Control of Stereochemistry at the Metal Center in Planar-Chiral Cyclopentadienyl Ruthenium Complexes with Anchor Phosphine on Complexation with Salicylideneaminato Ligands

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Received March 21, 2001

Reactions of planar-chiral cyclopentadienyl-phosphine ruthenium complexes [η^5,η^1-{C_5H_2-(Me)(R)$COO(CH_2)_2PPh_2$}$Ru(MeCN)_2$][PF_6] (**1a**, R = Me; **1b**, R = Ph) with sodium salicylideneaminato (**2**) led to the formation of salicylideneaminato complexes [η^5,η^1-{C_5H_2(Me)(R)-$COO(CH_2)_2PPh_2$}Ru(OArC=NR′)] (**3** and **4**, R = Me; **5** and **6**, R = Ph) inducing metal-centered chirality with a high selectivity (up to >99% de). The diastereoselectivity of products did not depend on the substituent on aromatic ring of salicylideneaminato ligands, but upon the substituents on the cyclopentadienyl group and on nitrogen of the imino group. X-ray diffraction and NMR studies including NOE measurements revealed that the configuration of the major isomers is $S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$. Similar reactions of planar-chiral cyclopentadienyl ruthenium complexes [η^5-{C_5H_2(Me)(R)COOEt}$Ru(PPh_3)(MeCN)_2$][PF_6] (**7**) (**7a**, R = Me; **7b**, R = Ph) having no anchor phosphine ligands with **2** also gave salicylideneaminato complexes [η^5-{C_5H_2(Me)(R)COOEt}Ru(PPh_3)(OC_6H_4C=NR′)] (**8** and **9**) with a low selectivity. Epimerization of a pure sample of the major product **5a** into a diastereomeric mixture of **5a** and **6a** showed that the diastereoselectivity at the ruthenium center is governed by the difference in thermodynamic stability between **3** and **4**, or **5** and **6**.

Introduction

Extensive studies on diastereoselectivity in the reactions of optically active organometallic complexes have been made in terms of molecular design of catalysts and understanding of the mechanism in asymmetric organic reactions.[1] Although organometallic complexes having chiral ligands such as chiral phosphines and amines have been the main objects of such studies for a long time, other types of optically active complexes have attracted much attention in recent years. Three-legged piano-stool complexes with three different ligands have metal-centered chirality,[2] while π-coordination of unsymmetrically substituted η^2-olefin and η^5-cyclopentadienyl (Cp) ligands generates planar chirality.[3] In particular, metal-centered chiral complexes, in which a metal atom serves as a reactive and asymmetric center, are of interest. However, application of those complexes is limited to stoichiometric reactions since racemization at the chiral metal center often takes place during reactions.[4] Thus, control of metal-centered chirality by using chiral ligands is a main subject to develop novel asymmetric reactions.[5] Recently, some attempts

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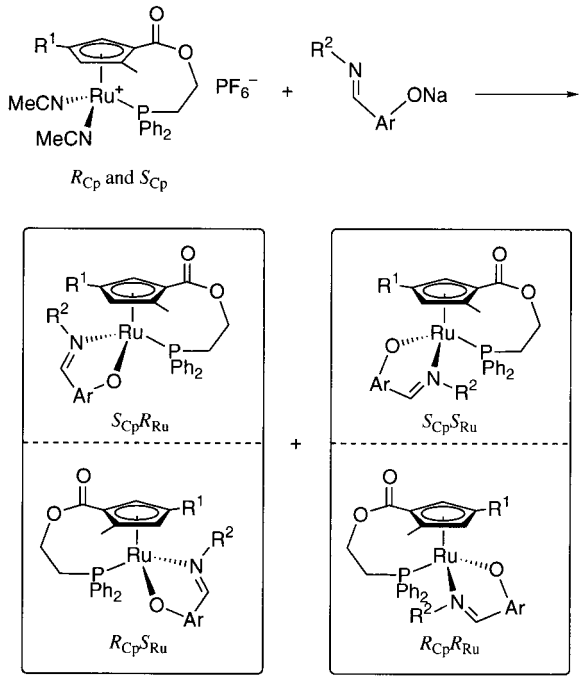
10.1021/om0102246 CCC: $20.00
Publication on Web 06/28/2001

of catalysis of metal-centered chiral complexes with chiral ligands in asymmetric Diels−Alder reactions were found in the literature.[6]

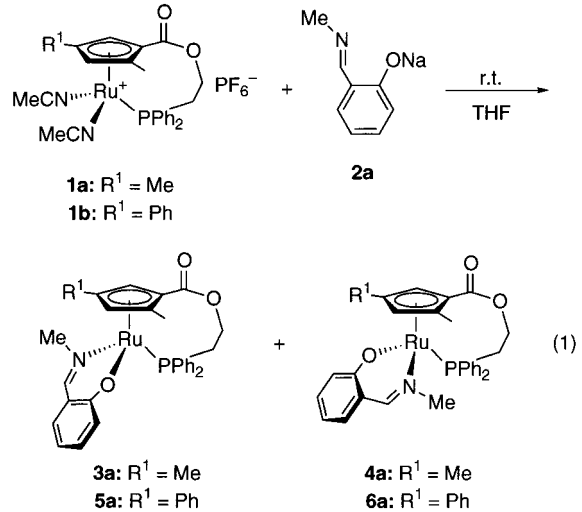
In the course of our study on planar-chiral complexes of late transition metals,[7] we prepared planar-chiral Cp′-phosphine ruthenium complexes [η^5,η^1-{C_5H_2(Me)(R)-$COO(CH_2)_2PPh_2$}Ru(MeCN)$_2$][PF_6] (**1**) (R = Me, Ph, Bu^t),[8] in which the anchor phosphine prevents the rotation of the Cp′ ring, constructing a good asymmetric environment around the ruthenium atom.[9] Efficiency of the planar-chiral Cp′-phosphine ligand was proved by the induction of metal-centered chirality with a high selectivity in the ligand exchange reactions with various phosphines and phosphites[10] and enantioface-selective π-coordination of prochiral dienes.[11] Similar results have been reported by Bergman[12] and Tani et al.[13] Now we have examined the selectivity at a metal center on complexation of salicylideneaminato ligands to planar-chiral Cp′-phosphine ruthenium complexes. Stereochemistry of metal-centered chirality in (η^6-arene)ruthenium complexes involving chiral salicylideneaminato ligands has been investigated by Chakravarty[14] and Brunner.[15] In their studies, relatively high selectivity was achieved by the chiral groups on the imino nitrogen. Application of these complexes as an enantioselective catalyst was attempted in olefin isomerization.[16] Herein we describe effective control of metal-centered chirality by planar-chiral Cp′-P ligands in ruthenium complexes having salicylideneaminato ligands. Since racemic mixtures were used as starting materials, resulting complexes form two pairs of diastereomers, each of which consists of a pair of enantiomers, as shown in Scheme 1. In this paper, all the stereostructures of the complexes are drawn with planar chirality of S_{Cp} for clarity.

Scheme 1



Results and Discussion

Treatment of planar-chiral cyclopentadienyl-phosphine ruthenium complex [η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2$-PPh_2}Ru(MeCN)$_2$][PF_6] (**1a**) with sodium salicylidenemethylaminato (**2a**) in THF at room temperature resulted in the formation of a diastereomeric mixture of [η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru(OC$_6H_4$C=NMe)] (**3a** and **4a**) in 50% yield (eq 1). The ^{31}P NMR spectrum of the product exhibited two singlet signals at δ 40.2 and 28.0 with an integral ratio of 74:26, indicating that the selectivity is 48% de. In the ^{1}H NMR spectrum, two



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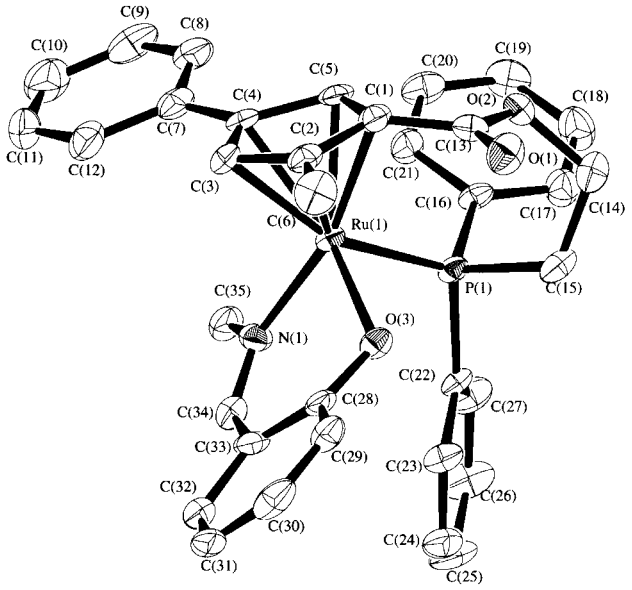


Figure 1. ORTEP view of **5a** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

sets of signals due to salicylidenemethylaminato complexes **3a** and **4a** appeared in the same integral ratio as mentioned above. To determine the configuration of the products, the differential NOE spectra were measured. For the major product **3a**, irradiation of the methyl signal at δ 1.91 gave rise to the NOE signals of two Cp′ protons and methyl protons on the imino nitrogen, suggesting that the signal at δ 1.91 is assignable to the methyl protons at the 4-position on the Cp′ ring and the imino group is close to the methyl group at the 4-position. On the other hand, no NOE was observed for the signal of methyl protons on the imino nitrogen but one Cp′ proton by irradiation of the methyl signal at δ 1.77. These data reveal that the signal at δ 1.77 is due to the methyl protons at the 2-position on the Cp′ ring and the imino group is situated apart from the methyl group at the 2-position. In the differential NOE spectra of the minor product **4a**, no NOE was observed between methyl protons on the imino nitrogen and those at the 4-position on the Cp′ ring for **4a**, while an NOE was observed between methyl protons on the imino nitrogen and those at the 2-position on the Cp′ ring. These results clearly show that the configuration of the major product **3a** is $S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$ on the basis of the priority sequence Cp′ > P > O > N, and the minor product **4a** has a configuration of $S_{Cp}S_{Ru}/R_{Cp}R_{Ru}$.[2]

Although similar reaction of [η^5,η^1-{C_5H_2(Me)(Ph)-$COO(CH_2)_2PPh_2$}Ru(MeCN)$_2$][PF_6] (**1b**), having a phenyl group at the 4-position instead of a methyl group as in **1a**, gave analogous products [η^5,η^1-{C_5H_2(Me)(Ph)-$COO(CH_2)_2PPh_2$}Ru(OC_6H_4C=NMe)] (**5a** and **6a**), the selectivity (90% de) was higher than that observed in the reaction of **1a**. The configuration of the major product **5a** was also suggested to be $S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$ by the NOE spectrum. Fortunately, single crystals of the major product **5a** were obtained by recrystallization from CH_2Cl_2−hexane. X-ray crystallography unequivocally revealed that the configuration of the major product **5a** is $S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$, as suggested from the NOE spectrum. The molecular structure of **5a** is illustrated in Figure 1. Structural parameters around the ruthenium atom (Table 1) are similar to those of (η^6-arene)Ru analogues.[14,15]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3g and 5a

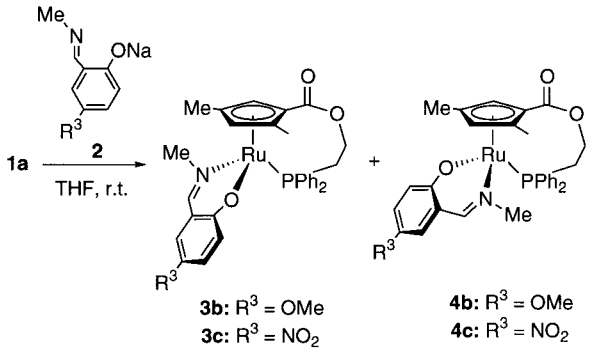
	3g	5a
Ru(1)−P(1)	2.336(2)	2.325(2)
Ru(1)−O(3)	2.092(4)	2.105(4)
Ru(1)−N(1)	2.105(5)	2.077(5)
Ru(1)−C(1)	2.153(6)	2.164(7)
Ru(1)−C(2)	2.239(7)	2.228(7)
Ru(1)−C(3)	2.251(7)	2.250(7)
Ru(1)−C(4)	2.199(7)	2.202(6)
Ru(1)−C(5)	2.135(6)	2.150(6)
O(3)−C(23 or 28)	1.298(8)	1.292(8)
N(1)−C(29 or 34)	1.296(8)	1.286(9)
P(1)−Ru(1)−O(3)	81.2(1)	86.8(1)
P(1)−Ru(1)−N(1)	93.9(2)	90.5(2)
O(3)−Ru(1)−N(1)	87.4(2)	85.7(2)
Ru(1)−O(3)−C(23 or 28)	1129.8(4)	20.4(4)
Ru(1)−N(1)−C(29 or 34)	1125.1(5)	24.9(5)

Table 2. Reactions of Complex 1a with Sodium Salicylideneaminato Derivatives 2

entry	NaOArC=NR[2]	products	yield (%)[a]	% de[b]	config[c]
1	**2a**	**3a** + **4a**	50	48	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$
2	**2b**	**3b** + **4b**	30[d]	47[e]	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$
3	**2c**	**3c** + **4c**	57[d]	29	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$
4	**2d**	**3d** + **4d**	81	52	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$
5	**2e**	**3e** + **4e**	87	47	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$

[a] Isolated yields. [b] Determined by ^{31}P NMR. [c] Configuration of major products determined by NOE spectra. [d] NMR yields. [e] Determined by ^{1}H NMR.

To elucidate the substituent effect on the aromatic ring of salicylideneaminato ligands toward the selectivity of the products (**3**/**4**), reactions with several kinds of salicylidenemethylaminato derivatives were performed (Table 2). Although reactions of **1a** with **2b** and **2c**, having a methoxy or nitro group, generated the corresponding salicylidenemethylaminato complexes (**3b**/**4b** and **3c**/**4c**), we could not isolate the products owing to



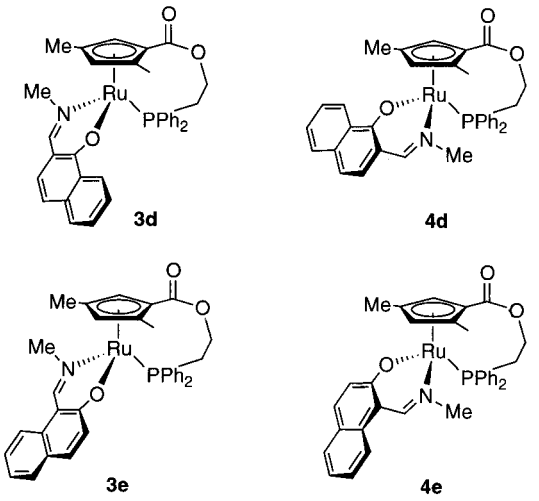
(2)

their low stability. Thus, yields, selectivity, and the configuration of the main products were determined by ^{1}H NMR spectra of the reaction mixtures. No significant differences in the selectivity of the products from that of **3a**/**4a** were observed in these reactions (entries 2 and 3). On treatment of complex **1a** with **2d** and **2e**, which have a naphthalene ring instead of a benzene ring, the products (**3d**/**4d** and **3e**/**4e**) were isolated in relatively high yields, but the selectivities were similar to that of **3a**/**4a** (entries 4 and 5). These results suggest that the electronic and steric effects of the substituents on the

Table 3. Reactions of Complexes 1 with Sodium Salicylideneaminato Derivatives

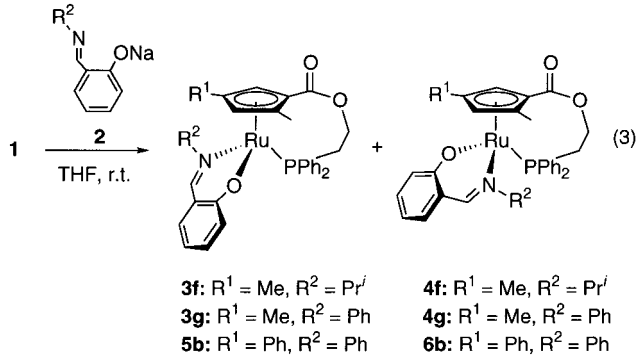
entry	complex	$NaOC_6H_4C{=}NR^2$	products	yield (%)[a]	% de[b]	config[c]
1	**1a**	**2a** (R^2 = Me)	**3a** + **4a**	50	48	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$[d]
2	**1a**	**2f** (R^2 = Pr^i)	**3f** + **4f**	11[e]	44	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$[f]
3	**1a**	**2g** (R^2 = Ph)	**3g** + **4g**	62	94	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$[g]
4	**1b**	**2a** (R^2 = Me)	**5a** + **6a**	54	90	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$[g]
5	**1b**	**2g** (R^2 = Ph)	**5b**	67	>99	$S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$[f]

[a] Isolated yields. [b] Determined by ^{31}P NMR. [c] Configuration of major products. [d] Determined by NOE spectra. [e] NMR yield. [f] Determined by comparison of chemical shifts in ^{31}P NMR spectra with those of other major products. [g] Determined by X-ray analyses.



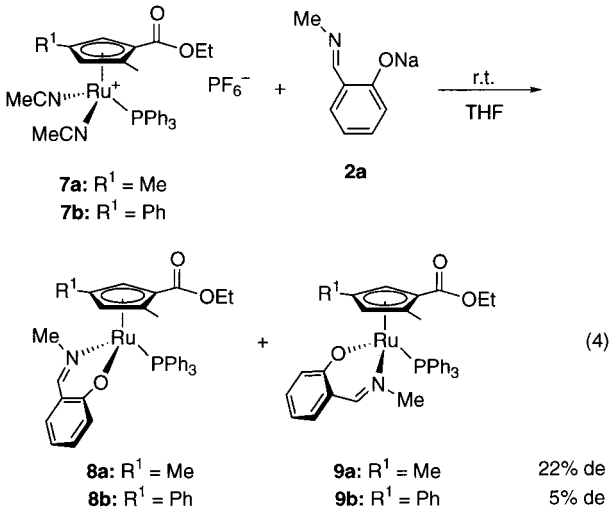
aromatic ring of salicylideneaminato ligands do not affect the selectivity of the products (**3**/**4**).

Then we investigated the substituent effect on the imino nitrogen and on the Cp′ ring (Table 3). While reaction of **1a** with sodium salicylideneisopropylaminato (**2f**) gave products **3f** and **4f** with a selectivity similar to that of **3a**/**4a** in a low yield (entry 2), the reaction with sodium salicylidenephenylaminato (**2g**) led to an increase in the selectivity of products **3g**/**4g** to 94% de (entry 3). The configuration of main product **3g** was determined by X-ray analysis to be $S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$. It should be noted that reaction of complex **1b** with **2g** gave a single product (**5b**), of which the stereochemistry



could not be determined by NOE spectra due to overlap of signals in the area of aromatic protons. However, comparison of the chemical shift (δ 35.3) in the ^{31}P NMR spectrum of **5b** with those of the major products **3g** and **5a** (δ 36.7 and 39.5), in contrast to those of the minor products **4g** and **6a** (δ 28.2 and 30.6), indicates that the configuration of **5b** is identical with those of **3g** and **5a**, and thus must be $S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$. These results clearly show that the phenyl groups on the Cp′ ring and/or on the imino nitrogen affect the diastereoselectivity of the products. However, the reaction of complex [η^5,η^1-{C_5H_2-(Me)(Bu^t)COO$(CH_2)_2PPh_2$}Ru$(MeCN)_2$][PF_6] (**1c**) with **2a** was accompanied by decomposition to give a complex mixture.

When planar-chiral cyclopentadienyl ruthenium complexes [η^5-{C_5H_2(Me)(R)COOEt}Ru$(PPh_3)(MeCN)_2$][PF_6] (**7**), having no anchor phosphine ligands, were treated with **2a**, salicylideneaminato complexes [η^5-{C_5H_2(Me)-(R)COOEt}Ru$(PPh_3)(OC_6H_4C{=}NR')$] (**8** and **9**) were obtained in moderate yields. Although the conformations of the major products **8a** and **8b** could not be assigned, the selectivities of the products (**8**/**9**) were lower than those in the corresponding reactions of **1**, suggesting that the anchor phosphine ligand has an important role of controlling the stereochemistry at metal center.[10,11]



Configuration at the metal center is fairly stable in chloroform at room temperature since a diastereomerically pure sample of **5a** slowly became a mixture of **5a** and **6a** in 94% de for 24 h, and 90% de for 4 days, of which the latter is the same composition as that of the products (**5a** and **6a**) formed from the reaction of **1b** with **2a**. Addition of 10% acetonitrile (v/v) into a chloroform solution of **5a** accelerated the epimerization of **5a**, giving a mixture of **5a** and **6a** in 90% de within 1 h. Rapid epimerization was observed in THF. When **5a** was dissolved in THF, the ^{31}P NMR spectrum of the solution showed within 15 min the signals of not only **5a** but also **6a** with 90% de. Furthermore, the ratio of **3a**/**4a** was dependent on the solvent, and the ratio lowered to 6% de (**3a**: major) in benzene, whereas in chloroform it was 48% de (Table 2, entry 1). These results clearly suggest that there is equilibrium between two diastereomers in a solution and the selectivity of products **3**/**4** or **5**/**6** could be determined by the difference of their thermodynamic stability.[15]

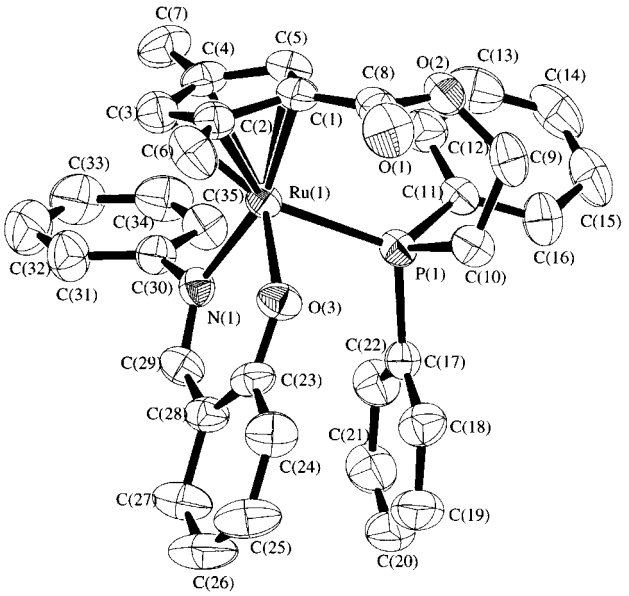


Figure 2. ORTEP view of **3g** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

From the results mentioned above, it became apparent that the selectivity of salicylideneaminato complexes **3**/**4** and **5**/**6** is under thermodynamic control and is improved by the 4-phenyl substituent on the cyclopentadienyl ligand and/or by the phenyl group on the nitrogen of the imino group. Especially, in the case where both substituents are phenyl groups (Table 3, entry 5), complex **5b** was produced as the sole product, suggesting that thermodynamic stability of diastereomer **5b** is much higher than that of diastereomer **6b**. To obtain information on the thermodynamic stability of complex **5b**, we have investigated the structure of **5b** using an optimized space-filling model as shown in Figure 3.[17] In this model, two phenyl rings bound to the cyclopentadienyl group and the imino nitrogen are almost parallel (the dihedral angle: 6°) with a distance of approximately 3.4 Å, suggesting a $\pi-\pi$ stacking between the two phenyl groups.[13c] Furthermore, a $\pi-\pi$ stacking was also found between one of the two phenyl rings on the phosphorus atom and the aromatic ring of the salicylideneaminato ligand since the distance and dihedral angle between them are about 3.4 Å and 16°, respectively. A similar phenomenon of the latter $\pi-\pi$ stacking was also found in the X-ray structure of **3g** shown in Figure 2. In contrast to **5b**, such $\pi-\pi$ stacking was not observed in the model of diastereomer **6b**. Therefore, the $\pi-\pi$ stacking makes a large contribution to improvement of the thermodynamic stability of **5b** compared with **6b**.

The CH$-\pi$ interaction between phenyl and methyl groups seems to play an important role for the preferable formation of **3g** and **5a** relative to **4g** and **6a**.[18] X-ray crystallography showed that the distances between the methyl proton and phenyl carbons lie in the range 3.33(1)−4.01(1) Å for **3g** and 3.52(1)−4.58(1) Å for **5a**, of which the minimum values are smaller than the sum (3.7 Å) of van der Waals radii of the methyl group (2.0 Å) and aromatic carbon (1.7 Å), and are

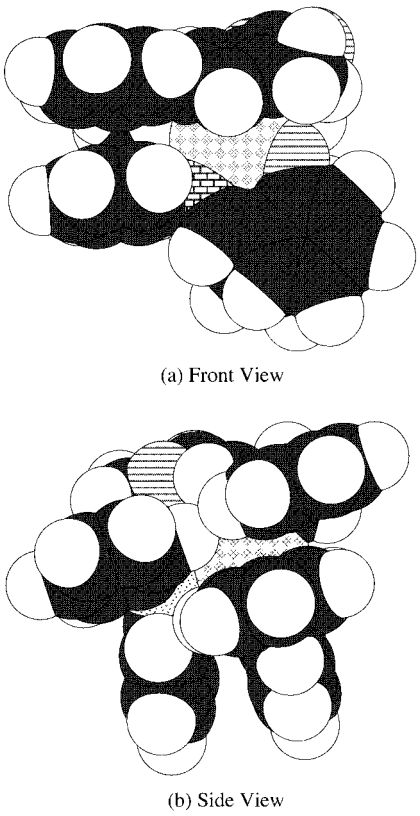
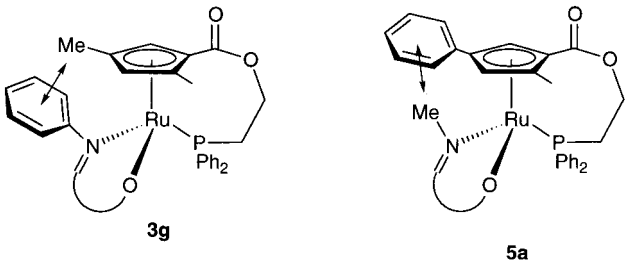


Figure 3. Space-filling model of **5b**.

comparable to those observed in transition metal complexes with CH$-\pi$ interaction.[19] It is noteworthy that in the ^{1}H NMR spectra signals due to the methyl protons with CH$-\pi$ interaction shifted to a higher magnetic field relative to those with no CH$-\pi$ interaction, and **3a** exhibited a signal due to the methyl protons on the Cp′ group at δ 1.91, while **3g** exhibited a signal at δ 0.59. The methyl protons on the imino group of **3a** and **5a** appeared at δ 3.43 and 2.75, respectively. These phenomena are caused by shielding due to the ring current of the phenyl groups, supporting the CH$-\pi$ interaction (see Scheme 2).

Scheme 2. CH$-\pi$ Interaction



Although we do not have enough evidence on the mechanism of epimerization between two diastereomers, a dissociative route may be reasonable taking account of remarkable acceleration by addition of acetonitrile. When an equimolar mixture of **3g** and **5a** was allowed to epimerize in THF, both complexes independently epimerized to give the corresponding diastereomeric mixtures **3g**/**4g** (94% de) and **5a**/**6a** (90% de), and

(17) MM calculation was performed by the PC Spartan Pro program.
(18) For reviews, see: Okawa, H. *Coord. Chem. Rev.* **1988**, *92*, 1. (b) Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201.

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no intermolecular processes forming **3a**/**4a** and **5b**/**6b** were observed. Thus, we propose that the epimerization proceeds via an intramolecular process involving dissociation and recoordination of the imino group.

In conclusion, we described thermodynamical control of metal-centered chirality in planar-chiral Cp′-P ruthenium complexes on complexation with salicylideneaminato ligands. Thermodynamic stability of the products is strongly influenced by $\pi-\pi$ stacking and CH$-\pi$ interaction between substituents on the Cp′ and the imino groups. Since an imino group increases the reactivity toward nucleophiles by coordination to a metal, we are making an effort to apply this finding to the development of a novel asymmetric reaction.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere. Hexane and THF were distilled over calcium hydride and sodium benzophenone ketyl, respectively. Other chemicals available commercially were used without further purification. The starting ruthenium complexes [η^5,η^1-{C_5H_2(Me)(R)COO$(CH_2)_2PPh_2$}Ru(MeCN)$_2$][PF_6] (**1**) were prepared as reported previouly.[8]

NMR spectra were taken on JEOL JNM-LA400, JEOL JNM-LA600, and Bruker ARX400 spectrometers. In ^{1}H and ^{13}C NMR spectra, $SiMe_4$ 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 a Perkin-Elmer system 2000 FT-IR and FAB mass spectra on a JEOL JMS-600H instrument. Elemental analyses were performed at The Material Analysis Center, ISIR, Osaka University.

Preparation of Salicylideneamines.[20] To a solution of a salicylaldehyde derivative (1.45 mmol) in hexane (10 mL) was added methylamine (40% in water) (0.20 mL), and the reaction mixture was stirred at room temperature for 1 h. After drying over Na_2SO_4, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to give a salicylideneamine derivative. When salicylideneamine was obtained as a solid, the resulting residue was washed with pentane.

1-OH-2-(MeN=CH)C_6H_3 (salicylidenemethylamine):[21] yellow oil, yield >99%. IR (cm^{-1}, neat): 1638 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.49 (d, J = 1.5 Hz, 3H, NCH_3), 6.87 (dt, J = 1.0, 7.4 Hz, 1H, Ph), 6.96 (d, J = 8.3 Hz, 1H, Ph), 7.24 (dd, J = 1.6, 7.7 Hz, 1H, Ph), 7.30 (dt, J = 1.5, 7.8 Hz, 1H, Ph), 8.35 (d, J = 1.2 Hz, 1H, N=CH), 13.50 (s, 1H, OH).

1-OH-2-(MeN=CH)-4-MeOC_6H_3 (4-methoxysalicylidenemethylamine):[22] yellow oil, yield >99%. IR (cm^{-1}, neat): 1642 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.49 (d, J = 1.2 Hz, 3H, NCH_3), 3.78 (s, 3H, OCH_3), 6.77 (d, J = 2.2 Hz, 1H, Ph), 6.88−6.93 (m, 2H, Ph), 8.31 (d, J = 1.5 Hz, 1H, N=CH), 12.95 (br, 1H, OH).

1-OH-2-(MeN=CH)-4-$NO_2C_6H_3$ (4-nitrosalicylidenemethylamine):[23] orange powder, yield 62%. IR (cm^{-1}, KBr): 1298 (ν_{N-O}), 1667 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.55 (d, J = 1.2 Hz, 3H, NCH_3), 6.96 (d, J = 9.2 Hz, 1H, Ph), 8.19 (dd, J = 2.7, 9.2 Hz, 1H, Ph), 8.23 (d, J = 2.7 Hz, 1H, Ph), 8.36 (d, J = 0.9 Hz, 1H, N=CH), 14.80 (br, 1H, OH).

1-OH-2-(MeN=CH)$C_{10}H_6$ (2-(methyliminomethyl)naphthalen-1-ol): yellow powder, yield 78%. IR (cm^{-1}, KBr): 1649 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.37 (d, J = 1.0 Hz, 3H, NCH_3), 6.79 (d, J = 8.8 Hz, 1H, naphthyl), 6.94 (d, J = 8.8 Hz, 1H, naphthyl), 7.42 (dt, J = 1.5, 7.4 Hz, 1H, naphthyl), 7.52−7.60 (m, 2H, naphthyl), 7.79 (d, J = 10.0 Hz, 1H, naphthyl), 8.45 (d, J = 8.1 Hz, 1H, N=CH), 13.39 (br, 1H, OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 37.73 (s, CH_3), 108.82 (s, naphthyl), 114.37 (s, naphthyl), 124.98 (s, naphthyl), 125.37 (s, naphthyl), 127.21 (s, naphthyl), 127.83 (s, naphthyl), 130.10 (s, naphthyl), 130.23 (s, naphthyl), 137.60 (s, naphthyl), 162.45 (s, naphthyl), 177.33 (s, C=N). FAB MS: m/z 185 (M^+). Mp: 114−115 °C. Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.91; H, 6.01; N, 7.67.

2-OH-1-(MeN=CH)$C_{10}H_6$ (1-(methyliminomethyl)naphthalen-2-ol):[24] yellow powder, yield 96%. IR (cm^{-1}, KBr): 1635 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.45 (d, J = 2.1 Hz, 3H, NCH_3), 6.92 (d, J = 9.5 Hz, 1H, naphthyl), 7.23 (t, J = 7.5 Hz, 1H, naphthyl), 7.43 (dt, J = 1.1, 7.7 Hz, 1H, naphthyl), 7.61 (d, J = 7.6 Hz, 1H, naphthyl), 7.68 (d, J = 9.2 Hz, 1H, naphthyl), 7.85 (d, J = 8.2 Hz, 1H, naphthyl), 8.71 (d, J = 8.9 Hz, 1H, N=CH), 14.36 (br, 1H, −OH).

1-OH-2-(Pr^{i}N=CH)C_6H_4 (salicylideneisopropylamine):[21] yellow oil, yield 99%. IR (cm^{-1}, neat): 1632 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.30 (d, J = 6.3 Hz, 6H, NCH(CH_3)$_2$), 3.55 (sept, J = 5.9 Hz, 1H, NC*H*(CH_3)$_2$), 6.86 (dt, J = 1.0, 7.4 Hz, 1H, Ph), 6.95 (d, J = 8.3 Hz, 1H, Ph), 7.24 (dd, J = 1.7, 7.6 Hz, 1H, Ph), 7.29 (dt, J = 1.8, 7.7 Hz, 1H, Ph), 8.36 (s, 1H, N=CH), 13.71 (br, 1H, OH).

1-OH-2-(PhN=CH)C_6H_4 (salicylidenephenylamine):[21] yellow powder, yield 99%. IR (cm^{-1}, KBr): 1617 ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.95 (dt, J = 1.0, 7.4 Hz, 1H, Ph), 7.03 (d, J = 7.8 Hz, 1H, Ph), 7.28−7.31 (m, 2H, Ph), 7.37−7.45 (m, 5H, Ph), 8.64 (s, 1H, N=CH), 13.27 (s, 1H, OH).

[η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru(O$C_6H_4$C=NMe)] (3a and 4a). NaH (60% oil suspension) (12 mg, 0.30 mmol) was washed with dry hexane (1 mL) three times and suspended in THF (1 mL). To this suspension was added salicylidenemethylamine (41 mg, 0.30 mmol), and the reaction mixture was stirred at room temperature for 15 min. After the reaction mixture was filtered, the filtrate was poured into a suspension of **1a** (136 mg, 0.20 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (1 mL) followed by the addition of hexane (5 mL). After insoluble materials were removed by filtration, the filtrate was concentrated under reduced pressure. Recrystallization from dichloromethane−hexane gave a mixture of **3a** and **4a** (59 mg, 50% yield, 48% de) as red crystals. IR (cm^{-1}, KBr): 1615 ($\nu_{C=N}$), 1688 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 600 MHz): for **3a**, δ 1.77 (s, 3H, Cp′CH_3), 1.91 (s, 3H, Cp′CH_3), 2.25 (dt, J = 4.8, 14.8 Hz, 1H, PCH_2), 3.22−3.28 (m, 1H, PCH_2), 3.43 (d, J = 0.9 Hz, 3H, NCH_3), 3.91 (ddt, J = 2.7, 4.7, 11.8 Hz, 1H, OCH_2), 4.42 (s, 1H, Cp′), 4.82 (d, J = 2.0 Hz, 1H, Cp′), 5.14 (ddd, J = 7.5, 11.0, 20.9 Hz, 1H, OCH_2), 6.14 (dt, J = 0.6, 7.2 Hz, 1H, Ph), 6.43 (dd, J = 1.8, 7.5 Hz, 1H, Ph), 6.77 (d, J = 8.4 Hz, 1H, Ph), 6.79−6.84 (m, 2H, Ph), 6.92−6.99 (m, 2H, Ph), 7.03 (t, J = 8.5 Hz, 2H, Ph), 7.24−7.35 (m, 1H, Ph), 7.42 (s, 1H, N=CH), 7.52−7.57 (m, 2H, Ph), 7.74−7.78 (m, 2H, Ph); for **4a**, δ 1.74 (s, 3H, Cp′CH_3), 2.07 (s, 3H, Cp′CH_3), 2.59−2.64 (m, 1H, PCH_2), 2.86−2.92 (m, 1H, PCH_2), 3.27 (s, 3H, NCH_3), 4.11−4.17 (m, 1H, OCH_2), 4.15 (s, 1H, Cp′), 4.75 (d, J = 2.2 Hz, 1H, Cp′), 5.06−5.13 (m, 1H, OCH_2), 6.12−6.14 (m, 1H, Ph), 6.45 (dd, J = 1.7, 7.6 Hz, 1H, Ph), 6.57 (d, J = 8.6 Hz, 1H, Ph), 6.79−6.84 (m, 2H, Ph), 6.92−6.99 (m, 2H, Ph), 7.11 (t, J = 9.0 Hz, 2H, Ph), 7.15 (s, 1H, N=CH), 7.24−7.35 (m, 1H, Ph), 7.52−7.57 (m, 2H, Ph), 7.85−7.88 (m, 2H, Ph). ^{31}P NMR ($CDCl_3$, 160 MHz): for **3a**, δ 40.2 (s); for **4a**, δ 28.0 (s). FAB MS: m/z 585 (M^+). Anal. Calcd for $C_{30}H_{30}NO_3PRu$: C, 61.64; H, 5.17; N, 2.40. Found: C, 61.38; H, 5.04; N, 2.55.

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[η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru($OC_6H_3(OMe)C{=}N$-Me)] (3b and 4b). These complexes were prepared from **1a** and **2b** by a method similar to that for **3a** and **4a**, but were not isolated. Yield and selectivity were determined by NMR spectra of the reaction mixture to be 30% and 47% de, respectively. ^{1}H NMR ($CDCl_3$, 400 MHz) for **3b**: δ 1.77 (s, 3H, Cp′CH_3), 1.91 (s, 3H, Cp′CH_3), 3.62 (s, 3H, NCH_3), 3.73 (s, 3H, OCH_3), 4.40 (s, 1H, Cp′), 4.82 (d, J = 2.2 Hz, 1H, Cp′), signals due to phenyl, N=CH, and CH_2CH_2P protons could not be assigned due to overlap of those of other products; for **4b**, δ 1.73 (s, 3H, Cp′CH_3), 2.06 (s, 3H, Cp′CH_3), 3.42 (d, J = 0.7 Hz, 3H, NCH_3), 4.13 (s, 1H, Cp′), 4.75 (s, 1H, Cp′), signals due to OCH_3, phenyl, and N=CH CH_2CH_2P protons could not be assigned due to overlap of those of other products. ^{31}P NMR ($CDCl_3$, 160 MHz): for **3b**, δ 39.5 (s); for **4b**, δ 27.0 (s).

[η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru($OC_6H_3(NO_2)C{=}N$-Me)] (3c and 4c). These complexes were prepared from **1a** and **2c** by a method similar to that for **3a** and **4a**, but were not isolated. Yield and selectivity were determined by NMR spectra of the reaction mixture to be 57% and 29% de, respectively. ^{1}H NMR ($CDCl_3$, 400 MHz): for **3c**, δ 1.75 (s, 3H, Cp′CH_3), 1.91 (s, 3H, Cp′CH_3), 3.55 (d, J = 0.9 Hz, 3H, NCH_3), 4.51 (s, 1H, Cp′), 4.85 (d, J = 2.1 Hz, 1H, Cp′), signals due to phenyl, N=CH, and CH_2CH_2P protons could not be assigned due to overlap of those of other products; for **4c**, δ 2.22 (s, 3H, Cp′CH_3), 3.41 (s, 3H, NCH_3), 4.59 (s, 1H, Cp′), signals due to Cp′CH_3, Cp-H, phenyl, N=CH, and CH_2CH_2P protons could not be assigned due to overlap of those of other products. ^{31}P NMR ($CDCl_3$, 160 MHz): for **3c**, δ 38.8 (s); for **4c**, δ 29.8 (s).

[η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru(1-$OC_{10}H_6C{=}NMe$-2)] (3d and 4d). A THF solution (1 mL) of sodium 2-(methyliminomethyl)naphthalen-1-olate (**2d**) prepared from 2-(methyliminomethyl)naphthalen-1-ol (56 mg, 0.30 mmol) and NaH (60% oil suspension) (12 mg, 0.30 mmol) as described above was added into a suspension of **1a** (136 mg, 0.20 mmol) in THF (10 mL), and the reaction mixture was stirred at room temperature for 1 h. After removal of the solvent under reduced pressure, the residue was purified by alumina column chromatography using benzene−dichloromethane = 1:1 (v/v) as an eluent. Evaporation of the solvent followed by drying in vacuo gave a mixture of **3d** and **4d** (102 mg, 81% yield, 52% de) as red powder. IR (cm^{-1}, KBr): 1595 ($\nu_{C=N}$), 1696 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 600 MHz): for **3d**, δ 1.79 (s, 3H, Cp′CH_3), 1.95 (s, 3H, Cp′CH_3), 2.23 (dt, J = 4.6, 14.6 Hz, 1H, PCH_2), 3.25−3.31 (m, 1H, PCH_2), 3.50 (d, J = 1.1 Hz, 3H, NCH_3), 3.94−3.99 (m, 1H, OCH_2), 4.50 (t, J = 1.8 Hz, 1H, Cp′), 4.88 (d, J = 2.2 Hz, 1H, Cp′), 5.20 (ddd, J = 7.1, 11.2, 20.8 Hz, 1H, OCH_2), 6.42 (d, J = 8.4 Hz, 1H, Ar), 6.49 (s, 1H, Ar), 6.52 (d, J = 8.4 Hz, 1H, Ar), 6.63 (dt, J = 1.1, 8.6 Hz, 2H, Ar), 6.68 (dt, J = 2.0, 7.7 Hz, 2H, Ar), 6.77 (t, J = 7.0 Hz, 1H, Ar), 6.97 (s, 1H, N=CH), 7.36−7.56 (m, 5H, Ar), 7.73−7.76 (m, 2H, Ar), 8.67 (dd, J = 0.7, 8.1 Hz, 12H, Ar); for **4d**, δ 1.87 (s, 3H, Cp′CH_3), 2.11 (s, 3H, Cp′CH_3), 2.56−2.62 (m, 1H, PCH_2), 2.91−2.96 (m, 1H, PCH_2), 3.25 (s, 1H, NCH_3), 4.15−4.20 (m, 1H, OCH_2), 4.34 (s, 1H, Cp′), 4.78 (d, J = 2.0 Hz, 1H, Cp′), 5.05−5.12 (m, 1H, OCH_2), 6.89−6.96 (m, 2H, Ar), 7.14 (s, 1H, N=CH), 7.23−7.26 (m, 1H, Ar), 7.36−7.56 (m, 8H, Ar), 7.95−7.99 (m, 2H, Ar), 8.36 (d, J = 7.9 Hz, 1H, Ar). ^{31}P NMR ($CDCl_3$, 160 MHz): for **3d**, δ 39.9 (s); for **4d**, δ 30.0 (s). FAB MS: m/z 635 (M^+). Anal. Calcd for $C_{34}H_{32}NO_3PRu$: C, 64.34; H, 5.08; N, 2.21. Found: C, 64.15; H, 4.91; N, 2.43.

[η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru(2-$OC_{10}H_6C{=}NMe$-1)] (3e and 4e). Reaction of **1a** (136 mg, 0.20 mmol) with sodium 1-(methyliminomethyl)naphthalen-2-olate (**2e**), prepared from 1-(methyliminomethyl)naphthalen-2-ol (56 mg, 0.30 mmol) and NaH (60% oil suspension) (12 mg, 0.30 mmol), by a method similar to that for **3d** and **4d** gave a mixture of **3e** and **4e** (110 mg, 87% yield, 47% de) as a red powder. IR (cm^{-1}, KBr): 1614 ($\nu_{C=N}$), 1696 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 600 MHz): for **3e**, δ 1.76 (s, 3H, Cp′CH_3), 1.93 (s, 3H, Cp′CH_3), 2.29 (dt, J = 4.9, 14.4 Hz, 1H, PCH_2), 3.18−3.24 (m, 1H, PCH_2), 3.44 (s, 3H, NCH_3), 3.94−3.99 (m, 1H, OCH_2), 4.38 (s, 1H, Cp′), 4.83 (d, J = 3.3 Hz, 1H, Cp′), 5.17 (ddd, J = 7.4, 11.4, 20.6 Hz, 1H, OCH_2), 6.78−7.89 (m, 16H, Ar), 7.81 (s, 1H, N=CH); for **4e**, δ 1.74 (s, 3H, Cp′CH_3), 2.08 (s, 3H, Cp′CH_3), 2.64−2.71 (m, 1H, PCH_2), 2.90−2.96 (m, 1H, PCH_2), 3.24 (s, 1H, NCH_3), 4.17 (s, 1H, Cp′), 4.21 (ddd, J = 5.9, 11.1, 16.7 Hz, 1H, OCH_2), 4.77−4.78 (m, 1H, Cp′), 5.08−5.17 (m, 1H, OCH_2), 6.78−7.89 (m, 16H, Ar), 8.02 (s, 1H, N=CH). ^{31}P NMR ($CDCl_3$, 160 MHz): for **3e**, δ 39.0 (s); for **4e**, δ 27.7 (s). FAB MS: m/z 635 (M^+). Anal. Calcd for $C_{34}H_{32}NO_3PRu$: C, 64.34; H, 5.08; N, 2.21. Found: C, 64.47; H, 4.99; N, 2.42.

[η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru($OC_6H_4C{=}NPr^i$)] (3f and 4f). These complexes were prepared from **1a** and **2f** by a method similar to that for **3a** and **4a**, but were not isolated. Yield and selectivity were determined by ^{31}P NMR spectra of the reaction mixture to be 11% and 44% de, respectively. Assignment of the ^{1}H NMR spectrum was difficult owing to overlap of those of other products. ^{31}P NMR ($CDCl_3$, 160 MHz): for **3f**, δ 39.3 (s); for **4f**, δ 27.6 (s).

[η^5,η^1-{$C_5H_2(Me)_2COO(CH_2)_2PPh_2$}Ru($OC_6H_4C{=}NPh$)] (3g and 4g). Reaction of **1a** (136 mg, 0.20 mmol) with sodium salicylidenephenylaminate (**2g**), prepared from salicylidenephenylamine (59 mg, 0.30 mmol) and NaH (60% oil suspension) (12 mg, 0.30 mmol), by a method similar to that for **3a** and **4a** gave a mixture of **3g** and **4g** (82 mg, 62% yield, 94% de) as red crystals. IR (cm^{-1}, KBr): 1605 ($\nu_{C=N}$), 1705 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 600 MHz): for **3g**, δ 0.59 (s, 3H, Cp′CH_3), 1.76 (d, J = 1.0 Hz, 3H, Cp′CH_3), 2.18 (dt, J = 4.3, 14.6 Hz, 1H, PCH_2), 3.26−3.31 (m, 1H, PCH_2), 3.75 (ddt, J = 2.7, 4.4, 11.7 Hz, 1H, OCH_2), 4.56 (s, 1H, Cp′), 4.57 (s, 1H, Cp′), 5.08 (ddd, J = 7.2, 10.9, 21.7 Hz, 1H, OCH_2), 6.12 (dt, J = 1.0, 7.8 Hz, 1H, Ph), 6.41 (dd, J = 1.7, 7.9 Hz, 1H, Ph), 6.79 (dt, J = 1.8, 7.8 Hz, 2H, Ph), 6.85 (d, J = 8.5 Hz, 1H, Ph), 6.91−6.94 (m, 3H, Ph), 7.02−7.04 (m, 2H, Ph), 7.07−7.12 (m, 2H, Ph), 7.21 (d, J = 1.5 Hz, 1H, N=CH), 7.25 (t, J = 7.8 Hz, 2H, Ph), 7.53−7.58 (m, 3H, Ph), 7.76 (dt, J = 1.5, 9.8 Hz, 2H, Ph); for **4g**, δ 0.89 (s, 3H, Cp′CH_3), 1.70 (d, J = 1.0 Hz, 3H, Cp′CH_3), 2.61 (dt, J = 4.4, 15.1 Hz, 1H, PCH_2), 3.05−3.11 (m, 1H, PCH_2), 3.70 (br, 1H, OCH_2), 3.98 (s, 1H, Cp′), 4.38 (s, 1H, Cp′), 5.13−5.23 (m, 1H, OCH_2), 5.98 (t, J = 7.7 Hz, 1H, Ph), 6.27 (dd, J = 1.7, 7.8 Hz, 1H, Ph), 6.50 (d, J = 8.8 Hz, 1H, Ph), 8.01 (t, J = 9.6 Hz, 2H, Ph); other phenyl and N=CH signals were not detected due to overlapping with those of **3g**. ^{31}P NMR ($CDCl_3$, 160 MHz): for **3g**, δ 36.7 (s); for **4g**, δ 28.2 (s). FAB MS: m/z 647 (M^+). Anal. Calcd for $C_{35}H_{32}NO_3PRu$: C, 65.01; H, 4.99; N, 2.17. Found: C, 65.08; H, 4.80; N, 2.35.

[η^5,η^1-{$C_5H_2(Me)(Ph)COO(CH_2)_2PPh_2$}Ru($OC_6H_4C{=}N$-Me)] (5a and 6a). Reaction of **1b** (148 mg, 0.20 mmol) with sodium salicylidenemethylaminate (**2a**), prepared from salicylidenemethylamine (41 mg, 0.30 mmol) and NaH (60% oil suspension) (12 mg, 0.30 mmol), by a method similar to that for **3a** and **4a** gave a mixture of **5a** and **6a** (54% yield, 90% de) as red crystals. IR (cm^{-1}, KBr): 1619 ($\nu_{C=N}$), 1700 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): for **5a**, δ 1.90 (s, 3H, Cp′CH_3), 2.27 (dt, J = 4.4, 14.9 Hz, 1H, PCH_2), 2.75 (d, J = 0.7 Hz, 3H, NCH_3), 3.15−3.23 (m, 1H, PCH_2), 4.05 (ddt, J = 2.2, 4.6, 12.0 Hz, 1H, OCH_2), 5.06 (t, J = 2.0 Hz, 1H, Cp′), 5.21 (ddd, J = 7.6, 11.2, 20.7 Hz, 1H, OCH_2), 5.45 (d, J = 1.7 Hz, 1H, Cp′), 6.21 (t, J = 7.2 Hz, 1H, Ph), 6.49 (dd, J = 1.8, 7.7 Hz, 1H, Ph), 6.73−6.82 (m, 6H, Ph), 6.92 (s, 1H, N=CH), 6.96 (dt, J = 1.5, 6.6 Hz, 1H, Ph), 7.07 (dt, J = 2.0, 7.7 Hz, 1H, Ph), 7.30 (d, J = 7.1 Hz, 1H, Ph), 7.35 (t, J = 7.3 Hz, 1H, Ph), 7.46 (d, J = 6.8 Hz, 2H, Ph), 7.52−7.61 (m, 3H, Ph), 7.69 (t, J = 8.4 Hz, 2H, Ph); for **6a**, δ 2.18 (d, J = 3.2 Hz, 3H, Cp′CH_3), 3.11 (s, 3H, NCH_3), 4.91 (s, 1H, Cp′), 5.36 (s, 1H, Cp′); signals assignable to phenyl, N=CH, and PCH_2CH_2 were not detected

Table 4. Crystallographic Data for Complexes 3g and 5a

	3g	5a
empirical formula	$C_{35}H_{32}NO_3PRu$	$C_{35}H_{32}NO_3PRu$
fw	646.69	646.69
cryst color, habit	red, prismatic	red, plate
cryst dimens	0.30 × 0.15 × 0.10 mm	0.40 × 0.40 × 0.05 mm
cryst system	monoclinic	monoclinic
lattice params	a = 12.558(7) Å	a = 13.949(3) Å
	b = 15.632(4) Å	b = 16.400(5) Å
	c = 15.330(4) Å	c = 12.994(2) Å
	β = 95.76(3)°	β = 106.91(1)°
	V = 2994(1) Å^3	V = 2844(1) Å^3
space group	$P2_1/c$ (# 14)	$P2_1/n$ (# 14)
Z value	4	4
D_{calcd}	1.434 g cm^{-3}	1.510 g cm^{-3}
F(000)	1328	1328
μ(Mo Kα)	6.13 cm^{-1}	6.46 cm^{-1}
temperature	−75 °C	−75 °C
no. of reflns measd		
total	7175	7826
unique	6864 (R_{int} = 0.063)	6519 (R_{int} = 0.085)
abs corr	ψ-scan	ψ-scan
p-factor	0.088	0.132
no. observations	3569 ($I > 3.0\sigma(I)$)	3852 ($I > 3.0\sigma(I)$)
no. variables	370	370
reflection/param ratio	9.65	10.41
residuals: R; R_w	0.052; 0.067	0.058; 0.084
goodness of fit indicator	1.02	1.11
max. shift/error in final cycle	0.00	0.01
max. peak in final diff map	1.46 e Å^{-3}	2.21 e Å^{-3} (near Ru)
min. peak in final diff map	−0.92 e Å^{-3}	−1.40 e Å^{-3}

due to overlapping with those of the major product. ^{31}P NMR ($CDCl_3$, 160 MHz): for **5a**, δ 39.5 (s); for **6a**, δ 30.6 (s). FAB MS: m/z 647 (M^+). Anal. Calcd for $C_{35}H_{32}NO_3PRu$: C, 65.01; H, 4.99; N, 2.17. Found: C, 64.79; H, 4.78; N, 2.23.

[η^5,η^1-{C_5H_2(Me)(Ph)COO(CH$_2$)$_2$PPh$_2$}Ru(OC$_6$H$_4$C=N-Ph)] (5b). Reaction of **1b** (148 mg, 0.20 mmol) with sodium salicylidenephenylaminate (**2g**), prepared from salicylidenephenylamine (59 mg, 0.30 mmol) and NaH (60% oil suspension) (12 mg, 0.30 mmol), by a method similar to that for **3a** and **4a** gave complex **5b** (67% yield, >99% de) as an orange powder. IR (cm^{-1}, KBr): 1604 ($\nu_{C=N}$), 1712 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.86 (s, 3H, Cp′CH_3), 2.19 (dt, J = 4.1, 14.3 Hz, 1H, PCH_2), 3.20−3.29 (m, 1H, PCH_2), 3.84−3.93 (m, 1H, OCH_2), 5.12 (ddd, J = 7.1, 10.5, 20.9 Hz, 1H, OCH_2), 5.20 (s, 1H, Cp′), 5.36 (s, 1H, Cp′), 6.14 (t, J = 7.3 Hz, 1H, Ph), 6.40 (dd, J = 1.5, 7.7 Hz, 1H, Ph), 6.66−6.76 (m, 7H, Ph), 6.80−6.93 (m, 8H, Ph), 7.17 (s, 1H, N=CH), 7.51−7.59 (m, 3H, Ph), 7.77 (t, J = 8.8 Hz, 2H, Ph). ^{31}P NMR ($CDCl_3$, 160 MHz): δ 35.3 (s). FAB MS: m/z 709 (M^+). Anal. Calcd for $C_{40}H_{34}NO_3PRu$: C, 67.79; H, 4.84; N, 1.98. Found: C, 67.53; H, 4.44; N, 1.90.

[η^5-{C_5H_2(Me)$_2$COOEt}Ru(PPh$_3$)(MeCN)$_2$][PF$_6$] (7a). To a dichloromethane solution (50 mL) of tris(acetonitrile) ruthenium complex [η^5-{C_5H_2(Me)$_2$COOEt}Ru(MeCN)$_3$][PF$_6$] (550 mg, 1.02 mmol) was added PPh_3 (270 mg, 1.02 mmol) at −78 °C, and the reaction mixture was stirred for 1 h at the same temperature. After removal of the solvent under reduced pressure, the residue was washed with ether. Drying in vacuo gave complex **7a** (770 mg, 99%) as a yellow powder. IR (cm^{-1}, KBr): 840 (ν_{P-F}), 1711 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.09 (t, J = 8.2 Hz, 3H, OCH$_2$CH_3), 1.52 (s, 3H, Cp′CH_3), 2.00 (d, J = 1.0 Hz, 3H, Cp′CH_3), 2.03 (d, J = 1.2 Hz, 3H, NCCH_3), 2.33 (d, J = 0.7 Hz, 3H, NCCH_3), 3.80−3.88 (m, 1H, OCH_2-CH$_3$), 3.96 (s, 1H, Cp′), 4.06−4.14 (m, 1H, OCH_2CH$_3$), 4.40 (s, 1H, Cp′), 7.26−7.34 (m, 5H, Ph), 7.45−7.46 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 3.3 (s, NCCH_3), 3.7 (s, NCCH_3), 12.2 (s, CH_3), 12.8 (s, CH_3), 14.1 (s, CH_3), 60.4 (s, OCH_2), 67.6 (s, Cp′), 77.6 (d, J_{P-C} = 5.8 Hz, Cp′), 81.6 (s, Cp′), 91.8 (s, Cp′), 106.2 (d, J_{P-C} = 2.5 Hz, Cp′), 126.6 (s, NCCH_3), 127.3 (s, NCCH_3), 128.5 (d, J_{P-C} = 9.9 Hz, Ph), 130.8 (s, Ph), 132.9 (s, Ph), 133.3 (s, Ph), 133.6 (d, J_{P-C} = 11.6 Hz, Ph), 169.1 (s, C=O). ^{31}P NMR ($CDCl_3$, 160 MHz): δ 48.7 (s). FAB MS: m/z 611 ($M^+ - PF_6$). Anal. Calcd for $C_{32}H_{34}F_6N_2O_2P_2Ru$: C, 50.86; H, 4.54; N, 3.71. Found: C, 51.04; H, 4.26; N, 3.86.

[η^5-{C_5H_2(Me)(Ph)COOEt}Ru(PPh$_3$)(MeCN)$_2$][PF$_6$] (7b). This complex was obtained from the reaction of ruthenium complex [η^5-{C_5H_2(Me)(Ph)COOEt}Ru(CH_3CN)$_3$][PF$_6$] (600 mg, 1.00 mmol) with PPh_3 (260 mg, 1.00 mmol) by a procedure similar to that for **7a** as a yellow powder (810 mg, 99% yield). IR (cm^{-1}, KBr): 839 (ν_{P-F}), 1711 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.10 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), 1.90 (d, J = 1.2 Hz, 3H, Cp′CH_3), 2.15 (d, J = 1.2 Hz, 3H, NCCH_3), 2.31 (d, J = 1.0 Hz, 3H, NCCH_3), 3.78−3.86 (m, 1H, OCH_2CH$_3$), 4.05−4.13 (m, 1H, OCH_2CH$_3$), 4.46 (s, 1H, Cp′), 5.27 (s, 1H, Cp′), 7.13−7.46 (m, 20H, Ph). ^{31}P NMR ($CDCl_3$, 160 MHz): δ 46.3 (s). FAB MS: m/z 673 ($M^+ - PF_6$). Anal. Calcd for $C_{37}H_{36}F_6N_2O_2P_2Ru$: C, 54.35; H, 4.44; N, 3.43. Found: C, 54.12; H, 4.32; N, 3.52.

[η^5-{C_5H_2(Me)$_2$COOEt}Ru(PPh$_3$)(OC$_6$H$_4$C=NMe)] (8a and 9a). Reaction of **7a** (151 mg, 0.20 mmol) with sodium salicylidenemethylaminate (**2a**), prepared from salicylidenemethylamine (41 mg, 0.30 mmol) and NaH (60% oil suspension) (12 mg, 0.30 mmol), by a method similar to that for **3a** and **4a** gave a mixture of **8a** and **9a** (62 mg, 50% yield, 22% de) as an orange powder. IR (cm^{-1}, KBr): 1620 ($\nu_{C=N}$), 1696 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 600 MHz): for the major product, δ 1.12 (s, 3H, Cp′CH_3), 1.14 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), 1.60 (s, 3H, Cp′CH_3), 3.38 (s, 3H, NCH_3), 3.75 (s, 1H, Cp′), 3.86−3.93 (m, 1H, OCH_2CH$_3$), 3.97−4.05 (m, 1H, OCH$_2$CH$_3$), 4.47 (s, 1H, Cp′), 6.13 (t, J = 7.2 Hz, 1H, Ph), 6.55−6.63 (m, 2H, Ph), 6.92 (dt, J = 1.7, 15.2 Hz, 1H, Ph), 7.23−7.30 (m, 5H, Ph), 7.39 (s, 1H, N=CH), 7.43−7.50 (m, 10H, Ph); for the minor product, δ 1.03 (t, J = 7.2 Hz, 3H, OCH$_2$CH_3), 1.53 (s, 3H, Cp′CH_3), 1.87 (s, 3H, Cp′CH_3), 3.42 (s, 3H, NCH_3), 3.72−3.85 (m, 2H, OCH_2CH$_3$), 3.91 (s, 1H, Cp′), 4.40 (s, 1H, Cp′), 6.22 (t, J = 7.4 Hz, 1H, Ph), 6.55−6.63 (m, 1H, Ph), 6.77 (dd, J = 1.7, 7.3 Hz, 1H, Ph), 6.98 (dt, J = 1.7, 15.4 Hz, 1H, Ph), 7.23−7.30 (m, 5H, Ph), 7.43−7.50 (m, 10H, Ph), 7.57 (s, 1H, N=CH). ^{31}P NMR ($CDCl_3$, 160 MHz): for the major product, δ 51.2 (s); for the minor product, δ 49.5 (s). FAB MS: m/z 663 (M^+). Anal. Calcd for $C_{36}H_{36}NO_3PRu$: C, 65.24; H, 5.48; N, 2.11. Found: C, 65.01; H, 5.24; N, 2.28.

[η^5-{C_5H_2(Me)(Ph)COOEt}Ru(PPh$_3$)(OC_6H_4C=NMe)] (8b and 9b). Reaction of **7b** (164 mg, 0.2 mmol) with sodium salicylidenemethylaminate (**2a**), prepared from salicylidenemethylamine (41 mg, 0.30 mmol) and NaH (60% oil suspension) (12 mg, 0.30 mmol), by a method similar to that for **3b** and **4a** gave a mixture of **8b** and **9b** (78 mg, 54% yield, 5% de) as an orange powder. IR (cm^{-1}, KBr): 1620 ($\nu_{C=N}$), 1698 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 600 MHz): for the major product, δ 1.04 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.93 (s, 3H, Cp′CH_3), 2.58 (s, 3H, NCH_3), 3.59−3.67 (m, 1H, OCH_2CH_3), 3.97−4.03 (m, 1H, OCH_2CH_3), 4.21 (s, 1H, Cp′), 5.14 (s, 1H, Cp′), 6.28 (t, J = 7.8 Hz, 1H, Ph), 6.70 (d, J = 8.5 Hz, 1H, Ph), 6.91−6.93 (m, 2H, Ph), 6.96−7.34 (m, 13H, Ph), 7.37 (s, 1H, N=CH), 7.49−7.53 (m, 7H, Ph); for the minor product, δ 1.09 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 1.99 (s, 3H, Cp′CH_3), 3.36 (s, 3H, NCH_3), 3.81−3.95 (m, 2H, OCH_2CH_3), 4.71 (d, J = 1.0 Hz, 1H, Cp′), 5.02 (d, J = 1.2 Hz, 1H, Cp′), 6.24 (t, J = 7.8 Hz, 1H, Ph), 6.56 (d, J = 8.3 Hz, 1H, Ph), 6.79−6.80 (m, 2H, Ph), 6.96−7.34 (m, 20H, Ph), 7.56 (s, 1H, N=CH). ^{31}P NMR ($CDCl_3$, 160 MHz): for the major product, 47.1 (s); for the minor product, 48.6 (s). FAB MS: m/z 725 (M^+). Anal. Calcd for $C_{41}H_{38}NO_3PRu$: C, 67.94; H, 5.28; N, 1.93. Found: C, 67.73; H, 5.08; N, 1.91.

X-ray Diffraction Analyses of Complexes 3g and 5a. Crystals suitable for X-ray diffraction were mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC7R automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at −75 °C. Reflections were collected by a $\omega-2\theta$ scan technique in the range $6° < 2\theta < 55°$ with a scan rate 16° min^{-1}. Three standard reflections were monitored at every 150 measurements; however no damage was observed in both measurements. Intensities were corrected for Lorentz and polarization effects, and for absorption using ψ-scan technique. The structures were solved by Patterson methods and refined by full-matrix least-squares minimizing of $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma_c^2(F_o) + 1/4(p^2F_o^2)]$. Anisotropic thermal parameters were used for all non-hydrogen atoms, while hydrogen atoms were included at the calculated positions (d_{C-H} = 0.95 Å), and their parameters were not refined. The fine cycles of full matrix least squares refinement were converged. All calculations were performed using the teXsan crystallographic software package. Crystallographic data are listed in Table 4.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture. The author (K.O.) gratefully acknowledges partial support of this work by Mitsubishi Chemical Corporation Fund. We thank The Material Analysis Center, ISIR, Osaka University, for support of spectral and X-ray measurements as well as microanalyses.

Supporting Information Available: Tables of atomic coordinates, all bond lengths and bond angles, and anisotropic displacement parameters for complexes **3g** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0102246