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Synthesis, Properties, and Molecular Structure of *trans*-Chloronitrosylbis(2,2′-bipyridine)ruthenium(2+): Trans and Cis Isomer Characteristics Compared

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A *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$ complex has been prepared. The form of the complex was confirmed by NMR spectroscopy (^{1}H and ^{13}C) and X-ray diffraction. Crystal data for [RuCl(NO)(C$_{10}$N$_2$H$_8$)$_2$](ClO$_4$)$_2$ are as follows: space group $P\bar{1}$, a = 10.355 (3) Å, b = 13.653 (3) Å, c = 10.114 (3) Å, α = 105.15 (2)°, β = 114.43 (2)°, γ = 77.52 (3)°, Z = 2, R = 0.049 for 2750 observed reflections. Differences between trans and cis isomers were substantiated in both their electrochemical properties and their reactivities toward ketones as nucleophiles.

Introduction

We have investigated the electrophilic behavior of coordinated nitrosyl in *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ [1-3] and that of *cis*-[RuCl(NO)(bpy)$_2$]$^{2+}$.[4,5] The latter complex has been reported by Meyer et al. to be a useful complex for such research.[6,7] In continuing this work on the reactivity of coordinated nitrosyl under various conditions, we have become interested in the synthesis of *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$, the isomeric twin of Meyer's complex.

Although the analogous *trans*-[Ru(OH)(NO)(bpy)$_2$]$^{2+}$ has been reported without detailed data,[8] our recent work showed that the nitrosyl complex having the hydroxo ligand at the trans position is a very poor electrophile.[9] The synthesis of *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$, which is expected to act as a better electrophile, is therefore necessary for continuation of our work.

This paper describes preparation of the title complex. Its characteristic properties are also investigated and compared with those of the cis isomer. A comparative study of characteristics between isomeric pairs is very rare for {RuNO}^{6} types of nitrosyl complexes, although their chemistry has extensively been investigated.[6,7] A few works on IR and X-ray structure studies have appeared.[10] The characteristics involving both chemical (electrophilic) and electrochemical relationships have never been compared.

Experimental Section

Table I. Crystallographic Data

formula: RuC$_{20}$H$_{16}$N$_5$Cl$_3$O$_9$	a = 10.355 (3) Å
fw = 675.81	b = 13.653 (3) Å
space group: $P\bar{1}$	c = 10.114 (3) Å
V = 1246.7 (6) Å^3	α = 105.15 (2)°
D_{calc} = 1.80 g cm^{-3}	β = 114.43 (2)°
D_{meas} = 1.83 g cm^{-3}	γ = 77.52 (3)°
μ(Mo Kα) = 9.80 cm^{-1}	radiation: Mo Kα (λ = 0.7107 Å)

Materials and Measurements. [RuCO$_3$(bpy)$_2$]· used as starting material, was prepared from *cis*-[RuCl$_2$(bpy)$_2$] according to a reported method.[11] The other complex, *trans*-[RuCl$_2$(bpy)$_2$], was prepared by a modification of a literature method.[8] Elemental analyses were performed by the Sophia University Analytical Facility. Cyclic voltammetry and normal-pulse voltammetry were carried out by using a Husō Model 321 polarograph with a stationary platinum disk electrode. When the voltammetry was performed with a rotating platinum disk electrode, a Yanagimoto speed controller was attached to the above system. IR spectra were measured on a Hitachi EPI G2 spectrometer. NMR spectra (^{1}H and ^{13}C) were recorded by using a JEOL JMN-270 spectrometer. Hydrated ruthenium trichloride was purchased from Nippon-Engelhard Co.

Preparations. *trans*-[RuCl(NO)(bpy)$_2$](PF$_6$)$_2$ and *trans*-[RuCl(NO)(bpy)$_2$](ClO$_4$)$_2$. *trans*-[RuCl$_2$(bpy)$_2$] was prepared first by the following procedure (a literature method was modified for the preparation of this complex[8]). A solution of [RuCO$_3$(bpy)$_2$] (120 mg in 100 cm^3 of 0.5 M HCl) was photolyzed in an ice bath under argon with a 250-W sun lamp for 3 h. The solution was then allowed to stand for 2 h at 4 °C (refrigerator), until precipitation appeared complete. The solid product was filtered off, washed first with water and then with ether, and finally air-dried. *trans*-[RuCl$_2$(bpy)$_2$] (80 mg) thus obtained was dissolved in water (50 cm^3) without heating; then, the solution was filtrated to remove insoluble matter. After the solution was charged with argon for 5 min, nitrogen monoxide gas was passed through the solution until the color changed from purple to yellow. To the yellow solution was added a minimum amount of NH$_4$PF$_6$, and then the mixture was kept in a refrigerator for 24 h. The pale yellow product was collected and washed with water, ethanol, and ether. Yield: 90 mg, 70%. Purification was performed by a nitrosyl–nitro conversion reaction (see eq 1 and 2). Anal. Calcd for C$_{20}$H$_{16}$N$_5$O$_1$P$_2$F$_{12}$Cl$_1$Ru$_1$: C, 31.31; N, 9.00; H, 1.98. Found: C, 31.32; N, 9.17; H, 2.10. The corresponding ClO$_4$ salt was obtained by the same procedure, using NaClO$_4$ as precipitant (attention should be paid to usage of NaClO$_4$, it is a potential explosive). Anal. Calcd for C$_{20}$H$_{16}$N$_5$O$_9$Cl$_3$Ru$_1$: C, 35.22; N, 10.25; H, 2.34. Found: C, 35.44; N, 10.33; H, 2.38.

Comments. Previous researchers of *trans*-[RuCl$_2$(bpy)$_2$] have pointed out that the dichloro complex of Ru(II) may contain *trans*-[RuCl(H$_2$O)(bpy)$_2$]$^+$ as a byproduct.[8] This presence was established by the following experiments: the suspended solution of *trans*-[RuCl$_2$(bpy)$_2$], obtained by the present procedure, was filtrated to remove insoluble matter. To this filtrate, an aqueous solution of NH$_4$PF$_6$ was added until a dark red crystalline material appeared. Analytical data of the product supports the chemical formula assignment as *trans*-[RuCl(H$_2$O)(bpy)$_2$]PF$_6$·H$_2$O. Anal. Calcd for RuCl(H$_2$O)(bpy)$_2$PF$_6$H$_2$O: C, 38.13; N, 8.90; H, 3.21. Found: C, 37.61; N, 8.77; H, 2.67. We belive that *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$ is formed mainly by the reaction between *trans*-[RuCl(H$_2$O)(bpy)$_2$]$^+$ and nitrogen monoxide. The insoluble matter obtained by the above procedure appears to be real *trans*-[RuCl$_2$(bpy)$_2$].

***trans*-[RuBr(NO)(bpy)$_2$](PF$_6$)$_2$.** The bromo complex was prepared by the same procedure as that employed for *trans*-[RuCl(NO)(bpy)$_2$](PF$_6$)$_2$, using *trans*-[RuBr$_2$(bpy)$_2$] (50 mg) instead of *trans*-[RuCl$_2$(bpy)$_2$]. Anal. Calcd for C$_{20}$N$_5$H$_{16}$OP$_2$F$_{12}$Br$_1$Ru$_1$: C, 30.11; N, 8.78; H, 2.01. Found: C, 29.59; N, 8.54; H, 1.87. Yield: 36 mg, 50%. The ClO$_4$ salt

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(9) For instance, nitrosyl ligand of *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ reacts with N$_3^-$ as an electrophile to give *trans*-[RuCl(N$_2$)(py)$_4$]$^+$, while that of *trans*-[Ru(OH)(NO)(py)$_4$]$^{2+}$ does not, under the same conditions. Instead of the electrophilic reaction observed in *trans*-[RuCl(NO)(py)$_4$]$^{2+}$, some replacement of pyridine ligands occurred to give *trans*-[Ru(OH)(N$_3$)$_2$(py)$_2$NO] and *trans*-[Ru(N$_3$)$_3$(py)$_2$NO]: Nishimura, H.; Matsuzawa, H.; Togano, M.; Mukaida, M.; Kakihana, H.; Bottomley, F. *J. Chem. Soc., Dalton Trans.*, in press.

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Table II. Positional Parameters ($\times 10^4$) for Non-Hydrogen Atoms

atom	x	y	z	B_{eq}/B_{iso}, Å^2
Ru	2558.9 (7)	2417.0 (4)	1263.2 (7)	2.75
Cl	4744.8 (21)	2058.1 (15)	3088.2 (22)	4.10
N(O)	955.9 (60)	2774.4 (43)	−133.8 (63)	3.41
O(N)	22.5 (60)	3098.0 (44)	−1052.2 (62)	5.61
N(1)	1659 (6)	2517 (4)	2828 (6)	3.18
N(2)	2665 (6)	3946 (4)	2359 (6)	3.38
N(3)	3589 (6)	2264 (4)	−208 (6)	3.29
N(4)	2652 (6)	849 (4)	344 (6)	2.97
C(12)	1989 (8)	3334 (5)	3954 (8)	3.58
C(13)	1618 (10)	3428 (6)	5149 (9)	5.26
C(14)	915 (9)	2696 (7)	5210 (10)	5.47
C(15)	544 (9)	1908 (6)	4018 (9)	4.81
C(16)	917 (8)	1836 (6)	2869 (9)	4.17
C(22)	2525 (8)	4141 (5)	3674 (8)	3.76
C(23)	2751 (10)	5090 (6)	4587 (9)	5.12
C(24)	3046 (10)	5849 (6)	4149 (11)	6.09
C(25)	3058 (10)	5662 (6)	2736 (10)	5.86
C(26)	2873 (9)	4704 (5)	1893 (9)	4.54
C(32)	3392 (7)	1381 (5)	−1262 (7)	3.16
C(33)	3782 (8)	1247 (6)	−2459 (9)	4.53
C(34)	4447 (9)	1985 (7)	−2551 (10)	5.70
C(35)	4724 (10)	2828 (7)	−1469 (11)	6.04
C(36)	4296 (9)	2951 (6)	−287 (10)	4.78
C(42)	2897 (7)	590 (5)	−914 (7)	3.12
C(43)	2833 (8)	−401 (6)	−1740 (8)	3.85
C(44)	2576 (8)	−1151 (6)	−1205 (10)	4.75
C(45)	2409 (9)	−888 (6)	116 (10)	4.89
C(46)	2444 (8)	107 (5)	880 (8)	3.87
Cl(1)	8319 (3)	1088 (2)	6483 (2)	5.28
Cl(2)	8048 (3)	4186 (2)	1492 (2)	5.28
O(11)	7503 (11)	286 (5)	5675 (9)	12.16
O(12)	9463 (7)	754 (5)	7718 (8)	7.80
O(13)	7421 (8)	1895 (5)	6978 (8)	8.24
O(14)	8732 (12)	1452 (10)	5632 (13)	18.34
O(21)	8165 (9)	3317 (5)	442 (8)	8.77
O(22)	8319 (13)	3874 (7)	2793 (9)	15.55
O(23)	6746 (8)	4747 (6)	1033 (10)	10.46
O(24)	9073 (10)	4797 (7)	1758 (12)	13.73

was obtained by the same procedure, using $NaClO_4$ as precipitant. Anal. Calcd for $C_{20}N_5H_{16}Cl_2O_9Br_1Ru_1$: C, 33.26; N, 9.70; H, 2.23. Found: C, 33.33; N, 9.82; H, 2.14.

***trans*-[RuCl(NO$_2$)(bpy)$_2$].** *trans*-[RuCl(NO)(bpy)$_2$](PF$_6$)$_2$ (50 mg) was suspended in water (10 cm^3). An aqueous solution of NaOH was added to the solution. The mixture was stirred for 24 h (pH of the solution was maintained at 11 throughout the procedure). A reddish brown solid was collected and then washed with water, ethanol, and ether. Yield: 19 mg, 60%. Anal. Calcd for $C_{20}H_{16}N_5O_2Cl_1Ru_1$: C, 48.52; N, 14.16; H, 3.26. Found: C, 47.42; N, 13.96; H, 2.97. The Cl ligand of the nitro complex is apparently trans to the NO_2 ligand, since *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$ is regenerated by acid decomposition.

***trans*-[RuCl(NO$_2$)(bpy)$_2$]PF$_6$.** *trans*-[RuCl(NO)(bpy)$_2$](PF$_6$)$_2$ (100 mg) was suspended in water (15 cm^3). NaClO solution (2 cm^3) was added to the suspended solution. The mixture was stirred for 24 h. A black material, which deposited, was collected and washed with water. Yield: 65 mg, 80%. Anal. Calcd for $C_{20}H_{16}N_5O_2P_1F_6Cl_1Ru_1$: C, 37.54; N, 10.95; H, 2.53. Found: C, 37.27; N, 10.83; H, 2.46.

X-ray Measurements. Crystal data are summarized in Table I. The reflections were collected by the ω-scan technique ($2\theta < 50°$) on a Rigaku AFC-6A automated four-circle diffractometer, with graphite Mo Kα radiation (0.7107 Å). The 2750 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure refinement. The intensities were collected for Lorentz and polarization factors, but no correction was made for absorption. All the calculation were carried out on a HITAC M-200H computer at the Computer Center of the University of Tokyo, using a local version of UNICS.[12] The atomic scattering factors were taken from tables.[13] The structure was solved by a heavy-atom method. The positions of Ru and Cl atoms were obtained from a three-dimensional Patterson function, while the positions of all the non-hydrogen atoms were successively located by Fourier syntheses. All hydrogen atoms were found at reasonable positions on the final difference Fourier map. Refinements using UNICS,[11] with all atoms except anisotropic H, resulted in $R_F = 0.049$ and $R_{wF} = 0.052$, where $R_F = \sum(F_o - F_c)/\sum(F_o)$ and $R_{wF} = [\sum w(F_o - F_c)^2/\sum(wF_o)^2]^{1/2}$, respectively. The $F_o - F_c$ data and the anisotropic temperature parameters are available as supplementary material. The final atomic coordinates and temperature factors are listed in Table II.

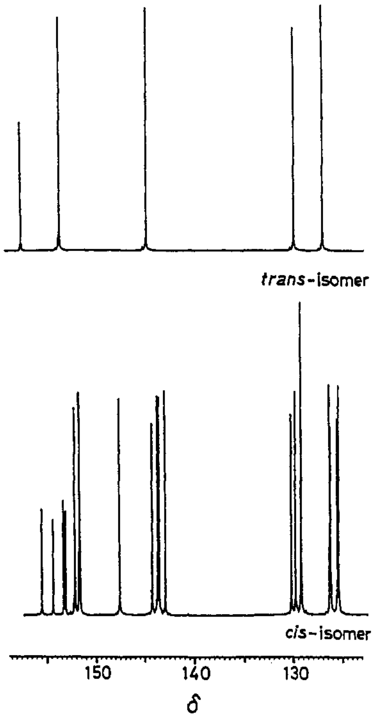

Figure 1. ^{13}C NMR spectra of *trans*-[RuCl(NO)(bpy)$_2$](PF$_6$)$_2$ and *cis*-[RuCl(NO)(bpy)$_2$](PF$_6$)$_2$ in CD_3CN.

Results and Discussion

Synthesis and Characterization. Synthesis of *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$ using a common nitrosylation agent (NO_2^-) was much more difficult than that of the cis isomer. We tried first a preparation of *trans*-[Ru(NO$_2$)$_2$(bpy)$_2$] based on the reaction of *trans*-[Ru(H$_2$O)$_2$(bpy)$_2$]$^{2+}$ with NO_2^-.[14] A dinitro complex of Ru(II) is often a useful material for the preparation of the corresponding nitrosyl complex. The decomposition of the dinitro complex by hydrochloric acid, however, always gave a mixture of *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$, *cis*-[RuCl(NO)(bpy)$_2$]$^{2+}$, and *trans*-[Ru(OH)(NO)(bpy)$_2$]$^{2+}$. A direct nitrosylation to *trans*-[RuCl$_2$(bpy)$_2$] using NO_2^- under acidic conditions also gave a mixture of *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$ and *cis*-[RuCl(NO)(bpy)$_2$]$^{2+}$. The reaction of *trans*-[RuCl(H$_2$O)(bpy)$_2$]$^+$ and NO gas was chosen finally as the most suitable method for the synthesis (see the Experimental Section).

Characteristic properties observed for *trans*-[RuCl(NO)(bpy)$_2$]$^{2+}$ and relevant complexes are shown in Table III. The diamagnetic property observed for all nitrosyl complexes is typical of the $\{RuNO\}^6$ type of complexes.[15] A characteristic nitrosyl stretching mode (ν(NO)) of the trans isomer was observed at 1910–1920 cm^{-1}, a frequency region lower by 20 cm^{-1} than that of the cis isomer. The trans isomer usually exhibits its ν(NO) mode at a lower frequency region than where the cis isomer does.[10] The ^1H NMR spectral pattern of the trans isomer (CD_3CN) is essentially the same as that reported for *trans*-[Ru(CH$_3$CN)$_2$(bpy)$_2$]$^{2+}$ [8] (δ = 9.08 (4 H, d), 8.70 (4 H, d), 8.57 (4 H, dd), 8.06 (4 H, dd)). The ^{13}C NMR spectrum of the trans isomer in CD_3CN solution is presented in Figure 1, along with that of the cis isomer, which was measured for comparison. The simple

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(15) Enemark, J.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. Mononitrosyl complexes are conveniently described as $\{RuNO\}^n$, where *n* is the number of the d electron on the metal when the NO group is formally bound as NO$^+$.

Table III. Complexes and Some of Their Properties

	IR[c]			CV[d]			
complex	ν(NO)	ν_{as}(NO)	ν_s(NO)	$E_{1/2}$	E_{p_c}	UV-vis λ (ϵ)[e]	ref
trans-$[RuCl(NO)(bpy)_2](PF_6)_2$	1912			−0.20	−0.82	460 (6.3×10) 308 (1.9×10^4)	
trans-$[RuCl(NO)(bpy)_2](ClO_4)_2$	1920						
trans-$[RuBr(NO)(bpy)_2](PF_6)_2$	1907						
trans-$[RuBr(NO)(bpy)_2](ClO_4)_2$	1914						
cis-$[RuCl(NO)(bpy)_2](PF_6)_2$	1934			−0.19	−0.99	480 (9.0×10) 324 (1.3×10^4) 295 (1.8×10^4)	
trans-$[RuCl(NO_2)(bpy)_2]$		1325	1290			503 (7.5×10^3) 334 (8.7×10^3) 294 (4.5×10^4) 237 (2.0×10^4)	38
cis-$[RuCl(NO_2)(bpy)_2]$		1338	1298	0.20			
trans-$[RuCl(NO_2)(bpy)_2]PF_6$[a]		1380	1320			630–640 (2.5×10^2) 312 (1.8×10^4)	25
cis-$[RuCl(NO_2)(bpy)_2]PF_6$[b]		1380	1320	0.20			

[a] $\mu_{eff} = 2.15\ \mu_B$. [b] $\mu_{eff} = 2.04\ \mu_B$. [c] In cm^{-1} (KBr). [d] In V vs Ag|$AgClO_4$ (0.1 mol dm^{-3} in CH_3CN) at 25 °C. [e] nm ($\epsilon/dm^3\ mol^{-1}\ cm^{-1}$).

Table IV. Important Bond Distances (Å) and Bond Angles (deg) of *trans*-$[RuCl(NO)(bpy)_2](ClO_4)_2$

Distances			
Ru–Cl	2.306 (2)	Ru–N(3)	2.108 (6)
Ru–N(O)	1.751 (6)	Ru–N(4)	2.096 (6)
Ru–N(1)	2.108 (6)	N(O)–O(N)	1.132 (9)
Ru–N(2)	2.092 (6)		
Angles			
Ru–N(O)–O(N)	170.4 (5)	Cl–Ru–N(2)	86.5 (2)
Cl–Ru–N(O)	175.2 (2)	Cl–Ru–N(3)	89.5 (2)
N(1)–Ru–N(2)	77.3 (3)	Cl–Ru–N(4)	87.6 (1)
N(2)–Ru–N(3)	103.6 (3)	N(O)–Ru–N(1)	95.9 (3)
N(3)–Ru–N(4)	76.7 (3)	N(O)–Ru–N(2)	90.2 (2)
N(4)–Ru–N(1)	102.0 (2)	N(O)–Ru–N(3)	88.0 (3)
Cl–Ru–N(1)	86.8 (2)	N(O)–Ru–N(4)	95.7 (2)

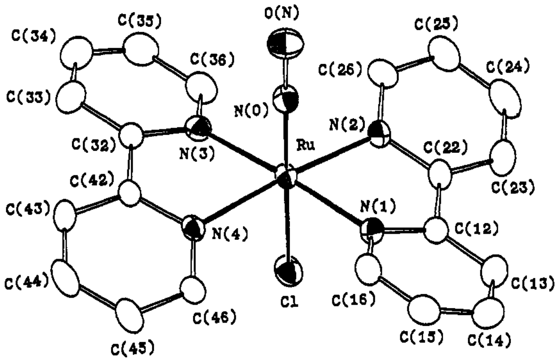

Figure 2. Molecular structure of *trans*-$[RuCl(NO)(bpy)_2]^{2+}$.

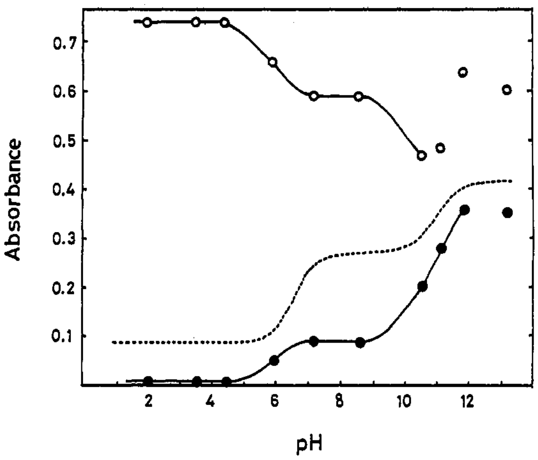

Figure 3. Dependence of UV absorption of *trans*- and *cis*-[RuCl(NO)(bpy)$_2$](PF$_6$)$_2$ on pH. Trans isomer (4.23×10^{-5} mol dm^{-3}): (○) 308 nm; (●) 480 nm. Cis isomer (6.2×10^{-5} mol dm^{-3}): (dotted line) 360 nm.

spectrum confirms the trans configuration, where two bpy molecules exist in positions essentially equivalent to each other (δ = 157.4 (s), 153.5 (s), 144.6 (s), 129.8 (s), 126.8 (s)).

The molecular structure of the trans isomer is shown in Figure 2. The cation has the expected trans-octahedral coordination geometry, with two bpy ligands in equatorial positions and with both chloro and nitrosyl ligands in axial positions. The bond distances and angles in the coordination sphere are given in Table IV. The Ru-N(nitrosyl) and N–O bond distances (1.751 (6) and 1.132 (9) Å, respectively) were comparable to those in known trans-type complexes.[16] The RuNO angle is approximately linear: the nitrosyl oxygen atom is directed so as to bisect the N(1)–Ru–N(4) angle, with a Ru–N–O angle of ca. 170° (Table IV).

The Ru–Cl distance (2.306 (2) Å) was shorter than that reported for *trans*-$[RuCl(NO)(py)_4]^{2+}$ (2.314 (1) Å).[17] It thus exhibits the shortest Ru–Cl distance among all $\{RuNO\}^6$ type complexes. The fact that the Ru–Cl bond (and also the Ru–N(nitrosyl) bond) has shortened relative to that of *trans*-$[RuCl(NO)(py)_4]^{2+}$ suggests that significant influence is exerted through the conjugated five-ring system, which consists of bridging carbons (C(12) and C(22), C(32) and C(42)), nitrogen atoms of each pyridine ring, and the Ru ion (in contrast, the N–O bond elongated by ca. 0.01 Å).

The Ru–N(bpy) bond distances of 2.108 (6)–2.092 (6) Å are very similar to those of other *trans*-bis(2,2′-bipyridine)ruthenium complexes.[14,18-20] A "bowed" type of distortion was found in the trans isomer. Either "bowed" or "twisted" distortion is necessary to minimize steric interaction due to 6,6′-hydrogen atoms of the bpy ligands. Direct comparison of the structural parameters between trans and cis isomers is important, but no structure analysis of the cis isomer has been performed.

Nitrosyl–Nitro Conversion. Addition of aqueous NaOH to the solution of *trans*-$[RuCl(NO)(bpy)_2]^{2+}$ immediately gave *trans*-$[RuCl(NO)_2(bpy)_2]$ as a solid, indicating that a nitrosyl-nitro conversion reaction ($-NO^+ + 2OH^- \rightleftarrows -NO_2^- + H_2O$) occurs, as is the case with *cis*-$[RuCl(NO)(bpy)_2]^{2+}$.[21] We tried to measure the equilibrium constant for the conversion reaction, to compare its value with that of cis isomer.[21] Accurate measurement was hampered by the facile precipitation of the nitro complex, *trans*-$[RuCl(NO_2)(bpy)_2]$, in the high pH region.

In Figure 3 are shown the results of the pH dependence of the UV spectral absorbance at several wavelengths. The experiment provides clear evidence for the existence of three different forms of the complexes in aqueous solution. These three forms can be

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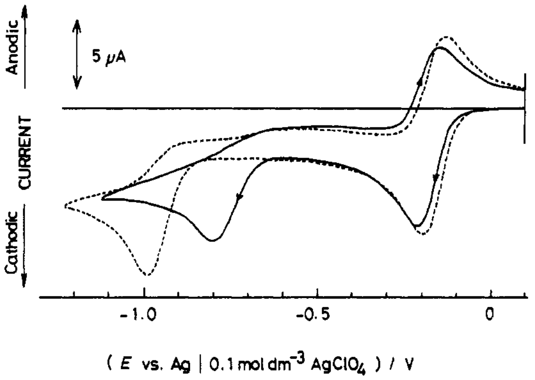

Figure 4. Cyclic voltammograms of: *trans*-$[\mathrm{RuCl(NO)(bpy)_2}](\mathrm{PF_6})_2$ (1.0 mmol $\mathrm{dm^{-3}}$; solid line) and *cis*-$[\mathrm{RuCl(NO)(bpy)_2}](\mathrm{PF_6})_2$ (1.0 mmol $\mathrm{dm^{-3}}$; dashed line), at a stationary platinum electrode in 0.1 mol $\mathrm{dm^{-3}}$ TEAP–$\mathrm{CH_3CN}$ at 25 °C (100 mV $\mathrm{s^{-1}}$).

assigned as *trans*-$[\mathrm{RuCl(NO)(bpy)_2}]^{2+}$ (pH < 5.3), *trans*-$[\mathrm{RuCl(NO_2H)(bpy)_2}]^+$ (5.3 < pH < 9.5), and *trans*-$[\mathrm{RuCl(NO_2)(bpy)_2}]$ (pH > 9.5), as was postulated by Meyer et al.[22] The following equilibrium occurs:

$$[\mathrm{RuCl(NO)(bpy)_2}]^{2+} \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftharpoons}} [\mathrm{RuCl(NO_2H)(bpy)_2}]^+ \qquad (1)$$
$$\mathrm{p}K_{\mathrm{a_1}} = 6.1$$

$$[\mathrm{RuCl(NO_2H)(bpy)_2}]^+ \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-\,(-H_2O)}}{\rightleftharpoons}} [\mathrm{RuCl(NO_2)(bpy)_2}] \qquad (2)$$
$$\mathrm{p}K_{\mathrm{a_2}} = 10.3$$

The pK values, estimated roughly for the trans isomer, are slightly lower than those of the cis isomer measured under the same experimental conditions: p$K_{\mathrm{a_1}}$ = 6.4 and p$K_{\mathrm{a_2}}$ = 11.0.[23]

Recently, we have reported a rare reaction that a nitro tetrakis(pyridine) complex of Ru(II), *trans*-$[\mathrm{RuCl(NO_2)(py)_4}]$, in $\mathrm{CH_3CN}$ is oxidized electrochemically to give an oxo complex of Ru(IV), *trans*-$[\mathrm{RuCl(O)(py)_4}]^+$, along with both *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$ and *trans*-$[\mathrm{RuCl(OH)(py)_4}]^+$.[24] The study of such electrochemical oxidation did not succeed for *trans*-$[\mathrm{RuCl(NO_2)(bpy)_2}]$, because of its lower solubility in organic solvents.

In the chemical oxidation using NaClO, *cis*-$[\mathrm{RuCl(NO_2)(bpy)_2}]$ undergoes a one-electron oxidation to give *cis*-$[\mathrm{RuCl(NO_2)(bpy)_2}]^+$, which is isolatable as the $\mathrm{PF_6}$ or the $\mathrm{ClO_4}$ salt.[25] The cis nitro complex of Ru(III) was reactive in $\mathrm{CH_3CN}$, and it changed successively to *cis*-$[\mathrm{RuCl(NO)(bpy)_2}]^{2+}$ and *cis*-$[\mathrm{RuCl(ONO_2)(bpy)_2}]^+$ by a disproportionation at the $\mathrm{NO_2}$ ligand.[26] Under the same oxidation conditions, *trans*-$[\mathrm{RuCl(NO_2)(bpy)_2}]$ gave *trans*-$[\mathrm{RuCl(NO_2)(bpy)_2}]^+$ as a $\mathrm{PF_6}$ salt (Table III). However, such a disproportionation reaction, observed for *cis*-$[\mathrm{RuCl(NO_2)(bpy)_2}]^+$, did not occur for *trans*-$[\mathrm{RuCl(NO_2)(bpy)_2}]^+$ owing again to its insolubility.

Electrochemical Behavior. The cyclic voltammograms of a $\mathrm{CH_3CN}$ solution of *trans*-$[\mathrm{RuCl(NO)(bpy)_2}]^{2+}$ exhibit a well-defined cathodic wave at around −0.20 V, together with the coupled anodic wave on the reverse scan (Figure 4). The peak current ratio $i_{\mathrm{p_c}}/i_{\mathrm{p_a}}$ is equal to unity and the peak potential separation $\Delta E = E_{\mathrm{p_c}} - E_{\mathrm{p_a}}$ = ca. 70 mV of the cathodic and anodic waves at all the scan rates used (200–50 mV $\mathrm{s^{-1}}$) corresponds to the value expected for a one-electron reversible couple, on the time scale of cyclic voltammetry. Plots of peak current vs the square root of the scan rate are linear, indicating that diffusion-controlled redox processes are occurring at the electrode.

At more negative potential region, the cyclic voltammograms of the trans isomer exhibit a irreversible cathodic peak at −0.82 V. The absence of any anodic wave, even when we used a fast scan rate (200 mV $\mathrm{s^{-1}}$) at low temperature (−40 °C), indicates a rapid decomposition of the two-electron-reduction species of the trans isomer. The latter reduction wave appears to involve no loss of nitrosyl ligand, so that the reduction can be described formally as similar to that of the cis isomer:

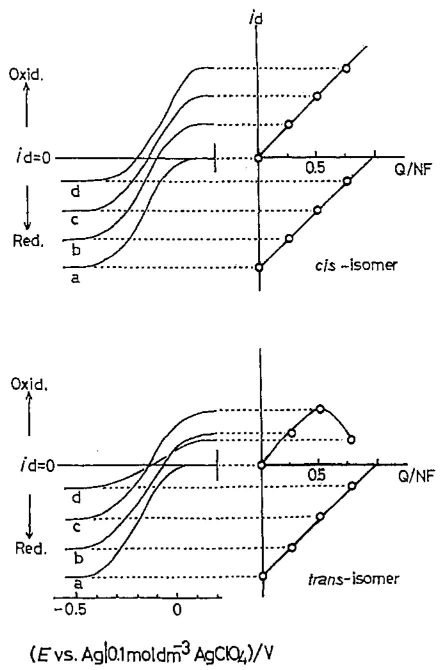

Figure 5. Voltammograms at a platinum rotating disk electrode monitoring the course of controlled-potential electrolysis (reduction) of the first wave of *trans*- and *cis*-$[\mathrm{RuCl(NO)(bpy)_2}](\mathrm{PF_6})_2$ (1.01 mmol $\mathrm{dm^{-3}}$) in $\mathrm{CH_3CN}$ and plots of i_{d} and Q/NF: (a) before electrolysis; (b and c) during electrolysis; (d) at the end of electrolysis (n = 0.78).

$$[\mathrm{RuCl(NO)(bpy)_2}]^{2+} + \mathrm{e^-} \rightleftarrows [\mathrm{RuCl(NO)(bpy)_2}]^+ \qquad (3)$$

$$[\mathrm{RuCl(NO)(bpy)_2}]^{+} + \mathrm{e^-} \rightarrow [\mathrm{RuCl(NO)(bpy)_2}] \qquad (4)$$

The site of the reduction is confirmed largely to the nitrosyl group, as has been proposed.[27]

The reduction potential for the first step (eq 3) is sensitive to the degree of dπ–pπ^* back-bonding between the metal and the nitrosyl group: the $E_{1/2}$ value of the first reduction step will decrease when greater dπ–pπ^* mixing for the metal atom and more extensive back-donation of electron density from the metal to the nitrosyl ligand are present.[28] In these isomers the potentials for the first reduction wave are remarkably close: $E_{1/2}$ = −0.20 V for the trans isomer and −0.19 V for the cis isomer, suggesting a smaller contribution of the trans–cis steric configuration to the dπ–pπ^* mixing. This result is rather surprising in view of the fact that the ligand at the trans position of nitrosyl should exert a large effect on the nature of the (M–NO) bonding. In practice, a considerable decreasing of the $E_{1/2}$ value was observed for *trans*-$[\mathrm{RuX(NO)(py)_4}]^{2+}$ (X = Cl, OH) when the Cl ligand was altered by OH.[29]

While the first reversible couple of both isomers appeared at the same potential region, a significant shift of $E_{\mathrm{p_c}}$ was observed for the second irreversible process: the cis isomer displays the reduction wave at a more negative potential (by 0.17 V) than does the trans isomer. The variation of $E_{\mathrm{p_c}}$ indicates some steric effect in the second irreversible process, since the dπ–pπ^* mixing seems to be less important in the once-reduced nitrosyl complexes.[28]

Another important feature of the trans and cis isomers was observed in the controlled-potential electrolysis, which was

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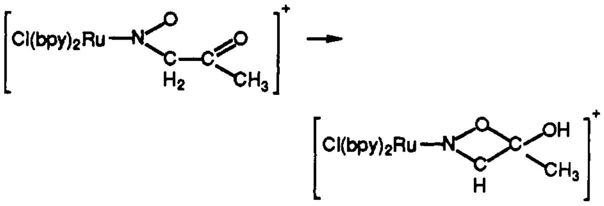
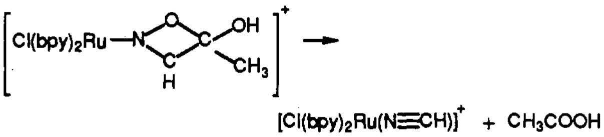
[29] $E_{1/2}$ = −0.69 V for *trans*-$[\mathrm{Ru(OH)(NO)(py)_4}]^{2+}$, −0.11 V for *trans*-$[\mathrm{RuCl(NO)(py)_4}]^{2+}$, and 0.08 V for *trans*-$[\mathrm{Ru(NO)(NH_3)(py)_4}]^{3+}$.[9]

monitored succesively by cyclic voltammetry. Exhaustive electrolysis of the trans isomer past the first reduction wave consumed 1 mol of electron/mol of the complex ($n = 1.0 \pm 0.03$ electron) at 25 °C (Figure 5). However, the height of the oxidation wave observed on the rotating-disk voltammograms of the reduced solution does not increase constantly, indicating a decomposition of *trans*-[RuCl(NO)(bpy)$_2$]$^+$ species. In contrast, the one-electron-reduction species of the cis isomer is stable enough to measure during the experiment. Meyer et al. have found for the cis isomer that the one-electron-reduction product generated by bulk electrolysis is stable for an indefinite period when protected from oxygen.[27]

Electrophilic Behavior of the Trans Isomer. Although *cis*-[RuCl(NO)(bpy)$_2$]$^{2+}$ is generally preferable for the investigation of the electrophilic behavior of coordinated nitrosyl,[6,7,30] the present trans isomer has a greater advantage as an electrophile than the cis isomer, at least in some cases. Our recent work showed that additions of small amounts of NH_4OH to a solution of *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ in acetone resulted in an intense pink coloration, due to the formation of an acetone adduct,[3] *trans*-[RuCl(py)$_4${N(O)CH$_2$C(O)CH$_3$}]$^+$; this appears to be a color reaction analogous to that in the standard test for ketones containing the $CH_3C(O)$–group.[31] The coloration does occur also in trans isomers, though attempts to isolate the colored species were unsuccessful.[32] However, an interesting material could be isolated instead of the pink species: prolonged standing (ca. 1 month) of the trans isomer in acetone without addition of NH_4OH, under room light, gave a deep brown solution, from which a black crystalline material deposited. The IR spectrum (4000–600 cm^{-1}) of the product showed a new strong absorption band at 2150 cm^{-1}, which was tentatively assigned to ν(C≡N). No other bands due to nitrosyl or an organic substance (CH_3 group) could be seen. Analytical data suggest the chemical formula [RuCl(bpy)$_2$(NCH)]PF$_6$·H$_2$O.[33] The product appears to be analogous to [Ru(NH$_3$)$_5$(NCH)]$^{2+}$ reported by Ford and by Isied and Taube.[34,35] The formation process of the present product could be explained as follows, according to the same reaction progress as reported for *trans*-[RuCl(NO)(py)$_4$]$^{2+}$:[3] (i) the trans isomer reacts first with acetone to give *trans*-[RuCl(bpy)$_2${N(O)CH$_2$C(O)CH$_3$}]$^+$, which is detected as a pink species; (ii) the acetone adduct would decompose into nitrile complex, *trans*-[RuCl(bpy)$_2$(NCH)]$^+$, via an intraligand cyclization and rearrangement



(5)



[Cl(bpy)$_2$Ru(N≡CH)]$^+$ + CH_3COOH (6)

Single crystals are clearly needed for further investigation. Our previous efforts to isolate the nitrile complex as a pure compound using *trans*-[RuCl(NO)(py)$_4$]$^{2+}$ failed.[3]

The coloration reaction did not occur in the cis isomer. Under the same conditions, the cis isomer gave simply *cis*-[RuCl(H$_2$O)(bpy)$_2$]PF$_6$·H$_2$O, which probably converted in a similar way to those complexes reported by both Meyer et al.[27] and by Swinehart et al.[36]

Walsh and Durham have reported that no thermal isomerization occurred in the *trans*-[RuXY(bpy)$_2$] type of complexes.[8] This seems true for our nitrosyl complex, from our check of cyclic voltammetry and NMR spectroscopy. There is, however, an unexplained observation: the UV–vis spectra of the trans isomer in CH_3CN solvent vary with time,[37] but a solution allowed to stand for 25 h still gave a cyclic voltammogram identical with that of the trans isomer which was measured immediately after the solution was prepared.

Supplementary Material Available: Tables of hydrogen atom positions, thermal parameters, distances and angles in the bpy ligands, and least-squares planes and a schematic diagram of the complex (6 pages); a table of $F_o - F_c$ data (20 pages). Ordering information is given on any current masthead page.

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(30) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 4340.

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(32) After this paper was submitted, the pink species was isolated successfully. A detailed characterization of the product is now under way.

(33) Anal. Calcd for RuCl(NCH)(C$_{10}$H$_8$N$_2$)$_2$PF$_6$: N, 11.3; C, 40.6; H, 2.8. Found: N, 10.8; C, 40.8; H, 2.7. It is diamagnetic.

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(37) A freshly prepared CH_3CN solution of the trans isomer exhibits an absorption band at 308 nm, along with a very weak band at 460 nm. A new peak appeared at 270 nm and increased in intensity with time, while the intensity of the band at 308 nm decreased. (In addition, another absorption band appeared at around 330 nm after 5 days.)

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