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Diastereoselectivity at chiral metal center of half-sandwich-type ruthenium complexes with planar-chiral cyclopentadienyl ligands in multiple ligand transfer reaction

Taku Katayama, Kiyotaka Onitsuka *, Shigetoshi Takahashi

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-047, Japan

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Abstract

The triple ligand transfer reaction between planar-chiral cyclopentadienyl–ruthenium complexes $[Cp'Ru(NCMe)_3][PF_6]$ (**1**) ($Cp' = 1$-$(COOR^2)$-2-Me-4-$R^1C_5H_2$; R^1 = Me, Ph, *t*-Bu) and iron complexes $CpFe(CO)(L)X$ (**2**) ($L = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3; X = I, Br) resulted in the formation of metal-centered chiral ruthenium complexes $Cp'Ru(CO)(L)X$ (**3**) in moderate yields with diastereoselectivities of up to 68% de. The configurations of some major diastereomers were determined to be $S^*_{Cp}R^*_{Ru}$ by X-ray crystallography. The diastereoselectivity of **3** was under kinetic control and not affected by the steric effect of the substituents on the Cp′ ring of **1** and the phosphine of **2**. Although the double ligand transfer reaction between $[Cp'Ru\{P(OMe)_3\}(NCMe)_2][PF_6]$ (**7**) and $CpFe(CO)_2X$ (**8**) produced $Cp'Ru\{P(OMe)_3\}(CO)X$ (**9**), the selectivity at the ruthenium center was low.

Keywords: Ruthenium; Iron; Ligand transfer; Planar chirality; Metal-centered chirality

1. Introduction

Much attention has been paid to the synthesis and reactivity of chiral organometallic complexes in order to obtain useful information for the development of new asymmetric catalysts and for understanding the mechanism of catalytic asymmetric reactions [1]. Although organometallic complexes with chiral ligands comprise the majority of such chemistry, other types of chiral complexes have become the focus of increasing interest in recent years. The metal-centered chiral complexes belong to such category [2]. Although a significant number of metal-centered chiral complexes have been prepared so far, the control of the stereochemistry at the metal center remains a challenging task.

We have examined the chemistry of planar-chiral cyclopentadienyl complexes of late transition metals [3] and showed that the metal-centered chirality is highly controlled in some reactions of the planar-chiral cyclopentadienyl–ruthenium complexes [4]. Recently, we found a novel multiple ligand transfer reaction between cyclopentadienyl–iron and cyclopentadienyl–ruthenium complexes [5]. When three ligands other than the cyclopentadienyl ligand are different from each other, a metal-centered chirality is generated on the resulting ruthenium complexes. Thus, we examined control of stereochemistry at the ruthenium center by planar-chiral cyclopentadienyl ligands in the multiple ligand transfer reaction. We present herein the full details of the diastereoselectivity at the chiral metal center of the planar-chiral cyclopentadienyl–ruthenium complexes in the multiple ligand transfer reaction. The preliminary results have appeared in a communication [6]. Although, we performed this study using racemic mixtures of planar-chiral cyclopentadienyl–ruthenium complexes as starting materials, all structures are drawn with the planar chirality of S_{Cp} for clarity.

* Corresponding author.
E-mail address: onitsuka@sanken.osaka-u.ac.jp (K. Onitsuka).

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2. Results and discussion

Planar-chiral trisubstituted cyclopentadienyl–ruthenium complex $[Cp'Ru(NCMe)_3][PF_6]$ (**1a**) was treated with cyclopentadienyl–iron complex $CpFe(CO)(PMe_3)I$ (**2a**) in CH_2Cl_2 under reflux for 3 h to give $Cp'Ru(CO)(PMe_3)I$ (**3a**) along with other ruthenium complexes, $Cp'Ru(CO)_2I$ (**4a**) and Cp′CpRu (**5**), and ferrocene (**6**) (Scheme 1). These complexes were isolated by column chromatography on silica gel, and fully characterized by spectral analyses. The ^{31}P NMR spectrum of complex **3a** showed two singlets at δ 11.9 and 13.0 with an integral ratio of 16:84, indicating that **3a** consists of two diastereomers in 68% de [7]. Consistent data were obtained in the ^1H NMR spectrum of **3a**. Since single crystals of the major diastereomer of **3a** were obtained by recrystallization of a diastereomeric mixture from ether–hexane, the configuration was determined by X-ray analysis to be $S^*_{Cp}R^*_{Ru}$ based on the priority sequence I > Cp′ > P > C (Fig. 1) [2,8]. When the diastereomerically pure sample of $(S^*_{Cp}R^*_{Ru})$-**3a** was heated in dichloromethane, no epimerization was observed.

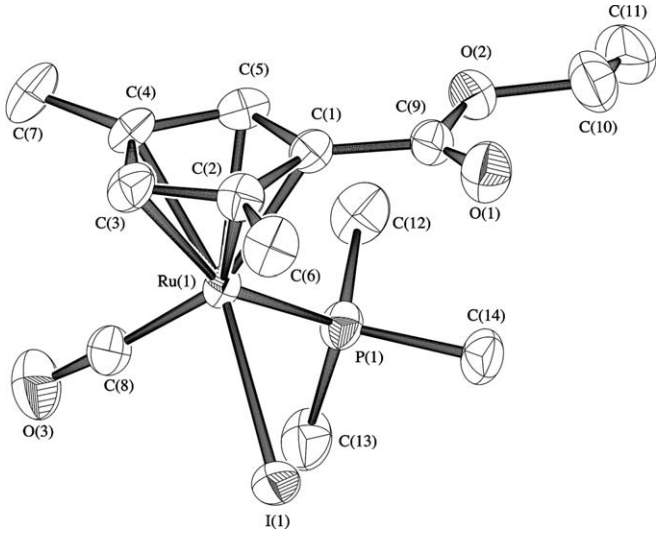
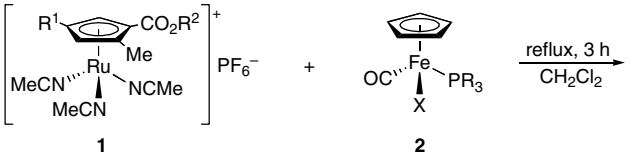


Fig. 1. ORTEP diagram of $(S^*_{Cp}R^*_{Ru})$-**3a** (major diastereomer). Hydrogen atoms are omitted for clarity.

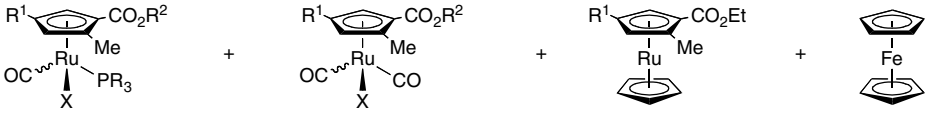
Then, we examined the reactions of **1** with several iron complexes **2**, the representative results of which are given in Table 1 together with the result mentioned above. The yield of **3** was slightly decreased in the order of phosphine ligands PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3 on **2**, and the highest diastereoselectivity of **3** was observed in the reaction with **2a** (entries 1–4). The reaction with **2e** having a bromide ligand gave **3d** in 12% yield with 34% de (entry 5), although the reaction with analogous chloride complex **2d** did not produce **3**. Similar phosphine effect on the yield and diastereoselectivity of **3** was observed in the reactions of **1b** that possessed a phenyl group on the Cp′ ring at 4-position (entries 6–8). The reaction of *t*-butyl analogue **1c**



1 **2**

Complex	R^1	R^2
1a	Me	Et
1b	Ph	Et
1c	Bu^t	Et
1d	Me	adamantyl

Complex	PR_3	X
2a	PMe_3	I
2b	PMe_2Ph	I
2c	$PMePh_2$	I
2d	PPh_3	I
2e	PPh_3	Br



3 **4** **5** **6**

Complex	R^1	R^2	PR_3	X
3a	Me	Et	PMe_3	I
3b	Me	Et	PMe_2Ph	I
3c	Me	Et	$PMePh_2$	I
3d	Me	Et	PPh_3	Br
3e	Ph	Et	PMe_3	I
3f	Ph	Et	PMe_2Ph	I
3g	Ph	Et	$PMePh_2$	I
3h	Bu^t	Et	PMe_3	I
3i	Me	adamantyl	PMe_3	I

Complex	R^1	R^2	X
4a	Me	Et	I
4b	Me	Et	Br
4c	Ph	Et	I
4d	Bu^t	Et	I
4e	Me	adamantyl	I

Complex	R^1
5a	Me
5b	Ph

Scheme 1. Triple ligand transfer from iron complex to ruthenium complex.

Table 1
Triple ligand transfer reactions between [Cp′Ru(NCMe)$_3$][PF$_6$] (**1**) and CpFe(CO)(L)X (**2**)

Entry	Substrates		Isolated yields of products (%)				Recovery of **2**
	Ru complex	Fe complex	Cp′Ru(CO)(L)X (**3**)[a]	Cp′Ru(CO)$_2$X (**4**)[a]	Cp′CpRu (**5**)[a]	Cp$_2$Fe (**6**)[b]	
1	**1a**	**2a**	49 (68, $S^*_{Cp}R^*_{Ru}$)[c] (**3a**)	12 (**4a**)	6 (**5a**)	12	17
2	**1a**	**2b**	38 (22, not determined)[c] (**3b**)	22 (**4a**)	5 (**5a**)	30	11
3	**1a**	**2c**	20 (28, $S^*_{Cp}R^*_{Ru}$)[c] (**3c**)	24 (**4a**)	6 (**5a**)	18	21
4	**1a**	**2d**		35 (**4a**)	2 (**5a**)		24
5	**1a**	**2e**	12 (34, $S^*_{Cp}R^*_{Ru}$)[c] (**3d**)	31 (**4b**)	12 (**5a**)	1	
6	**1b**	**2a**	36 (22, not determined)[c] (**3e**)	17 (**4c**)	2 (**5b**)	20	23
7	**1b**	**2b**	29 (14, $S^*_{Cp}R^*_{Ru}$)[c] (**3f**)	22 (**4c**)	1 (**5b**)	22	19
8	**1b**	**2c**	16 (4, not determined)[c] (**3g**)	26 (**4c**)	9 (**5b**)	13	15
9	**1c**	**2a**	48 (40, $S^*_{Cp}R^*_{Ru}$)[c] (**3h**)	18 (**4d**)		10	9
10	**1d**	**2a**	41 (56, $S^*_{Cp}R^*_{Ru}$)[c] (**3i**)	12 (**4e**)			

[a] Yields are based on ruthenium complex **1**.
[b] Yields are based on iron complex **2**.
[c] %De determined by ^{1}H and ^{31}P NMR analyses and the configuration of the major diastereomer are indicated in parentheses.

with **2a** gave **3h** in 48% yield with 40% de, whereas the reaction of **1d** that had a very bulky ester group with **2a** produced **3i** in 41% yield with 56% de. These results suggested that the steric effect of the substituents on the Cp′ ring on the diastereoselectivity of **3** was small.

The configurations of the major diastereomers of **3c**, **3d**, **3f**, **3h** and **3i** were also determined by X-ray crystallography. To our surprise, **3c** formed single crystals with two diastereomers in the ratio of 74:26. The structures of the major diastereomers were confirmed by measuring the ^{31}P NMR spectra of the single crystals of **3c** as well as the other compounds. The molecular structures of the major diastereomers given in Figs. 2–6 are similar to each other and clearly show that these major diastereomers have the $S^*_{Cp}R^*_{Ru}$ configuration. In these complexes, no epimerization was observed even on refluxing with CH_2Cl_2, suggesting that the diastereoselectivity of the present reaction is under kinetic control.

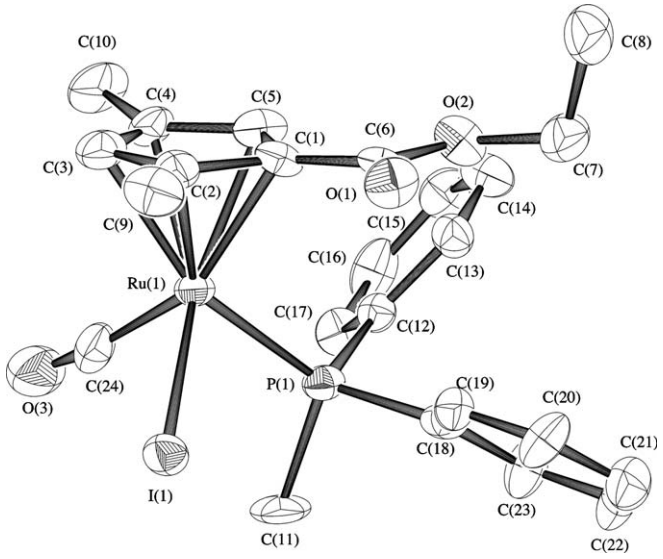


Fig. 2. ORTEP diagram of ($S^*_{Cp}R^*_{Ru}$)-**3c** (major diastereomer). Hydrogen atoms are omitted for clarity.

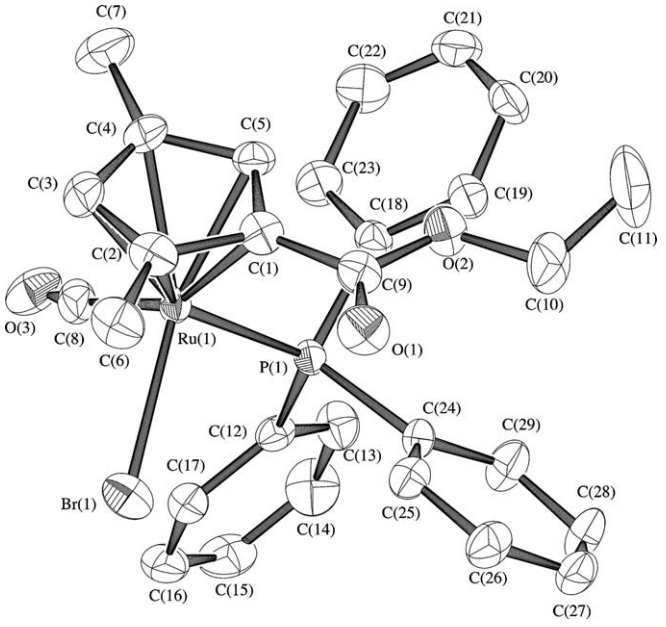


Fig. 3. ORTEP diagram of ($S^*_{Cp}R^*_{Ru}$)-**3d** (major diastereomer). Hydrogen atoms are omitted for clarity.

On treatment of [Cp′Ru{P(OMe)$_3$}(NCMe)$_2$][PF$_6$] (**7**) with CpFe(CO)$_2$X (**8**) in refluxing CH_2Cl_2 for 3 h, similar multiple ligand transfer reactions took place to give Cp′Ru{P(OMe)$_3$}(CO)X (**9**) in low to moderate yields (Scheme 2). The results are summarized in Table 2. Although no ruthenium complexes other than **9** were isolated in these reactions, the diastereoselectivities of **9** were low. Unfortunately, the configurations of the major diastereomers of **9** could not be identified at all.

When the reaction of **1a** with **2a** was performed at 0 °C, dinuclear ruthenium complex (**10a**) was formed (Scheme 3). Although we could not isolate **10a** from the reaction mixture due to low stability, the structure was confirmed by spectral analyses by comparing with the data of analogous ruthenium complex [5]. Similar dinuclear ruthenium complexes having double halide bridges have been prepared

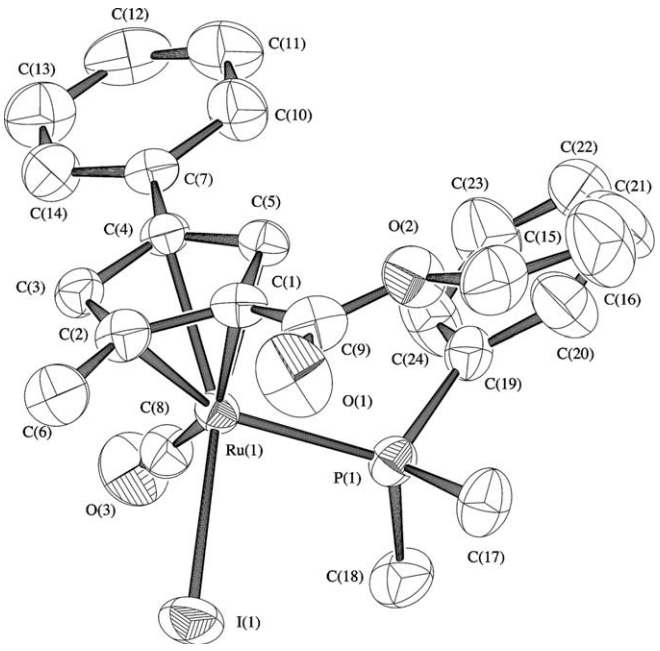


Fig. 4. ORTEP diagram of $(S^*_{Cp}R^*_{Ru})$-**3f** (major diastereomer). Hydrogen atoms are omitted for clarity.

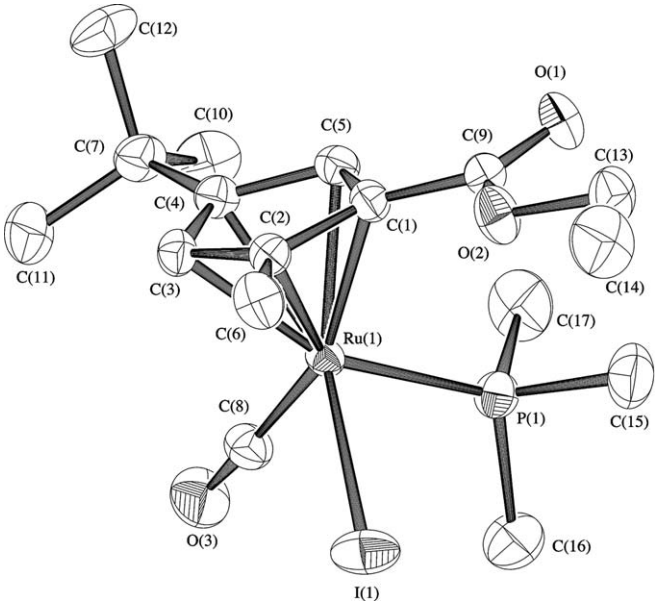


Fig. 5. ORTEP diagram of $(S^*_{Cp}R^*_{Ru})$-**3h** (major diastereomer). Hydrogen atoms are omitted for clarity.

[9]. Since **1a** was a racemic mixture, **10a** consisted of two diastereomers of *dl* and *meso* forms. Treatment of **10a** with PMe_3 instantly produced **3a,** inducing metal-centered chirality, whereas **10a** slowly decomposed in solution, generating **4a**.

From the results described above, the reaction pathway is proposed, as illustrated in Scheme 4. Heterodinuclear complex (**11**) is generated by the dissociation of two acetonitrile ligands from **1** and the subsequent reaction with

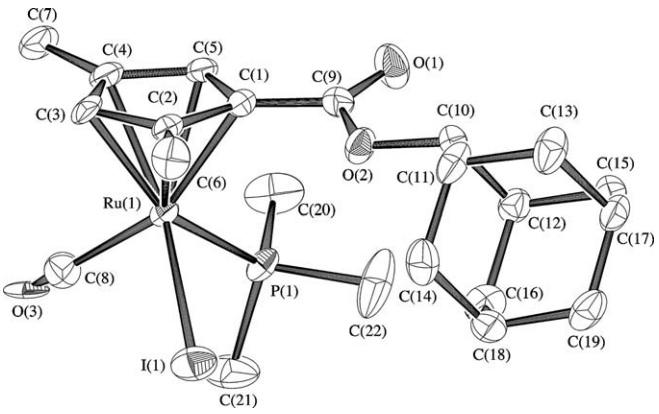


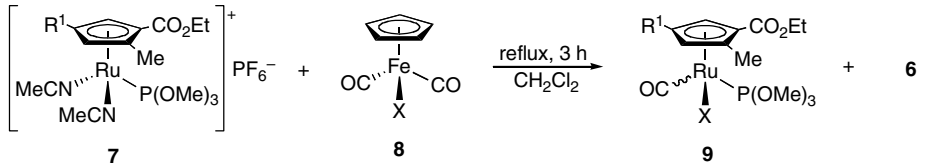
Fig. 6. ORTEP diagram of $(S^*_{Cp}R^*_{Ru})$-**3i** (major diastereomer). Hydrogen atoms are omitted for clarity.

2 [10]. Cationic iron complex (**13**), which is unstable and easily decomposed to give ferrocene **6** and free phosphine ligand, is eliminated from **11** to form neutral ruthenium complex **9** or **12**. The dissociation of acetonitrile from **12** leads to dimerization to give **10**, which is then converted into **3** by reacting with phosphine and partially into **4** by decomposition. In the reaction between **7** and **8**, the configuration at the ruthenium center in **9** is determined in the first step where **11** is formed as the intermediate. From the results in Table 2, the diastereoselectivity of this step should be low. On the other hand, the metal-centered chirality is also generated in **12**, but is lost in the step forming **10**. Thus, the configuration at the ruthenium center in **3** is determined in the last step, in which the diastereoselectivity would be slightly higher than that in the first step. The small steric effect of the substituents on the Cp′ ring of **1** and/or the phosphine of **2** on the diastereoselectivity of **3** may be due to the free rotation of the Cp′ ring, generating sufficient space to coordinate the ruthenium atom of **10**. Since the highest selectivity was achieved in the reaction between **1a** and **2a**, the electronic effect of the phosphine may be important for the diastereoselective reaction of **10**.

In summary, we have shown the control of the stereochemistry at the chiral metal center of planar-chiral cyclopentadienyl–ruthenium complexes in the multiple ligand transfer reaction. These results should provide useful information to understand the mechanism of asymmetric reactions using planar-chiral cyclopentadienyl–ruthenium complexes. Further studies that focus on the application to asymmetric catalysis are in progress.

3. Experimental

All reactions were carried out under an argon atmosphere, whereas the workup was performed in air. Dichloromethane were dried over calcium hydride and distilled before use. Other chemicals available from commercial suppliers were used without further purification. Ruthenium complexes $[\eta^5\text{-}\{C_5H_2(Me)(R)(COOEt)\}Ru(NC\text{-}$



7

Complex	R^1
7a	Me
7b	Ph
7C	Bu^t

8

Complex	X
8a	I
8b	Br

9

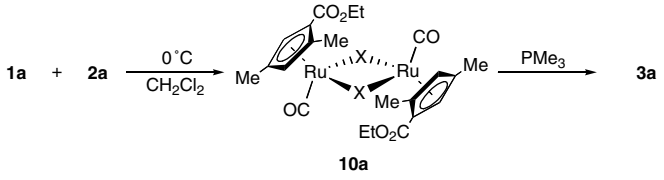
Complex	R^1	X
9a	Me	I
9b	Me	Br
9c	Ph	I
9d	Ph	Br
9e	Bu^t	I

Scheme 2. Double ligand transfer from iron complex to ruthenium complex.

Table 2
Double ligand transfer reactions between $[Cp'Ru\{P(OMe)_3\}(NCMe)_2][PF_6]$ (**7**) and $CpFe(CO)_2X$ (**8**)

Entry	Substrates		Isolated yields of products (%)		Recovery of **8**
	Ru complex	Fe complex	$Cp'Ru\{P(OMe)_3\}(CO)X$ (**9**)[a]	Cp_2Fe (**6**)[b]	
1	**7a**	**8a**	53 (0)[c] (**3a**)	4	43
2	**7a**	**8b**	26 (12)[c] (**3b**)	3	72
3	**7b**	**8a**	40 (8)[c] (**3c**)		55
4	**7b**	**8b**	15 (0)[c] (**3c**)		79
5	**7c**	**8a**	69 (14)[c] (**3d**)		26

[a] Yields are based on ruthenium complex **7**.
[b] Yields are based on iron complex **8**.
[c] %De's determined by ^1H and ^{31}P NMR analyses are indicated in parentheses.



10a

Scheme 3.

$Me)_3][PF_6]$ **1a**–**1c** were prepared as reported previously [3d], and iron complexes **2a** [11], **2b**–**2d** [12], **2e** [13] were prepared according to methods in the literature.

NMR spectra were measured on JEOL JNM-LA400 spectrometer using $SiMe_4$ as an internal standard for ^1H and ^{13}C NMR spectra and 85% H_3PO_4 as an external reference for ^{31}P NMR, respectively. IR and FAB mass spectra were obtained on Perkin–Elmer system 2000 FT-IR and JEOL JMS-600H instrument, respectively. Elemental analyses were performed at The Material Analysis Center, ISIR, Osaka University.

3.1. $[\{\eta^5\text{-}C_5H_2(Me)_2(COOAdm)\}Ru(NCMe)_3][PF_6]$ (**1d**)

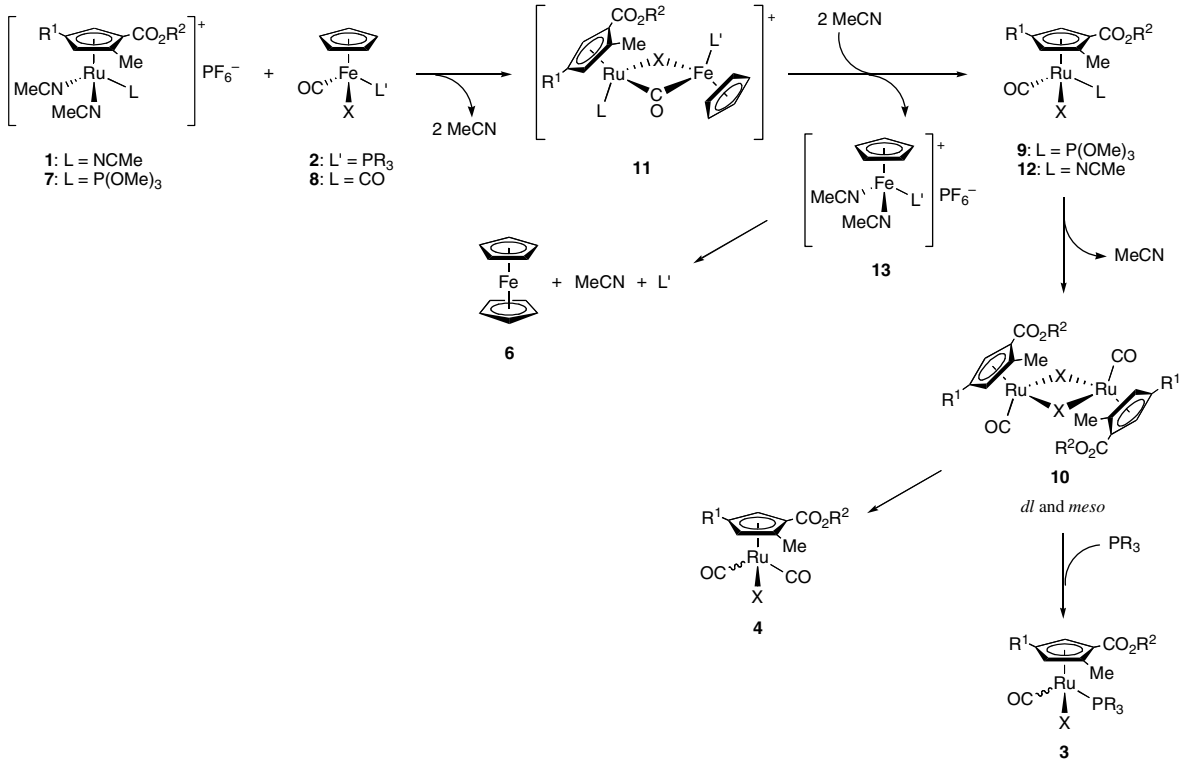
The title complex was prepared from **1a** and 2-adamantanol by a similar method reported previously. IR (cm^{-1}, KBr): 1704 ($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.63–1.70 (2H, m, Adm), 1.77 (3H, s, $Cp'CH_3$), 1.78–1.93 (8H, m, Adm), 2.00 (3H, s, $Cp'CH_3$), 2.07–2.18 (4H, m, Adm), 2.54 (9H, s, CH_3CN), 4.15 (1H, s, Cp′), 4.75 (1H, s, Cp′), 5.01 (1H, broad s, Adm). ^{13}C NMR (acetone-d_6): δ 3.2, 12.5, 13.1, 27.8, 28.1, 32.4, 32.6, 32.7, 32.9, 36.8, 36.9, 37.9, 62.6, 67.0, 72.9, 77.4, 89.9, 98.1, 126.2, 169.7. Anal. Calc. for $C_{24}H_{32}F_6N_3O_2PRu$: C, 45.00; H, 5.04; N, 6.56; P, 4.84; F, 17.79. Found: C, 44.84; H, 5.11; N, 6.74; P, 5.01; F, 17.80%.

3.2. General procedure of triple ligand transfer reactions between $[\{\eta^5\text{-}C_5H_2(Me)(R)(COOEt)\}Ru(NCMe)_3][PF_6]$ (**1**) and $(\eta^5\text{-}C_5H_5)Fe(CO)(PR'_3)X$ (**2**)

A dichloromethane solution (30 mL) containing ruthenium complex **1** (1.0 mmol) and iron complex **2** (1.0 mmol) was refluxed for 3 h. After removal of the solvent, the products were separated by silica gel column chromatography using dichloromethane or a mixture of dichloromethane/ethyl acetate.

3.3. $[\eta^5\text{-}C_5H_2(Me)_2(COOEt)]Ru(CO)(PMe_3)I$ (**3a**)

The title complex was obtained as a mixture of two diastereomers (68% de) in 49% yield. The major isomer $(S^*_{Cp}R^*_{Ru})$-**3a** was isolated by recrystallization from diethyl ether–hexane as orange crystals. $(S^*_{Cp}R^*_{Ru})$-**3a**: IR (cm^{-1}, KBr): 1939 (ν_{CO}), 1715 ($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.27 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.74 (9H, d, $J_{PH} = 10.7$ Hz, PCH_3), 1.94 (3H, s, $Cp'CH_3$), 2.45 (3H, d, $J = 2.0$ Hz, $Cp'CH_3$), 4.16 (2H, m, CH_2CH_3), 5.14 (1H, s,



Scheme 4. Proposed reaction pathway.

Cp′), 5.45 (1H, d, $J = 2.2$ Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 14.2, 14.7, 16.0, 20.5 (d, $J_{PC} = 35$ Hz), 60.8, 82.3, 87.0 (d, $J_{PC} = 7$ Hz), 87.2, 95.4, 115.6, 166.2, 204.4 (d, $J_{PC} = 22$ Hz). ^{31}P NMR (acetone-d_6): δ 13.0. Mass: m/z 498 (M^+). Anal. Calc. for $C_{14}H_{22}IO_3PRu$: C, 33.82; H, 4.46; P, 6.23; I, 25.52. Found: C, 33.64; H, 4.62; P, 6.46; I, 25.57%. ($S^*_{Cp}S^*_{Ru}$)-**3a**: ^{1}H NMR (acetone-d_6): δ 1.23 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.71 (9H, d, $J_{PH} = 10.5$ Hz, PCH_3), 2.11 (3H, s, Cp′CH_3), 2.31 (3H, s, Cp′CH_3), 4.16 (2H, m, CH_2CH_3), 5.08 (1H, s, Cp′), 5.58 (1H, s, Cp′). ^{31}P NMR (acetone-d_6): δ 11.9.

3.4. [η^5-$C_5H_2(Me)_2(COOEt)$]Ru(CO)(PMe_2Ph)I (**3b**)

The title complex was obtained as a mixture of two diastereomers (22% de) in 38% yield. Recrystallization from dichloromethane–hexane gave red crystals, in which the minor isomer ($S^*_{Cp}S^*_{Ru}$)-**3b** was enriched into 74% de. IR (cm^{-1}, KBr): 1949 (ν_{CO}), 1712 ($\nu_{C=O}$). Mass: m/z 560 (M^+). Anal. Calc. for $C_{19}H_{24}IO_3PRu$: C, 40.80; H, 4.32; P, 5.54; I, 22.69. Found: C, 41.00; H, 4.51; P, 5.67; I, 22.53%. ($S^*_{Cp}R^*_{Ru}$)-**3b**: ^{1}H NMR (acetone-d_6): δ 1.24 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.62 (3H, s, Cp′CH_3), 2.00 (3H, d, $J_{PH} = 10.3$ Hz, PCH_3), 2.09 (3H, d, $J = 10.7$ Hz, PCH_3), 2.39 (3H, d, $J = 2.2$ Hz, Cp′CH_3), 4.02 (2H, m, CH_2CH_3), 4.74 (1H, d, $J = 2.2$ Hz, Cp′), 5.09 (1H, s, Cp′), 7.46–7.53 (3H, m, PC_6H_5), 7.71–7.73 (2H, m, PC_6H_5). ^{13}C NMR (acetone-d_6): δ 14.3, 14.6, 16.8 (d, $J_{PC} = 34$ Hz), 20.4 (d, $J_{PC} = 38$ Hz), 60.8, 82.2, 86.9 (d, $J_{PC} = 7$ Hz), 90.4, 94.7, 114.5 (d, $J_{PC} = 4$ Hz), 129.3 (d, $J_{PC} = 10$ Hz), 130.4 (d, $J_{PC} = 10$ Hz), 130.5 (d, $J_{PC} = 2$ Hz), 139.9 (d, $J_{PC} = 50$ Hz), 165.9, 203.9 (d, $J_{PC} = 21$ Hz). ^{31}P NMR (acetone-d_6): δ 22.2. ($S^*_{Cp}S^*_{Ru}$)-**3b**: ^{1}H NMR (acetone-d_6): δ 1.20 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.76 (3H, s, Cp′CH_3), 1.92 (3H, d, $J_{PH} = 10.0$ Hz, PCH_3), 2.10 (3H, d, $J_{PH} = 10.3$ Hz, PCH_3), 2.15 (3H, d, $J = 1.2$ Hz, Cp′CH_3), 4.17 (2H, m, CH_2CH_3), 4.90 (1H, s, Cp′), 5.29 (1H, d, $J = 2.0$ Hz, Cp′), 7.46–7.53 (3H, m, PC_6H_5), 7.68–7.70 (2H, m, PC_6H_5). ^{13}C NMR (acetone-d_6): δ 13.5, 14.5, 15.7, 19.8 (d, $J_{PC} = 34$ Hz), 20.6 (d, $J_{PC} = 37$ Hz), 60.7, 80.0, 88.7 (d, $J_{PC} = 5$ Hz), 90.7 (d, $J_{PC} = 3$ Hz), 101.4, 109.0, 129.1 (d, $J_{PC} = 10$ Hz), 130.6 (d, $J_{PC} = 3$ Hz), 131.0 (d, $J_{PC} = 10$ Hz), 138.3 (d, $J_{PC} = 49$ Hz), 166.4, 204.3 (d, $J_{PC} = 21$ Hz). ^{31}P NMR (acetone-d_6): δ 23.0.

3.5. [η^5-$C_5H_2(Me)_2(COOEt)$]Ru(CO)($PMePh_2$)I (**3c**)

The title complex was obtained as a mixture of two diastereomers (28% de) in 20% yield. Recrystallization from dichloromethane–hexane gave red crystals, in which the major isomer ($S^*_{Cp}R^*_{Ru}$)-**3c** was enriched into 48% de. IR (cm^{-1}, KBr): 1940 (ν_{CO}), 1712 ($\nu_{C=O}$). Mass: m/z 622 (M^+). Anal. Calc. for $C_{24}H_{26}IO_3PRu$: C, 46.39; H, 4.22; P, 4.98; I, 20.42. Found: C, 46.26; H, 4.21; P, 5.05; I, 20.38%. ($S^*_{Cp}R^*_{Ru}$)-**3c**: 1H NMR (acetone-d_6): δ 1.10 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.67 (3H, s, Cp′CH_3), 2.34 (3H, d, $J_{PH} = 9.5$ Hz, PCH_3), 2.48 (3H, d, $J = 2.0$ Hz, Cp′CH_3),

3.93 (2H, m, CH_2CH$_3$), 4.62 (1H, dd, $J = 2.0$, 1.7 Hz, Cp′), 5.07 (1H, d, $J = 1.7$ Hz, Cp′), 7.43–7.50 (6H, m, PC$_6$H$_5$), 7.54–7.72 (4H, m, PC$_6$H$_5$). ^{13}C NMR (acetone-d_6): δ 13.5, 14.2, 15.7, 20.0 (d, $J_{PC} = 35$ Hz), 60.6, 82.5, 85.1 (d, $J_{PC} = 7$ Hz), 89.7, 91.5, 115.8, 128.3 (d, $J_{PC} = 6$ Hz), 128.5 (d, $J_{PC} = 10$ Hz), 130.2, 130.6, 132.1 (d, $J_{PC} = 10$ Hz), 133.4 (d, $J_{PC} = 11$ Hz), 135.6 (d, $J_{PC} = 47$ Hz), 138.2 (d, $J_{PC} = 51$ Hz), 165.7, 203.7 (d, $J_{PC} = 21$ Hz). ^{31}P NMR (acetone-d_6): δ 36.0. ($S^*_{Cp}S^*_{Ru}$)-**3c**: ^{1}H NMR (acetone-d_6): δ 1.15 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 1.72 (3H, s, Cp′CH_3), 2.29 (3H, d, $J_{PH} = 11.6$ Hz, PCH_3), 3.79 (3H, s, Cp′CH_3), 3.93 (2H, m, CH_2CH$_3$), 4.91 (1H, s, Cp′), 5.18 (1H, d, $J = 1.7$ Hz, Cp′), 7.42–7.49 (6H, m, PC$_6$H$_5$), 7.54–7.69 (4H, m, PC$_6$H$_5$). ^{13}C NMR (acetone-d_6): δ 13.7, 14.2, 14.3, 21.3 (d, $J_{PC} = 36$ Hz), 60.7, 79.2, 87.4 (d, $J_{PC} = 6$ Hz), 96.1, 103.5, 108.8, 128.4 (d, $J_{PC} = 4$ Hz), 128.5 (d, $J_{PC} = 4$ Hz), 130.4, 132.5 (d, $J_{PC} = 11$ Hz), 132.6 (d, $J_{PC} = 11$ Hz), 136.3 (d, $J_{PC} = 51$ Hz), 136.8 (d, $J_{PC} = 47$ Hz), 166.4, 203.3 (d, $J_{PC} = 20$ Hz). ^{31}P NMR (acetone-d_6): δ 36.5.

3.6. [η^5-$C_5H_2(Me)_2(COOEt)$]Ru(CO)($PMePh_2$)Br (**3d**)

The title complex was obtained as a mixture of two diastereomers (34% de) in 12% yield. The major isomer ($S^*_{Cp}R^*_{Ru}$)-**3d** was isolated by recrystallization from dichloromethane–hexane as orange crystals. ($S^*_{Cp}R^*_{Ru}$)-**3d**: IR (cm^{-1}, KBr): 1952 (ν_{CO}), 1704 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.02 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 1.69 (3H, s, Cp′CH_3), 2.23 (3H, d, $J = 2.0$ Hz, Cp′CH_3), 3.97 (1H, d, $J = 2.0$ Hz, Cp′), 3.98 (2H, m, CH_2CH$_3$), 5.02 (1H, d, $J = 2.0$ Hz, Cp′), 7.41–7.50 (9H, m, PC$_6$H$_5$), 7.65–7.70 (6H, m, PC$_6$H$_5$). ^{31}P NMR (acetone-d_6): δ 50.0. Mass: m/z 637 (M$^+$). Anal. Calc. for $C_{29}H_{28}BrO_3PRu$: C, 54.73; H, 4.43; P, 4.87; Br, 12.55. Found: C, 54.98; H, 4.14; P, 4.93; I, 12.32%. ($S^*_{Cp}S^*_{Ru}$)-**3d**: ^{1}H NMR (acetone-d_6): δ 1.15 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 1.53 (3H, s, Cp′CH_3), 2.20 (3H, d, $J = 1.0$ Hz, Cp′CH_3), 3.71 (2H, m, CH_2CH$_3$), 4.53 (1H, d, $J = 2.0$ Hz, Cp′), 4.93 (1H, d, $J = 2.0$ Hz, Cp′), 7.41–7.50 (9H, m, PC$_6$H$_5$), 7.55–7.60 (6H, m, PC$_6$H$_5$). ^{31}P NMR (acetone-d_6): δ 54.5.

3.7. [η^5-$C_5H_2(Me)(Ph)(COOEt)$]Ru(CO)(PMe_3)I (**3e**)

The title complex was obtained as a mixture of two diastereomers (22% de) in 36% yield. Recrystallization from dichloromethane–hexane gave red crystals, in which the major isomer ($S^*_{Cp}R^*_{Ru}$)-**3e** was enriched into 74% de. IR (cm^{-1}, KBr): 1940 (ν_{CO}), 1714 ($\nu_{C=O}$). Mass: m/z 560 (M$^+$). Anal. Calc. for $C_{19}H_{24}IO_3PRu$: C, 40.80; H, 4.32; P, 5.54; I, 22.69. Found: C, 40.77; H, 4.27; P, 5.32; I, 22.87%. ($S^*_{Cp}R^*_{Ru}$)-**3e**: ^{1}H NMR (acetone-d_6): δ 1.30 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 1.49 (9H, d, $J_{PH} = 10.7$ Hz, PCH_3), 2.49 (3H, s, Cp′CH_3), 4.22 (2H, m, CH_2CH$_3$), 5.84 (1H, d, $J = 1.7$ Hz, Cp′), 6.27 (1H, d, $J = 1.7$ Hz, Cp′), 7.26–7.41 (3H, m, Cp′C$_6H_5$), 7.60–7.62 (2H, m, Cp′C$_6H_5$). ^{13}C NMR (acetone-d_6): δ 14.8, 15.8, 20.1 (d, $J_{PC} = 36$ Hz), 60.9, 83.3 (d, $J_{PC} = 4$ Hz), 86.1, 88.1, 96.5, 112.1 (d, $J_{PC} = 3$ Hz), 126.6, 128.9, 129.6, 133.2, 165.9, 204.0 (d, $J_{PC} = 22$ Hz). ^{31}P NMR (acetone-d_6): δ 13.3. ($S^*_{Cp}S^*_{Ru}$)-**3e**: ^{1}H NMR (acetone-d_6): δ 1.31 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 1.60 (9H, d, $J_{PH} = 10.5$ Hz, PCH_3), 2.51 (3H, d, $J = 1.5$ Hz, Cp′CH_3), 4.22 (2H, m, CH_2CH$_3$), 5.82 (1H, s, Cp′), 6.25 (1H, dd, $J = 2.0$, 1.7 Hz, Cp′), 7.26–7.41 (3H, m, Cp′C$_6H_5$), 7.62–7.64 (2H, m, Cp′C$_6H_5$). ^{13}C NMR (acetone-d_6): δ 14.7, 15.2, 20.3 (d, $J_{PC} = 36$ Hz), 60.8, 81.6, 83.4, 88.8 (d, $J_{PC} = 3$ Hz), 97.0, 111.4, 127.2, 128.7, 129.5, 133.5, 166.3, 203.17 (d, $J_{PC} = 21$ Hz). ^{31}P NMR (acetone-d_6): δ 13.3.

3.8. [η^5-$C_5H_2(Me)(Ph)(COOEt)$]Ru(CO)(PMe_2Ph)I (**3f**)

The title complex was obtained as a mixture of two diastereomers (14% de) in 29% yield. The major isomer ($S^*_{Cp}R^*_{Ru}$)-**3f** was isolated by recrystallization from dichloromethane-hexane as red crystals. ($S^*_{Cp}R^*_{Ru}$)-**3f**: IR (cm^{-1}, KBr): 1955 (ν_{CO}), 1714 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.29 (3H, t, $J = 7.3$ Hz, CH$_2$CH_3), 1.64 (3H, d, $J_{PH} = 10.0$ Hz, PCH_3), 1.96 (3H, d, $J_{PH} = 10.5$ Hz, PCH_3), 2.19 (3H, s, Cp′CH_3), 4.17 (2H, m, CH_2CH$_3$), 5.38 (1H, d, $J = 1.7$ Hz, Cp′), 6.09 (1H, d, $J = 1.7$ Hz, Cp′), 7.18–7.47 (8H, m, PC$_6$H$_5$), 7.54–7.59 (2H, m, PC$_6$H$_5$). ^{13}C NMR (acetone-d_6): δ 14.4, 14.7, 19.5 (d, $J_{PC} = 38$ Hz), 19.7 (d, $J_{PC} = 35$ Hz), 60.8, 82.0 (d, $J_{PC} = 3$ Hz), 87.4 (d, $J_{PC} = 3$ Hz), 87.5, 99.0, 110.6, 126.8, 128.6, 129.0 (d, $J_{PC} = 10$ Hz), 129.3, 130.6 (d, $J_{PC} = 3$ Hz), 131.0 (d, $J_{PC} = 10$ Hz), 132.4, 137.6 (d, $J_{PC} = 47$ Hz), 165.9, 203.4 (d, $J_{PC} = 22$ Hz). ^{31}P NMR (acetone-d_6): δ 23.3. Mass: m/z 622 (M$^+$). Anal. Calc. for $C_{24}H_{26}IO_3PRu$: C, 46.39; H, 4.42; P, 4.98; I, 20.42. Found: C, 46.32; H, 4.23; P, 4.76; I, 20.50%. ($S^*_{Cp}S^*_{Ru}$)-**3f**: ^{1}H NMR (acetone-d_6): δ 1.30 (3H, t, $J = 7.3$ Hz, CH$_2$CH_3), 1.89 (3H, d, $J_{PH} = 10.3$ Hz, PCH_3), 1.93 (3H, d, $J_{PH} = 11.2$ Hz, PCH_3), 2.50 (3H, d, $J = 1.7$ Hz, Cp′CH_3), 4.20 (2H, m, CH_2CH$_3$), 5.53 (1H, dd, $J = 2.0$, 1.7 Hz, Cp′), 5.56 (1H, s, Cp′), 7.05–7.07 (2H, m, C$_6H_5$), 7.18–7.47 (2H, m, C$_6H_5$). ^{13}C NMR (acetone-d_6): δ 14.7, 15.8 (d, $J_{PC} = 34$ Hz), 15.9, 20.4 (d, $J_{PC} = 39$ Hz), 61.0, 73.9, 83.8 (d, $J_{PC} = 5$ Hz), 89.8, 96.2, 113.0 (d, $J_{PC} = 3$ Hz), 126.4, 128.7, 129.3, 129.3 (d, $J_{PC} = 9$ Hz), 130.2 (d, $J_{PC} = 10$ Hz), 130.4 (d, $J_{PC} = 3$ Hz), 132.3, 139.4 (d, $J_{PC} = 50$ Hz), 165.8, 203.9 (d, $J_{PC} = 22$ Hz). ^{31}P NMR (acetone-d_6): δ 22.4.

3.9. [η^5-$C_5H_2(Me)(Ph)(COOEt)$]Ru(CO)($PMePh_2$)I (**3g**)

The title complex was obtained as a mixture of two diastereomers (4% de) in 16% yield. IR (cm^{-1}, KBr): 1953 (ν_{CO}), 1712 ($\nu_{C=O}$). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.18 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 1.33 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 2.04 (3H, d, $J_{PH} = 9.5$ Hz, PCH_3), 2.16 (3H, d, $J_{PH} = 9.8$ Hz, PCH_3), 2.35 (3H, s, Cp′CH_3), 2.61 (3H, s,

Cp′CH_3), 3.99 (2H, m, C$H_2$$CH_3$), 4.09 (2H, m, C$H_2$$CH_3$), 5.27 (1H, s, Cp′), 5.32 (1H, s, Cp′), 5.31 (1H, d, $J = 1.7$ Hz, Cp′), 5.38 (1H, d, $J = 1.7$ Hz, Cp′), 6.96–6.98 (2H, m, C_6H_5), 7.06–7.08 (2H, m, C_6H_5), 7.19–7.50 (13H, m, C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 14.3, 14.4, 14.5, 16.0, 19.3 (d, $J_{PC} = 36$ Hz), 20.4 (d, $J_{PC} = 36$ Hz), 60.9, 61.0, 80.9, 83.1, 82.2 (d, $J_{PC} = 6$ Hz), 86.7 (d, $J_{PC} = 4$ Hz), 88.5 (d, $J_{PC} = 2$ Hz), 89.1, 97.3, 101.5, 109.5, 114.5, 126.3, 126.8, 128.4 (d, $J_{PC} = 11$ Hz), 128.5 (d, $J_{PC} = 11$ Hz), 128.5 (d, $J_{PC} = 11$ Hz), 128.4, 128.5, 128.8, 129.0, 130.2 (d, $J_{PC} = 2$ Hz), 130.4 (d, $J_{PC} = 3$ Hz), 130.5 (d, $J_{PC} = 2$ Hz), 130.7 (d, $J_{PC} = 2$ Hz), 131.6, 131.7, 132.0 (d, $J_{PC} = 10$ Hz), 132.4 (d, $J_{PC} = 10$ Hz), 132.6 (d, $J_{PC} = 11$ Hz), 133.4 (d, $J_{PC} = 11$ Hz), 135.3 (d, $J_{PC} = 41$ Hz), 135.8 (d, $J_{PC} = 42$ Hz), 136.9 (d, $J_{PC} = 48$ Hz), 138.3 (d, $J_{PC} = 51$ Hz), 165.6, 166.1, 203.1 (d, $J_{PC} = 22$ Hz), 203.3 (d, $J_{PC} = 22$ Hz). ^{31}P NMR (acetone-d_6): δ 36.0, 36.2. Mass: *m/z* 684 (M^+). Anal. Calc. for $C_{29}H_{28}IO_3PRu$: C, 50.96; H, 4.13; P, 4.53; I, 18.57. Found: C, 50.71; H, 4.11; P, 4.29; I, 18.82%.

3.10. [η^5-$C_5H_2(Me)(Bu^t)(COOEt)$]$Ru(CO)(PMe_3)I$ (**3h**)

The title complex was obtained as a mixture of two diastereomers (40% de) in 48% yield. The major isomer ($S^*_{Cp}R^*_{Ru}$)-**3h** was isolated by recrystallization from diethyl ether as orange crystals. ($S^*_{Cp}R^*_{Ru}$)-**3h**: IR (cm^{-1}, KBr): 1940 (ν_{CO}), 1683 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.21 (9H, s, C(CH_3)$_3$), 1.28 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.74 (9H, d, $J_{PH} = 10.5$ Hz, PCH_3), 2.54 (3H, d, $J = 2.0$ Hz, Cp′CH_3), 4.17 (2H, m, C$H_2$$CH_3$), 5.10 (1H, d, $J = 2.0$ Hz, Cp′), 5.37 (1H, dd, $J = 2.7$, 2.0 Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 14.6, 16.8, 20.5 (d, $J_{PC} = 36$ Hz), 31.2, 31.4, 60.9, 81.4, 81.9, 82.3 (d, $J_{PC} = 7$ Hz), 114.8, 118.5 (d, $J_{PC} = 3$ Hz), 166.4, 204.9 (d, $J_{PC} = 21$ Hz). ^{31}P NMR (acetone-d_6): δ 10.9. Mass: *m/z* 540 (M^+). Anal. Calc. for $C_{17}H_{28}IO_3PRu$: C, 37.86; H, 5.23; P, 5.74; I, 23.53. Found: C, 38.09; H, 5.25; P, 5.88; I, 23.38%. ($S^*_{Cp}S^*_{Ru}$)-**3h**: 1H NMR (acetone-d_6): δ 1.27 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.28 (9H, s, C(CH_3)$_3$), 1.69 (9H, d, *J*PH = 10.5 Hz, P(CH_3)$_3$), 2.23 (3H, d, $J = 2.7$ Hz, Cp′CH_3), 4.17 (2H, m, C$H_2$$CH_3$), 4.99 (1H, d, $J = 2.0$ Hz, Cp′), 5.84 (1H, dd, $J = 2.4$, 2.0 Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 14.4, 15.0, 19.1 (d, $J_{PC} = 36$ Hz), 31.2, 32.0, 60.7, 74.9, 79.4, 94.1 (d, $J_{PC} = 5$ Hz), 106.2, 118.5 (d, $J_{PC} = 5$ Hz), 166.3, 204.8 (d, $J_{PC} = 22$ Hz). ^{31}P NMR (acetone-d_6): δ 9.6.

3.11. [η^5-$C_5H_2(Me)_2(COOAdm)$]$Ru(CO)(PMe_3)I$ (**3i**)

The title complex was obtained as a mixture of two diastereomers (56% de) in 41% yield. ($S^*_{Cp}R^*_{Ru}$)-**3i** was isolated by recrystallization from dichloromethane–hexane as orange crystals. IR (cm^{-1}, KBr): 1941 (ν_{CO}), 1714 ($\nu_{C=O}$). Mass: *m/z* 604 (M^+). Anal. Calc. for $C_{22}H_{32}IO_3PRu$: C, 43.79; H, 5.35; P, 5.13; I, 21.03. Found: C, 43.77, H, 5.23; P, 5.07; I, 20.85%. ($S^*_{Cp}R^*_{Ru}$)-**3i**: ^{1}H NMR ($CDCl_3$): δ 1.55–1.61 (2H, m, Adm), 1.69–1.80 (3H, m, Adm), 1.72 (9H, d, $J = 10.5$ Hz, PCH_3), 1.85 (4H, m, Adm), 1.95 (3H, s, Cp′CH_3), 2.01–2.07 (3H, m, Adm), 2.17–2.20 (1H, m, Adm), 2.75 (3H, s, Cp′CH_3), 4.99 (1H, s, Cp′), 5.03 (1H, broad s, Adm), 5.25 (1H, s, Cp′). ^{31}P NMR ($CDCl_3$): δ 7.4. ($S^*_{Cp}S^*_{Ru}$)-**3i**: 6.0.

3.12. [η^5-$C_5H_2(Me)_2(COOEt)$]$Ru(CO)_2I$ (**4a**)

IR (cm^{-1}, KBr): 2048, 1990 (ν_{CO}), 1715 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.29 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.20 (3H, s, Cp′CH_3), 2.56 (3H, s, Cp′CH_3), 4.24 (2H, m, C$H_2$$CH_3$), 5.52 (1H, d, $J = 1.7$ Hz, Cp′), 5.99 (1H, d, $J = 1.7$ Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 14.2, 14.5, 15.1, 61.7, 84.0, 88.5, 88.8, 106.7, 118.8, 164.5, 197.0, 197.2. Mass: *m/z* 450 (M^+). Anal. Calc. for $C_{12}H_{13}IO_4Ru$: C, 32.09; H, 2.92; I, 28.34. Found: C, 31.83; H, 2.66; I, 28.34%.

3.13. [η^5-$C_5H_2(Me)_2(COOEt)$]$Ru(CO)_2Br$ (**4b**)

IR (cm^{-1}, KBr): 2053, 2003 (ν_{CO}), 1722 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.29 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.08 (3H, s, Cp′CH_3), 2.32 (3H, s, Cp′CH_3), 4.24 (2H, m, C$H_2$$CH_3$), 5.53 (1H, d, $J = 1.7$ Hz, Cp′), 5.90 (1H, d, $J = 1.7$ Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 13.7, 14.0, 14.5, 61.7, 83.5, 86.5, 88.6, 106.9, 121.5, 164.6, 197.0, 197.3. Mass: *m/z* 402 (M^+). Anal. Calc. for $C_{12}H_{13}BrO_4Ru$: C, 35.84; H, 3.26; Br, 19.87. Found: C, 36.12; H, 3.05; Br, 20.11%.

3.14. [η^5-$C_5H_2(Me)(Ph)(COOEt)$]$Ru(CO)_2I$ (**4c**)

IR (cm^{-1}, KBr): 2040, 1999 (ν_{CO}), 1704 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.32 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.68 (3H, s, Cp′CH_3), 4.29 (2H, m, C$H_2$$CH_3$), 6.24 (1H, d, $J = 2.0$ Hz, Cp′), 6.71 (1H, d, $J = 2.0$ Hz, Cp′), 7.37–7.44 (3H, m, C_6H_5), 7.72–7.74 (2H, m, C_6H_5). ^{13}C NMR (acetone-d_6): δ 14.7, 15.5, 61.8, 85.1, 85.7, 87.2, 105.3, 119.4, 127.4, 129.9, 130.4, 130.9, 164.4, 196.4, 197.0. Mass: *m/z* 512 (M^+). Anal. Calc. for $C_{17}H_{15}IO_4Ru$: C, 39.94; H, 2.96; I, 24.82. Found: C, 40.19; H, 3.09; I, 24.71%.

3.15. [η^5-$C_5H_2(Me)(Bu^t)(COOEt)$]$Ru(CO)_2I$ (**4d**)

IR (cm^{-1}, KBr): 2041, 1998 (ν_{CO}), 1722 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.27 (9H, s, C(CH_3)$_3$), 1.28 (3H, t, $J = 7.3$ Hz, CH_2CH_3), 2.58 (3H, s, Cp′CH_3), 4.23 (2H, m, C$H_2$$CH_3$), 5.70 (1H, d, $J = 1.7$ Hz, Cp′), 6.16 (1H, d, $J = 1.7$ Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 14.6, 15.4, 31.3, 31.4, 61.5, 84.2, 87.8, 89.1, 117.6, 118.4, 164.2, 196.9, 197.7. Mass: *m/z* 492 (M^+). Anal. Calcd for $C_{15}H_{19}IO_4Ru$: C, 36.67; H, 3.90; I, 25.83. Found: C, 36.80; H, 4.11; I, 25.71%.

3.16. [η^5-$C_5H_2(Me)_2(COOAdm)$]$Ru(CO)_2I$ (**4e**)

IR (cm^{-1}, KBr): 2042, 1990 (ν_{CO}), 1716 ($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.60–1.63 (2H, m, Adm), 1.77–1.91 (8H, m, Adm), 2.04 (2H, m, Adm), 2.14–2.18 (2H, m, Adm), 2.20 (3H, s, Cp′CH_3), 2.61 (3H, s, Cp′CH_3), 5.04 (1H, broad, Adm), 5.54 (1H, s, Cp′), 6.09 (1H, s, Cp′). ^{13}C NMR (acetone-d_6): δ 14.1, 15.4, 27.8, 28.0, 32.5, 32.5, 32.7, 32.7, 36.8, 36.9, 37.9, 78.7, 84.4, 88.9, 89.0, 106.0, 118.7, 163.9, 197.0, 197.2. Mass: m/z 556 (M^+). Anal. Calc. for $C_{20}H_{23}IO_4PRu$: C, 43.25; H, 4.17; I, 22.85. Found: C, 43.46; H, 4.09; I, 22.82%.

3.17. [η^5-$C_5H_2(Me)_2(COOEt)$]$Ru(C_5H_5)$ (**5a**)

IR (cm^{-1}, KBr): 1711($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.23 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.90 (3H, s, Cp′CH_3), 2.17 (3H, s, Cp′CH_3), 4.13 (2H, m, CH_2CH_3), 4.46 (5H, s, C_5H_5), 4.76 (1H, s, Cp′), 4.99 (1H, s, Cp′). ^{13}C NMR (acetone-d_6): δ 14.7, 15.0, 15.3, 60.0, 73.1, 74.0, 74.8, 78,5, 88.3, 89.3, 171.1. Mass: m/z 332 (M^+). Anal. Calc. for $C_{15}H_{18}O_2Ru$: C, 54.37; H, 5.48. Found: C, 54.21; H, 5.57%.

3.18. [η^5-$C_5H_2(Me)(Ph)(COOEt)$]$Ru(C_5H_5)$ (**5b**)

IR (cm^{-1}, KBr): 1713($\nu_{C=O}$). ^1H NMR (CD_2Cl_2): δ 1.31 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.30 (3H, s, Cp′CH_3), 4.22 (2H, m, CH_2CH_3), 4.44 (5H, s, C_5H_5), 5.22 (1H, s, Cp′), 5.53 (1H, s, Cp′), 7.16 (1H, t, $J = 7.3$ Hz, C_6H_5), 7.23 (2H, t, $J = 7.3$ Hz, C_6H_5), 7.39 (2H, d, $J = 7.3$ Hz, C_6H_5). ^{13}C NMR (CD_2Cl_2): δ 14.6, 15.4, 60.3, 71.2, 73.7, 75.5, 75.8, 90.4, 90.6, 126.8, 126.9, 128.4, 137.7, 171.0. Mass: m/z 394 (M^+). Anal. Calc. for $C_{20}H_{20}O_2Ru$: C, 61.06; H, 5.12. Found: C, 61.03; H, 4.88%.

3.19. Synthesis of [{η^5-$C_5H_2(Me)_2(COOEt)$}$Ru(NCMe)_2$-{$P(OMe)_3$}][PF_6] (**7a**)

To an acetonitrile solution (20 mL) of **1a** (2.67 g, 5.0 mmol) was added trimethylphosphite (0.8 mL, 6.1 mmol). After stirring at room temperature for 5 min, the solvent was evaporated. The residue was washed with diethyl ether, and dried under reduced pressure to give yellow powder (3.05 g, 99%). IR (cm^{-1}, KBr): 1712 ($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.28 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.79 (3H, s, Cp′CH_3), 2.02 (3H, d, $J = 1.7$ Hz, Cp′CH_3), 2.60 (3H, d, $J = 1.2$ Hz, CH_3CN), 2.61 (3H, d, $J = 1.2$ Hz, CH_3CN), 3.67 (9H, d, $J = 11.7$ Hz, OCH_3), 4.19 (2H, m, CH_2CH_3), 4.71 (1H, s, Cp′), 4.98 (1H, d, $J = 1.7$ Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 3.6, 12.6, 12.8, 14.6, 52.2 (d, $J_{PC} = 3$ Hz), 60.9, 71.3, 78.2 (d, $J_{PC} = 7$ Hz), 80.1, 94.6, 108.2, 128.5, 168.4. ^{31}P NMR (acetone-d_6): δ 156.2. Anal. Calc. for $C_{17}H_{28}N_2O_5P_2F_6Ru$: C, 33.07; H, 4.57; N, 4.54; P, 10.03; F, 18.46. Found: C, 33.33; H, 4.32; N, 4.52; P, 10.23; F, 18.22%.

3.20. [{η^5-$C_5H_2(Me)(Ph)(COOEt)$}$Ru(NCMe)_2$-{$P(OMe)_3$}] [PF_6] (**7b**).

The title complex was prepared by a similar method to that for **7a** in 98% yield. IR (cm^{-1}, KBr): 1714 ($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.31 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.14 (3H, d, $J = 2.0$ Hz, Cp′CH_3), 2.40 (3H, d, $J = 1.2$ Hz, CH_3CN), 2.52 (3H, d, $J = 1.0$ Hz, CH_3CN), 3.51 (9H, d, $J = 11.7$ Hz, OCH_3), 4.22 (2H, m, CH_2CH_3), 5.45 (1H, s, Cp′), 5.73 (1H, d, $J = 1.7$ Hz, Cp′), 7.31–7.39 (3H, m, C_6H_5), 7.57–7.59 (2H, m, C_6H_5). ^{13}C NMR (acetone-d_6): δ 3.4, 3.5, 13.1, 14.6, 52.2 (d, $J_{PC} = 3$ Hz), 61.2, 70.5, 77.6 (d, $J_{PC} = 8$ Hz), 78.8, 93.4, 108.2, 127.5, 128.6 128.8, 129.1, 129.6, 133.1, 168.5. ^{31}P NMR (acetone-d_6): δ 154.0. Anal. Calc. for $C_{22}H_{30}N_2O_5P_2F_6Ru$: C, 38.89; H, 4.45; N, 4.12; P, 9.12; F, 16.78. Found: C, 38.77; H, 4.62; N, 4.42; P, 9.23; F, 16.90%.

3.21. [{η^5-$C_5H_2(Me)(Bu^t)(COOEt)$}$Ru(NCMe)_2$-{$P(OMe)_3$}][PF_6] (**7c**)

The title complex was prepared by a similar method to that for **7a** in 99% yield. IR (cm^{-1}, KBr): 1716 ($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.18 (9H, s, $C(CH_3)_3$), 1.28 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.05 (3H, d, $J = 2.9$ Hz, Cp′CH_3), 2.59 (3H, d, $J = 1.5$ Hz, CH_3CN), 2.63 (3H, d, $J = 1.5$ Hz, CH_3CN), 3.69 (9H, d, $J = 11.5$ Hz, OCH_3), 4.15 (2H, m, CH_2CH_3), 5.07 (1H, d, $J = 1.7$ Hz, Cp′), 5.14 (1H, dd, $J = 2.9$, 1.7 Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 3.5, 13.1, 14.6, 31.0, 31.4, 52.5 (d, $J_{PC} = 4.1$ Hz), 61.1, 67.5, 79.7, 80.5 (d, $J_{PC} = 10$ Hz), 106.0, 108.5, 128.7, 129.8, 169.2. ^{31}P NMR (acetone-d_6): δ 153.3. Anal. Calc. for $C_{20}H_{34}N_2O_5P_2F_6Ru$: C, 36.42; H, 5.20; N, 4.25; P, 9.39; F, 17.28. Found: C, 36.24; H, 5.07; N, 4.07; P, 9.19; F, 17.33%.

3.22. General procedure of double ligand transfer reactions between [{η^5-$C_5H_2(Me)(R)(COOEt)$}Ru{$P(OMe)_3$}-$(NCMe)_2$][PF_6] (**7**) and (η^5-C_5H_5)$Fe(CO)_2X$ (**8**)

Ruthenium complex **7** (1.0 mmol) and iron complex **8** (1.0 mmol) was dissolved in A dichloromethane (30 mL), and the reaction mixture was stirred for 3 h under reflux. After removal of the solvent, the products were separated by silica gel column chromatography using dichloromethane or a mixture of dichloromethane/ethyl acetate.

3.23. [η^5-$C_5H_2(Me)_2(COOEt)$]$Ru[P(OMe)_3](CO)I$ (**9a**)

This complex was obtained as a mixture of two diastereomers (0% de) in 53% yield. IR (cm^{-1}, KBr): 1965 (ν_{CO}), 1714 ($\nu_{C=O}$). ^1H NMR (acetone-d_6): δ 1.27 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.28 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.04 (3H, s, Cp′CH_3), 2.44 (3H, d, $J = 2.0$ Hz, Cp′CH_3), 3.66 (9H, d, $J = 12.0$ Hz, OCH_3), 3.67 (9H, d,

$J = 12.0$ Hz, OCH_3), 4.17 (2H, m, CH_2CH_3), 5.06 (1H, s, Cp′), 5.13 (1H, s, Cp′), 5.45 (1H, d, $J = 1.7$ Hz, Cp′), 5.53 (1H, s, Cp′). ^{13}C NMR (acetone-d_6): δ 13.9, 14.0, 14.5, 14.6, 53.8 (d, $J_{PC} = 5$ Hz), 53.9 (d, $J_{PC} = 4$ Hz), 60.8, 61.0, 81.7 (d, $J_{PC} = 7$ Hz), 83.2, 86.9 (d, $J_{PC} = 3$ Hz), 87.2, 87.8, 88.3 (d, $J_{PC} = 5$ Hz), 100.7, 102.7, 114.2, 115.1, 165.7, 165.8, 202.9 (d, $J_{PC} = 29$ Hz), 203.1 (d, $J_{PC} = 28$ Hz). ^{31}P NMR (acetone-d_6): δ 155.0, 155.5. Mass: m/z 545 (M^+). Anal. Calc. for $C_{14}H_{22}IO_6PRu$: C, 30.84; H, 4.07; P, 5.68; I, 23.27. Found: C, 30.69; H, 4.32; P, 5.48; I, 23.53%.

3.24. [η^5-$C_5H_2(Me)_2(COOEt)$]Ru[$P(OMe)_3$](CO)Br (**9b**)

This complex was obtained as a mixture of two diastereomers (12% de) in 26% yield. IR (cm^{-1}, KBr): 1965 (ν_{CO}), 1714 ($\nu_{C=O}$). Mass: m/z 499 (M^+). Anal. Calc. for $C_{14}H_{22}BrO_6PRu$: C, 33.75; H, 4.45; P, 6.22; Br, 16.04. Found: C, 33.95; H, 4.56; P, 6.04; Br, 15.92. Major isomer of **9b**: ^{1}H NMR (acetone-d_6): δ 1.27 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.88 (3H, s, Cp′CH_3), 2.23 (3H, s, Cp′CH_3), 3.69 (9H, d, $J = 12.2$ Hz, OCH_3), 4.17 (2H, m, CH_2CH_3), 5.10 (1H, s, Cp′), 5.44 (1H, d, $J = 1.7$ Hz, Cp′). 13C NMR (acetone-d_6): δ 13.4, 14.0, 14.6, 53.5 (d, $J_{PC} = 5$ Hz), 60.8, 80.9, 84.9, 88.4 (d, $J_{PC} = 5$ Hz), 102.8, 116.7, 165.9, 202.1 (d, $J_{PC} = 30$ Hz). ^{31}P NMR (acetone-d_6): δ 153.4. Minor isomer of **9b**: ^{1}H NMR (acetone-d_6): δ 1.27 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.94 (3H, s, Cp′CH_3), 2.20 (3H, d, $J = 2.9$ Hz, Cp′CH_3), 3.68 (9H, d, $J = 12.2$ Hz, OCH_3), 4.17 (2H, m, CH_2CH_3), 5.18 (1H, d, $J = 2.2$ Hz, Cp′), 5.34 (1H, s, Cp′). ^{13}C NMR (acetone-d_6): δ 13.7, 13.8, 14.5, 53.4 (d, $J_{PC} = 5$ Hz), 60.9, 82.9, 85.4, 86.8 (d, $J_{PC} = 9$ Hz), 100.2, 118.4, 166.0, 203.3 (d, $J_{PC} = 30$ Hz). ^{31}P NMR (acetone-d_6): δ 153.0.

3.25. [η^5-$C_5H_2(Me)(Ph)(COOEt)$]Ru[$P(OMe)_3$](CO)I (**9c**)

This complex was obtained as a mixture of two diastereomers (8% de) in 40% yield. The major isomer was isolated by recrystallization from diethyl ether as orange needles. Major isomer of **9c**: IR (cm^{-1}, KBr): 1972 (ν_{CO}), 1695 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.31 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.54 (3H, s, $J_{PH} = 2.2$ Hz, Cp′CH_3), 3.51 (9H, d, $J = 12.0$ Hz, OCH_3), 4.22 (2H, m, CH_2CH_3), 5.81 (1H, d, $J = 2.0$ Hz, Cp′), 6.15 (1H, d, $J = 2.0$ Hz, Cp′), 7.27–7.38 (3H, m, C_6H_5), 7.59–7.61 (2H, m, C_6H_5). ^{13}C NMR (acetone-d_6): δ 14.6, 15.3, 53.7 (d, $J_{PC} = 5.0$ Hz), 60.9, 84.0, 84.1 (d, $J_{PC} = 7$ Hz), 87.8, 99.1, 113.4, 126.8, 129.0, 129.3, 132.2, 165.3, 202.6 (d, $J_{PC} = 31$ Hz). ^{31}P NMR (acetone-d_6): δ 152.9. Mass: m/z 608 (M^+). Anal. Calc. for $C_{19}H_{24}O_6PIRu$: C, 37.58; H, 3.98; P, 5.10; I, 20.89. Found: C, 37.87; H, 4.11; P, 5.29; I, 20.70%. Minor isomer of **9c**: ^{1}H NMR (acetone-d_6): δ 1.31 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.49 (3H, s, $J = 1.5$ Hz, Cp′CH_3), 3.49 (9H, d, $J = 12$ Hz, OCH_3), 4.22 (2H, m, CH_2CH_3), 5.77 (1H, d, $J = 2.0$ Hz, Cp′), 6.29 (1H, dd, $J = 2.0$, 1.7 Hz, Cp′), 7.27–7.38 (3H, m, C_6H_5), 7.58–7.60 (2H, m, C_6H_5). ^{13}C NMR (acetone-d_6): δ 14.7, 14.8, 53.5 (d, $J_{PC} = 5$ Hz), 60.8, 83.1 (d, $J_{PC} = 7$ Hz), 85.3, 86.9 (d, $J_{PC} = 3$ Hz), 100.5, 113.9, 127.0, 128.8, 129.0, 132.1, 165.4, 202.2 (d, $J_{PC} = 30$ Hz). ^{31}P NMR (acetone-d_6): δ 153.3.

3.26. [η^5-$C_5H_2(Me)(Ph)(COOEt)$]Ru[$P(OMe)_3$](CO)-Br (**9d**)

This complex was obtained as a mixture of two diastereomers (0% de) in 15% yield. IR (cm^{-1}, KBr): 1952 (ν_{CO}), 1715 ($\nu_{C=O}$). ^{1}H NMR (acetone-d_6): δ 1.30 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.31 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.31 (3H, d, $J = 2.7$ Hz, Cp′CH_3), 2.33 (3H, s, Cp′CH_3), 3.49 (9H, d, $J = 12.2$ Hz, OCH_3), 3.58 (9H, d, $J = 12.0$ Hz, OCH_3), 4.23 (2H, m, CH_2CH_3), 5.83 (1H, d, $J = 1.7$ Hz, Cp′), 5.88 (1H, dd, $J = 2.0$, 1.7 Hz, Cp′), 6.03 (1H, d, $J = 2.0$ Hz, Cp′), 6.25 (1H, dd, $J = 2.0$, 2.0 Hz, Cp′), 7.26–7.38 (3H, m, C_6H_5), 7.56–7.59 (2H, m, C_6H_5), 7.59–7.61 (2H, m, C_6H_5). ^{13}C NMR (acetone-d_6): δ 14.1, 14.6, 14.7, 53.2 (d, $J_{PC} = 5$ Hz), 53.4 (d, $J_{PC} = 5$ Hz), 60.9, 61.0, 82.6 (d, $J_{PC} = 10$ Hz), 84.2, 83.8 (d, $J_{PC} = 9$ Hz), 84.8, 85.3, 85.9 (d, $J_{PC} = 3$ Hz), 98.5, 99.8, 116.8, 118.3, 127.0, 127.4, 129.0, 129.1, 129.3, 129.5, 132.5, 132.6, 165.7, 202.6 (d, $J_{PC} = 30$ Hz), 202.9 (d, $J_{PC} = 31$ Hz). ^{31}P NMR (acetone-d_6): δ 150.5, 151.0. Mass: m/z 561 (M^+). Anal. Calc. for $C_{14}H_{22}O_6PIRu$: C, 40.73; H, 4.32; P, 5.53; Br, 14.26. Found: C, 40.51; H, 4.36; P, 5.49; Br, 14.14%.

3.27. [η^5-$C_5H_2(Me)(Bu^t)(COOEt)$]Ru[$P(OMe)_3$]-(CO)I (**9e**)

This complex was obtained as a mixture of two diastereomers (14% de) in 69% yield. IR (cm^{-1}, KBr): 1972 (ν_{CO}), 1695 ($\nu_{C=O}$). Mass: m/z 588 (M^+). Anal. Calc. for $C_{17}H_{26}O_6PIRu$: C, 34.76; H, 4.81; P, 5.27; I, 21.61. Found: C, 34.98; H, 4.67; P, 5.17; I, 21.34. Major isomer of **9e**: ^{1}H NMR (acetone-d_6): δ 1.27 (9H, s, $C(CH_3)_3$), 1.27 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.20 (3H, d, $J = 3.7$ Hz, Cp′CH_3), 3.64 (9H, d, $J = 12.0$ Hz, OCH_3), 4.17 (2H, m, CH_2CH_3), 5.07 (1H, d, $J = 2.0$ Hz, Cp′), 5.85 (1H, dd, $J = 3.7$, 2.0 Hz, Cp′). ^{13}C NMR (acetone-d_6): δ 13.8, 14.8, 31.5, 31.7, 53.7 (d, $J_{PC} = 5$ Hz), 60.6, 81.1, 83.3, 94.1 (d, $J_{PC} = 7$ Hz), 108.9, 117.4 (d, $J_{PC} = 5$ Hz), 165.5, 203.5 (d, $J_{PC} = 31$ Hz). ^{31}P NMR (acetone-d_6): δ 153.9. Minor isomer of **9e**: ^{1}H NMR (acetone-d_6): δ 1.20 (9H, s, $C(CH_3)_3$), 1.28 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 2.55 (3H, d, $J = 3.2$ Hz, Cp′CH_3), 3.66 (9H, d, $J = 11.7$ Hz, OCH_3), 4.17 (2H, m, CH_2CH_3), 5.23 (1H, dd, $J = 3.7$, 2.0 Hz, Cp′), 5.43 (1H, s, Cp′). ^{13}C NMR (acetone-d_6): δ 14.4, 16.0, 31.2, 31.3, 54.0 (d, $J_{PC} = 5$ Hz), 60.8, 82.7, 83.7, 84.6 (d, $J_{PC} = 12$ Hz), 114.8, 117.9 (d, $J = 7$ Hz), 165.7, 203.6 (d, $J_{PC} = 29$ Hz). ^{31}P NMR (acetone-d_6): δ 151.7.

Table 3
Crystallographic data

Complex	**3a**	**3c**	**3d**	**3f**	**3h**	**3i**
Chemical formula	$C_{14}H_{22}IO_3PRu$	$C_{24}H_{26}IO_3PRu$	$C_{29}H_{28}BrO_3PRu$	$C_{24}H_{26}IO_3PRu$	$C_{17}H_{28}IO_3PRu$	$C_{22}H_{32}IO_3PRu$
Formula weight	497.27	621.42	636.49	621.42	539.35	603.44
Crystal size (mm)	$0.65 \times 0.50 \times 0.50$	$0.40 \times 0.35 \times 0.35$	$0.40 \times 0.25 \times 0.20$	$0.70 \times 0.55 \times 0.25$	$0.30 \times 0.30 \times 0.25$	$0.50 \times 0.35 \times 0.35$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	Cc (no. 9)	$P\bar{1}$ (no.2)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)
a (Å)	10.067(2)	9.547(3)	10.144(3)	9.502(2)	31.548(4)	13.568(2)
b (Å)	9.951(2)	17.797(4)	18.353(2)	16.434(3)	7.955(2)	16.115(2)
c (Å)	18.322(1)	14.607(3)	14.689(2)	8.420(3)	17.899(2)	10.733(3)
α (°)	90	90	90	98.93(3)	90	90
β (°)	100.410(8)	103.62(2)	93.96(2)	103.98(2)	111.442(10)	99.70(1)
γ (°)	90	90	90	103.73(2)	90	90
V (Å^3)	1805.2(4)	2412.2(10)	2728.1(8)	1207.5(6)	4180(1)	2313.3(7)
Z	4	4	4	2	8	4
D_{calc} (g cm^{-3})	1.830	1.711	1.550	1.709	1.714	1.733
μ (Mo Kα) (cm^{-1})	26.71	20.19	21.30	20.16	23.14	21.02
Reflections collected	4352	5849	3298	5884	4895	5586
Unique reflections [R_{int}]	4122 [0.023]	5526 [0.023]	3127 [0.063]	5548 [0.013]	4810 [0.008]	5303 [0.024]
Observed reflections	2889 ($I > 3.0\sigma(I)$)	4611 ($I > 2.0\sigma(I)$)	2815 ($I > 2.0\sigma(I)$)	4932 ($I > 2.0\sigma(I)$)	4432 ($I > 2.0\sigma(I)$)	4630 ($I > 2.0\sigma(I)$)
Variables	181	293	316	271	208	248
R	0.029	0.065	0.039	0.030	0.030	0.051
R_w	0.069	0.122	0.052	0.050	0.064	0.100
Goodness-of-fit	1.78	1.64	1.41	1.09	1.24	1.58

3.28. X-ray diffraction analyses

Crystals suitable for X-ray diffraction were mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC5R or AFC7R automated four-circles diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at −75 °C. The structures were solved by Patterson methods and refined by full-matrix least-squares using the TEXSAN crystallographic software package. Crystallographic data are listed in Table 3.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 142961 and 285029–285033 for complexes **3a**, **3c**, **3d**, **3f**, **3h** and **3i**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk. or www: http://www.ccdc.cam.ac.uk).

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