for a zinc complex, the competition of proton for the ligand at pH 7.4 substantially reduces the effective stability of the complex.

Although quantitative studies have not been done, ligand substitution involving either CuL^+ or ZnL^+ occurs rapidly. Hence the comparison of the thermodynamics of ligand substitution is a useful means of predicting the behavior of these complexes in biological systems. Studies to be reported elsewhere which do examine the reactions of metal complexes of HL with biomolecules appear to support the utility of such work.[19] A strong case has already been made for the usefulness of model studies with bis(thiosemicarbazonato)copper and -zinc complexes, which have antitumor effects, for it has now been shown that the biochemical and cellular reactivity of these chelates can be understood in some detail on the basis of their physicochemical properties.[8,14,20,26-30]

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Registry No. CuL^+, 60804-19-5; $CuLen^+$, 60804-20-8; $Cu(en)_2{}^{2+}$, 45650-15-5; ZnL^+, 60804-21-9.

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Contribution from the W. R. Kenan, Jr. Laboratory, Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

Reversible Electron Transfer in Ruthenium Nitrosyl Complexes

R. W. CALLAHAN and T. J. MEYER*

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Electrochemical studies in acetonitrile show that the nitrosyl complexes $[(bpy)_2Ru(NO)X]^{n+}$ (bpy is 2,2′-bipyridine; X = N_3^-, Cl^-, NO_2^- ($n = 2$); X = NH_3, pyridine, CH_3CN ($n = 3$)) undergo reversible, one-electron reductions in the potential range 0.1–0.6 V vs. the SSCE at room temperature and a further, irreversible reduction at more cathodic potentials. The one-electron reduction product $[(bpy)_2Ru(NO)Cl]I$ has been isolated. A nearly linear correlation is observed between $\nu(NO)$ and $E_{1/2}$ for the reversible reduction wave. The results of IR, EPR, ESCA, Mössbauer, spectral, and chemical studies are consistent with a picture in which there is extensive $d\pi(Ru)$ to $\pi^*(NO)$ back-bonding, and yet the site of reduction remains largely $\pi^*(NO)$ in character. The results of electron-transfer studies indicate that activation barriers for electron-transfer processes to and from the nitrosyl ligands are relatively low.

Introduction

The chemistry of metal nitrosyl complexes remains a source of chemical interest, in part because the area illustrates certain problems and ambiguities which are largely unresolved in many chemical systems. The problems include the question of the oxidation-state formalism in cases where metal and ligand levels may be closely matched energetically, a quantitative understanding of the relative roles of σ and π bonding in determining the electronic structure and stereochemistry of metal complexes, the role of the metal in determining the reactivity of coordinated ligands and of the ligands in determining the reactivity of a metal center.

Recently, the electronic structures of metal nitrosyl complexes have been treated by using molecular orbital theory and by applying the qualitative molecular orbital ideas developed by Walsh.[1-6] The picture of electronic structure which is evolving is highly developed, at least qualitatively, and introduces some interesting and experimentally testable ideas concerning electronic structure and reactivity.

Nitrosyl complexes are known to undergo a variety of reactions.[2,5,7,8] Among the most chemically useful complexes are the strong-field d^6 complexes of iron(II) and ruthenium(II). Certain of these complexes undergo chemical reactions which are consistent with the presence of a nitrosyl group having nitrosonium ion (NO^+) like reactivity. Reactions observed include typical acid–base behavior at the electrophilic nitrosyl group and, in addition, both diazotization and nitrosation of activated aromatic amines.[7,9-13]

Perhaps the simplest chemical reaction to consider in such complexes is electron transfer. The nitrosonium ion is known to be a relatively strong oxidant,[14] and reversible electron transfer has been reported for the nitroprusside ion.[15,16] An understanding of the origin of the electron-transfer properties in these complexes is of importance in terms of both electronic structure and chemical reactivity. The work described here has appeared, in part, in a preliminary communication.[17]

Experimental Section

Measurements. Ultraviolet–visible and near-infrared spectra were recorded using Cary Models 14 and 17 and Bausch and Lomb 210 spectrophotometers. Infrared spectra were obtained using a Perkin-Elmer 421 spectrometer. Electrochemical measurements were vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C and are uncorrected for junction potentials. The measurements were made using a PAR Model 173 potentiostat for potential control with a PAR Model 176 universal programmer as a sweep generator for voltammetric experiments. X-ray photoelectron spectra were obtained using a Du Pont 650 B electron spectrometer equipped with a Du Pont Instruments multichannel analyzer.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared as previously described.[18] Acetonitrile (MCB, Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical measurements and used without drying for spectral measurements. Water was deionized and then distilled from alkaline permanganate. All other solvents (Reagent grade) were used without further purification. Lithium perchlorate and tetra-*n*-butylammonium idodide were obtained commercially and used without further purification. Argon was deaerated by passing through acidic solutions of Cr^{2+} and dried by passing through sulfuric acid. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Preparations. The preparations of the salts $[(bpy)_2RuCl_2]\cdot 2H_2O$,[19] $[(bpy)_2Ru(NO_2)_2]\cdot H_2O$,[20] and $[(bpy)_2Ru(NO)Cl](PF_6)_2$[20] (bpy is 2,2′-bipyridine) have been described previously. The general procedure for the preparation of the remaining nitrosyl complexes is as follows. Initially, the nitrosyl group in $[(bpy)_2Ru(NO)NO_2](PF_6)_2$ was replaced by solvent by the reaction between the nitrosyl group and azide ion[21]

$$[(bpy)_2Ru(NO)NO_2]^{2+} + N_3^- + S \rightarrow [(bpy)_2Ru(S)NO_2]^+ + N_2 + N_2O \qquad (1)$$

(S = acetone or methanol)

The solvent complex generated in reaction 1 was then allowed to react with an excess of the appropriate ligand A

$$[(bpy)_2Ru(S)NO_2]^+ + A \rightarrow [(bpy)_2Ru(A)NO_2]^{n+} + S \qquad (2)$$

($A = N_3^-$, $n = 0$; $A = NH_3$, py, CH_3CN, $n = 1$)

The coordinated nitrite in the product of reaction 2 was then converted into coordinated nitrosyl by reaction with acid[22]

$$[(bpy)_2Ru(A)NO_2]^{n+} + 2H^+ \rightarrow [(bpy)_2Ru(A)NO]^{(n+2)+} + H_2O \qquad (3)$$

($A = N_3^-$, $n = 0$; $A = NH_3$, py, CH_3CN, $n = 1$)

$[(bpy)_2Ru(NO)N_3](PF_6)_2$. The salt $[(bpy)_2Ru(NO)NO_2](PF_6)_2$ (653 mg, 0.838 mmol) was dissolved in acetone (~10 ml) and tetra-*n*-butylammonium chloride (~0.5 g) was added. The chloride salt immediately precipitated and was collected on a glass frit and washed with several portions (~30 ml) of acetone. The complex was then dissolved in water (~10 ml) and an excess of sodium azide (~1.0 g, 15 mmol) was added. The solution was heated (~70–80 °C) for 15 min and allowed to cool. The dark black powder which precipitated, presumably $[(bpy)_2Ru(NO_2)N_3]$, was washed with several portions (~30 ml) of water. The complex was suspended in stirred methanol (~40 ml) and 65% HPF_6 (1–2 ml) was added. After 10–15 min, the suspension–solution was added with stirring to anhydrous ether (~300 ml). The resulting precipitate was collected, redissolved in acetone (~30 ml), and filtered into stirred anhydrous ether (~300 ml). The resulting light yellow-brown precipitate was collected on a glass frit and air-dried; yield 280 mg (43%). Anal. Calcd for $[(bpy)_2Ru(NO)N_3](PF_6)_2$: C, 30.98; H, 2.08; N, 14.45. Found: C, 31.18; H, 2.15; N, 14.17.

$[(bpy)_2Ru(NO)NH_3](PF_6)_3$. The salt $[(bpy)_2Ru(NO)NO_2](PF_6)_2$ (609 mg, 0.781 mmol) was converted into the chloride salt by the procedure used above and dissolved in water (~10–15 ml). The solution was protected from light and an equimolar amount of NaN_3 (51 mg in ~5 ml of H_2O) was added dropwise to the stirred solution. The solution was heated (~70–80 °C) for 10–15 min. A 28% NH_3 solution (~2 ml) was added and the solution was allowed to reflux for 0.5 h in the absence of light. A saturated solution of NH_4PF_6 (~5–10 ml) was added, and the solution was cooled to give a dark red precipitate. The precipitate was dried in a vacuum desiccator over Drierite and then dissolved in a 1:1 acetone–dichloromethane mixture (~30 ml) in the absence of light. The solution was filtered into stirred anhydrous ether (~300 ml) to give a red precipitate, presumably $[(bpy)_2Ru(NH_3)NO_2](PF_6)$. The complex was suspended in stirred methanol (~40 ml) and 60% HPF_6 (1–2 ml) was added. After 0.5 h, the solution–suspension was filtered into stirred anhydrous ether (~300 ml) to produce a light brown precipitate. The complex was collected on a glass frit, washed with dichloromethane (~30 ml), and dissolved in acetone (~30 ml). The acetone solution was filtered into stirred anhydrous ether (~300 ml). The resulting light brown precipitate was collected on a glass frit and air-dried; yield 200 mg (37%). Anal. Calcd. for $[(bpy)_2Ru(NO)NH_3](PF_6)_3$: C, 26.83; H, 2.14; N, 9.39. Found: C, 27.06; H, 2.17; N, 9.40.

$[(bpy)_2Ru(NO)(py)](PF_6)_3$. The salt $[(bpy)_2Ru(NO)NO_2](PF_6)_2$ (725 mg, 0.930 mmol) was dissolved in acetone (~10 ml) and protected from light. An equimolar amount of KN_3 (75 mg) was then dissolved in methanol (5–10 ml) and added dropwise to the above solution. Freshly distilled pyridine (~1 ml) was added to the stirred solution and the reaction allowed to proceed for ~1.5 h. The solution was added to stirred anhydrous ether (~300 ml) to produce a precipitate. The precipitate was dissolved in dichloromethane (~30 ml), protected from light, and filtered into stirred pentane (~300 ml). (Not all of the precipitate would dissolve in CH_2Cl_2; a brick red product is left behind after filtering.) The resulting dark orange precipitate was collected on a glass frit and air-dried. The precipitate, $[(bpy)_2Ru(NO_2)(py)](PF_6)$, was then dissolved in acetonitrile (~10–15 ml) and 60% HPF_6 (1–2 ml) was added to the stirred solution. After 10–15 min, the solution was added to stirred, anhydrous ether (~300 ml). The precipitate which formed was collected and redissolved in acetone (~10–15 ml). The solution was filtered into stirred anhydrous ether (~300 ml) to give a light yellow solid which was collected and air-dried; yield 350 mg (39%). Anal. Calcd. for $[(bpy)_2Ru(NO)(py)](PF_6)_3$: C, 31.36; H, 2.21. Found: C, 31.58; H, 2.40.

$[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_3$. The salt $[(bpy)_2Ru(NO)NO_2](PF_6)_2$ (402 mg, 0.516 mmol) was dissolved in acetonitrile (10–15 ml), and an equimolar amount of KN_3 (25 mg in ~5–10 ml of methanol) was added dropwise to the stirred solution. The reaction was allowed to proceed for ~1 h in the absence of light. The solution was added to stirred anhydrous ether (~300 ml). The resulting precipitate was collected and dissolved in CH_2Cl_2 (~30 ml) in the absence of light. The solution was filtered into stirred pentane (~300 ml) to precipitate a dark orange solid, presumably $[(bpy)_2Ru(NO_2)(CH_3CN)](PF_6)$. The precipitate was collected and dissolved in acetonitrile (~15 ml). Sixty percent HPF_6 (~1–2 ml) was added to the stirred solution. After 10–15 min, the solution was added to stirred anhydrous ether (~300 ml) precipitating a light yellow compound. The compound was collected, dissolved in acetone, and filtered into stirred anhydrous ether giving a pale yellow solid; yield 300 mg (63%). Anal. Calcd for $[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_3$: C, 28.74; H, 2.08. Found: C, 29.45; H, 2.32.

$[(bpy)_2Ru(NO)Cl]I$. The salt $[(bpy)_2Ru(NO)Cl](PF_6)_2$ (311 mg, 0.404 mmol) was dissolved in acetone and protected from light. The solution was then thoroughly deaerated with argon and stirred. A saturated solution of tetra-*n*-butylammonium iodide (~5–10 ml) in acetone was prepared, protected from light, thoroughly deaerated, and added slowly via a syringe technique to the solution of the nitrosyl complex. An immediate brown-green coloration appeared. The reaction proceeded for 5–10 min during which time a dark black precipitate formed. The precipitate was collected on a glass frit, washed twice with 5-ml portions of acetone, and dried overnight in a vacuum desiccator; yield 130 mg (53%). Anal. Calcd for $[(bpy)_2Ru(NO)Cl]I$: C, 39.65; H, 2.66; N, 11.56; I, 20.95. Found: C, 39.50; H, 2.72; N, 11.49; I, 20.80.

Reduction of $[(bpy)_2Ru(NO)(CH_3CN)]^{3+}$. The salt $[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_3$ (19.1 mg, 0.04 mmol) and an equimolar amount of $[(bpy)_2RuCl_2]\cdot 2H_2O$ (10.8 mg) were placed in a 2-ml volumetric flask which was then thoroughly deaerated and protected from light. CD_3CN (~1.5 ml) which had been previously deaerated was added to the flask using syringe techniques and stirred. The infrared spectrum of the solution was recorded, using a deaerated 0.1-mm NaCl cell in the 2000–1400-cm^{-1} region. The typical ν(NO) band (1970 cm^{-1}) of $[(bpy)_2Ru(NO)(CH_3CN)]^{3+}$ had disappeared, and a new intense band had appeared at 1665 cm^{-1}. $[(bpy)_2RuCl_2]^+$ does not have intense bands in this region. The solvent was removed from the CD_3CN solution. The infrared spectrum (KBr) of the remaining solid showed the intense band slightly shifted to 1655 cm^{-1}.

Photolysis of $[(bpy)_2Ru(NO)Cl]^{2+}$. Small-scale photolyses (~10^{-4} M in acetonitrile) were carried out in the following manner. Solutions of the nitrosyl complex (air saturated) were placed in a merry-go-round apparatus and irradiated by a Hanovia 450-W medium-pressure mercury lamp. The 313-nm line was isolated by using a combination of a Corning glass filter and a solution filter as previously described.[23] The reaction was assumed to be over when no further increases in the absorbance maximum (425 nm) of the product ($[(bpy)_2Ru^{III}(CH_3CN)Cl]^{2+}$) occurred.

Preparative-scale irradiations were carried out in a Rayonet Photochemical reactor using RPR-3000 lamps which emit a broad band of ultraviolet radiation centered at 300 nm. The salt $[(bpy)_2Ru(NO)Cl](PF_6)_2$ (121 mg, 0.157 mmol) was dissolved in acetonitrile (~50 ml) and placed in the reactor. Oxygen was bubbled through the stirring solution during the reaction. (For the determination of free NO, oxygen was *not* bubbled through the solution. Instead, the vessel containing the solution of the nitrosyl complex was initially evacuated under vacuum. At the end of the photolysis, NO was shown to be the only gas present by mass spectral analysis.) UV-VIS spectra of aliquots of the reaction solution showed that formation of the product (λ_{max} 425 nm) was complete after ~1 h. The solution was then added to stirred anhydrous ether (~300 ml) to precipitate the light yellow-green product. The salt $[(bpy)_2Ru^{III}(CH_3CN)Cl](PF_6)_2$ was collected and dried overnight in a vacuum desiccator; yield 100 mg (82%).

The product was characterized spectrally. Addition of 60% N_2H_4 (1–2 drops) to acetonitrile solutions (~10 ml, ~10^{-4} M) of the complex produced an electronic spectrum that was quantitatively identical with that of $[(bpy)_2Ru^{II}(CH_3CN)Cl]^+$.[24] (The reaction of hydrazine with the product complex is a net redox reaction in which Ru(III) is reduced to Ru(II).[25]) In addition, a medium-strength band (2290 cm^{-1}) is observed in the infrared spectrum of the complex (NaCl pellet) which can be assigned as $\nu(C{\equiv}N)$.[26]

Spectrophotometric Titration of $[(bpy)_2Ru(NO)CH_3CN]^{3+}$ by $Ru(bpy)_2Cl_2$. The titration was carried out in the absence of light using deaerated acetonitrile. Aliquots of $[(bpy)_2Ru(NO)(CH_3CN)]^{3+}$ were added to solutions of $[(bpy)_2RuCl_2]$ and the changes in absorbance monitored. To establish the reaction stoichiometry, a Yoe–Jones plot was made of absorbance (550 nm, λ_{max} for $[(bpy)_2RuCl_2]$) vs. (moles of $[(bpy)_2Ru(NO)(CH_3CN)]^{3+}$ added)/(moles of $[(bpy)_2RuCl_2]$). ($[(bpy)_2Ru(NO)(CH_3CN)]^{3+}$ and $[(bpy)_2Ru(NO)(CH_3CN)]^{2+}$ are essentially transparent in the 550-nm region.) Solutions of $[(bpy)_2RuCl_2]^+$ could be reduced essentially quantitatively (using the hydrazine reduction technique described above) to give back $[(bpy)_2RuCl_2]$ as shown spectrally. The titration established the reaction stoichiometry as

$$[(bpy)_2RuCl_2] + [(bpy)_2Ru(NO)(CH_3CN)]^{3+} \rightarrow [(bpy)_2RuCl_2]^+ + [(bpy)_2Ru(NO)(CH_3CN)]^{2+} \quad (4)$$

Estimate of the Rate of Self-Exchange in the Electron-Transfer Reaction $[(bpy)_2Ru(^{14}NO)Cl]^+$ + $[(bpy)_2Ru(^{15}NO)Cl]^{2+}$ → $[(bpy)_2Ru(^{14}NO)Cl]^{2+}$ + $[(bpy)Ru(^{15}NO)Cl]^+$. Solutions of $[(bpy)_2Ru(^{15}NO)Cl]^{2+}$ (3.2×10^{-3} M) and $[(bpy)_2Ru(^{14}NO)Cl]^+$ (3.1×10^{-3} M) were prepared in acetonitrile using $[(bpy)_2Ru(^{15}NO)Cl](PF_6)_2$ and $[(bpy)_2Ru(^{14}NO)Cl]I$. The solutions were introduced simultaneously into an infrared cell using a continuous-flow mixing apparatus. The infrared spectrum of the mixture was then recorded in the region 1870–2000 cm^{-1}. Two bands, essentially equally intense, were observed at 1940 cm^{-1} ($\nu(^{14}NO)$) and 1900 cm^{-1} ($\nu(^{15}NO)$), indicating that the reaction had reached equilibrium by the end of the mixing and recording procedure (~1 min). No further changes were noted in the spectrum over longer periods of time.

Results

Electrochemistry. Shown in Figure 1 is a cyclic voltammogram of $[(bpy)_2Ru(NO)Cl]^{2+}$ in acetonitrile (bpy is 2,2′-bipyridine). Voltammograms for all the nitrosyl complexes gave one cathodic wave in the potential region 0.6–0.1 V. Voltammetric half-wave potentials vs. the saturated sodium chloride electrode for this process are given in Table I. The potentials are formally reduction potentials except for a usually small correction term for differences in diffusion coefficients[27] and refer to the reactions

$$[(bpy)_2Ru(NO)A]^{n+} + e^- \rightarrow [(bpy)_2Ru(NO)A]^{(n+1)+} \qquad E_{1/2}(1)$$
$$(A = N_3^-, Cl^-, NO_2^-; n = 2: \quad A = NH_3, py, CH_3CN; n = 3)$$

(For the complexes reported here, the A ligand is apparently cis to the nitrosyl group.[20])

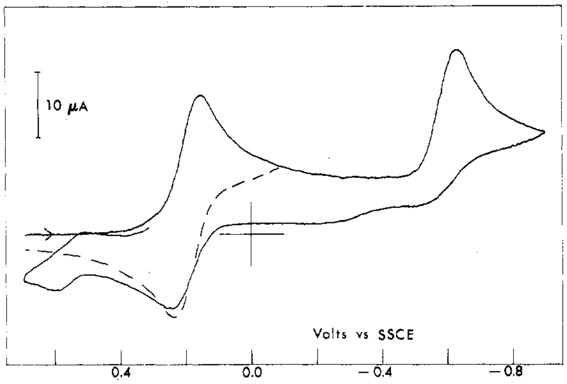


Figure 1. Cyclic voltammogram (200 mV/s) of $[(bpy)_2Ru(NO)Cl]^{2+}$ (1.1×10^{-3} M) in 0.1 M TBAH–CH_3CN at 22 ± 2 °C vs. the saturated sodium chloride calomel electrode. The dashed line shows the single-sweep voltammogram where the cathodic sweep is reversed before reaching the second reduction wave.

Table I. Electrochemical Data for the Ruthenium Nitrosyl Complexes[a,b]

Complex	$E_{1/2}(1)$, V (n)	$E_{p,c}(2)$,[c] V (n)
$[(bpy)_2Ru(NO)N_3]^{2+}$	0.18 (0.92)	−0.63
$[(bpy)_2Ru(NO)Cl]^{2+}$	0.20[d] (0.94)	−0.60
$[(bpy)_2Ru(NO)NO_2]^{2+}$	0.33	−0.56
$[(bpy)_2Ru(NO)NH_3]^{3+}$	0.36	−0.48
$[(bpy)_2Ru(NO)py]^{3+}$	0.53 (0.95)	−0.37
$[(bpy)_2Ru(NO)CH_3CN]^{3+}$	0.56[e] (0.98)	−0.35 (0.90)

[a] Potential measurements were at a Pt electrode and are referred to the saturated sodium chloride calomel electrode in 0.1 M TBAH-CH_3CN at 25 ± 2 °C. The estimated error in the potential measurements is ±0.01 V. [b] n values, given in parentheses, refer to the number of electrons transferred in a constant-potential reduction on the diffusion plateaus of the waves indicated. [c] Cathodic peak potentials using a 200-mV/s scan rate. [d] Value shifts to 0.29 and 0.04 V in acetone (0.1 M TBAH) and water (0.1 M NaCl), respectively. [e] Value shifts to 0.46 V in 0.1 M $LiClO_4$-acetonitrile.

The reversible waves have been labeled $E_{1/2}(1)$. They arise from the one-electron reduction of the complexes as shown by coulometric experiments (Table I). The electrode reactions were all essentially electrochemically reversible. The reversibility was shown by plots of E vs. log $(i_l - i)/i$ for voltammetry experiments and by differences in anodic and cathodic peak potentials from cyclic voltammetry experiments (ΔE_p = 60–75 mV).[28]

Voltammograms of the nitrosyl complexes gave another cathodic wave in the region −0.35 to −0.65 V. Coulometric experiments using $[(bpy)_2Ru(NO)(CH_3CN)]^{2+}$ suggest that the waves correspond to a further one-electron reduction of the complexes. The second reduction results in some decomposition as can be seen in the cyclic voltammogram for $[(bpy)_2Ru(NO)Cl]^{2+}$. The second reduction process is irreversible even using fast scan rates (~10 V/s) in cyclic voltammetry experiments. In Table I the second reduction is denoted as $E_{p,c}(2)$ from cyclic voltammetry experiments at 200 mV/s. No voltammetric waves corresponding to the oxidation of the complexes were observed out to 2.0 V.

Solutions of the one-electron reduction products could be generated by bulk electrolysis under argon. The reduced solutions were stable indefinitely when protected from oxygen as shown by electrochemical experiments. Cyclic voltammograms of the reduced solutions were identical with those of the starting complexes. Exposure of the solutions to air resulted in significant decomposition (~50% in 1 h); the solutions are light stable.

Infrared Spectra. Table II gives $\nu(NO)$ values for each of the nitrosyl complexes. The one-electron reduction products, $[(bpy)_2Ru(NO)Cl]I$ and $[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_2$,

Table II. Nitrosyl Stretching Frequencies

Compd	ν(NO),[a] cm^{-1}
$[(bpy)_2Ru(NO)N_3](PF_6)_2$	1923
$[(bpy)_2Ru(NO)Cl](PF_6)_2$	1940 (1925)[b]
$[(bpy)_2Ru(NO)Cl]I$	1640[c] (1611)[b]
$[(bpy)_2Ru(NO)NO_2](PF_6)_2$	1948
$[(bpy)_2Ru(NO)NH_3](PF_6)_3$	1950
$[(bpy)_2Ru(NO)py](PF_6)_3$	1953
$[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_3$	1970 (1956)[b]
$[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_2$[d]	1665[c] (1655)[b]

[a] Values are given in CH_3CN unless otherwise noted. The estimated error is ±2 cm^{-1}. [b] KBr pellet. [c] In CD_3CN. [d] Recorded in the presence of $[(bpy)_2RuCl_2](PF_6)$ (see Experimental Section).

Table III. Electronic Spectra

Complex	λ_{max},[a] nm	$10^{-4}\epsilon$,[b] M^{-1} cm^{-1}
$[(bpy)_2Ru(NO)N_3]^{2+}$	322	1.29
	286	2.24
$[(bpy)_2Ru(NO)Cl]^{2+}$	323	1.23
	294	1.70
$[(bpy)_2Ru(NO)Cl]^{+}$	350	0.540
	310 sh	
	293	2.65
$[(bpy)_2Ru(NO)NO_2]^{2+}$	323	1.09
	296	1.95
$[(bpy)_2Ru(NO)NH_3]^{3+}$	324	
	289	
$[(bpy)_2Ru(NO)py]^{3+}$	325 sh	
	299	
$[(bpy)_2Ru(NO)CH_3CN]^{3+}$	326 sh	
	300	2.12

[a] In acetonitrile, ±2 nm. [b] Estimated error in ϵ values is ±5%.

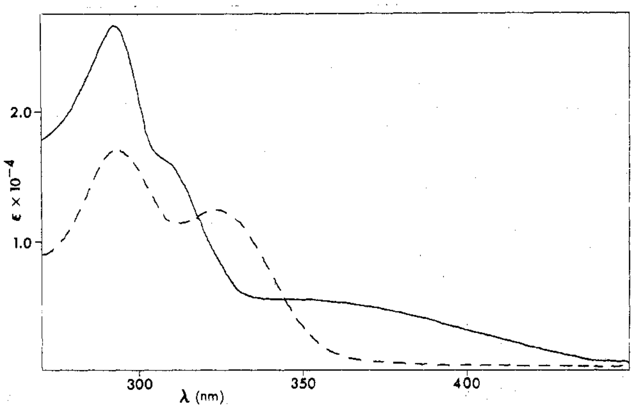


Figure 2. Electronic spectra of $[(bpy)_2Ru(NO)Cl]^{2+}$ (- - -) and $[(bpy)_2Ru(NO)Cl]^{+}$ (—) in acetonitrile.

have ν(NO) at 1611 and 1655 cm^{-1} (KBr pellets). The assignment of the bands as ν(NO) was confirmed by ^{15}N-labeling experiments using $[(bpy)_2Ru(^{15}NO)Cl]^{+}$ in CD_3CN (ν(NO) 1640 cm^{-1} for $[(bpy)_2Ru(NO)Cl]^{+}$ and ν(NO) 1608 cm^{-1} for $[(bpy)_2Ru(^{15}NO)Cl]^{+}$).

Electronic Spectra. Electronic spectral data for the nitrosyl complexes are given in Table III. In Figure 2 are shown the electronic spectra of $[(bpy)_2Ru(NO)Cl]^{2+}$ and $[(bpy)_2Ru(NO)Cl]^{+}$ in acetonitrile. The electronic spectrum of $[(bpy)_2Ru(NO)Cl]I$ dissolved in acetonitrile is identical with that obtained by the electrochemical reduction of $[(bpy)_2Ru(NO)Cl]^{2+}$ in the same solvent.

EPR. In Figure 3 is shown the EPR spectrum of the one-electron reduction product of $[(bpy)_2Ru(NO)Cl]^{2+}$ at 77 K in frozen acetone. Also shown is the EPR spectrum of $[Fe(CN)_5NO]^{3-}$ at 77 K in frozen aqueous solution. Solutions of $[(bpy)_2Ru(NO)Cl]^{+}$ were generated electrochemically under argon. Solutions were then transferred via a syringe technique to a deaerated EPR cell which had a rubber septum top. The solution was freeze–thaw degassed on a vacuum line and the tube sealed with a flame. The room-temperature EPR spectrum exhibited only a broad (~2500 G), irregularly shaped band.

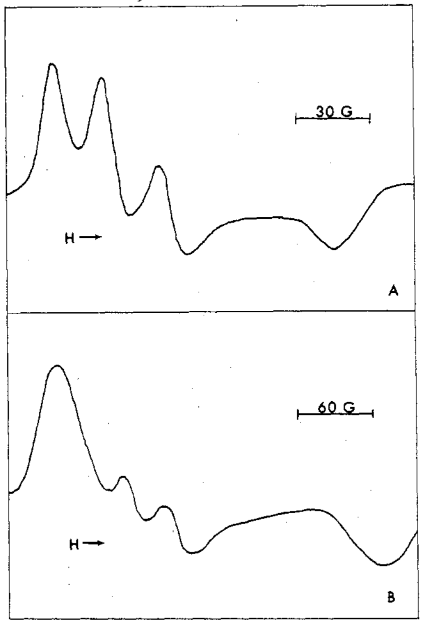


Figure 3. EPR spectra of (A) $[Fe(CN)_5NO]^{3-}$ in frozen aqueous solution at 77 K (reproduced from ref 29) and (B) $[(bpy)_2Ru(NO)Cl]^{+}$ in frozen acetone solution at 77 K.

Photochemistry. The photoreaction of $[(bpy)_2Ru(NO)Cl]^{2+}$ apparently occurs only with ultraviolet radiation since the complexes are indefinitely stable in visible light. A mixture of products, $[(bpy)_2Ru(CH_3CN)Cl]^{+}$ and $[(bpy)_2Ru(CH_3CN)Cl]^{2+}$ as shown by comparison to known spectra,[24] is obtained if the solutions are degassed with argon prior to irradiation. If the photolyses are carried out using air- (or oxygen-) saturated solutions or solutions which have been freeze–thaw degassed, $[(bpy)_2Ru(CH_3CN)Cl]^{2+}$ is obtained cleanly. Photolyses of freeze–thaw degassed solutions resulted in the evolution of NO as shown by mass spectral analysis. No other gases were detected.

Self-Exchange Reaction. The reaction

$$[(bpy)_2Ru(^{15}NO)Cl]^{2+} + [(bpy)_2Ru(^{14}NO)Cl]^{+} \xrightarrow{k_{11}} [(bpy)_2Ru(^{15}NO)Cl]^{+} + [(bpy)_2Ru(^{14}NO)Cl]^{2+} \quad (5)$$

was followed in the infrared region. From the IR data, the reaction reaches equilibrium in less than 1 min when both complexes are present at 3×10^{-3} M. From this observation, at least 4 half-lives ($t_{1/2}$) had passed during 60 s so that $t_{1/2} \leq 15$ s. Assuming the reaction to be second order gives $k_{11} \geq 2 \times 10$ s^{-1} at room temperature.

Discussion

Site of Reduction in the Nitrosyl Complexes. The nitroprusside ion, $Fe(CN)_5NO^{2-}$, is isoelectronic with the ruthenium complexes in that both are formally d^6 cases, and in both cases the metal ion is surrounded by strong back-bonding ligands. The nitroprusside ion shares with the ruthenium complexes a high ν(NO) stretching frequency (1944 cm^{-1} for $[Fe(CN)_5NO]^{2-}$ in a KBr pellet),[30] diamagnetism, and the ability to undergo a reversible one-electron reduction.

Kolthoff and Toren first reported an electrochemically reversible reduction of the nitroprusside ion in aqueous solution.[15]

$$[Fe(CN)_5NO]^{2-} + e^{-} \rightarrow [Fe(CN)_5NO]^{3-}$$

The reduction occurs at $E_{1/2} = -0.4$ V vs. the SCE and is independent of pH.

Kolthoff and Toren suggested that the site of reduction was confined largely to the nitrosyl group, the reaction *formally* represented as

$$\mathrm{Fe^{II}\text{-}NO^{+}} \xrightarrow[+e^{-}]{} \mathrm{Fe^{II}\text{-}NO^{0}}$$

Recent EPR[29] and magnetically perturbed Mössbauer studies[32] on the reduced nitroprusside ion have demonstrated that the unpaired spin density is indeed confined largely to the nitrosyl group. Also, recent molecular orbital studies on the nitroprusside ion[37] have shown that the lowest lying unoccupied orbitals are largely π^*(NO) in character.[31]

The experimental evidence suggests that the site of reduction in the analogous ruthenium complexes is also confined largely to the nitrosyl group.

(1) Upon reduction, ν(NO) shifts dramatically to lower energies (Table II). Such a decrease is expected since the nitric oxide bond order would be reduced with the addition of an electron to the ligand π^* system. The magnitude of the shifts, ~300 cm^{-1}, is approximately the same as when free NO$^+$ is reduced to NO.[9]

(2) In contrast to normal bis(2,2′-bipyridine)ruthenium(III)–bis(2,2′-bipyridine)ruthenium(II) couples,[28] $E_{1/2}(1)$ for the $[(bpy)_2Ru(NO)(CH_3CN)]^{3+/2+}$ couple shifts 0.1 V to a lower potential when the supporting electrolyte is changed from 0.1 M TBAH to 0.1 M $LiClO_4$. Specific medium effects might be expected if electron transfer occurred to and from a group on the periphery of the complex.

(3) The EPR spectrum of $[(bpy)_2Ru(NO)Cl]^+$ in frozen acetone at 77 K is qualitatively identical with the frozen aqueous solution spectrum of the reduced nitroprusside complex (Figure 3). In reduced nitroprusside ion, the EPR spectrum exhibits the expected ^{14}N hyperfine splitting, but essentially no metal hyperfine was observed using samples enriched in ^{57}Fe.[29] By contrast, a large ^{57}Fe hyperfine interaction has been observed for the ion $[Fe(CN)_4NO]^{2-}$.[29,31]

(4) The nitrosyl/reduced nitrosyl redox potentials fall in the same range as potentials for typical bis(2,2′-bipyridine)Ru(III)–bis(2,2′-bipyridine)ruthenium(II) couples. However, in contrast to the Ru(II) complexes, the reduced nitrosyl complexes are oxygen sensitive. Exposure of solutions of the reduced ion $[(bpy)_2Ru(NO)(CH_3CN)]^{2+}$ to air for ~1 h leads to several products as shown by cyclic voltammetry. One of the products is $[(bpy)_2Ru(NO_2)(CH_3CN)]^+$ as shown by comparison with known E_p values for the complex.[24] Oxygen is known to react with nitrosyl groups having low ν(NO) values to give coordinated nitrite.[33]

Both nitroprusside ion and the ruthenium complexes undergo a second one-electron reduction, but disagreement exists as to the species produced.[15,16,34] Kolthoff and Toren suggested that the wave corresponded to a further one-electron reduction of the nitrosyl group.[15]

Unfortunately, the ruthenium nitrosyl complexes undergo decomposition upon reduction past the second wave ($E_{p,c}(2)$ in Table I), and it is not possible to determine the nature of the reduced product which is formed initially. Coulometric studies with $[(bpy)_2Ru(NO)(CH_3CN)]^{2+}$ (Table II) suggest that the reductions are one-electron processes. One of the products following the two successive one-electron reductions of $[(bpy)_2Ru(NO)(CH_3CN)]^{3+}$ is $[(bpy)_2Ru(NO_2)(CH_3CN)]^+$ by comparison with known E_p values for the complex.[24] The origin of the nitrite complex is perhaps one-electron reduction of Ru^{II}–NO^0 to give Ru^{II}–NO^- followed by a rapid reaction with trace oxygen (or some other oxygen source such as another nitrosyl complex) to give coordinated nitrite. (Bulk electrolyses were performed on solutions which had been vigorously deaerated with argon prior to and during the reduction process.) However, the overall chemistry is not this simple since several other products are observed which cannot be identified by comparisons with E_p and $E_{1/2}$ values for known complexes.

Electronic Structure. In the electronic spectra of the nitrosyl complexes (Table III), the intense band at ~290 nm is most likely the same $\pi \rightarrow \pi^*$(bpy) transition that is commonly found in this region for typical bis(2,2′-bipyridine)ruthenium(II) complexes.[35] The band does not shift in the reduced ion $[(bpy)_2Ru(NO)Cl]^+$, but it does become more intense. The band at ~323 nm for the nitrosyl complexes is conceivably a $d\pi$(Ru) $\rightarrow \pi^*$(bpy) transition. Similar transitions are observed in related complexes but at much lower energies.[35] If this assignment is correct, there must be a strong back-bonding interaction leading to a large stabilization of the metal $d\pi$ levels.

A $t_2 \rightarrow \pi^*$(NO) transition is also expected for the nitrosyl complexes.[36a] Armor and Pell[36b] observed the transition (420–480 nm) in the series of cis-tetraammine–nitrosyl complexes $[(NH_3)_4Ru(NO)X]^{n+}$ (X = OH$^-$, Cl$^-$, Br$^-$, I$^-$, n = 2; X = OH$_2$, n = 3). The intensities of the bands are weak (ϵ <50 M^{-1} cm^{-1}). Such bands should occur at higher energies in the 2,2′-bipyridine–nitrosyl complexes because of stabilization of the $d\pi$ levels by back-bonding with 2,2′-bipyridine. The bands are probably not observed because they are obscured by the more intense $d\pi \rightarrow \pi^*$(bpy) and $\pi \rightarrow \pi^*$(bpy) transitions.

In the reduced nitrosyl complex $[Ru(bpy)_2(NO)Cl]^+$ there is a broad band at ~350 nm, and a shoulder appears at 310 nm (Figure 2). Back-bonding should be less in the reduced complexes because of increased electron density in π^*(NO) and possibly because of a significant bending of the Ru–N–O bond angle. Both bands have relatively high oscillator strengths, the lower energy band because of its large band width. High oscillator strengths suggest considerable charge-transfer character in the transitions involved but the detailed origins of the two absorption bands are not clear.

ESCA measurements on $[Ru(bpy)_2(NO)Cl]I$ show the Ru($3d_{5/2}$) binding energy at 280.5 eV (relative to the arbitrarily assigned C(1s) binding energy of the 2,2′-bipyridine ligands at 284.4 eV). This value is intermediate between binding energies in related (2,2′-bpy) complexes of Ru(II) (279.9 ± 0.2 eV) and Ru(III) (281.8 ± 0.3 eV) but is nearer the value for Ru(II).[25] For the starting nitrosyl complex as its PF_6^- salt, the Ru($3d_{5/2}$) binding energy appears at 286.6 eV which is on the high-energy side of the C(1s) peak.

A plot of ν(NO) vs. $E_{1/2}(1)$ for the nitrosyl complexes is shown in Figure 4. There is, at least qualitatively, a direct relation between the two quantities which is not surprising since both are dependent upon the electronic properties of the nitrosyl group. The origin of the variations in ν(NO) and $E_{1/2}$ with the cis ligand may be threefold. Azide and chloride ions are π-donating ligands, and nitrite ion, pyridine, and acetonitrile, π-back-bonding ligands. The two different types of ligands should influence the ability of the Ru ion to back-bond to the nitrosyl group, but in opposite ways. The difference in charge for the two sets of complexes (2+ vs. 3+) may also affect the availability of $d\pi$-electron density to NO. The $E_{1/2}$ values are also sensitive (but probably weakly at I = 0.1 M) to changes in the charge type of the couples (3+/2+ compared to 2+/+). In any case, the linear correlation implied by the data in the figure indicates that the oxidizing strength of the complexes increases with the NO$^+$-like character of the nitrosyl group.

The electronic structure of nitroprusside ion has been studied using molecular orbital theory.[37] In nitroprusside ion, strong, symmetry-allowed $d\pi$–π^*(NO) interactions lead to a considerable stabilization of the $d\pi$ levels, and the lowest

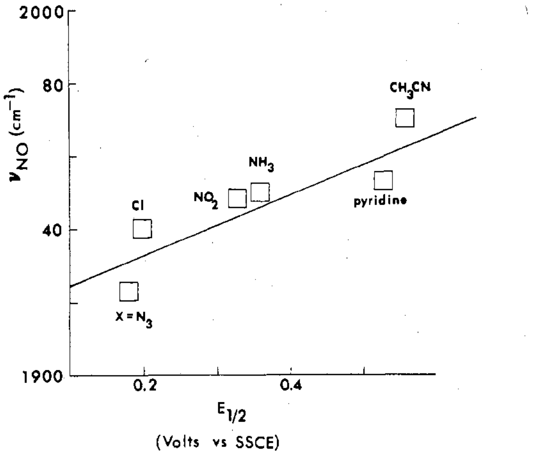


Figure 4. Plot of ν(NO) for the $[(bpy)_2Ru(NO)X]^{n+}$ complexes vs. $E_{1/2}$ for the reaction $[(bpy)_2Ru(NO)X]^{n+} + e^- \rightarrow [(bpy)_2Ru(NO)X]^{(n-1)+}$. The boxes give the estimated uncertainties in the two measured values.

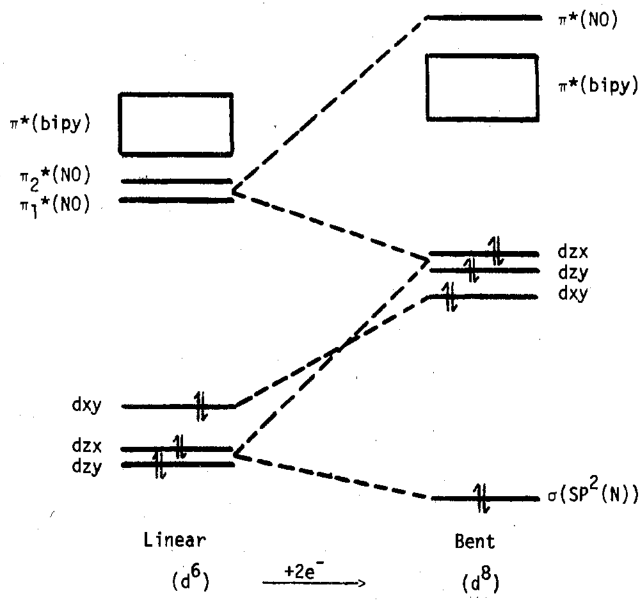


Figure 5. Schematic correlation diagram for the $[(bpy)_2Ru(NO)(L)]^{n+}$ complexes interrelating the linear and bent six-coordinate nitrosyl cases. The $d_{x^2-y^2}$ and d_{z^2} orbitals are not included and for the linear d^6 case they may lie near π*(NO) in energy.[36a] With a bending in the NO group mixing between π*(NO) and d_{z^2} may be important.[6]

unoccupied levels are largely (~73%) π*(NO) in character. A related, but qualitative, MO scheme is given on the left-hand side of the correlation diagram in Figure 5 for the ruthenium complexes. In the scheme the z axis is taken along the Ru–NO bond, and the differential interactions of the dπ orbitals with π*(bpy) have been taken into account.

The high ν(NO) stretching frequencies and chemical reactivity of the bound NO group argue that in comparing the 2,2′-bipyridylruthenium nitrosyl complexes to most other d^6 cases, the energy separation between dπ(Ru) and π*(NO) is significant, and the dπ(Ru) character in π*(NO) is appreciable but *relatively* low. A considerable amount of nitrosonium ion character is retained in the bound nitrosyl group. The remaining ligands are important in determining the properties of the nitrosyl group. The high ν(NO) stretching frequencies and chemical reactivity of the group are surely attributable to competitive dπ–π*(bpy) back-bonding. The presence of the bipyridine groups probably also accounts for the relatively high stability of the reduced nitrosyl complexes. In the ion $[Ru(NH_3)_5NO]^{3+}$ where the remaining coordination positions are occupied by saturated ligands, a reversible one-electron reduction has been reported.[42] However, the reduction occurs at a considerably lower reduction potential, and the reduced product is stable only on the cyclic voltammetry time scale. In addition to the effect of the bipyridine groups, the variations in ν(NO) and $E_{1/2}$ with cis ligand show that relatively subtle changes in the remaining ligands can lead to chemically significant changes in the Ru–NO interaction. The nearly parallel increases in ν(NO) and $E_{1/2}$ are not surprising. The $E_{1/2}$ values are essentially reduction potentials (ε) in the medium used vs. the SSCE. With regard to an external reference (the SSCE half-cell), the oxidizing strength of NO$^+$ is decreased upon binding because of electron donation from the metal. As the extent of donation increases, the electron content at NO increases further, decreasing its oxidizing strength (Scheme I). If electron donation occurs at least in part by dπ → π*(NO) interaction, the N–O bond order and ν(NO) will be affected, and both ν(NO) and $E_{1/2}$ should respond to changes in the cis ligand. The essentially linear correlation in Figure 4 suggests that changes in total electron content at –NO (as measured by ε) are roughly proportional to the extent of dπ → π*(NO) donation. The correlation shows that ν(NO) provides a rough measure of the oxidizing strength of the –NO group. From Figure 4 the sensitivity of ν(NO) to oxidizing strength is 84 cm^{-1}/V from the slope, or 1.0×10^{-3} V/V.

Scheme I

—$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + Cl^-(satd)$ (SSCE ref)
ε ↓ —$[RuB_2(NO)Cl]^{2+/+}$
reduction potential —$[RuB_2(NO)py]^{3+/2+}$
(oxidizing strength) —$NO^{+/0}$

The effect of the dπ–π*(NO) interaction on the ruthenium ion is profound. The properties of related bis(2,2′-bipyridyl) complexes of ruthenium(II) are determined largely by the accessibility of electrons in the filled dπ levels. Reversible Ru(III)–Ru(II) redox couples are observed in potential range 0.17–1.51 V in 0.1 M $[N(n\text{-}Bu)_4]PF_6$ vs. the SSCE; intense dπ → π*(bpy) absorption bands appear in the range 555–410 nm.[28] In both cases the energies involved increase as the back-bonding ability of the cis ligands increases. The nitrosyl group is the extreme case since the Ru(III)–Ru(II) potentials are >2.0 V, and dπ–π*(bpy) transitions appear well into the ultraviolet region. From Figure 5 for the linear d^6 case, the highest filled level is d_{xy}. Oxidation to Ru(III) would entail removing an electron from d_{xy}. However, by symmetry d_{xy} cannot interact with π*(NO) and the effect of the Ru–NO interaction on the ability of the complexes to be oxidized must be indirect. The effect can be viewed as a synergistic phenomenon where loss of dπ-electron density leaves the metal center electron deficient, stabilizing all bonding and nonbonding levels largely Ru in character.

The picture developed above is in accord with the ESCA results. The high 3d$_{5/2}$ binding energy is consistent with considerable loss of electron density from the ruthenium. Essentially the same conclusions have been reached by Haymore and Ibers for the compound $Os(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$ where the Os center is viewed as being Os(–II) and the nitrosyl groups are viewed as being very effective at removing electron density from the metal.[43] Reduction at the ligand ($[Ru(bpy)_2(\dot{N}O)Cl]^+$) decreases the binding energy to a value near that in related Ru(II) complexes indicating that the effect of the Ru–$\dot{N}$O interaction at Ru is more nearly that found for conventional ligands.

The electronic structures of the reduced nitrosyl complexes are of interest in light of recent theoretical work on six-coordinate nitrosyls.[2,3,5,6] Figure 5 shows a correlation diagram which interrelates linear and bent six-coordinate complexes taken essentially from the review by Enemark and Feltham.[2]

The starting nitrosyl complexes have the configuration $(d\pi)^6$ and RuNO is expected to be linear. Additional electrons must enter antibonding levels, and if two electrons are added, the pattern of levels associated with the bent nitrosyl case is expected to apply. In fact this occurs in the net chemical reaction in eq 6[22] which in the formal sense involves donation

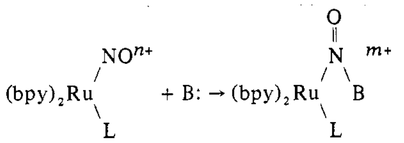
$$(bpy)_2Ru(NO)Cl^{2+} + 2OH^- \rightarrow (bpy)_2Ru(NO_2)Cl + H_2O \qquad (6)$$

of an electron pair from O^{2-} to the nitrosyl group. In the nitrite product, the RuNO bond angle is expected to be ~120°. The pattern of levels associated with the bent nitrosyl case is appropriate for a nitrite product since $d\pi$–π^*(bpy) CT bands appear and a Ru(II) → Ru(III) oxidation occurs in the potential range expected.[28]

Addition of a single electron probably leads to a case somewhere between the two extremes in Figure 5. The available evidence for the related ions $[Fe(CN)_5NO]^{3-}$ and $[Fe(das)_2(NO)X]^+$ (X = Cl, Br; das is *o*-phenylenebis(dimethylarsine)) indicates that the Fe–NO linkages are significantly bent.[2] The low ν(NO) values and greatly decreased $3d_{5/2}$ binding energy for the salt $[(bpy)_2Ru(NO)Cl]I$ are consistent with a bending of RuNO and destabilization of the $d\pi$ levels. However, both the absence of well-defined $d\pi$–π^*(bpy) bands, as found for example in the nitrite complexes, and the EPR data are consistent with the ordering of levels given for the linear case where the unpaired electron is in a level largely π^*(NO) in character.

Viewing the reduced complexes as containing Ru^{II}–$\dot{N}O$ may be useful in terms of predicting chemical reactivity. However, as in other cases, where the use of simple oxidation-state formalisms is troubling, a detailed and intuitively satisfying picture of electronic structure remains elusive.

Reactivity of the Nitrosyl Group. The ability of the bis(2,2′-bipyridyl)ruthenium nitrosyl complexes to undergo relatively facile reactions with OH^-,[22] N_3^-,[38] and aromatic amines[10,11] probably depends on two factors. Competitive back-bonding with bipyridine decreases the $d\pi$–π^*(NO) interaction sufficiently so that the nitrosyl group retains a considerable amount of nitrosonium ion character. The nitrogen atom of the nitrosyl group remains electron deficient and provides a site for a Lewis acid–base interaction (eq 7)



$$(bpy)_2Ru(NO^{n+})(L) + B: \rightarrow (bpy)_2Ru(N(=O)B)(L)^{m+} \qquad (7)$$

which is probably the initial step in much of the net chemistry observed. It is also important that the acceptance of an electron pair by the nitrosyl group can be accommodated without gross structural changes in the complex, except at the nitrogen atom.

Electron transfer to the nitrosyl group is formally a related process in which the added electron enters a largely ligand-based level. The barrier to electron transfer must be low since couples like $[(bpy)_2Ru(NO)Cl]^{2+/+}$ are electrochemically reversible.

The rate of reaction 8 was studied in acetonitrile using the

$$[(bpy)_2RuCl_2] + [(bpy)_2Ru(NO)(CH_3CN)]^{3+} \xrightarrow{k_{12}} [(bpy)_2RuCl_2]^+ + [(bpy)_2Ru(NO)(CH_3CN)]^{2+} \qquad (8)$$

$\Delta\mathcal{E} = 0.26$ V

stopped-flow technique. Assuming that the reaction is first order in each reactant gives a lower limit for k_{12} at 25 °C of 10^6 M^{-1} s^{-1}. Using the Marcus cross-reaction equation (eq 9) and neglecting the f factor which should be small[39] allows

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (9)$$

an estimate to be made for the rate constant for the $[(bpy)_2Ru(NO)(CH_3CN)]^{3+/2+}$ self-exchange reaction (k_{11}). The self-exchange rate for $[(bpy)_2RuCl_2]^{+/0}$ is $\sim 10^5$ M^{-1} s^{-1} in CH_3CN,[40] and using that value and $K_{12} = 2.5 \times 10^4$ gives $k_{11} \geq 4 \times 10^2$ M^{-1} s^{-1}. From the infrared experiment described earlier, k_{11} for the couple $[(bpy)_2Ru(NO)Cl]^{2+/+}$ is ≥ 20 M^{-1} s^{-1}.

Only lower limits are available for the self-exchange rates, but it appears that electron transfer based on the nitrosyl group is relatively facile. The low barrier to electron exchange is consistent with only minor structural differences between the nitrosyl and reduced nitrosyl complexes.

It is worth noting that some of the nitrosyl complexes are moderately strong oxidants. The Ru(III) complex $[(bpy)_2RuCl_2]^+$ is less strongly oxidizing than $[(bpy)_2Ru(NO)(CH_3CN)]^{3+}$ by ~0.3 V. The low reorganizational barrier to electron transfer, the strengths of the reagents as oxidants, and the ability to vary $E_{1/2}$ by variations in the cis ligand may make the nitrosyl complexes and related reagents useful chemical oxidants.

Photochemistry. Wolfe and Swinehart have recently examined the photochemistry of the nitroprusside ion.[41] The complex was observed to undergo the photoreaction

$$[Fe^{II}(CN)_5(NO^+)]^{2-} + H_2O \xrightarrow[\substack{366\text{ nm}\\ \text{or}\\ 436\text{ nm}}]{} [Fe^{III}(CN)_5H_2O]^{2-} + NO$$

In the formal sense, the reaction involves net electron transfer from the metal to the nitrosyl group. The authors suggested a mechanism whereby excitation of a $t_2 \rightarrow \pi^*$(NO) transition (~400 nm) resulted in the expulsion of nitric oxide.

The photoreaction of the formally isoelectronic ruthenium nitrosyl complex $[(bpy)_2Ru(NO)Cl]^{2+}$ (eq 10) is entirely

$$[(bpy)_2Ru^{II}(NO^+)Cl]^{2+} + CH_3CN \xrightarrow[313\text{ nm}]{} [(bpy)_2Ru^{III}(CH_3CN)Cl]^{2+} + NO \qquad (10)$$

analogous except that the reaction was carried out in acetonitrile. No evidence has been obtained to suggest a detailed mechanism for the photoreaction. It is certainly conceivable that the same mechanism occurs in the ruthenium nitrosyl photoreaction as in the nitroprusside reaction due to the similarities of the two complexes. However, since the $t_2 \rightarrow \pi^*$(NO) transitions are apparently obscured by the more intense $\pi \rightarrow \pi^*$(bpy) and $t_2 \rightarrow \pi^*$(bpy) transitions, an interpretation of the photochemical results for the ruthenium complex in terms of the excited state or states involved is more difficult.

Solutions of $[(bpy)_2Ru(NO)Cl]^{2+}$ photolyzed in argon-saturated acetonitrile produced both $[(bpy)_2Ru^{II}(CH_3CN)Cl]^+$ and $[(bpy)_2Ru^{III}(CH_3CN)Cl]^{2+}$ in a ratio of ~1:3 as estimated from the electronic spectra of the complexes. Solutions of the nitrosyl complex photolyzed in air-saturated acetonitrile or photolyzed under a vacuum produced only $[(bpy)_2Ru^{III}(CH_3CN)Cl]^{2+}$. A possible explanation is that the back-reaction

$$NO + [(bpy)_2Ru^{III}(CH_3CN)Cl]^{2+} \rightarrow [(bpy)_2Ru^{II}(CH_3CN)Cl]^+ + NO^+$$

may occur unless the evolved NO is removed from solution by reaction with O_2 or by removal under vacuum. Bubbling NO through acetonitrile solutions of $[(bpy)_2Ru^{III}(CH_3CN)Cl]^{2+}$ did result in generation of some of the Ru(II) product. More quantitative studies are clearly needed in order to fully explain the observed behavior.

The photoreaction provides a useful synthetic route for the preparation of $[(bpy)_2Ru^{III}(CH_3CN)Cl](PF_6)_2$ (see Experimental Section). The reaction time is relatively short (~1 h for millimolar solutions), and the product can be produced cleanly under the appropriate conditions. By using other ruthenium(II) nitrosyl complexes, the photoreaction should be adaptable for the synthesis of a variety of Ru(III) complexes.

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Registry No. $[(bpy)_2Ru(NO)N_3](PF_6)_2$, 61278-44-2; $[(bpy)_2Ru(NO)Cl](PF_6)_2$, 29102-12-3; $[(bpy)_2Ru(NO)Cl]I$, 54866-03-4; $[(bpy)_2Ru(NO)NO_2](PF_6)_2$, 29240-99-1; $[(bpy)_2Ru(NO)NH_3](PF_6)_3$, 61278-45-3; $[(bpy)_2Ru(NO)py](PF_6)_3$, 29241-00-7; $[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_3$, 61303-15-9; $[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_2$, 61303-16-0; $(bpy)_2RuCl_2$, 15746-57-3.

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Contribution from the Departments of Chemistry, University of Massachusetts, Boston, Massachusetts 02125,
University of Vermont, Burlington, Vermont 05401, and University of Massachusetts, Amherst, Massachusetts 01002

Paramagnetic Complexes Produced in the Electrochemical and Chemical Reduction of Cyclopentadienyl–Cobalt– and –Rhodium–Cyclopentadienone Complexes

HANS van WILLIGEN, WILLIAM E. GEIGER, Jr.,* and MARVIN D. RAUSCH

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The reduction of π-tetraphenylcyclopentadienone–π-cyclopentadienyl complexes of cobalt and rhodium has been studied by electrochemical methods and by electron spin resonance spectroscopy. All of the compounds studied undergo a reversible one-electron reduction, but only the cobalt compounds gave anions stable enough to allow ESR studies. Frozen solutions of $CpCo(tpc)^-$ and the anion radical of π-tetrakis(pentafluorophenyl)cyclopentadienone(π-cyclopentadienyl)cobalt, $[(f\text{-}tpc)CoCp]^-$, show highly anisotropic nonaxial ESR spectra. The ESR data as well as the electrochemical potentials are consistent with a high degree of metal character in the orbital involved in the reduction, leading to the designation of the reduced complexes as having the d^9 electron configuration, Co(0) and Rh(0). All of the complexes studied undergo further electrochemical reductions to uncharacterized products.

Introduction

Redox properties of organometallic π complexes have been increasingly investigated in recent years, and one of the major questions to be answered in such studies concerns the relative contributions of the metal and ligand moieties to the redox orbital.[1-3] Complexes involving ligands which can be isolated and hence be subjected to separate redox studies are especially attractive, and considerable efforts have been made to judge the metal vs. ligand contributions in molecules of this type.[4-6]

A group of complexes which seemed nicely amenable to such a study involved tetraphenylcyclopentadienone (Ph_4C_5O, I, tpc) and tetrakis(pentafluorophenyl)cyclopentadienone ($(Ph_F)_4C_5O$,

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* To whom correspondence should be addressed at the University of Vermont.