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Multiple ligand transfer reaction between $[CpRu(L)(AN)_2][PF_6]$ ($L = AN$, CO, $P(OMe)_3$; $AN =$ acetonitrile) and $CpFe(CO)L'X$ ($L' = CO$, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(OPh)_3$; $X = Cl$, Br, I)

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Abstract

Treatment of ruthenium complexes $[CpRu(AN)_3][PF_6]$ (**1a**) ($AN = $ acetonitrile) with iron complexes $CpFe(CO)_2X$ (**2a**–**2c**) ($X = Cl$, Br, I) and $CpFe(CO)L'X$ (**6a**–**6g**) ($L' = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, $P(OPh)_3$; $X = Cl$, Br, I) in refluxing CH_2Cl_2 for 3 h results in a triple ligand transfer reaction from iron to ruthenium to give stable ruthenium complexes $CpRu(CO)_2X$ (**3a**–**3c**) ($X = Cl$, Br, I) and $CpRu(CO)L'X$ (**7a**–**7g**) ($L' = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, $P(OPh)_3$; $X = Br$, I), respectively. Similar reaction of $[CpRu(L)(AN)_2][PF_6]$ (**1b**: $L = CO$, **1c**: $P(OMe)_3$) causes double ligand transfer to yield complexes **3a**–**3c** and **7a**–**7h**. Halide on iron, CO on iron or ruthenium, and two acetonitrile ligands on ruthenium are essential for the present ligand transfer reaction. The dinuclear ruthenium complex **11a** $[CpRu(CO)(\mu\text{-}I)]_2$ was isolated from the reaction of **1a** with **6a** at 0°C. Complex **11a** slowly decomposes in CH_2Cl_2 at room temperature to give **3a**, and transforms into **7a** by the reaction with PMe_3. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ligand transfer reactions; Half-sandwich ruthenium complexes; Crystal structures

1. Introduction

Much attention has recently focused on half-sandwich ruthenium complexes $CpRuL_2X$ with a three-legged piano stool structure due to their potentials in precise organic syntheses [1]. Although traditional synthetic routes to such ruthenium complexes relied on $CpRu(CO)_2Cl$ and $CpRu(PPh_3)_2Cl$ as starting materials [2], convenient routes have been developed by use of ruthenium complexes with easily exchangeable ligands [3–6]. Especially the tris(acetonitrile) complex $[CpRu(AN)_3][PF_6]$ (**1a**) ($AN = CH_3CN$) is useful as a precursor since it has three weak-coordinated ligands which can be exchanged by various ligands stepwise to give $[CpRu(L)(AN)_2][PF_6]$, $[CpRu(L)_2(AN)][PF_6]$ and $[CpRu(L)_3][PF_6]$ [3,4]. Therefore, complex **1a** can be regarded as a pseudo coordinatively unsaturated species $[CpRu]^+$. On the other hand, it has been reported that the reaction of a coordinatively unsaturated complex with an appropriate complex generates di- or multinuclear complexes [7]. Recently novel clusters have been prepared by the reaction of **1a** with anionic metal carbonyl clusters [8]. Thus, we have examined the reactivity of complex **1a** with some transition metal complexes and found that the reaction with iron complexes $CpFe(CO)L'X$ (**2**) ($L' = CO$, PR_3, $P(OR)_3$; $X = Cl$, Br, I) resulted in a multiple ligand transfer reaction from iron to ruthenium to give half-sandwich ruthenium complexes $CpRu(CO)L'X$. In the present paper we wish to report the scope and limitation of this multiple ligand transfer from iron to ruthenium and discuss the reaction mechanism.

2. Results and discussion

When $[CpRu(AN)_3](PF_6)$ (**1a**) was treated with $CpFe(CO)_2I$ (**2a**) in refluxing CH_2Cl_2 for 3 h, $CpRu(CO)_2I$ (**3a**) was isolated in 84% yield and 14% of the starting iron complex **2a** was recovered. The struc-

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Table 1
Multiple ligand transfer reaction between $[CpRu(AN)_3][PF_6]$ (**1a**) and $CpFe(CO)(L')X$ (**2a**–**2d**, **6a**–**6g**)

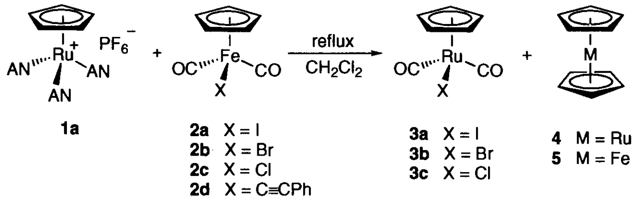
Run	Substrate			Yield of products (%) [a]				Recovery of Fe complex (%) [a]
	Fe complex	L′	X	$CpRu(CO)_2X$	$CpRu(CO)(L')X$	Cp_2Ru **4** [b]	Cp_2Fe **5** [b]	
1	**2a**	CO	I	84 **3a**				14
2	**2b**	CO	Br	79 **3b**		1	5	
3	**2c**	CO	Cl	35 **3c**		21	21	
4	**2d**	CO	C≡CPh			10	10	
5	**6a**	PMe_3	I	11 **3a**	44 **7a**	14	19	18
6	**6b**	PMe_2Ph	I	18 **3a**	36 **7b**	7	25	17
7	**6c**	PMe_2Ph	I	22 **3a**	32 **7c**	9	26	10
8	**6d**	PPh_3	I	27 **3a**	31 **7d**	1	1	10
9	**6e**	$P(OPh)_3$	I	26 **3a**	34 **7e**	3	11	6
10	**6f**	PPh_3	Br	30 **3b**	28 **7f**	16	26	
11	**6g**	$P(OPh)_3$	Br	24 **3b**	18 **7g**	15	2	11

[a] Isolated yields.

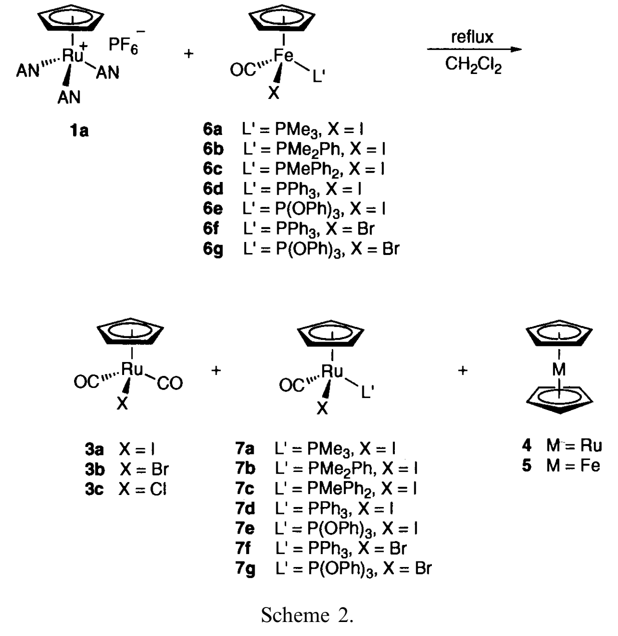
[b] Yields were estimated from the ^1H-NMR spectrum of the mixture of **4** and **5**.

ture of the resulting complex **3a** suggested that two CO ligands along with one iodide ligand were transferred from iron to ruthenium. Though the ligand transfer between transition metal complexes is often found in organometallic chemistry, multiple transfer is quite rare [9]. Thus, we investigated this ligand transfer reaction in detail, and the results are summarized in Table 1. Reactions of **1a** with **2b** (X = Br) and **2c** (X = Cl) also caused the ligand transfer to give **3b** and **3c**, respectively (runs 2 and 3). In these reactions ruthenocene **4** and ferrocene **5** were also produced (Scheme 1). Although the starting iron complexes **2b** and **2c** were completely consumed, the fate of iron is not clear since other identifiable iron complexes were not detected. Yields of **3a**–**3c** depend on the nature of the halide and decrease in the order I > Br > Cl, whereas yields of metallocenes **4** and **5** increase in the order I < Br < Cl. On the other hand, treatment of **1a** with iron acetylide **2d** (X = C≡CPh) did not give $CpRu(CO)_2(C{\equiv}CPh)$ but small amounts of **4** and **5**, suggesting that the halide ligand on iron is essential to the present ligand transfer reaction (run 4). Analogous iron complexes $CpFe(CO)(PR_3)X$ (**6a**–**6g**) with phosphine or phosphite ligands also reacted with **1a** to give ruthenium phosphine or phosphite complexes $CpRu(CO)(PR_3)X$ (**7a**–**7g**) and $CpRu(CO)_2X$ (**3a**–**3b**) along with metallocenes **4** and **5** (runs 5–11, Scheme 2). In these reactions yields of **3a** increase in the order $PMe_3 < PMe_2Ph < PMePh_2 < PPh_3$, while yields of **7a**–**7d** decrease in the order $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$. It should be noted that no ruthenium complex but $[CpFe\{P(OPh)_3\}_2(AN)][PF_6]$ (**9a**) was isolated from the reaction of **1a** with bis(phosphite) complex $CpFe\{P(OPh)_3\}_2Br$ (**8**) (Scheme 3). This result suggests that CO ligand on iron has an important role in the ligand transfer reaction.

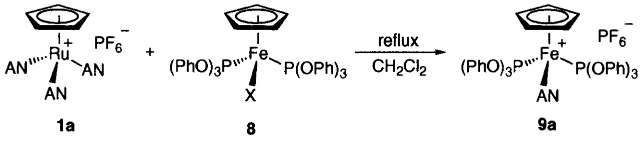
The molecular structure of complex **9a** was determined by X-ray crystallography. Selected bond distances and angles are listed in Table 2. As shown in Fig. 1, complex **9a** has a typical three-legged piano stool structure. The Fe–P bond distances are 2.144(1) and 2.1653(9) Å, which are slightly shorter than those of $[CpFe\{P(OMe)_3\}_2(AN)][PF_6]$ (**9b**) (2.181(6) and 2.175(6) Å) [10]. This is probably due to the difference



Scheme 1.



Scheme 2.



Scheme 3.

Table 2
Selected bond distances (Å) and angles (°) for **9a**

Fe(1)–P(1)	2.144(1)	Fe(1)–P(2)	2.1653(9)
Fe(1)–N(1)	1.918(3)	Fe(1)–C(1)	2.102(3)
Fe(1)–C(2)	2.104(3)	Fe(1)–C(3)	2.122(3)
Fe(1)–C(4)	2.123(3)	Fe(1)–C(5)	2.092(3)
N(1)–C(6)	1.133(4)		
P(1)–Fe(1)–P(2)	93.97(3)	P(1)–Fe(1)–N(1)	89.86(8)
P(2)–Fe(1)–N(1)	95.46(8)	Fe(1)–N(1)–C(6)	173.7(3)

of π-acid character between $P(OPh)_3$ and $P(OMe)_3$. Consequently the Fe–C(Cp) distances of **9a** (average distance 2.109 Å) are slightly longer than those of **9b** (average distance: 2.092 Å). In contrast, the Fe–N distance of **9a** (1.918(3) Å) is consistent with that of **9b** (1.923(15) Å). Although the cone angle of $P(OPh)_3$ is larger than that of $P(OMe)_3$ [10], no significant differences are found in the bond angles around iron between complexes **9a** and **9b**.

Next we investigated the effect of the ligand on ruthenium in the ligand transfer reaction (Scheme 4, Table 3). Treatments of $[CpRu(CO)(AN)_2](PF_6)$ (**1b**) with $CpFe(CO)_2X$ (**2a**–**2c**) also gave $CpRu(CO)_2X$ (**3a**–**3c**), respectively (runs 1–3). Conversions of iron complexes **2a**–**2c**, however, are lower than those in the reactions with **1a**. Reactions of **1b** with $CpFe(CO)(PR_3)X$ (**6a**–**6g**) produced complex **3a** or **3b** as a major product, suggesting that the CO ligand moves from iron to ruthenium in preference to phosphine and phosphite (runs 4–8). Formation of iron complexes **9a** and **9c** indicates the phosphorus ligand transfer between iron complexes which released the CO and halide ligands. It may be of interest that the reaction of **1b** with **8** afforded **3b** and **7g** in low yields (run 9). This result indicates that the carbonyl ligand on ruthenium is effective for the ligand transfer. When $[CpRu\{P(OMe)_3\}(AN)_2](PF_6)$ (**1c**) was treated with $CpFe(CO)_2X$ (**2a**–**2c**), $CpRu(CO)\{P(OMe)_3\}X$ (**7h**–**7j**) were isolated as a sole ruthenium complex (runs 10–12, Scheme 4). Reaction of **1c** with **6a** gave **7h** in 90% yield (run 13). In this reaction $CpRu(PMe_3)\{P(OMe)_3\}X$ (**10**) could not be detected, suggesting that the phosphine transfer did not occur at all. As observed in the reaction of **1a** with **8**, treatment of **1c** with **8** gave iron complex **9a** since there are no CO ligands on both ruthenium and iron (run 14). Complexes $[CpRu(CO)_2(AN)][PF_6]$ (**1d**) and $[CpRu\{P(OMe)_3\}_2(AN)][PF_6]$ (**1e**) having one acetonitrile ligand did not react with **2b** at all, and an almost quantitative amount of **2b** was recovered (runs 15 and 16). These results clearly show that at least two acetonitrile ligands are

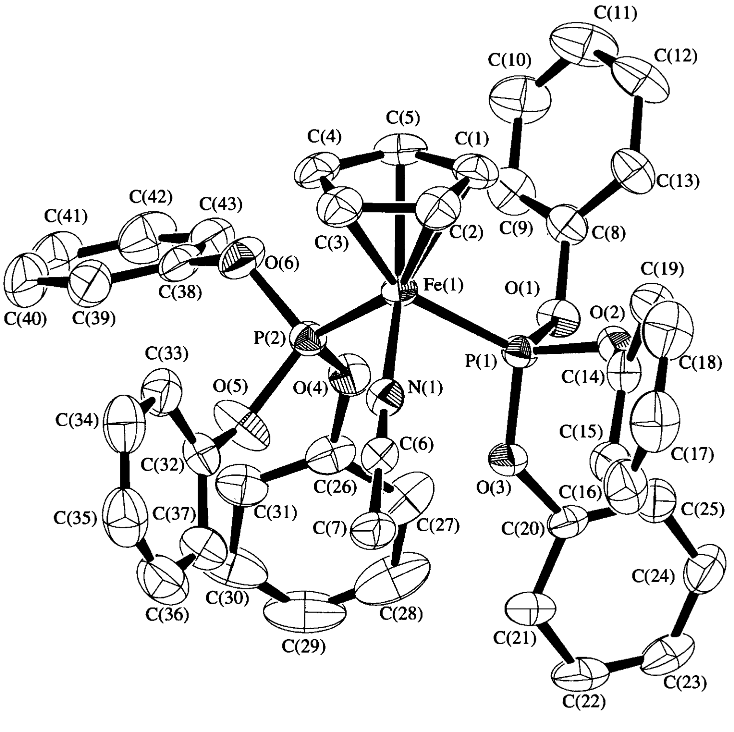


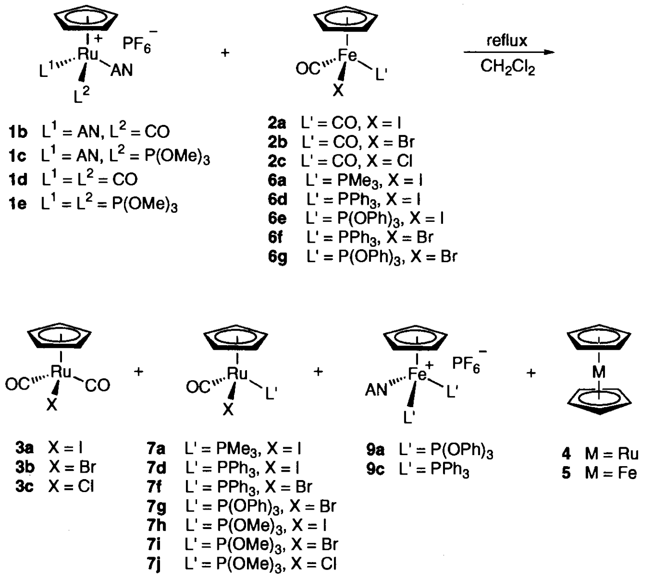
Fig. 1. Molecular structure of complex **9a**. Hydrogen atoms and PF_6^- have been omitted for clarity.

Table 3
Multiple ligand transfer reaction between [CpRu(AN)(L^1)(L^2)][PF_6] (**1b**–**1e**) and CpFe(CO)(L′)X (**2a**–**2d** and **6a**–**6g**) and CpFe$(L)_2$X (**8**)

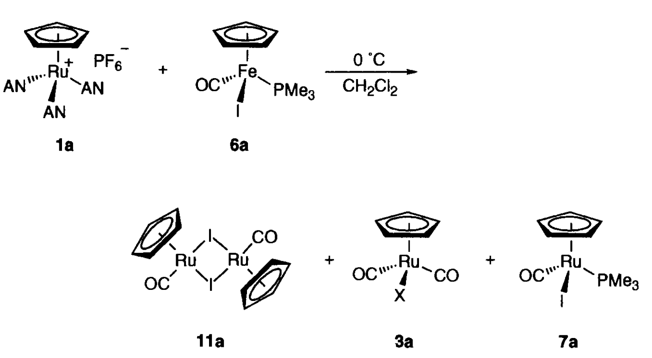
Run	Substrate				Yield of products (%) [a]					Recovery of Fe complex (%)
	Ru complex	L^1	L^2	Fe complex	CpRu$(CO)_2$X	CpRu(CO)(L)X	Cp_2Ru **4** [b]	[CpFe$(L)_2$(AN)][PF_6]	Cp_2Fe **5** [b]	
1	**1b**	AN	CO	**2a**	71 **3a**					26
2	**1b**	AN	CO	**2b**	43 **3b**					53
3	**1b**	AN	CO	**2c**	21 **3c**				10	73
4	**1b**	AN	CO	**6a**	62 **3a**	6 **7a**			10	12
5	**1b**	AN	CO	**6d**	58 **3a**	4 **7d**	5		5	21
6	**1b**	AN	CO	**6e**	75 **3a**			28 **9a**	1	20
7	**1b**	AN	CO	**6f**	48 **3b**	16 **7f**	4	47 **9c**	7	
8	**1b**	AN	CO	**6g**	59 **3b**	2 **7g**		22 **9a**	4	30
9	**1b**	AN	CO	**8**	11 **3b**	16 **7g**		42 **9a**		
10	**1c**	AN	$P(OMe)_3$	**2a**		87 **7h**				12
11	**1c**	AN	$P(OMe)_3$	**2b**		48 **7i**			9	50
12	**1c**	AN	$P(OMe)_3$	**2c**		23 **7j**			18	40
13	**1c**	AN	$P(OMe)_3$	**6a**		90 **7h**			7	3
14	**1c**	AN	$P(OMe)_3$	**8**				33 **9a**		
15	**1d**	CO	CO	**2b**						97
16	**1e**	$P(OMe)_3$	$P(OMe)_3$	**2b**						96

[a] Isolated yields.

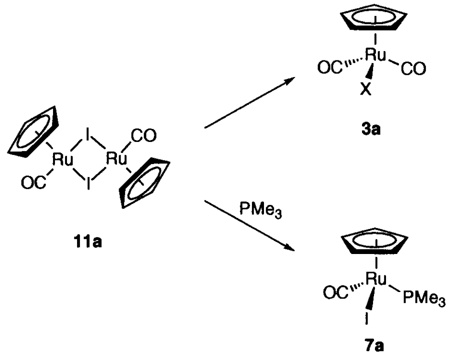
[b] Yields were estimated from the ^{1}H-NMR spectrum of the mixture of **4** and **5**.



Scheme 4.



Scheme 5.

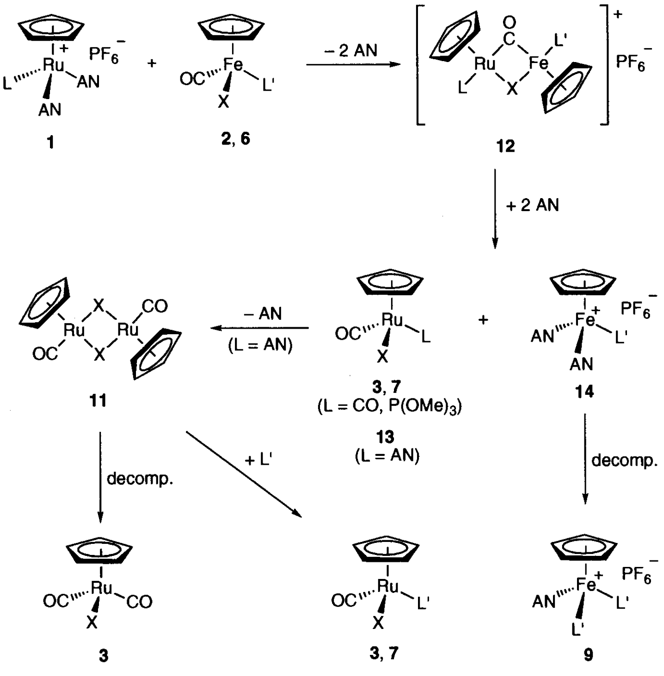


Scheme 6.

required on ruthenium for the present ligand transfer reaction.

When the reaction of **1a** with **6a** was performed at 0°C, a new ruthenium complex **11a** $[CpRu(CO)(\mu\text{-}I)]_2$ along with small amounts of **3a** and **7a** was obtained (Scheme 5). Although complex **11a** could not be isolated as an analytically pure sample due to low stability, unequivocal identification was achieved by spectral analyses. The FAB mass spectrum showed a molecular ion peak of $m/z = 644$, which corresponds to the dinuclear complex possessing two of each Cp, CO, and iodide ligands. In the IR spectrum of **11a** a strong absorption was observed at 1953 cm^{-1}, suggesting that the CO ligands do not bridge two ruthenium atoms but coordinate to ruthenium in an η^1 fashion. One sharp singlet signal appeared at δ 4.50 in the ^{1}H-NMR spectrum. These data strongly suggest **11a** to be a dinuclear ruthenium complex with two halogen bridges. Complex **11a** was unstable in CH_2Cl_2 at room temperature and slowly transformed into **3a** and unidentified complexes. However, treatment of **11a** with PMe_3 instantly gave **7a** in a quantitative yield (Scheme 6).

From the experimental results described above, requisites for the present multiple ligand transfer reaction may be concluded as follows: (1) halide ligands on iron, (2) CO ligands on iron or ruthenium, (3) at least two acetonitrile ligands on ruthenium. A proposed reaction mechanism involving dinuclear complex **12** as a key intermediate is illustrated in Scheme 7. Coordinatively unsaturated ruthenium species provided by dissociation of two acetonitrile ligands react with iron complexes to generate complex **12** with both halide and carbonyl bridges. When **1b** or **1c** is used as a starting material, the ligand transfer from iron to ruthenium is achieved by cleavage of Fe–X and Fe–CO bonds to give stable ruthenium complexes **3a**–**3c** and **7a**–**7j**. Therefore, yields of the products are fairly high on the basis of the conversion of iron complexes in most of the cases shown in Table 1. In contrast, the reactions of **1a**



Scheme 7.

produce labile ruthenium complex **13**, which undergoes a dimerization with the loss of acetonitrile to give complex **11**. Iron complex **14** with two acetonitrile ligands is also produced as a result of the transfer of halide and CO ligands followed by the coordination of acetonitrile liberated from ruthenium. Complex **14** would be unstable to convert into other iron complexes such as ferrocene with liberating free ligands L′. Reactions of **11** with free ligands L′ (CO, phosphine or phosphite) provide stable ruthenium complexes **3a**–**3c** and **7a**–**7g** while complexes **3a**–**3c** are also produced from decomposition of **11**. Ligand exchange of acetonitrile on **14** with L′ (phosphine or phosphite) gives stable cationic iron complexes **9a** and **9c**. Metallocenes **4** and **5** may be produced by the reaction with a cyclopentadienyl ligand released by decomposition of ruthenium and iron complexes.

In conclusion, we have shown a novel multiple ligand transfer reaction between ruthenium complexes $[CpRu(L)(AN)_2][PF_6]$ (**1a**–**1c**) and iron complexes CpFe(CO)L′X (**2a**–**2c** and **6a**–**6g**) to yield CpRu(CO)LX or CpRu(CO)L′X (**3a**–**3c** and **7a**–**7h**). Such a multiple ligand transfer reaction between transition metal complexes is quite rare [9]. Although most of the ruthenium complexes obtained in this study have already been synthesized by other methods, the multiple ligand transfer reaction may provide new chemistry of Group 8 metal complexes and may be applicable to the synthesis of new cyclopentadienyl–ruthenium complexes.

3. Experimental

All reactions were carried out under an atmosphere of argon, but the workup was performed in air. ^{1}H- and ^{13}C-NMR spectra were measured in acetone-d_6 using $SiMe_4$ as an internal standard and recorded on a JEOL JNM-LA400 spectrometer. IR and mass spectra were taken on a Perkin–Elmer system 2000 FTIR and JEOL JMS-600H instrument, respectively. Elemental analyses were performed by The Material Analysis Center, ISIR, Osaka University.

Dichloromethane was dried over calcium hydride and distilled before use. All other chemicals available from commercial sources were used without further purification. Ruthenium complexes $[CpRu(L)(AN)_2][PF_6]$ (**1a**: L = AN, **1b**: L = CO, **1c**: L = $P(OMe)_3$) [3], $[CpRu(CO)_2(AN)][PF_6]$ (**1d**) [11] and $[CpRu\{P(OMe)_3\}_2(AN)][PF_6]$ (**1e**) [3] were prepared by published procedures. Iron complexes $CpFe(CO)_2I$ (**2a**) [12], $CpFe(CO)_2Br$ (**2b**) [13], $CpFe(CO)_2Cl$ (**2c**) [14], $CpFe(CO)_2(C{\equiv}CPh)$ (**2d**) [15], $CpFe(CO)(PMe_3)I$ (**6a**) [16], CpFe(CO)(L′)I (**6b**: L′ = PMe_2Ph, **6c**: L′ = $PMePh_2$, **6d**: L′ = PPh_3, **6e**: L′ = $P(OPh)_3$) [17], $CpFe(CO)(PPh_3)Br$ (**6f**) [18], $CpFe(CO)\{P(OPh)_3\}Br$ (**6g**) [19], and $CpFe\{P(OPh)_3\}_2Br$ (**8**) [20] were prepared according to the literature methods.

Typical procedure for the ligand transfer reaction between $[CpRu(AN)_2(L)]PF_6$ (**1a**–**1c**) (L = AN, $P(OMe)_3$, CO) and CpFe(CO)(L′)X (**2a**–**2c**, **6a**–**6g**) (L′ = CO, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(OPh)_3$; X = I, Br, Cl) is as follows.

A dichloromethane solution (30 ml) of $[CpRu(MeCN)_2(L)]PF_6$ (1.0 mmol) and CpFe(CO)(L′)X (1.0 mmol) was refluxed for 3 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane or a mixture of dichloromethane–ethyl acetate as an eluent followed by recrystallization.

All of the resulting ruthenium complexes were characterized by spectral analyses. Spectroscopic data of $CpRu(CO)_2X$ (**3a**: X = I, **3b**: X = Br, **3c**: X = Cl) [21], $CpRu(CO)(PMe_3)Br$ (**7a**) [22], CpRu(CO)(L′)I (**7b**: L′ = PMe_2Ph, **7c**: L′ = $PMePh_2$, **7d**: L′ = PPh_3, **7e**: L′ = $P(OPh)_3$) [23], CpRu(CO)(L′)Br (**7f**: L′ = PPh_3, **7g**: L′ = $P(OPh)_3$) [24], $CpRu(CO)\{P(OMe)_3\}I$ (**7h**) [23], $CpRu(CO)\{P(OMe)_3\}X$ (**7i**: X = Br, **7j**: X = Cl) [24], and $[CpFe(PPh_3)_2(AN)][PF_6]$ (**9c**) [25] were identical to those found in the literature. Spectroscopic data for a new cationic iron complex $[CpFe\{P(OPh)_3\}_2(AN)][PF_6]$ (**9a**) are as follows.

9a: ^{1}H-NMR (acetone-d_6): δ 2.48 (3H, s, CH_3CN), 4.33 (5H, s, Cp), 7.27 (6H, t, $J = 7.3$ Hz, Ph), 7.33 (12H, d, $J = 8.1$ Hz, Ph), 7.43 (12H, d, $J = 7.8$ Hz, Ph). ^{13}C-NMR (acetone-d_6): δ 6.35 (CH_3CN), 81.56 (Cp), 122.29 (Ph), 126.63 (Ph), 131.26 (Ph), 137.65 (*ipso*-C of Ph), 152.42 (CH_3CN). FAB MS: m/z 783 (M^+-PF_6). Anal. Calc. for $C_{43}H_{38}F_6FeNO_6P_3$: C, 55.68; H, 4.13; N, 1.51; P, 10.02; F, 12.29. Found: C, 55.87; H, 4.00; N, 1.66; P, 9.93; F, 12.44%.

3.1. X-ray crystallography of $[CpFe\{P(OPh)_3\}_2(AN)][PF_6]$ (9a)

A single crystal suitable for X-ray diffraction was obtained by recrystallization from dichloromethane–hexane and mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC7R automated four-circle diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å) at − 50°C. Intensities were corrected for Lorentz and polarization effects and for absorption using ψ-scan technique. The structure was solved by Patterson methods (DIRDIF94). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares minimizing $Rw(|F_o| - |F_c|)^2$ ($w = 1/\sigma^2(F_o)$). The hydrogen atoms were included at the calculated positions ($d_{C-H} = 0.95$ Å) and their parameters were not refined. The final

Table 4
Crystallographic data for **9a**

Chemical formula	$C_{43}H_{38}F_6FeNO_6P_3$
Formula weight	912.50
Crystal size (mm)	0.65 × 0.40 × 0.25
Crystal system	Monoclinic
Space group	C_c (no. 9)
Unit cell parameters	
a (Å)	10.644(2)
b (Å)	19.652(5)
c (Å)	20.249(4)
β (°)	97.88(2)
V (Å^3)	4195(1)
Z	4
D_{calc} (g cm^{-3})	1.468
μ (Mo–K$_\alpha$) (cm^{-1})	5.49
No. of reflections collected	5069
No. of unique reflections	4849 ($R_{int} = 0.026$)
No. of observed reflections	4544 ($I > 3.0\sigma(I)$)
No. of variables	542
R	0.028
R_w	0.041
Goodness of fit	1.08

cycle of full-matrix least-squares refinement was converged. All calculation was performed using the TEXSAN crystallographic software package. Crystallographic data are listed in Table 4.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 142961 for complex **9a**. 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; e-mail: deposit@ccdc.cam.ac.uk. or www: http://www.ccdc.cam.ac.uk).

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