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Short communication

Synthesis, structure, and electrochemical behavior of a new dinuclear Rh(III) complex bridged by a bpp^- ligand (bpp^- = 3,5-bis(2-pyridyl)pyrazolate)

Take-aki Koizumi *, Yusuke Ohkura, Erika Tsuda

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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ABSTRACT

The new dinuclear rhodium complex $[(Cp^*RhCl)_2(bpp)](PF_6)$ ($[\mathbf{1}](PF_6)$, Cp^* = pentamethylcyclopentadienyl, bpp = 3,5-bis(2-pyridyl)pyrazolate) was synthesized by the reaction of $[Cp^*RhCl_2]_2$ with 3,5-bis(2-pyridyl)pyrazole (bppH). $[\mathbf{1}](PF_6)$ was characterized by ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy and X-ray diffraction. The distance between the two Rh atoms in $[\mathbf{1}](PF_6)$ is 4.746(3) Å. A cyclic voltammogram of $[\mathbf{1}](PF_6)$ in acetonitrile shows three-step reduction peaks at $E_{pc} = -1.44$, -1.68 and -1.88 V (vs. Fc^+/Fc), which are assigned to the reduction of the two Rh(III) centers and the bpp^- ligand, respectively. $[\mathbf{1}](PF_6)$ catalyzes the reduction reaction of NAD^+ (nicotinamide adenine dinucleotide) using HCO_2^- as a reductant.

A new dinuclear rhodium complex $[(Cp^*RhCl)_2(bpp)](PF_6)$ ($[\mathbf{1}](PF_6)$, bpp = 3,5-bis(2-pyridyl)pyrazolate) was synthesized and characterized by NMR spectroscopy and X-ray crystallography. $[\mathbf{1}](PF_6)$ catalyzes the reduction reaction of NAD^+ (nicotinamide adenine dinucleotide) using HCO_2^- as a reductant

Rhodium complexes bearing one pentamethylcyclopentadienyl (Cp^*) ligand are reactive in a variety of interesting ways and exhibit catalytic activities based on the coordinative lability of the Cp^* ligand [1]. Previously, hydrogen transfer reactions to convert formate [2] and 2-propanol [3] to carbonyl compounds, catalyzed by $[Cp^*RhCl(N\text{-}N)]$ type complexes (N-N = a bidentate ligand coordinated to the metal center by two N atoms such as 2,2′-bipyridyl) have been studied. Multinuclear complexes containing multiple $[Cp^*Rh]$ units are expected to develop by the regulation of Rh–Rh distance [4]. 3,5-Bis(2-pyridyl)pyrazolate (bpp^-), which is shown in Chart 1, contains four N atoms that form two chelating sites for coordination with metals.

Dinuclear complexes with bpp^- as the bridging ligand have been prepared using various transition metals. In particular, first-row transition metals, such as Fe [5] and Cu [6] have mainly been used for the synthesis of the bpp^--coordinated complexes, and their magnetic properties have been reported. On the other hand, studies on second-row transition metals are limited. Several groups have studied dinuclear Ru complexes bearing a bridging bpp^- ligand in order to discover catalysts capable of oxidizing water [7]. There are very few synthetic examples of complexes of other second-row transition metals [8]. In the case of rhodium, only one example of a bpp^--coordinated mononuclear Rh complex, $[Cp^*RhCl(bppH)](PF_6)$, was reported by Rao et al. [9] A dinuclear Rh complex with a bridging bpp^- ligand has not been reported to date. In this paper, we report the first synthesis of a dinuclear Rh complex with a bridging bpp^- ligand, $[(Cp^*RhCl)_2(bpp)](PF_6)$ ($[\mathbf{1}](PF_6)$). The molecular structure and electrochemical properties of the complex are presented.

The dinuclear Rh complex $[\mathbf{1}](PF_6)$ was prepared by the reaction of $[Cp^*RhCl_2]_2$ with equimolecular amount of 3,5-bis(2-pyridyl)pyrazole (bppH), as shown in Scheme 1.

After anion exchange with NH_4PF_6, $[\mathbf{1}](PF_6)$ was obtained as an orange powder in 90% yield. The ESI-MS spectrum of $[\mathbf{1}](PF_6)$ shows $m/z = 767$ as a monocation pattern. The IR spectrum of the mononuclear Rh-bppH complex, $[Cp^*RhCl(bppH)](PF_6)$, showed a strong band at 3429 cm^{-1}, corresponding to the stretching frequencies of the N–H bond in the pyrazole ring [9]. In contrast, complex $[\mathbf{1}](PF_6)$ shows no peak in this region, indicating that $[\mathbf{1}](PF_6)$ does not contain an N–H proton due to the coordination of both Rh moieties to the bpp^- ligand.

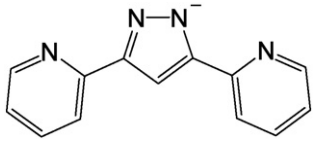

Chart 1. Structure of bpp^-.

* Corresponding author.
E-mail address: tkoizumi@res.titech.ac.jp (T. Koizumi).

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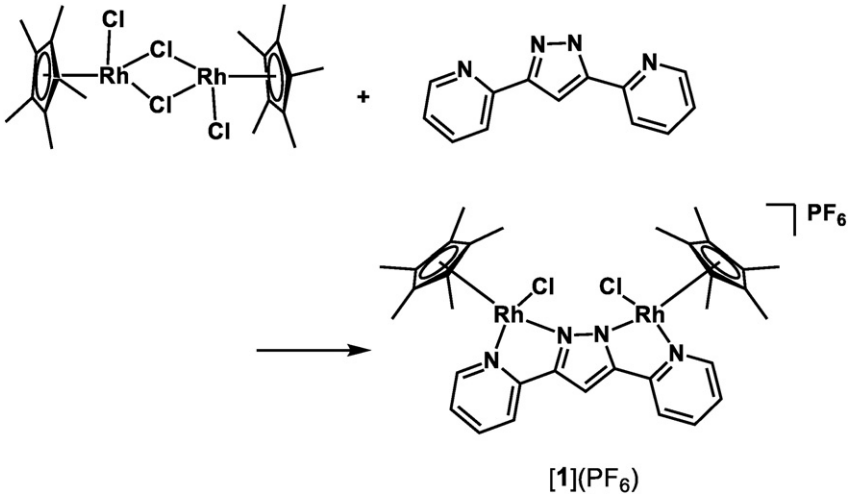

Scheme 1. Synthesis of complex [**1**](PF_6).

The ^{1}H NMR spectrum of [**1**](PF_6) in acetone-d_6 shows one Cp* resonance at δ 1.67 and five resonances for the bpp$^-$ ligand in the aromatic region. The peak ratios and numbers indicate that [**1**](PF_6) has a symmetrical structure.

[**1**](PF_6) was recrystallized from a CH_3CN–Et_2O solution to obtain good quality crystals for X-ray crystallography. Fig. 1 depicts the molecular structure of the cationic part of [**1**](PF_6) determined by X-ray crystallography.

In [**1**]$^+$, two [Cp*RhCl] units are coordinated to the bpp$^-$ ligand, and the two Cp* ligands (and two Cl ligands) coordinated to each Rh center are situated on mutually opposing sides of the bpp$^-$ ligand. The distance between Rh1–Rh2 is 4.746(3) Å, which is longer than that of [(η^6-benzene)$_2$Ru$_2$Cl$_2$(bpp)](BF_4) (4.395 Å) [9]. The dihedral angles between the pyrazolate ring and two pyridyl rings in the bpp ligand are 14.3(3)° and 17.0(3)°, respectively. Although they are larger than those of [(η^6-benzene)$_2$Ru$_2$Cl$_2$(bpp)](BF_4) (1.55° and 9.19°) [9], the bpp ligand has an almost planar structure. The slightly twisted structure of the bpp ligand in [**1**](PF_6) is considered to be due to the steric repulsion between the two Cp* ligands; the nearest C···C distance is 3.46(2) Å (C9–C17). The distances of Rh-Cp*$_{centroid}$ are 1.782(3) and 1.780(3) Å, respectively, which are similar to those of [Cp*RhCl(bpy)](ClO_4) (1.782 Å, bpy = 2,2′-bipyridine) [10] and [Cp*RhCl(Phen)](ClO_4) (1.776 Å, Phen = 1,10-phenanthroline) [11]. The bond lengths of Rh1–Cl1 and Rh2–Cl2 are 2.374(3) and 2.399(3) Å, respectively. They are similar or slightly longer than those of the [Cp*RhCl(N-N)] complexes (2.363(3)–2.394(2) Å, N-N = a bidentate ligand which contains a 2,2′-bipyridine structure) [2f,10–12].

The electronic spectrum of [**1**](PF_6) in CH_3CN is shown in Fig. 2, in which [**1**](PF_6) shows an absorption maximum at λ = 313 and 400 nm. The absorption band observed at λ = 313 nm is assigned to the π–π*/n–π* transitions [9], and the band at λ = 400 nm may be assigned to a metal-to-ligand charge transfer (MLCT) transition. These two absorption peaks are shifted to longer wavelengths than those of [Cp*RhCl(bppH)](PF_6) ([**2**](PF_6)), where λ = 292 and 366 nm. The bathochromic shift seems to be produced by expansion of the π-conjugation of the almost coplanarly fixed bpp ligand.

Electrochemical studies of [**1**](PF_6) and [**2**](PF_6) were performed in a CH_3CN solution. Fig. 3 displays the cyclic voltammogram (CV) of [**1**](PF_6), which exhibited three reduction peaks at E_{pc} = −1.42, −1.81 and −2.16 V (vs. Fc^+/Fc). The first two reduction waves are observed with re-oxidation waves at −1.15 and −1.73 V (vs. Fc^+/Fc), respectively. Each redox process can be assigned to one of the Rh(III)/Rh(I) redox process of the two Rh metal centers [13]. The latter reduction process may be assigned to the reduction of the bpp$^-$ ligand. On the other hand, [**2**](PF_6) shows one irreversible reduction peak at E_{pc} = −1.42 V (vs. Fc^+/Fc) (Fig. S1 in Supporting Information). This reduction process is considered to be the Rh(III)/Rh(I) redox process of the Rh metal center in [**2**](PF_6). The irreversibility of the CV of [**1**](PF_6) and [**2**](PF_6) suggests that the complexes undergoes structural changes through the Rh(III)-Rh(I) reduction–oxidation process.

[Cp*RhCl(N-N)] complexes have been used for reduction of NAD^+ to regenerate co-enzyme NADH using formate in relation to biocatalytic reduction [2b,2d,2e,14]. Because [**1**](PF_6) contains two [Cp*Rh]

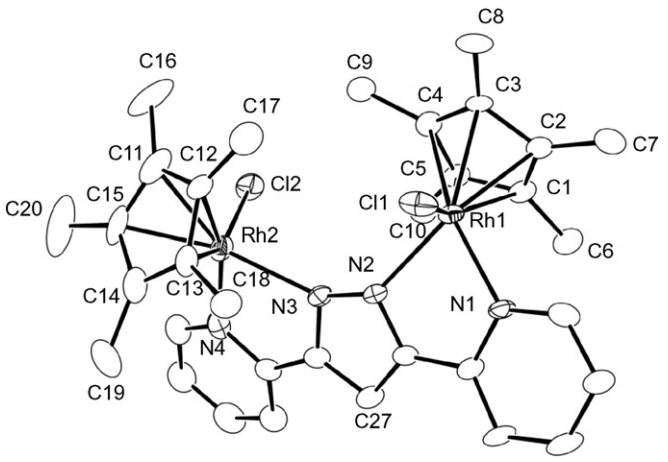

Fig. 1. ORTEP drawing of the cation in [**1**](PF_6) with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

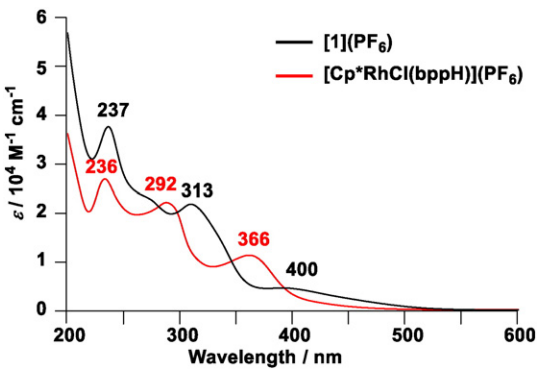

Fig. 2. UV–vis spectra of [**1**](PF_6) and [Cp*RhCl(bppH)](PF_6) in acetonitrile.