Oxidation of Coordinated Diamines in Bis(2,2'-bipyridine) Complexes of Ruthenium

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A series of diaminebis(2,2'-bipyridine) complexes of ruthenium(II), e.g., [Ru(bipy)2(en)]$^{2+}$, has been prepared and the spectral and redox properties were investigated. The ethylenediamine and *trans*-1,2-diaminocyclohexane complexes undergo net four-electron oxidations, either chemically or electrochemically, giving the corresponding α,α'-diimine complexes. The chemical and spectral properties of the α,α'-diimine complexes are similar to those of [Ru(bipy)3]$^{2+}$. Complexes containing 2-(aminomethyl)pyridine and 1,2-diamino-2-methylpropane undergo net two-electron oxidations, in which the single CH2–NH2 linkage has undergone oxidative dehydrogenation to the imine. Electrochemical and titrimetric data (using Ce(IV)) in acetonitrile show that the diamine oxidative dehydrogenation reactions are initiated by oxidation of ruthenium(II) to ruthenium(III), and that the reactions probably occur in a stepwise manner via monoimine intermediates.

Introduction

Metal ions have been found to catalyze the oxidative dehydrogenation of coordinated amines to imines. The oxidation of macrocyclic amine complexes to imine complexes was investigated by Curtis[1] and Busch et al.,[2] and their studies have provided some insight into the mechanism of oxidative dehydrogenation. It was observed that the macrocyclic amine complexes of Ni^{2+}, Cu^{2+}, and Fe^{2+} undergo oxidative dehydrogenation whereas the complexes of Co^{3+} are resistant to oxidation. This indicated that the net reaction involved prior oxidation of the metal ion followed by oxidation of the ligand and reduction of the metal ion.

Elsbernd and Beattie[3] reported that [Ru^{II}(en)3]$^{2+}$ (en is ethylenediamine) undergoes a net four-electron oxidation, and Lane, Lester, and Basolo[4] showed that the reaction involved oxidative dehydrogenation of ethylenediamine to give an α,α'-diimine (dim) complex of Ru(II)

$$(1)$$
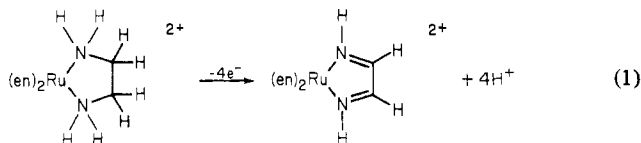
Mahoney and Beattie[5] have since reported that [Ru(phen)2(en)]$^{2+}$ undergoes a four-electron oxidation giving [Ru(phen)2(dim)]$^{2+}$. They also found Ru(III) intermediates in the oxidations of both [Ru(phen)2(en)]$^{2+}$ and [Ru(en)3]$^{2+}$. Similar oxidative dehydrogenation reactions have been observed for diamine complexes of tetracyanoferrate(II);[6] isolation of the tetracyanoethylenediamineiron(III) ion demonstrated the intermediacy of Fe(III) in the net reaction.

We have become interested in redox processes involving coordinated ligands, and in how such processes are affected by a variety of molecular features.[7-10] As part of this interest, we have studied the oxidation of a series of diaminebis(2,-2'-bipyridine)ruthenium(II) complexes. In the study, evidence has been found which indicates that the oxidative dehydrogenation reactions proceed in a stepwise manner through Ru(III) intermediates.

Experimental Section

Measurements. Ultraviolet–visible spectra were obtained on Cary Model 14, Cary Model 17, or Unicam Model SP-800B spectrophotometers. Molar extinction coefficients were determined from absorbance measurements on three or more concentrations. Absorbances were checked on a Gilford Model 240 spectrometer. Infrared spectra were obtained using a Perkin-Elmer Model 421 spectrometer or a Digilab Model FTS-14 interferometer. ^{1}H NMR spectra were obtained on a Jeol C-60-HL spectrometer, using D2O solutions with *t*-BuOH as an internal reference.

All electrochemical measurements were made vs. the saturated

sodium chloride calomel electrode (SSCE) at 25 ± 2°C, and are uncorrected for junction potentials. All potentials reported are reduction potentials vs. the SSCE. Potential control for electrochemical experiments was obtained with a Princeton Applied Research Model 173 Potentiostat/Galvanostat. The waveform generator for voltammetric experiments was a Princeton Applied Research Model 175 Universal Programmer. Voltammograms and slow scan cyclic voltammograms were recorded on a Hewlett-Packard Model 7004B X–Y recorder. Fast scan cyclic voltammograms were obtained from photographs of the trace of a Tektronix Model 564B storage oscilloscope. Values of *n*, where *n* is the total number of equivalents of electrons transferred in exhaustive electrolyses at constant potentials, were calculated after measuring the total area under current vs. time curves for the complete reaction. Reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurements were carried out at platinum electrodes in solutions deaerated with a stream of dry, prepurified nitrogen. Platinum electrodes were cleaned by the procedure recommended by Adams.[11] Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.
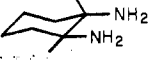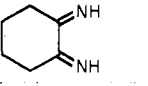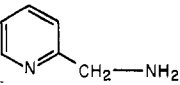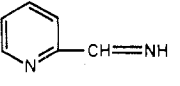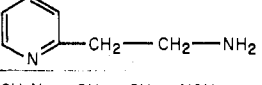
Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[12] recrystallized three times from hot ethanol–water mixtures, and vacuum dried at 80°C for 12 hr. Acetonitrile (MCB Spectrograde) was dried over Davison 4 Å molecular sieves for electrochemical measurements and used without drying for spectral measurements. Water was deionized and then distilled from alkaline permanganate. The ligands ethylenediamine, *trans*-1,2-diaminocyclohexane, 1,3-propylenediamine, 1,2-diamino-2-methylpropane, 2-(2'-aminoethyl)pyridine, and 2-(aminomethyl)pyridine were purchased commercially and used without further purification. (A list of the ligands used in this study, as well as their formulas and abbreviations, is given in Table I). The complexes [Ru(bipy)2Cl2]·2H2O,[13] [Ru(bipy)3](ClO4)2,[14] and [Ru(bipy)2-(NH3)2](ClO4)2·3H2O[15] were prepared as previously described. All other chemicals were commercially available in reagent quality and were used without further purification.

[Ru(bipy)2(LL)](ClO4)2 (LL = Ethylenediamine (en), *trans*-**1,2-Diaminocyclohexane (dach), 1,2-Diamino-2-methylpropane (damp), 2-(2'-Aminoethyl)pyridine (AEPy), and 2-(Aminomethyl)pyridine (AMPy)).** The diamine complexes were prepared by essentially the same procedure described for the preparation of the complexes [Ru(bipy)2(en)](ClO4)2[15] and [Ru(phen)2(en)]I2·2H2O.[16] The complex [Ru(bipy)2Cl2]·2H2O (0.50 g) was suspended in a 1:1 (by volume) water–methanol solution (30 ml) of the ligand (3 g). The mixture was heated at reflux on a steam bath for 1 hr under an atmosphere of nitrogen. The condenser was removed and the methanol was boiled off under a stream of nitrogen. The deep red solution was cooled and filtered. The filtrate was returned to the steam bath and warmed to 80–90°C. A saturated aqueous solution of NaClO4 was added dropwise to the warm solution until the onset of precipitation. Slow cooling to room temperature gave deep red crystals which were collected by suction filtration, washed with small portions of ice cold water and methanol, and air dried. The products could be recrystallized from hot water containing a small amount of NaClO4. Yields were 70% or greater.

Anal. Calcd for [Ru(bipy)2(en)](ClO4)2: C, 39.3; H, 3.60; N, 12.5. Found: C, 39.3; H, 3.71; N, 12.3. Calcd for [Ru(bipy)2-

* N. F. Curtis, *Chem. Commun.*, 881 (1966); *Coord. Chem. Rev.*, **3**, 3 (1968).

Table I. Abbreviations and Chemical Formulas for Amine and Imine Ligands

Ligand	Formula	Abbreviation
Ethylenediamine	H_2N—CH_2—CH_2—NH_2	en
1,2-Diiminoethane	HN=CH—CH=NH	dim
trans-1,2-Diamino-cyclohexane	[structure with NH₂, NH₂]	dach
1,2-Diiminocyclo-hexane	[structure with NH, NH]	dich
1,2-Diamino-2-methylpropane	[structure: CH₃, NH₂—C—CH₂—NH₂, CH₃]	damp
2-Amino-2-methyl-propanalimine	[structure: CH₃, CH₃—C—CH=NH, NH₂]	iamp
1,3-Propylenedi-amine (trimethyl-enediamine)	NH_2—CH_2—CH_2—CH_2—NH_2	tn
2-(Aminomethyl)-pyridine	[pyridine structure with CH_2—NH_2]	AMPy
2-(Iminomethyl)-pyridine	[pyridine structure with CH=NH]	IMPy
2-(2'-Aminoethyl)-pyridine	[pyridine structure with CH_2—CH_2—NH_2]	AEPy
Glyoxalbismethyl-imine	CH_3N=CH—CH=NCH_3	GMI

Table II. Half-Wave Potentials and Electronic Spectra for Diaminebis(2,2'-bipyridine)ruthenium(II) Complexes in Acetonitrile

Compd	$E_{1/2}$, V[a]	λ_{max}, nm (ϵ)[b]
$Ru(bipy)_2(NH_3)_2{}^{2+}$	0.92	490 (9300)
		345 (7600)
		290 (54000)
		243 (20000)
$Ru(bipy)_2(en)^{2+}$	0.96	485 (9900)
		344 (7600)
		291 (60000)
		243 (21000)
$Ru(bipy)_2(dach)^{2+}$	0.96	488 (9900)
		344 (7600)
		292 (58000)
		244 (21000)
$Ru(bipy)_2(damp)^{2+}$	0.99	487 (10000)
		345 (7600)
		292 (58000)
		244 (21000)
$Ru(bipy)_2(tn)^{2+}$	~0.98	492 (8500)
		348 (6600)
		292 (52000)
		244 (18000)
$Ru(bipy)_2(AMPy)^{2+}$	1.12	471 (10000)
		422 (sh) (6300)
		339 (11000)
		298 (55000)
		244 (23000)
$Ru(bipy)_2(AEPy)^{2+}$	1.12	471 (9000)
		425 (sh) (5600)
		338 (9700)
		289 (54000)
		243 (23000)

[a] $E_{1/2}$ values vs. the saturated sodium chloride calomel electrode (SSCE) in 0.1 M N(n-C_4H_9)$_4$PF$_6$ at 25 ± 2°C. [b] λ_{max} values ± 2 nm; ϵ values ±5%.
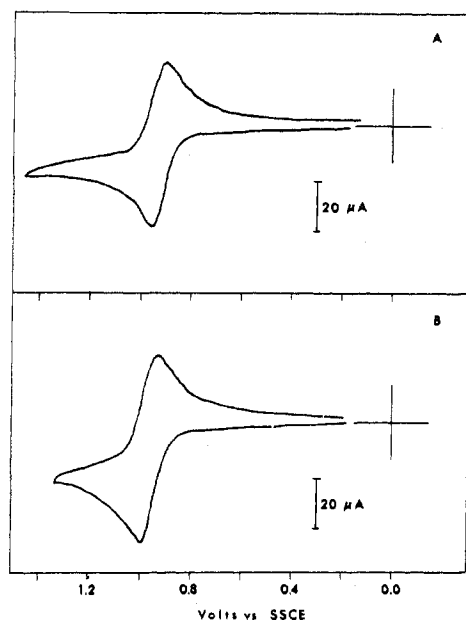
[Ru(bipy)2(damp)]³⁺/²⁺ couple (0.99 V).

Conversion of perchlorate or hexafluorophosphate salts of the above cations to the chloride salt for ¹H NMR measurements was achieved by precipitation (using tetra-*n*-butylammonium chloride) from acetone solution.

Spectrophotometric Titrations with Ce(IV). Some of the oxidative dehydrogenation reactions were studied by spectrophotometric titrations in 0.1 M aqueous HClO₄ and acetonitrile solutions, using Ce(IV) as oxidant. The concentration of Ce(IV) was determined spectrophotometrically,[17] and the solutions were used immediately and protected from the light. Titrations were carried out by adding aliquots of oxidant to solutions of the complex, and monitoring the changes in absorbance in the range 600–320 nm. Some of the reactions studied required rapid mixing of the ruthenium and Ce(IV) solutions, which was accomplished by using a hand-driven device patterned after a stopped-flow syringe drive train.
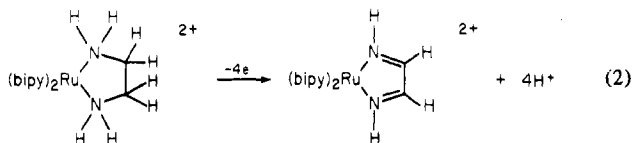
Results and Discussion

Net Electrochemical Oxidation of Bound Diamine Ligands. The complex [Ru(bipy)₂(NH₃)₂]²⁺ undergoes an electrochemically reversible one-electron oxidation at a platinum electrode in acetonitrile, as shown by the cyclic voltammogram in Figure 1A. Under the same experimental conditions, the complex [Ru(bipy)₂(en)]²⁺ also undergoes an electrochemically reversible one-electron oxidation on the cyclic voltammetry time scale (Figure 1B).[18] The similarity in reduction potentials for the series of diamine complex 3+/2+ couples studied and that for the [Ru(bipy)₂(NH₃)₂]³⁺/²⁺ (Table II) indicates that this oxidation occurs in all cases at the ruthenium.

Exhaustive electrolysis of acetonitrile solutions of [Ru(bipy)₂(en)]²⁺ at a constant potential (1.15 V) on the diffusion plateau for the voltammetric wave gave a coulometric n value of 3.82. The product of the electrolytic oxidation was identified by spectral and electrochemical measurements (see below) as the α,α'-diimine complex, [Ru(bipy)₂(dim)]²⁺. The net

(dach)](ClO₄)₂: C, 43.0; H, 4.16; N, 11.6. Found: C, 43.0; H, 4.00; N, 11.4. Calcd for [Ru(bipy)₂(damp)](ClO₄)₂: C, 41.2; H, 4.03; N, 12.0. Found: C, 41.0; H, 3.95; N, 11.9. Calcd for [Ru-(bipy)₂(AEPy)](ClO₄)₂: C, 44.2; H, 3.57; N, 11.4. Found: C, 43.9; H, 3.45; N, 10.8. Calcd for [Ru(bipy)₂(AMPy)](ClO₄)₂: C, 43.3; H, 3.36; N, 11.7. Found: C, 43.5, H, 3.28; N, 11.5.

[Ru(bipy)₂(tn)](PF₆)₂·2H₂O (tn = 1,3-Propylenediamine). The complex was prepared as described above. The salt was precipitated by the addition of a filtered aqueous solution of NH₄PF₆ to a filtered, aqueous solution of the complex. The product was purified by re-precipitation from acetone–ether and vacuum dried overnight.

Anal. Calcd for [Ru(bipy)₂(tn)](PF₆)₂·2H₂O: C, 34.0; H, 3.72; N, 10.3. Found: C, 33.1; H, 3.06; N, 10.6.

[Ru(bipy)₂(LL)](PF₆)₂ (LL = 1,2-Ethylenediimine (dim), 1,2-Diiminocyclohexane (dich), 2-(Iminomethyl)pyridine (IMPy)). The corresponding diaminebis(bipyridine)ruthenium(II) complex (100 mg) was dissolved in 1.0 M aqueous HCl (30 ml). The solution was oxidized by exhaustive electrolysis at constant potential which was anodic of $E_{1/2}$. It is essential that the potentials not be made so anodic that the desired diimine products are oxidized. Electrolysis was continued until the current had fallen to about 1% of the initial current. The product was precipitated from solution by the addition of a filtered, saturated, aqueous solution of NH₄PF₆ (2 ml). The product was purified by reprecipitation from acetone–ether.

Anal. Calcd for [Ru(bipy)₂(dim)](PF₆)₂: C, 34.8; H, 2.65; N, 11.1; F, 30.0. Found: C, 34.7; H, 2.75; N, 10.9; F, 29.8. Calcd for [Ru(bipy)₂(dich)](PF₆)₂·2H₂O: C, 36.8; H, 3.56; N, 9.9; F, 26.8. Found: C, 36.9; H, 3.26; N, 9.9; F, 26.6. Calcd for [Ru(bipy)₂-(IMPy)](PF₆)₂: C, 38.6; H, 2.75; N, 10.4; F, 28.2. Found: C, 38.3; H, 2.68; N, 10.3; F, 28.0.

[Ru(bipy)₂(iamp)]²⁺ (iamp = 2-Amino-2-methylpropanalimine). This complex was prepared in situ and not isolated. Attempts to isolate salts of the complex failed to give a pure material. Solutions of the complex were prepared from solutions of [Ru(bipy)₂(damp)]²⁺ in 0.1 M TBAH–CH₃CN by exhaustive electrolysis at the $E_{1/2}$ of the

Figure 1. Cyclic voltammograms (200 mV/sec) of (A) [Ru-(bipy)$_2$(NH$_3$)$_2$]$^{2+}$ (1.0 × 10^{-3} M), and (B) [Ru(bipy)$_2$(en)]$^{2+}$ (1.2 × 10^{-3} M) in acetonitrile solution (0.1 M TBAH).
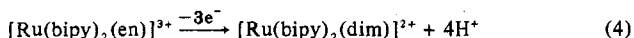
stoichiometry of the oxidation is given by eq 2.

The oxidation process thus consists of two parts: initial oxidation of the metal to Ru(III)

$$[Ru(bipy)_2(en)]^{2+} \xrightarrow{-e^-} [Ru(bipy)_2(en)]^{3+} \quad (3)$$

followed by oxidation of the coordinated ligand

$$[Ru(bipy)_2(en)]^{3+} \xrightarrow{-3e^-} [Ru(bipy)_2(dim)]^{2+} + 4H^+ \quad (4)$$
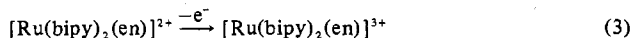
In acetonitrile, for [Ru(bipy)$_2$(en)]$^{2+}$, and also for [Ru(bipy)$_2$(dach)]$^{2+}$, the initial one-electron oxidation is faster than the subsequent oxidation of the ligand. At slow voltammetry scan rates (0.2 V/sec), recapture of [Ru(bipy)$_2$(en)]$^{3+}$ by reduction at the electrode is more rapid than ligand oxidation, and the voltammetric waves are reversible.

In aqueous solution (1.0 M HCl or 1.0 M NaCl), electrochemical oxidation of [Ru(bipy)$_2$(en)]$^{2+}$ (or [Ru(bipy)$_2$(dach)]$^{2+}$) at a Pt electrode was irreversible, even by fast cyclic voltammetry (100 V/sec). Exhaustive electrolysis at 0.80 V (vs. SSCE) in 1.0 M HCl gave the corresponding α,α'-diimine complexes quantitatively and provided a convenient synthetic route to these complexes.

The ligand 2-(aminomethyl)pyridine (AMPy) contains one imine (pyridine) and one amine nitrogen atom, so that the α,α'-diimine linkage is half present initially. Exhaustive electrolysis of [Ru(bipy)$_2$(AMPy)]$^{2+}$ in acetonitrile at a potential on the diffusion plateau for oxidation (1.20 V) gave a coulometric n value of 1.96 and the α,α'-diimine complex as the sole product:
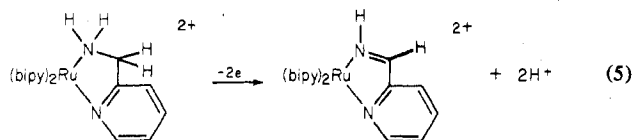
Cyclic voltammetry of [Ru(bipy)$_2$(AMPy)]$^{2+}$ at slow scan rates was irreversible, but at faster scan rates (≥5 V/sec) the
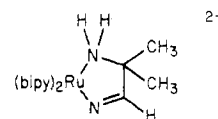
Table III. Half-Wave Potentials and Electronic Spectra of Diiminebis(2,2'-bipyridine)ruthenium(II) Complexes in Acetonitrile

Compd	$E_{1/2}$, V^a	λ_{max}, nm (ϵ)^b
Ru(bipy)$_3$$^{2+}$	1.29	450 (14000)
		283 (80000)
		242 (25000)
Ru(bipy)$_2$(dim)$^{2+}$	1.33	454 (14000)
		280 (46000)
		242 (17000)
Ru(bipy)$_2$(dich)$^{2+}$	1.20	472 (16000)
		285 (48000)
		242 (18000)
Ru(bipy)$_2$(iamp)$^{2+}$	1.06	475 (9000)
		335 (9100)
Ru(bipy)$_2$(IMPy)$^{2+}$	1.27	470 (13000)
		430 (sh)
		345 (sh)
		315 (sh)
		286 (51000)
		245 (18000)
		242 (20000)

^{a} Vs. the SSCE in 0.1 M N(n-C$_4$H$_9$)$_4$PF$_6$ at 25 ± 2°C. ^{b} λ_{max} values are ±2 nm; ϵ values ±5%.

cyclic voltammetric data were consistent with a reversible one-electron oxidation. Since the [Ru(bipy)$_2$(AMPy)]$^{3+/2+}$ potential (1.12 V) is higher than the potentials of the diamine complexes, the Ru(III) complex would be more strongly oxidizing and a higher rate of ligand oxidation (e.g., eq 4) is not unexpected.

The ligand 1,2-diamino-2-methylpropane (damp) has a skeletal framework similar to ethylenediamine, but oxidative dehydrogenation can only occur at one –CH$_2$–NH$_2$ group, leading to a coordinated monoimine. Cyclic voltammetry in acetonitrile solution shows that [Ru(bipy)$_2$(damp)]$^{2+}$ undergoes an electrochemically reversible one-electron oxidation. Exhaustive electrolysis at $E_{1/2}$ gave an n value of 1.76 and near-quantitative conversion to a single product whose redox and spectral properties are consistent with a monoimine complex.

When electrolysis was carried out at potentials more anodic than $E_{1/2}$, further oxidation processes, involving the ion [Ru(bipy)$_2$(iamp)]$^{2+}$, occurred. The electrochemical oxidation of [Ru(bipy)$_2$(damp)]$^{2+}$ in aqueous solution was completely irreversible, and attempts to prepare the monoimine complex [Ru(bipy)$_2$(iamp)]$^{2+}$ by exhaustive electrolysis were frustrated by competitive processes involving oxidation of bound iamp. In both these cases, it is apparent that both [Ru(bipy)$_2$(damp)]$^{2+}$ and [Ru(bipy)(iamp)]$^{2+}$ are oxidizable, and that the oxidation rates are comparable. Because of the further ligand oxidation, a possible complicating reaction here, and in related systems, is bimolecular electron transfer giving the Ru(III) form of the ligand-oxidized complex,

$$[Ru(bipy)_2(damp)]^{3+} + [Ru(bipy)_2(iamp)]^{2+} \rightleftharpoons$$
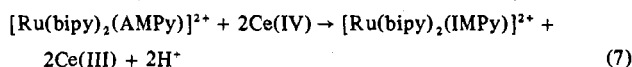$$[Ru(bipy)_2(damp)]^{2+} + [Ru(bipy)_2(iamp)]^{3+} \quad (6)$$

Equation 6 is an equilibrium in which the forward reaction is slightly disfavored thermodynamically (using $E_{1/2}$ data in Tables II and III). From rate data on other bis(2,2'-bipyridine)ruthenium(III)–(II) electron transfer reactions,[20] the forward reaction should still be rapid, and if followed by rapid Ru(III) ligand oxidation accounts for such phenomena as the dependence of products on rates of mixing with chemical oxidants and our inability to prepare imine complexes in such systems.

The ligands 1,3-propylenediamine (tn) and 2-(2'-amino-ethyl)pyridine (AEPy) contain one methylene group more than ethylenediamine and 2-(aminomethyl)pyridine, respectively, and hence cannot give conjugated α,α'-diimines upon oxidation. The complexes $[Ru(bipy)_2(tn)]^{2+}$ and $[Ru(bipy)_2$-$(AEPy)]^{2+}$ undergo electrochemically reversible one-electron oxidations in acetonitrile solutions, as determined by cyclic voltammetry. Exhaustive electrolyses on the diffusion plateaus of the oxidation waves gave high n values and a variety of products (as shown by cyclic voltammetry), consistent with oxidation past the imine stage.
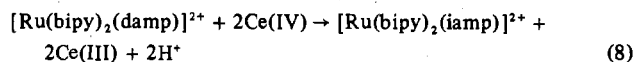
Oxidations by Ce(IV). Spectrophotometric Titrations. The oxidative dehydrogenation reactions could also be carried out chemically using Ce(IV). The Ce(IV) oxidations were studied by spectrophotometric titrations.

The spectrophotometric titration of $[Ru(bipy)_2(AMPy)]^{2+}$ with Ce(IV) in either acetonitrile or 0.1 M aqueous HClO$_4$ gave a smooth conversion to $[Ru(bipy)_2(IMPy)]^{2+}$ (isosbestic points at 388 and 513 nm) with the stoichiometry given in eq 7. The addition of more than 2 equiv of Ce(IV) per mole of

$$[Ru(bipy)_2(AMPy)]^{2+} + 2Ce(IV) \rightarrow [Ru(bipy)_2(IMPy)]^{2+} +$$
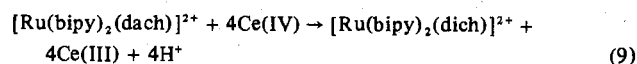$$2Ce(III) + 2H^+ \tag{7}$$

ruthenium did not give a smooth conversion to the imine product. It appears that further oxidation of the ligand occurs, giving products which we have not characterized.

The oxidation of $[Ru(bipy)_2(damp)]^{2+}$ with Ce(IV) in acetonitrile led to the formation of $[Ru(bipy)_2(iamp)]^{2+}$, with the stoichiometry given in eq 8. The reactions were clean only

$$[Ru(bipy)_2(damp)]^{2+} + 2Ce(IV) \rightarrow [Ru(bipy)_2(iamp)]^{2+} +$$
$$2Ce(III) + 2H^+ \tag{8}$$

if the Ce(IV) and ruthenium solutions were mixed rapidly and 1 mol or less of Ce(IV) was added per mole of ruthenium. If these conditions were met, isosbestic points were observed at 477, 379, and 360 nm, and the observed spectra were consistent with the sums of the spectra of $[Ru(bipy)_2(damp)]^{2+}$ and $[Ru(bipy)_2(iamp)]^{2+}$ in the ratios expected from the stoichiometry given in eq 8. These results are understandable if the reaction of Ce(IV) with $[Ru(bipy)_2(damp)]^{2+}$ is faster than the oxidative dehydrogenation reaction, and the rate of further ligand oxidation of $[Ru(bipy)_2(iamp)]^{2+}$ is competitive with the initial oxidative dehydrogenation. The Ce(IV) oxidation of bis(2,2'-bipyridine)ruthenium(II) complexes is known to be very rapid.[20]

Titration of $[Ru(bipy)_2(dach)]^{2+}$ with Ce(IV) indicated a 4:1 stoichiometry with the formation of $[Ru(bipy)_2(dich)]^{2+}$, eq 9. Addition of 4 mol of Ce(IV) per mole of ruthenium

$$[Ru(bipy)_2(dach)]^{2+} + 4Ce(IV) \rightarrow [Ru(bipy)_2(dich)]^{2+} +$$
$$4Ce(III) + 4H^+ \tag{9}$$

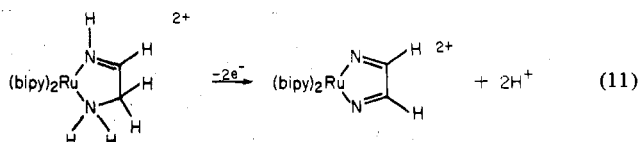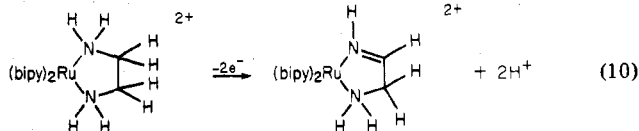gave a spectrum identical with that of an analyzed sample of $[Ru(bipy)_2(dich)]^{2+}$ prepared electrochemically. An isosbestic point occurred at 380 nm for all additions up to 4 mol of Ce(IV) per mole of ruthenium. However, the lack of an isosbestic point in the region of the 472-nm absorbance of $[Ru(bipy)_2(dich)]^{2+}$ and the 488-nm absorbance of $[Ru(bipy)_2(dach)]^{2+}$ indicated interference in this region from a third species. The likely explanation of this combination of observations is that an intermediate exists which contains one imine and one amine linkage. The addition of more than 4 mol of Ce(IV) per mole of ruthenium leads to complicated product spectra, probably due to the further oxidation of the α,α'-diimine ligand. The data indicate that the oxidative dehydrogenation leading to $[Ru(bipy)_2(dich)]^{2+}$ is faster than further oxidation of the coordinated dich ligand.

Spectrophotometric titrations of the complex $[Ru-(bipy)_2(en)]^{2+}$ with Ce(IV) were extremely complicated. The

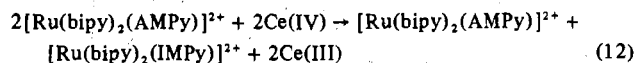data indicate that complications arise both from competitive further oxidation of the product, $[Ru(bipy)_2(dim)]^{2+}$, and from the interference of a species containing a half-oxidized ligand, with a single imine linkage ($HN\!=\!CHCH_2NH_2$).

Mechanism of Oxidative Dehydrogenation. These studies indicate that the diamine ligand oxidation, reaction 4, can be further broken down into two stepwise processes, the first involving oxidation to a monoimine intermediate (eq 10), and
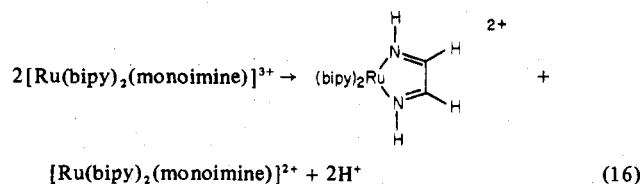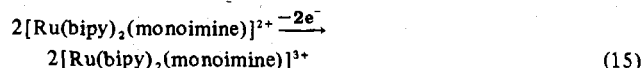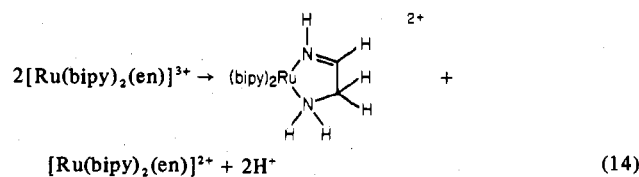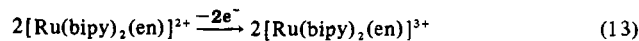
$$\tag{10}$$

$$\tag{11}$$

the second involving oxidation of the monoimine to the α,α'-diimine (eq 11). Analogous equations could be written for the oxidative dehydrogenation of the dach ligand.
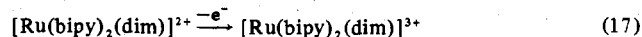
For the complexes $[Ru(bipy)_2(AMPy)]^{2+}$ and $[Ru-(bipy)_2(damp)]^{2+}$, only one of these two-electron steps is possible. On addition of a 1:1 stoichiometric quantity of Ce(IV) to a solution of either of these complexes, a clean oxidation occurs producing an equimolar mixture of the starting complex and the corresponding two-electron oxidation product, as indicated in eq 12 for the AMPy species:

$$2[Ru(bipy)_2(AMPy)]^{2+} + 2Ce(IV) \rightarrow [Ru(bipy)_2(AMPy)]^{2+} +$$
$$[Ru(bipy)_2(IMPy)]^{2+} + 2Ce(III) \tag{12}$$

From the instantaneous color changes observed on the addition of Ce(IV) to solutions of the diamine complexes (spectrophotometric titrations), preliminary kinetic studies on the Ce(IV) oxidation of $[Ru(bipy)_2(en)]^{2+}$ and $[Ru-(bipy)_2(AMPy)]^{2+}$,[20] and the electrochemical results, the initial step in the oxidation process involves oxidation of ruthenium(II) to ruthenium(III). Furthermore, in the Ce(IV) titration of $[Ru(bipy)_2(dach)]^{2+}$ there is clear evidence for an intermediate of a monoimine type. Detailed mechanistic information about the oxidative dehydrogenation step is not available. However, under conditions where stoichiometric amounts of oxidant are added, an overall pattern of *net* reactions can be written, and this is illustrated for $[Ru-(bipy)_2(en)]^{2+}$ below:

$$2[Ru(bipy)_2(en)]^{2+} \xrightarrow{-2e^-} 2[Ru(bipy)_2(en)]^{3+} \tag{13}$$

$$2[Ru(bipy)_2(en)]^{3+} \rightarrow (bipy)_2Ru \qquad + $$
$$[Ru(bipy)_2(en)]^{2+} + 2H^+ \tag{14}$$

$$2[Ru(bipy)_2(monoimine)]^{2+} \xrightarrow{-2e^-}$$
$$2[Ru(bipy)_2(monoimine)]^{3+} \tag{15}$$

$$2[Ru(bipy)_2(monoimine)]^{3+} \rightarrow (bipy)_2Ru \qquad + $$
$$[Ru(bipy)_2(monoimine)]^{2+} + 2H^+ \tag{16}$$

On further oxidation,

$$[Ru(bipy)_2(dim)]^{2+} \xrightarrow{-e^-} [Ru(bipy)_2(dim)]^{3+} \tag{17}$$

$$[Ru(bipy)_2(dim)]^{3+} \rightarrow \text{further ligand oxidation} \tag{18}$$

Figure 2. Infrared spectra (KBr pellets) of (A) [Ru(bipy)$_2$(en)]-(ClO$_4$)$_2$ and (B) [Ru(bipy)$_2$(dim)](PF$_6$)$_2$ in the regions 3400–2800 and 1650–1350 cm^{-1}.

In cases where eq 18 is sufficiently rapid, electron transfer as in eq 6 can occur giving a pathway for the depletion of the imine complexes by further ligand oxidation.

Electrochemical and Chemical Behavior of the Imine Complexes. The ruthenium(II) complexes of the α,α'-diimines reported here are stable for several hours in aqueous 1.0 M acid and in 0.1 M base solution. In neutral solution, the complexes showed little (if any) decomposition after several days. In acetonitrile solution, the complexes were also found to be unchanged after several days, even when unprotected from light.

The redox properties of the α,α'-diimine complexes were investigated by electrochemical techniques, both in aqueous solution and in acetonitrile. In aqueous solution, using 0.5 M p-toluenesulfonic acid (HTos) as the supporting electrolyte, cyclic voltammetry experiments show that the α,α'-diimine complexes [Ru(bipy)$_2$(dim)]$^{2+}$, [Ru(bipy)$_2$(dich)]$^{2+}$, and [Ru(bipy)$_2$(IMPy)]$^{2+}$, undergo electrochemically irreversible oxidations at a Pt electrode. However, in 0.1 M TBAH–CH$_3$CN, the complexes each undergo a reversible, or nearly reversible, one-electron oxidation at Pt, apparently involving the oxidation of Ru(II) to Ru(III).
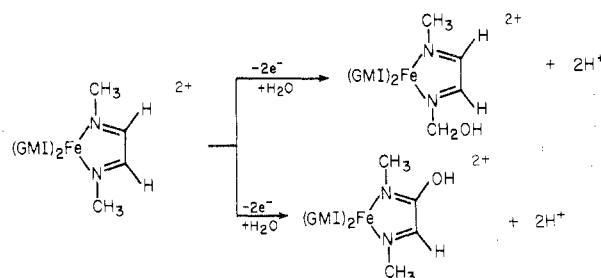
$$[\text{Ru}^{\text{II}}(\text{bipy})_2(\alpha,\alpha'\text{diimine})]^{2+} \xrightarrow{-e} [\text{Ru}^{\text{III}}(\text{bipy})_2(\alpha,\alpha'\text{-diimine})]^{3+}$$

At slow scan rates (0.2 V/sec), the ratio of the cathodic to anodic peak currents (i_c/i_a) is less than one in all cases. However, at faster scan rates (10 V/sec) the ratio of i_c/i_a is one and no additional waves appeared in the cyclic voltammograms, indicating that decomposition had not occurred. Exhaustive electrolysis at controlled potentials more positive than $E_{1/2}$ gave large n values; the products were not characterized. Apparently, the further oxidations result in the oxidation of the α,α'-diimine ligands.

Cyclic voltammetry of the α,α'-diimine complexes in 0.1 M TBAH–CH$_3$CN also shows an electrochemically irreversible reduction in addition to the usual 2,2'-bipyridine reductions which occur at more cathodic potentials.[21] The products of the reduction waves are apparently bound, reduced radical anions in which the reduction is localized mainly on an imine linkage. Reduction of [Ru(bipy)$_2$(dim)]$^{2+}$ by exhaustive

electrolysis gave a variety of products, as shown by cyclic voltammetry, and was not pursued further. Sodium borohydride reacts slowly with the α,α'-diimine complexes in either water or acetonitrile, but does not give well-defined products.

The α,α'-diimine complexes [Ru(bipy)$_2$(dim)]$^{2+}$, [Ru(bipy)$_2$(dich)]$^{2+}$, and [Ru(bipy)$_2$(IMPy)]$^{2+}$ have stability and chemical and physical properties reminiscent of [Ru(bipy)$_3$]$^{2+}$. On the cyclic voltammetry time scale the ruthenium(III) complexes [Ru(bipy)$_2$(α,α'-diimine)]$^{3+}$ are stable (the [Ru(bipy)$_2$(α,α'-diimine)]$^{3+/2+}$ couples are electrochemically reversible, or nearly reversible). However, on longer time scales, the ruthenium(III) complexes are unstable, apparently because of further oxidation processes involving the coordinated ligands. We have not investigated the subsequent reactions in detail. Chum and Krumholz[22] have investigated ligand oxidation reactions in iron(II) α,α'-diimine complexes like [Fe(GMI)]$^{2+}$ (GMI is CH$_3$—N=CH—CH=N—CH$_3$) and have found reactions such as,

The reactions of the α,α'-diimine ligands in the coordination sphere of the ruthenium complexes may be similar.

The subsequent α,α'-diimine oxidation presents a synthetic difficulty in the conversion of diamines into α,α'-diimines. It is essential that controlled-potential electrolysis methods be used to avoid oxidation of the α,α'-diimine complexes once formed. The reaction potentials for the α,α'-diimine (1.20 to 1.33 V, Table III) and diamine couples (0.96 to 0.99 V, Table II) are sufficiently different so that electrolyses can be carried out cleanly on the diffusion plateau of the [Ru(bipy)$_2$(diamine)]$^{3+/2+}$ wave.

Infrared Spectra. Infrared spectra were helpful in the characterization of the α,α'-diimine complexes.

The infrared spectra of the complexes [Ru(bipy)$_2$(en)]-(ClO$_4$)$_2$ and [Ru(bipy)$_2$(dim)](PF$_6$)$_2$ in the regions 3400–2800 and 1650–1350 cm^{-1} are illustrated in Figure 2. For the complex [Ru(bipy)$_2$(en)]$^{2+}$, the absorptions at 3315, 3280, and 3195 cm^{-1} can be assigned as N–H stretching vibrations ($\nu_{\text{N–H}}$). The absorption at 1618 cm^{-1} can be assigned as an N–H deformation ($\delta_{\text{N–H}}$). Upon oxidation to [Ru(bipy)$_2$-(dim)]$^{2+}$, the N–H stretching region simplifies to one absorption at 3325 cm^{-1}, as expected for an imine complex. Also as expected, the N–H deformation near 1600 cm^{-1} disappears for the imine complexes. A new absorption appears at 1480 cm^{-1} for the salt [Ru(bipy)$_2$(dim)](ClO$_4$)$_2$. A pure –C=N– stretching vibration would be expected to appear around 1600 cm^{-1}.[23,24] Nakamoto has carried out a normal coordinate analysis of the ion [Fe(GMI)$_3$]$^{2+}$, and has identified a band at 1530 cm^{-1} as a combination mode, which is made up predominantly of a –C=N– stretching vibration.[25] The band at 1480 cm^{-1} for [Ru(bipy)$_2$(dim)](ClO$_4$)$_2$ can reasonably be assigned to a combination mode consisting largely of the conjugated –C=N– stretch of the α,α'-diimine ligand ($\nu_{\text{C=N}}$). The characteristic $\nu_{\text{N–H}}$, $\delta_{\text{N–H}}$, and $\nu_{\text{C=N}}$ bands for some of the ruthenium(II) amine and α,α'-diimine complexes studied are summarized in Table IV. The C=N stretching mode could not be found for the complex [Ru(bipy)$_2$(IMPy)]$^{2+}$. There are many strong absorptions due to the bipyridine ligands in this region, and the band of interest may well be

Table IV. Infrared Spectra of Bis(2,2'-bipyridine)ruthenium(II) Amine and Imine Complexes

| Complex	ν(N–H)$_{as}$, cm^{-1}		ν(N–H)$_s$, cm^{-1}	δ(N–H), cm^{-1}	ν(C=N), cm^{-1}
[Ru(bipy)$_2$(en)](ClO$_4$)$_2$	3315	3280	3195	1618	
[Ru(bipy)$_2$(dim)](PF$_6$)$_2$	3325				1480
[Ru(bipy)$_2$(dach)](ClO$_4$)$_2$	3280	3252	3178	1615	
[Ru(bipy)$_2$(dich)](PF$_6$)$_2$	3300				1450
[Ru(bipy)$_2$(AMPy)](ClO$_4$)$_2$	3300	3267	3185	1615	
[Ru(bipy)$_2$(IMPy)](PF$_6$)$_2$	3322				

hidden. Also the intensity of the band may be diminished due to poor conjugation of the –C=N– group with the pyridine group. King and Douglas[23] observed that the –C=N– vibration was very weak in the monoalkylimine complex ((CH$_3$)$_2$C=NH)Cr(CO)$_5$.

¹H NMR Spectra. The ¹H NMR spectra of the imine complexes in D$_2$O solution were of limited use for characterization since the –N=CH resonance was hidden by the very complicated resonances due to the bipyridine ligands (δ = 7.0–9.0 ppm). The spectra were however consistent with the complex formulations given above; for example, the >CH$_2$ and –NH$_2$ resonances in [Ru(bipy)$_2$(en)]$^{2+}$ (centered at 2.8 and 3.5 ppm, respectively, relative to *t*-BuOH at 1.23 ppm) were absent in the spectrum of [Ru(bipy)$_2$(dim)]$^{2+}$.

Electrochemical and Electronic Spectral Data. Electronic spectra (absorption maxima and molar extinction coefficients) and half-wave potentials in acetonitrile solution are given in Table II for [Ru(bipy)$_2$(NH$_3$)$_2$]$^{2+}$ and for the diamine-bis(2,2'-bipyridine) complexes of ruthenium(II) studied here. In Table III, similar data are presented for [Ru(bipy)$_3$]$^{2+}$ and for the various imine complexes considered in this work.

Ruthenium(III)/ruthenium(II) reduction potentials are known to be dependent upon the presence of back-bonding ligands in the coordination sphere,[26–28] the potential increasing as the number of back-bonding ligands is increased. Qualitatively, this change in potential can be attributed to a stabilization of the ruthenium(II) oxidation state by increased back-bonding: back-bonding is thought to be insignificant between ruthenium(III) and pyridine-type ligands.[26] Such a trend is evident from the data in Table II: the $E_{1/2}$ values for the chelated diamine couples [Ru(bipy)$_2$(en)]$^{3+/2+}$, [Ru(bipy)$_2$(dach)]$^{3+/2+}$, [Ru(bipy)$_2$(damp)]$^{3+/2+}$, and [Ru(bipy)$_2$(tn)]$^{3+/2+}$ are close to that for [Ru(bipy)$_2$(NH$_3$)$_2$]$^{3+/2+}$, whereas the $E_{1/2}$ values for the pyridine–amine couples [Ru(bipy)$_2$(AMPy)]$^{3+/2+}$ and [Ru(bipy)$_2$(AEPy)]$^{3+/2+}$ are at considerably more anodic potentials.

If the back-bonding argument is correct, the data in Table III indicate that imine ligands undergo appreciable back-bonding with ruthenium(II) in bis(2,2'-bipyridine) complexes. The Ru(III)/Ru(II) potentials for [Ru(bipy)$_2$(dim)]$^{2+}$ and [Ru(bipy)$_2$(dich)]$^{2+}$ are at considerably higher potentials than the corresponding diamine complexes, and the potentials for all three α,α'-diimine complexes fall in the same range (1.20–1.33 V) as the potential for the [Ru(bipy)$_3$]$^{3+/2+}$ couple. The ligands 2,2'-bipyridine and 1,10-phenanthroline are high in the spectrochemical series and capable of strong back-bonding,[29] and it has been suggested[30] that it is the α,α'-diimine linkage

$$\underset{N}{\overset{|}{\diagdown}}C{-}C\underset{N}{\overset{|}{\diagup}}$$
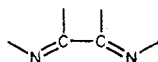
which is the important bonding feature responsible for the back-bonding. The similarities in properties between [Ru(bipy)$_3$]$^{2+}$ and the α,α'-diimine complexes reported here are consistent with this suggestion. However, it is not clear that *linked* imine systems are necessary to explain the effects observed. The linked imine system benefits from the chelate effect, and the chemical link may be the origin of the unusual chemical stability of the α,α'-diimine complexes. However, the spectral and redox properties of [Ru(bipy)$_2$(py)$_2$]$^{2+}$ are
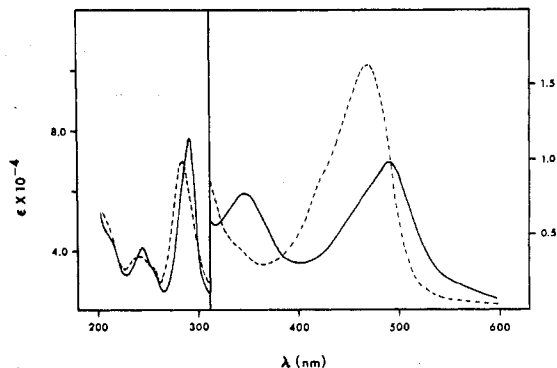
Figure 3. Electronic spectra of [Ru(bipy)$_2$(dach)]$^{2+}$ (—) and [Ru(bipy)$_2$(dich)]$^{2+}$ (- - -) in acetonitrile solution.

essentially identical with those for [Ru(bipy)$_3$]$^{2+}$.[14] The electronic effects of the α,α'-diimine ligand, particularly with regard to back-bonding, may originate primarily from the two imine linkages, irrespective of a chemical link between them.

The reduction potential for the monoimine couple [Ru(bipy)$_2$(iamp)]$^{3+/2+}$ is higher than that for its precursor diamine couple [Ru(bipy)$_2$(damp)]$^{3+/2+}$, but is similar to that for the pyridine–amine couple [Ru(bipy)$_2$(AMPy)]$^{3+/2+}$. The similarity indicates the monoimine linkage may be similar to a pyridine group in back-bonding ability.

The electronic spectra of *cis*-bis(2,2'-bipyridine)ruthenium(II) complexes are also sensitive to the presence of back-bonding ligands in the two remaining coordination positions.[15,28] The spectrum of [Ru(bipy)$_2$(NH$_3$)$_2$]$^{2+}$ has two broad maxima in the visible region, which have previously been assigned as d(Ru(II)) → π*(bipy) MLCT transitions.[15] There are also two maxima in the uv region, which have been assigned as 2,2'-bipyridine π → π* transitions.[15] From the data in Table II it can be seen that the electronic spectra of the diamine complexes of bis(2,2'-bipyridine)ruthenium(II) are all very similar to the spectrum of [Ru(bipy)$_2$(NH$_3$)$_2$]$^{2+}$. The spectrum of the complex [Ru(bipy)$_2$(dach)]$^{2+}$ is shown in Figure 3.

The spectra of the complexes [Ru(bipy)$_2$(AMPy)]$^{2+}$ and [Ru(bipy)$_2$(AEPy)]$^{2+}$ differ slightly from the spectra of the diamine complexes, there being additional transitions at 422 and 425 nm, respectively. An assignment of these bands as d(Ru(II)) → π*(py) MLCT transitions is reasonable since similar transitions are known for related complexes.

As the number of back-bonding ligands in bis(2,2'-bipyridine)ruthenium(II) complexes increases, the energy of the bands in the visible region increases and for complexes with back-bonding ligands in both sites there is typically only one d(Ru(II)) → π*(bipy) MLCT transition.[31] Distinct shoulders are also sometimes observed since the broad absorption bands are clearly a composite of allowed transitions.[15] The energy of the first d → π* transition is observed to increase from [Ru(bipy)$_2$(NH$_3$)$_2$]$^{2+}$ (490 nm) to [Ru(bipy)$_3$]$^{2+}$ (450 nm), and those for the α,α'-diimine complexes occur between 454 and 472 nm, which again indicates considerable back-bonding from the metal to the α,α'-diimine ligand. The spectrum of [Ru(bipy)$_2$(dich)]$^{2+}$ is shown in Figure 3.

The electronic spectrum of the monoimine complex [Ru(bipy)$_2$(iamp)]$^{2+}$ is quite similar to the visible spectrum of the

pyridine–amine complex [Ru(bipy)$_2$(AMPy)]$^{2+}$, but lacks the d(Ru) → π*(pyridine) MLCT band at 422 nm as expected. The complex [Ru(bipy)$_2$(IMPy)]$^{2+}$ has a very complicated electronic spectrum, but this is expected since transitions in the MLCT region are expected to appear due to d(Ru) → π*(L) transitions, where L = 2,2'-bipyridine, pyridine, and the imine group.

The effects of back-bonding in the α,α'-diimine complexes are felt both at the metal (redox and spectral properties) and also at the ligand. For example, simple organic imines are known to be unstable with respect to hydrolysis,[32] yet coordinated α,α'-diimine ligands are remarkably stable in aqueous solution.

The complexes [Ru(bipy)$_2$(AEPy)]$^{2+}$ and [Ru(bipy)$_2$-(tn)]$^{2+}$ do not have stable imine oxidation products. Because of the structures of the ligands, the imine oxidation products cannot be α,α'-diimines. It is probable that oxidation of these ligands gives first an imine intermediate, e.g.,
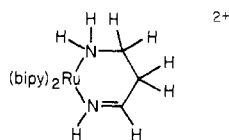
which is unstable with respect to further oxidation at the imine site. The instability of nondelocalized imines appears to be further evidence for the unusual stability of the α,α'-diimine linkage.

Registry No. [Ru(bipy)$_2$Cl$_2$], 19542-80-4; [Ru(bipy)$_3$](ClO$_4$)$_2$, 15635-95-7; [Ru(bipy)$_2$(NH$_3$)$_2$](ClO$_4$)$_2$, 56993-99-8; [Ru(bipy)$_2$-(en)](ClO$_4$)$_2$, 31659-06-0; [Ru(bipy)$_2$(dach)](ClO$_4$)$_2$, 56889-66-8; [Ru(bipy)$_2$(damp)](ClO$_4$)$_2$, 56889-68-0; [Ru(bipy)$_2$(AEPy)](ClO$_4$)$_2$, 56889-70-4; [Ru(bipy)$_2$(AMPy)](ClO$_4$)$_2$, 56889-72-6; [Ru-(bipy)$_2$(tn)](PF$_6$)$_2$, 56889-74-8; [Ru(bipy)$_2$(dim)](PF$_6$)$_2$, 56889-76-0; [Ru(bipy)$_2$(dich)](PF$_6$)$_2$, 56889-78-2; [Ru(bipy)$_2$(IMPy)](PF$_6$)$_2$, 56889-80-6; [Ru(bipy)$_2$(iamp)]$^{2+}$, 56889-81-7; Ce(IV), 16065-90-0.

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