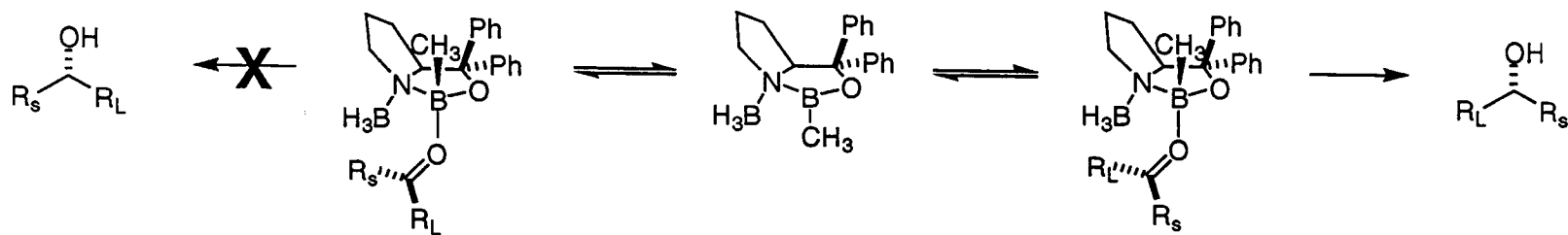
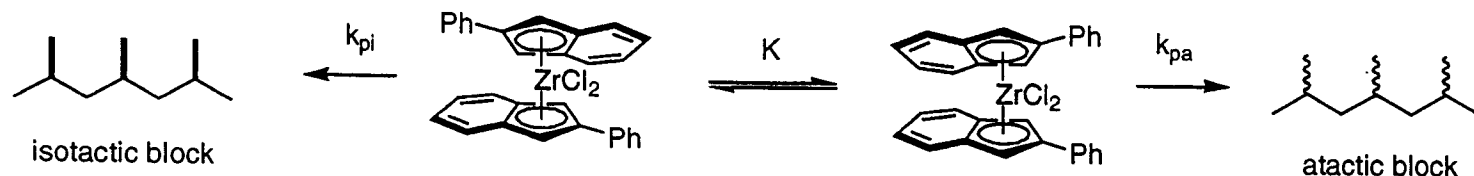


# Polypropylene Synthesis: Use of Dynamic Catalysts

## Single State Catalyst:



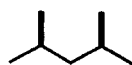
## Two State Catalyst:



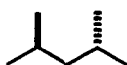
- In catalysis as we understand it, a catalyst has a desired state and an undesired one.
- Effort is spent trying to minimize reaction through this undesired state.
- What if we need to control both states?
- How can we design a two state catalyst capable of producing 2 stereochemical outcomes in a controlled fashion?

# Polypropylene Stereochemistry

**stereochemical dyads:**

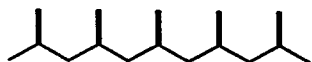


*syn = m*

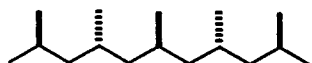


*anti = r*

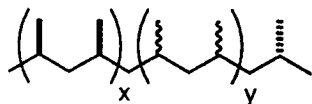
**stereochemical pentads:**



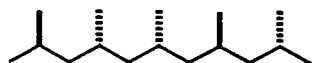
isotactic polypropylene  
*mmmm*



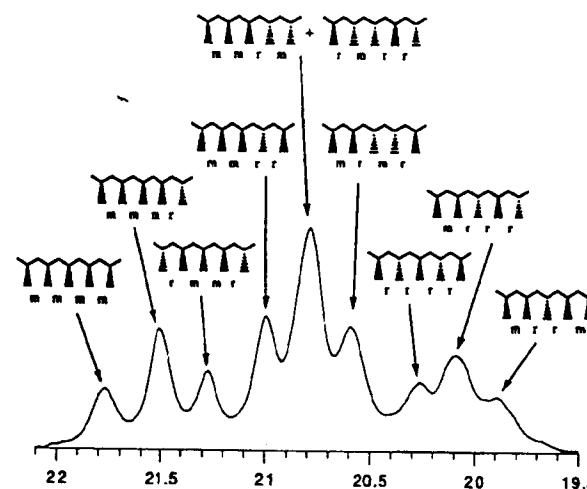
syndiotactic polypropylene  
*rrrr*



isotactic block polypropylene



atactic polypropylene  
*rmrr*

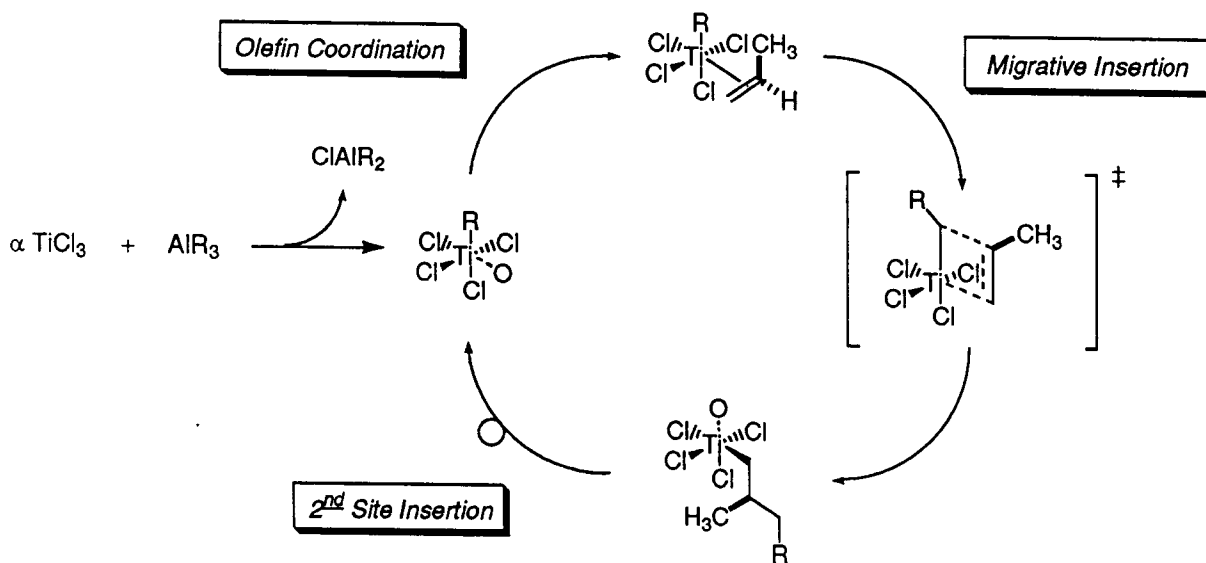


The chemical shift of a particular methyl group is sensitive to the relative configurations of the neighbouring methyl groups. Hence, the pentad is a commonly used measure for  $\alpha$  olefin stereochemistry since this is the highest level of resolution available at ~ 100 MHz NMR.

- A wide range of polypropylene geometries are possible, yielding a wide range of physical properties.
- NMR is a convenient and accurate method for determination of stereochemical content.

Most microstructures can be easily accessed through careful choice of catalyst.

## Ziegler Natta Catalysis



*"Up to now, there is no direct proof for the structures proposed; most of them are the result of speculations or derived from indirect experimental indications."*

- Muelhaupt, 1980

- Ziegler Natta catalysis is a widely used form of heterogeneous catalysis which can generate various isotactic polyolefins.
- Cossee proposed a two site mechanism where the polymer chain undergoes insertion into a coordinated olefin ( *Tetrahedron Lett.* **1960**, 17, 12-21 ).
- Stereoselectivity is induced by the nature of the neighbouring titanium atoms in the matrix.

Despite the amazing success of these systems, little rationale design is possible.

# Isotactic Polypropylene Synthesis

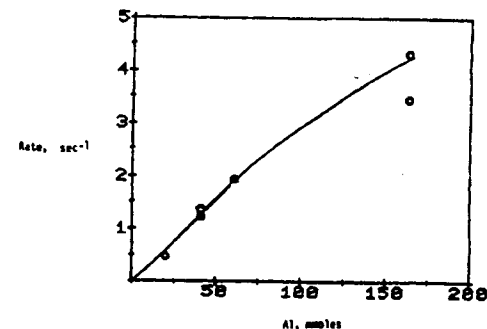
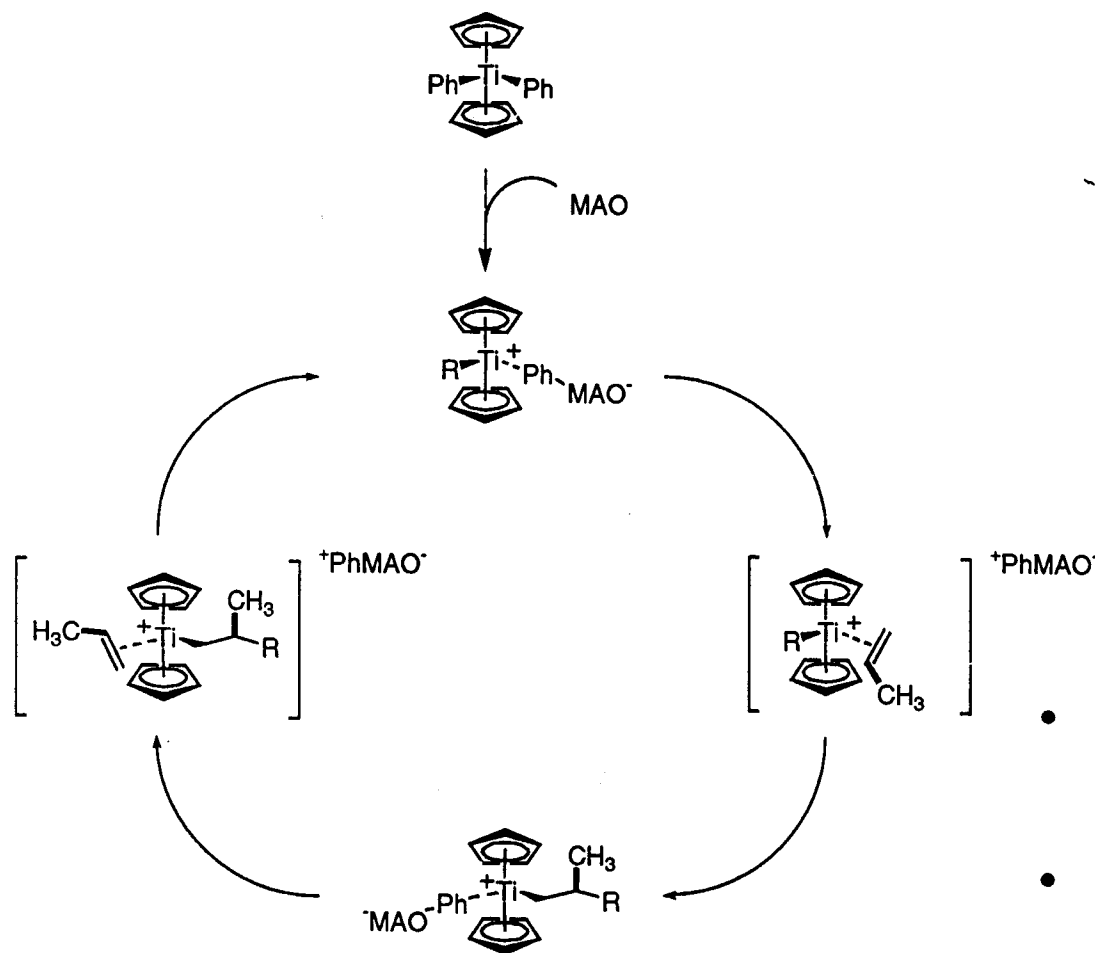


Figure 1. Integral polymerization rate dependence on concentration of total aluminum at  $-60^\circ\text{C}$ . Rate: moles of propylene consumed per mole of  $\text{Cp}_2\text{Ti}(\text{Ph})_2$  per second (Table I).

Table I. Yields and Molecular Weights Obtained with  $\text{Cp}_2\text{Ti}(\text{Ph})_2$  at Different Aluminum Concentrations<sup>a</sup>

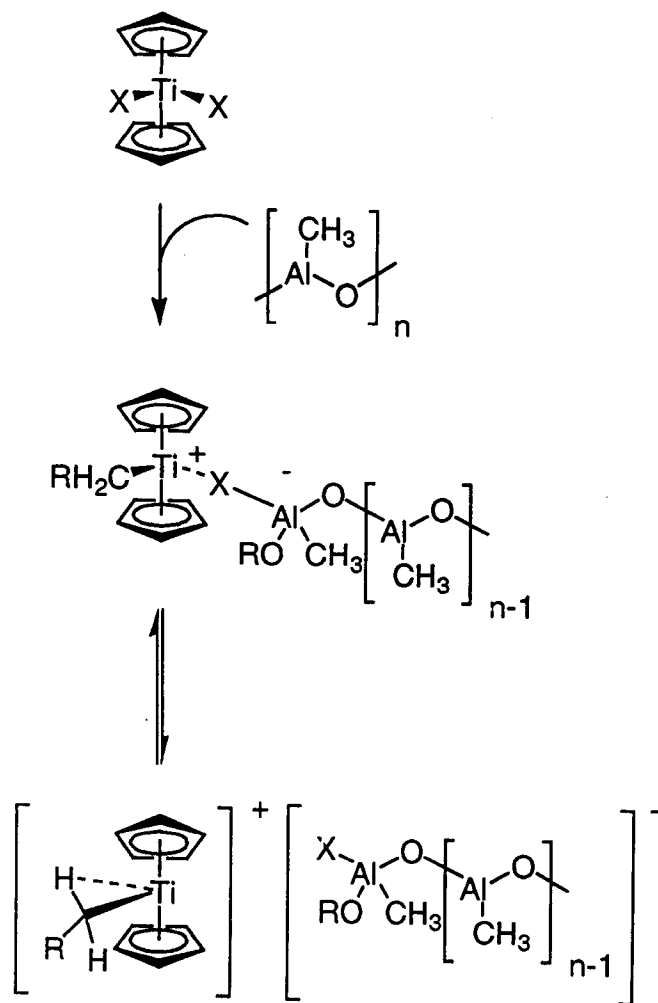
Ti, mmol	Al, mmol	$\text{C}_3\text{H}_6$ , mol	yield, g	turnovers, <sup>b</sup> $\text{s}^{-1}$	$10^{-4} \bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.062	20.5	4.0	4.5	0.48	7.47	1.9
0.056	41.0	4.8	11.4	1.22	14.4	1.9
0.017	41.0	4.0	3.4	1.35	17.6	1.6
0.061	61.5	4.0	17.6	1.92	16.7	1.7
0.066	164	5.4	34.5	3.43	27.1	1.7
0.065	164	4.3	39.5	4.47	30.7	1.6

<sup>a</sup> Polymerization conditions:  $400\text{ cm}^3$  of toluene,  $-60^\circ\text{C}$ , 1 h. These polymerizations were initiated by adding propylene. All others by injection of the catalyst. <sup>b</sup> Rate in moles of propylene/mole of Ti/s.

- The first homogeneous catalysts were simple titanocenes.
- Activation with methyl aluminoxane provided catalysts capable of polymerizing  $\alpha$  olefins.

Ewen, J.A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

# Activation Processes: The Role of MAO



- Early catalytic systems employed alkyl aluminum chlorides as activators.
- Vollmer discovered that adventitious water greatly accelerated the reaction.
- Methyl aluminoxane ( MAO ) is a undefined hydrolysis product of trimethyl aluminum.

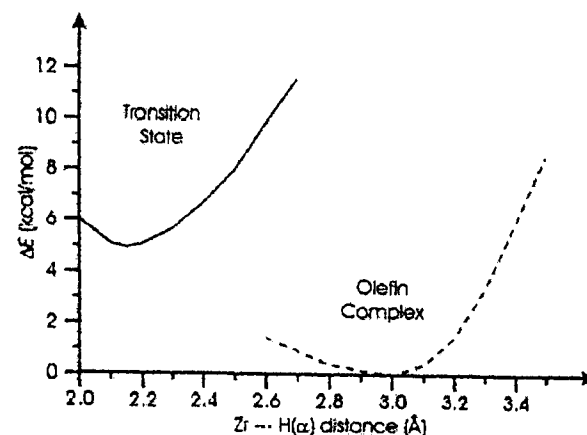
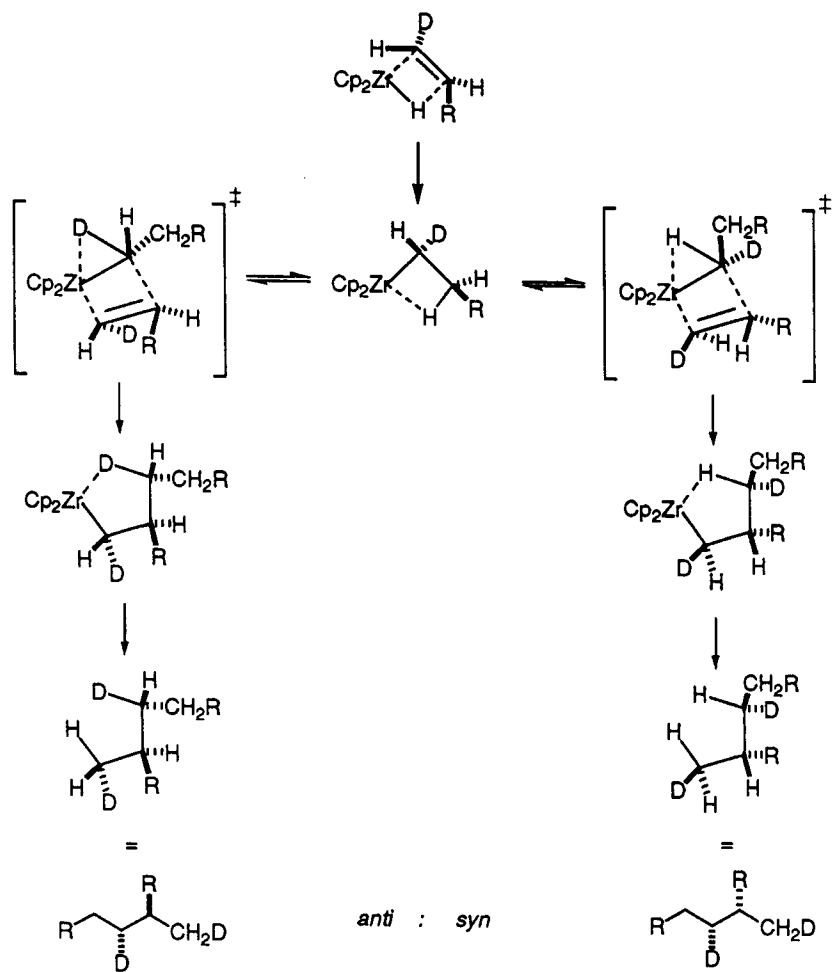
Table 1. Ethylene polymerization with the system bis(cyclopentadienyl)dimethyltitanium(IV), trimethylaluminum, and water.

Yield of polyethylene [g/l]	Time [h]	Temp. [°C]	Titanium concentration [mol/l]	Amount of water added [mol/l]	Rel. Mol. Wt. (viscometric)
33.6	112	21	$7 \times 10^{-4}$	$< 0.25 \times 10^{-3}$	3800000
43.2	1.5	21	$7 \times 10^{-4}$	$4.6 \times 10^{-3}$	200000
57.6	1.5	50	$3.5 \times 10^{-4}$	$4.6 \times 10^{-3}$	90000
34.2	1.5	12	$1.1 \times 10^{-4}$	$7.5 \times 10^{-3}$	---

- Based on careful studies, it has been determined that two MAOs are required.
- The dissociation of the MAO counterion is promoted by agostic interactions with the methylene and methine protons of the growing alkyl chain.

Vollmer, H-J. *Angew. Chem., Int. Ed. Eng.* **1976**, *15*, 630.

# The Role of Agostic Interactions



**Figure 16.** Relative energies of the transition state (continuous line) and of the olefin complex (dashed line) for propene insertion into the Zr-methyl bond of the  $\text{H}_2\text{-Si}(\text{Cp})_2\text{ZrCH}_3^+$  system, as a function of the Zr-H( $\alpha$ ) distance.<sup>175</sup>

- Experimental evidence for these effects was gained through stereochemical analysis of the polymer formed from (E)-1-deuteriohexene.
- The selectivity was not dependent on use of a chiral catalyst:
  - $\text{rac}(\text{EBTHI})_2\text{ZrCl}_2$  / *syn* : *anti* 2.55 : 1
  - $\text{Cp}_2\text{ZrCl}_2$  / *syn* : *anti* 1.3 : 1

# The Insertion Event: Orbital Interactions and Control

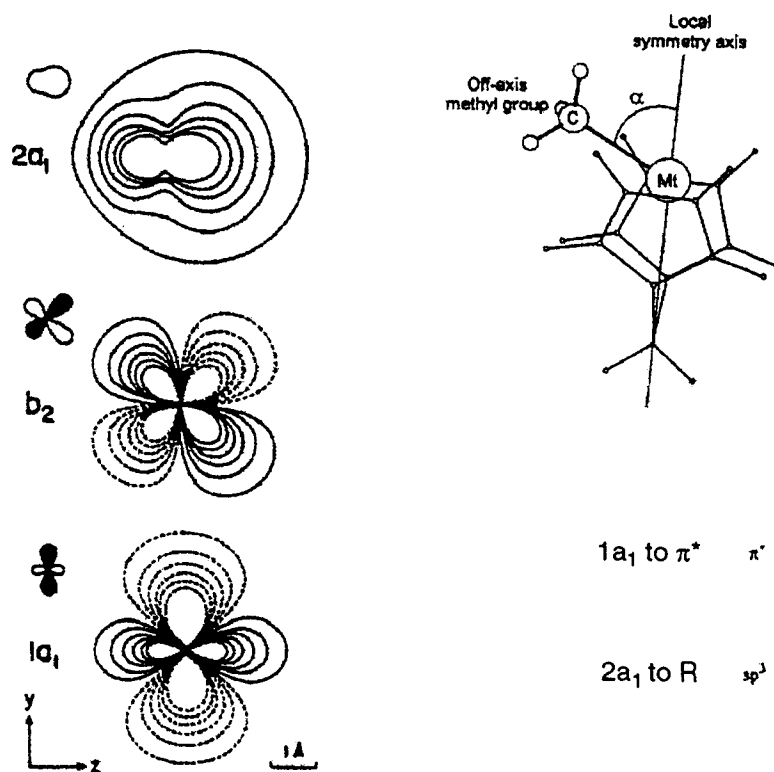


Figure 1. Contour diagram in the  $yz$  plane of the three most important extended Hückel molecular orbitals of the generic bent metallocene  $\text{Cp}_2\text{Mt}$ . Solid and dashed lines correspond to positive and negative contour of the wave function.<sup>56</sup>

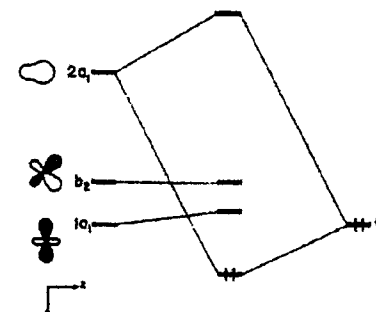


Figure 5. Interaction diagram for the generic  $d^0$  bent metallocene  $\text{Cp}_2\text{Mt}$ , on the left, and  $\text{H}^+$ , on the right. The orbitals are sketched in the  $yz$  plane.<sup>56</sup>

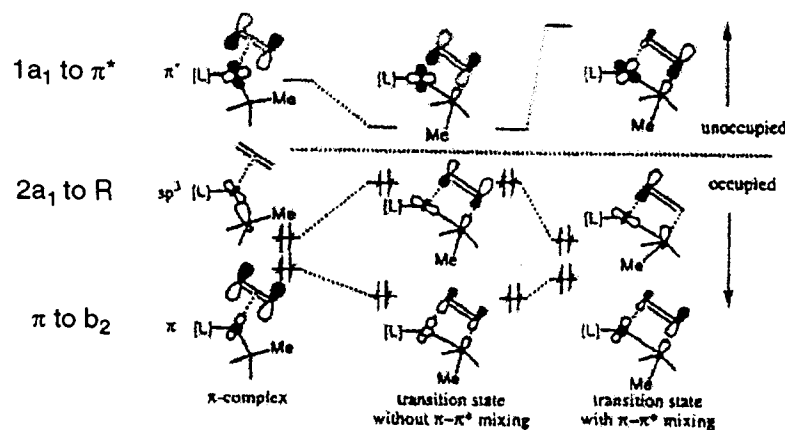


Figure 13. Molecular orbital diagram of the mixing process involved in the insertion of olefin into a metal-carbon bond. Orbital occupations are shown for the formal  $d^0$  configuration on the metal.<sup>191</sup>

# Stereochemistry of a $C_{2v}$ Catalyst

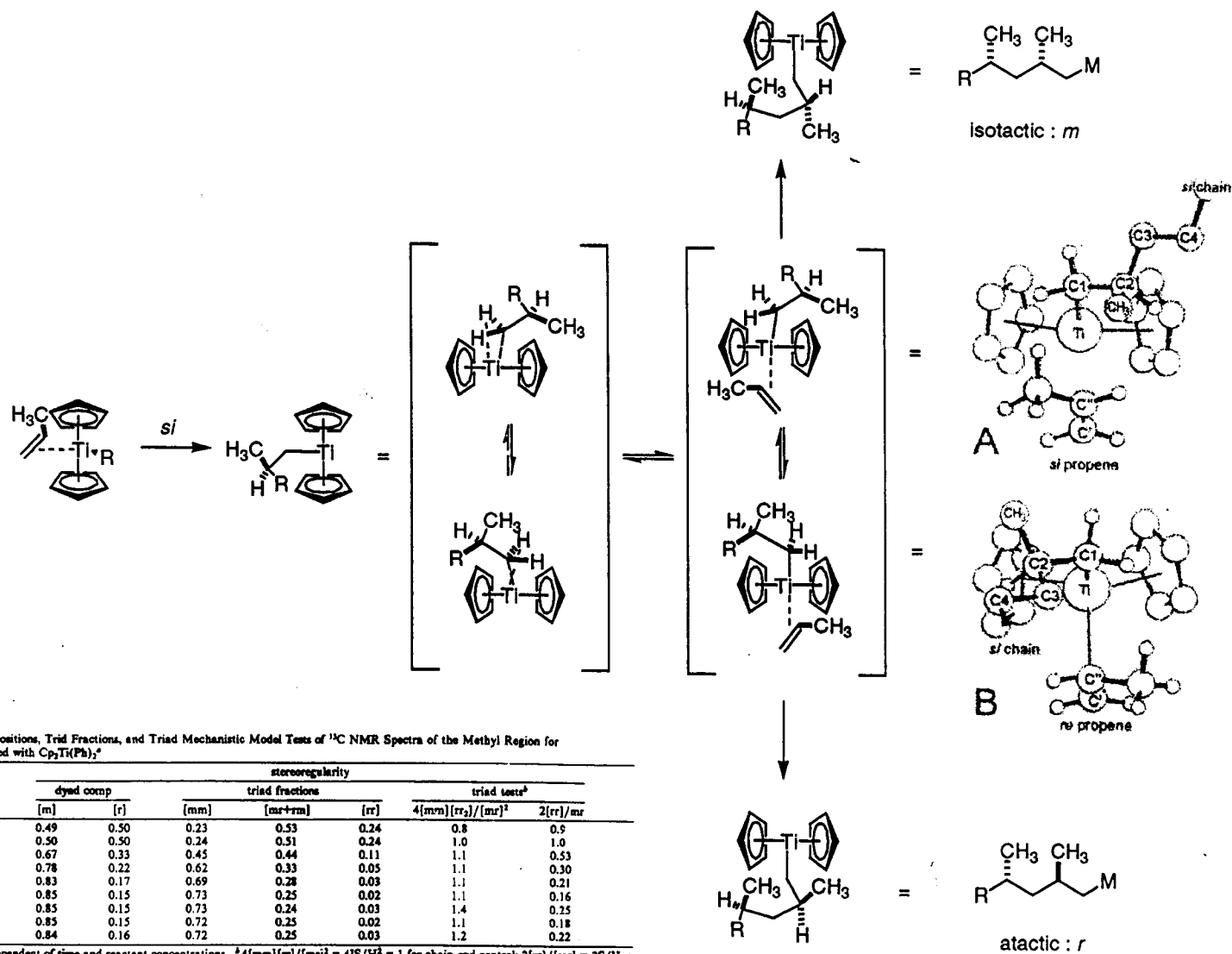


Table IV. Dyad Compositions, Triad Fractions, and Triad Mechanistic Model Tests of  $^{13}\text{C}$  NMR Spectra of the Methyl Region for Polypropylenes Obtained with  $\text{Cp}_2\text{Ti}(\text{Ph})_2$ <sup>a</sup>

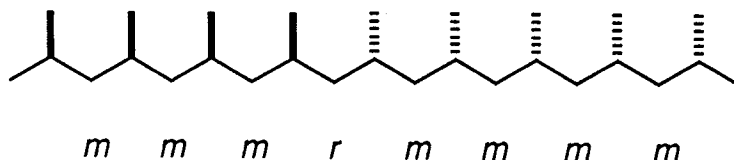
polym temp. °C	stereoregularity						
	dyad comp		triad fractions			triad tests <sup>b</sup>	
	[m]	[r]	[mm]	[mr+rm]	[rr]	$4[\text{mm}][\text{rr}]/[\text{mr}]^2$	$2[\text{rr}]/\text{mr}$
50	0.49	0.50	0.23	0.53	0.24	0.8	0.9
25	0.50	0.50	0.24	0.51	0.24	1.0	1.0
0	0.67	0.33	0.45	0.44	0.11	1.1	0.53
-15	0.78	0.22	0.62	0.33	0.05	1.1	0.30
-30	0.83	0.17	0.69	0.28	0.03	1.1	0.21
-45	0.85	0.15	0.73	0.25	0.02	1.1	0.16
-60	0.85	0.15	0.73	0.24	0.03	1.4	0.25
-75	0.85	0.15	0.72	0.25	0.02	1.1	0.18
-85	0.84	0.16	0.72	0.25	0.02	1.2	0.22

<sup>a</sup> Stereoregularity independent of time and reactant concentrations. <sup>b</sup>  $4[\text{mm}][\text{rr}]/[\text{mr}]^2 = 4\text{IS}/\text{H}^2 = 1$  for chain-end control;  $2[\text{rr}]/[\text{mr}] = 2\text{S}/\text{H} = 1$  for site control



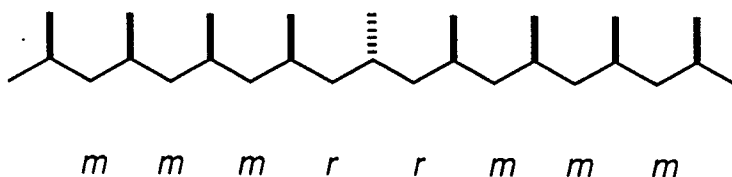
# Chain End vs. Catalytic Site Control

## Chain End Control:



$$mmmr : mmrr : mmrm : mrrm = 1 : 0 : 1 : 0$$

## Catalytic Site Control:

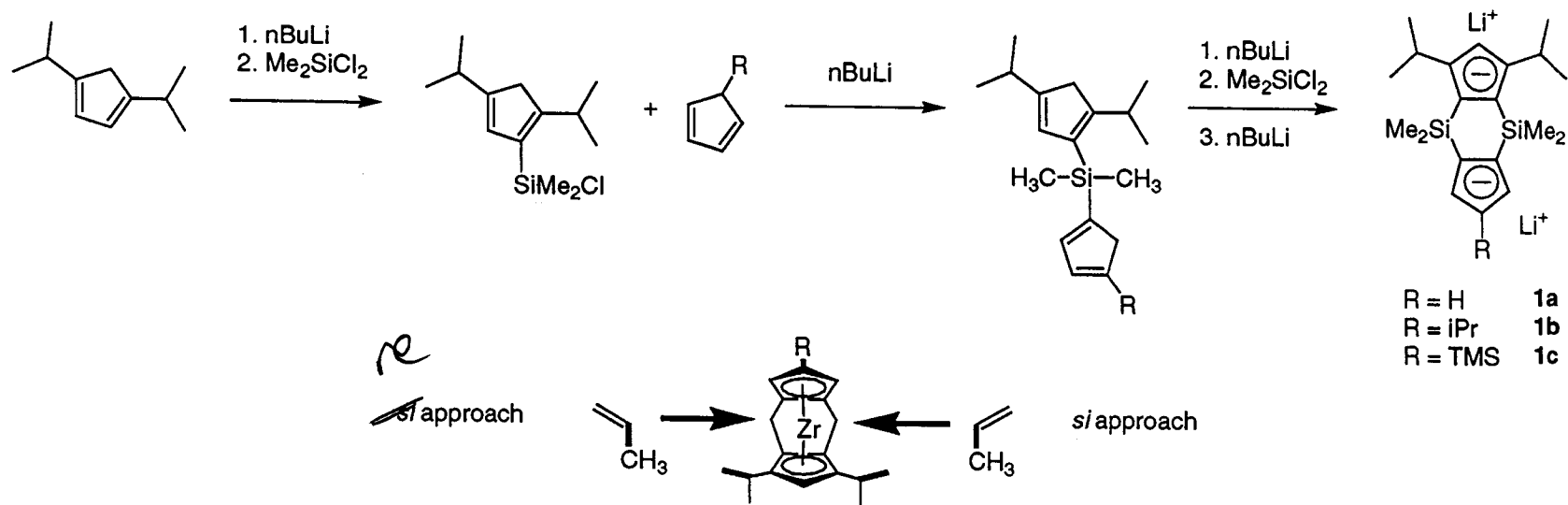


$$mmmr : mmrr : mmrm : mrrm = 2 : 2 : 0 : 1$$

- Assuming a selective polymerization process, the type of stereochemical control can be determined by analysis of the types of errors observed in an isotactic sequence.
- In chain end control, monomer misinsertion will cause a change in the sense of insertion selectivity, evidenced by single *r* dyads.
- In catalytic site control, a monomer misinsertion will be corrected by the influence of the catalyst, leading to *rr* triads.

Analysis of polymer stereochemistry reveals insights about polymerization mechanism.

# Syndiotactic Polypropylene Synthesis



- Design of a rigid C<sub>1</sub> symmetric catalyst provides for two enantiotopic binding sites.
- The double silyl bridges aid in maintaining the stereochemical integrity of the catalyst.

Bercaw, J.E. *J. Am. Chem. Soc.* **1996**, *118*, 11988.

# Stereochemistry of a $C_1$ Catalyst

entry	catalyst	$[C_3H_6]$ (M)	activity <sup>a</sup>	$[r]$ (%)	$T_m$ (°C)	$M_n$	$M_w/M_n$
1	1a	0.8	$3 \times 10^{3h}$	90.6	109	$2.9 \times 10^4$	1.9
2	1a	1.5	$1.3 \times 10^{3h}$	95.0	125	nd <sup>c</sup>	nd
3	1a	2.1	$2.9 \times 10^{3h}$	94.7	131	$6.1 \times 10^4$	3.0
4	1a	2.8	$3.1 \times 10^{3h}$	95.9	139	$9.0 \times 10^4$	4.2
5	1a	3.4	$5.3 \times 10^{3h}$	97.1	140	$1.01 \times 10^5$	1.5
6	1b	0.8	$1.9 \times 10^4$	80.2	nd	$3.4 \times 10^3$	2.3
7	1b	1.5	$1.9 \times 10^4$	91.8	d	$5.9 \times 10^3$	2.4
8	1b	2.1	$3.5 \times 10^4$	92.7	d	$1.46 \times 10^4$	1.7
9	1b	2.9	$5.9 \times 10^4$	95.1	118	$1.15 \times 10^5$	3.0
10	1b	3.4	$1.04 \times 10^5$	97.1	127	$1.66 \times 10^5$	1.8
11	1c	0.8	$7 \times 10^3$	81.5	d	$3.8 \times 10^3$	1.9
12	1c	1.5	$2.4 \times 10^4$	86.7	d	$4.9 \times 10^4$	2.2
13	1c	2.1	$4.3 \times 10^4$	90.7	102	$7.7 \times 10^4$	1.7
14	1c	2.8	$5.4 \times 10^4$	93.6	119	nd	nd
15	1c	3.4	$5.7 \times 10^4$	96.5	124	$1.33 \times 10^5$	1.8

<sup>a</sup> Defined as grams of polymer per gram of Zr per hour. <sup>b</sup> A different sample of methylalumoxane cocatalyst was employed for entries 1–5. The activity data are therefore not comparable with entries 6–15. <sup>c</sup> Not determined. <sup>d</sup> No melting point observed by DSC.

entry	catalyst	$T$ (°C)	activity <sup>a</sup>	$[r]$ (%)	$T_m$ (°C)	$M_n$	$M_w/M_n$
16	1a	20	$2.8 \times 10^6$	97.1	151	$1.25 \times 10^6$	1.9
17	1a	50	$7.9 \times 10^6$	96.6	140	$3.3 \times 10^6$	2.3
18	1a	70	$16.9 \times 10^6$	94.1	119	$1.6 \times 10^7$	3.2
19	1b	20	$3.2 \times 10^5$	99.4	151	$9.8 \times 10^5$	2.0
20	1b	50	$1.4 \times 10^6$	94.5	123	$2.9 \times 10^6$	2.0
21	1b	70	$9.2 \times 10^5$	90.6	b	$1.3 \times 10^6$	2.3
22	1c	20	$3.5 \times 10^5$	97.9	152	$7.9 \times 10^5$	1.8
23	1c	50	$8.3 \times 10^5$	96.0	124	$2.6 \times 10^6$	2.1
24	1c	70	$7.3 \times 10^5$	91.3	b	$1.4 \times 10^6$	2.2

<sup>a</sup> Defined as grams of polymer per gram of Zr per hour. <sup>b</sup> No melting point observed by DSC. <sup>c</sup> These two runs were carried out earlier with a differing catalyst:MAO ratio (1:325) and with propylene of generally lower purity than for the other runs.

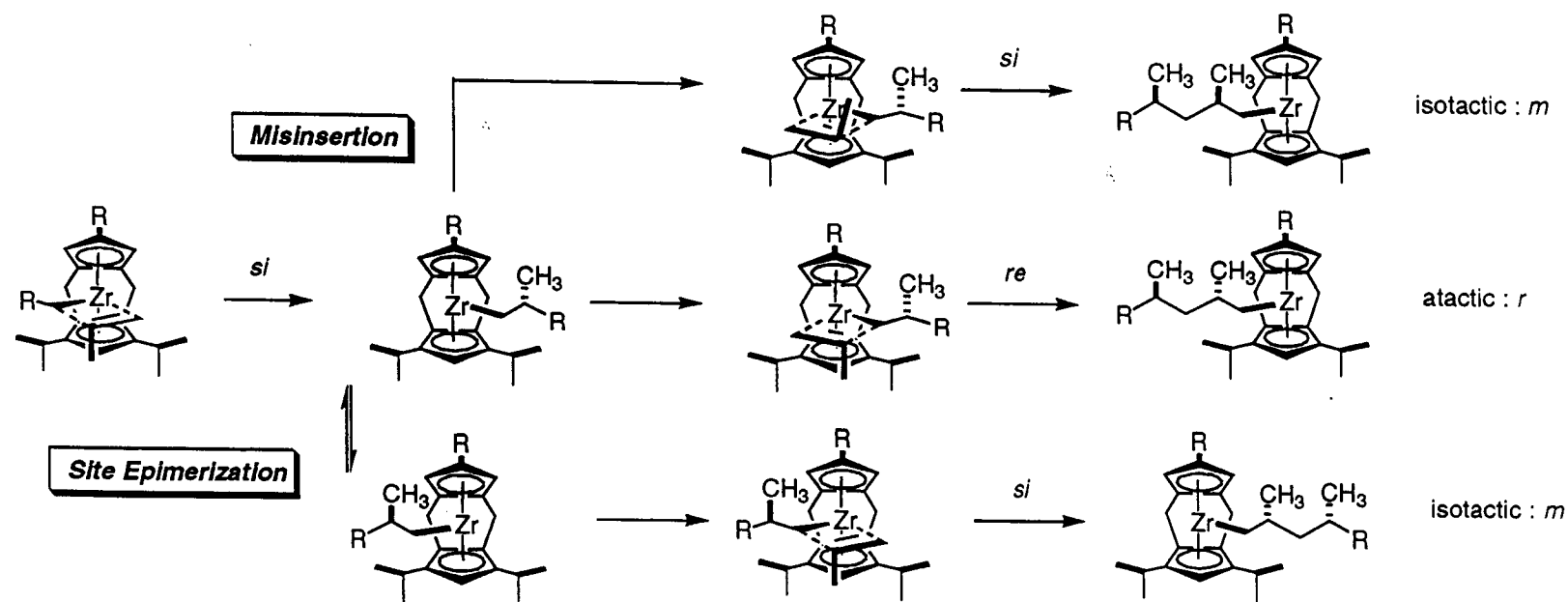
[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mrrmm]+[mrrr]	[mrrmr]	[rrrr]	[mrrrr]	[mrrrm]
		1.7	3.6	11.6		68.6	14.4	
		<1	1.5	5.1		79.5	13.5	
		<1	2.1	4.7		83.6	9.0	
		<1	2.0	3.5		86.1	7.7	
		<1	1.9	2.7		90.7	4.2	
1.4		3.0	6.0	19.9	5.1	41.5	20.4	2.5
			2.3	12.6	<1	68.2	17.0	
		<1	1.4	10.3	<1	71.6	13.3	2.6
			1.3	8.6		82.6	7.4	
				5.5		89.0	5.5	
<1	1.2	2.4	5.3	18.8	4.2	47.2	18.0	1.7
		1.7	3.6	16.7	3.4	59.0	15.0	
		<1	2.1	13.0	1.3	68.9	13.5	
			2.4	7.8		75.8	12.7	1.2
				7		81.6	11.3	

[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mrrmm]+[mrrr]	[mrrmr]	[rrrr]	[mrrrr]	[mrrrm]
		0.8	1.5	0.9		93.4	3.5	
		<1	2.0	2.4		90.6	4.9	
		<1	3.0	7.3	<1	79.5	10.0	
		-	-	1.2		97.5	1.2	
		1.6	1.9	4.2		81.0	11.1	
		1.8	2.4	12.9	<1	68.4	14.3	
		0.3	0.6	1.6		94.2	3.3	
		-	1.2	4.8		83.8	10.1	
		<1	3	13.6	<1	65.8	17.1	

Bercaw, J.E. *J. Am. Chem. Soc.* **1999**, *121*, 564.

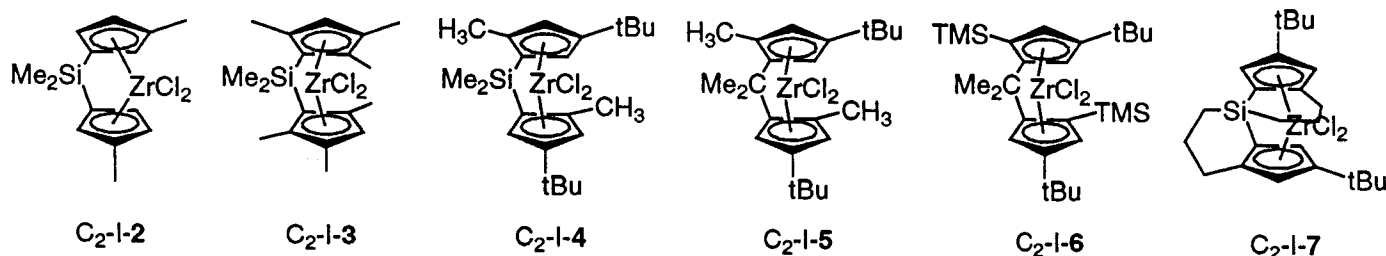
- The inverse relationship of monomer concentration to errors is indicative of a second order process competing with a first order process.
- The direct relationship between errors and temperature agrees with this conclusion.

# Stereochemistry of a $C_4$ Catalyst



- Only site epimerization can account for the observed effects of temperature and monomer concentration.
- These catalysts are clearly under a catalyst site control mechanism.

# Isotactic Polypropylene Synthesis Revisited



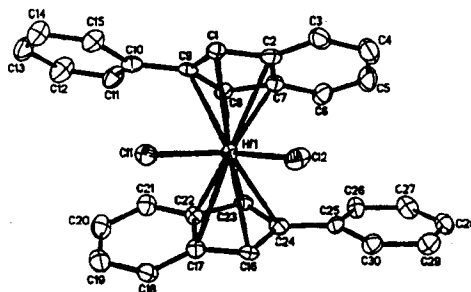
catalyst	$T_p$ , °C	Al <sub>MAO</sub> /Zr, molar ratio	propene (solvent)	activity, kg <sub>PP</sub> /(mmol <sub>Zr</sub> ·h)	$M_w$	$M_w/M_n$	$T_m$ , °C	% mmmm <sup>a</sup>	% 2,1 <sup>a</sup>
<i>rac</i> -C <sub>2</sub> H <sub>4</sub> (3-Me-Cp) <sub>2</sub> ZrCl <sub>2</sub>	40	2 000	3 bar (toluene)	5.8	19 600	2.3	133	92.2	nr
<i>rac</i> -C <sub>2</sub> H <sub>4</sub> (3- <i>i</i> -Pr-Cp) <sub>2</sub> ZrCl <sub>2</sub>	40	2 000	3 bar (toluene)	4.5	19 400	2.2	136	94.6	nr
<i>rac</i> -C <sub>2</sub> H <sub>4</sub> (3- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub>	40	2 000	3 bar (toluene)	1.0	17 400	2.5	141	97.6	nr
<i>rac</i> -Me <sub>2</sub> Si(3-Me-Cp) <sub>2</sub> ZrCl <sub>2</sub> ( <i>C</i> <sub>2</sub> -I-2)	30	10 000	3 bar (toluene)	16.3	13 700	2.3	148	92.5	nr
<i>rac</i> -Me <sub>2</sub> Si(3- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub>	30	10 000	3 bar (toluene)	0.3	9 500	2.3	149	93.4	nr
<i>rac</i> -Me <sub>2</sub> Si(2,4-Me <sub>2</sub> -Cp) <sub>2</sub> ZrCl <sub>2</sub>	30	10 000	3 bar (toluene)	11.1	86 500	1.9	160	97.1	nr
<i>rac</i> -Me <sub>2</sub> Si(2,4-Me <sub>2</sub> -Cp) <sub>2</sub> ZrCl <sub>2</sub>	70	15 000	liquid propene	97	31 000		149	89.2	nr
<i>rac</i> -Me <sub>2</sub> Si(2,3,5-Me <sub>3</sub> -Cp) <sub>2</sub> ZrCl <sub>2</sub> ( <i>C</i> <sub>2</sub> -I-3)	30	10 000	3 bar (toluene)	1.6	133 900	2.0	162	97.7	nr
<i>rac</i> -Me <sub>2</sub> Si(2,3,5-Me <sub>3</sub> -Cp) <sub>2</sub> ZrCl <sub>2</sub> ( <i>C</i> <sub>2</sub> -I-3)	50	15 000	liquid propene	207	184 500	1.9	161	96.4	0.3
<i>rac</i> -Me <sub>2</sub> Si(2-Me-4- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub> ( <i>C</i> <sub>2</sub> -I-4)	50	300	nr	5	4 000 ( <i>M</i> <sub>n</sub> )	2.7	149	97	0.2
<i>rac</i> -Me <sub>2</sub> Si(2-Me-4- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub> ( <i>C</i> <sub>2</sub> -I-4)	70	15 000	liquid propene	10	19 000		155	94.3	nr
<i>rac</i> -Me <sub>2</sub> C(3- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub>	50	3 000	liquid propene	15	17 000 ( <i>M</i> <sub>w</sub> )		153	99.5 <sup>c</sup>	0.4
<i>rac</i> -Me <sub>2</sub> C(2-Me-4- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub> ( <i>C</i> <sub>2</sub> -I-5)	50	8 000	liquid propene	73	103 000	1.9	162	99.5 <sup>c</sup>	0.16
<i>rac</i> -Me <sub>2</sub> Si(2-Me <sub>2</sub> Si-4- <i>t</i> -Bu-Cp) <sub>2</sub> YHf <sub>2</sub> ( <i>C</i> <sub>2</sub> -I-6)	25	none	25% v/v (MeC <sub>3</sub> H <sub>11</sub> )	very low	4 200 ( <i>M</i> <sub>n</sub> )	2.3	157	97.0	
<i>C</i> <sub>2</sub> -I-7	50	1 200	2 bar (toluene)	2	9 800	1.8	128	97	2.5 <sup>d</sup>

<sup>a</sup> From <sup>13</sup>C NMR. The values are referred to the total methyl signals. <sup>b</sup> Total of regioerrors (see section VII). <sup>c</sup> On primary insertions only. <sup>d</sup> 3,1 units. nr = not reported.

- Knowing that these metals form two site catalysts, it would seem logical that C<sub>2</sub> symmetric ligands would make excellent catalysts.
- A variety of highly active, rigid and sterically biased systems have been developed.
- The C<sub>2</sub> symmetry gives a catalyst with two enantiotopic sites.

# Isotactic Block Polypropylene?

Hf(1)–C(1)	2.538(6)
Hf(1)–C(7)	2.517(10)
Hf(1)–C(9)	2.542(6)
Hf(1)–C(17)	2.618(6)
Hf(1)–C(23)	2.454(6)
average	2.533
Hf(1)–C(2)	2.591(7)
Hf(1)–C(8)	2.461(8)
Hf(1)–C(16)	2.547(5)
Hf(1)–C(22)	2.516(5)
Hf(1)–C(24)	2.542(6)
average	2.531



Hf(2)–C(32)	2.582(6)
Hf(2)–C(38)	2.459(9)
Hf(2)–C(46)	2.528(6)
Hf(2)–C(52)	2.563(6)
Hf(2)–C(54)	2.485(7)
average	2.523
Hf(2)–C(31)	2.511(2)
Hf(2)–C(37)	2.551(7)
Hf(2)–C(39)	2.543(7)
Hf(2)–C(47)	2.614(6)
Hf(2)–C(53)	2.471(7)
average	2.538

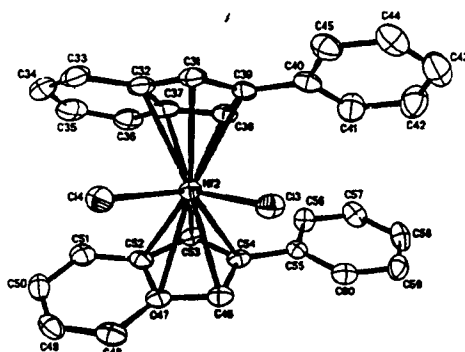
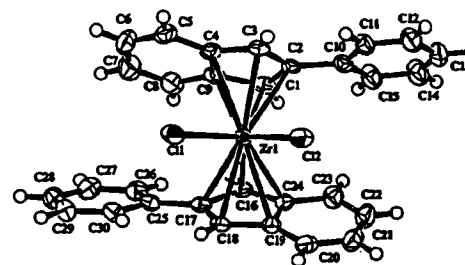
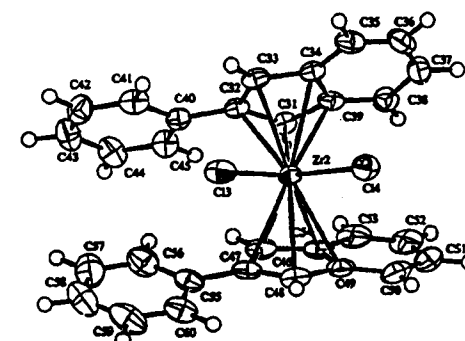


Figure 2. ORTEPs of *anti*- and *syn*-bis(2-phenylindenyl)hafnium dichloride (2).



Zr(1)–C(1)	2.482(5)
Zr(1)–C(2)	2.561(3)
Zr(1)–C(3)	2.558(3)
Zr(1)–C(4)	2.612(4)
Zr(1)–C(9)	2.531(5)
average	2.548
Zr(1)–C(16)	2.465(3)
Zr(1)–C(17)	2.551(3)
Zr(1)–C(18)	2.564(3)
Zr(1)–C(19)	2.622(3)
Zr(1)–C(24)	2.527(3)
average	2.545

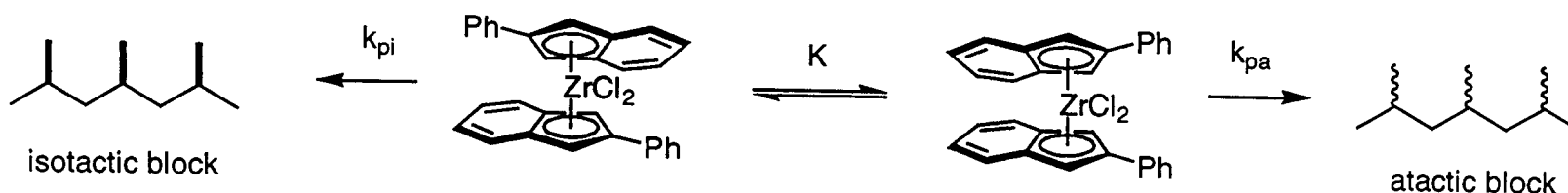


Zr(2)–C(31)	2.476(4)
Zr(2)–C(32)	2.504(4)
Zr(2)–C(33)	2.523(3)
Zr(2)–C(34)	2.624(3)
Zr(2)–C(39)	2.570(3)
average	2.539
Zr(2)–C(46)	2.485(5)
Zr(2)–C(47)	2.553(4)
Zr(2)–C(48)	2.529(3)
Zr(2)–C(49)	2.591(3)
Zr(2)–C(54)	2.559(4)
average	2.543

Figure 3. ORTEPs of *anti*- and *syn*-bis(2-phenylindenyl)zirconium dichloride (1).

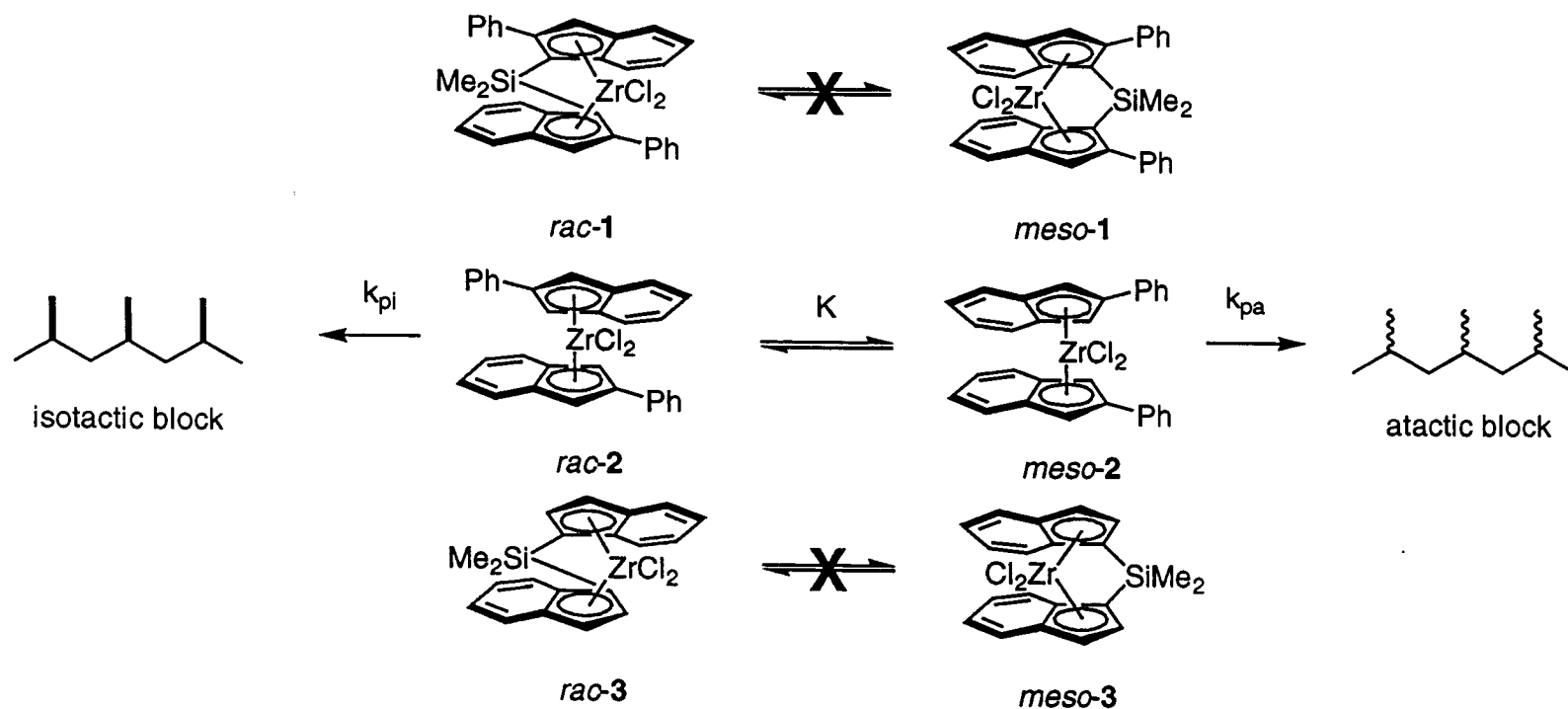
- In order to better understand the cause of this phenomenon, investigations were preformed to understand the solid- and solution state behavior of 1 and 2.
- Both 1 and 2 interconverted between their *rac* and *meso* forms quickly compared to the NMR timescale at  $-100\text{ }^{\circ}\text{C}$ .
- Conversion to the dibenzyl derivatives allowed for NMR dynamics to be preformed:
  - Dibenzyl 1 :  $\Delta H = 7.8 \pm 2.3\text{ kcal / mol}$ ,  $\Delta S = -15.4 \pm 10.1\text{ cal / mol}$ ,  $k = 6700 \pm 300\text{ s}^{-1}$  @  $20\text{ }^{\circ}\text{C}$
  - Dibenzyl 2 :  $\Delta H = 7.1 \pm 3.0\text{ kcal / mol}$ ,  $\Delta S = -17.3 \pm 11.0\text{ cal / mol}$ ,  $k = 6800 \pm 300\text{ s}^{-1}$  @  $20\text{ }^{\circ}\text{C}$

# Oscillating Catalysts



- In order to explain their results, the authors proposed a model where the isomerization of the complex was competitive with the rates of polymerization.
- If isomerization were faster than polymerization ( C-H control ) the polymer would be atactic.
- If isomerization were slower than polymerization, the polymer would be purely isotactic or atactic.
- NMR results with the dibenzyl metallocenes seem to be in error since they neglect the steric influence of the growing polymer chain and the cationic nature of the metal center.
- Again, this mechanism agrees with the concentration dependence on the selectivity.

# Modelling the Dynamic Catalyst



Waymouth, R.M. *J. Am. Chem. Soc.* **1998**, *120*, 11316.

- In an attempt to model the behavior of the two rotameric forms of **2**, the *rac* and *meso* isomers of **1** and **3** were synthesized.
- By comparing the activities and selectivities of the different complexes, it is hoped that the solution state behavior of **2** can be approximated.



# Stereochemistry of the ansa-Linked Catalysts

Table 1. Summary of Polymerization Results Using 1-*rac*, 1-*meso*, and 3

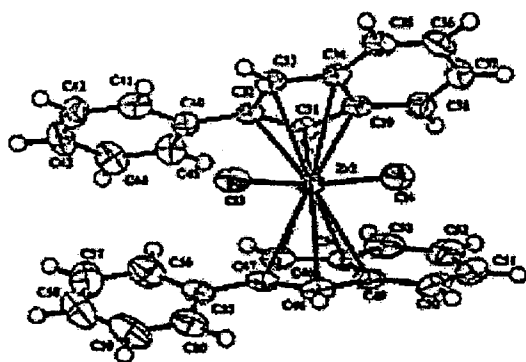
catalyst	% <i>rac</i>	yield (g)	prodvity <sup>a</sup>	%mmmm <sup>b</sup>	% <i>ru</i> <sup>b</sup>	$M_w^c (\times 10^{-3})$	$M_w/M_n$	IR index	$T_m$ (°C)
1	100	4.01	2408	86	96	425	2.6	0.9	139
1	100	3.88	2327	87	96	410	3.1	0.9	139
1	100	4.29	2573	88	96	495	4.1	0.9	138
1	0	6.82	4092	7.0	50	150	2.1	0.2	
1	0	6.59	3951	6.2	48	125	2.0	0.2	
1	0	6.76	4058	6.2	49	194	2.2	0.2	
1 <sup>d</sup>	100	2.20	3270			1850	2.9		nd <sup>e</sup>
1 <sup>d</sup>	0	1.74	2610			1470	3.1		nd
3	100	10.39	6234	92	98	121	2.2	nd	nd
3	45	1.75	1050 <sup>f</sup>	91	98	nd	nd	nd	nd

Table 2. Summary of Polymerization Results Using Mixtures of 1-*rac* and 1-*meso*

entry	% <i>rac</i>	yield (g)	prodvity <sup>a</sup>	%mmmm <sup>b</sup>	% <i>m</i> <sup>b</sup>	$M_w^c (\times 10^{-3})$	$M_w/M_n$	IR index	$T_m$ (°C)	$\Delta H_f$ (J/g)
1	42	4.00	2400	34	64	293	3.1	0.41	139	21.3
2	57	5.29	3172	39	69	312	3.3	0.48	138	26.1
3	61	5.09	3052	45	73	345	3.4	0.56	138	28.7
4	75	4.47	2680	57	79	374	3.9	0.64	139	49.9
5	2PhInd <sup>d</sup> (2)	4.59	2756	39	73	502	3.6	0.50	138	16.9

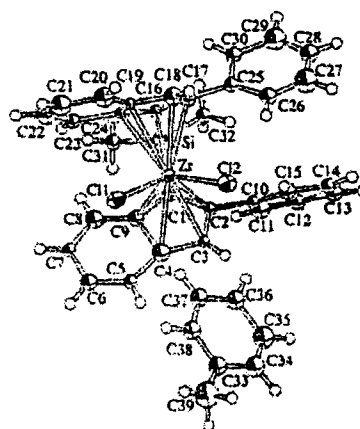
- The *rac* isomer is more selective but far less active than the *meso*.
- This trend appears unique to the polymerization of propylene.
- Based on %*m*, comparison of different mixtures of *rac*- and *meso*- 1 to 2 suggest that it exists as a ~70:30 mixture of *rac* : *meso* forms.
- After comparison to *rac*- and *meso*- 3, this behavior seems to be a unique consequence of the 2-phenyl substituent.

# Theory vs. Experiment



*meso-2*

Cp-Zr-Cp = 131° / Ph - Ind = 10°



*meso-1*

Cp-Zr-Cp = 125° / Ph - Ind = 60°

Table 3. Calculated and Experimental Productivities for 1-*rac* and 1-*meso*

entry	method <sup>a</sup>	rac productivity	meso productivity
6	%mmmm	2408 (166) <sup>b</sup>	4037 (30)
7	%m	2471 (155)	4033 (14)
8	% isotactic polymer	2652 (253)	3977 (77)
9	$\Delta H_t$	2545 (149)	4648 (784)
10	exptl	2436 <sup>c</sup>	4034 <sup>d</sup>

<sup>a</sup> Variable plotted against %rac. <sup>b</sup> Standard error. <sup>c</sup> Average of entries 1, 2, and 3 in Table 1. <sup>d</sup> Average of entries 4, 5, and 6 in Table 1.

$$BL_a / BL_i = K_{eq} [k_{p-meso} / k_{p-rac}]$$

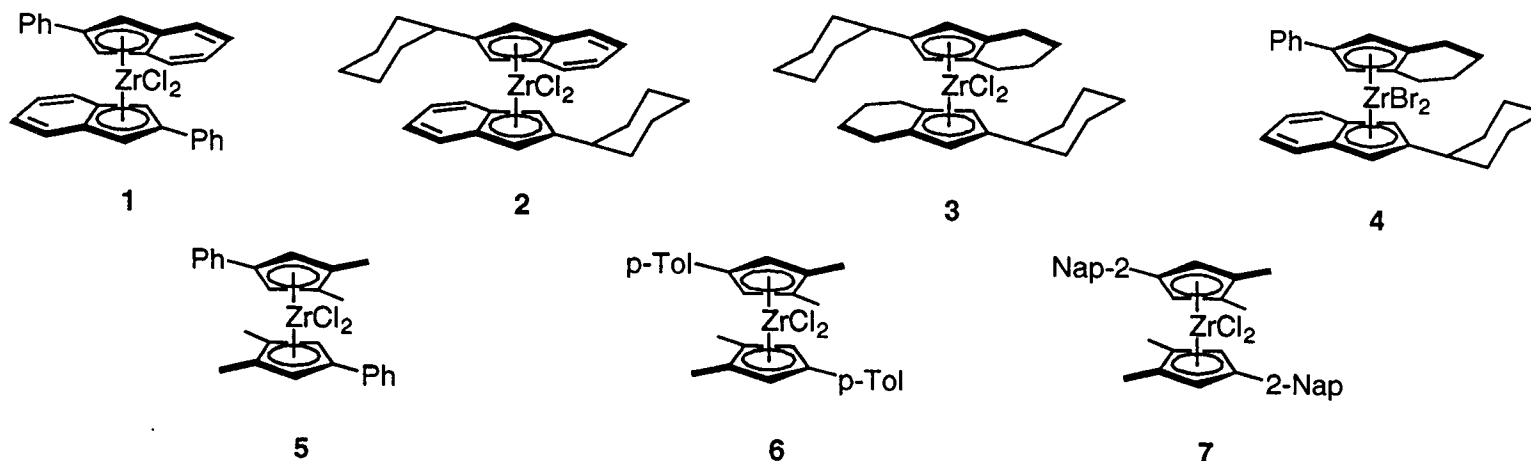
assuming  $K_{eq} = 0.7 \dots$

$$BL_a / BL_i = 1.3$$

$$\alpha_{meso} = 0.55 / \alpha_{rac} = 0.98$$

- Minor structural differences exist between *meso-1* and *2*, most notably the angle between the planes of the indenyl and phenyl rings.
- Calculations based on the different productivities of *meso-* and *rac-1* estimate that the atactic blocks are slightly longer than isotactic ones.
- Calculations using the predicted equilibrium constant can be applied to a two state polymerization model to closely approximate observed catalyst activities.

## Role of Indenyl Substituents



- A systematic study of the influence of the substitution pattern on the indenyl rings may provide clues for design of a more tunable catalysts.
- Catalysts **2** through **4** were prepared to assess the importance of  $\pi$  stacking.
- Catalysts **5** and **6** were prepared to assess the requirement of the indenyl ring.
- Catalyst **7** was prepared to probe the benefit of steric bulk at the 2 position.

Waymouth, R.A. *Organometallics* **1997**, 16, 5909.

# The Role of Indenyl Substituents

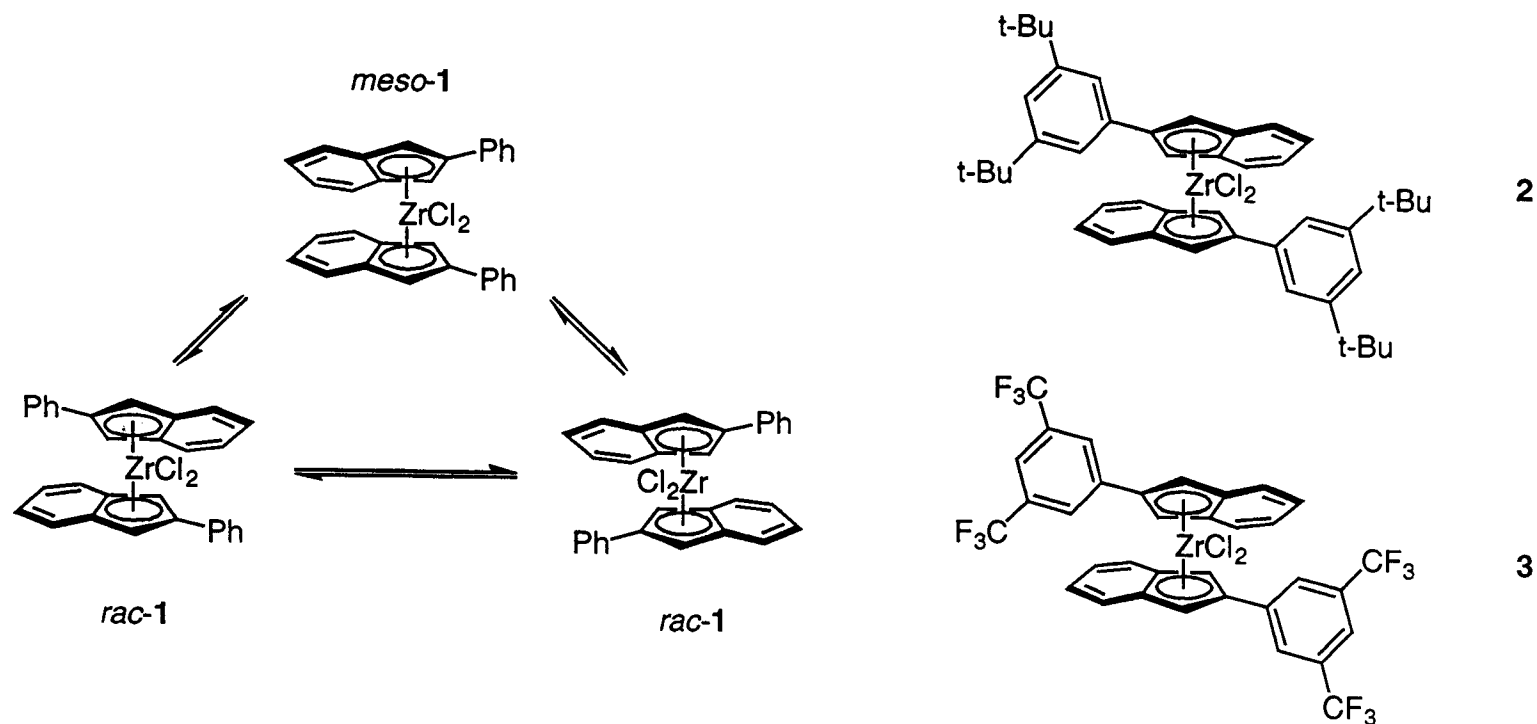
Table 1. Summary of Polymerization Results Using Unbridged Metallocenes<sup>a</sup>

entry	catalyst	propylene press (psig)	productivity <sup>b</sup>	% <i>mmmm</i> <sup>c</sup>	% <i>m</i>	$M_w^d (\times 10^{-3})$	$M_w/M_n$
1	1	50 <sup>e</sup>	1380	31	69	310	3.2
2		75 <sup>f</sup>	1480	35	71	399	3.8
3		bulk <sup>g</sup>	2525	32	70	542	3.5
4	2	50	374	11	57	117	3.8
5		75	602	11	55	131	3.9
6		bulk	2340	15	62	219	3.3
7	3	50	940	3	46	20	1.9
8		75	2020	3	45	27	1.9
9		bulk	2390	5	52	40	1.9
10	4	50	531	6	49	52	2.6
11		75	957	7	51	78	2.9
12		bulk	3394	13	58	186	3.1
13	5	50	3657	10	59	146	2.0
14		75	4511	10	58	215	2.2
15		bulk	8797	10	59	392	3.2
16	6	50	2325	10	59	201	3.1
17		75	3235	10	58	290	2.9
18		bulk	7120	10	60	323	3.1
19	7	50	867	10	59	94	2.1
20		75	1027	11	59	140	2.2
21		bulk	2833	11	61	217	2.7

<sup>a</sup> Conditions:  $T = 20\text{ }^\circ\text{C}$ ;  $[\text{Zr}] = 5.0 \times 10^{-5}\text{ M}$ ;  $[\text{Al}]/[\text{Zr}] = 1000$ . <sup>b</sup> Kilograms of polypropylene per mole of Zr per hour. <sup>c</sup> Determined by <sup>13</sup>C NMR spectroscopy. <sup>d</sup> Determined by gel permeation chromatography versus polypropylene standards. <sup>e</sup>  $[\text{C}_3\text{H}_6] = 3.24\text{ M}$ . <sup>f</sup>  $[\text{C}_3\text{H}_6] = 4.49\text{ M}$ . <sup>g</sup> 100 of mL liquid propylene and 25 mL of toluene.

- Elimination of  $\pi$  stacking interactions has a drastic effect of the %*mmmm*.
- Replacement of the indenyl ring with a trisubstituted cyclopentadiene does not effect %*m*, but does decrease %*mmmm*.
- Addition of the bulky 2-naphthyl substituent is also detrimental to selectivity and activity.

# Peripheral Substitutions



- In order to effect the rate of ligand rotation, it was hypothesized that steric or electronic differentiation of the 2-phenyl substituents might lead to changes in %*mmmm* rather than %*m*.

Waymouth, R.A. *Macromolecules* **2002**, 35, 5382.

# Steric Hinderance to Rotation

Table 1. Propylene Polymerizations at Various Temperatures Using 1/MMAO and 2/MMAO<sup>a</sup>

entry	catalyst	[C <sub>3</sub> H <sub>6</sub> ] (M)	P (psig)	T <sub>p</sub> (°C)	r <sub>max</sub> (mmol/min)	[mmmm] <sup>b</sup>	M <sub>n</sub> (g/mol) <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>
1	1	1.1 <sup>d</sup>	n/a	20	nd <sup>e</sup>	0.44	100 000	3.0
2	1	1.2	10	20	0.63	0.18	35 700	2.6
3	1	1.2	24	40	0.67	0.09	11 200	2.4
4	1	1.2	48	60	0.78	0.05	3 900	2.2
5	2	1.2	10	20	nd <sup>e</sup>	0.40	70 700	2.8
6	2	1.2	24	40	0.68	0.29	31 900	4.8
7	2	1.2	48	60	1.37	0.17	13 600	4.1

<sup>a</sup> Polymerization conditions: [Zr] = 1.0 × 10<sup>-6</sup> M; [Al]/[Zr] = 3160; [C<sub>3</sub>H<sub>6</sub>] = 1.16 M; t<sub>rxn</sub> = 60 min. <sup>b</sup> By <sup>13</sup>C NMR. <sup>c</sup> By high-temperature GPC. <sup>d</sup> Synthesized in 90 mL of liquid propylene + 10 mL of toluene. <sup>e</sup> Not determined.

Table 2. Pentad Distributions of Polypropylenes Synthesized at Various Monomer Concentrations Using 2/MMAO<sup>a</sup>

entry	[C <sub>3</sub> H <sub>6</sub> ] (M)	prod <sup>b</sup>	M <sub>n</sub> (g/mol) <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	T <sub>m,max</sub> (°C) <sup>d</sup>	ΔH <sub>f</sub> (J/g) <sup>e</sup>	[mmmm] <sup>f</sup>	[mmmr]	[rmmr]	[mmrr]	[+mmrr]	[mmmr]	[rrrr]	[mrrr]	[+mrrr]
8	1.2	4000	70 700	2.8	45, 120	27.9	0.40	0.17	0.03	0.10	0.15	0.05	0.02	0.04	0.04
9	1.7	1890	100 000	3.2	45, 130	58.0	0.59	0.13	0.02	0.06	0.10	0.08	0.01	0.02	0.08
10	2.2	2490	90 100	3.2	46, 140	60.5	0.65	0.11	0.02	0.05	0.08	0.03	0.01	0.02	0.08
11	2.7	2020	154 000	3.5	51, 149	75.2	0.70	0.10	0.02	0.04	0.07	0.02	0.01	0.01	0.02
12	3.3	2420	162 000	3.6	145	64.4	0.76	0.09	0.01	0.03	0.06	0.02	0.01	0.01	0.02
13	3.8	4850	119 000	3.3	45, 144	67.6	0.75	0.09	0.01	0.04	0.06	0.02	0.00	0.01	0.02
14	11 <sup>g</sup>	2140	64 700	3.8	155	93.0	0.78	0.08	0.02	0.03	0.04	0.01	0.01	0.01	0.01

<sup>a</sup> Polymerization conditions: [Zr] = 2.0 × 10<sup>-6</sup> M; [Al] = 3.16 × 10<sup>-2</sup>; [Al]/[Zr] = 15 800; T<sub>p</sub> = 20 °C; t<sub>rxn</sub> = 60 min. <sup>b</sup> Productivity in kg PP/(mol Zr h). <sup>c</sup> By high-temperature GPC. <sup>d</sup> By DSC. <sup>e</sup> By <sup>13</sup>C NMR. <sup>f</sup> Synthesized in 90 mL of liquid propylene + 10 mL of toluene.

- Increased temperature decreases %*mmmm*, in line with competition of a 1<sup>st</sup> and 2<sup>nd</sup> order process.
- Increased monomer concentration also increases %*mmmm*.
- The ligand **2** has far more isotactic blocks than **1**.
- The error distribution of polypropylene produced by **2** suggests a catalyst site control mechanism.

## Electronic Hinderance to Rotation?

expt	cat.	method	conditions <sup>d</sup>	prodvty <sup>a</sup>	$M_n^b$	$M_w/M_n^b$	<i>rr</i> (%)	<i>mmmm</i> <sup>c</sup> (%)
1	1	B <sup>d</sup>	35 psig, 20 °C	952	232 000	3.8	63	23
2	1	B	50 psig, 20 °C	832	250 000	3.3	66	27
3	1	B	75 psig, 20 °C	1480	399 000	3.8	68	29
4	1	B	100 psig, 20 °C	960	435 000	3.0	70	31
15	3	B	35 psig, 20 °C	206	454 000	4.0	85	56
16	3	B	50 psig, 20 °C	582	470 000	3.9	85	59
17	3	B	75 psig, 20 °C	624	631 000	4.3	88	64
18	3	B	100 psig, 20 °C	638	608 000	5.6	87	67

<sup>a</sup> In kg of PP/(mol of Zr·h). <sup>b</sup> Determined by GPC vs polypropylene. <sup>c</sup> Determined by <sup>13</sup>C NMR spectroscopy. <sup>d</sup> [M] =  $5.0 \times 10^{-3}$  M, [Al]/[Zr] = 1000,  $t = 1$  h. Method A, [M]/MAO in 20 mL of toluene injected under 200 psig Ar; method B, [M]/MAO in 20 mL of toluene injected under P + 5 psig propylene.

- Again, increased monomer concentration leads to increases in %*mmmm*.
- The ligand **3** yields comparable isotactic dyad content ( %*m* ), but much greater isotactic block content ( %*mmmm* ).
- The loss in productivity seems to be contradictory with the assumption that more electron poor ligands give more strongly cation metal centers.
- However, this increased electrophilicity may also be traced to increases in rate of deactivation processes.

Waymouth, R.A. *J. Am. Chem. Soc.* **1997**, *119*, 11174.

# Assessment of Electronic Effects

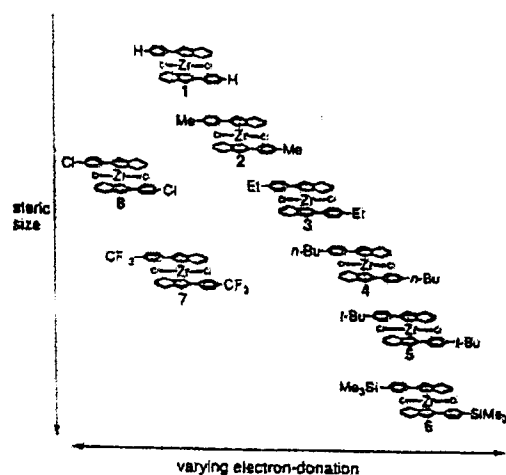


Fig. 2. Variation of substituents for  $(2-(4-R-C_6H_4)indenyl)_2ZrCl_2$  catalysts.

Catalyst $(2-(4-R)PhInd)_2ZrCl_2$	Pressure (psig) <sup>a</sup>	Productivity (kgPP/mol Zr/h)	$M_w^b$ (kg/mol)	$M_w/M_n$	[ $\eta$ ] %	[mmmm] % <sup>c</sup>
1 (R=H)	25	863	220	3.66	66	27
2 (R=CH <sub>3</sub> )	50	1780	303	4.34	71	33
3 (R=Et)	25	842	163	3.29	69	32
4 (R=nBu)	50	1290	311	3.76	72	39
5 (R=iBu)	25	780	211	3.58	69	31
6 (R=TMS)	50	1544	343	4.15	73	37
7 (R=CF <sub>3</sub> )	25	697	217	3.49	67	29
8 (R=Cl)	50	1289	351	4.16	71	37
	25	578	219	3.23	67	29
	50	1174	357	3.66	71	34
	25	786	173	2.97	68	29
	50	1344	317	3.67	70	33
	25	775	138	2.84	62	21
	50	1281	190	3.21	66	26
	25	331	102	3.60	60	20
	50	689	149	4.00	66	27

<sup>a</sup>[Zr] =  $5 \times 10^{-5}$  M, [Al]/[Zr] = 1000; 100 ml toluene total volume, 1 h, 20°C (solution runs); 80 ml liquid propylene, 20 ml toluene, 2-40 min, 20°C (bulk runs).

<sup>b</sup>Determined by high-temperature GPC vs. polypropylene standards.

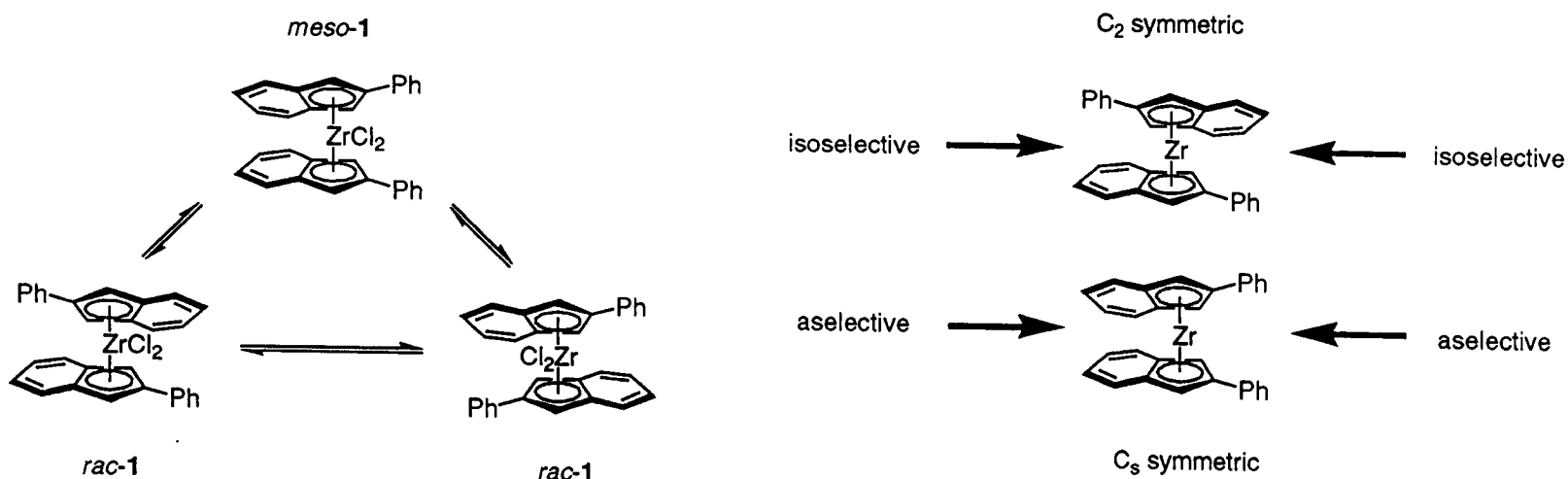
<sup>c</sup>Triad distribution determined from <sup>13</sup>C NMR (300 MHz, tetrachloroethane, 100°C).

- Addition of substituents of varying electronic properties at the remote 4 position does not yield an obvious trend with respect to productivity or selectivity.
- Comparison of the trend with steric parameters yields an equally unsatisfactory correlation.

Waymouth, R.A. *J. Mol. Cat. A* 1998, 136, 23.

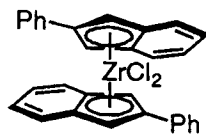


# Oscillating Catalysts

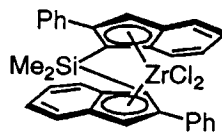


- It has been demonstrated that a two state, dynamic catalyst is a good choice for synthesis of stereoblock polymers.
- The differing reactivities of the isoselective and aselektive states provide an interesting handle on selectivity.
- Control over the rate of catalyst isomerization vs. polymerization yields polymers with different properties.
- Can the steric differences between the two sites be utilized to induce selective copolymerization of different monomers?

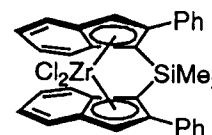
# Ethylene / Propylene Co-polymerization



1



anti-3



syn-3

Table 4. Ethylene/Propylene Copolymerization Parameters for *ansa*-Metallocenes *anti*-3, *anti*-4 and *syn*-3, *syn*-4<sup>a</sup>


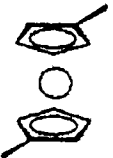
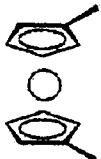
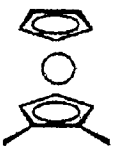
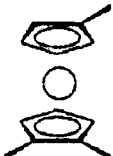
$N_{exp}^b$	metallocene	$X_e/X_p$ in feed <sup>c</sup>	% E in polymer <sup>d</sup>	avg prod <sup>e</sup>	$r_e r_p^f$	$r_e^f$	$r_p^f$	$M_n$ ( $\times 10^{-3}$ ) <sup>g</sup>
5	(1) <sup>h</sup>	0.065	25		$1.3 \pm 0.20$	$5.4 \pm 0.9$	$0.24 \pm 0.04$	688
2	( <i>anti</i> -3)	0.132–0.137	34–38	3500	0.53	$2.64 \pm 0.15$	$0.20 \pm 0.01$	66
3		0.062	21–22		$0.62 \pm 0.10$	$2.99 \pm 0.42$	$0.20 \pm 0.03$	54
3	( <i>syn</i> -3)	0.136–0.137	39–41	2000	$0.79 \pm 0.05$	$4.63 \pm 0.34$	$0.16 \pm 0.01$	44
2		0.062–0.062	22		$1.08 \pm 0.06$	$6.00 \pm 0.31$	$0.18 \pm 0.01$	54

<sup>a</sup> Conditions: 100 mL of liquid propylene/20 mL of toluene,  $T_p = 20^\circ\text{C}$ , time = 20 min,  $[\text{Zr}] = (1-10) \times 10^{-6}$  M, MAO = 130 mg.  
<sup>b</sup> Number of experiments used for determination of the average reactivity ratios. <sup>c</sup> The range of the ratios of the mole fractions of ethylene ( $X_e$ ) and propylene ( $X_p$ ). <sup>d</sup> The range of mol % E in copolymers determined using  $^{13}\text{C}$  NMR. <sup>e</sup> In kg of PE/(mol of Zr h), averaged over several runs; see Supporting Information. <sup>f</sup> Determined using  $^{13}\text{C}$  NMR and diads equations according to Kakugo. <sup>g</sup> Determined by high temperature GPC. <sup>h</sup> Kravchenko, R.; Waymouth, R. M. *Macromolecules* 1998, 31, 1–6.

- The catalysts 1 and 3 can generate EP copolymers.
- The rate of ethylene incorporation is much higher for *syn*-3 as compared to *anti*-3.
- The unlinked catalyst and *syn*-3 have a higher tendency to form blocks of propylene than does the C2 symmetric *anti*-3.
- These differences suggesting a strong steric differentiation between sites in the *rac* and *meso* catalyst structures.

Waymouth, R.A. *Macromolecules* 2002, 35, 2882.

# Metallocene Polymerization Catalysts: Trends?

Symmetry		Sites	Polymer
$C_{2v}$ Achiral		A, A Homotopic	Atactic
$C_2$ Chiral		E, E Homotopic	Isotactic
$C_s$ Achiral		A, A Diastereotopic	Atactic
$C_2$ Prochiral		E, -E Enantiotopic	Syndiotactic
$C_1$ Chiral		E, A Diastereotopic	Hemi-isotactic

<sup>a</sup> E = enantioselective site; A = nonselective site.

- As we have seen, the symmetry properties of a particular catalyst are somewhat predictive in terms of the stereochemistry of the polymer that is formed.
- This led to the recent formation of Ewen's Symmetry Rules ( see *J. Mol. Cat. A* **1998**, 128, 103 ).
- The formation of isotactic block polymers fits into these rules since it employs a catalyst which alternates between  $C_2$  chiral and  $C_s$  achiral states.
- Extension of this system to copolymerization has yielded promising results based on the steric differentiation of the two sites.

