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Synthesis of enantiopure planar-chiral cyclopentadienyl-ruthenium binuclear complexes bridged by aromatic systems †

Mari Yamamoto, Kiyotaka Onitsuka, Mitsunari Uno and Shigetoshi Takahashi *

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

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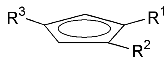
Planar-chiral trisubstituted cyclopentadienyl-ruthenium binuclear complexes [(Cp^{3}Ru)$_2$(μ-η^6,η^6-arene)][PF$_6$]$_2$ (Cp^3 = (R_{C1})- or (S_{C1})-1-Pr^{i}NHCO-2,4-Me$_2$C$_5$H$_2$) bridged by aromatic π-ligands such as biphenyl **b**, triphenylene **c**, diphenylmethane **d**, and 9,10-dihydroanthracene **e** were synthesized and isolated in an enantiomerically pure form. The molecular structures of (S_{C1})-[Cp^{3}Ru(η^6-biphenyl)][PF$_6$] (S)-**1b**(Cp^3), [{(S_{C1})-Cp^{3}Ru}$_2$(η^6,η^6-biphenyl)][PF$_6$]$_2$ (R,R)-**3b**(Cp^3), and [Cp^{3}Ru(η^6-triphenylene)][PF$_6$] **1c**(Cp^3) were established by X-ray crystallography. These complexes were characterized by optical and electrochemical analyses.

Introduction

Multinuclear transition metal complexes linked by π-electron conjugation have attracted considerable interest due to their potential applications in electronic, magnetic, and optical materials. In particular, multinuclear polymetallocenes bridged by π-aromatic systems have been extensively studied with regard to molecular electronics due to communication among the metals through π-electron conjugation.[1,2] If these complexes are optically active, unusual electronic, magnetic, and optical properties might be expected, and helical-chiral metallocene oligomers have already been studied in terms of such characteristics.[3] Although there have been several reports on multinuclear π-polyarene complexes,[1,2,4–6] there are relatively few reports on optically active forms.[7]

Recently, we reported a new method for the synthesis of enantiopure planar-chiral cyclopentadienyl-ruthenium complexes by using a trisubstituted cyclopentadiene (Cp^{1}H, Table 1) with a removable chiral auxiliary, an (l)-menthyl group.[8,9] A usual reaction of Cp^{1}Na with a ruthenium source gives a mixture of diastereomers **1a**(Cp^1), which can also be obtained from an ester exchange reaction between [Cp^{2}Ru(C$_6$H$_6$)][PF$_6$] and (l)-menthol[9] (Scheme 1). The diastereomers (S)-**1a** and (R)-**1a** are separated by fractional recrystallization. (η^5-Cyclopentadienyl)(η^6-benzene)ruthenium complexes **1a** are readily converted to tris(acetonitrile) complexes, [Cp^{1}Ru(CH$_3$CN)$_3$][PF$_6$] **2**, by a photoreaction with acetonitrile, which is a useful precursor for a CpRu moiety. Complexes **2** can easily be re-converted to π-arene complexes **1** by treatment with arenes[10,11] (Scheme 2). Thus, the photoreaction of diastereopure (S)-**1a**(Cp^1) in acetonitrile, followed by ligand exchange with benzene again gave (η^5-Cp^1)(η^6-benzene)ruthenium without any detectable change in optical purity, indicating that racemization of the Cp^1-Ru moiety is not involved in the photoreaction.[9] We applied this transformation to the synthesis of enantiopure planar-chiral cyclopentadienyl bi-ruthenium complexes bridged by polyaromatic π-ligands such as biphenyl and triphenylene.

Table 1 Abbreviations of cyclopentadienyl ligands



Cp^n	R^1	R^2	R^3
Cp^1	CH$_3$	CH$_3$	CO$_2$(l)-menthyl
Cp^2	CH$_3$	CH$_3$	CO$_2$C$_2$H$_5$
Cp^3	CH$_3$	CH$_3$	CONH^{i}Pr
Cp^4	H	H	CO$_2$CH$_3$

Results and discussion

Synthesis of enantiopure planar-chiral [bis(η^5-cyclopentadienylruthenium)](μ-π-polyarene) complexes

For the synthesis of planar-chiral bis(cyclopentadienylruthenium)(polyarene) complexes, we initially chose biphenyl as a bridging π-aromatic ligand. There may be two routes, direct (A) and stepwise (B), to [bis(η^5-cyclopentadienylruthenium)]-μ-biphenyl complex **3b** (Scheme 3). We first examined the direct route, and a preliminary experiment using a racemic mixture of [Cp^{2}Ru(AN)$_3$][PF$_6$] **2** (Cp^2, see Table 1) showed that stepwise route B is preferable with respect to the yield of **3b**, since **2** is not very stable in refluxing dichloroethane and considerable decomposition of **2** was observed during the reaction. Therefore, we adopted the stepwise reaction for the synthesis of optically active planar-chiral [bis(η^5-cyclopentadienylruthenium)-μ-biphenyl][PF$_6$]$_2$ complexes **3b**. Thus, a racemic mixture of [Cp^{2}Ru(C$_6$H$_6$)][PF$_6$] **1a**(Cp^2) was converted to **2**(Cp^2) by photolysis in acetonitrile, followed by treatment with an equiamount of biphenyl in dichloromethane at 40 °C for 3 h to give planar-chiral mononuclear complex [Cp^{2}Ru(η^6-C$_6$H$_5$-C$_6$H$_5$)] **1b**(Cp^2) in good yield. When complex **1b**(Cp^2) was again reacted with tris(acetonitrile) complex **2**(Cp^2) in 1,2-dichloroethane under reflux, biphenyl-bridging binuclear complex **3b**(Cp^2) was obtained as a pale yellow powder in 81% yield.

Using this method, we attempted to prepare an optically pure planar-chiral analog of **3b** (Scheme 4). Thus, [(S_{C1})-Cp^{1}Ru-(C$_6$H$_6$)][PF$_6$] (S)-**1a**(Cp^1) was converted to tris(acetonitrile) complex **2**, which was reacted with an equiamount of biphenyl

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† Electronic supplementary information (ESI) available: physical and spectral data of enantiopure mononuclear and binuclear complexes. See http://www.rsc.org/suppdata/dt/bl/b107051g/

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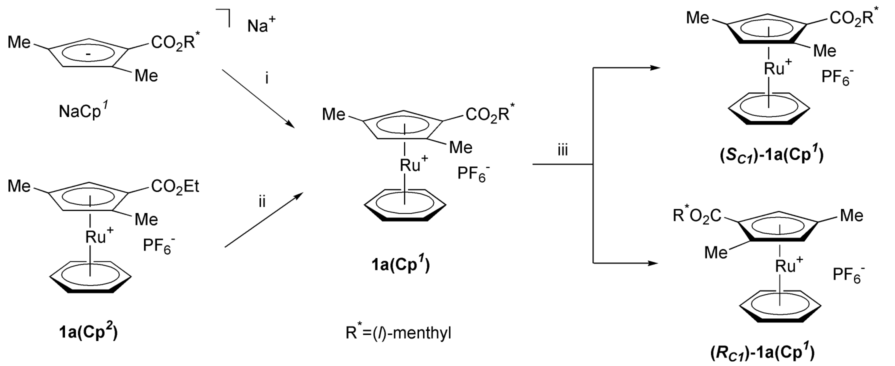
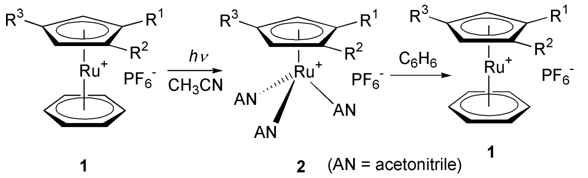
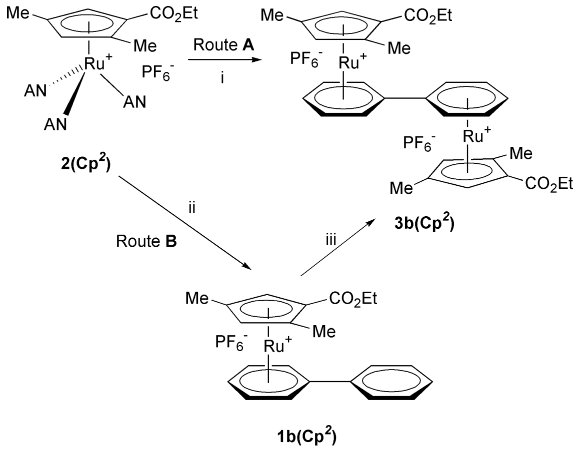


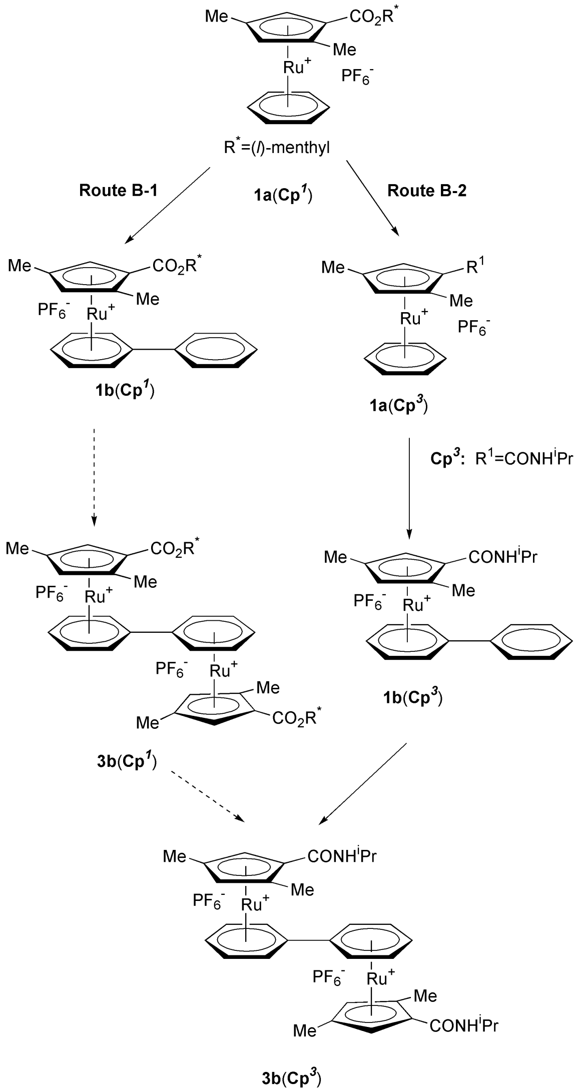
Scheme 1 Synthesis of diastereomers. *Reagents*: i, [Ru(C_6H_6)Cl_2]$_2$; ii, (1) hydrolysis, (2) $(COCl)_2$, (3) (*l*)-menthol; iii, fractional recrystallization.



Scheme 2 Arene ligand-exchange reaction.



Scheme 3 Syntheses of binuclear complex **3b**. *Reagents*: i, 1/2 biphenyl; ii, biphenyl; iii, **2**(Cp^2).



Scheme 4 Syntheses of enantiopure planar-chiral complexes.

in dichloromethane under reflux for 3 h to give planar-chiral mononuclear complex [(S_{C1})-Cp^1Ru(η^6-C_6H_5-C_6H_5)] (*S*)-**1b**-(Cp^1) in 87% yield. To synthesize a planar-chiral binuclear complex bridged by a biphenyl ligand according to Route B-1 in Scheme 4, mononuclear complex (*S*)-**1b**(Cp^1) was treated with tris(acetonitrile) complex (*S*)-**2**(Cp^1) in refluxing 1,2-dichloroethane. However, the formation of binuclear complex **3b**(Cp^1) was not observed, probably due to the steric effect of a sterically large menthyl group, since an X-ray structural analysis[12] of a Cp^1Co complex showed that the menthyl group lies perpendicular to the Cp ring. Therefore, we chose another synthetic route, Route B-2 (Scheme 4), in which enantiopure complex **1a**(Cp^3) with a smaller substituent is used as a starting material. Enantiopure [(S_{C1})-Cp^3Ru(C_6H_6)][PF_6] (*S*)-**1a**(Cp^3), which has a trisubstituted cyclopentadienyl ligand bearing an isopropylamide group and is easily prepared from (*S*)-**1a**(Cp^1),[9] was converted to [Cp^3Ru(CH_3CN)$_3$][PF_6] (*S*)-**2**(Cp^3) by a photoreaction in CH_3CN, followed by a reaction with excess biphenyl (**b**) in dichloromethane under reflux for 3 h to afford mononuclear complex [Cp^3Ru(η^6-C_6H_5-C_6H_5)][PF_6] (*S*)-**1b**(Cp^3) in 84% yield. In the ^{1}H and ^{13}C NMR spectra, signals due to the hydrogens and carbons of a phenyl group coordinating to a Ru atom showed an upfield shift relative to those of the non-coordinating ring,[5] indicating hexahapto coordination of the biphenyl ligand to the ruthenium atom (Experimental section). Mononuclear complex (*S*)-**1b**(Cp^3) further reacted with (*S*)-**2**(Cp^3) in 1,2-dichloroethane under reflux to afford a C_2-symmetric binuclear complex [{(S_{C1})-Cp^3Ru}$_2$(μ-η^6,η^6-biphenyl)][PF_6]$_2$ (*S*,*S*)-**3b**(Cp^3) in 73% yield. Reflecting the C_2 symmetry of the molecule, the Cp^3Ru(η^6-C_6H_5-) units were equivalent with regard to both ^{1}H and ^{13}C{^{1}H} NMR spectra.

Optically pure (*R*)-isomers [(R_{C1})-Cp^3Ru(η^6-biphenyl)][PF_6] (*R*)-**1b**(Cp^3) and [{(R_{C1})-Cp^3Ru}$_2$(μ-η^6,η^6-biphenyl)][PF_6]$_2$ (*R*,*R*)-**3b**(Cp^3) were similarly prepared from [(S_{C1})-Cp^3Ru-(η^6-benzene)][PF_6] (*R*)-**1a**(Cp^3).[9] Binuclear complex [{(S_{C1})-Cp^3Ru:(R_{C1})-Cp^3Ru}(μ-η^6,η^6-biphenyl)][PF_6]$_2$ (*R*,*S*)-**3b**(Cp^3) was also prepared by reacting (*R*)-**1b**(Cp^3) with (*S*)-**2**(Cp^3). These optically active complexes were identified by usual analyses including optical rotations and circular dichroism (CD) spectra. Planar-chiral mono-ruthenium complexes (*R*)-**1b**(Cp^3) and (*S*)-**1b**(Cp^3) showed the same melting point and absolute value of $[\alpha]_D$ (Table 2). The CD spectrum of (*R*)-**1b**(Cp^3) is the

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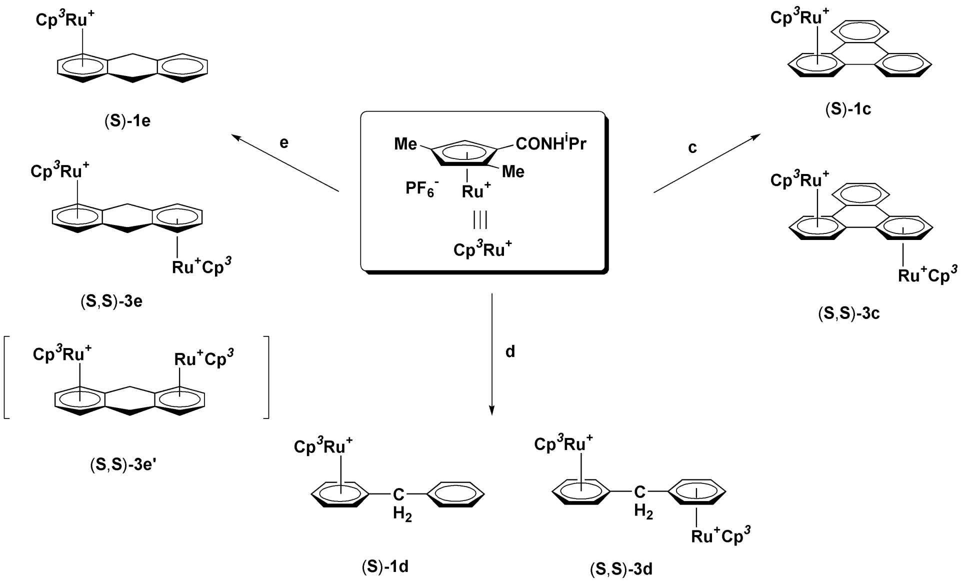
Table 2 Physical data of enantiomers

Complex	Yield (%)[a]	mp/°C	$[\alpha]_D^{25}$/deg	(in CH_3CN)[b]
(*R*)-**1b**(Cp^3)	90	141.5–142.0	−59.3	(*c* 0.497)
(*S*)-**1b**(Cp^3)	84	141.5–142.0	+59.3	(*c* 0.500)
(*R*,*R*)-**3b**(Cp^3)	94	218.5–219.0[c]	−40.8	(*c* 0.500)
(*S*,*S*)-**3b**(Cp^3)	73	217.5–218.5[c]	+39.9	(*c* 0.517)
(*S*,*R*)-**3b**(Cp^3)	95	255.0–255.5[c]	0	(*c* 0.507)
(*S*)-**1c**(Cp^3)	83	251.0–251.5[c]	+117.4	(*c* 0.499)
(*S*,*S*)-**3c**(Cp^3)	79	218.8–219.8[c]	+94.5	(*c* 0.504)
(*S*)-**1d**(Cp^3)	73	170.2–170.7	+40.5	(*c* 0.478)
(*S*,*S*)-**3d**(Cp^3)	99	109.0–110.0	+39.5	(*c* 0.504)
(*S*)-**1e**(Cp^3)	69	155.2–155.7	+38.7	(*c* 0.499)
(*S*,*S*)-**3e**(Cp^3)	94	244.0–244.5[c]	+43.7	(*c* 0.503)

[a] Based on **2**(Cp^3) used. [b] *c*/g per 100 ml. [c] Decomposition.



Scheme 5 Synthesis of mono- and binuclear complexes linked by polyaromatics.

mirror-image of that of (*S*)-**1b**(Cp^3) (Fig. 1a). A similar relationship was observed between the spectra of (*R*,*R*)-**3b**(Cp^3) and (*S*,*S*)-**3b**(Cp^3) (Fig. 1b), indicating that (*R*)-**1b**(Cp^3) and (*S*)-**1b**(Cp^3) as well as (*R*,*R*)-**3b**(Cp^3) and (*S*,*S*)-**3b**(Cp^3) are pairs of enantiomers. *Meso* isomer (*R*,*S*)-**3b**(Cp^3) had an $[\alpha]_D$ of almost zero and no Cotton effect in the CD spectrum, as expected (Fig. 1b).

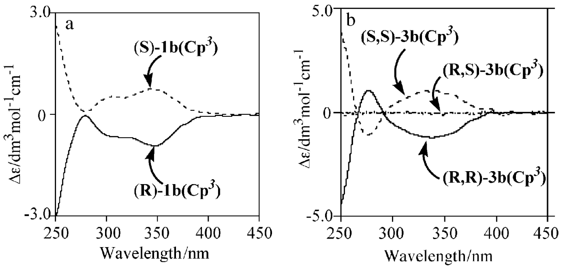


Fig. 1 (a) CD Spectra of (*R*)- and (*S*)-**1b**(Cp^3). (b) CD Spectra of (*R*,*R*)-, (*S*,*S*)- and (*R*,*S*)-**3b**(Cp^3).

Several binuclear complexes **3c**–**e**, in which planar-chiral Cp–Ru moieties are linked by polyaromatic π-ligands, such as triphenylene (**c**), diphenylmethane (**d**), and 9,10-dihydroanthracene (**e**), were also synthesized in a similar manner (Scheme 5). Isolated yields are summarized in Table 2 along with $[\alpha]_D$ values and melting or decomposition points. The reaction of dihydroanthracene (**e**) with (*S*)-**2**(Cp^3) in a molar ratio of 1 : 2 yielded binuclear complex (*S*,*S*)-**3e**(Cp^3) as a sole product, while its isomer (*S*,*S*)-**3e′**(Cp^3) was not observed, probably due to steric constraints imposed by the large cyclopentadienylruthenium moiety. Similarly, the reaction of triphenylene (**c**) with excess (*S*)-**2**(Cp^3) gave binuclear complex (*S*,*S*)-**3c**(Cp^3). The binuclear complex bridged by triphenylene should be obtained as a mixture of diastereomers (Fig. 2).

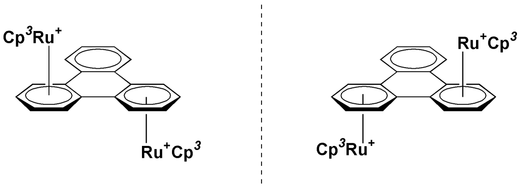


Fig. 2 A diastereomeric pair of (*S*,*S*)-**3c**(Cp^3).

Actually, the ^1H NMR spectrum suggested that the resulting product was a 1 : 1 mixture of diastereomers, which could not be separated. There is still one free benzene ring in **3c**(Cp^3), and we tried to react the third moiety of $CpRu^+$, but failed, probably due to steric hindrance. These results suggest that two moieties of Cp^3Ru are unable to combine simultaneously with a π-system on the same side of a triphenylene ligand.

The planar-chiral complexes synthesized in the present study were characterized by usual analyses (Experimental section), and some were examined by X-ray crystallography.

Molecular structures of (*S*)-1b(Cp^3), (*R*,*R*)-3b(Cp^3), and 1c(Cp^3)

Recrystallization of (*S*)-**1b**(Cp^3) and (*R*,*R*)-**3b**(Cp^3) from a mixture of ethanol, acetonitrile and ether gave single crystals suitable for X-ray analysis. Single crystals of **1c**(Cp^3) were obtained by recrystallization from a racemic mixture, but not

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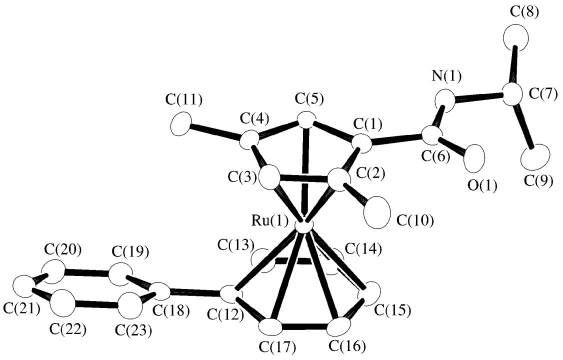

Fig. 3 Molecular structure of (*S*)-**1b**(Cp^3); all hydrogen atoms and the PF_6 anion have been omitted for clarity (as in all the present structures).

from the enantiomers. The molecular structure of (*S*)-**1b**(Cp^3) is illustrated in Fig. 3. The Cp^3 and η^6-phenyl rings, which are bonded to a Ru atom, are nearly parallel to one another (dihedral angle, 1.4°). The two phenyl rings of biphenyl are twisted relative to each other by 18.1°. The amide group is almost coplanar with the Cp^3 ring (dihedral angle, 0.8°). The bond distances and angles of Cp–Ru as well as C_6H_5-Ru are within normal ranges.[5,6]

The molecular structure of (*R*,*R*)-**3b**(Cp^3) is depicted in Fig. 4. The bond distances and angles found in (*R*,*R*)-**3b**(Cp^3) are similar to those reported for $[(CpRu)_4(\eta^6,\eta^6,\eta^6,\eta^6\text{-quaterphenyl})][PF_6]_4$.[5] The Cp^3 and η^6-phenyl rings are nearly parallel to one another (dihedral angles, 2.2° and 1.1°) and the torsion angle between the two phenyl rings of biphenyl is 14.4°. The molecular structure of **1c**(Cp^3) is shown in Fig. 5. The dihedral angle between the Cp^3 ring and C_6 ring **1** bonded to a Ru atom is 4.9°, which is slightly larger than that of (*S*)-**1b**(Cp^3) or (*R*,*R*)-**3b**(Cp^3). C_6 ring **2** bends to the opposite side of the Cp^3 ring to avoid steric repulsion by the isopropyl group (dihedral angle between rings **1** and **2**, 11.1°). On the other hand, ring **3** bends in the direction of the Cp^3 ring to maintain the aromaticity of triphenylene (dihedral angle between rings **1** and **3**, 6.9°). Crystal data are given in Table 3.

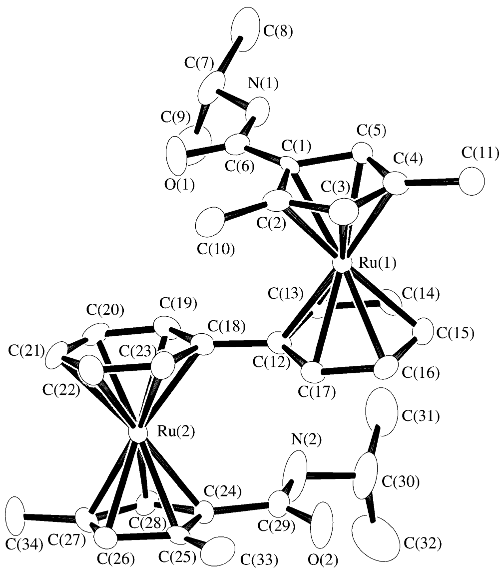

Fig. 4 Molecular structure of (*R*,*R*)-**3b**(Cp^3).

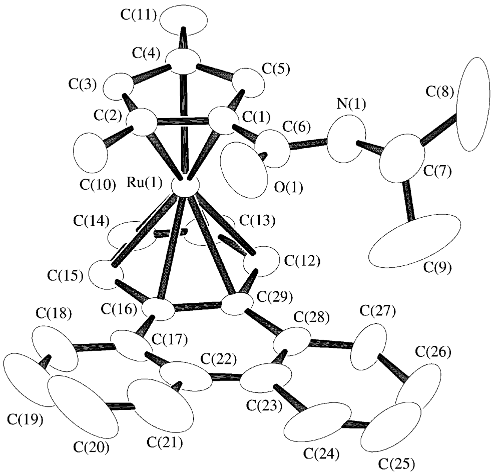

Fig. 5 Molecular structure of **1c**(Cp^3).

Electrochemistry

To evaluate the electronic effect of trisubstituted cyclopentadienyl ligands on the ruthenium center and to determine whether there is communication between two ruthenium centers bridged by a π-aromatic ligand, we measured redox potentials of the complexes by cyclic voltammetry (CV). Both the mono- and binuclear complexes underwent reduction in acetonitrile at a Pt electrode. The potentials of the complexes with reference to an internal ferrocene standard are listed in Table 4. To compare the effects of substituents on the cyclopentadienyl ligand, we also prepared mononuclear complexes $[Cp^4Ru(\eta^6\text{-biphenyl})][PF_6]$ (Cp^4 = $C_5H_4CO_2Me$) **1b**(Cp^4) and $[(C_5H_5)Ru(\eta^6\text{-biphenyl})][PF_6]$ **1b**(C_5H_5), and binuclear complexes $[(Cp^4Ru)_2(\mu\text{-biphenyl})][PF_6]_2$ **3b**(Cp^4) and $[\{(C_5H_5)Ru\}_2(\mu\text{-biphenyl})][PF_6]_2$ **3b**(C_5H_5), and then recorded their CVs. The potentials of complexes **1b** and **3b** should reflect the electronic effects of the cyclopentadienyl ligand on the central metal. In fact, reversible or irreversible reduction was observed for these complexes, and the reduction potentials of trisubstituted cyclopentadienyl complexes **1b** as well as **3b** bearing an ester or an amide group on the cyclopentadienyl ligand were more positive than those of non-substituted cyclopentadienyl complexes **1b**(C_5H_5) and **3b**(C_5H_5). As expected, the most positive potential was observed for **1b**(Cp^4) as well as **3b**(Cp^4), which only has an electron-withdrawing ester group on the cyclopentadienyl ligand. The general pattern of voltammograms consists of one irreversible reduction peak for mononuclear complexes **1b** containing an η^6-biphenyl ligand, as reported for a $(C_5Me_5)Ru$ analog.[13] In contrast to the case of mononuclear complexes **1b**, a characteristic feature of voltammograms of binuclear complexes **3b** is the single reversible wave found at $E_{1/2} = -1.06$ to -1.25 V *vs.* SCE. Compared with the corresponding binuclear iron complexes,[14] ruthenium complexes **3b** showed a different behavior and did not show a second wave up to a potential of −2.5 V. Comparison of the peak height of **3b** with that of ferrocene used as an internal reference at the same concentration showed that the waves of **3b** correspond to a one-electron process. This is in contrast to a binuclear $(C_5Me_5)Ru$ analog which reportedly undergoes irreversible one-electron reduction.[13] Binuclear **3b** shows more positive reduction potential than mononuclear **1b**, suggesting that there is some interaction between the two ruthenium centers bridged by a biphenyl ligand in **3b**. We also recorded the CV of mono- and binuclear triphenylene complexes. Mononuclear complex **1c**(Cp^3) showed one reversible wave, whereas binuclear **3c**(Cp^3) showed two reversible waves. A similar phenomenon has been reported for $(C_5Me_5)Ru$ analogs with condensed-ring compounds such as triphenylene and anthracene.[15]

Experimental

General

All reactions except hydrolysis were performed under an atmosphere of argon. ^1H and ^{13}C NMR spectra were measured

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Table 3 Crystal and refinement data for (*S*)-**1b**(Cp^3), (*R*,*R*)-**3b**(Cp^3), and **1c**(Cp^3)

Complex	(*S*)-**1b**(Cp^3)·EtOH	(*R*,*R*)-**3b**(Cp^3)	**1c**(Cp^3)
Chemical formula	$C_{25}H_{32}NO_2RuPF_6$	$C_{34}H_{42}N_2O_2Ru_2P_2F_{12}$	$C_{29}H_{28}NORuPF_6$
M	624.57	1002.79	652.58
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P1$ (no. 1)	$P1$ (no. 1)	$P\bar{1}$ (no. 2)
a/Å	8.331(3)	10.576(2)	12.050(2)
b/Å	9.722(3)	11.833(3)	12.101(3)
c/Å	8.317(2)	8.557(3)	10.445(2)
α/deg	95.87(2)	92.90(3)	111.74(2)
β/deg	99.12(2)	112.03(2)	103.61(2)
γ/deg	74.53(3)	76.36(2)	72.34(2)
V/Å^3	639.7(4)	963.8(5)	1335.0(6)
Z value	1	1	2
μ/cm^{-1}	7.43	9.59	7.14
Total data collected	3155	4677	6419
Unique data	2953 ($R_{int} = 0.025$)	4437 ($R_{int} = 0.024$)	6129 ($R_{int} = 0.021$)
Observed data	2951 ($I > 3\sigma(I)$)	3949 ($I > 3\sigma(I)$)	5250 ($I > 3\sigma(I)$)
R	0.016	0.030	0.057
R_w	0.021	0.035	0.088
GOF	1.05	1.08	1.25

Table 4 Electrochemical data[a]

[compound]$^{n+}$		E_{pc}	E_{pa}	$E_{1/2}$[b]
Cp^{4}Ru(η^6-biphenyl)	**1b**(Cp^4)	−1.56		
Cp^{2}Ru(η^6-biphenyl)	**1b**(Cp^2)	−1.65		
Cp^{3}Ru(η^6-biphenyl)	**1b**(Cp^3)	−1.75		
(C_5H_5)Ru(η^6-biphenyl)	**1b**(C_5H_5)	−1.80		
(Cp^{4}Ru)$_2$(η^6,η^6-biphenyl)	**3b**(Cp^4)	−1.08	−1.03	−1.06
(Cp^{2}Ru)$_2$(η^6,η^6-biphenyl)	**3b**(Cp^2)	−1.16	−1.12	−1.14
(Cp^{3}Ru)$_2$(η^6,η^6-biphenyl)	**3b**(Cp^3)	−1.34	−1.10	−1.22
(C_5H_5Ru)$_2$(η^6,η^6-biphenyl)	**3b**(C_5H_5)	−1.30	−1.20	−1.25
Cp^{3}Ru(η^6-triphenylene)	**1c**(Cp^3)	−1.54	−1.30	−1.42
(Cp^{3}Ru)$_2$(η^6,η^6-triphenylene)	**3c**(Cp^3)	−1.31	−1.22	−1.27
		−1.86	−1.63	−1.75[c]

[a] Measured in acetonitrile solution of 0.1 M *n*-Bu_4NClO_4 at room temperature at a scan rate of 200 mV s^{-1}. [b] $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials in V, respectively, and are referred to SCE based on a simultaneous measurment of the ferrocene redox potential (0.40 V). [c] Second wave.

in d$_6$-acetone on a JEOL JNM LA-400 (400 MHz) or BRUKER ARX-400 (400 MHz). IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR. Mass spectrometry was performed with a Shimadzu GCMS-QP-2000 spectrometer. Optical rotation was measured on a JASCO DIP-1000 digital polarimeter and circular dichroism spectra were taken on a JASCO circular dichroism J-725. Cyclic voltammograms were recorded on a BAS 100B/W (CV-50). CV cells were fitted with Pt working electrodes, Pt wire counter electrodes, and Ag/Ag$^+$ reference electrodes. Unless stated otherwise, commercial-grade chemicals were used without further purification. Trisubstituted cyclopentadienyl-ruthenium complexes (*R*)-**1a**-(Cp^1), (*S*)-**1a**(Cp^1), and **1a**(Cp^2) were prepared as reported elsewhere.[9]

Preparation of enantiopure mononuclear complexes

(*S*)-1a(Cp^3). [(S_{C1})-(η^5-1-(*l*)-Menthyloxycarbonyl-2,4-dimethylcyclopentadienyl)(η^6-benzene)ruthenium](hexafluorophosphate) (*S*)-**1a**(Cp^1) (2.11 g, 3.52 mmol) was heated under reflux in a mixture of acetonitrile (50 ml) and water (50 ml) saturated with Na_2CO_3. After continuous stirring for 8 h, the reaction mixture was neutralized with 6M HCl and then evaporated to dryness. The residue was extracted with acetonitrile and the solution was dried over anhydrous sodium sulfate. Evaporation of the solvent from the resulting solution gave a carboxylic acid derivative as pale yellow solids. The carboxylic acid was suspended in 60 ml of dichloromethane, and a few drops of DMF and oxaryl chloride (1 ml) were then added to the suspension. The mixture was vigorously stirred for 6 h at room temperature to give the corresponding acid chloride. After the removal of dichloromethane and excess oxaryl chloride under reduced pressure, the resulting solid was dissolved in 10 ml of acetonitrile. The solution was added dropwise to a solution of isopropylamine (35.2 mmol) and a small amount of 4-dimethylaminopyridine in acetonitrile (60 ml). The mixture was stirred at room temperature overnight and the solvent was removed under reduced pressure. The crude product was suspended in water, and ammonium hexafluorophosphate (1.15 g, 7.04 mmol) was added. The mixture was extracted with dichloromethane and the extract was dried over anhydrous sodium sulfate and passed through an alumina column. Purification by recrystallization from ethanol gave [(S_{C1})-{η^5-1-isopropylaminocarbonyl-2,4-dimethylcyclopentadienyl}(η^6-benzene)ruthenium](hexafluorophosphate) (*S*)-**1a**(Cp^3) as pale yellow needles (1.25 g, 71%). mp 207.0–207.5 °C. (Found: C, 40.81; H, 4.14; N, 2.86; F, 22.87; P, 6.03. $C_{17}H_{22}F_6NOPRu$ requires C, 40.64; H, 4.41; N, 2.79; F, 22.69; P, 6.17%); ν_{max}/cm^{-1} (C=O), 1666 (KBr); δ_H (acetone-d$_6$) 7.26(1 H, br, NH), 6.27(6 H, s, η^6-C_6H_6), 5.88(1 H, s, Cp–H), 5.63(1 H, s, Cp–H), 4.15–4.05(1 H, m, C*H*(CH_3)$_2$), 2.27(3 H, s, Cp–CH_3), 2.04(3 H, s, Cp–CH_3), 1.20(3 H, d,*J* = 6.6 Hz, CH(C*H*$_3$)) and 1.16(3 H, d, *J* = 6.6 Hz, CH(C*H*$_3$)); δ_C(acetone-d$_6$) 163.4(s, C=O), 100.7(s, *Cp*–CH_3), 99.3(s, *Cp*–CH_3), 91.4(s, *Cp*–CONH^{i}Pr), 88.8(s, η^6-C_6H_6), 85.6(s, Cp–H), 81.0(s, Cp–H), 42.5(s, *C*H(CH_3)), 22.5(s, CH(*C*H$_3$)), 22.3(s, CH(*C*H$_3$)), 13.4(s, Cp–*C*H$_3$) and 13.3(s, Cp–*C*H$_3$); *m*/*z* 358 (M$^+$ − PF_6).

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(*S*)-1b(Cp^3). In a quartz glass vessel, (*S*)-**1a**(Cp^3) (301 mg, 0.60 mmol) was dissolved in 100 ml of acetonitrile. The solution was irradiated with ultraviolet light using a 500-W high-pressure mercury lamp for 15 h. Evaporation of the acetonitrile from the solution gave tris(acetonitrile) complex [Cp^{3}Ru(CH$_3$-CN)$_3$][PF$_6$] **2**(Cp^3) as an orange solid. A mixture of solid **2**(Cp^3) and biphenyl (925 mg, 6.0 mmol) was dissolved in 50 ml of dichloromethane, and the solution was stirred under reflux for 3 h. The solvent was evaporated under reduced pressure and excess biphenyl was removed by extraction with ether. Purification by recrystallization from ethanol gave [(S_{C1})-{η^5-1-isopropylaminocarbonyl-2,4-dimethylcyclopentadienyl}(η^6-biphenyl)ruthenium](hexafluorophosphate) (*S*)-**1b**(Cp^3) as pale yellow needles (291 mg, 84%). mp 141.5–142.0 °C (Found: C, 47.95; H, 4.27; N, 2.32; F, 19.65; P, 5.19. $C_{23}H_{26}F_6NOPRu$ requires C, 47.75; H, 4.53; N, 2.42; F, 19.70; P, 5.35%; ν_{max}/cm^{-1} (C=O) 1666; δ_H(acetone-d$_6$) 7.85–7.83 (2 H, m, Ph$_{ortho}$), 7.57–7.54 (3 H, m, Ph$_{meta}$, Ph$_{para}$), 7.20 (1 H, br, NH), 6.79 (1 H, d, *J* = 6.3 Hz, η^6-Ph$_{ortho}$), 6.75 (1 H, d, *J* = 6.6 Hz, η^6-Ph$_{ortho}$), 6.45–6.36 (3 H, m, η^6-Ph$_{meta}$, η^6-Ph$_{para}$), 5.80 (1 H, s, Cp–H), 5.55 (1 H, s, Cp–H), 4.04–3.95 (1 H, m, C*H*(CH$_3$)$_2$), 2.06 (3 H, s, Cp–CH$_3$), 1.87 (3H, s, Cp–CH$_3$) and 1.11 (6H, d, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$); δ_C(acetone-d$_6$) 163.1 (s, C=O), 134.2 (s, C$_6$H$_5$), 131.2 (s, C$_6$H$_5$), 130.2 (s, C$_6$H$_5$), 128.8 (s, C$_6$H$_5$), 104.9 (s, η^6-C$_6$H$_5$), 100.7 (s, *Cp*–CH$_3$), 99.4 (s, *Cp*–CH$_3$), 92.1 (s, *Cp*–CONH^{i}Pr), 88.9 (s, η^6-C$_6$H$_5$), 88.7 (s, η^6-C$_6$H$_5$), 88.5 (s, η^6-C$_6$H$_5$), 87.5 (s, η^6-C$_6$H$_5$), 87.3 (s, η^6-C$_6$H$_5$), 85.9 (s, Cp–H), 81.5 (s, Cp–H), 42.6 (s, *C*H(CH$_3$)), 22.4 (s, CH(*C*H$_3$)), 22.4 (s, CH(*C*H$_3$)), 13.0 (s, Cp–*C*H$_3$) and 12.7 (s, Cp–*C*H$_3$); *m*/*z* 434 (M$^+$ − PF$_6$).

Enantiopure mononuclear complexes (*R*)-**1b**(Cp^3), (*S*)-**1c**(Cp^3), (*S*)-**1d**(Cp^3) and (*S*)-**1e**(Cp^3) were similarly prepared from (*R*)- or (*S*)-**1a**(Cp^3) with arenes. Complexes **1b**(Cp^2) and **1b**(Cp^4) were prepared by a similar method using **1a**(Cp^2) and **1a**(Cp^4), respectively, with biphenyl. The analytical data, including ^{1}H and ^{13}C NMR, IR, and mass spectra, are provided as ESI.†

Preparation of enantiopure binuclear complexes

(*S*,*S*)-3b(Cp^3). In a quartz glass vessel, (*S*)-**1a**(Cp^3) (100 mg, 0.20 mmol) was dissolved in 100 ml of CH$_3$CN. The solution was irradiated with ultraviolet light using a 500-W high-pressure mercury lamp for 15 h. The reaction solution was evaporated to dryness and tris(acetonitrile) complex [Cp^3-Ru(CH$_3$CN)$_3$][PF$_6$] **2** was obtained. A mixture of solid **2** and (*S*)-**1b**(Cp^3) (58 mg, 0.10 mmol) was dissolved in 50 ml of 1,2-dichloroethane, and the solution was stirred at 83 °C for 3 h. The solvent was evaporated under reduced pressure and purification by recrystallization from ethanol–acetonitrile–ether gave [{(S_{C1})-Cp^{3}Ru}$_2$(μ-η^6,η^6-biphenyl)][PF$_6$]$_2$ (*S*,*S*)-**3b**(Cp^3) as pale yellow needles (74 mg, 73%). mp 217.5–218.0 °C(dec.) (Found: C, 40.84; H, 4.01; N, 2.95; F, 22.52; P, 6.39. $C_{34}H_{42}F_{12}N_2O_2$-P_2Ru_2 requires C, 40.72; H, 4.22; N, 2.79; F, 22.73; P, 6.18%); ν_{max}/cm^{-1} (C=O) 1665 (KBr); δ_H(acetone-d$_6$) 7.41 (2 H, br, NH), 6.94–6.92 (4 H, m, η^6-Ph$_{ortho}$), 6.59–6.53 (6 H, m, η^6-Ph$_{meta}$, η^6-Ph$_{para}$), 5.90 (2 H, s, Cp–H), 5.64 (2 H, s, Cp–H), 3.96–3.92 (2 H, m, C*H*(CH$_3$)$_2$), 2.09 (6 H, s, Cp–CH$_3$), 1.96 (6 H, s, Cp–CH$_3$), 1.13 (6 H, d, *J* = 6.6 Hz, CH(C*H*$_3$)) and 1.10 (6 H, d,*J* = 6.6 Hz, CH(C*H*$_3$)); δ_C(acetone-d$_6$) 162.6 (s, C=O), 101.7 (s, η^6-C$_6$H$_5$), 100.5 (s, *Cp*–CH$_3$), 97.3 (s, *Cp*–CH$_3$), 93.5 (s, *Cp*–CONH^{i}Pr), 89.3 (s, η^6-C$_6$H$_5$), 88.9 (s, η^6-C$_6$H$_5$), 88.9 (s, η^6-C$_6$H$_5$), 87.7 (s, η^6-C$_6$H$_5$), 87.4 (s, η^6-C$_6$H$_5$), 86.2 (s, Cp–H), 82.0 (s,Cp–H), 42.6 (s, *C*H(CH$_3$)), 22.4 (s, CH(*C*H$_3$)), 22.3 (s, CH(*C*H$_3$)), 13.1 (s, Cp–*C*H$_3$), 12.6 (s, Cp–*C*H$_3$); *m*/*z* 859 (M$^+$ − PF$_6$) and 713 (M$^+$ − 2PF$_6$).

Enantiopure binuclear complexes (*R*,*R*)-**3b**(Cp^3), (*S*,*R*)-**3b**-(Cp^3), (*S*,*S*)-**3c**(Cp^3), (*S*,*S*)-**3d**(Cp^3), and (*S*,*S*)-**3e**(Cp^3) were similarly prepared from (*R*)- or (*S*)-**1a**(Cp^3) with the corresponding mononuclear complexes. Complexes **3b**(Cp^2) and **3b**(Cp^4) were prepared by a similar method using **1a**(Cp^2) and **1a**(Cp^4), respectively, with the corresponding mononuclear complexes. The analytical data, including ^{1}H and ^{13}C NMR, IR, and mass spectra, are provided in the ESI.†

X-Ray diffraction analyses

Crystals suitable for X-ray diffraction were mounted on a glass fiber with epoxy resin. Measurements were performed on a Rigaku AFC7R automated four circles diffractometer for (*S*)-**1b**(Cp^3), (*R*,*R*)-**3b**(Cp^3), and **1c**(Cp^3) using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) at −75 °C. An empirical absorption collection was made for (*S*)-**1b**(Cp^3) and **1c**(Cp^3) using the ψ-scan technique. The structures were solved by Patterson methods (DIRDIF92 Patty or SAPI). Absolute configurations were determined on the basis of those of the starting materials. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares refinement while minimizing $\Sigma\omega(|F_o| - |F_c|)^2$. The hydrogen atoms were included at the calculated positions (*d*C–H = 0.95 Å) and their parameters were not refined. The final cycles of full-matrix least-squares refinement were converged. All calculations were performed using the teXsan crystallographic software package.

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See http://www.rsc.org/suppdata/dt/b1/b107051g/ for crystallographic data in CIF or other electronic format.

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