Polymerization of Propylene by Nonbridged Zirconocene Complexes

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Nonbridged zirconocene dichlorides, $(1,2\text{-Me}_2\text{-4-RC}_5\text{H}_2)_2\text{ZrCl}_2$ (R = Me (**3**), Ph (**4**), *p*-FC_6H_4 (**5**), 2-furyl (**6**), 2-thienyl (**7**), and Fc (**8**)), and *meso*- and *rac*-$(1\text{-Me-3-PhC}_5\text{H}_3)_2\text{ZrCl}_2$ (**9** and **10**), in the presence of MAO show a high catalytic activity ($8.1\sim17.4 \times 10^6$ gPP/molZr · h) in the polymerization of propylene and produce almost an *atactic* elastomeric polymer of high molecular weight (*M*w = $10.5 \sim 23.2 \times 10^4$). In contrast, *rac*-$(1\text{-Me-3-}t\text{-BuC}_5\text{H}_3)_2\text{ZrCl}_2$ (**12**) shows very low activity and produces a rather high *isotactic* polymer of low molecular weight.

Recently, Waymouth *et al.* discovered that bis(2-phenylindenyl)zirconium dichloride (**1**) in the presence of methylaluminoxane (MAO) produced elastomeric polypropylene with alternating *isotactic* and *atactic* blocks and they proposed that, in this catalyst, two active sites for *isotactic* and *atactic* polymerization were generated alternately by hindered rotation of the indenyl ligands.[1] Rappé *et al.* pointed out the importance of π-stacking of phenyl groups attached to the indenyl ligands to other aromatic rings within the complex to make the barrier between *rac* and *meso* conformers competitive with the propylene insertion barrier.[2] In this respect, it is interesting to examine the catalytic activity and the stereoregulating ability of nonbridged metallocene with or without phenyl groups in the polymerization of propylene (Figure 1).[3]

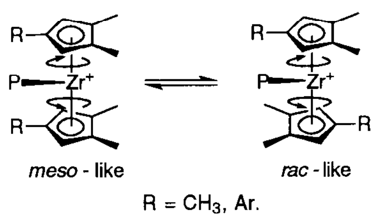
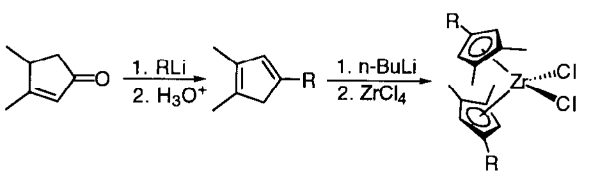


Figure 1. Alternation between chiral and achiral forms during the polymerization reaction.

Waymouth complex **1** and the related bis(2-methylindenyl) zirconium dichloride (**2**) have been prepared starting from 2-indanone.[1] We prepared zirconium complexes of general formula $(1,2\text{-Me}_2\text{-4-RC}_5\text{H}_2)_2\text{ZrCl}_2$ (R = Me (**3**), Ph (**4**)[4], *p*-FC_6H_4 (**5**), 2-furyl (**6**), 2-thienyl (**7**), and Fc (**8**))[5] starting from 3,4-dimethyl-2-cyclopentenone (Scheme 1); in these



3 : R = Me　**4** : R = Ph　**5** : R = *p*-FC_6H_4　**6** : R = 2-furyl　**7** : R = 2-thienyl　**8** : R = Fc

Scheme 1.

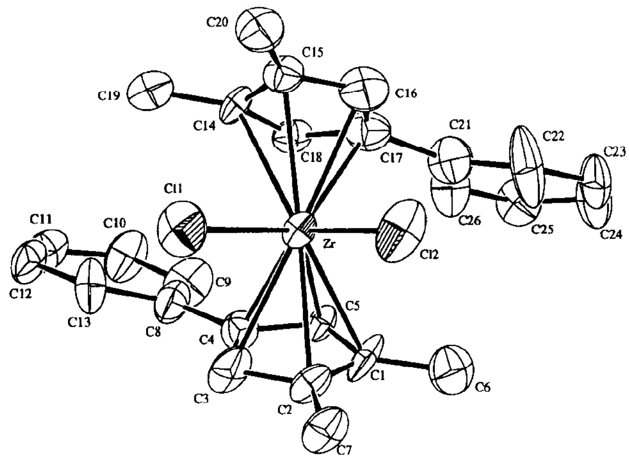
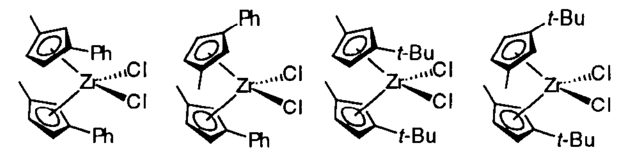


Figure 2. Molecular structure of complex **4**, showing the atom-labeling scheme.

complexes two adjacent methyl groups are the replacement of the benzo moiety of the indenyl group in **1** or **2**. Their ^{1}H NMR spectra at 25 °C revealed time-averaged molecular C_{2v} symmetry consistent with rapid rotation of the cyclopentadienyl rings around the Cp(centroid)-Zr axis. It was found that the process could not be frozen out at -90 °C in the case of **4**. Metallocenes **3**, **4**, **5**, **7**, and **8** were characterized by X-ray crystallography.[6] They all crystallized in a racemic-like conformation. The molecular structure of **4** is shown in Figure 2, as a representative. Bite angles, ∠Cp(centroid)-Zr-Cp(centroid), are 132.6, 131.5, 131.0, 131.0, and 131.8° for **3**, **4**, **5**, **7**, and **8**, respectively, and almost the same as that (131°) reported for **1** (racemic rotamer). Dihedral angles between the plane defined by the cyclopentadienyl rings and the aryl rings are 18.83 and 13.63° for **4**, 15.31° for **5**, and 10.50° for **7**, which are slightly larger than the value (≤ 10°) reported for **1**.

Similarly, the mixtures of *meso*- and *rac*-$(1\text{-Me-3-PhC}_5\text{H}_3)_2\text{ZrCl}_2$ (**9** and **10**) and *meso*- and *rac*- $(1\text{-Me-3-}t\text{-BuC}_5\text{H}_3)_2\text{ZrCl}_2$ (**11** and **12**) were prepared. They were separated by recystallization and their stereochemistry was deduced from ^{1}H NMR spectra of their methyl derivatives, $(1\text{-Me-3-RC}_5\text{H}_3)_2\text{ZrMe}_2$, zirconium-bonded methyl protons being observed as two singlets due to the *meso*-isomers and as one singlet due to the *rac*-isomers.



9　**10**　**11**　**12**

Table 1. Propylene polymerization using zirconocene dichlorides and MAO[a]

complex	activity[b] x 10^{-6}	appearance	Mw[c] x 10^{-4}	Mn/Mw	[mmmm][d] %
1[e]	0.87	rubber	12.0	4.02	25.8
2	3.0	rubber	10.0	-	12.0
3	17.38	rubber	13.2	2.39	10.8
4	9.95	rubber	16.0	2.11	12.4
5	8.39	rubber	15.0	3.04	14.3
6	14.36	rubber	23.2	3.20	12.8
7	8.89	rubber	15.7	2.01	12.3
8	1.46	rubber	6.0	2.26	n.d.
9	11.12	rubber	11.2	2.73	8.8
10	8.12	rubber	10.5	2.45	13.0
11	0.3	wax	0.26	-	2.2
12	0.5	wax	0.19	-	49.8

[a]Conditions: [Al]/[M] = 10^4, T = 30 °C, t = 60 min., P = 3 kg/cm^{2}G. [b]Grams of polypropylene per mole of metal per hour. [c]Determined by gel permeation chromatography. [d]Determined by ^{13}C NMR. [e]Present result.

Polymerizations of propylene were carried out using these complexes in the presence of MAO and the results are summarized in Table 1. All complexes except **11** and **12** afforded elastomeric polypropylene. The catalyst derived from **2** showed higher productivity than that derived from **1**, but produced polymers of lower *isotactic* pentad value. These findings suggest the importance of phenyl substituents in determining the microstructure of the resulting polymer. Interestingly, the catalyst derived from **3** which had no aryl substituents was the most productive among the catalysts studied, although the *isotactic* pentad value was rather low.[7] Catalysts derived from **4** and **5** which contained one aryl substituent produced polymers having slightly higher *isotactic* pentad values than that by **3**. Complexes **6** and **7** having an aromatic heterocycle showed the same order of catalytic activity and tacticity as **4** and **5**. Complex **8** having a bulky ferrocenyl substituent revealed decreased activity and gave a polymer of low molecular weight. Complexes **9** (*meso*-isomer) and **10** (*rac*-isomer) exhibited activity similar to **4** and **5** and produced an elastomeric polymer. Introduction of a bulky *tert*-butyl substituent on the cyclopentadienyl ring resulted in a considerable decrease in the catalytic activity as shown in the polymerization by **11** and **12**. However, **12** (*rac*-isomer) produced polypropylene of rather high isotacticity. This may arise from restricted rotation of the cyclopentadienyl ring to generate an isospecific site preferentially.

References and notes

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2 M. A. Pietsch and A. K. Rappé, *J. Am. Chem. Soc.*, **118**, 10908 (1996).

3 For polymerization by nonbridged metallocene bearing bulky chiral substituents: G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermühle, C. Krüger, M. Nolte, and S. Werner, *J. Am. Chem. Soc.*, **115**, 4590 (1993); M. Knickmeier, G. Erker, and T. Fox, *J. Am. Chem. Soc.*, **118**, 9623 (1996).

4 Polymerization of propylene by **4** was reported recently: J. L. M. Petoff, M. D. Bruce, R. M. Waymouth, A. Masood, T. K. Lal, R. W. Quan, and S. J. Behrend, *Organometallics*, **16**, 5909 (1997).

5 **3**: 79 %. ^{1}H NMR (CDCl$_3$): δ 5.99 (s, 4 H, CpH), 2.15 (s, 6 H, CH$_3$), 2.06 (s, 12 H, CH$_3$).
4: 11 %. ^{1}H NMR (CDCl$_3$): δ 7.43-7.51 (m, 8 H, arom. H), 7.27-7.33 (m, 2 H, arom. H), 6.27 (s , 4 H, CpH), 1.77 (s, 12 H, CH$_3$).
5: 41 %. ^{1}H NMR (CDCl$_3$): δ 7.41-7.45 (m, 4 H, arom. H), 7.12-7.17 (m, 4 H, arom. H), 6.21 (s , 4 H, CpH), 1.80 (s, 12 H, CH$_3$).
6: 10 %. ^{1}H NMR (CDCl$_3$): δ 7.49 (d, 2 H, arom. H), 6.48 (dd, 2 H, arom. H), 6.43 (s, 4 H, CpH), 6.39 (d, 2 H, arom. H), 1.81 (s, 12 H, CH$_3$).
7: 72 %. ^{1}H NMR (CDCl$_3$): δ 7.23-7.25 (m, 2 H, arom. H), 7.06-7.11 (m, 4 H, arom. H), 6.28 (s, 4 H, CpH), 1.80 (s, 12 H, CH$_3$).
8: 65 %. ^{1}H NMR (CDCl$_3$): δ 5.95 (s, 4 H, CpH), 4.46 (t, 4 H, CpH), 4.32 (t, 4 H, CpH), 4.00 (s, 10 H, CpH), 1.83 (s, 12 H, CH$_3$).

6 Crystallographic data for **3**: $C_{16}H_{22}Cl_2Zr$, Fw = 376.48, monoclinic, space group Cc (# 9), a = 17.063(3) Å, b = 6.836(2) Å, c = 16.492(2) Å, β = 122.489(7)°, V = 1622.6(5) Å^3, Z = 4, D_{calc} = 1.541 g cm^{-3}, R = 0.027, Rw = 0.029 for 1327 reflection with $I > 3\sigma(I)$.
Crystallographic data for **4**: $C_{26}H_{26}Cl_2Zr$, Fw = 500.62, monoclinic, space group $C2/c$ (# 15), a = 15.574(3) Å, b = 14.947(2) Å, c = 20.757(4) Å, β = 104.37(2)°, V = 4680(1) Å^3, Z = 8, D_{calc} = 1.421 g cm^{-3}, R = 0.069, Rw = 0.071 for 1598 reflection with $I > 3\sigma(I)$.
Crystallographic data for **5**: $C_{26}H_{24}F_2Cl_2Zr$, Fw = 536.60, tetragonal, space group $P4_12_12$ (# 92), a = 13.037(1) Å, c = 14.613(2) Å, V = 2483.5(5) Å^3, Z = 4, D_{calc} = 1.435 g cm^{-3}, R = 0.040, Rw = 0.044 for 1226 reflection with $I > 3\sigma(I)$.
Crystallographic data for **7**: $C_{22}H_{22}S_2Cl_2Zr$, Fw = 512.66, monoclinic, space group $C2/c$ (# 15), a = 17.706(1) Å, b = 8.881(1) Å, c = 14.460(1) Å, β = 101.115(5)°, V = 2231.2(3) Å^3, Z = 4, D_{calc} = 1.526 g cm^{-3}, R = 0.043, Rw = 0.058 for 1698 reflection with $I > 3\sigma(I)$.
Crystallographic data for **8**: $C_{34}H_{34}Cl_2Fe_2Zr$, Fw = 716.46, monoclinic, space group $P2_1/c$ (# 14), a = 10.068(3) Å, b = 24.305(4) Å, c = 12.835(2) Å, β = 104.24(2)°, V = 3044(1) Å^3, Z = 4, D_{calc} = 1.563 g cm^{-3}, R = 0.049, Rw = 0.050 for 2265 reflection with $I > 3\sigma(I)$.

7 The hafnium analogue of **3** shows comparable productivity (16.23 x 10^6 gPP/molHf · h) and produces a rubberlike polymer having very high molecular weight (Mw = 64.0 x 10^4).