Supplementary Data for

# A mixed-valence diruthenium complex, triply bridged by mixed-moieties of chloro and methoxo ligands.

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## I. Synthesis of [{Ru(ebpma)}$_2$(μ-Cl)(μ-OCH$_3$)$_2$](PF$_6$)$_2$

*fac*-[Ru$^{III}$Cl$_3$(ebpma)] (50 mg, 0.12 mmol) and zinc powder (25 mg) were suspended in methanol (15 cm$^3$), and the mixture was stirred at room temperature for 15 hrs to give green solution. The zinc was then filtered out, ammonium hexafluorophosphate (50 mg, 0.31 mmol) was added, and the solvent was removed by a rotary evaporator. After a small amount of H$_2$O was added to the remaining green solid, the product was then filtered. The green solid was recrystallized from a water-acetone mixture (20 cm$^3$, 1:4 *v/v*). The green complex was collected by filtration, washed with water, ethanol, and diethyl ether, and dried *in vacuo*.

Yield: 37 mg, 66%. Elemental Analysis: calcd for C$_{30}$H$_{40}$ClF$_{12}$N$_6$O$_2$P$_2$Ru$_2$: C, 34.51; H, 3.86; N, 8.05%. Found: C, 34.35; H, 3.57; N; 7.88%. FAB MS (*m/z*): 900 (M-PF$_6$), 755 (M-2PF$_6$).

## II. Characterization of the diruthenium complex

### II-1  X-ray structural analysis

Single crystals were obtained by diffusion of diethyl ether into CH$_3$COCH$_3$ solution. The intensity data were collected on a Rigaku Mercury CCD diffractometer, using graphic monochromatized MoK$\alpha$ radiation (0.71069 Å). All the calculations were carried out using the Crystal Structure software package. Structures were solved by a direct method, expanded using Fourier techniques and refined using full-matrix least-squares techniques.
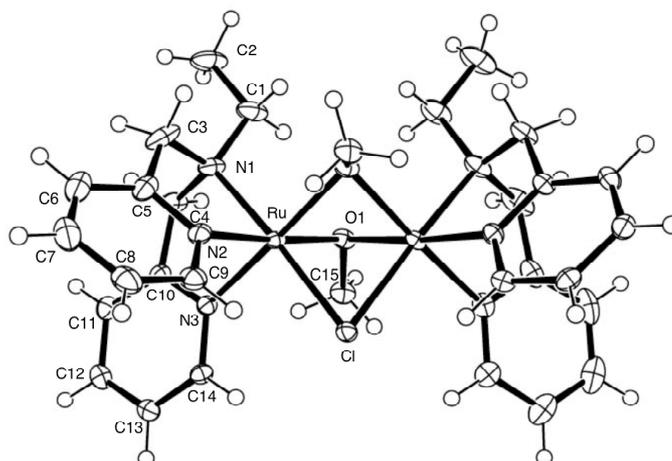
**Fig. S1** Structure of [{Ru(ebpma)}$_2$($\mu$-Cl)($\mu$-OCH$_3$)$_2$]$^{2+}$ with atom labeling.

## II-2 Electrochemical properties

**Cyclic voltammetry.** Cyclic voltammetric measurements were made on CH$_3$CN solution containing 0.1 mol dm$^{-3}$ tetraethylammonium perchlorate (TEAP, Nakarai Tesque. Ltd.) as supporting electrolyte with a platinum disk working electrode ($\phi$ = 1.6 mm), and an Ag | 0.01 mol dm$^{-3}$ AgNO$_3$ reference electrode by using a BAS 100B/W Electrochemical Analyzer. At the end of each measurement, ferrocene (0.07 V in CH$_3$CN(TEAP) *vs.* Ag | 0.01 mol dm$^{-3}$ AgNO$_3$ (CH$_3$CN)) was added as an internal standard to correct redox potentials.

Cyclic voltammogram (CV) of the diruthenium complex in CH$_3$CN showed two reversible waves at 0.22 and -0.65 V (Fig. S2). The redox potential was independent with scan rate.
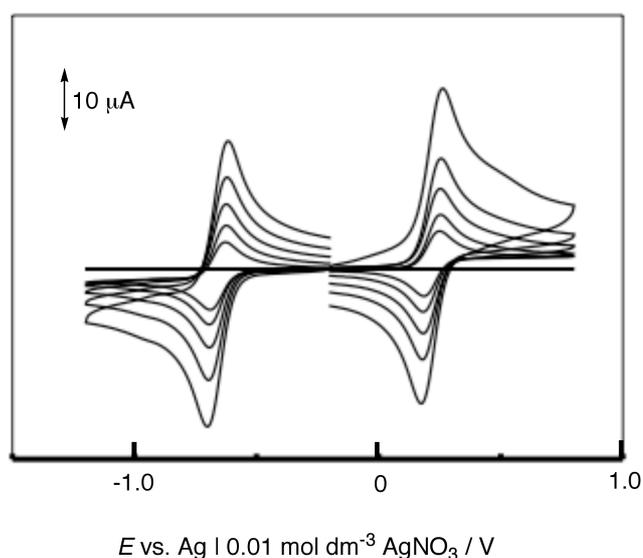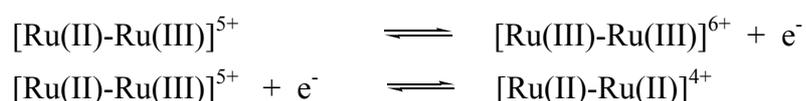


*E* vs. Ag | 0.01 mol dm$^{-3}$ AgNO$_3$ / V

**Fig. S2** CV of [{Ru(ebpma)}$_2$($\mu$-Cl)($\mu$-OCH$_3$)$_2$](PF$_6$)$_2$ in CH$_3$CN with scan rate 25, 50, 100, 200, 400 mV/s at 25°C.

**Controlled-potential electrolysis (CPE).** CPE was made in a three-compartment cell with a platinum gauze working electrode in the first-compartment, an auxiliary electrode in the second-compartment, and an reference electrode in the third-compartment using a Huso polarograph Model 312 and 343B digital coulometer. After the electrolyses, changes of the species were monitored by CV and hydrodynamic voltammograms (HDVs). The HDVs were made with a rotating platinum disk working electrode ($\phi$ = 3.0 mm) using a BAS RDE-2 rotating electrode. At the end of each measurement, ferrocene was added as an internal standard to correct redox potentials.

The electrolysis was performed under an applied voltage of -0.70 and 0.50 V. The number of electrons was determined by the relation of the change in wave height of HDV (a diffusion current) with the quantity of electricity consumed during electrolysis (Fig. S3 for the oxidation wave at 0.22 V and Fig. S4 for the reduction wave at -0.65 V). These results revealed these waves corresponded to one-electron oxidation and reduction processes.

$$[Ru(II)\text{-}Ru(III)]^{5+} \quad \rightleftharpoons \quad [Ru(III)\text{-}Ru(III)]^{6+} + e^-$$
$$[Ru(II)\text{-}Ru(III)]^{5+} + e^- \quad \rightleftharpoons \quad [Ru(II)\text{-}Ru(II)]^{4+}$$

The CVs of the complex in $CH_3CN$ solution that had been left for hours under Ar after electrolysis were measured. The reduced (Ru(II)-Ru(II)) and oxidized isovalence species (Ru(III)-Ru(III)) were stable for a few hours.
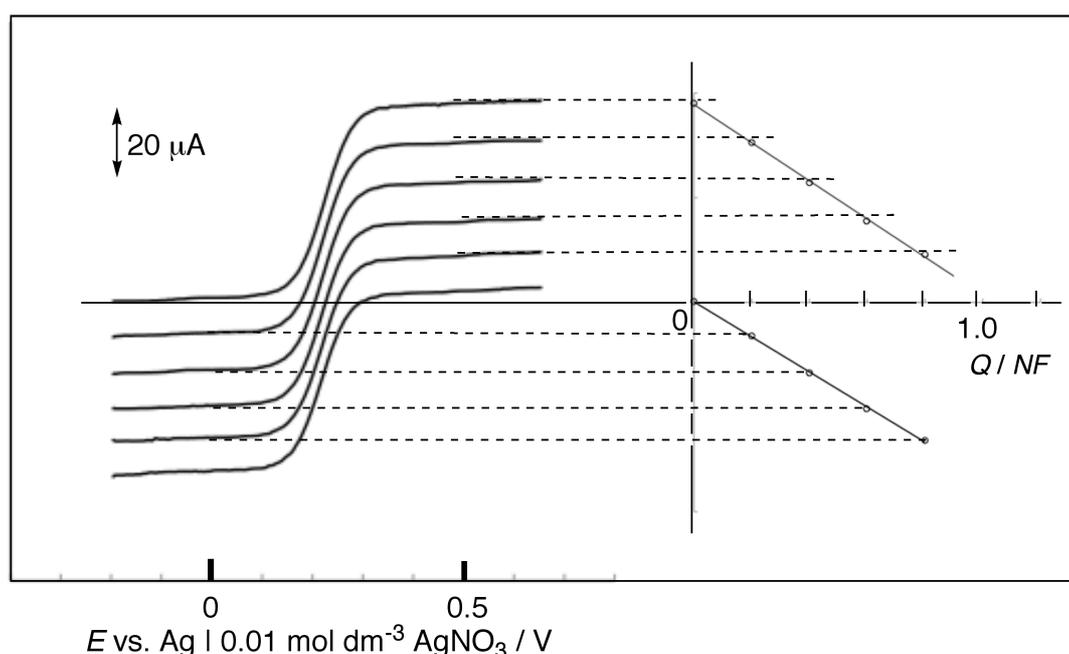


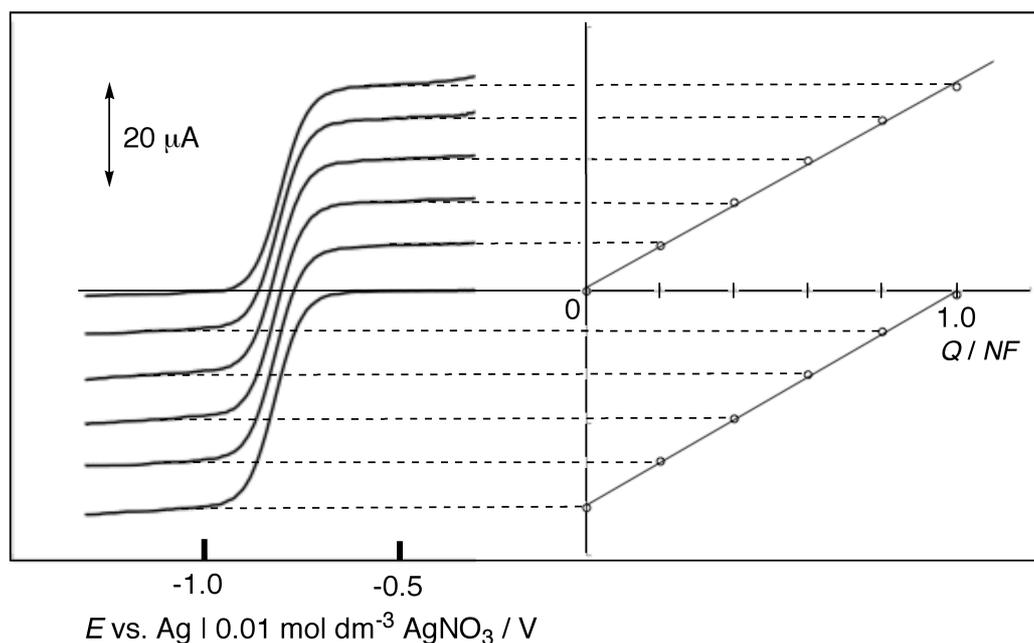**Fig. 3.** Change of HDV and Plot of the Limiting Current vs. *Q/NF* of the oxidation wave.

**Fig. S4** Change of HDV and Plot of the Limiting Current vs. *Q/NF* of the reduction wave.

**Comproportionation constant ($K_C$).** The comproportionation constant $K_C$ was estimated from the $E_{1/2}$ separation between Ru(III)-Ru(III)/Ru(III)-Ru(II) and Ru(III)-Ru(II)/Ru(II)-Ru(II) redox couples.

$$RT \ln K_c = nF(\Delta E)$$
$$\Delta E = 0.22 - (-0.65) = 0.87 \text{ V}$$
$$K_C = 5.1 \times 10^{14}$$

This value indicated that the complex would be categorized into Class III according to Robin-Day classification.

**II-3  Spectroscopic properties**

**UV-vis / Near-IR spectroscopy.**  UV-vis and Near-IR spectra were measured on Shimadzu MultiSpec-1500 spectrophotometer and UV-3100 using a quartz cell of 1 cm path length.
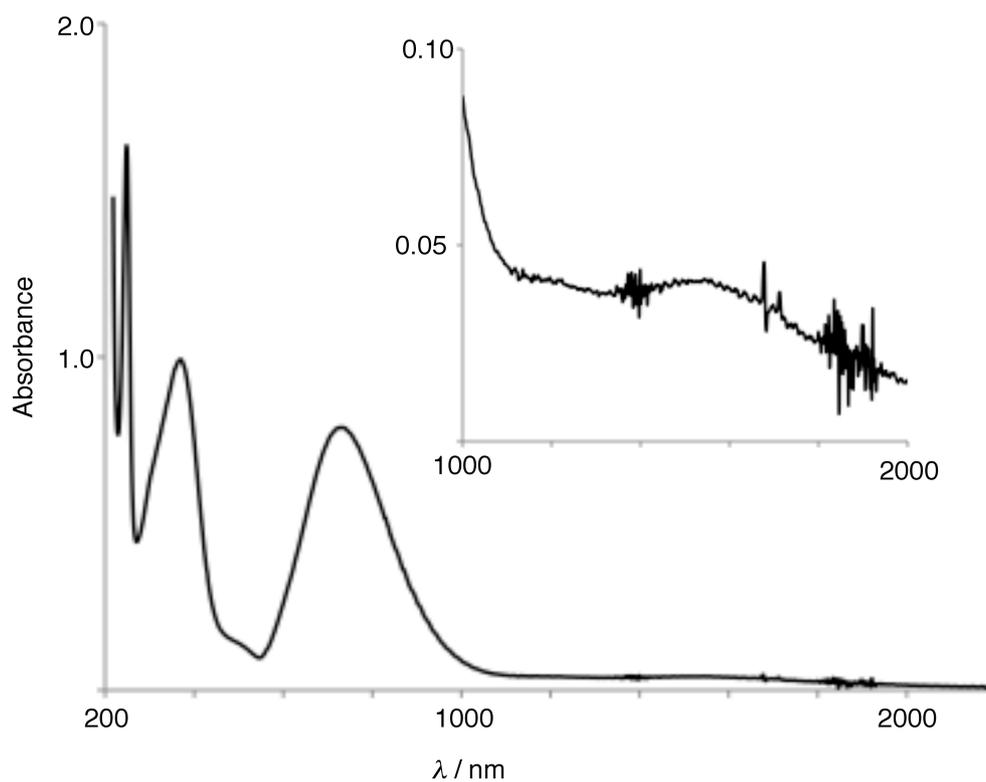
**Fig. S5** UV-vis / Near-IR spectrum of $[\{Ru(ebpma)\}_2(\mu\text{-}Cl)(\mu\text{-}OCH_3)_2](PF_6)_2$ $(1.00 \times 10^{-4}\ mol\ dm^{-3})$ in $CH_3CN$.

**Table 1** UV-vis spectral data of $[\{Ru(ebpma)\}_2(\mu\text{-}Cl)(\mu\text{-}OCH_3)_2](PF_6)_2$.

| solvent | $\lambda_{max}$ / nm | $\varepsilon$ / $10^4\ M^{-1}\ cm^{-1}$ |
|---|---|---|
| $CH_2Cl_2$ | 249 | 1.265 |
| | 369 | 0.763 |
| | 733 | 0.599 |
| $CH_3COCH_3$ | 730 | 0.825 |
| $CH_3CN$ | 248 | 1.421 |
| | 370 | 0.899 |
| | 729 | 0.724 |
| DMF | 370 | 1.000 |
| | 735 | 0.624 |
| DMSO | 369 | 1.331 |
| | 374 | 1.369 |
| | 733 | 1.043 |
| $CH_3OH$ | 248 | 1.699 |
| | 370 | 1.190 |
| | 731 | 1.022 |
| $CH_3NO_2$ | 733 | 0.822 |

**Spectroelectrochemistry.** Spectroelectrochemical experiments were performed using an OTTLE (Optically Transparent Thin-Layer Electrode) cell. [{Ru(ebpma)}$_2$($\mu$-Cl)($\mu$-OCH$_3$)$_2$](PF$_6$)$_2$ was dissolved in CH$_3$CN to prepare a solution whose concentration was 5 mmol dm$^{-3}$.
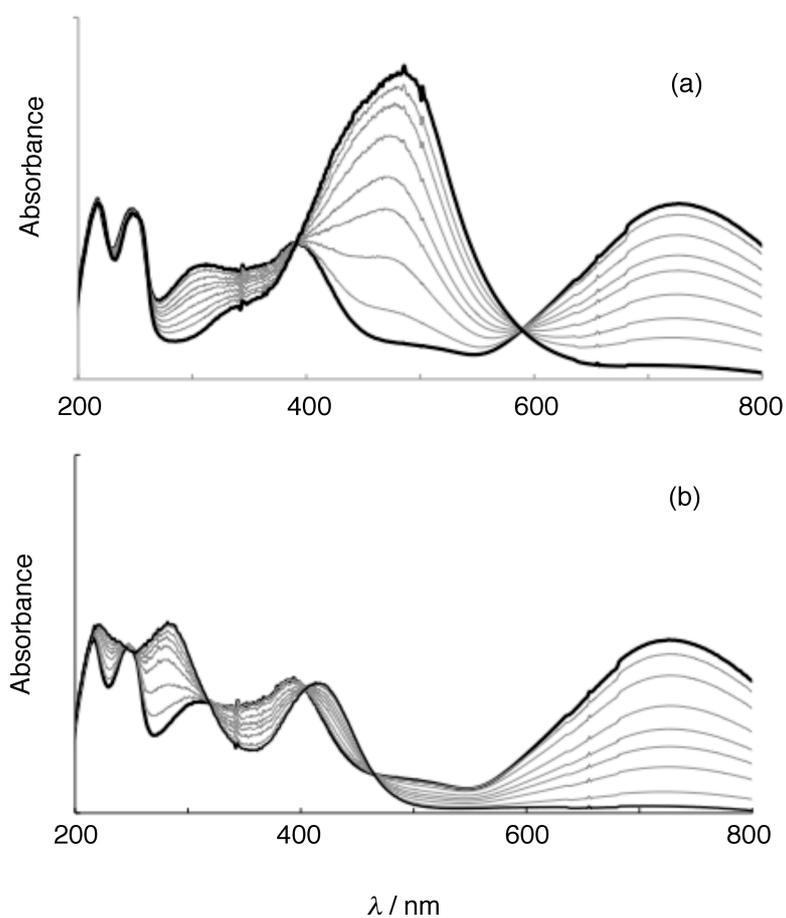


**Fig. S6** UV-vis spectrum in CH$_3$CN; (a) the reductive CPE at -0.70 V, (b) the oxidative CPE at 0.50 V.