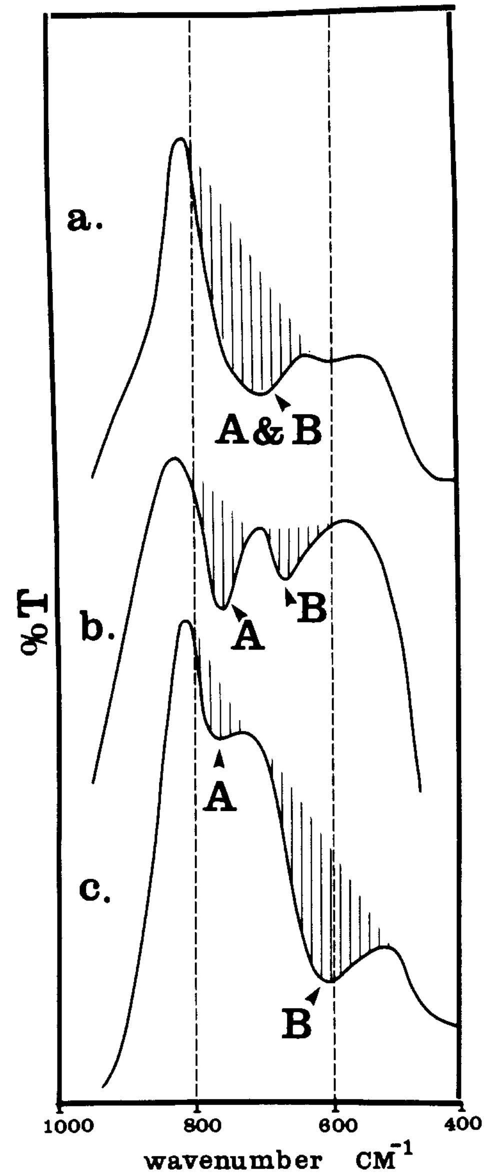

Figure 1. Comparison of the symmetric stretching vibration region of the infrared spectra of three metallosilicate gels showing successful incorporation of the metal into the silicate function: (a) aluminosilicate, (b) ferrisilicate, (c) gallosilicate. A refers to the Si–O–Si symmetric stretching vibration; B refers to the Si–O–T symmetric stretching vibration. The shift in B between parts b and c is consistent with the difference in the reduced mass of the two trivalent elements. Si–O–Si and Si–O–Al are indistinguishable for the aluminosilicate gel in part a.

formation of the Si–O–Ga linkage as a function of time when the colloidal silica Ludox (Du Pont Corp.) is used as a source of silica in this preparation. It is understandable that incorporation of the trivalent element would be slow due to the presence of small 150-Å beads of polymeric silica composing the colloidal material. A disruption of the Si–O–Si linkages must occur before incorporation of the trivalent element into the silica polymer. Initially, when Ludox is used as the source of silica only the Si–O–Si linkage is observed at 800 cm^{-1} in the symmetric stretching vibration region. This is shown in Figure 2a. No band associated with the formation of Si–O–Ga linkages appears. With time, 1–5 h, as the gallium begins to incorporate into the silica polymer, it is observed in the infrared spectrum as a formation and growth in intensity of the Si–O–Ga band at 611 cm^{-1}. This is shown in Figure 2b. A small shift in the Si–O–Si vibration to lower wavenumber is seen as the Si–O–Ga vibration appears.

It is anticipated that infrared spectroscopy may prove to be a powerful tool to assist in determining the range of metals that may complex with silica and ultimately form crystalline molecular sieve structures. In addition, the use of these elements as labels may provide insight into the understanding of the gel phase of molecular sieve synthesis.

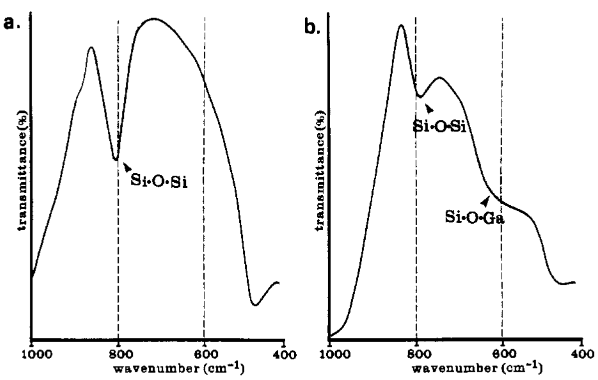

Figure 2. Incorporation of the trivalent gallium ion into the silicate fragment as a function of time followed by using the symmetric stretching vibration region of the infrared spectrum. (a) Initially, when Ludox is used as a source of silica no Si–O–Ga vibration is observed. (b) With time, 1–5 h, the band associated with the Si–O–Ga vibration appears.

Experimental Procedure

Gels were prepared by addition of the acidified (6.1 g of H_2SO_4) Al^{3+}, Fe^{3+}, and Ga^{3+} ions prepared from the corresponding nitrate (ca. 3 g $M(NO_3)_3 \cdot xH_2O$ (M = Al, Fe, Ga) in 25 g of H_2O) to a water solution of sodium metasilicate (24 g of $Na_2SiO_3 \cdot H_2O$ in 25 g of H_2O). The solid gel was separated from the liquid by filtration, washed with water, and dried at 50 °C. Preparation of samples for IR studies is described in ref 3.

Registry No. $Al(NO_3)_3$, 13473-90-0; $Fe(NO_3)_3$, 10421-48-4; $Ga(NO_3)_3$, 13494-90-1; silica, 7631-86-9; sodium metasilicate, 6834-92-0; sodium aluminosilicate, 1344-00-9; sodium ferrisilicate, 51142-60-0; sodium gallosilicate, 104619-11-6.

Contribution from the Department of Chemistry,
Faculty of Science and Technology, Sophia University,
Chiyoda-ku, Kioi-cho 7, Tokyo, Japan 102

First Synthesis of a Nitro Complex of Ruthenium(III), as a Key Intermediate in the Oxidation of Nitro Ligand To Give both Nitrosyl and Nitrato Ligands

Hirotaka Nagao, Masao Mukaida,* Kunio Shimizu,
F. Scott Howell, and Hidetake Kakihana

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Recent investigations of the nitrosyl ligand coordinated to a transition metal have revealed a variety of interesting reactions.[1] For example, the oxidation of *cis*-$[RuCl(NO)(bpy)_2]^{2+}$ gives the corresponding nitrato complex via a reactive nitro complex of Ru(III).[2] We recently reported that the oxidation of *trans*-$[RuCl(NO)(py)_4]^{2+}$, under basic conditions, gave an oxo complex of Ru(IV), *trans*-$[RuCl(O)(py)_4]^{+}$, the first example of this type of complex.[3] If the same oxidation procedure is applied to *cis*-$[RuCl(NO)(bpy)_2]^{2+}$, the nitro complex of Ru(III), $[RuCl(NO_2)(bpy)_2]^{+}$, which can be regarded as a key intermediate for the preparation of the nitrato complex of Ru(III), was obtained as a black crystalline material. Isolation of the nitro complex of

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(1) (a) Swinehart, J. H. *Coord. Chem. Rev.* **1967**, *2*, 385–402. (b) Bottomley, F. *Acc. Chem. Res.* **1978**, *11*, 158–163. (c) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53–76.

(2) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruna, H. D.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1896–1903.

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0020-1669/86/1325-4312$01.50/0

Ru(III) is noteworthy because the complex has been considered to exist only as a kinetic transient.[4] In fact, there appears to be no known stable monomeric nitro complex of Ru(III), despite various reported efforts.[5] We here communicate the first syntheses of $[RuX(NO_2)(bpy)_2]Y$ [**1** (X = Cl, Y = ClO_4); **2** (X = Cl, Y = PF_6); **3** (X = Br, Y = ClO_4); **4** (X = Br, Y = PF_6)] by the oxidation of the corresponding nitrosyl complex with NaClO solution. It appears that the basic reaction medium for the oxidation is the key to successful isolation of the unstable, hitherto unisolatable compound.

Experimental Section

Reagents. Hydrated ruthenium trichloride was purchased from Nippon-Engelhardt; analytical grade chemicals were used in all cases. It should be noted that the preparation of the present complexes was carried out by using freshly obtained sodium hypochlorite solution (Wako Co.) whose concentration of available chlorine was near 10%. *cis*-$[RuX(NO)(bpy)_2]Y_2$ (X = Cl, Br; Y = ClO_4, PF_6) were prepared by a literature method from *cis*-$[Ru(NO_2)_2(bpy)_2]$.[6] The dinitro complex was prepared by the use of *cis*-$[RuCl_2(bpy)_2]Cl$ (in place of the *cis*-$[RuCl_2(bpy)_2]$ used by Godwin and Meyer), which was synthesized conveniently by use of a ruthenium blue solution.[7] The procedure to give the blue solution has recently been modified.[8]

Instruments. IR spectra were measured on a Hitachi EPI G2 spectrometer. UV-vis spectra were recorded on a Hitachi 200-20 spectrophotometer. Magnetic moments were measured by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. Elemental analyses were performed by both the Sophia University Analytical Facility and the Institute of Chemical and Physical Research, Wako Saitama 351, Japan. The cyclic voltammetry was carried out by using a Fuso Polarograph Model 312 with a stationary platinum disk electrode (o.d. = 1.99 mm).[9] Conductivity data were obtained with a Metrohm Konduktoskop E356.

Syntheses. $[RuCl(NO_2)(bpy)_2]ClO_4$ (1). Method A. A 50-mg sample of *cis*-$[RuCl(NO)(bpy)_2](ClO_4)_2$ was dissolved in 10 mL of water by heating. A 2-mL aliquot of NaClO was added to the solution after it was cooled down to room temperature. The mixed solution immediately became dark red, turning gradually to dark green as it stood at room temperature. The pH of the solution increased to approximately 12. The black crystalline material that deposited was collected, washed with cold water, and then dried in vacuo. Anal. Calcd for $[RuCl(NO_2)(bpy)_2]ClO_4$: C, 40.42; H, 2.72; N, 11.79. Found: C, 40.44; H, 2.65; N, 11.63. UV-vis spectral data (λ_{max}/nm (ϵ/M^{-1} cm^{-1})) in CH_3CN (Dotite Spectrosol): 630–640 (300), 312 (20200). Yield: 70–80%. Method A is convenient for the preparation of the perchlorate salt of the complex from the corresponding nitrosyl complex, which is soluble in water, since the appearance of the dark green solution is taken as a measure of the effective oxidation progress.

$[RuCl(NO_2)(bpy)_2]PF_6$ (2). Method B. A 100-mg sample of the corresponding nitrosyl complex, which was milled by using an agate mortar, was suspended in 10 mL of water. After 2 mL of NaClO solution had been added, the solution was stirred for 3 h and then it was kept at room temperature for 8 h without stirring. A black solid material was obtained and collected, washed with cold water, and then dried in vacuo. Yields were usually greater than 85%. Anal. Calcd for $[RuCl(NO_2)(bpy)_2]PF_6$: C, 37.54; H, 2.53; N, 10.95; PF_6, 22.66. Found: C, 37.26; H, 2.41; N, 10.78; PF_6, 22.51. UV-vis spectral data: 630–640 (250), 312 (18000).

$[RuBr(NO_2)(bpy)_2]ClO_4$ (3) and $[RuBr(NO_2)(bpy)_2]PF_6$ (4). These complexes were prepared by the same procedure as that used for **2**, with $[RuBr(NO)(bpy)_2]Y_2$ (Y = ClO_4, PF_6) used as a starting material. Anal. Calcd for $[RuBr(NO_2)(bpy)_2]ClO_4$: C, 37.60; H, 2.53; N, 10.97. Found: C, 37.35; H, 2.47; N, 10.79. Calcd for $[RuBr(NO_2)(bpy)_2]PF_6$: C, 35.10; H, 2.36; N, 10.24. Found: C, 34.89; H, 2.22; N, 10.03.

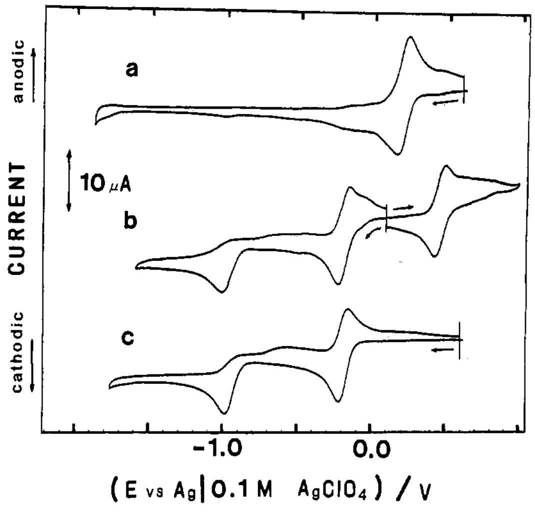

Figure 1. Cyclic voltammograms for $[RuCl(NO_2)(bpy)_2]PF_6$ and *cis*-$[RuCl(NO)(bpy)_2](PF_6)_2$ (used as an authentic sample) at a stationary platinum disk electrode in 0.1 mol dm^{-3} TEAP + AN at 25 °C (scan rate 50 mV s^{-1}): (a) $[RuCl(NO_2)(bpy)_2]^+$ (2.39 mmol dm^{-3}), measured immediately after the solution was prepared; (b) $[RuCl(NO_2)(bpy)_2]^+$ (4.00 mmol dm^{-3}), measured for the solution that was allowed to stand for 7 days under argon (initial potential is 0.1 V for both reductive and oxidative scan); (c) *cis*-$[RuCl(NO)(bpy)_2]^{2+}$ (1.75 mmol dm^{-3}).

Table I. IR Absorption Bands for $[RuCl(NO_2)(bpy)_2]PF_6$ and Related Complexes[a]

complex	ν(N–O)/cm^{-1}		ref
$[RuCl(NO_2)(bpy)_2]PF_6$	1380 (1360)	1320 (1298)	this work
$[RuCl(NO_2)(bpy)_2]$	1338	1298	6
$[RuCl(ONO)(bpy)_2]$	1396	1133	13
$[Ru(ONO_2)(bpy)_2(py)]PF_6$	1460	1288	2

[a] The figures in parentheses are for $[RuCl(^{15}NO_2)(bpy)_2]PF_6$.

Results and Discussion

Addition of NaClO to an aqueous solution of *cis*-$[RuCl(NO)(bpy)_2]^{2+}$ gave immediately a dark red solution, due to the formation of $[RuCl(NO_2)(bpy)_2]$. The nitro complex of Ru(II) is formed under basic conditions by the nitrosyl–nitro conversion reaction.[1a,6] The crystalline product, obtained from the resultant solution, was stable when stored in a desiccator but decomposed slowly in organic solvents or in the presence of moisture.[10] The nitro complex of Ru(III) was identified by the following experiments. Satisfactory elemental analyses were obtained for all of the products. The effective magnetic moment of 2.35 μ_B for **1** supports its characterization as a Ru(III) complex with an octahedral environment, though the value is a little higher than those of related Ru(III) complexes. IR spectra of the nitro group in the products were observed at 1380 and 1320 cm^{-1}. Both bands shifted to lower frequency in an ^{15}N-labeling experiment. As seen in Table I, the IR spectra indicate N-bound nitro coordination, rather than an O-bound nitrito or nitrato complex.[11,12] Both bands due to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ increased by ca. 20–40 cm^{-1} upon oxidation.[2,13] Conductivity data of **1**, measured immediately after it was dissolved in CH_3CN, suggest it to be a 1:1 electrolyte, since the slope of the $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ plot is nearly identical with that of $[RuCl_2(bpy)_2]ClO_4$ used for a comparison.[14]

The cyclic voltammogram of **1**, in CH_3CN, exhibits a single reversible reduction wave at a potential that is reasonable for Ru(III)/Ru(II) reduction ($E_{1/2}$ = 0.19 V vs. Ag|$AgClO_4$ (0.1 mol

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(4) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 4821–4822.

(5) (a) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2384–2386. (b) Griffith, W. P. *The Chemistry of the Rare Platinum Compounds*; Interscience: New York, 1967; p 159.

(6) Godwin, J. B.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 2150–2153.

(7) Bottomley, F.; Mukaida, M. *Inorg. Chim. Acta* **1985**, L29–30.

(8) Endo, A.; Shimizu, K.; Sato, G. P.; Mukaida, M. *Chem. Lett.* **1984**, 437–440.

(9) Aoyagi, K.; Yukawa, Y.; Mukaida, M.; Shimizu, K.; Takeuchi, T.; Kakihana, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1493–1499.

(10) The products always show a very weak IR band assignable to ν(NO), due to contamination by *cis*-$[RuCl(NO)(bpy)_2]^{2+}$. A partial decomposition probably occurred because water was used as the washing solvent.

(11) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; pp 220–226.

(12) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 3rd ed.; Interscience: New York, pp 639–641.

(13) Adeymi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994–999.

(14) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587–4591.

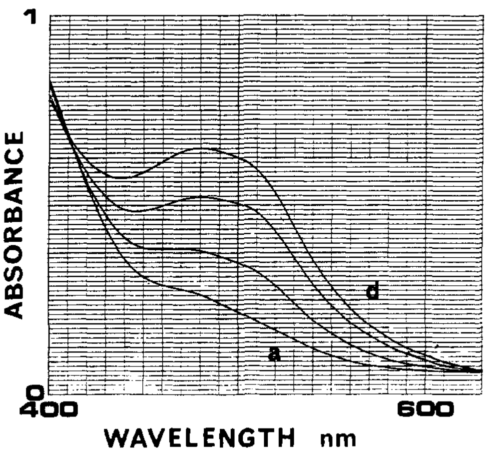
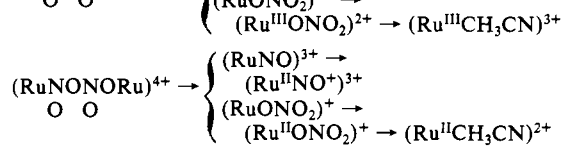


Figure 2. UV–vis spectra change of the decomposition reaction of $[RuCl(NO_2)(bpy)_2]ClO_4$ (**1**) (1.5×10^{-4} mol dm^{-3}) dissolved in CH_3CN at room temperature: (a) immediately after; (b) 40 min after; (c) 120 min after; (d) 240 min after.

dm^{-3} in CH_3CN)), as shown in Figure 1a. The wave was judged to be due to a one-electron-transfer process by analysis of the normal pulse voltammetry data. The potential observed for the one-electron reduction of **1** ($E_{1/2} = 0.19$ V) is identical with that in the one-electron oxidation of the corresponding nitro complex of Ru(II), $[RuCl(NO_2)(bpy)_2]$, supporting the proposed formulation, $[RuCl(NO_2)(bpy)_2]^+$.[15] When the reductive potential scan, starting at 0.1 V, was run again after the solution was allowed to stand for 1 h the cyclic voltammogram was changed. The peak current at 0.19 V was seen to decrease, accompanied by the appearance of new reduction peaks at −0.19 and −0.99 V. In addition, oxidative potential scanning from 0.1 V also gave a new peak at 0.47 V. On further standing, the peak current of these three waves increased, accompanied by a decrease in the wave at 0.19 V. In another experiment, the CH_3CN solution containing **1** was kept independently for 7 days under argon, in order to elucidate the final products in the decomposition reaction. With time, traces of $[RuCl(NO_2)(bpy)_2]$ separated out as a brown precipitate from the decomposed solution.[16] The cyclic voltammograms of the filtrate are shown in Figure 1b: three waves, at 0.47, −0.19, and −0.99 V, developed, while the wave at 0.19 V disappeared. The potentials observed at −0.19 and −0.99 V are in agreement with those of the authentic sample of $[RuCl(NO)(bpy)_2]^{2+}$.[17] Certain nitrosyl complexes have been known to undergo two one-electron reductions, reversible and irreversible one-electron reductions, centered on the nitrosyl ligand.[17-19] Another wave at 0.47 V, observed by oxidative potential scanning, could be ascribed to the one-electron oxidation of $[RuCl(CH_3CN)(bpy)_2]^+$ by comparison to the available data.[20,21]

The appearance of small amounts of $[Ru^{II}Cl(NO_2)(bpy)_2]$ as a brown precipitate and the detection of complex ions $[RuCl(NO)(bpy)_2]^{2+}$ and $[Ru^{II}Cl(CH_3CN)(bpy)_2]^+$ by cyclic voltammetry are consistent with the mechanism reported by Meyer et al.[2] They proposed, based on both electrochemical and spectrometric experiments, that the oxidation of the nitro complex of Ru(II) to Ru(III) leads to a facile disproportionation with nitro–nitrito isomerization of the nitro ligand, yielding finally $[Ru^{II}Cl(NO)(bpy)_2]^{2+}$, $[Ru^{II}Cl(NO_2)(bpy)_2]$, and $[Ru^{III}Cl(ONO_2)(bpy)_2]^+$. On the other hand, **1** in CH_3CN gave $[Ru^{II}Cl(NO)(bpy)_2]^{2+}$, $[Ru^{II}Cl(NO_2)(bpy)_2]$, and $[Ru^{II}Cl(CH_3CN)(bpy)_2]^+$ in place of the nitrato complex of Ru(II) or Ru(III) as its decomposition products. The formation of the solvated complex could be understood by assuming that the decomposition reaction of $[Ru^{III}Cl(NO_2)(bpy)_2]^+$ proceeds exclusively to produce $[RuCl(NO)(bpy)_2]^{2+}$ and $[Ru^{II}Cl(ONO_2)(bpy)_2]$, under these conditions, and that the resultant nitrato complex of Ru(II) undergoes solvolysis to give $[Ru^{II}Cl(CH_3CN)(bpy)_2]^+$. $[Ru^{II}Cl(NO_2)(bpy)_2]$, observed as a brown precipitate, appears to be minor, although the equilibrium concentration of these three species was not estimated. The occurrence of $[Ru^{II}Cl(NO_2)(bpy)_2]$ could be explained by assuming that $[Ru^{III}Cl(NO_2)(bpy)_2]^+$ reacted with $[Ru^{II}Cl(\dot{N}O)(bpy)_2]^+$, which would be present as a transient in the decomposition reaction. The assumption of the existence of $[Ru^{II}Cl(\dot{N}O)(bpy)_2]^+$, along with the formation of $[Ru^{II}Cl(CH_3CN)(bpy)_2]^+$, is plausible if the decomposition reaction proceeds, via a dimeric intermediate of $[Ru^{III}Cl(NO_2)(bpy)_2]^+$, by the following two formally different routes:



$$\underset{\mathrm{O}\quad\mathrm{O}}{(\mathrm{RuNONORu})^{4+}} \rightarrow \left\{\begin{array}{l} (\mathrm{Ru\dot{N}O})^{2+} \rightarrow \\ \quad (\mathrm{Ru^{II}NO^{+}})^{3+} + e^{-} \\ (\mathrm{RuONO_2})^{2+} \rightarrow \\ \quad (\mathrm{Ru^{III}ONO_2})^{2+} \rightarrow (\mathrm{Ru^{III}CH_3CN})^{3+} \end{array}\right. \qquad (1)$$

$$\underset{\mathrm{O}\quad\mathrm{O}}{(\mathrm{RuNONORu})^{4+}} \rightarrow \left\{\begin{array}{l} (\mathrm{RuNO})^{3+} \rightarrow \\ \quad (\mathrm{Ru^{II}NO^{+}})^{3+} \\ (\mathrm{RuONO_2})^{+} \rightarrow \\ \quad (\mathrm{Ru^{II}ONO_2})^{+} \rightarrow (\mathrm{Ru^{II}CH_3CN})^{2+} \end{array}\right. \qquad (2)$$

The reaction to give $[Ru^{II}Cl(NO_2)(bpy)_2]$ by use of $(Ru^{II}ONO_2)^+$, prior to undergo the solvation, is also expected to occur; the $(Ru^{II}ONO_2)^+$ species has been known to act as an reductant toward $[Ru^{III}Cl(NO_2)(bpy)_2]^+$.[22]

The complex $[RuCl(NO)(bpy)_2]^{2+}$, which resulted from the solvolysis, also appeared when **1** was refluxed with EtOH; concentration of the resultant solution gave the nitrosyl complex in 30–40% yield. It should be noted that the present work on the isolation of the nitro complex of Ru(III), along with the identification of its decomposition products, provides evidence to support the mechanism reported by Meyer et al.[2] for the oxidation of the nitro ligand coordinated to Ru(II). There are also two other possible structures of the dimeric form, $[Ru_2(NO_2)_2Cl_2(bpy)_4]^{2+}$, having a –(O)N–O–O–N(O)– or a –(O)N–O–N(O)–O– bridging unit.[2,23] Although they can not be ruled out, they seem less likely. X-ray structural work was attempted, but single crystals prepared so far were too small to obtain reflection data.

Acknowledgment. Thanks are due to Mieko Kurihara for her technical assistance. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

Registry No. **1**, 104600-82-0; **2**, 104600-83-1; **3**, 104600-85-3; **4**, 104600-86-4; *cis*-$[RuCl(NO)(bpy)_2](ClO_4)_2$, 83700-49-6; *cis*-$[RuBr(NO)(bpy)_2](ClO_4)_2$, 104600-87-5; *cis*-$[RuCl(NO)(bpy)_2](PF_6)_2$, 29102-12-3; *cis*-$[RuBr(NO)(bpy)_2](PF_6)_2$, 29390-56-5; $[RuCl(NO_2)(bpy)_2]$, 29241-02-9; $[Ru^{II}Cl(CH_3CN)(bpy)_2]^+$, 76023-73-9; $[RuCl(NO)(bpy)_2]^+$, 54866-04-5; $[RuCl(NO)(bpy)_2]$, 54865-99-5; NaClO, 7681-52-9; NO, 10102-43-9; HNO_2, 7782-77-6.

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(15) The potential datum for the oxidation of $[RuCl(NO_2)(bpy)_2]$, reported by Meyer et al. was 0.57 V vs. SSCE. The observed difference in the potential data is due to different experimental conditions, as described in ref 20.

(16) The precipitate could be identified as $[RuCl(NO_2)(bpy)_2]$ by IR spectra. However, participation of the species as an impurity in the product can be ruled out, because no isotopic shift by ^{15}N substitution is observed for the bands near the 1400–1300-cm^{-1} region, where a strong band characteristic for NO_2^- ligand in $[RuCl(NO_2)(bpy)_2]$ has generally been found.

(17) Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 574–581.

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(19) Bottomley, F.; Mukaida, M. *J. Chem. Soc., Dalton Trans.* **1982**, 1933–1937.

(20) There is a large difference in the potential data, due to experimental conditions, between Meyer's data and our data on *cis*-$[RuCl(NO)(bpy)_2]^{2+}$. They reported that $E_{1/2}$ for $[RuCl(NO)(bpy)_2]^{2+/+}$ was 0.20 V and E_{pc} for $[RuCl(NO)(bpy)_2]^{+/0}$ was −0.60 V vs. SSCE. We found $E_{1/2} = -0.19$ V and $E_{pc} = -0.99$ V vs. Ag|$AgClO_4$ (0.1 mol dm^{-3}), respectively. The potential datum ($E_{1/2}$) in $[Ru^{II}Cl(CH_3CN)(bpy)_2]^+$, under the conditions is then estimated by subtracting the above difference from the value of Meyer et al. (0.86–0.39 = 0.47 V).

(21) Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A. Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211–2215.

(22) Another scheme for the oxidation of nitro ligand in $[Ru(NO_2)(bpy)_2(py)]^+$ has been reported, in which only two species, $[Ru(ONO_2)(bpy)_2(py)]^+$ and $[Ru(NO)(bpy)_2(py)]^{3+}$, were formed at the one-electron-oxidation stage with no formation of the corresponding nitro complex of Ru(II), $[Ru(NO_2)(byp)_2(py)]^+$. See ref 2.

(23) Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528–1534.