

Dimeric complexes of ruthenium(II) and rhodium(III) bridged by 1,1'-bis(diphenylphosphinomethyl)ferrocene

Jian-Fang Ma¹, Yasuhiro Yamamoto^{*}

Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, 274, Japan

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Abstract

Reactions of bis[dichloro(arene)ruthenium] or bis[dichloro(pentamethylcyclopentadienyl)rhodium] with 1,1'-bis[(diphenylphosphino)methyl]ferrocene (dpmf) gave the dpmf-*P,P'* bridged complexes. The reactions of the arene ruthenium complexes with 1,1'-bis[diphenylphosphino]ferrocene (dppf) formed the bridged and chelated complexes. The structures of complexes were confirmed by X-ray analysis. The cyclic voltammetry of ruthenium complexes was measured. © 1997 Elsevier Science S.A.

1. Introduction

Chemistry of 1,1'-bis(diphenylphosphino)ferrocene (dppf) has been well provided [1]. Since 1,1'-bis[(diphenylphosphino)methyl]ferrocene (dpmf) formed by introduction of a methylene group between the cyclopentadienyl ring and phosphorus atom could be more flexible than dppf, it has the possibility of various conformers between two cyclopentadienyl rings. We have reported the preparation of new dpmf ligand and its reaction with [PdCl₂(MeCN)₂] to give the cyclic dimer [Pd₂Cl₄(dpmf)₂] [2]. We report here the preparation of linear arene ruthenium and pentamethylcyclopentadienyl rhodium complexes bridged by the dpmf ligand and their electrochemical behaviors, in which for comparison the reaction with dppf was also carried out.

When arene ruthenium complex [(η^6 -1,2,3,4-Me₄C₆H₂)₂Ru₂Cl₄] **1a** was treated with dpmf in CH₂Cl₂ at room temperature in a 1:1 ratio, orange crystals **2a**, formulated as [(η^6 -1,2,3,4-Me₄C₆H₂)₂Ru₂Cl₄(μ -dpmf-*P,P'*)], were isolated in 75% yield.^{2,3} The ¹H NMR spectrum in CDCl₃ showed

three signals at δ 1.58, 2.04 (d, $J_{\text{PH}} = 2.0$ Hz) and 4.16 (d, $J_{\text{PH}} = 3.2$ Hz) ppm consisting of a 6:6:2 intensity ratio for two kinds of methyl groups and aromatic protons on the arene rings, in which one of two methyl groups did not show the coupling with the P atom. This behavior has been observed in the ruthenium complexes of the phosphines having the 2,6-dimethoxyphenyl groups [3]. The CH₂ protons appeared at δ 3.19 ppm and cyclopentadienyl ones at 3.46 and 3.56 ppm as singlets. The ³¹P{¹H} NMR spectrum showed a singlet at δ 32.4 ppm. The X-ray analysis showed that two arene ruthenium moieties are bridged through the dpmf ligand and have a piano-stool structure (Fig. 1).⁴ The

³ **2a** (75%). ¹H NMR (CDCl₃; 250 MHz): δ 1.58 (s, C₆Me₂), 2.04 (d, $J_{\text{PH}} = 2.0$ Hz, C₆Me₂), 3.19 (bs, PCH₂), 3.46 (s, C₅H₂), 3.56 (s, C₅H₂), 4.16 (d, $J_{\text{PH}} = 3.3$ Hz, C₆H₂), 7.2–7.6 (m, Ph). ³¹P{¹H} NMR (CDCl₃; 100 MHz): δ 32.4 ppm. **2b** (53%). ¹H NMR (CDCl₃; 250 MHz): δ 1.64 (s, C₆Me₆), 3.07 (s, PCH₂), 3.47 (s, C₅H₂), 4.51 (s, C₅H₂), 7.2–7.6 (m, Ph). ³¹P{¹H} NMR (CDCl₃; 100 MHz): δ 30.6 ppm.

⁴ Crystal data: C₅₆H₆₀Cl₄P₂Ru₂Fe (orange), triclinic P1 (No. 2), $a = 12.802(6)$ Å, $b = 19.111(6)$ Å, $c = 11.438(4)$ Å, $\alpha = 98.93(3)^\circ$, $\beta = 108.57(3)^\circ$, $\gamma = 90.42(3)^\circ$, $V = 2615(1)$ Å³, $z = 2$. Data were collected on a Rigaku AFC5s diffractometer in the range $50^\circ > 2\theta > 3^\circ$ (9219 independent reflections). The structure was solved by direct methods and refined by full-matrix least-squares technique (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were induced in calculated positions) to $R = 0.057$ and $R_w = 0.054$ ($w = 1/\sigma^2(F_o)$) for 4114 reflections ($I > 3\sigma(I)$).

^{*} Corresponding author.

¹ On leave from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

² Elemental analysis was in agreement with the calculated value. The chemical shifts of ³¹P{¹H} NMR spectra were calibrated to 85% H₃PO₄ as an external reference.

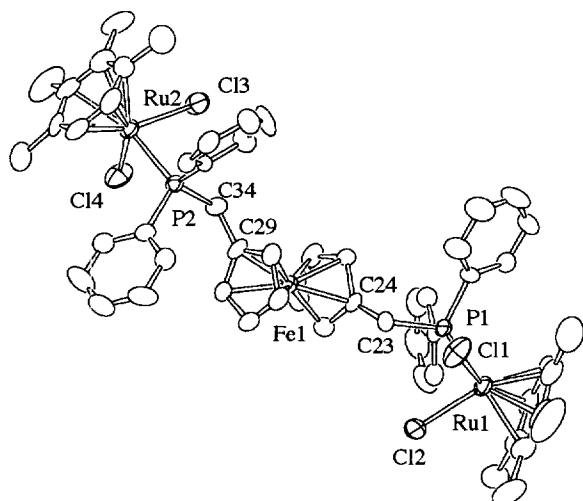


Fig. 1. Molecular structure of $[(\eta^6\text{-}1,2,3,4\text{-Me}_4\text{C}_6\text{H}_2)_2\text{Ru}_2\text{Cl}_4(\mu\text{-dpmf-}P,P')]$ **2a**. Preliminary materials. (1) $[(\eta^6\text{-}1,2,3,4\text{-Me}_4\text{C}_6\text{H}_2)_2\text{Ru}_2\text{Cl}_4(\mu\text{-dpmf-}P,P')]$ **2a**. (a) Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$; (b) anisotropic thermal parameters; and (c) bond lengths and angles.

Ru–P bond length is 2.340(3) Å, longer than those in other ruthenium phosphine complexes [4–6]. The average torsion angle of the C23C24Fe1C29 and C24Fe1C29C34 bonds is 75(1)°. The two Cp rings have an anticlinal eclipsed conformation. A similar complex **2b** was obtained from the reaction of $[(\eta^6\text{-Me}_6\text{C}_6)_2\text{Ru}_2\text{Cl}_4]$ **1b** with dpmf^{2,3}. When dpmf was treated with bis[dichloro(pentamethylcyclopentadienyl)rhodium] $[\text{Cp}_2^*\text{Rh}_2\text{Cl}_4]$ in CH_2Cl_2 at room temperature, the complex formulated as $[\text{Cp}_2^*\text{Rh}_2\text{Cl}_4(\text{dpmf})]$ **3** was obtained⁵ and the structure is assumed to have a linear phosphine-bridged structure similar to **2a** and **2b**. The ^1H NMR spectrum showed two well-defined doublets at δ 1.29 ($J_{\text{PH}} = 3.5$ Hz) and 3.67 ($J_{\text{PH}} = 6.3$ Hz) in a 30:4 intensity ratio, assignable to methyl and methylene protons, respectively. The cyclopentadienyl protons appeared at δ 3.19 and 3.62 ppm as singlets. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a doublet at δ 33.9 ($J_{\text{RHP}} = 141$ Hz). These spectral data were in agreement with the proposed structure.

It is known that the reaction of $[(p\text{-cymene})_2\text{Ru}_2\text{Cl}_4]$ with dppf gave $[(p\text{-cymene})_2\text{Ru}_2\text{Cl}_4(\mu\text{-dppf-}P,P')]$, but the detailed structural analysis has not been examined [7]. The reaction of **1a** with dppf was carried out and produced $[(\eta^6\text{-}1,2,3,4\text{-Me}_4\text{C}_6\text{H}_2)_2\text{Ru}_2\text{Cl}_4(\mu\text{-dppf-}P,P')]$ **4a** in 75% yield.⁶

⁵ **3** (85%). ^1H NMR(CDCl_3 ; 250 MHz): δ 1.29 (d, $J_{\text{PH}} = 3.5$ Hz, C_5Me_5), 3.19 (s, C_5H_2), 3.62 (bs, C_5H_2), 3.67 (d, $J_{\text{PH}} = 6.3$ Hz, PC_6H_2), 7.3–7.7 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; 100 MHz): δ 33.9 ($J_{\text{RHP}} = 141$ ppm).

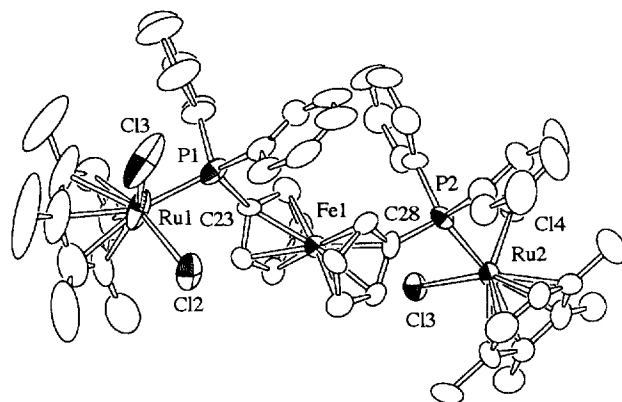


Fig. 2. Molecular structure of $[(\eta^6\text{-}1,2,3,4\text{-Me}_4\text{C}_6\text{H}_2)_2\text{Ru}_2\text{Cl}_4(\mu\text{-dppf-}P,P')]$ **4a**. Preliminary materials. (2) $[(\eta^6\text{-}1,2,3,4\text{-Me}_4\text{C}_6\text{H}_2)_2\text{Ru}_2\text{Cl}_4(\mu\text{-dppf-}P,P')]$ **4a**. (a) Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$; (b) anisotropic thermal parameters; and (c) bond lengths and angles.

The two methyl protons of the arene ring appeared at δ 1.68 (s) and 2.05 (d, $J_{\text{PH}} = 2.5$ Hz) ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum appeared at δ 20.7 ppm, in the higher magnetic field by ca. 10 ppm than that of the corresponding dpmf complex. The X-ray analysis showed that the molecule also has a phosphine bridged structure.⁷ The average torsion angle of the P1C23Fe1C28 and P2C28Fe1C23 bond is $-65(1)^\circ$ and two Cp rings showed an anticlinal staggered conformation (Fig. 2). The Ru–P bond lengths are 2.352(4) and 2.349(4) Å, not different from that of **2a**. A reaction of **1a** with dppf was carried out in a 1:2 ratio in the presence of NaPF_6 to give the chelated complex $[(\eta^6\text{-}1,2,3,4\text{-Me}_4\text{C}_6\text{H}_2)\text{RuCl}(\text{dppf-}P,P')][\text{PF}_6]$ **5a**.⁸ Complex $[(\eta^6\text{-Me}_6\text{C}_6)\text{RuCl}(\text{dppf-}P,P')][\text{PF}_6]$ **5b**

⁶ **4a** (75%). ^1H NMR(CDCl_3 ; 250 MHz): δ 1.68 (s, C_6Me_2), 2.046 (d, $J_{\text{PH}} = 2.5$ Hz, C_6Me_2), 3.96 (d, $J_{\text{PH}} = 3.5$ Hz, C_6H_2), 4.06, 4.08 (s, C_5H_2), 7.2–7.7 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; 100 MHz): δ 20.7 ppm.

⁷ Crystal data: $\text{C}_{55}\text{H}_{58}\text{Cl}_6\text{P}_2\text{Ru}_2\text{Fe}$ (orange), triclinic $P1$ (No. 2), $a = 15.044(7)$ Å, $b = 17.664(3)$ Å, $c = 10.586(2)$ Å, $\alpha = 99.64(2)^\circ$, $\beta = 113.9(1)^\circ$, $\gamma = 94.74(2)^\circ$, $V = 2744(1)$ Å³, $z = 2$. Data were collected on a Rigaku AFC5s diffractometer in the range $50^\circ > 2\theta > 3^\circ$ (9660 independent reflections). The structure was solved by Patterson methods (DIRDIF92 Patty) and refined by full-matrix least-squares technique (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were induced in calculated positions) to $R = 0.069$ and $R_w = 0.077$ ($w = 1/\sigma^2(F_o)$) for 4356 reflections ($I > 3\sigma(I)$).

⁸ **5a** (26%). ^1H NMR (CDCl_3 ; 250 MHz): δ 1.28 (bs, C_6Me_2), 1.92 (bs, C_6Me_2), 4.01, 4.30, 4.84, 5.04 (bs, C_5H), 4.84 (bs, C_6H_2), 7.4–7.7 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; 100 MHz): δ 36.7, -144.5 (hep.) ppm. **5b** (26%). ^1H NMR (CDCl_3 ; 250 MHz): δ 1.53 (s, C_6Me_6), 3.98, 4.11, 4.25, 4.94 (bs, C_5H), 7.4–7.9 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; 100 MHz): δ 34.0 (s, dppf), -144.5 (hep.) $J_{\text{PF}} = 709$ Hz, $P\text{F}$ ppm.

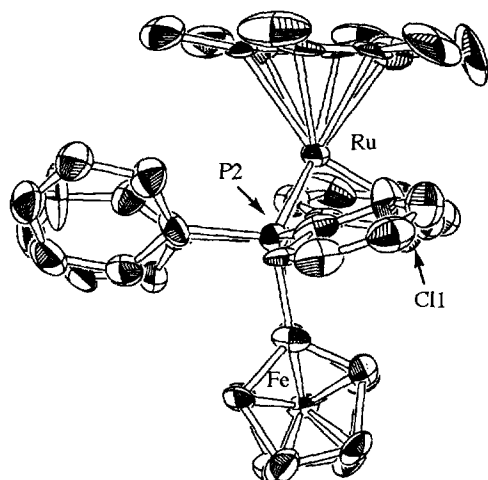


Fig. 3. Molecular structure of $[(\eta^6\text{-Me}_6\text{C}_6)\text{RuCl}(\text{dppf-}P,P')](\text{PF}_6)$ **5b**. Preliminary materials. (3) $[(\eta^6\text{-Me}_6\text{C}_6)_2\text{Ru}_2\text{Cl}_4(\text{dppf-}P,P')]$ **5b**. (a) Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$; (b) anisotropic thermal parameters; and (c) bond lengths and angles.

was obtained in 79% yield from $[(\eta^6\text{-Me}_6\text{C}_6)_2\text{Ru}_2\text{Cl}_4]$ and dppf in the presence of NaPF_6 .⁷ In ^1H NMR spectrum of these complexes **5a** and **5b**, the cyclopentadienyl ring protons appeared in the region from δ 4.0 to 5.0 ppm as four singlets. This magnetic nonequivalence is responsible for the rigid ferrocene moiety as depicted in Fig. 3.⁹ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a peak at 36.7 ppm in lower magnetic field than that of **2a**.

The cyclic voltammograms showed two quasi-reversible redox couples at -0.02 and 0.67 V for **2a** and at 0.01 and 0.62 V for **2b**, respectively; former redox-

couple for each complex is an $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ couple and the latter one is a $\text{Ru}^{2+} \rightleftharpoons \text{Ru}^{3+}$ couple.¹⁰ Based on the redox potential of a $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair, the electron-withdrawing ability of the groups suggested to decrease in the order of $(\text{C}_6\text{Me}_6)\text{RuCl}_2 > (\text{C}_6\text{H}_2\text{Me}_4)\text{RuCl}_2$. The redox potential of the $\text{Ru}^{2+} \rightleftharpoons \text{Ru}^{3+}$ couple in the $\text{C}_6\text{Me}_4\text{H}_2$ complex is more positive than that of the C_6Me_6 one, depending on electron-richness on the arene ring. A similar trend was observed for the dppf complexes. The shift of the $\Delta E_{1/2}$ value of the $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ couple ($E_{1/2}(\text{complex}) - E_{1/2}(\text{free}) = \text{ca. } 0.1\text{--}0.16$ V) in the dppf complexes is larger than that (ca. 0.02 V) of the dpmf ones. It is reasonable that the presence of the methylene group between the Cp ring and P atom is the cause of decrease of electronic effect for the iron ion. Further developments are currently underway.

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⁹ Crystal data: $\text{C}_{46}\text{H}_{46}\text{ClP}_3\text{F}_6\text{RuFe}$ (orange), monoclinic $P2_1/n$ (No. 14), $a = 15.036(4)$, $b = 17.192(5)$, $c = 15.983(3)$ Å, $\beta = 92.92(2)$, $V = 4126(1)$ Å³, $z = 4$. Data were collected on a Rigaku AFC5s diffractometer in the range $50^\circ > 2\theta > 3^\circ$ (7524 independent reflections). The structure was solved by Patterson methods (DIRDIF92 Patty) and was refined by full-matrix least-squares technique (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were induced in calculated positions) to $R = 0.070$ and $R_w = 0.079$ ($w = 1/\sigma^2(F_o)$) for 3389 reflections ($I > 3\sigma(I)$).

¹⁰ The complex (0.1 mM) were measured at the sweep rate of 0.2 V s^{-1} in a 0.1 M $n\text{-BuNClO}_4/\text{MeCN}$. A Ag/AgNO_3 (0.1 M)/0.1 M $[n\text{-Bu}_4\text{N}](\text{ClO}_4)/\text{MeCN}$ system was used as a reference electrode and all potentials were calibrated relative to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ (1 mM in MeCN).