Headline Articles

An Anion Receptor Based on Poly-Substituted Cobalticinium Complexes

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

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

(Received July 31, 1995)

Various derivatives of poly-substituted cobalticinium complexes have been synthesized by using substituted cyclopentadienes with a convertible carboxylic group. By ^{1}H NMR titration experiments, these complexes were shown to behave as a receptor for anions such as Cl^-, Br^-, AcO^-, and p-TsO^-. Planar-chiral anilide derivative **3a** showed chiral recognition toward camphor-10-sulfonate though the difference of the association constants was 10%. The molecular structure including the absolute configuration of **3a** have been established by an X-ray crystallographic analysis. The results suggest the hydrophobic cavity constructed by the substituents on the cyclopentadienyl ligands may be an important component for the successful anion complexation.

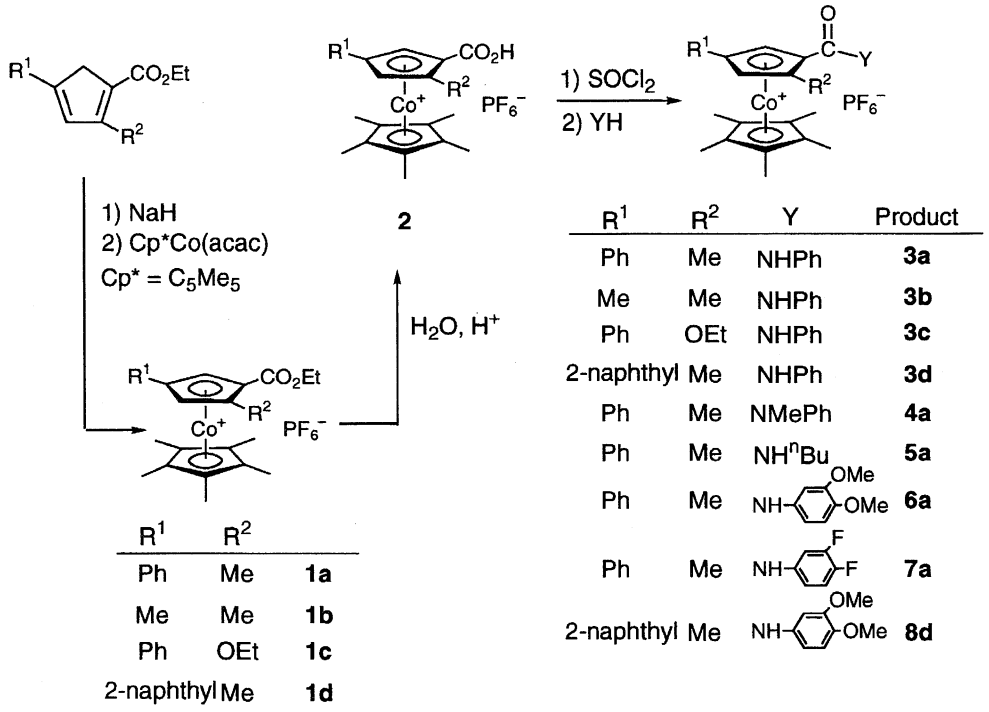
Organic and inorganic anions are known to be important in chemical and biochemical processes, and their recognition by abiotic receptors is an area of current interest.[1] In contrast to a large variety of host compounds which form host–guest complexes with cations, there are only a few abiotic receptors for organic anions.[2] For example, Lewis-acid-containing ligands[3] and quaternary ammonium salts[4] have been reported so far. In particular, metallocene compounds such as ferrocene[5] and cobalticinium salts[6] have received much attention as ion-receptors based on their redox-active moieties. Beer et al. have prepared mono- or di-substituted cobalticinium amide complexes, and demonstrated electrochemical recognition for anions such as halides and nitrates.[6] Cobalticinium cations are, however, chemically inactive toward electrophilic substitutions on the cyclopentadienyl ring and there are few reports[7] about poly-substituted cobalticinium complexes in comparison with ferrocene derivatives.

During the last few years, we have reported the syntheses of several planar-chiral cobalticinium complexes bearing poly-substituted cyclopentadienyl ligands.[8] Our method for preparing such poly-substituted cobalticinium complexes is based on use of a trisubstituted cyclopentadiene having a convertible ester group and we have obtained planar-chiral complexes in an enantiomerically pure form.[9,10] Now, we have investigated their behavior toward anions and found that they act as an anion receptor for not only inorganic but also organic anions.[8a] The results of ^{1}H NNR titration experiments and an X-ray structural analysis have indicated that the hydrophobic cavity constructed by the substituents on the cyclopentadienyl ligands is an important component for the anion complexation. We report here the properties as an anion receptor of poly-substitued cobalticinium complexes having an amide group on the cyclopentadienyl ligand.

Results and Discussion

Synthesis of Planar-Chiral Cobalticinium Complexes. Cobalticinium complexes containing poly-substituted cyclopentadienyl ligands may be good candidates for anion receptors because the substituents as well as the cationic metal center may potentially construct a hydrophobic cavity which would be suitable to accommodate organic anions. Although the preparative method of poly-substitued cobalticinium complexes is limited because of the low reactivity of cobalticinium complexes toward electrophilic substitution reactions on the cyclopentadienyl ligand, they can be rather easily prepared by our new method.[8] Thus, we have now prepared ester (**1**), carboxylic acid (**2**), and amide derivatives (**3**—**8**) as shown in Scheme 1. Moreover planar chiral cobalticinium complexes are also prepared by our method and in some cases (**3a**, **3b**) enantiomerically pure complexes have been isolated. Our method has an advantage for preparing various derivatives having a functional group via the carboxylic acid. Complexes (**3**—**8**) have also been prepared to evaluate the effects of substituents on the anion complexation (vide infra).

^{1}H NMR Titration Studies. Beer et al. reported that mono- or di-substituted cobalticinium amide derivatives act as an anion receptor.[6,11] Their results showed that simple monoester derivatives of cobalticinium complexes had no



R¹	R²	Y	Product
Ph	Me	NHPh	**3a**
Me	Me	NHPh	**3b**
Ph	OEt	NHPh	**3c**
2-naphthyl	Me	NHPh	**3d**
Ph	Me	NMePh	**4a**
Ph	Me	NH^{n}Bu	**5a**
Ph	Me		**6a**
Ph	Me		**7a**
2-naphthyl	Me		**8d**

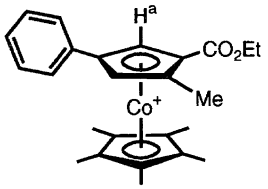
R¹	R²	
Ph	Me	**1a**
Me	Me	**1b**
Ph	OEt	**1c**
2-naphthyl	Me	**1d**

Scheme 1. Syntheses of poly-substituted cobalticinium complexes.

interaction with anions.[11a] We examined the behavior of our ethyl ester derivative **1a** (R^1 = Ph, R^2 = Me) as a receptor by a ^{1}H NMR titration method. Thus, addition of tetraethylammonium *p*-toluenesulfonate (NEt_4^+*p*-TsO^-) to **1a** resulted in a down-field shift of the proton (H^a) at 5-position on the cyclopentadienyl ligand. The titration curve obtained from the experiment using $CDCl_3$ as a solvent is shown in Fig. 1, in which the change of chemical shift due to H^a is plotted against the molar equivalents of added *p*-TsO^-. The association constant (K_a) has been estimated at 7.7×10^2 M^{-1} by use of a least-squares fit computer program (1 M = 1 mol dm^{-3}).

Similar NMR titration experiments were done for complexes **1**, **3**, **4**, and **5**, and the association constants estimated for the complexation with anions such as halides and *p*-TsO^- are summarized in Table 1. It should be noted that in our case a substantial binding was observed between ester derivative **1a** and *p*-TsO^-, though Beer et al. detected no interaction for a simple mono-substituted cobalticinium complex having an ester group, suggesting that a hydrophobic cavity constructed by R^1 and R^2 together with methyl groups on the pentamethylcyclopentadienyl ligand was an important component for successful complexation with an anion.

Anilide **3a** was found to form host–guest complexes with a variety of inorganic and organic anions. The titration experiment for **3a** with *p*-TsO^- showed a large value of K_a (1.4×10^4 M^{-1}) in $CDCl_3$. The titration curve of **3a** with *p*-TsO^- traced by ^{1}H NMR is illustrated in Fig. 2, which shows the formation of a 1 : 1 host–guest complex. It is noteworthy that the complexation causes large downfield shifts of the amide proton (H^b) and the proton (H^a) on the trisubstituted cyclopentadienyl ligand. For example, shifts



1a

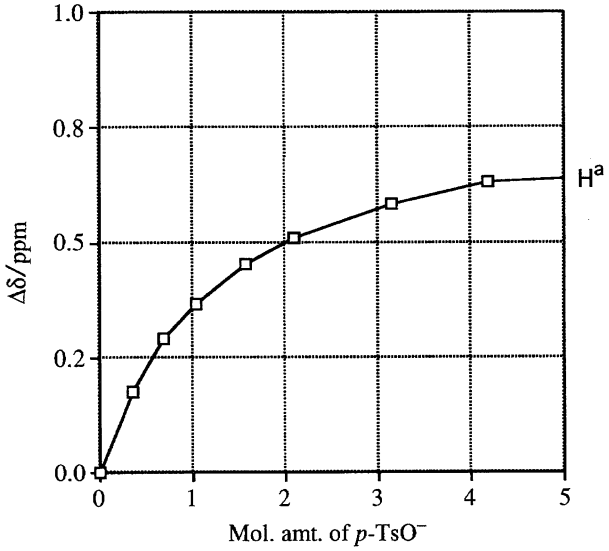


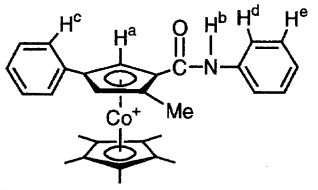
Fig. 1. ^{1}H NMR titration curve of **1a** with *p*-TsO^-.

of $\Delta\delta$ = 1.8 ppm for the H^b and 1.0 ppm for H^a were observed on addition of equimolar amount of *p*-TsO^-, implying that a CO–NH···X^- hydrogen bonding is a significant contributing factor to the overall anion complexation process. In the titra-

Table 1. Association Constants with Anions (25 °C, $CDCl_3$)

Host complex	Guest anion	K_a/M^{-1}
3a	Br^- a)	ca. 10^4 c)
3a	Cl^- a)	ca. 10^4 c)
3a	AcO^- a)	ca. 10^5 c)
3a	*p*-TsO^- b)	1.4×10^4 c)
3b	*p*-TsO^-	8.8×10^3 c)
3c	*p*-TsO^-	8.6×10^2 c)
4a	*p*-TsO^-	3.8×10^2 d)
5a	*p*-TsO^-	2.6×10^3 c)
1a	*p*-TsO^-	7.7×10^2 d)

a) Tetrabutylammonium salt was used. b) Tetraethylammonium salt was used. c) The value was calculated for H^b. c) The value was calculated for H^a.



3a

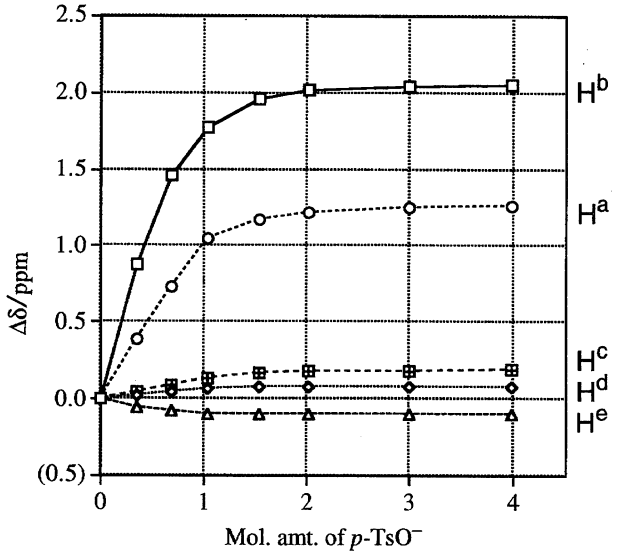


Fig. 2. ^1H NMR titration curves of **3a** with *p*-TsO^-.

tion experiments of **3a** with Cl^-, Br^-, and AcO^-, the same phenomenon was observed ($\Delta\delta$ for H^b: Cl^-, 2.3; Br^-, 1.8; AcO^-, 3.4 ppm). The binding site is, therefore, undoubtedly the same in all the cases and is presumably located near the H^a and H^b groups in a hydrophobic cavity surrounded by a cobalt atom and substituents on two cyclopentadienyl ligands.

To find details about the anion complexation process, we did titration experiments for several derivatives **3**—**5**. Complexes **3a**, **3b**, and **5a** bearing an appending amide NH unit, which is capable to form a favorable hydrogen bond with a guest anion, afforded larger values of K_a than those of **1a**, **3c**, and **4a**. The poor association ($K_a = 8.6\times10^2$ M^{-1}) between **3c** and *p*-TsO^- may be due to the contribution of an intramolecular hydrogen bond between NH and the neighboring OEt group which prevents the hydrogen bonding of NH with a guest anion (Fig. 3). This may be supported by the infrared spectrum (taken for a sample in solid state) in which **3c** showed an amide NH stretching absorption at 3380 cm^{-1} lower wavenumber than **3a** at 3410 cm^{-1}. Furthermore, in the ^1H NMR spectrum, the resonance due to the NH of **3c** (8.84 ppm) was observed in a lower field relative to that of **3a** (8.49 ppm). These results suggest an intramolecular hydrogen bonding between NH and OEt group. *N*-Butyl amide **5a** gave a smaller value of K_a than that of anilide **3a**. This may be due to the weaker hydrophobic effect of **5a** in comparison with anilide derivative **3a**. From these results, tentative model of the host–guest complex [**3a**·*p*-TsO^-] is shown in Fig. 4. This may be supported by the X-ray crystallographic analysis of **3a** (vide infra).

X-Ray Structural Analysis of (+)-3a. To establish the molecular structure of **3a** including the absolute configuration, an X-ray diffraction study of (+)-**3a** has been done. Recrystallization of (+)-**3a** from ethanol gave single crystals suitable for an X-ray analysis. The measurement was done with Cu $K\alpha$ radiation. The cobalt anomalous dispersion term for Cu $K\alpha$ ($\Delta f'' = 3.608$)[12] is much larger than that for Mo $K\alpha$ ($\Delta f'' = 0.973$) and this effect has an advantage even considering the problem due to the higher crystal absorption when using Cu $K\alpha$ radiation. The Bijvoet pairs were treated as independent reflections. In the course of the refinement with all observed reflections, two refinements were used. The refinement with the configuration shown in this article with anisotropic thermal parameters for non-H atoms gave the *R* factor 0.045 and R_w 0.054. On the other hand in the model with the opposite enantiomer they were 0.117 (*R*) and 0.154 (R_w), even though the calculation was repeated from the isotropic stage. From these results, we have identified the absolute configuration of (+)-**3a** around the Cp-M moiety to be *R*. The molecular structure is illustrated in Fig. 5 together with atom labeling scheme. All the bond lengths are typical. The two Cp rings are planar, nearly parallel to

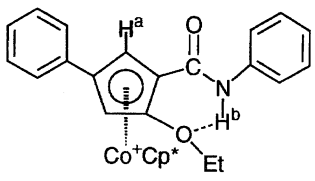


Fig. 3. Tentative model of **3c** (top view).

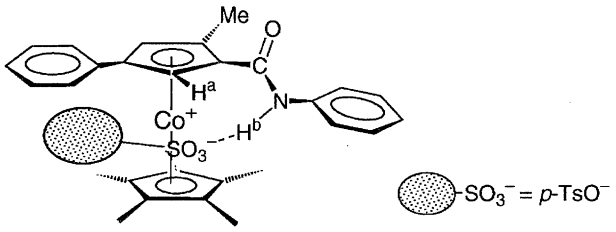


Fig. 4. Tentative model of host–guest complex [**3a**·*p*-TsO^-] (side view).

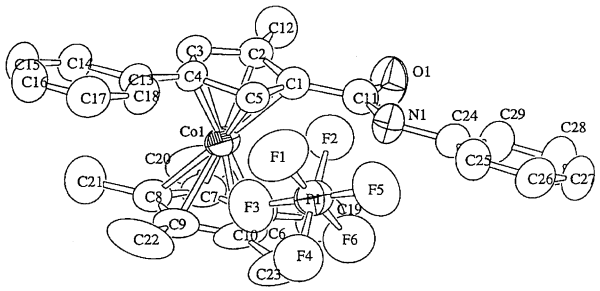


Fig. 5. ORTEP drawing of (1*R*)-(+)-**3a** with atom labelling scheme. Hydrogen atoms have omitted for clarity.

one another (dihedral angle, 2.67°). The conformation is midway between the fully eclipsed and staggered. The dihedral angles between trisubstituted cyclopentadiene and two phenyl rings (C18—23, C24—29) are 10.11° and 11.92°, respectively. It is noteworthy that there seems to be a cavity constructed by anilide and phenyl (R^1) together with methyl groups on the pentamethylcyclopentadienyl ligand, and the amide proton (H^b) and the proton (H^a) at the 5-position on the cyclopentadienyl ligand are located closely. As predicted by the large downfield shift of both H^a and H^b protons in the NMR spectra, the binding site may exist in the neighborhood of these protons.

Chiral Recognition. As our cobalticinium complexes have a planar chirality, a chiral recognition may be expected in a host–guest complexation. Thus, tetrabutylammonium (+)-camphor-10-sulfonate [(+)-camph] was used as a chiral guest toward the host cobalticinium complex (±)-**3a**. Addition of the chiral sulfonate to a solution of (±)-**3a** in $CDCl_3$ also caused a large shift (1—2 ppm downfield) of proton signals due to H^a and H^b. However, the resultant titration curve of **3a** was significantly different from that with *p*-TsO^-, and the NH signal of **3a** was split into two peaks (the difference of chemical shift: 19 Hz). The splitting indicates the formation of diastereomeric host–guest complexes [(+)-camph·(+)-**3a** and (+)-camph·(−)-**3a**]. The two peaks were crossed with each other before reaching an equilibrium state, suggesting the different K_a between the diastereomeric complexes of (+)-**3a** and (−)-**3a**. In the case of (±)-**3b** with (+)-camph, the H^a signal as well as H^b was split into two peaks (the difference of chemical shift: 17 Hz), but they were not crossed with each other.

Although complexes **4a** and **5a**, which showed small association constants with camphor-10-sulfonate, did not induce splitting of the NMR signals, **6**—**8d** with large association constants afforded similar titration curves to **3a**. The association constants between cobalticinium complexes **3**—**8** and camphorsulfonate are summarized in Table 2. The association constants of **6a** and **7a**, which have electron-donating or -withdrawing substituents on the anilide group, indicate almost no electric effects of the substituents on complexation with the anion.

A quantitative study was done to estimate the degree of chiral recognition. Enantiomeric pure (+)-**3a** was prepared from carboxylic acid (+)-**2a** by the method reported previously.[8b] The association constants for the complexation of (+)-**3a** with (+)-and (−)-camphorsulfonate were calculated by the ^{1}H NMR titration method in a 1 : 1 mixture of $CDCl_3/CD_3CN$ at 25 °C. The association constants K_a and K'_a, (K_a = [(+)-**3a**·(+)-camph]/[(+)-**3a**]·[(+)-camph]; K'_a = [(+)-**3a**·(−)-camph]/[(+)-**3a**]·[(−)-camph]), have been estimated to be 1900 and 1700 M^{-1}, respectively. Consequently cobalticinium complex (+)-**3a** is able to recognize the chirality of camphorsulfonate, though the ability of recognition is not high.

Table 2. Association Constants with Camphor-10-sulfonate (25 °C, $CDCl_3$)

Host-complex	K_a/M^{-1}
3a	1.8×10^4 b)
3b	1.1×10^4 b)
3c	1.9×10^3 b)
4a	6.1×10^2 a)
5a	5.8×10^3 a)
6a	1.8×10^4 b)
7a	2.5×10^4 b)
8d	1.7×10^4 b)

a) The value was calculated for H^a. b) The value was calculated for H^b.

In conclusion, we have studied the properties as an anion receptor based on poly-substituted cobalticinium complexes. These complexes, which have a hydrophobic cavity constructed by substituents on cyclopentadienyl ligands, are capable of receiving anions such as *p*-TsO^- and have potentials to recognize the chirality of guest anions. One of features of our cobalticinium anion receptor is to have a convertible function which may be appropriately designed for a binding site.

Experimental

All the reactions except for hydrolysis were done under an atmosphere of nitrogen or argon. Melting points are uncorrected. ^{1}H 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. Upfiled 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) or JEOL JMX-DX300 (FAB) spectrometer. Elemental analysis was done by using a Perkin–Elmer 240C. Optical rotatory powers were measured on a JASCO DIP-370 digital polarimeter. Solvents were dried in usual manners and distilled. Unless stated to the contrary, commercial grade chemicals were used without further purification. Trisubstituted cyclopentadienes and complexes **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** were prepared by the reported methods.[8b]

Synthesis of Ethylester Derivatives (1c, 1d). The reaction of $Co(acac)_2$ (2.62 g, 10 mmol) with 1 equimolar amount of C_5Me_5Li in THF (50 mL) at −78 °C afforded $C_5Me_5Co(acac)$. To this reaction mixture was added a solution of sodium 2-ethoxy-1-ethoxycarbonyl-4-phenylcyclopentadienide (Cp′Na) generated from Cp′H (2.58 g, 10 mmol) and NaH (60% in mineral oil; 0.44 g, 11 mmol) in THF (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 24 h, then was poured over 100 mL of 6 M hydrochloric acid. Ether (50 mL) was added

to the resulting solution, the aqueous layer was separated and then washed with ether to remove unreacted cyclopentadienes. To the aqueous solution dropwise addition of a saturated solution of ammonium hexafluorophosphate (4.89 g, 30 mmol) in water afforded compound **1c** as yellow precipitates. Recrystallization from MeOH gave pure **1c** as yellow powders in 30% yield (1.80 g).

1c: Mp 206.0—206.5 °C; IR (Nujol) 1740, 1240 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 7.70 (d, 2H, J = 7.2 Hz), 7.56—7.46 (m, 3H), 6.30 (d, 1H, J = 2.2 Hz), 5.51 (d, 1H, J = 1.9 Hz), 4.47—4.37 (m, 2H), 4.35—4.26 (m, 2H), 1.65 (s, 15H), 1.50 (t, 3H, J = 7.1 Hz), 1.45 (t, 3H, J = 7.1 Hz); Mass (EI) m/z 451 (M^+-PF_6). Found: C, 52.42; H, 5.41; P, 4.93; F, 19.03%. Calcd for $C_{26}H_{32}O_3CoPF_6$: C, 52.36; H, 5.41; P, 5.19; F, 19.11%.

Complex **1d** was prepared following the method for **1c** starting with 1-ethoxycarbonyl-2-methyl-4-naphthyl-1,3-cyclopentadiene.

1d: Orange powder (Yield 51%); mp 276.5—277.0 °C (decomp); IR (Nujol) 1725, 1255, and 1240 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.23 (s, 1H), 8.10—7.54 (m, 6H), 6.03 (d, 1H, J = 2.0 Hz), 5.89 (d, 1H, J = 2.0 Hz), 4.44 (dq, 2H, J = 7.2, 2.0 Hz), 2.25 (s, 3H), 1.61 (s, 15H), 1.49 (t, 3H, J = 7.1 Hz); Mass (EI) m/z 471 (M^+-PF_6). Found: C, 56.26; H, 5.03; P, 5.14; F, 18.74%. Calcd for $C_{29}H_{32}O_2CoPF_6$: C, 56.50; H, 5.23; P, 5.02; F, 18.49%.

Hydrolysis of 1c and 1d. Ethylester derivative **1c** (2.78 g, 4.7 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 yellow solids which were dissolved in 50 mL of hot water. Dropwise addition of ammonium hexafluorophosphate (3.83 g, 24 mmol) in water produced pale yellow precipitates, which were purified by recrystallization from EtOH. Orange needles (2.51 g) of carboxylic acid **2c** were obtained in 95% yield.

2c: Mp 196.0—197.0 °C (decomp); IR (Nujol) 1720 cm^{-1}; ^1H NMR (360 MHz, CD_3OD) δ = 7.77—7.75 (m, 2H), 7.58—7.53 (3H, m), 6.10 (d, 1H, J = 2.0 Hz), 6.97 (d, 1H, J = 2.0 Hz), 4.21 (q, 1H, J = 6.8 Hz), 4.19 (q, 1H, J = 7.0 Hz), 1.66 (s, 15H), 1.50 (t, 3H, J = 7.1 Hz); Mass (FAB) m/z 423 (M^+-PF_6). Found: C, 50.73; H, 4.91; P, 5.30; F, 20.09%. Calcd for $C_{24}H_{28}O_3CoPF_6$: C, 50.72; H, 4.97; P, 5.45; F, 20.06%.

The same treatment of **1d** gave **2d**, which was used for the next reaction without further purification.

2d: Orange powder (Yield 83%); mp 240.0—243.0 °C (decomp); IR (Nujol) 3700—3200, 1720 cm^{-1}; ^1H NMR (360 MHz, CD_3OD) δ = 8.32 (s, 1H), 8.05—7.59 (m, 6H), 6.21 (s, 1H), 5.96 (s, 1H), 2.29 (s, 3H), 1.66 (s, 15H).

Synthesis of Amide Derivatives. Carboxylic acid **2c** (0.57 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 resultant solid was dissolved in acetonitrile (20 mL). The solution was added to a solution of aniline (0.47 g, 5.0 mmol) in acetonitrile (10 mL). The mixture was stirred at room temperature overnight and the solvent was removed in vacuo. The crude product was dissolved in MeOH and ammonium hexafluorophosphate (0.49 g, 3.0 mmol) was added. Evaporation of MeOH and washing with water gave orange solids, which were purified by recrystallization from MeOH. Orange plates (0.52 g) were obtained in 82% yield.

3c: Orange plates (Yield 82%); mp 248.0—249.5 °C (decomp); IR (Nujol) 3380, 1680, and 1605 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 8.84 (s, 1H), 7.69—7.41 (m, 10H), 6.24 (d, 1H, J = 2.0 Hz), 5.69 (d, 1H, J = 1.8 Hz), 4.61—4.45 (m, 2H), 1.66 (s, 15H), 1.65 (t, 3H, J = 7.2 Hz); Mass (FAB) m/z 498 (M^+-PF_6) Found: C, 56.22; H, 4.89; N, 2.31; P, 4.60; F, 17.54%. Calcd for $C_{30}H_{33}NO_2CoPF_6$: C, 56.00; H, 5.17; N, 2.18; P, 4.81; F, 17.71%.

Anilide derivative **3d** was prepared following the method for **3c** starting with **2d**.

3d: Orange-red needles (Yield 56%); mp 260 °C (decomp); IR (Nujol) 1675, 1600, and 1535 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 8.85 (s, 1H), 8.29 (s, 1H), 8.13—7.13 (m, 11H), 6.72 (s, 1H), 5.24 (s, 1H), 2.11 (s, 3H), 1.54 (s, 15H); Mass (EI) m/z 471 (M^+-PF_6). Found: C, 60.04; H, 5.05; N, 2.33; P, 4.39; F, 16.98%. Calcd for $C_{33}H_{33}NOCoPF_6$: C, 59.74; H, 5.01; N, 2.11; P, 4.67; F, 17.18%.

N-Methylanilide derivative **4a** was prepared following the method for **3c** starting with **2a** and *N*-methylaniline.

4a: Yellow needles (Yield 72%); mp 274.0—275.0 °C (decomp); IR (Nujol) 1650, 1600 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 7.45—7.43 (m, 3H), 7.34—7.30 (m, 5H), 7.07 (d, 2H, J = 7.2 Hz), 5.50 (d, 1H, J = 1.6 Hz), 4.83 (d, 1H, J = 1.8 Hz), 3.48 (s, 3H), 2.05 (s, 3H), 1.66 (s, 15H); Mass (EI) m/z 482 (M^+-PF_6). Found: C, 57.25; H, 5.19; N, 2.31; P, 4.73; F, 18.29%. Calcd for $C_{30}H_{33}NOCoPF_6$: C, 57.42; H, 5.30; N, 2.23; P, 4.94; F, 18.17%.

N-Butyl amide derivative **5a** was prepared following the method for **3c** starting with **2a** and *N*-butyl amine.

5a: Orange plates (Yield 89%); mp 202.0—203.0 °C (decomp); IR (Nujol) 3445, 1670 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 7.64 (d, 2H, J = 6.5 Hz), 7.55—7.45 (m, 3H), 7.11 (s, 1H), 6.20 (d, 1H, J = 1.7 Hz), 5.19 (d, 1H, J = 1.7 Hz), 3.56—3.46 (m, 1H), 3.39—3.30 (s, 3H), 2.26 (s, 3H), 1.72—1.66 (m, 2H), 1.63 (s, 15H), 1.46—1.36 (m, 2H), 0.96 (t, 3H, J = 7.3 Hz); Mass (EI) m/z 448 (M^+-PF_6). Found: C, 54.70; H, 5.77; N, 2.14; P, 5.47; F, 19.06%. Calcd for $C_{27}H_{35}NOCoPF_6$: C, 54.64; H, 5.94; N, 2.36; P, 5.22; F, 19.21%.

3,4-Dimethoxyanilide derivative **6a** was prepared following the

Table 3. Experimental Parameters for the X-Ray Diffraction Study of (1*R*)-(+)-**3a**

Formula	$C_{29}H_{31}NOPF_6Co$
Molecular weight	613.47
Crystal data	
Crystal color, habit	Yellow, prismatic
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	17.346(2)
b/Å	19.965(2)
c/Å	8.131(2)
V/Å^3	2816.0(7)
Z	4
D_{calcd}/g cm^{-1}	1.447
Measurement	
Crystal size/mm	0.35×0.25×0.15
Radiation	Cu $K\alpha$ (1.54178 Å, Ni filtered)
No. of reflections	
independent	4463
used $F_o \geq 3\sigma \mid F_o \mid$	3344
Absorption	
μ/cm^{-1}	58.80
correction ψ scan	
correction factor	max 1.0
	min 0.70
Decay/I	No
Refimement	
R	0.045(0.117) [a]
R_w	0.054(0.154) [a]

a) Values in parentheses are for the enantiomer, (*S*)-**3a**.

method for **3c** starting with **2a** and 3,4-dimethoxyaniline.

6a: Orange needles (Yield 70%); mp 220.5—221.0 °C (decomp); IR (Nujol) 3425, 1680, and 1610 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 8.27 (s, 1H), 7.65—7.60 (m, 3H), 7.44—7.40 (m, 3H), 7.32 (d, 1H, J = 2.2 Hz), 6.86 (d, 1H, J = 8.8 Hz), 6.11 (s, 1H), 5.35 (s, 1H), 3.98 (s, 3H), 3.89 (s, 3H), 2.18 (s, 3H), 1.57 (s, 15H); Mass (EI) m/z 528 (M^+-PF_6). Found: C, 55.41; H, 5.06; N, 2.24; P, 4.84; F, 17.04%. Calcd for $C_{31}H_{35}NO_3CoPF_6$: C, 55.28; H, 5.24; N, 2.08; P, 4.60; F, 16.92%.

3,4-Difluoroanilide derivative **7a** was prepared following the method for **3c** starting with **2a** and 3,4-difluoroaniline.

7a: Orange needles (Yield 86%); mp 262.0—263.0 °C (decomp); IR (Nujol) 3420, 1695, and 1620 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 8.57 (s, 1H), 8.03—7.97 (m, 1H), 7.67 (d, 2H, J = 7.6 Hz), 7.50—7.47 (m, 4H), 7.18 (q, 1H), 6.28 (s, 1H), 5.31 (s, 1H), 2.24 (s, 3H), 1.61 (s, 15H); Mass (EI) m/z 504 (M^+-PF_6). Found: C, 53.38; H, 4.21; N, 2.07; P, 4.45; F, 23.42%. Calcd for $C_{29}H_{29}NOCoPF_6$: C, 53.63; H, 4.50; N, 2.16; P, 4.77; F, 23.40%.

3,4-Dimethoxyanilide derivative **8d** was prepared following the method for **3c** starting with **2d** and 4-aminoveratrole.

8d: Orange needles (Yield 54%); mp 269.0—272.0 °C (decomp); IR (Nujol) 3420, 1680, and 1600 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ = 8.28—6.87 (m, 11H), 6.25 (s, 1H), 5.34 (s, 1H), 4.02 (s, 3H), 3.92 (s, 3H), 2.12 (s, 3H), 1.55 (s, 15H); Mass (EI) m/z 578 (M^+-PF_6). Found: C, 57.93; H, 5.02; N, 1.93; P, 4.23; F, 15.51%. Calcd for $C_{35}H_{37}NO_3CoPF_6$: C, 58.10; H, 5.15; N, 1.94; P, 4.28; F, 15.75%.

General Procedure for NMR Titration and Determination of Association Constants. For an example, the titration experiment of anilide **3a** with *p*-toluenesulfonate is as follows. A 0.0022 M solution of **3a** in $CDCl_3$ (2.68 mg in 2 mL) was prepared in a 2 mL volumetric flask. 0.50 mL of the solution was taken into a 5 mm NMR tube. A 0.054 M solution of Et_4N^+p-TsO^- in $CDCl_3$ (32.3 mg in 2.00 mL) was prepared in a 2 mL volumetric flask. An initial NMR spectrum of the solution of **3a** was taken, and the initial chemical shifts both of the H^a and H^b were measured to be 6.29 and 8.49 ppm.[13] The solution of Et_4N^+p-TsO^- was then added, initially in 7 μL portions and the chemical shift of the protons was recorded after each addition. After 1 equimolar amount of guest was added, the sample size was increased to 10 μL. After a total of 41 μL had been added, the sample size was increased to 20 μL. The portions were added until no further change in the chemical shift of the protons was observed (usually 4—10 mol. amt.). The temperature of the NMR probe was 25 °C. The association constant

Table 4. Atomic Coordinates with Equivalent Isotropic Temperature Factors for (1*R*)-(+)-**3a**

Atom	x	y	z	B_{eq} [a]	Atom	x	y	z	B_{eq} [a]
Co(1)	0.28769(4)	0.29629(3)	0.43319(8)	4.18(1)	C(26)	0.5699(3)	0.3821(2)	1.0786(6)	6.1(1)
P(1)	0.49291(7)	0.15187(7)	0.8470(2)	5.77(3)	C(27)	0.5772(3)	0.4509(3)	1.0720(7)	6.9(1)
F(1)	0.4720(2)	0.2034(1)	0.9027(4)	8.11(8)	C(28)	0.5252(3)	0.4874(2)	0.9838(7)	6.6(1)
F(2)	0.4476(2)	0.1419(2)	0.6771(5)	10.4(1)	C(29)	0.4664(2)	0.4572(2)	0.9003(6)	5.6(1)
F(3)	0.4472(2)	0.0941(1)	0.9230(6)	11.8(1)	H(1)	0.4031	0.3055	0.8230	5.9095
F(4)	0.5571(2)	0.1045(2)	0.7867(5)	11.9(1)	H(2)	0.1329	0.2809	0.4701	5.2962
F(5)	0.5359(2)	0.1661(2)	1.0112(4)	9.07(9)	H(3)	0.3342	0.2321	0.7060	4.8301
F(6)	0.5358(2)	0.2136(2)	0.7667(4)	10.9(1)	H(4)	0.2072	0.4455	0.6187	8.0446
O(1)	0.3204(2)	0.4381(1)	0.7439(5)	6.76(9)	H(5)	0.1690	0.4220	0.4561	8.0446
N(1)	0.3982(2)	0.3526(2)	0.8249(5)	4.89(9)	H(6)	0.1262	0.4127	0.6220	8.0446
C(1)	0.2831(2)	0.3284(2)	0.6715(5)	4.49(10)	H(7)	0.1198	0.1713	0.3930	6.4789
C(2)	0.2115(2)	0.3449(2)	0.5897(5)	4.43(9)	H(8)	0.0934	0.0573	0.3544	8.2456
C(3)	0.1795(2)	0.2848(2)	0.5310(5)	4.47(10)	H(9)	0.1686	−0.0235	0.4798	8.0976
C(4)	0.2270(2)	0.2299(2)	0.5775(5)	3.92(9)	H(10)	0.2704	0.0084	0.6467	7.8415
C(5)	0.2920(2)	0.2569(2)	0.6620(5)	4.06(9)	H(11)	0.2966	0.1215	0.6946	6.1414
C(6)	0.3952(2)	0.2910(3)	0.3342(6)	6.4(1)	H(12)	0.4811	0.2339	0.4283	13.0228
C(7)	0.3620(3)	0.3550(3)	0.3031(6)	5.8(1)	H(13)	0.5104	0.3022	0.3626	13.0228
C(8)	0.2943(3)	0.3448(2)	0.2123(6)	5.6(1)	H(14)	0.4671	0.2986	0.5294	13.0228
C(9)	0.2845(3)	0.2746(3)	0.1882(5)	5.8(1)	H(15)	0.4380	0.4188	0.4090	11.6065
C(10)	0.3474(3)	0.2418(2)	0.2646(6)	6.1(1)	H(16)	0.4016	0.4482	0.2504	11.6065
C(11)	0.3357(2)	0.3780(2)	0.7479(6)	4.8(1)	H(17)	0.3543	0.4461	0.4123	11.6065
C(12)	0.1747(3)	0.4130(2)	0.5695(7)	6.5(1)	H(18)	0.2586	0.4409	0.1768	10.5748
C(13)	0.2116(2)	0.1577(2)	0.5485(5)	4.41(9)	H(19)	0.2400	0.3951	0.0279	10.5748
C(14)	0.1505(2)	0.1382(2)	0.4463(6)	5.4(1)	H(20)	0.1902	0.3909	0.1861	10.5748
C(15)	0.1352(3)	0.0704(2)	0.4233(7)	6.8(1)	H(21)	0.1881	0.2723	0.0531	12.1903
C(16)	0.1792(3)	0.0228(2)	0.4972(7)	6.8(1)	H(22)	0.2467	0.2173	0.0028	12.1903
C(17)	0.2393(3)	0.0416(2)	0.5959(7)	6.4(1)	H(23)	0.1981	0.2091	0.1618	12.1903
C(18)	0.2554(2)	0.1090(2)	0.6233(6)	5.1(1)	H(24)	0.3642	0.1536	0.3856	12.4212
C(19)	0.4699(3)	0.2801(4)	0.4214(8)	11.0(2)	H(25)	0.3221	0.1441	0.2189	12.4212
C(20)	0.3920(4)	0.4232(3)	0.3482(8)	10.2(2)	H(26)	0.4102	0.1575	0.2222	12.4212
C(21)	0.2405(3)	0.3986(3)	0.1449(7)	9.2(2)	H(27)	0.5057	0.3042	0.9980	6.5305
C(22)	0.2238(4)	0.2404(3)	0.0934(7)	9.8(2)	H(28)	0.6054	0.3560	1.1398	7.3349
C(23)	0.3633(4)	0.1669(3)	0.2732(8)	10.3(2)	H(29)	0.6178	0.4730	1.1285	8.2196
C(24)	0.4577(2)	0.3884(2)	0.9073(5)	4.5(1)	H(30)	0.5302	0.5348	0.9801	7.8156
C(25)	0.5104(2)	0.3514(2)	0.9954(6)	5.4(1)	H(31)	0.4313	0.4835	0.8373	6.9359

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

was obtained using Eqs. 1 and 2.[14] Here, x is the

$$K_a = x/([M]_0 - x)([A]_0 - x) \quad (1)$$

$$x = [M]_0(\Delta\delta/\Delta\delta c) \quad (2)$$

concentration of the 1 : 1 complex in the equilibrium, $[M]_0$ and $[A]_0$ are initial concentrations of **3a** and *p*-TsONEt$_4$, respectively, $\Delta\delta$ is the induced change in chemical shift of H^a or H^b proton signal, and $\Delta\delta c$ is the limiting shift, corresponding to the induced change after 100% complexation. From a series of measured $\Delta\delta$

$$\Delta\delta = [1/K_a + [M]_0 + [A]_0 - \{(1/K_a + [M]_0 + [A]_0)\}^2 - 4[M]_0[A]_0\}^{1/2}]\Delta\delta c/(2[M]_0)$$

together with known $[A]_0$ and $[M]_0$ values, the K_a could be calculated by nonlinear least-squares method (modified Newton–Gauss type). Eight different concentrations of $[A]_0$ were measured.

In the case of the titration of (+)-**3a** with (+) or (−)-camphor sulfonate, we did the experiment for 4 times (in $CDCl_3/CD_3CN$=1/1) and their average was adapted.

Preparation of Tetrabutylammonium (+)-(*S*)-Camphor-10-sulfonate. To a solution of (+)-(*S*)-camphor-10-sulfonic acid monohydrate 1.93 g (7.7 mmol) in water (50 mL) was added 1.0

Table 5. Selected Bond Distances (Å) and Bond Angles (°) in (1*R*)-(+)-**3a**

a) Bond distances				C(7)–C(6)–C(10)	107.7(6)	C(7)–C(6)–C(19)	123.6(7)
Co(1)–C(1)	2.041(6)	Co(1)–C(2)	2.071(5)	C(10)–C(6)–C(19)	128.7(7)	Co(1)–C(7)–C(6)	69.7(4)
Co(1)–C(3)	2.047(5)	Co(1)–C(4)	2.059(5)	Co(1)–C(7)–C(8)	69.5(4)	Co(1)–C(7)–C(20)	128.3(4)
Co(1)–C(5)	2.020(5)	Co(1)–C(6)	2.040(6)	C(6)–C(7)–C(8)	108.2(6)	C(6)–C(7)–C(20)	126.7(7)
Co(1)–C(7)	2.043(6)	Co(1)–C(8)	2.040(6)	C(1)–Co(1)–C(2)	40.8(2)	C(1)–Co(1)–C(3)	68.2(2)
Co(1)–C(9)	2.032(6)	Co(1)–C(10)	2.037(5)	C(1)–Co(1)–C(4)	69.0(2)	C(1)–Co(1)–C(5)	41.4(2)
P(1)–F(1)	1.536(4)	P(1)–F(2)	1.606(4)	C(1)–Co(1)–C(6)	109.7(2)	C(1)–Co(1)–C(7)	133.4(2)
P(1)–F(3)	1.605(5)	P(1)–F(4)	1.549(4)	C(1)–Co(1)–C(8)	172.7(3)	C(1)–Co(1)–C(9)	145.9(3)
P(1)–F(5)	1.559(4)	P(1)–F(6)	1.581(4)	C(1)–Co(1)–C(10)	115.4(3)	C(2)–Co(1)–C(3)	40.1(2)
O(1)–C(11)	1.230(6)	N(1)–C(11)	1.356(7)	C(2)–Co(1)–C(4)	68.3(2)	C(2)–Co(1)–C(5)	68.8(2)
N(1)–C(24)	1.412(6)	C(1)–C(2)	1.434(7)	C(2)–Co(1)–C(6)	116.9(2)	C(2)–Co(1)–C(7)	110.6(2)
C(1)–C(5)	1.436(7)	C(1)–C(11)	1.487(7)	C(2)–Co(1)–C(8)	133.0(3)	C(2)–Co(1)–C(9)	171.3(3)
C(2)–C(3)	1.410(6)	C(2)–C(12)	1.513(7)	C(2)–Co(1)–C(10)	148.1(3)	C(3)–Co(1)–C(4)	40.6(2)
C(3)–C(4)	1.423(7)	C(4)–C(5)	1.420(7)	C(3)–Co(1)–C(5)	68.3(2)	C(3)–Co(1)–C(6)	147.9(3)
C(4)–C(13)	1.483(7)	C(6)–C(7)	1.412(8)	C(3)–Co(1)–C(7)	116.3(2)	C(3)–Co(1)–C(8)	109.2(2)
C(6)–C(10)	1.421(8)	C(6)–C(19)	1.510(9)	C(3)–Co(1)–C(9)	131.9(3)	C(3)–Co(1)–C(10)	170.5(3)
C(7)–C(8)	1.423(8)	C(7)–C(20)	1.518(8)	C(4)–Co(1)–C(5)	40.7(2)	C(4)–Co(1)–C(6)	171.2(2)
C(8)–C(9)	1.421(9)	C(8)–C(21)	1.460(9)	C(4)–Co(1)–C(7)	146.5(2)	C(4)–Co(1)–C(8)	113.9(2)
C(9)–C(10)	1.402(9)	C(9)–C(22)	1.525(9)	C(4)–Co(1)–C(9)	107.4(2)	C(4)–Co(1)–C(10)	131.2(2)
C(10)–C(23)	1.484(8)	C(13)–C(14)	1.416(7)	C(5)–Co(1)–C(6)	132.7(2)	C(5)–Co(1)–C(7)	172.6(3)
C(13)–C(18)	1.368(7)	C(14)–C(15)	1.395(8)	C(5)–Co(1)–C(8)	144.9(2)	C(5)–Co(1)–C(9)	113.3(3)
C(15)–C(16)	1.370(9)	C(16)–C(17)	1.368(9)	C(5)–Co(1)–C(10)	108.1(2)	C(6)–Co(1)–C(7)	40.5(2)
C(17)–C(18)	1.389(7)	C(24)–C(25)	1.384(7)	C(6)–Co(1)–C(8)	68.5(3)	C(6)–Co(1)–C(9)	68.4(2)
C(24)–C(29)	1.385(7)	C(25)–C(26)	1.379(7)	C(6)–Co(1)–C(10)	40.8(2)	C(7)–Co(1)–C(8)	40.8(2)
C(26)–C(27)	1.379(8)	C(27)–C(28)	1.359(8)	C(7)–Co(1)–C(9)	68.5(3)	C(7)–Co(1)–C(10)	68.2(2)
C(28)–C(29)	1.380(8)			C(8)–Co(1)–C(9)	40.8(3)	C(8)–Co(1)–C(10)	68.3(3)
				C(9)–Co(1)–C(10)	40.3(3)	F(1)–P(1)–F(2)	89.6(2)
b) Bond angles				F(1)–P(1)–F(3)	89.6(3)	F(1)–P(1)–F(4)	93.0(3)
F(1)–P(1) –F(5)	92.6(3)	F(1)–P(1)–F(6)	176.8(3)	C(8)–C(7)–C(20)	125.1(7)	Co(1)–C(8)–C(7)	69.7(4)
F(2)–P(1)–F(3)	88.2(2)	F(2)–P(1)–F(4)	177.2(3)	Co(1)–C(8)–C(9)	69.3(4)	Co(1)–C(8)–C(21)	129.2(4)
F(2)–P(1)–F(5)	89.2(2)	F(2)–P(1)–F(6)	87.6(2)	C(7)–C(8)–C(9)	107.5(6)	C(7)–C(8)–C(21)	128.3(7)
F(3)–P(1)–F(4)	90.6(3)	F(3)–P(1)–F(5)	176.6(3)	C(9)–C(8)–C(21)	124.1(7)	Co(1)–C(9)–C(8)	69.9(3)
F(3)–P(1)–F(6)	88.8(3)	F(4)–P(1)–F(5)	91.8(3)	Co(1)–C(9)–C(10)	70.0(4)	Co(1)–C(9)–C(22)	126.1(5)
F(4)–P(1)–F(6)	89.8(3)	F(5)–P(1)–F(6)	88.8(3)	C(8)–C(9)–C(10)	108.2(6)	C(8)–C(9)–C(22)	128.3(8)
C(11)–N(1)–C(24)	127.5(5)	Co(1)–C(1)–C(2)	70.7(3)	C(10)–C(9)–C(22)	123.5(8)	Co(1)–C(10)–C(6)	69.7(3)
Co(1)–C(1)–C(5)	68.5(3)	Co(1)–C(1)–C(11)	125.6(4)	Co(1)–C(10)–C(9)	69.7(3)	Co(1)–C(10)–C(23)	127.9(5)
C(2)–C(1)–C(5)	107.3(5)	C(2)–C(1)–C(11)	124.7(5)	C(6)–C(10)–C(9)	108.4(6)	C(6)–C(10)–C(23)	124.6(8)
C(5)–C(1)–C(11)	128.0(6)	Co(1)–C(2)–C(1)	68.5(3)	C(9)–C(10)–C(23)	126.9(7)	O(1)–C(11)–N(1)	123.6(5)
Co(1)–C(2)–C(3)	69.1(3)	Co(1)–C(2)–C(12)	128.6(4)	O(1)–C(11)–C(1)	120.1(5)	N(1)–C(11)–C(1)	116.3(5)
C(1)–C(2)–C(3)	107.4(5)	C(1)–C(2)–C(12)	128.5(5)	C(4)–C(13)–C(14)	119.4(5)	C(4)–C(13)–C(18)	121.6(5)
C(3)–C(2)–C(12)	124.1(5)	Co(1)–C(3)–C(2)	70.9(3)	C(14)–C(13)–C(18)	119.0(5)	C(13)–C(14)–C(15)	119.5(6)
Co(1)–C(3)–C(4)	70.2(3)	C(2)–C(3)–C(4)	109.7(4)	C(14)–C(15)–C(16)	120.1(6)	C(15)–C(16)–C(17)	120.4(6)
Co(1)–C(4)–C(3)	69.3(3)	Co(1)–C(4)–C(5)	68.1(3)	C(16)–C(17)–C(18)	120.5(6)	C(13)–C(18)–C(17)	120.5(5)
Co(1)–C(4)–C(13)	128.8(4)	C(3)–C(4)–C(5)	106.8(4)	N(1)–C(24)–C(25)	117.3(5)	N(1)–C(24)–C(29)	124.2(5)
C(3)–C(4)–C(13)	127.3(5)	C(5)–C(4)–C(13)	125.9(5)	C(25)–C(24)–C(29)	118.5(5)	C(24)–C(25)–C(26)	121.4(5)
Co(1)–C(5)–C(1)	70.1(3)	Co(1)–C(5)–C(4)	71.1(3)	C(25)–C(26)–C(27)	119.4(6)	C(26)–C(27)–C(28)	119.5(6)
C(1)–C(5)–C(4)	108.7(5)	Co(1)–C(6)–C(7)	69.9(3)	C(27)–C(28)–C(29)	121.8(6)	C(24)–C(29)–C(28)	119.5(6)
Co(1)–C(6)–C(10)	69.5(3)	Co(1)–C(6)–C(19)	128.0(5)				

equimolar amount of a 40% water solution of tetrabutylammonium hydroxide (5.00 g). The resulting mixture was stirred for 30 min at room temperature. The solvent was evaporated in vacuo, and the resulting solid was recrystallized from hexane-ethyl acetate. Colorless needles (3.03 g) were obtained in 83% yield.

Mp 133.0—134.0 °C; IR (Nujol) 1740 cm^{-1}; ^1HNMR (270 MHz, $CDCl_3$) δ=3.35—3.27 (m, 8H), 2.91—0.91 (m, 9H), 1.72—1.61 (m, 8H), 1.45 (q, 8H, J=7.3 Hz), 1.14 (s, 3H), 1.01 (t, 12H, J=7.3 Hz), 0.83 (s, 3H); $[\alpha]_D^{15}$=+25.1° ($CHCl_3$, c 1.19). Found: C, 65.68; H, 10.73; N, 2.76; S, 6.65%. Calcd for $C_{26}H_{51}NO_4S$: C, 65.92; H, 10.85 N, 2.96; S, 6.77%.

Similarly tetrabutylammonium (−)-(*R*)-camphor-10-sulfonate was prepared in 86% yield.

Mp 134.5—135.0 °C; $[\alpha]_D^{25}$=−25.1° ($CHCl_3$, c 1.08). Found: C, 66.10; H, 10.81; N, 2.76; S, 6.58%. Calcd for $C_{26}H_{51}NO_4S$: C, 65.92; H, 10.85 N, 2.96; S, 6.77%.

X-Ray Crystallographic Analysis for (+)-3a. Enantiomeric complex (+)-**3a** was prepared following the method for **3c** from starting with (+)-**2a**. (+)-**3a** gave the same IR, ^1HNMR, and mass spectral data as the racemic isomers.[8b)]

(+)-3a: Orange needles (Yield 86%), mp 280.5—282.0 °C (decomp); $[\alpha]_D^{25}$=+47.5° (MeOH, c 0.390). Found: C, 56.73; H, 5.30; N, 2.18; P, 5.00; F, 18.52%. Calcd for $C_{29}H_{31}ONCoPF_6$: C, 56.78; H, 5.09; N, 2.28; P, 5.05; F, 18.58%.

The experimental conditions and the summary of structure analysis are shown in Table 3. For (+)-**3a**, X-ray diffraction date was collected on a Rigaku AFC5R four-circle diffractometer. The structure was solved by heavy-atom Patterson methods (SAPI 91). Hydrogen atoms were placed in appropriate trigonal or tetrahedral positions. All calculations were done using the teXsan crystallographic software package of Molecular Structure Corporation. Fractional coordinates are listed in Table 4 and bond distances and angles in Table 5.[15)] Additional data, including anisotropic temperature factors are available from the authors.

This work is supported by Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture. The authors are grateful to the JSPS Fellowship for Japan Junior Scientists to N. K.

References

1) a) A. Galán, D. Andreu, A. M. Echavarren, P. Prodos, and J. de Mendoza, *J. Am. Chem. Soc.*, **114**, 1511 (1992); b) K. Konishi, K. Yahara, H. Toshishige, T. Aida, and S. Inoue, *J. Am. Chem. Soc.*, **116**, 1337 (1994); c) S. Arimori, H. Murakami, M. Takeuchi, and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, **1995**, 961.

2) H. -J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **30**, 1417 (1991).

3) a) M. E. Jung and H. Xia, *Tetrahedron Lett.*, **29**, 297 (1988); b) X. Yang, Z. Zheng, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **115**, 193 (1993).

4) F. P. Schmidtchen, *Angew. Chem., Int. Ed. Engl.*, **16**, 720 (1977).

5) G. De Santis, L. Fabbrizzi, M. Licchelli, P. Pallavicini, and A. Perotti, *J. Chem. Soc., Dalton Trans.*, **1992**, 3283.

6) P. D. Beer, C. Hazlewood, D. Hesek, J. Hodacova, and S. E. Stokes, *J. Chem. Soc., Dalton Trans.*, **1993**, 1327.

7) a) N. E. Murr and E. Laviron, *Can. J. Chem.*, **54**, 3357 (1976); b) R. Boese, D. Bläser, R. L. Halterman, and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, **27**, 553 (1988).

8) a) M. Uno, N. Komatsuzaki, K. Shirai, and S. Takahashi, *J. Organomet. Chem.*, **462**, 343 (1993); b) N. Komatsuzaki, M. Uno, K. Shirai, T. Tanaka, M. Sawada, and S. Takahashi, *J. Organomet. Chem.*, **498**, 53 (1995).

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

10) M. Uno, K. Ando, N. Komatsuzaki, T. Tsuda, T. Tanaka, M. Sawada, and S. Takahashi, *J. Organomet. Chem.*, **462**, 303 (1993).

11) a) P. D. Beer, D. Hesek, J. Hodacova, and S. E. Stokes, *J. Chem. Soc., Chem. Commun.*, **1992**, 270; b) P. D. Beer, M. G. B. Drew, C. Hazlewood, D. Hesek, J. Hodacova, and S. E. Stokes, *J. Chem. Soc., Chem. Commun.*, **1993**, 229; c) P. D. Beer and A. R. Graydon, *J. Organomet. Chem.*, **466**, 241 (1994).

12) "International Tables for X-Ray Crystallography," Kynoch Press, Birminham (1974), Vol. 4, p. 149.

13) Control studies indicated that in the absence of binding partner, the chemical shifts of H^a and H^b were not dependent on the concentration.

14) a) M. Sawada, Y. Okumura, M. Shizuma, Y. Takai, Y. Hidaka, H. Yamada, T. Tanaka, T. Kaneda, K. Hirose, S. Misumi, and S. Takahashi, *J. Am. Chem. Soc.*, **115**, 7381 (1993); b) F. Diederich, *Angew. Chem., Int. Ed. Engl.*, **27**, 362 (1988); c) H. Tsukube and H. Sohmiya, *J. Org. Chem.*, **56**, 875 (1991).

15) The complete $F_o - F_c$ data are deposited as Document No. 69002 at the Office of the Editor of Bull. Chem. Soc. Jpn.