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Synthesis of planar-chiral cobalticinium complexes and their properties as chiral anion receptors *

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Abstract

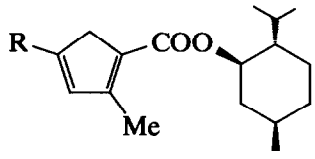
The first enantiomerically pure planar-chiral cobalticinium complexes have been synthesized and shown to behave as anion receptors which can recognize the chirality of camphor-10-sulfonate.

1. Introduction

Chiral organotransition metal complexes have been extensively studied due to their catalytic behaviour in asymmetric organic synthesis. The synthesis and catalysis of planar-chiral cyclopentadienyl complexes are of particular current interest [1]. Recently we reported a new method for the synthesis of enantiomerically pure planar-chiral ferrocenes and cyclopentadienylrhodium complexes [2]. We have now applied this method to the synthesis of a cobalt complex, cobalticinium salt, which is the cationic form of cobaltocene and has a structure isoelectronic with ferrocene [3]. Cobalticinium complexes have attracted attention for their attributes as functional materials [4] and as anion receptors [5].

2. Results and discussion

One of the features of our method for preparing planar-chiral cyclopentadienyl complexes is to use a trisubstituted cyclopentadiene having a removable chiral auxiliary, namely a (−)-menthyl group [2]. For the synthesis of planar-chiral cobalticinium complexes we used chiral cyclopentadienes (Cp^1H; **1a** and **1b**). In order to avoid the formation of a *meso* isomer, a cobalt source in the form of mono(cyclopentadienyl)cobalt compound, $(C_5Me_5)Co(acac)$ [6] was reacted with the anion prepared from chiral cyclopentadiene **1**.



1a: R = Me
1b: R = Ph

The reactions gave cobaltocene derivatives, $(C_5Me_5)Co(Cp^1)$, which were oxidized by a customary method to cobalticinium complexes and isolated as a hexafluorophosphate (Scheme 1). ^1H NMR and HPLC analyses showed that the cobalticinium complexes thus obtained consist of two diastereomers **2X** and **3X** ($X = PF_6$). During the synthesis of **2aX** and **3aX** (R = Me), asymmetric induction by the chiral (−)-menthyl group was observed to a slight extent. The separation of diastereomer **2aX** from **3aX** was accomplished by fractional crystallization. Pure **2aX** was isolated from recrystallization in ethanol, and pure **3aX** from recrystallization in ethanol-water. However, the separation of **2bX** from **3bX** (R = Ph) needed help with preparative HPLC (ODS column, methanol–water). Isolated yields are summarized in Table 1 along with $[\alpha]_D$ values of the diastereomers, though absolute configurations of the enantiomers have not yet been determined.

Conversion of diastereomeric complexes into enantiomeric was carried out for **2aX** and **3aX**. Thus, the chiral auxiliary, (−)-menthyl group, was removed from

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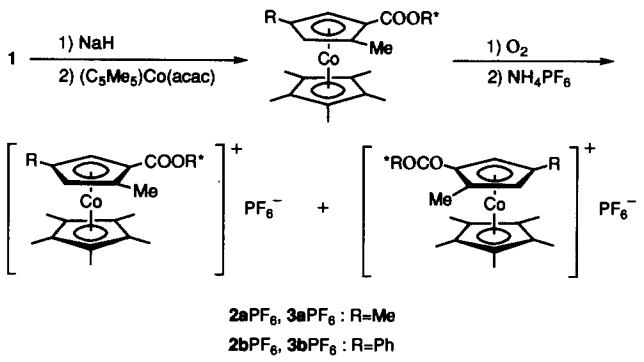


Scheme 1. Synthesis of diastereomers [R* = (−)-menthyl].

diastereomer **2aX** by hydrolysis in concentrated aqueous HCl and we successfully obtained an optically pure enantiomer, (+)-**4aX** as a carboxylic acid derivative (Scheme 2). Similarly (−)-**4aX** was obtained from **3aX**. Enantiomers (+)- and (−)-**4aX** are useful intermediates for leading to planar-chiral cobalticinium complexes having a variety of functional groups on the cyclopentadienyl ring. For example, enantiomer (+)-**4aX** was transformed to an acid chloride followed by condensation with aniline to afford an optically pure amide (−)-**5aX** [7]. The same treatment of (−)-**4aX** yielded (+)-**5aX** which showed the same melting point and absolute value of $[\alpha]_D$ as (−)-**5aX** (Table 2). The circular dichroism spectra indicated (+)- and (−)-**5aX** to be a pair of optically pure enantiomers. Enantiomers **4aX** and **5aX** provide the first examples of planar-chiral ionic metallocenes.

TABLE 1. Synthesis of planar-chiral cobalticinium complexes

Product (X = PF_6)	Yield(%) [a]	$[\alpha]_D$ (deg.) (in $CHCl_3$)
2aX+**3aX**	65 (**2a**:**3a** = 1:0.7) [b]	
2aX	25	+1 [c] (c 0.453)
3aX	17	−67.2 [c] (c 0.399)
2bX+**3bX**	85 (**2b**:**3b** = 1:1) [b]	
2bX	7	−16 [d] (c 0.285)
3bX	9	−39.5 [d] (c 0.326)

[a] Isolated yield based on cobalt source.
[b] Ratio was determined by HPLC.
[c] Temp. 15°C.
[d] Temp. 22°C.

TABLE 2. Physical data of enantiomeric complexes **4aX** and **5aX** (X = PF_6)

	M.p. (°C)	$[\alpha]^{15}D$ (deg.) (in CH_3OH)
(+)-**4aX**	270 (dec.)	+1 (c 0.317)
(−)-**4aX**	270 (dec.)	−1 (c 0.312)
(+)-**5aX**	216.0–217.0	+18.2 (c 0.727)
(−)-**5aX**	216.0–217.0	−17.3 (c 0.723)

Recently Beer *et al.* reported that cobalticinium complexes act as an receptor for anions such as halides and nitrates [5]. We have also examined the behaviour of **5X** towards anions and found that our cobalticinium complexes recognize not only organic as well as inorganic anions but also the chirality of guest species. For example, in the ^1H NMR spectrum of **5bX** taken in $CDCl_3$ solution, addition of tetraethylammonium *p*-toluenesulfonate resulted in a remarkable shift of the NH(H^a) and Cp(H^b) signals. A titration experiment indicated the formation of a host-guest complex with clear 1:1 stoichiometry (Fig. 1). The association constant between **5b** and *p*-toluenesulfonate has been estimated as 10^4 M^{-1} by a nonlinear curve fitting procedure. Subsequently, tetrabutylammonium (+)-camphor-10-sulfonate was employed as a chiral guest. Addition of the chiral sulfonate to a solution of (±)-**5bX** in $CDCl_3$ also caused a remarkable shift (1–2 ppm downfield) of proton signals for the NH and Cp. The result obtained from the ^1H NMR titration experiment

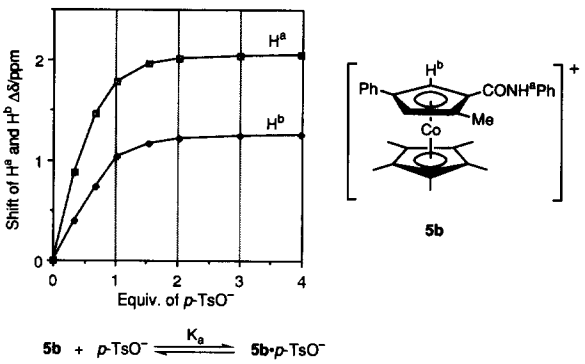
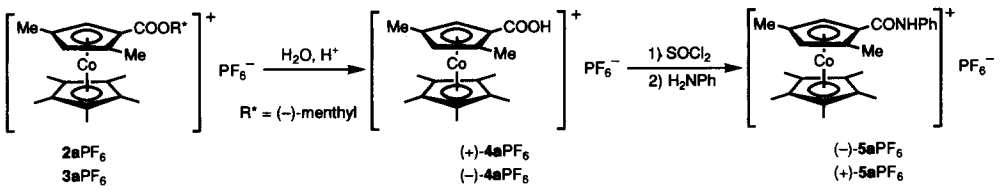


Fig. 1. ^1H NMR titration curve for **5b** (in $CDCl_3$).



Scheme 2. Synthesis of enantiomers $5aPF_6$.

has indicated that the cobalticinium host recognizes the chiralty of the guest and the difference between K_a and $K_{a'}$ (K_a = [(+)-**5b** · (+)-camphorsulfonate]/ [(+)-**5b**][(+)-camphorsulfonate]; $K_{a'}$ = [(−)-**5b** · (+)-camphorsulfonate]/ [(−)-**5b**][(+)-camphorsulfonate]) is estimated at about 10%. Further work is now in progress to examine the potential of the planar-chiral cobalticinium complexes for chiral recognition.

Experimental details

The new compounds were characterized by elemental analyses and IR, ^{1}H NMR (360 MHz), and mass spectra.

Selected data for new compounds are as follows.

1a: ^{1}H NMR ($CDCl_3$): δ = 6.05 (s, 1H), 4.75 (dt, 1H, J = 11.0, 4.3 Hz), 3.22–3.20 (m, 2H), 2.30 (t, 3H, J = 2.5 Hz), 2.07 (d, 3H, J = 1.4 Hz), 0.90 (d, 6H, J = 6.8 Hz), 0.78 (d, 3H, J = 6.7 Hz), 2.0–0.80 (m, 9H); $[\alpha]^{22}$D −79.2° (*c* 0.361, $CHCl_3$).

2aPF_6: ^{1}H NMR ($CDCl_3$): δ = 5.21 (d, 1H, J = 1.6 Hz), 5.16 (d, 1H, J = 1.9 Hz), 4.89 (dt, 1H, J = 11.0, 4.6 Hz), 2.13–1.05 (m, 9H), 2.11 (s, 3H), 2.00 (s, 3H), 1.89 (s, 15H), 0.97 (d, 3H, J = 6.4 Hz), 0.93 (d, 3H, J = 7.0 Hz), 0.77 (3H, d, J = 7.0 Hz).

2bPF_6: ^{1}H NMR ($CDCl_3$): δ = 7.66–7.50 (m, 5H), 5.94 (d, 1H, J = 1.8 Hz), 5.71 (d, 1H, J = 1.8 Hz), 4.94 (dt, 1H, J = 10.8, 4.4 Hz), 2.27 (s, 3H), 2.15–1.06 (m, 9H), 1.66 (s, 15H), 0.98 (d, 3H, J = 6.7 Hz), 0.96 (d, 3H, J = 6.9 Hz), 0.79 s(3H, d, J = 6.9 Hz).

3aPF_6: ^{1}H NMR ($CDCl_3$): δ = 5.34 (d, 1H, J = 1.7 Hz), 5.16 (d, 1H, J = 1.7 Hz), 4.87 (dt, 1H, J = 11.2, 4.5 Hz), 2.12–1.05 (m, 9H), 2.15 (s, 3H), 2.03 (s, 3H), 1.91 (s, 15H), 0.97 (d, 3H, J = 6.6 Hz), 0.93 (d, 3H, J = 7.0 Hz), 0.76 (3H, d, J = 7.0 Hz).

3bPF_6: ^{1}H NMR ($CDCl_3$): δ = 7.65–7.50 (m, 5H), 5.97 (d, 1H, J = 1.8 Hz), 5.74 (d, 1H, J = 2.1 Hz), 4.96 (dt, 1H, J = 11.0, 4.6 Hz), 2.25 (s, 3H), 2.17–1.07 (m, 9H), 1.66 (s, 15H), 0.99 (d, 3H, J = 6.7 Hz), 0.94 (d, 3H, J = 6.9 Hz), 0.79 (3H, d, J = 6.9 Hz).

(+)-**4a**PF_6: ^{1}H NMR (CD_3OD): δ = 5.32 (d, 1H, J = 1.9 Hz), 5.02 (d, 1H, J = 1.4 Hz), 2.13 (s, 3H), 1.97 (s, 3H), 1.89 (s, 15H); Mass (FAB): *m/z* 331 [M − PF_6]$^+$.

(+)-**5a**PF_6: ^{1}H NMR ($CDCl_3$): δ = 8.36 (s, 1H), 7.79 (d, 2H, J = 7.8 Hz), 7.36 (t, 2H, J = 7.6 Hz), 7.16 (t, 1H, J = 7.3 Hz), 5.92 (d, 1H, J = 1.2 Hz), 4.67 (d, 1H, J = 1.0 Hz), 2.22 (s, 3H), 2.00 (s, 3H), 1.89 (s, 15H); Mass (EI): *m/z* 406 [M − PF_6]$^+$.

The (−)-**4a**PF_6 and (−)-**5a**PF_6 gave the same spectral data as the (+)-isomers.

Acknowledgments

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References

1 R.L. Halterman, *Chem. Rev., 92* (1992) 965 and references therein; T. Hayashi, A. Yamamoto, M. Hojo, K. Kishi, Y. Ito, E. Nishioka, H. Miura and K. Yanagi, *J. Organomet. Chem., 370* (1989) 129; R.C. Petter and C.I. Milberg, *Tetrahedron Lett., 30* (1989) 5085.

2 M. Uno, K. Ando, N. Komatsuzaki and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, (1992) 964.

3 Related Co complexes have been reported, but they were not optically resolved: N.E. Murr and E. Laviron, *Can. J. Chem., 54* (1976) 3357; R. Boese, D. Bläser, R.L. Halterman and K.P.C. Vollhardt, *Angew. Chem., Int. Ed. Engl., 27* (1988) 553.

4 C.E. Carraher, Jr., in F. Millichi and C.E. Carraher, Jr. (eds.), *Interfacial Synthesis, Vol. 2*, Marcel Dekker, New York, 1977, p. 367; J.E. Sheats, *J. Organomet. Chem. Library, 7* (1979) 461; K. Sakamoto, H. Nishihara and K. Aramaki, *J. Chem. Soc., Dalton Trans.*, (1992) 1877.

5 P.D. Beer, D. Hesek, J. Hodacova and S.E. Stokes, *J. Chem. Soc., Chem. Commun.*, (1992) 270; P.D. Beer, M.G.B. Drew, C. Hazlewood, D. Hesek, J. Hodacova and S.E. Stokes, *J. Chem. Soc., Chem. Commun.*, (1993) 229.

6 E.E. Bunel, L. Valle and J.M. Manriquez, *Organometallics, 4* (1985) 1680.

7 J.E. Sheats and M.D. Rausch, *J. Org. Chem., 35* (1970) 3245.