



# Preparation, structure, and dynamic and electrochemical behaviors of dinuclear rhodium(I) complexes with bridging formamidinato ligands



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## ARTICLE INFO

### Article history:

Received 27 August 2015

Received in revised form

16 October 2015

Accepted 4 December 2015

Available online 15 December 2015

### Keywords:

Dirhodium(I) complexes

Formamidinato ligand

Crystal structures

Dynamic NMR

Cyclic voltammogram

## ABSTRACT

Dinuclear rhodium(I) complexes, [Rh(4-Me-pf)(cod)]<sub>2</sub> (**1**), [Rh(3,5-Me<sub>2</sub>-pf)(cod)]<sub>2</sub> (**2**), [Rh(4-Me-pf)(nbd)]<sub>2</sub> (**3**), [Rh(3,5-Me<sub>2</sub>-pf)(nbd)]<sub>2</sub> (**4**), and [Rh(2,6-F<sub>2</sub>-pf)(nbd)]<sub>2</sub> (**5**), have been synthesized and characterized by X-ray structure analysis, <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR, UV–vis, ESI-TOF-MS, and elemental analysis. In these complexes, two rhodium atoms are bridged by two formamidinato ligands and each rhodium atom is coordinated by one chelating cod or nbd ligand to form an approximately square planar coordination structure with two nitrogen atoms and two double bonds. The Rh–Rh distances are in the range of 3.2668 to 2.9726 Å, suggesting a direct bonding interaction between two rhodium atoms. Variable temperature NMR studies in CD<sub>2</sub>Cl<sub>2</sub> solution have revealed that **1–5** exhibit a novel dynamic behavior, that is, an interconversion between two enantiomers. The activation parameters for racemization have been determined by the line shape analyses of the <sup>1</sup>H and <sup>19</sup>F NMR spectra taken at various temperatures. Variable temperature NMR studies have also revealed that the rotation rates of the four aryl groups around N–C(aryl) bonds are extremely different in each complex. The cyclic voltammetry study has shown that the oxidation potentials corresponding to Rh<sup>3+</sup>/Rh<sup>2+</sup> are 0.41 V in the cod complexes (**1** and **2**) while those in the nbd complexes (**3–5**) have shown negative shift by ca. 0.2 V. The reasons for the difference in dynamic behaviors and redox properties among these complexes have been discussed.

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## 1. Introduction

A wide variety of studies have been done on the binuclear transition metal complexes, which include i) theoretical, spectroscopic, and magnetic studies to reveal metal–metal interactions, ii) structural modeling of biological molecules, and iii) catalytic activities for various reactions [1–11]. The aim of these explorations has been the use of transition metal ions such as rhodium and

iridium ions with bridging ligands to improve the stability and reactivity of the binuclear transition metal complexes. Since the first reports on binuclear chloride-bridged rhodium(I) complexes [Rh(μ-Cl)(cod)]<sub>2</sub> and [Rh(μ-Cl)(nbd)]<sub>2</sub> carrying 1,5-cyclooctadiene (cod) and 2,5-norbornadiene (nbd) as diene ligands [12–14], a number of analogous rhodium(I) complexes such as [Rh(L)(cod)]<sub>2</sub> (L = carboxylato, pyrazolato, and pyridine-2-olato) [7–9,15–19] and [Rh(L)(nbd)]<sub>2</sub> (L = carboxylato, pyrazolato, and pyridine-2-olato) have been investigated [8,9,20–22]. Some of these complexes have exhibited catalytic activities in the reactions such as hydroformylation, hydrogenation, and polymerization [7–9,23–27]. More recently, *N,N'*-bis(alkylphenyl or alkoxyphenyl)formamidinato anions (R<sub>m</sub>-pf<sup>−</sup>) have been extensively used as bridging ligands in transition metal chemistry [28–38], particularly in the preparation of binuclear paddle–wheel complexes [M<sub>2</sub>(R<sub>m</sub>-pf)<sub>4</sub>]<sup>0,1+,2+</sup> (M = Rhodium or Iridium ion) [39–45]. For example,

**Abbreviations:** 4-Me-pf, *N,N'*-bis(4-methylphenyl)formamidinato; 3,5-Me<sub>2</sub>-pf, *N,N'*-bis(3,5-dimethylphenyl)formamidinato; 2,6-F<sub>2</sub>-pf, *N,N'*-bis(2,6-difluorophenyl)formamidinato; cod, 1,5-cyclooctadiene; nbd, 2,5-norbornadiene.

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binuclear rhodium(II) complex  $[\text{Rh}_2(\text{R}_m\text{-pf})_4]$  was prepared by the reaction of dirhodium(II) mixed ligand complex  $\text{Rh}_2(\text{R}_m\text{-pf})_2(\text{O}_2\text{CCF}_3)_2$  with molten  $\text{H}(\text{R}_m\text{-pf})$  [46,47]. During the surveillance of the literature, we have found several papers reported by Piraino et al. [36,37,46–48] on the characterization and electrochemical studies of formamidinate-bridged rhodium(I) dimers,  $[\text{Rh}(4\text{-Me-pf})(\text{cod})]_2$  (**1**) and  $[\text{Rh}(4\text{-Me-pf})(\text{nbd})]_2$  (**3**). We were very much interested in these complexes as potent reducing agents. We have considered that the catalytic activity of these complexes can be finely tuned by the introduction of various substituents at the nitrogen and carbon atoms of the bridged ligands. Furthermore, the Rh–Rh catalytic center can be modulated sterically and electronically by the nature of diene ligands. Thus, the elucidation of the structural, spectroscopic, and redox properties of  $[\text{Rh}(\text{R}_m\text{-pf})(\text{L})]_2$  ( $\text{L} = \text{carboxylato}$ ,  $\text{pyrazolato}$ , and  $\text{pyridine-2-olato}$ ) is essential for the development of efficient catalysts. In this paper, we will report the syntheses, molecular structures, dynamic behavior, and redox properties of various formamidinate bridged binuclear complexes such as  $[\text{Rh}(4\text{-Me-pf})(\text{cod})]_2$  (**1**),  $[\text{Rh}(3,5\text{-Me}_2\text{-pf})(\text{cod})]_2$  (**2**),  $[\text{Rh}(4\text{-Me-pf})(\text{nbd})]_2$  (**3**),  $[\text{Rh}(3,5\text{-Me}_2\text{-pf})(\text{nbd})]_2$  (**4**), and  $[\text{Rh}(2,6\text{-F}_2\text{-pf})(\text{nbd})]_2$  (**5**) as shown in Scheme 1.

## 2. Experimental

### 2.1. Synthesis

$[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$  and  $[\text{Rh}(\mu\text{-Cl})(\text{nbd})]_2$  were prepared by the methods of Giordano et al. and Abel et al., respectively [12–14]. The formamidinate ligands were prepared using the modified method in literature [49].  $[\text{Rh}(4\text{-Me-pf})(\text{cod})]_2$  (**1**) and  $[\text{Rh}(3,5\text{-Me}_2\text{-pf})(\text{cod})]_2$  (**2**) were obtained by the reaction of  $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$  with  $\text{H}(\text{R}_m\text{-pf})$  ( $\text{R}_m = 4\text{-Me}$  and  $3,5\text{-Me}_2$ ) in toluene (Scheme 2), according to the method developed by Piraino et al. [48].  $[\text{Rh}(4\text{-Me-pf})(\text{nbd})]_2$  (**3**),  $[\text{Rh}(3,5\text{-Me}_2\text{-pf})(\text{nbd})]_2$  (**4**), and  $[\text{Rh}(2,6\text{-F}_2\text{-pf})(\text{nbd})]_2$  (**5**) were similarly obtained by the reaction of  $[\text{Rh}(\mu\text{-Cl})(\text{nbd})]_2$  with  $\text{H}(\text{R}_m'\text{-pf})$  ( $\text{R}_m' = 4\text{-Me}$ ,  $3,5\text{-Me}_2$ , and  $2,6\text{-F}_2$ ) in toluene (Scheme 3) [48].

#### 2.1.1. Typical procedure

In the preparation of **1–5**, we have slightly modified the method developed by Piraino et al. [48] and obtained the complexes in better yield. As shown in Schemes 2 and 3, a toluene solution containing  $\text{KOBu}^t$  (2.10 mmol) and the formamidinate ligands (2.10 mmol) was stirred for 12 h at room temperature, to which  $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$  or  $[\text{Rh}(\mu\text{-Cl})(\text{nbd})]_2$  (1.00 mmol) was added. The mixture was stirred for 6 h at room temperature. After condensation of the solution, *n*-hexane was added to the concentrated solution. The solution was kept at room temperature for a few days.

Orange colored single crystals were obtained from the solution. These crystals were filtered, washed with hexane, and dried under vacuum. Analytically pure samples were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ .

#### 2.1.2. $[\text{Rh}(4\text{-Me-pf})(\text{cod})]_2$ (**1**)

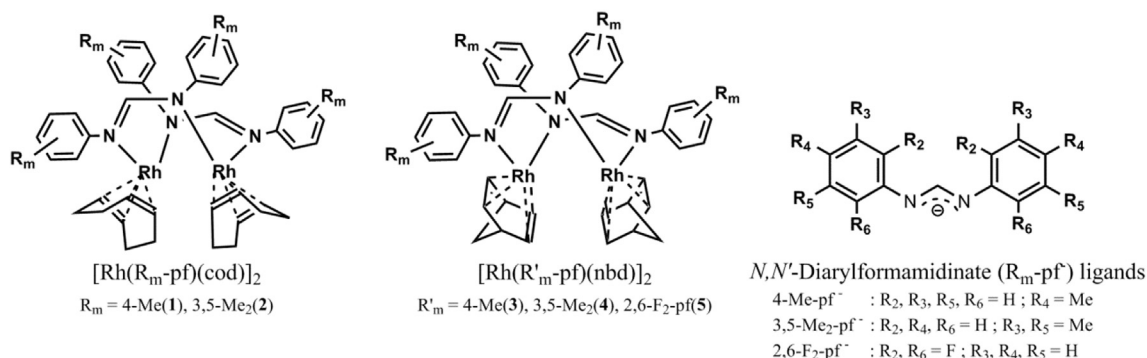
This complex was originally prepared and characterized by Piraino et al. [48]. We have added full  $^1\text{H}$  NMR data together with the assignments. UV–vis, IR, Reflectance, and HR-MS (ESI-TOF) data are also listed below. **1** was isolated in 80.2% yield (697 mg, 0.802 mmol). *Anal. Calcd.* for  $\text{C}_{46}\text{H}_{54}\text{N}_4\text{Rh}_2$ : C, 63.60; H, 6.27; N, 6.45%. *Found:* C, 63.41; H, 6.18; N, 6.29%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz, 298 K):  $\delta = 1.79$  (*cod*-CH<sub>2</sub>, 4H, m), 1.91 (*cod*-CH<sub>2</sub>, 4H, m), 2.29 (*p*-CH<sub>3</sub>, 12H, s), 2.54 (*cod*-CH<sub>2</sub>, 4H, m), 2.91 (*cod*-CH<sub>2</sub>, 4H, br), 3.82 (*cod*-CH, 4H, br), 4.35 (*cod*-CH, 4H, br), 7.02 (*m*-H, 8H, d,  $J = 8.0$  Hz), 7.18 (*o*-H, 8H, br), and 7.19 ppm (CH, 2H, t,  $J_{\text{Rh-H}} = 1.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz, 298 K):  $\delta = 20.8$  (*p*-CH<sub>3</sub>, q,  $J_{\text{C-H}} = 126$  Hz), 31.0 (*cod*-CH<sub>2</sub>, t,  $J_{\text{C-H}} = 127$  Hz), 31.4 (*cod*-CH<sub>2</sub>, t,  $J_{\text{C-H}} = 127$  Hz), 76.1 (*cod*-CH, br), 84.7 (*cod*-CH, br), 125.0 (*o*-C, d,  $J_{\text{C-H}} = 160$  Hz), 129.1 (*m*-C, d,  $J_{\text{C-H}} = 156$  Hz), 132.4 (*p*-C, s), 150.3 (*ipso*-C, s), and 165.0 ppm (CH, d,  $J_{\text{C-H}} = 169$  Hz). UV–vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon: 10^4 \text{ mol}^{-1}\text{dm}^3 \text{ cm}^{-1}$ ) = 241 (5.4, sh), 276 (8.2), 355 (1.7, sh), and 455 nm (0.7). Reflectance:  $\lambda_{\text{max}} = 296, 340, 379,$  and 460 nm. IR (KBr):  $\nu_{\text{N-C-N}} = 1561$  and  $\nu_{\text{C-H}} = 2829\text{--}3014 \text{ cm}^{-1}$ . HR-MS (ESI-TOF): *Calcd.* for  $[\text{M}]^+$ : 868.2453; *Found:* 868.2450 *m/z*.

#### 2.1.3. $[\text{Rh}(3,5\text{-Me}_2\text{-pf})(\text{cod})]_2$ (**2**)

**2** was isolated in 82.3% (761 mg, 0.823 mmol). *Anal. Calcd.* for  $\text{C}_{50}\text{H}_{62}\text{N}_4\text{Rh}_2$ : C, 64.93; H, 6.76; N, 6.06%. *Found:* C, 64.81; H, 6.54; N, 6.02%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz, 298 K):  $\delta = 1.83$  (*cod*-CH<sub>2</sub>, 4H, br), 1.92 (*cod*-CH<sub>2</sub>, 4H, br), 2.30 (*m*-CH<sub>3</sub>, 24H, s), 2.61 (*cod*-CH<sub>2</sub>, 4H, br), 2.92 (*cod*-CH<sub>2</sub>, 4H, br), 3.90 (*cod*-CH, 4H, br), 4.35 (*cod*-CH, 4H, br), 6.68 (*p*-H, 4H, s), 7.05 (*o*-H, 8H, br), and 7.21 ppm (CH, 2H, t,  $J_{\text{Rh-H}} = 2.0$  Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz, 298 K):  $\delta = 21.6$  (*m*-CH<sub>3</sub>, q,  $J_{\text{C-H}} = 126$  Hz), 31.2 (*cod*-CH<sub>2</sub>, t,  $J_{\text{C-H}} = 131$  Hz), 31.4 (*cod*-CH<sub>2</sub>, t,  $J_{\text{C-H}} = 126$  Hz), 76.5 (*cod*-CH, br), 84.4 (*cod*-CH, br), 123.2 (*o*-C, d,  $J_{\text{C-H}} = 163$  Hz), 124.5 (*p*-C, d,  $J_{\text{C-H}} = 167$  Hz), 137.7 (*m*-C, s), 152.7 (*ipso*-C, s), and 164.6 ppm (CH, d,  $J_{\text{C-H}} = 170$  Hz). UV–vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon: 10^4 \text{ mol}^{-1}\text{dm}^3 \text{ cm}^{-1}$ ) = 308 (2.1), 357 (1.0, sh), and 461 nm (0.4). Reflectance:  $\lambda_{\text{max}} = 310$  and 479 nm. IR (KBr):  $\nu_{\text{N-C-N}} = 1550$  and  $\nu_{\text{C-H}} = 2825\text{--}3018 \text{ cm}^{-1}$ . HR-MS (ESI-TOF): *Calcd.* for  $[\text{M}]^+$ : 924.3079; *Found:* 924.3094 *m/z*.

#### 2.1.4. $[\text{Rh}(4\text{-Me-pf})(\text{nbd})]_2$ (**3**)

This complex was originally prepared and characterized by Piraino et al. [48]. We have added full  $^1\text{H}$  NMR data together with the assignments. UV–vis, IR, Reflectance, and HR-MS (ESI-TOF) data are also listed below. **3** was isolated in 60.2% (504 mg, 0.602 mmol).



Scheme 1. Structural scheme of  $N,N'$ -diarylformamidinate ligands,  $[\text{Rh}(\text{R}_m\text{-pf})(\text{cod})]_2$  (**1–2**), and  $[\text{Rh}(\text{R}'_m\text{-pf})(\text{nbd})]_2$  (**3–5**).

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