

Synthesis and Characterization of Ruthenium Complexes Having Tridentate *N*-Ethyl-*N*,*N*-bis(2-pyridylmethyl)amine Coordinating in a Facial or Meridional Fashion

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Ruthenium complexes containing a tridentate *N*-ethyl-*N*,*N*-bis(2-pyridylmethyl)amine (*N*,*N*-bis(2-pyridylmethyl)-ethylamine: bpea) ligand having two different types of nitrogen donors, one an amine and the other pyridine rings connected with flexible CH_2-arms, were synthesized and characterized. A trichlororuthenium isomeric pair of *fac*- and *mer*-[$RuCl_3$(bpea)] was synthesized from $RuCl_3 \cdot nH_2O$ in a H_2O–C_2H_5OH solution. A reaction of *fac*-[$RuCl_3$(bpea)] in an C_2H_5OH–H_2O–CH_3CN solution under refluxing conditions afforded a triacetonitrile complex, *fac*-[$Ru(CH_3CN)_3$-(bpea)]$(PF_6)_2$. Four nitrosylruthenium complexes, *trans*(NO, py), *cis*(NO, Cl), *fac*-[$RuCl_2$(NO)(bpea)]PF_6, *trans*(NO, OH), *cis*(NO, NO_2), *mer*-[$Ru(NO_2)$(OH)(NO)(bpea)]PF_6, *trans*(NO, OCH_3), *cis*(NO, Cl), *mer*-[RuCl(OCH_3)(NO)-(bpea)]PF_6 and *trans*(NO, OH), *cis*(NO, Cl), *mer*-[RuCl(OH)(NO)(bpea)]PF_6, were synthesized and characterized by X-ray crystallography. The bpea of three nitrosylruthenium complexes bearing an electron-donating ligand such as hydroxo or methoxo as an ancillary ligand coordinated in a meridional fashion.

Ruthenium complexes containing polypyridine ligand(s) such as 2,2′-bipyridine (bpy) and 2,2′:6′,2″-terpyridine (trpy) have received much attention and have been investigated in a great variety of areas in connection with their photochemical, electrochemical, and spectroscopic properties.[1–9] Bis(2,2′-bipyridine)ruthenium-type complexes, $[RuX_2(bpy)_2]^{n+}$, have been well investigated and used in many studies on electro- and photochemical properties and electron-transfer reactions between a metal complex and some substances.[1–4] The trpy ligand has also been used for similar aims in studies on metal complexes containing the bpy ligand and on their chemical properties and affinities toward DNA in connection with biochemical aspects.[5–9] We have reported the syntheses of $[RuXY(NO)(trpy)]^{2+}$-type complexes, their reactions with anionic monodentate ligands such as NO_2^-, Br^-, N_3^-, and CH_3O^-, and the relationship between coexisting ligands and configuration around the Ru center.[10,11] The configurational changes were explained on the basis of the interaction between the nitrosyl ligand and ancillary ligands, and reactivity of those complexes, especially that of the nitrosyl moiety, was strongly influenced by a combination of ligands around the central metal.[12] Six-coordination metal complexes containing the trpy ligand have three variable coordination sites, and reactivity of these complexes can be regulated by the nature of the ancillary ligands. The trpy ligand coordinates to a ruthenium center as a tridentate ligand with three pyridyl nitrogen atoms only in a meridional configuration, on account of the firm and direct connections between the adjacent pyridine rings. Bis(pyridylalkyl)amine ligands have been used for several metal complexes as a tridentate pyridyl-containing ligand.[13–23]

N-Ethyl-*N*,*N*-bis(2-pyridylmethyl)amine (*N*,*N*-bis(2-pyridylmethyl)ethylamine: bpea), shown in Figure 1, can coordinate to a metal center in both meridional and facial configurations with two pyridyl and one amino nitrogen atoms, because of the flexible CH_2-arms between them.[14–23] Ruthenium complexes containing a bpea ligand coordinating in a facial fashion have been synthesized and structurally characterized,[15–18] while in Mn and Fe complexes, bpea coordinated in both meridional and facial configurations.[19,22] Recently, ruthenium complexes containing the bpea ligand coordinating in both meridional and facial fashions were synthesized and investigated by DFT calculations, and the first meridional ruthenium complex has been structurally characterized by Romero, Llobet, et al.[14,15] The geometric configuration around the ruthenium center of the bpea complexes relates to their reactiv-

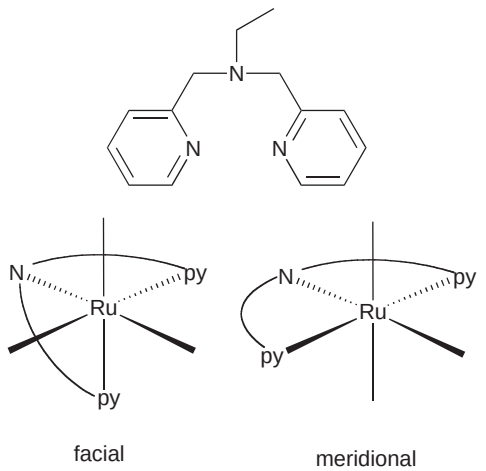

Figure 1. *N*-Ethyl-*N*,*N*-bis(2-pyridylmethyl)amine (bpea) and steric configuration around Ru.

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ity. The purpose of this work is to synthesize and characterize rare meridional-type complexes using the strong π-acid nitrosyl ligand to clarify relations between the combinations of the ligands and properties of the complexes.

In this paper, we describe syntheses of trichloro- and triacetonitrileruthenium complexes containing the bpea ligand, $[RuCl_3(bpea)]$ and $[Ru(CH_3CN)_3(bpea)]^{2+}$, and nitrosylruthenium complexes, $[RuXY(NO)(bpea)]^+$ (X and Y are anionic monodentate ligands such as Cl^-, NO_2^-, OH^-, and OCH_3^-), and structures of these complexes with indication that the coordination mode, meridional or facial, of the bpea ligand depends on the nature of the X and Y ligands.

Experimental

Measurements. IR spectra were recorded on a Perkin-Elmer FT 2000 FTIR spectrophotometer using samples prepared as KBr disks. Elemental analyses were carried out with a Perkin-Elmer 2400-II. ^{1}H and ^{13}C NMR spectra were obtained with a JEOL JML-LA500 spectrometer. UV–vis spectra were obtained on a Shimadzu MultiSpec-1500 diode array spectrophotometer. Cyclic voltammetric measurements were made in acetonitrile solutions containing 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte with a platinum disk working electrode (ϕ = 1.6 mm), and a Ag|0.01 mol dm^{-3} $AgNO_3$ reference electrode which was purchased from BAS Inc. using a BAS 100B/W Electrochemical Analyzer.

Preparation of the Ruthenium Complexes. $RuCl_3 \cdot nH_2O$ (content of Ru: 41.24 wt %) was purchased from Furuya Kinzoku Inc. $K_2[RuCl_5(NO)]$ was prepared by a procedure reported in the literature.[24] The bpea ligand was prepared according to a literature procedure.[21]

***fac*-[Ru^{III}Cl$_3$(bpea)] (*fac*-1).** A dark brown H_2O–C_2H_5OH solution (2:3 v/v, 100 cm^3) of $RuCl_3 \cdot nH_2O$ (500 mg, 2.04 mmol) was refluxed until the color of the solution changed to dark blue (a Ru-blue solution). To the magnetically stirred dark blue solution, hydrochloric acid (4 cm^3) and bpea (462 mg, 2.04 mmol) were added to give a brown solution. The brown solution was refluxed for 3 h and concentrated to ca. 5 cm^3 on a hot plate. It was then allowed to stand in a refrigerator overnight to give a brown precipitate. The brown complex obtained was collected by filtration and washed with H_2O, CH_3OH, and diethyl ether. Yield: 613 mg (69%). Anal. Calcd for $C_{14}H_{17}N_3Cl_3Ru$: C, 38.68; H, 3.94; N, 9.67%. Found: C, 38.52; H, 3.93; N, 9.43%. MS (ESI$^+$): m/z 459 (M + Na).

***mer*-[Ru^{III}Cl$_3$(bpea)] (*mer*-1).** A Ru-blue solution was prepared from $RuCl_3 \cdot nH_2O$ (500 mg, 2.04 mmol) in H_2O–C_2H_5OH (2:3 v/v, 20 cm^3). To the magnetically stirred Ru-blue solution, hydrochloric acid (4 cm^3) and bpea (462 mg, 2.04 mmol) were added to give a brown solution. The brown solution was refluxed for 20 min and concentrated to ca. 5 cm^3 to give a brown solid. The brown solid was a mixture of *fac*- and *mer*-[Ru^{III}Cl$_3$(bpea)]. Yield: 529 mg. 100 mg of this brown solid was dissolved in CH_3CN and the complexes were isolated by alumina column chromatography. The first yellow fraction, eluted with CH_3CN, was evaporated to dryness with a rotary evaporator. Diethyl ether was added to the yellow solid formed. The complex was collected by filtration and washed with diethyl ether. Yield: 20 mg (8%). Anal. Calcd for $C_{14}H_{17}N_3Cl_3Ru$: C, 38.68; H, 3.94; N, 9.67%. Found: C, 38.81; H, 3.69; N, 9.60%. MS (ESI$^+$): m/z 459 (M + Na).

***fac*-[Ru^{II}(CH$_3$CN)$_3$(bpea)](PF$_6$)$_2$·(CH$_3$)$_2$CO (*fac*-2(PF$_6$)$_2$·(CH$_3$)$_2$CO).** *fac*-**1** (100 mg, 0.230 mmol) was suspended in H_2O–C_2H_5OH (1:1 v/v, 100 cm^3), and CH_3CN (2 cm^3) was added to the suspended solution. The mixture was refluxed for 5 h to give a yellow solution. The volume of the solution was reduced and NH_4PF_6 (200 mg) was added as a precipitant. The yellow product obtained was collected by filtration and washed with H_2O, C_2H_5OH, and diethyl ether. The complex was recrystallized from $(CH_3)_2CO$ several times. Yield: 147 mg (86%). Anal. Calcd for $C_{23}H_{32}N_6OF_{12}P_2Ru$: C, 34.55; H, 4.03; N, 10.51%. Found: C, 34.22; H, 3.77; N, 10.49%. ^{1}H NMR (CD_3CN, 500 MHz): δ 1.36 (3H, t, J = 7.0 Hz, CH_3(ethyl)), 2.39 (6H, s, CH_3CN), 2.65 (3H, s, CH_3CN), 3.52 (2H, q, J = 7.0 Hz, CH_2(ethyl)), 4.31 (2H, d, J = 16.5 Hz, CH_2), 4.44 (2H, d, J = 16.8 Hz, CH_2), 7.27 (2H, t, J = 6.3 Hz, 5-H(py)), 7.32 (2H, d, J = 7.9 Hz, 3-H(py)), 7.74 (2H, t, J = 7.8 Hz, 4-H(py)), 8.72 (2H, d, J = 5.8 Hz, 6-H(py)). MS (FAB$^+$): m/z 597 (M − PF_6).

***trans*(NO, py), *cis*(NO, Cl), *fac*-[RuCl$_2$(NO)(bpea)]PF$_6$ (*fac*-3PF$_6$).** $K_2[RuCl_5(NO)]$ (100 mg, 0.26 mmol) and bpea (70 mg, 0.31 mmol) were suspended in H_2O (20 cm^3). This mixture was refluxed for 1 h to give a brown solution. This solution was cooled to room temperature and NH_4PF_6 (100 mg) was added as a precipitant. The brown product obtained was collected by filtration and washed with H_2O, CH_3OH, and diethyl ether. Yield: 65 mg (44%). Anal. Calcd for $C_{14}H_{17}N_4OF_6PCl_2Ru$: C, 29.28; H, 2.98; N, 9.76%. Found: C, 29.66; H, 2.83; N, 9.60%. IR (KBr, cm^{-1}): 1914 (NO). ^{1}H NMR (CD_3CN, 500 MHz): δ 1.48 (3H, t, J = 7.3 Hz, CH_3(ethyl)), 3.64 (1H, m, CH_2(ethyl)), 4.28 (1H, m, CH_2(ethyl)), 4.72 (1H, d, J = 16.2 Hz, CH_2), 4.80 (1H, d, J = 18.0 Hz, CH_2), 5.10 (1H, d, J = 16.2 Hz, CH_2), 5.19 (1H, d, J = 18.0 Hz, CH_2), 7.52–7.55 (2H, m, 3-H and 5-H(py)), 7.60 (1H, t, J = 6.7 Hz, 5′-H(py)), 7.63 (1H, d, J = 7.9 Hz, 3′-H(py)), 8.02–8.07 (2H, m, 4-H and 4′-H(py)), 9.09 (1H, d, J = 5.8 Hz, 6-H(py)), 9.20 (1H, d, J = 5.8 Hz, 6-H(py)). MS (FAB$^+$): m/z 429 (M − PF_6).

***trans*(NO, OH), *cis*(NO, NO$_2$), *mer*-[Ru(NO$_2$)(OH)(NO)(bpea)]PF$_6$ (*mer*-4PF$_6$).** **Procedure A:** $K_2[RuCl_5(NO)]$ (100 mg, 0.17 mmol) was dissolved in H_2O (10 cm^3) and $NaNO_2$ (200 mg, 2.90 mmol) was added. This solution was refluxed for 2 h to give a yellow solution. An C_2H_5OH solution (3 cm^3) of bpea (60 mg, 0.26 mmol) was added to the yellow solution. The mixed solution was refluxed for 2 h to give a brown solution. After its volume was reduced to 5 cm^3 by evaporation, it was allowed to stand at room temperature overnight to give an ocher solution containing a viscous black material. The supernatant was decanted and NH_4PF_6 (100 mg) was added as a precipitant. The yellow complex obtained was collected by filtration and washed with H_2O. Yield: 26 mg (17%). Anal. Calcd for $C_{14}H_{18}N_5O_4F_6PRu$: C, 29.69; H, 3.20; N, 12.37%. Found: C, 29.74; H, 3.03; N, 12.34%. IR (KBr, cm^{-1}): 1874 (NO). ^{1}H NMR (CD_3CN, 500 MHz): δ 1.15 (3H, t, J = 7.0 Hz, CH_3(ethyl)), 3.31 (2H, q, J = 7.0 Hz, CH_2(ethyl)), 4.72 (2H, d, J = 16.2 Hz, CH_2), 5.19 (2H, d, J = 16.2 Hz, CH_2), 5.23 (1H, s, OH), 7.68–7.72 (4H, m, 3-H and 5-H(py)), 8.18 (2H, t, J = 7.9 Hz, 4-H(py)), 8.67 (2H, d, J = 5.5 Hz, 6-H(py)). MS (FAB$^+$): m/z 422 (M − PF_6).

Procedure B: *fac*-**1** (100 mg, 0.23 mmol) and $NaNO_2$ (100 mg, 1.45 mmol) were suspended in H_2O (20 cm^3). The suspension was refluxed for 1 h to give a brown solution. The solution was evaporated to 5 cm^3 on a hot plate. It was then cooled to room temperature and NH_4PF_6 (100 mg) was added as a precipitant. The yellow product formed was collected by filtration and washed with H_2O. Yield: 53 mg (41%).

Procedure C: This procedure was similar to Procedure B,

Table 1. Crystallographic Data of Ruthenium Complexes

	fac-**1**	*mer*-**1**	*fac*-**2**$(PF_6)_2\cdot(CH_3)_2CO$
Formula	$C_{14}H_{17}N_3Cl_3Ru$	$C_{14}H_{17}N_3Cl_3Ru$	$C_{23}H_{32}N_6OF_{12}P_2Ru$
Fw	434.74	434.74	799.54
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	7.2107(18)	8.728(2)	12.034(2)
b/Å	12.523(9)	13.251(4)	18.280(3)
c/Å	18.119(8)	14.105(4)	14.982(3)
β/°	93.817(7)	92.4006(11)	104.7050(5)
V/Å^3	1632.5(14)	1629.9(8)	3187.7(10)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.769	1.771	1.666
μ (Mo Kα)/cm^{-1}	14.46	14.49	6.92
T/°C	25	25	−150
No. of refls	11317	11936	24807
No. of unique refls	3561	3614	7294
R/wR[a)]	0.0465/0.1048	0.0398/0.0949	0.0619/0.1327
GOF	1.168	1.163	1.142

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|(I > 2\sigma(I))$. $wR = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$ (all reflection).

except that *fac*-**2**$(PF_6)_2$ (100 mg, 0.14 mmol) was used as the starting complex instead of *fac*-**1**. The yellow product was collected by filtration and washed with H_2O. Yield: 39 mg (51%).

Procedure D: *fac*-**3**PF_6 (100 mg, 0.17 mmol) and $NaNO_2$ (30 mg, 0.43 mmol) were dissolved in H_2O (20 cm^3). This mixture was refluxed for 8 h to give a brown solution. The solution was evaporated to 5 cm^3 on a hot plate. It was then cooled to room temperature and NH_4PF_6 (100 mg) was added as a precipitant. The yellow product was collected by filtration and washed with H_2O. Yield: 51 mg (53%).

The obtained complexes by procedures B, C, and D were identified as *mer*-**4**PF_6 by IR, CV, and ^{1}H NMR.

***trans*(NO, OCH$_3$), *cis*(NO, Cl), *mer*-[RuCl(OCH$_3$)(NO)(bpea)]PF$_6$ (*mer*-5PF$_6$).** *fac*-**3**PF_6 (100 mg, 0.17 mmol) and $NaOCH_3$ (15 mg, 0.28 mmol) were suspended in CH_3OH (20 cm^3). This suspension was refluxed for 5 h to give a reddish brown solution. This solution was cooled to room temperature and NH_4PF_6 (100 mg) was added as a precipitant. The reddish brown product formed was collected by filtration and washed with CH_3OH and diethyl ether. Yield: 67 mg (68%). Anal. Calcd for $C_{15}H_{20}N_4O_2F_6PClRu$: C, 31.62; H, 3.54; N, 9.83%. Found: C, 31.64; H, 3.52; N, 10.05%. IR (KBr, cm^{-1}): 1822 (NO). ^{1}H NMR (CD_3CN, 500 MHz): δ 1.20 (3H, t, J = 7.0 Hz, CH_3(ethyl)), 3.43 (2H, q, J = 7.0 Hz, CH_2(ethyl)), 3.49 (3H, s, CH_3), 4.78 (2H, d, J = 15.9 Hz, CH_2), 5.13 (2H, d, J = 16.1 Hz, CH_2), 7.68–7.72 (4H, m, 3-H and 5-H(py)), 8.17 (2H, t, J = 7.9 Hz, 4-H(py)), 8.81 (2H, d, J = 5.5 Hz, 6-H(py)). MS (FAB$^+$): m/z 425 (M − PF_6).

***trans*(NO, OH), *cis*(NO, Cl), *mer*-[RuCl(OH)(NO)(bpea)]PF$_6$ (*mer*-6PF$_6$).** *mer*-**5**PF_6 (50 mg, 0.09 mmol) and KCl (7 mg, 0.09 mmol) were suspended in H_2O (10 cm^3). This suspension was refluxed for 3 h to give an ochre solution. The volume of the solution was reduced to ca. 5 cm^3 on a hot plate. After the solution was cooled to room temperature, NH_4PF_6 (100 mg) was added as a precipitant. The yellow product formed was collected by filtration and washed with H_2O. Yield: 35 mg (71%). Anal. Calcd for $C_{14}H_{18}N_4O_2F_6PClRu$: C, 30.25; H, 3.26; N, 10.08%. Found: C, 30.14; H, 3.08; N, 10.04%. IR (KBr, cm^{-1}): 1865 (NO). ^{1}H NMR (CD_3CN, 500 MHz): δ 1.20 (3H, t, J = 7.0 Hz, CH_3(ethyl)), 3.43 (2H, q, J = 7.0 Hz, CH_2(ethyl)), 4.67 (1H, s, OH), 4.78 (2H, d, J = 15.9 Hz, CH_2), 5.26 (2H, d, J = 15.6 Hz, CH_2), 7.67 (2H, t, J = 6.6 Hz, 5-H(py)), 7.71 (2H, d, J = 7.9 Hz, 3-H(py)), 8.15 (2H, t, J = 7.9 Hz, 4-H(py)), 8.77 (2H, d, J = 6.4 Hz, 6-H(py)). MS (FAB$^+$): m/z 411 (M − PF_6).

Reaction of *mer*-1 in Hydrochloric Acid Solution. *mer*-**1** (20 mg) was suspended in H_2O (10 cm^3) with hydrochloric acid (37%, 0.2 cm^3). The suspension was refluxed for 3 h, and was then cooled to room temperature to give a brown solid. The brown solid was collected by filtration and washed with H_2O, CH_3OH, and diethyl ether. The obtained complex was identified as *fac*-**1** by UV–vis, CV, and ^{1}H NMR. Yield: 15 mg (75%).

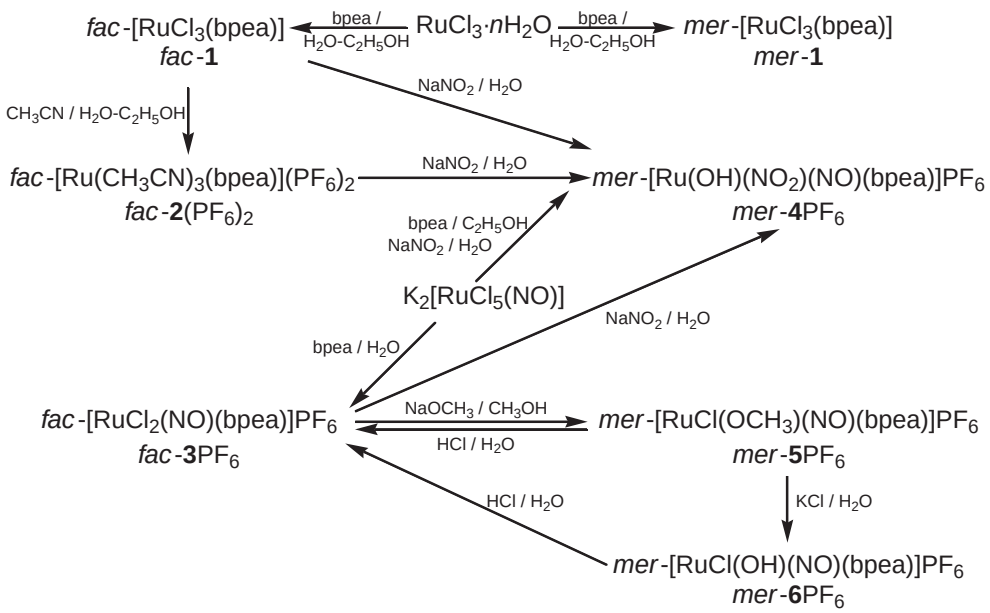
Reactions of *mer*-5PF$_6$ and *mer*-6PF$_6$ in Hydrochloric Acid Solution. The starting complex, *mer*-**5**PF_6 (50 mg) or *mer*-**6**PF_6 (50 mg), was suspended in H_2O (10 cm^3) with hydrochloric acid (37%, 0.2 cm^3). The suspension was refluxed for 3 h, and was then cooled to room temperature. NH_4PF_6 (100 mg) was added as a precipitant to give a brown solid. The solid was collected by filtration and washed with H_2O, CH_3OH, and diethyl ether. The obtained complex was identified as *fac*-**3**PF_6 by IR, CV, and ^{1}H NMR. Yield: 40 mg (81%) for *mer*-**5**PF_6, and 40 mg (83%) for *mer*-**6**PF_6.

X-ray Crystallography. Single crystals of *fac*-**1**, *fac*-**3**PF_6, *mer*-**4**PF_6, and *mer*-**6**PF_6 were obtained by recrystallization from their CH_3CN and diethyl ether solutions, and those of *fac*-**2**$(PF_6)_2\cdot(CH_3)_2CO$ from its $(CH_3)_2CO$ solution. Those of *mer*-**1** were obtained by slow evaporation of its CH_3CN–H_2O solution. Single crystals of *mer*-**5**PF_6 were obtained as a mixture of *mer*-**5**$^+$ and *fac*-**3**$^+$, the starting complex, by slow evaporation of a *mer*-**5**$^+$ and *fac*-**3**$^+$ solution, while no single crystals were obtained by recrystallization from pure *mer*-**5**PF_6 solutions of CH_3CN, CH_3NO_2, or $(CH_3)_2CO$. The crystallographic data are summarized in Tables 1 and 2. Intensity data were collected on a Rigaku Mercury CCD diffractometer, using graphite-monochromated Mo Kα radiation (0.71069 Å). All the calculations were carried out using the Crystal Structure software package.[25] Structures were solved by direct methods, expanded using Fourier techniques, and refined using full-matrix least-squares techniques on F^2 using SHELXL97.[26] Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-676914 for *fac*-**1**, CCDC-676915 for *mer*-**1**,

Table 2. Crystallographic Data of Nitrosylruthenium Complexes

	fac-**3**PF_6	*mer*-**4**PF_6	*fac*-**3**·*mer*-**5**$(PF_6)_2$	*mer*-**6**PF_6
Formula	$C_{14}H_{17}N_4OF_6Cl_2PRu$	$C_{14}H_{18}N_5O_4F_6PRu$	$C_{29}H_{37}N_8O_3F_{12}Cl_3P_2Ru_2$	$C_{14}H_{18}N_4O_2F_6ClPRu$
Fw	574.25	566.36	1144.09	555.81
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pca2_1$	$P2_1/a$	$P2_12_12_1$
a/Å	8.5731(8)	11.3688(5)	15.042(3)	11.791(3)
b/Å	20.175(2)	11.3324(4)	16.310(4)	12.316(3)
c/Å	12.2537(11)	15.7182(6)	17.468(4)	13.697(4)
β/°	104.562(4)		101.097(3)	
V/Å^3	2051.3(3)	2025.07(14)	4205.4(16)	1989.2(9)
Z	4	4	4	4
D_{calcd}/g cm^{-3}	1.859	1.858	1.807	1.856
μ (Mo Kα)/cm^{-1}	11.69	9.40	10.81	10.76
T/°C	25	25	25	25
No. of refls	14921	14887	31764	15643
No. of unique refls	4592	4603	9255	4554
R/wR[a)]	0.0567/0.1351	0.0313/0.0761	0.0554/0.1360	0.0297/0.0767
GOF	1.194	1.120	1.145	1.058

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|(I > 2\sigma(I))$. $wR = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$ (all reflection).



Scheme 1. Synthetic routes of the complexes with abbreviations.

CCDC-676916 for *fac*-**2**$(PF_6)_2$·$(CH_3)_2CO$, CCDC-676917 for *fac*-**3**PF_6, CCDC-676918 for *mer*-**4**PF_6, CCDC-676919 for *mer*-**5**·*fac*-**3**$(PF_6)_2$, and CCDC-676920 for *mer*-**6**PF_6. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Syntheses of Ruthenium Complexes. The synthetic routes for preparation of the ruthenium(II) and -(III) complexes and nitrosylruthenium complexes are summarized in Scheme 1 with their abbreviations.

Trichlororuthenium(III) complex, [$Ru^{III}Cl_3$(bpea)], has been synthesized by reaction of $RuCl_3 \cdot nH_2O$ with bpea in dry-CH_3OH.[16] In several other solvents such as ethanol, acetone, and acetonitrile, the reactions of $RuCl_3 \cdot nH_2O$ with bpea afforded a mixture of the trichloro complex and some unidentified complexes, which was confirmed with cyclic voltamograms (CVs) of the mixtures. In the present work, we used a Ru-blue solution that was useful for synthesis of Ru^{III} and Ru^{II} complexes from $RuCl_3 \cdot nH_2O$ in H_2O–C_2H_5OH mixed solvents. *fac*-[$Ru^{III}Cl_3$(bpea)] (*fac*-**1**) was synthesized by using a Ru-blue solution that was made as a H_2O–C_2H_5OH (2:3 v/v, 100 cm^3) solution.[27] The Ru-blue solution, to which an equimolar amount of bpea and concd HCl were added, was refluxed for 3 h to give *fac*-**1** in 69% yield. A similar procedure with 20 cm^3 of the Ru-blue solution containing $Ru^{III}Cl_3 \cdot nH_2O$

(500 mg) and 20 min refluxing afforded a mixture of *fac*- and *mer*-$[Ru^{III}Cl_3(bpea)]$ as a brown solid. *mer*-$[Ru^{III}Cl_3(bpea)]$ (*mer*-**1**) was isolated by alumina column chromatography with CH_3CN as the eluant. The formation ratio of *mer*-**1**, which was confirmed by the height of the reduction wave of the CV, decreased with increasing reaction time. From these reaction mixtures, after filtering out *fac*-**1**, the bis(bpea)ruthenium(II) complex, $[Ru^{II}(bpea)_2]^{2+}$, which had been previously synthesized and characterized,[18] and a small amount of *mer*-**1** were isolated by adding NH_4PF_6 and reducing the volume of the solution. The reaction conditions were varied to optimize the formation of *mer*-**1**. The conducted reactions always afforded mixtures of *fac*-**1**, *mer*-**1**, and $[Ru^{II}(bpea)_2]^{2+}$. The amount of *mer*-**1** decreased with increasing reaction time. It was suggested that the bpea ligand coordinated to the Ru center in both facial and meridional modes at first and then a configuration change occurred during heating under the synthetic conditions. Indeed, the reaction of *mer*-**1** in hydrochloric acid under refluxing conditions gave *fac*-**1**. Isolation of *mer*-**1** from the mixture obtained in the reaction solution after the 20 min reflux was successful by alumina column chromatography using an CH_3CN eluant.

Trichlororuthenim(III) complex, *fac*-**1**, seemed to be a useful starting complex for syntheses of ruthenium complexes, although synthesis of new ruthenium(III) complexes from *fac*-**1** by substitution reactions was unsuccessful under several reaction conditions. Syntheses of ruthenium(II) complexes by reduction of $[RuCl_3(bpea)]$ with $N(C_2H_5)_3$ and replacement of the chloro ligands have been reported.[15–18] Reaction of *fac*-**1** in C_2H_5OH–H_2O–CH_3CN (25:25:1) mixed solvent under refluxing conditions for 5 h afforded a triacetonitrile complex of ruthenium(II), *fac*-**2**$(PF_6)_2$ in good yield. Although isolation of mono- and bis-substituted complexes was attempted in other solvents and using $N(C_2H_5)_3$ as a reducing agent, those complexes were not obtained in a pure form.

$[RuCl_5(NO)]^{2-}$ is a useful starting complex for the synthesis of corresponding nitrosylruthenium complexes containing chloro ligand(s). A reaction of $[RuCl_5(NO)]^{2-}$ with an equimolar amount of bpea afforded a dichloronitrosyl complex *fac*-$\mathbf{3}^+$ in H_2O. The yield of *fac*-**3**PF_6 was slightly low due to its good solubility in H_2O and organic solvents such as CH_3CN and CH_3COCH_3. *fac*-**3**PF_6 was obtained from the reactions using an excess amount of bpea and in the presence of KCl in nearly the same yield. Attempts at synthesis of a mer form isomer and isolation from reaction mixtures were unsuccessful. The complex formulated as $[RuCl_2(NO)(bpea)]PF_6$ was thus stable in a facial fashion.

New nitrosylruthenium complexes were synthesized from *fac*-**3**PF_6 as a starting complex. Reactions of *fac*-**3**PF_6 with nucleophiles such as NO_2^-, CH_3O^-, and OH^- were carried out under several conditions. A reaction of *fac*-**3**PF_6 with $NaNO_2$ in H_2O afforded a hydroxonitronitrosyl complex, $[Ru(NO_2)(OH)(NO)(bpea)]^+$ ($\mathbf{4}^+$), whose configuration was of a meridional form. *mer*-**4**PF_6 was also obtained by a nitrosylation reaction of *fac*-**1** and *fac*-**2**$(PF_6)_2$ with $NaNO_2$ in H_2O. In the reaction of *fac*-**1**, $NaNO_2$ functioned as a reducing agent and was the source of the nitrosyl and the nitro ligands. A similar formation reaction of a nitrosyl complex had occurred in the reaction of $[RuCl_2(pyca)_2]^-$ (pyca = 2-pyridinecarboxylato) with $NaNO_2$ in H_2O.[28] Another synthetic route of *mer*-$\mathbf{4}^+$ was a simple substitution reaction of $[Ru(NO_2)_4(OH)(NO)]^{2-}$, which was synthesized from $[RuCl_5(NO)]^{2-}$,[24,29] with the bpea ligand in H_2O–C_2H_5OH. Some reactions of *fac*-**3**PF_6 with $NaNO_2$ were carried out in other solvents such as CH_3OH, CH_3COCH_3, and CH_3CN, and gave mixtures of a few nitrosyl complexes containing *mer*-**4**PF_6. Thus, the hydroxo ligand of $\mathbf{4}^+$ came from H_2O used as the solvent and contributed to regulating the configuration around the Ru center by interacting with the nitrosyl ligand.

A reaction of *fac*-**3**PF_6 with $NaOCH_3$ in dry-CH_3OH gave *trans*(NO, OCH_3), *cis*(NO, Cl), *mer*-$[RuCl(OCH_3)(NO)(bpea)]$-PF_6 (*mer*-**5**PF_6). This reaction was similar to that of $[RuCl_2(NO)(terpy)]^+$ with $NaOCH_3$ under the same reaction conditions.[10] When NaOH was used as a reaction substrate, *mer*-$\mathbf{5}^+$ was also obtained in CH_3OH and a new nitrosyl complex, whose FAB-MS spectrum showed $m/z = 439$ indicating formation of $[RuCl(OCH_2CH_3)(NO)(bpea)]^+$, was generated in C_2H_5OH. Thus, the alkoxo ligand of the reaction product would come from the solvent. The configuration of $\mathbf{6}^+$ was determined as meridional by the same reason as for *mer*-$\mathbf{4}^+$.

An aqueous solution of *mer*-**5**PF_6 in the presence of an equimolar amount of KCl gave *trans*(NO, OH), *cis*(NO, Cl), *mer*-$[RuCl(OH)(NO)(bpea)]PF_6$ (*mer*-**6**PF_6), which was formed by a solvolysis reaction of $\mathbf{5}^+$ in H_2O with substitution of the methoxo ligand by a hydroxo ligand. Although *mer*-**6**PF_6 was also obtained from the reaction in the absence of KCl, the presence of KCl resulted in a better yield and a higher purity of the obtained complex. These reactions were investigated in the presence of Cl^- as an incoming ligand for synthesis of $[RuCl_2(NO)(bpea)]^+$ in a meridional form, which was a geometric isomer of *fac*-$\mathbf{3}^+$. Further details of these reactions are described in a later section.

Properties of Trichloro and Triacetonitrile Complexes. Redox potentials of oxidation and reduction waves in CH_3CN at −40 °C and UV–vis spectral data of *fac*-**1**, *mer*-**1**, and *fac*-**2**$(PF_6)_2$ are summarized in Table 3.

fac-**1**, *mer*-**1**, and *fac*-**2**$(PF_6)_2$ were soluble in acetonitrile, acetone, dichloromethane, and nitromethane. ^1H NMR spectra of *fac*-**1** and *mer*-**1** revealed their paramagnetic properties. CVs of *fac*-**1**, *mer*-**1**, and *fac*-**2**$(PF_6)_2$ in CH_3CN are shown in Figure 2. These results indicate that both *fac*-**1** and *mer*-**1** are characterized as in the Ru^{III} oxidation state.

The CVs of *fac*-**1** and *mer*-**1** in CH_3CN at −40 °C revealed two redox waves and that of *fac*-**2**$(PF_6)_2$ one redox wave within the potential window. The profiles of the CVs of *fac*-**1** at 25 and −40 °C were different from each other, and so were those of *mer*-**1**, as shown in Figures 2a–2d. The CVs at −40 °C showed two reversible redox waves at −0.56 and 1.01 V for *fac*-**1** (Figure 1b), and −0.63 and 1.01 V for *mer*-**1** (Figure 1d), respectively. The redox waves at 1.01 V of *fac*-**1** and *mer*-**1** were assigned to reversible one-electron couples of Ru^{III} and Ru^{IV}, and those at −0.56 and −0.63 V to Ru^{III} and Ru^{II}. These redox waves were confirmed as those of a Nernstian one-electron process by normal pulse voltammetry (NPV). These redox potential values of *fac*-**1** and *mer*-**1**, (Ru^{IV}/Ru^{III}) and (Ru^{III}/Ru^{II}) couples, revealed that the oxidation state of Ru^{III} was stable compared to those of similar polypyridine ruthenium complexes.[30] At 25 °C, the

Table 3. Properties of Complexes

Complex	E/V		ν(NO)/cm^{-1}	λ_{max}/nm ($10^{-4}\varepsilon$/M^{-1} cm^{-1})
	Reduction	Oxidation		
fac-**1**	−0.56[a]	1.01[b]		244(0.81), 324(0.45), 343(0.43), 400(0.24)
mer-**1**	−0.63[a]	1.01[b]		243(0.82), 333(0.45), 390(0.52), 466(0.08)
fac-**2**$(PF_6)_2$	1.06[a]			246(1.18), 332(0.92)
fac-**3**PF_6	−0.58, −1.43[c]		1914	265(0.63), 367(0.04)
mer-**4**PF_6	−0.91, −1.68[c]		1874	260(1.13)
mer-**5**PF_6	−1.04, −1.81[c]		1822	267(0.89), 288(sh), 378(0.07)
mer-**6**PF_6	−1.04, −1.77[c]		1865	265(0.81), 290(sh), 357(0.06)

a) Ru^{III}/Ru^{II}. b) Ru^{IV}/Ru^{III}. c) $(RuNO)^{3+}/(RuNO)^{2+}$, $(RuNO)^{2+}/(RuNO)^{+}$.

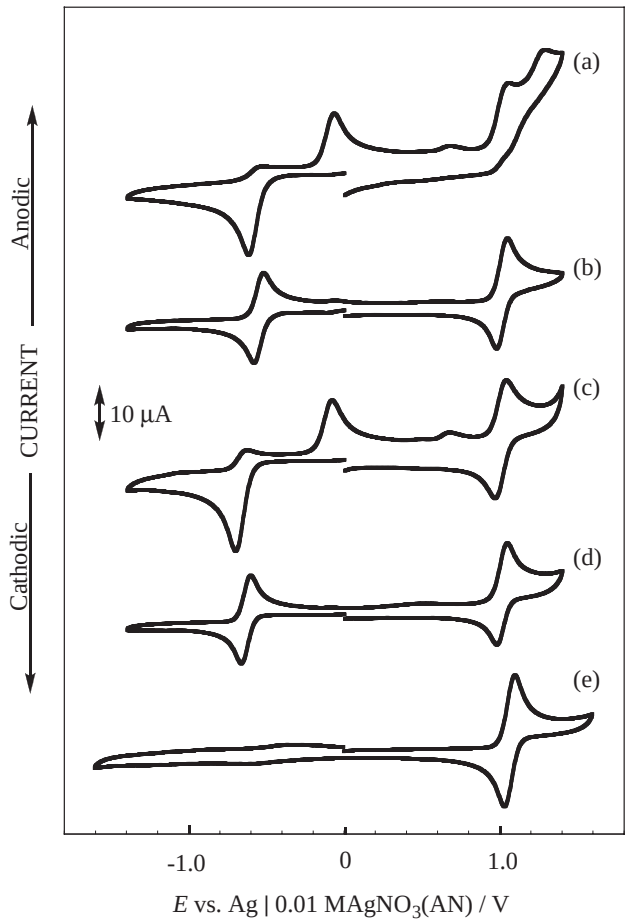


Figure 2. CVs of *fac*- and *mer*-$[RuCl_3(bpea)]$ (*fac*-**1** and *mer*-**1**) and *fac*-$[Ru(CH_3CN)_3(bpea)](PF_6)_2$ (*fac*-**2**$(PF_6)_2$) in CH_3CN with scan rate 200 mV s^{-1}: (a) *fac*-**1** at 25 °C, (b) *fac*-**1** at −40 °C, (c) *mer*-**1** at 25 °C, (d) *mer*-**1** at −40 °C, (e) *fac*-**2** at −40 °C.

CVs of both *fac*-**1** and *mer*-**1** with reductive scans from 0 V revealed irreversible reduction waves assigned to reduction from Ru^{III} to Ru^{II}, and the corresponding oxidation waves disappeared in the reverse oxidative scans from −1.5 V (Figures 2a and 2c). In the continuous oxidative scan, new waves were observed at around −0.1 V. The reduction forms of *fac*-**1** and *mer*-**1** were unstable at 25 °C and formed new species whose oxidation waves appeared at around −0.1 V within the CV's time scale. These CV profiles of both complexes at 25 °C indicate that one-electron-reduced species, *fac*- and *mer*-$[Ru^{II}Cl_3(bpea)]^-$, are unstable and changed to new species showing an oxidation wave at around −0.1 V, while those at −40 °C revealed a reversible processes of Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II}. The reduction processes were confirmed as a one-electron reduction process by controlled potential electrolysis (CPE) at −0.8 V, and the formation of new complexes showing a redox couple at around −0.1 V was confirmed by CVs after CPE. Those CVs showed that the wave of the Ru^{III}/Ru^{II} couple disappeared and new waves at −0.1 and 0.8 V appeared. The wave at −0.1 V was observed on the reverse positive scan from −1.4 V, that caused the reduction of *fac*-**1** and *mer*-**1** to occur, and the wave at 0.8 V was assigned to an oxidation wave of the free Cl^- ion. Detailed studies on isolation and identification of these products are now in progress. While the CV of *mer*-**1** at 25 °C with an oxidative scan from 0 V was the same as that at −40 °C, the CV of *fac*-**1** at 25 °C revealed two irreversible oxidation waves at 1.04 and 1.28 V. The oxidation wave at 1.04 V was assigned to oxidation from Ru^{III} to Ru^{IV} and that at 1.28 V to a new species which formed from the oxidation form of *fac*-**1**.

The ^1H NMR spectrum of *fac*-**2**$(PF_6)_2$ in CD_3CN showed two signals for the CH_3CN ligands and eight signals for the bpea ligand consisting of two signals for the ethyl group bonded to the amine nitrogen at 1.36 and 3.52 ppm for the CH_3 and CH_2 and four signals for the pyridyl groups and two signals for the bridging CH_2 groups between 7.3–8.8 and 4.3–4.4 ppm, respectively. The CV of *fac*-**2**$(PF_6)_2$ showed one reversible redox couple at 1.06 V attributed to the Ru^{II} and Ru^{III} couple (Figure 1e), which was confirmed as that of a Nernstian one-electron process by NPV. The CV profiles measured at 25 and −40 °C were essentially the same.

Properties of Nitrosylruthenium Complexes. Each of the nitrosylruthenium complexes obtained in this work showed a strong N–O stretching mode, ν(NO), and two stepwise reduction waves within the potential window. The ν(NO), reduction potentials and λ_{max} with ε of the nitrosyl complexes are given in Table 3. The CV profiles of these nitrosylruthenium complexes in CH_3CN at −40 °C were similar to those of $\{RuNO\}^6$-type complexes as shown in Figures 3a–3d. The first reduction processes were assigned to a reversible $(RuNO)^{3+}/(RuNO)^{2+}$ couple whose peak current ratio I_{pa}/I_{pc} was nearly

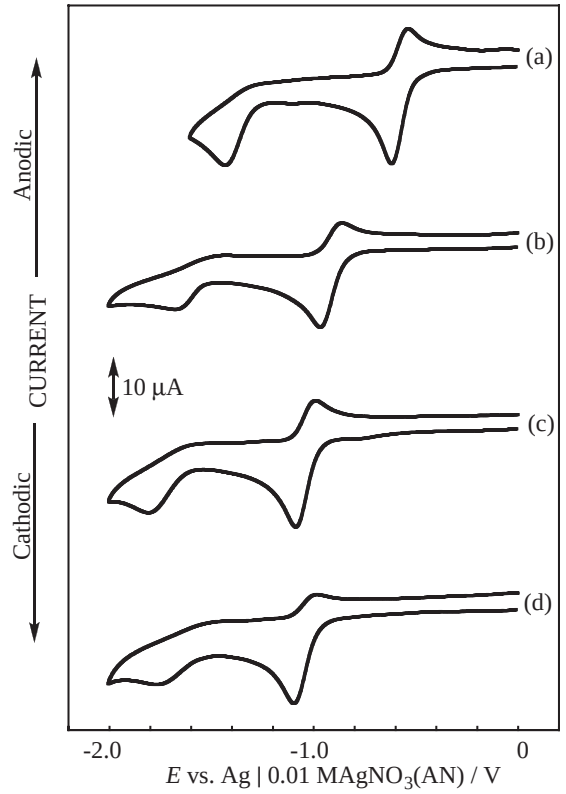


Figure 3. CVs of nitrosylruthenium complexes in CH_3CN with the scan rate 200 mV s^{-1} at −40 °C: (a) *fac*-**3**PF_6, (b) *mer*-**4**PF_6, (c) *mer*-**5**PF_6, (d) *mer*-**6**PF_6.

equal to unity in the CVs with a reverse scan to observe the first wave, and were confirmed as those of a Nernstian one-electron process by NPV. The second one was assigned to irreversible reduction of the $(RuNO)^{2+}$ species to $(RuNO)^{+}$ in accordance with those of previously reported $\{RuNO\}^6$-type nitrosyl complexes.[10–12,28] There was no appreciable difference in the CV profile measured at 25 and −40 °C nor between the complexes having *fac*- and *mer*-coordination modes of the bpea ligand. The reduction potential values of these nitrosyl complexes changed with varying compositions of the coexisting ligands such as Cl^-, NO_2^-, OH^-, and OCH_3^-.

The values of the ν(NO) band in IR spectroscopy and the reduction potentials of the nitrosyl complexes depended on electron density and reactivity of the nitrosyl ligand, and they correlated with each other.[31] The synthesized complexes showed a strong ν(NO) band over a range between 1822 and 1914 cm^{-1} and the reduction potential of the (RuNO)-moiety between −0.58 and −1.04 V in CH_3CN. These values of the present complexes are within the normal region like those of nitrosylruthenium complexes containing polypyridine ligand such as bpy and trpy, and the structural parameters of the (RuNO)-moieties, the Ru–N and N–O distances and the Ru–N–O angle, revealed these nitrosyl complexes to be classified as $\{RuNO\}^6$-type.[10–12,32] The ^{1}H NMR spectra of these nitrosyl complexes revealed differences in spectral pattern of the bpea ligand between fac and mer forms. There were two types of CH_2 units in the bpea ligand: one in the ethyl group bonded to the amine nitrogen and another in two bridging units between the amine and the pyridyl groups. The signals of the six protons of *fac*-**3**$^+$ were observed at different chemical shifts; two proton signals for the ethyl group at 3.64 and 4.28 ppm and four signals for the bridging methylene groups at 4.72, 4.80, 5.10, and 5.19 ppm with coupling constants of 16 and 18 Hz, while the mer form nitrosyl complexes, *mer*-**4**$^+$, -**5**$^+$, and -**7**$^+$, showed only three signals; one multiplet proton signal for the ethyl group at around 3.3–3.4 ppm and two proton signals for the bridging methylene groups at around 4.2–5.3 ppm with a coupling constant of 16 Hz. Thus, a geometric configuration of this type of nitrosyl complex, $[RuXY(NO)(bpea)]^{n+}$, was predictable from spectral patterns of the CH_2 units in ^{1}H NMR spectroscopy. The electronic spectrum revealed dπ(Ru)–π^*(bpea) transitions and a weak d–d transition overlapped with the dπ(Ru)–π^*(NO) transition by comparison with those found in the literature.[15,17] The dπ(Ru)–π^*(bpea) transitions were shifted to a higher energy region compared with those of non-nitrosyl complexes. These shifts were due to the stabilization of dπ(Ru) orbitals by the strong π-acid NO ligand.

Table 4. Selected Bond Distances/Å and Angles/° for *fac*-**1**, *mer*-**1**, and *fac*-**2**$^{2+}$

	fac-**1**	*mer*-**1**	*fac*-**2**$^{2+}$
Ru–N(amine)	2.134(3)	2.127(2)	2.101(3)
Ru–N(py)	2.066(3)	2.064(2)	2.051(3)
	2.092(3)	2.056(2)	2.060(2)
Ru–X			
trans-amine[a)]	X = Cl	X = Cl	X = $NCCH_3$
	2.3485(12)	2.3603(11)	2.047(3)
cis-amine[b)]	X = Cl	X = Cl	X = $NCCH_3$
	2.3709(12)	2.3383(8)	2.041(2)
	2.3643(11)	2.3721(10)	2.036(3)
X–Ru–X	91.60(4)	88.53(3)	87.60(12)
	91.56(4)	177.18(3)	86.26(14)
	93.51(4)	89.27(3)	90.41(12)
N(py)–Ru–N(amine)	81.41(13)	81.90(10)	82.72(13)
	78.57(13)	82.55(10)	82.17(12)
N(py)–Ru–N(py)	92.62(12)	164.45(10)	83.88(12)
N(amine)–Ru–X(*trans*-amine)	167.75(9)	178.34(7)	178.20(11)

a) The ligand located at the trans position toward the amine nitrogen atom. b) Ligands located at the cis position toward the amine nitrogen atom.

Structures of Complexes. Each of the structurally characterized complexes, $[RuXYZ(bpea)]^n$, revealed a distorted octahedral coordination geometry around the Ru atom with three nitrogen atoms of the bpea and three ancillary ligands (X, Y, and Z). Selected structural parameters are summarized in Tables 4 and 5. Structures of *fac*-**1** and *mer*-**1** are shown in Figure 4 and those of the complex cations (*fac*-**2**$^{2+}$, *fac*-**3**$^+$, *mer*-**4**$^+$, *mer*-**5**$^+$, and *mer*-**6**$^+$) in Figures 5–9.

The bpea ligand can coordinate in both the meridional and facial configurations with two pyridyl and one amino nitrogen atoms. The mer form of octahedral manganese complexes has been structurally characterized,[20] and the first mer form ruthenium complex has been recently synthesized and characterized by X-ray crystallography.[14] The facial coordination mode of the bpea ligand was confirmed in *fac*-**1**, *fac*-**2**$^{2+}$, and *fac*-**3**$^+$, and the meridional in *mer*-**1**, *mer*-**4**$^+$, *mer*-**5**$^+$, and *mer*-**6**$^+$.

Table 5. Selected Bond Distances/Å and Angles/° for *fac*-$\mathbf{3}^{+}$, *mer*-$\mathbf{4}^{+}$, *mer*-$\mathbf{5}^{+}$, and *mer*-$\mathbf{6}^{+}$

	fac-$\mathbf{3}^{+}$	*mer*-$\mathbf{4}^{+}$	*mer*-$\mathbf{5}^{+}$ [a]	*mer*-$\mathbf{6}^{+}$
Ru–N(amine)	2.137(3)	2.119(2)	2.093(3)	2.096(2)
Ru–N(py)	2.090(3)	2.078(2)	2.082(3)	2.082(3)
	2.103(3)	2.079(2)	2.073(3)	2.071(2)
Ru–X				
trans-amine[b]	X = Cl	X = NO_2	X = Cl	X = Cl
	2.3588(11)	2.096(3)	2.3945(13)	2.3808(10)
Ru–Y	Y = Cl[c]	Y = OH[d]	Y = OCH_3[d]	Y = OH[d]
	2.3646(13)	1.941(2)	1.943(3)	1.953(2)
Ru–N(NO)	1.746(4)	1.755(3)	1.751(3)	1.751(2)
N–O(NO)	1.131(5)	1.147(5)	1.145(5)	1.139(4)
X–Ru–Y	90.21(5)	87.09(13)	91.65(9)	88.25(7)
X–Ru–N(NO)	90.39(14)	89.05(15)	86.46(10)	87.49(9)
Y–Ru–N(NO)	91.90(14)	175.20(13)	178.02(13)	175.73(11)
N(py)–Ru–N(amine)	82.23(13)	82.40(11)	81.43(12)	82.10(10)
	80.99(12)	82.44(11)	83.15(11)	82.45(10)
N(py)–Ru–N(py)	82.58(13)	162.94(11)	163.18(13)	163.77(11)
N(amine)–Ru–X(*trans*-amine)	171.64(9)	172.72(14)	176.44(10)	172.39(8)
Ru–N–O(NO)	176.0(5)	173.4(3)	170.6(3)	170.2(2)

a) The cation was crystallized with *fac*-$\mathbf{3}^{+}$ and two PF_6^-. b) The ligand located at the trans position toward the amine nitrogen atom. c) The ligand located at the cis position toward the NO ligand and the trans position toward the amine nitrogen atom. d) Ligands located at the trans position toward the NO ligand.

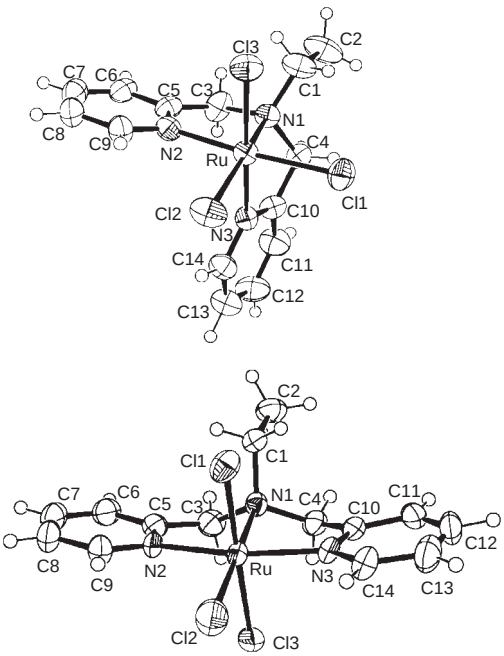


Figure 4. Structure of *fac*-**1** and *mer*-**1** with non-hydrogen atom labeling.

The bond distances between Ru and the amine nitrogen atom were longer than those between Ru and the pyridyl nitrogen atoms in the same complex, due to the difference in nature between σ-donor amine and weak π-acceptor pyridine. The bond lengths of Ru–N(py) were similar to those of previously reported bpea complexes and polypyridine complexes (Ru^{III}–N 2.04–2.06 Å and Ru^{II}–N 2.05–2.10 Å).[33,34] The bond angles of N(py)–Ru–N(amine) (78.57(13)–82.72(13)°) of both the

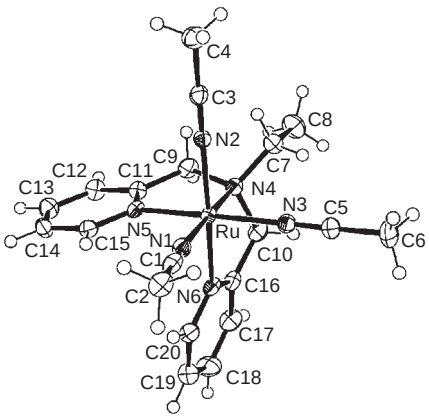


Figure 5. Structure of *fac*-$\mathbf{2}^{2+}$ with non-hydrogen atom labeling.

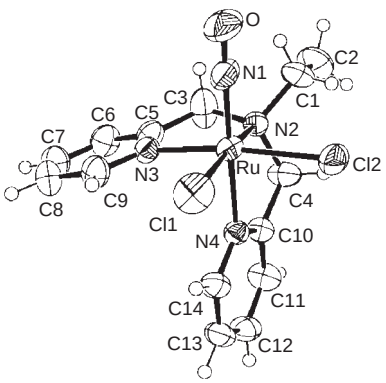


Figure 6. Structure of *fac*-$\mathbf{3}^{+}$ with non-hydrogen atom labeling.

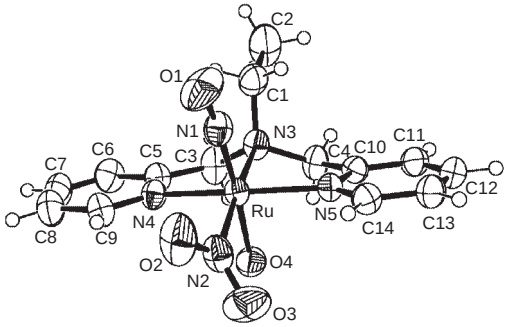


Figure 7. Structure of *mer*-$\mathbf{4}^{+}$ with non-hydrogen atom labeling.

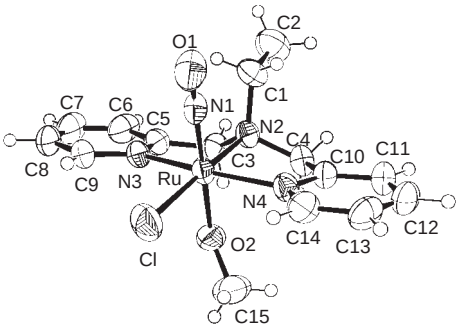


Figure 8. Structure of *mer*-$\mathbf{5}^{+}$ with non-hydrogen atom labeling.

fac and the mer configurations and those of N(py)–Ru–N(py) of the fac (83.88(12) and 82.58(13)°) and the mer configuration (162.94(11)–164.45(10)°) were distorted from ideal octahedral angles, except for that of *fac*-**1** in which the only amine nitrogen atom of its bpea was located in the distorted octahedral positions. Structural features of the bpea ligand coordinated to the metal center with distortion were explained by the difference in Ru–N bonds and the spatially constrained nature of the bpea ligand. The bond angles involving the ancillary ligands such Cl, CH_3CN, NO, NO_2, OH, and OCH_3 through the Ru center (X–Ru–X, X–Ru–Y, X–Ru–N(NO), and Y–Ru–N(NO) in Tables 4 and 5) were close to the ideal right angle or straight angle.

Trichlororuthenium(III) complexes, *fac*-**1** and *mer*-**1**, were the first structurally characterized Ru^{III} complexes containing the bpea ligand. The bond lengths of Ru–Cl and Ru–N were typical for Ru^{III} complexes.[34,35] The isomeric pair of trichlororuthenium(III) complexes, *fac*-**1** and *mer*-**1**, showed different bond distances between the Ru and the Cl atoms. For *fac*-**1**, the distances between Ru and Cl located in the trans positions toward the pyridyl nitrogen atoms were longer than those in the cis position, indicating a weak trans effect of the pyridyl rings of the bpea. Three nitrogen atoms of the bpea ligand of the reported complexes were situated in distorted positions with the N(amine)–Ru–N(py), N(py)–Ru–N(py), N(amine)–Ru–X, and N(py)–Ru–X angles of ca. 80°.[15–18] These angles of *fac*-**1** and *mer*-**1** indicated different distortions from the ideal octahedron: only the amine nitrogen atom was dislocated from the ideal position in *fac*-**1**, while two pyridyl nitrogen atoms of *mer*-**1** were dislocated due to the spatially constrained nature of the bpea ligand.

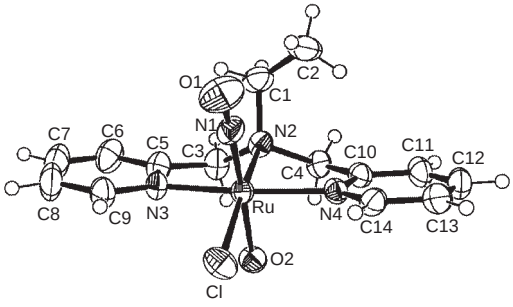


Figure 9. Structure of *mer*-$\mathbf{6}^{+}$ with non-hydrogen atom labeling.

Structural parameters of the Ru–NO moieties (Ru–N; 1.746(4)–1.755(3) Å and N–O bond distances; 1.131(5)–1.147(5) Å, and Ru–N–O angle; 170.2(2)–176.0(5)°) in nitrosyl complexes, *fac*-$\mathbf{3}^{+}$, *mer*-$\mathbf{4}^{+}$, *mer*-$\mathbf{5}^{+}$, and *mer*-$\mathbf{6}^{+}$, revealed a typical linearly coordinated NO ligand. Thus, the present nitrosyl complexes are classified as $\{RuNO\}^6$-type complexes. The structural parameters of {Ru(bpea)} moiety revealed the Ru–N(py) bond lengths were slightly longer than those of ruthenium complexes having no nitrosyl ligand. This lengthening tendency was attributed to coordination of the strong π-acceptor NO ligand in analogy with complexes having a π-acceptor ligand such as CO.[34,36] In nitrosyl complexes containing a OH^- or OCH_3^- ligand, *mer*-$\mathbf{4}^{+}$, *mer*-$\mathbf{5}^{+}$, and *mer*-$\mathbf{6}^{+}$, the bpea ligand coordinated in a meridional fashion. The nitrosyl ligand interacted with an electron-donor ligand, and then the electron-donor ligand coordinated in a trans-position toward the nitrosyl ligand, similarly to *trans*-$[Ru(OCH_3)(pyca)_2(NO)]$ (pyca = 2-pyridinecarboxylato), which was formed by a substitution of Cl in *cis*-$[RuCl(pyca)_2(NO)]$ with OCH_3^- followed by an isomerization reaction from the cis form to the trans.[12] These results indicated that the interaction between the nitrosyl and the ancillary ligands was important in regulating the coordinating geometry of the bpea ligand.

Conversions between Fac and Mer Complexes. The bpea ligand has flexible CH_2-arms and therefore potentially coordinates both in facial and meridional fashions. In our experiments with the synthesis of trichloro complex $[Ru^{III}Cl_3(bpea)]$, a fac form complex (*fac*-**1**) was obtained in a high yield under 3 h reflux and a mer form complex (*mer*-**1**) was also obtained as a mixture with *fac*-**1** by applying a short reaction time. The results of experiments with varying reaction times indicated *fac*-**1** was more stable than *mer*-**1** under the refluxing conditions in the presence of excess hydrochloric acid. While *mer*-**1** was stable in an CH_3CN solution under refluxing conditions, a brown aqueous solution of *mer*-**1** changed to a dark blue solution by refluxing. Attempts to isolate and identify the products from the blue solution were unsuccessful. A hydrochloric acid solution of *mer*-**1** was refluxed for 3 h to give a brown precipitate. The brown complex showed absorption bands at 244, 324, 343, and 400 nm in the UV–vis spectrum and two reversible waves at 1.01 and −0.56 V in the CV in an CH_3CN solution. This brown complex was identified as *fac*-**1** by comparing characteristic data shown in Table 3. A reaction of *mer*-**1** in aqueous solution without hydrochloric acid afforded a blue solution, while *mer*-**1** was quantitatively isolated in its reaction in CH_3CN. Several attempts of isolation from

the blue solution were unsuccessful. Similar reactions of mer–fac changes in nitrosylruthenium complexes occurred in a hydrochloric acid solution. Reactions were performed under similar reaction conditions using mer form complexes containing a nitrosyl ligand. In reactions of **5**PF_6 and **6**PF_6 in a hydrochloric acid solution under refluxing conditions, brown complexes were isolated by addition of NH_4PF_6 as a precipitant. These complexes showed a strong IR band at 1914 cm^{-1} and a reversible couple at −0.58 V and an irreversible wave at −1.43 V in CH_3CN in common. The obtained complexes were identified as *fac*-**3**$^+$ based on those data in addition to ^{1}H NMR spectral data. Conformational changes from a mer form to a fac form thus occurred during the reactions in the presence of hydrochloric acid. The configuration of the products was determined by an interaction between the nitrosyl and an ancillary ligand as described above. The products having both nitrosyl and hydroxo or methoxo ligands in the trans position to each other were more stable, and the bpea ligand coordinated to the Ru center in a meridional fashion. Thus, these results indicate that the coordinating fashion of the bpea ligand can be controlled by a combination of ancillary ligands.

Conclusion

The tridentate *N*-ethyl-*N*,*N*-bis(2-pyridylmethyl)amine (bpea) ligand having two different types of nitrogen donors, one an amine and the other pyridine rings connected with flexible CH_2-arms was used as supporting ligand to synthesize ruthenium complexes. The bpea ligand was able to coordinate to the ruthenium center in facial and meridional fashions, and its coordination mode was determined by a combination of ancillary ligands such as nitrosyl, Cl^-, NO_2^-, OH^-, OCH_3^-, and CH_3CN. The fac form complex was slightly more stable than the corresponding mer form due to the spatially constrained nature of the bpea ligand. Syntheses of both *fac*- and *mer*-[$RuCl_3$(bpea)] were successful in simple reaction procedures, although the yield of the mer form complex was lower than that of the fac one. Nitrosyl ligands function as a weak σ-donor and a strong π-acceptor coordinated to the ruthenium center and interact with co-existing ligands through the central metal. The nitrosyl ligand in the present synthesized complexes regulated the configuration around the ruthenium center, similar to that in [RuL(pyca)$_2$(NO)]-type complexes due to its strong π-acid character. The configuration of the synthesized nitrosyl complexes indicated that the decreasing order of electron-donating nature was: OR^- (R = H and CH_3) > py(bpea) > $Cl^- \approx NO_2^-$. Geometric configurations around the ruthenium center depended on the nature of the co-existing ligands that strongly influenced the nitrosyl ligand. In this work, synthesis of fac and mer form complexes with the same formula as the nitrosylruthenium complex was unsuccessful. Studies on synthesis of isomeric pairs of nitrosyl complexes using pyridine as an ancillary ligand are in progress.

Supporting Information

The electronic spectra of *fac*-**1**, *mer*-**1**, and *fac*-**2**(PF_6)$_2$ (Figure S1), *fac*-**3**PF_6, *mer*-**4**PF_6, *mer*-**5**PF_6, and *mer*-**6**PF_6 (Figure S2), ^{1}H NMR spectra of *fac*-**2**(PF_6)$_2$ (Figure S3), *fac*-**3**PF_6, *mer*-**4**PF_6, *mer*-**5**PF_6, and *mer*-**6**PF_6 (Figure S4), the controlled potential electrolysis of *fac*-**1** (Figure S5) and of *mer*-**1** (Figure S6), CVs after controlled potential electrolysis (Figure S7), and CVs of *fac*-**3**PF_6, *mer*-**4**PF_6, *mer*-**5**PF_6, and *mer*-**6**PF_6 (Figure S8). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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