

Polymerization of Propylene by Nonbridged Zirconocene Complexes

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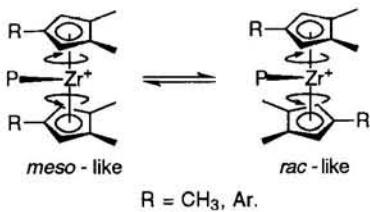
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Nonbridged zirconocene dichlorides, $(1,2\text{-Me}_2\text{-4-RC}_5\text{H}_2)_2\text{ZrCl}_2$ (**3**) ($\text{R} = \text{Me}$), (**4**) ($\text{R} = \text{Ph}$), (**5**) ($\text{R} = p\text{-FC}_6\text{H}_4$), (**6**) ($\text{R} = 2\text{-furyl}$), (**7**) ($\text{R} = 2\text{-thienyl}$), and (**8**) ($\text{R} = \text{Fc}$), 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 ($8.1\text{--}17.4 \times 10^6 \text{ gPP/molZr} \cdot \text{h}$) 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.

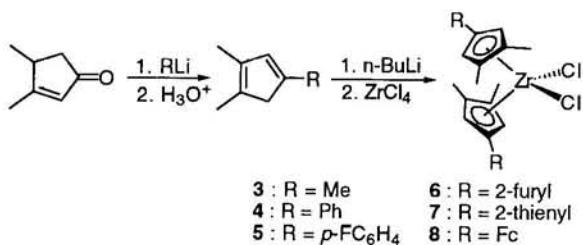
Recently, Waymouth *et al.* discovered that bis(2-phenylindenyl)zirconium dichloride (**1**) in the presence of methylaluminoxane (MAO) produced elastomeric polypropylene with alternating *isotactic* and *atactic* blocks and they proposed that, in this catalyst, two active sites for *isotactic* and *atactic* 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



$\text{R} = \text{CH}_3, \text{Ar}$

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 $(1,2\text{-Me}_2\text{-4-RC}_5\text{H}_2)_2\text{ZrCl}_2$ ($\text{R} = \text{Me}$ (**3**)), ($\text{R} = \text{Ph}$ (**4**)), ($\text{R} = p\text{-FC}_6\text{H}_4$ (**5**)), ($\text{R} = 2\text{-furyl}$ (**6**)), ($\text{R} = 2\text{-thienyl}$ (**7**)), and ($\text{R} = \text{Fc}$ (**8**))⁵ starting from 3,4-dimethyl-2-cyclopentenone (Scheme 1); in these



Scheme 1.

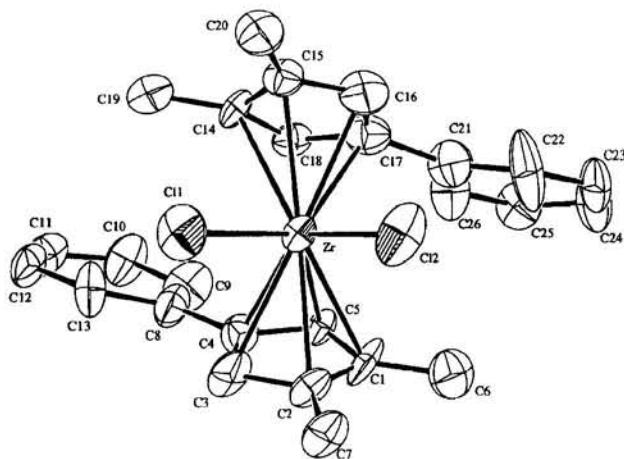


Figure 2. Molecular structure of complex **4**, showing the atom-labeling scheme.

complexes two adjacent methyl groups are the replacement of the benzo moiety of the indenyl group in **1** or **2**. Their ^1H 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, $\angle \text{Cp}(\text{centroid})\text{-Zr-Cp}(\text{centroid})$, 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 ($\leq 10^\circ$) 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 recrystallization and their stereochemistry was deduced from ^1H 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.

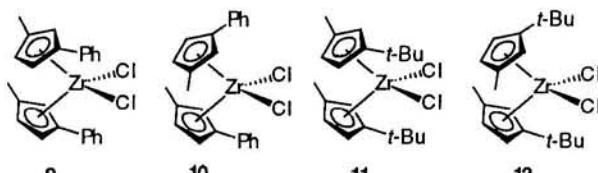


Table 1. Propylene polymerization using zirconocene dichlorides and MAO^a

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

^aConditions: [Al]/[M] = 10⁴, T = 30 °C, t = 60 min., P = 3 kg/cm² G.^bGrams of polypropylene per mole of metal per hour. ^cDetermined by gel permeation chromatography. ^dDetermined by ¹³C NMR. ^ePresent 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

- 1 G. W. Coates and R. M. Waymouth, *Science*, **267**, 217 (1995); E. Hauptman, R. M. Waymouth, and J. W. Ziller, *J. Am. Chem. Soc.*, **117**, 11586 (1995); M. D. Bruce, G. W. Coates, E. Hauptman, R. M. Waymouth, and J. W. Ziller, *J. Am. Chem. Soc.*, **119**, 11172 (1997).
- 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 %. ¹H NMR (CDCl₃): δ 5.99 (s, 4 H, CpH), 2.15 (s, 6 H, CH₃), 2.06 (s, 12 H, CH₃).
4: 11 %. ¹H NMR (CDCl₃): 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, CH₃).
5: 41 %. ¹H NMR (CDCl₃): 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, CH₃).
6: 10 %. ¹H NMR (CDCl₃): 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, CH₃).
7: 72 %. ¹H NMR (CDCl₃): 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, CH₃).
8: 65 %. ¹H NMR (CDCl₃): 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, CH₃).
- 6 Crystallographic data for **3**: C₁₆H₂₂Cl₂Zr, 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) Å³, Z = 4, D_{calc} = 1.541 g cm⁻³, R = 0.027, R_w = 0.029 for 1327 reflection with I > 3σ(I).
Crystallographic data for **4**: C₂₆H₂₆Cl₂Zr, 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) Å³, Z = 8, D_{calc} = 1.421 g cm⁻³, R = 0.069, R_w = 0.071 for 1598 reflection with I > 3σ(I).
Crystallographic data for **5**: C₂₆H₂₄F₂Cl₂Zr, Fw = 536.60, tetragonal, space group P4₁2₁2 (# 92), a = 13.037(1) Å, c = 14.613(2) Å, V = 2483.5(5) Å³, Z = 4, D_{calc} = 1.435 g cm⁻³, R = 0.040, R_w = 0.044 for 1226 reflection with I > 3σ(I).
Crystallographic data for **7**: C₂₂H₂₂S₂Cl₂Zr, 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) Å³, Z = 4, D_{calc} = 1.526 g cm⁻³, R = 0.043, R_w = 0.058 for 1698 reflection with I > 3σ(I).
Crystallographic data for **8**: C₃₄H₃₄Cl₂Fe₂Zr, Fw = 716.46, monoclinic, space group P2₁/c (# 14), a = 10.068(3) Å, b = 24.305(4) Å, c = 12.835(2) Å, β = 104.24(2)°, V = 3044(1) Å³, Z = 4, D_{calc} = 1.563 g cm⁻³, R = 0.049, R_w = 0.050 for 2265 reflection with I > 3σ(I).
- 7 The hafnium analogue of **3** shows comparable productivity (16.23 × 10⁶ gPP/molHf·h) and produces a rubberlike polymer having very high molecular weight (Mw = 64.0 × 10⁴).