

# A novel heterobimetallic rotation system: characterization of palladium(II) complexes with 2-pyridylethylferrocenecarboxamides

Toshiyuki Moriuchi, Isao Ikeda, Toshikazu Hirao \*

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan*

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## Abstract

2-(4-Pyridyl)ethylferrocenecarboxamide (4-PEFA) and 2-(2-pyridyl)ethylferrocenecarboxamide (2-PEFA) served as monodentate ligands to form the corresponding 2:1 trans-complexes with  $\text{PdCl}_2(\text{MeCN})_2$ . The rotational barrier of the two pyridyl rings in  $\text{PdCl}_2(2\text{-PEFA})_2$  was  $14.9 \text{ kcal mol}^{-1}$ , being in sharp contrast to the free rotation of  $\text{PdCl}_2(4\text{-PEFA})_2$  above  $25^\circ\text{C}$ . These complexes provide examples for heterobimetallic rotation systems.

**Keywords:** Palladium(II) complex; Ferrocene ligand; Heterobimetallics; Fe; Pd

## 1. Introduction

Metallocenes are often compared with an atomic ball bearing, since two cyclopentadienyl rings rotate with respect to each other about the metal center. Such a system is envisaged to be applied to a molecular receptor. Complexation of particular molecules [1] or ions [2] with metallocene receptors has become an interesting area in both organic and inorganic chemistry. Molecular design including coordination sites is a key factor to achieve an efficient system. A previous paper demonstrated that 2- and 4-aminopyridines react with 1,1'-ferrocenedicarboxylic acid chloride in a different way to give the imide-bridged [3]ferrocenophane and ferrocenedicarboxamide respectively [3]. Pyridyl pendant moieties are considered to participate in coordination [4], which allows us to construct a heterobimetallic ball bearing system. We herein report a synthesis and characterization of the novel palladium(II) complexes with ferrocene ligands possessing a 2- or 4-pyridyl coordination moiety.

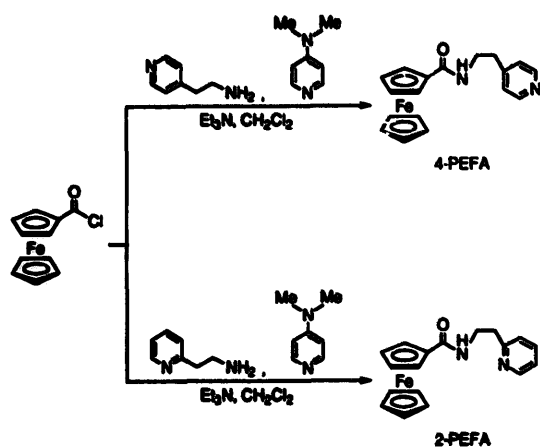
## 2. Results and discussion

The ferrocene ligands, 2-(4-pyridyl)ethylferrocenecarboxamide (4-PEFA) and 2-(2-pyridyl)ethylferrocenecarboxamide (2-PEFA), were readily prepared from ferrocenecarboxylic acid chloride and 4- and 2-(2-aminoethyl)pyridine, respectively, as shown in Scheme 1.

Complexation behavior of both ligands possessing one pendant group was investigated. Treatment of 4-PEFA with  $\text{PdCl}_2(\text{MeCN})_2$  afforded the 2:1 trans-palladium complex,  $\text{PdCl}_2(4\text{-PEFA})_2$ , in a 72% yield (Eq. (1)). The structure of the isolated complex was elucidated by spectral data. The same down-field shift of both pyridyl protons in  $^1\text{H-NMR}$  implies the equal coordination of two pyridyl nitrogen atoms to palladium. The trans-conformation was confirmed by far infra-red Pd–Cl stretching frequency [5].

The site of the pyridyl nitrogen atom is considered to affect the complexation. Use of 2-PEFA possessing the 2-pyridyl group instead 4-PEFA also led to the formation of the 2:1 trans-complex with  $\text{PdCl}_2(\text{MeCN})_2$  in an 84% yield (Eq. (2)). Spectral data support the similar complexation as observed in  $\text{PdCl}_2(4\text{-PEFA})_2$ , but it should be noted that two different kinds of the down-

\* Corresponding author.



field pyridyl proton were observed at 25°C. This result indicates the rotational barrier of the pendant pyridyl group about palladium, which was ascertained by the variable-temperature  $^1\text{H-NMR}$  spectra. The spectra of  $\text{PdCl}_2(2\text{-PEFA})_2$  at various temperatures are shown in Fig. 1. The peaks coalesced above 90°C and lowering the temperature resulted in the separation of the resonances for the pyridyl protons. The isomer ratio calculated from the peak area of these new peaks was about 50/50 at 40°C, but 36/64 at -40°C. The rotational barrier  $E_a$  for the isomerism was calculated as 14.9 kcal mol $^{-1}$  from the Arrhenius equation. Such a barrier was not detected in the case of  $\text{PdCl}_2(4\text{-PEFA})_2$ . Ortho substitution of a pyridine ring largely reflected on the rotation isomerism.

The redox properties of the palladium complexes thus obtained were investigated by cyclic voltammetry (Table 1). Compared with the parent ferrocene, the iron redox couple of 4-PEFA and 2-PEFA was shifted toward more positive values due to the electron-withdrawing carbamoyl group. In both cases, the complexation

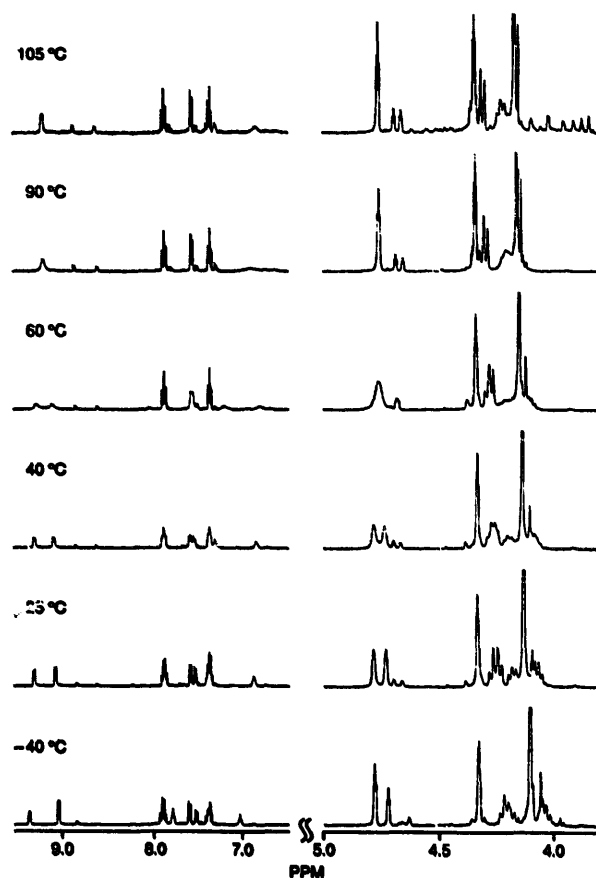
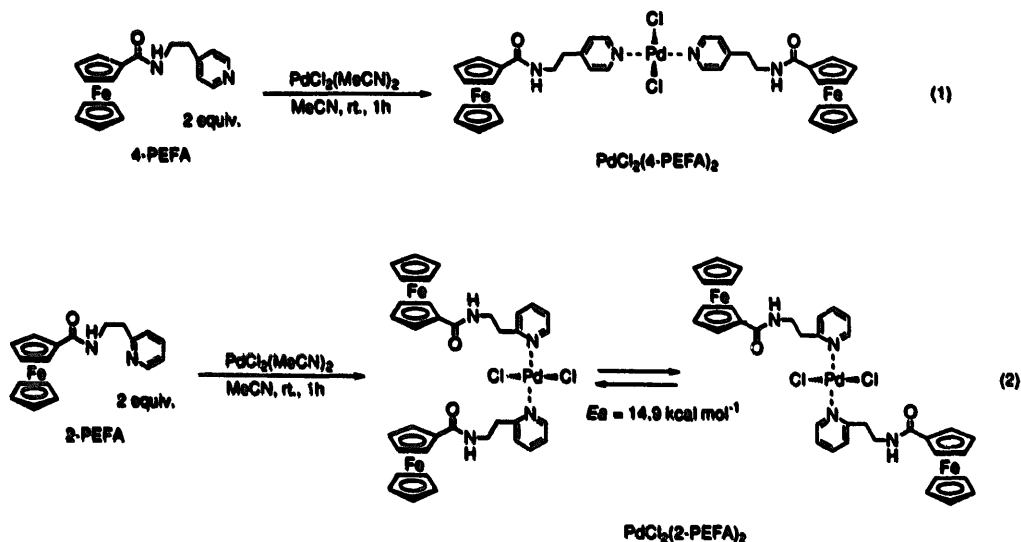


Fig. 1. Variable-temperature 400 MHz  $^1\text{H-NMR}$  spectra of  $\text{PdCl}_2(2\text{-PEFA})_2$ .

did not affect the electronic environment of iron, indicating no essential interaction between palladium and iron in these conformations.

These complexes provide examples for hetero-bimetallic systems for free and restricted rotation depending on the structure of coordination ligands.



### 3. Experimental details

All chemicals and solvents were dried and purified by usual methods. Melting points were measured using a Yanagimoto micromelting point apparatus and are uncorrected. Infra-red spectra were recorded on a Perkin–Elmer FT-IR 1605. Far infra-red spectra were recorded on an Hitachi 270-50 spectrophotometer.  $^1\text{H-NMR}$  spectra were recorded on a JEOL JNM-GSX-400 (400 MHz) spectrometer and a Bruker AM-600 (600 MHz) spectrometer with tetramethylsilane as an internal standard.  $^{13}\text{C-NMR}$  spectra were recorded on a Bruker AM-600 (150 MHz) spectrometer. The fast atom bombardment mass spectra were run on a JEOL JMS-DX303HF spectrometer. The cyclic voltammetry measurements were performed on a Hokuto Denko potentiostat–galvanostat HA-301S and a Hokuto Denko function generator HB-104S with a three-electrode system consisting of a glassy-carbon working electrode, a platinum auxiliary electrode, and a KCl-saturated calomel reference electrode. Cyclic voltammograms were recorded with Graphtec WX 1000.

#### 3.1. Syntheses

##### 3.1.1. 2-(4-Pyridyl)ethylferrocenecarboxamide (4-PEFA)

To a stirred mixture of 4-(2-aminoethyl)pyridine (0.366 g, 3.0 mmol), 4-dimethylaminopyridine (9.2 mg, 0.075 mmol), and triethylamine (1.525 g, 15 mmol) in dichloromethane (10 ml) was dropwise added ferrocenecarboxylic acid chloride (0.75 g, 3.0 mmol) in dichloromethane (20 ml) under nitrogen at 0°C. The mixture was stirred at 0°C for 7 h and then at room temperature for 17 h. The resulting mixture was diluted with dichloromethane (20 ml), washed with saturated  $\text{NaHCO}_3$  aqueous solution and brine, and dried over  $\text{MgSO}_4$ . The solvent was evaporated in vacuo and the residue was chromatographed over an alumina column eluting with dichloromethane. 4-PEFA was isolated in an 86% yield as an orange plate by recrystallization from dichloromethane.

M.p. 153–155°C (uncorrected); IR (KBr,  $\text{cm}^{-1}$ ) 3300 (NH), 1632 (C=O), 1544 (C=C);  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.48 (dd, 2H,  $J = 4.4, 1.7$  Hz, Py), 7.27

(dd, 2H,  $J = 4.4, 1.7$  Hz, Py), 6.54(br, 1H, NH), 4.61 (t, 2H,  $J = 2.0$  Hz, Cp), 4.31 (t, 2H,  $J = 2.0$  Hz, Cp), 4.09 (s, 5H, Cp), 3.56 (q, 2H,  $J = 7.0$  Hz,  $\text{CH}_2$ ), 2.90 (t, 2H,  $J = 7.0$  Hz,  $\text{CH}_2$ );  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  170.1 (C=O), 150.3 (Py), 149.4 (Py), 125.0 (Py), 77.3 (*ipso* Cp), 70.7 (Cp), 70.1 (Cp), 68.6 (Cp), 39.7 ( $\text{CH}_2$ ), 35.4 ( $\text{CH}_2$ ); MS (FAB)  $m/z$  335 ( $\text{M}^+ + 1$ ). Anal. Found: C, 63.61; H, 5.51; N, 8.30.  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{FeO} \cdot 0.25\text{H}_2\text{O}$ . Calc.: C, 63.83; H, 5.51; N, 8.27%.

##### 3.1.2. 2-(2-Pyridyl)ethylferrocenecarboxamide (2-PEFA)

To a stirred mixture of 2-(2-aminoethyl)pyridine (0.245 g, 2.0 mmol), 4-dimethylaminopyridine (6.0 mg, 0.05 mmol), and triethylamine (1.016 ml, 10 mmol) in dichloromethane (10 ml) was dropwise added ferrocenecarboxylic acid chloride (0.50 g, 2.0 mmol) in dichloromethane (20 ml) under nitrogen at 0°C. The mixture was stirred at 0°C for 7 h and then at room temperature for 17 h. The resulting mixture was diluted with dichloromethane (20 ml), washed with saturated  $\text{NaHCO}_3$  aqueous solution and brine, and dried over  $\text{MgSO}_4$ . The solvent was evaporated in vacuo and the residue was chromatographed over an alumina column eluting with dichloromethane. 2-PEFA was isolated in an 85% yield as an orange yellow needle by recrystallization from dichloromethane.

M.p. 143–144°C (uncorrected); IR (KBr,  $\text{cm}^{-1}$ ) 3300 (NH), 1628 (C=O), 1556 (C=C);  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.56 (ddd, 1H,  $J = 4.9, 1.8, 1.1$  Hz, Py), 7.69 (dt, 1H,  $J = 7.7, 1.8$  Hz, Py), 7.29 (dt, 1H,  $J = 7.7, 1.1$  Hz, Py), 7.20 (ddd, 1H,  $J = 7.7, 4.9, 1.1$  Hz, Py), 6.79 (br, 1H, NH), 4.62 (t, 2H,  $J = 1.9$  Hz, Cp), 4.31 (t, 2H,  $J = 1.9$  Hz, Cp), 4.09 (s, 5H, Cp), 3.65 (q, 2H,  $J = 6.7$  Hz,  $\text{CH}_2$ ), 3.03 (t, 2H,  $J = 6.7$  Hz,  $\text{CH}_2$ );  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  170.0 (C=O), 160.5 (Py), 149.9 (Py), 137.1 (Py), 124.0 (Py), 122.1 (Py), 77.5 (*ipso* Cp), 70.7 (Cp), 70.1 (Cp), 68.6 (Cp), 39.3 ( $\text{CH}_2$ ), 38.0 ( $\text{CH}_2$ ); MS (FAB)  $m/z$  335 ( $\text{M}^+ + 1$ ). Anal. Found: C, 64.52; H, 5.47; N, 8.44.  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{FeO}$ . Calc.: C, 64.69; H, 5.43; N, 8.38%.

##### 3.1.3. $\text{PdCl}_2(4\text{-PEFA})_2$

A mixture of 4-PEFA (13.4 mg, 0.04 mmol) and  $\text{PdCl}_2(\text{MeCN})_2$  (5.2 mg, 0.02 mmol) in acetonitrile (2.0 ml) was stirred under nitrogen at room temperature for 1 h. The reaction mixture was filtered and concentrated.  $\text{PdCl}_2(4\text{-PEFA})_2$  was isolated in a 72% yield as a yellow needle by recrystallization from acetonitrile.

M.p. 207–210°C (decomp.); IR (KBr,  $\text{cm}^{-1}$ ) 3259 (NH), 1619 (C=O), 1535 (C=C), 368 (Pd–Cl);  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{CN}$ , 25°C)  $\delta$  8.64 (dd, 4H,  $J = 5.1, 1.5$  Hz, Py), 7.35 (dd, 4H,  $J = 5.1, 1.5$  Hz, Py), 6.58 (br, 2H, NH), 4.61 (t, 4H,  $J = 1.7$  Hz, Cp), 4.32 (t, 4H,  $J = 1.7$  Hz, Cp), 4.11 (s, 10H, Cp), 3.57 (q, 4H,  $J = 6.7$  Hz,  $\text{CH}_2$ ), 2.96 (t, 4H,  $J = 6.7$  Hz,  $\text{CH}_2$ );

Table 1  
Redox potential

Ferrocene derivative and complex	$E_{1/2}^a$
Ferrocene	0.330
4-PEFA	0.564
$\text{PdCl}_2(4\text{-PEFA})_2$	0.558
2-PEFA	0.556
$\text{PdCl}_2(2\text{-PEFA})_2$	0.567

<sup>a</sup> V vs. saturated calomel reference electrode.

$^{13}\text{C}$ -NMR (150 MHz,  $d_6$ -DMSO, 25°C)  $\delta$  169.0 (C=O), 152.7 (Py), 152.3 (Py), 125.6 (Py), 76.5 (*ipso* Cp), 69.8 (Cp), 69.3 (Cp), 68.0 (Cp), 38.6 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ); MS (FAB)  $m/z$  846 ( $\text{M}^+ + 1$ ). Anal. Found: C, 51.05; H, 4.28; N, 6.66; Cl, 8.13.  $\text{C}_{36}\text{H}_{36}\text{N}_4\text{Cl}_2\text{Fe}_2\text{O}_2\text{Pd}$ . Calc.: C, 51.13; H, 4.29; N, 6.63; Cl, 8.38%.

### 3.1.4. $\text{PdCl}_2(2\text{-PEFA})_2$

A mixture of 2-PEFA (13.4 mg, 0.04 mmol) and  $\text{PdCl}_2(\text{MeCN})_2$  (5.2 mg, 0.02 mmol) in acetonitrile (2.0 ml) was stirred under nitrogen at room temperature for 1 h. The reaction mixture was filtered and concentrated.  $\text{PdCl}_2(2\text{-PEFA})_2$  was isolated in an 84% yield as a yellow needle by recrystallization from chloroform:acetonitrile (1:1 v/v).

M.p. 158–161°C (decomp.); IR (KBr,  $\text{cm}^{-1}$ ) 3230 (NH), 1621 (C=O), 1544 (C=C), 344 (Pd–Cl);  $^1\text{H}$ -NMR (600 MHz,  $\text{CD}_3\text{CN}$ , 25°C)  $\delta$  9.29 (d, 1.8H,  $J = 5.6$  Hz, Py), 9.05 (d, 2.2H,  $J = 5.6$  Hz, Py), 7.90–7.84 (m, 4H, Py), 7.60 (d, 2.2H,  $J = 7.8$  Hz, Py), 7.54 (d, 1.8H,  $J = 7.8$  Hz, Py), 7.42–7.36 (m, 6.2H, Py and NH), 6.90 (br, 1.8H, NH), 4.78 (t, 4.4H,  $J = 1.7$  Hz, Cp), 4.73 (t, 3.6H,  $J = 1.7$  Hz, Cp), 4.32 (t, 8H,  $J = 1.7$  Hz, Cp), 4.27–4.23 (m, 8H,  $\text{CH}_2$ ), 4.19–4.15 (m, 3.6H,  $\text{CH}_2$ ), 4.12–4.01 (m, 24.4H, Cp and  $\text{CH}_2$ );  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CD}_3\text{CN}$ , 25°C)  $\delta$  170.6 (C=O), 162.3 (Py), 162.0 (Py), 153.6 (Py), 153.3 (Py), 139.7 (Py), 139.6 (Py), 126.9 (Py), 126.5 (Py), 123.9 (Py), 123.8 (Py), 78.8 (*ipso* Cp), 77.1 (*ipso* Cp), 70.9 (Cp), 70.8 (Cp), 70.2 (Cp), 70.1 (Cp), 69.0 (Cp), 68.9 (Cp), 40.2 ( $\text{CH}_2$ ), 40.0 ( $\text{CH}_2$ ), 39.1 ( $\text{CH}_2$ ), 39.0 ( $\text{CH}_2$ ); MS (FAB)  $m/z$  846 ( $\text{M}^+ + 1$ ). Anal. Found: C, 48.25; H, 4.10; N, 6.22; Cl, 13.80.  $\text{C}_{36}\text{H}_{36}\text{N}_4\text{Cl}_2\text{Fe}_2\text{O}_2\text{Pd} \cdot 0.5\text{CHCl}_3$ . Calc.: C, 48.42; H, 4.06; N, 6.19; Cl, 13.71%.

### 3.2. Electrochemical experiments

All electrochemical measurements were carried out at 25°C under an atmospheric pressure of nitrogen, which was previously passed through a solution of the

same composition as the electrolysis solution. Cyclic voltammograms were obtained in the dichloromethane solutions containing 0.1 M  $\text{Bu}_4\text{NClO}_4$  as a supporting electrolyte ([ferrocene derivatives] =  $1 \times 10^{-3}$  M). Potentials were determined with reference to a KCl saturated calomel electrode at 100 mV  $\text{s}^{-1}$  scan rate.

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