

Supporting Information

for

**Formation and Structure of an (Iminium Ion)ruthenium Complex,
and Reaction of the (Iminium Ion)-moiety Toward Alcohols**

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I. Synthesis of ethylbis(2-pyridylethyl)amine (ebpea)

A solution of $\text{CH}_3\text{SO}_2\text{Cl}$ (18.3 g, 0.16 mol) in diethyl ether (80 cm^3) was slowly added to a solution of 2-(2-hydroxyethyl)pyridine (19.7 g, 0.16 mol) and $\text{N}(\text{Et})_3$ (24.0 g) in CH_2Cl_2 (80 cm^3) on an ice bath. A light brown solution of 2-(2-methenesulfonateethyl)pyridine was formed. The 2-(2-methenesulfonateethyl)pyridine was extracted with a mixed solution of CH_2Cl_2 (640 cm^3) and an aqueous NaHCO_3 solution (9.720 g NaHCO_3 in 200 cm^3 H_2O). The extracted solution was evaporated with a rotary evaporator to give a chestnut-colored solution. A solution of $\text{NH}_2\text{C}_2\text{H}_5$ (70%, 6.4 cm^3 , 0.08 mol), $\text{N}(\text{Et})_3$ (12.0 g), and CH_2Cl_2 (40 cm^3) were added to the solution. This mixture was then refluxed at 50°C for 9 hrs. This solution was extracted with a mixed solution of CH_2Cl_2 (480 cm^3) and the aqueous NaHCO_3 solution (9.720 g NaHCO_3 in 200 cm^3 H_2O). The extracted solution was evaporated with a rotary evaporator to give a chestnut-colored solution. This solution was purified by alumina and silica column chromatography. Yield: 7.574 g (37%). ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 500MHz): δ 0.87 (3H, t, $J = 7$, $\text{CH}_3(\text{ethyl})$), 2.50 (2H, q, $J = 7$ Hz, $\text{CH}_2(\text{ethyl})$), 2.77 (8H, m, CH_2), 7.11 (2H, ddd, $J = 1, 5, 8$ Hz, 5-H(py)), 7.15 (2H, dd, $J = 1, 8$ Hz, 3-H(py)), 7.58 (2H, td, $J = 2, 8$ Hz, 4-H(py)), 8.42 (2H, ddd, $J = 1, 2, 5$ Hz, 6-H(py)). ^{13}C NMR (CDCl_3 , 500MHz): δ 11.72, 35.56, 47.09, 53.10, 120.71, 122.99, 135.87, 148.79, 160.34. MS (EI^+): m/z 255 (ebpea^+). The purity of the product was confirmed by GC-MS.

II. Syntheses of ruthenium complexes

***mer*(Cl, Cl, Cl)-[$\text{RuCl}_3(\eta^2\text{-NCHCH}_2\text{py}(\text{C}_2\text{H}_4\text{py})\text{C}_2\text{H}_5)$] (*mer*-[1]):** A dark brown solution (3:2 v/v) of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (Ru content 42.60 wt%, 400 mg, 1.68 mmol) in $\text{EtOH-H}_2\text{O}$ 40 cm^3 was refluxed until a color changed to dark blue (Ru-blue). Then 432 mg (1.69 mmol) of ebpea was added to the magnetically stirred dark blue solution to give a dark green solution. After this solution was refluxed for 15 minutes, 8 cm^3 of hydrochloric acid was added to give a dark brown solution. The solution was refluxed for 30 minutes and then cooled at room temperature to give a dark brown precipitate that was collected by filtration and washed with H_2O , EtOH , and diethyl ether. Yield: 255 mg (42%). Anal. calcd for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{OCl}_3\text{Ru}$: C, 40.05; H, 4.62; N, 8.76%. Found; C, 40.02; H, 4.20; N, 8.96%. ^1H NMR($(\text{CD}_3)_2\text{SO}$, 500 MHz): δ 1.06 (3H, t, $J = 7$ Hz, $\text{CH}_3(\text{ethyl})$), 2.75 (1H, m, CH_2), 2.93 (1H, q, $J = 5, 17$ Hz, CH_2), 3.60 (2H, overlapped with $(\text{CD}_3)_2\text{SO}$, $\text{CH}_2(\text{ethyl})$), 4.18 (2H, m, CH_2), 4.30 (1H, d, $J = 19$ Hz, CH_2), 4.78 (1H, q, $J = 5, 19$ Hz, CH_2), 6.56 (1H, d, $J = 5$ Hz, CH), 7.20-7.31 (4H, m, 3-H(py), 5-H(py)), 7.71 (2H, m, 4-H(py)), 8.90, 9.42 (2H, d, exchangeable, 6-H(py)).

***fac*-[$\text{Ru}^{\text{III}}\text{Cl}_3(\text{ebpea})$] (*fac*-[2]):** A dark brown solution (3:2 v/v) of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (Ru content 42.60 wt%, 400 mg, 1.68 mmol) in $\text{EtOH-H}_2\text{O}$ 40 cm^3 was refluxed until a color changed to dark blue (Ru-blue). Then 432 mg (1.69 mmol) of ebpea was added to the magnetically stirred dark blue solution to give a dark green solution. After this solution was refluxed for 15 minutes, 4 cm^3 of hydrochloric acid was added to give a dark brown solution. The brown solution was refluxed for 30

min and then cooled to room temperature to give a dark brown precipitate, *mer*(Cl, Cl, Cl)-[RuCl₃(η²-NCHCH₂py(C₂H₄py)C₂H₅)]. The resulted solid was removed by filtration. Then filtrate was allowed to stand at room temperature for two nights to give a brown precipitate that was collected by filtration and washed with H₂O, EtOH, and diethyl ether. Yield: 547 mg (73%). Anal. calcd for C₁₆H₂₁N₃Cl₃Ru: C, 41.52; H, 4.57; N, 9.08%. Found; C, 41.18; H, 4.53; N, 9.06%. FAB MS: 487 (M+Na).

***mer*-[Ru^{III}Cl₃(ebpea)] (*mer*-[2]):** A suspended solution of *mer*-[1] (20 mg, 0.043 mmol) in MeOH (20 cm³) was magnetically stirred for 6 hrs to give a yellow solution. The volume of the yellow solution was reduced to dryness with a rotary evaporator. EtOH was added to the formed light brown solid. The complex was collected by filtration and washed with H₂O, EtOH, and diethyl ether. Yield: 15 mg (75%). Anal. calcd for C₁₆H₂₁N₃Cl₃Ru: C, 41.52; H, 4.57; N, 9.08%. Found; C, 41.02; H, 4.39; N, 8.92%. FAB MS: 487 (M+Na).

III. NMR spectra

¹H and ¹³C NMR spectra were obtained with a JEOL JML-LA500 spectrometer and a JEOL AL300 spectrometer.

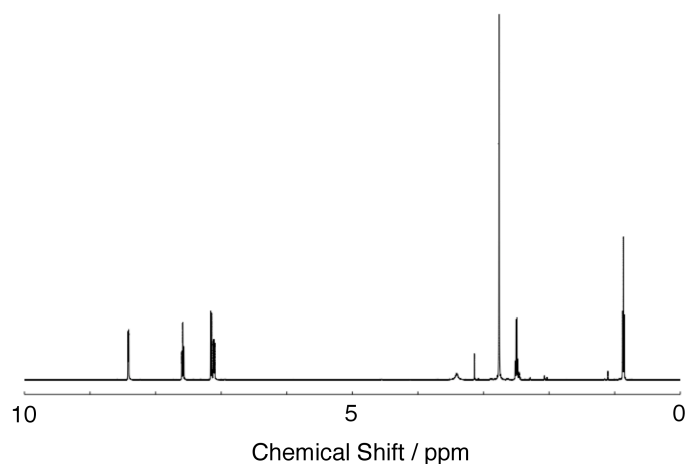


Figure S1. ¹H NMR spectrum of ethylbis(2-pyridylethyl)amine in CDCl₃.

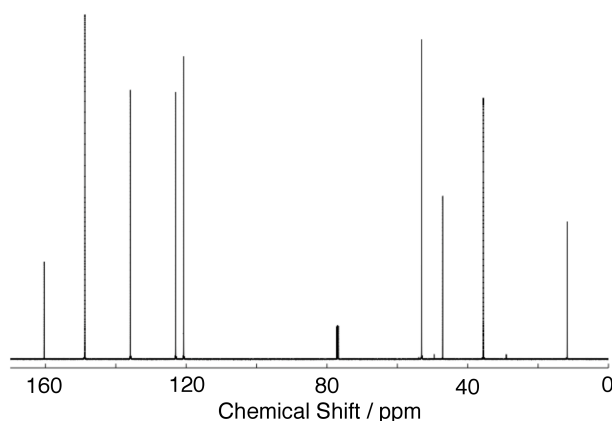


Figure S2. ¹³C NMR spectrum of ethylbis(2-pyridylethyl)amine in CDCl₃.

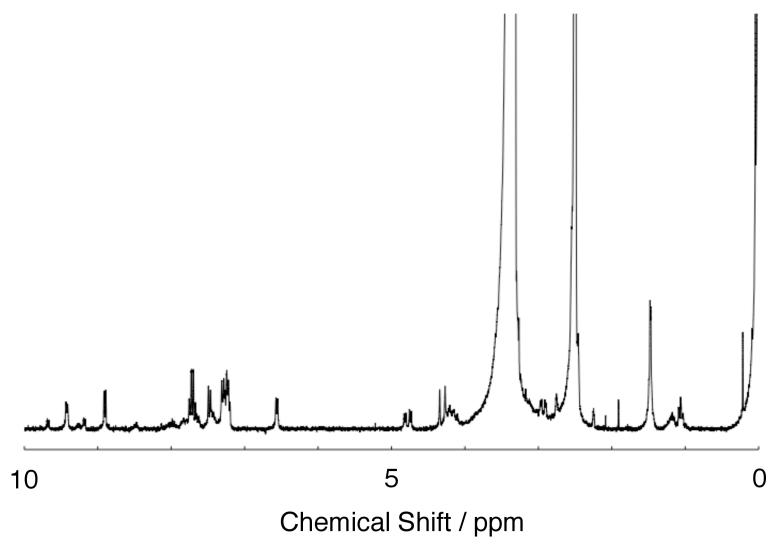


Figure S3. ^1H NMR spectrum of $\text{mer}(\text{Cl}, \text{Cl}, \text{Cl})\text{-}[\text{RuCl}_3(\eta^2\text{-NCHCH}_2\text{py}(\text{C}_2\text{H}_4\text{py})\text{C}_2\text{H}_5)]$ in $(\text{CD}_3)_2\text{SO}$.

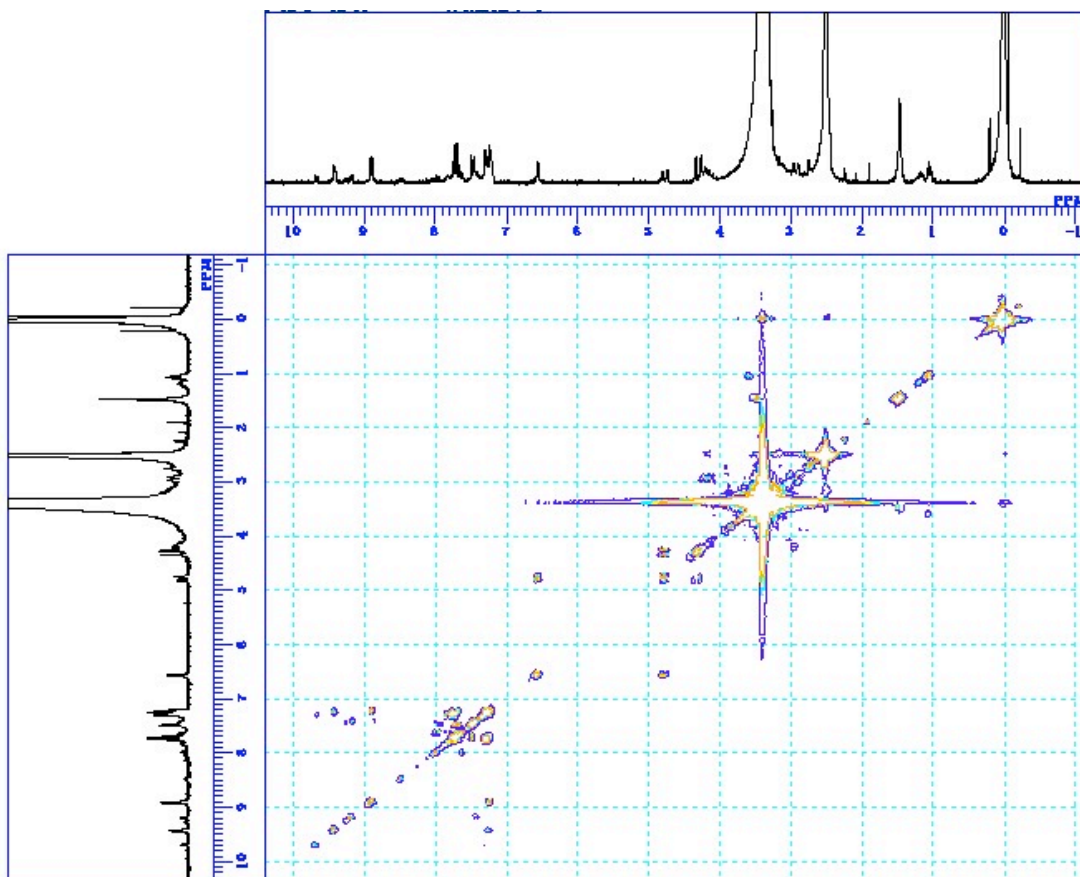


Figure S4. 2D NMR spectrum of $\text{mer}(\text{Cl}, \text{Cl}, \text{Cl})\text{-}[\text{RuCl}_3(\eta^2\text{-NCHCH}_2\text{py}(\text{C}_2\text{H}_4\text{py})\text{C}_2\text{H}_5)]$ in $(\text{CD}_3)_2\text{SO}$.

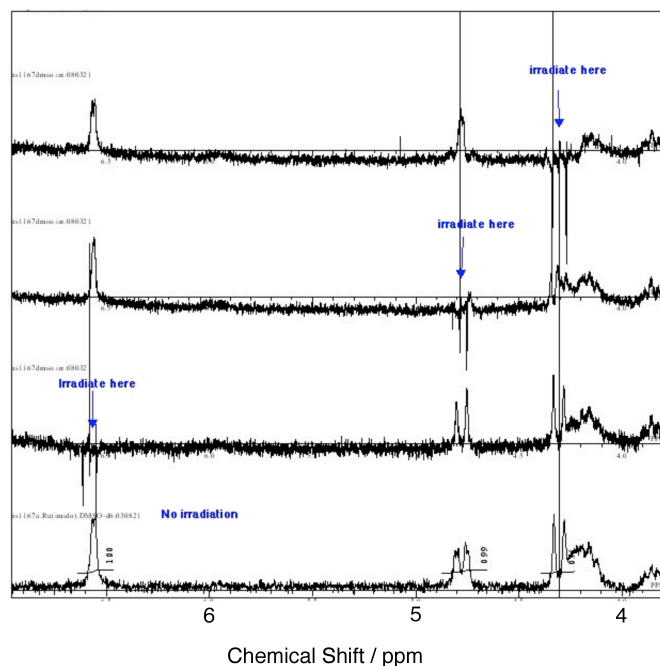


Figure S5. Homo-decoupling spectra of *mer*(Cl, Cl, Cl)-[RuCl₃(η²-NCHCH₂py(C₂H₄py)C₂H₅)] in (CD₃)₂SO.

IV. Cyclic voltammetry

Cyclic voltammetry was made on a CH₂Cl₂ solutions containing in 0.1 mol dm⁻³ tetrabutylammonium hexafluorophosphate (TBAH, Wako.) as supporting electrolyte with a platinum disk working electrode ($\phi = 1.6$ mm), and an Ag|0.01 mol dm⁻³ AgNO₃ reference electrode by using a BAS 100B/W Electrochemical Analyzer. At the end of each measurement, ferrocene (0.07 V) was added as an internal standard to correct redox potentials.

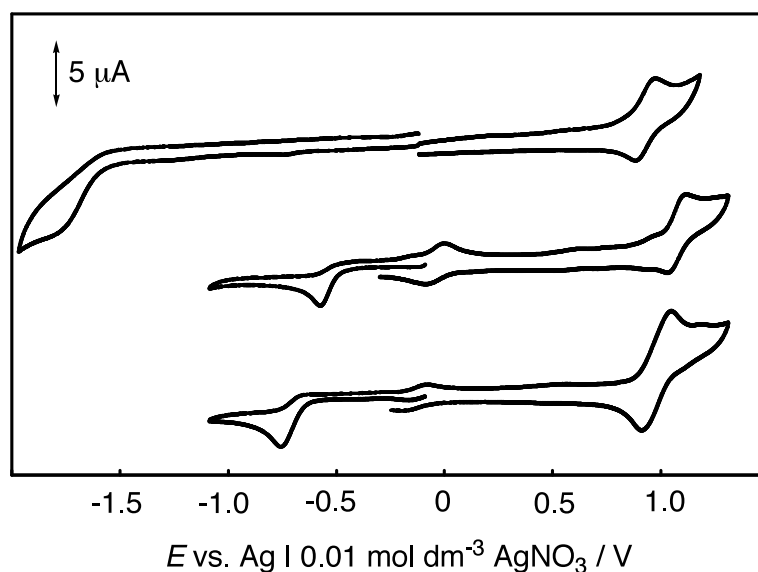


Figure S6. Cyclic voltammograms of (a) *mer*(Cl, Cl, Cl)-[RuCl₃(η²-NCHCH₂py(C₂H₄py)C₂H₅)] in CH₂Cl₂ with scan rate 100 mV/s at -40°C, (b) *fac*-[Ru^{III}Cl₃(ebpea)] in CH₂Cl₂ with scan rate 100 mV/s at -40°C, (c) *mer*-[Ru^{III}Cl₃(ebpea)] in CH₂Cl₂ with scan rate 100 mV/s at -40°C.

V. X-Ray crystallography

Table S1. Selected bond distances /Å and angles /° for *mer*-[1] and *fac*-[2].

	<i>mer</i> -[1]	<i>fac</i> -[2]
Ru-N1	2.154(3)	2.2013(18)
Ru-N2	2.083(3)	2.0961(17)
Ru-N3	2.113(3)	2.1255(16)
Ru-Cl1	2.3853(10)	2.3703(6)
Ru-Cl2	2.3822(10)	2.3507(4)
Ru-Cl3	2.4333(10)	2.3852(4)
Ru-C3	2.101(4)	-
N1-C1	1.506(4)	1.510(2)
N1-C3	1.378(5)	1.516(2)
N1-C5	1.492(4)	1.496(2)
C1-C2	1.516(6)	1.528(3)
C3-C4	1.508(5)	1.519(3)
C5-C6	1.522(6)	1.527(3)
Cl1-Ru-Cl2	84.66(3)	88.61(2)
Cl1-Ru-Cl3	80.75(3)	84.772(18)
Cl2-Ru-Cl3	165.40(3)	90.012(16)
N1-Ru-N2	90.99(12)	88.21(7)
N1-Ru-N3	90.90(11)	93.46(6)
N2-Ru-N3	176.89(15)	93.37(6)
N1-Ru-Cl1	169.98(10)	174.56(4)
N1-Ru-Cl2	85.32(10)	95.60(4)
N1-Ru-Cl3	109.27(10)	91.77(4)
C3-Ru-N1	37.77(14)	-
C3-Ru-N2	79.52(14)	-
C3-Ru-N3	103.45(14)	-
N1-C1-C2	112.9(3)	117.90(17)
N1-C3-C4	123.7(3)	117.16(17)
N1-C5-C6	113.0(3)	113.46(17)