

Synthesis of planar-chiral cobalticinium complexes

Nobuko Komatsuzaki, Mitsunari Uno, Kazuhiko Shirai, Takanori Tanaka, Masami Sawada, Shigetoshi Takahashi *

Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan

Received 28 December 1994; in revised form 15 February 1995

Abstract

Planar-chiral cobalticinium complexes having a carboxylic function were synthesized in an enantiomerically pure form and transformed into several derivatives such as amide, ester and alcohol. The molecular structure including absolute configuration of **8b** was established by a single-crystal X-ray structure analysis. Based on the configuration of the (–)-menthyl group, the absolute configuration of **8b** around the Cp–M moiety was determined to be *R*.

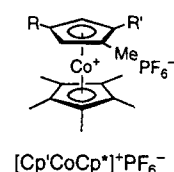
Keywords: Cobalt; Cyclopentadienyl; Optical resolution; X-ray diffraction; Chirality

1. Introduction

Cyclopentadienyl–metal complexes have wide application in organic syntheses [1]. In particular, planar-chiral metallocenes have attracted much interest because they play an important role in enantioselective organic syntheses [2]. Recently, we have reported a new method for the synthesis of enantiomerically pure planar-chiral ferrocenes, Cp′Rh(cycloocta-1,5-diene) [3] and Cp′Co(tetraphenylcyclobutadiene) (Cp′ = trisubstituted cyclopentadienyls) [4]. One of the features of our method for preparing such planar-chiral complexes is to use a trisubstituted cyclopentadiene having a removable chiral auxiliary such as a (–)-menthyl group. Now we have attempted to apply our method to the synthesis of cobaltocene; however, cobaltocene is air sensitive and it can be very difficult to perform the resolution of a diastereomeric mixture. It is well known that cobaltocene is easily oxidized by release of one electron to give a cobalticinium cation which has the isoelectronic structure of ferrocene. We therefore decided to perform the resolution of a more stable cobalticinium salt, because cobaltocene and cobalticinium cation are redox-active.

Planar-chiral cobaltocene and cobalticinium complexes have not been reported so far [5]. This may be the reason why, unlike ferrocene, cobalticinium cation

is chemically inactive towards electrophilic substitutions, and the number of derivatives in this series is limited, although cobalticinium complexes have attracted attention in terms of functional materials [6] and anion receptors [7]. Here, we report on the first syntheses of optically pure planar-chiral cobalticinium complexes, [Cp′CoCp*]⁺PF₆[–] (Cp* = pentamethylcyclopentadienyl) [8], and the absolute configuration determined by an X-ray crystallographic analysis.

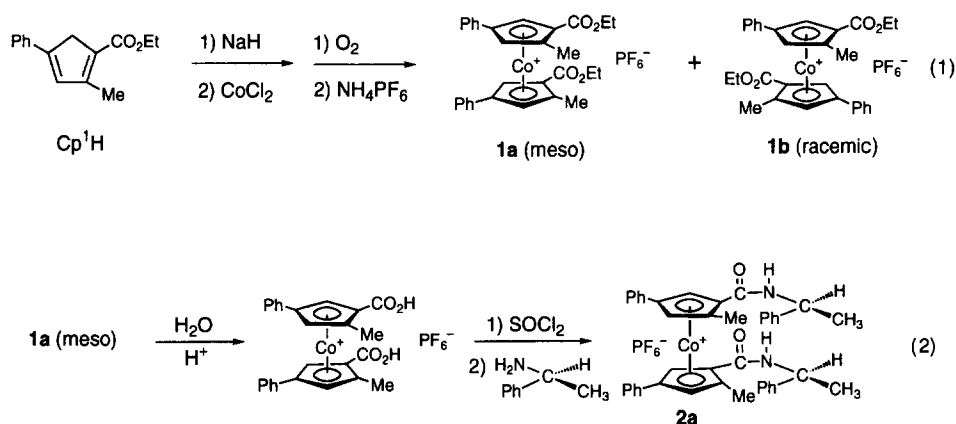


2. Results and discussion

2.1. Synthesis of planar-chiral cobalticinium complexes

First, we synthesized planar-chiral cobalticinium complexes using an achiral trisubstituted cyclopentadiene, 1-ethoxycarbonyl-2-methyl-4-phenylcyclopenta-1,3-diene Cp¹H [9], by the usual method [10]. Thus, cobaltocene Cp₂Co, which was prepared from the reaction of CoCl₂ with Cp¹Na, was oxidized in hydrochloric

* Corresponding author.

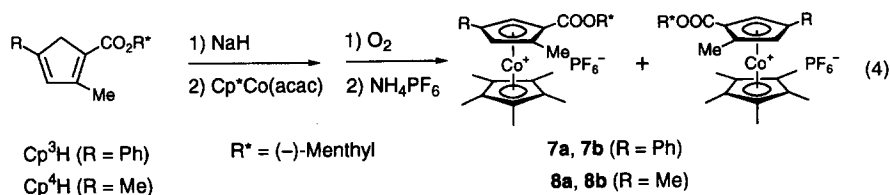
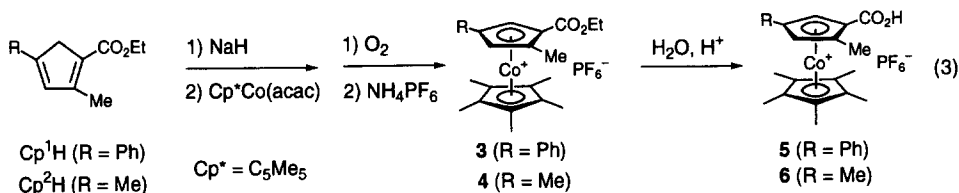


ric acid to a cobalticinium complex, $[\text{Cp}_2^1\text{Co}]^+$, and isolated as a hexafluorophosphate salt (Eq. 1).

The salt is not hygroscopic and exhibits moderate solubility in both water and polar organic solvents such as dichloromethane and acetone. The ^1H NMR spectrum indicated that the salt consists of equimolar amounts of two diastereomers, which were separated from each other by fractional recrystallization from methanol, giving **1a** (m.p. 243°C) and **1b** (m.p. 207°C) as orange needles. Diastereomer **1a** was assigned to a *meso* form and **1b** to a racemic isomer as follows. Diastereomeric mixture **1** was converted into amide derivatives **2** by reaction with $(-)\text{-}\alpha\text{-phenylethylamine}$ via carboxylic acid intermediates (see below). The ^1H NMR spectrum and HPLC analysis showed that amide derivatives **2** consist of three diastereomers with a molar ratio of 2:1:1, of which the first comes from *meso* and the last two from racemic isomers. We isolated the amide **2a** derived from the *meso* isomer by fractional recrystallization from ethanol. Amide **2a** exhibited the same ^1H NMR spectrum as the amide derivative which was prepared starting from **1a** (Eq. 2). Hence **1a** may be

a *meso* isomer. This assignment is confirmed by comparison of the ^1H NMR spectra of **1a** and **2a**; the spectrum of **2a** indicated loss of a σ_h -symmetric element observed for **1a** due to the introduction of a chiral group on the two cyclopentadienyl ligands. For example, **1a** showed a resonance attributable to the protons at the 3-position on cyclopentadienyl ligands at δ 6.16 ppm, while the corresponding resonances of **2a** appeared at δ 5.73 and 6.00 ppm with the same intensity, indicating magnetic unequivalence of one cyclopentadienyl ligand to the other in **2a**. These NMR data also suggest that **1a** must be a *meso* isomer. The stereochemistry of **1b**, therefore, can be assigned to be racemic.

In order to avoid the formation of a *meso* isomer, we used a monocyclopentadienyl cobalt compound, $(\text{C}_5\text{Me}_5)\text{Co}(\text{acac})$ [11], as a cobalt source for the preparation of cobaltocene. The cobaltocene $(\text{C}_5\text{Me}_5)\text{CoCp}'$ thus obtained was similarly oxidized to a cobalticinium complex and isolated as a hexafluorophosphate (Eq. 3). In the presence (fivefold excess) of a chiral shift reagent, $(R)\text{-}(-)\text{-}2,2,2\text{-trifluoro-1-(9-anthryl)ethanol}$ [12], the ^1H



NMR analysis indicated both **3** and **4** to be a pair of enantiomers. For example, two sets of resonances due to the 2- and 4-methyl protons on the cyclopentadienyl ring of **4** ($R = \text{Me}$) were observed: δ 2.04 and 2.03 ppm for 2-Me, and δ 1.89 and 1.88 ppm for 4-Me with an intensity ratio of 1:1. A similar spectrum was observed for **3** ($R = \text{Ph}$).

We have now found that **3** and **4** easily undergo hydrolysis in HCl to give a carboxylic acid **5** ($R = \text{Ph}$) and **6** ($R = \text{Me}$), respectively, in good yield (Eq. 3), although the hydrolysis of free cyclopentadiene did not yield a carboxylic acid. This reactivity of **3** and **4** suggests that optically pure enantiomers of planar-chiral cobalticinium complexes may be isolated if we obtain the diastereomeric planar-chiral cobalticinium complexes using chiral cyclopentadienes Cp^3H and Cp^4H [3,4]. We then prepared $[(\text{C}_5\text{Me}_5)\text{CoCp}^4]^+ \text{PF}_6^-$ (**8** ($R = \text{Me}$)) according to Eq. 4. HPLC analyses showed that the cobalticinium complexes **8** thus obtained consist of two diastereomers, **8a** and **8b**, with a ratio of 1:0.7, which indicates asymmetric induction to a slight extent by the chiral (–)-menthyl group in the formation of diastereomers **8**. In the ^1H NMR spectrum of **8**, one set of resonances due to 2-methyl protons on the cyclopentadienyl ring appeared at δ 2.11 and 2.15 ppm with an intensity ratio of 1:0.7, indicating that the diastereomers **8a** and **8b** are distinguished from one another by ^1H NMR. Cobalticinium complex **7** ($R = \text{Ph}$) was also characterized by the same method and the results indicated that it was diastereomers **7a** and **7b** with a ratio of 1:1. The separation of diastereomer **8a** from **8b** was accomplished by fractional crystallization. Pure **8a** was isolated by recrystallization from ethanol and pure **8b** from ethanol–water. However, the separation of **7a** from **7b** required the use of preparative HPLC (ODS column, methanol–water eluent). Isolated yields are summarized in Table 1 along with $[\alpha]_D$ values of the diastereomers.

Conversion of diastereomers **7** and **8** into enantiomers by removing the chiral auxiliary on a cyclopent-

Table 1
Synthesis of planar-chiral cobalticinium complexes

Product	Yield (%) ^a	$[\alpha]_D$ (°) (in CHCl_3)
7a + 7b	85 (7a : 7b = 1:1) ^b	
7a	7	–16 ^c (c 0.285)
7b	9	–39.5 ^c (c 0.326)
8a + 8b	65 (8a : 8b = 1:0.7) ^b	
8a	25	+1 ^d (c 0.453)
8b	17	–67.2 ^d (c 0.399)

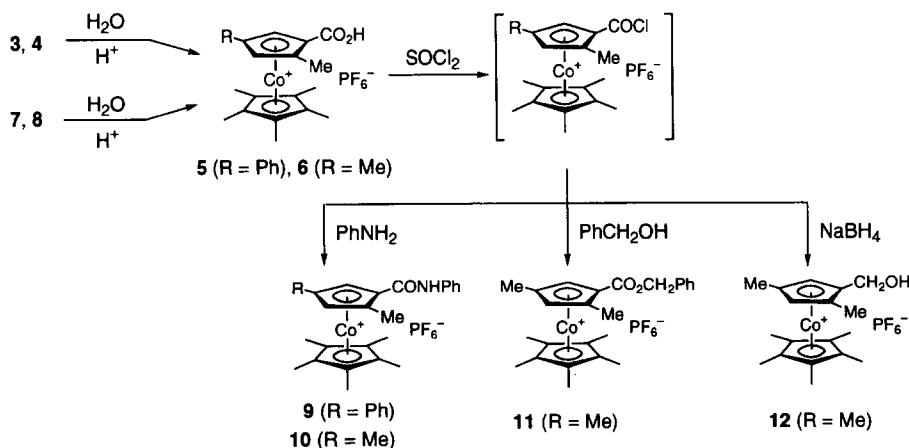
^a Isolated yield based on cobalt source.

^b Ratio was determined by HPLC.

^c Temperature 22°C.

^d Temperature 15°C.

tadienyl ring was carried out by hydrolysis. The (–)-menthyl group was removed from **8a** ($R = \text{Me}$) by an acid-promoted hydrolysis and we successfully obtained an optically pure enantiomer, (+)-**6**, as a carboxylic acid. Enantiomer (–)-**6** was obtained from **8b**, and (+)-**5** and (–)-**5** ($R = \text{Ph}$) were obtained from **7a** and **7b** ($R = \text{Ph}$), respectively, in the same manner. Optically pure **5** and **6** thus obtained may be useful precursors for the synthesis of optically active planar-chiral cobalticinium complexes having a variety of functional groups on the cyclopentadienyl ring. We then investigated the conversion of the carboxylic group of **6** into other groups. Thus, an acid chloride was prepared from **6** by the reaction with thionyl chloride [13], and then converted into anilide **10** by condensation with aniline, and benzyl ester **11** by condensation with benzyl alcohol. By treatment with sodium borohydride, **7** was reduced to alcohol derivative **12**. Among the above reactions, esterification and amidation were also carried out for enantiomers (+)- and (–)-**6** and we obtained optically pure (–)-**10** and (+)-**11** from (+)-**6** (Scheme 1). Similarly, (+)-**10** and (–)-**11** were prepared from (–)-**6**. These enantiomer pairs showed the same melting point and absolute value of $[\alpha]_D$ (Table 2). The circular dichroism (CD) spectrum of (+)-**6** is the same as the mirror image of that of (–)-**6**. A similar relationship of the spectra was observed for (+)- and (–)-**10**.

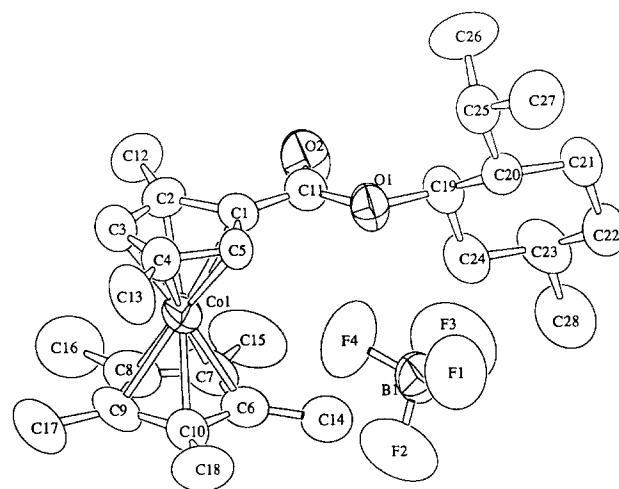


Scheme 1.

Table 2

Physical data for enantiomeric complexes **5**, **6**, **10** and **11**

Starting complex	Product	M.p. (°C)	$[\alpha]_D$ (°) (in CH ₃ OH)
7a	(+)- 5	207.2–208.8	+73.0 ^a (c 1.006)
7b	(-)- 5	207.3–208.5	-73.4 ^a (c 1.015)
8a	(+)- 6	270 (decomp.)	+1 ^b (c 0.317)
8b	(-)- 6	270 (decomp.)	-1 ^b (c 0.312)
(-)- 6	(+)- 10	216.0–217.0	+18.2 ^c (c 0.727)
(+)- 6	(-)- 10	216.0–217.0	-17.3 ^c (c 0.723)
(+)- 6	(+)- 11	131.0–131.5	+49.6 ^d (c 0.520)
(-)- 6	(-)- 11	131.5–132.0	-47.6 ^d (c 0.506)

^a Temperature 28°C.^b Temperature 15°C.^c Temperature 17°C.^d Temperature 25°C.Fig. 1. ORTEP drawing of **8b** with atom labelling scheme. Hydrogen atoms have been omitted for clarity.

2.2. Molecular structure of **8b**

In order to establish the absolute configuration of planar-chiral cobalticinium complexes, an X-ray diffraction study of **8b** (R = Me) was performed. Recrystallization of **8b** from ethanol–water gave single crystals suitable for X-ray analysis when the counter anion, hexafluorophosphate, of **8b** was replaced with tetrafluoroborate. The molecular structure is illustrated in Fig. 1 together with the atom labelling scheme.

The two Cp rings are planar and nearly parallel to one another (dihedral angle, 1.86°), and in a staggered conformation, as seen in the crystal structure of cobaltocene [14]. The distances within the cyclopentadienyl

rings average 1.420 and 1.423 Å for the pentamethylcyclopentadienyl and trisubstituted cyclopentadienyl rings, respectively. The Co–C (trisubstituted cyclopentadienyl ring) distances are in the range 2.033(4)–2.060(5) Å with an average of 2.047 Å; these values are also almost the same as that (2.041 Å) found between Co and a pentamethylcyclopentadienyl ring. The bond distances and angles found in **8b** are essentially similar to those found in [CpCoC₅H₄COOH][PF₆] [15]. The substituents on the cyclopentadienyl ring, such as methyl and menthoxy carbonyl groups, seem to have no influence on the

Table 3

Microanalytical data

Compound	Molecular formula	Analyses: found (%) (calc. (%))				
		C	H	N	P	F
1a	C ₃₀ H ₃₀ O ₄ CoPF ₆	54.44 (54.72)	4.35 (4.59)		4.63 (4.70)	17.56 (17.31)
1b		54.75	4.35		4.62	17.22
2a	C ₄₂ H ₄₀ O ₂ N ₂ CoPF ₆	52.37 (52.28)	5.12 (5.30)	2.60 (2.54)	5.81 (5.62)	20.67 (20.67)
3	C ₂₅ H ₃₀ O ₂ CoPF ₆	53.03 (53.01)	5.12 (5.34)		5.25 (5.47)	20.76 (20.12)
4	C ₂₀ H ₂₈ O ₂ CoPF ₆	47.34 (47.63)	5.76 (5.60)		6.00 (6.14)	22.40 (22.60)
5	C ₂₃ H ₂₆ O ₂ CoPF ₆	51.10 (51.31)	4.62 (4.87)		5.91 (5.75)	21.60 (21.17)
(+)- 5		51.21	5.09		5.83	21.00
(-)- 5		51.22	4.65		5.69	21.06
6	C ₁₈ H ₂₄ O ₄ CoPF ₆	45.67 (45.39)	5.07 (5.08)		6.45 (6.50)	24.11 (23.93)
(+)- 6		45.20	4.96		6.31	23.91
(-)- 6		45.14	5.17		6.40	23.65
7a	C ₃₃ H ₄₄ O ₂ CoPF ₆	58.31 (58.58)	6.26 (6.55)		4.55 (4.58)	16.89 (16.85)
7b		58.38	6.26		4.43	16.62
8a	C ₂₈ H ₄₂ O ₂ CoPF ₆	55.00 (54.73)	6.99 (6.89)		5.19 (5.04)	18.45 (18.55)
		55.00	6.44		4.84	18.42
8b	C ₂₈ H ₄₂ O ₂ CoBF ₄	60.47 (60.45)	7.51 (7.61)			13.41 (13.66)
9	C ₂₉ H ₃₁ ONCoPF ₆	56.82 (56.78)	5.08 (5.09)	2.22 (2.28)	5.21 (5.05)	18.67 (18.58)
10	C ₂₄ H ₂₉ ONCoPF ₆	52.37 (52.28)	5.12 (5.30)	2.60 (2.54)	5.81 (5.62)	20.67 (20.67)
(+)- 10		52.00	5.14	2.58	5.50	20.67
(-)- 10		51.99	5.21	2.60	5.53	20.75
11	C ₂₅ H ₃₀ OCOPF ₆	53.02 (53.01)	5.02 (5.34)		5.27 (5.47)	20.25 (20.12)
(+)- 11		52.85	5.22		5.35	20.34
(-)- 11		52.81	5.26		5.33	19.97
12	C ₁₈ H ₂₆ OCOPF ₆	47.07 (46.77)	5.50 (5.67)		6.59 (6.70)	24.56 (24.66)

bond distances. Based on the known configuration of the (–)-menthyl group, the absolute configuration of **8b** around the Cp–M moiety has been determined to be *R*. Complexes (–)-**6**, (+)-**10** and (–)-**11**, therefore, must possess *R* stereochemistry, while (+)-**6**, (–)-**10** and (+)-**11** have the *S* configuration.

In conclusion, we have succeeded in synthesizing planar-chiral cobalticinium complexes by using chiral cyclopentadienes and achieved optical resolution. The complexes described here provide rare examples of optically pure ionic metallocenes with a planar chirality [16].

3. Experimental section

3.1. General

All the reactions except for hydrolysis were carried out under an atmosphere of nitrogen or argon. Melting points are uncorrected. ^1H NMR spectra were measured in CDCl_3 or CD_3OD with SiMe_4 as an internal standard and recorded on a Bruker AM360 or JEOL EX-270 spectrometer. Upfield shifts are quoted as negative. IR spectra were recorded on a Hitachi Model 295 spectrometer. Mass spectrometry was performed with a Shimadzu QP-2000 GC–MS (EI, 70 eV) or JEOL JMX-DX300 (FAB) spectrometer. Elemental analysis was carried out by using a Perkin-Elmer Model 240C, instrument; the data are summarized in Table 3. Optical rotatory powers were measured on a Jasco DIP-370 digital polarimeter. Solvents were dried in the usual manner and distilled. Unless stated to the contrary, commercial-grade chemicals were used without further purification. Trisubstituted cyclopentadienes (Cp^{1-4}H) were prepared by the reported methods [4,9].

3.2. Synthesis of $\text{Cp}^1_2\text{CoPF}_6$ (**1**)

A solution of Cp^1Na generated from Cp^1H (5.48 g, 24 mmol) and NaH (60% in mineral oil; 1.04 g, 26 mmol) in THF (50 ml) was added to a THF solution (100 ml) of CoCl_2 (1.30 g, 10 mmol). The mixture was stirred under reflux for 3 h. The solvent was evaporated and the black residue was dissolved in 200 ml of 6 M hydrochloric acid. The aqueous solution was washed with diethyl ether to remove unreacted Cp^1H . The mixture of **1a** (*meso*) and **1b** (racemic) was precipitated as an orange powder by dropwise addition of a saturated solution of ammonium hexafluorophosphate (3.26 g, 20 mmol) in water. The yield was 4.80 g (73%). They were separated by recrystallization from MeOH.

1a (*meso*): M.p. 243.0–245.0°C (decomp.). Infrared (Nujol): 1740, 1250 cm^{-1} . ^1H NMR (360 MHz, CDCl_3): δ 7.50–7.15 (m, 10H); 6.28 (d, 2H, $J = 1.7$ Hz); 6.16 (d, 2H, $J = 1.7$ Hz); 4.39–4.23 (m, 4H); 2.25 (s, 3H);

1.43 (t, 6H, $J = 7.2$ Hz). Mass (EI): m/z 513 ($\text{M}^+ - \text{PF}_6$).

1b (racemic): M.p. 207.0–208.0°C (decomp.). Infrared (Nujol): 1740, 1250 cm^{-1} . ^1H NMR (360 MHz, CDCl_3): δ 7.50–7.15 (m, 10H); 6.28 (d, 2H, $J = 2.0$ Hz); 6.22 (d, 2H, $J = 2.0$ Hz); 4.39–4.23 (m, 4H); 1.87 (s, 3H); 1.43 (t, 6H, $J = 7.2$ Hz). Mass (EI): m/z 513 ($\text{M}^+ - \text{PF}_6$).

3.3. Synthesis of **2a**

This compound was prepared via carboxylic acids by the method for **9** (see below) starting with **1a** and (–)- α -phenylethylamine, and was obtained as an orange powder (yield 98%). M.p.: 261.0–262.0°C. Infrared (Nujol): 3425, 1665 cm^{-1} . ^1H NMR (360 MHz, CD_3OD): δ 7.87–7.20 (m, 20H); 6.25 (d, 1H, $J = 1.7$ Hz); 6.13 (d, 1H, $J = 1.7$ Hz); 6.00 (d, 1H, $J = 1.7$ Hz); 5.73 (d, 1H, $J = 1.7$ Hz); 5.16 (q, 1H, $J = 7.0$ Hz); 4.82 (q, 1H, $J = 7.0$ Hz); 2.02 (s, 3H); 2.01 (s, 3H); 1.55 (d, 3H, $J = 7.0$ Hz); 1.43 (d, 3H, $J = 7.0$ Hz). Mass (FAB): m/z 663 ($\text{M}^+ - \text{PF}_6$).

3.4. Synthesis of $\text{Cp}^1\text{Co}(\text{C}_5\text{Me}_5)\text{PF}_6$ (**3**)

The reaction of $\text{Co}(\text{acac})_2$ (5.14 g, 20 mmol) with 1 equiv. of $\text{C}_5\text{Me}_5\text{Li}$ in THF (100 ml) at -78°C afforded $\text{C}_5\text{Me}_5\text{Co}(\text{acac})$. To the reaction mixture was added a solution of Cp^1Na generated from Cp^1H (4.56 g, 20 mmol) and NaH (60% in mineral oil; 0.88 g, 22 mmol) in THF (100 ml) at 0°C . The mixture was allowed to warm to room temperature and stirring was continued for 24 h, then the mixture was poured over 200 ml of 6 M hydrochloric acid. Diethyl ether (100 ml) was added to the resulting solution and the layers were separated. The aqueous solution was washed with diethyl ether to remove unreacted cyclopentadienes. After dropwise addition of a saturated solution of ammonium hexafluorophosphate (8.15 g, 50 mmol) in water, compound **3** was obtained as a yellow precipitate. Recrystallization from MeOH gave yellow needles in 75% yield (8.56 g). M.p.: 203.0–204.0°C. Infrared (Nujol): 1730, 1245 cm^{-1} . ^1H NMR (360 MHz, CDCl_3): δ 7.66–7.53 (m, 5H); 5.91 (d, 1H, $J = 1.8$ Hz); 5.78 (d, 1H, $J = 1.8$ Hz); 4.46–4.43 (m, 2H); 2.28 (s, 3H); 1.64 (s, 15H); 1.47 (t, 3H, $J = 7.1$ Hz). Mass (EI): m/z 421 ($\text{M}^+ - \text{PF}_6$).

3.5. Synthesis of $\text{Cp}^2\text{Co}(\text{C}_5\text{Me}_5)\text{PF}_6$ (**4**)

This compound was prepared following the method for **3** starting with Cp^2H . Yellow needles were obtained (yield 61%). M.p.: 176.0–177.0°C. Infrared (Nujol): 1730, 1245 cm^{-1} . ^1H NMR (360 MHz, CDCl_3): δ 5.26 (d, 1H, $J = 1.9$ Hz); 5.13 (d, 1H, $J = 1.9$ Hz); 4.41–4.33 (m, 2H); 2.14 (s, 3H); 2.00 (s, 3H); 1.87 (s, 15H); 1.42 (t, 3H, $J = 7.1$ Hz). Mass (EI): m/z 359 ($\text{M}^+ - \text{PF}_6$).

3.6. Synthesis of 5

Ethyl ester derivative **3** (2.56 g, 4.5 mmol) was suspended in 300 ml of concentrated hydrochloric acid and heated for 24 h at 80°C with constant stirring. The reaction mixture was evaporated to give a yellow solid, which was dissolved in 50 ml of hot water. Dropwise addition of ammonium hexafluorophosphate (3.75 g, 23 mmol) in water produced a pale yellow precipitate of the carboxylic acid **5**, which was purified by recrystallization from EtOH. The yield was 2.25 g (93%). M.p.: 215.0–216.0°C. Infrared (Nujol): 3300–2700, 1720 cm^{-1} . ^1H NMR (360 MHz, CD_3OD): δ 7.79–7.55 (m, 5H); 6.20 (d, 1H, $J = 1.9$ Hz); 5.92 (d, 1H, $J = 1.9$ Hz); 2.26 (s, 3H); 1.66 (s, 15H). Mass (EI): m/z 393 ($\text{M}^+ - \text{PF}_6^-$).

3.7. Synthesis of 6

The procedure described for **5**, but starting with **4**, gave compound **6** as a yellow powder (yield 90%). M.p.: 270°C (decomp.). Infrared (Nujol): 3300–2500, 1710 cm^{-1} . ^1H NMR (360 MHz, CD_3OD): δ 5.42 (s, 1H); 5.09 (s, 1H); 2.14 (s, 3H); 1.99 (s, 3H); 1.90 (s, 15H). Mass (FAB): m/z 331 ($\text{M}^+ - \text{PF}_6^-$).

3.8. Synthesis of $\text{Cp}^3\text{Co}(\text{C}_5\text{Me}_5)\text{PF}_6$ (**7**)

This compound was prepared following the method for **3** starting with Cp^3H . Separation of **7a** from **7b** was carried out by a preparative HPLC on ODS (20.0 $\times$ 250 mm column, Wakosil-II 5C18HG) with $\text{MeOH}-\text{H}_2\text{O}$ (3:1, v/v, 0.1 M AcOH, AcONa) as eluent. Purification was performed by recrystallization from MeOH.

7a: Yellow–orange needles. M.p.: 258.5–259.0°C. Infrared (Nujol): 1725, 1250 cm^{-1} . ^1H NMR (360 MHz, CDCl_3): δ 7.66–7.50 (m, 5H); 5.91 (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 (3H, d, $J = 6.9$ Hz). Mass (EI): m/z 531 ($\text{M}^+ - \text{PF}_6^-$).

7b: Yellow–orange needles. M.p.: 267.0–267.5°C. Infrared (Nujol): 1725, 1250 cm^{-1} . ^1H NMR (360 MHz, CDCl_3): δ 7.65–7.50 (m, 5H); 5.97 (d, 1H, $J = 1.9$ Hz); 5.74 (d, 1H, $J = 1.9$ 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). Mass (EI): m/z 531 ($\text{M}^+ - \text{PF}_6^-$). The yields and $[\alpha]_D$ are summarized in Table 1.

3.9. Synthesis of $\text{Cp}^4\text{Co}(\text{C}_5\text{Me}_5)\text{PF}_6$ (**8**)

This compound was prepared following the method for **3** starting with Cp^4H . After addition of ammonium

hexafluorophosphate, the solution was extracted with CH_2Cl_2 . Evaporation of the CH_2Cl_2 solution gave a mixture of **8a** and **8b** as an orange oil. Recrystallization gave pure **8a** from EtOH and **8b** from EtOH– H_2O (3:2, v/v).

8a: Yellow–orange needles. M.p.: 188.0–188.5°C. Infrared (Nujol): 1730, 1240 cm^{-1} . ^1H NMR (360 MHz, 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). Mass (EI): m/z 469 ($\text{M}^+ - \text{PF}_6^-$).

8b: Yellow–orange needles. M.p.: 227.0–227.5°C. Infrared (Nujol): 1730, 1240 cm^{-1} . ^1H NMR (360 MHz, 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). Mass (EI): m/z 469 ($\text{M}^+ - \text{PF}_6^-$). The yields and $[\alpha]_D$ are summarized in Table 1.

The tetrafluoroborate of **8b** for X-ray crystallographic analysis was similarly prepared and recrystallized from EtOH, m.p. 165.0–167.0°C.

3.10. Synthesis of (+)- and (–)-**5** and (+)- and (–)-**6**

Removal of the (–)-menthyl group from **7a**, **7b**, **8a** and **8b** by hydrolysis was performed following the method for **6**.

(+)-**5** (Starting from **7a**): orange needles (yield 97%).

(–)-**5** (Starting from **7b**): orange needles (yield 96%).

(+)-**6** (Starting from **8a**): yellow powder (yield 99%).

(–)-**6** (Starting from **8b**): yellow powder (yield 99%).

These enantiomers gave the same IR, ^1H NMR and mass spectral data as racemic isomers **5** and **6**. Melting points and $[\alpha]_D$ are summarized in Table 2.

3.11. Synthesis of 9

Carboxylic acid **5** (0.54 g, 1.0 mmol) was refluxed with thionyl chloride (20 ml) for 3 h to give the corresponding acid chloride. After removal of thionyl chloride in vacuo, the solid was dissolved in acetonitrile (10 ml). The solution was added to a solution of aniline (0.19 g, 2.0 mmol) in acetonitrile (10 ml). The resulting mixture was stirred at room temperature overnight and the solvent was removed in vacuo. The crude product was dissolved in MeOH and ammonium hexafluorophosphate (0.82 g, 5.0 mmol) was added. After removal of MeOH from the mixture and washing with water, an orange product was obtained. Purification was performed by recrystallization from EtOH. Orange needles (0.50 g) were obtained in 82% yield. M.p.: 244.0–245.0°C (decomp.). Infrared (Nujol): 3410, 1680, 1600 cm^{-1} . ^1H NMR (360 MHz, CDCl_3): δ 8.49 (s, 1H); 7.86 (d, 2H, $J = 7.8$ Hz); 7.68 (d, 2H, $J = 7.1$ Hz);

7.47–7.38 (m, 3H); 7.40 (t, 2H, $J = 7.8$ Hz); 7.19 (t, 1H, $J = 7.2$ Hz); 6.27 (s, 1H); 5.33 (s, 1H); 2.23 (s, 3H); 1.61 (s, 15H). Mass (EI): m/z 468 ($M^+ - PF_6^-$).

3.12. Synthesis of **10**

The procedure described for **9**, but starting with **6**, gave compound **10** as orange needles (yield 84%). M.p.: 214.0–215.0°C. Infrared (Nujol): 3430, 1680 cm^{-1} . 1H NMR (360 MHz, $CDCl_3$): δ 8.32 (s, 1H) 7.78 (d, 2H, $J = 7.6$ Hz); 7.35 (dd, 2H, $J = 7.6, 8.3$ Hz); 7.15 (t, 1H, $J = 7.4$ Hz); 5.84 (s, 1H); 4.77 (s, 1H); 2.21 (s, 3H); 1.99 (s, 3H); 1.88 (s, 15H). Mass (EI): m/z 406 ($M^+ - PF_6^-$).

3.13. Synthesis of **11**

Carboxylic acid **6** (0.48 g, 1.0 mmol) was refluxed with thionyl chloride (20 ml) for 3 h to give the corresponding acid chloride. After removal of thionyl chloride in vacuo, the solid was dissolved in acetonitrile (10 ml). The solution was added to a solution of benzyl alcohol (0.32 g, 3.0 mmol) in triethylamine (5 ml) and acetonitrile (10 ml). The resulting mixture was stirred at room temperature overnight to generate triethylammonium chloride as a white precipitate. After filtering off the precipitates, the solvent was removed in vacuo to give a brown oil, which was dissolved in CH_2Cl_2 and then washed with water. The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated. The residue was dissolved in MeOH and ammonium hexafluorophosphate (0.33 g, 2.0 mmol) was added. After removal of MeOH from the mixture and washing with water, an orange product was obtained. Purification was performed by recrystallization from MeOH. Orange needles (0.40 g) were obtained in 71% yield. M.p.: 169.0–169.5°C (decomp.). Infrared (Nujol): 1720 cm^{-1} . 1H NMR (270 MHz, $CDCl_3$): δ 7.49–7.39 (m, 5H); 5.35 (dd, 1H, $J = 1.4, 1.9$ Hz); 5.30 (dd, 1H, $J = 1.4, 1.9$ Hz); 5.22 (s, 1H); 5.14 (s, 1H); 2.13 (s, 3H); 2.00 (s, 3H); 1.76 (s, 15H). Mass (EI): m/z 421 ($M^+ - PF_6^-$).

3.14. Synthesis of (+)- and (–)-**10** and (+)- and (–)-**11**

These compounds were prepared following the method for the racemic isomers **10** and **11**, respectively.

(+)-**10** (Starting from (–)-**6**): orange powder (yield 92%).

(–)-**10** (Starting from (+)-**6**): orange powder (yield 91%).

(+)-**11** (Starting from (+)-**6**): yellow needles (yield 68%).

(–)-**11** (Starting from (–)-**6**): yellow needles (yield 73%).

These enantiomers gave the same IR, 1H NMR and mass spectral data as racemic isomers **10** and **11**. Melting points and $[\alpha]_D$ are summarized in Table 2.

3.15. Synthesis of **12**

Carboxylic acid **6** (0.48 g, 1.0 mmol) was refluxed with thionyl chloride (20 ml) for 3 h to give the corresponding acid chloride. After removal of thionyl chloride in vacuo, the solid was suspended in THF (20 ml). To the suspension of acid chloride was added sodium borohydride (76 mg, 2.0 mmol) at room temperature and the mixture was refluxed for 5 h. The mixture was quenched by saturated aqueous NH_4Cl , 30 ml of diethyl ether were added to the resulting solution and the layers were separated. The aqueous solution was washed with diethyl ether and ammonium hexafluorophosphate (0.49 g, 3.0 mmol) was added to generate a

Table 4
Atomic coordinates with equivalent isotropic temperature factors for **8b**

Atom	x	y	z	B_{eq}^a
Co(1)	–0.16645(3)	0.0009	–0.17217(3)	4.308(10)
F(1)	–0.3000(4)	0.6018(4)	–0.1303(3)	12.3(1)
F(2)	–0.1835(3)	0.4977(7)	–0.0819(2)	13.7(1)
F(3)	–0.2116(4)	0.5099(10)	–0.1976(2)	18.1(2)
F(4)	–0.2926(4)	0.3920(4)	–0.1379(3)	13.6(2)
O(1)	–0.2106(2)	0.2474(3)	–0.3202(2)	4.81(7)
O(2)	–0.1664(3)	0.0678(3)	–0.3716(2)	7.18(9)
C(1)	–0.2358(3)	0.0527(5)	–0.2662(2)	4.43(10)
C(2)	–0.2404(3)	–0.0831(5)	–0.2583(3)	5.1(1)
C(3)	–0.2800(3)	–0.1070(5)	–0.1951(3)	5.3(1)
C(4)	–0.3027(2)	0.0120(6)	–0.1653(2)	4.86(9)
C(5)	–0.2758(3)	0.1107(4)	–0.2093(2)	4.09(10)
C(6)	–0.0564(4)	0.1143(6)	–0.1391(3)	5.9(1)
C(7)	–0.0308(3)	0.0056(9)	–0.1770(2)	6.6(1)
C(8)	–0.0553(3)	–0.1058(6)	–0.1416(3)	6.3(1)
C(9)	–0.0969(4)	–0.0699(6)	–0.0822(3)	6.3(1)
C(10)	–0.0980(3)	0.0676(5)	–0.0797(3)	5.1(1)
C(11)	–0.2001(3)	0.1201(4)	–0.3249(2)	4.7(1)
C(12)	–0.2101(4)	–0.1858(5)	–0.3060(3)	7.3(1)
C(13)	–0.3481(3)	0.0285(6)	–0.0993(3)	6.9(1)
C(14)	–0.0401(4)	0.2494(7)	–0.1570(3)	8.8(2)
C(15)	0.0158(3)	0.006(1)	–0.2431(3)	10.2(2)
C(16)	–0.0366(5)	–0.2449(7)	–0.1614(4)	9.9(2)
C(17)	–0.1324(5)	–0.1524(7)	–0.0276(3)	8.2(2)
C(18)	–0.1344(5)	0.1544(7)	–0.0272(3)	8.2(2)
C(19)	–0.1756(3)	0.3273(5)	–0.3745(2)	4.9(1)
C(20)	–0.2337(3)	0.4485(4)	–0.3829(2)	4.37(9)
C(21)	–0.1933(3)	0.5355(5)	–0.4353(2)	5.4(1)
C(22)	–0.0936(3)	0.5645(6)	–0.4131(3)	6.3(1)
C(23)	–0.0377(3)	0.4436(6)	–0.4027(3)	6.9(1)
C(24)	–0.0777(3)	0.3576(6)	–0.3508(3)	6.2(1)
C(25)	–0.3344(3)	0.4213(5)	–0.4023(3)	5.5(1)
C(26)	–0.3572(4)	0.3462(8)	–0.4682(4)	8.9(2)
C(27)	–0.3892(4)	0.5450(6)	–0.4054(3)	7.5(2)
C(28)	0.0610(4)	0.4722(9)	–0.3764(4)	10.1(2)
B(1)	–0.2408(4)	0.5026(9)	–0.1392(3)	6.7(1)

^a $B_{eq} = 8/3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$.

yellow precipitates, followed by recrystallization from EtOH to give a yellow powder. The yield was 0.19 g (41%). M.p: 290.0–291.0°C (decomp.). Infrared (Nujol): 3600–3200, 1030 cm^{-1} . ^1H NMR (270 MHz, CDCl_3): δ 4.96 (s, 1H); 4.63 (s, 1H); 4.34 (s, 2H); 2.93 (bs, 1H); 1.91 (s, 15H); 1.89 (s, 3H); 1.85 (s, 3H). Mass (FAB): m/z 317 ($\text{M}^+ - \text{PF}_6^-$).

3.16. X-ray crystallographic analysis for **8b**

Crystal data for **8b**: $\text{C}_{28}\text{H}_{42}\text{O}_2\text{CoBF}_4$, $M = 556.38$, monoclinic, space group $C2$, $a = 14.929(2)$, $b = 10.397(2)$, $c = 19.042(1)$ Å, $\beta = 96.791(8)^\circ$, $V = 2934$ Å³, $Z = 4$, $D_c = 1.259$ g cm^{-3} , $D_m = 1.259$ g cm^{-3} , $F(000) = 1176$, Mo $K\alpha$ radiation with $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 6.32$ cm^{-1} ; 6083 reflections were collected on a Rigaku AFC-5FOS four-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation) in the $\omega - 2\theta$ scan mode to $2\theta_{\text{max}} = 65^\circ$. The structure was solved by heavy-atom Patterson methods (SAPI 91) and refined to give $R = 0.043$, $R_w = 0.050$ for 2407 independent reflections [$I > 3\sigma(I)$]. Hydrogen atoms were placed in appropriate trigonal or tetrahedral positions. All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corporation. Absolute stereochemistry was determined based on the (–)-menthyl group on the cyclopentadienyl ring of **8b**. Fractional coordinates are listed in Table 4, bond distances in Table 5 and bond angles in Table 6. Additional data, including hydrogen atomic coordinates, anisotropic temperature factors and lists of

Table 5
Selected bond distances (Å) in **8b**

Atoms	Distance	Atoms	Distance
Co(1)–C(1)	2.033(4)	Co(1)–C(2)	2.060(5)
Co(1)–C(3)	2.036(5)	Co(1)–C(4)	2.058(4)
Co(1)–C(5)	2.048(4)	Co(1)–C(6)	2.060(6)
Co(1)–C(7)	2.039(4)	Co(1)–C(8)	2.023(5)
Co(1)–C(9)	2.034(5)	Co(1)–C(10)	2.050(5)
F(1)–B(1)	1.382(9)	F(2)–B(1)	1.305(6)
F(3)–B(1)	1.243(6)	F(4)–B(1)	1.387(10)
O(1)–C(11)	1.337(5)	O(1)–C(19)	1.470(5)
O(2)–C(11)	1.202(5)	C(1)–C(2)	1.423(6)
C(1)–C(5)	1.431(6)	C(1)–C(11)	1.471(7)
C(2)–C(3)	1.426(7)	C(2)–C(12)	1.505(7)
C(3)–C(4)	1.419(8)	C(4)–C(5)	1.414(7)
C(4)–C(13)	1.505(6)	C(6)–C(7)	1.418(9)
C(6)–C(10)	1.437(7)	C(6)–C(14)	1.472(9)
C(7)–C(8)	1.410(10)	C(7)–C(15)	1.507(6)
C(8)–C(9)	1.405(8)	C(8)–C(16)	1.528(9)
C(9)–C(10)	1.431(7)	C(9)–C(17)	1.492(9)
C(10)–C(18)	1.495(9)	C(19)–C(20)	1.528(6)
C(19)–C(24)	1.511(6)	C(20)–C(21)	1.525(6)
C(20)–C(25)	1.530(6)	C(21)–C(22)	1.528(6)
C(22)–C(23)	1.510(8)	C(23)–C(24)	1.508(7)
C(23)–C(28)	1.529(7)	C(25)–C(26)	1.483(8)
C(25)–C(27)	1.522(7)		

Table 6
Selected bond angles ($^\circ$) in **8b**

Atoms	Angle	Atoms	Angle
C(1)–Co(1)–C(2)	40.7(2)	C(1)–Co(1)–C(3)	68.5(2)
C(1)–Co(1)–C(4)	68.7(2)	C(1)–Co(1)–C(5)	41.0(2)
C(1)–Co(1)–C(6)	115.0(2)	C(1)–Co(1)–C(7)	111.0(2)
C(1)–Co(1)–C(8)	135.5(2)	C(1)–Co(1)–C(9)	174.0(2)
C(1)–Co(1)–C(10)	144.8(2)	C(2)–Co(1)–C(3)	40.7(2)
C(2)–Co(1)–C(4)	68.5(2)	C(2)–Co(1)–C(5)	68.4(2)
C(2)–Co(1)–C(6)	145.0(2)	C(2)–Co(1)–C(7)	114.5(2)
C(2)–Co(1)–C(8)	109.9(2)	C(2)–Co(1)–C(9)	133.6(2)
C(2)–Co(1)–C(10)	173.4(2)	C(3)–Co(1)–C(4)	40.6(2)
C(3)–Co(1)–C(5)	67.9(2)	C(3)–Co(1)–C(6)	174.0(2)
C(3)–Co(1)–C(7)	144.1(3)	C(3)–Co(1)–C(8)	113.2(2)
C(3)–Co(1)–C(9)	108.1(2)	C(3)–Co(1)–C(10)	133.5(2)
C(4)–Co(1)–C(5)	40.3(2)	C(4)–Co(1)–C(6)	135.0(2)
C(4)–Co(1)–C(7)	175.3(3)	C(4)–Co(1)–C(8)	142.8(2)
C(4)–Co(1)–C(9)	112.1(2)	C(4)–Co(1)–C(10)	108.8(2)
C(5)–Co(1)–C(6)	111.1(2)	C(5)–Co(1)–C(7)	136.5(3)
C(5)–Co(1)–C(8)	176.2(2)	C(5)–Co(1)–C(9)	143.1(2)
C(5)–Co(1)–C(10)	113.8(2)	C(6)–Co(1)–C(7)	40.5(3)
C(6)–Co(1)–C(8)	68.2(2)	C(6)–Co(1)–C(9)	68.9(2)
C(6)–Co(1)–C(10)	40.9(2)	C(7)–Co(1)–C(8)	40.6(3)
C(7)–Co(1)–C(9)	68.7(2)	C(7)–Co(1)–C(10)	68.5(2)
C(8)–Co(1)–C(9)	40.5(2)	C(8)–Co(1)–C(10)	68.3(2)
C(9)–Co(1)–C(10)	41.0(2)	C(11)–O(1)–C(19)	117.2(3)
Co(1)–C(1)–C(2)	70.7(3)	Co(1)–C(1)–C(5)	70.0(2)
Co(1)–C(1)–C(11)	127.0(3)	C(2)–C(1)–C(5)	108.0(5)
C(2)–C(1)–C(11)	125.4(5)	C(5)–C(1)–C(11)	126.5(4)
Co(1)–C(2)–C(1)	68.6(3)	Co(1)–C(2)–C(3)	68.7(3)
Co(1)–C(2)–C(12)	127.6(4)	C(1)–C(2)–C(3)	107.0(5)
C(1)–C(2)–C(12)	128.2(5)	C(3)–C(2)–C(12)	124.8(5)
Co(1)–C(3)–C(2)	70.5(3)	Co(1)–C(3)–C(4)	70.5(3)
C(2)–C(3)–C(4)	109.2(4)	Co(1)–C(4)–C(3)	68.9(3)
Co(1)–C(4)–C(5)	69.5(2)	Co(1)–C(4)–C(13)	127.2(3)
C(3)–C(4)–C(5)	107.3(4)	C(3)–C(4)–C(13)	125.8(5)
C(5)–C(4)–C(13)	126.9(5)	Co(1)–C(5)–C(1)	68.9(2)
Co(1)–C(5)–C(4)	70.2(2)	C(1)–C(5)–C(4)	108.5(4)
Co(1)–C(6)–C(7)	69.0(3)	Co(1)–C(6)–C(10)	69.2(3)
Co(1)–C(6)–C(14)	128.5(4)	C(7)–C(6)–C(10)	107.5(5)
C(7)–C(6)–C(14)	125.5(6)	C(10)–C(6)–C(14)	127.0(6)
Co(1)–C(7)–C(6)	70.5(3)	Co(1)–C(7)–C(8)	69.1(3)
Co(1)–C(7)–C(15)	126.6(3)	C(6)–C(7)–C(8)	108.1(4)
C(6)–C(7)–C(15)	127.0(8)	C(8)–C(7)–C(15)	125.0(9)
Co(1)–C(8)–C(7)	70.3(3)	Co(1)–C(8)–C(9)	70.1(3)
Co(1)–C(8)–C(16)	128.0(4)	C(7)–C(8)–C(9)	109.4(6)
C(7)–C(8)–C(16)	126.5(6)	C(9)–C(8)–C(16)	124.1(6)
Co(1)–C(9)–C(8)	69.3(3)	Co(1)–C(9)–C(10)	70.1(3)
Co(1)–C(9)–C(17)	127.4(4)	C(8)–C(9)–C(10)	107.4(6)
C(8)–C(9)–C(17)	129.5(6)	C(10)–C(9)–C(17)	123.0(6)
Co(1)–C(10)–C(6)	69.9(3)	Co(1)–C(10)–C(9)	68.9(3)
Co(1)–C(10)–C(18)	126.5(4)	C(6)–C(10)–C(9)	107.7(5)
C(6)–C(10)–C(18)	123.2(6)	C(9)–C(10)–C(18)	129.1(6)
O(1)–C(11)–O(2)	124.1(4)	O(1)–C(11)–C(1)	111.4(4)
O(2)–C(11)–C(1)	124.6(4)	O(1)–C(19)–C(20)	107.2(3)
O(1)–C(19)–C(24)	108.7(4)	C(20)–C(19)–C(24)	112.1(4)
C(19)–C(20)–C(21)	107.1(3)	C(19)–C(20)–C(25)	113.7(4)
C(21)–C(20)–C(25)	113.9(4)	C(20)–C(21)–C(22)	112.6(4)
C(21)–C(22)–C(23)	112.2(4)	C(22)–C(23)–C(24)	108.9(4)
C(22)–C(23)–C(28)	112.2(6)	C(24)–C(23)–C(28)	110.0(5)
C(19)–C(24)–C(23)	111.9(4)	C(20)–C(25)–C(26)	115.0(4)
C(20)–C(25)–C(27)	111.2(4)	C(26)–C(25)–C(27)	110.1(5)
F(1)–B(1)–F(2)	106.9(6)	F(1)–B(1)–F(3)	111.2(7)
F(1)–B(1)–F(4)	104.5(5)	F(2)–B(1)–F(3)	119.0(6)
F(2)–B(1)–F(4)	105.3(7)	F(3)–B(1)–F(4)	108.8(7)

observed and calculated structure factors, are available from the authors.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. The authors are grateful to a JSPS Fellowship for Japan Junior Scientists to N.K. The authors gratefully acknowledge Dr. M. Shiro, Dr. M. Yamasaki and Mr. S. Yoshimachi of Rigaku Corporation for X-ray crystallographic analyses.

References

- [1] S.G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Pergamon Press, Oxford, 1982.
- [2] R.L. Halterman, *Chem. Rev.*, **92** (1992) 965, and references cited 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; O. Riant, O. Samuel and H.B. Kagan, *J. Am. Chem. Soc.*, **115** (1993) 5835.
- [3] M. Uno, K. Ando, N. Komatsuzaki and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, (1992) 964.
- [4] M. Uno, K. Ando, N. Komatsuzaki, T. Tanaka, M. Sawada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, (1993) 1549; M. Uno, K. Ando, N. Komatsuzaki, T. Tsuda, T. Tanaka, M. Sawada and S. Takahashi, *J. Organomet. Chem.*, **473** (1994) 303; M. Uno, K. Shirai, K. Ando, N. Komatsuzaki, T. Tanaka, M. Sawada and S. Takahashi, *Chem. Lett.*, (1995) 7.
- [5] 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.
- [6] 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. Libr.*, **7** (1979) 461; K. Sakamoto, H. Nishihara and K. Aramaki, *J. Chem. Soc., Dalton Trans.*, (1992) 1877.
- [7] P.D. Beer, D. Heseck, J. Hodacova and S.E. Stokes, *J. Chem. Soc., Chem. Commun.*, (1992) 270; P.D. Beer, M.G.B. Drew, C. Hazlewood, D. Heseck, J. Hodacova and S.E. Stokes, *J. Chem. Soc., Chem. Commun.*, (1993) 229.
- [8] M. Uno, N. Komatsuzaki, K. Shirai and S. Takahashi, *J. Organomet. Chem.*, **462** (1993) 343.
- [9] M. Hatanaka, Y. Himeda and I. Ueda, *J. Chem. Soc., Chem. Commun.*, (1990) 526.
- [10] G. Wilkinson, *J. Am. Chem. Soc.*, **74** (1952) 6148.
- [11] E.E. Bunel, L. Valle and J.M. Manriquez, *Organometallics*, **4** (1985) 1680.
- [12] W.H. Pirkle, D.L. Sikkenga and M.S. Pavlin, *J. Org. Chem.*, **42** (1977) 384.
- [13] J.E. Sheats and M.D. Rausch, *J. Org. Chem.*, **35** (1970) 3245.
- [14] W. Bünder and E. Weiss, *J. Organomet. Chem.*, **92** (1975) 65.
- [15] P.E. Riley and R.E. Davis, *J. Organomet. Chem.*, **152** (1978) 209.
- [16] V.I. Sokolov, I.A. Mamedyarova, M.N. Nefedova and G. Snatzke, *J. Organomet. Chem.*, **438** (1992) C26.