were not accessible to experiment. However, it is anticipated that the stability constant of the Eu^{2+} adduct with macrocycle **1** should be near to the constant measured for Sm^{2+}. From a comparison with the data of Gansow et al.,[5] it appears that ligand **1** should be as effective as cryptate [2.2.1] for the stabilization of europium in the divalent oxidation state (the nature of the solvents being not taken into account).

Other macrocycles of suitable size should give rise to complexometric and stabilization effects similar to the ones described here. Polarographic and potentiometric investigations of these new facets of the properties of macrocycles are now in progress.

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Oxidation of the Ligand in Nitro Complexes of Ruthenium(III)

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Nitro complexes of bis(bipyridyl)ruthenium(III) are unstable with respect to oxidation of the coordinated nitro ligand. For the complexes $Ru(bpy)_2(L)NO_2^+$ (L = NH_3, py (pyridine), pyr (pyrazine), CH_3CN, PPh_3) and $Ru(bpy)_2(Cl)NO_2$, electrochemical oxidation to the ruthenium(III) state results in production of the corresponding nitrosyl and nitrato complexes in a 1:1 ratio. A two-electron oxidation of the nitro ligand to nitrate occurs, and the corresponding reduction is delocalized over two sites, one at the metal ($Ru^{III} \rightarrow Ru^{II}$) and one at the ligand ($RuNO^+ \rightarrow Ru\dot{N}O$). For the chloro complex the rate of disappearance of $Ru^{III}(bpy)_2(Cl)NO_2^+$ is first order in Ru(III) and the rate constant, determined by monitoring the reaction by cyclic voltammetry, is $1.8 \times 10^{-3}\ s^{-1}$ in acetonitrile at room temperature. For the pyridyl complex, variable scan-rate cyclic voltammetry experiments show the intervention of an intermediate past the initial oxidation step. A mechanism is suggested for the oxidation of coordinated nitrite which consists of an initial rearrangement of the nitro ligand from N bound to O bound. The O-bound isomer is a reactive intermediate which undergoes a bimolecular oxygen atom transfer reaction probably with the corresponding $Ru^{II}-NO_2$ complex to give the observed products. The acid–base properties of the $Ru(bpy)_2(py)NO_2^+$–$Ru(bpy)_2(py)NO^{3+}$ acid–base pair and formal reduction potentials for the chloro and pyridyl complexes as two-electron-acceptor, oxide ion donor oxidants have been determined. In basic solutions, oxidation of the nitro group becomes catalytic and the nitrato complex is the sole product of the oxidation.

Introduction

We are attempting to design 2,2′-bipyridyl complexes of ruthenium which can function as redox catalysts. As potential catalytic systems, the complexes are attractive because of the stability of the Ru–bpy chemical link, the availability of possible multiple electron donor or acceptor properties based either on metal[1,2] or ligand[3,4] redox sites, the existence of dimeric and oligomeric multimetallic complexes,[5] and the versatility of the background synthetic chemistry for making controlled chemical modifications.[5a,6] The complexes are also attractive from the kinetic point of view since they retain the same basic coordination number in a series of different oxidation states and, where known, the kinetic barriers to electron transfer are low as shown by electron-transfer self-exchange studies.[4a,7]

In earlier work it was shown that relatively facile oxidation of ligands coordinated to $(bpy)_2$ complexes of ruthenium can occur (eq 1 and 2). The reactions in eq 1 and 2 are known

$$Ru(bpy)_2(N_3)_2 + CH_3CN \xrightarrow{-e^-} Ru(bpy)_3(CH_3CN)N_3^+ + {}^3/_2N_2 \quad (1)^8$$

$$Ru(bpy)_2(NH_2CH_2R)_2^{2+} \xrightarrow{-8e^-} Ru(bpy)_2(N{\equiv}CR)_2^{2+} + 8H^+ \quad (2)^9$$

to occur by initial oxidation of Ru(II) to Ru(III). For the case where bound amines are oxidized (eq 2), the initial Ru(II) → Ru(III) step is followed by a series of net two-electron oxidative dehydrogenation steps at the bound amine ligands.

In this paper a third example is described where a bound ligand is oxidized following oxidation of Ru(II) to Ru(III). The chemistry involves oxidation of a bound nitro to a nitrato

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group. The appearance of the reaction, which was described in a preliminary communication,[10] helps explain the apparent nonexistence of stable, monomeric nitro complexes of Ru(III)[11] and more importantly suggests that Ru(III)–nitro complexes, which do exist, but as transient intermediates, may have useful properties as oxygen atom transfer catalysts.[12]

Experimental Section

Ultraviolet–visible spectra were obtained by using a Bausch and Lomb Model UV-210 spectrometer. All electrochemical measurements were at platinum electrodes, and all potentials are reported vs. the saturated sodium chloride calomel electrode (SSCE) at 22 ± 2 °C and were uncorrected for junction potentials. Potential control for electrochemical experiments was obtained by using a Princeton Applied Research Model 173 potentiostat/galvanostat. The wave-form generator for voltammetric experiments was a Princeton Applied Research Model 175 universal programmer. Slow-scan (50–500 mV/s) cyclic voltammograms were recorded on a Hewlett-Packard Model 7004B X-Y recorder. Fast-scan cyclic voltammograms were obtained from photographs of the trace from a Tektronix Model 564B storage oscilloscope. For fast-scan cyclic voltammograms, IR compensation was used. Values of n, where n is the number of equivalents of electrons transferred per complex in exhaustive electrolyses at constant potentials, were calculated from the total area under current vs. time curves. Reactions were judged to be complete when the current had fallen below 1% of the initial value.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) and tetraethylammonium perchlorate (TEAP) were prepared by standard techniques and used as the supporting electrolyte in electrochemical experiments. The acetonitrile (MCB spectrograde) used in electrochemical measurements was dried over Davidson 4-Å molecular sieves. All other chemicals were commercially available and were of reagent quality and used without further purification.

Synthesis of Complexes. $[Ru(bpy)_2(NO_2)_2]\cdot H_2O$,[13] $[Ru(bpy)_2(NO)Cl](PF_6)_2$,[13] and $Ru(bpy)_2(NO_2)Cl\cdot H_2O$[14] were prepared as described previously.

$[Ru(bpy)_2(NO)(NO_2)](PF_6)_2$. $Ru(bpy)_2(NO_2)_2$ (1 g) was suspended in acetonitrile (20 mL) in subdued light. One milliliter of 70% HPF_6 was added dropwise with stirring, and the mixture was stirred for 2 min and then filtered into an excess of diethyl ether. The solid which precipitated was collected by filtration, washed with ether, and air-dried; yield 96%. The complex could be recrystallized from acetonitrile–ether solvent mixtures.

$[Ru(bpy)_2(py)(NO_2)]PF_6$. $[Ru(bpy)_2(NO)(NO_2)](PF_6)_2$ (2.425 g) was dissolved in deaerated acetone (30 mL), and a stoichiometric amount of KN_3 (0.252 g), dissolved in methanol (8 mL), was added dropwise with stirring in subdued light. The mixture was stirred for 10 min. Pyridine (5 mL) was added, and the solution was stirred for 2 h. The mixture was filtered into excess diethyl ether, giving a red-brown precipitate which was filtered, washed with ether, and dried in vacuo. Purification of the solid was achieved by chromatography on a column of alumina, using acetonitrile as an eluant under subdued light conditions. The eluant was evaporated to dryness giving a bright red product. It was recrystallized by slow addition of petroleum ether (bp 40–60 °C) to a methylene chloride solution of the complex. The electronic spectrum of the complex in water included an intense band at λ_{max} 414 nm (ϵ 7400) and in acetonitrile $\lambda_{max} = 449$ nm (ϵ 7800) and $\lambda_{max} = 336$ nm (ϵ 10 000). Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(C_5H_5N)(NO_2)]PF_6$: C, 43.93; H, 3.10; N, 12.30. Found: C, 44.10; H, 3.00; N, 12.15.

$[Ru(bpy)_2(py)(NO)](PF_6)_3$. $[Ru(bpy)_2(py)(NO_2)]PF_6$ (0.50 g) was suspended in acetonitrile (10 mL) in the dark, and 70% HPF_6 (1 mL) was added with stirring. The mixture was stirred for 2 min and then filtered into excess diethyl ether. The precipitated solid was collected by filtration, washed with ether, and dried in vacuo; yield 95%. The solid was recrystallized from acetone–ether. The procedure given here is a slight modification of a procedure given earlier.[4]

$[Ru(bpy)_2(CH_3CN)(NO_2)]PF_6$. This salt was synthesized by using a procedure analogous to that given for $[Ru(bpy)_2(py)(NO_2)]PF_6$ except that CH_3CN was substituted for py. The salt was purified by converting it to the nitrosyl form (by treatment with HPF_6 as mentioned above) followed by reconversion to the nitro complex. For the nitrosyl → nitro conversion, $[Ru(bpy)_2(CH_3CN)(NO)](PF_6)_3$ (0.5 g) was suspended in H_2O (20 mL) and 3 drops of a 50% NaOH solution was added. The mixture was stirred for 5 min. The solid was collected by filtration, washed with ice-cold water, and dried in vacuo.

$[Ru(bpy)_2(NH_3)(NO_2)]PF_6$. $[Ru(bpy)_2(NO)(NO_2)](PF_6)_2$ (0.110 g) was dissolved in deaerated CH_2Cl_2 (150 mL). Tetraphenylarsonium azide (0.060 g; stoichiometric) was added, and the solution was stirred in subdued light for 2 h. Ammonia was then bubbled through the solution for 2 h, after which the solution was filtered into a large excess of diethyl ether. The resulting solid was collected by filtration, washed with ether, and dried in vacuo; yield 40%.

$[Ru(bpy)_2(PPh_3)(NO_2)](PF_6)$ (Ph = Phenyl). This complex was prepared by the method given for $[Ru(bpy)_2(py)(NO_2)](PF_6)$ except that PPh_3 was substituted for py. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2P(C_6H_5)_3(NO_2)](PF_6)$: C, 52.66; H, 3.61; N, 8.05. Found: C, 51.58; H, 3.41; N, 8.05.

$[Ru(bpy)_2(pyr)(NO_2)](PF_6)$ (pyr = Pyrazine). $[Ru(bpy)_2(NO)(NO_2)](PF_6)_2$ (0.40 g) was dissolved in 20 mL of deaerated acetone, and sodium azide (0.033 g) was added as a methanol solution. The resulting solution was then added to a solution of 1.02 g of pyr in acetone. This solution was stirred and gently heated for 30 min and then added to diethyl ether, and the solid product was collected by filtration. The product was purified by chromatography on a basic alumina column using acetone as eluant. The eluted product was evaporated to dryness, redissolved in a minimum amount of acetone, and precipitated with diethyl ether. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(C_4H_4N_2)(NO_2)]PF_6\cdot 2H_2O$: C, 40.46; H, 2.26; N, 13.76. Found: C, 41.75; H, 2.73; N, 13.87.

$[Ru(bpy)_2(NO_3)Cl]Cl$. $Ru(bpy)_2(NO_2)Cl$ (0.05 g) was dissolved in CH_3CN (100 mL), and triethylamine (3 drops) and water (3 drops) were added. Chlorine was bubbled through the solution which caused a color change from red to yellow. The solution was added dropwise to 250 mL of ether and cooled to 5 °C. The solid which precipitated was collected by filtration and air-dried; yield 40%. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(NO_3)Cl]Cl$: C, 43.97; H, 2.95; N, 12.82. Found: C, 43.24; H, 3.26; N, 12.64.

$[Ru(bpy)_2(py)(NO_3)]PF_6$. A solution of 1.42 g of $(NH_4)_2Ce(NO_3)_6$ in water (3 mL) was added to a solution of 0.589 g of $[Ru(bpy)_2(py)(NO_2)]PF_6$ in acetonitrile to give a greenish solution and a tan precipitate. After filtration, the green solution was added to diethyl ether and the resulting precipitate was collected by filtration. The solid was dissolved in water, and saturated aqueous NH_4PF_6 was added. The resulting precipitate was collected by filtration and extracted with CH_3CN. The extract was chromatographed on an alumina column with $[Ru(bpy)_2(py)(NO_3)]PF_6$ being eluted with CH_2Cl_2/CH_3CN. The eluant was rotary evaporated to small volume and precipitated by addition of diethyl ether, and the solid was collected by filtration; yield 20%. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(C_5H_5N)(NO_3)](PF_6)$: C, 42.93; H, 3.03; N, 12.07. Found: C, 42.71; H, 2.99; N, 11.52. In addition to the expected bands for bpy and py vibrations, the infrared spectrum of $[Ru(bpy)_2(py)(NO_3)]PF_6$ exhibits bands suggesting the existence of O-bound, unidentate nitrate (~1460, 1288, 1000 cm^{-1}).[15] The visible spectrum exhibits a λ_{max} at 478 nm (ϵ 8000) in acetonitrile solution. A more convenient, photochemical preparation of $[Ru(bpy)_2(py)(NO_3)]PF_6$ is described elsewhere.[16]

$[Fe(bpy)_3](PF_6)_3$. $[Fe(bpy)_3](PF_6)_2$, prepared by standard techniques,[17] was oxidized with excess $(NH_4)_2Ce(NO_3)_6$ in acetonitrile. The precipitate which formed was collected by filtration and dissolved in water, and $[Fe(bpy)_3](PF_6)_3$ was precipitated by addition of HPF_6. The precipitate was collected, dissolved in acetonitrile, and reprecipitated by addition of ether. The purity of $[Fe(bpy)_3](PF_6)_3$ was checked by cyclic voltammetry. On standing in solution or as a solid, $Fe(bpy)_3^{3+}$ is readily reduced apparently by moisture in the air or

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Table I. Rate Constants for the Reaction $3Ru(bpy)_2(Cl)NO_2^+ \rightarrow Ru(bpy)_2(Cl)NO_2 + Ru(bpy)_2(Cl)NO_3^+ + Ru(bpy)_2(Cl)NO^{2+}$ at 22 ± 2 °C in Acetonitrile

run no.	initial concn of $Ru(bpy)_2(Cl)NO_2^+$, mM	10^3k, s^{-1}	method,[a] oxidant[b]
1	0.05	4.3	vis, $Fe(bpy)_3^{3+}$
2	0.12	4.2	vis, $Fe(bpy)_3^{3+}$
		av 4.2	
3	0.7	2.2	CV, $Fe(bpy)_3^{3+}$
4	1.8	2.3	CV, $Fe(bpy)_3^{3+}$
5	1.9	1.8	CV, $Ru(bpy)_3^{3+}$
6	3.9	0.9	CV, $Fe(bpy)_3^{3+}$
		av 1.8	

[a] vis: Rate constant values were determined from absorbance (507 nm) vs. time data after mixing $Ru(bpy)_2(Cl)NO_2$ with the oxidant. No additional electrolyte was added. CV: Rate constant values were determined by cyclic voltammetry by measuring oxidative peak currents for the $Ru(bpy)_2(Cl)NO^{2+}/Ru(bpy)_2(Cl)NO^+$ couple as a function of time following the chemical oxidation step. The region −0.2 to 1.0 volts vs. SSCE was scanned at appropriate time intervals at 200 mV/s in the cyclic voltammetry experiment. Solutions were 0.1 M in $[NEt_4](ClO_4)$. [b] $[Fe(bpy)_3](PF_6)_3$ was added as a solid directly to the solution to be oxidized. When $Ru(bpy)_3^{3+}$ was used as oxidant, it was generated electrochemically in solution immediately prior to use.

by solvent contaminants. The absence of $Fe(bpy)_3^{2+}$ in samples of $Fe(bpy)_3^{3+}$ is indicated by the absence of the intense red color of $Fe(bpy)_3^{2+}$.

Determination of the Rate Constant for Disproportionation of $Ru^{III}(bpy)_2(Cl)NO_2^+$. By Cyclic Voltammetry. For cases where $Fe(bpy)_3^{3+}$ was used as oxidant, a weighed quantity of $Ru(bpy)_2(Cl)NO_2$ was added to about 6 mL of acetonitrile (0.1 M TEAP) and the solution was stirred to dissolve at least part of the $Ru(bpy)_2(Cl)NO_2$. A slight molar deficiency of solid $[Fe(bpy)_3](PF_6)_3$ was added at which time all of the suspended material dissolved. The reaction which followed was assumed to be that shown in eq 3 based

$$3Ru(bpy)_2(Cl)NO_2^+ \rightarrow Ru(bpy)_2(Cl)NO_2 + Ru(bpy)_2(Cl)NO_3^+ + Ru(bpy)_2(Cl)NO^{2+} \quad (3)$$

on prior electrochemical results (see below). Cyclic voltammograms (scan rate 200 mV/s; limits −0.2 to +0.9 V vs. SSCE) were recorded as soon as possible after mixing and were recorded then at frequent intervals throughout a period of 30 min. When $Ru(bpy)_3^{3+}$ was used as oxidant, a weighed quantity of $[Ru(bpy)_3](PF_6)_2$ was exhaustively oxidized in acetonitrile (0.1 M TEAP) at 1.40 V vs. SSCE and a weighed quantity of solid $Ru(bpy)_2(Cl)NO_2$ was then added to the solution. The reaction was followed in the same fashion as when $Fe(bpy)_3^{3+}$ was used as oxidant. For each case, the rate of appearance of $Ru(bpy)_2(Cl)NO^{2+}$ was determined by the increase in the anodic peak current, i_p, for the $Ru(bpy)_2(Cl)NO^{2+}/Ru(bpy)_2(Cl)NO^+$ couple ($E_{p,a}$ = 0.21 V). The treatment of the kinetic data is outlined below.

By Spectrophotometry. Acetonitrile solutions of $Ru(bpy)_2(Cl)NO_2$ and $[Fe(bpy)_3](PF_6)_3$ were mixed in appropriate proportions to give a slight molar excess of $Ru(bpy)_2(Cl)NO_2$. The solution was added to a cuvette and placed in the spectrophotometer. The absorbance change at λ_{max} 507 nm for $Ru(bpy)_2(Cl)NO_2$) was monitored and absorbance vs. time data recorded. An initial rapid ($t_{1/2} \approx$ 2–4 min) increase was observed, followed by a slow decrease. The initial increase in absorbance, A, was attributed to the appearance of $Ru(bpy)_2(Cl)NO_2$ via eq 3, and the data was treated accordingly as outlined below. The origin of the slow secondary absorbance change is not clear. It should be noted that corresponding changes were not observed when the system was monitored by cyclic voltammetry but admittedly under conditions where the concentration of initial complex was higher.

Data Treatment. Kinetic data for the formation of $Ru(bpy)_2(Cl)NO^{2+}$, measured by changes in peak current (i_p) in the electrochemical experiments, or for the appearance of $Ru(bpy)_2(Cl)NO_2$, measured by changes in absorbance (A) in the spectral experiments, were analyzed by the Swinbourne method.[18] The parameter, i_p or A, at time t was plotted vs. the same parameter at time $t + \tau$, where τ is a constant time interval which was chosen as 2 min in this case. Smooth curves were drawn for the i_p or A vs. time data and then the data obtained from these plots by extrapolation were used in the Swinbourne analysis. Straight-line Swinbourne plots were obtained with slopes greater than 1 and the intersection of the straight lines with the line of slope equal to 1 were in good agreement with the infinity values either observed or obtained by extrapolation. The infinity values were used to treat the i_p or A data by standard first-order techniques, and the rate constants in Table I were obtained. The insensitivity of the observed rate constants to the concentration of $Ru(bpy)_2(Cl)NO_2^+$ confirms the first-order nature of the reaction.

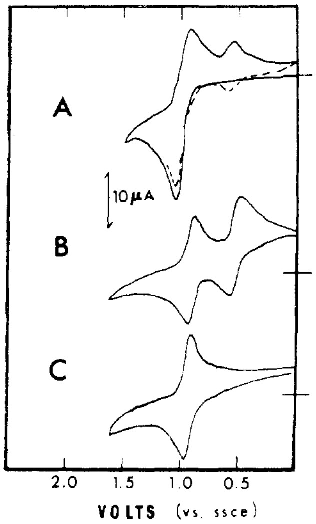

Figure 1. Cyclic voltammograms (200 mV/s) in acetonitrile (0.1 M $[NEt_4](ClO_4)$) at 22 ± 2 °C: (A) $Ru(bpy)_2(py)NO_2^+$; (B) solution A after exhaustive electrolysis at +1.2 V (n = 1.5); (C) solution A with added H_2O (1%) and 2,6-lutidine (1%) after exhaustive electrolysis at +1.2 V (n = 3.0).

Measurement of K for the Equilibrium $Ru(bpy)_2(py)NO^{3+} + 2OH^- \rightleftharpoons Ru(bpy)_2(py)NO_2^+ + H_2O$. The equilibrium constant for the nitrosyl–nitro equilibrium was determined spectrophotometrically at 25.0 ± 0.1 °C in water at I = 1.0 M (NaCl). Constant pH was maintained in the experiment by using potassium hydrogen phthalate (0.010 M) as buffer. The equilibrium constant was determined by adding an aliquot of an aqueous solution of $[Ru(bpy)_2(py)NO](PF_6)_3$ to each of ten 50-mL flasks (to give a complex concentration of $\sim 1.2 \times 10^{-4}$ M). In addition, NaCl (2.92 g), an aliquot of potassium hydrogen phthalate (to make the buffer concentration 0.010 M), and sufficient 0.1 M $HClO_4$ or 0.10 M NaOH to vary the pH of the solutions over the range pH 2–6 were added. The solutions were allowed to sit at 25.0 ± 0.1 °C in a water bath for 12 h. Each solution was then measured spectrophotometrically in the visible region with the absorbance at λ 414 nm [λ_{max} for $Ru(bpy)_2(py)(NO_2)^+$] being especially noted, and the pH of each solution was recorded. At the two extremes of pH used, only $Ru(bpy)_2(py)NO)^{3+}$ or $Ru(bpy)_2(py)(NO_2)^+$ were present in any appreciable amount. For the intermediate pH cases, the amounts of the two species were calculated from the absorbance at λ 414 nm. Since the nitrosyl complex is essentially transparent at this wavelength, the absorbance measurement with the known molar extinction coefficient for the nitro complex gave its concentration, and the concentration of nitrosyl complex was determined by mass balance. From the results of three separate experiments under conditions where both the nitrosyl and nitro complexes were present in appreciable amounts, an average value of K(25.0 °C, I = 1.0 M) = $(1.0 \pm 0.3) \times 10^{20}$ M^{-2} was found.

Results and Discussion

Oxidation of Bound Nitrite to Nitrate. A cyclic voltammogram of a solution containing the complex $Ru(bpy)_2(py)NO_2^+$ in acetonitrile (0.1 M TEAP) is shown in Figure 1A. The initial oxidative sweep shows a wave at a potential which is reasonable for a Ru(II) → Ru(III) oxidation ($E_{p,a}$ = 1.06 V), but the oxidation is chemically irreversible, at least in part. On the back, reductive sweep, a new wave appears, and a second sweep through the same potential region indicates that

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Scheme I

$$2Ru^{II}(bpy)_2(py)NO_2^+ \xrightarrow{-2e^-} 2Ru^{III}(bpy)_2(py)NO_2^{2+}$$

$$2Ru^{III}(bpy)_2(py)NO_2^{2+} \rightarrow Ru^{II}(bpy)_2(py)NO^{3+} + Ru^{II}(bpy)_2(py)NO_3^+$$

$$Ru^{II}(bpy)_2(py)NO_3^+ \overset{-e^-}{\text{——}} Ru^{III}(bpy)_2(py)NO_3^{2+}$$

Table II. Electrochemical Data in 0.1 M $[N(n\text{-}Bu)_4(PF_6)]$–Acetonitrile Solution at 22 ± 2 °C[a]

	couple or process		
	oxidn of $Ru(bpy)_2(L)NO_2^+$	$Ru(bpy)_2(L)(NO)^{3+/2+}$	$Ru(bpy)_2(L)(NO_3)^{2+/+}$
L	$E_{p,a}$ V	$E_{1/2}$, V	$E_{1/2}$, V
PPh_3	1.25	0.56	1.07[b]
CH_3CN	1.17	0.56	1.02[b]
pyr (pyrazine)	1.14	0.57	1.00[b]
py (pyridine)	1.06	0.53	0.91
NH_3	0.85	0.30	0.70[b]
Cl	0.57[c]	0.19[d]	0.45[e]

[a] Values are reported vs. the SSCE determined by cyclic voltammetry at a scan rate of 200 mV/s. [b] The nitrato complex was not isolated. The $E_{1/2}$ values were obtained by following electrolytic oxidation of solutions of $Ru(bpy)_2(L)(NO_2)^+$. [c] The $Ru(bpy)_2(Cl)(NO_2)^{+/0}$ couple is reversible at this scan rate, and the value quoted is the $E_{1/2}$ value. If the interpretation given below is correct for the results of scan rate dependent cyclic voltammetry experiments, it follows that $E_{1/2} = 1.00$ V for the $Ru(bpy)_2(py)NO_2^{2+/+}$ couple in acetonitrile ($I = 0.1$ M). [d] The couple is $Ru(bpy)_2(Cl)(NO)^{2+/+}$. [e] The couple is $Ru(bpy)_2(Cl)(NO_3)^{+/0}$.

the new wave is associated with a reversible couple. The cyclic voltammogram suggests that initial oxidation of Ru(II) to Ru(III) may occur (eq 4) but that the Ru(III) intermediate is unstable and undergoes further chemistry following the oxidative step.

$$Ru^{II}(bpy)_2(py)(NO_2)^+ \xrightarrow{-e^-} Ru^{III}(bpy)_2(py)(NO_2)^{2+} \quad (4)$$

Figure 1B shows a cyclic voltammogram of an identical solution following exhaustive electrolysis at 1.20 V. The electrochemical stoichiometry was $n = 1.5$ by coulometry. The voltammogram shows that two new products are formed in essentially equal amounts and that both have chemically reversible redox couples in the potential region studied.

Comparisons with voltammograms for known complexes show that the wave with $E_{1/2} = 0.53$ V corresponds to the reversible nitrosyl couple $Ru(bpy)_2(py)NO^{3+}/Ru(bpy)_2(py)(NO)^{2+}$,[4] and the wave with $E_{1/2} = 0.91$ V corresponds to the $Ru^{III}(bpy)_2(py)(NO_3)^{2+}/Ru^{II}(bpy)_2(py)NO_3)^+$ couple. From the results of the voltammetry and coulometry experiments, the net electrochemical reaction which occurs is shown in eq 5. The nitrosyl and nitrato complexes are both found in the oxidized forms of their respective couples.

$$2Ru(bpy)_2(py)(NO_2)^+ \xrightarrow{-3e^-} Ru(bpy)_2(py)(NO)^{3+} + Ru(bpy)_2(py)(NO_3)^{2+} \quad (5)$$

The nature of the reaction strongly suggests that oxygen transfer occurs between nitro groups on two different ruthenium complexes following oxidation of Ru(II) to Ru(III). As discussed in the next section, the n value of 1.5 and the nature of the reaction products observed are consistent with the series of reactions shown in Scheme I.

As summarized in Table II, similar results were obtained upon oxidation of the Ru(II)–nitro complexes $Ru(bpy)_2(CH_3CN)(NO_2)^+$, $Ru(bpy)_2(NH_3)(NO_2)^+$, $Ru(bpy)_2(PPh_3)(NO_2)^+$, $Ru(bpy)_2(pyr)(NO_2)^+$ (pyr is pyrazine), and $Ru(bpy)(Cl)(NO_2)$ in acetonitrile solution. In all cases, coulometry experiments, where the potential was set at a value on the diffusion plateau of the oxidation wave, gave $n = 1.5$, and two new products appeared as shown by cyclic voltammetry. In each case, one of the products was shown to be the corresponding nitrosyl complex by voltammetric comparisons with known samples under the same conditions. For the chloro and the pyridyl complexes, the second product was shown to be $Ru^{III}(bpy)_2(Cl)(NO_3)^+$ and $Ru^{III}(bpy)_2(py)(NO_3)^{2+}$, respectively, by spectral and electrochemical comparisons with a known sample prepared as described in the Experimental Section. In each of the other cases, the assumption that the second products are the corresponding Ru^{III}–nitrato complexes seems reasonable given the similarities in the electrochemical details of the reactions.

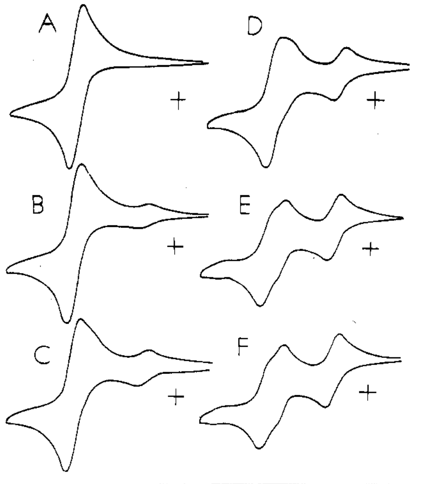


Figure 2. Reaction of $Ru(bpy)_2(Cl)NO_2^+$ according to eq 3 as followed by cyclic voltammetry in acetonitrile (0.1 M $[NEt_4](ClO_4)$ solution, 200 mV/s). Time after oxidation to Ru(III): (A) 1 min; (B) 2 min; (C) 3 min; (D) 5.5 min; (E) 12 min; (F) 16 min.

There is a distinguishing feature in the case of the chloro complex. At scan rates of 200 mV/s or faster, the $Ru(bpy)_2(Cl)(NO_2)^{+/0}$ couple is chemically and electrochemically reversible, which shows that the reaction or reactions following the Ru(II) → Ru(III) oxidation step are relatively slow.

The Rate and Mechanism of Oxidation of the Bound NO_2^- Ligand. As mentioned in the previous section, the $Ru(bpy)_2(Cl)(NO_2)^{+/0}$ couple is chemically reversible on the cyclic voltammetry time scale ($v = 200$ mV/s). The Ru(III) form of the couple is sufficiently long-lived in solution that it can be generated by chemical means and the subsequent chemistry, which leads to the nitrosyl and nitrato complexes, eq 3, can be followed by cyclic voltammetry or spectrophotometry.

The experiments were carried out as follows. Solutions of $Ru(bpy)_2(Cl)(NO_2)$ in acetonitrile were oxidized with 1 equiv of $Fe(bpy)_3^{3+}$ or $Ru(bpy)_3^{3+}$ and the subsequent changes in spectral or electrochemical properties were observed with time. In cyclic voltammetry experiments (0.1 M TEAP), the decrease in the height of the wave due to the $Ru(bpy)_2(Cl)(NO_2)^{+/0}$ couple was accompanied by an increase in the height of the waves due to the $Ru(bpy)_2(Cl)(NO)^{2+/+}$ and $Ru(bpy)_2(Cl)(NO_3)^{+/0}$ couples (Figure 2). The initial electron-transfer step is clearly very rapid and no evidence for intermediates was observed. When 1 equiv of the oxidant was used, the final products are $Ru^{II}(bpy)_2(Cl)(NO_2)$, $Ru^{III}(bpy)_2(Cl)(NO_3)^+$, and $Ru^{II}(bpy)_2(Cl)(NO)^{2+}$ in a ratio of approximately 1:1:1. The observed ratio is consistent with the stoichiometry derived from the mechanisms shown in Scheme II and eq 3.

Scheme II

$$3\mathrm{Ru^{II}(bpy)_2(Cl)(NO_2)} + 3\mathrm{M(bpy)_3}^{3+} \rightarrow 3\mathrm{Ru^{III}(bpy)_2(Cl)(NO_2)^+} + 3\mathrm{M(bpy)_3}^{2+} \quad (\mathrm{M = Fe\ or\ Ru})$$

$$2\mathrm{Ru^{III}(bpy)_2(Cl)(NO_2)^+} \rightarrow \mathrm{Ru^{II}(bpy)_2(Cl)(NO_3)} + \mathrm{Ru^{II}(bpy)_2(Cl)(NO)^{2+}}$$

$$\mathrm{Ru^{III}(bpy)_2(Cl)(NO_2)^+} + \mathrm{Ru^{II}(bpy)_2(Cl)(NO_3)} \rightarrow \mathrm{Ru^{II}(bpy)_2(Cl)(NO_2)} + \mathrm{Ru^{III}(bpy)_2(Cl)(NO_3)^+}$$

Assuming that the peak current for the Ru(bpy)$_2$(Cl)(NO)$^{2+/+}$ couple is proportional to the concentration of Ru(bpy)$_2$(Cl)(NO)$^{2+}$, the disappearance of Ru^{III}(bpy)$_2$(Cl)(NO$_2$)$^+$, following its formation by the rapid oxidation of Ru^{II}(bpy)$_2$(Cl)(NO$_2$) using M(bpy)$_3^{3+}$ as oxidant, follows first-order kinetics. From the stoichiometry and kinetic measurements (Table I), the rate law for the reaction is

$$\frac{d[\mathrm{Ru^{II}(bpy)_2(Cl)(NO)^{2+}}]}{dt} = -\frac{1}{3}\frac{d[\mathrm{Ru^{III}(bpy)_2(Cl)(NO_2)^+}]}{dt} = k[\mathrm{Ru^{III}(bpy)_2(Cl)(NO_2)^+}] \quad (6)$$

Rate constants for this reaction were evaluated by using the Swinbourne method as described in the Experimental Section. The results of four separate experiments gave an average value of $k = 1.8 \times 10^{-3}$ s^{-1} at $I = 0.1$ M and at 22 ± 2 °C.

The reaction was also followed by monitoring changes in absorbance at 507 nm which is an absorbance maximum for Ru^{II}(bpy)$_2$(Cl)(NO$_2$). A kinetic treatment of the spectral data gave 4.2×10^{-3} s^{-1} as an average value of two experiments. The value obtained spectrally is consistent with that observed in the cyclic voltammetry experiment, considering the accuracy of the data and the difference in conditions for the two types of experiments. The electrochemical experiment was carried out at $I = 0.1$ M with added TEAP while in the spectral experiment, there was no added electrolyte.

Attempts to measure the rate constant for the related reaction involving Ru^{III}(bpy)$_2$(py)(NO$_2$)$^{2+}$ were unsuccessful. Stopped-flow kinetic studies were carried out in acetonitrile by using Ce(IV) to oxidize Ru^{II}(bpy)$_2$(py)(NO$_2$)$^+$ to Ru^{III}(bpy)$_2$(py)(NO$_2$)$^{2+}$. The only reaction which could definitely be identified was the initial oxidation reaction (eq 7) which was first order both in Ce^{IV} and in Ru(bpy)$_2$(py)(NO$_2$)$^+$ and occurred with a rate constant of 1.7×10^6 M^{-1} s^{-1} at 25.0 ± 0.1 °C ($I = 0.1$ M).

$$\mathrm{Ru^{II}(bpy)_2(py)NO_2^+} + \mathrm{Ce(IV)} \rightarrow \mathrm{Ru^{III}(bpy)_2(py)NO_2^{2+}} + \mathrm{Ce(III)} \quad (7)$$

However, following electrochemical oxidation of Ru^{II}(bpy)$_2$(py)NO$_2^+$ to Ru^{III}(bpy)$_2$(py)NO$_2^{2+}$, detailed insight into the overall mechanism can be gained by cyclic voltammetry although the interpretation of the data is intricate. In Figure 3 is shown a series of *single-sweep* cyclic voltammograms at varying sweep rates which can be interpreted on the basis of Scheme III. The critical part of the scheme is the rapid isomerization of the nitro group from N-bound, Ru^{III}–NO$_2$, to O-bound, Ru^{III}–ONO, following oxidation to Ru(III).

At the fastest scan rate, Figure 3A (50 V/s), oxidation of (bpy)$_2$(py)Ru^{II}NO$_2^+$ to Ru(III) at $E_{p,a} = 1.06$ V results in the appearance of a reduction wave for a new couple at $E_{p,c} = 0.72$ V. A following scan, returning in the oxidative direction, shows the oxidative component of the reductive wave at 0.72 V, and the reversibility of the new couple ($E_{1/2} \approx 0.80$ V) is seen clearly by low-temperature cyclic voltammetry in 0.1 M [N(*n*-C$_4$H$_9$)$_4$]ClO$_4$-*n*-BuCN. The behavior described here is especially well-defined upon attachment of the [(bpy)$_2$(NO$_2$)Ru^{II}py~] group to a platinum electrode surface, results which will be reported in a later publication. A sample of the nitrito isomer, (bpy)$_2$(py)RuONO$^+$, is not available for comparison, but the potential of the wave at $E_{p,c} = 0.72$ V is consistent with potentials for other Ru(III)/Ru(II) couples which contain related ligands.[16]

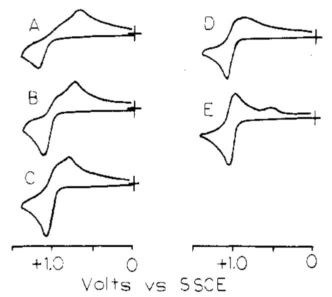
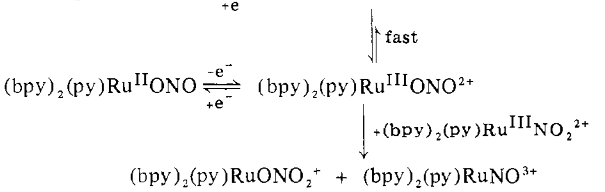


Figure 3. Scan-rate dependence of single-sweep cyclic voltammograms of solutions containing Ru(bpy)$_2$(py)NO$_2^+$ in acetonitrile (0.1 M [NEt$_4$](ClO$_4$)): (A) 50 V/s; (B) 20 V/s; (C) 5 V/s; (D) 3 V/s; (E) 0.5 V/s.

Scheme III



$$\begin{tikzcd}
\mathrm{(bpy)_2(py)Ru^{II}NO_2^+} \arrow[r, shift left, "-e^-"] & \mathrm{(bpy)_2(py)Ru^{III}NO_2^{2+}} \arrow[l, shift left, "+e^-"] \arrow[d, shift right] \\
\mathrm{(bpy)_2(py)Ru^{II}ONO} \arrow[r, shift left, "-e^-"] & \mathrm{(bpy)_2(py)Ru^{III}ONO^{2+}} \arrow[l, shift left, "+e^-"] \arrow[u, shift right, "\text{fast}"'] \arrow[d, "+\mathrm{(bpy)_2(py)Ru^{III}NO_2^{2+}}"] \\
& \mathrm{(bpy)_2(py)RuONO_2^+} + \mathrm{(bpy)_2(py)RuNO^{3+}}
\end{tikzcd}$$

At slower scan rates, a wave at $E_{p,c} = 0.95$ V grows in at the expense of the Ru–ONO$^{2+/+}$ wave at $E_{p,c} = 0.72$ V. The wave at 0.95 V appears to be the reductive component of the oxidative wave at $E_{p,a} = 1.06$ V for the Ru–NO$_2^{2+/+}$ couple. What this means in terms of Scheme III is that initial oxidation of Ru^{II}–NO$_2^+$ to Ru^{III}–NO$_2^{2+}$ is followed by rapid isomerization to Ru^{III}–ONO^{2+}. The Ru^{III}–NO$_2^{2+}$ $\rightleftharpoons$ Ru^{III}–ONO^{2+} equilibrium lies in favor of the nitrito isomer, and at rapid scan rates it can be recaptured at the electrode by reduction to Ru^{II}–ONO$^+$. However, at slower scan rates, the conversion, Ru^{III}–ONO^{2+} → Ru^{III}–NO$_2^{2+}$, is competitive with the cyclic voltammetry time scale. Reduction of Ru(III) now occurs through Ru^{III}–NO$_2^{2+}$ because the potential for reduction is ~0.2 V more positive than the potential for reduction of Ru^{III}–ONO.

In the interpretation given in Scheme III, at even slower scan rates, a further complication appears which leads to the nitrosyl and nitrato products. At slow scan rates, before Ru^{III}–ONO^{2+} can be reduced to Ru(II) either directly at the electrode or through Ru^{III}–NO$_2^{2+}$, a bimolecular reaction occurs, probably with Ru(bpy)$_2$(py)NO$_2^{2+}$, to give the final products. The competition is shown in Figure 3E (0.5 V/s), where, in addition to the Ru^{III}–NO$_2^{2+/+}$ wave, the reductive wave for the Ru(bpy)$_2$(py)NO$^{3+/2+}$ couple is clearly observed and, presumably, a wave at $E_{p,c} = 0.91$ V for the Ru(bpy)$_2$(py)ONO$_2^{2+/+}$ couple is present as a barely detectable shoulder on the Ru–NO$_2^{2+/+}$ wave. It should be noted that Figure 3 shows *single-sweep* cyclic voltammograms so that the oxidative components for the nitrosyl and nitrato couples do not appear.

Cyclic voltammograms at varying scan rates for the complexes Ru(bpy)$_2$(PPh$_3$)NO$_2^+$ and Ru(bpy)$_2$(py)NO$_2^+$ suggest that although the same net reaction and mechanism exist for the related systems, the kinetic details do vary somewhat with changes in the ligand cis to the nitro group.[19]

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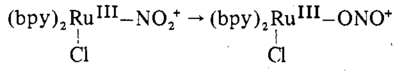
[19] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

The electrochemical experiments suggest strongly that, unlike the chloro complex, the rate-determining step for ligand oxidation in the pyridyl complex is a bimolecular reaction involving the reactive intermediate $(bpy)_2(py)Ru^{III}ONO^{2+}$. A similar mechanism may be involved for the chloro complex as well, but because the reaction is slower and the rate-determining step first order in $Ru(bpy)_2(Cl)NO_2^+$, presumably to give $Ru^{III}(bpy)_2(Cl)ONO^+$, any information about possible reactions which occur following the rate-determining step is lost.

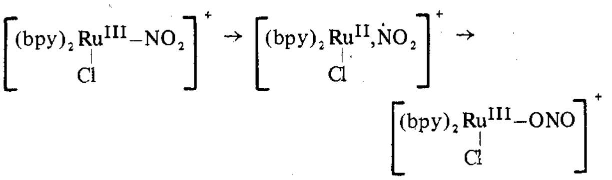
By combining the mechanistic information available for the chloro and the pyridyl complexes and assuming a common mechanism, it is possible to develop an overall scheme which explains the observed reactivity of the $Ru^{II}-NO_2$ complexes on oxidation.

For the chloro complex, initial oxidation of Ru(II) to Ru(III) is followed by a first-order reaction. The first-order nature of the process suggests that it involves an internal reorganization in the Ru(III) state, and, given the electrochemical result on the pyridyl complex, the most likely reorganization is an isomerization of the ligand from N- to O-bound, eq 8. Such a step must appear somewhere in the overall mechanism since in the net reaction the oxidative conversion of an N-bound nitro to O-bound nitrato ligand occurs.



$$(bpy)_2\underset{\mathrm{Cl}}{Ru^{III}}-NO_2^+ \rightarrow (bpy)_2\underset{\mathrm{Cl}}{Ru^{III}}-ONO^+ \tag{8}$$

An isomerization reaction like that in eq 8 would be expected to have substantial redox character given the usual inertia to substitution expected for complexes of Ru(III). In the limiting case the net reaction could involve an initial intramolecular electron-transfer step followed by recapture of loosely bound NO_2 before it can escape into solution

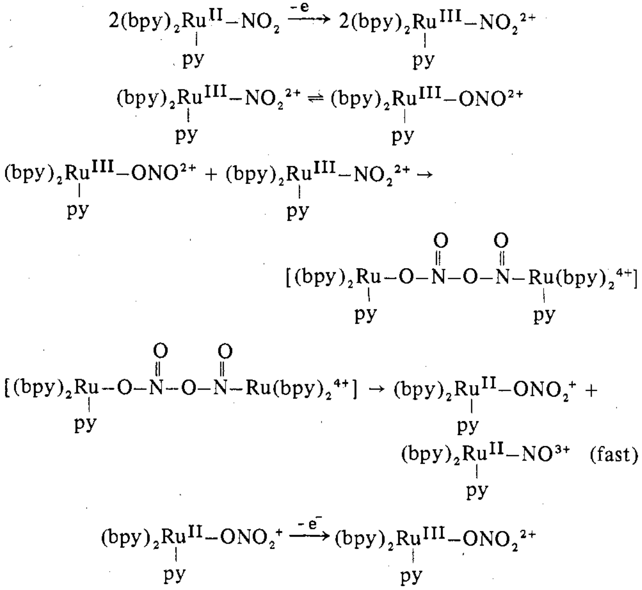


$$\left[(bpy)_2\underset{\mathrm{Cl}}{Ru^{III}}-NO_2\right]^+ \rightarrow \left[(bpy)_2\underset{\mathrm{Cl}}{Ru^{II}},\dot{N}O_2\right]^+ \rightarrow \left[(bpy)_2\underset{\mathrm{Cl}}{Ru^{III}}-ONO\right]^+ \tag{9}$$

Such a mechanism is entirely analogous to the proposed mechanism for the photochemical isomerization of $Co(NH_3)_5NO_2^{2+}$ following photolysis into ligand to metal charge-transfer absorption bands.[20]

The suggestion of an initial intramolecular redox step is consistent with several available facts. It fits the substantial rate enhancement for the pyridyl complex following oxidation of $Ru(bpy)_2(py)NO_2^+$. For the pyridyl complex $Ru(bpy)_2(py)ONO^{2+}$ is the immediately observed product even at a scan rate of 50 V/s. The origin of the rate enhancement is apparently that the pyridyl complex is a considerably stronger one-electron oxidant. Closely related chemistry has been observed for a series of complexes where there is a bound, oxidizable ligand (I^-, Br^-, NCS^-, CN^-).[1a] Electrochemically generated Ru(III) complexes rapidly produce Ru(II) and the oxidized ligand (I_2 etc). In the case of the bound azide ligand, the rate of net intramolecular ligand oxidation also follows the oxidizing strength of the metal site.[8] Although the data are limited, the suggested increase in rate constant as ionic strength decreases (Table I) is also consistent with an intramolecular redox step because of the decrease in intramolecular charge separation ($Ru^{III}-NO_2^- \rightarrow Ru^{II}-\dot{N}O_2$) in the activation process.[8]

Scheme IV



$$2(bpy)_2\underset{\mathrm{py}}{Ru^{II}}-NO_2 \xrightarrow{-e^-} 2(bpy)_2\underset{\mathrm{py}}{Ru^{III}}-NO_2^{2+}$$

$$(bpy)_2\underset{\mathrm{py}}{Ru^{III}}-NO_2^{2+} \rightleftharpoons (bpy)_2\underset{\mathrm{py}}{Ru^{III}}-ONO^{2+}$$

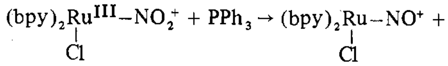
$$(bpy)_2\underset{\mathrm{py}}{Ru^{III}}-ONO^{2+} + (bpy)_2\underset{\mathrm{py}}{Ru^{III}}-NO_2^{2+} \rightarrow \left[(bpy)_2\underset{\mathrm{py}}{Ru}-O-\overset{\overset{\displaystyle O}{\|}}{N}-O-\overset{\overset{\displaystyle O}{\|}}{N}-\underset{\mathrm{py}}{Ru}(bpy)_2^{4+}\right]$$

$$\left[(bpy)_2\underset{\mathrm{py}}{Ru}-O-\overset{\overset{\displaystyle O}{\|}}{N}-O-\overset{\overset{\displaystyle O}{\|}}{N}-\underset{\mathrm{py}}{Ru}(bpy)_2^{4+}\right] \rightarrow (bpy)_2\underset{\mathrm{py}}{Ru^{II}}-ONO_2^+ + (bpy)_2\underset{\mathrm{py}}{Ru^{II}}-NO^{3+} \quad \text{(fast)}$$

$$(bpy)_2\underset{\mathrm{py}}{Ru^{II}}-ONO_2^+ \xrightarrow{-e^-} (bpy)_2\underset{\mathrm{py}}{Ru^{III}}-ONO_2^{2+}$$

With the pyridyl complex as the example, the initial oxidation and isomerization steps are combined with a necessary bimolecular step to complete the overall mechanism as shown in Scheme IV. When taken together, the set of reactions accounts for both the final product distribution and the appearance of an intermediate if the intermediate is $(bpy)_2(py)RuONO^{2+}$. There is a fundamental difference in reactivity between the chloro and pyridyl complexes. For the pyridyl complex, isomerization to the reactive O-bound isomer is rapid and the rate-determining step is its bimolecular reaction with a second $Ru^{II}-NO_2$ complex. For the chloro complex, isomerization is slow and becomes the rate-determining step.

The existence of a dimeric intermediate or activated complex in Scheme IV is almost demanded in the mechanism since the nature of the products suggests strongly that a net O-atom transfer occurs from one NO_2 group to the second. Although we have not carried out a labeling study on the ligand oxidation reaction, a labeling study has shown that O-atom transfer does occur in the reaction[12]



$$(bpy)_2\underset{\mathrm{Cl}}{Ru^{III}}-NO_2^+ + PPh_3 \rightarrow (bpy)_2\underset{\mathrm{Cl}}{Ru}-NO^+ + OPPh_3 \tag{10}$$

In terms of possible redox catalytic systems, the bimolecular redox step is of considerable interest since it is in this step that net oxygen-atom transfer occurs. The favorable reactivity of the Ru(III)–nitro system lies in its ability to donate an oxide ion in conjunction with the availability of two one-electron-acceptor sites, one at the metal ($Ru^{III} \rightarrow Ru^{II}$) and one at the nitrosyl ligand ($Ru-NO^+ \rightarrow Ru-\dot{N}O$). Chemical and electrochemical studies[4] have shown that the nitrosyl complexes are themselves mild, reversible oxidants where the electron-acceptor properties are largely localized on the nitrosyl ligand.[2]

$$(bpy)_2\underset{\mathrm{L}}{Ru}-NO^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} (bpy)_2\underset{\mathrm{L}}{Ru}-\dot{N}O^{2+} \tag{11}$$

For the oxidation of PPh_3 by $Ru^{III}(bpy)_2(Cl)NO_2^+$, the results of the labeling experiment mentioned above are consistent with an O-atom transfer reactivity for the Ru(III)–nitro complex analogous to the bimolecular step shown in Scheme IV.[12] The existence of such a pathway is mechanistically appealing because the electron-acceptor properties of the oxidant are delocalized over two different sites in the molecule, and both sites are known to undergo rapid electron transfer as shown by self-exchange studies.[4a,7] Furthermore, other than loss of the

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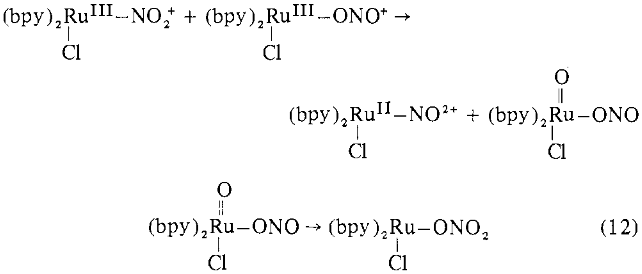
[20] (a) D. A. Johnson and K. A. Pashman, *Inorg. Nucl. Chem. Lett.*, **11**, 23 (1975); (b) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

oxygen atom, no major structural changes are required at the oxidant.

There are other mechanistic possibilities for some of the steps in Scheme IV, and although they cannot be ruled out, they seem less likely. One is that in the bimolecular step, O-atom transfer actually occurs to the metal to give a seven-coordinate $\mathrm{Ru^{IV}{=}O}$ complex (eq 12). Seven-coordination



$$(\mathrm{bpy})_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Ru}^{\mathrm{III}}}}-\mathrm{NO}_2^+ + (\mathrm{bpy})_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Ru}^{\mathrm{III}}}}-\mathrm{ONO}^+ \rightarrow (\mathrm{bpy})_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Ru}^{\mathrm{II}}}}-\mathrm{NO}^{2+} + (\mathrm{bpy})_2\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Ru}}}}}-\mathrm{ONO}$$

$$(\mathrm{bpy})_2\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Ru}}}}}-\mathrm{ONO} \rightarrow (\mathrm{bpy})_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Ru}}}-\mathrm{ONO}_2 \qquad (12)$$

is known for Ru(IV),[21] and the six-coordinate complex $(\mathrm{bpy})_2(\mathrm{py})\mathrm{Ru^{IV}{=}O^{2+}}$ has been isolated and characterized.[2]

Equilibrium Constant and Reduction Potential Values. An acid–base equilibrium exists between the nitrosyl and nitro forms of the bis(bipyridyl)ruthenium(II) complexes in aqueous solution, eq 13.[14,22] For the chloro complex, an equilibrium

$$\mathrm{Ru(bpy)_2(Cl)(NO)^{2+} + 2OH^- \rightleftarrows Ru(bpy)_2(Cl)(NO_2) + H_2O} \qquad (13)$$

constant for eq 13 of $K = (1.6 \pm 0.4) \times 10^9\ \mathrm{M}^{-2}$ has been determined[14] by spectrophotometric titration techniques at 25.0 ± 0.2 °C in 1.0 M aqueous NaCl solution. Since quantitative information concerning the acid–base equilibrium is necessary both for the calculation of redox potentials and for the development of catalytic cycles based on the redox chemistry of the bound nitro group, we have measured the equilibrium acid–base properties of the pyridyl complex in the same medium (eq 14).

$$\mathrm{Ru(bpy)_2(py)(NO)^{3+} + 2OH^- \rightleftarrows Ru(bpy)_2(py)(NO_2)^+ + H_2O} \qquad (14)$$

The spectrophotometric procedure was described in the Experimental Section. For eq 14, $K(25.0\ °\mathrm{C}, I = 1.0\ \mathrm{M}) = (1.0 \pm 0.3) \times 10^{20}\ \mathrm{M}^{-2}$. In terms of relative concentrations of the nitro and nitrosyl forms in eq 13 and 14, the equilibrium constants show that the two forms are present in equal amounts at pH 9.2 for the chloro system and at pH 3.8 for the pyridyl system. The sizable increase in the acidity of the nitrosyl group for the pyridyl, compared to the chloro complex, is paralleled by an increase in the $E_{1/2}$ value for the couple $\mathrm{RuNO^+/RuNO}$ (Table II)[4] and by an increase in the ν(NO) stretching frequency.[4] The evidence provided by such experiments suggests that the electron-deficient nature of the nitrosyl group can be systematically modulated by making variations in the cis ligand. Apparently, the differences between the chloro and pyridyl systems are due to increased electron donation to the metal from the chloro group when compared to the pyridyl group.

It is possible to determine formal reduction potential values for the chloro and pyridyl Ru(III)–nitro complexes acting as two-electron-acceptor, oxide ion donor oxidants, by using values of $\Delta G = -RT \ln K$ for the acid–base equilibria in eq 13 and 14 and formal potentials for the $\mathrm{RuNO^+/Ru\dot{N}O}$ and $\mathrm{Ru^{III}NO_2/Ru^{II}NO_2}$ couples in the same medium. The calculations for $\mathrm{Ru^{III}(bpy)_2(Cl)(NO_2)^+}$ are shown in Scheme V. A similar calculation can be made for $\mathrm{Ru^{III}(bpy)_2(py)(NO_2)^{2+}}$ by using $K = 1.0 \times 10^{20}\ \mathrm{M}^{-2}$, $E_{1/2}(\mathrm{Ru(bpy)_2(py)(NO)^{3+/2+}}) = 0.53$ V,[23] $E_{1/2} = 1.16$ V ($E_{\mathrm{p,a}} = 1.21$ V)[23] for the $\mathrm{Ru(bpy)_2(py)NO_2^{2+/+}}$ couple. The resulting formal potential is $E_{\mathrm{F}} \simeq 0.26$ V (25.0 °C, 1 M NaCl; ≥ 0.67 V at pH 7).

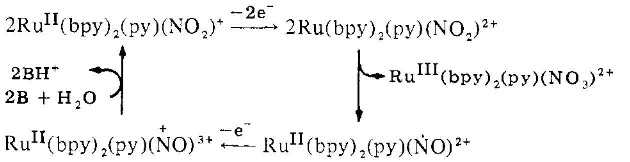
Scheme V[a]

Reaction	$-\Delta G°'$, V
$\mathrm{H_2O + Ru^{II}(bpy)_2(Cl)(NO_2) \rightarrow Ru^{II}(bpy)_2(Cl)(NO)^{2+} + 2OH^-}$	−0.54
$\mathrm{Ru^{III}(bpy)_2(Cl)(NO_2)^+ + e^- \rightarrow Ru^{II}(bpy)_2(Cl)(NO_2)}$	0.90[23]
$\mathrm{Ru(bpy)_2(Cl)(NO)^{2+} + e^- \rightarrow Ru(bpy)_2(Cl)(\dot{N}O)^+}$	0.27[23]
$\mathrm{H_2O + Ru^{III}(bpy)_2(Cl)(NO_2)^+ + 2e^- \rightarrow Ru^{II}(bpy)_2(Cl)(\dot{N}O)^+ + 2OH^-}$	

E_{F}(NHE, 25.0 °C) = 0.31 V (0.72 V at pH 7)

[a] In 1.0 M aqueous NaCl at 25 °C.

Scheme VI[a]



[a] B is collidine or 2,6-lutidine.

The similarity in the potential values for the two complexes is worth noting. It arises because even though the oxidized forms of the pyridyl $\mathrm{Ru^{III}NO_2/Ru^{II}NO_2}$ and $\mathrm{RuNO^+/Ru\dot{N}O}$ couples are considerably more strongly oxidizing than the chloro ones, there is a compensation effect which arises from the more acidic character of the nitrosyl group in the pyridyl case (note Scheme V).

Catalytic Oxidation of the Bound Nitro Group to Nitrate. Based on the acid–base and redox chemistry of the nitro complexes, it is possible to predict that oxidation of the nitro to nitrato complexes can be made catalytic. According to eq 5, in a single cycle, a three-electron oxidation occurs to give equal amounts of $\mathrm{Ru(bpy)_2(py)(NO_3)^{2+}}$ and $\mathrm{Ru(bpy)_2(py)(NO)^{3+}}$. However, if the pH of the solution is maintained at a sufficiently high level, the nitrosyl complex will be converted into the nitro complex according to eq 14.

Electrolysis at 1.2 V of an acetonitrile solution containing $\mathrm{Ru(bpy)_2(py)(NO_2)^+}$ with added water (1% by volume) and 2,6-lutidine (or collidine) (1%) results in the production of $\mathrm{Ru(bpy)_2(py)(NO_3)^{2+}}$ as the sole product (Figure 1C), and the n value is 3. These results are consistent with the series of reactions shown in Scheme VI.

The existence of the catalytic scheme, which is quantitative, is worth noting since it sets the conditions for and may presage a series of applications where the $\mathrm{Ru^{III}NO_2}$ complexes are used as net O atom transfer catalysts.

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Registry No. $\mathrm{[Ru(bpy)_2(py)(NO_2)]PF_6}$, 36309-80-5; $\mathrm{[Ru(bpy)_2(CH_3CN)(NO_2)]PF_6}$, 35986-82-4; $\mathrm{[Ru(bpy)_2(NH_3)(NO_2)]PF_6}$, 72402-33-6; $\mathrm{[Ru(bpy)_2(PPh_3)(NO_2)]PF_6}$, 72378-54-2; $\mathrm{[Ru(bpy)_2(pyr)(NO_2)]PF_6}$, 49734-31-8; $\mathrm{Ru(bpy)_2Cl(NO_2)^+}$, 63771-54-0; $\mathrm{[Ru(bpy)_2(py)(NO)](PF_6)_3}$, 29241-00-7; $\mathrm{[Ru(bpy)_2(CH_3CN)}$-

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(NO)](PF$_6$)$_3$, 61303-15-9; Ru(bpy)$_2$(PPh$_3$)(NO)$^{3+}$, 72378-55-3; Ru(bpy)$_2$(pyr)(NO)$^{3+}$, 72378-56-4; Ru(bpy)$_2$(NH$_3$)(NO)$^{3+}$, 54866-01-2; Ru(bpy)$_2$Cl(NO)$^{2+}$, 31847-83-3; Ru(bpy)$_2$(PPh$_3$)(NO)$^{2+}$, 72378-57-5; Ru(bpy)$_2$(CH$_3$CN)(NO)$^{2+}$, 54866-05-6; Ru(bpy)$_2$(pyr)(NO)$^{2+}$, 72378-58-6; Ru(bpy)$_2$(py)(NO)$^{2+}$, 72378-59-7; Ru(bpy)$_2$(NH$_3$)(NO)$^{2+}$, 72378-60-0; Ru(bpy)$_2$Cl(NO)$^+$, 54866-04-05; [Ru(bpy)$_2$(NO$_3$)Cl]Cl, 72402-34-7; Ru(bpy)$_2$(PPh$_3$)(NO$_3$)$^{2+}$, 72378-61-1; Ru(bpy)$_2$(CH$_3$CN)(NO$_3$)$^{2+}$, 72378-62-2; Ru(bpy)$_2$(pyr)(NO$_3$)$^{2+}$, 72390-14-8; Ru(bpy)$_2$(py)(NO$_3$)$^{2+}$, 72402-35-8; Ru(bpy)$_2$(NH$_3$)(NO$_3$)$^{2+}$, 72378-63-3; [Ru(bpy)$_2$(py)(NO$_3$)]PF$_6$, 72378-65-5; Ru(bpy)$_2$(PPh$_3$)(NO$_3$)$^+$, 72378-66-6; Ru(bpy)$_2$(CH$_3$CN)(NO$_3$)$^+$, 72378-67-7; Ru(bpy)$_2$(pyr)(NO$_3$)$^+$, 72390-12-6; Ru(bpy)$_2$(NH$_3$)(NO$_3$)$^+$, 72378-68-8; Ru(bpy)$_2$Cl(NO$_3$), 72390-13-7; [Ru(bpy)$_2$(NO)(NO$_2$)](PF$_6$)$_2$, 58575-13-6; Ru(bpy)$_2$(NO$_2$)$_2$, 29241-01-8; Ru(bpy)$_2$(NO$_2$)Cl, 34398-51-1; [Fe(bpy)$_3$](PF$_6$)$_2$, 70811-29-9; [Fe(bpy)$_3$](PF$_6$)$_3$, 28190-88-7; Ru(bpy)$_3$$^{3+}$, 18955-01-6.

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Effect of Lattice Anions on the Racemization of Optically Active Metal Chelate Salts in the Solid State. 1.[1] [Fe(phen)$_3$]X$_2$, [Fe(bpy)$_3$]X$_2$, [Ni(phen)$_3$]X$_2$, and [Ni(bpy)$_3$]X$_2$, Where X$^-$ = Cl$^-$, Br$^-$, I$^-$, or ClO$_4$$^-$

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The kinetics of racemization of the anhydrous complexes (+)-[Fe(phen)$_3$]X$_2$, (+)-[Fe(bpy)$_3$]X$_2$, (−)-[Ni(phen)$_3$]X$_2$, and (−)-[Ni(bpy)$_3$]X$_2$, where phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine, and X$^-$ = Cl$^-$, Br$^-$, I$^-$, or ClO$_4$$^-$, have been studied in the solid state. The halide salts of the complexes were found to undergo a very rapid initial loss of optical activity and subsequently to racemize at a lower rate. The former process has been assigned to a process enhanced by lattice defects and the latter to a first-order process with respect to the complex. Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined for the first-order racemization. A similarity between the racemization mechanisms of the phenanthroline and bipyridine complexes of nickel was noted in terms of an isokinetic relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. $\Delta H^{\ddagger}$ values for all the iron complexes were found to be identical, whereas those for the nickel complexes decrease with the lattice anion in the order X$^-$ = ClO$_4$$^-$ > I$^-$ > Br$^-$ > Cl$^-$. Temperatures at which thermal decomposition of the complexes takes place were determined by both thermogravimetric and differential thermal analysis methods. The results for the nickel complexes showed the temperatures to be linearly related to the $\Delta H^{\ddagger}$ values and the thermal decomposition and racemization processes to be related by the donicity of lattice anions. Different racemization mechanisms involving a 7-coordinate and a trigonal-prismatic intermediate are proposed for the nickel and iron complexes, respectively, and are consistent with the different effects of lattice anions in the kinetic data between them. A retarding effect of lattice water on the rate of racemization was observed.

Introduction

From the results of kinetics studies it was concluded that the major path for racemization of the [Fe(phen)$_3$]$^{2+}$ ion in aqueous media[2] and various solvent systems[3] is an intramolecular process. The intramolecular mechanism has been thought to proceed by a twisting process.[2,4] It was suggested originally that racemization of [Ni(phen)$_3$]$^{2+}$ and [Ni(bpy)$_3$]$^{2+}$ occurred by an intramolecular process.[5] However, later measurements of racemization and dissociation rates showed that both the rates were experimentally the same in aqueous solution, indicating racemization by dissociation.[6,7] In nonaqueous solvents, exchange rates were also shown to be the same as the rates of racemization in the same solvent system;[7] a dissociative intermolecular mechanism is believed to be operative in the various solvents used.[8,9]

Solvent effects on the racemization of the nickel complexes could not be related to the solvent viscosity or to the dielectric constant of the solvent.[5,8,10] We reported that the rates of racemization of [Ni(phen)$_3$]$^{2+}$ in various solvents are related to Gutmann's donor number of the solvents and that this can be accounted for by a process involving encounter between the complex ion and a solvent molecule and the subsequent formation of a 7-coordinate intermediate with the solvent molecule followed by a rapid dissociation process.[11] Moreover, we showed that the racemization of the complex ion is accelerated by the pairing of the complex ion with a counteranion in water–*t*-BuOH mixtures (the mole fraction of *t*-BuOH > 0.5) and the rates increase with the anion in the order ClO$_4$$^-$ < I$^-$ < Br$^-$ < Cl$^-$.[12] The dependence of the rates on the anions might arise from the donicity of anions, although the anions are solvated by water and *t*-BuOH. In order to explore this possibility, we have investigated the effect of lattice anions of the solid-state racemization of a series of anhydrous halide

Table I. Elemental Analysis

compd	% calcd			% found		
	C	H	N	C	H	N
(+)-[Fe(phen)$_3$]Br$_2$·6H$_2$O	50.02	4.20	9.72	49.99	4.41	9.52
(+)-[Fe(phen)$_3$]I$_2$·3H$_2$O	47.81	3.34	9.29	48.07	3.29	9.20
(+)-[Fe(bpy)$_3$]Br$_2$·6H$_2$O	45.48	4.58	10.61	44.69	4.81	10.42
(+)-[Fe(bpy)$_3$]I$_2$·5H$_2$O	41.50	3.95	9.68	41.35	4.16	9.97
(−)-[Ni(phen)$_3$]I$_2$·4H$_2$O	46.74	3.49	9.08	46.17	3.54	8.99
(−)-[Ni(bpy)$_3$]Cl$_2$·6H$_2$O	51.02	5.14	11.90	47.49	5.18	11.36
(−)-[Ni(bpy)$_3$]Br$_2$·6H$_2$O	45.31	4.56	10.57	44.93	4.57	10.07
(−)-[Ni(bpy)$_3$]I$_2$·6H$_2$O	40.52	4.08	9.45	40.70	4.04	9.60

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