Optical Resolution of Planar-Chiral Cyclopentadienyl-Rhodium and -Iron Complexes by Liquid Chromatography Using Aqueous β-Cyclodextrin

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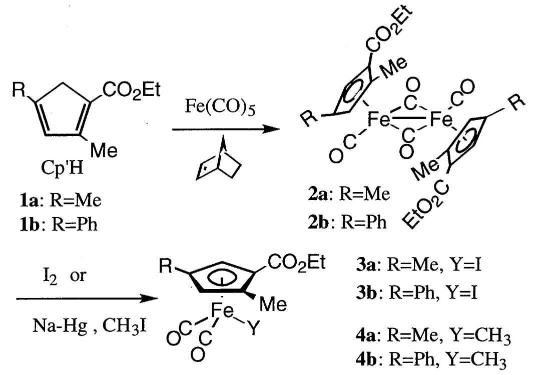
Racemates of planar-chiral cyclopentadienyl-rhodium and -iron complexes, Cp'Rh(cod) and Cp'Fe(CO)$_2$Y (Cp': trisubstituted cyclopentadienyls, Y=alkyl or halogen) are optically resolved on a preparative scale into enantiomers with efficincies of 100 and 50%ee, respectively, by liquid chromatography on a polyamide column using aqueous β–cyclodextrin as a mobile phase.

Planar-chiral cyclopentadienyl-metal complexes (Cp'-M; Cp' = unsymmetrically substituted cyclopentadienyls) have received a great deal of attention in recent years.[1] However only a few reports on the synthesis of optically pure Cp'-M complexes with a planar chirality have appeared in literatures because there are few efficient methods available for optical resolution of chiral organometallic complexes on a preparative scale. Previously we reported the syntheses of planar-chiral cyclopentadienyl-cobalt and -rhodium complexes starting form chiral cyclopentadienes bearing a (-)-menthyl group.[2] On the other hand, cyclodextrins(CDs) can form inclusion complexes with a wide variety of guest compounds including organometallic complexes,[3] and gas chromatography with cyclodextrin derivatives have emerged as a practical and widely applicable method for the resolution of many kinds of chiral organic and organometallic compounds.[4] We previously demonstrated that racemates of α-ferrocenylalcohol were successfully resolved by liquid chromatography on a preparative scale using aqueous α-CD as a mobile phase.[5] Now we have found the chromatographic method with CDs to be applied to the resolution of planar-chiral organometallic complexes. Here we wish to report the first optical resolution of planar-chiral cyclopentadienyl-metal complexes by liquid chromatography on a preparative scale using polyamide as a stationary phase and aqueous β-cyclodextrin as a mobile phase.

Cyclopentadienylirondicarbonyl complexes are known as a useful reagent and catalyst for organic syntheses.[6] We prepared new planar-chiral cyclopentadienyl-iron complexes, Cp'Fe(CO)$_2$Y (Y=alkyl or halogen), from 1,2,4-trisubstituted cyclopentadienes[7] by the method shown in Scheme 1.[8] Thus, heating cyclopentadienes **1** with iron carbonyl in the presence of norbornene as a hydrogen acceptor afforded a high yield of cyclopentadienylirondicarbonyl dimers **2** (**2a**: 85% yield, **2b**: 74% yield), which were converted upon treatment with iodine to iodoiron complexes **3**. Purification by column chromatography on silica gave iodoiron complexes **3a** and **3b** in 94 and 92% yield, respectively. Cyclopentadienylirondicarbonyl dimers **2** were alkylated to methyliron species **4** and purification by column chromatography on alumina afforded methyl iron complexes **4a** and **4b** in 71 and 54% yield, respectively, as a racemate. Complexes **3** and **4** were identified by ^{1}H NMR and IR spectroscopies and elemental analyses. Planar-chiral cyclopentadienyl-rhodium complexes, Cp'Rh(1,5-cyclooctadiene) **5**, were prepared by the method similar to that reported previously.[2]

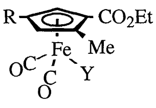
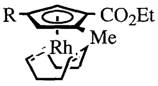


Scheme 1.

Then we examined mutual interaction between guest planar-chiral complexes **3**, **4**, and **5** and host cyclodextrins. When fine solids of the guest complexes were added to a saturated aqueous solution of cyclodextrins and stirred at 30 °C for 3 h, all of the guests exhibited strong interaction with the host and formed inclusion complexes. The inclusion complexes which precipitated were collected and washed with water to remove remaining cyclodextrin. Nonincluded metal complexes were removed by washing the residue with dichloromethane. During this process, the included guest complexes were not liberated from the cyclodextrin cavity. The inclusion complexes were characterized by spectral analyses and stoichiometries were determined by elemental and atomic absorption analyses, which showed that the planar-chiral cyclopentadienyl complexes form 2:1 (host : guest) inclusion complexes with β- and γ-CD, while no inclusion complexes were formed with α-CD which has the smallest cavity among them (Table 1).

On the basis of the results mentioned above, optical resolution of the racemates was performed by liquid chromatography using aqueous β-CD as a mobile phase and polyamide as a stationary phase on a preparative schale. A glass column (50 X 0.8 cm) was packed with polyamide 6 (Baker, for t.l.c.) by a slurry technique. A medium-pressure liquid chromatography system was equipped with a u. v. detector. The flow rate was 0.70 - 1.30 ml/min and 10 - 30 mg of racemic complexes were charged. Figures 1 and 2 show the chromatograms of the resolution for racemic methyliron complex **4b** and for racemic rhodium complex **5a**, respectively, on use of 0.01M β-CD as an eluent. The chromatograms clearly indicate efficient resolution of the racemates into the enantiomers. However, this method was not effective for the optical resolution of racemic methyliron complex **4a**.

Table 1. Inclusion complexes

Guest Complexes				Yield , % [a]		
	R	Y		α–CD	β–CD	γ–CD
	Me	I	**3a**	0	64	62
	Ph	I	**3b**	0	4	55
	Me	Me	**4a**	0	77	59
	Ph	Me	**4b**	0	36	58
	Me		**5a**	0	21	78
	Ph		**5b**	0	5	54

[a] Based on 2 : 1 inclusion complexes (CD : guest).

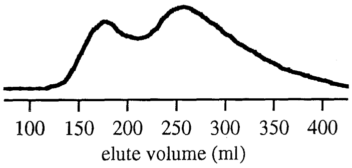


Figure 1. Chromatogram of Cp'Fe$(CO)_2CH_3$ **4b**.

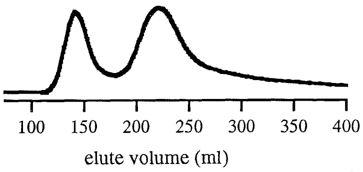


Figure 2. Chromatogram of Cp'Rh(cod) **5a**.

The enantiomers eluted as an inclusion complex could be isolated readily by extraction with diethylether. The optical purity was determined by HPLC using DAICEL chiral cell OD column with hexane-2-propanol as an eluate. Typically 10 mg of racemic cyclopentadienyliron complex **4b** was partially resolved into two enantiomeric fractions and each fraction contains 3 mg of (+)- or (-)-**4b** with about 50%ee. On the other hand, 30 mg of Cp'Rh(cod) **5a** was resolved into two enantiomeric fractions; fraction 1 contains 8 mg of pure (-)-**5a** and fraction 2 contains 13 mg of (+)-**5a** with 50%ee. Optically pure (+)-**5a** (5 mg) was obtained by reresolution of fraction 2. Enantiomerically pure (+)- and (-)-**5a** exhibit $[\alpha]_D$ of +14° and -14° (c 0.31, $CHCl_3$ 23°C), respectively, and the circular dichroism spectra indicated the isolated products to be a pair of enantiomers. However, this method could not be applied for iodoiron complexes **3** because they are somewhat unstable in water.

Consideration with CPK structural models suggest that the molecules of methyliron complex **4b** and Cp'Rh(cod) **5a** are too large to be included in the cavity of α-CD and even of single β- and γ- CD, but two molecules of β- and γ- CD are large enough to accommodate the complexes. Indeed this is consistent with the composition of the isolated inclusion complexes. The chromatogram of Cp'Rh(cod) **5a** shows that the (-)-isomer is eluted faster than the (+)-one, indicating stronger interaction of the (-)-isomer with β-CD.

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9 **4b**: IR (nujol) $\nu_{C=O}$ 2025, 1970, 1730 cm^{-1}; ^1H NMR (C_6D_6) 7.03 (s, 5H), 5.62 (d, J = 2.0 Hz), 4.44 (d, J = 2.0 Hz), 4.13 - 3.97 (m, 2H), 2.01 (s, 3H), 1.03 (t, J = 7.1 Hz, 3H), 0.41 (s, 3H). Anal. Found: C, 60.98; H, 5.07%. Calcd for $C_{18}H_{18}O_4Fe$: C, 61.04; H, 5.12%.

10 CD inclusion complexes **4b**: IR (nujol) $\nu_{C=O}$ 2030, 1970, 1720 cm^{-1}; Anal. Found: C, 44.02; H, 6.17; Fe, 1.85%. Calcd for 2β-CD-**4b** + 8 H_2O: $C_{102}H_{174}O_{82}Fe$: C, 44.26; H, 6.34; Fe, 2.02%.

11 CD inclusion complexes **5a**: IR (nujol) $\nu_{C=O}$ 1710 cm^{-1}; Anal. Found: C, 44.51; H, 6.29; Rh, 3.51%. Calcd for 2β-CD-**5a** + 5 H_2O: $C_{102}H_{175}O_{77}Rh$: C, 44.77; H, 6.45; Fe, 3.76%.