Preparation and Electrochemical Properties of Polynuclear Organometallic Complexes Derived from Ferrocene-Containing Bidentate Ligands

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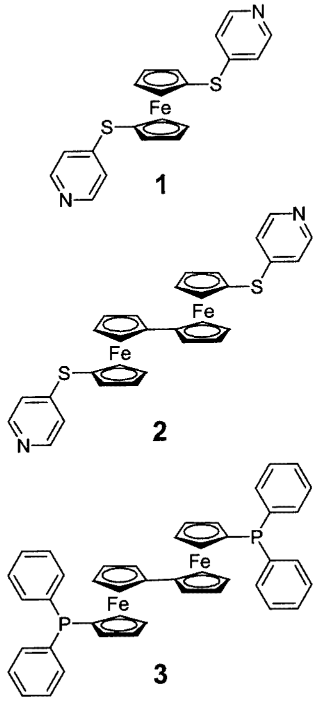
Keywords: Bridging ligands / Cyclic voltammetry / Ruthenium / Rhodium / Iridium / Metallocenes

The reaction of the ferrocene-containing bridging ligands 1,1′-bis(4-pyridylthio)ferrocene (**1**), 1′,1′′′-bis(4-pyridylthio)biferrocene (**2**), and 1′,1′′′-bis(diphenylphosphanyl)biferrocene (**3**), with the chloro-bridged dinuclear complexes $[(p\text{-cymene})\mathrm{RuCl}(\mu\text{-Cl})]_2$ and $[\mathrm{Cp^*MCl}(\mu\text{-Cl})]_2$ (M = Rh, Ir) affords trinuclear and tetranuclear metal complexes in good yields: $[\{(p\text{-cymene})\mathrm{RuCl}(\mu\text{-Cl})\}_2(\mu\text{-L})]$ (**4**: L = **1**; **7**: L = **2**; **10**: L = **3**), $[\{\mathrm{Cp^*MCl}(\mu\text{-Cl})\}_2(\mu\text{-L})]$ (**5**: L = **1**, M = Rh; **6**: L = **1**, M = Ir, **8**: L = **2**, M = Rh; **9**: L = **2**, M = Ir; **11**: L = **3**, M = Rh; **12**: L = **3**, M = Ir). The molecular structures of **3** and **5** have been determined by X-ray structure analysis. These complexes show quasi-reversible redox processes of the bridging ligands as well as irreversible redox processes of the terminal metal ions. Reaction of $[\{\mathrm{Cp^*MCl}(\mu\text{-Cl})\}_2(\mu\text{-}\mathbf{1})]$ with $\mathrm{AgPF_6}$ affords $[\{(\mathrm{Cp^*M})_4(\mu\text{-Cl})_4\}(\mu\text{-}\mathbf{1})_2](\mathrm{PF_6})_4$ (**13**: M = Rh, **14**: M = Ir), which are chloro-bridged polynuclear complexes.

Introduction

Metal-containing supramolecules and coordination polymers have attracted much interest in recent years, and a variety of supramolecular compounds have been prepared by the spontaneous self-assembly of metal ions and spacer ligands.[1−10] Recently it has been shown that supramolecular architectures can be constructed in a stepwise manner, using organometallic compounds.[11−16] Molecular squares and boxes have been synthesized by combining bidentate ligands, which have organometallic building blocks containing octahedral metals of Ru,[11,12] Rh[13,14] or Ir[15,16], with arene, cyclopentadienyl or pentamethylcyclopentadienyl (Cp*) groups.

The redox activities of ferrocene and biferrocene derivatives are well documented,[17] and we have recently synthesized redox-active bridging ligands containing ferrocene and have characterized their coordination polymers.[18] The syntheses of organometallic polynuclear compounds of Ru, Rh, and Ir with ferrocene- and biferrocene-based bidentate ligands are reported here. These compounds may be useful as redox-active building blocks for supramolecules showing multi-step redox properties. This paper describes the preparation and electrochemical properties of a series of tri- and tetranuclear organometallic complexes containing bidentate ligands of 1,1′-bis(4-pyridylthio)ferrocene (**1**), 1′,1′′′-bis(4-pyridylthio)biferrocene (**2**), and 1′,1′′′-bis(diphenylphosphanyl)biferrocene (**3**), as shown in Scheme 1: $[\{(p\text{-cymene})\mathrm{RuCl}(\mu\text{-Cl})\}_2(\mu\text{-L})]$ (**4**: L = **1**; **7**: L = **2; 10**: L = **3**), $[\{\mathrm{Cp^*MCl}(\mu\text{-Cl})\}_2(\mu\text{-L})]$ (**5**: L = **1**, M = Rh; **6**: L = 1, M = Ir, **8**: L = **2**, M = Rh; **9**: L = **2**, M = Ir; **11**: L = **3**, M = Rh; **12**: L = **3**, M = Ir). Coupling reactions of the trinuclear complexes were also investigated; treatment of **5** or **6** with $\mathrm{AgPF_6}$ afforded $[\{(\mathrm{Cp^*M})_4(\mu\text{-Cl})_4\}(\mu\text{-}\mathbf{1})_2](\mathrm{PF_6})_4$ (**13**: M = Rh, **14**: M = Ir), which are chloro-bridged polynuclear complexes.



Scheme 1. Ferrocene-based bridging ligands: 1,1′-bis(4-pyridylthio)ferrocene (**1**), 1′,1′′′-bis(4-pyridylthio)biferrocene (**2**), and 1′,1′′′-bis(diphenylphosphanyl)biferrocene (**3**)

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Results and Discussion

Preparation and Properties of the Bridging Ligands 1, 2, and 3

The bidentate ligands 1,1′-bis(4-pyridylthio)ferrocene (**1**), 1′,1′′′-bis(4-pyridylthio)biferrocene (**2**), and 1′,1′′′-bis(diphenylphosphanyl)biferrocene (**3**) were chosen so as to generate bridged polynuclear complexes, rather than chelate ones. The ligand **1** was synthesized as reported previously,[18] and **2** and **3** were synthesized from dilithiobiferrocene. The ligand **3** is a biferrocene analogue of 1,1′-bis(diphenylphosphanyl)ferrocene (dppf), although dppf mostly forms chelate complexes.[17,19−23] The molecular structure of **3** has been characterized by X-ray crystallography. An ORTEP[24] view of the compound is shown in Figure 1 along with the numbering scheme. The molecule sits on a crystallographic inversion centre and the phosphorus atoms are arranged in opposite directions, demonstrating the versatility of this ligand as a bidentate. The distances from the iron atom to the Cp planes are approximately 1.64 Å, which is typical for neutral ferrocene. The bond lengths and angles around the phosphorus atom are similar to those found in dppf.[25]

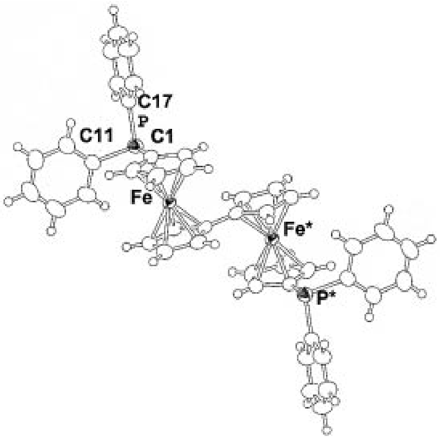


Figure 1. An ORTEP drawing of the molecular structure **3** with the atom numbering scheme; displacement ellipsoids are shown at the 50% probability level; selected bond lengths (Å) and angles (°): P(1)−C(1) 1.815(3), P(1)−C(11) 1.847(2), P(1)−C(17) 1.836(2), C(1)−P(1)−C(11) 99.4(1), C(1)−P(1)−C(17) 102.1(1), C(11)−P(1)−C(17) 101.2(1)

The redox properties of **2** and **3** were investigated by cyclic voltammetry. Complex **2** shows two quasi-reversible redox waves of the biferrocenyl moiety at $E_{1/2}$ = 0.14 V and 0.37 V (vs. $FeCp_2/FeCp_2^+$), exhibiting slight positive shifts relative to biferrocene, due to the electron-withdrawing effect of the pyridinethio moieties. The complex **3** exhibits several complicated redox waves; these could not be analyzed, although peaks corresponding to the oxidations of the biferrocene moiety were identified at $E_{1/2}$ = 0.03 V and 0.40 V (vs. $FeCp_2/FeCp_2^+$). The redox behaviour might be analogous to that of dppf,[26] in which oxidation is accompanied by reactions such as intermolecular coupling of the phosphorus groups, giving rise to complicated behaviour.

Preparation and Characterization of the Polynuclear Complexes

Reactions of the ferrocene-containing ligands **1**−**3** with the chloro-bridged dinuclear complexes [(*p*-cymene)RuCl(μ-Cl)]$_2$ and [Cp*MCl(μ-Cl)]$_2$ (M = Rh, Ir) produced tri- and tetranuclear metal complexes **4**−**12**, in good yields. Satisfactory analytical data were obtained for all products. The NMR spectroscopic and elemental analysis data confirm the 2:1 molar ratio of the organometallic moieties and the bridging ligands. These compounds are air-stable and are soluble in common polar organic solvents.

The trinuclear molecular structure of **5** was confirmed by X-ray structure analysis. An ORTEP view of the trinuclear complex is shown in Figure 2, along with the numbering scheme. The coordination environment of the rhodium atom is pseudooctahedral, with N(1)−Rh(1)−Cl(1), N(1)−Rh(1)−Cl(2), N(2)−Rh(2)−Cl(3), N(2)−Rh(2)−Cl(4) angles of 88.7(3), 87.0(2), 89.1(3), and 86.8(3) °, respectively, and Rh(1)−N(1) and Rh(2)−N(2) distances of 2.117(8) and 2.127(9) Å, respectively. The cyclopentadienyl rings are located ca. 1.77 Å away from the rhodium atom. The conformation of the two ferrocenyl rings is synclinal (eclipsed) with an S···S separation of ca. 4.26 Å. The ferrocenyl rings are planar and located 1.65 Å away from the iron atom.

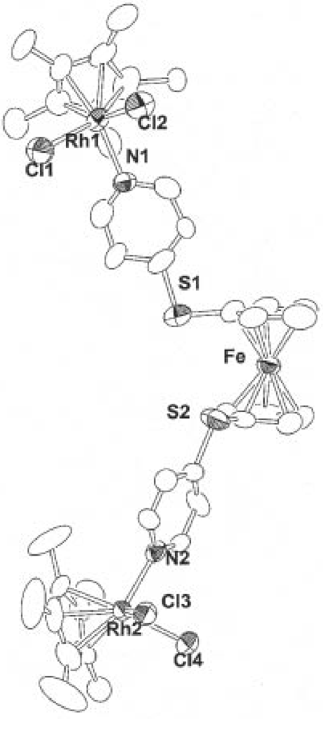


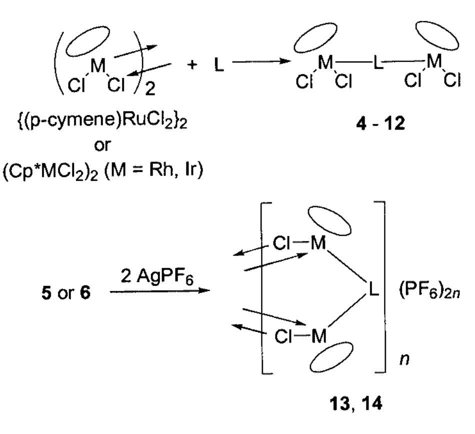
Figure 2. An ORTEP drawing of the molecular structure **5** with the atom numbering scheme; displacement ellipsoids are shown at the 50% probability level; selected bond lengths (Å) and angles (°): Rh(1)−N(1) 2.117(8), Rh(2)−N(2) 2.127(9), S(1)−C(1) 1.743(13), S(1)−C(11) 1.782(11), S(2)−C(6) 1.711(13), S(2)−C(16) 1.766(11), C(1)−S(1)−C(11) 103.5(6), C(6)−S(2)−C(16) 104.6(6)

The ^1H NMR spectra of the pyridine-ligated complexes **4**−**9** show two doublets at around δ(H_α) = 8.6 and δ(H_β) =

6.8 ppm, which are assigned to the metal-coordinated pyridine ring protons. The chemical shifts of the pyridyl α-protons are shifted downfield by 0.3−0.4 ppm relative to those of the free ligands of **1** [$\delta(H_\alpha) = 8.31$, $\delta(H_\beta) = 6.89$ ppm][18] and **2** [$\delta(H_\alpha) = 8.24$, $\delta(H_\beta) = 6.83$ ppm]. The NMR spectroscopic signals of the ferrocenyl protons in complexes **4−10** are observed at almost identical positions to those of the corresponding free ligands **1−3**. The signals of the ferrocenyl protons in **11** and **12** are very broad at room temperature, and become sharper when the temperature is lowered to −60 °C.

The ^{31}P NMR spectroscopic signals of the phosphane-ligated complexes **10−12** are observed at $\delta = 18.99$, 22.33 and −8.53 ppm, respectively, and show significant low-field shifts relative to the free ligand **3**. The chemical shifts have reasonable values for metal-coordinated phosphorus atoms.[27−29]

Self-coupling reactions of the trinuclear complexes **5** or **6** were performed by treating these complexes with $AgPF_6$. The yields were low — 27% and 16% for **13** and **14**, respectively — and recovery of the starting materials was mainly observed, with no significant side products. Based on the spectroscopic data, elemental analysis data, and the 18-electron rule, these products are considered to be chloro-bridged polynuclear complexes. Infrared spectra of the products exhibit characteristic P−F stretching vibrations at 1112, 848 and 558 cm^{-1}, showing the presence of the PF_6^- anion. The ^1H NMR spectroscopic signals of the Cp* protons are observed at higher fields than those of the precursors **5** and **6**, which may be a consequence of changes in the electron density on the metal centres. The ^1H NMR spectroscopic signals of the bridging moieties are observed at slightly lower fields than the precursors. Although we could not determine the crystal structures of **13** and **14**, we speculate that these complexes are most likely to have dimeric structures, i.e. *n* = 2 in Scheme 2, because of their close resemblance to the tetranuclear chloro-bridged complexes of $[\{Cp^*M(\mu\text{-}Cl)\}_4L_2]X_4$ (M = Rh, Ir).[13,14] The present complexes are soluble in common organic solvents such as dichloromethane, acetonitrile, and methanol, suggesting that they are oligomers and not coordination polymers.[18]



Scheme 2. General reaction scheme

Electrochemical Properties of the Trinuclear and Tetranuclear Complexes

The redox properties of complexes **4−10** were investigated by cyclic voltammetry. Figure 3 and 4 show the cyclic voltammograms in dichloromethane solutions. The redox potentials are listed in Table 1. Cyclic voltammetry studies on complex **4** revealed that there are two oxidation waves at 0.50 and 0.93 V (vs. $FeCp_2/FeCp_2^+$), and one reduction wave at 0.34 V. The redox waves around 0.4 V are assigned to the redox processes of the ferrocene moiety, and the oxidation wave at 0.93V is assigned to that of the Ru^{II} to Ru^{III} process.

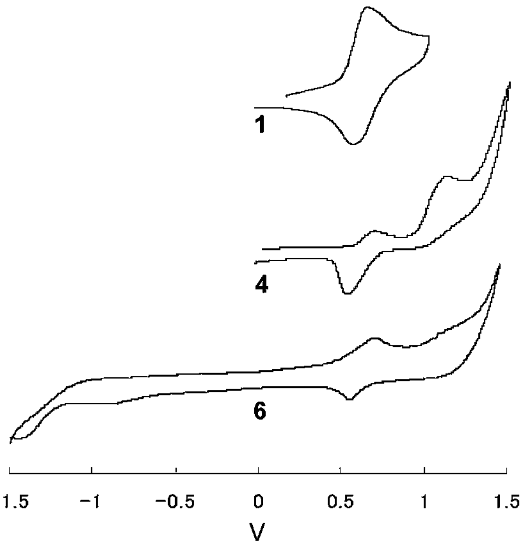


Figure 3. Cyclic voltammograms (vs. Ag/Ag^+) of **1**, **4** and **6**

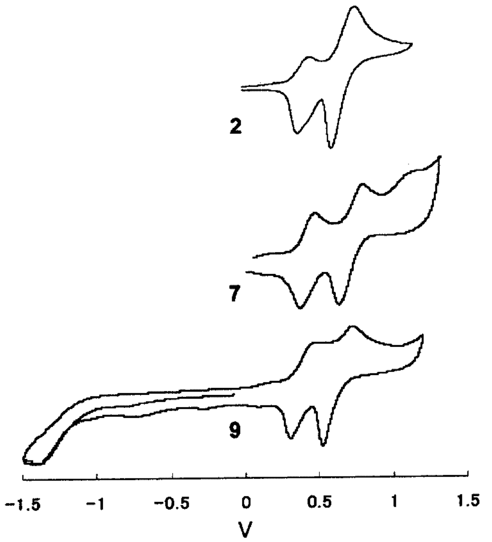


Figure 4. Cyclic voltammograms (vs. Ag/Ag^+) of **2**, **7** and **9**

The cyclic voltammogram of complex **5** exhibits an irreversible reduction wave of the Rh^{III} state at −1.60 V, and a quasi-reversible redox wave of the bridging ligand at $E_{1/2}$ = 0.45 V. Similarly, the cyclic voltammogram of the iridium

Table 1. Redox potentials (in *V* vs. $FeCp_2/FeCp_2^+$)

Compound	E_{pc}	E_{pc}	E_{pa}	E_{pc}	E_{pa}	E_{pa}
	(Rh, Ir)	(1st ferrocene)		(2nd ferrocene)		(Ru)
1		0.38	0.48			
2		0.11	0.17	0.30	0.44	
3		–	0.03[a]	0.21 [a]	0.55	
4		0.34	0.50			0.93
5	−1.60	0.35	0.52			
6	−1.54	0.41	0.57			
7		0.13	0.22	0.36	0.51	0.84
8	−1.64	0.09	0.27	0.25	0.50	
9	−1.64	0.10	0.28	0.34	0.54	
10		–	0.02	–	0.30	0.73

[a] Several unresolved redox waves were also present

complex **6** exhibits an irreversible reduction wave of the metal ion at −1.54 V, and a quasi-reversible redox wave of the bridging ligand at $E_{1/2}$ = 0.47 V. It seems that the redox potentials of the ferrocene moiety roughly increase in the order $E_{1/2}$ (**1**) < $E_{1/2}$ (**5**: M = Rh) < $E_{1/2}$ (**6**: M = Ir). This tendency is consistent with the stronger electron-withdrawing nature of the Ir complex than that of the Rh complex.

The biferrocene-containing ruthenium complex **7** shows two quasi-reversible and one irreversible oxidation wave. The reversible ones [$E_{1/2}(1)$ = 0.17 V, $E_{1/2}(2)$ = 0.44 V] are assigned to the redox processes of the biferrocene moiety, and the irreversible one (E_{pa} = 0.84 V) to that of the ruthenium ion. The rhodium and iridium complexes of **8** and **9** show two quasi-reversible and one irreversible reduction wave on scanning from 0 to −1.5 V. It seems that the redox potentials of the biferrocene moiety roughly increase in the order $E_{1/2}$ (**2**) < $E_{1/2}$ (**8**: M = Rh) < $E_{1/2}$ (**9**: M = Ir), showing a similar tendency to the derivatives of **1**. Since the redox spectra of the terminal metal ions exhibit only one wave in **4**−**9**, it follows that interactions between the terminal metal ions through the bridging ligand are negligible.

The diphenylphosphanyl-coordinated complexes **10**−**12** show highly complicated redox behaviours compared with the pyridine-coordinated complexes **4**−**9**. The redox behaviour of complex **10** is slightly clearer than that of its precursor **3**; three oxidation processes for the biferrocene moiety and the Ru^{II} centre can be discerned, although these are irreversible. It is conceivable that the addition of the end-capping groups prevents chemical reactions such as intermolecular coupling,[26] which complicate the redox processes of **3**. The first oxidation process of the biferrocene moiety in **10** is quasi-reversible on scanning from 0 to 0.15 V, although both the first and the second waves become irreversible on scanning from 0 to 0.40 V. In complexes **4**−**9**, the redox processes of the ferrocene moiety are only slightly affected by the coordination of the metal ions. This is probably because the sulfur bridge terminates the conjugation between the ferrocene moiety and the pyridyl group. By contrast, coordination of the metal ions to the phosphorus atom in **3** leads to significant interaction between the metal ions and the ferrocene moieties, which could complicate the redox behaviour of **10**−**12**.

Experimental Section

General Remarks: All reactions were carried out by Schlenk techniques under nitrogen. Reagent grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting complexes $[(p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ [30] and $[Cp^*MCl(\mu\text{-}Cl)]_2$ (M = Rh, Ir),[31,32] and the bridging ligand **1**[18] were prepared by a published procedure.

Elemental analyses were performed using a Yanagimoto C−H−N recorder (MT-3) and Elementar Vario EL. Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer as KBr pellets in the 4000−400 cm^{-1} range. NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. Chemical shifts are cited relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P). Cyclic voltammograms were obtained with an ALS/chi electrochemical-analyzer, model 600A. The working electrode was a glassy disk electrode with an Ag/Ag^+ reference electrode. NBu_4ClO_4 and CH_2Cl_2 were used as the supporting electrolyte and solvent, respectively.

Synthesis of 1′,1′′′-Bis(4-pyridylthio)biferrocene (2): A THF solution (10 mL) of 4,4′-dipyridyl disulfide (660 mg, 3 mmol) was added dropwise to a suspension of dilithiobiferrocene, prepared from dibromobiferrocene (528 mg, 1 mmol), in THF (30 mL) at −80 °C for 4 h, and left to stir at room temperature for 4 h. The resulting brown solution was filtered, the solvent evaporated, and the orange residue dissolved in chloroform. Concentration of the solution to ca. 10 mL and addition of diethyl ether gave **2** as an orange solid. Further purification was achieved by recrystallization from chloroform/acetonitrile (1:1 v/v) as an orange solid that was obtained in a yield of 53% (312 mg). $C_{30}H_{24}Fe_2N_2S_2$ (588.36): calcd. C 61.20, H 4.11, N 4.76; found C 60.91, H 4.12, N 4.56. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.16 (m, 4 H), 4.26 (m, 4 H), 4.34 (m, 4 H), 4.51 (m, 4 H), 6.83 (m, 4 H), 8.24 (m, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1} (m), 1575 (s), 1479 (m), 1409 (m), 802 (m), 705 (s), 494 (m), 418 (m).

Synthesis of 1′,1′′′-Bis(diphenylphosphanyl)biferrocene (3): The procedure was similar to that described for the preparation of **2**, except that diphenylphosphanyl chloride (0.54 mL, 3 mmol) was used instead of 4,4′-dipyridyl disulfide. The product **3** was obtained in 68% (502 mg) yield. Crystals suitable for X-ray measurements were grown by slow diffusion of diethyl ether into a solution of **3** in chloroform at ambient temperature. $C_{44}H_{36}Fe_2P_2$ (738.41): calcd. C 71.56, H 4.91; found C 71.47, H 4.91. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.87 (m, 4 H), 4.01 (m, 4 H), 4.11 (m, 4 H), 4.18 (m, 4 H), 7.37−7.27 (m, 20 H) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ = −16.09 ppm. IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} (m), 1477 (m), 1433 (s), 1159 (m), 1033 (m), 836 (m), 829 (m), 805 (m), 742 (s), 697 (s), 495 (s), 419 (s).

Synthesis of $[\{(p\text{-cymene})RuCl(\mu\text{-}Cl)\}_2(\mu\text{-}1)]$ (4): A dichloromethane solution (10 mL) of 1,1′-bis(4-pyridylthio)ferrocene (20 mg, 0.05 mmol) was added to a solution of $[(p\text{-cymene})RuCl(\mu\text{-}Cl)]_2$ (31 mg, 0.05 mmol) in dichloromethane (5 mL), and the mixture was stirred for 5 h at room temperature. The resulting orange solution was evaporated to dryness and the red residue recrystallized from dichloromethane/diethyl ether (1:1 v/v). The orange solid of **4** was obtained in a yield of 74% (38 mg). $C_{40}H_{44}Cl_4FeN_2Ru_2S_2$ (1016.73): calcd. C 47.25, H 4.36, N 2.76; found C 46.95, H 4.42, N 2.85. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.29 (d, 12 H), 2.10 (s, 6 H), 2.97 (sept, $J_{H,H}$ = 7.0 Hz, 2 H), 4.47 (m, 4 H), 4.58 (m, 4 H), 5.19 (d, $J_{H,H}$ = 3.0 Hz, 4 H), 5.41 (d, $J_{H,H}$ = 3.0 Hz, 4 H), 6.86 (m, 4 H), 8.66 (m, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1} (m), 2965 (m), 2872 (m), 1594 (s), 1481 (m), 1417 (m), 1219 (m), 1110 (m), 1061 (m), 815 (m), 724 (m), 514 (m), 418 (m).

Synthesis of [{Cp*RhCl(μ-Cl)}$_2$(μ-1)]·CH_2Cl_2 (5): The procedure was similar to that described for the preparation of **4**, except that [Cp*RhCl(μ-Cl)]$_2$ (31 mg, 0.05 mmol) was used instead of [(*p*-cymene)RuCl(μ-Cl)]$_2$. The orange solid of **5** was obtained in a yield of 95% (47 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.57 (s, 30 H), 4.47(m, 4 H), 4.58 (m, 4 H), 6.92 (m, 4 H), 8.62 (m, 4 H) ppm. $C_{41}H_{48}Cl_6FeN_2Rh_2S_2$ (1107.35): calcd. C 44.47, H 4.27, N 2.53; found C 44.4, H 4.5, N 2.5. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.66 (s, 30 H), 4.61 (m, 4 H), 4.66 (m, 4 H), 6.93 (m, 4 H), 8.31 (m, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 1636 cm^{-1} (m), 1592 (s), 1479 (m), 1417 (m), 1375 (m), 1216 (m), 1109 (m), 1062 (m), 1025 (m), 896 (m), 817 (m), 726 (m), 504 (m), 419 (s).

Synthesis of [{Cp*IrCl(μ-Cl)}$_2$(μ-1)] (6): The procedure was similar to that described for the preparation of **4**, except that [Cp*IrCl(μ-Cl)]$_2$ (39 mg, 0.05 mmol) was used instead of [(*p*-cymene)RuCl(μ-Cl)]$_2$. The yellow solid of **6** was obtained in a yield of 87% (51 mg). $C_{40}H_{46}Cl_4FeIr_2N_2S_2$ (1201.04): calcd. C 40.00, H 3.86, N 2.33; found C 39.73, H 3.89, N 2.20. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.56 (s, 30 H), 4.49 (m, 4 H), 4.58 (m, 4 H), 6.88 (d, $J_{H,H}$ = 3.4 Hz, 4 H), 8.61 (d, $J_{H,H}$ = 3.2 Hz, 4 H) ppm. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.63 (s, 30 H) 4.61 (m, 4 H), 4.67 (m, 4 H), 6.95 (m, 4 H), 8.31 (m, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 2917 cm^{-1} (m), 1636 (m), 1595 (s), 1478 (m), 1419 (m), 1380 (m), 1215 (m), 1111 (m), 1061 (m), 1029 (m), 896 (m), 816 (m), 728 (m).

Synthesis of [(*p*-cymene)RuCl(μ-Cl)}$_2$(μ-2)](7): The procedure was similar to that described for the preparation of **4**, except that **2** (30 mg, 0.05 mmol) was used instead of **1**. The orange solid of **7** was obtained in a yield of 52% (31 mg). $C_{50}H_{52}Cl_4Fe_2N_2Ru_2S_2$ (1200.75): calcd. C 50.00, H 4.37, N 2.33; found C 49.71, H 4.46, N 2.44. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.27 (d, 12 H), 2.07 (s, 6 H), 2.95 (sept, $J_{H,H}$ = 7.0 Hz, 2 H), 4.12 (m, 4 H), 4.27 (m, 4 H), 4.35 (m, 4 H), 4.49 (m, 4 H), 5.14 (d, $J_{H,H}$ = 3.0 Hz, 4 H), 5.36 (d, $J_{H,H}$ = 3.0 Hz, 4 H), 6.80 (m, 4 H), 8.58 (m, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 3085 cm^{-1} (w), 3037 (w), 2961 (w), 2870 (w), 1593 (s), 1480 (m), 1418 (m), 1111 (m), 1059 (m), 1026 (m), 890 (m), 816 (m), 725 (m), 500 (m), 419 (m).

Synthesis of [Cp*RhCl(μ-Cl)}$_2$(μ-2)]·CH_2Cl_2 (8): The procedure was similar to that described for the preparation of **5**, except that **2** (30 mg, 0.05 mmol) was used instead of **1**. The orange solid of **8** was obtained in a yield of 52% (32 mg). $C_{51}H_{56}Cl_6Fe_2N_2Rh_2S_2$ (1291.37): calcd. C 47.43, H 4.37, N 2.17; found C 47.6, H 4.5, N 2.1. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.54 (s, 30 H), 4.12 (m, 4 H), 4.27 (m, 4 H), 4.35 (m, 4 H), 4.50 (m, 4 H), 6.86 (m, 4 H), 8.55 (m, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 2870 cm^{-1} (w), 1636 (m), 1592 (s), 1478 (m), 1417 (m), 1374 (m), 1215 (m), 1165 (m), 1109 (m), 1061 (m), 1024 (m), 890 (m), 817 (m), 725 (m), 499 (m).

Synthesis of [{Cp*IrCl(μ-Cl)}$_2$(μ-2)]·(CH_2Cl_2)$_{1.5}$ (9): The procedure was similar to that described for the preparation of **6**, except that **2** (30 mg, 0.05 mmol) was used instead of **1**. The yellow solid of **9** was obtained in a yield of 67% (46 mg). $C_{51.5}H_{57}Cl_3Fe_2Ir_2N_2S_2$ (1370.65): calcd. C 40.90, H 3.80, N 1.85; found C 41.20, H 3.89, N 1.72. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.54 (s, 30 H), 4.14 (m, 4 H), 4.28 (m, 4 H), 4.36 (m, 4 H), 4.51 (m, 4 H), 6.82 (m, 4 H), 8.58 (m, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1} (w), 2913 (w), 1595 (s), 1479 (m), 1420 (m), 1377 (m), 1215 (m), 1167 (m), 1111 (m), 1062 (m), 1031 (m), 891 (m), 822 (m), 727 (m), 500 (m).

Synthesis of [{(*p*-cymene)RuCl(μ-Cl)}$_2$(μ-3)]·CH_2Cl_2 (10): The procedure was similar to that described for the preparation of **4**, except that **3** (37 mg, 0.05 mmol) was used instead of **1**. The orange solid of **10** was obtained in a yield of 45% (32 mg). $C_{65}H_{66}Cl_6Fe_2P_2Ru_2$ (1435.73): calcd. C 54.37, H 4.63; found C 54.63, H 4.71. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.96 (d, 12 H), 1.75 (s, 6 H), 2.52 (sept, $J_{H,H}$ = 7.0 Hz, 2 H), 3.61 (m, 4 H), 3.89 (m, 4 H), 4.00 (m, 4 H), 4.30 (m, 4 H), 5.07 (s, 8 H), 7.43−7.37 (m, 12 H), 7.85−7.80 (m, 8 H) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ = 18.99 ppm. IR (KBr): $\tilde{\nu}$ = 3044 cm^{-1} (w), 2958 (w), 2868 (w), 1482 (m), 1437 (s), 1384 (m), 1159 (m), 1095 (m), 1032 (s), 825 (s), 742 (s), 694 (s), 540 (m), 517 (s), 472 (s), 450 (s).

Synthesis of [{Cp*RhCl(μ-Cl)}$_2$(μ-3)]·(CH_2Cl_2)$_{0.5}$ (11): The procedure was similar to that described for the preparation of **5**, except that **3** (37 mg, 0.05 mmol) was used instead of **1**. The orange solid of **11** was obtained in a yield of 79% (54 mg). $C_{64.5}H_{67}Cl_5Fe_2P_2Rh_2$ (1398.95): calcd. C 55.38, H 4.83; found C 55.8, H 5.0. ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C): δ = 1.27 (s, 30 H), 3.93−3.70 (m, 4 H), 4.28−4.02 (m, 8 H), 4.50 (m, 4 H), 7.55−7.30 (m, 12 H), 8.10−7.82 (m, 8 H) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ = 22.33 (d) ppm. IR (KBr): $\tilde{\nu}$ = 2359 cm^{-1} (w), 1483 (m), 1434 (s), 1373 (m), 1305 (m), 1192 (m), 1159 (m), 1113 (m), 1094 (m), 1023 (m), 834 (m), 748 (m), 697 (m), 540 (s), 479 (m).

Synthesis of [{Cp*IrCl(μ-Cl)}$_2$(μ-3)] (12): The procedure was similar to that described for the preparation of **6**, except that **3** (37 mg, 0.05 mmol) was used instead of **1**. The orange solid of **12** was obtained in a yield of 71% (54 mg). $C_{64}H_{66}Cl_4Fe_2Ir_2P_2$ (1535.12): calcd. C 50.07, H 4.33; found C 49.8, H 4.3. ^{1}H NMR (400 MHz, $CDCl_3$, −60 °C): δ = 1.25 (s, 30 H), 3.82−3.75 (m, 4 H), 4.20−3.90 (m, 8 H), 4.60−4.25 (m, 4 H), 7.50−7.20 (m, 12 H), 8.10−7.70 (m, 8 H) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ = −8.53 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3072 cm^{-1} (w), 2912 (w), 1636 (m), 1435 (s), 1374 (m), 1159 (m), 1098 (m), 1085 (m), 1030 (m), 836 (m), 749 (m), 697 (m), 545 (s), 518 (m), 476 (m).

Synthesis of [{(Cp*Rh)$_4$(μ-Cl)$_4$}(μ-1)$_2$](PF_6)$_4$·CH_2Cl_2 (13): A diethyl ether solution (30 mL) of $AgPF_6$ (26 mg, 0.1 mmol) was added to a solution of **5** (52 mg, 0.05 mmol) in dichloromethane (30 mL), and the mixture was stirred for 12 h at room temperature. The resulting orange solution was filtered, the solvents evaporated to dryness and the red residue recrystallized from dichloromethane/diethyl ether (1:1 v/v). The orange solid of **13** was obtained in a yield of 27% (21 mg). $C_{81}H_{94}Cl_6F_{24}Fe_2N_4P_4Rh_4S_4$ (2567.81): calcd. C 37.89, H 3.69, N 2.18; found C 38.08, H 3.34, N 2.02. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.54 (s, 60 H), 4.72 (m, 8 H), 4.76 (m, 8 H), 7.31 (m, 8 H), 8.36 (m, 8 H) ppm. IR (KBr): $\tilde{\nu}$ = 1596 cm^{-1} (s), 1482 (m), 1422 (m), 1377 (m), 1112 (m), 1062 (m), 1023 (m), 844 (s).

Synthesis of [{(Cp*Ir)$_4$(μ-Cl)$_4$}(μ-1)$_2$](PF_6)$_4$ (14): The procedure was similar to that described for the preparation of **13**, except that **6** (61 mg, 0.05 mmol) was used instead of **5**. The yellow solid of **14** was obtained in a yield of 16% (16 mg). $C_{80}H_{92}Cl_4F_{24}Fe_2Ir_4N_4P_4S_4$ (2840.14): calcd. C 33.83, H 3.26, N 1.97; found C 33.44, H 3.00, N 2.18. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 1.55 (s, 60 H), 4.73 (m, 8 H), 4.77 (m, 8 H), 7.31 (m, 8 H), 8.43 (m, 8 H) ppm. IR (KBr): $\tilde{\nu}$ = 1598 cm^{-1} (s), 1483 (m), 1458 (m), 1425 (m), 1387 (m), 1230 (m), 1140 (m), 1115 (m), 1061 (m), 1031 (m), 848 (s).

X-ray Crystallographic Study: Crystals of compound **3** or **5** were mounted on a glass fibre and transferred to the diffractometer. The X-ray data were collected with a Rigaku AFC-5S four-circle diffractometer (**3**) or a Rigaku Mercury CCD diffractometer (**5**) using graphite-monochromated Mo-K_α radiation. Crystal data, data col-

Table 2. Crystal data and structure refinement of **3** and **5**

	3	**5**
Empirical formula	$C_{44}H_{36}Fe_2P_2$	$C_{41}H_{48}Cl_6FeN_2Rh_2S_2$
Molecular weight	738.41	1107.34
Temperature [K]	296	296
Radiation used (λ [Å])	Mo-K_α (0.71069)	Mo-K_α (0.71069)
Crystal description	prismatic, orange	prismatic, orange
Crystal size [mm]	0.8×0.6×0.1	0.15×0.1×0.1
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a [Å]	9.000(3)	16.776(3)
b [Å]	9.144(3)	11.883(2)
c [Å]	14.061(3)	26.952(4)
α [°]	110.91(2)	
β [°]	59.43(2)	110.127(7)
γ [°]	117.46(3)	
V [Å^3]	872.6(5)	5044.5(12)
$2\theta_{max}$ [°]	55.0	55.0
Z	1	4
F(000)	382	2232
$\rho_{calcd.}$ [g·cm^{-3}]	1.405	1.458
μ [mm^{-1}]	9.54	13.57
Total reflections	4250	24822
Unique reflections	4246	10881
R (int)	0.027	0.087
$R1$, $wR2$ [$I > 3\sigma(I)$][a]	0.0439, 0.1122	0.089, 0.177
Goodness-of-fit on F^2	1.546	0.87
Max./min. el. dens. [e Å^{-3}]	0.70/ −0.43	1.56/ −0.75

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR2 = [\Sigma w(F_0{}^2 - F_c{}^2)^2/\Sigma w(F_0{}^2)^2]^{1/2}$.

lection parameters, and analysis statistics for **3** and **5** are listed in Table 2. All calculations were performed using the teXsan crystallographic software package.[33] The structures were solved by direct methods (SIR 92[34] and SHELX-97[35]) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and absorption correction was applied. The hydrogen atoms were inserted at the calculated positions and allowed to ride on their respective parent atoms.

CCDC-181949 (**3**) and CCDC-184341 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to Prof. Tadashi Sugawara and Dr. Michio M. Matsushita (The University of Tokyo) for help with X-ray measurements. We thank Mr. Jouji Seta (Toho University) for help with ^{31}P NMR spectroscopy measurements. We also thank Prof. Hiroshi Moriyama (Toho University) for his assistance and Ms. Yumiko Sato (Toho University) the for elemental analyses. We are indebted to Mr. Masaru Nakama (WarpStream Ltd., Tokyo) for the Web-DB computer system.

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Received April 23, 2002
[I02211]