Chiral Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium 2,2'-Biphenolate. Separation and Application to Asymmetric Polymerization

Shigeki HABAUE, Hiroshi SAKAMOTO, and Yoshio OKAMOTO[†]Department of Applied Chemistry, School of Engineering, Nagoya University,
Chikusa-ku, Nagoya 464-01, Japan

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Enantiomerically pure ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**1**) has become increasingly important as a precatalyst for catalytic asymmetric reactions in synthetic organic chemistry and polymer chemistry.¹ However, the only method of preparation is kinetic resolution of ($\pm$)-**1** with optically active lithium (1,1'-binaphthyl)-2,2'-diolate followed by removal of unreacted **1** with alumina.^{2–4} The binaphtholate adduct **2** can be converted to the optically pure **1** again.⁵ We recently reported the first successful resolution of racemic ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium derivatives by high-performance liquid chromatography (HPLC) on cellulose tris(3,5-dimethylphenylcarbamate) coated on silica-gel (Chiralcel OD).^{6,7} This paper reports a preparative separation of the optically pure ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium 2,2'-biphenolate (**3**) by HPLC and its application as a catalyst to the asymmetric cyclopolymerization of 1,5-hexadiene.

EXPERIMENTAL

General

¹H NMR spectra were measured on a Varian Gemini-2000 (400 MHz) or UNITY-INOVA (500 MHz) spectrometer in CDCl₃ with tetramethylsilane as the internal standard. CD spectra were taken on a JASCO J-720L apparatus with a 0.1-mm cell in CHCl₃ solution. Optical rotation was measured with a JASCO DIP-181 polarimeter.

Toluene was distilled from Na wire, and then distilled again from *n*-BuLi under high vacuum just before use. The zirconocene complex ($\pm$)-**1** was generously supplied by Tosoh Co. A co-catalyst methylaluminoxane (MAO) in toluene was kindly provided by Tosoh Akzo Co. 1,5-Hexadiene (TCI) was distilled under high vacuum from calcium hydride just before polymerization.

Preparation of ($\pm$)-**3**

2,2'-Biphenolate complex ($\pm$)-**3** was prepared from ($\pm$)-**1** and lithium (1,1'-biphenyl)-2,2'-diolate in benzene followed by removal of unreacted **1** with alumina (ICN biochemicals) according to the literatures.⁵ The obtained complex was used in chromatographic separation as a benzene solution without further purification.

Polymerization Procedure

Polymerization was carried out in a glass ampule equipped with a three-way stopcock, and purified reagents were transferred into the ampule with syringes under a dry nitrogen atmosphere. The polymerization was typically carried out using zirconocene **3** (8.0×10^{-3} mmol), MAO (1.85 M, 1.3 mmol), and monomer (1.3 mmol) in toluene at 30°C. After mixing zirconocene and MAO in toluene at room temperature for 5 min, a monomer was added. The polymerization was stopped by carefully adding 2 mL of methanol at 0°C and then the polymer was precipitated in a large amount of 1N HCl-methanol (1:6). The polymer was washed with methanol and dried *in vacuo*. Methanol insoluble polymer was obtained quantitatively.

RESULTS AND DISCUSSION

Separation of ($\pm$)-**3**

2,2'-Biphenolate complex ($\pm$)-**3** was separated into enantiomers by HPLC on a silica-gel column coated with cellulose tris(3,5-dimethylphenylcarbamate) as a chiral stationary phase using the eluent, *n*-hexane-ethyl alcohol = 20:1 as shown in Figure 1.⁶ Chromatographic separation was performed using a preparative column (50 $\times$ 2.0 (i.d.) cm) and JASCO PU 980 chromatograph equipped with a UV detector (JASCO UV 970, monitored at 295 nm) and polarimetric detector (JASCO OR 990) at room temperature. A benzene solution of the racemic sample, including about 13 mg of ($\pm$)-**3** was injected into a chromatographic system (eluent, *n*-hexane-ethyl alcohol = 20:1; flow rate, 10 mL min⁻¹). The purity of the recovered complex (+)-**3** and (–)-**3** was confirmed by chiral HPLC (Figure 2), ¹H, ¹³C NMR, and elemental analyses; ¹H NMR (500 MHz, CDCl₃) δ 1.3–1.8 (m, 8H, CH₂), 2.10 (m, 4H, CH₂), 2.60 (m, 4H, CH₂), 3.12 (m, 2H, CH₂), 3.28 (m, 2H, CH₂), 5.70 (s, 4H, Cp-H), and 6.7–7.2 (m, 8H, aromatic); ¹³C NMR (125 MHz, CDCl₃) δ 161.7, 131.9, 131.8, 130.3, 128.3,

[†] To whom all correspondence should be addressed.

Figure 1. HPLC trace of zirconocene **3** on a silica-gel column coated with cellulose tris(3,5-dimethylphenylcarbamate). Column, 50 × 2.0 (i.d.) cm; eluent, *n*-hexane-ethanol = 20:1 (v/v); flow rate, 10 mL min⁻¹; monitored at 295 nm.

Figure 2. HPLC traces of (+)-**3** (97%ee) (a) and (-)-**3** (>99%ee) on a silica-gel column coated with cellulose tris(3,5-dimethylphenylcarbamate). Column, 25 × 0.46 (i.d.) cm; eluent, *n*-hexane-ethanol = 20:1 (v/v); flow rate, 0.5 mL min⁻¹; monitored at 295 nm.

128.2, 123.0, 119.2, 118.6, 114.6, 106.2, 27.5, 23.6, 22.8, 22.33, and 22.27; *Elemental Analysis*. Found: C = 71.19%, H = 6.23% for (+)-**3** and C = 70.81%, H = 6.38% for (-)-**3**. Calcd for C₃₂H₃₂O₂Zr: C = 71.20%, H = 5.98%. The specific rotation ($[\alpha]_{435}^{25}$) of the isolated (+)- and (-)-**3** was estimated to be +2200° ($c=0.12$) and -2000° ($c=0.07$), respectively, in CHCl₃. Figure 3 demonstrates the circular dichroism (CD) spectra of the enantiomers in CHCl₃, which were mirror images of each other.

Application of **3**

Waymouth *et al.* reported that the asymmetric cyclopolymerization of 1,5-hexadiene using the optically active

Figure 3. CD spectra of (+)-**3** (a) and (-)-**3** (b).

Table I. Cyclopolymerization of 1,5-hexadiene using optically active zirconocene catalyst (**3**)^a

Entry	Zirconocene	[Monomer]/ [Al]/[Zr]	Yield ^b	Trans ^c	$[\alpha]_{435}^{25}$ ^d
			%	%	deg
1	(+)- 3	160/160/1	34	73	-40
2	(-)- 3	170/180/1	39	71	+46

^a Polymerization was carried out using MAO as a cocatalyst in toluene at 30°C for 0.5 h, [monomer] = 0.2 M. ^b Methanol insoluble and CHCl₃ soluble part. ^c Determined by ¹³C NMR. ^d Measured in CHCl₃ at 25°C ($c=0.50$).

2,2'-binaphtholate complex **2** yields optically active poly(methylene-1,3-cyclopentane) (poly(MCP)) based on a main-chain chiral configuration.^{4,8} They obtained optically active poly(MCP)s possessing molar optical rotations $[\Phi]_{405}^{28} = +51^\circ$ and -51° ($c=0.8$, CHCl₃) using (*R,R*)-**2** and (*S,S*)-**2**, respectively. (+)-**3** and (-)-**3** complexes were also used for the polymerization of 1,5-hexadiene (Table I). After polymerization in the presence of excess methylaluminoxane (MAO) at 30°C for 0.5 h in toluene, methanol-insoluble and CHCl₃-soluble poly(MCP)s were obtained in 34% and 39% yields, and showed specific rotations $[\alpha]_{435}^{25} = -40^\circ$ ($[\Phi]_{435}^{25} = -33^\circ$) and $+46^\circ$ ($[\Phi]_{435}^{25} = +38^\circ$), respectively. These values seem comparable to the results of Waymouth *et al.*, taking into account differences of wavelengths for optical rotation. This may be because the binaphtholate and biphenolate ligands would not participate in the polymerization.^{4b} The results indicate that the absolute configurations of (+)-**3** and (-)-**3** are (*S*) and (*R*), respectively, in comparison with those of 2,2'-binaphtholate complexes.

In conclusion, the first isolation of optically pure ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium 2,2'-biphenolate complexes, (+)-**3** and (-)-**3**, was accom-

plished by HPLC using cellulose tris(3,5-dimethylphenyl-carbamate) as the chiral stationary phase, and its ability to function as an asymmetric catalyst was demonstrated in the asymmetric cyclopolymerization of 1,5-hexadiene. A new method for the preparation of enantiomerically pure *ansa*-zirconocene complexes was established.

REFERENCES

1. (a) M. T. Didiuk, J. P. Morken, and A. H. Hoveyda, *J. Am. Chem. Soc.*, **117**, 7097 (1995). (b) M. S. Visser and A. H. Hoveyda, *Tetrahedron*, **51**, 4383 (1995). (c) W. Kaminsky, A. Ahlers, and N. Möller-Lindenhof, *Angew. Chem., Int. Ed. Engl.*, **28**, 1216 (1989). (d) P. Pino, P. Cioni, and J. Wei, *J. Am. Chem. Soc.*, **109**, 6189 (1987). (e) W. Kaminsky, K. Küpler, and S. Niedoba, *Makromol. Chem., Makromol. Symp.*, **3**, 377 (1986).
2. (a) F. R. W. P. Wild, M. Wasiucionek, G. Huttner, and H. H. Brinzinger, *J. Organomet. Chem.*, **288**, 63 (1985). (b) S. Collins, B. A. Kuntz, N. J. Taylor, and D. G. Ward, *J. Organomet. Chem.*, **342**, 21 (1988).
3. The asymmetric reactions using optically active **2** have been reported. (a) P. Pino, M. Galimberti, P. Prada, and G. Consiglio, *Makromol. Chem.*, **191**, 1677 (1990). (b) M. S. Visser, J. P. A. Harriety, and A. M. Hoveyda, *J. Am. Chem. Soc.*, **118**, 3779 (1996).
4. (a) G. W. Coates and R. M. Waymouth, *J. Am. Chem. Soc.*, **113**, 6270 (1991). (b) G. W. Coates and R. M. Waymouth, *J. Am. Chem. Soc.*, **115**, 91 (1993).
5. (a) F. R. W. P. Wild, L. Zsolnai, Huttner, and H. H. Brinzinger, *J. Organomet. Chem.*, **232**, 233 (1982). (b) R. B. Grossman, W. M. Davis, and S. L. Buchwald, *J. Am. Chem. Soc.*, **113**, 2321 (1991). (c) A. Schäfer, E. Karl, L. Zsolnai, G. Huttner, and H. H. Brinzinger, *J. Organomet. Chem.*, **328**, 87 (1987).
6. S. Habaue, H. Sakamoto, and Y. Okamoto, *Chem. Lett.*, 383 (1996).
7. (a) E. Yashima and Y. Okamoto, *Bull. Chem. Soc. Jpn.*, **68**, 3289 (1995). (b) Y. Okamoto and Y. Kaida, *J. Chromatogr. A*, **666**, 403 (1994). (c) Y. Okamoto, M. Kawashima, and K. Hatada, *J. Chromatogr.*, **363**, 173 (1986).
8. (a) G. Wulff, *Angew. Chem., Int. Ed. Engl.*, **28**, 21 (1989). (b) Y. Okamoto and T. Nakano, *Chem. Rev.*, **94**, 349 (1994).