Supplementary Information

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

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(1) Electrochemical properties of fac-[Ru\textsuperscript{lll}Cl\textsubscript{3}(ebpma)]
CVs of fac-[Ru\textsuperscript{lll}Cl\textsubscript{3}(ebpma)] in CH\textsubscript{3}CN at room temperature and -40°C are shown in Figure S1(a) and (b). Controlled potential electrolysis (CPE) of fac-[Ru\textsuperscript{lll}Cl\textsubscript{3}(ebpma)] in CH\textsubscript{3}CN 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 CH\textsubscript{3}CN; (a) and (b) fac-[Ru\textsuperscript{lll}Cl\textsubscript{3}(ebpma)] at room temperature and -40°C, (c) after the CPE at 1.1 V of fac-[Ru\textsuperscript{lll}Cl\textsubscript{3}(ebpma)].

Analysis of NPV for the oxidation wave
Normal pulse voltammetry was carried out in CH\textsubscript{3}CN at -40°C with sampling time of 20, 40, and 60 ms. These NPVs were analyzed using the Nernst equation below.

\[
\ln \left( \frac{i_o}{i_a-i_o} \right) = \frac{nF}{RT} (E - E_{1/2})
\]

The slopes of the line are close to the ideal value (49.8 V\textsuperscript{-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}Cl_3(ebpma)] in CH_3CN 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}Cl_3(ebpma)], [Ru^{III}Cl_2(NCCH_3)(b pca)]·H_2O, [Ru^{II}(NCCH_3)_3(bpca)]PF_6 and [Ru^{III}Cl_3(Hbpca)] were recorded on a Shimazu 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}Cl_3(ebpma)] (a), [Ru^{III}Cl_2(NCCH_3)(b pca)]·H_2O (b), [Ru^{II}(NCCH_3)_3(bpca)]PF_6 (c), and [Ru^{III}Cl_3(Hbpca)] (d).
(3) NMR spectra of [Ru^{II}(NCCH_{3})_{3}(bpca)]PF_{6}.

![NMR spectrum image]

**Fig. S4** ¹H NMR spectrum of [Ru^{II}(NCCH_{3})_{3}(bpca)]PF_{6} in CD_{3}CN.

(4) X-ray crystallography for [Ru^{III}Cl_{2}(NCCH_{3})(bpca)]·0.5NaClO_{4}.

Single crystals of [Ru^{III}Cl_{2}(NCCH_{3})(bpca)]·0.5NaClO_{4} were obtained by recrystallization from a CH_{3}CN-H_{2}O solution containing NaClO_{4} and then vapor diffusion of ether into the solution.

![Crystal structure image]

**Fig. S5** Structure of [Ru^{III}Cl_{2}(NCCH_{3})(bpca)]·0.5NaClO_{4} and structural network between Na^{+}, Cl⁻ and bpca⁻ ligands.
(5) UV-vis spectra of ruthenium complexes.

![UV-vis spectra](image)

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

(6) Controlled potential electrolysis (CPE) experiment of [Ru$^{III}$Cl$_2$(Hbpca)]

The CV of [Ru$^{III}$Cl$_2$(Hbpca)] was shown in (a). CPE was performed at -0.6 V ($Q/NF = 0.9$) in CH$_3$CN 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 [Ru$^{II}$Cl$_2$(NCCH$_3$)(bpca)] (-0.41 and 1.17 V) and [Ru$^{II}$(NCCH$_3$)$_3$(bpca)]$^+$ (0.68 V) under electrochemical conditions with a Cl$^-$ dissociation, whose wave showed around 0.7 V and overlapped with the wave of [Ru$^{II}$(NCCH$_3$)$_3$(bpca)]$^+$. Finally, the wave of [Ru$^{II}$Cl$_2$(NCCH$_3$)(bpca)] disappeared and the wave around 0.7 V were bigger in a few days.
**Fig. S7** Cyclic voltammograms in CH$_3$CN 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.