

## Propylene polymerization with unbridged *rac*- or *meso*-bis[1-(*p*-tolyl)indenyl]dichloro zirconium/methylaluminoxane catalyst

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Received: 8 January 1996/Revised version: 12 March 1996/Accepted: 13 March 1996

### Summary

A novel unbridged metallocene complex, (1-TolInd)<sub>2</sub>ZrCl<sub>2</sub> (Tol = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) was prepared. *Meso*-like (1-TolInd)<sub>2</sub>ZrCl<sub>2</sub> afforded a syndiotactic-dominant polypropylene having a short syndiotactic length at low temperatures (-30 °C). This stereosequence is due either to a weakly chain-end controlled or to a syndiotactic site controlled polymerization with site isomerization. *Racemic* isomer produced a completely atactic PP even at -30 °C.

### Introduction

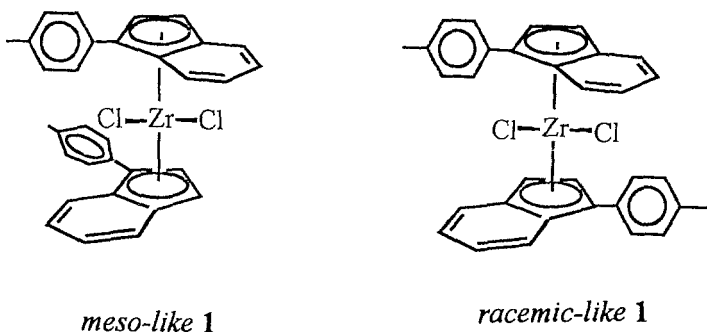
Chiral *ansa*-metallocene complexes have been extensively employed as catalyst precursors for the highly isospecific (C<sub>2</sub>-symmetric)<sup>1,2</sup> and syndiospecific (C<sub>s</sub>-symmetric)<sup>3</sup> polymerization of propylene. The presence of a bridging group restricts the mobility of the π-ligands providing a rigid system which transfers the chirality information of the *ansa*-metallocene onto the growing polymer chain in an enantiomorphic site controlled process. In recent years, however, unbridged mono-substituted indenyl (RInd)<sub>2</sub>MX<sub>2</sub> complexes have received a considerable attention due to their versatile catalytic properties caused by facile interconversion of the rotameric forms by a rotation of π-ligands during polymerization. Erker et al. have analyzed the overall stereochemical consequences of unbridged (1-RInd)<sub>2</sub>MX<sub>2</sub> complexes and reported that partly isotactic polypropylene can be obtained either with *rac*-like or *meso*-like unbridged complexes<sup>4-7</sup>.

We have prepared an unbridged metallocene complex, (1-TolInd)<sub>2</sub>ZrCl<sub>2</sub> (1, Tol = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), which exists as *rac*-like and *meso*-like diastereomers (Scheme 1). Interestingly, the *rac*-like 1/MAO catalyst (MAO = methylaluminoxane) produces an atactic polypropylene (PP), whereas the *meso*-like 1/MAO

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catalyst at low temperatures ( $-30\text{ }^{\circ}\text{C}$ ) affords an syndiotactic-dominant PP.



Scheme 1. *Bis(1-p-tolylyindenyl)zirconium dichloride (1)*.

### Experimental Section

**Materials;** Polymerization grade propylene (Korea Petrochem. Ind. Co., Korea) and extra pure grade nitrogen were further purified by passing through columns of Fisher RIDOX and 5A/13X molecular sieves. Extra pure grade toluene and analytical grade tetrahydrofuran (THF) were purified by refluxing over sodium metal in a nitrogen atmosphere. Analytical grade diethylether and dichloromethane were distilled over calcium dihydride in a nitrogen atmosphere. MAO was purchased from Tosol-Akzo as a toluene solution. Other materials were purchased from Aldrich Chemical Company, Inc. and were used without further purification.

**Synthesis of complex 1;** The reaction of 1-indanone with *p*-tolylmagnesiumbromide followed by dehydration of an alcohol intermediate with aqueous HCl gave 1-*p*-tolylindene in 76 % yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  7.70~7.28 (multiplet, 8 H), 6.57 (triplet, 1H), 3.52 (doublet, 2H), 2.45 (singlet, 3H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  145.0, 144.8, 144.0, 137.3, 133.2, 130.3, 129.2, 127.6, 126.1, 124.7, 124.1, 120.3, 30.1, 21.2. Mass spectrum:  $m/z$  206 ( $\text{M}^+$ ). The reaction of lithiated 1-*p*-tolylindene (2 equiv.) with  $\text{ZrCl}_4$  in diethylether was performed according to previously described procedures<sup>4-7</sup> to produce a mixture of two diastereomers in a ratio of 1:1 (*meso*-like 1 : *rac*-like 1) in 74 % yield. Repeated recrystallization in dichloromethane at  $-20\text{ }^{\circ}\text{C}$  gave the *meso*-like 1 as bright yellow crystal (34 %) and the mother liquor was evaporated to give *rac*-like 1 as an orange-yellow solid (33 %). *meso*-like 1:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ )  $\delta$  7.86~7.15 (multiplet, 16H), 6.52

(doublet, 2H), 5.95 (doublet, 2H), 2.40 (singlet, 3H). Mass spectrum:  $m/z$  570 ( $M^+$ ,  $^{90}\text{Zr}$ ,  $^{35}\text{Cl}$ ). *rac*-like 1 :  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  7.80~7.11 (multiplet, 16H), 6.33 (doublet, 2H), 5.88 (doublet, 2H), 2.47 (singlet, 3H). Mass spectrum:  $m/z$  570 ( $M^+$ ,  $^{90}\text{Zr}$ ,  $^{35}\text{Cl}$ ).

Polymerization and analytical procedures; Solution polymerization reactions in toluene were carried out at a propylene pressure of 1.2 atm, agitating with a Teflon magnetic spinbar in a 500 ml glass reactor. Toluene (200 ml) was introduced into the reactor, the temperature was increased to polymerization temperature, and then toluene was saturated with propylene. A prescribed amount of MAO and Zr catalyst dissolved in toluene were injected into the reactor by a tuberculin syringe, and then the polymerization was started. After the polymerization was terminated by injecting ethanol, the produced polymer was quenched by an excess of acidified methanol (*ca.* 5 times of the amount of toluene used). The precipitated polymer was separated from the polymerization medium by cooling to -30 °C, washed with fresh ethanol, and dried *in vacuo*.

Measurements; Intrinsic viscosity,  $[\eta]$ , of the polymer in decalin was determined using a modified Ubbelohde viscometer at  $135 \pm 0.1$  °C by one-point intrinsic viscosity.<sup>8</sup> Viscosity average molecular weight ( $M_v$ ) of PP was calculated from a Mark-Houwink equation<sup>9</sup>,  $[\eta] = 1,0 \times 10^{-4} M_v^{0.80}$ .  $^{13}\text{C}$  NMR (75 MHz) spectra of the resulting PP were recorded at 100 °C on a Bruker AMX-300 FT NMR spectrometer. The PP samples were dissolved in 1,2,4-trichlorobenzene/benzene- $d_6$  (4/1 by vol.) up to a concentration of 15 wt-% at 130 °C in NMR tubes (10 mm o.d.).

### Results and Discussion

The reaction of lithiated 1-*p*-tolylindene (2 equiv.) with  $\text{ZrCl}_4$  in diethyl ether produced a *ca.* 1 : 1 mixture of the metallocene diastereomer *rac*-1 and *meso*-1. Pure *rac*-1 and *meso*-1 complexes could be obtained by fractional crystallization in dichloromethane. Due to the average overall molecular symmetry in solution, both *rac*-1 ( $C_2$ ) and *meso*-1 ( $C_s$ ) complexes reveal a single resonance (*rac*-1 :  $\delta$  2.45 ; *meso*-1 :  $\delta$  2.40) for each pair of methyl groups of the tolyl moieties. The diastereomer assignment is based on the preparation of the dimethyl derivatives of complexes 1. The dimethyl derivatives were prepared from the reaction of complex 1 with  $\text{CH}_3\text{Li}$  in THF. The dimethylated product derived from *rac*-1 exhibits only one methyl resonance at  $\delta$  -0.83 whereas that from *meso*-1 shows two methyl resonances at  $\delta$  -0.56 and -0.87 in a 1 : 1 ratio.

Table 1. Comparison for propylene polymerization results of (1-*p*-Tol)Ind)<sub>2</sub>ZrCl<sub>2</sub> (1) catalysts with the other unbridged metallocenes.

catalyst	Zr ( $\mu\text{mol}$ )	T <sub>p</sub> ( $^{\circ}\text{C}$ )	t <sub>p</sub> (h)	yield (g)	A <sup>a</sup>	M <sub>v</sub> <sup>b</sup> $\times 10^{-4}$	M <sub>n</sub> <sup>c</sup> $\times 10^{-4}$	M <sub>w</sub> /M <sub>n</sub>	rrrrr <sup>d</sup> (%)
<i>meso</i> -like 1 <sup>e</sup>	8	25	2	2.84	147.5	- <sup>i</sup>	-	-	7 <sup>g</sup>
	16	-30	6	12.0	104.0	20.0	15.0	2.52	19 <sup>g</sup>
<i>rac</i> -like 1 <sup>e</sup>	8	25	2	2.83	147.2	31.0	- <sup>i</sup>	-	-
	12	-30	6	13.0	150.5	7.7	-	-	6
Cp <sub>2</sub> ZrCl <sub>2</sub> <sup>h</sup>		0	7		400	- <sup>i</sup>	0.531	2.4	- <sup>i</sup>
		20	6		300	-	0.119	1.9	-
(2-PhInd) <sub>2</sub> - ZrCl <sub>2</sub> <sup>j</sup>		25	0.25		310	- <sup>i</sup>	6.7	2.7	9.2
		0	0.25		710	-	18.3	2.6	12.3
		-25	0.25		1,100	-	33.0	2.2	16.1
4b-A <sup>k</sup>		-30	3		35	26.0	- <sup>i</sup>	-	76
		-5	3		24	10.0	-	-	77
4a-A <sup>l</sup>		-30	3		220	13.4	-	-	24
		-5	3		30	2.6	-	-	33

a) Activity. Unit; kg-polymer/(mol-Zr.h.atm).

b) Calculated from intrinsic viscosity ( $[\eta] = 1.0 \times 10^4 [M_v]^{0.8}$ ).

c) Determined by g.p.c. versus polystyrene.

d) Determined by <sup>13</sup>C NMR spectrum.

e) Polymerization conditions : 1.2 bar, toluene (250 ml), MAO (50 mmol-Al).

f) not measured.

g) percentage of rrrr pentad sequence.

h) Cited from ref. (11). Polymerization conditions : 2 bar, Zr = 31  $\mu\text{mol}$ , Al = 31 mmol.

i) not provided.

j) Cited from ref. (10) . (2-phenylindenyl) dichlorozirconium, 1 bar, [Zr]=1.4x10<sup>4</sup> M, [Al]/[Zr] = 1,033.

k) *Racemic*-bis(1-neoisomenthyl indenyl) zirconium dichloride cited from ref. (4). Toluene (250 ml) + propylene (30~50ml), [Al]/[Zr]=700.

l) *Racemic*-bis(1-neomenthylindenyl)zirconium dichloride cited from ref. (4).

Kruger et al.<sup>7</sup> synthesized bis(1-cyclohexyl-4,5,6,7-tetrahydroindenyl)ZrCl<sub>2</sub> (2) and characterized both *meso*- and *rac*-diastereomers of 2 by X-ray crystal structure study. 2 might be analogous to complex 1. Accordingly, the molecular structure of 1 could be induced by an analogous method. As observed by authors, in the crystal the molecular structure of complex *rac*-2 is C<sub>2</sub>-Symmetric, with the annulated six-membered ring systems arranged towards the open front side of the bent metallocene wedge and the cyclohexyl substituents oriented anti-periplanarly in the lateral sectors. In

contrast, complex *meso*-2 has only one of the ligands arranged in this way, the cyclohexyl substituent of the other one pointing towards a central front position and the annulated six-membered ring being situated in the lateral position ( $C_1$ -symmetry). Erker et al.<sup>4</sup> also discussed there existed the various conformational structures for bis(tetrahydroindenyl)MX<sub>2</sub> and bis(indenyl)MX<sub>2</sub> with alkyl-substituents at  $\alpha$ -carbon of C<sub>5</sub> ring in solution state. Dynamic NMR spectroscopy in solution indicated the presence of at least three different rotameric forms in both *racemic*- and *meso*-diastereomers.

In Table 1, the activities of propylene polymerization and the molecular weights of produced PP over both *meso*-like and *racemic*-like of 1 activated with MAO were compared with the other unbridged metallocenes reported earlier by Erker<sup>4</sup>, Waymouth<sup>10</sup> and Mulhaupt<sup>11</sup>. The activities of both diastereomers of 1 having substituted indenyl  $\pi$ -ligands with bulky phenyl ring at  $\alpha$ -positional carbon of C<sub>5</sub> ring are lower than those of over Cp<sub>2</sub>ZrCl<sub>2</sub> or (2-PhInd)<sub>2</sub>ZrCl<sub>2</sub> (3) with  $\beta$ -carbon-substituted ligands. It should be noticed that the molecular weights of polypropylenes (PPs) produced with all complexes having 1- or 2-substituted ligands are much higher than those over Cp<sub>2</sub>ZrCl<sub>2</sub>. The causes of these propylene polymerization properties could be rationalized from the analysis of the conformational structure of two each ligands at solution state. The high molecular weight PPs over both diastereomers of 1 are probably formed because the existences of C<sub>6</sub>-ring system or *p*-tolyl substituent toward the open front side of the vent metallocene wedge suppress the  $\beta$ -H transfer reaction and consequent chain termination<sup>12</sup>.

As shown in Fig. 1, the <sup>13</sup>C-NMR spectra of the produced polymers at -30 °C indicate that PP obtained with *meso*-like 1 has dominantly syndiotactic stereosequences and PP obtained with *racemic*-like 1 is completely atactic. With other known 1-substituted unbridged zirconocene, (1-RInd)<sub>2</sub>ZrCl<sub>2</sub> both *rac*-like diastereomers (R = cholestanyl, neoisomenthyl) and a *meso*-like diastereomer (tetrahydroindenyl, R= neoiso pinocamphyl) have been reported to produce isotactic PP (mmmm ca. 80%) and partly isotactic PP at -30 °C, respectively, by Erker et al..<sup>6-7</sup>

Several causes for this stereosequence of syndiotactic-dominant PP over *meso*-like 1 are possible. First, in solution of -30 °C, *meso*-like 1 may exist as some frozen rotameric isomers, one of these isomers appears to be a syndiospecific coordination geometry and the others can be aspecific, thus, syndiotactic chains are formed by syndiospecific center and atactic polymers are formed by atactic geometry, respectively. However, this phenomena should be excluded from results that Soxhlet extractions of polymer in both hexane and pentane did not fractionate the insoluble polymer and that melting point did not exist in DSC

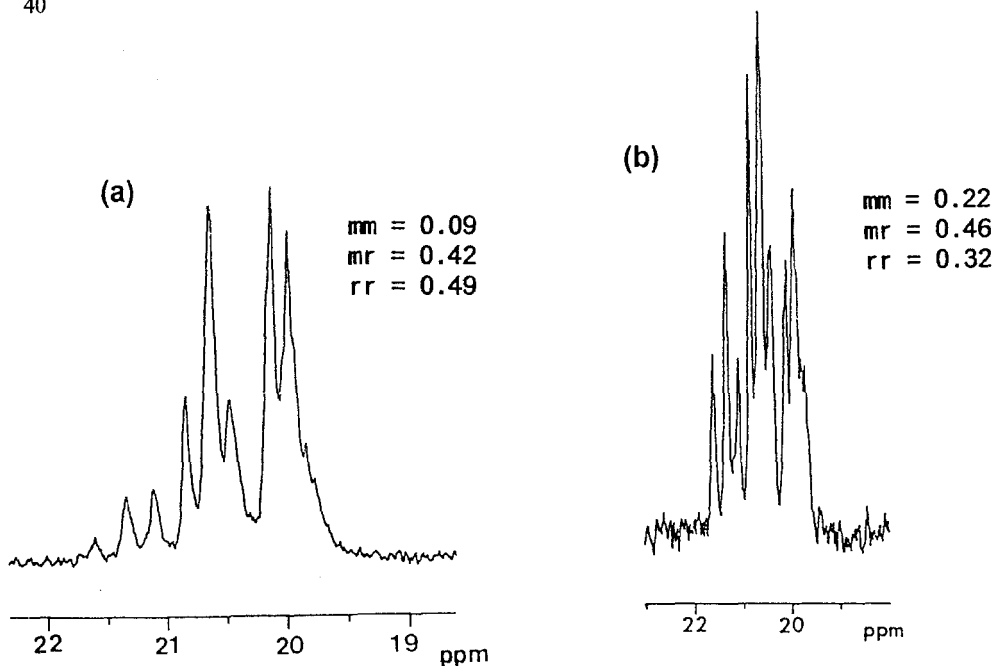


Fig. 1.  $^{13}\text{C}$  NMR spectra of methyl region of PP prepared with (a) *meso*-like 1/MAO and (b) *rac*-like 1/MAO catalyst at  $-30^\circ\text{C}$ .

analysis, thus, practically syndiotactic chains might not be contained. Second, in contrast to first cause, the conformer equilibration might occur in *meso*-like 1. With more stable syndiospecific coordination geometries than the other conformers, this rotameric equilibration produces syndiotactic-dominant PP. Tactic block lengths  $n_{\text{iso}}$  and  $n_{\text{syn}}$  could be calculated from the integration of the methyl signal groups in accordance with the literature as the equations,  $n_{\text{iso}} = 2 (mm)/(mr) + 1$  and  $n_{\text{syn}} = 2 (rr)/(mr) + 1$ .<sup>13</sup> From triad intensity data in Fig. 1(a), the value of syndiotactic block length of syndiotactic-dominant PP produced by *meso*-like 1 is very small as 3.33. Judging from this short block length of syndioblocks, the ratio of monomer insertion rate to rotameric isomerization rate may be small because this equilibration appears to be very fast even at low temperature ( $-30^\circ\text{C}$ ). The number of propagating propylene molecules per a active center and per second is 0.79 mol-propylene/mol-Zr-sec in accordance with the activity on the assumption that all of zirconium centers are active. Accordingly, isomerization rate between syndiotactic and atactic conformational isomers is  $0.24 \text{ sec}^{-1}$  on the calculation from activity and tactic block length. However, short tactic length has not been associated with the formation of syndiotactic-atactic block PP by analogous rotameric oscillation between *anti*- and *syn*-conformers of 2-substituted indenyl unbridged-complex,  $(2\text{-PhInd})_2\text{ZrCl}_2$  reported recently by Coates and Waymouth.<sup>10</sup>

Third cause is that there seems to be a weak chain-end-controlled syndiotacticity or a site control with isomerization in *meso*-like 1. The triad distribution indicate either the chain end control mechanism with  $P_r = 0.7$ , ( $P_r$  is the conditional probability of a syndiotactic placement in the Bernoullian propagating model) or the syndiotactic control with site isomerization errors,  $P_r = 0.7$ .<sup>14</sup> The data with this resolution is consistent with syndiotactic polypropylene containing *meso* dyads as the primary steric defect. Erker and Fritz<sup>15</sup> observed syndioselective control in the formation of PP with  $(Cp^iPr)_2TiPh_2/MAO$  at the temperature range from  $-10$  to  $+10$  °C while below  $-10$  °C, PP were formed with isoselective control.

In conclusion, we suggest *meso*-like 1 complexes can make a syndiotactic-dominant PP having a short tactic block length by means of chain end control mechanism or site isomerization mechanism.

### References

1. W. Kaminsky, K. Kulper, H. H. Brintzinger, F. R. W. P. Wild, *Angew. Chem. Int. Ed. Engl.* 24, 507 (1985).
2. J. A. Ewen, *J. Am. Chem. Soc.*, 106, 6355 (1984).
3. J. A. Ewen, L. J. Robert, A. Razavi, J. D. Ferrara, *J. Am. Chem. Soc.*, 110, 6255 (1988).
4. G. Erker, M. Albach, M. Knickmeier, D. Wingbermahle, C. Kruger, M. Nolte, S. Werner, *J. Am. Chem. Soc.* 115, 4590 (1993).
5. Erker, B. Tomme, *J. Am. Chem. Soc.* 114, 4004 (1992).
6. G. Erker, M. Albach, C. Kruger, S. Werner, *J. Organomet. Chem.* 450, 1 (1993).
7. C. Kruger, F. Lutz, M. Nolte, G. Erker, M. Aulbach, *J. Organomet. Chem.* 452, 79 (1993).
8. J. H. J. Elliott, *J. Appl. Polym. Sci.*, 19, 2947 (1970).
9. J. B. Kissinger, R.E. Hughes, *J. Phys. Chem.*, 63, 2002 (1959).
10. G. W. Coates, R. M. Waymouth, *Science* 267, 217 (1995).
11. D. Fischer, R. Mulhaupt, *J. Organomet. Chem.* C7, 417 (1991).
12. W. Roll, H. H. Brintzinger, B. Rieger, R. Zolk, *Angew. Chem. Int. Ed. Engl.* 29(3), 279 (1990).
13. W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, J. Rohrmann, *Makromol. Chem.* 193, 1643 (1992).
14. J. A. Ewen, M. J. Elder, R. L. Jones, S. Curtis, H. N. Cheng, In *Catalytic Olefin Polymerization* Eds: T. Keii, K. Soga, Kodansa Elsevier, Tokyo, 1990, p439.
15. G. Erker, C. Fritze, *Angew. Chem. Int. Ed. Engl.*, 31(2), 199(1992).