Optical Resolution of Chiral Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium Derivatives by High-Performance Liquid Chromatography

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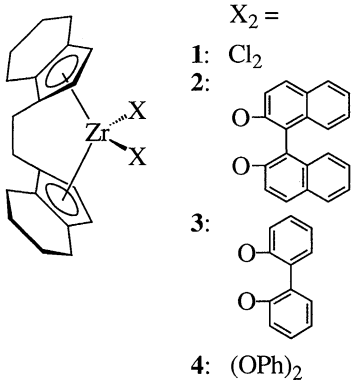
Optical resolution of racemic C_2-symmetric ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium derivatives was accomplished by high-performance liquid chromatography using cellulose tris(3,5-dimethylphenylcarbamate) as a chiral stationary phase.

In recent years, great interest has been focused on *ansa*-zirconocene complexes as catalysts for obtaining stereoregular polymers in the polymerization of α-olefins. Especially, C_2-symmetric ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride **1**[1] is well-known to behave as a homogeneous catalyst for isotactic specific propylene polymerization.[2] Furthermore, enantiomerically pure **1** has been used as a precatalyst for catalytic asymmetric reactions.[3] However, only the method of its preparation is the kinetic resolution of (±)-**1** with optically active lithium (1,1'-binaphthyl)-2,2'-diolate followed by removal of unreacted **1** with alumina. The binaphtholate adduct **2** can be converted to the optically pure **1** again.[4] Here, we report the first successful resolution of racemic ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium derivatives (**2** and **3**) by high-performance liquid chromatography (HPLC) on cellulose tris(3,5-dimethylphenylcarbamate) coated on silica-gel (Chiralcel OD).[5]



The binaphtholate complex (±)-**2**,[6] which was prepared from (±)-**1**[7] and racemic lithium (1,1'-binaphthyl)-2,2'-diolate followed by removal of unreacted **1** with alumina according to the literatures,[4] was resolved into enantiomers by HPLC on cellulose tris(3,5-dimethylphenylcarbamate) as a chiral stationary phase using the eluent, *n*-hexane / ethyl alcohol = 90 / 10 as shown in Figure 1. Chromatography was performed using a Jasco PU 980 chromatograph equipped with a UV detector (Jasco UV 970, monitored at 318 nm) and a polarimetric detector (Jasco OR 990). Two peaks indicated a positive and a negative optical rotations, and the second-peak was identified as (R, R)-**2** isomer

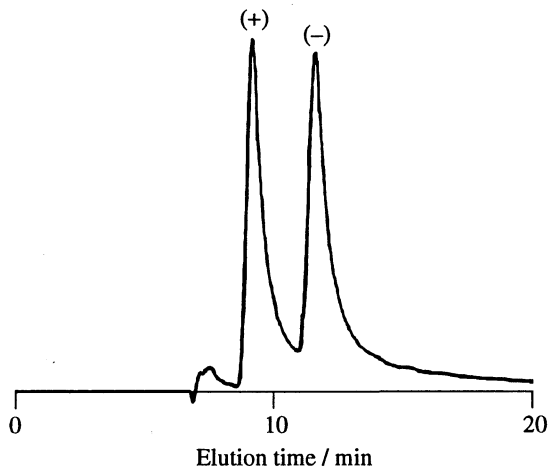


Figure 1. HPLC trace of zirconocene **2** on a silica-gel column coated with cellulose tris(3,5-dimethylphenylcarbamate). Column: 25 x 0.46(id) cm; eluent: *n*-hexane / ethanol 9:1 v/v; flow rate: 0.5 mL / min; monitored at 318 nm.

by using the (R, R)-**2** prepared from (±)-**1** and (R)-[lithium (1,1'-binaphthyl)-2,2'-diolate] by kinetic resolution.

2,2'-Biphenolate complex (±)-**3** was also prepared in the same manner as the complex **2** without further purification.[8] Figure 2 demonstrates the HPLC separation of the complex (±)-**3** by using cellulose tris(3,5-dimethylphenylcarbamate). The separation into enantiomers was efficiently performed showing positive optical rotation for the first-peak and negative one for the second. And about 0.4 mg of the racemic sample could be separated completely using an analytical column, indicating that preparative resolution is possible with a larger column. However, the dichloride (±)-**1** was not separated into enantiomers by HPLC under the same conditions. In addition, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium bisphenoxide (±)-**4** was not also efficiently resolved by the above HPLC method. These results indicate that the bidentate phenolate ligands play an important role for the efficient separation on the chiral stationary phase.

In conclusion, C_2-symmetric ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium derivatives possessing the bidentate phenolate ligands (**2** and **3**) were efficiently separated into enantiomers by HPLC on cellulose tris(3,5-dimethylphenylcarbamate) as a chiral stationary phase. These results suggest the development of a new method for the preparation of enantiomerically pure *ansa*-zirconocene complexes as well as the estimation of purity. Further work on the isolation of enantiomers of the complexes **2** and **3** by HPLC separation and their application to asymmetric reactions is under current investigation.

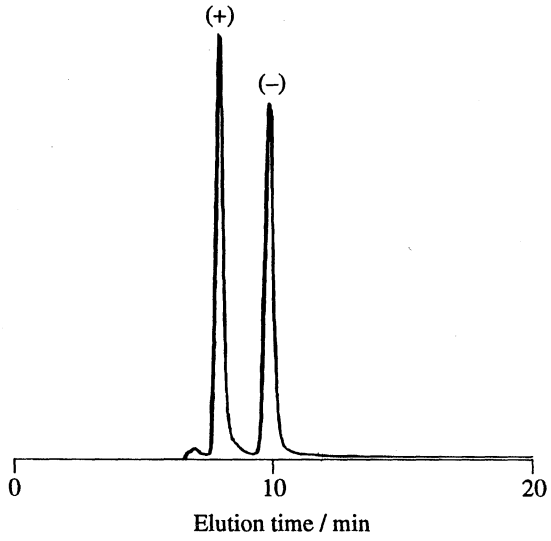


Figure 2. HPLC trace of zirconocene **3** on a silica-gel column coated with cellulose tris(3,5-dimethylphenylcarbamate). Column: 25 x 0.46(id) cm; eluent: *n*-hexane / ethanol 9:1 v/v; flow rate: 0.5 mL / min; monitored at 318 nm.

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7 The complex (±)-**1** was generously supplied by Tosoh Co.

8 ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.3 - 1.8 (m, 8H, CH_2), 2.10 (m, 4H, CH_2), 2.60 (m, 4H, bridge-CH_2), 3.26 (m, 4H, CH_2), 5.62 (d, 2H, J = 3 Hz, Cp-H), 5.71 (d, 2H, J = 3 Hz, Cp-H), 6.7 - 6.9 (m, 4H, aromatic), 7.2 - 7.5 (m, 4H, aromatic).