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Regulation of Geometry around the Ruthenium Center of Bis(2-pyridinecarboxylato) Complexes by the Nitrosyl Moiety: Syntheses, Structures, and Theoretical Studies

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cis-[Ru(NO)Cl(pyca)$_2$] (pyca = 2-pyridinecarboxylato), in which the two pyridyl nitrogen atoms of the two pyca ligands coordinate at the trans position to each other and the two carboxylic oxygen atoms at the trans position to the nitrosyl ligand and the chloro ligand, respectively (type **I** shown as in Chart 1), reacted with $NaOCH_3$ to generate *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**). The geometry of this complex was confirmed to be the same as the starting complex by X-ray crystallography: $C_{13.5}H_{13}N_3O_{6.5}Ru$; monoclinic, $P2_1/n$; $a = 8.120(1)$, $b = 16.650(1)$, $c = 11.510(1)$ Å; $\beta = 99.07(1)°$; $V = 1536.7(2)$ Å^3; $Z = 4$. The cis–trans geometrical change reaction occurred in the reactions of *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**) in water and alcohol (ROH, R = CH_3, C_2H_5) to form [{*trans*-Ru(NO)(pyca)$_2$}$_2$(H$_3$O$_2$)]$^+$ (type **V**) and *trans*-[Ru(NO)(OR)(pyca)$_2$] (type **V**). The reactions of the trans-form complexes, *trans*-[Ru(NO)(H$_2$O)(pyca)$_2$]$^+$ (type **V**) and *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **V**), with Cl^- in hydrochloric acid solution afforded the cis-form complex, *cis*-[Ru(NO)Cl(pyca)$_2$] (type **I**). The favorable geometry of [Ru(NO)X(pyca)$_2$]$^{n+}$ depended on the nature of the coexisting ligand X. This conclusion was confirmed by theoretical, synthetic, and structural studies. The mono-pyca-containing nitrosylruthenium complex $(C_2H_5)_4N$[Ru(NO)Cl$_3$(pyca)] was synthesized by the reaction of [Ru(NO)Cl$_5$]$^{2-}$ with Hpyca and characterized by X-ray structural analysis: $C_{14}H_{24}N_3O_3Cl_3Ru$; triclinic, $P\bar{1}$, $a = 7.631(1)$, $b = 9.669(1)$, $c = 13.627(1)$ Å; $\alpha = 83.05(2)$, $\beta = 82.23(1)$, $\gamma = 81.94(1)°$; $V = 981.1(1)$ Å^3; $Z = 2$. The type **II** complex of *cis*-[Ru(NO)Cl(pyca)$_2$] was synthesized by the reaction of [Ru(NO)Cl$_3$(pyca)]$^-$ or [Ru(NO)Cl$_5$]$^{2-}$ with Hpyca and isolated by column chromatography. The structure was determined by X-ray structural analysis: $C_{12}H_8N_3O_5ClRu$; monoclinic, $P2_1/n$; $a = 10.010(1)$, $b = 13.280(1)$, $c = 11.335(1)$ Å; $\beta = 113.45(1)°$; $V = 1382.4(2)$ Å^3; $Z = 4$.

Introduction

It is now well-known that nitric oxide plays fundamental roles in biochemical processes.[1,2] The interests in nitric oxide in chemical and biochemical studies are its reactions and interactions with the metal centers. Nitrogen monoxide bonds to a metal center via two types of coordinating modes, linearly and bent bonding: A linearly bonded nitrosyl ligand functions as a poor σ-donor and a strong π-acceptor, and a bent one as a strong σ-donor. Many linearly bonded nitrosyl complexes have been synthesized and characterized,[1−3] and a few theoretical study on reactions of the coordinated nitrosyl moiety have been recently reported.[4] The structural trans effects of the linearly bonded nitrosyl ligand in

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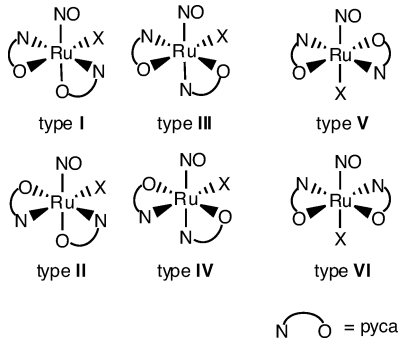
Chart 1. Six Geometrical Isomers of $[Ru(NO)X(pyca)_2]^{n+}$ Complexes



octahedral transition metal complexes have been discussed in terms of their stable structures which are correlated with the nature of the ligand at the trans position to the NO ligand.[3] These nitrosyl complexes receive much attention not only as useful models for biological systems to understand metal−NO interactions but also as reaction mediators and regulators. The reaction behaviors and structural features of the nitrosyl ligand correlate with a contribution of electrons around central metal: the character of the bond between a metal and NO has been classified by the Enemark−Feltham notation, $\{M(NO)_x\}^n$, where n is the sum of the number of electrons in the d orbitals of the metal (M) and in the π^* orbital of NO.[5] In our investigations on syntheses, structures, and reactions of the $\{RuNO\}^6$-type nitrosylruthenium complexes, the nitrosyl ligand plays an important role in the stability of complexes and rearrangement of coexisting ligands such as NO_2^- in N- and O-bonded modes.[6]

$[Ru(NO)X(pyca)_2]^{n+}$ has six geometrical isomers (four isomers of cis form, isomers **I**−**IV**, and two isomers of trans form, isomers **V** and **VI**) as shown in Chart 1. Some isomerization reactions of metal nitrosyl complexes have been investigated and reported: linkage isomerization of the N- and O-bonded nitrosyl ligands;[7] geometrical isomerization.[8,9] Although a few geometrical isomerizations of $\{RuNO\}^6$-type complexes accompanying the dissociation of the NO molecule have been reported,[9] the mechanisms of isomerization reactions and the function of the nitrosyl ligand are not clear at present. We have reported that reactions of *cis*-$[Ru(NO)X(pyca)_2]^{n+}$ (type **I**) (X = Cl, NO_2, $n = 0$; X = H_2O, $n = 1$) with OH^-, N_3^-, and OCH_3^- were accompanied by the rare cis−trans geometrical changes to form trans-type isomers, $[\{trans\text{-}Ru(NO)(pyca)_2\}_2(H_3O_2)]^+$ (type **V**) and *trans*-$[Ru(NO)(OCH_3)(pyca)_2]$ (type **V**).[10] These geometrical changes quantitatively occur without NO evolution,[10] indicating the metal−NO bond is not activated and cleavage does not occur during isomerization. Thus, our reaction system of the $[Ru(NO)X(pyca)_2]^{n+}$ series differs from photoactivation of the metal−NO bond with NO evolution, and the relation among the nitrosyl and the coming and the leaving ligands is important for the stability of the complexes. This paper describes syntheses, structural determinations, reactions of $[Ru(NO)X(pyca)_2]^{n+}$ (X = Cl, NO_2, OR (R = CH_3, C_2H_5), $n = 0$; X = H_2O, $n = 1$), and theoretical studies on the stability of these geometrical isomers to understand the interactions between NO and coexisting ligands through the Ru center. Synthesis and characterization of three different types of isomers, types **I**, **II**, and **V**, have been successful by employing a suitable kind of X ligand in $[Ru(NO)X(pyca)_2]^{n+}$ and reaction conditions, and the stability of each isomer is theoretically explained by the sum of contributions of trans pairs in the complex.

Experimental Section

Materials. $K_2[Ru(NO)Cl_5]$,[11] *cis*-$[Ru(NO)Cl(pyca)_2]$ (type **I**),[12] *cis*-$[Ru(NO)(NO_2)(pyca)_2]$ (type **I**),[6] and *trans*-$[Ru(NO)(H_2O)(pyca)_2]ClO_4 \cdot 0.5H_2O$ (type **V**)[10] were prepared according to the methods in the literature.

Caution! *Although the complexes as perchlorate salts are stable, they are potentially explosive and should be handled with care.*

Synthesis of *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type I). To a methanol solution (20 cm^3) of *cis*-$[Ru(NO)Cl(pyca)_2]$ (type **I**) (200 mg, 0.49 mmol) was added $NaOCH_3$ (28 mg, 0.52 mmol) while stirring. The solution was stirred for 12 h at room temperature. The solution was concentrated to ca. 5 cm^3 using a rotary evaporator, and diethyl ether was added to give a brown precipitate. The product was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 120 mg (61%). Anal. Found: C, 38.19; H, 2.54; N, 10.36. Calcd for $C_{13}H_{11}N_3O_6Ru$: C, 38.43; H, 2.73; N, 10.34. $\nu(NO) = 1861\ cm^{-1}$. NMR: δ_H (CD_3CN) 3.44 (3H, s, CH_3), 7.88 (1H, t, 5-py), 7.93 (1H, t, 5-py), 8.20 (2H, d, 3-py), 8.29 (1H, t, 4-py), 8.36 (1H, t, 4-py), 8.76 (1H, d, 6-py), 8.90 (1H, d, 6-py); δ_C (CD_3CN) 60.5 ($-CH_3$), 116.7 (5-py), 117.0 (5-py), 117.2 (3-py), 117.8 (3-py), 126.8 (4-py), 127.5 (4-py), 128.2 (6-py), 129.5 (6-py), 141.5 (2-py), 142.7 (2-py), 146.6 ($-COO^-$), 150.2 ($-COO^-$).

Reaction of *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type I) in Methanol To Form *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type V). A methanol solution (20 cm^3) of *cis*-$[Ru(NO)(OCH_3)(pyca)_2]$ (type **I**) (50 mg, 0.12 mmol) was refluxed for 1 h to give a yellow solution. The yellow solution was concentrated using a rotary evaporator to ca. 5 cm^3. Diethyl ether was added to the solution to give a yellow precipitate. The product was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 38 mg (76%). This

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complex has been synthesized by a different method and characterized.[10] ν(NO) = 1838 cm^{-1}.

Reaction of *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type I) in Ethanol To Form *trans*-[Ru(NO)(OC$_2$H$_5$)(pyca)$_2$] (Type V). A suspension of *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**) (50 mg, 0.12 mmol) in C_2H_5-OH (20 cm^3) was refluxed for 1 hour to give a yellow solution. The solution was concentrated using a rotary evaporator to ca. 5 cm^3. Diethyl ether was added to the solution to give a yellow precipitate. The product was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 30 mg (58%). Anal. Found: C, 40.01; H, 2.96; N, 9.93. Calcd for $C_{14}H_{13}N_3O_6Ru$: C, 40.00; H, 3.12; N, 10.00. ν(NO) = 1815 cm^{-1}. δ_H (CD_3CN): 0.50 (3H, t, CH_3), 3.33 (1H, q, CH_2), 3.61 (1H, q, CH_2), 7.86 (2H, t, 5-py), 8.18 (2H, d, 3-py), 8.32 (2H, t, 4-py), 8.75 (1H, d, 6-py); δ_C (CD_3CN) 19.7 (CH_3), 64.4 (CH_2), 128.2 (5-py), 130.0 (3-py), 143.4 (4-py), 150.1 (6-py), 152.1 (2-py), 172.7 (COO^-).

Reaction of *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type V) with HCl To Form *cis*-[Ru(NO)Cl(pyca)$_2$] (Type I). An aqueous hydrochloric acid solution (20 cm^3, pH 1.8) of *trans*-[Ru(NO)(OCH$_3$)-(pyca)$_2$] (type **V**) (50 mg, 0.12 mmol) and KCl (200 mg, 2.7 mmol) was refluxed for 2 h to give an orange solution. This solution was cooled to room temperature to give an orange precipitate. The product was collected by filtration, washed with cold water, ethanol, and diethyl ether, and dried in vacuo. Yield: 26 mg (51%). ν(NO) = 1890 cm^{-1}.

Reaction of *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type V) with NaNO$_2$ To Form *cis*-[Ru(NO)(NO$_2$)(pyca)$_2$] (Type I). A suspension of *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **V**) (50 mg, 0.12 mmol) and $NaNO_2$ (200 mg, 2.9 mmol) in $C_2H_5OH-H_2O$ (10:1 v/v; 55 cm^3) was refluxed for 3 h to give a yellow solution. The solution was concentrated to ca.. 5 cm^3 by evaporating the solvent by heating to give a yellow precipitate. The product was collected by filtration, washed with cold water, ethanol, and diethyl ether, and dried in vacuo. Yield: 15 mg (29%). ν(NO) = 1907 cm^{-1}.

Reaction of *trans*-[Ru(NO)(H$_2$O)(pyca)$_2$]ClO$_4$·0.5H$_2$O (Type V) with HCl To Form *cis*-[Ru(NO)Cl(pyca)$_2$] (Type I). An aqueous hydrochloric acid solution (pH 2.0) of *trans*-[Ru(NO)-(H$_2$O)(pyca)$_2$]ClO$_4$·0.5H$_2$O (type **V**) (50 mg, 0.10 mmol) and KCl (200 mg, 2.7 mmol) was refluxed for 3 h to give an orange solution. This solution was cooled to room temperature to give an orange precipitate. The product was collected by filtration, washed with cold water, ethanol, and diethyl ether, and dried in vacuo. Yield: 26 mg (51%). ν(NO) = 1890 cm^{-1}.

Reaction of *trans*-[Ru(NO)(H$_2$O)(pyca)$_2$]ClO$_4$·0.5H$_2$O (Type V) with NaNO$_2$ To Form *cis*-[Ru(NO)(NO$_2$)(pyca)$_2$] (Type I). A suspension of *trans*-[Ru(NO)(H$_2$O)(pyca)$_2$]ClO$_4$·0.5H$_2$O (type **V**) (50 mg, 0.10 mmol) and $NaNO_2$ (140 mg, 2.0 mmol) in C_2H_5-$OH-H_2O$ (10:1 v/v, 55 cm^3) was refluxed for 3 h to give a yellow solution. The solution was concentrated to ca. 5 cm^3 by evaporating the solvent by heating to give a yellow precipitate. The product was collected by filtration, washed with cold water, ethanol, and diethyl ether, and dried in vacuo. Yield: 15 mg (29%). ν(NO) = 1907 cm^{-1}.

Reaction of [Ru(NO)Cl$_5$]$^{2-}$ with Hpyca To Form [Ru(NO)Cl$_3$-(pyca)]$^-$. To an aqueous solution (10 cm^3) of K_2[Ru(NO)Cl_5] (250 mg, 0.65 mmol) was added a solution of Hpyca (75 mg, 0.61 mmol), the pH of which had been adjusted to pH 4.5 with an aqueous NaOH solution. The mixed solution was refluxed for 1 h and concentrated to ca. 5 cm^3 by evaporating the solvent by heating. The solution was cooled, allowed to stand overnight, and filtrated. To the filtrate was then added $(C_2H_5)_4NCl$ as precipitant. The filtrate was allowed to stand overnight to give an orange precipitate. The product was collected by filtration, washed with ethanol and ether, and dried in vacuo. Yield: 40 mg (13%). ν(NO) = 1849 cm^{-1}.

Isolation of *cis*-[Ru(NO)Cl(pyca)$_2$] (Type II). *cis*-[Ru(NO)Cl-(pyca)$_2$] (type **II**) has been isolated by two different procedures. (i) The pH of an aqueous solution (20 cm^3) of K_2[Ru(NO)Cl_5] (250 mg, 0.65 mmol) and Hpyca (250 mg, 2.0 mmol) was adjusted to pH 6.8 with an aqueous 1 mol dm^{-3} NaOH solution. The solution was refluxed for 3 h. The solution was then concentrated to ca. 5 cm^3 by evaporating the solvent by heating, cooled, and allowed to stand overnight. An orange crude product was deposited. It was collected by filtration, washed with C_2H_5OH and ether, and dried in vacuo. The obtained mixed material was separated into components by column chromatography (Sephadex LH-20; water). The first orange band was collected and concentrated with a rotary evaporator. The formed orange precipitate was collected by filtration, washed with C_2H_5OH and ether, and dried in vacuo. Yield: 35 mg (13%). ν(NO) = 1864 cm^{-1}. Anal. Found: C, 34.91; H, 1.79; N, 9.97. Calcd for $C_{12}H_8N_3O_5ClRu$: C, 35.09; H, 1.96; N, 10.23. The second band was a solution of *cis*-[Ru(NO)Cl(pyca)$_2$] (type **I**). (ii) The pH of an aqueous solution (15 cm^3) of Et_4N[Ru-(NO)Cl_3(pyca)] (50 mg, 0.10 mmol) and Hpyca (13 mg, 0.10 mmol) was adjusted to pH 4.5 with an aqueous 1 mol dm^{-3} NaOH solution. The solution was refluxed for 2 h. The solution was then concentrated to ca. 5 cm^3 by evaporating the solvent by heating, cooled, and allowed to stand overnight. An orange crude product was deposited. It was collected by filtration, washed with C_2H_5-OH and ether, and dried in vacuo. The separation into components by column chromatography was carried out in the same way described as in the procedure i. Yield: 5 mg (12%).

X-ray Crystallography. Single crystals of *cis*-[Ru(NO)(OCH$_3$)-(pyca)$_2$]·0.5CH_3OH (type **I**) and $(C_2H_5)_4$N[Ru(NO)Cl_3(pyca)] were obtained by recrystallization from the methanol solutions and then vapor diffusion of ether into those solutions. A single crystal of *cis*-[Ru(NO)Cl(pyca)$_2$] (type **II**) was obtained by slow evaporation of the aqueous solution of the complex. The intensity data for *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$]·0.5CH_3OH (type **I**) were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer, and those for $(C_2H_5)_4$N[Ru(NO)Cl_3(pyca)] and *cis*-[Ru(NO)Cl(pyca)$_2$] (type **II**) on a Rigaku Mercury CCD diffractometer, using graphite-monochromatized Mo Kα radiation (0.710 69 Å). All the calculations were carried out using the Crystal Structure software package.[13] Structures were solved by direct methods, expanded using Fourier techniques, and refined using full-matrix least-squares techniques. The crystallographic data are summarized in Table 1.

Molecular Orbital Calculations. All calculations were performed using the Gaussian 98 program.[14] The geometry optimizations were carried out without symmetry constraint at the B3LYP level of density functional theory, which consists of a hybrid Becke + Hartree−Fock exchange and Lee−Yang−Parr correlation func-

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Table 1. Crystallographic Data for *cis*-[Ru(NO)(OCH_3)(pyca)$_2$]·0.5CH_3OH (Type **I**), $(C_2H_5)_4N$[Ru(NO)Cl_3(pyca)], and *cis*-[Ru(NO)Cl(pyca)$_2$] (Type **II**)

formula	$C_{13.5}H_{13}N_3O_{6.5}Ru$	$C_{14}H_{24}N_3O_3\,Cl_3Ru$	$C_{12}H_8N_3O_5ClRu$
fw	422.34	489.79	410.74
color of cryst	brown	orange	orange
cryst system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	8.120 (1)	7.631(1)	10.010(1)
b, Å	16.650(1)	9.669(1)	13.280(1)
c, Å	11.510(1)	13.627(1)	11.335(1)
α, deg		83.05(2)	
β, deg	99.07(1)	82.23(1)	113.45(1)
γ, deg		81.94(1)	
V, Å^3	1536.7(2)	981.1(1)	1382.4(2)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.83	1.66	1.97
μ(Mo Kα), cm^{-1}	10.61	12.24	13.55
T, °C	−150	−150	23
R[a]	0.043	0.050	0.032
GOF	1.37	0.87	1.11

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $I < 2\sigma(I)$.

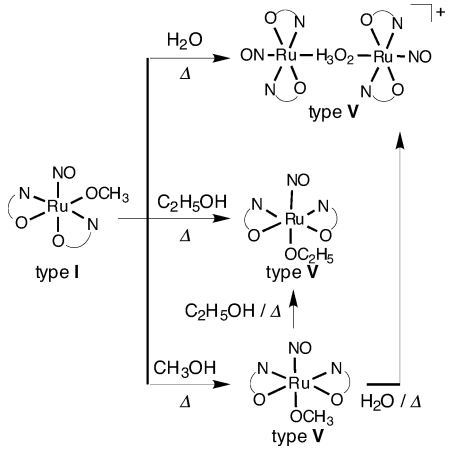
tional with nonlocal corrections,[15] with the LANL2DZ effective core potential and basis set.[16] No second derivatives were calculated. Since the optimization was performed without symmetry constraint, the optimized structures were assumed to be at local minima. At the B3LYP/LANL2DZ-optimized geometries the energies were recalculated with the B3LYP method using a larger LANL2DZdpd basis set,[17] which consists of LANL2DZ + diffuse + polarization basis sets.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer FT-1650 FTIR spectrophotometer using samples prepared as KBr disks. Elemental analyses were performed by the Sophia University Analytical Facility. ^{1}H NMR and ^{13}C NMR spectra were obtained with a JEOL JML-LA500 spectrometer. Cyclic voltammetric measurements were made on acetonitrile solutions 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 using a BAS 100B/W electrochemical analyzer. At the end of each measurement, ferrocene was added as an internal standard to correct redox potentials.

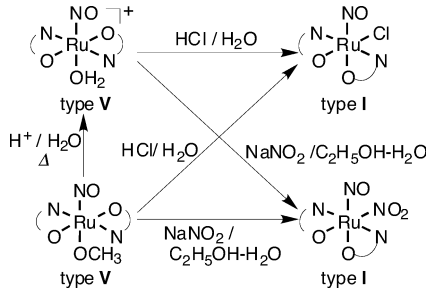
Results

Syntheses and Reactions. *cis*-[Ru(NO)(OCH_3)(pyca)$_2$] (type **I**) has been synthesized by a reaction of *cis*-[Ru(NO)-Cl(pyca)$_2$] (type **I**) with $NaOCH_3$ in methanol at room temperature without reflux. Reactions of *cis*-[Ru(NO)-(OCH_3)(pyca)$_2$] (type **I**) including the result of the previous paper are summarized in Scheme 1.[10] *cis*-[Ru(NO)(OCH_3)-(pyca)$_2$] (type **I**) is convertible into [{*trans*-Ru(NO)(pyca)$_2$}$_2$-(μ-H_3O_2)]PF_6 (type **V**), a hydroxide hydrate anion-bridged complex, in an aqueous solution by heating.[10] It is also convertible into *trans*-[Ru(NO)(OC_2H_5)(pyca)$_2$] (type **V**) in C_2H_5OH. The geometry of *trans*-[Ru(NO)(OC_2H_5)(pyca)$_2$] (type **V**) is confirmed by ^{1}H and ^{13}C NMR spectra showing four and six signals assigned to the two symmetrically coordinated pyca ligands, respectively, in addition to two

Scheme 1. Reactions of *cis*-[Ru(NO)(OCH_3)(pyca)$_2$] (Type I)



Scheme 2. Reactions from the Trans Form (Type **V**) to the Cis Form (Type **I**)



^{13}C signals assigned to the $C_2H_5O^-$ ligand. When a methanol solution of *cis*-[Ru(NO)(OCH_3)(pyca)$_2$] (type **I**) is refluxed, *trans*-[Ru(NO)(OCH_3)(pyca)$_2$] (type **V**) is isolated in a high yield, and the same reaction also takes place in the dark. *trans*-[Ru(NO)(OCH_3)(pyca)$_2$] (type **V**) in an aqueous solution affords [{*trans*-Ru(NO)(pyca)$_2$}$_2$(μ-H_3O_2)]$^+$ (type **V**) by heating under reflux and in the ethanoic solution *trans*-[Ru-(NO)(OC_2H_5)(pyca)$_2$] (type **V**).

The geometrical change reactions from the type **V** to the type **I** of [Ru(NO)X(pyca)$_2$]$^{n+}$ are summarized in Scheme 2. The hydrochloric acid solution of *trans*-[Ru(NO)X-(pyca)$_2$]$^{n+}$ (type **V**) (X = CH_3O, $n = 0$; X = H_2O, $n = 1$) gives *cis*-[Ru(NO)Cl(pyca)$_2$] (type **I**) by heating under reflux,

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Table 2. Stretching N−O Wave numbers and Reduction Potentials of Synthesized and Related Nitrosylruthenium Complexes

complex	ν(NO), cm^{-1} [a]	$E_{1/2}$, V[b]	E_{pc}, V[b]	ref
cis-[Ru(NO)Cl(pyca)$_2$] (type **I**)	1890	−0.71[c]	−1.48[c]	10, 12
cis-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**)	1861	−0.90[c]	−1.68[c]	this work
cis-[Ru(NO)(NO$_2$)(pyca)$_2$] (type **I**)	1907	−0.60[c]	−1.46[c]	6
cis-[Ru(NO)Cl(pyca)$_2$] (type **II**)	1864	−0.71[c]	−1.44[c]	this work
trans-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **V**)	1838	−1.12[c]	−1.71[c]	10
trans-[Ru(NO)(OC$_2$H$_5$)(pyca)$_2$] (type **V**)	1815	−1.15[c]	−1.85[c]	this work
trans-[Ru(NO)(H$_2$O)(pyca)$_2$]ClO$_4$ (type **V**)	1940	−0.53[d]	−1.23[d]	10
[{*trans*-Ru(NO)(pyca)$_2$}$_2$(H$_3$O$_2$)]PF$_6$ (type **V**)	1895, 1910			10
mer(Cl),*trans*(NO,O)-(C$_2$H$_5$)$_4$N[Ru(NO)Cl$_3$(pyca)]	1849	−1.15[c,e]		this work

[a] KBr disk. [b] Vs Ag|0.1 mol dm^{-3} AgNO$_3$(AN). [c] In CH$_3$CN containing TEAP. [d] In DMF containing TEAP. [e] An irreversible process, E_{pc}.

Table 3. Selected Bond Distances (Å) and Angles (deg) in *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type **I**), (C$_2$H$_5$)$_4$N[Ru(NO)Cl$_3$(pyca)], and *cis*-[Ru(NO)Cl(pyca)$_2$] (Type **II**)

	[Ru(NO)(OCH$_3$)(pyca)$_2$] type **I**	(C$_2$H$_5$)$_4$N[Ru(NO)Cl$_3$(pyca)]	[Ru(NO)Cl(pyca)$_2$] type **II**
Ru−N(nitrosyl)	1.737(3)	1.729(4)	1.743(2)
Ru−X			
X = OCH$_3^-$	2.040(3)		
X = Cl$^-$		2.364(1)	2.370(1)
		2.359(1)	
		2.382(1)	
Ru−N(pyca)	2.079(3)[a]	2.072(3)[a]	2.074(2)[a]
	2.041(3)		2.060(2)
Ru−O(pyca)	1.999(2)[a]	2.015(3)[a]	2.007(2)[a]
	2.068(2)		2.014(2)
N−O(nitrosyl)	1.160(4)	1.163(5)	1.139(3)
Ru−N−O(nitrosyl)	176.3(3)	173.4(3)	170.7(2)

[a] Oxygen or nitrogen atom of pyca at the trans position to NO.

and the H$_2$O−C$_2$H$_5$OH solution in the presence of excess nitrite anion yields *cis*-[Ru(NO)(NO$_2$)(pyca)$_2$] (type **I**).

The mono-pyca complex *mer*(Cl),*trans*(NO,O)-[Ru(NO)Cl$_3$(pyca)]$^-$ has been synthesized by the reaction of [Ru(NO)Cl$_5$]$^{2-}$ with equimolar Hpyca[12] and characterized by the X-ray crystal structural analysis. *mer*(Cl), *trans*(NO,O)-[Ru(NO)Cl$_3$(pyca)]$^-$ reacts with the equimolar amount of Hpyca to give a type **I** of *cis*-[Ru(NO)Cl(pyca)$_2$] as the main product and a type **II** as a byproduct. These two isomers of [Ru(NO)Cl(pyca)$_2$] are successfully separated from the reaction mixture by column chromatography.

IR Spectroscopy. Wavenumbers of a characteristic stretching N−O mode (ν(NO)) of synthesized and related nitrosylruthenium complexes are presented in Table 2. Four nitrosylruthenium complexes synthesized in this work show a strong NO stretching vibration at 1815−1861 cm^{-1} and CO stretching vibrations(s) of pyca ligand(s) at 1650−1700 cm^{-1}. The observed values of wavenumber of the ν(NO) band are reasonable, compared with those of similar nitrosylruthenium complexes previously reported.[6,10,12]

Electrochemistry. Two reduction potentials of the present and previous nitrosylruthenium complexes, which can be assigned to the ligand-based reductions of the (RuNO) moiety, (RuNO)$^{3+/2+}$ and (RuNO)$^{2+/+}$, respectively, are summarized in Table 2.[18] *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**) shows a reversible redox couple at $E_{1/2} = -0.90$ V and an irreversible reduction wave at $E_{pc} = -1.68$ V, in addition to an irreversible oxidation wave at $E_{pa} = 1.20$ V, which is based on the oxidation of the metal center. *cis*-[Ru(NO)Cl(pyca)$_2$] (type **II**) exhibits typical reduction processes similar to the corresponding type **I** complex, a reversible wave at $E_{1/2} = -0.71$ V and an irreversible one at $E_{pc} = -1.44$ V. *trans*-[Ru(NO)(OC$_2$H$_5$)(pyca)$_2$] (type **V**) shows a reversible wave at $E_{1/2} = -1.15$ V and an irreversible one at $E_{pc} = -1.85$ V. These waves are observed at slightly negative region as compared with those of the type **V** complex containing a methoxo ligand instead of an ethoxo one. The mono-pyca complex *mer*(Cl),*trans*(NO,O)-(C$_2$H$_5$)$_4$N[Ru(NO)Cl$_3$(pyca)] shows only an irreversible reduction wave at $E_{pc} = -1.15$ V, and no other reduction wave is observed within the potential window (∼ca. 2.00 V).

X-ray Structures. The selected bond distances and angles of three new complexes, *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**), *mer*(Cl),*trans*(NO,O)-(C$_2$H$_5$)$_4$N[Ru(NO)Cl$_3$(pyca)], and *cis*-[Ru(NO)Cl(pyca)$_2$] (type **II**), are summarized in Table 3. In all these complexes, the bond distances of Ru−N(pyca) and those of Ru−O(pyca) are similar to those of previously reported ruthenium complexes containing pyca ligands,[6,10,12,19] and the nitrosyl ligand is essentially linearly coordinated to the ruthenium center.

The structure of *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**) is shown in Figure 1.[20] The geometry of this complex is confirmed as a type **I** as shown in Chart 1. The bond distance between Ru and the oxygen atom of the methoxo ligand is almost the same as those of previously reported {RuNO}^{6}-type complexes[21] and slightly longer than that of *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **V**).[10]

The geometry of the mono-pyca complex, (C$_2$H$_5$)$_4$N[Ru(NO)Cl$_3$(pyca)], is such that three chloro ligands locate in

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Table 4. Comparison of Calculated and Experimental Values of Major Structural Parameters (Bond Distances in Å and Bond Angles in deg) of $[Ru(NO)Cl(pyca)_2]$

	cis form				trans form	
param	**I**[a]	**II**[b]	**III**	**IV**	**V**	**VI**
Ru−N(nitrosyl)	1.768 (1.75)	1.765 (1.743)	1.768	1.769	1.772	1.775
N−O(nitrosyl)	1.190 (1.12)	1.197 (1.139)	1.186	1.187	1.194	1.197
Ru−Cl	2.475 (2.361)	2.439 (2.370)	2.463	2.449	2.403[c]	2.409[c]
Ru−N(pyca)	2.098 (2.07)	2.125 (2.074)	2.107[c]	2.098[c]	2.074	2.153
	2.080(2.05)	2.122(2.060)	2.108	2.101	2.074	2.153
Ru−O(pyca)	2.003[c] (2.02[c])	2.014[c] (2.007[c])	2.056	2.069	2.071	2.035
	2.058 (2.01)	2.122 (2.014)	2.108	2.101	2.071	2.035
Ru−N−O(nitrosyl)	172.8 (172)	171.2 (170.7)	170.6	170.6	180.0	172.1

[a] Experimental values in parentheses from ref 12. [b] Experimental values of this work in parentheses. [c] Distances between Ru and the atom at the trans position to the nitrosyl ligand.

Table 5. Comparison of Calculated and Experimental Values of Major Structural Parameters (Bond Distances in Å and Bond Angles in deg) of $[Ru(NO)(OCH_3)(pyca)_2]$

	cis form				trans form	
param	**I**[a]	**II**	**III**	**IV**	**V**[b]	**VI**
Ru−N(nitrosyl)	1.771 (1.737)	1.771	1.769	1.770	1.788 (1.760)	1.791
N−O(nitrosyl)	1.204 (1.160)	1.208	1.195	1.198	1.202 (1.143)	1.199
Ru−OCH_3	2.001 (2.040)	1.972	1.991	1.983	1.946[c] (1.964[c])	1.933[c]
Ru−N(pyca)	2.110 (2.079)	2.118	2.122[c]	2.119[c]	2.090 (2.074)	2.148
	2.073 (2.041)	2.164	2.090	2.143	2.079 (2.073)	2.150
Ru−O(pyca)	2.023[c] (1.999[c])	2.033[c]	2.073	2.079	2.068 (2.035)	2.061
	2.104 (2.068)	2.164	2.121	2.075	2.087 (2.036)	2.064
Ru−N−O(nitrosyl)	169.7 (176.3)	168.9	170.6	170.9	165.5 (173.3)	169.2

[a] Experimental values of this work in parentheses. [b] Experimental values in parentheses from ref 10. [c] Distances between Ru and the atom at the trans position to the nitrosyl ligand.

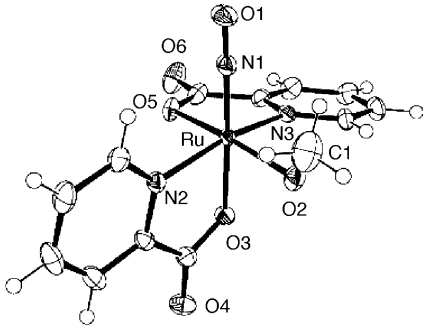

Figure 1. Structure of *cis*-$[Ru(NO)(OCH_3)(pyca)_2]$ (type **I**).

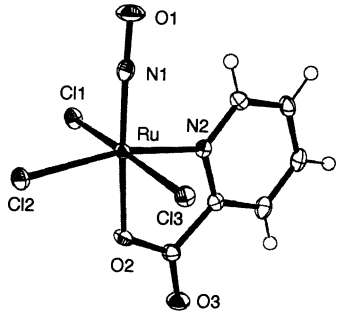

Figure 2. Structure of $[Ru(NO)Cl_3(pyca)]^-$.

the meridional position and the nitrosyl ligand is at the trans position to the carboxylic oxygen atom of the pyca ligand as shown in Figure 2 i.e., *mer*(Cl),*trans*(NO,O)-$(C_2H_5)_4N$-$[Ru(NO)Cl_3(pyca)]$. The Ru−Cl distances are almost the same as those of previously reported complexes.[22]

The structure of *cis*-$[Ru(NO)Cl(pyca)_2]$ (type **II**) has been confirmed as shown in Figure 3. The nitrogen atom of the nitrosyl ligand is located at the trans position to the oxygen atom of the pyca ligand, and two pyridine nitrogen atoms of two pyca ligands are at the cis position to each other. The bond distance of Ru−Cl is similar to those of *mer*-(Cl),*trans*(NO,O)-$(C_2H_5)_4N[Ru(NO)Cl_3(pyca)]$.

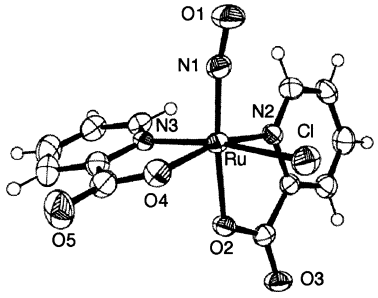

Figure 3. Structure of *cis*-$[Ru(NO)Cl(pyca)_2]$ (type **II**).

Computational Work. The structural parameters obtained by the B3LYP/LANL2DZ calculations are listed for the isomers of $[Ru(NO)Cl(pyca)_2]$ in Table 4 and for the isomers of $[Ru(NO)(OCH_3)(pyca)_2]$ in Table 5 together with the

(20) The structural chemical formula is $[Ru(NO)(OCH_3)(pyca)_2]\cdot 0.5CH_3OH$; the methyl carbon atom of the methanol of crystallization is located at a special position, and the hydroxyl oxygen atom of the methanol is at a general position with an occupancy of 0.5. Hydrogen atoms of this methanol molecule are not included in the final refining cycle. These carbon and oxygen atoms can be distinguished by the O−H···O hydrogen bonds between the oxygen atom of the methanol molecule and the oxygen atom (O2) of the coordinated methoxo ligand (2.629(7) Å) and between the oxygen atom of the methanol and the carboxylic oxygen atoms (O3 and O4) of the pyca ligand (3.424(8) and 3.556(9) Å).

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Table 6. Comparison of Relative Energies of $[Ru(NO)X(pyca)_2]$ (X = Cl and CH_3O) Isomers (kcal/mol) and Their Energy Component Analysis (See Text) at the B3LYP/LANL2DZdpd Level at B3LYP/LANL2DZ-Optimized Geometries

	cis form				trans form	
param	**I**	**II**	**III**	**IV**	**V**	**VI**
			$X = Cl^-$			
$\Delta E([Ru(NO)X(pyca)_2]_{opt})$	0.00	8.65	7.31	4.79	1.64	14.25
$\Delta E([RuX(pyca)_2]_{opt})$	0.00	12.73	5.14	2.67	−1.67	19.88
ΔBE	0.00 (−43.33)[a]	−4.08 (−47.41)	2.17 (−41.16)	2.12 (−41.21)	3.31 (−40.02)	−5.63 (−48.96)
ΔDEF	0.00 (12.56)	−0.74 (11.82)	−2.58 (9.98)	−1.72 (10.84)	−0.91 (11.65)	−7.94 (4.62)
ΔINT	0.00 (−55.89)	−3.34 (−59.23)	4.76 (−51.13)	3.84 (−52.05)	4.23 (−51.66)	2.31 (−53.58)
			$X = CH_3O^-$			
$\Delta E([Ru(NO)X(pyca)_2]_{opt})$	0.00	2.86	4.06	2.85	−5.10	4.08
$\Delta E([RuX(pyca)_2]_{opt})$	0.00	2.64	2.90	1.64	−4.12	8.38
ΔBE	0.00 (−37.63)	0.22 (−37.41)	1.16 (−36.47)	1.21 (−36.42)	−0.97 (−38.60)	−4.30 (−41.93)
ΔDEF	0.00 (10.64)	4.49 (15.13)	2.79 (13.43)	2.11 (12.75)	2.19 (12.83)	3.28 (13.92)
ΔINT	0.00 (−48.27)	−4.27 (−52.54)	−1.63 (−49.90)	−0.90 (−49.17)	−3.16 (−51.43)	−7.58 (−55.85)

[a] Absolute values of the BE, DEF, and INT energies in parentheses.

experimental ones in the parentheses. Optimized geometries of the trans form have nearly C_{2v} symmetry. As a whole, the calculated values agree reasonably well with the experimental ones, although the former values are in general slightly longer than the latter values. The calculations also reproduce the experimentally obtained differences in the corresponding bond distances between the isomers of the cis form, types **I** and **II** of $[Ru(NO)Cl(pyca)_2]$, and between the isomers of the cis form, type **I,** and the trans form, type **V** of $[Ru(NO)(OCH_3)(pyca)_2]$, except for the Ru−Cl and Ru−O(pyca) distances in $[Ru(NO)Cl(pyca)_2]$.

The comparison of the calculated relative energies among the isomers of $[Ru(NO)X(pyca)_2]$ (X = Cl and OCH_3) at the B3LYP/LANLD2Zdpd level at the B3LYP/LANLD2Z-optimized geometries is shown in Table 6. We did not include the zero-point energy correction (ZPC) or the correction for the basis set superposition error (BSSE). Since all the isomers to be compared have the same numbers of various ligands, these corrections are expected to be similar among the isomers, and the errors introduced by neglecting these are anticipated to be a few kcal/mol at most. The qualitative conclusions derived from these values will not be effected by these small errors. The B3LYP/LANLD2Z energies are similar and will not be discussed here for brevity (see Supporting Information).

The relative stability $\Delta E([Ru(NO)X(pyca)_2]_{opt})$ of various geometrical isomers of $[Ru(NO)X(pyca)_2]$ (here and hereafter, Δ stands the energy relative to the type **I** complex and the subscript, opt, indicates that the structure is optimized) can be divided into the following contributions:

$$\Delta E([Ru(NO)X(pyca)_2]_{opt}) = \Delta E([RuX(pyca)_2]_{opt}) + \Delta BE$$

Here $\Delta E([RuX(pyca)_2]_{opt})$ is the relative stability of the corresponding geometrical isomers of the five-coordination complex, with subscript "opt" meaning optimized structures for individual species, and ΔBE is the relative binding energy of an isomer (relative to the type **I** complex) between the five-coordination isomer $[Ru(NO)X(pyca)_2]_{opt}$ and the nitrogen oxide, where the binding energy is defined as

$$BE = E([Ru(NO)X(pyca)_2]_{opt}) - (E([Ru^{III}X(pyca)_2]_{opt}) + E(NO_{opt}))$$

The BE can be further divided into the deformation energy (DEF), the energy required to deform the individual fragments from their equilibrium structures to those in the specific geometrical isomer of the complex, and the interaction energy (INT) of the deformed NO and five-coordinate complex fragment:[23]

$$BE = DEF + INT$$

$$DEF = (E([Ru^{III}X(pyca)_2]_{cmplx}) - E([Ru^{III}X(pyca)_2]_{opt})) + (E(NO_{cmplx}) - E(NO_{opt}))$$

$$INT = E([Ru(NO)X(pyca)_2]_{opt}) - (E([Ru^{III}X(pyca)_2]_{cmplx}) + E(NO_{cmplx}))$$

Here the subscript cmplx stands for the structure of the fragment that is optimized for the complex $[Ru(NO)X(pyca)_2]$.

To quantify the origin of the order of relative stability of geometrical isomers of the complex $[Ru(NO)X(pyca)_2]$, an analysis of trans effects has been performed. In this analysis, the relative stabilization energy of each isomer was assumed to be sum of contributions of trans pairs that exist in the isomer; for instance, the type **V** isomer of the six-coordinate complex has one trans N−N, one trans O−O, and one trans NO−X contribution. The contributions of all trans pairs were determined by the least-squares fit of the stabilities of 20 isomers (cis form, types **II**−**IV,** and trans form, types **V** and **VI**, X = Cl and CH_3O and 5-coordinate and 6-coordinate).[24] The analysis yielded the following values (in kcal/mol) as contribution of trans pairs: Cl−O (−5.3) < NO−MeO

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(23) Khoroshun, D. V.; Musaev, D. G.; Morokuma, K. *Mol. Phys.* **2002**, *100*, 523−532.

(−2.1) ∼ O−O (−2.1) < NO−Cl (−0.6) ∼ N−N (−0.5) < Cl−N (−0.3) < NO−O (0.5) < MeO−O (1.7) < MeO−N (2.0) < NO−N (2.2) < N−O (4.6). For instance, Cl−O trans pair stabilizes the system by 5.3 kcal/mol, while the N−O pair with both atoms having strong trans effects destabilizes the system by as much as 4.6 kcal/mol.

Discussion

Synthesis of *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (Type I). While the reaction of *cis*-[Ru(NO)Cl(pyca)$_2$] (type **I**) with NaOCH$_3$ in methanol under reflux gave *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **V**), in which a cis−trans geometrical change occurred,[10] the same reaction at room temperature without reflux gave *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**), in which a simple substitution occurred. The nitrosyl ligand is essentially linearly coordinated to the ruthenium center, and the cyclic voltammogram (CV) shows two reduction waves and one oxidation wave in CH$_3$CN. Thus, *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**) is classified into a {RuNO}^{6} configuration by the structural feature. It is rare for nitrosylruthenium complexes containing pyca ligands to show the oxidation wave at 1.20 V within the potential window of CH$_3$CN.[18] A comparison of the ν(NO) and reduction potential values between the cis form (type **I**) and the trans form (type **V**) of [Ru(NO)(OCH$_3$)(pyca)$_2$] reveals that the ν(NO) band and the two reduction waves for the cis form (type **I**) complex (ν(NO) = 1861 cm^{-1}, $E_{1/2}$ = −0.90 V and E_{pc} = −1.68 V) are observed at a higher wavenumber and in a higher potential region than those of the trans form (type **V**) complex (ν(NO) = 1838 cm^{-1}, $E_{1/2}$ = −1.12 V and E_{pc} = −1.71 V), respectively. The reduction potentials and ν(NO) values of nitrosyl complexes reflect the electron density at the (RuNO) moiety.[4a,25] These results thus indicate that the nitrosyl ligand of the trans-form (type **V**) complex is strongly influenced by the coexisting ligands, compared with that of the cis form (type **I**), and the electronic effect of the CH$_3$O$^-$ group to the nitrosyl ligand at the trans position is stronger than that at the cis position.

Geometrical Change Reaction between Types I and V Complexes. The reaction from the cis form, type **I**, to the trans form, type **V,** of [Ru(NO)(OCH$_3$)(pyca)$_2$] suggests that *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**) is an intermediate of the previously reported reaction from *cis*-[Ru(NO)Cl(pyca)$_2$] (type **I**) to *trans*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **V**) with a cis−trans geometrical change.[10] Reactions of the type **I** and the type **V** of [Ru(NO)(OCH$_3$)(pyca)$_2$] as starting complexes shown in Scheme 1 indicate that the sixth ligand (X) in a [Ru(NO)X(pyca)$_2$]-type complex such as with RO$^-$ and OH$^-$ (H$_2$O) ligand prefers to be at the trans position to the nitrosyl ligand rather than at the cis position. On the other hand, reactions of *trans*-[Ru(NO)X(pyca)$_2$]$^{n+}$ (type **V**) (X = CH$_3$O, n = 0; X = H$_2$O, n = 1) in the hydrochloric acid solution shown in Scheme 2 indicate the chloro and the nitro ligands will coordinate to the Ru center at the cis position to the nitrosyl ligand in the (Ru(NO)(pyca)$_2$) moiety.

Function of Nitrosyl Ligand in Formation of [Ru(NO)Cl(pyca)$_2$]. The mono-pyca complex [Ru(NO)Cl$_3$(pyca)]$^-$ has three geometrical isomers.[26] The isolated mono-pyca complex from the reaction of [Ru(NO)Cl$_5$]$^{2-}$ has been characterized as *mer*(Cl),*trans*(NO,O)-(C$_2$H$_5$)$_4$N[Ru(NO)Cl$_3$(pyca)] by the X-ray structural analysis. The geometry of [Ru(NO)Cl$_3$(pyca)]$^-$ seems reasonable, considering the results on the stabilities of isomers for [Ru(NO)X(pyca)$_2$]$^{n+}$-type complexes. The nitrosyl complex having the carboxylic oxygen atom of the pyca ligand that coordinates at the trans position to the NO ligand is more stable than that having the chloro ligand or pyridyl nitrogen atom of the pyca ligand, which is classified by synthetic and theoretical studies on [Ru(NO)X(pyca)$_2$]$^{n+}$-type complexes.

cis-[Ru(NO)Cl(pyca)$_2$] (type **II**) is obtained from the reaction of *mer*(Cl),*trans*(NO,O)-[Ru(NO)Cl$_3$(pyca)]$^-$ with an equimolar amount of Hpyca followed by column chromatographic isolation. The nitrosyl ligand is essentially linearly coordinated to the ruthenium center indicating *cis*-[Ru(NO)(OCH$_3$)(pyca)$_2$] (type **I**) is classified into a {RuNO}^{6} configuration, and CV shows two reduction waves in CH$_3$CN. Although both of the types **I** and **II** complexes of *cis*-[Ru(NO)Cl(pyca)$_2$] show the (RuNO)$^{3+/2+}$ couple at the same potential, the ν(NO) of the type **I** complex is observed in a higher wavenumber region (1890 cm^{-1}) than that of the type **II** (1864 cm^{-1}). The bond distances of Ru−O (carboxyl oxygen at the cis position to the nitrosyl ligand) for the types **I** and **II** complexes are almost the same, and that of Ru−O (carboxyl oxygen of the pyca ligand at the trans position of the nitrosyl ligand) for the type **II** complex is shorter than that of the type **I**. Those observations of IR spectra and the structural parameters indicate that the nitrosyl ligand in the type **II** complex withdraws a π-electron from the carboxylato ligand to a higher extent than the type **I** complex through a dπ-orbital. The bond distance of Ru−N (pyridine nitrogen of the pyca ligand at the cis position to the nitrosyl ligand) for the type **II** complex is longer than that for the type **I**. Differences in structural parameters can be explained by a combination of π-donor and π-acceptor ligands and the order of the trans pair stability, Cl−O (−5.3) < N−N (−0.5) < Cl−N (−0.3), between the pyca and Cl ligands by theoretical studies on contribution of the trans pair described in the Computational Work section. In both of the types **I** and **II** complexes of [Ru(NO)Cl(pyca)$_2$], the nitrosyl ligand locates at the trans position to the π-donor ligand of the carboxylato group of the pyca ligand. In the formation process of *cis*-[Ru(NO)Cl(pyca)$_2$] (type **I**), which is formed by the reaction of [Ru(NO)Cl$_5$]$^{2-}$ with excess Hpyca, it is highly probable that *mer*(Cl),*trans*(NO,O)-[Ru(NO)Cl$_3$(pyca)]$^-$ is first formed and then *cis*-[Ru(NO)Cl(pyca)$_2$] (type **I**) is formed by the substitution reaction of two chloro ligands with a pyca molecule.

Calculated vs Experimental Structural Parameters for [Ru(NO)X(pyca)$_2$] (X = Cl and OCH$_3$). A comparison of the Ru−Cl bond distances (Table 4) among the six isomers

(24) All the trans-pair contributions are not linearly independent. However, one can still perform the least-squares fitting by the use of singular vector decomposition. See for instance: Golub, G, H.; van Loan, C. F. *Matrix,* 3rd ed.; Johns Hopkins University Press: Baltimore, MD, 1996; p 582.

(25) Ford, P. C.; Lorkovic, I. M. *Chem. Rev.* **2002**, *102*, 993−1017.

(26) One is the facial isomer in which three chloro ligands coordinate in a facial configuration, the second one is the meridional isomer in which three chloro ligands coordinate in a meridional configuration and the nitrosyl ligand is at the trans position to the pyridyl nitrogen, and the third one is another meridional isomer in which three chloro ligands coordinate in a meridional configuration and the nitrosyl ligand is at the trans position to the carboxylic oxygen atom of the pyca ligand.

of $[Ru(NO)Cl(pyca)_2]$ clearly reveals the trans effect between the nitrosyl and chloro ligands; the Ru−Cl bond distances of the trans-form isomers are definitely shortened compared with those of the cis-form isomers. The trans effect is also observed between the nitrosyl and carboxylato ligands in the four cis-form isomers of $[Ru(NO)Cl(pyca)_2]$ but not between the nitrosyl and pyridine ligands. Similar observations can also be made for $[Ru(NO)(OCH_3)(pyca)_2]$ (Table 5), although the effect of the nitrosyl ligand is more significant in $[Ru(NO)(OCH_3)(pyca)_2]$ than in $[Ru(NO)Cl(pyca)_2]$. The calculations also clarify that while the two pyca ligands in each of the types **V** and **VI** isomers of $[Ru(NO)Cl(pyca)_2]$ symmetrically coordinate to the ruthenium center, the coordination of the pyca ligands is asymmetric in the trans-form isomers of $[Ru(NO)(OCH_3)(pyca)_2]$ and consequently the methoxo ligand is differently oriented against the two pyca ligands.

Calculated Stability of Geometrical Isomers for $[Ru(NO)X(pyca)_2]$ (X = Cl and OCH_3). Table 6 clearly indicates for both X = Cl and CH_3O that the order of relative stability of the six-coordination complexes ($\Delta E([Ru(NO)X(pyca)_2]_{opt}$) is almost the same as that of the five-coordination counterparts ($\Delta E([RuX(pyca)_2]_{opt}$); that is to say, the relative stability of the six-coordinate nitrosyl complexes (which changes as much as 14.25 kcal/mol for X = Cl and 9.18 kcal/mol for X = CH_3O) is determined essentially by that of the parent five-coordinate complexes (which changes as much as 21.55 kcal/mol for X = Cl and 12.50 kcal/mol for X = CH_3O). The relative binding energy ΔBE (which changes as much as 8.94 kcal/mol for X = Cl and 5.51 kcal/mol for X = CH_3O) or the components, ΔDEF and ΔINT, are minor contributors to the relative stability of $[Ru(NO)X(pyca)_2]$ but give some insight into the interaction of the NO ligand with the five-coordinate complex. In both X = Cl and OCH_3 series, the difference in the BE among the six isomers (cis form, types **I**−**IV,** and trans form, types **V** and **VI**) is small, and the INT values are larger than the DEF values. In X = Cl series, the difference in the DEF values among the six isomers is small. The INT values of types **I** and **II** are larger than the other isomers due to the π-electron effect of the carboxylato moiety of the pyca ligand at the trans position to the nitrosyl ligand. On the other hand, the profiles of the differences in the BE, the INT, and the DEF values are different from each other in the X = OCH_3 series. These results indicate that in the stabilities of isomers except for type **VI** obvious differences are not found and the synthetically isolable isomers, types **I**, **II,** and **V**, are due to the stabilities of the isomers having a π-donor moiety such as the methoxo and the carboxylato ligand at the trans position to the nitrosyl ligand.

The contributions of trans pairs can be used to explain the origin of the relative stability of various isomers. For instance in $[Ru(NO)Cl(pyca)_2]$, type **I** is most stable because it has one trans Cl−O pair (stabilizing) and no trans N−O pair (destabilizing), type **V** form is next because it has no Cl−O and no N−O, and type **VI** forming with no Cl−O and two N−O is the most unstable. In $[Ru(NO)(CH_3O)(pyca)_2]$, type **V** is most stable because it has one trans O−O pair (stabilizing) and one NO−OMe pair (stabilizing) and no N−O pair (destabilizing), type **I** forms with no O−O, no NO−OMe, and no N−O is next, and type **VI** forming with one O−O and two N−O is the most unstable. The above contributions also qualitatively explain why the order of stability of six-coordinate complexes is similar to that of five-coordinate complexes.

Conclusion

The stable structures of nitrosyl complexes have been explained by considering the structural trans effect and the inverse structural trans effect which depend on the nature of the ligand at the trans position to the nitrosyl ligand.[3] The present geometrical change reaction of $[Ru(NO)X(pyca)_2]^{n+}$ complexes can also be explained by the correlation between the coexisting ligands at the trans and cis positions. It is important for regulating the geometries of these complexes that the nitrosyl ligand functions as a strong π-acceptor ligand and affects other coexisting ligands, pyca and X. In other words, the geometry of the complex would be determined by positional relationship among NO, X, and the carboxylato and pyridine of the pyca ligands. The careful synthetic experiments indicate the isolable isomers in this series of nitrosylruthenium complexes are types **I**, **II,** and **V**. These experimental results are supported by the theoretical investigations. The experimental and theoretical results show types **I** and **II** are more stable than types **III** and **IV** since the nitrosyl ligand prefers the carboxylato group to the pyridyl group at the trans position. The decreasing order of a favorable ligand sited at the trans position to the nitrosyl ligand is $CH_3O^- > RCOO^- > Cl^- \sim$ py. It is worthy to note that geometrical reactions occur not only from the cis form to the trans form but also from the trans form to the cis form with use of appropriate X ligands. Finally, we conclude that the interaction of the nitrosyl ligand through the ruthenium ion strongly depends on the electronic features of the coexisting ligand in the series of $[Ru(NO)X(pyca)_2]^{n+}$ complexes.

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Supporting Information Available: Crystallographic details for *cis*-$[Ru(NO)(OCH_3)(pyca)_2]\cdot 0.5CH_3OH$ (type **I**), $(C_2H_5)_4N[Ru(NO)Cl_3(pyca)]$, and *cis*-$[Ru(NO)Cl(pyca)_2]$ (type **II**), in CIF format, and the total energies of optimized structures for $[Ru(NO)Cl(pyca)_2]$ and $[Ru(NO)(OCH_3)(pyca)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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