (2)	1235 (2)	499 (3)	50.3 (8)
C(4′)	4543 (3)	1215 (2)	321 (4)	67 (1)
C(5′)	5111 (3)	1985 (3)	1061 (4)	82 (1)
C(6′)[b]	4781 (3)	2082 (3)	2487 (4)	61 (1)
C(66′)[c]	4612 918)	2459 (16)	1773 (24)	63 (5)
C(7′)	3535 (2)	2233 (2)	2572 (3)	52.6 (9)
C(7A′)	2841 (2)	1700 (2)	1572 (2)	41.9 (7)
C(8′)	853 (3)	2107 (2)	2270 (4)	66 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Occupancy 0.85. [c] Occupancy 0.15.

Table III. Selected Interatomic Distances and Angles for Compound 4[a]

	Bond Lengths (Å)[b]		
Zr–Cl(1)	2.4203 (6)	Zr–Cl(2)	2.4568 (7)
Zr–C(1)	2.485 (3)	Zr–C(1′)	2.496 (2)
Zr–C(2)	2.436 (3)	Zr–C(2′)	2.439 (3)
Zr–C(3)	2.506 (3)	Zr–C(3′)	2.505 (3)
Zr–C(3a)	2.585 (3)	Zr–C(3a′)	2.602 (3)
Zr–C(7a)	2.567 (3)	Zr–C(7a′)	2.561 (2)
Zr–Cen(1)	2.213 (3)	Zr–Cen(1′)	2.220 (3)
	Bond Angles (deg)[b]		
Cl(1)–Zr–Cl(2)	98.65 (2)	Cl(1)–Zr–Cen(1)	107.2 (1)
Cl(1)–Zr–Cen(1′)	107.8 (1)	Cl(2)–Zr–Cen(1)	107.6 (1)
Cl(2)–Zr–Cen(1′)	107.2 (1)	Cen(1)–Zr–Cen(1′)	125.2 (1)

[a] A complete list of distances and angles is contained in the supplementary material. See Figure 1 for the numbering scheme used. [b] Cen(1) and Cen(1′) are the two centroids of the cyclopentadienyl rings corresponding to the unprimed and primed carbon atoms, respectively.

Polymerization of propylene with use of mixtures of compounds *rac*-**1** and *meso*-**1** or compounds **2**–**4** and methylaluminoxane were conducted in toluene solution, and the results are summarized in Table IV. On the basis of the work of Ewen,[2a] it was expected that polymerizations with mixtures of racemic and meso catalysts would lead to the production of poly(propylene) that was a mixture of isotactic and atactic material.[8] As shown in Table IV, the crude polymer produced was a mixture of isotactic and atactic material in the case of compounds *rac*-**1** and *meso*-**1**

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[6] For the preparation of compounds **2** and **3** see: (a) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21. (b) Wild, F. W. R. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63. (c) Wild, F. W. R. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

[7] During the preparation of compound **2**, the crude product is washed with ether to remove a polymeric byproduct.[6] The meso isomer of **2** is much more soluble in ether and is therefore removed during this step. Concentration of the filtrate provides small amounts of the meso isomer (rac:meso ratios typically >5:1).

[8] The term isotactic can be a source of confusion. In this paper we use the term to refer to poly(propylene) that has a high degree of chain microtacticity (or stereoregularity) as revealed by ^{13}C NMR spectroscopy, rather than the amount of polymer insoluble in e.g. boiling heptane. Similarly, atactic polymer is defined here as poly(propylene) that lacks long-range, stereochemical order—i.e., the mole fraction of meso and racemic diads is more or less equal.

Scheme I

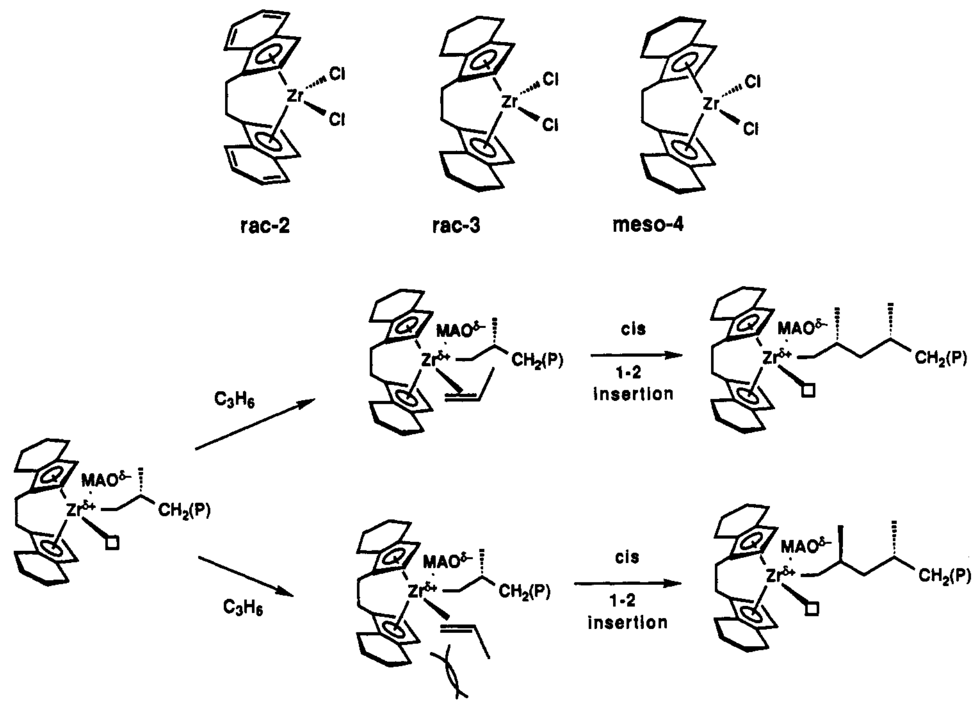

Table IV. Poly(propylene) Preparation and Properties[a]

entry no.	catalyst (amt, mg)	X_{meso}[b]	yield, g	R_p[c]	R_p(rac)[c,d]	R_p(meso)[c,d]	w_a[e]	% mmmm[f]	T_m, °C[f]	M_w[f]	M_w/M_n[f]
1	**1a** (1.9)	0.45	81.5	3720	5800	1200	0.142	92.2	133	19600	2.33
2	**1b** (1.9)	0.54	57.0	2700	4500	1100	0.230	94.6	136	19400	2.19
3	**1c** (2.0)	0.58	8.9	479	1000	78	0.095	97.6	141	17400	2.52
4	**2** (2.3)	pure *rac*	42.5[g]	15700	15700			89.0	137	39000	1.95
5	**3** (2.6)	pure *rac*	18.5[g]	6800	6800			85.9	129	20000	2.10
6	**4** (2.5)	pure *meso*	18.3[h]	630		630	1.0[i]	8.3[i]	oil	2400[j]	

[a] Polymerizations were conducted in 500 mL of toluene, containing 600 mg of methylaluminoxane ($M_n \approx 1300$; [Al]:[Zr] ≈ 2000:1), that was saturated with propylene (3.0 bar) at 40 °C. Polymerizations were initiated by injecting the catalyst dissolved in 5 mL of toluene and were run for 4 h unless otherwise noted. Polymerizations were stopped by venting the monomer and draining the polymer slurry under N_2 into a small volume of methanol. [b] Mole fraction of meso catalyst as determined by ^{1}H NMR spectroscopy. [c] Rate of polymerization (kg of poly(propylene)/(mol of Zr·h)). [d] Calculated from the weight fraction of atactic polymer (w_a) and the mole fraction of meso catalyst present (X_{meso}), assuming equal concentrations of active sites for both isomers. [e] Weight fraction of atactic polymer as determined by ^{13}C NMR spectroscopy. [f] Fraction insoluble in pentane at 25 °C. [g] The polymerization time was 30 min. [h] The polymerization time was 5 h. [i] The ^{13}C NMR spectrum of this polymer was consistent with it being atactic material ($P = 0.55$; see Table V). [j] This value is M_n and was estimated from the ^{13}C NMR spectrum.

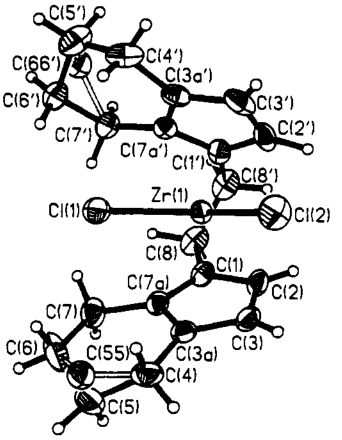

Figure 1. Ortep diagram for *meso*-(ethylenebis(η^5-tetrahydroindenyl))zirconium dichloride (**4**) with 50% probability thermal ellipsoids depicted. Carbon atoms C(5) and C(6'), each with site occupancies of 0.85, are thermally disordered with C(55) and C(66'), each with site occupancies of 0.15.

(entries 1–3, Table IV), as revealed by the ^{13}C NMR spectra of these materials (see Table V), whereas isotactic polymer was obtained with use of compounds **2** and **3** (entries 4 and 5, Table IV) and atactic polymer was produced with use of compound **4** (entry 6, Table IV).

The crude polymers, with the exception of that produced with compounds **2**–**4**, were extracted with pentane at 25 °C to remove atactic material.[2a] The pentane-insoluble fractions were analyzed by ^{13}C NMR spectroscopy, DSC, and GPC (Tables IV and V). The crude, unfractionated polymers produced were also analyzed by ^{13}C NMR spectroscopy (Table V). By use of the value of β, determined by analysis of pentad intensities obtained from the ^{13}C NMR spectra of the pentane-insoluble portion of the polymer (Table V), the weight fraction of atactic material (w_a) present in the corresponding crude polymer was calculated from the pentad intensities obtained from ^{13}C NMR spectra of these materials (Tables IV and V).[2a,9]

An unexpected result that ensues from this analysis is that the weight fraction of atactic (i.e. stereorandom)

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[9] The stereoselective copolymerization parameter and the weight fraction of atactic polymer can, in principle, be determined by a statistical analysis of all the pentad intensities in the crude, unfractionated polymer.[2a] However, an accurate analysis is not possible if significant overlap between some of the pentad resonances and signals due to regioirregular units or polymer end groups exists. This was *certainly* the case for the crude, unfractionated polymers prepared with catalysts *rac*-**1** and *meso*-**1**.

Table V. ^{13}C NMR Intensities of Methyl Pentads of Polypropylene[a]

catalyst	mmmm	mmmr	rmmr	mmrr	mmrm + rmrr[b]	rmrm	rrrr	rrrm[b]	mrrm
rac-**1a**/*meso*-**1a**[c]	0.92_2 (0.922)	0.04_5 (0.030)		0.02_3 (0.030)					0.01_0 (0.015)
rac-**1a**/*meso*-**1a**[d]	0.80_0 (0.800)	0.04_1 (0.043)	0.01_0 (0.009)	0.03_9 (0.043)	0.03_0 (0.036)	0.01_6 ().018)	0.01_6 (0.009)	0.02_8 (0.018)	0.02_0 (0.022)
rac-**1b**/*meso*-**1b**[e]	0.94_2 (0.941)	0.02_4 (0.023)		0.02_4 (0.023)					0.01_0 (0.011)
rac-**1b**/*meso*-**1b**[f]	0.73_8 (0.740)	0.06_0 (0.046)	0.01_2 (0.014)	0.03_3 (0.046)	0.06_2 (0.056)	0.02_4 (0.028)	0.01_3 (0.014)	0.03_7 (0.028)	0.02_4 (0.023)
rac-**1c**/*meso*-**1c**[g]	0.97_6 (0.976)	0.01_1 (0.0095)			0.009_0 (0.0095)				0.004_0 (0.0047)
rac-**1c**/*meso*-**1c**[h]	0.87_0 (0.889)	0.01_9 (0.020)	0.007_6 (0.006)	0.01_5 (0.020)	0.03_4 (0.024)	0.01_9 (0.012)	0.009_2 (0.006)	0.01_8 (0.012)	0.008_2 (0.010)
2[i]	0.89_0 (0.890)	0.05_2 (0.042)		0.04_4 (0.042)					0.01_5 (0.021)
3[j]	0.85_9 (0.865)	0.06_9 (0.054)		0.04_9 (0.054)					0.02_3 (0.027)
4[k]	0.08_3 (0.092)	0.14_2 (0.151)	0.08_0 (0.061)	0.15_4 (0.122)	0.21_9 (0.250)	0.11_7 (0.122)	0.05_6 (0.040)	0.08_8 (0.099)	0.06_0 (0.061)
		0.30_5[l] (0.304)			0.49_0[l] (0.494)			0.20_4[l] (0.200)	

[a] Observed intensities with calculated intensities in parentheses. [b] These signals were always overlapping with signals due to regioirregularities and/or end groups[2j] for unfractionated polymers prepared from catalysts *rac*-**1a–c** and *meso*-**1a–c**. [c] Pentane-insoluble portion; parameters $\beta = 0.983$, $w_a = 0.0$. [d] Unfractionated polymer; parameters $\beta = 0.983$, $w_a = 0.142$. [e] Pentane-insoluble portion; parameters $\beta = 0.988$, $w_a = 0.0$. [f] Unfractionated polymer; parameters $\beta = 0.988$, $w_a = 0.230$. [g] Pentane-insoluble portion; parameters $\beta = 0.995$, $w_a = 0.0$. [h] Unfractionated polymer; parameters $\beta = 0.995$, $w_a = 0.095$. [i] Unfractionated polymer; parameters $\beta = 0.977$, $w_a = 0.0$. A similar value of β was determined from the ^{13}C NMR spectrum of pentane-insoluble material. [j] Unfractionated polymer; parameters $\beta = 0.971$, $w_a = 0.0$. [k] Unfractionated polymer; parameter $P = 0.55$. [l] These values are the observed and calculated intensities for the mm-, mr-, and rr-centered triads.

polymer (w_a) produced does *not*, even closely, correspond to the mole fraction (X_{meso}) of the meso compounds present in the catalyst mixtures used. This is dramatically illustrated in the case of polymerizations with compounds *meso*-**1c** and *rac*-**1c**; 58% of the catalyst mixture is comprised of *meso*-**1c**, yet less than 10% by weight of the polymer produced is atactic or stereorandom! These results are in marked contrast to earlier work with mixtures of diastereomeric, titanium-based catalysts.[2a] The implication of the present results is that the intrinsic activity of the meso isomers is considerably less than that of their racemic counterparts and/or that a smaller percentage of the meso compound is converted into an active catalytic species. Using the former assumption, it is possibly to determine the individual polymerization activities of compounds *rac*-**1** and *meso*-**1**, and these are summarized in Table IV. In every case the racemic isomer is more active than the corresponding meso compound and the difference in activity is seen to dramatically increase as the substituent is made more bulky (compare entries 1 vs 3, Table IV). This hypothesis is further reinforced by comparing the activities of *meso*-**4** and *rac*-**3**, where a similar difference is observed (entries 5 and 6).

Racemic compounds **1** produce poly(propylene) that possesses a higher degree of chain microtacticity than that formed with catalysts **3** and **4**. Perhaps, the more conformationally rigid indenyl systems[10] prevent close approach of the monomer to the ligand framework prior to insertion—the "looser" diastereomeric transition states are thus closer in energy (Scheme I). Other explanations involving the intermediacy of α- or β-agostically stabilized species are also compatible with the results reported here in that a more rigid ligand framework may selectively destabilize e.g. α-agostic structures, thus leading to a decrease in the stereoselectivity of olefin insertion.[11]

Chain microtacticity is seen to be controlled by the steric environment at the metal center—i.e., the more hindered compounds (e.g. *rac*-**1c**, R = *t*Bu, entry 3) provide more highly isotactic polymer than the less sterically encumbered catalysts (e.g. *rac*-**1a**, R = Me, entry 1). This result seems entirely consistent with our initial hypothesis, as outlined in Scheme I. Furthermore, catalytic activity is seen to decline with increasing steric hindrance at the metal center in compounds **1**.

As might be expected, for polymers with closely equivalent molecular weight, the degree of crystallinity, as indirectly reflected by the melting temperatures, correlates with the degree of chain microtacticity (Table IV, entries 1–3 and 5). The low melting temperatures observed are probably the result of regioirregular insertions (both 2,1 and 1,3) during polymerization—regioirregularities were detected in all the polymers prepared. There seems to be no clear correlation between catalyst structure and the level of regioirregularities observed (typically on the order of 1–2%).

Interestingly, signals due to regioirregularities arising from 2,1-insertion of propylene were absent or very weak in the ^{13}C NMR spectra of poly(propylene) prepared with catalysts *rac*-**1b**, *rac*-**1c**, and **3**, although signals due to 1,3-insertion were observed in all samples. Qualitatively, it appears that as steric hindrance is increased at the metal center 1,3-insertion is favored at the expense of 2,1-insertion, although the total levels of regioirregularities are approximately constant. There has been the suggestion in the literature to the effect that 3,1-insertion proceeds

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(10) There are two conformations (δ and λ) available to the ansa ligand in these compounds, which have C_2 symmetry and can interconvert by rotation about the C–C bond of the ethylene bridge. The conformation adopted by the indenyl and tetrahydroindenyl compounds in the solid state has the substituents on the Cp rings in a forward position.[2f,6] The ^{1}H and ^{13}C NMR spectra of these compounds are invariant with temperature, suggesting that this conformation is highly favored in solution as well. In contrast, the ^{1}H and ^{13}C NMR spectra of compound **1c** (M = Ti) exhibit line-broadening behavior at low temperatures, consistent with a low-energy chemical exchange process that may involve conformer interconversion: Collins, S.; Hong, Y.; Ramachandran, R.; Taylor, N. J., submitted for publication in *Organometallics*.

(11) (a) Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 1289. (c) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566 and references therein.

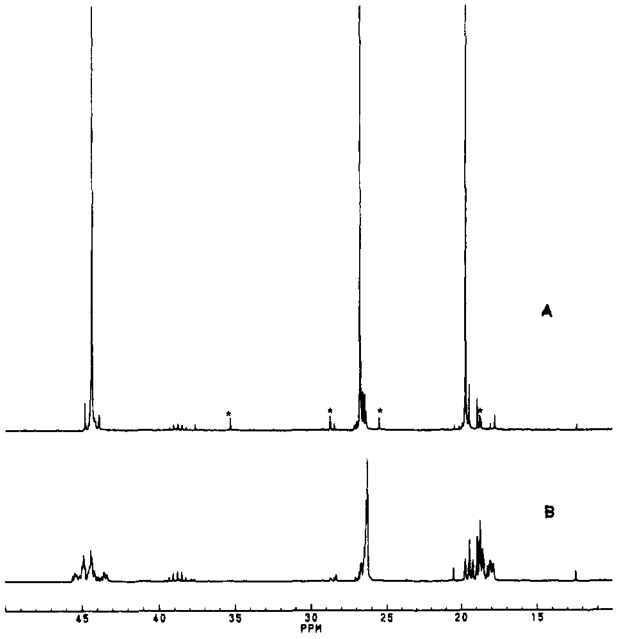


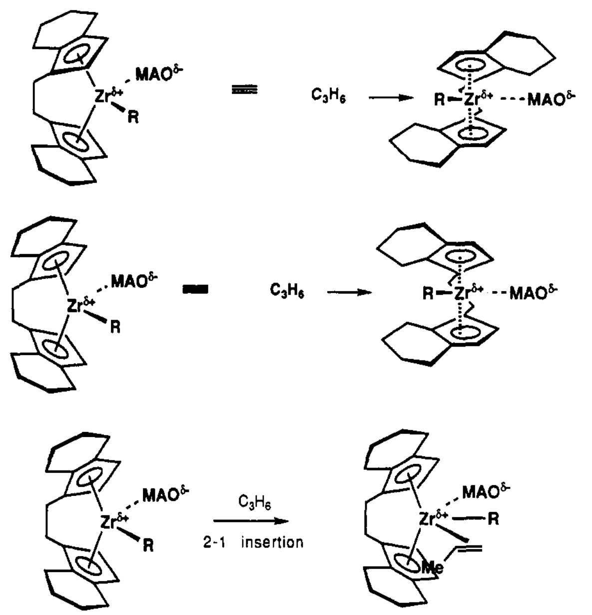
Figure 2. ^{13}C NMR spectra of isotactic (A) and atactic (B) poly(propylene) prepared with catalysts **3** and **4**, respectively. The intensities of these spectra have been normalized with respect to the intensity of the signal due to the methyl group of an *n*-propyl end group at 12.35 ppm,[2j] taking into account the different values of M_n measured from the spectra. Signals due to regioirregularities arising from 1,3-insertion[2j] of propylene are indicated with an asterisk.

via 2,1-insertion, followed by β-hydride elimination and subsequent 1,2-insertion of the polymer vinyl end group into the metal–hydrogen bond of the catalysts.[12] The present results would suggest that this process is facilitated with the more sterically hindered catalysts, perhaps via sterically accelerated, β-hydride elimination.

Quite surprisingly, the atactic polymer produced with meso compound **4** contained hardly any regioirregularities due to 2,1- or 1,3-insertion compared to the polymer obtained with its racemic isomer **3** (Figure 2).[13] This result assumes greater significance when viewed in the context of the polymer produced with compound **1d** (R = H). The polymer produced with compound **1d** (R = H) was atactic but had considerable levels (i.e. ~2%) of regioirregularities.[14] Also, as can be appreciated from Figure 2, the polymer produced with compound **4** is not ideally atactic; the intensity of the mm-centered triad is greater than that of the rr-centered triad. The pentad intensities observed (Table V) conform better to the chain-end control model ($4[mm][rr]/[mr]^2 = 1.04$) than to the enantiomorphic-site control model ($2[rr]/[mr] = 0.83$).[2a] The observed pentad intensities can be reproduced with use of the chain-end control model with $P = 0.55$ (Table V).[2a] This value corresponds to a very modest difference in energy (~0.2 kcal mol^{-1} at 40 °C) between diastereomeric transition states for monomer insertion.

We have found it useful to view the gross features of the interaction of the active, catalytic species in these polymerization (i.e. cationic, d^0, 14e$^-$ metallocenes)[3] with the methylaluminoxane counterion as being similar to that of a small molecule adsorbed on a surface.[15] Using this model (Scheme II), it is quite easy to rationalize some of the results seen; presumably the meso isomers interact with the MAO most strongly from their less hindered side at a lateral coordination site. Assuming the growing polymer chain occupies the central site, incoming monomer will thus be forced to coordinate at the remaining lateral site that is sterically blocked by the alkyl substituents on the Cp rings. The lower activities of the meso isomers, as compared to those of their racemic counterparts, as well as the dramatic reduction in activities of the meso isomers (as compared to those of their racemic counterparts) as the steric hindrance at the metal center is increased (i.e. Table IV; compare entries 1 and 3) are consistent with this analysis. Moreover, the unusual result concerning the lower level of regioirregularities in the atactic polymer prepared with catalyst **4** can also be rationalized by using these arguments. Secondary (2,1) insertion requires that the monomer coordinate to the metal with its methyl group directed inward toward the ansa ligand. If the meso catalyst is coordinated to the MAO counterion at the less hindered lateral site, then the more hindered site, accessible to incoming monomer, presents a significant steric barrier to 2,1-insertion by virtue of having both Cp rings substituted by alkyl groups.

Scheme II



It should be noted that all the polymers prepared have closely equivalent molecular weights.[16] This implies that the ratio of propagation to chain-transfer rates is nearly constant for these different catalysts. The exception is the polymer produced with the indenyl compound **2**, the molecular weight of which is nearly double that of the others. The reasons for this discrepancy are of interest, particularly in view of the fact that the hafnium analogues of

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(12) Rieger, B.; Mu, X.; Mallin, D. T.; Rausch, M. D.; Chien, J. C. W. *Macromolecules* **1990**, *23*, 3559.

(13) The ^{13}C NMR spectra of the pentane-soluble fractions of polymers prepared with catalysts **1a–c** all contained resonances due to regioirregularities (<2%). However, since considerable amounts of isotactic polymer (of low molecular weight) were present in these fractions, it was not possible to unambiguously determine whether the atactic polymer produced by compounds *meso*-**1a–c** was also more regioregular.

(14) Collins, S.; Gauthier, W. J., unpublished observations.

(15) A reviewer has pointed out that the same conclusions could be reached without invoking the intermediacy of cationic species as is implied here. We do not wish to imply that fully charge-separated species are involved; it is our opinion that there probably is association or coordination of the metallocene with the MAO, at least in the resting state of these catalysts. The concept that MAO functions as a support in these polymerizations has been suggested previously: Giannetti, E.; Nicoletti, G. M.; Mazzocchi, R. *J. Polym. Sci., Polymer Chem. Ed.* **1985**, *23*, 2117.

(16) This does not result from the fractionation procedure employed; the unfractionated polymers also had very similar, but somewhat lower, values of M_W while the dispersity, as expected, was higher.

compounds **2** and **3** produce much higher molecular weight polymer,[2f] an effect that is likely electronic in nature. Future studies with compounds of similar steric but different electronic environments will address this important question.[17]

Finally, we note that reports concerning the polymerization of propylene with tetramethylethylene-[18a] or dimethylsilyl-bridged[18] analogues of compounds **1** have appeared recently. With respect to the tetramethylethylene-bridged analogue of compound **1** (R = *t*Bu),[18a] the polymer obtained was much less stereoregular (62% mmmm) low melting (T_m = 103 °C) and low in molecular weight (M_w = 775), while the polymerization activity of this catalyst was lower than that of compound **1** (R = *t*Bu). Direct comparison of these results to those obtained here is tenuous at best, given the different experimental conditions employed.[19]

Concluding Remarks

It is apparent from the results presented in this paper, as well as the work of others,[2,18] that the polymerization activity of metallocene compounds and the microstructure of the polymer produced are quite sensitive to rather subtle steric effects in these catalyst systems (e.g. meso vs racemic or e.g. *i*Pr vs *t*-Bu). It is satisfying to be able to account for most of these differences using the simple (and intuitive) models presented in this paper (i.e. Schemes I and II). However, it is clear that the specific interaction of the MAO cocatalyst with the metallocene in these catalyst systems remains to be addressed.

Experimental Section

All solvents and reagents were obtained from commercial sources and purified as required. Tetrahydrofuran and toluene (Fischer Optima Grade, 250 ppt S) were dried and deoxygenated by distillation from benzophenone ketyl. The complex $ZrCl_4 \cdot 2THF$ was prepared by the method of Manzer.[20] Solutions of *n*-butyllithium in hexane were titrated prior to use. A toluene solution of $AlMe_3$ (2.0 M) was used as received. Propylene (CP grade 99.5%) used for polymerization was purchased from Linde Co. and deoxygenated and dried by passage through columns of BASF R3-11 catalyst and 4-Å molecular sieves. Polymerizations were conducted in a 1-L Zipperclave reactor (Autoclave Engineers) equipped with a spiral-wound external cooling jacket. Coolant mixture was passed through the jacket with use of a NesLab RTE-110 refrigerating circulator. Temperature control (to 0.5 °C) was maintained by using an RTD-220 temperature controller, which monitored the reaction solution temperature and cycled the circulator heater on or off as required. Routine ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 250 or AC 200 spectrometer. Samples were dissolved in $CDCl_3$ solution, and chemical shifts are referenced relative to residual $CHCl_3$ (δ 7.26 ppm), unless otherwise noted. The ^{13}C NMR spectra of poly(propylene) were obtained with a Bruker WM 300 or AM 250 spectrometer at 120 °C (pulse width 30°; sweep width 150 ppm; delay time 2.0 s with BB decoupling). Samples of the polymer were dissolved in 1,2,4-trichlorobenzene (1,2,4-TCB), containing 0.1% Irganox 1010 and ~10% DMSO-d_6, so as to give a final concentration of ~10 wt %. Chemical shifts are referenced with respect to that of the mmmm pentad at 19.7$_1$ ppm.[2j] GPC analyses were conducted with a Waters 150C chromatograph equipped with differential refractive index, Viscotek Model 100 continuous differential viscometer, and LDC/Milton Roy KMX-6 low-angle, laser light scattering detectors. Jordi mixed-bed and 1000-Å linear columns (1000–25 000 and 25 000–1 000 000) were employed, and samples (1% by weight in 1,2,4-TCB containing 0.1% Irganox 1010) were eluted with 1,2,4-TCB at 145 °C at a flow rate of 1.5 mL/min. DSC measurements were conducted with a Du Pont Instruments Series 99 thermal analyzer (previously calibrated with indium metal) at a heating rate of 10 °C/min from 40 to 170 °C. Repetitive runs were conducted until three constant melting endotherms were obtained.

Preparation of Metallocene Compounds 1. General Procedure. A solution of 1,2-bis(3-alkylcyclopentadienyl)ethane (5.0 mmol) in THF (25 mL) was cooled to −78 °C under argon in a two-necked round-bottom (rb) flask equipped with a gas inlet and condenser, a septum inlet, and a stirbar. *n*-Butyllithium (2.5 M in hexane, 11.0 mmol) was added dropwise via syringe. The pale yellow solution was then warmed to room temperature and stirred for 30 min at this temperature, at which time the dilithio salt had separated from solution. The mixture was cooled to −20 °C, and a solution of $ZrCl_4 \cdot 2THF$ (5.0 mmol) in 25 mL of THF was added slowly via syringe over 10–15 min to the vigorously stirred suspension. When this mixture was warmed to room temperature, a pale yellow solution was obtained. The solution was heated to reflux for 12 h to ensure complete reaction. The solution was cooled to room temperature and the solvent removed in vacuo to dryness to give a pale orange foam. The residue was extracted with dry toluene–CH_2Cl_2 (1:1) and filtered through a small pad of dry Celite, which was washed with additional toluene. The filtrate was concentrated in vacuo to give crude material, which was purified by gel chromatography on ~20 g of BioBeads SX-1, with toluene as eluent to remove polymeric material. Fractions containing the desired metallocene, as determined by ^1H NMR spectroscopy of a portion of each, were combined and concentrated in vacuo to give spectroscopically pure material (30–50% yield). Analytical samples of each diastereoisomeric mixture were obtained by crystallization from ether (R = Me) or hexane–ether (R = *i*Pr, *t*Bu).

***rac*- and *meso*-(Ethylenebis(η^5-3-methylcyclopentadienyl))zirconium Dichlorides (*rac*-1a and *meso*-1a).** *rac*-**1a** and *meso*-**1a** (ratio of rac:meso 1.2:1): ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 6.37 (pseudotriplet, J = 2.5 Hz, 1.09 H) and 6.28 (pseudotriplet, J = 2.6 Hz, 0.91 H), 5.92 (pseudotriplet, J = 2.8 Hz, 1.09 H) and 6.04 (pseudotriplet, J = 2.8 Hz, 0.91 H), 5.74 (pseudotriplet, J = 2.5 Hz, 1.09 H) and 5.65 (pseudotriplet, J = 2.5 Hz, 0.91 H), 3.12–3.07 (m, total 4 H), 2.26 (s, 3.27 H) and 2.30 (s, 2.73 H). *rac*-**1a**: ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 134.9, 132.8, 121.9, 111.2, 110.2, 30.54, 15.38. *meso*-**1a**: ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm) 134.9, 132.9, 122.3, 111.3, 110.2, 30.54, 15.51. High-resolution mass spectrum (m/z): calculated for $C_{14}H_{16}{}^{35}Cl_2{}^{90}Zr$, 343.967$_2$; found (EI), 343.968$_3$. Anal. Calcd for $C_{14}H_{16}Cl_2Zr$: C, 48.54; H, 4.66. Found: C, 48.89; H, 4.91. A mixture of the title compounds (100 mg, 0.29 mmol, meso:rac 1:1.3) was converted to the corresponding dimethyl analogues by reaction with MeLi (2.2 equiv) in hexane (5 mL) at 25 °C (12 h). Concentration of the mixture in vacuo and extraction of the solid obtained with C_6D_6 followed by filtration under Ar gave a solution of the dimethyl derivatives with the following spectral characteristics: ^1H NMR (200 MHz, C_6D_6) δ (ppm) 6.15–6.10 (overlapping pseudotriplets, total 2 H), 5.43 (pseudotriplet, J = 2 Hz, 0.87 H) and 5.35 (pseudotriplet, J = 2 Hz, 1.13 H), 5.20 (pseudotriplet, J = 2 Hz, 1.13 H) and 5.15 (pseudotriplet, J = 2 Hz, 0.87 H), 2.22 (br s, 4 H), 2.17 (s, 2.6 H), 2.15 (s, 3.4 H), −0.14 (s, 1.3 H), −0.22 (s, 3.4 H) and −0.28 (s, 1.3 H).

***rac*- and *meso*-(Ethylenebis(η^5-3-isopropylcyclopentadienyl))zirconium Dichlorides (*rac*-1b and *rac*-1b).** *rac*-**1b** and *meso*-**1b** (rac:meso 1.0:1.5): ^1H NMR (250 MHz,

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[17] It should be noted that a number of ethylene and propylene polymerization studies employing catalysts with different electronic *and* steric properties have been conducted. See for example: (a) Ewen, J. A.; Haspeslagh, L.; Elder, M. J.; Atwood, J. L. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1988; p 281. (b) Chien, J. C. W.; Razavi, A. *J. Polym. Sci., Part A* 1988, *26*, 2369.

[18] (a) Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. (b) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853.

[19] These results have to be viewed in the context of the results that were also obtained for polymerization of propylene with catalyst **3**.[18a] The poly(propylene) produced with compound **3** under conditions ostensibly similar to those reported here (or elsewhere)[2] was (a) lower in molecular weight (M_W = 3000), (b) higher in polydispersity (M_W/M_n = 2.9), (c) less isotactic (49% mmmm), and (d) lower melting (T_m = 85 °C). In our hands, and under the conditions reported ([Al]:[Zr] = 300:1, 11.2 mg of compound **3**, 400 mL of toluene, 2 bar of propylene, 50 °C, 50 min),[18a] we obtained poly(propylene) (R_p = 3300 with the following characteristics: 70.1% mmmm, M_W = 4300, M_W/M_n = 1.8, T_m = 110 °C.

[20] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 136.

CDCl$_3$) δ (ppm) 6.48 (pseudotriplet, J = 2.7 Hz, 0.80 H) and 6.38 (pseudotriplet, J = 2.7 Hz, 1.2 H), 5.93 (pseudotriplet, J = 2.9 Hz, 0.80 H) and 6.08 (pseudotriplet, J = 2.9 Hz, 1.2 H), 5.77 (pseudotriplet, J = 2.5 Hz, 0.80 H) and 5.68 (pseudotriplet, J = 2.5 Hz, 0.91 H), 3.2–3.0 (m, total 6 H), 1.23 (d, J = 6.8 Hz, 2.4 H) and 1.24 (d, J = 6.8 Hz, 3.6 H), 1.15 (d, J = 7.0 Hz, total 6 H). *rac*-**1b**: ^{13}C NMR (62.5 MHz, CDCl$_3$) δ (ppm) 143.3, 134.8, 120.0, 110.0, 109.2, 30.67, 28.57, 24.90, 21.2. *meso*-**1b**: ^{13}C NMR (62.5 MHz, CDCl$_3$) δ (ppm) 143.5, 134.9, 120.1, 110.0, 108.8, 30.58, 28.33, 24.79, 21.20. High-resolution mass spectrum (m/z): calculated for $C_{18}H_{24}{}^{35}Cl_2{}^{90}Zr$, 400.029$_8$; found (EI), 400.031$_2$. Anal. Calcd for $C_{18}H_{24}Cl_2Zr$: C, 53.71; H, 6.01. Found: C, 53.94; H, 5.69. A mixture of the title compounds (100 mg, 0.25 mmol, meso:rac 1.2:1) was converted to the corresponding dimethyl analogues by reaction with MeLi as described above. The crude mixture of dimethyl compounds obtained had the following NMR spectrum: ^{1}H NMR (250 MHz, C_6D_6) δ (ppm) 6.2–6.3 (overlapping pseudotriplets, 2 H) and 5.42 (pseudotriplet, J = 2 Hz, 1.1 H), 5.33 (pseudotriplet, J = 2 Hz, 0.9 H), 5.28 (pseudotriplet, J = 2 Hz, 0.9 H), 5.24 (pseudotriplet, J = 2 Hz, 1.1 H), 2.8–3.1 (overlapping septets, J = 6.0 Hz, total 2 H), 2.1–2.3 (m, 4 H), 1.25 (d, J = 6.0 Hz, 6 H), 1.15 (overlapping doublets, J = 6.0 Hz, 6 H), −0.10 (s, 1.6 H), −0.17 (s, 2.7 H), −0.24 (s, 1.6 H).

***rac*- and *meso*-(Ethylenebis(η^5-3-*tert*-butylcyclopentadienyl))zirconium Dichlorides (*rac*-1c and *meso*-1c).** *rac*-**1c** and **meso-1c** (rac:meso 1.0:1.5): ^{1}H NMR (250 MHz, CDCl$_3$) δ (ppm) 6.65 (pseudotriplet, J = 2.8 Hz, 0.57 H) and 6.61 (pseudotriplet, J = 2.9 Hz, 1.43 H), 6.13 (pseudotriplet, J = 2.9 Hz, 0.57 H) and 6.32 (pseudotriplet, J = 2.9 Hz, 1.43 H), 6.02 (pseudotriplet, J = 2.6 Hz, 0.57 H) and 5.96 (pseudotriplet, J = 2.6 Hz, 1.43 H), 3.2–3.0 (m, total 4 H), 1.33 (s, 5.14 H) and 1.36 (s, 12.86 H). *rac*-**1c**: ^{13}C NMR (62.5 MHz, CDCl$_3$) δ (ppm) 145.8, 133.5, 122.2, 109.2, 108.9, 33.32, 30.46 [C(CH_3)$_3$], 30.18. *meso*-**1c**: ^{13}C NMR (62.5 MHz, CDCl$_3$) δ (ppm) 144.8, 132.3, 121.1, 110.5, 109.6, 33.32, 30.70 [C(CH_3)$_3$], 30.50. High-resolution mass spectrum (m/z): calculated for $C_{20}H_{28}{}^{35}Cl_2{}^{90}Zr$, 428.061$_1$; found (EI) 428.056$_8$. Anal. Calcd for $C_{20}H_{28}Cl_2Zr$: C, 55.79; H, 6.55. Found: C, 55.90; H, 6.93. A mixture of the title compounds (150 mg, 0.35 mmol, meso:rac 1.5:1) was converted to the corresponding dimethyl analogues by reaction with MeLi as described above. The crude mixture of dimethyl compounds obtained had the following NMR spectrum: ^{1}H NMR (250 MHz, C_6D_6) δ (ppm) 6.3 (overlapping pseudotriplets, 2 H), 5.59 (pseudotriplet, J = 2 Hz, 1.2 H), 5.49 (overlapping pseudotriplets, J = 2 Hz, 2 H), 5.54 (pseudotriplets, J = 2 Hz, 0.8 H), 2.25 (two broad s, total 4 H), 1.36 (s, 18 H), 0.06 (s, 2.4 H), 0.05 (s, 1.8 H), 0.04 (s, 1.8 H).

***meso*-(Ethylenebis(η^5-tetrahydroindenyl))zirconium Dichloride (4).** ^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) 6.30 (d, J = 3.0 Hz, 2 H), 6.05 (d, J = 3.0 Hz, 2 H), 3.2–2.8 (complex multiplet, total 8 H), 2.6–2.2 (complex multiplet, total 4 H), 2.1–1.75 (complex multiplet, total 4 H), 1.7–2.4 (complex multiplet, total 4 H). ^{13}C NMR (50.0 MHz, CDCl$_3$): δ (ppm) 132.4, 130.4, 125.5, 121.2, 107.8, 28.33, 24.02, 23.12, 22.18, 21.95. High-resolution mass spectrum (m/z): calculated for $C_{20}H_{25}{}^{35}Cl_2{}^{90}Zr$, 424.029$_8$; found (EI), 424.028$_2$. Anal. Calcd for $C_{20}H_{24}Cl_2Zr$: C, 56.32; H, 5.67. Found: C, 56.43; H, 5.74. Single crystals, suitable for X-ray diffraction studies, were grown by slow evaporation of a toluene solution of the title compound.

X-ray Structural Determination of Compound 4. Relevant crystal, collection, and refinement data are summarized in Table I.

A crystal of dimensions 0.33 × 0.38 × 0.40 mm was mounted on a Nicolet-Siemens R3m diffractometer. Intensity data were obtained with use of graphite-monochromated Mo Kα radiation. Accurate unit cell dimensions were determined with use of 25 general reflections ($22 < 2\theta < 32°$) well distributed in reciprocal space. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 measurements. Absorption corrections to the data were made with use of the ψ-scan method (transmission factors 0.50–0.55).

The structure was solved by standard Patterson and Fourier methods with use of Nicolet SHELXTLPLUS software and a DEC Microvax II computer. Anisotropic refinement of all heavy atoms allowed location of the hydrogen atoms from a difference map, which were included in the refinement with isotropic thermal parameters. This refinement converged with R = 0.0290 and R_W = 0.0335; however, residual electron density (0.59 e Å^{-3}) in both six-membered rings that was still present in a difference map and the large thermal parameters associated with C(5) and C(6′) compared to those of their neighbors suggested that C(5) and C(6′) were thermally disordered. Atoms C(55), C(66′), and C(5), C(6′) with site occupancies of 0.15 and 0.85, respectively, were included in the refinement, which converged with R = 0.0256 and R_W = 0.0299 (maximum residual electron density 0.48 e Å^{-3} associated with Cl(2)).

Selected bond lengths and angles appear in Table III, and atomic coordinates and isotropic thermal parameters appear in Table II, while complete lists of bond lengths and angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters have been deposited as supplementary material (Tables S1–S4 inclusive) along with a table of structure factors.

Preparation of Methylaluminoxane (MAO). $Al_2(SO_4)_3 \cdot 16H_2O$ (23.64 g, 37.50 mmol, corresponding to 0.6000 mol of H_2O) was suspended in dry, degassed toluene (250 mL) in a 1-L three-necked round-bottom flask equipped with a large, magnetic stirbar, a dropping funnel (capacity 500 mL), an argon inlet, and a medium-porosity Schlenk fit connected to a second, 1-L round-bottom flask. Trimethylaluminum (TMA, 2.0 M, in toluene, 300 mL, 0.6 mol) was added to the dropping funnel via cannula under argon. Approximately 100 mL of this solution was slowly added dropwise to the vigorously stirred suspension of aluminum sulfate at 25 °C until vigorous CH_4 evolution had ceased. The remainder of the TMA solution was then added over 15–20 min at 25 °C. The suspension was heated to 60 °C and maintained at this temperature for 4 h at which time CH_4 evolution had effectively ceased. The mixture was then cooled to room temperature and filtered through the Schlenk frit by applying a slight vacuum to the receiver flask. After filtration was complete, the filter cake was washed with ~100 mL of dry, degassed toluene. The receiver flask was quickly disconnected from the Schlenk frit and placed under argon. The toluene and excess TMA were removed in vacuo, and the viscous liquid was placed under vacuum (10^{-2} mmHg) until a solid foam was obtained. The flask, still under vacuum, was transferred to a Vacuum Atmospheres glovebox, and the solid MAO was scraped out and stored until required; yield 8.0 g, 21% based on the formula (CH_3AlO). Cryoscopy in benzene under N_2 gave $M_n \approx 1300 \pm 100$.

Polymerization Procedure. MAO (600 mg) was dissolved in 10.0 mL of dry toluene in a 50-mL sample bomb in a glovebox. The bomb was connected to a port on the Zipperclave reactor, and the contents were flushed into the reactor with use of 500 mL of dry toluene under nitrogen pressure. The bomb was disconnected and the reactor saturated with propylene at 45 psi and 40 °C while the mixture was stirred at 1500 rpm. Mixtures of compounds *rac*-**1** and *meso*-**1** (ca. 1.0–2.0 mg) were dissolved in 5.0 mL of dry toluene in an rb flask under nitrogen. The solution was transferred to the reactor by gastight syringe through a septum port. Propylene uptake was monitored with use of a mass-flow controller interfaced to a chart recorder. Polymerizations were stopped after the times listed in Table I by venting the monomer and draining the polymer slurry through a ball valve in the bottom of the reactor, under N_2, into a 1-L flask containing 10 mL of MeOH. The solvent was removed in vacuo. For polymerizations employing catalysts **1a–c**, **2**, and **3**, the crude polymer was slurried in MeOH (200 mL). The MeOH was then removed in vacuo to azeotropically remove residual toluene. The polymer was then suspended in 3 M HCl·MeOH (1:1; 100 mL), the suspension was agitated in a blender for 10–15 min and then filtered, and the residue was washed with MeOH (50 mL) (concentration of the filtrate gave a small quantity of white powder, totally soluble in 3 M HCl). The polymer cake was dried in vacuo at 60 °C to constant weight. For polymerizations employing catalyst **4**, the polymer slurry was concentrated to dryness in vacuo to constant weight. In the case of polymerizations with catalysts **1a–c**, a weighed portion of the crude polymer obtained was washed with pentane at 25 °C to constant weight; the soluble portion contained both atactic and isotactic polymer (^{13}C NMR), and the insoluble portion was analyzed by NMR, GPC, and DSC methods with the results summarized in Table III.

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Supplementary Material Available: Complete lists of bond lengths and angles and tables of H atom coordinates and isotropic thermal parameters and heavy-atom anisotropic thermal parameters for compound 4 (5 pages); a table of structure factors for compound 4 (12 pages). Ordering information is given on any current masthead page.

Notes

Molecular and Crystal Structure of 2,2′,5,5′-Tetramethyl-1,1′-distibaferrocene: A Short Sb···Sb Inter-Ring Contact

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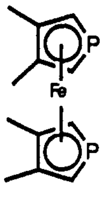
Summary: 2,2′,5,5′-Tetramethyl-1,1′-distibaferrocene (**13**) was obtained from the reaction of 1-phenyl-2,5-dimethylstibole with lithium followed by $FeCl_2$. Red crystals of **13** form in *Pc* space group with $Z = 2$, $a = 6.811$ (1) Å, $b = 11.336$ (3) Å, $c = 8.918$ (3) Å, and $\beta = 102.80$ (2)°. The full structure has been determined and shows a ferrocene-like arrangement with a close (3.68 Å) inter-ring Sb···Sb contact.

The group 15 heterobenzenes 1–5 are an important series in which elements of an entire column of the periodic table have been incorporated into aromatic rings.[1-3] The comparison of properties, particularly structural properties,[4-6] of 1–5 has provided insight into the concepts of aromaticity and π-bonding between carbon and the heavier main-group elements.[1-3] The group 15 diheteroferrocenes 6–10 form a similar series that can be compared with the heterobenzenes. Derivatives of 6,[7] 7,[8-10] 8,[8,11-13] and 9[8,14] have been reported. Prior structural data are available for 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (11)[9] and 2,2′,5,5′-tetramethyl-1,1′-diarsaferrocene (12).[12] We report here on the crystal and molecular structure of 2,2′,5,5′-tetramethyl-1,1′-distibaferrocene (13).

1 E = N
2 P
3 As
4 Sb
5 Bi

6 E = N
7 P
8 As
9 Sb
10 Bi



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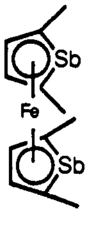
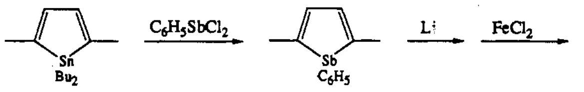
12



13

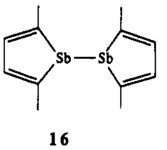
Results and Discussion

Compound 13 was prepared by a route modified compared to that previously reported.[14] The exchange reaction of phenylantimony dichloride with 1,1-dibutyl-2,5-dimethylstannole (14) gave a 63% yield of 1-phenyl-2,5-di-



13

14 15



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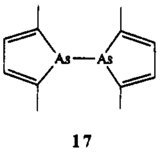

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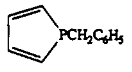

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