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Synthesis and structure of planar-chiral (1,2,4-trisubstituted cyclopentadienyl)cobalt(tetraarylcyclobutadiene) complexes containing three different chiralities in one molecule *

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Abstract

The first diastereomerically pure planar-chiral cyclopentadienyl–cobalt complexes (**4** and **5**) have been synthesised by the reaction of $CoCl(PPh_3)_3$ with a trisubstituted cyclopentadienyl anion having a (−)-menthyl group in the presence of diarylacetylenes. Removal of the menthyl group from **4a** and **5a** afforded the first optically pure enantiomers of planar-chiral cyclopentadienylcobalt complexes, (+)- and (−)-**6**, and (+)- and (−)-**7**. The molecular structure including absolute configuration of **4a** has been established by a single-crystal X-ray structure analysis. Crystallographic data for **4a**: orthorhombic, space group $P2_12_12_1$; $a = 18.602(10)$, $b = 15.629(3)$, $c = 13.893(3)$ Å; $Z = 4$; $R = 0.051$, $R_w = 0.057$. The structure of **4a** indicates that there exist three different chiralities [planar (Cp′–Co moiety), central {(−)-menthyl group}, and helical (C_4Ar_4-moiety) chirality] in one molecule. These complexes provide not only the first optically pure planar-chiral Cp′–Co complexes but also the first examples containing three different chiralities in one molecule.

Key words: Cobalt; Cyclobutadiene; Optical resolution; X-ray diffraction; Crystal structure

1. Introduction

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 works, Schlögl and others have developed a synthetic route to planar-chiral ferrocenes and then expanded it to several 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 kinds of metals with planar chirality have appeared in the literature [3,4], although there are numerous works on non-chiral Cp–M complexes of various metals. The reason for limited synthesis and optical resolution of planar-chiral Cp′–M complexes may be due to their chemical instability, and in addition a convenient method for the preparation of unsymmetrically substituted cyclopentadienes has not been reported so far [5]. On the other hand, Cp–M complexes have widely been utilized in organic syntheses [6]. Particularly, in the past few years planar-chiral Cp′–M complexes have been regarded with much interest as mediators of enantioselective organic reactions [3] and as a host-guest system [4].

Recently a novel synthetic method for unsymmetrically trisubstituted cyclopentadienes was reported by Ueda *et al.* [7]. Since the method produces cyclopentadienes having an ester group, we can easily introduce a removable chiral auxiliary on the cyclopentadiene ring by an alcohol exchange reaction. The chiral cyclopentadienes may offer a new route leading to diastereomeric planar-chiral Cp′–M complexes. In fact, we successfully synthesized enantiomerically pure planar-chiral ferrocenes and cyclopendadienyl–rhodium complexes *via* diastereomers which were formed from the reaction of $FeCl_2$ or $[Rh(cod)Cl]_2$ (cod = cycloocta-1,5-diene) with a trisubstituted cyclopentadiene having a (−)-menthyl group [8]. Here we wish to report the synthesis and

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structure of the first optically pure planar-chiral cyclopentadienyl–cobalt complexes [9,10], which uniquely contain three different types of chirality, *i.e.* planar, carbon-centered and helical chirality, in one molecule.

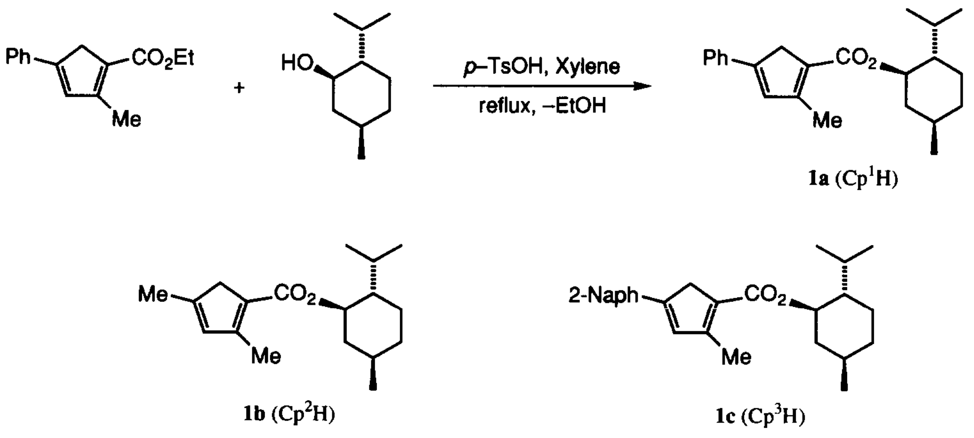
2. Results and discussion

2.1. Syntheses of planar-chiral Cp′–Co complexes

A non-chiral trisubstituted cyclopentadiene was prepared by the reaction of 2-bromoacetophenone with triphenylphosphonium bromide [7], and then transformed to a chiral cyclopentadiene by an alcohol exchange reaction as shown in Scheme 1. In the presence of a catalytic amount of *p*-toluenesulfonic acid, 1-ethoxycarbonyl-2-methyl-4-phenyl-1,3-cyclopentadiene was allowed to react with (−)-menthol in xylene under reflux. The alcohol exchange reaction proceeded smoothly to give (−)-menthyl ester **1a** (Cp^1H) after purification by column chromatography on silica and subsequent distillation. Furthermore, we have prepared other cyclopentadienes, **1b** (Cp^2H) and **1c** (Cp^3H), bearing a (−)-menthyl group in the same manner starting from 2,4-dimethyl-1-ethoxycarbonyl-1,3-cyclopentadiene and 1-ethoxycarbonyl-2-methyl-4-(2-naphthyl)-1,3-cyclopentadiene, respectively.

Firstly we synthesized planar-chiral Cp′Co(cod) complexes using cyclopentadiene **1a** (Cp^1H) by a reported method [11] (Scheme 2). The reaction of $CoCl(PPh_3)_3$ with Cp^1Na, generated from **1a** with NaH, and 1,5-cod in toluene/tetrahydrofuran gave $Cp^1Co(cod)$ as a mixture of two diastereomers, **2a** and **3a**, after purification by column chromatography on silica. In the ^1H NMR spectrum, two sets of resonances due to two protons on the cyclopentadienyl ring appeared at δ 5.09, 4.96, and 4.87 with the intensity ratio of 1:2:1, indicating that diastereomers **2a** and **3a** are distinguished from one another by ^1H NMR. A similar spectrum was observed for the Rh analogues as reported previously [8]. However, our attempts with preparative HPLC on silica have failed in the separation of **2a** from **3a** although complete resolution has already been achieved for the Rh analogues by the same HPLC method. Hence both **2a** and **3a** were converted to cyclobutadiene complexes, Cp^1Co(tetraphenylcyclobutadiene), by the treatment with diphenylacetylene in xylene under reflux (Scheme 2, path A). The reaction gave a pair of diastereomers, **4a** and **5a**, together with a small amount of hexaphenylbenzene. The resultant diastereomers **4a** and **5a** were easily separated by column chromatography on silica with hexane/benzene as an eluent. Isolated yields are summarized in Table 1 (run 1) along with their $[\alpha]_D$ values. We have also performed the direct syntheses of **4a** and **5a** starting from $CoCl(PPh_3)_3$, cyclopentadiene **1a**, and diphenylacetylene (Scheme 2, path B), and obtained a pair of the diastereomers in moderate yields (Table 1, run 2).

Since the direct method (path B) is more convenient for the synthesis of cobalt–cyclobutadiene complexes, it has been applied to the preparation of several Cp^1Co(tetraarylcyclobutadiene) complexes using diarylacetylenes such as bis(3,5-dimethylphenyl)acetylene and di(4-chlorophenyl)acetylene (Scheme 2). Similarly, the method was used for Cp^2– and Cp^3–Co complexes and we have successfully obtained the pairs of diastereomers listed in Tables 1 and 2. In all cases except run 5, the reaction afforded a pair of diastereomers, **4** and **5**, in moderate yields. The reaction with bis(2,4,6-trimethylphenyl)acetylene (run 5) did not afford a cy-



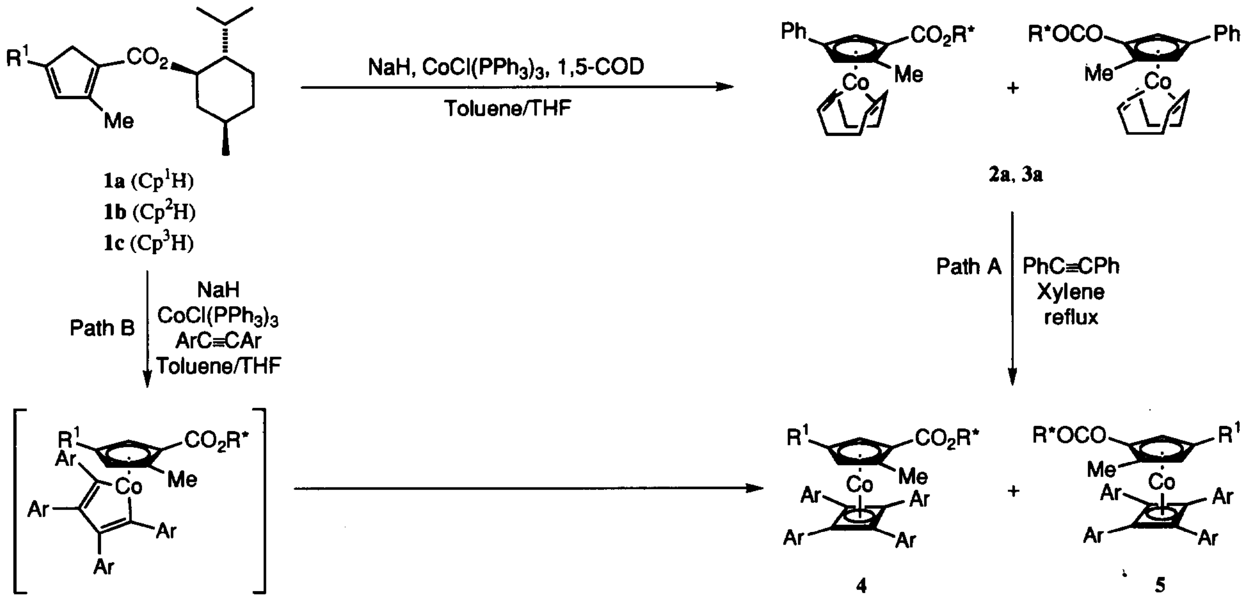
1a (Cp^1H)

1b (Cp^2H)

1c (Cp^3H)

2-Naph = 2-naphthyl

Scheme 1. Preparation of trisubstituted cyclopentadiene bearing a (−)-menthyl group.



4a, 5a: R^1=Ph, Ar=Ph
4b, 5b: R^1=Ph, Ar=3,5-$Me_2C_6H_3$
4c, 5c: R^1=Ph, Ar=4-ClC_6H_4
4e, 5e: R^1=Me, Ar=Ph
4f, 5f: R^1=2-naphthyl, Ar=Ph
R*=(−)-menthyl

Scheme 2. Synthesis of planar-chiral cyclopentadienyl–cobalt complexes.

clobutadiene complex probably due to the steric hindrance of the two methyl groups at the *ortho*-position on the phenyl ring. The diastereomer pairs synthesized here were similarly separated by column chromatography.

Conversion of diastereomeric complexes into enantiomeric ones by removing the (−)-menthyl group on cyclopentadienyl ligands was carried out for **4a** and **5a**. The reduction of **4a** with methyllithium in THF gave enantiomer (+)-**6**, and with $LiAlH_4$ afforded (+)-**7** in good yield. Removal of (−)-menthyl group from diastereomer **5a** was performed in the same manner and gave (−)-**6** and (−)-**7** (Scheme 3). Enantiomers (+)- and (−)-**6** showed the same melting points and the same absolute values of $[\alpha]_D$ (Table 3). The circular dichromism (CD) spectrum of (+)-**6** is the same as the mirror image of that of (−)-**6** (Fig. 1). In the presence of a chiral shift reagent, (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol [12] (fivefold excess), the ^1H NMR

TABLE 1. Synthesis of planar chiral $Cp^1Co(Ar_4C_4)$ complexes

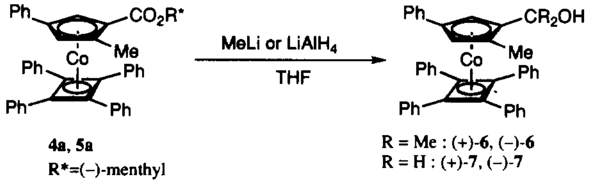
Run	Path	Product	Ar	Yield (%)	$[\alpha]_D$ (°) (in $CHCl_3$)
1	A	**4a**	Ph	28 [a]	+46 [c] (*c* 0.502)
		5a		36 [a]	−5.6 [c] (*c* 0.547)
2	B	**4a**	Ph	27 [b]	
		5a		35 [b]	
3	B	**4b**	3,5-$Me_2C_6H_3$	29 [b]	+93 [d] (*c* 0.515)
		5b		32 [b]	−7.7 [d] (*c* 0.521)
4	B	**4c**	4-ClC_6H_4	16 [b]	+7 [e] (*c* 0.121)
		5c		18 [b]	−2 [e] (*c* 0.266)
5	B	**4d**	2,4,6-$Me_3C_6H_2$	0 [b]	–
		5d		0 [b]	–

[a] Isolated yield based on $Cp^2(Co(cod)$. [b] Isolated yield based on $CoCl(PPh_3)_2$. [c] Temperature 16°C. [d] Temperature 31°C. [e] Temperature 14°C.

TABLE 2. Syntheses of planar-chiral $Cp'Co(Ph_4C_4)$

Run	Product	Cp′ (R^1)	Yield [a] (%)	$[\alpha]_D$ (°) (in $CHCl_3$)
2	**4a**	Cp^1 (Ph)	27	+46 [b] (*c* 0.502)
	5a		35	−5.6 [b] (*c* 0.547)
6	**4e**	Cp^2 (Me)	21	26 [c] (*c* 0.508)
	5e		26	−43 [c] (*c* 0.507)
7	**4f**	Cp^3 (2-Naph [d])	26	+25 [b] (*c* 0.498)
	5f		44	−62 [b] (*c* 0.288)

[a] Isolated yield based on $CoCl(PPh_3)_3$. [b] Temperature 16°C. [c] Temperature 31°C. [d] 2-Npah = 2-naphthyl.



4a, **5a**
R*=(−)-menthyl

R = Me : (+)-**6**, (−)-**6**
R = H : (+)-**7**, (−)-**7**

Scheme 3. Removal of the (−)-menthyl group.

TABLE 3. Removal of (−)-mentyl group from diastereomers

Product	Yield [a] (%)	$[\alpha]_D$ (°)	M.p. (°C)
(+)-**6**	87	+62 (*c* 0.535) [b]	172–173
(−)-**6**	79	−62 (*c* 0.534) [b]	172–173
(+)-**7**	87	+32 (*c* 0.511) [c]	225–226
(−)-**7**	90	−33 (*c* 0.288) [c]	225–226

[a] Isolated yield based on **4a** or **5a**. [b] Temperature 15°C; solvent, C_6H_6. [c] Temperature 14°C; solvent, toluene.

analysis indicated (+)- and (−)-**6** to be a pair of pure enantiomers. The same relation between (+)- and (−)-**7** was also observed. These complexes provide the first examples of optically pure planar-chiral cyclopentadienyl-cobalt complexes.

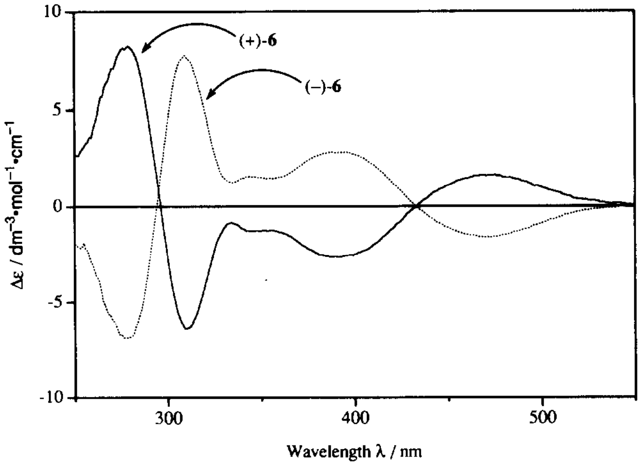


Fig. 1. CD spectra of (+)- and (−)-**6**.

2.2. Molecular structure of 4

In order to establish the absolute configuration of planar-chiral cobalt complexes, an X-ray diffraction study of **4** has been performed. Recrystallization of **4a** from hexane/benzene gave single crystals suitable for an X-ray analysis. Figure 2 depicts an ORTEP drawing

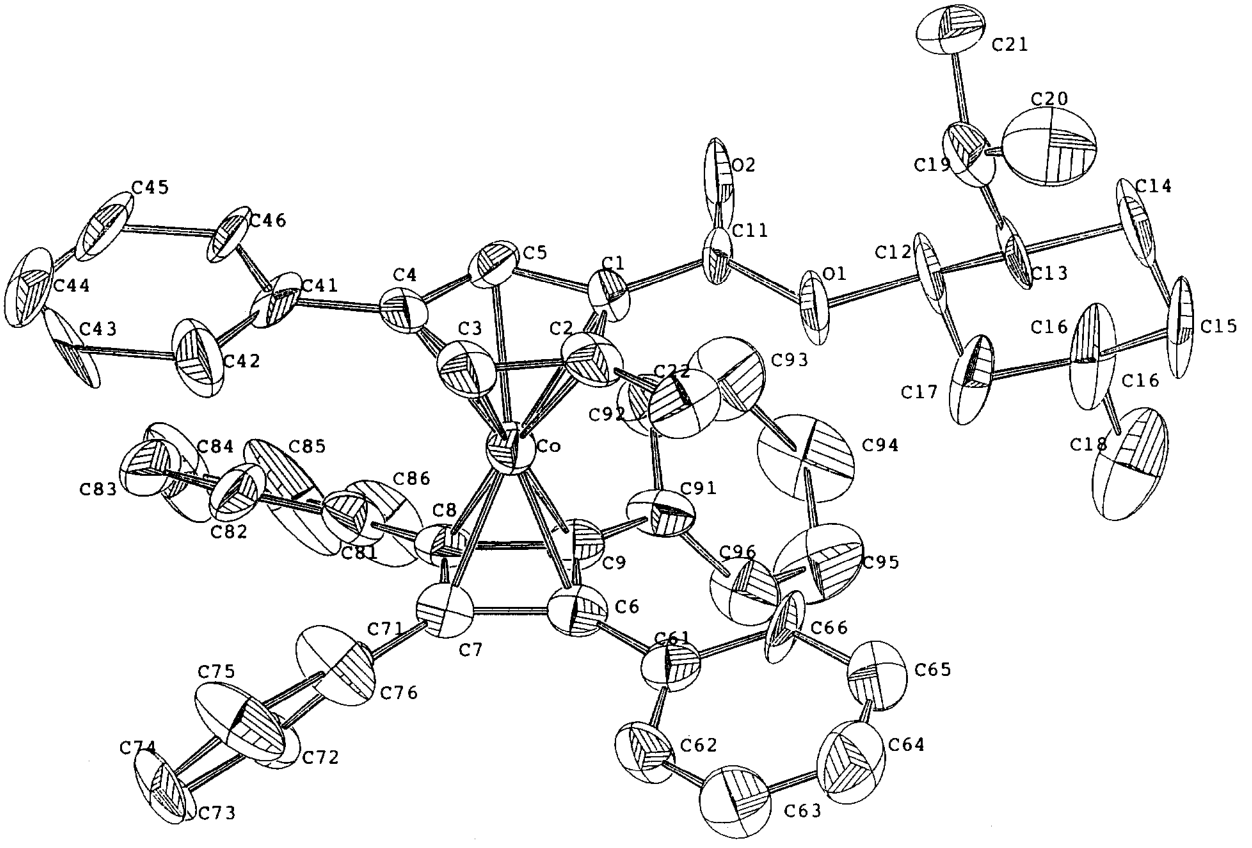


Fig. 2. ORTEP drawing of **4a** with atom labelling scheme.

of the established molecular structure of **4a**. Bond distances within the cyclopentadienyl ring range from 1.416(7) to 1.438(7) Å with an average bond length of 1.429 Å, and the Co–C(Cp) distances are in the range of 2.071(5)–2.098(5) Å with an average of 2.084 Å. These values are slightly longer (0.040 and 0.030 Å) than those (1.389 and 2.054 Å) found for the corresponding non-substituted cyclopentadienyl complex, (η^5-C_5H_5)Co(tetraarylcyclobutadiene) [13]. The substituents on the cyclopentadienyl ring such as phenyl and menthoxycarbonyl groups seem to have little influence on the bond distances. Bond distances within the cyclobutadiene ring appear normal and range from 1.457(7) to 1.473(7) Å with an average bond length of 1.464 Å. The CoC(cyclobutadiene) distances range from 1.986(5) to 1.990(5) Å with an average of 1.989 Å and are almost the same as reported values (1.980 Å) for (η^5-C_5H_5)Co(C_4Ar_4). The dihedral angle between the best planes defined by the carbon atoms of the four- and five-membered rings is 0.864°. The configuration of cyclopentadienyl and cyclobutadiene ligands around the Co metal is essentially similar to those of achiral (η^5-C_5H_5)M(cyclobutadiene) (M = Co, Rh) complexes [13,14]. Based on the known configuration of the (–)-menthyl group, the absolute configuration of **4a** around the Cp^1–M moiety has been determined to be *S*. Furthermore, the crystallographic analysis has revealed that **4a** has an interesting structure, in which the four phenyl groups on the cyclobutadiene ring are twisted in only one direction about their bonds to the cyclobutadiene ring, that is, the four phenyl groups form a unique four-blade windmill arrangement. The tortion angles of C7–C6–C61–C62, C8–C7–C71–C72, C9–C8–C81–C86, and C6–C9–C91–C96 are 12.4°, 41.3°, 22.0°, and 40.6°, respectively. This windmill unit has no asymmetric carbon but induces a helical chirality (point group D_4). Thus, the absolute stereochemistry of the windmill moiety has been determined to be *P* also based on the (–)-menthyl group. The established molecular structure shows that diastereomer **4a** has, in addition to planar and central chiralities, a helical chirality.

Taking a view of the molecular structure of **4a**, the location of the (–)-menthyl group between two phenyl groups of the windmill and the distance between C17 of the menthyl group and C66 of the windmill moiety (3.89(1) Å) suggest that the helical chirality on a C_4 ring may be controlled by the menthyl group on a cyclopentadienyl ligand. As can be seen in the physical data, including CD spectra of **6** and **7**, removal of the menthyl group from the cyclopentadienyl ligand results in loss of the helical chirality, also indicating that the helical chirality induced by four phenyl groups may be governed by the (–)-menthyl group on the C_5 ring.

The complexes described here are not only the first optically pure planar chiral Cp′–Co complexes but also the first examples containing three different chiralities, that is planar (Cp′–M moiety), carbon-centered [(–)menthyl group], and helical (or axial, Ph_4C_4 moiety) chirality, in one molecule.

3. Experimental section

3.1. General

All the reactions were carried out under an atmosphere of nitrogen or argon. Melting points and boiling points are uncorrected. ^{1}H NMR spectra were measured in $CDCl_3$ or C_6D_6 with $SiMe_4$ as an internal standard and recorded on a Bruker AM360 or a Jeol EX-270 spectrometer. Upfield shifts are quoted as negative. IR spectra were recorded on a Hitachi 295 spectrometer. Mass spectrometry was performed with a Shimadzu QP-2000 GC-MS (EI, 70 eV) spectrometer. Elemental analysis was carried out by using a Perkin Elmer 240C. Optical rotatory powers were measured on a Jasco DIP-370 digital polarimeter. Solvents were dried in the usual manner and distilled. $CoCl(PPh_3)_3$ [15], diarylacetylenes [16], and non-chiral trisubstituted cyclopentadienes [7] were prepared by the reported methods.

3.2. Preparation of 1-{(1R,2S,5R)-menthoxycarbonyl}-2-methyl-4-phenyl-1,3-cyclopentadiene (*1a*)

A mixture of 1-ethoxycarbonyl-2-methyl-4-phenyl-1,3-cyclopentadiene (17.0 g, 100 mmol), (–)-menthol (19.0 g, 120 mmol), and *p*-toluenesulfonic acid monohydrate (0.60 g, 3 mmol) in xylene (600 ml) was allowed to react under reflux for 3 days. Evaporation of the solvent at 70°C under reduced pressure gave a dark brown viscous oil, from which the product was isolated by column chromatography on silica with hexane/Et_2O (10:1) as an eluent and then purified by distillation under reduced pressure to give pure **1a** as a pale yellow oil in 64% yield.

B.p.: 190–195°C (0.4 mmHg). Anal. Found: C, 81.84; H, 8.84. $C_{23}H_{30}O_2$ calcd.: C, 81.62; H, 8.93%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.57–7.24 (m, 5H); 6.76 (s, 1H); 4.82 (dt, $J = 10.9$, 4.2 Hz, 1H); 3.71 (m, 2H); 2.40 (t, $J = 2.3$ Hz, 3H); 0.90 (d, $J = 7.4$ Hz, 6H); 0.80 (d, $J = 7.0$ Hz, 3H); 2.00–0.90 (m, 9H). Infrared (neat): 1690, 1210 cm^{-1}. Mass: m/z 338 (M^+). $[\alpha]_D^{22}$ –60.6° (*c* 1.18, $CHCl_3$).

3.3. Preparation of 2,4-dimethyl-1-{(1R,2S,5R)-menthoxycarbonyl}-1,3-cyclopentadiene (*1b*)

The procedure described for **1a**, but starting with 1-ethoxycarbonyl-2,4-dimethyl-1,3-cyclopentadiene gave compound **1b** as a pale yellow oil. Yield 60%.

B.p.: 117–119°C (0.4 mmHg). Anal. Found: C, 78.21; H, 10.21 $C_{18}H_{28}O_2$ calcd.: C, 78.00; H, 10.31%. ^1H NMR (360 MHz, $CDCl_3$): δ 6.05 (s, 1H); 4.75 (dt, $J = 11.0$, 4.3 Hz, 1H); 3.21 (m, 2H); 2.30 (t, $J = 4.0$ Hz, 3H); 2.07 (d, $J = 1.4$ Hz, 3H); 0.90 (d, $J = 6.2$ Hz, 6H); 0.78 (d, $J = 6.7$ Hz, 3H); 2.0–0.80 (m, 9H). Infrared (neat): 1700, 1250 cm^{-1}. Mass: m/z 276 (M^+). $[\alpha]_D^{22}$ −79.2° (c 0.361, $CHCl_3$).

3.4. Preparation of 1-{(1R,2S,5R)-menthoxycarbonyl}-2-methyl-4-(2-naphthyl)-1,3-cyclopentadiene (1c)

The procedure described for **1a**, but starting with 1-ethoxycarbonyl-2-methyl-4-(2-naphthyl)-1,3-cyclopentadiene gave compound **1c** as colorless crystals, which was purified by recrystallization from $EtOH/C_6H_6$. Yield 49%.

M.p.: 117–119°C. Anal. Found: C, 83.27; H, 8.02 $C_{27}H_{32}O_2$ calcd.: C, 83.46; H, 8.30%. ^1H NMR (270 MHz, $CDCl_3$): δ 7.98 (s, 1H); 7.78–7.45 (m, 6H); 6.88 (s, 1H); 4.84 (dt, $J = 10.9$, 4.3 Hz, 1H); 3.84 (bs, 2H); 2.43 (t, $J = 2.3$ Hz, 3H); 0.94 (d, $J = 7.3$ Hz, 3H); 0.93 (d, $J = 6.6$ Hz, 3H); 0.82 (d, $J = 6.9$ Hz, 3H); 2.14 0.82 (m, 9H). Infrared (neat): 1690, 1240 cm^{-1}. Mass: m/z 388 (M^+). $[\alpha]_D^{29}$ −51.4° (c 0.544, $CHCl_3$).

3.5. Synthesis of $Cp^1Co(cod)$ (2a and 3a)

To a suspension of $CoCl(PPh_3)_3$ (1.35 g, 1.5 mmol) in toluene (10 ml) at room temperature was added 1,5-cyclooctadiene (0.6 ml). After stirring for a few minutes, a solution of Cp^1Na generated from Cp^1H (0.81 g, 2.4 mmol) and NaH (60% in mineral oil; 0.10 g, 2.5 mmol) in THF (10 ml) was added to the suspension. The mixture was allowed to react under reflux for 3 h. After evaporation of the solvent, the resultant dark brown viscous oil was purified by column chromatography on silica. Using benzene as eluant, a reddish orange band was collected. Removal of the solvent gave a pair of diastereomers **2a** and **3a** as a reddish orange oil.

Anal.: Found: H, 7.92; C, 73.95. $C_{31}H_{41}CoO_2$ calcd: H, 8.19; C, 73.79%. ^1H NMR (360 MHz, C_6D_6): δ 7.30–7.06 (m, 5H); 5.34 (dt, $J = 10.5$, 4.3 Hz, 0.5H); 5.31 (dt, $J = 10.5$, 4.3 Hz, 0.5H); 5.09 (d, $J = 2.3$ Hz, 0.5H); 4.96 (d, $J = 2.3$ Hz, 1H); 4.87 (d, $J = 2.3$ Hz, 0.5H); 3.63–3.53 (m, 2H); 3.03–2.95 (m, 2H); 2.56–0.75 (m, 29H). Infrared (neat): 1700, 1230 cm^{-1}. Mass: m/z 504 (M^+).

3.6. Conversion of $Cp^1Co(cod)$ (2a and 3a) to $Cp^1Co(C_4Ph_4)$ (4a and 5a)

$Cp^1Co(cod)$ (0.23 g, 0.46 mmol) and diphenylacetylene (0.82 g, 4.6 mmol) in xylene (10 ml) were allowed to react under reflux for 3 days. The reaction mixture was evaporated to give a dark brown oil, which was purified by column chromatography on silica. Development with hexane-benzene (4:1, v/v) gave two orange bands. The first band was one (**5a**) of the two diastereomers of $Cp'Co(C_4Ph_4)$ and the second was the other diastereomer **4a**. Recrystallization gave pure **4a** (hexane/benzene) and **5a** (benzene/EtOH).

4a: Deep red crystals. M.p.: 232–233°C: Anal. Found: C, 81.56; H, 6.71. $C_{51}H_{49}CoO_2$ calcd., C81.36; H, 6.56%. ^1H NMR (270 MHz, $CDCl_3$): δ 7.09–7.25 (m, 21H); 7.01 (t, $J = 7.4$ Hz, 2H); 6.87 (d, $J = 6.9$ Hz, 2H); 5.58 (d, $J = 2.0$ Hz, 1H); 4.95 (d, $J = 2.0$ Hz, 1H); 4.57 (dt, $J = 10.6$, 4.3 Hz); 1.80 (s, 3H); 0.83 (d, $J = 7.3$ Hz, 3H); 0.82 (d, $J = 6.6$ Hz, 3H); 0.64 (d, $J = 6.9$ Hz, 3H); 1.86–0.65 (m, 8H); 0.57 (q, $J = 11.7$ Hz, 1H). Infrared: 1715, 1235 cm^{-1}. Mass: m/z 752 (M^+).

5a: Orange crystals. M.p.: 191.8–192.8°C. Anal. Found: C, 81.40; H, 6.28. $C_{51}H_{49}CoO_2$ calcd., C, 81.36; H, 6.56%. ^1H NMR (270 MHz, $CDCl_3$): a 7.08–7.25 (m, 21H); 7.02 (t, $J = 7.4$ Hz, 2H); 6.92 (d, $J = 6.9$ Hz, 2H); 5.37 (d, $J = 2.0$ Hz, 1H); 4.99 (d, $J = 2.0$ Hz, 1H); 4.49 (dt, $J = 10.6$, 4.0 Hz, 1H); 1.90 (s, 3H); 0.87 (d, $J = 7.3$ Hz, 3H); 0.82 (d, $J = 6.3$ Hz, 3H); 0.70 (d, $J = 6.9$ Hz, 3H); 0.75–1.86 (m, 8H); 0.38 (q, $J = 11.2$ Hz, 1H). Infrared: 1720, 1230 cm^{-1}. Mass: m/z 752 (M^+).

3.7. Synthesis of $Cp'Co(C_4Ar_4)$ (4 and 5) by the reaction of $CoCl(PPh_3)_3$ with trisubstituted chiral cyclopentadiene (Cp'H) and diarylacetylene

To a suspension of $CoCl(PPh_3)_3$ (2.64 g, 3 mmol) in toluene (50 ml) at room temperature were added diarylacetylene (7 mmol) and a solution of Cp'Na, generated from Cp'H (3.5 mmol) and NaH (60% in mineral oil; 0.16 g, 4 mmol), in THF (10 ml). The mixture was allowed to react under reflux for 5 h. The resultant mixture was placed on a 2.5 cm × 15 cm column of activated alumina and eluated by benzene. The eluate was evaporated to give a dark brown solid, which was purified by column chromatography on silica. Development with hexane/benzene (4 : 1, v/v) gave two orange bands; the first and the second bands were found to be **5** and **4**, respectively. Recrystallization gave pure **4** (benzene/hexane) and **5** (benzene/EtOH).

4b: Yellow-orange crystals. M.p.: 115–116°C. Anal. Found: C, 81.94; H, 7.59. $C_{59}H_{65}CoO_2$ calcd.: C, 81.92; H, 7.57%. ^1H NMR (360 MHz, $CDCl_3$): δ 7.12 (d, $J = 7.2$ Hz, 1H); 7.04 (t, $J = 7.2$ Hz, 2H); 6.88 (s, 8H); 6.86 (d, $J = 7.2$ Hz, 2H); 6.85 (s, 4H); 5.55 (d, $J = 2.0$ Hz, 1H); 4.79 (d, $J = 1.8$ Hz, 1H); 4.55 (dt, $J = 10.5$, 4.3 Hz, 1H); 2.18 (s, 24H); 1.73 (s, 3H); 1.84–0.67 (m, 8H); 0.82 (d, $J = 7.0$ Hz, 3H); 0.81 (d, $J = 6.5$ Hz, 3H); 0.67 (d, $J = 7.0$ Hz, 3H); 0.52 (q, $J = 11.7$ Hz, 1H). Infrared (Nujol): 1710, 1230 cm^{-1}. Mass: m/z 864 (M^+).

5b: Yellow-orange crystals. M.p.: 111–112°C. Anal. Found: C, 81.82; H, 7.49. $C_{59}H_{65}CoO_2$ calcd.: C, 81.92; H, 7.57%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.13 (d, $J = 7.2$ Hz, 1H); 7.06 (t, $J = 7.2$ Hz, 2H); 6.89 (s, 8H); 6.86 (d, $J = 7.2$ Hz, 2H); 6.84 (s, 4H); 5.15 (d, $J = 1.8$ Hz, 1H); 4.92 (d, $J = 2.0$ Hz, 1H); 4.50 (dt, $J = 10.8$, 4.5 Hz, 1H); 2.18 (s, 24H); 1.81 (s, 3H); 1.79–0.70 (m, 8H); 0.83 (d, $J = 7.0$ Hz, 3H); 0.82 (d, $J = 6.5$ Hz, 3H); 0.72 (d, $J = 7.0$ Hz, 3H); 0.38 (q, $J = 11.7$ Hz, 1H). Infrared (Nujol): 1720, 1230 cm^{-1}. Mass: m/z 864 (M^+).

4c: Orange crystals. M.p.: 280–281°C. Anal. Found: C, 68.98; H, 4.93; Cl, 15.80. $C_{51}H_{45}Cl_4CoO_2$ calcd.: C, 68.78; H, 5.09; Cl, 15.92%. 1H NMR (360 MHz, $CDCl_3$): δ 7.18 (d, $J = 6.5$ Hz, 1H); 7.12–7.03 (m, 18H); 6.90 (d, $J = 7.6$ Hz, 2H); 5.55 (d, $J = 2.0$ Hz, 1H); 4.94 (bs, 1H); 4.61 (dt, $J = 10.3$, 4.3 Hz, 1H); 1.85 (bs, 3H); 1.79–0.65 (m, 8H); 0.88 (d, $J = 7.5$ Hz, 3H); 0.85 (d, $J = 7.0$ Hz, 3H); 0.66 (d, $J = 6.7$ Hz, 3H); 0.56 (q, $J = 11.7$ Hz, 1H). Infrared (Nujol): 1715, 1230 cm^{-1}. Mass: m/z 888 (M^+).

5c: Deep red crystals. M.p.: 242–244°C. Anal. Found: C, 68.83; H, 5.10; Cl, 15.67. $C_{51}H_{45}Cl_4CoO_2$ calcd.: C, 68.78; H, 5.09; Cl, 15.92%. 1H NMR (360 MHz, $CDCl_3$): δ 7.19 (d, $J = 7.0$ Hz, 1H); 7.11–7.04 (m, 18H); 6.93 (d, $J = 7.4$ Hz, 2H); 5.34 (bs, 1H); 4.97 (bs, 1H); 4.54 (dt, $J = 10.3$, 4.0 Hz, 1H); 1.91 (bs, 3H); 1.85–0.83 (m, 8H); 0.88 (d, $J = 6.7$ Hz, 6H); 0.71 (d, $J = 6.7$ Hz, 3H); 0.36 (q, $J = 11.6$ Hz, 1H). Infrared (Nujol): 1720, 1235 cm^{-1}. Mass: m/z 888 (M^+).

4e: Orange crystals. M.p.: 90–91°C. Anal. Found: C, 80.20; H, 6.62. $C_{46}H_{47}CoO_2$ calcd.: C, 79.98; H, 6.86%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.41–7.19 (m, 20H); 5.05 (d, $J = 1.8$ Hz, 1H); 4.55 (dt, $J = 10.7$, 4.3 Hz, 1H); 4.47 (d, $J = 1.8$ Hz, 1H); 1.74 (s, 3H); 1.79–0.60 (m, 8H); 1.47 (s, 3H); 0.82 (d, $J = 6.5$ Hz, 3H); 0.78 (d, $J = 6.9$ Hz, 3H); 0.63 (d, $J = 7.0$ Hz, 3H); 0.52 (q, $J = 11.2$ Hz, 1H). Infrared (Nujol): 1715, 1215 cm^{-1}. Mass: m/z 690 (M^+).

5e: Orange crystals. M.p.: 86–87°C. Anal. Found: C, 79.76; H, 6.48. $C_{46}H_{47}CoO_2$ calcd.: C, 79.98; H, 6.86%. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.41–7.20 (m, 20H); 4.87 (d, $J = 1.8$ Hz, 1H); 4.64 (d, $J = 1.8$ Hz, 1H); 4.44 (dt, $J = 10.6$, 4.4 Hz, 1H); 1.84 (s, 3H); 1.65–0.70 (m, 8H); 1.47 (s, 3H); 0.87 (d, $J = 7.0$ Hz, 3H); 0.80 (d, $J = 6.5$ Hz, 3H); 0.69 (d, $J = 7.0$ Hz, 3H); 0.32 (q, $J = 11.5$ Hz, 1H). Infrared (Nujol): 1710, 1215 cm^{-1}. Mass: m/z 690 (M^+).

4f: Orange crystals. M.p.: 118–120°C. Anal. Found: C, 81.69; H, 6.17. $C_{55}H_{51}CoO_2$ calcd.: C, 82.27; H, 6.40%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.75–7.71 (m, 1H); 7.48–7.40 (m, 6H); 7.20–7.00 (m, 20H); 5.69 (d, $J = 2.0$ Hz, 1H); 5.08 (d, $J = 2.3$ Hz, 1H); 4.59 (dt, $J = 10.9$, 4.3 Hz, 1H); 1.84 (s, 3H); 1.78–0.65 (m, 8H); 0.85 (d, $J = 7.0$ Hz, 3H); 0.83 (d, $J = 6.8$ Hz, 3H); 0.65 (d, $J = 7.0$ Hz, 3H); 0.59 (q, $J = 11.2$ Hz, 1H). Infrared (Nujol): 1715, 1225 cm^{-1}. Mass: m/z 802 (M^+).

TABLE 4. Atomic coordinates with equivalent isotropic temperature factors for **4a**

Atom	x	y	z	B_{eq} [a]
Co	0.05358(4)	0.72922(4)	0.07365(4)	2.72(1)
O1	0.1184(2)	0.5498(2)	−0.0870(3)	4.3(1)
O2	0.2200(2)	0.6245(3)	−0.0589(3)	6.1(1)
C1	0.1255(3)	0.6292(3)	0.0562(3)	3.4(1)
C2	0.0628(3)	0.5980(3)	0.1032(3)	3.5(1)
C3	0.0552(3)	0.6452(3)	0.1896(3)	3.9(1)
C4	0.1133(3)	0.7054(3)	0.1986(4)	3.9(1)
C5	0.1572(3)	0.6950(3)	0.1144(3)	3.4(1)
C6	−0.0312(2)	0.7546(3)	−0.0088(4)	2.9(1)
C7	−0.0285(2)	0.8107(3)	0.0763(4)	2.9(1)
C8	0.0363(3)	0.8510(3)	0.0385(3)	3.0(1)
C9	0.0344(3)	0.7954(3)	−0.0456(3)	3.0(1)
C11	0.1608(3)	0.6022(3)	−0.0359(4)	3.8(1)
C12	0.1476(3)	0.5182(4)	−0.1787(4)	4.6(2)
C13	0.1306(3)	0.4229(4)	−0.1833(4)	4.9(2)
C14	0.1581(4)	0.3915(5)	−0.2838(5)	6.5(2)
C15	0.1215(4)	0.4388(4)	−0.3657(5)	6.0(2)
C16	0.1340(3)	0.5345(4)	−0.3598(4)	5.7(2)
C17	0.1102(4)	0.5669(4)	−0.2600(4)	5.1(2)
C18	0.0932(5)	0.5851(5)	−0.4382(5)	7.9(3)
C19	0.1596(4)	0.3727(4)	−0.0958(5)	6.1(2)
C20	0.1333(5)	0.2799(5)	−0.0979(6)	8.8(3)
C21	0.2413(4)	0.3765(6)	−0.0841(7)	8.5(3)
C22	0.0129(3)	0.5257(3)	0.0745(5)	4.4(1)
C41	0.1262(3)	0.7667(4)	0.2767(4)	4.7(2)
C42	0.0756(4)	0.7760(5)	0.3508(4)	6.3(2)
C43	0.0887(6)	0.8369(5)	0.4231(5)	9.5(3)
C44	0.1471(6)	0.8870(5)	0.4228(6)	10.3(3)
C45	0.1975(5)	0.8765(5)	0.3510(6)	8.3(3)
C46	0.1872(4)	0.8169(4)	0.2781(5)	6.3(2)
C61	−0.0818(3)	0.6914(3)	−0.0479(4)	3.3(1)
C62	−0.1515(3)	0.6843(4)	−0.0118(5)	4.6(2)
C63	−0.1985(3)	0.6220(4)	−0.0490(5)	5.8(2)
C64	−0.1763(4)	0.5689(4)	−0.1218(5)	6.0(2)
C65	−0.1076(4)	0.5761(4)	−0.1588(5)	5.3(2)
C66	−0.0613(3)	0.6376(4)	−0.1210(4)	4.5(2)
C71	−0.0768(3)	0.8357(3)	0.1553(3)	3.2(1)
C72	−0.0950(3)	0.9220(3)	0.1657(4)	3.9(1)
C73	−0.1388(3)	0.9488(4)	0.2402(5)	4.8(2)
C74	−0.1651(3)	0.8922(4)	0.3054(4)	5.2(2)
C75	−0.1487(4)	0.8079(5)	0.2966(5)	6.3(2)
C76	−0.1062(3)	0.7784(4)	0.2205(5)	5.0(2)
C81	0.0768(3)	0.9291(3)	0.0632(4)	3.7(1)
C82	0.0843(3)	0.9545(3)	0.1584(5)	4.7(2)
C83	0.1223(4)	1.0291(4)	0.1806(6)	6.6(2)
C84	0.1509(4)	1.0776(4)	0.1085(7)	8.0(3)
C85	0.1445(4)	1.0547(4)	0.0150(7)	8.0(3)
C86	0.1053(4)	0.9794(4)	−0.0099(5)	5.7(2)
C91	0.0748(3)	0.7967(3)	−0.1365(4)	3.5(1)
C92	0.1499(3)	0.8021(4)	−0.1360(4)	4.5(2)
C93	0.1880(4)	0.8113(5)	−0.2213(5)	6.5(2)
C94	0.1522(4)	0.8160(5)	−0.3075(5)	6.9(2)
C95	0.0788(4)	0.8100(5)	−0.3092(4)	6.7(2)
C96	0.0404(3)	0.8002(4)	−0.2244(4)	4.9(2)

[a] $B_{eq} = (4/3)\Sigma_i \Sigma_j [\beta_{ij}(a_i a_j)]$.

5f: Yellow-orange crystals. M.p.: 109–111°C. Anal.

Found: C, 82.26; H, 6.52. $C_{55}H_{51}CoO_2$ calcd.: C, 82.27; H, 6.40%. ^1H NMR (270 MHz, $CDCl_3$): δ 7.75–7.72 (m, 1H); 7.49–7.39 (m, 6H); 7.19–7.00 (m, 20H); 5.48 (d, $J = 2.0$ Hz, 1H); 5.12 (d, $J = 2.0$ Hz, 1H); 4.53 (dt, $J = 10.6$, 4.3 Hz, 1H); 1.94 (s, 3H); 1.68–0.72 (m, 8H); 0.89 (d, $J = 7.3$ Hz, 3H); 0.83 (d, $J = 6.3$ Hz, 3H); 0.72 (d, $J = 6.9$ Hz, 3H); 0.44 (q, $J = 10.9$ Hz, 1H). Infrared (Nujol): 1720, 1220 cm^{-1}. Mass: m/z 802 (M^+).

*3.8. Removal of (−)-menthyl group from **4a** and **5a** by the reaction with MeLi*

To a solution of **4a** (or **5a**) (0.753 g, 1 mmol) in THF (60 ml) at 0°C was added a solution of MeLi (1.4 M in Et_2O, 3 ml, 4.2 mmol), and the mixture was allowed to react at room temperature for 30 min. The mixture was quenched by saturated NH_4Cl aq. and the organics were extracted with ether. The extract was evaporated to give a red brown viscous oil. (−)-Menthol was removed by sublimation under reduced pressure at 100°C and the residue was purified by column chromatography on silica with hexane/Et_2O (3 : 1, v/v) as eluant, followed by recrystallization from hexane to give (+)-**6** or (−)-**6**.

TABLE 5A. Selected bond distances (Å) of **4a**

Co–C1	2.071(5)	C16–C17	1.541(9)
Co–C2	2.098(5)	C16–C18	1.545(10)
Co–C3	2.078(5)	C19–C20	1.531(10)
Co–C4	2.094(5)	C19–C21	1.528(11)
Co–C5	2.079(5)	C41–C42	1.401(9)
Co–C6	1.989(5)	C41–C46	1.380(10)
Co–C7	1.989(4)	C42–C43	1.405(10)
Co–C8	1.990(5)	C43–C44	1.339(14)
Co–C9	1.986(5)	C44–C45	1.378(13)
O1–C11	1.339(6)	C45–C46	1.389(10)
O1–C12	1.470(7)	C61–C62	1.394(8)
O2–C11	1.199(7)	C61–C66	1.372(7)
C1–C11	1.500(7)	C62–C63	1.406(9)
C1–C2	1.423(7)	C63–C64	1.373(10)
C1–C5	1.434(7)	C64–C65	1.381(10)
C2–C22	1.515(7)	C65–C66	1.394(9)
C2–C3	1.416(7)	C71–C72	1.399(7)
C3–C4	1.438(8)	C71–C76	1.386(8)
C4–C41	1.467(7)	C72–C73	1.381(8)
C4–C5	1.436(7)	C73–C74	1.356(9)
C6–C7	1.473(7)	C74–C75	1.359(10)
C6–C9	1.469(7)	C75–C76	1.398(9)
C7–C8	1.458(7)	C81–C82	1.389(9)
C8–C9	1.457(7)	C81–C86	1.390(9)
C6–C61	1.469(7)	C82–C83	1.398(9)
C7–C71	1.471(7)	C83–C84	1.364(12)
C8–C81	1.475(7)	C84–C85	1.354(14)
C9–C91	1.470(7)	C85–C86	1.426(9)
C12–C13	1.525(9)	C91–C92	1.399(7)
C12–C17	1.530(8)	C91–C96	1.379(7)
C13–C14	1.566(10)	C92–C93	1.389(9)
C13–C19	1.544(9)	C93–C94	1.372(10)
C14–C15	1.518(10)	C94–C95	1.369(11)
C15–C16	1.516(10)	C95–C96	1.385(8)

TABLE 5B. Selected bond angles (°) of **4a**

C1–C2–C22	129.6(5)	C12–C17–C16	111.8(5)
C1–C2–C3	106.9(4)	C13–C12–C17	111.1(5)
C1–C5–C4	107.8(4)	C13–C14–C15	111.6(6)
C2–C1–C11	130.8(4)	C13–C19–C20	110.7(6)
C2–C1–C5	108.9(4)	C13–C19–C21	114.3(6)
C2–C3–C4	109.9(5)	C14–C13–C19	115.4(5)
C3–C2–C22	123.4(5)	C14–C15–C16	111.8(6)
C3–C4–C41	127.9(5)	C15–C16–C17	109.2(5)
C3–C4–C5	106.4(4)	C15–C16–C18	113.0(6)
C4–C41–C42	120.1(6)	C17–C16–C18	109.0(6)
C4–C41–C46	121.0(5)	C20–C19–C21	110.9(6)
C5–C1–C11	120.2(4)	C41–C42–C43	118.7(7)
C5–C4–C41	125.7(5)	C41–C46–C45	120.3(7)
C6–C61–C62	121.1(5)	C42–C41–C46	118.8(6)
C6–C61–C66	120.5(5)	C42–C43–C44	122.2(8)
C6–C7–C71	137.4(4)	C43–C44–C45	119.0(8)
C6–C7–C8	89.8(4)	C44–C45–C46	120.9(8)
C6–C9–C8	90.0(4)	C61–C62–C63	120.1(6)
C6–C9–C91	136.9(4)	C61–C66–C65	122.0(6)
C7–C6–C61	136.0(4)	C62–C61–C66	118.4(5)
C7–C6–C9	89.6(4)	C62–C63–C64	120.1(6)
C7–C71–C72	118.7(4)	C63–C64–C65	120.2(6)
C7–C71–C7	123.9(5)	C64–C65–C66	119.2(6)
C7–C8–C81	134.1(4)	C71–C72–C73	120.8(5)
C7–C8–C9	90.6(4)	C71–C76–C75	120.3(6)
C8–C7–C71	131.2(4)	C72–C71–C76	117.4(5)
C8–C81–C82	120.6(5)	C72–C73–C74	121.1(6)
C8–C81–C86	119.6(5)	C73–C74–C75	119.4(6)
C8–C9–C91	132.0(4)	C74–C75–C76	121.0(6)
C9–C6–C61	134.0(4)	C81–C82–C83	120.0(6)
C9–C8–C81	133.8(4)	C81–C86–C85	119.0(7)
C9–C91–C92	120.4(5)	C82–C81–C86	119.7(5)
C9–C91–C96	121.6(5)	C82–C83–C84	119.9(7)
O1–C11–C1	111.6(4)	C83–C84–C85	121.6(7)
O1–C11–O2	125.3(5)	C84–C85–C86	119.7(7)
O1–C12–C13	106.7(4)	C91–C92–C93	120.8(5)
O1–C12–C17	107.7(5)	C91–C96–C95	121.2(6)
O2–2C11–C1	123.1(5)	C92–C91–C96	117.7(5)
C11–O1–C12	116.5(4)	C92–C93–C94	120.1(6)
C12–C13–C14	106.0(5)	C93–C94–C95	119.7(6)
C12–C13–C19	112.9(5)	C94–C95–C96	120.5(6)

(+)-**6**: Deep red crystals. M.p.: 172–173°C. Anal. Found: C, 82.44; H, 5.90. $C_{43}H_{37}OCo$ calcd.: C, 82.15; H, 5.93%. ^1H NMR (360 MHz, C_6D_6): δ 7.51 (dd, $J = 7.9$, 1.6 Hz, 8H); 7.04–6.92 (m, 17H); 5.17 (d, 1H, $J = 1.9$ Hz); 4.76 (d, $J = 1.9$ Hz, 1H); 2.10 (s, 3H); 1.48 (s, 1H); 1.36 (s, 3H); 1.34 (s, 3H). Mass: m/z 628 (M^+).

(−)-**6**: Deep red crystals. M.p.: 172–173°C. Anal. Found: C, 82.22; H, 5.82. $C_{43}H_{37}OCo$ calcd.: C, 82.15; H, 5.93%. ^1H NMR (360 MHz, C_6D_6): δ 7.51 (dd, $J = 7.9$, 1.6 Hz, 8H); 7.04–6.92 (m, 17H); 5.17 (d, 1H, $J = 1.9$ Hz); 4.76 (d, $J = 1.9$ Hz, 1H); 2.10 (s, 3H); 1.48 (s, 1H); 1.36 (s, 3H); 1.34 (s, 3H). Mass: m/z 628 (M^+).

3.9. Removal of (−)-menthyl group from **4a** and **5a** by the reaction with $LiAlH_4$

To a solution of **4a** (or **5a**) (0.149 g, 0.2 mmol) in THF (20 ml) at 0°C was added $LiAlH_4$ (0.010 g, 0.25 mmol), and the mixture was then allowed to react at room temperature for 5 h. The mixture was quenched by saturated NH_4Cl aq. and the organics were extracted with ether. The extract was evaporated to give a red brown viscous oil. (−)-Menthol was removed by sublimation under reduced pressure at 100°C and the residue was purified by column chromatography on alumina with hexane/Et_2O (3:1, v/v) as eluant, followed by recrystallization from hexane to give (+)-**7** or (−)-**7**.

(+)-**7**: Yellow powder. M.p.: 225–226°C. Anal. Found: C, 81.74; H, 5.31. $C_{41}H_{33}CoO$ calcd.: C, 81.99; H, 5.54%. ^1H NMR (360 MHz, C_6D_6): δ 7.42–6.93 (m, 25H); 5.05 (d, $J = 1.8$ Hz, 1H); 4.77 (d, $J = 1.8$ Hz, 1H); 4.07 (dd, $J = 12.8$, 5.7 Hz, 1H); 4.04 (dd, $J = 12.8$, 5.7 Hz, 1H); 1.59 (s, 3H); 0.77 (t, $J = 5.7$ Hz, 1H). Mass: m/z 600 (M^+).

(−)-**7**:.Yellow powder. M.p.: 225–226°C. Anal. Found: C, 81.87; H, 5.28. $C_{41}H_{33}CoO$ calcd.: C, 81.99; H, 5.54%. ^1H NMR (360 MHz, C_6D_6): δ 7.42–6.92 (m, 25H); 5.05 (d, $J = 1.8$ Hz, 1H); 4.77 (d, $J = 1.8$ Hz, 1H); 4.07 (dd, $J = 12.8$, 5.8 Hz, 1H); 4.04 (dd, $J = 12.8$, 5.8 Hz, 1H); 1.59 (s, 3H); 0.78 (t, $J = 5.8$ Hz, 1H). Mass: m/z 600 (M^+).

3.10. X-Ray crystallographic analysis for **4a**

Crystal data for **4a**: $C_{51}H_{49}O_2Co$, $M = 752.88$, orthorhombic, space group $P2_12_12_1$, $a = 18.602(10)$, $b = 15.629(3)$, $c = 13.893(3)$ Å, $V = 4039$ Å^3, $Z = 4$, $D_c = 1.239$ g cm^{-3}, $D_m = 1.239$ g cm^{-3}, $F(000) = 1592$, Mo-Kα radiation with $\lambda = 0.7107$ Å, μ(Mo-Kα) = 4.85 cm^{-1}. A total of 5175 reflections were collected on a Rigaku AFC-5FOS four-circle diffractometer (graphite-monochromated Mo-Kα radiation) in the ω–2θ scan mode to $2\theta_{max} = 55°$. The structure was solved by direct methods (MULTAN 80, Rigaku RASA system on FACOM S-3500) and refined to give $R = 0.051$, $R_w = 0.057$ for 3643 independent reflections [$F > 3\sigma(F)$]. Absolute stereochemistry was determined based on the (−)-menthyl group on the cyclopentadienyl ring of **4a**. Fractional coordinates are listed in Table 4 and bond distances and angles in Table 5. Additional data, including hydrogen atomic coordinates, anisotropic temperature factors and lists of observed and calculated structure factors are available from the authors.

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