

A New Route to Planar-chiral Cyclopentadienyl-Iron(II) and -Rhodium(I) Complexes

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Diastereoisomerically pure planar-chiral cyclopentadienyl-metal complexes, **3** and **4**, are prepared by the reaction of the cyclopentadiene **2** having a (-)-menthyl group with FeCl₂ or [Rh(cod)Cl]₂ (cod = cycloocta-1,5-diene); removal of the (-)-menthyl group from **4** affords the first optically pure enantiomers, (+)-**5** and (-)-**5**.

Since the discovery of planar-chiral ferrocenes,¹ many planar-chiral cyclopentadienyl-metal (Cp'-M; Cp' = unsymmetrically substituted cyclopentadienyls) complexes have been reported. In pioneering work, Schlögl and others have developed synthetic routes to planar-chiral ferrocenes and expanded to other Cp'-M complexes, e.g. (Cp')₂Ru, (Cp')Mn(CO)₃.² However, few reports on the optically pure Cp'-M complexes of other metals with planar chirality have appeared,³ though there are numerous reports on Cp'-M complexes of various metals. The reason may be that the synthesis and optical resolution of the planar-chiral Cp'-M complexes are limited by their chemical instabilities, and in addition a convenient method for the preparation of unsymmetrically substituted cyclopentadienes has not yet been reported.⁴ In the past few years, planar-chiral metallocenes have been of much interest because they play an important role as a chiral auxiliary for enantioselective organic syntheses^{3a-8} and an allosteric host-guest system.^{3h}

Recently a novel synthetic method for trisubstituted cyclopentadienes was shown by Ueda *et al.*⁵ By using this method we can easily prepare cyclopentadienes having a alkoxy carbonyl group which is used for the introduction of a removable chiral auxiliary such as the (-)-menthyl group on the cyclopentadiene ring by a simple alcohol-exchange reaction. Thus, the method may offer a new route leading to diastereoisomeric planar-chiral Cp'-M complexes. Here we report new and convenient routes for the syntheses of planar-chiral ferrocenes and Cp'-Rh complexes, of which the latter provides the first example of enantiomeric planar-chiral Cp'-Rh complexes.⁶

The preparation of a cyclopentadiene derivative having a chiral group was performed as follows. In the presence of a catalytic amount of toluene-*p*-sulfonic acid (*p*-TsOH), **1** prepared by Ueda's method was allowed to react with (-)-menthol in xylene under reflux (Scheme 1). The alcohol-exchange reaction proceeded smoothly and the resultant

(-)-menthyl ester **2** was purified by chromatography on silica and distillation.

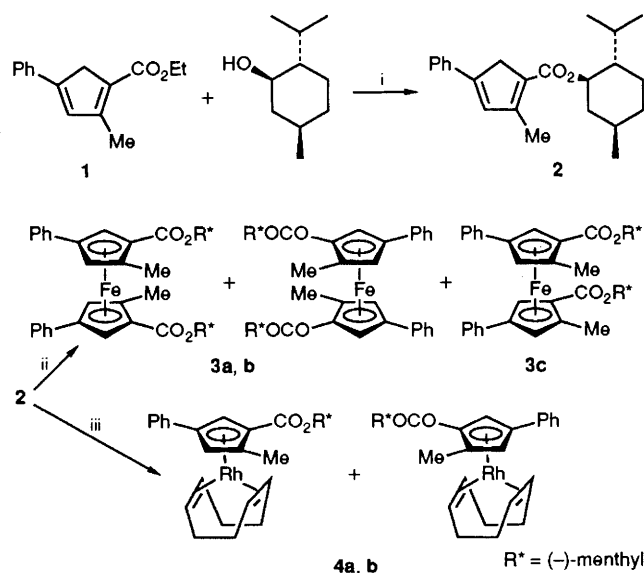
Then we synthesized the planar-chiral ferrocenes and Cp'-Rh complexes using the prepared chiral cyclopentadiene derivative by the usual methods (Scheme 1).⁷ Purification by column chromatography on silica gave ferrocenes **3** and Cp'-Rh complexes **4**, as a mixture of diastereoisomers. ¹H NMR and HPLC analyses indicated that the products consist of three isomers (**3a**, **b** and **c**) for the ferrocenes and two isomers (**4a** and **b**) for the Cp'-Rh complexes. In the case of the ferrocene synthesis, an asymmetric induction by the chiral (-)-menthyl group was observed (Table 1).

Optical resolution of the mixture of diastereoisomers was performed by preparative HPLC on silica with hexane-benzene as eluate. Isolated yields are summarized in Table 1 along with [α]_D values of the diastereoisomers. Converting diastereoisomeric complexes into enantiomeric complexes was carried out for the Cp'-Rh complexes **4** by the reaction with phenyllithium (Scheme 2). Removal of the chiral auxiliary, (-)-menthyl group, from diastereoisomers afforded

Table 1 Synthesis of planar-chiral C₅H₅-M complexes

Product	Yield(%) ^a Total/isolated	[α] _D (in CHCl ₃)
3	67 (3a : 3b : 3c = 2 : 3 : 5) ^b	
3a	4	238 ^c (c 0.286)
3b	28	-271 ^c (c 0.413)
3c	21	-13 ^c (c 0.324)
4	90 (4a : 4b = 1 : 1) ^b	
4a	31	66 ^d (c 1.00)
4b	26	-75 ^d (c 1.00)

^a Based on metal source. ^b Ratio was determined by HPLC. ^c Temp. 20 °C. ^d Temp. 18 °C.



Scheme 1 Reagents and conditions: i, *p*-TsOH, xylene, reflux; ii, FeCl₂; iii, [Rh(cod)Cl]₂

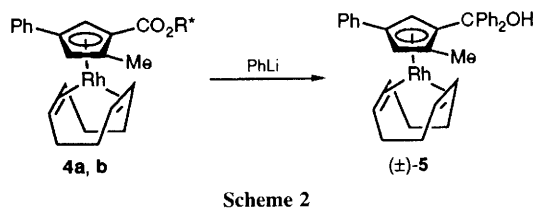


Table 2 Physical data of enantiomeric complexes **5**

	M.p./°C	[α] _D ²⁶ (in CHCl ₃)
(+)- 5	173.7-174.5	125 (c 1.02)
(-)- 5	173.8-174.3	-126 (c 0.951)

enantiomers, (+)- and (-)-**5**,[†] which showed the same melting points and absolute values of $[\alpha]_D$ (Table 2). In the presence of a chiral shift reagent such as (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol⁸ (fivefold excess), the ¹H NMR analysis indicated that the optical purity of (-)-**5** was up to at least 95% enantiomeric excess, and the circular dichroism spectra indicated the products to be a pair of enantiomers.

[†] The new compounds were characterized by elemental analyses and IR and ¹H NMR (in CDCl₃, 360 MHz) spectra.

Selected data: **2**, yellow oil, $\nu_{\max}/\text{cm}^{-1}$ (neat) 1700 (CO); ¹H NMR, δ 7.28–7.57 (m, 5H), 6.76 (s, 1H), 4.82 (dt, 1H, *J* 4.6, 10.9 Hz), 3.71 (bq, 2H, *J* 2.5 Hz), 2.40 (t, 3H, *J* 2.5 Hz), 0.92 (d, 6H, *J* 7.4 Hz), 0.90–2.00 (m, 8H), 0.80 (d, 3H, *J* 7.0 Hz); $[\alpha]_D^{25} -61$, *c*, 1.15, CHCl₃. **3a**, orange crystals, $\nu_{\max}/\text{cm}^{-1}$ (Nujol) 1725 (CO); ¹H NMR, δ 4.78 (dt, 2H, *J* 4.3, 10.8 Hz), 4.33 (s, 2H), 3.97 (s, 2H), 2.08 (s, 6H), 1.93 (s, 6H), 0.96 (d, 6H, *J* 7.0 Hz), 0.93 (d, 6H, *J* 6.5 Hz), 0.84 (d, 6H, *J* 6.9 Hz), 0.82–2.17 (m, 16H). **3b**, orange crystals, $\nu_{\max}/\text{cm}^{-1}$ (Nujol) 1725 (CO); ¹H NMR, δ 4.79 (dt, 2H, *J* 4.3, 7.7 Hz), 4.31 (s, 2H), 3.96 (s, 2H), 2.08 (s, 6H), 1.95 (s, 6H), 0.96 (d, 6H, *J* 6.8 Hz), 0.93 (d, 6H, *J* 7.1 Hz), 0.81–2.20 (m, 16H), 0.79 (d, 6H, *J* 7.1 Hz). **3c**, orange crystals, $\nu_{\max}/\text{cm}^{-1}$ (Nujol) 1725 (CO); ¹H NMR, δ 4.79 (dt, 1H, *J* 4.0, 7.9 Hz), 4.77 (dt, 1H, *J* 4.3, 8.0 Hz), 4.35 (s, 2H), 3.97 (s, 2H), 2.15 (s, 3H), 2.14 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H), 0.95 (d, 3H, *J* 6.8 Hz), 0.95 (d, 3H, *J* 7.1 Hz), 0.93 (d, 3H, *J* 7.1 Hz), 0.91 (d, 3H, *J* 7.4 Hz), 0.82 (d, 3H, *J* 6.8 Hz), 0.81–2.18 (m, 16H), 0.77 (d, 3H, *J* 7.1 Hz). (+)-**5**, yellow crystals, ¹H NMR (in C₆D₆), δ 6.92–7.87 (m, 15H), 5.47 (d, 1H, *J* 2.1 Hz), 4.66 (d, 1H, *J* 2.1 Hz), 3.93–4.00 (m, 2H), 3.86 (s, 1H), 3.11–3.18 (m, 2H), 2.20–2.34 (m, 2H), 2.05–2.18 (m, 2H), 1.78–1.95 (m, 4H), 1.45 (s, 3H). (-)-**5**, yellow crystals, ¹H NMR (in C₆D₆), δ 6.92–7.87 (m, 15H), 5.46 (d, 1H, *J* 2.1 Hz), 4.65 (d, 1H, *J* 2.1 Hz), 3.93–4.00 (m, 2H), 3.88 (s, 1H), 3.11–3.18 (m, 2H), 2.20–2.34 (m, 4H), 1.78–1.95 (m, 4H), 1.45 (s, 3H).

The convenient synthetic route described here leads to a fairly wide range of new planar-chiral cyclopentadienyl-organometallic compounds which build up new chiral environments around the central metals.

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References

- 1 J. B. Thomson, *Tetrahedron Lett.*, 1959, 26.
- 2 K. Schlögl, *Top. Stereochem.*, 1967, **1**, 39; *J. Organomet. Chem.*, 1986, **300**, 219; D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann and I. Ugi, *J. Am. Chem. Soc.*, 1970, **92**, 5389; D. E. Bublitz and K. L. Rinehart Jr., *Org. React. (NY)*, 1969, **17**, 1.
- 3 (a) F. Le Moigne, A. Dormond, J. C. Leblanc, C. Moise and J. Tirouflet, *J. Organomet. Chem.*, 1973, **54**, C13; (b) F. R. W. P. Wild, L. Zsolnai, G. Huttner and H. H. Brintzinger, *J. Organomet. Chem.*, 1982, **232**, 233; (c) J. Okuda, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 47 and references cited therein; (d) R. L. Halterman, K. P. C. Vollhardt and M. E. Welker, *J. Am. Chem. Soc.*, 1987, **109**, 8105; (e) R. L. Halterman and K. P. C. Vollhardt, *Organometallics*, 1988, **7**, 883; (f) L. A. Paquette, J. A. McKinney, M. L. McLaughlin and A. L. Rheingold, *Tetrahedron Lett.*, 1986, **27**, 5599; (g) T. Hayashi, A. Yamamoto, M. Hojo, K. Kishi, Y. Ito, E. Nishioka, H. Miura and K. Yanagi, *J. Organomet. Chem.*, 1989, **370**, 129 and references cited therein; (h) R. C. Petter and C. I. Milberg, *Tetrahedron Lett.*, 1989, **30**, 5085.
- 4 D. W. Macomber, W. P. Hart and M. D. Rausch, *Adv. Organomet. Chem.*, 1982, **21**, 1.
- 5 M. Hatanaka, Y. Himeda and I. Ueda, *J. Chem. Soc., Chem. Commun.*, 1990, 526.
- 6 Related Co complexes were reported, but they were not optically resolved: N. E. Murr and E. Laviron, *Can. J. Chem.*, 1976, **54**, 3357; R. Boese, D. Bläser, R. L. Halterman and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 553.
- 7 G. Wilkinson, *Org. Synth. IV*, 1963, 473; J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.
- 8 W. H. Pirkle, D. L. Sikkenga and M. S. Pavlin, *J. Org. Chem.*, 1977, **42**, 384.