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Synthesis and characterization of planar-chiral cyclopentadienylruthenium–vinylidene complexes

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Abstract

Enantiopure planar-chiral cyclopentadienylruthenium–vinylidene complexes, (S_{Cl})- and (R_{Cl})-[(η^5-C_5H_2-1-COR^1-2-Me-4-R^2)$Ru(PPh_3)_2$(=C=CHR^3)][PF_6] (**4**: R^1 = O-(*l*)- and O-(*d*)-menthyl; **8**: R^1 = NH^tBu. R^2 = Me, Ph; R^3 = Ph, H), were synthesized starting from [(η^5-C_5H_2-1-COR^1-2-Me-4-R^2)$Ru(\eta^6$-C_6H_6)][PF_6], and characterized by optical and spectra methods including ^{1}H, ^{13}C, and ^{31}P-NMR, and CD spectra. The reaction rate of [(η^5-C_5H_2-1-CO_2Et-2,4-Me_2)$Ru(PPh_3)_2(MeCN)_3$][PF_6] with phenylacetylenes leading to vinylidene complexes increases in the order: $HCCC_6H_4NO_2 < HCCC_6H_5 < HCCC_6H_4OMe$. Analysis by cyclic voltammetry showed that trisubstituted cyclopentadienyl ligands C_5H_2-1-CO_2Et-2-Me-4-R^2 (R^2 = Me, Ph, ^{t}Bu, Naph etc.) act as a weak electron-donor compared with non-substituted cyclopentadienyl one in ruthenium–phenylacetylide complexes.

Keywords: Planar chiral; Enantiomer; Cyclopentadienyl; Vinylidene complexes; Ruthenium

1. Introduction

Most of optically active organometallic catalysts conventionally used in asymmetric organic syntheses contain, as their chiral sources, chiral ligands in which the chirality is based mainly on carbon-centered or axial chirality as seen in many examples of chiral phosphine, amine, acid, and alcohol ligands [1]. However, there have been few applications of planar chirality as a chiral source to optically active catalysts [2–4] although planar chirality is characteristic of organometallic π-complexes [5] such as π-olefin, -cyclopentadienyl, and -arene complexes. In particular, planar-chiral cyclopentadienyl–metal complexes may be a promising candidate as a novel chiral catalyst for asymmetric organic syntheses because racemization arising from a change in coordination mode from η^5 into η^1 or dissociation of the cyclopentadienyl ligand is unlikely to occur, therefore, rigid asymmetric environment can be kept at the metal center. In addition a cyclopentadienyl ligand is an anionic one and forms a different family of chiral oraganometallic complexes from neutral compounds like phosphines. The efficiency of planar-chiral cyclopentadienyl complexes has proved particularly valuable in the asymmetric Diels–Alder reactions and the polymerization of olefins by early transition metal catalysts [3,6]. In contrast to early transition metals few studies on planar-chiral cyclopentadienyl complexes of late transition metals have been made [4], except extremely stable planar-chiral ferrocene [2] and ruthenocene [7] derivatives. Half-sandwich complexes of such late transition metals having a piano-stool structure, however, may be expected to show high catalytic activities. Indeed, some cyclopentadieyl-iron and -ruthenium complexes of a half-sandwich structure are known to behave as an effective catalyst in organic reactions [8]. Among reactive ruthenium complexes we were interested in ruthenium vinylidene complexes, carbene related species, since they have been proposed as key intermediates in a number of catalytic transformations involving terminal alkynes [9]. Previously we have shown synthetic methods [10] for planar-chiral cyclopentadienyl complexes of late transition metals such as iron, cobalt, rhodium, and ruthenium. Now we have expanded the method to the synthesis of planar-chiral

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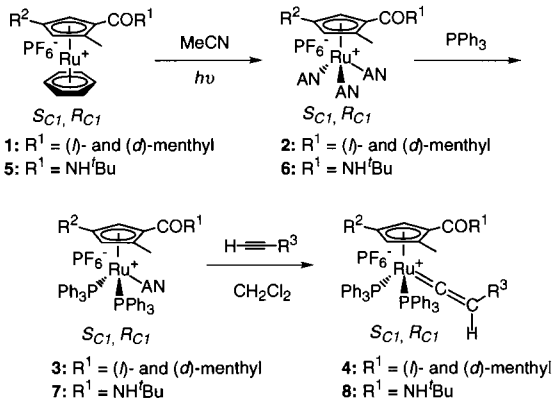
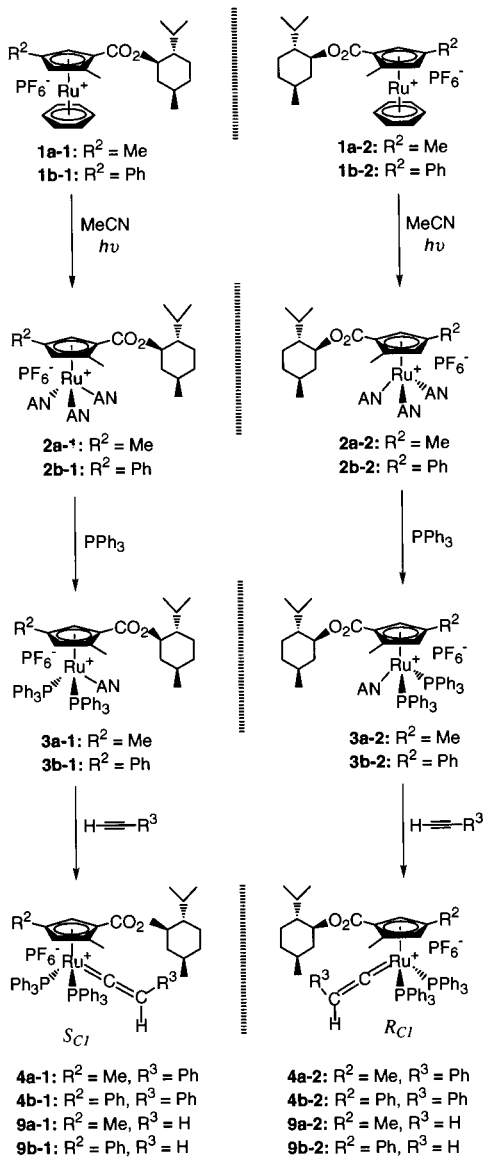


Scheme 1.



Scheme 2.

cyclopentadienylruthenium–vinylidene complexes, and successfully obtained them as an enantiopure form. Herein we report the synthesis and characterization of enantiopure planar-chiral (trisubstituted cyclopentadienyl)ruthenium complexes bearing a vinylidene ligand as well as the electronic property of the trisubstituted cyclopentadienyl ligand in comparison with non-substituted- (Cp) and pentamethyl-cyclopentadienyl (CMe_5) ones.

2. Results and discussion

The planar-chiral cyclopentadienylruthenium–vinylidene complexes (**4** and **8**) have been synthesized from the reactions outlined in Scheme 1.

Since separation of a diastereo mixture as well as optical resolution of a racemic mixture of planar-chiral cyclopentadienylruthenium–vinylidene complexes was difficult mainly due to low crystallinity and stability, we choose stepwise transformation to the optically active ruthenium-vinylidene complexes starting from (S_{Cl})- or (R_{C1})-planar-chiral (η^5-trisubstituted cyclopentadienyl)ruthenium(η^6-benzene) hexafluorophosphate [(η^5-C_5H_2-1-COR^1-2-Me-4-R^2)Ru(η^6-C_6H_6)][PF_6] (**1**) which was prepared in an optically pure form by a convenient method developed previously [10c]. According to the synthetic route, irradiation to enantiopure complex **1a-1** (S_{Cl}, R^1 = O-(*l*)-menthyl, R^2 = Me) with UV light in acetonitrile caused the dissociation of a benzene ligand to give an acetonitrile-coordinated complex, (S_{Cl})-[(η^5-C_5H_2-1-COR^1-2,4-Me_2)Ru($MeCN)_3$][PF_6] (**2a-1**: R^1 = O-(*l*)-menthyl) [11]. During this ligand exchange reaction, dissociation and re-coordination of the planar-chiral cyclopentadienyl ligand resulting in a racemization of planar chirality did not occur at all, and optically pure complex **2a-1** was isolated in an almost quantitative yield (Scheme 2). Similar treatment of (R_{C1})-[(η^5-C_5H_2-1-COR^1-2,4-Me_2)Ru(η^6-C_6H_6)][PF_6] (**1a-2**: R^1 = O-(*d*)-menthyl) gave (R_{C1})-[(η^5-C_5H_2-1-COR^1-2,4-Me_2)Ru($MeCN)_3$][PF_6] (**2a-2**), and tris(acetonitrile) complexes **2a-1** and **2a-2** were confirmed to be a pair of enanitomers by optical and spectral analyses. Then, we reacted tris(acetonitrile) complex **2a-1** with two equivalents of triphenylphosphine in dichloromethane to afford bis(triphenylphosphine) complex, (S_{Cl})-[(η^5-C_5H_2-1-COR^1-2,4-Me_2)Ru($PPh_3)_2$(MeCN)]-[PF_6] (**3a-1**: R^1 = O-(*l*)-menthyl), in a good yield, in which two molecules of acetonitrile ligands were replaced by triphenylphosphine, and even use of a large excess of the phosphine did not give tris(triphenylphosphine) derivative [(η^5-C_5H_2-1-COR^1-2,4-Me_2)Ru-($PPh_3)_3$][PF_6], but formed bis(triphenylphosphine) one (**3**) as a sole product, in which one acetonitrile ligand remains on the ruthenium. An *R* isomer, (R_{C1})-[(η^5-

Table 1
Optical rotation, melting point and C=C stretching of vinylidene complexes

Entry	Complex	Optically rotation (°) [a]	Melting point (°C)	$\nu_{C=C}$ (cm^{-1}) [b]
1	**4a-1**	−46.4 (*c* 0.347)	138–139	1626
2	**4a-2**	+46.4 (*c* 0.300)	138–139	1626
3	**4b-1**	−42.5 (*c* 0.258)	137–138	1650
4	**4b-2**	+42.5 (*c* 0.283)	137–138	1650
5	**8a-1**	+10.5 (*c* 0.418)	119–120	1624
6	**8a-2**	−10.4 (*c* 0.431)	119–120	1624
7	**9a-1**	−76.9 (*c* 0.200)	142–143	1626
8	**9a-2**	+76.5 (*c* 0.200)	142–143	1626
9	**9b-1**	−34.3 (*c* 0.255)	152–153	1626
10	**9b-2**	+34.8 (*c* 0.287)	152–153	1627
11	**10a-1**	+22.3 (*c* 0.235)	113–114	1624
12	**10a-2**	−22.3 (*c* 0.200)	113–114	1623
13 [c]	**15**		105–110 (dec.)	1622, 1640
14 [d]	[d]		190 (dec.)	1616

[a] In CH_3CN.
[b] KBr disc.
[c] See Ref. [12].
[d] Complex: $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(=C=CH_2)][PF_6]$. See Ref. [13].

C_5H_2-1-COR^1-2,4-Me_2)$Ru(PPh_3)_2(MeCN)][PF_6]$ (**3a-2**: R^1 = O-(*d*)-menthyl), was similarly prepared from **2a-2**. Complexes **3a** were identified by means of optical and spectral analyses. They showed optical rotations with the same absolute value, but with an opposite sign each other. Enantiomer **3a-1** exhibited the same ^{31}P-NMR spectrum as **3a-2**, showing two sets of doublet signals at 37.6 and 43.2 ppm due to diastereotopic phosphorus ligands (see Section 3).

It is well known that neutral and cationic cyclopentadienylruthenium(II) complexes are converted to ruthenium-vinylidene complexes by treatment of terminal acetylenes [9a,b,12]. The conversion of the neutral complexes requires a scavenger for removing halogen ligands, however cationic ruthenium complexes produce vinylidene complexes by simply mixing with acetylenes in an appropriate solvent. We performed the reaction of **3** with the acetylenes to obtain the first planar-chiral cyclopentadienylruthenium–vinylidene complexes. Thus, complex **3a-1** was reacted with ten equivalents of phenylacetylene in dichlomethane at room temperature for 18 h. The solution turned from yellow to red in color suggesting the formation of a vinylidene complex. Addition of hexane to the dichloromethane solution caused precipitation of vinylidene complex **4a-1**, (S_{Cl})-$[(\eta^5\text{-}C_5H_2\text{-}1\text{-}COR^1\text{-}2,4\text{-}Me_2)Ru(PPh_3)_2(=C=CHPh)][PF_6]$ (R^1 = O-(*l*)-menthyl), as red solids. Similarly, R_{Cl} isomer **4a-2** was prepared from **3a-2** (Scheme 2). Optically active vinylidene complexes **4a-1** and **4a-2** were characterized by optical and spectral methods. The IR and NMR spectra of **4a-1** were identical with those of **4a-2** (Tables 1 and 2). They showed the C=C stretching vibration in the IR spectra at 1626 cm^{-1} which is within the normal region reported for ruthenium vinylidene complexes [12,13]. In the ^{13}C-NMR spectra, **4a-1** and **4a-2** exhibited an apparent triplet signal (J_{P-C} = 15.1 Hz) attributable to the α–C of vinylidene ligand at 356.9 ppm in a very low field. It is well recognized that the carbon resonance due to Ru=C appears at such a low field and this strongly deshielded resonance for α–C is a characteristic feature of vinylidene complexes [14,15d], clearly indicating that **4a** contains a vinylidene moiety.

Table 2
^{13}C Chemical shift of vinylidene α-carbon and ^{31}P chemical shift of vinylidene complexes

[a]Entry	Complex	^{13}C Chemical shift (ppm)	^{31}P Chemical shift (ppm)
1	**4a-1**	356.90 (t, J_{P-C} = 15.1 Hz)	37.56 (d, J_{P-P} = 27.9 Hz), 43.16 (d, J_{P-P} = 27.8 Hz)
2	**4a-2**	356.95 (t, J_{P-C} = 15.1 Hz)	37.54 (d, J_{P-P} = 27.9 Hz), 43.16 (d, J_{P-P} = 27.9 Hz)
3	**4b-1**	363.66 (t, J_{P-C} = 17.1 Hz)	31.87 (d, J_{P-P} = 26.6 Hz), 45.58 (bs)
4	**4b-2**	363.68 (t, J_{P-C} = 18.2 Hz)	31.80 (d, J_{P-P} = 26.0 Hz), 45.55 (bs)
5	**8a-1**	358.54 (t, J_{P-C} = 15.3 Hz)	42.40 (d, J_{P-P} = 27.3 Hz), 44.91 (d, J_{P-P} = 28.1 Hz)
6	**8a-2**	358.54 (t, J_{P-C} = 15.3 Hz)	42.38 (d, J_{P-P} = 27.3 Hz), 44.89 (d, J_{P-P} = 28.3 Hz)
7	**9a-1**	352.31 (t, J_{P-C} = 17.1 Hz)	38.43 (d, J_{P-P} = 28.1 Hz), 45.61 (d, J_{P-P} = 28.2 Hz)
8	**9a-2**	352.33 (t, J_{P-C} = 17.1 Hz)	38.43 (d, J_{P-P} = 28.1 Hz), 45.62 (d, J_{P-P} = 28.1 Hz)
9	**9b-1**	355.90 (t, J_{P-C} = 19.2 Hz)	35.17 (d, J_{P-P} = 26.3 Hz), 44.51 (bs)
10	**9b-2**	355.99 (t, J_{P-C} = 18.1 Hz)	35.17 (d, J_{P-P} = 25.9 Hz), 44.50 (bs)
11	**10a-1**	352.85 (t, J_{P-C} = 17.0 Hz)	36.78 (d, J_{P-P} = 28.4 Hz), 46.20 (d, J_{P-P} = 28.8 Hz)
12	**10a-2**	352.85 (t, J_{P-C} = 17.0 Hz)	36.75 (d, J_{P-P} = 28.9 Hz), 46.21 (d, J_{P-P} = 28.8 Hz)
13	**15**	358.9 (t, J_{P-C} = 24.0 Hz) [b]	43.00 (s)
14 [c]	[c]	349.94 (t, J_{P-C} = 15.2 Hz)	49.37 (s)

[a] In $CDCl_3$.
[b] See Ref. [12].
[c] Complex: $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(=C=CH_2)][PF_6]$, in CD_3CN. See reference [13].

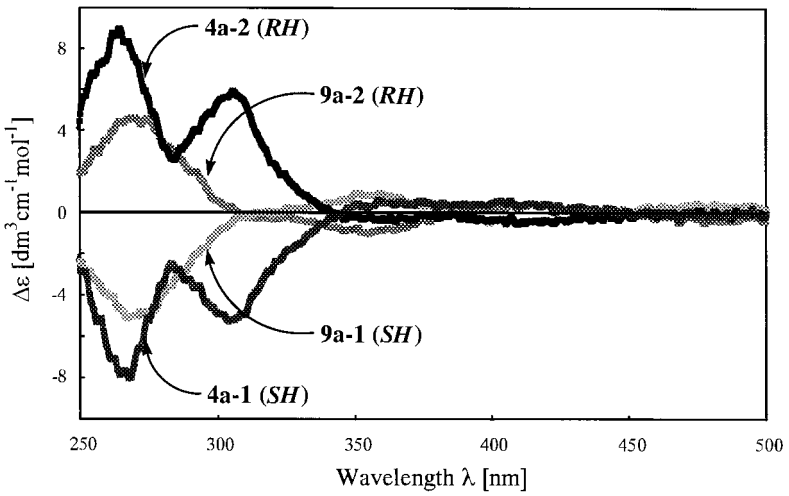


Fig. 1. CD spectra of ruthenium complexes **4a** and **9a**.

Complexes **4a-1** and **4a-2** showed the same melting point at 138–139°C, and the same absolute value in optical rotation with an opposite sign: $[\alpha]_D$: $-46.3°$ for **4a-1**, $+46.4°$ for **4a-2** in an acetonitrile solution. The circular dichroisum (CD) spectra of them are mirror symmetrical each other in all ranges (Fig. 1). A careful NMR experiment showed that the samples of **4a-1** and **4a-2** were not contaminated with impurities such as their diastereomers (R_{Cl})-[(η^5-C_5H_2-1-COR^1-2,4-Me_2)-$Ru(PPh_3)_2$(=C=CHPh)][PF_6] (R^1 = O-(*l*)-menthyl) and (S_{Cl})-[(η^5-C_5H_2-1-COR^1-2,4-Me_2)$Ru(PPh_3)_2$(=C=CH-Ph)][PF_6] (R^1 = O-(*d*)-menthyl), unequivocally indicating that **4a-1** and **4a-2** are a pair of enantiomers. Optically active phenyl-substituted analogs (S_{Cl})- and (R_{Cl})-**4b** (R^2 = Ph) were similarly prepared from (S_{Cl})- and (R_{Cl})-[(η^5-C_5H_2-1-COR^1-2-Me-4-Ph)$Ru(\eta^6$-$C_6H_6)$]-[PF_6] (**1b**: R^1 = O-(*l*)- and O-(*d*)-menthyl), respectively, via tris(acetonitrile) complex **2b** (R^2 = Ph) and then bis(triphenylphosphine)(acetonitrile) complexes **3b** (R^2 = Ph).

Vinylidene complexes **4a** and **4b** carry two chiral elements, i.e. a planar chirality and a carbon-centered chirality in the menthyl group, in a molecule. We have also synthesized optically active cyclopentadienylruthenium–vinylidene complexes possessing only planar chirality. In this case we used, as a starting material, planar-chiral (S_{Cl})- and (R_{Cl})-[(η^5-C_5H_2-1-$CONH^tBu$-2-Me-4-R^2)$Ru(\eta^6$-$C_6H_6)$][PF_6] (**5**) (Scheme 1). Enantiomers, (S_{Cl})-**5a-1** (R^2 = Me) and (R_{Cl})-**5a-2** (R^2 = Me) were prepared from (S_{Cl})-**1a-1** and (R_{Cl})-**1a-2**, respectively, via hydrolysis of the menthyl groups followed by condensation with *tert*-butylamine as reported previously [10b,c]. Enantiopure [(η^5-C_5H_2-1-$CONH^tBu$-2,4-Me_2)$Ru(\eta^6$-$C_6H_6)$][PF_6] (**5a-1**) (S_{Cl} isomer) and **5a-2** (R_{Cl} isomer) were irradiated with UV light in acetonitrile [11], followed by the reaction of triphenylphosphine to give bis(triphenylphosphine)(acetonitrile) complexes **7a-1** and **7a-2**, respectively. Treatment of these complexes with phenylacetylene yielded planar-chiral vinylidene complexes (S_{Cl})- and (R_{Cl})-[(η^5-C_5H_2-1-$CONH^tBu$-2,4-Me_2)Ru(=C=CHPh)][PF_6] **8a**, which have fully been identified by optical and spectral analyses (Tables 1 and 2, Fig. 2).

There have appeared several papers dealing with mechanistic studies on the transformation of vinylidenes from terminal acetylenes [15], but a few reporting the effect of acetylene substituents on the transformation reaction [15d]. The reaction of **3a-1** with trimethylsilylacetylene, $HCCSiMe_3$, caused the cleavage of the C–Si bond to form a non-substituted vinylidene complex, (S_{Cl})-[(η^5-C_5H_2-1-COR^1-2,4-Me_2)$Ru(PPh_3)_2$-(=C=CH_2)][PF_6] (**9a-1**: R^1 = O-(*l*)-menthyl), as often observed in some cases [13]. Similarly, planar-chiral vinylidene complexes **9a-2**, **9b-1**, and **9b-2** were obtained in an enantiopure form from the reactions of **3a-2**, **3b-1**, and **3b-2**, respectively, with trimethylsilylacetylene. Complexes **7a** bearing an amide group on a cyclopentadienyl ligand underwent the same reaction with trimethylsilylacetylene as **3a** and formed optically pure **10a** (Fig. 3). Methyl propionate, $HCCCO_2Me$, which is a strong electron-acceptor, reacted with **3a** to give a complex mixture, from which no definite product was isolated. To know the substituent effect of acetylenes in somewhat details, the reaction rates of [(η^5-C_5H_2-1-COR^1-2,4-Me_2)$Ru(PPh_3)_2$(MeCN)][PF_6] (**11a**: R^1 = OEt) with phenylacetylene derivatives bearing a substituent at the 4-position of the phenyl ring were monitored by a ^{31}P-NMR spectroscopy Eq. (1). The experiment was performed using a racemic mixture of **11a** at 25°C and the formation rate of vinylidene complexes **12a** was traced by ^{31}P-NMR.

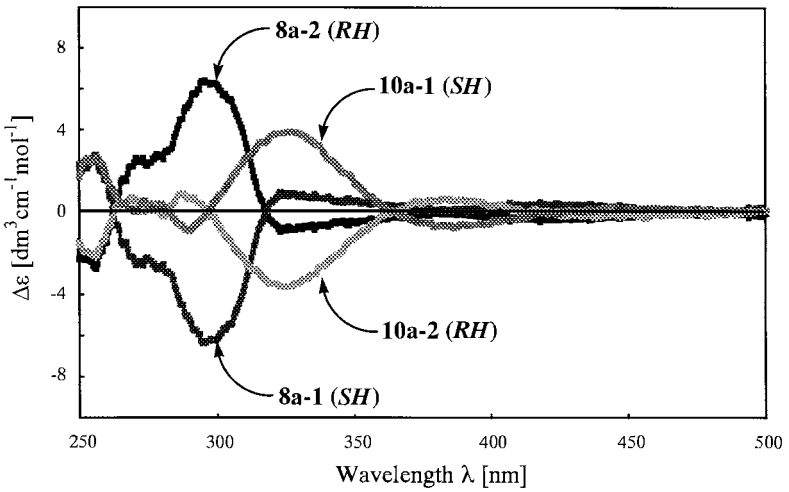
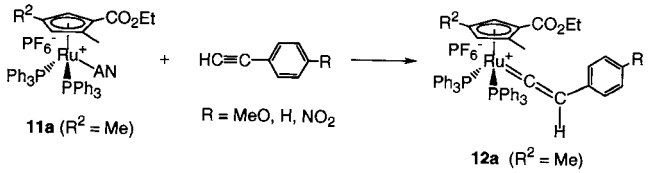


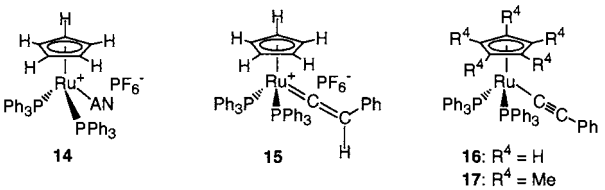
Fig. 2. CD spectra of ruthenium complexes **8a** and **10a**.



(1)

The result (Fig. 4) showed that among phenylacetylene derivatives 4-RC_6H_4CCH (R = H, OMe, and NO_2) employed in this experiment, 4-methoxyphenylacetylene reacted with **11a** faster than phenylacetylene to give vinylidene complex **12a**, whereas the reaction of 4-nitrophenylacetylene proceeded slower than that of phenylacetylene. These results suggest that acetylenes having an electron-donating substituent show a higher reactivity toward **11a** giving vinylidene complexes **12a**, and the same order in the reactivity of acetylenes was observed in the reactions of non-substituted cyclopentadienylruthenium analog **14** [16]. This is a reverse tendency in the substituent effect as compared with the case of cobalt complexes [15b]. The trisubstituted cyclopentadienylruthenium complexes react with phenylacetylene slower than non-substituted cyclopentadienylruthenium analog, implying that steric bulkiness and/or weaker electron-donating nature (vide infra) of the trisubstituted cyclopentadienyl ligand causes a slower reaction leading to vinylidene complexes.

The planar-chiral vinylidene complexes prepared in the present work are thermally stable and show a definite melting point without decomposition (Table 1), although C_5H_5 and C_5Me_5 analogs are known to melt being accompanied with decomposition [12,13]. Our trisubstituted cyclopentadienylruthenium complexes are soluble in polar organic solvents such as dichloromethane, acetone, and acetonitrile, but insoluble in hexane, benzene, and diethylether. Ruthenium-vinylidene complexes commonly react with methanol to give methoxycarbene complexes [17], whereas the present (trisubstituted cyclopentadienyl)ruthenium-vinylidene complexes can be dissolved in warm methanol, but do not show any reactivities toward methanol. Even with oxygen gas these complexes do not react, although a cyclopentadienylruthenium–vinylidene complex is converted to a cyclopentadienylruthenium(carbonyl) complex by the action of O_2 [18].



Previously we reported a novel catalysis of cationic $[CpRu(MeCN)_3]^+$, by which norbornene undergoes a cyclopropanation with propargyl alcohol [19]. Toward this novel transformation of propargyl alcohol, the trisubstituted cyclopentadienylruthenium catalysts, for example, $[(\eta^5\text{-}C_5H_2\text{-}1\text{-}COR^1\text{-}2,4\text{-}Me_2)Ru(MeCN)_3][PF_6]$ (**2a**) exhibited a higher activity than both C_5H_5Ru and C_5Me_5Ru analogs. The reaction was thought to proceed via ruthenium-alkylidene or ruthenacyclopentene as a key intermediate. In this connection, we attempted to evaluate the effect of trisubstituted cyclopentadienyl ligand on the Ru=C=C moiety in $[(\eta^5\text{-}C_5H_2\text{-}1\text{-}COR^1\text{-}$

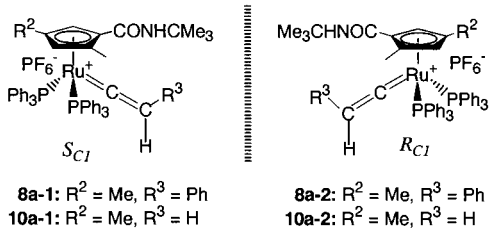


Fig. 3. A pair of enantiopore planar-chiral cyclopentadienylruthenium–vinyliedene compleces **8** and **10**.

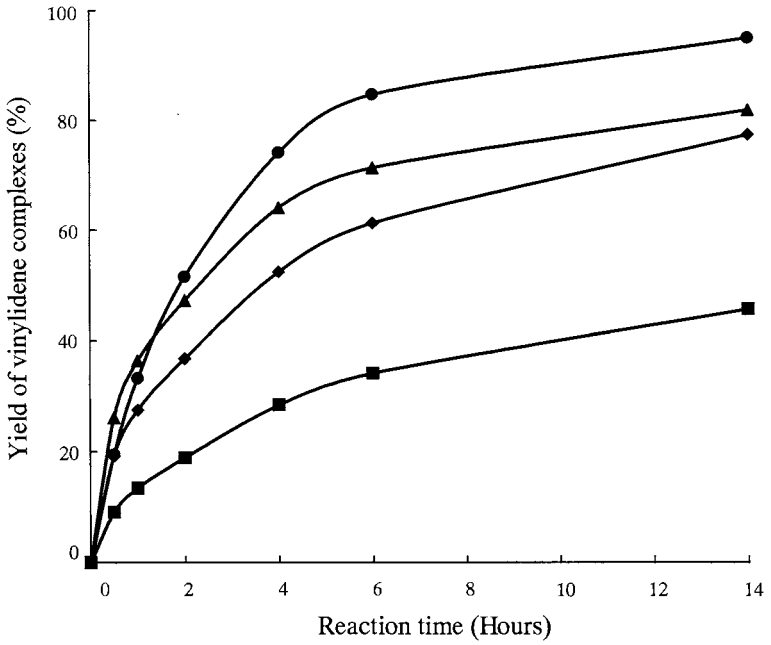
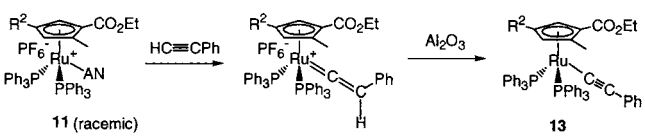


Fig. 4. Reaction rates of ruthenium complexes **11a** with phenylacetylene derivatives $HCCC_6H_4R$. —▲—: R = MeO; —◆—: R = H; —■—: $R = NO_2$; —●—: The reaction of complex **14** with $HCCC_6H_5$.

2,4-Me_2)$Ru(PPh_3)_2$(=C=CHR)][PF_6] (**4** and **8**). The donor-acceptor properties of the trisubstituted cyclopentadienyl ligand were estimated in comparison with C_5H_5 and C_5Me_5, by means of spectral analyses; for example, the C=C stretching vibration of vinylidene was measured by IR, and the P and C chemical shifts of phosphine ligand and α-C in the alkylidene ligand by NMR. The data obtained are summarized in Tables 1 and 2 along with those of C_5H_5 and C_5Me_5 analogs. The C=C stretching vibration of the complexes appeared around 1625 cm^{-1} in the IR spectra and is almost unaffected by the substituents on cyclopentadienyl ligand except **4b** and even by those on the vinylidene ligand. The C_5Me_5 complex showed the absorption at 1616 cm^{-1}, suggesting that increase in the electron-donating property of C_5Me_5 causes a slight shift of the absorption to a lower wavenumber in the comparison with a C_5H_5 analog. In ^{13}C-NMR spectra all the complexes listed in Table 2 showed the characteristic low-field resonances (352–364 ppm) attributable to the α–C of Ru=C=C species. However, no significant influence by the substituents on the α–C chemical shift were observed and even the C_5Me_5 complex exhibited the resonance at 350 ppm. In ^{31}P-NMR spectra the planar-chiral complexes showed two doublets due to diastereotopic phosphorus ligands in the region of 36.8–46.2 ppm except **4b** and **9b**. Complexes **4b** and **9b**, both of which bear a phenyl group on the cyclopentadienyl ligand, similarly showed two phosphorus resonances, but one of the two appeared as an apparent broad signal. This anomaly would presumably be due to an influence of the π-electron system of the phenyl group on a cyclopentadienyl ligand, and some unsuccessful attempts to determine the stereo structure of the complexes were made. The C_5H_5 and C_5Me_5 complexes exhibited resonance at 43 and 49 ppm, respectively. On the basis of such a little difference in phosphorus chemical shifts as well as the through-space influence of a phenyl group the substitutent effect on the metal can not be discussed. The spectral analyses chosen here seem to be obtuse for estimating the electronic property of the trisubstituted cyclopentadienyl ligands. Therefore we electrochemically analyzed the central metal, Ru, directly bound to a cyclopentadienyl ligand. Unfortunately the cyclic voltamograms of the vinylidene complexes did not show a definite oxidation potential, and the Ru-vinylidene complexes were transformed into stable Ru–acetylide complexes **13** by treatment with alumina Eq. (2). Complexes **13** showed quasi-reversible waves in cyclic voltamograms and the results are summarized in Table 3 along with the data obtained from (η^5-C_5H_5)$Ru(PPh_3)_2$(CCPh) (**16**) and (η^5-C_5Me_5)Ru-$(PPh_3)_2$(CCPh) (**17**).

The oxidation potential (E_{pa}) of complex **13a** was observed at a potential higher than those of complexes **16** and **17**, indicating that the trisubstituted cyclopenta-



a: R^2 = Me; **b:** R^2 = Ph; **c:** R^2 = ^{t}Bu; **d:** R^2 = α-Naph; **e:** R^2 = 4-BrC_6H_4.

(2)

dienyl ligand bearing one ethoxycarbonyl and two methyl groups has an weaker electron-donating poperty than a C_5H_5 ligand. To examine in somewhat detail the effect of substituents, we also prepared complexes **13b**–**e** bearing phenyl, *tert*-butyl, α-naphthyl and 4-bromophenyl groups on a cyclopentadienyl ligand. Complexes **13b**–**e** showed similar voltamograms (Table 3), and among complexes **13a**–**e** the highest oxidation potential was observed for **13e** having a 4-BrC_6H_4 group, whereas the lowest potential for a *t*-butyl group. The same tendency was also observed for the reduction potentials (E_{pc}). Based on these results, we may estimate the donor-acceptor properties of cyclopentadienyl ligands in the ruthenium complexes, that is, the electron-donating property increases in the order, 4-(4-BrC_6H_4)-Cp′ < 4-α-Naphthyl-Cp′ ~ 4-Ph-Cp′ < 4-Me-Cp′ < 4-^{t}Bu-Cp′ ≪ C_5H_5 ≪ C_5Me_5 (Cp′ = 1-CO_2Et-2-MeC_5H_2). It should be noted that the delicate control of electron-donating property of 1-COR^1-2-Me-4-R^2-C_5H_2 ligands may be attained by the choice of substituent R^2.

Table 3
Redox potentials of complexes **13a**–**e**, **16** and **17** [a]

Entry	Complex	E_{pc} (V)	E_{pa} (V)
1	**13a**	0.24	0.32
2	**13b**	0.25	0.36
3	**13c**	0.21	0.30
4	**13d**	0.26	0.34
5	**13e**	0.30	0.38
6	**16**	0.14	0.23
7	**17**	−0.05	0.03

[a] In 0.1 M ^{n}Bu_4NPF_6–CH_2Cl_2 at 0.1 V s^{-1}. Ferrocene: $\Delta E_{1/2} = +0.19$, $I_{pa} \fallingdotseq 2I_{pc}$.

3. Experimental

3.1. General

All reactions were carried out under an argon atmosphere, but the work up was performed in air. CH_2Cl_2 was dried over calcium hydride and then distilled. Other chemicals commercially available were used without further purification. Planar-chiral [(η^5-trisubstituted cyclopentadienyl)ruthenium(η^6-benzene)][PF_6] complexes, (S_{Cl})- and (R_{C1})-[(η^5-C_5H_2-1-COR^1-2-Me-4-R^2)-Ru(η^6-C_6H_6)][PF_6], (R^1 = O-(*l*)-menthyl, O-(*d*)-menthyl, NH^{t}Bu; R^2 = Me, Ph) [10b,c], [(η^5-C_5H_5)Ru-(PPh_3)$_2$(MeCN)][PF_6] [16], (η^5-C_5H_5)Ru(PPh_3)$_2$(CCPh) [12], and (η^5-C_5Me_5)Ru(PPh_3)$_2$(CCPh) [13] were prepared according to the methods reported by us and others.

Melting points were measured on Yamato melting point apparatus mode MP 21 and are corrected. NMR spectra were taken on JEOL JNM-LA400, JEOL JNM-LA600 and Bruker ARX400 spectrometers. In ^{1}H and ^{13}C-NMR, $SiMe_4$ was used as an internal standard, and an external 85% H_3PO_4 reference was used for ^{31}P-NMR. IR spectra were obtained on Perkin-Elmer system 2000 FT-IR, FAB mass spectra on a JEOL JMS-600H instrument. Optical rotations and CD spectra were measured on JASCO DIP-1000 and JASCO J-725 instruments, respectively. Cyclic voltammograms were recorded on BAS 100 B/W (CV-50) in CH_2Cl_2 solutions of 0.1 M n-Bu_4NPF_6, and the scan rate was 0.1 V s^{-1}. CV cells were fitted with Pt working electrodes, Pt wire counter electrodes, and Ag/Ag^+ reference electrodes. All potentials were represented versus Cp_2Fe/Cp_2Fe^+ (+0.19 V vs. Ag/Ag^+), which were obtained by the measurement of ferrocene under the same conditions. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University.

3.2. Syntheses of planar-chiral trisubstituted cyclopentadienylrutheniumtris(acetonitrile) complexes (2)

3.2.1. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2,4-Me_2}Ru(MeCN)$_3$][PF_6] (2a-1)

Ruthenium complex (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2,4-Me_2}Ru(η^5-C_6H_6)][PF_6] (**1a-1**) (0.19 g, 0.32 mmol) was dissolved in MeCN (50 ml) under an argon atmosphere and the solution was irradiated with ultraviolet light for 18 h. Removal of the solvent under reduced pressure gave ruthenium complex **2a-1** (0.20 g, 99% yield) as an orange powder. IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1705 ($\nu_{C=O}$). ^{1}H-NMR (CD_3CN, 400 MHz): δ 0.76 (d, J = 6.8 Hz, 3H, menthyl–CH_3), 0.89 (d, J = 5.9 Hz, 6H, menthyl–CH_3), 0.93–1.12 (m, 2H, menthyl), 1.38–1.54 (m, 2H, menthyl), 1.65–1.69 (m, 2H, menthyl), 1.70 (s, 3H, Cp–CH_3), 1.89 (s, 3H, Cp–CH_3), 1.93 (s, 9H, NCCH_3), 4.07 (s, 1H, Cp–*H*), 4.66 (s, 1H, Cp–H), 4.72 (dt, J = 4.4, 10.8 Hz, 1H, menthyl). ^{13}C-NMR (CD_3CN, 100 MHz): δ 12.51 (s), 13.26 (s), 16.68 (s), 21.30 (s), 22.37 (s), 24.06 (s), 27.12 (s), 32.21 (s), 34.97 (s), 41.77 (s), 48.06 (s), 62.57 (s), 68.63 (s), 74.53 (s), 74.97 (s), 88.14 (s), 97.70 (s), 126.20 (s), 170.57 (s). FAB MS: m/z 500 (M^+–PF_6). Mp: 120–121°C. $[\alpha]_D^{20}$: −63.3° (*c* 0.453, MeCN). Calc. for $C_{24}H_{36}F_6N_3O_2PRu$: C, 44.64; H, 5.62; N, 6.51. Anal. Found: C, 44.71; H, 5.41; N, 6.60.

3.2.2. (R_{C1})-[{η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2,4-Me_2}Ru(MeCN)$_3$][PF_6] (2a-2)

This compound was prepared from **1a-2** by the method similar to that for **2a-1** (99%, orange powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1706 ($\nu_{C=O}$). ^{1}H-NMR (CD_3CN, 400 MHz): δ 0.76 (d, J = 7.1 Hz, 3H, menthyl–CH_3), 0.89 (d, J = 6.0 Hz, 6H, menthyl–CH_3), 0.94–1.14 (m, 2H, menthyl), 1.38–1.54 (m, 2H, menthyl), 1.65–1.69 (m, 2H, menthyl), 1.70 (s, 3H,

Cp–CH_3), 1.89 (s, 3H, Cp–CH_3), 1.93 (s, 9H, NCCH_3), 4.07 (s, 1H, Cp–*H*), 4.66 (s, 1H, Cp–*H*), 4.72 (dt, $J = 4.4$, 10.9 Hz, 1H, menthyl). ^{13}C-NMR (CD_3CN, 100 MHz): δ 12.51 (s), 13.25 (s), 16.64 (s), 21.28 (s), 22.35 (s), 24.02 (s), 27.09 (s), 32.19 (s), 34.95 (s), 41.75 (s), 48.04 (s), 62.55 (s), 68.60 (s), 74.51 (s), 74.94 (s), 88.15 (s), 97.72 (s), 126.21 (s), 170.56 (s). FAB MS: *m*/*z* 500 (M^+–PF_6). Mp: 120–121°C. $[\alpha]_D^{20}$: +64.0° (*c* 0.371, MeCN). Calc. for $C_{24}H_{36}F_6N_3O_2PRu$: C, 44.64; H, 5.62; N, 6.51. Anal. Found: C, 44.85; H, 5.41; N, 6.54.

3.2.3. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2-Me-4-Ph}Ru(MeCN)$_3$][PF_6] (**2b-1**)

This compound was prepared from **1b-1** by the method similar to that for **2a-1** (99%, orange powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1712 ($\nu_{C=O}$). ^{1}H-NMR (CD_3CN, 600 MHz): δ 0.78 (d, $J = 7.0$ Hz, 3H, menthyl–CH_3), 0.91 (d, $J = 7.0$ Hz, 6H, menthyl–CH_3), 1.02–1.15 (m, 2H, menthyl), 1.44–1.51 (m, 2H, menthyl), 1.67–1.71 (m, 2H, menthyl), 1.93 (s, 9H, NCCH_3), 2.03 (s, 3H, Cp–CH_3), 4.68 (s, 1H, Cp–*H*), 4.80–4.84 (m, 1H, menthyl), 5.35 (d, $J = 1.6$ H, 1H, Cp–H), 7.34–7.36 (m, 3H, Ph), 7.45–7.46 (m, 2H, Ph). ^{13}C-NMR (CD_3CN, 150 MHz): δ 13.43 (s), 16.74 (s), 21.24 (s), 22.34 (s), 24.06 (s), 27.29 (s), 32.23 (s), 34.96 (s), 42.11 (s), 48.21 (s), 62.91 (s), 64.98 (s), 74.88 (s), 88.99 (s), 99.72 (s), 126.47 (s), 127.94 (s), 129.27 (s), 129.73 (s), 133.94 (s), 170.16 (s). FAB MS: *m*/*z* 562 (M^+–PF_6). Mp: 82–83°C. $[\alpha]_D^{20}$: −220.1° (*c* 0.186, MeCN). Calc. for $C_{29}H_{38}F_6N_3O_2PRu$: C, 49.21; H, 5.42; N, 5.94. Anal. Found: C, 49.48; H, 5.21; N, 5.75.

3.2.4. (R_{Cl})-[η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2-Me-4-Ph}Ru(MeCN)$_3$][PF_6] (**2b-2**)

This compound was prepared from **1b-2** by the method similar to that for **2a-1** (99%, orange powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1711 ($\nu_{C=O}$). ^{1}H-NMR (CD_3CN, 600 MHz): δ 0.78 (d, $J = 7.0$ Hz, 3H, menthyl–CH_3), 0.91 (d, $J = 6.8$ Hz, 6H, menthyl–CH_3), 1.01–1.15 (m, 2H, menthyl), 1.44–1.51 (m, 2H, menthyl), 1.67–1.71 (m, 2H, menthyl), 1.93 (s, 9H, NCCH_3), 2.03 (s, 3H, Cp–CH_3), 4.68 (s, 1H, Cp–*H*), 4.80–4.84 (m, 1H, menthyl), 5.35 (d, $J = 1.6$ H, 1H, Cp–*H*), 7.34–7.36 (m, 3H, Ph), 7.45–7.46 (m, 2H, Ph). ^{13}C-NMR (CD_3CN, 150 MHz): δ 13.43 (s), 16.80 (s), 21.27 (s), 22.38 (s), 24.12 (s), 27.32 (s), 32.26 (s), 35.00 (s), 42.14 (s), 48.25 (s), 62.99 (s), 64.98 (s), 74.88 (s), 88.99 (s), 99.69 (s), 126.46 (s), 127.98 (s), 129.29 (s), 129.74 (s), 134.00 (s), 170.12 (s). FAB MS: *m*/*z* 562 (M^+–PF_6). Mp: 82–83°C. $[\alpha]_D^{20}$: +220.2° (*c* 0.109, MeCN). Calc. for $C_{29}H_{38}F_6N_3O_2PRu$: C, 49.21; H, 5.42; N, 5.94. Anal. Found: C, 49.38; H, 5.24; N, 5.68.

3.3. Syntheses of planar-chiral trisubstituted cyclopentadienylrutheniumtris(acetonitrile) bis(triphenylphosphine) complexes (**3**)

3.3.1. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2,4-Me_2}Ru(PPh_3)$_2$(MeCN)][PF_6] (**3a-1**)

A mixture of **2a-1** (0.20 g, 0.32 mmol) and triphenylphosphine (0.16 g, 0.64 mmol) in CH_2Cl_2 (30 ml) was stirred at room temperature for 12 h. After concentration of the reaction mixture under reduced pressure, the solution was chromatographed on Al_2O_3 with CH_2Cl_2:acetone = 3:1. The eluent was evaporated and dried in vacuo to give **3a-1** (0.33 g, 98% yield) as a yellow powder. IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1702 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.73 (d, $J = 6.8$ Hz, 3H, menthyl–CH_3), 0.81 (d, $J = 6.8$ Hz, 3H, menthyl–CH_3), 0.85–1.10 (m, 2H, menthyl), 0.96 (d, $J = 6.3$ Hz, 3H, menthyl–CH_3), 1.24 (s, 3H, Cp–CH_3), 1.23–1.33 (m, 2H, menthyl), 1.42–1.61 (m, 1H, menthyl), 1.66–1.73 (m, 3H, menthyl), 1.94 (d, $J = 2.0$ Hz, 3H, Cp–CH_3), 1.94–2.00 (m, 1*H*, menthyl), 2.27 (s, 3H, NCCH_3), 4.13 (s, 1H, Cp–H), 4.56 (s, 1H, Cp–H), 4.79 (dt, $J = 4.6$, 10.7 Hz, 1H, menthyl), 6.80 (t, $J = 9.3$ Hz, 6H, Ph), 7.10–7.45 (m, 24H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 4.91 (s), 11.93 (s), 13.14 (s), 15.76 (s), 20.90 (s), 22.00 (s), 22.74 (s), 25.69 (s), 31.50 (s), 33.94 (s), 41.41 (s), 46.58 (s), 70.45 (s), 75.87 (s), 85.24 (s), 96.89 (d, $J = 3.3$ Hz), 107.34 (s), 127.80–134.19 (m), 169.89 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 39.63 (d, $J_{P-P} = 32.8$ Hz), 42.40 (d, $J_{P-P} = 32.7$ Hz). FAB MS: *m*/*z* 942 (M^+–PF_6). Mp: 120–121°C. $[\alpha]_D^{20}$: −27.1° (*c* 0.360, MeCN). Calc. for $C_{56}H_{60}F_6NO_2P_3Ru$: C, 61.81; H, 5.56; N, 1.29. Anal. Found: C, 61.79; H, 5.31; N, 1.35.

3.3.2. (R_{Cl})-[{η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2,4-Me_2}Ru(PPh_3)$_2$(MeCN)][PF_6] (**3a-2**)

This compound was prepared from **3a-2** by the method similar to that for **3a-1** (95%, yellow powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1702 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.73 (d, $J = 6.8$ Hz, 3H, menthyl–CH_3), 0.81 (d, $J = 6.8$ Hz, 3H, menthyl–CH_3), 0.86–1.09 (m, 2H, menthyl), 0.96 (d, $J = 6.3$ Hz, 3H, menthyl–CH_3), 1.24 (s, 3H, Cp–CH_3), 1.23–1.33 (m, 2H, menthyl), 1.42–1.61 (m, 1H, menthyl), 1.66–1.73 (m, 3H, menthyl), 1.94 (d, $J = 2.2$ Hz, 3H, Cp–CH_3), 1.94–2.00 (m, 1*H*, menthyl), 2.27 (s, 3H, NCCH_3), 4.13 (s, 1H, Cp–*H*), 4.56 (s, 1H, Cp–*H*), 4.79 (dt, $J = 4.4$, 10.9 Hz, 1H, menthyl), 6.80 (t, $J = 8.9$ Hz, 6H, Ph), 7.09–7.45 (m, 24H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 5.00 (s), 11.97 (s), 13.20 (s), 15.79 (s), 20.94 (s), 22.05 (s), 22.78 (s), 25.72 (s), 31.55 (s), 34.00 (s), 41.45 (s), 46.63 (s), 70.48 (s), 75.91 (s), 85.23 (s), 96.91 (d, $J = 4.2$ Hz), 107.36 (s), 127.81–134.15 (m), 170.00 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 39.67 (d, $J_{P-P} = 32.7$ Hz), 42.46 (d, $J_{P-P} = 32.7$ Hz). FAB MS: *m*/*z* 942 (M^+–PF_6).

M.p.: 120–121°C. $[\alpha]_D^{20}$: +27.8° (*c* 0.304, MeCN). Calc. for $C_{56}H_{60}F_6NO_2P_3Ru$: C, 61.81; H, 5.56; N, 1.29. Anal. Found: C, 62.03; H, 5.63; N, 1.33.

3.3.3. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2-Me-4-Ph}$Ru(PPh_3)_2(MeCN)][PF_6]$ (**3b-1**)

This compound was prepared from **3b-1** by the method similar to that for **3a-1** (97%, yellow powder). IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1700 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.66 (d, $J = 7.1$ Hz, 3H, menthyl–CH_3), 0.81 (d, $J = 7.1$ Hz, 3H, menthyl–CH_3), 0.90–0.96 (m, 2H, menthyl), 0.97 (d, $J = 6.4$ Hz, 3H, menthyl–CH_3), 1.05–1.10 (m, 2H, menthyl), 1.16–1.21 (m, 1H, menthyl), 1.40 (s, 3H, Cp–CH_3), 1.52–1.75 (m, 4H, menthyl), 4.69–4.73 (m, 1H, menthyl), 4.72 (s, 1H, Cp–*H*), 4.96 (s, 1H, Cp–*H*), 6.57 (t, $J = 9.1$ Hz, 6H, Ph), 7.06 (t, $J = 7.0$ Hz, 6H, Ph), 7.22–7.55 (m, 23H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 4.83 (s), 13.10 (s), 16.47 (s), 20.50 (s), 22.15 (s), 23.60 (s), 26.40 (s), 31.46 (s), 31.70 (s), 41.52 (s), 46.46 (s), 69.50 (s), 75.87 (s), 80.80 (s), 92.84 (s), 109.83 (s), 127.68–134.30 (m), 169.70 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 38.62 (d, $J_{P-P} = 32.5$ Hz), 42.04 (bs). FAB MS: *m/z 1004* (M^+–PF_6). Mp: 132–133°C. $[\alpha]_D^{20}$: −165.9° (*c* 0.300, MeCN). Calc. for $C_{61}H_{62}F_6NO_2P_3Ru$: C, 63.69; H, 5.44; N, 1.22. Anal. Found: C, 63.97; H, 5.48; N, 1.18.

3.3.4. (R_{Cl})-[{η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2-Me-4-Ph}$Ru(PPh_3)_2(MeCN)][PF_6]$ (**3b-2**)

This compound was prepared from **3b-2** by the method similar to that for **3a-1** (99%, yellow powder). IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1700 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.67 (d, $J = 7.0$ Hz, 3H, menthyl–CH_3), 0.82 (d, $J = 7.0$ Hz, 3H, menthyl–CH_3), 0.90–0.96 (m, 2H, menthyl), 0.98 (d, $J = 6.4$ Hz, 3H, menthyl–CH_3), 1.03–1.10 (m, 2H, menthyl), 1.19–1.22 (m, 1H, menthyl), 1.42 (s, 3H, Cp–CH_3), 1.53–1.78 (m, 4H, menthyl), 4.70–4.75 (m, 1H, menthyl), 4.75 (s, 1H, Cp–*H*), 4.94 (s, 1H, Cp–*H*), 6.58 (t, $J = 9.1$ Hz, 6H, Ph), 7.08 (t, $J = 7.0$ Hz, 6H, Ph), 7.22–7.56 (m, 23H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 4.81 (s), 13.09 (s), 16.46 (s), 20.49 (s), 22.13 (s), 23.59 (s), 26.38 (s), 31.44 (s), 31.69 (s), 34.16 (s), 41.50 (s), 46.45 (s), 69.78 (s), 75.85 (s), 80.78 (s), 92.83 (s), 109.83 (s), 127.65–134.28 (m), 169.67 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 38.59 (d, $J_{P-P} = 32.5$ Hz), 42.09 (bs). FAB MS: *m/z 1004* (M^+–PF_6). Mp: 132–133°C. $[\alpha]_D^{20}$: +165.1° (*c* 0.312, MeCN). Calc. for $C_{61}H_{62}F_6NO_2P_3Ru$: C, 63.69; H, 5.44; N, 1.22. Anal. Found: C, 63.64; H, 5.41; N, 1.17.

3.3.5. (S_{Cl})-[{η^5-C_5H_2-1-(CONH^{t}Bu)-2,4-Me_2}-$Ru(PPh_3)_2(MeCN)][PF_6]$ (**7a-1**)

(S_{Cl})-[{η^5-C_5H_2-1-(CONH^{t}Bu)-2,4-Me_2}Ru(η^5-C_6H_6)]-[PF_6] **5a-1** was prepared from **1a-1** via hydrolysis and then treatment with *tert*-butylamine according to the method reported previously [10b,c]. Thus obtained **5a-1** was used as a starting material for the preparation of **7a-1**. A solution of **5a-1** (0.35 g, 0.68 mmol) in MeCN (50 ml) under an argon atmosphere was irradiated with ultraviolet light for 18 h. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2. To the solution triphenylphosphine (0.36 g, 1.36 mmol) was added, and stirred at room temperature for 12 h. After concentration of the reaction mixture under reduced pressure, the residue was chromatographed on Al_2O_3 with CH_2Cl_2:acetone = 3:1. The eluate was evaporated and dried in vacuo to give **7a-1** (0.66 g, 97% yield) as a yellow powder. IR (cm^{-1}, KBr): 842 (ν_{P-F}), 1657 ($\nu_{C=O}$), 3416 (ν_{N-H}). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.27 (dd, $J = 1.5$, 3.4 Hz, 3H, Cp–CH_3), 1.33 (s, 9H, –C(CH_3)$_3$), 1.99 (d, $J = 2.0$ Hz, 3H, Cp–CH_3), 2.30 (s, 3H, NCCH_3), 3.71 (s, 1H, –CON*H*–), 4.44 (s, 1H, Cp–*H*), 4.85 (s, 1H, Cp–*H*), 6.73 (t, $J = 18.2$ Hz, 6H, Ph), 7.11–7.45 (m, 24H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 5.03 (s), 11.94 (s), 13.39 (s), 28.79 (s), 51.97 (s), 72.22 (s), 83.26 (d, $J_{P-C} = 7.4$ Hz), 93.84 (d, $J_{P-C} = 5.8$ Hz), 98.84 (d, $J_{P-C} = 4.0$ Hz), 108.84 (d, $J_{P-C} = 2.5$ Hz), 128.04–134.44 (m), 167.92 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 39.53 (d, $J_{P-P} = 33.1$ Hz), 42.54 (d, $J_{P-P} = 33.2$ Hz). FAB MS: *m/z* 859 (M^+–PF_6). Mp: 135–136°C. $[\alpha]_D^{20}$: +12.1° (*c* 0.463, MeCN). Calc. for $C_{50}H_{51}F_6N_2OP_3Ru$: C, 59.82; H, 5.12; N, 2.79. Anal. Found: C, 59.90; H, 5.12; N, 2.90.

3.3.6. (R_{Cl})-[{η^5-C_5H_2-1-(CONH^{t}Bu)-2,4-Me_2}$Ru(PPh_3)_2(MeCN)][PF_6]$ (**7a-2**)

This compound was prepared from **5a-2** by the method similar to that for **7a-1** (97%, yellow powder). IR (cm^{-1}, KBr): 841 (ν_{P-F}), 1657 ($\nu_{C=O}$), 3417 (ν_{N-H}). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.28 (dd, $J = 1.7$, 3.4 Hz, 3H, Cp–CH_3), 1.33 (s, 9H, –C(CH_3)$_3$), 1.99 (d, $J = 2.4$ Hz, 3H, Cp–CH_3), 2.30 (s, 3H, NCCH_3), 3.72 (s, 1H, –CON*H*–), 4.44 (s, 1H, Cp–*H*), 4.85 (s, 1H, Cp–H), 6.73 (t, $J = 17.8$ Hz, 6H, Ph), 7.12–7.44 (m, 24H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 4.99 (s), 11.92 (s), 13.36 (s), 28.76 (s), 51.96 (s), 72.25 (s), 83.23 (d, $J_{P-C} = 7.4$ Hz), 93.84 (d, $J_{P-C} = 5.8$ Hz), 98.80 (d, $J_{P-C} = 3.3$ Hz), 108.80 (d, $J_{P-C} = 3.3$ Hz), 128.03–134.41 (m), 167.89 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 39.55 (d, $J_{P-P} = 33.1$ Hz), 42.54 (d, $J_{P-P} = 33.2$ Hz). FAB MS: *m/z* 859 (M^+–PF_6). Mp: 135–136°C. $[\alpha]_D^{20}$: −12.1° (*c* 0.493, MeCN). Calc. for $C_{50}H_{51}F_6N_2OP_3Ru$: C, 59.82; H, 5.12; N, 2.79. Anal. Found: C, 59.94; H, 5.24; N, 2.80.

3.4. Syntheses of planar-chiral trisubstituted cyclopentadienylruthenium–vinylidene complexes (**4**)

3.4.1. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2,4-Me_2}$Ru(PPh_3)_2$(=C=CHPh)][PF_6] (**4a-1**)

To a solution of ruthenium complex **3a-1** (86.0 mg, 0.08 mmol) in CH_2Cl_2 (5 ml) was added phenylacetylene (80.7 mg, 0.79 mmol) and stirred at room temperature

for 18 h. After removal of the solvent under reduced pressure, the residue was dissolved with CH_2Cl_2 (2 ml), and to the CH_2Cl_2 solution addition of hexane (10 ml) resulted in the precipitation of **4a-1**. Purification of the complex was performed by repeating re-precipitation from CH_2Cl_2, giving **4a-1** (82 mg, 90% yield) as a reddish–brown powder. IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1626 ($\nu_{C=C}$), 1704 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.78 (d, $J = 6.6$ Hz, 3H, menthyl–CH_3), 0.82 (t, $J = 6.0$ Hz, 3H, menthyl–CH_3), 0.92–0.98 (m, 1H, menthyl), 1.03–1.09 (m, 1H, menthyl), 1.28–1.38 (m, 2H, menthyl), 1.48 (s, 3H, Cp–CH_3), 1.68–1.74 (m, 3H, menthyl), 1.80–1.84 (m, 1H, menthyl), 1.98–2.00 (m, 1H, menthyl), 4.90 (dt, $J = 4.4$, 10.8 Hz, 1H, menthyl), 4.99 (s, 1H, =C*H*Ph), 5.23 (s, 1H, Cp–*H*), 5.60 (s, 1H, Cp–*H*), 6.93 (d, $J = 7.7$ Hz, 2H, Ph), 7.00–7.09 (m, 13H, Ph), 7.16–7.19 (m, 8H, Ph), 7.25–7.27 (m, 6H, Ph), 7.35 (t, $J = 7.3$ Hz, 3H, Ph), 7.41 (d, $J = 7.4$ Hz, 3H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 11.65 (s), 13.42 (s), 15.79 (s), 20.90 (s), 21.88 (s), 22.23 (s), 25.88 (s), 33.82 (s), 34.02 (s), 41.29 (s), 46.86 (s), 93.30 (s), 98.87 (s), 99.24 (s), 110.00 (s), 113.50 (s), 118.92 (s), 127.04–133.89 (m), 164.99 (s), 356.90 (t, $J_{P-C} = 15.1$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 37.56 (d, $J_{P-P} =$ 27.9 Hz), 43.16 (d, $J_{P-P} = 27.8$ Hz). FAB MS: m/z 1003 (M^+–PF_6). Mp: 138–139°C. $[\alpha]_D^{20}$: −46.4° (c 0.347, MeCN). Calc. for $C_{62}H_{63}F_6O_2P_3Ru$: C, 64.79; H, 5.53. Anal. Found: C, 64.52; H, 5.59.

3.4.2. (R_{Cl})-[{η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2,4-Me_2}$Ru(PPh_3)_2$(=C=CHPh)][PF_6] (**4a-2**)

This compound was prepared from **3a-2** by the method similar to that for **4a-1** (89%, reddish–brown powder). IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1626 ($\nu_{C=C}$), 1703 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.78 (d, $J = 6.9$ Hz, 3H, menthyl–CH_3), 0.82 (t, $J = 6.4$ Hz, 3H, menthyl–CH_3), 0.92–0.98 (m, 1H, menthyl), 1.02–1.09 (m, 1H, menthyl), 1.28–1.38 (m, 2H, menthyl), 1.48 (s, 3H, Cp–CH_3), 1.68–1.72 (m, 3H, menthyl), 1.79–1.84 (m, 1H, menthyl), 1.98–2.00 (m, 1H, menthyl), 4.90 (dt, $J = 4.4$, 10.4 Hz, 1H, menthyl), 4.99 (s, 1H, =C*H*Ph), 5.23 (s, 1H, Cp–*H*), 5.60 (s, 1H, Cp–*H*), 6.93 (d, $J = 7.1$ Hz, 2H, Ph), 7.00–7.09 (m, 13H, Ph), 7.16–7.18 (m, 8H, Ph), 7.25–7.27 (m, 6H, Ph), 7.35 (t, $J = 7.4$ Hz, 3H, Ph), 7.42 (d, $J = 7.4$ Hz, 3H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 11.70 (s), 13.45 (s), 15.82 (s), 20.92 (s), 21.91 (s), 22.25 (s), 25.90 (s), 33.84 (s), 34.04 (s), 41.32 (s), 46.89 (s), 93.33 (s), 98.90 (s), 99.20 (s), 110.00 (s), 113.55 (s), 118.95 (s), 126.84–133.92 (m), 164.99 (s), 356.95 (t, $J_{P-C} = 15.1$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 37.54 (d, $J_{P-P} = 27.9$ Hz), 43.16 (d, $J_{P-P} = 27.9$ Hz). FAB MS: m/z 1003 (M^+–PF_6). Mp: 138–139°C. $[\alpha]_D^{20}$: +46.4° (c 0.300, MeCN). Calc. for $C_{62}H_{63}F_6O_2P_3Ru$: C, 64.79; H, 5.53. Anal. Found: C, 64.99; H, 5.79.

3.4.3. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2-Me-4-Ph}$Ru(PPh_3)_2$(=C=CHPh)][PF_6] (**4b-1**)

This compound was prepared from **3b-1** by the method similar to that for **4a-1** (74%, reddish–brown powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1650 ($\nu_{C=C}$), 1704 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.69 (d, $J = 6.8$ Hz, 3H, menthyl–CH_3), 0.85 (d, $J = 7.0$ Hz, 3H, menthyl–CH_3), 0.96–1.01 (m, 1H, menthyl), 0.99 (d, $J = 6.2$ Hz, 3H, menthyl–CH_3), 1.05–1.13 (m, 1H, menthyl), 1.20–1.33 (m, 1H, menthyl), 1.60–1.78 (m, 4H, menthyl), 1.66 (s, 3H, Cp–CH_3), 2.26–2.28 (m, 1H, menthyl), 4.82 (dt, $J = 4.1$, 10.8 Hz, 1H, menthyl), 5.26 (s, 1H, =C*H*Ph), 5.65 (s, 1H, Cp–*H*), 5.84 (s, 1H, Cp–*H*), 6.07 (d, $J = 7.1$ Hz, 2H, Ph), 6.57 (t, $J = 9.2$ Hz, 1H, Ph), 6.65–6.71 (m, 8H, Ph), 6.76 (t, $J = 7.2$ Hz, 1H, Ph), 6.94–7.00 (m, 6H, Ph), 7.05–7.15 (m, 5H, Ph), 7.18–7.25 (m, 6H, Ph), 7.29–7.42 (m, 6H, Ph), 7.45–7.53 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 13.39 (s), 14.00 (s), 16.60 (s), 20.52 (s), 22.16 (s), 22.27 (s), 23.74 (s), 26.64 (s), 31.51 (s), 34.07 (s), 34.17 (s), 41.63 (s), 46.74 (s), 76.60 (s), 89.54 (s), 90.75 (s), 99.75 (s), 111.12 (s), 118.99 (s), 125.39 (s), 126.28–134.17 (m), 165.72 (s), 363.66 (t, $J_{P-C} = 17.1$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 31.87 (d, $J_{P-P} = 26.6$ Hz), 45.58 (bs). FAB MS: m/z 1065 (M^+–PF_6). Mp: 137–138°C. $[\alpha]_D^{20}$: −42.5° (c 0.258, MeCN). Calc. for $C_{67}H_{65}F_6O_2P_3Ru$: C, 66.43; H, 5.41. Anal. Found: C, 66.20; H, 5.34.

3.4.4. (R_{Cl})-[{η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2-Me-4-Ph}$Ru(PPh_3)_2$(=C=CHPh)][PF_6] (**4b-2**)

This compound was prepared by the method from **3b-2** similar to that for **4a-1** (80%, reddish–brown powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1650 ($\nu_{C=C}$), 1704 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.69 (d, $J = 6.8$ Hz, 3H, menthyl–CH_3), 0.85 (d, $J = 7.0$ Hz, 3H, menthyl–CH_3), 0.96–1.02 (m, 1H, menthyl), 0.99 (d, $J = 6.0$ Hz, 3H, menthyl–CH_3), 1.05–1.14 (m, 1H, menthyl), 1.21–1.33 (m, 1H, menthyl), 1.60–1.78 (m, 4H, menthyl), 1.67 (s, 3H, Cp–CH_3), 2.26–2.28 (m, 1H, menthyl), 4.82 (dt, $J = 4.1$, 10.8 Hz, 1H, menthyl), 5.26 (s, 1H, =C*H*Ph), 5.65 (s, 1H, Cp–H), 5.83 (s, 1H, Cp–H), 6.07 (d, $J = 7.3$ Hz, 2H, Ph), 6.57 (t, $J = 9.2$ Hz, 1H, Ph), 6.65–6.71 (m, 8H, Ph), 6.76 (t, $J = 7.0$ Hz, 1H, Ph), 6.93–7.00 (m, 6H, Ph), 7.05–7.15 (m, 5H, Ph), 7.18–7.25 (m, 6H, Ph), 7.30–7.42 (m, 6H, Ph), 7.45–7.53 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 13.38 (s), 14.00 (s), 16.59 (s), 20.52 (s), 22.15 (s), 22.28 (s), 23.75 (s), 26.65 (s), 31.50 (s), 34.07 (s), 34.17 (s), 41.63 (s), 46.74 (s), 76.61 (s), 89.52 (s), 90.76 (s), 99.76 (s), 111.12 (s), 118.99 (s), 125.39 (s), 126.27–134.16 (m), 165.71 (s), 363.67 (t, $J_{P-C} = 19.2$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 31.80 (d, $J_{P-P} = 26.6$ Hz), 45.55 (bs). FAB MS: m/z 1065 (M^+–PF_6). Mp: 137–138°C. $[\alpha]_D^{20}$: +42.5° (c 0.283, MeCN). Calc. for $C_{67}H_{65}F_6O_2P_3Ru$: C, 66.43; H, 5.41. Anal. Found: C, 66.50; H, 5.36.

*3.4.5. (S_{Cl})-[{η^5-C_5H_2-1-(CONH^{t}Bu)-2,4-Me_2}-Ru(PPh_3)$_2$(=C=CHPh)][PF_6] (**8a-1**)*

This compound was prepared from **7a-1** by the method similar to that for **4a-1** (93%, reddish–brown powder). IR (cm^{-1}, KBr): 842 (ν_{P-F}), 1624 ($\nu_{C=C}$), 1657 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.36 (s, 9H, –C(CH_3)$_3$), 1.52 (s, 3H, Cp–CH_3), 1.81 (s, 3H, Cp–CH_3), 4.67 (s, 1H, =C*H*Ph), 4.81 (s, 1H, Cp–*H*), 5.62 (s, 1H, Cp–*H*), 5.65 (s, 1H, –CON*H*–), 6.70–7.43 (m, 35H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 12.41 (s), 13.19 (s), 28.47 (s), 52.35 (s), 93.87 (d, J_{P-C} = 1.6 Hz), 95.95 (s), 97.51 (s), 110.63 (d, J_{P-C} = 2.1 Hz), 117.49 (s), 118.07 (s), 126.58–134.15 (m), 163.34 (s), 358.54 (t, J_{P-C} = 15.3 Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 42.40 (d, J_{P-P} = 27.3 Hz), 44.91 (d, J_{P-P} = 28.1 Hz). FAB MS: m/z 920 (M^+–PF_6). Mp: 119–120°C. $[\alpha]_D^{20}$: +10.5° (c 0.418, MeCN). Calc. for $C_{56}H_{54}F_6NOP_3Ru$: C, 63.15; H, 5.11; N, 1.32. Anal. Found: C, 63.29; H, 4.92; N, 1.20.

*3.4.6. (R_{Cl})-[{η^5-C_5H_2-1-(CONH^{t}Bu)-2,4-Me_2}-Ru(PPh_3)$_2$(=C=CHPh)][PF_6] (**8a-2**)*

This compound was prepared from **7a-2** by the method similar to that for **4a-1** (99%, reddish–brown powder). IR (cm^{-1}, KBr): 841 (ν_{P-F}), 1624 ($\nu_{C=C}$), 1657 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.35 (s, 9H, –C(CH_3)$_3$), 1.52 (s, 3H, Cp–CH_3), 1.81 (s, 3H, Cp–CH_3), 4.67 (s, 1H, =CHPh), 4.81 (s, 1H, Cp–*H*), 5.61 (s, 1H, Cp–*H*), 5.64 (s, 1H, –CON*H*–), 6.70–7.43 (m, 35H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 12.43 (s), 13.20 (s), 28.47 (s), 52.36 (s), 93.87 (d, J_{P-C} = 1.7 Hz), 95.97 (s), 97.51 (s), 110.63 (d, J_{P-C} = 2.5 Hz), 117.50 (s), 118.07 (s), 126.60–134.16 (m), 163.35 (s), 358.54 (t, J_{P-C} = 15.3 Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 42.38 (d, J_{P-P} = 27.3 Hz), 44.89 (d, J_{P-P} = 28.3 Hz). FAB MS: m/z 920 (M^+–PF_6). Mp: 119–120°C. $[\alpha]_D^{20}$: −10.4° (c 0.431, MeCN). Calc. for $C_{56}H_{54}F_6NOP_3Ru$: C, 63.15; H, 5.11; N, 1.32. Anal. Found: C, 63.47; H, 4.99; N, 1.41.

*3.4.7. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2,4-Me_2}Ru(PPh_3)$_2$(=C=CH_2)][PF_6] (**9a-1**)*

To a solution of ruthenium complex **3a-1** (80.0 mg, 0.07 mmol) in CH_2Cl_2 (5 ml) was added trimethylsilylacetylene (0.14 g, 1.47 mmol) and stirred at room temperature for 18 h. After removal of the solvent under reduced pressure, the residue was dissolved with CH_2Cl_2 (2 ml), and to the CH_2Cl_2 solution addition of hexane (10 ml) resulted in a reddish–brown precipitation. Purification of the complex was performed by repeating re-precipitation from CH_2Cl_2, giving **9a-1** (52 mg, 75% yield) as a reddish–brown powder. IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1626 ($\nu_{C=C}$), 1703 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.79 (d, J = 6.8 Hz, 3H, menthyl–CH_3), 0.84 (d, J = 7.0 Hz, 3H, menthyl–CH_3), 0.93–0.99 (m, 1H, menthyl), 1.02 (d, J = 6.4 Hz, 3H, menthyl–CH_3), 1.07–1.18 (m, 2H, menthyl), 1.28–1.33 (m, 1H, menthyl), 1.39 (s, 3H, Cp–CH_3), 1.40–1.44 (m, 1H, menthyl), 1.72–1.83 (m, 3H, menthyl), 1.76 (s, 3H, Cp–CH_3), 2.16–2.18 (m, 1H, menthyl), 4.41 (s, 2H, =CH_2), 4.55 (s, 1H, Cp–*H*), 4.86 (s, 1H, Cp–*H*), 4.90 (dt, J = 4.4, 10.9 Hz, 1H, menthyl), 7.01–7.04 (m, 6H, Ph), 7.10–7.13 (m, 6H, Ph), 7.20–7.23 (m, 6H, Ph), 7.30–7.33 (m, 6H, Ph), 7.36–7.38 (m, 3H, Ph), 7.43–7.45 (m, 3H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 11.85 (s), 13.09 (s), 15.93 (s), 20.98 (s), 22.06 (s), 22.26 (s), 25.92 (s), 33.96 (s), 34.06 (s), 41.68 (s), 47.01 (s), 76.55 (s), 91.74 (s), 95.33 (s), 97.82 (s), 101.05 (s), 109.07 (s), 115.07 (s), 128.29—134.05 (m), 165.32 (s), 352.31 (t, J_{P-C} = 17.1 Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 38.43 (d, J_{P-P} = 28.1 Hz), 45.61 (d, J_{P-P} = 28.2 Hz). FAB MS: m/z 927 (M^+–PF_6). Mp: 142–143°C. $[\alpha]_D^{20}$: −76.9° (c 0.200, MeCN). Calc. for $C_{56}H_{59}F_6O_2P_3Ru$: C, 62.67; H, 5.55. Anal. Found: C, 62.92; H, 5.81.

*3.4.8. (R_{Cl})-[{η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2,4-Me_2}Ru(PPh_3)$_2$(=C=CH_2)][PF_6] (**9a-2**)*

This compound was prepared from **3a-2** by the method similar to that for **9a-1** (61%, mustard–yellow powder). IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1626 ($\nu_{C=C}$), 1703 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.79 (d, J = 6.8 Hz, 3H, menthyl–CH_3), 0.84 (d, J = 7.0 Hz, 3H, menthyl–CH_3), 0.93–0.99 (m, 1H, menthyl), 1.02 (d, J = 6.6 Hz, 3H, menthyl–CH_3), 1.08–1.17 (m, 2H, menthyl), 1.27–1.32 (m, 1H, menthyl), 1.39 (s, 3H, Cp–CH_3), 1.40–1.44 (m, 1H, menthyl), 1.72–1.83 (m, 3H, menthyl), 1.76 (s, 3H, Cp–CH_3), 2.16–2.18 (m, 1H, menthyl), 4.41 (s, 2H, =CH_2), 4.55 (s, 1H, Cp–*H*), 4.86 (s, 1H, Cp–*H*), 4.90 (dt, J = 4.3, 10.8 Hz, 1H, menthyl), 7.01–7.04 (m, 6H, Ph), 7.10–7.13 (m, 6H, Ph), 7.20–7.22 (m, 6H, Ph), 7.30–7.32 (m, 6H, Ph), 7.36–7.38 (m, 3H, Ph), 7.42–7.45 (m, 3H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 11.85 (s), 13.08 (s), 15.94 (s), 20.99 (s), 22.06 (s), 22.26 (s), 25.92 (s), 33.97 (s), 34.05 (s), 41.69 (s), 47.02 (s), 76.55 (s), 91.74 (s), 95.33 (s), 97.82 (s), 101.07 (s), 109.09 (s), 115.10 (s), 128.29–134.05 (m), 165.34 (s), 352.33 (t, J_{P-C} = 17.1 Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 38.43 (d, J_{P-P} = 28.1 Hz), 45.62 (d, J_{P-P} = 28.1 Hz). FAB MS: m/z 927 (M^+–PF_6). Mp: 142–143°C. $[\alpha]_D^{20}$: +76.5° (c 0.200, MeCN). Calc. for $C_{56}H_{59}F_6O_2P_3Ru$: C, 62.67; H, 5.55. Anal. Found: C, 62.91; H, 5.68.

*3.4.9. (S_{Cl})-[{η^5-C_5H_2-1-(CO_2-(l)-menthyl)-2-Me-4-Ph}Ru(PPh_3)$_2$(=C=CH_2)][PF_6] (**9b-1**)*

This compound was prepared from **3b-1** by the method similar to that for **9a-1** (81%, mustard–yellow powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1627 ($\nu_{C=C}$), 1705 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.73 (d, J = 6.6 Hz, 3H, menthyl–CH_3), 0.87 (d, J = 7.3 Hz, 3H, menthyl–CH_3), 0.98 (d, J = 5.8 Hz, 3H, menthyl–CH_3),

1.08–1.14 (m, 1H, menthyl), 1.27–1.34 (m, 2H, menthyl), 1.56 (s, 3H, Cp–CH_3), 1.64–1.81 (m, 2H, menthyl), 2.15–2.17 (m, 1H, menthyl), 4.20 (s, 2H, =CH_2), 4.82 (dt, $J = 3.4$, 10.4 Hz, 1H, menthyl), 5.04 (s, 1H, Cp–*H*), 5.22 (s, 1H, Cp–*H*), 6.71–6.74 (m, 6H, Ph), 7.06–7.14 (m, 13H, Ph), 7.36–7.49 (m, 16H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 13.00 (s), 14.00 (s), 16.56 (s), 20.65 (s), 22.10 (s), 22.27 (s), 23.62 (s), 26.56 (s), 31.51 (s), 34.14 (s), 41.62 (s), 47.09 (s), 76.39 (s), 89.94 (s), 91.49 (d, $J_{P-C} = 8.5$ Hz), 97.69 (s), 99.29 (s), 110.23 (s), 115.99 (s), 126.23–134.17 (m), 165.41 (s), 355.90 (t, $J_{P-C} = 19.2$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 35.17 (d, $J_{P-P} = 26.3$ Hz), 44.51 (bs). FAB MS: *m*/*z* 989 (M^+–PF_6). Mp: 152–153°C. $[\alpha]_D^{20}$: −34.3° (*c* 0.255, MeCN). Calc. for $C_{61}H_{61}F_6O_2P_3Ru$: C, 64.53; H, 5.42. Anal. Found: C, 64.36; H, 5.23.

*3.4.10. (R_{Cl})-[{η^5-C_5H_2-1-(CO_2-(d)-menthyl)-2-Me-4-Ph}Ru(PPh_3)$_2$(=C=CH_2)][PF_6] (**9a-2**)*

This compound was prepared from **3b-2** by the method similar to that for **9a-1** (86%, mustard–yellow powder). IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1626 ($\nu_{C=C}$), 1704 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.73 (d, $J = 7.0$ Hz, 3H, menthyl–CH_3), 0.89 (d, $J = 7.1$ Hz, 3H, menthyl–CH_3), 0.98 (d, $J = 6.4$ Hz, 3H, menthyl–CH_3), 1.08–1.15 (m, 1H, menthyl), 1.28–1.34 (m, 2H, menthyl), 1.55 (s, 3H, Cp–CH_3), 1.65–1.80 (m, 2H, menthyl), 2.17–2.19 (m, 1H, menthyl), 4.22 (s, 2H, =CH_2), 4.82 (dt, $J = 3.6$, 10.4 Hz, 1H, menthyl), 5.02 (s, 1H, Cp–*H*), 5.24 (s, 1H, Cp–*H*), 6.70–6.74 (m, 6H, Ph), 7.07–7.14 (m, 13H, Ph), 7.35–7.49 (m, 16H, Ph). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 13.01 (s), 13.99 (s), 16.55 (s), 20.65 (s), 22.11 (s), 22.28 (s), 23.60 (s), 26.56 (s), 31.51 (s), 34.14 (s), 41.62 (s), 47.08 (s), 76.39 (s), 89.93 (s), 91.47 (d, $J_{P-C} = 8.5$ Hz), 97.70 (s), 99.29 (s), 110.23 (s), 115.99 (s), 126.21–134.17 (m), 165.41 (s), 355.99 (t, $J_{P-C} = 18.1$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 35.17 (d, $J_{P-P} = 25.9$ Hz), 44.50 (bs). FAB MS: *m*/*z* 989 (M^+–PF_6). Mp: 152–153°C. $[\alpha]_D^{20}$: +34.8° (*c* 0.287, MeCN). Calc. for $C_{61}H_{61}F_6O_2P_3Ru$: C, 64.53; H, 5.42. Anal. Found: C, 64.25; H, 5.62.

*3.4.11. (S_{Cl})-[{η^5-C_5H_2-1-(CONH^{t}Bu)-2,4-Me_2}-Ru(PPh_3)$_2$(=C=CH_2)][PF_6] (**10a-1**)*

This compound was prepared from **7a-1** by the method similar to that for **9a-1** (95%, mustard–yellow powder). IR (cm^{-1}, KBr): 842 (ν_{P-F}), 1624 ($\nu_{C=C}$), 1657 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.42 (s, 3H, Cp–CH_3), 1.45 (s, 9H, –C(CH_3)$_3$), 1.81 (s, 3H, Cp–CH_3), 4.22 (s, 1H, Cp–H), 4.33 (s, 2H, =CH_2), 4.48 (s, 1H, Cp–*H*), 5.55 (s, 1H, –CON*H*–), 6.89–7.69 (m, 30H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 12.06 (s), 12.94 (s), 28.49 (s), 28.76 (s), 52.44 (s), 92.71 (d, $J_{P-C} =$ 3.3 Hz), 97.08 (s), 98.55 (d, $J_{P-C} = 4.2$ Hz), 108.43 (s), 116.47 (s), 128.24–134.69 (m), 163.66 (s), 352.85 (t, $J_{P-C} = 17.0$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 36.78 (d, $J_{P-P} = 28.4$ Hz), 46.20 (d, $J_{P-P} = 28.8$ Hz). FAB MS: *m*/*z* 844 (M^+–PF_6). Mp: 113–114°C. $[\alpha]_D^{20}$: +22.3° (*c* 0.235, MeCN). Calc. For $C_{50}H_{50}F_6NOP_3Ru$: C, 60.73; H, 5.10; N, 1.42. Anal. Found: C, 60.85; H, 4.94; N, 1.62.

*3.4.12. (R_{Cl})-[{η^5-C_5H_2-1-(CONH^{t}Bu)-2,4-Me_2}-Ru(PPh_3)$_2$(=C=CH_2)][PF_6] (**10a-2**)*

This compound was prepared from **7a-2** by the method similar to that for **9a-1** (92%, mustard–yellow powder). IR (cm^{-1}, KBr): 841 (ν_{P-F}), 1623 ($\nu_{C=C}$), 1657 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.42 (s, 3H, Cp–CH_3), 1.45 (s, 9H, –C(CH_3)$_3$), 1.81 (s, 3H, Cp–CH_3), 4.21 (s, 1H, Cp–H), 4.33 (s, 2H, =CH_2), 4.49 (s, 1H, Cp–*H*), 5.54 (s, 1H, –CON*H*–), 6.89–7.69 (m, 30H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 12.02 (s), 12.92 (s), 28.45 (s), 28.75 (s), 52.49 (s), 92.71 (d, $J_{P-C} =$ 3.9 Hz), 97.06 (s), 98.54 (d, $J_{P-C} = 4.3$ Hz), 108.39 (s), 116.46 (s), 128.23–134.70 (m), 163.67 (s), 352.85 (t, $J_{P-C} = 17.0$ Hz). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 36.75 (d, $J_{P-P} = 28.9$ Hz), 46.21 (d, $J_{P-P} = 28.8$ Hz). FAB MS: *m*/*z* 844 (M^+–PF_6). Mp: 113–114°C. $[\alpha]_D^{20}$: −22.3° (*c* 0.263, MeCN). Calc. For $C_{50}H_{50}F_6NOP_3Ru$: C, 60.73; H, 5.10; N, 1.42. Anal. Found: C, 60.63; H, 5.24; N, 1.70.

3.5. Other cyclopentadienylruthenium complexes

*3.5.1. [(η^5-C_5H_2-1-CO_2Et-2-Me-4-R^2)Ru(PPh_3)$_2$-(MeCN)][PF_6] (**11**: R^2 = Me, Ph, ^{t}Bu, α-Naph, and 4-BrC_6H_4)*

These compounds were prepared as a racemic mixture from the corresponding [(η^5-C_5H_2-1-CO_2Et-2-Me-4-R^2)Ru(η^6-C_6H_6)][PF_6] [10c] by the method similar of that for **3a**–**1**.

Complex **11a** (R^2 = Me): 99% yield, yellow powder. IR (cm^{-1}, KBr): 841 (ν_{P-F}), 1703 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.17 (t, $J = 7.2$ Hz, 3H, –OCH_2CH$_3$), 1.31 (s, 3H, Cp–CH_3), 1.92 (s, 3H, Cp–CH_3), 2.34 (s, 3H, NCCH_3), 3.94–4.02 (m, 1H, –OCH_2CH$_3$), 4.12 (s, 1H, Cp–*H*), 4.13–4.21 (m, 1H, –OCH_2CH$_3$), 4.53 (s, 1H, Cp–*H*), 6.79 (t, $J = 8.9$ Hz, 6H, Ph), 7.11–7.44 (m, 24H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 5.06 (s), 12.00 (s), 12.80 (s), 14.15 (s), 60.72 (s), 65.83 (s), 69.40 (s), 84.84 (d, $J_{P-C} = 6.5$ Hz), 94.72 (d, $J_{P-C} = 3.3$ Hz), 99.24 (s), 109.25 (s), 127.80–134.50 (m), 169.68 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 38.88 (d, $J_{P-P} = 33.0$ Hz), 44.15 (d, $J_{P-P} = 33.0$ Hz). FAB MS: *m*/*z* 832 (M^+–PF_6). Calc. for $C_{48}H_{46}F_6NO_2P_3Ru$: C, 59.02; H, 4.75; N, 1.43. Anal. Found: C, 59.20; H, 4.83; N, 1.25.

Complex **11b** (R^2 = Ph): 97% yield, yellow powder. IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1711 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.22 (t, $J = 7.2$ Hz, 3H, –OCH$_2$CH_3), 1.51 (s, 3H, Cp–CH_3), 2.09 (s, 3H, NCCH_3), 3.97–4.05 (m, 1H, –OCH_2CH$_3$), 4.18–4.26

(m, 1H, –OCH_2CH$_3$), 4.73 (s, 1H, Cp–*H*), 4.83 (s, 1H, Cp–*H*), 6.67 (t, $J = 8.9$ Hz, 6H, Ph), 6.83 (t, $J = 9.0$ Hz, 1H, Ph), 7.08–7.52 (m, 28H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 4.52 (s), 12.87 (s), 14.06 (s), 61.18 (d, $J_{P-C} = 13.3$ Hz), 71.74 (s), 82.43 (d, $J_{P-C} = 10.7$ Hz), 89.29 (d, $J_{P-C} = 3.3$ Hz), 99.01 (d, $J_{P-C} = 4.9$ Hz), 108.57 (s), 127.47–134.23 (m), 168.69 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 37.78 (d, $J_{P-P} = 33.1$ Hz), 41.12 (d, $J_{P-P} = 33.2$ Hz). FAB MS: m/z 894 (M^+–PF_6). Calc. for $C_{53}H_{48}F_6NO_2P_3Ru$: C, 61.27; H, 4.66; N, 1.35. Anal. Found: C, 61.50; H, 4.76; N, 1.25.

Complex **11c** ($R^2 = {}^t$Bu): 98% yield, yellow powder. IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1708 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, $J = 9.3$ Hz, 3H, –OCH$_2$CH_3), 1.27 (s, 9H, Cp–C(CH_3)$_3$), 1.56 (s, 3H, Cp–CH_3), 2.22 (s, 3H, NCCH_3), 3.63–3.71 (m, 1H, –OCH_2CH$_3$), 3.86 (s, 1H, Cp–*H*), 4.22–4.30 (m, 1H, –OCH_2CH$_3$), 4.37 (d, $J = 4.9$ Hz, 1H, Cp–*H*), 6.69 (t, $J = 8.9$ Hz, 6H, Ph), 7.13–7.48 (m, 24H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 5.23 (s), 13.45 (s), 13.90 (s), 30.65 (s), 32.03 (s), 61.07 (s), 70.32 (s), 77.90 (d, $J_{P-C} = 9.9$ Hz), 84.04 (d, $J_{P-C} = 6.6$ Hz), 107.23 (s), 124.78 (s), 127.83–134.67 (m), 169.37 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 35.62 (d, $J_{P-P} = 31.5$ Hz), 41.26 (d, $J_{P-P} = 31.4$ Hz). FAB MS: m/z 874 (M^+–PF_6). Calc. for $C_{51}H_{52}F_6NO_2P_3Ru$: C, 60.12; H, 5.14; N, 1.37. Anal. Found: C, 60.03; H, 4.88; N, 1.48.

Complex **11d** ($R^2 =$ α-naphthyl): 88% yield, yellow powder. IR (cm^{-1}, KBr): 841 (ν_{P-F}), 1711 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.27 (t, $J = 13.4$ Hz, 3H, –OCH$_2$CH_3), 1.57 (s, 3H, Cp–CH_3), 2.10 (s, 3H, NCCH_3), 4.03–4.11 (m, 1H, –OCH_2CH$_3$), 4.21–4.29 (m, 1H, –OCH_2CH$_3$), 4.89 (s, 1H, Cp–*H*), 4.96 (s, 1H, Cp–*H*), 6.63 (t, $J = 9.0$ Hz, 6H, Ar), 7.05 (dt, $J = 2.0$ Hz, 7.7 Hz, 6H, Ar), 7.24–7.99 (m, 25H, Ar). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 4.56 (s), 12.98 (s), 14.11 (d, $J_{P-C} = 5.8$ Hz), 61.16 (s), 71.75 (s), 83.13 (s), 90.30 (s), 97.77 (s), 108.73 (d, $J_{P-C} = 2.4$ Hz), 124.92 (s), 126.40–134.24 (m), 168.78 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 37.96 (d, $J_{P-P} = 33.1$ Hz), 40.38 (bs). FAB MS: m/z 944 (M^+–PF_6). Calc. For $C_{57}H_{50}F_6NO_2P_3Ru$: C, 62.87; H, 4.63; N, 1.29. Anal. Found: C, 63.01; H, 4.58; N, 1.41.

Complex **11e** ($R^2 = 4$-BrC_6H_4): 93% yield, yellow powder. IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1711 ($\nu_{C=O}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.23 (t, $J = 7.2$ Hz, 3H, –OCH$_2$CH_3), 1.47 (s, 3H, Cp–CH_3), 2.15 (s, 3H, NCCH_3), 4.02–4.11 (m, 1H, –OCH_2CH$_3$), 4.19–4.27 (m, 1H, –OCH_2CH$_3$), 4.77 (s, 1H, Cp–*H*), 4.84 (s, 1H, Cp–H), 6.65 (t, $J = 8.9$ Hz, 6H, Ph), 7.00–7.61 (m, 28H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 4.70 (s), 12.85 (s), 14.03 (s), 61.13 (s), 71.09 (s), 81.95 (d, $J_{P-C} = 3.3$ Hz), 90.88 (s), 96.98 (d, $J_{P-C} = 4.1$ Hz), 109.20 (s), 123.11 (s), 127.83–134.10 (m), 168.72 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 37.49 (d, $J_{P-P} = 33.1$ Hz), 40.80 (d, $J_{P-P} = 33.2$ Hz). FAB MS: m/z 972 (M^+–PF_6). Calc. for $C_{53}H_{47}BrF_6NO_2P_3Ru$: C, 56.95; H, 4.24; N, 1.25. Anal. Found: C, 57.08; H, 4.48; N, 1.27.

*3.5.2. [(η^5-C_5H_2-1-CO_2Et-2-Me-4-R^2)Ru(PPh_3)$_2$-(CCPh)][PF_6] (**13**: $R^2 =$ Me, Ph, ^{t}Bu, α-Naph, and 4-BrC_6H_4)*

These compounds were prepared as a racemic mixture from the corresponding [(η^5-C_5H_2-1-CO_2Et-2-Me-4-R^2)Ru(PPh_3)$_2$(MeCN)][PF_6] **11**.

Complex **13a** ($R^2 =$ Me): To a solution of ruthenium complex **11a** 0.49 g (0.50 mmol) in CH_2Cl_2 (20 ml) was added phenylacetylene (0.51 g, 5.00 mmol) and stirred at room temperature for 18 h. After removal of the solvent under reduced pressure, the residual oil was chromatographed on alumina using benzene as an eluent. The solvents were evaporated and the resulting yellow solid was dried in vacuo, giving a yellow powder of **12a** in 96% yield. IR (cm^{-1}, KBr): 1694 ($\nu_{C=O}$), 2076 ($\nu_{C\equiv C}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.19 (t, $J = 7.1$ Hz, 3H, –OCH$_2$CH_3), 1.26 (s, 3H, Cp–CH_3), 1.99 (s, 3H, Cp–CH_3), 3.76 (s, 1H, Cp–*H*), 3.98–4.11 (m, 2H, –OCH_2CH$_3$), 4.11 (s, 1H, Cp–*H*), 7.00–7.38 (m, 29H, Ph), 7.55(t, $J = 17.5$ Hz, 3H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 12.90 (s), 13.09 (s), 14.19 (s), 59.76 (s), 79.71 (s), 85.57 (d, $J_{P-C} = 8.2$ Hz), 93.06 (d, $J_{P-C} = 5.7$ Hz), 101.22 (d, $J_{P-C} = 4.9$ Hz), 109.09 (d, $J_{P-C} = 2.4$ Hz), 111.72 (s), 123.12 (s), 126.87–138.88 (m), 168.54 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 44.37 (d, $J_{P-P} = 34.2$ Hz), 52.60 (d, $J_{P-P} = 34.2$ Hz). FAB MS: m/z 892 (M^+). Calc. for $C_{54}H_{48}O_2P_2Ru$: C, 72.72; H, 5.42. Anal. Found: C, 72.35; H, 5.50.

Complex **13b** ($R^2 =$ Ph): 89%, yellow powder. IR (cm^{-1}, KBr): 1695 ($\nu_{C=O}$), 2078 ($\nu_{C\equiv C}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.09 (t, $J = 7.1$ Hz, 3H, –OCH_2CH$_3$), 1.74 (s, 3H, Cp–CH_3), 3.65–3.74 (m, 1H, –OCH_2CH$_3$), 3.90–4.04 (m, 1H, –OCH_2CH$_3$), 4.04 (d, $J = 1.2$ Hz, 1H, Cp–*H*), 5.10 (s, 1H, Cp–*H*), 6.91 (t, $J = 6.7$ Hz, 6H, Ph), 7.00–7.59 (m, 28H, Ph), 7.65 (t, $J = 9.0$, 6H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 13.43 (s), 14.05 (s), 59.86 (s), 79.90 (s), 86.31 (s), 88.94 (s), 100.44 (d, $J_{P-C} = 4.2$ Hz), 107.96 (s), 112.55 (s), 123.12 (s), 126.63–138.14 (m), 167.56 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 45.34 (d, $J_{P-P} = 35.1$ Hz), 49.84 (d, $J_{P-P} = 35.1$ Hz). FAB MS: m/z 954 (M^+). Calc. for $C_{59}H_{50}O_2P_2Ru$: C, 74.28; H, 5.28. Anal. Found: C, 73.99; H, 5.33.

Complex **13c** ($R^2 = {}^t$Bu): 24% yield, yellow powder. IR (cm^{-1}, KBr): 1689 ($\nu_{C=O}$), 2075 ($\nu_{C\equiv C}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.16 (t, $J = 7.1$ Hz, 3H, –OCH_2CH$_3$), 1.18 (s, 9H, Cp–C(CH_3)$_3$), 3.44 (s, 1H, Cp–*H*), 3.56–3.64 (m, 1H, –OCH_2CH$_3$), 4.02–4.10 (m, 1H, –OCH_2CH$_3$), 4.22 (s, 1H, Cp–*H*), 7.01–7.57 (m, 35H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 13.77 (s), 14.45 (d, $J_{P-C} = 5.0$ Hz), 30.91 (s), 32.31 (s), 60.02 (s), 66.16 (s), 79.39 (s), 80.34 (d, $J_{P-C} = 9.1$ Hz), 85.75 (d, $J_{P-C} = 7.4$ Hz), 107.92 (d, $J_{P-C} = 2.5$ Hz), 115.09 (s), 123.37 (s), 126.62–141.58 (m), 169.25 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 39.52 (d, $J_{P-P} = 32.5$ Hz), 51.96 (d, $J_{P-P} = 32.3$ Hz). FAB MS: m/z 934 (M^+). Calc. for

$C_{57}H_{54}O_2P_2Ru$: C, 73.29; H, 5.83. Anal. Found: C, 73.22; H, 5.87.

Complex **13d** ($R^2 = \alpha$–naphthyl): 97% yield, yellow powder. IR (cm^{-1}, KBr): 1698 ($\nu_{C=O}$), 2079 ($\nu_{C\equiv C}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, $J = 7.2$ Hz, 3H, –OCH_2CH$_3$), 1.90 (s, 3H, Cp–CH_3), 3.67–3.76 (m, 1H, –OCH_2CH$_3$), 3.92–4.00 (m, 1H, –OCH_2CH$_3$), 4.14 (s, 1H, Cp–H), 5.20 (d, $J = 2.2$ Hz, 1H, Cp–H), 6.84 (t, $J = 6.8$ Hz, 6H, Ar), 7.00–7.77 (m, 36H, Ar). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 13.56 (s), 14.05 (s), 59.86 (s), 79.61 (d, $J_{P-C} = 5.0$ Hz), 87.02 (d, $J_{P-C} = 5.7$ Hz), 90.07 (s), 99.39 (s), 107.99 (d, $J_{P-C} = 1.7$ Hz), 112.88 (s), 123.17 (s), 124.91–137.99 (m), 167.66 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 45.48 (d, $J_{P-P} = 34.1$ Hz), 48.88 (d, $J_{P-P} = 34.1$ Hz). FAB MS: m/z 1004 (M^+). Calc. for $C_{63}H_{52}O_2P_2Ru$: C, 75.36; H, 5.22. Anal. Found: C, 74.88; H, 5.28.

Complex **13e** ($R^2 = 4$-BrC_6H_4): 90% yield, yellow powder. IR (cm^{-1}, KBr): 1695 ($\nu_{C=O}$), 2079 ($\nu_{C\equiv C}$). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.10 (t, $J = 7.1$ Hz, 3H, –OCH_2CH$_3$), 1.73 (s, 3H, Cp–CH_3), 3.70–3.78 (m, 1H, –OCH_2CH$_3$), 3.92–4.00 (m, 1H, –OCH_2CH$_3$), 4.02 (s, 1H, Cp–*H*), 5.04 (s, 1H, Cp–*H*), 6.85–7.42 (m, 33H, Ph), 7.61 (t, $J = 17.6$ Hz, 6H, Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 13.40 (s), 14.03 (s), 59.91 (s), 80.16 (s), 85.89 (s), 89.76 (s), 98.70 (s), 108.30 (s), 112.74 (s), 120.28 (s), 123.32 (s), 126.88–137.91 (m), 167.51 (s). ^{31}P-NMR ($CDCl_3$, 160 MHz): δ 44.91 (d, $J_{P-P} = 34.0$ Hz), 49.47 (d, $J_{P-P} = 32.2$ Hz). FAB MS: m/z 1032 (M^+–PF_6). Calc. for $C_{59}H_{49}BrO_2P_2Ru$: C, 68.60; H, 4.78. Anal. Found: C, 68.85; H, 4.88.

*3.6. NMR trace experiments on the reactions of [(η^5-C_5H_2-1-CO_2Et-2,4-Me_2)Ru(PPh_3)$_2$(MeCN)][PF_6] (**11a**) with phenylacetylenes 4-RC_6H_4CCH (R = H, OMe, and NO_2).*

To a solution of ruthenium complex **11a** (0.06 mmol) in CH_2Cl_2 (0.5m l) was added ten equivalents of phenylacetylenes in an-NMR tube at 25°C. The rate of formation of the vinylidene complexes were traced by ^{31}P-NMR. In this reaction, any ruthenium complexes other than the starting material and vinylidene complex were not observed.

4. Conclusions

A new family of enantiopure planar-chiral cyclopentadienylruthenium–vinylidene complexes, (S_{Cl})- and (R_{Cl})-[(η^5-C_5H_2-1-COR^1-2-Me-4-R^2)Ru(PPh_3)$_2$(=C=CHR^3)][PF_6], reported here may provide the first examples of chiral cyclopentadienylruthenium-alkylidene complexes which have the potential use as reactive chiral ruthenium complexes possessing an asymmetric environment around the central ruthenium atom arising from planar chirality. In addition the redox property of ruthenium in the complexes can be finely tunable by the type of substituents on the cyclopentadienyl ligand.

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