

Supplementary Information

Formation of Bis(2-pyridylcarbonyl)aminato by Oxidation of Ethylbis(2-pyridylmethyl)amine on Trichloridoruthenium(III) Complex

Hirota Nagao*, Naoto Shimura, and Haruka Yonezawa

Department of Materials and Life Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

(1) Electrochemical properties of *fac*-[Ru^{III}Cl₃(ebpma)]

CVs of *fac*-[Ru^{III}Cl₃(ebpma)] in CH₃CN at room temperature and -40°C are shown in Figure S1(a) and (b). Controlled potential electrolysis (CPE) of *fac*-[Ru^{III}Cl₃(ebpma)] in CH₃CN was performed at 1.1 V. After CPE, a new oxidation wave was observed at 1.2 V as shown in Fig. S1(c).

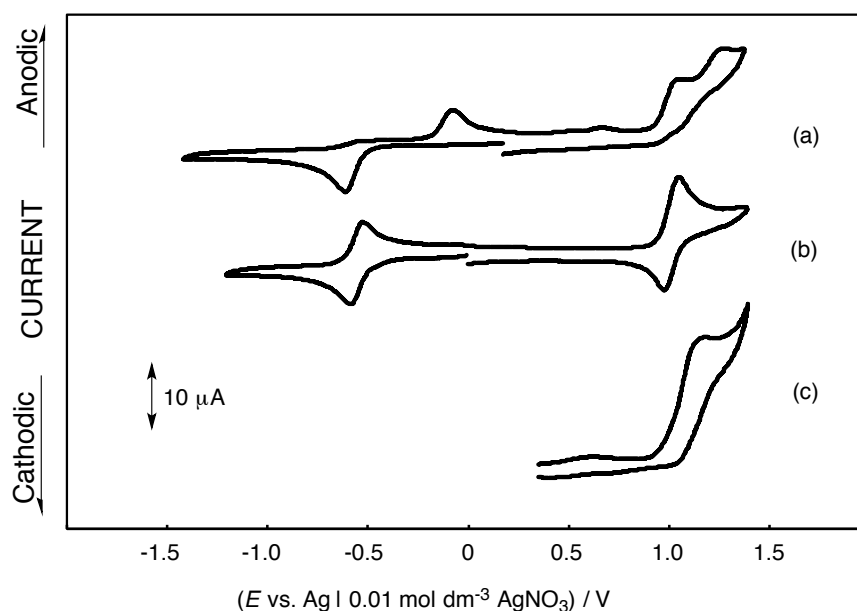


Fig. S1 Cyclic voltammograms in CH₃CN; (a) and (b) *fac*-[Ru^{III}Cl₃(ebpma)] at room temperature and -40°C, (c) after the CPE at 1.1 V of *fac*-[Ru^{III}Cl₃(ebpma)].

Analysis of NPV for the oxidation wave

Normal pulse voltammetry was carried out in CH₃CN at -40°C with sampling time of 20, 40, and 60 ms. These NPVs were analyzed using the Nernst equation below.

$$\ln\left(\frac{i_o}{i_d - i_o}\right) = \frac{nF}{RT}(E - E_{1/2})$$

The slopes of the line are close to the ideal value (49.8 V⁻¹) for one-electron process ($n = 1$), indicating that the oxidation wave is one-electron process.

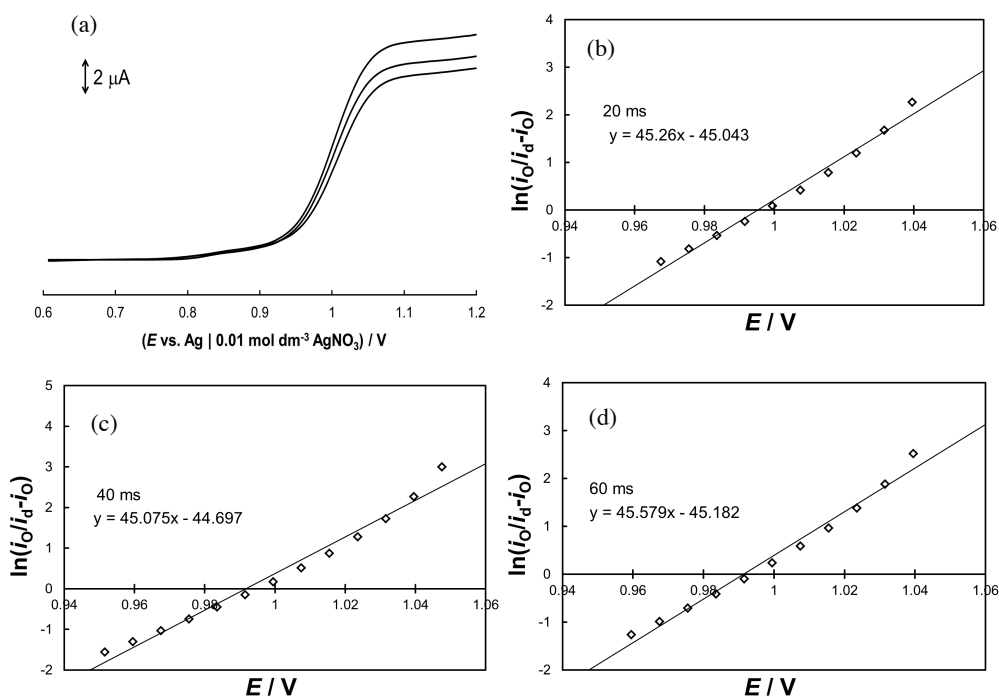


Fig. S2 Normal pulse voltammograms of *fac*-[Ru^{III}Cl₃(ebpma)] in CH₃CN at -40°C (a) and the plots of $\ln(i_o/(i_d-i_o))$ vs. E (b)-(d).

(2) IR spectra of ruthenium complexes

IR spectra of *fac*-[Ru^{III}Cl₃(ebpma)], [Ru^{III}Cl₂(NCCH₃)(bpca)]·H₂O, [Ru^{II}(NCCH₃)₃(bpca)]PF₆ and [Ru^{III}Cl₃(Hbpca)] were recorded on a Shimadzu IR Affinity-1 spectrophotometer using samples prepared as KBr disks. The characteristic CO stretching band of bis(2-pyridylcarbonyl)aminato ligand was observed around 1700 cm⁻¹ as shown in (b) and (c).

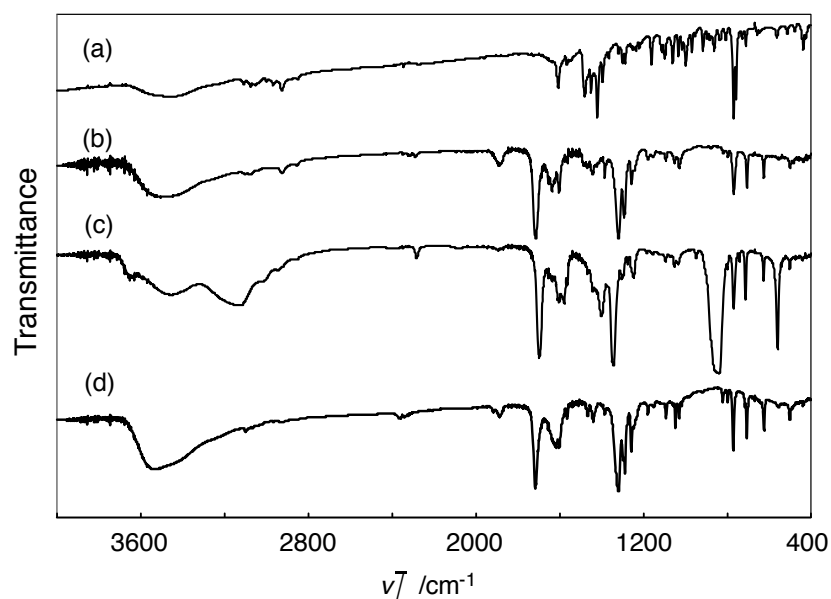


Fig. S3 IR spectra of *fac*-[Ru^{III}Cl₃(ebpma)] (a), [Ru^{III}Cl₂(NCCH₃)(bpca)]·H₂O (b), [Ru^{II}(NCCH₃)₃(bpca)]PF₆ (c), and [Ru^{III}Cl₃(Hbpca)] (d).

(3) NMR spectra of $[\text{Ru}^{\text{II}}(\text{NCCH}_3)_3(\text{bpca})]\text{PF}_6$.

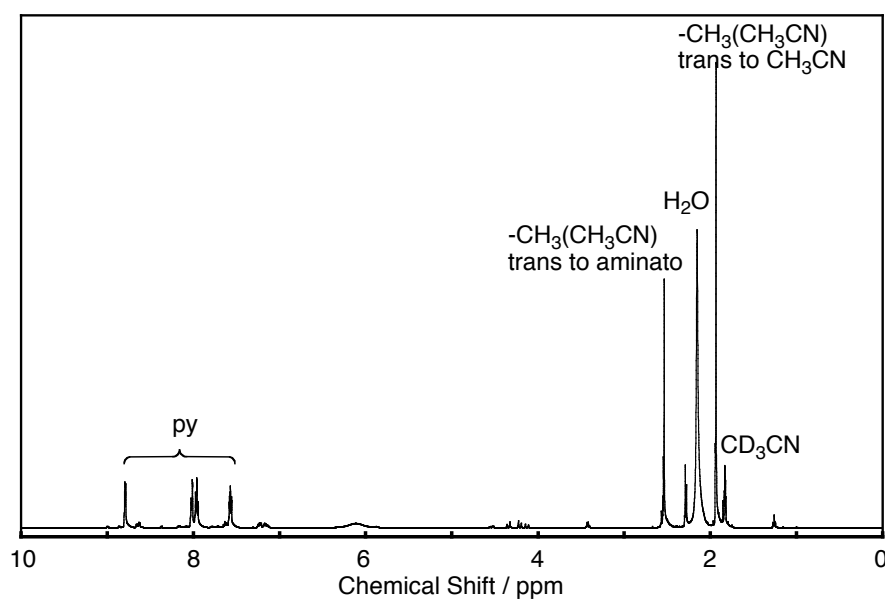


Fig. S4 ^1H NMR spectrum of $[\text{Ru}^{\text{II}}(\text{NCCH}_3)_3(\text{bpca})]\text{PF}_6$ in CD_3CN .

(4) X-ray crystallography for $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{NCCH}_3)(\text{bpca})]\cdot 0.5\text{NaClO}_4$.

Single crystals of $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{NCCH}_3)(\text{bpca})]\cdot 0.5\text{NaClO}_4$ were obtained by recrystallization from a $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solution containing NaClO_4 and then vapor diffusion of ether into the solution.

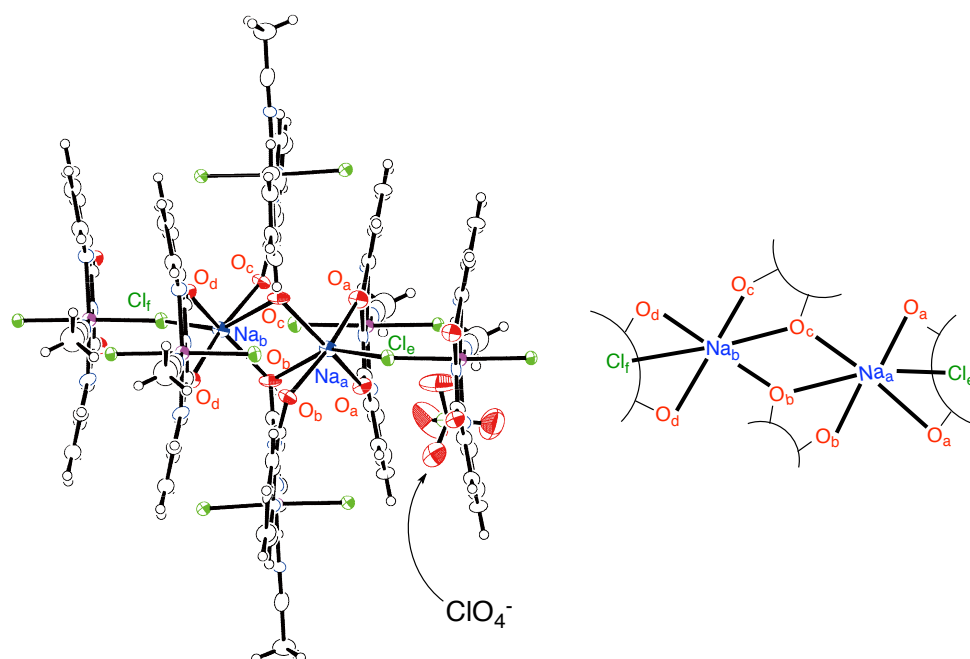


Fig. S5 Structure of $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{NCCH}_3)(\text{bpca})]\cdot 0.5\text{NaClO}_4$ and structural network between Na^+ , Cl^- and bpca^- ligands.

(5) UV-vis spectra of ruthenium complexes.

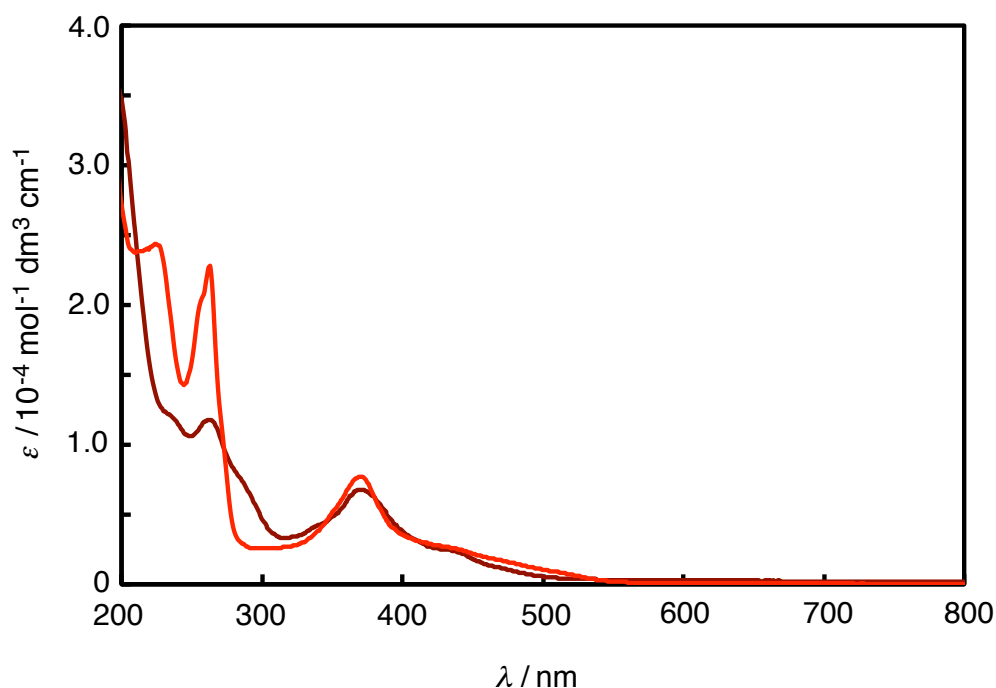


Fig. S6 UV-vis spectra of $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{NCCH}_3)(\text{bpca})]$ (brown line) and $[\text{Ru}^{\text{II}}(\text{NCCH}_3)_3(\text{bpca})]\text{PF}_6$ (red line) in CH_3CN .

(6) Controlled potential electrolysis (CPE) experiment of $[\text{Ru}^{\text{III}}\text{Cl}_3(\text{Hbpca})]$

The CV of $[\text{Ru}^{\text{III}}\text{Cl}_3(\text{Hbpca})]$ was shown in (a). CPE was performed at -0.6 V ($Q/NF = 0.9$) in CH_3CN at -40°C and the first reduction wave -0.31 V disappeared as shown (b). During the CPE experiment, the evolution of H_2 was observed by GC. Further reduction at -1.2 V ($Q/NF = 1.2$) afforded CV of (c). This CV revealed the formation of $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{NCCH}_3)(\text{bpca})]$ (-0.41 and 1.17 V) and $[\text{Ru}^{\text{II}}(\text{NCCH}_3)_3(\text{bpca})]^+$ (0.68 V) under electrochemical conditions with a Cl^- dissociation, whose wave showed around 0.7 V and overlapped with the wave of $[\text{Ru}^{\text{II}}(\text{NCCH}_3)_3(\text{bpca})]^+$. Finally, the wave of $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{NCCH}_3)(\text{bpca})]$ disappeared and the wave around 0.7 V were bigger in a few days.

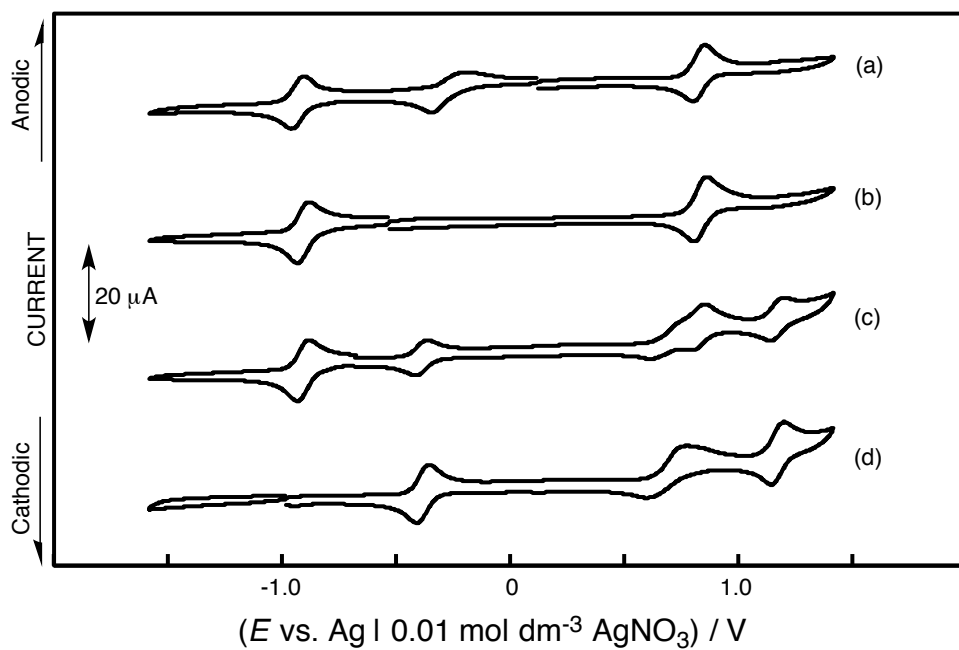


Fig. S7 Cyclic voltammograms in CH_3CN at -40°C ; (a) before electrolysis, (b) after CPE at -0.6 V ($Q/NF = 0.9$), (c) further reduction CPE at -1.2 V ($Q/NF = 1.2$) and (d) after standing for 1 day.