

Synthesis and Properties of Planar-Chiral (η^6-Benzene)(η^5-cyclopentadienyl)ruthenium(II) Complexes in an Optically Pure Form

Yuji Matsushima, Nobuko Komatsuzaki, Yoshiki Ajioka, Mari Yamamoto, Hidetomo Kikuchi, Yasuyuki Takata, Noriko Dodo, Kiyotaka Onitsuka, Mitsunari Uno, and Shigetoshi Takahashi*

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047

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Planar-chiral cyclopentadienylruthenium complexes [Ru(η^5-1-CO_2R^*-2-Me-4-$R^1C_5H_2$)(η^6-C_6H_6)][X] (**4** and **8**) (R^* = (*l*)- or (*d*)-menthyl; R^1 = Me, Ph, *t*-Bu, 2-Naphthyl, or 4-BrC_6H_4; X = PF_6 or BPh_4) were synthesized in a diastereomerically pure form. The absolute configuration of **8b** and **4c** (R^1 = Ph, *t*-Bu) were determined by an X-ray crystallographic analysis and those of the others were assigned on the basis of their optical properties including their CD spectra. Enantiopure complexes (S_{C1})-[Ru(η^5-1-CONHBu^t-2-Me-4-$R^1C_5H_2$)(η^6-C_6H_6)][PF_6] **9** and -[Ru(η^5-1-CONHBu^t-2-Me-4-$R^1C_5H_2$)(η^6-C_6H_6)] [BPh_4] **10**, and (R_{C1})-**9** and -**10** were prepared from direct hydrolysis of diastereomeric complexes, followed by the reaction of amines. Replacement reactions of the bromo group in **9e** (R^1 = 4-BrC_6H_4) gave alkyl, phenyl, and ethynyl derivatives. Complexes [Ru(η^5-1-CO_2Et-2-Me-4-$R^1C_5H_2$)(η^6-C_6H_6)][PF_6] **6** were also transformed to planar-chiral [Ru(η^5-1-CO_2Et-2-Me-4-$R^1C_5H_2$)($CH_3CN)_3$][X], which underwent ligand exchange reactions to afford carbonyl, phosphine, and π-arene complexes.

The chemistry of chiral organometallic complexes is attracting increasing interest, particularly in organic syntheses and in materials science. There are three types of chiral organometallic complexes[1]: one bearing chiral ligands and others containing a metal-centered chirality or a planar chirality. Most of known chiral organometallic complexes belong to the former category and bear chiral phosphine and amine ligands, whereas relatively few examples have been known so far for the latter two types of chiral complexes. Planar chirality arises from the π-coordination of prochiral ligands such as unsymmetrically substituted cyclopentadienyls,[2] arenes,[3] and olefins,[4] and is thus characteristic of organometallic π-complexes. Currently several efforts have been made to facilitate the syntheses of planar-chiral cyclopentadienyl metal complexes in terms of their potentials as mediators or catalysts in asymmetric organic syntheses.[2] Planar-chiral cyclopentadienyl metal complexes have advantages in use as a catalyst since coordination of a cyclopentadienyl ligand to a metal atom is generally so strong that there is almost no chance of ligand dissociation resulting in racemization. In fact planar-chiral cyclopentadienyl-group 4 metal complexes are successfully used as catalysts in asymmetric organic syntheses and stereoregular polymerizations.[5] However, there are few examples of planar-chiral cyclopentadienyl complexes of late transition metals except for planar-chiral ferrocene,[6] ruthenocene,[7] and their derivatives, which are extremely stable. Recently we have found a new method for the synthesis of planar-chiral (η^5-cyclopentadienyl)iron,[8] -cobalt,[9] and -rhodium.[10] Now we apply our method with modification to the synthesis of ruthenium analogs, planar-chiral (η^5-cyclopentadienyl)ruthenium(II) complexes. The complexes, [Ru(η^5-Cp′)(η^6-benzene)]$^+$, are easily transformed to [Ru(η^5-Cp′)($CH_3CN)_3$]$^+$ by a photoreaction with acetonitrile,[11] which may be a precursor for a coordinatively unsaturated Cp′Ru$^+$ species possessing a planar chirality. Since several reports have revealed the novel reactivity and catalysis of ruthenium complexes,[12] new types of chiral ruthenium complexes are of special interest as catalysts for asymmetric organic syntheses. Here we wish to report# the convenient and useful synthesis of planar-chiral [Ru(η^5-Cp′)(η^6-benzene)]$^+$[X]$^-$ in an optically pure form.

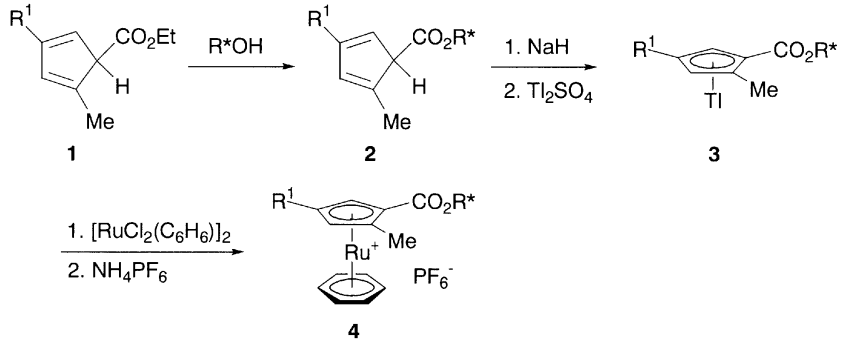
Results and Discussion

Although some preparative methods for *ligand-chiral* cyclopentadienyl-ruthenium complexes are already known,[13] no general methods have appeared in the literature so far for the synthesis of enantiopure planar-chiral cyclopentadienyl-ruthenium complexes, except ruthenocene derivatives.[7] Previously we showed a new method for the synthesis of planar-chiral cyclopentadienyl-metal complexes by use of 1,2,4-trisubstituted cyclopentadienes **2** bearing a removable chiral auxiliary like an (*l*)-menthyl group. By essentially the same procedure as utilized for the preparation[9] of planar-chiral cyclopentadienyl cobalt complexes, [Ru(η^5-Cp′)(η^6-benzene)]$^+$[PF_6]$^-$ (**4a**), was prepared by use of 1-(*l*)-menthyloxycarbonyl-2,4-dimethylcyclopentadiene **2a** as a 1 : 1 mixture of diastereomers (Synthetic Route A in Scheme 1).

Separation of **4a** into a pair of diastereomers **4a-1** and **4a-2** was successfully performed by fractional recrystallization

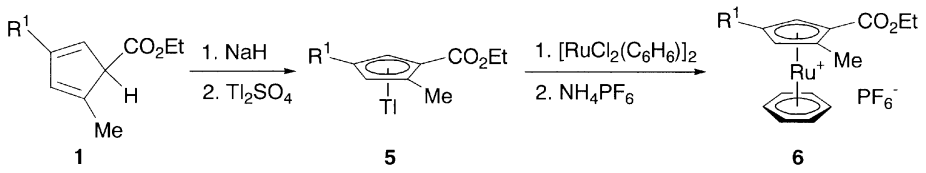
A preliminary result has already communicated in Ref. 14.

Synthetic Route A

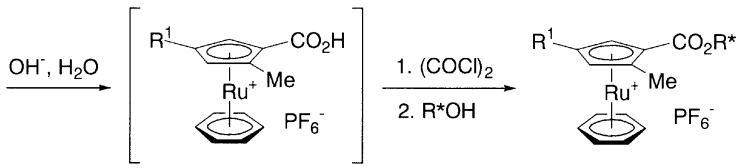


(**4a**: R^1 = Me; R* = (*l*)-menthyl)

Synthetic Route B



6a: R^1 = Me, 67 %
6b: R^1 = Ph, 73%
6c: R^1 = t-Bu, 45%
6d: R^1 = 2-Naphthyl, 72%
6e: R^1 = 4-BrC_6H_4, 58%



4 (R* = (*l*)-menthyl)
4' (R* = (*d*)-menthyl)

4a: R^1 = Me, 49%
4b: R^1 = Ph, 76%
4c: R^1 = t-Bu, 72%
4d: R^1 = 2-Naphthyl, 70 %
4e: R^1 = 4-BrC_6H_4, 76%

4'b: R^1 = Ph, 74%
4'c: R1 = t-Bu, 71%
4'e: R^1 = 4-BrC_6H_4, 73%

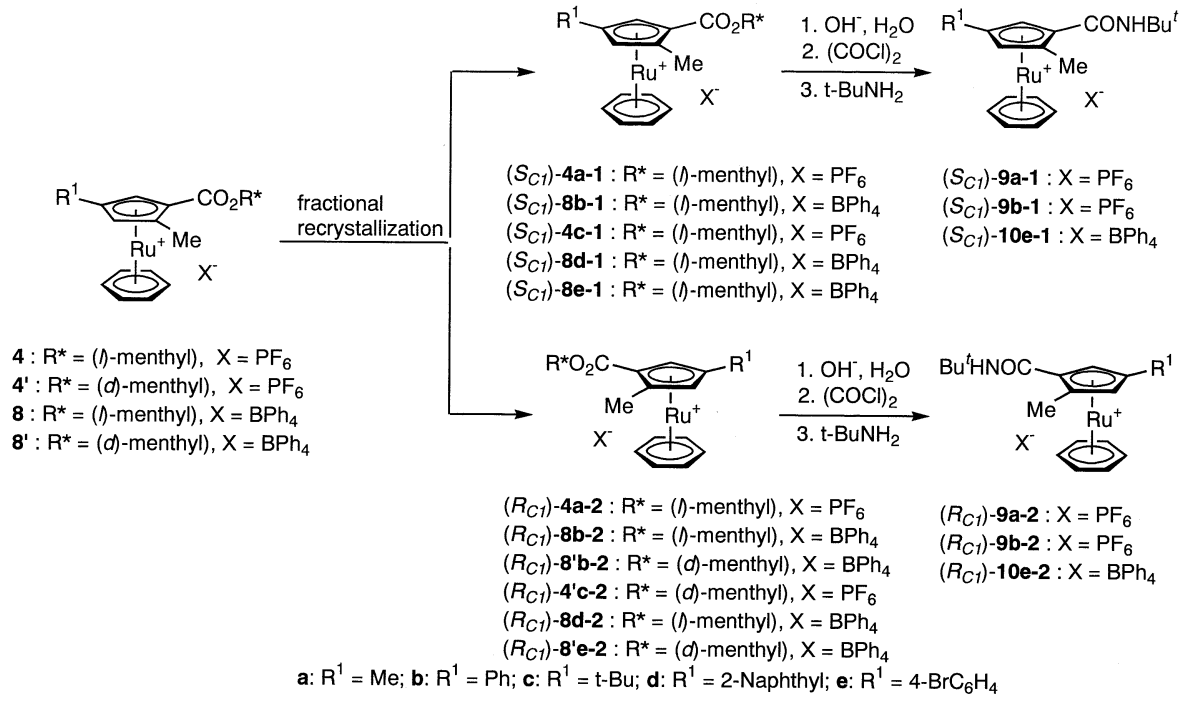
Scheme 1.

from EtOH/H_2O.[14] Diastereopure complexes **4a-1** and **4a-2** were isolated as hexafluorophosphate and characterized by spectroscopic analyses including mass spectra (See Experimental Section). The absolute configuration of **4a-1** was established to be S_{Cl}[##] on the basis of the absolute structure of the (*l*)-menthyl group by an X-ray crystallographic method.[14]

To obtain planar-chiral ruthenium complexes in an enantiomerically pure form, we attempted to remove the chiral auxiliary on the cyclopentadienyl ligand from **4a**, and successfully found that direct hydrolysis of the ester group in cationic complexes **4a** under basic conditions gave carboxylic acid **7a**. Treatment of **7a** with oxalyl chloride and then with *t*-butylamine gave enantiopure amide derivative **9a-1** (R = *t*-Bu) (Scheme 2). Similarly, enantiopure R_{Cl} isomer **9a-2** (R = *t*-Bu) was prepared from **4a-2**. Complexes **9a-1** and **9a-2** were confirmed to be a pair of enantiomers by melting points and by optical rotatory powers (Table 1) as well as by circular dichroism (CD) spectra.

It should be noted that the ester group on cyclopentadienyl ligand in cationic cyclopentadienylruthenium complex **4a** undergoes hydrolysis to give carboxylic acid **7a** without any decomposition, although an attempt to prepare cyclopentadienecarboxylic acid from free alkoxycarbonylcyclopentadiene **1** by hydrolysis resulted in failure and **1** decomposed to form no definite products under the hydrolysis conditions. The hydrolysis of **4a** to a carboxylic acid, followed by transformation to an acid chloride and then re-esterification with an appropriate al-

##The representation of planar chirality is based on the absolute cofiguration of the 1-position of cyclopentadienyl ligand.



Scheme 2.

Table 1. Optical Rotation and Melting Point of Ruthenium Complexes

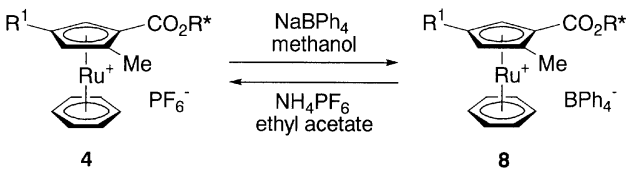
Complex	$[\alpha]_D^{20}$/°	Melting point/°C
S_{C1}-**4a-1**	+3.00 (*c* 0.222)[a]	209.5–210.5
R_{C1}-**4a-2**	−54.7 (*c* 0.220)[a]	175.0–175.5
S_{C1}-**8b-1**	−17.0 (*c* 0.252)[a]	178.0–179.0
R_{C1}-**8b-2**	−1.00 (*c* 0.279)[a]	186.0–187.0
R_{C1}-**8′b-2**	+17.3 (*c* 0.244)[a]	178.0–179.0
S_{C1}-**4c-1**	−43.4 (*c* 0.445)[b]	244.0–245.0
R_{C1}-**4′c-2**	+43.4 (*c* 0.453)[b]	244.0–245.0
S_{C1}-**8d-1**	−21.6 (*c* 0.534)[b]	189.0–189.5
R_{C1}-**8d-2**	−1.25 (*c* 0.583)[b]	120.5–121.5
S_{C1}-**8e-1**	−27.8 (*c* 0.404)[b]	122.0–122.5
R_{C1}-**8′e-2**	+27.3 (*c* 0.524)[b]	122.0–122.5
S_{C1}-**9a-1**	−41.6 (*c* 0.327)[b]	197.0–197.5
R_{C1}-**9a-2**	+42.3 (*c* 0.329)[b]	197.0–197.5
S_{C1}-**9b-1**	−29.0 (*c* 0.381)[b]	225.0–225.5
R_{C1}-**9b-2**	+28.9 (*c* 0.397)[b]	225.0–225.5
S_{C1}-**10e-1**	−22.0 (*c* 0.450)[b]	203.0–206.0[c]
R_{C1}-**10e-2**	+22.0 (*c* 0.514)[b]	202.0–206.0[c]

a) In chloroform. b) In acetonitrile. c) Decomposition point.

cohol, provides us an alternative and convenient method for the synthesis of various planar-chiral cyclopentadienylruthenium complexes. Thus, a racemic mixture of planar-chiral (η^6-benzene)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium hexafluorophosphate **6a**, which was prepared directly from cyclopentadiene **1a**, was easily transformed into a mixture of diastereomers (η^6-benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2,4-dimethylcyclopentadienyl]ruthenium hexafluorophosphate **4a** by hydrolysis in aqueous acetonitrile under basic conditions at 80 °C, followed by esterification with (*l*)-menthol (Synthetic Route B in Scheme 1).

The trisubstituted cyclopentadienyl ligands have advantages in that they can modulate their steric and electronic properties by varying the substituents on the ligand. We prepared 1,2,4-trisubstituted cyclopentadienes having phenyl (**1b**), *t*-butyl (**1c**), 2-naphthyl (**1d**), and 4-bromophenyl (**1e**) groups at the 4-position of cyclopentadienyl ligand.[15] Such use leads to the synthesis of planar-chiral cyclopentadienylruthenium complexes bearing a variety of substituents on the cyclopentadienyl ligand. Thus, 1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadiene **1b** was converted to racemic (η^6-benzene)(η^5-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)ruthenium hexafluorophosphate **6b** in 73% yield according to the reaction in Scheme 1. Hydrolysis of **6b**, followed by transformation to acid chloride and then by esterification with (*l*)-menthol, afforded a mixture of diastereomers **4b** in 76% yield. Some attempts to separate the mixture into a pair of diastereomers **4b-1** and **4b-2** by fractional recrystallization failed. As the solubility and crystallinity of cationic complexes depend on the kind of anions, the counter anion, PF_6^-, in **4b** was replaced for BPh_4^- by treatment with $NaBPh_4$ in methanol (Scheme 3).

Fortunately the tetraphenylborate complexes **8b** were successfully separated into a pair of diastereomers **8b-1** and **8b-2** by fractional recrystallization from ethyl acetate (Scheme 2). Diastereomer **8b-1** was obtained in 48% yield, whereas **8b-2** was isolated in a lower yield (7%), since the latter is much



Scheme 3.

more soluble in ethyl acetate. As mentioned below, the absolute configuration of **8b-1** has been established to be an S_{C1} configuration. To obtain more efficiently a planar-chiral complex possessing an R_{C1} configuration, we prepared (η^6-benzene)[η^5-1-(*d*)-menthyloxycarbonyl-2-methyl-4-phenylcyclopentadienyl]ruthenium tetraphenylborate **8′b** from **6b** by use of (*d*)-menthol. Fractional recrystallization of **8′b** from ethyl acetate gave diastereomer **8′b-2** in a higher isolated yield. The physical data on **8b** and **8′b** are shown in Table 1. The CD spectra of **8b-1** and **8′b-2** exhibited mirror-symmetry, clearly indicating that they are a pair of enantiomers (Fig. 1).

The absolute configuration around Cp′-Ru of **8b-1** has been established to be S_{C1} on the basis of the absolute structure of the (*l*)-menthyl group by an X-ray crystallographic analysis. Figure 2 depicts an ORTEP drawing of the molecular structure of **8b-1**. The bond distances and angles found in **8b-1** are very similar to those found in **4a-1**[14] and [(CpRu)$_2$(η^6,η^6-dibenzo-*p*-quinodimethane)][PF_6]$_2$.[16] The absolute configuration of **8b-2**, therefore, should be R_{C1}.

Similarly, planar-chiral cyclopentadienylruthenium complexes **4c**, **4d**, and **4e** were also synthesized starting from cyclopentadienes **1c**, **1d**, and **1e**, respectively, and separated into respective pairs of diastereomers **4c-1** and **4′c-2**, **8d-1** and **8d-2**, and **8e-1** and **8′e-2** by fractional recrystallization. Especially, the planar-chiral complex **4c-1** (R = *t*-Bu) was obtained in a high yield (82%) simply by recrystallization from ethanol. Their physical data are listed in Table 1, and the CD spectra are shown in Fig. 3. Fortunately, we could obtain good single crystals of **4c-1** by recrystallization from ethanol, and X-ray crystallographic analysis has established the absolute configuration of **4c-1**. The ORTEP diagram (Fig. 4) reveals that the absolute configuration around Cp′-Ru of **4c-1** is S_{C1}. CD spectra of enantiomers **4c-1** and **4′c-2** resemble those of diastereomers **4a-1** and **4a-2**, respectively, indicating that the CD spectra reflect the absolute configuration around Cp′-Ru.[14] Although we have not yet established the absolute configurations of diastereomers other than **4a**, **8b**, and **4c** by a crystallographic method, the similarity in CD spectra of the complexes suggests their absolute configurations. Thus, the CD spectra of **8d-1** and **8e-1** closely resemble that of **8b-1**, suggesting an S_{C1} configuration, whereas an R_{C1} configuration may be assigned for **8d-2** and **8′e-2**.

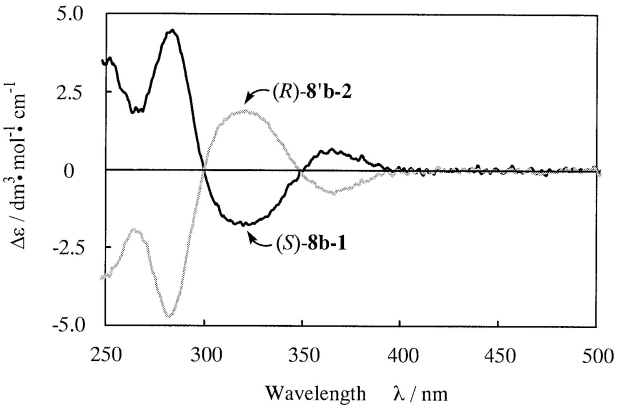


Fig. 1. CD spectra of ruthenium complexes **8b-1** and **8′b-2**.

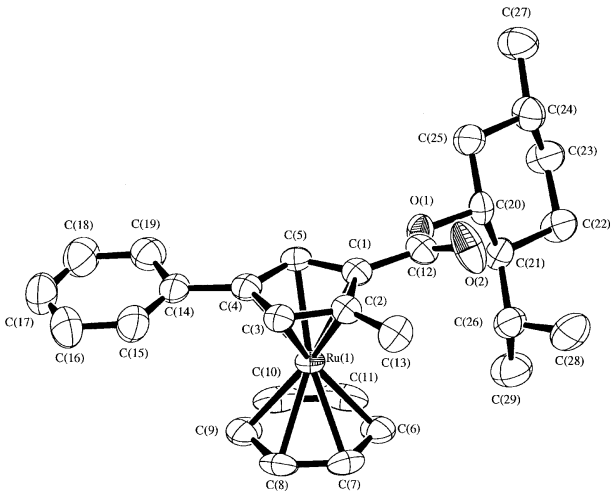


Fig. 2. ORTEP drawing of ruthenium complex S_{C1}-**8b-1**. Hydrogen atoms and a counter anion are omitted for clarity.

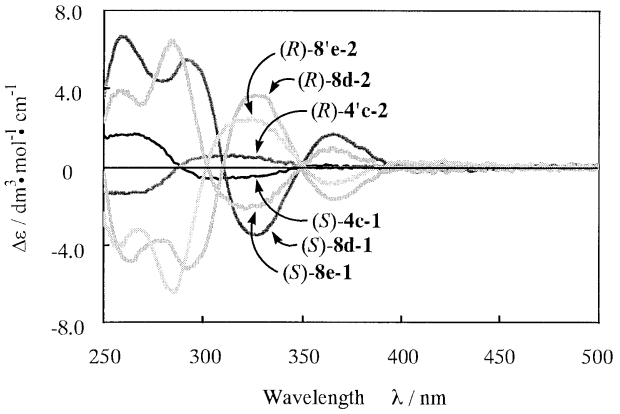


Fig. 3. CD spectra of ruthenium complexes **4c**, **8d**, and **8e**.

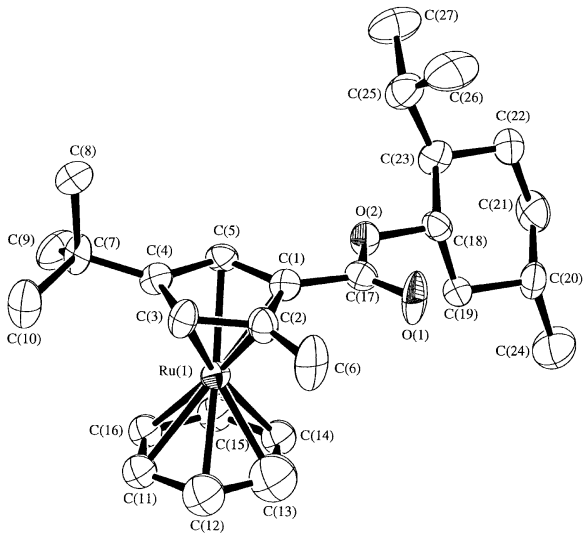


Fig. 4. ORTEP drawing of ruthenium complex S_{C1}-**4c-1**. Hydrogen atoms, a counter anion and the disordered η^6-benzene group with low occupancy are omitted for clarity.

Hydrolysis of diastereomers **8b-1**, **8b-2**, **8e-1**, and **8′e-2**, followed by treatment with oxalyl chloride and then with *t*-butylamine, afforded pairs of enantiopure amide derivatives **9b-1** and **9b-2**, and **10e-1** and **10e-2**, respectively, in good yields (Scheme 2). Their optical data are shown in Table 1, and the CD spectra in Fig. 5. These data give us the valuable information that, simply on the basis of the optical rotation as well as CD spectrum, we may predict the absolute configuration of planar-chiral 4-phenylcyclopentadienylruthenium complexes; that is, a positive optical rotation suggests an R_{C1} configuration of the complexes, whereas a negative one may be assigned to an S_{C1} configuration.

Diastereomers **4e** and enantiomers **8e** serve as useful starting materials for the further variations of planar-chiral cyclopentadienylruthenium complexes, because **4e** and **8e** have an exchangeable bromo group on the ligand. For example, **8e** was at first transformed to an amido derivative (**9e**), since the ester group of **8e** possibly undergoes hydrolysis in the presence of water under basic conditions. Then, treatments of **9e** with alkyllithium,[17] phenylboronic acid,[18] and trimethylsilylacetylene[19] in the presence of a palladium catalyst gave complexes **11**, **12**, and **13**, respectively, which carry alkylphenyl, biphenylyl, and (trimethylsilylethynyl)phenyl groups on the cyclopentadienyl ligand (Scheme 4).

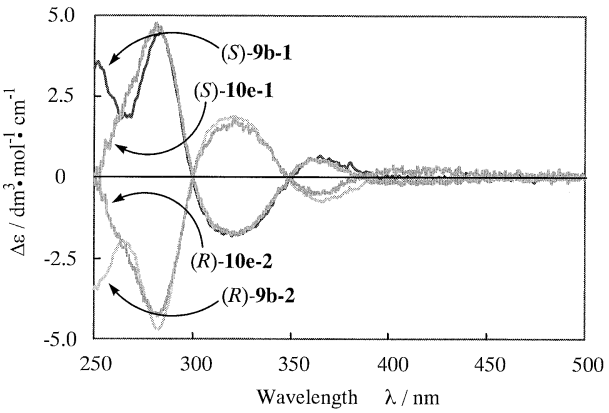
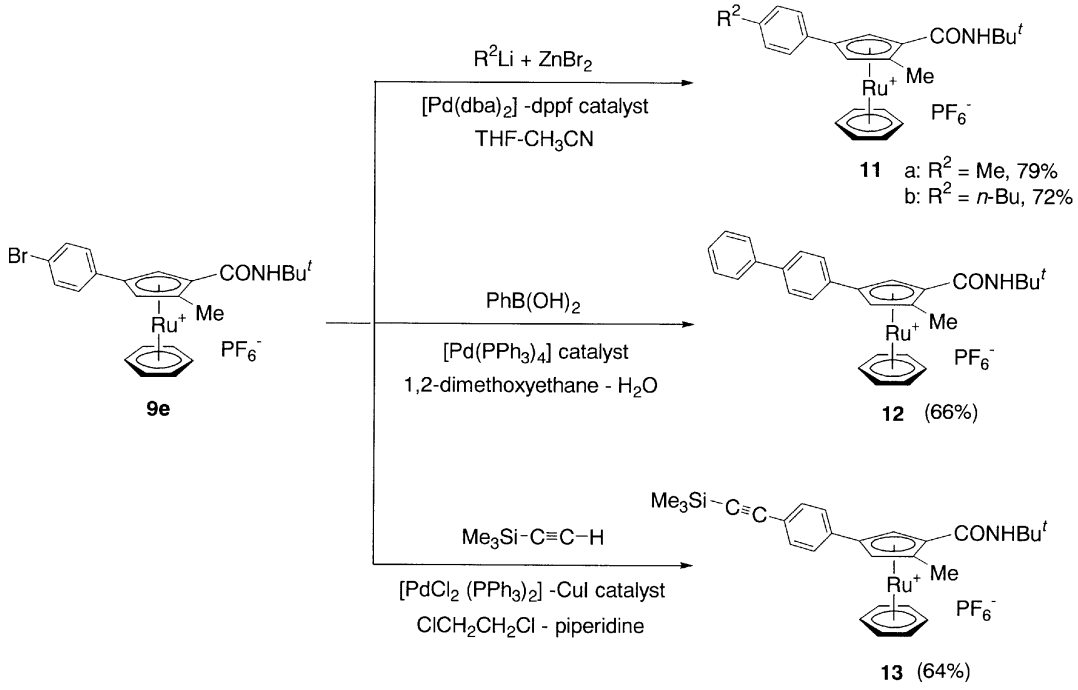


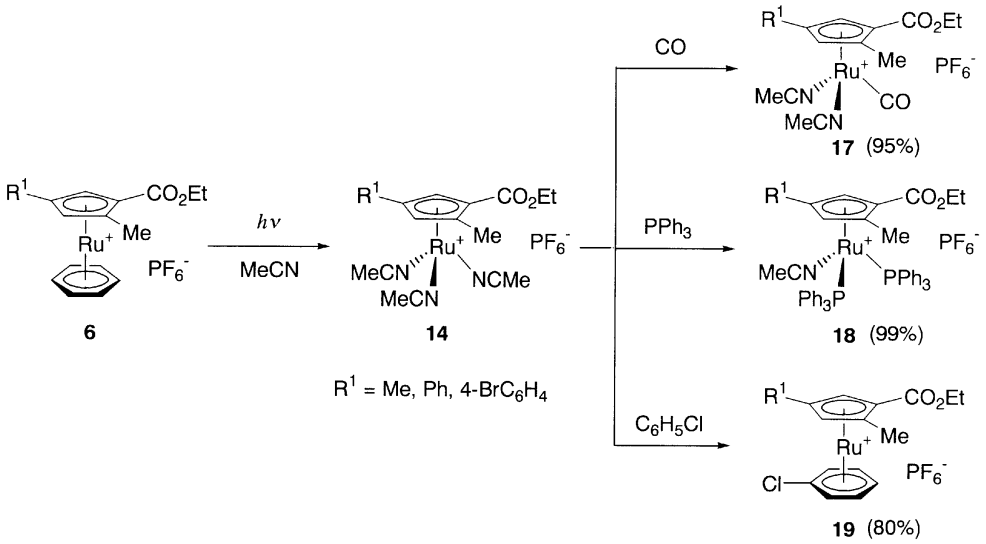
Fig. 5. CD spectra of ruthenium complexes **9b** and **10e**.

The η^6-benzene complexes, $[Ru(\eta^5\text{-Cp}')(\eta^6\text{-benzene})]^+$, have a stable 18-electron configuration; however, they are easily transformed by a photoreaction in acetonitrile to versatile tris(acetonitrile)cyclopentadienylruthenium complexes **14**, $[Ru(\eta^5\text{-Cp}')(CH_3CN)_3]^+$,[11] which may be regarded as a precursor of coordinatively unsaturated $Cp'Ru^+$ species. Thus, irradiation to complex **6a** in acetonitrile gave tris(acetonitrile) complexes **14a** in almost quantitative yield (Scheme 5). However similar treatment of **8b** having BPh_4^- as a counter anion gave a mixture of **15b** and **16b** (Scheme 6). The latter product involves a coordination of the phenyl group of the counter anion. To avoid the participation of the anion, we tried replacement of the BPh_4 for another anion and found that the treatment of $[RuCp'(L)][BPh_4]$ with NH_4PF_6 in ethyl acetate yielded a desired salt, $[RuCp'(L)][PF_6]$, due to the low solubility of NH_4BPh_4 in ethyl acetate (Scheme 3). Thus obtained tris(acetonitrile) complexes **14** are reactive and undergo several ligand-exchange reactions. For example, the acetonitrile ligands in **14** are easily replaced with carbon monoxide and triphenylphosphine to produce new planar-chiral cyclopentadienyl ruthenium complexes **17** and **18**.[11] Treatment of **14** with arenes reproduces η^6-arene complexes **19**.

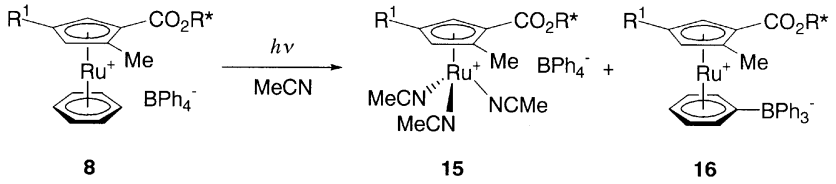
In conclusion, we have synthesized a variety of planar-chiral trisubstituted cyclopentadienylruthenium complexes in an optically pure form. They provide the first examples of optically pure planar-chiral ruthenium complexes with a half-sandwich



Scheme 4.



Scheme 5.



Scheme 6.

structure.

Experimental

All reactions were carried out under an atmosphere of nitrogen or argon, but the workup was performed in air. Melting and decomposition points are corrected. ^{1}H and ^{13}C NMR spectra were measured in acetone-d_6 or $CDCl_3$ with $SiMe_4$ as an internal standard and recorded on JEOL EX-270 (270 MHz), JEOL JNM-LA400 (400 MHz), and JEOL JNM-LA600 (600 MHz) spectrometers. Chemical shifts are given in ppm. IR and mass spectra were taken on a Perkin–Elmer system 2000 FT-IR and a JEOL JMS-600H instrument, respectively. Optical rotations and CD spectra were measured on a JASCO DIP-1000 polarimeter and a JASCO J-725 spectropolarimeter, respectively. Optical purity was determined by HPLC using a DAICEL chiral cell OD column or by ^{1}H NMR spectrum using a shift reagent [Eu(hfc)$_3$] [hfc = 3-(heptafluoropropylhydroxymethylene)-D-camphorate]. Elemental analyses were performed by the Materials Analysis Center, ISIR, Osaka University. Diethyl ether and THF were distilled over benzophenone ketyl under argon just before use. Dichloromethane and acetonitrile were dried over calcium hydride and then distilled. 1-Ethoxycarbonyl-2,4-dimethylcyclopentadiene **1a**, 1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadiene **1b**, 1-ethoxycarbonyl-2-methyl-4-(*t*-butyl)cyclopentadiene **1c**, and 1-(*l*)-menthyloxycarbonyl-2,4-dimethylcyclopentadiene [**2a**, $[\alpha]_D^{25}$: –58.9° (*c* 1.12, acetone)] were prepared by the method previously reported.[9,15] Other chemicals available commercially were used without further purification.

Synthesis of 1-Ethoxycarbonyl-2-methyl-4-(2-naphthyl)cyclopentadiene (1d). This compound was prepared by the method reported previously[15] from 2-bromoacetonaphthone. (52% yield). Mp 94.0–94.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97–7.69 (m, 7H, $C_{10}H_7$), 6.89 (s, 1H, CH), 4.29 (q, 2H, J = 7.1 Hz, CH_2CH_3), 3.86 (d, 2H, J = 2.2 Hz, CH_2), 2.44 (d, 3H, J = 2.2 Hz, CH_3), 1.37 (t, 3H, J = 7.1 Hz, CH_2CH_3). IR (KBr) 1682 cm^{-1} (C=O). MS (FAB) *m/z* 278. Found: C, 81.72; H, 6.38%. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52%.

Synthesis of 1-Ethoxycarbonyl-2-methyl-4-(4-bromophenyl)cyclopentadiene (1e). This compound was prepared by the method reported previously[15] from 4-bromophenacyl bromide (44% yield). Mp 178.0–178.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, 2H, J = 8.5 Hz, C_6H_4), 7.41 (d, 2H, J = 8.5 Hz, C_6H_4), 4.26 (q, 2H, J = 7.1 Hz, CH_2CH_3), 3.68 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.35 (t, 3H, J = 7.1 Hz, CH_2CH_3). IR (KBr) 1682 cm^{-1} (C=O). MS (FAB) *m/z* 307. Found: C, 58.43; H, 4.71; Br, 25.89%. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92; Br, 26.01%.

Synthesis of (η^6-Benzene)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium Hexafluorophosphate (6a). To a solution of sodium hydride (60% in oil, 0.88 g, 22 mmol) in THF (10 ml) was added a THF (20 ml) solution of 1-ethoxycarbonyl-2,4-dimethylcyclopentadiene **1a** (3.32 g, 20 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. This solution was added dropwise to an aqueous solution of thallium(I) sulfate (5.0 g, 9.5 mmol), and the mixture was stirred overnight at room temperature to give a pale brown precipitate, which was collected and washed with ether several times. The resulting solid was dried in vacuo and then dissolved in acetonitrile. To this solution was added (η^6-benzene)dichlororuthenium dimer, [(η^6-C_6H_6)Cl_2Ru]$_2$, (5.0 g, 10 mmol). The reaction mixture was stirred overnight at room temperature and then filtered through Celite. The filtrate was concentrated and to the residual oil was added an aqueous solution of ammonium hexafluorophosphate (6.54 g, 40 mmol). The aqueous solution was extracted with dichloromethane (200 ml × 3) and the combined extracts were dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure,

the residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and the residue was purified by recrystallization from ethanol to give 6.22 g (67% yield) of ruthenium complex **6a** as pale yellow needles. Mp 178.0–178.5 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 6.53 (s, 6H, C_6H_6), 5.90 (d, 1H, J = 1.7 Hz, CpH), 5.74 (d, 1H, J = 1.7 Hz, CpH), 4.32 (dq, 1H, J = 1.7, 7.3 Hz, CH_2CH$_3$), 4.31 (dq, 1H, J = 1.7, 7.3 Hz, CH_2CH$_3$), 2.31 (s, 3H, CpCH$_3$), 2.09 (s, 3H, CpCH$_3$), 1.35 (t, 3H, J = 7.3 Hz, CH$_2$CH_3). IR (KBr) 1712 cm^{-1} (C=O). MS (FAB) m/z 345 ($M^+ - PF_6$). Found: C, 39.49; H, 3.84; F, 23.21; P, 6.20%. Calcd for $C_{16}H_{19}F_6O_2PRu$: C, 39.27; H, 3.91; F, 23.29; P, 6.33%.

Synthesis of (η^6-Benzene)(η^5-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)ruthenium Hexafluorophosphate (6b). This complex was prepared using **1b** by the same method as that for **6a** (73% yield). Mp 145.0–146.0 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 7.74–7.69 (m, 2H, Ph), 7.45–7.42 (m, 3H, Ph), 6.51 (d, 1H, J = 1.7 Hz, CpH), 6.39 (d, 1H, J = 1.7 Hz, CpH), 6.28 (s, 6H, C_6H_6), 4.90 (dq, 1H, J = 2.3, 7.3 Hz, CH_2CH$_3$), 4.89 (dq, 1H, J = 2.3, 7.3 Hz, CH_2CH$_3$), 2.43 (s, 3H, CpCH$_3$), 1.39 (t, 3H, J = 7.3 Hz, CH$_2$CH_3). IR (KBr) 1725 cm^{-1} (C=O). MS (FAB) m/z 407 ($M^+ - PF_6$). Found: C, 45.79; H, 3.82; F, 20.57; P, 5.63%. Calcd for $C_{21}H_{21}F_6O_2PRu$: C, 45.74; H, 3.84; F, 20.67; P, 5.62%.

Synthesis of (η^6-Benzene)[η^5-1-ethoxycarbonyl-2-methyl-4-(*t*-butyl)cyclopentadienyl]ruthenium Hexafluorophosphate (6c). This complex was prepared using **1c** by the same method as that for **6a** (45% yield). Mp 160.5–162.0 °C. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.13 (s, 6H, C_6H_6), 5.64 (d, 1H, J = 2.0 Hz, CpH), 5.62 (d, 1H, J = 2.0 Hz, CpH), 4.36 (q, 2H, J = 7.3 Hz, CH_2CH$_3$), 2.30 (s, 3H, CpCH$_3$), 1.39 (t, 3H, J = 7.3 Hz, CH$_2$CH_3), 1.18 (s, 9H, C(CH$_3$)$_3$). IR (KBr) 1724 cm^{-1} (C=O). MS (FAB) m/z 387 ($M^+ - PF_6$). Found: C, 42.89; H, 4.68; F, 21.49; P, 5.65%. Calcd for $C_{19}H_{25}F_6O_2PRu$: C, 42.94; H, 4.74; F, 21.45; P, 5.83%.

Synthesis of (η^6-Benzene)[η^5-1-ethoxycarbonyl-2-methyl-4-(2-naphthyl)cyclopentadienyl]ruthenium Hexafluorophosphate (6d). This complex was prepared using **1d** by the same method as that for **6a** (72% yield). Mp 223.0–224.0 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.29 (s, 1H, $C_{10}H_7$), 7.96–7.92 (m, 3H, $C_{10}H_7$), 7.80–7.78 (m, 1H, $C_{10}H_7$), 7.60–7.57 (m, 2H, $C_{10}H_7$), 6.64 (s, 1H, CpH), 6.52 (s, 1H, CpH), 6.30 (s, 6H, C_6H_6), 4.43–4.34 (m, 2H, CH_2CH$_3$), 2.46 (s, 3H, CpCH$_3$), 1.40 (t, 3H, J = 7.1 Hz, CH$_2$CH_3). IR (KBr) 1714 cm^{-1} (C=O). MS (FAB) m/z 457 ($M^+ - PF_6$). Found: C, 50.01; H, 3.68%. Calcd for $C_{25}H_{23}F_6O_2PRu$: C, 49.92; H, 3.85%.

Synthesis of (η^6-Benzene)[η^5-1-ethoxycarbonyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl]ruthenium Hexafluorophosphate (6e). This complex was prepared using **1e** by the same method as that for **6a** (58% yield). Mp 239.0–239.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.68 (d, 2H, J = 8.5 Hz, C_6H_4), 7.58 (d, 2H, J = 8.5 Hz, C_6H_4), 6.54 (s, 1H, CpH), 6.04 (s, 1H, CpH), 6.03 (s, 6H, C_6H_6), 4.42–4.30 (m, 2H, CH_2CH$_3$), 2.42 (s, 3H, CpCH$_3$), 1.38 (t, 3H, J = 7.1 Hz, CH$_2$CH_3). IR (KBr) 1722 cm^{-1} (C=O). MS (FAB) m/z 485 ($M^+ - PF_6$). Found: C, 40.05; H, 3.27; Br, 12.69; F, 17.87; P, 4.80%. Calcd for $C_{21}H_{20}BrF_6O_2PRu$: C, 40.02; H, 3.20; Br, 12.68; F, 18.08; P, 4.91%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2,4-dimethylcyclopentadienyl]ruthenium Hexafluorophosphate (4a). To a solution of **6a** (1.47 g, 3 mmol) in acetonitrile (50 ml) was added K_2CO_3 (5% in water, 50 ml) and the mixture was refluxed for 3 h. This solution was neutralized by 6 M HCl (1 M = 1 mol dm^{-3}). The solvent was evaporated under reduced pressure and the residue was dissolved in acetonitrile. This solution was dried over $MgSO_4$ and filtered. After removal of the solvent, the residue was washed with dichloromethane several times. To the suspension of the resulting solid in dichloromethane (20 ml) were added oxalyl chloride (1 ml) and DMF (a catalytic amount) with stirring in the dark at room temperature. After 2 h, the solvent was evaporated under reduced pressure, and the residue was dissolved in acetonitrile (10 ml). This solution was added to an acetonitrile solution (20 ml) containing (*l*)-menthol (1.40 g, 9 mmol), triethylamine (3 ml), and 4-dimethylaminopyridine (5 mg). The reaction mixture was stirred for 3 h and the precipitate formed was removed by filtration. The filtrate was concentrated and to the residual oil was added an aqueous solution of ammonium hexafluorophosphate (1.47 g, 9 mmol). The aqueous solution was extracted with dichloromethane (10 ml × 3) and the combined extracts were dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure, the residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and then the resulting solid was purified by recrystallization from ethanol to give 0.88 g (49% yield) of ruthenium complex **4a** as pale yellow needles. Diastereomers were separated with recrystallization by EtOH–H_2O (5:1). **4a-1(S_{C1} form)**: 26% yield. Mp 209.5–210.5 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 6.34 (s, 6H, C_6H_6), 5.92 (s, 1H, CpH), 5.76 (s, 1H, CpH), 4.87 (dt, 1H, J = 4.3, 10.6 Hz, OCH), 2.33 (s, 3H, CpCH$_3$), 2.09 (s, 3H, CpCH$_3$), 1.80–1.00 (m, 9H, menthyl), 0.98 (d, 3H, J = 7.3 Hz, menthyl), 0.95 (d, 3H, J = 6.6 Hz, menthyl), 0.86 (d, 3H, J = 6.9 Hz, menthyl). IR (KBr) 1722 cm^{-1} (C=O). Mass (FAB) m/z 455 ($M^+ - PF_6$). Found: C, 48.04; H, 5.50; F, 19.23; P, 5.23%. Calcd for $C_{24}H_{33}F_6O_2PRu$: C, 48.08; H, 5.55; F, 19.01; P, 5.17%. **4a-2(R_{C1} form)**: 4% yield. Mp 175.0–175.5 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 6.36 (s, 6H, C_6H_6), 5.93 (s, 1H, CpH), 5.76 (s, 1H, CpH), 4.87 (dt, 1H, J = 4.6, 10.9 Hz, OCH), 2.32 (s, 3H, CpCH$_3$), 2.10 (s, 3H, CpCH$_3$), 1.82–1.00 (m, 9H, menthyl), 0.97 (d, 3H, J = 6.6 Hz, menthyl), 0.94 (d, 3H, J = 6.9 Hz, menthyl), 0.82 (d, 3H, J = 6.9 Hz, menthyl). IR (KBr) 1728 cm^{-1} (C=O). MS (FAB) m/z 455 ($M^+ - PF_6$). Found: C, 48.07; H, 5.40; F, 19.20; P, 5.07%. Calcd for $C_{24}H_{33}F_6O_2PRu$: C, 48.08; H, 5.55; F, 19.01; P, 5.17%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-phenylcyclopentadienyl]ruthenium Hexafluorophosphate (4b). This complex was prepared using **6b** by the same method as that for **4a** (76% yield). ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.71–7.68 (m, 3H, Ph), 7.42–7.40 (m, 2H, Ph), 6.52 (t, 1H, J = 1.7 Hz, CpH), 6.39 (s, 1H, CpH), 6.25 (s, 6H, C_6H_6), 4.92 (dt, 1H, J = 4.4, 11.0 Hz, OCH), 2.42 (s, 3H, CpCH$_3$), 2.10–1.98 (m, 2H, menthyl), 1.79–1.74 (m, 2H, menthyl), 1.61–1.53 (m, 2H, menthyl), 1.28–1.11 (m, 2H, menthyl), 0.99–0.94 (m, 7H, menthyl), 0.88–0.82 (m, 3H, menthyl). IR (KBr) 1725 cm^{-1} (C=O). MS (FAB) m/z 517 ($M^+ - PF_6$). Found: C, 52.38; H, 5.13%. Calcd for $C_{29}H_{35}F_6O_2PRu$: C, 52.65; H, 5.33%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-(*t*-butyl)cyclopentadienyl]ruthenium Hexafluorophosphate (4c). This complex was prepared using **6c** by the same method as that for **4a** (72% yield). Diastereomers were separated by recrystallization from ethanol. **4c-1(S_{C1} form)**: 82% yield. Mp 244.0–245.0 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 6.40 (s, 6H, C_6H_6), 5.88 (t, 1H, CpH), 5.77 (s, 1H, CpH), 4.89 (dt, 1H, J = 4.4, 10.7 Hz, OCH), 2.33 (s, 3H, CpCH$_3$), 2.13–2.10 (m, 1H, menthyl), 1.97–1.88 (m, 2H, menthyl), 1.77–1.72 (m, 2H, menthyl), 1.57–1.51 (m, 2H, menthyl), 1.21 (s, 9H, C(CH$_3$)$_3$), 1.19–1.09 (m, 2H, menthyl), 0.94 (dd, 6H, J = 7.1, 8.8 Hz, menthyl), 0.81 (d, 3H, J = 7.1 Hz, menthyl). IR (KBr) 1723 cm^{-1} (C=O). Mass (FAB) m/z 497 ($M^+ - PF_6$). Found: C, 50.26; H, 6.03%. Calcd for

$C_{27}H_{39}F_6O_2PRu$: C, 50.54; H, 6.13%.

Synthesis of (η^6-Benzene)[η^5-1-(*d*)-menthyloxycarbonyl-2-methyl-4-(*t*-butyl)cyclopentadienyl]ruthenium Hexafluorophosphate (4′c). This complex was prepared using (*d*)-menthol by the same method as that for **4c** (71% yield). Diastereomers were separated by recrystallization from ethanol. **4′c-2(R_{C1} form)**: 82% yield. The spectroscopic data indicated (R_{C1})-**4′c-2** and (S_{C1})-**4c-1** to be a pair of enantiomers. Found: C, 50.32; H, 6.38%. Calcd for $C_{27}H_{39}F_6O_2PRu$: C, 50.54; H, 6.13%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-(2-naphthyl)cyclopentadienyl]ruthenium Hexafluorophosphate (4d). This complex was prepared using **6d** by the same method as that for **4a** (70% yield). ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.28 (d, 1H, J = 2.4 Hz, $C_{10}H_7$), 7.96–7.93 (m, 3H, $C_{10}H_7$), 7.79–7.77 (m, 1H, $C_{10}H_7$), 7.61–7.56 (m, 2H, $C_{10}H_7$), 6.67 (d, 1H, J = 3.2 Hz, CpH), 6.53 (s, 1H, CpH), 6.21 (s, 6H, C_6H_6), 4.97–4.93 (m, 1H, OCH), 2.47 (d, 3H, J = 3.2 Hz, $CpCH_3$), 2.16 (br, 1H, menthyl), 1.77 (br, 2H, menthyl), 1.61–1.58 (m, 2H, menthyl), 1.39–0.76 (m, 13H, menthyl). IR (KBr) 1728 cm^{-1} (C=O). Mass (FAB) *m/z* 567 ($M^+ - PF_6$). Found: C, 55.41; H, 5.18; F, 15.82; P, 4.26%. Calcd for $C_{33}H_{37}F_6O_2PRu$: C, 55.69; H, 5.24; F, 16.02; P, 4.35%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl]ruthenium Hexafluorophosphate (4e). This complex was prepared using **6e** by the same method as that for **4a** (76% yield). ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.65–7.62 (m, 2H, C_6H_4), 7.58–7.56 (m, 2H, C_6H_4), 6.55 (s, 1H, CpH), 6.37 (s, 1H, CpH), 6.24 (s, 6H, C_6H_6), 4.96–4.87 (m, 1H, OCH), 2.42 (d, 3H, J = 3.4 Hz, $CpCH_3$), 1.95–1.88 (br, 3H, menthyl), 1.79–1.75 (br, 2H, menthyl), 0.99–0.93 (m, 6H, menthyl), 0.85 (d, 3H, J = 7.1 Hz, menthyl). IR (KBr) 1725 cm^{-1} (C=O). Mass (FAB) *m/z* 597 ($M^+ - PF_6$). Found: C, 47.03; H, 4.81%. Calcd for $C_{29}H_{34}BrF_6O_2PRu$: C, 47.04; H, 4.63%.

Synthesis of (η^6-Benzene)[η^5-1-(*d*)-menthyloxycarbonyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl]ruthenium Hexafluorophosphate (4′e). This complex was prepared using (*d*)-menthol by the same method as that for **4e** (73% yield). Spectroscopic data of **4′e** are the same as **4e** within experimental error. Found: C, 47.00; H, 4.59%. Calcd for $C_{29}H_{34}BrF_6O_2PRu$: C, 47.04; H, 4.63%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-phenylcyclopentadienyl]ruthenium Tetraphenylborate (8b). To a solution of **4b** (1.72 g, 2 mmol) in methanol was added a methanol solution of $NaBPh_4$ (2.05 g, 6 mmol). This solution was stirred for 30 min at room temperature. The precipitate was filtrated. The resulting solid was washed with methanol and dried under vacuum (99% yield). Diastereomers were separated by recrystallization from ethyl acetate. **8b-1(S_{C1} form)**: 48% yield. Mp 178.0–179.0 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 7.46–7.36 (m, 2H, Ph), 7.23–7.19 (m, 3H, Ph), 7.04 (t, 8H, J = 7.3 Hz, Ph), 6.91 (t, 4H, J = 7.3 Hz, Ph), 5.97 (d, 1H, J = 1.7 Hz, CpH), 5.57 (d, 1H, J = 1.7 Hz, CpH), 5.19 (s, 6H, C_6H_6), 4.89 (dt, 1H, J = 4.5 Hz, OCH), 2.21 (s, 3H, $CpCH_3$), 2.05–1.07 (m, 11H, menthyl), 0.96 (d, 6H, J = 5.6 Hz, menthyl), 0.82 (d, 3H, J = 6.9 Hz, menthyl). IR (KBr) 1724 cm^{-1} (C=O). Mass (FAB) *m/z* 517 ($M^+ - BPh_4$). Found: C, 76.05; H, 6.45%. Calcd for $C_{53}H_{55}BO_2Ru$: C, 76.15; H, 6.63%. **8b-2(R_{C1} form)**: 7% yield. Mp 186.0–187.0 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 7.45–7.34 (m, 2H, Ph), 7.26–7.18 (m, 3H, Ph), 7.03 (t, 8H, J = 7.3 Hz, Ph), 6.91 (t, 4H, J = 7.3 Hz, Ph), 5.97 (d, 1H, J = 1.7 Hz, CpH), 5.53 (s, 1H, CpH), 5.16 (s, 6H, C_6H_6), 4.88 (dt, 1H, J = 4.6 Hz, OCH), 2.18 (s, 3H, $CpCH_3$), 2.04–1.07 (m, 11H, menthyl), 0.99 (d, 6H, J = 6.6 Hz, menthyl), 0.83 (d, 3H, J = 6.9 Hz, menthyl). IR (KBr) 1722 cm^{-1} (C=O). Mass (FAB) *m/z* 517 ($M^+ - BPh_4$). Found: C, 76.11; H, 6.44%. Calcd for $C_{53}H_{55}BO_2Ru$: C, 76.15; H, 6.63%.

Synthesis of (η^6-Benzene)[η^5-1-(*d*)-menthyloxycarbonyl-2-methyl-4-phenylcyclopentadienyl]ruthenium Tetraphenylborate (8′b-2). This complex was prepared using **6′b** by the same method as that for **8b** (99% yield). Diastereomers were separated by recrystallization from ethyl acetate. The spectroscopic data indicated (R_{C1})-**8′b-2** and (S_{C1})-**8b-1** to be a pair of enantiomers. Found: C, 75.61; H, 6.20%. Calcd for $C_{53}H_{55}BO_2Ru$: C, 76.15; H, 6.63%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-(2-naphthyl)cyclopentadienyl]ruthenium Tetraphenylborate (8d). This complex was prepared using **4d** by the same method as that for **8b** (99% yield). Diastereomers were separated by recrystallization from chloroform–hexane. **8d-1(S_{C1} form)**: 24% yield. Mp 189.0–189.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.25 (s, 1H, $C_{10}H_7$), 7.95–7.90 (m, 3H, $C_{10}H_7$), 7.76 (m, 1H, $C_{10}H_7$), 7.59–7.58 (m, 2H, $C_{10}H_7$), 7.34–7.33 (m, 8H, Ph), 6.91 (t, 8H, J = 7.3 Hz, Ph), 6.76 (t, 4H, J = 7.3 Hz, Ph), 6.67 (s, 1H, CpH), 6.50–6.48 (m, 1H, CpH), 6.27–6.22 (m, 6H, C_6H_6), 4.95 (dt, 1H, J = 6.3, 11.0 Hz, OCH), 2.45 (d, 3H, J = 2.7 Hz, $CpCH_3$), 2.18–2.15 (br, 1H, menthyl), 1.78–1.76 (br, 2H, menthyl), 1.59–1.57 (br, 2H, menthyl), 1.30–1.14 (m, 2H, menthyl), 0.98–0.95 (m, 7H, menthyl), 0.84 (d, 3H, J = 7.1 Hz, menthyl). IR (KBr) 1728 cm^{-1} (C=O). Mass (FAB) *m/z* 567 ($M^+ - BPh_4$). Found: C, 77.11; H, 6.20%. Calcd for $C_{57}H_{57}BO_2Ru$: C, 77.27; H, 6.48%. **8d-2(R_{C1} form)**: 10% yield. Mp 120.5–121.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.27 (s, 1H, $C_{10}H_7$), 7.95–7.90 (m, 3H, $C_{10}H_7$), 7.76 (dd, 3H, J = 1.7, 8.5 Hz, $C_{10}H_7$), 7.60–7.57 (m, 2H, $C_{10}H_7$), 7.33 (br, 8H, Ph), 6.91 (t, 8H, J = 7.3 Hz, Ph), 6.76 (t, 4H, J = 7.3 Hz, Ph), 6.66 (s, 1H, CpH), 6.50 (s, 1H, CpH), 6.24 (d, 6H, J = 2.4 Hz, C_6H_6), 4.95 (dt, 1H, J = 6.3, 11.0 Hz, OCH), 2.46 (s, 3H, $CpCH_3$), 2.16–2.13 (br, 1H, menthyl), 1.80–1.75 (br, 2H, menthyl), 1.63–1.57 (br, 2H, menthyl), 1.26–1.13 (m, 3H, menthyl), 0.98 (dd, J = 6.6, 15.1 Hz, 6H, menthyl), 0.89 (d, 3H, J = 6.8 Hz, menthyl). IR (KBr) 1717 cm^{-1} (C=O). Mass (FAB) *m/z* 567 ($M^+ - BPh_4$). Found: C, 77.01; H, 6.59%. Calcd for $C_{57}H_{57}BO_2Ru$: C, 77.27; H, 6.48%.

Synthesis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl]ruthenium Tetraphenylborate (8e). This complex was prepared using **4e** by the same method as that for **8b** (99% yield). Diastereomers were separated by recrystallization from ethyl acetate. **8e-1(S_{C1} form)**: 31% yield. Mp 122.0–122.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.64 (d, 2H, J = 8.8 Hz, C_6H_4), 7.57 (d, 2H, J = 8.8 Hz, C_6H_4), 7.33 (br, 8H, Ph), 6.91 (t, 8H, J = 7.3 Hz, Ph), 6.77 (t, 4H, J = 7.3 Hz, Ph), 6.55 (d, 1H, J = 1.7 Hz, CpH), 6.37 (d, 1H, J = 1.7 Hz, CpH), 6.24 (s, 6H, C_6H_6), 4.93 (dt, 1H, J = 4.4, 11.0 Hz, OCH), 2.41 (s, 3H, $CpCH_3$), 1.78–1.74 (br, 2H, menthyl), 1.60–1.54 (br, 2H, menthyl), 0.97–0.93 (m, 7H, menthyl), 0.83 (d, 3H, J = 6.8 Hz, menthyl). IR (KBr) 1725 cm^{-1} (C=O). Mass (FAB) *m/z* 596 ($M^+ - BPh_4$). Found: C, 69.93; H, 5.58; Br, 8.71%. Calcd for $C_{53}H_{54}BBrO_2Ru$: C, 69.59; H, 5.95; Br, 8.73%.

Synthesis of (η^6-Benzene)[η^5-1-(*d*)-menthyloxycarbonyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl]ruthenium Tetraphenylborate (8′e). This complex was prepared using **4′e** by the same method as that for **8b** (99% yield). Diastereomers were separated by recrystallization from ethyl acetate. **8′e-2(R_{C1} form)**: 35% yield. The spectroscopic data indicated (R_{C1})-**8′e-2** and (S_{C1})-**8e-1** to be a pair of enantiomers. Found: C, 69.33; H, 5.70%. Calcd for $C_{53}H_{54}BBrO_2Ru$: C, 69.59; H, 5.95%.

Synthesis of (S_{C1})-[(η^6-Benzene)(η^5-1-*t*-butylcarbamoyl-2,4-dimethylcyclopentadienyl)ruthenium] Hexafluorophosphate (9a-1). To a solution of **4a-1** (1.20 g, 2 mmol) in acetonitrile (30 ml) was added K_2CO_3 (5% in water, 30 ml) and the mixture was refluxed for 3 h. This solution was neutralized by 6 M HCl. The solvent was evaporated under reduced pressure and the residue was dissolved in acetonitrile. This solution was dried over $MgSO_4$ and filtered. After removal of the solvent, the residue was washed with dichloromethane several times. To the suspension of the resulting solid in dichloromethane (10 ml) were added oxalyl chloride (1 ml) and DMF (a catalytic amount) with stirring in the dark at room temperature. After 2 h, the solvent was evaporated under reduced pressure, and the residue was dissolved in acetonitrile (10 ml). This solution was added to an acetonitrile solution (20 ml) containing *t*-butylamine (1 ml) and 4-dimethylaminopyridine (5 mg). The reaction mixture was stirred for 3 h and the precipitate formed was removed by filtration. The filtrate was concentrated under reduced pressure. The residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and then the resulting solid was purified by recrystallization from ethanol to give 0.78 g (75% yield) of ruthenium complex **9a-1** as white powder. Mp 197.0–197.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 6.97 (br, 1H, NH), 6.27 (s, 6H, C_6H_6), 5.90 (s, 1H, CpH), 5.62 (s, 1H, CpH), 2.28 (s, 3H, $CpCH_3$), 2.07 (s, 3H, $CpCH_3$), 1.42 (s, 9H, $C(CH_3)_3$). IR (KBr) 3426 (NH), 1662 cm^{-1} (C=O). MS (FAB) *m/z* 372 ($M^+ - PF_6$). Found: C, 41.90; H, 4.58; N, 2.77%. Calcd for $C_{18}H_{24}F_6NOPRu$: C, 41.86; H, 4.68; N, 2.71%.

Synthesis of (R_{C1})-[(η^6-Benzene)(η^5-1-*t*-butylcarbamoyl-2,4-dimethylcyclopentadienyl)ruthenium] Hexafluorophosphate (9a-2). This complex was prepared using **4a-2** by the same method as that for **9a-1** (74% yield). The spectroscopic data indicated (R_{C1})-**9a-2** and (S_{C1})-**9a-1** to be a pair of enantiomers. Found: C, 41.99; H, 4.54; N, 2.76%. Calcd for $C_{18}H_{24}F_6NOPRu$: C, 41.86; H, 4.68; N, 2.71%.

Synthesis of (S_{C1})-[(η^6-Benzene)(η^5-1-*t*-butylcarbamoyl-2-methyl-4-phenylcyclopentadienyl)ruthenium] Hexafluorophosphate (9b-1). This complex was prepared using **8b-1** by the same method as that for **9a-1** (42% yield). Mp 225.0–225.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.65–7.60 (m, 2H, Ph), 7.40–7.38 (m, 3H, Ph), 7.18 (br, 1H, NH), 6.51 (s, 1H, CpH), 6.24 (s, 1H, CpH), 6.19 (s, 6H, C_6H_6), 2.37 (s, 3H, $CpCH_3$), 1.43 (s, 9H, $C(CH_3)_3$). IR (KBr) 3430 (NH), 1664 cm^{-1} (C=O). MS (FAB) *m/z* 434 ($M^+ - PF_6$). Found: C, 47.51; H, 4.33; N, 2.32%. Calcd for $C_{23}H_{26}F_6NOPRu$: C, 47.75; H, 4.53; N, 2.42%.

Synthesis of (R_{C1})-[(η^6-Benzene)(η^5-1-*t*-butylcarbamoyl-2-methyl-4-phenylcyclopentadienyl)ruthenium] Hexafluorophosphate (9b-2). This complex was prepared using **8′b-2** by the same method as that for **9a-1** (49% yield). The spectroscopic data indicated (R_{C1})-**9b-2** and (S_{C1})-**9b-1** to be a pair of enantiomers. Found: C, 47.77; H, 4.43; N, 2.33%. Calcd for $C_{23}H_{26}F_6NOPRu$: C, 47.75; H, 4.53; N, 2.42%.

Synthesis of (η^6-Benzene)[η^5-1-*t*-butylcarbamoyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl]ruthenium Hexafluorophosphate (9e). This complex was prepared using **6e** by the same method as that for **9a-1** (66% yield). Mp 257.0–257.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.60–7.55 (m, 4H, C_6H_4), 7.21 (br, 1H, NH), 6.56 (s, 1H, CpH), 6.27 (s, 1H, CpH), 6.23 (s, 6H, C_6H_6), 2.38 (s, 3H, $CpCH_3$), 1.43 (s, 9H, $C(CH_3)_3$). IR (KBr) 3426 (NH), 1665 cm^{-1} (C=O). MS (FAB) *m/z* 512 ($M^+ - PF_6$). Found: C, 42.09; H, 3.80; Br, 11.88; F, 17.56; N, 2.32; P, 4.76%. Calcd for $C_{23}H_{25}BrF_6NOPRu$: C, 42.02; H, 3.83; Br, 12.15; F, 17.34; N, 2.13; P, 4.71%.

Synthesis of (S_{C1})-[(η^6-Benzene){η^5-1-*t*-butylcarbamoyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl}ruthenium] Hexafluorophosphate (10e-1). This complex was prepared using **8e-1** by the same method as that for **9a-1** (76% yield). Mp 203.0–206.0 °C (decomp). ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.60–7.55 (m, 4H, C_6H_4), 7.33 (br, 8H, Ph), 7.21 (br, 1H, NH), 6.91 (t, 8H, *J* = 7.3 Hz, Ph), 6.77 (t, 4H, *J* = 7.3 Hz, Ph), 6.56 (s, 1H, CpH), 6.27 (s, 1H, CpH), 6.23 (s, 6H, C_6H_6), 2.38 (s, 3H, $CpCH_3$), 1.43 (s, 9H, $C(CH_3)_3$). IR (KBr) 3427 (NH), 1666 cm^{-1} (C=O). MS (FAB) *m/z* 512 ($M^+ - BPh_4$). Found: C, 67.92; H, 5.20; Br, 9.69; N, 1.65%. Calcd for $C_{47}H_{45}BBrNORu$: C, 67.88; H, 5.45; Br, 9.61; N, 1.68%.

Synthesis of (R_{C1})-[(η^6-Benzene){η^5-1-*t*-butylcarbamoyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl}ruthenium] Hexafluorophosphate (10e-2). This complex was prepared using **8e-2** by the same method as that for **9a-1** (75% yield). The spectroscopic data indicated (R_{C1})-**10e-2** and (S_{C1})-**10e-1** to be a pair of enantiomers. Found: C, 67.68; H, 5.35; Br, 9.51; N, 1.69%. Calcd for $C_{47}H_{45}BBrNORu$: C, 67.88; H, 5.45; Br, 9.61; N, 1.68%.

Synthesis of (η^6-Benzene)(η^5-1-*t*-butylcarbamoyl-2-methyl-4-tolylcyclopentadienyl)ruthenium Hexafluorophosphate (11a). To a solution of zinc dibromide (0.68 g, 3 mmol) in THF (1 ml) was added methyllithium (1.4 M in THF, 2 ml) at 0 °C for 30 min. This solution was added to an acetonitrile-THF solution (1:4, 2.5 ml) containing **9e** (0.33 g, 0.5 mmol), $Pd(dba)_2$ (14 mg, 0.025 mmol), and dppf (14 mg, 0.025 mmol). The reaction mixture was refluxed for 12 h and, after removal of the solvent, to the residual oil was added an aqueous solution of ammonium hexafluorophosphate (0.24 g, 1.5 mmol). The aqueous solution was extracted with dichloromethane (20 ml × 3) and the combined extracts were dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure, the residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and the residue was purified by recrystallization from ethanol to give 0.24 g (79% yield) of ruthenium complex **11a** as pale yellow needles. Mp 266.5–267.0 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.51 (d, 2H, *J* = 8.3 Hz, C_6H_4), 7.21 (m, 3H, C_6H_4, NH), 6.50 (s, 1H, CpH), 6.22 (s, 1H, CpH), 6.19 (s, 6H, C_6H_6), 2.36 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 1.42 (s, 9H, $C(CH_3)_3$). IR (KBr) 3427 (NH), 1663 cm^{-1} (C=O). MS (FAB) *m/z* 448 ($M^+ - PF_6$). Found: C, 48.38; H, 4.82; N, 2.30; F, 18.99; P, 5.00%. Calcd for $C_{24}H_{28}F_6NOPRu$: C, 48.65; H, 4.76; N, 2.36; F, 19.24; P, 5.23%.

Synthesis of (η^6-Benzene)[η^5-1-*t*-butylcarbamoyl-2-methyl-4-(4-butylphenyl)cyclopentadienyl]ruthenium Tetraphenylborate (11b). This complex was prepared using *n*-butyllithium and $NaBPh_4$ by the same method as that for **11a** (72% yield). Mp 202.0–202.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.52 (d, 2H, *J* = 8.3 Hz, C_6H_4), 7.35–7.30 (m, 8H, Ph), 7.24 (d, 2H, *J* = 8.3 Hz, C_6H_4), 6.91 (t, 8H, *J* = 7.3 Hz, Ph), 6.76 (t, 4H, *J* = 7.3 Hz, Ph), 6.49 (s, 1H, NH), 6.23 (s, 1H, CpH), 6.19 (s, 1H, CpH), 6.16 (s, 6H, C_6H_6), 2.62 (t, 2H, *J* = 7.8 Hz, CH_2), 2.36 (s, 3H, $CpCH_3$), 1.62–1.55 (m, 2H, CH_2), 1.43 (s, 9H, $C(CH_3)_3$), 1.39–1.30 (m, 2H, CH_2), 0.92 (t, 3H, *J* = 7.3 Hz, CH_3). IR (KBr) 3393 (NH), 1663 cm^{-1} (C=O). MS (FAB) *m/z* 490 ($M^+ - PF_6$). Found: C, 75.51; H, 6.68; N, 1.60%. Calcd for $C_{51}H_{54}BNORu$: C, 75.73; H, 6.73; N, 1.73%.

Synthesis of (η^6-Benzene)(η^5-1-*t*-butylcarbamoyl-2-methyl-4-biphenylylcyclopentadienyl)ruthenium Hexafluorophosphate (12). A mixture of **9e** (0.66 g, 1 mmol), $PhB(OH)_2$ (0.69 g, 6 mmol), Na_2CO_3 (0.63 g, 6 mmol), and $[Pd(PPh_3)_4]$ (10 mg, 0.01 mmol) in 1,2-dimethoxyethane (12 ml) and water (8 ml) was refluxed for 3 h. This solution was neutralized by 6 M HCl. After re-

moval of the solvent, to the residual oil was added an aqueous solution of ammonium hexafluorophosphate (0.48 g, 3 mmol). The aqueous solution was extracted with dichloromethane (40 ml × 3) and the combined extracts were dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure, the residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and the residue was purified by recrystallization from ethanol to give 0.43 g (66% yield) of ruthenium complex **12** as pale yellow needles. Mp 224.0–224.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.74–7.67 (m, 6H, Ph), 7.59 (t, 2H, J = 7.1 Hz, Ph), 7.42–7.40 (m, 1H, Ph), 6.59 (s, 1H, CpH), 6.31 (s, 1H, CpH), 6.23 (s, 6H, C_6H_6), 2.40 (s, 3H, $CpCH_3$), 1.44 (s, 9H, $C(CH_3)_3$). IR (KBr) 3428 (NH), 1668 cm^{-1} (C=O). MS (FAB) *m/z* 510 ($M^+ - PF_6$). Found: C, 53.09; H, 4.37; N, 2.18%. Calcd for $C_{29}H_{30}F_6NOPRu$: C, 53.21; H, 4.62; N, 2.14%.

Synthesis of (η^6-Benzene)[η^5-1-*t*-butylcarbamoyl-2-methyl-4-(4-trimethylsilyletynylphenyl)cyclopentadienyl]ruthenium Hexafluorophosphate (13). A mixture of **9e** (0.74 g, 1.16 mmol), trimethylsilylacetylene (0.66 g, 6.6 mmol), [$PdCl_2(PPh_3)_2$] (40 mg, 0.05 mmol), PPh_3 (30 mg, 10 mmol), and CuI (11 mg, 5 mmol) in acetonitrile (5 ml) and piperidine (10 ml) was refluxed for 12 h. After removal of the solvent, to the residual oil was added an aqueous solution of ammonium hexafluorophosphate (0.48 g, 3 mmol). The aqueous solution was extracted with dichloromethane (40 ml × 3) and the combined extracts were dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure, the residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and the residue was purified by recrystallization from ethanol to give 0.50 g (64% yield) of ruthenium complex **13** as pale yellow needles. Mp 146.5–147.0 °C. ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.63 (d, 2H, J = 8.3 Hz, C_6H_4), 7.45 (d, 2H, J = 8.3 Hz, C_6H_4), 6.59 (s, 1H, CpH), 6.30 (s, 1H, CpH), 6.22 (s, 6H, C_6H_6), 2.38 (s, 3H, $CpCH_3$), 1.43 (s, 9H, $C(CH_3)_3$), 0.23 (s, 9H, $Si(CH_3)_3$). IR (KBr) 3422 (NH), 2159 (C_2), 1669 cm^{-1} (C=O). MS (FAB) *m/z* 530 ($M^+ - PF_6$). Found: C, 49.70; H, 4.86; F, 17.05; N, 2.29; P, 4.49%. Calcd for $C_{28}H_{34}F_6NOPRuSi$: C, 49.85; H, 5.08; F, 16.89; N, 2.08; P, 4.59%.

Synthesis of Tris(acetonitrile)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium Hexafluorophosphate (14a). Ruthenium complex **6a** (0.98 g, 2 mmol) was dissolved in acetonitrile (100 ml) under an argon atmosphere and the solution was irradiated with ultraviolet light for 18 h. Removal of the solvent under reduced pressure gave 1.07 g (99% yield) of ruthenium complex **14a** as an orange powder. Mp 98.0–102.0 °C (decomp). ^{1}H NMR (acetone-d_6, 270 MHz) δ 4.66 (s, 1H, CpH), 4.22 (dq, 1H, J = 3.0, 7.3 Hz, CH_2CH_3), 4.19 (dq, 1H, J = 3.0, 7.3 Hz, CH_2CH_3), 2.55 (s, 9H, CH_3CN), 1.97 (s, 3H, $CpCH_3$), 1.77 (s, 3H, $CpCH_3$), 1.30 (t, 3H, J = 7.3 Hz, CH_2CH_3). IR (KBr) 1708 cm^{-1} (C=O). Found: C, 35.77; H, 4.12; F, 21.22; N, 7.71; P, 5.77%. Calcd for $C_{16}H_{22}F_6N_3O_2PRu$: C, 35.96; H, 4.15; F, 21.33; N, 7.86; P, 5.80%.

Synthesis of Tris(acetonitrile)(η^5-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)ruthenium Hexafluorophosphate (14b). This complex was prepared using **6b** by the same method as that for **14a** (99% yield). Mp 65.0–68.0 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 7.59–7.56 (m, 3H, Ph), 7.41–7.39 (m, 2H, Ph), 5.43 (s, 1H, CpH), 4.85 (s, 1H, CpH), 4.33–4.23 (m, 2H, CH_2CH_3), 2.45 (s, 9H, CH_3CN), 1.35 (t, 3H, J = 7.3 Hz, CH_2CH_3). IR (KBr) 1716 cm^{-1} (C=O). Found: C, 42.07; H, 3.85; F, 19.01; N, 6.97; P, 5.00%. Calcd for $C_{21}H_{24}F_6N_3O_2PRu$: C, 42.29; H, 4.06; F, 19.11; N, 7.04; P, 5.19%.

Synthesis of Tris(acetonitrile)[η^5-1-ethoxycarbonyl-2-methyl-4-(4-bromophenyl)cyclopentadienyl]ruthenium Hexafluorophosphate (14e). This complex was prepared using **6e** by the same method as that for **14a** (99% yield). Mp 138.5–139.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, 2H, J = 8.5 Hz, C_6H_4), 7.26 (d, 2H, J = 8.5 Hz, C_6H_4), 5.21 (s, 1H, CpH), 4.51 (s, 1H, CpH), 4.34–4.24 (m, 2H, CH_2CH_3), 2.34 (s, 9H, CH_3CN), 2.17 (s, 3H, $CpCH_3$), 1.35 (t, 3H, J = 7.1 Hz, CH_2CH_3). IR (KBr) 1714 cm^{-1} (C=O). Found: C, 37.08; H, 3.18; Br, 11.77; F, 16.86; N, 6.11; P, 4.55%. Calcd for $C_{21}H_{23}BrF_6N_3O_2PRu$: C, 37.35; H, 3.43; Br, 11.83; F, 16.88; N, 6.22; P, 4.59%.

Synthesis of Bis(acetonitrile)(carbonyl)(η^5-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)ruthenium Hexafluorophosphate (17). Ruthenium complex **14b** (0.42 g, 0.7 mmol) was dissolved in acetonitrile (20 ml) under an argon atmosphere and the carbon monoxide was bubbled through this solution for 30 min. Removal of the solvent under reduced pressure gave 0.39 g (95% yield) of ruthenium complex **17** as a reddish-brown powder. Mp 37.0–46.0 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 7.72–7.60 (m, 3H, Ph), 7.49–7.45 (m, 2H, Ph), 6.47 (d, 1H, J = 1.7 Hz, CpH), 5.94 (d, 1H, J = 1.7 Hz, CpH), 4.39–4.26 (m, 2H, CH_2CH_3), 2.56 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.35 (t, 3H, J = 7.3 Hz, CH_2CH_3). IR (KBr) 1991 (C=O), 1721 cm^{-1} (C=O). MS (FAB) *m/z* 439 ($M^+ - PF_6$). Found: C, 41.16; H, 3.44; F, 19.55; N, 4.63; P, 5.57%. Calcd for $C_{20}H_{21}F_6N_2O_3PRu$: C, 41.17; H, 3.63; F, 19.54; N, 4.80; P, 5.31%.

Synthesis of (Acetonitrile)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)bis(tirphenylphosphine)ruthenium Hexafluorophosphate (18). A mixture of **14a** (0.53 g, 1.0 mmol) and triphenylphosphine (2.62 g, 10 mmol) in acetonitrile (50 ml) was stirred at room temperature for 12 h. After removal of the solvent under reduced pressure, the precipitate was washed with ether several times and the residue was dissolved in dichloromethane. This solution was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated and dried in vacuo (99% yield). Mp 119.5–120.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.11 (m, 24H, Ph), 6.82–6.78 (m, 6H, Ph), 4.53 (s, 1H, CpH), 4.21–4.13 (m, 1H, CH_2CH_3), 4.12 (s, 1H, CpH), 4.02–3.94 (m, 1H, CH_2CH_3), 2.34 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.18 (t, 3H, J = 7.3 Hz, CH_2CH_3). IR (KBr) 1709 cm^{-1} (C=O). MS (FAB) *m/z* 832 ($M^+ - PF_6$). Found: C, 59.20; H, 4.83; F, 11.57; N, 1.25; P, 9.32%. Calcd for $C_{48}H_{46}F_6NO_2P_3Ru$: C, 59.02; H, 4.75; F, 11.67; N, 1.43; P, 9.51%.

Synthesis of (η^6-Chlorobenzene)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium Hexafluorophosphate (19). A mixture of **14a** (0.17 g, 0.32 mmol) and chlorobenzene (179 mg, 1.6 mmol) in 1,2-dichloroethane (50 ml) was refluxed for 12 h. After removal of the solvent under reduced pressure, the precipitate was washed with ether several times and the residue was dissolved in dichloromethane. This solution was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated and the residue was purified by recrystallization from ethanol to give 0.13 g (80% yield) of ruthenium complex **19** as colorless needles. Mp 142.0–142.5 °C. ^{1}H NMR (acetone-d_6, 270 MHz) δ 6.74 (dd, 2H, J = 5.6, 6.6 Hz, Ph), 6.51 (dd, 2H, J = 5.9, 6.6 Hz, Ph), 6.41 (d, 1H, J = 5.9 Hz, Ph), 5.98 (d, 1H, J = 1.7 Hz, CpH), 5.80 (d, 1H, J = 1.7 Hz, CpH), 4.33 (q, 2H, J = 7.3 Hz, CH_2CH_3), 2.30 (s, 3H, $CpCH_3$), 2.08 (s, 3H, $CpCH_3$), 1.36 (t, 3H, J = 7.3 Hz, CH_2CH_3). IR (KBr) 1717 cm^{-1} (C=O). MS (FAB) *m/z* 379 ($M^+ - PF_6$). Found: C, 36.88; H, 3.41; F, 21.65; P, 5.67%. Calcd for $C_{16}H_{18}ClF_6O_2PRu$: C, 36.69; H, 3.46; F, 21.76; P, 5.91%.

X-ray Diffraction Analysis of (η^6-Benzene)[η^5-1-(*l*)-menthyloxycarbonyl-2-methyl-4-phenylcyclopentadienyl]ruthenium Tetraphenylborate (S_{C1}-8b-1) and (η^6-Benzene)[η^5-1-(*l*)-men-

thyloxycarbonyl-2-methyl-4-(*t*-butyl)cyclopentadienyl]ruthenium Hexafluorophosphate (S_{C1}-4c-1). Crystals suitable for X-ray diffraction were mounted on a glass fiber with epoxy resin. All measurements were performed on Rigaku AFC5R and AFC7R automated four-circle diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). Reflections were collected in the range of $6° < 2\theta < 55°$ at –70 °C with a scan rate 8° min^{-1} for S_{C1}-**8b-1** and at –75 °C with a scan rate 16° min^{-1} for S_{C1}-**4c-1**. Three standard reflections were monitored at every 150 measurements and no damage was observed in any measurements. Intensities were corrected for Lorentz and polarization effects and for absorption using ψ-scan technique. The structures were solved by Patterson methods and refined by full-matrix least-squares minimizing of $\Sigma w(|F_o| - |F_c|)^2$ ($w = 1/\sigma^2(F_o)$). Absolute configurations were based on the stereochemistry of the (*l*)-menthyl group. Anisotropic thermal parameters were used for all non-hydrogen atoms except for carbon atoms of the η^6-benzene ligands and fluorine atoms of the hexafluorophosphate anion, which were refined as a rigid group, for S_{C1}-**4c-1**. The η^6-benzene ligands and the hexafluorophosphate anion of S_{C1}-**4c-1** were disordered. The hydrogen atoms were included at calculated positions ($d_{C\text{-}H}$ = 0.95 Å) and their parameters were not refined. The final cycles of full matrix least squares refinements converged. Crystallographic data are as follows.

***S*$_{C1}$-8b-1**: $C_{53}H_{55}BO_2Ru$, MW = 835.90, yellow, monoclinic, $P2_1$ (#4), a = 9.836(1), b = 20.625(6), c = 11.313(2) Å, β = 106.24(1)°, V = 2203.4(8) Å^3, Z = 2, μ = 3.95 cm^{-1}, R = 0.038 and R_w = 0.044 for 514 parameters against 4386 reflections with $I > 3\sigma(I)$ out of 5212 unique reflections (R_{int} = 0.026), GOF = 1.09.

***S*$_{C1}$-4c-1**: $C_{27}H_{39}F_6O_2PRu$, MW = 641.64, colorless, monoclinic, $C2$ (#5), a = 14.876(2), b = 10.615(2), c = 18.632(2) Å, β = 94.222(8)°, V = 2934.3(5) Å^3, Z = 4, μ = 6.49 cm^{-1}, R = 0.060 and R_w = 0.083 for 274 parameters against 2572 reflections with $I > 3\sigma(I)$ out of 3546 unique reflections (R_{int} = 0.029), GOF = 1.14.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 153431–153432, and the final atomic parameters and structure factors have been deposited as Document No. 74018 at the Office of the Editor of *Bull. Chem. Soc. Jpn.*

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