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Thermal and Light-Induced Decomposition of Azido(bis-2,2'-bipyridine) Complexes of Ruthenium(III)

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The ruthenium(II) complexes Ru(bipy)₂(N₃)₂ (bipy is 2,2'-bipyridine) and Ru(bipy)₂(L)(N₃)⁺ (L is acetonitrile or pyridine) are oxidized rapidly to ruthenium(III) either electrochemically or chemically, using Br₂ or Ce(IV). The ruthenium(III) complexes undergo thermal and light-induced decomposition reactions in acetonitrile in which *net* azide → metal electron transfer occurs

$$CH_3CN + Ru(bipy)_2(N_3)_2^+ \xrightarrow[\text{room temp}]{h\nu \text{ or}} Ru(bipy)_2(CH_3CN)N_3^+ + {}^3/_2 N_2$$
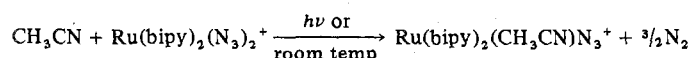
The results of a series of kinetic studies are consistent with either rate-determining intramolecular electron transfer (N₃⁻ → Ru(III)) or metal–nitrene formation. Gas evolution studies in the presence of acrylamide have shown that free azide radicals N₃⁰ do not appear as intermediates in either the thermal or light-induced decomposition reactions of Ru(bipy)₂(N₃)₂⁺. No evidence for dinitrogen complexes as intermediates has been found in solution, but infrared evidence has been obtained for the appearance of an intermediate dinitrogen complex at a low steady-state level in the solid-state decomposition of [Ru(bipy)₂(N₃)₂]Br.

Metal azide complexes commonly undergo thermal and/or light-induced decomposition reactions. The mechanistic details of the decomposition reactions in solution have been elucidated to a considerable degree recently by the use of flash photolysis techniques[2,3] and the results of both product isolation studies and of scavenging experiments for intermediates.[3–10]

For the systems which have been studied, it appears that strong, one-electron oxidants (e.g., Co(III),[11] Mn(III)[12]) react with N₃⁻ to give azide radicals, N₃⁰, and the reduced form of the oxidant. Azide radicals are also produced in the light-induced decomposition of Co(III)[2,4] and of other metal azide[5,13] complexes. On the other hand, for the thermal decomposition reactions of ruthenium(III) azides[6,10] and the thermal and light-induced reactions of iridium(III) azides,[3,7,8] evidence has been obtained for the appearance of intermediate metal–nitrene complexes, e.g., Ru(NH₃)₅NH³⁺. In the ultraviolet-catalyzed decomposition of Rh(NH₃)₅N₃²⁺, evidence has been found for simultaneous paths involving both N₃⁰ and metal–nitrene formation.[9]

We have prepared a series of azidobis(2,2'-bipyridine) complexes of ruthenium(II) and have found that they can be rapidly oxidized to the corresponding ruthenium(III) complexes either chemically or electrochemically. The ruthenium(III) complexes once formed undergo both thermal and light-induced decomposition reactions involving the bound azide group. We have been able to study the thermal reactions in some detail since they are amenable to a kinetic investigation.

Experimental Section

Measurements. Ultraviolet–visible spectra were recorded on Cary Model 14, Cary Model 17, Unicam Model SP-800B, or Gilford Model 240 spectrophotometers. Infrared spectra were obtained using a Perkin-Elmer Model 421 spectrophotometer. All electrochemical measurements were made at platinum electrodes vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2° and are uncorrected for junction potentials. In all electrochemical experiments, standard three-electrode operational amplifier circuitry was used as previously described,[14] or a Princeton Applied Research Model 173 Potentiostat/Galvanostat was used for potential control and current

measurements with a Princeton Applied Research Model 175 Universal Programmer as a wave form generator for voltammetry and cyclic voltammetry experiments. Voltammograms and slow scan rate cyclic voltammograms were recorded on a Hewlett-Packard Model 7004B X-Y recorder. Fast scan rate 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 electrons transferred in an exhaustive electrolysis at constant potential, 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 its initial value.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[15] recrystallized three times from hot ethanol–water mixtures, and vacuum dried at 80° for 12 hr. Acetonitrile (MCB "Spectrograde") for use in electrochemical experiments was dried over Davison 4-Å molecular sieves before use. Dichloromethane (Fisher "Spectranalyzed") was used without further purification. Pyridine (Reagent Grade) was purified by distillation from KOH. Water was deionized and redistilled from alkaline KMnO₄. The complexes Ru(bipy)₂Cl₂·2H₂O and [Ru(bipy)₂(NO)py](PF₆)₃ were prepared as previously described.[16] Tetraphenylarsonium azide was prepared by the method of Bosnich and Dwyer.[17] All other solvents and chemicals were of commercially available reagent or spectrograde quality and were used without further purification.

Preparation of Compounds. All elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

cis-**Ru(bipy)₂(N₃)₂·H₂O.** Ru(bipy)₂Cl₂·2H₂O (1.61 g, 3.09 mmol) was suspended in 35 ml of H₂O containing 3.00 g of NaN₃ (46 mmol). The mixture was heated to reflux under nitrogen for 1 hr with stirring. Upon cooling deep purple crystals formed which were collected by filtration, washed with water, and air-dried. The product was then dried overnight in a vacuum desicator over Drierite; 88% yield. Anal. Calcd for RuC₁₀H₁₈N₁₀O: C, 46.60; H, 3.52; N, 27.17. Found: C, 46.11; H, 3.70; N, 26.25.

[Ru(bipy)₂(N₃)(py)](PF₆)·H₂O (py is Pyridine). Ru(bipy)₂-(N₃)₂·H₂O (185 mg, 0.346 mmol) was dissolved in about 25 ml of pyridine. A concentrated solution of Br₂ in acetonitrile (0.173 mmol, 0.39-ml total volume) was added with stirring. The solution immediately turned green and was allowed to stand in the dark at room temperature with stirring for ~15 hr. The solution gradually turned from green to red-brown. The product was then precipitated by

dropwise addition to 150 ml of diethyl ether. The solid was collected by filtration, immediately dissolved in ~25 ml of H_2O, and reprecipitated as the hexafluorophosphate salt by the addition of several milliliters of a saturated solution of NH_4PF_6 in H_2O. The PF_6^- salt was collected by filtration, washed with H_2O, and dried overnight in a vacuum desiccator over Drierite. The product was then reprecipitated from CH_2Cl_2–pentane and air-dried; yield 73%. Reaction time could be shortened to about 3 hr by heating the solution at ~40°; however this method led to small amounts of impurities (~5%) as shown by voltammetry experiments. Anal. Calcd for $RuC_{25}H_{23}N_8F_6PO$: C, 43.05; H, 3.03; N, 16.06. Found: C, 43.90; H, 3.12; N, 16.20.

[Ru(bipy)₂(N₃)(CH₃CN)](PF₆)·H₂O. This salt was prepared under conditions identical with that for [Ru(bipy)2(N3)(py)](PF6)·H2O except that the bromine oxidation was carried out in pure acetonitrile. Anal. Calcd for $RuC_{22}H_{21}N_8F_6PO$: C, 40.07; H, 3.20; N, 16.99. Found: C, 40.65; H, 3.17; N, 15.99.

[Ru(bipy)₂(CH₃CN)₂](PF₆)₂. Ru(bipy)2Cl2·2H2O (0.40 g, 0.77 mmol) was suspended in 25 ml of a 1:1 (v/v) mixture of acetonitrile and water and heated on a steam bath under nitrogen for 1.5 hr. The solution was then filtered while still hot and reheated just to boiling on a hot plate. A 5-ml amount of a saturated aqueous solution of NH4PF6 was added, and the mixture was allowed to cool slowly to room temperature and then was cooled in an ice bath. The precipitate was collected by filtration, washed with 20 ml of cold water, and air-dried; yield 83%. Anal. Calcd for $RuC_{24}H_{22}N_6P_2F_{12}$: C, 36.70; H, 2.82; N, 10.70. Found: C, 36.65; H, 2.77; N, 10.63.

Solutions of Ru(bipy)₂(py)(CH₂CN)²⁺. To a solution of Ru-(bipy)2(py)(NO)3+ in acetonitrile was added a stoichiometric amount of tetraphenylarsonium azide in acetonitrile

$$Ru(bipy)_2(py)(NO)^{3+} + N_3^- + CH_3CN \rightarrow$$
$$Ru(bipy)_2(py)(CH_3CN)^{2+} + N_2 + N_2O$$
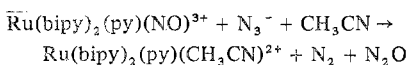
The reaction of azide ion with bis(2,2'-bipyridine)nitrosylruthenium(II) complexes has been described previously.[18,19]

Kinetic Studies. Solutions of Br2 and Ce(IV) in acetonitrile were standardized as previously described.[20] The rate of decomposition of Ru(bipy)2(N3)2+ in acetonitrile was monitored by following the changes in absorbance on a Gilford Model 240 spectrophotometer. The reaction was begun by adding a stoichiometric amount of Br2 in acetonitrile to a solution of Ru(bipy)2(N3)2·H2O in acetonitrile. Rate constants were calculated from the slope of first-order plots which were linear for at least 3 half-lives. Changes in the ionic strength of the solvent medium were made with N(n-C4H9)4PF6. The rates of decomposition of the complexes Ru(bipy)2(N3)(L)2+ (L is py or CH3CN) in acetonitrile were followed by monitoring the changes in absorbance on a Cary Model 14 spectrophotometer. The reactions were initiated by the addition of a stoichiometric amount of Ce(IV) in acetonitrile to a solution of the corresponding ruthenium(II)–azide complex in acetonitrile. The stoichiometries of the reactions of Ce(IV) with Ru(bipy)2(N3)L+ in acetonitrile were shown to be 1:1 by spectrophotometric titrations. Rate constants were calculated from first-order rate plots which were linear for at least 3 half-lives. The temperature was maintained at 25.0 ± 0.2° in the sample compartments of the spectrophotometers using Forma Temp Model 2095 or Model 2220 constant-temperature baths. In all cases, rate constants were independent of the wavelength used to monitor the reactions. Because of the sensitivity of the ruthenium(III)–azide complexes to light, all kinetic measurements were made on solutions protected from room light with aluminum foil.

Photolyses. Solutions of Ru(bipy)(N3)2+ were generated in acetonitrile as described in the previous section. Solutions were irradiated with a GE 275-W sun lamp, using Pyrex glassware.

Quantitative Determination of Evolved Nitrogen. Solutions of [Ru(bipy)2Cl2]PF6 in acetonitrile were standardized by measuring the absorbance at 380 nm (ϵ_{380} 5650).[21] The ion Ru(bipy)2Cl2+ was used as the oxidant because of ease of handling and because of its long-term stability in acetonitrile. The initial electron-transfer reaction that occurs

$$Ru(bipy)_2Cl_2^+ + Ru(bipy)_2(N_3)_2 \rightarrow Ru(bipy)_2Cl_2 +$$
$$Ru(bipy)(N_3)_2^+$$
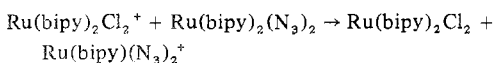
is rapid and from electrochemical measurements is favored by 0.13 V. Reactions were carried out in a vessel consisting of two 100-ml round-bottom flasks joined by a Y tube. The two reactants, Ru-

Table I. $E_{1/2}$ Values for the Azido and Solvent Complexes

Compd	$E_{1/2}$,^{a} V	Compd	$E_{1/2}$,^{a} V
Ru(bipy)₂(N₃)₂	0.17,^{b} 1.25^c	Ru(bipy)₂(py)-(CH₃CN)²⁺	1.36^b
Ru(bipy)₂(N₃)-(py)⁺	0.58^b		
Ru(bipy)₂(N₃)-(CH₃CN)⁺	0.65^b	Ru(bipy)₂(CH₃-CN)₂²⁺	1.44^b
		[(C₆H₅)₄As]N₃	0.73^c

^{a} $E_{1/2}$ values were determined in 0.1 M TBAH–CH₃CN at a Pt electrode and are referenced to SSCE at 25 ± 2°. ^{b} Electrochemically reversible. The $E_{1/2}$ values are essentially reduction potentials for the various Ru(III)–Ru(II) couples, e.g., Ru(bipy)₂-(N₃)₂⁺ + e → Ru(bipy)₂(N₃)₂. ^{c} The values are not reduction potentials. The $E_{1/2}$ values refer to irreversible oxidation processes. No reverse reduction waves are observed by cyclic voltammetry.

### Table II. Infrared (ν_{N_3}) and Electronic Spectra of Ruthenium–Azide and Solvent-Coordinated Complexes

Compd	λ_{max} (ϵ),^{a} nm	ν_{N_3},^{b} cm⁻¹
Ru(bipy)₂(N₃)₂·H₂O	555 (7100)	2029 b^c
	383 (8340)	2060 sh, 2030^d
	298 (41,000)	
	243 (28,500)	
Ru(bipy)₂(N₃)₂⁺	582 (~3060)	2007^c
	405 (4950)	2004^d
	289 (29,700)	
	240 (34,800)	
Ru(bipy)₂(py)(N₃)⁺	498 (7370)	2031^c
	352 (9980)	
	292 (46,900)	
	244 (25,800)	
Ru(bipy)₂(CH₃CN)(N₃)⁺	474 (6650)	2040^c
	346 (7450)	
	289 (48,300)	
	240 (25,600)	
Ru(bipy)₂(CH₃CN)₂²⁺	425 (8590)	
	283 (52,500)	
	240 (17,400)	
Ru(bipy)₂(py)(CH₃CN)²⁺	437 (7730)	
	410 sh	
	320 sh	
	284 (51,100)	
	250 (21,800)	

^{a} All electronic spectra were obtained in acetonitrile. The estimated error in the molar extinction coefficients (ϵ) is ±5%. ^{b} N₃ asymmetric stretching vibration. ^{c} Acetonitrile solution spectra. ^{d} KBr pellet.

(bipy)2Cl2+ and Ru(bipy)2(N3)2, were placed in the separate flasks, connected to a vacuum line via a stopcock, the solutions were degassed, and the vessel was evacuated. The reaction was initiated by mixing the two reactants. The initial, rapid electron transfer was followed by the slower decomposition of Ru(bipy)2(N3)2+. The decomposition of Ru(bipy)2(N3)2+ was allowed to proceed to completion, the solution was frozen with liquid nitrogen, and the evolved gas was measured using a Toepler pump.[22]

Results[23]

Chemical Oxidations. The oxidation of Ru(bipy)2(N3)2·H2O by 1 equiv of Br2 in acetonitrile or pyridine leads in a net reaction to the evolution of N2 and the ruthenium(II) solvent-coordinated complexes Ru(bipy)2(N3)(L)+ (L is py or CH3CN). The stoichiometry of the net reaction in acetonitrile, as shown by spectral and gas evolution studies (see below), is given in reaction 1. The identity and concentration

$$Ru(bipy)_2(N_3)_2 + \frac{1}{2}Br_2 + CH_3CN \rightarrow$$
$$Ru(bipy)_2(CH_3CN)(N_3)^+ + Br^- + \frac{3}{2}N_2 \qquad (1)$$
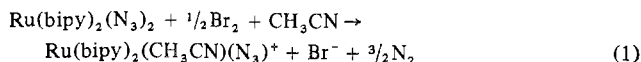
of the ruthenium ion product were determined by spectral and electrochemical measurements using the $E_{1/2}$ and molar extinction coefficient values given in Tables I and II, respectively. The products of the chemical oxidation studies described below were determined in the same manner. It should be noted that the available evidence indicates that the

2,2'-bipy complexes have the cis configuration around ruthenium, and there is no evidence to indicate that the configuration changes in the reactions described here.[24]
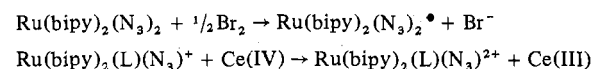
Reaction 1 is useful synthetically. The complexes Ru(bipy)$_2$(CH$_3$CN)(N$_3$)$^+$ and Ru(bipy)$_2$(py)(N$_3$)$^+$ were prepared and isolated as PF$_6^-$ salts by carrying out the oxidation of Ru(bipy)$_2$(N$_3$)$_2$·H$_2$O by Br$_2$ on a synthetically useful scale in either acetonitrile or pyridine.

As shown by spectrophotometric titrations and product studies, the complexes Ru(bipy)$_2$(L)(N$_3$)$^+$ (L is py or CH$_3$CN) react with 1 equivalent of Ce(IV) in acetonitrile by the net reaction

$$Ru(bipy)_2(L)(N_3)^+ + Ce(IV) + CH_3CN \rightarrow$$
$$Ru(bipy)_2(L)(CH_3CN)^{2+} + Ce(III) + \tfrac{3}{2}N_2 \quad (2)$$
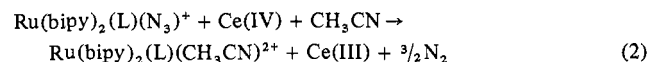
Additional Ce(IV) in acetonitrile appears to oxidize the ruthenium(II) complexes to ruthenium(III), Ru(bipy)$_2$(L)-(CH$_3$CN)$^{3+}$, as expected, but the ruthenium(III) complexes have not been fully characterized.

The Br$_2$ oxidation of Ru(bipy)$_2$(N$_3$)$_2$·H$_2$O and the Ce(IV) oxidations of Ru(bipy)$_2$(L)(N$_3$)$^+$ (L is py or CH$_3$CN) occur by a rapid (on the time scale of mixing) initial electron-transfer step

$$Ru(bipy)_2(N_3)_2 + \tfrac{1}{2}Br_2 \rightarrow Ru(bipy)_2(N_3)_2{}^\bullet{}^+ + Br^-$$

$$Ru(bipy)_2(L)(N_3)^+ + Ce(IV) \rightarrow Ru(bipy)_2(L)(N_3)^{2+} + Ce(III)$$

As discussed below the oxidized ruthenium products can best be characterized as azido complexes of ruthenium(III). The ruthenium(III)–azide complexes undergo a subsequent net decomposition reaction, to give the ultimate observed products

$$Ru(bipy)_2(N_3)_2{}^+ + CH_3CN \rightarrow Ru(bipy)_2(CH_3CN)(N_3)^+ +$$
$$\tfrac{3}{2}N_2 \quad (3)$$

$$Ru(bipy)_2(L)(N_3)^{2+} + CH_3CN \rightarrow Ru(bipy)_2(L)(CH_3CN)^{2+} +$$
$$\tfrac{3}{2}N_2 \quad (4)$$
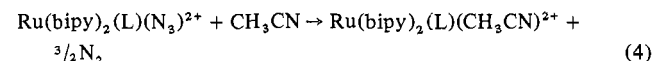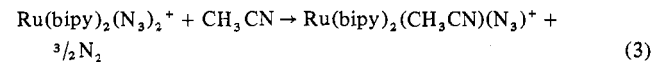
(reactions 3 and 4).

As expected by combining reactions 1 and 2 (where L is CH$_3$CN), Ru(bipy)$_2$(N$_3$)$_2$·H$_2$O reacts quantitatively with 2 mol of Ce(IV) in acetonitrile to give N$_2$ and the bis(acetonitrile) complex (reaction 5).

$$Ru(bipy)_2(N_3)_2 + 2Ce(IV) + 2CH_3CN \rightarrow$$
$$Ru(bipy)_2(CH_3CN)_2{}^{2+} + 2Ce(III) + 3N_2 \quad (5)$$
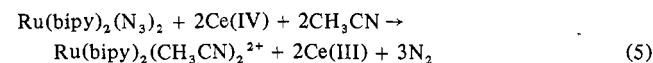
Electrochemical Oxidations. Ru(bipy)$_2$(N$_3$)$_2$ undergoes two one-electron oxidations in 0.1 M TBAH–CH$_3$CN as indicated by the cyclic voltammograms in Figure 1. The first oxidation is electrochemically reversible on both the voltammetric and cyclic voltammetric time scales. However, the second oxidation is electrochemically irreversible by cyclic voltammetry even at scan rates >100 V/sec. At slow scan rates a third oxidation wave ($E_{1/2}$ = 1.44 V) appears in the cyclic voltammogram. The peak current for the third oxidation wave is dependent upon the scan rate and disappears at fast scan rates ($\geq$10.0 V/sec). The third oxidation wave was absent in cyclic voltammograms of Ru(bipy)$_2$(N$_3$)$_2$ in 0.1 M TBAH–CH$_2$Cl$_2$ in the potential range 0–1.5 V vs. SSCE.

Exhaustive electrolytic oxidation of Ru(bipy)$_2$(N$_3$)$_2$ past the first wave yielded a coulometric n value of 1.02. Cyclic voltammetry immediately after the electrolysis was complete indicated that the dominant product was Ru(bipy)$_2$(N$_3$)$_2^+$ and that only a small amount of decomposition had occurred. If the electrolyzed solution was allowed to stand in the absence of light for several hours, extensive decomposition took place giving Ru(bipy)$_2$(CH$_3$CN)(N$_3$)$^+$ ($E_{1/2}$ = 0.69 V) quantitatively as calculated using the molar extinction coefficients in Table II.

Controlled-potential electrolysis past the irreversible second oxidation wave of Ru(bipy)$_2$(N$_3$)$_2$ with simultaneous coulo-
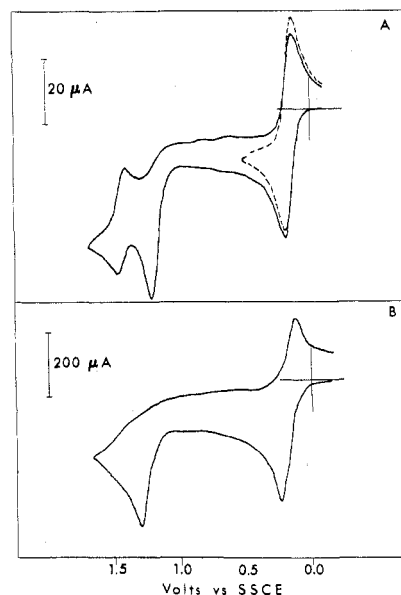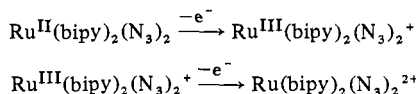

Figure 1. Cyclic voltammograms of Ru(bipy)$_2$(N$_3$)$_2$ in 0.1 M TBAH–CH$_3$CN at a Pt electrode: (A) 0.10 V/sec; (B) 10.0 V/sec. Figures are drawn on a scale such that the current is normalized with respect to scan rate.

metry indicated that the second wave was also a one-electron oxidation. However, the initial product of the oxidation decomposed on the time scale of the electrolysis (minutes) giving Ru(bipy)$_2$(CH$_3$CN)$_2^{2+}$ ($E_{1/2}$ = 1.44 V) quantitatively, as shown by spectral and electrochemical measurements.

The cyclic voltammogram for Ru(bipy)$_2$(N$_3$)$_2$ (Figure 1) has two oxidation waves corresponding to the processes

$$Ru^{II}(bipy)_2(N_3)_2 \xrightarrow{-e^-} Ru^{III}(bipy)_2(N_3)_2{}^+$$

$$Ru^{III}(bipy)_2(N_3)_2{}^+ \xrightarrow{-e^-} Ru(bipy)_2(N_3)_2{}^{2+}$$

The second oxidation involves loss of an electron from the intact ruthenium(III)–azide complex since the extent of decomposition of Ru(bipy)$_2$(N$_3$)$_2^+$ once formed at the electrode is insignificant on the cyclic voltammetry time scale (see below). The second oxidation, which is irreversible, must involve direct oxidation of a coordinated azide ion

$$(bipy)_2(N_3)Ru^{III}(N_3{}^-)^+ \xrightarrow{-e^-} (bipy)_2(N_3)Ru^{III}(N_3{}^0)^{2+}$$
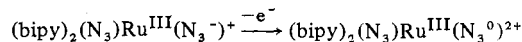
Direct oxidation of coordinated azide ion is a feasible process; the oxidation of free azide ion in acetonitrile which is also irreversible occurs at 0.73 V (Table I). Oxidation of ruthenium giving a Ru(IV) complex is unlikely. Ru(bipy)$_2$Cl$_2^+$ can be oxidized to Ru(bipy)$_2$Cl$_2^{2+}$, but only at a far more anodic potential ($\sim$1.9 V).[25]

In summary, cyclic voltammograms of Ru(bipy)$_2$(N$_3$)$_2$ at slow sweep rates (Figure 1A) and product analysis of controlled-potential electrolytic oxidations show that the product of the second oxidation wave, once formed, decomposes to give the bis(acetonitrile) complex Ru(bipy)$_2$(CH$_3$CN)$_2^{2+}$ ($E_{1/2}$ = 1.44 V). At fast scan rates the wave for the bis-(acetonitrile) complex is not observed. At neither scan rate is a wave observed attributable to the reduction of Ru^{III}-(bipy)$_2$(N$_3$)(N$_3^0$)$^{2+}$. A reasonable interpretation of the cyclic voltammetry results is that the initial one-electron oxidation product decomposes giving a fairly long-lived intermediate or intermediates
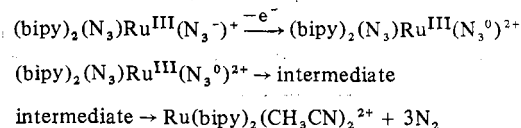
$$(bipy)_2(N_3)Ru^{III}(N_3{}^-)^+ \xrightarrow{-e^-} (bipy)_2(N_3)Ru^{III}(N_3{}^0)^{2+}$$

$$(bipy)_2(N_3)Ru^{III}(N_3{}^0)^{2+} \rightarrow intermediate$$

$$intermediate \rightarrow Ru(bipy)_2(CH_3CN)_2{}^{2+} + 3N_2$$

Table III. Rate Constants for the Decomposition of
Ruthenium(III)–Azide Complexes in Acetonitrile

Compd	k_{obsd},[a] sec^{-1}
$Ru(bipy)_2(N_3)_2^+$	$(1.07 \pm 0.11) \times 10^{-4}$ [b]
$Ru(bipy)_2(py)(N_3)^{2+}$	$(1.38 \pm 0.06) \times 10^{-2}$
$Ru(bipy)_2(CH_3CN)(N_3)^{2+}$	$(2.07 \pm 0.17) \times 10^{-2}$

[a] First-order rate constants at $25.0 \pm 0.2°$. Rate constants are
the average of four to eight runs. Error limits are reported as the
range of observed rate constants. [b] Note that for comparisons
with the other systems $k = 0.54 \times 10^{-4}$ sec^{-1} because of the
statistical factor of 2.

The intermediate cannot be $Ru(bipy)_2(CH_3CN)(N_3)^{2+}$ since
its lifetime is appreciable on the cyclic voltammetry time scale
(Table III) and its characteristic voltammetric wave (Table
I) is not observed in the cyclic voltammogram.

As shown by voltammetry, the complexes $Ru(bipy)_2$-
$(CH_3CN)(N_3)^+$ undergo only a single, reversible one-electron
oxidation (Table I) in the potential region 0–1.7 V in 0.1 M
TBAH–CH$_3$CN vs. SSCE. Coulometry experiments showed
that one-electron oxidations occur; however, on the longer time
scale for electrolysis (minutes), decomposition occurs giving
solvent-bound complexes, $Ru(bipy)_2(L)(CH_3CN)^{2+}$ (L is py
or CH$_3$CN), quantitatively.

The half-wave potentials for the complexes studied are
summarized in Table I. Electrochemical reversibility was
determined from plots of log $[i/(i_1 - i)]$ vs. E from voltammetry
experiments and from the determination of ΔE_p and the ratio
of cathodic to anodic peak currents in cyclic voltammetry
experiments. The ΔE_p value was larger than the theoretical
value of 59 mV in fast-scan cyclic voltammograms due to
uncompensated resistance between the reference and working
electrodes. Reversibility was established in the cyclic vol-
tammetry experiments by comparisons with the systems
$Ru(bipy)_2Cl_2^+$–$Ru(bipy)_2Cl_2^0$ and $Ru(bipy)_2(py)(Cl)^{2+}$–
$Ru(bipy)_2(py)(Cl)^+$ which are known to be reversible.

In cases where the oxidations are electrochemically re-
versible, the $E_{1/2}$ values are essentially reduction potentials
in the medium used and refer to reactions such as

$$Ru(bipy)_2(N_3)_2^+ + e \rightarrow Ru(bipy)_2(N_3)_2$$
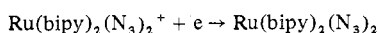
The potentials in Table I differ from reduction potentials only
by a usually small term involving diffusion coefficients.

Electronic and Infrared Spectra. The electronic and infrared
(ν_{N_3}) spectra for the complexes studied are summarized in
Table II. The decomposition reaction of $Ru(bipy)_2(N_3)_2^+$ in
acetonitrile was sufficiently slow at ice-bath temperatures so
that electronic and infrared (ν_{N_3}) spectra could be obtained
in solution. The intermediates formed in the oxidations of
$Ru(bipy)_2(N_3)(L)^+$ (L is py or CH$_3$CN) by Ce(IV) de-
composed too rapidly to obtain their spectra in any convenient
way.

The ruthenium(II) complexes show two absorption maxima
in their visible and near-uv spectra which have been assigned
in similar complexes as d(Ru) $\rightarrow$ π^*(bipy) MLCT transitions.[26]

The infrared absorptions in Table II can be assigned to the
N$_3^-$ asymmetric stretching vibration. Infrared spectra were
obtained both in acetonitrile and in the solid state for freshly
prepared $Ru(bipy)_2(N_3)_2^+$. Measurements in acetonitrile
indicated a smooth conversion of $Ru(bipy)_2(N_3)_2^+$ (ν_{N_3} 2007
cm^{-1}) to $Ru(bipy)_2(N_3)(CH_3CN)^+$ (ν_{N_3} 2040 cm^{-1}) with no
evidence for an intermediate dinitrogen complex. Infrared
spectra of $[Ru(bipy)_2(N_3)_2]Br$ in a KBr pellet (ν_{N_3} 2028 cm^{-1})
indicate that the decomposition reaction proceeds via a di-
nitrogen intermediate. The evidence for an intermediate
monomeric dinitrogen complex is the appearance and sub-
sequent disappearance of a band at 2150 cm^{-1}. The intensity
of the band at 2150 cm^{-1} is always weak indicating that the
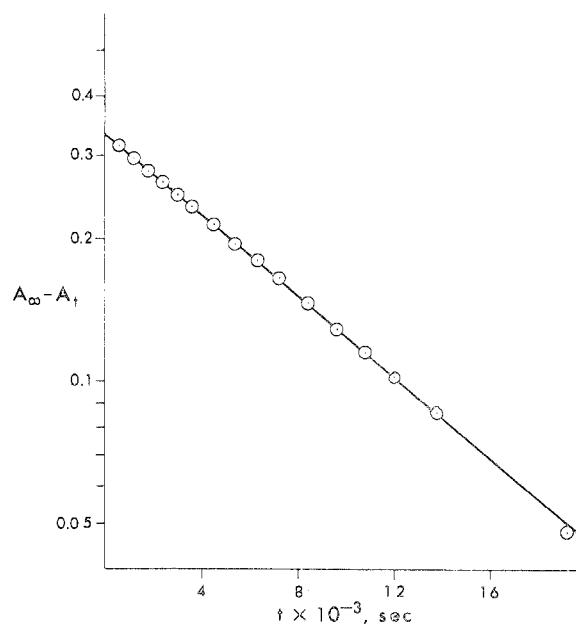dinitrogen complex is present in only a low steady-state amount.

Figure 2. First-order rate plot for the decomposition of
$Ru(bipy)_2(N_3)_2^+$ in acetonitrile at $25.0 \pm 0.2°$.

Kinetics of the Decomposition Reactions. In all cases, the
ruthenium(II)–azide complexes could be rapidly oxidized in
acetonitrile to the ruthenium(III)–azide complexes which
subsequently decomposed in a slower step giving rutheni-
um(II)–acetonitrile complexes and N$_2$. The lifetime of the
ruthenium(III) intermediates in acetonitrile at 25° was long
enough for the kinetics of the decomposition reactions to be
studied by conventional techniques.

The rates of decomposition of the ruthenium(III)–azide
complexes were measured by monitoring the reactions
spectrophotometrically. The ruthenium(III)–azide complexes
were generated in solution by the oxidation of the corresponding
ruthenium(II) complexes using either Br$_2$ (for $Ru(bipy)_2$-
$(N_3)_2^+$) or Ce(IV) (for $Ru(bipy)_2(L)(N_3)^{2+}$). After mixing
solutions which contained the appropriate oxidant and the
appropriate ruthenium(II) complex, the changes in absorbance
of the solutions vs. time were followed at various wavelengths
where absorbance changes were large.

As shown by the first-order, integrated rate plot in Figure
2, reaction 3 is first order in Ru(III) (eq 6). The rate constants

$$\frac{d[Ru(bipy)_2(CH_3CN)(N_3)^+]}{dt} = k[Ru(bipy)_2(N_3)_2^+] \qquad (6)$$

obtained from first-order plots are independent of the con-
centration of $Ru(bipy)_2(N_3)^+$ in the range $(1.0-2.4) \times 10^{-4}$
M and are also independent of ionic strength in the range 1.0
$\times 10^{-4}$–1.0 $\times 10^{-2}$ M.

The ruthenium(III) complexes, which are rapidly formed
in the Ce(IV) oxidation of the complexes $Ru(bipy)_2(L)(N_3)^+$
(L is py or CH$_3$CN) in acetonitrile, decompose according to
reaction 4. These reactions were also found to be first order
in ruthenium(III) complex. First-order rate plots were linear
for 3–4 half-lives. The rate constants at 25.0° for the reactions
studied are summarized in Table III.

Photolysis Experiments. The decomposition of Ru-
(bipy)$_2$(N$_3$)$_2^+$ in acetonitrile is strongly light catalyzed.
Irradiation of a solution 1.0×10^{-4} M in complex at 3–4° using
a GE 275-W sun lamp led to complete decomposition in about
15 min. The thermal decomposition of $Ru(bipy)_2(N_3)_2^+$ is
negligible after 15 min at 3–4°. The light-catalyzed de-
composition reaction did not cleanly yield $Ru(bipy)_2(N_3)$-
$(CH_3CN)^+$. There was evidence in the visible spectrum of
the photolyte for the complex $Ru(bipy)_2(CH_3CN)_2^{2+}$ which,

as shown by blank experiments, arises from the light-catalyzed reaction

$$Ru(bipy)_2(N_3)(CH_3CN)^+ + CH_3CN \xrightarrow{h\nu}$$
$$Ru(bipy)_2(CH_3CN)_2{}^{2+} + N_3{}^-$$
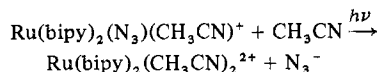
Determination of Evolved Nitrogen. Quantitative determination of the evolved gas from the thermal decomposition of $Ru(bipy)_2(N_3)_2{}^+$ in acetonitrile indicates 1.5 ± 0.1 mol of nitrogen are released per mole of ruthenium complex. Measurements of the gas evolved from the light-catalyzed decomposition of $Ru(bipy)_2(N_3)_2{}^+$ also gave 1.5 ± 0.1 mol of nitrogen per mole of ruthenium complex. The evolved nitrogen from the thermal and light-catalyzed decomposition reactions was also measured in solutions containing a 200-fold excess of acrylamide. Under these conditions there was no significant quenching in the production of nitrogen for either the thermal or the light-catalyzed decomposition reactions.

Discussion

Site of Oxidation in the Ruthenium–Azide Complexes.
Azide complexes of bis(2,2'-bipyridine)ruthenium(II) undergo rapid one-electron oxidation reactions either chemically using Ce(IV) or Br2 or electrochemically. From their properties, the products of the reactions can be formulated simply as azide complexes of ruthenium(III).

Reduction potentials for the Ru(III)–Ru(II) azido complex couples $Ru(bipy)_2(N_3)_2{}^{+,0}$ and $Ru(bipy)_2(L)(N_3)^{2+,+}$ fall in the same range as potentials for closely related halide complexes. For example, $E_{1/2}$ values in 0.1 M TBAH–CH3CN solutions are 0.17 and 0.30 V for the $Ru(bipy)_2(N_3)_2{}^{+,0}$ and $Ru(bipy)_2Cl_2{}^{+,0}$ couples and 0.58 and 0.79 V for the $Ru(bipy)_2(py)(N_3)^{2+,+}$ and $Ru(bipy)_2(py)Cl^{2+,+}$ couples. The slight shift to lower energy in the asymmetric ν_{N_3} stretching frequency when $Ru(bipy)_2(N_3)_2$ is oxidized to $Ru(bipy)_2(N_3)_2{}^+$ (Table II) is also consistent with an oxidation state change of Ru(II) to Ru(III).

The ultraviolet–visible spectrum of $Ru(bipy)_2(N_3)_2{}^+$ is very similar to the spectrum of the ion $Ru(bipy)_2Cl_2{}^+$.[21] The comparison is meaningful since for bis(2,2'-bipyridine) complexes of ruthenium(II) and ruthenium(III) there are characteristic $\pi \rightarrow \pi^*$(bipy) and d(Ru) $\rightarrow$ π^*(bipy) bands which are sensitive to both the oxidation state and the coordination environment of the metal ion.[24,28,29] A striking difference in the spectra of the two ions is the appearance of an intense band at 582 nm for $Ru(bipy)_2(N_3)_2{}^+$. Given the thermal and light-catalyzed decompositions of $Ru(bipy)_2(N_3)_2{}^+$, which are formally intramolecular redox processes ($N_3{}^- \rightarrow$ Ru(III)), and the greater oxidizability of $N_3{}^-$ compared to Cl^-,[30] it seems reasonable to assign the relatively low-energy, intense band at 582 nm to an $N_3{}^- \rightarrow$ Ru(III) LMCT transition.

The Rate-Determining Step in the Decomposition of the Ruthenium(III)–Azide Complexes.
The decomposition of the ruthenium(III) azide complexes (reactions 3 and 4) is first order in Ru(III) (eq 6). Two mechanisms consistent with the first-order rate law suggest themselves: the first involves prior dissociation of azide ion, and the second, rate-determining nitrene formation.[6]

A mechanism for the decomposition of $Ru(bipy)_2(N_3)_2{}^+$ involving prior, rate-determining loss of azide ion, followed by rapid, outer-sphere oxidation of $N_3{}^-$ (reactions 7 and 8), can be ruled out. The most compelling argument is that the
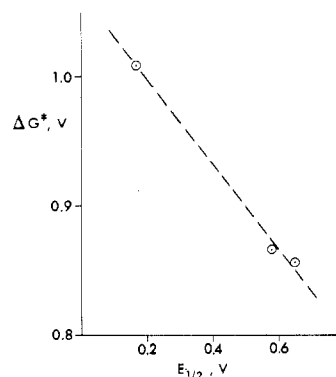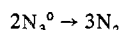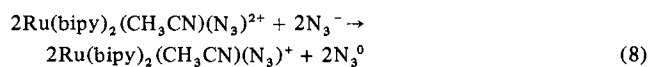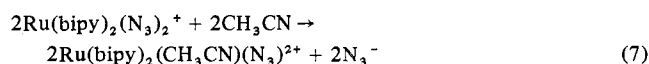
$$2Ru(bipy)_2(N_3)_2{}^+ + 2CH_3CN \rightarrow$$
$$2Ru(bipy)_2(CH_3CN)(N_3)^{2+} + 2N_3{}^- \quad (7)$$

$$2Ru(bipy)_2(CH_3CN)(N_3)^{2+} + 2N_3{}^- \rightarrow$$
$$2Ru(bipy)_2(CH_3CN)(N_3)^+ + 2N_3{}^0 \quad (8)$$
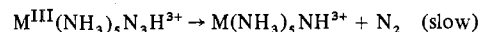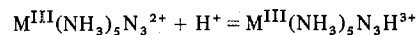
$$2N_3{}^0 \rightarrow 3N_2$$

Figure 3. Plot of $\Delta G^{\ddagger}$ at 25° for the decomposition of the ruthenium(III)–azide complexes in acetonitrile vs. $E_{1/2}$ of the Ru(III)–Ru(II) couples.

evolution of nitrogen in the thermal decomposition reaction is not quenched in the presence of acrylamide, yet acrylamide is known to be an efficient scavenger for $N_3{}^0$.[5,9] $N_3{}^0$ is the expected one-electron outer-sphere oxidation product since evidence for it has been found in light-catalyzed decomposition of metal–azide complexes[2,4,5,9] and in thermal reactions involving powerful one-electron oxidants.[11] It is also expected that if the solvolysis reaction (eq 7) were rate determining, the observed first-order rate constant should be somewhat sensitive to changes in ionic strength. If Ru^{III}–$N_3{}^-$ bond breaking is important in the activation process, the activated complex will have a considerable dipolar character, and the rate constant is expected to have a noticeable ionic strength dependence.[31] In fact the observed rate constant for reaction 3 is insensitive to changes in ionic strength in the range $I = 1.0 \times 10^{-4}$–1.0×10^{-2}. It is also unlikely that the ruthenium(III)–azide complexes are sufficiently labile to account for the observed first-order rate constants. The complexes $Ru(bipy)_2(N_3)_2$[32] and $Ru(bipy)_2Cl_2{}^+$ [21] are substitution inert and stable indefinitely in acetonitrile.[32]

In the thermal decomposition of azido complexes of Ru(III)[6] and Ir(III),[7] kinetic studies have shown that a term exists in the rate law which is first order in [H+] and first order in metal complex. The path has been interpreted in terms of prior protonation of the coordinated azide, followed by rate-determining formation of metal–nitrene complexes

$$M^{III}(NH_3)_5N_3{}^{2+} + H^+ = M^{III}(NH_3)_5N_3H^{3+}$$

$$M^{III}(NH_3)_5N_3H^{3+} \rightarrow M(NH_3)_5NH^{3+} + N_2 \quad (slow)$$

For azidoammine complexes of ruthenium(III), e.g., $Ru(NH_3)_5N_3{}^{2+}$ and cis-$Ru(en)_2(N_3)_2{}^+$, a path has also been found in water and nonaqueous solvents which is first order in metal complex and independent of acid. A related mechanism, involving rate-determining formation of a deprotonated nitrene complex, has been proposed for the path

$$Ru^{III}(NH_3)_5(N_3)^{2+} \rightarrow Ru(NH_3)_5N^{2+} + N_2$$
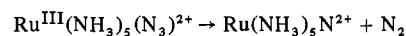
It is interesting to note that the ultimate products of the two paths are different. Under appropriate conditions the dimer $(NH_3)_5Ru(N_2)Ru(NH_3)_5{}^{4+}$ can be made to be the dominant ruthenium-containing product for the acid-dependent path, while the dimer has not been observed to be a product of the acid-independent path.
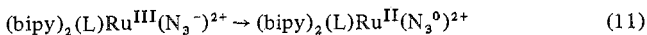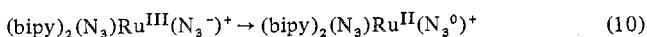
For the three reactions reported here which have been studied kinetically, a plot of the free energy of activation ($\Delta G^{\ddagger}$) at 25° vs. $E_{1/2}$ for the Ru(III)–Ru(II) couples is given in Figure 3. Because of the limited data available, the linear relation implied by the drawn, dashed line in the figure is only that. The importance of the dashed line is that it emphasizes that the rates of decomposition of the azido complexes increase with the relative oxidizing power of the ruthenium(III) center.

The $E_{1/2}$ values are essentially reduction potentials for the Ru(III)–Ru(II) couples in the medium used, and they clearly vary with the ligand cis to the *azide* group.

From the results of a variety of experiments the order of increasing back-bonding ability of the cis ligands in bis(2,-2'-bipyridine) complexes of ruthenium(II) is CH₃CN > py >> N₃⁻, Cl⁻. The effect of the back-bonding ability of the cis ligand is clearly seen in the ν_{NO} stretching frequencies for the nitrosyl complexes Ru(bipy)₂(NO)L^{n+} [16,33] ($n = 2$, L = Cl, Br, I, N₃, NO₂; $n = 3$, L = py, CH₃CN, H₂O) and in electrochemical and spectral data.[26,29] In the nitrosyl complexes the extent of back-bonding of Ru to the nitrosyl group decreases as the back-bonding ability of the cis ligand increases. This trend is observed both in ν_{NO} stretching frequencies and in $E_{1/2}$ values for the one-electron reduction of the coordinated nitrosyl group.[33]
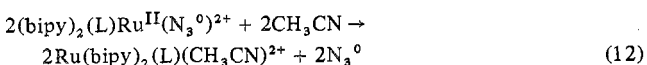
The importance of back-bonding in metal–nitrene chemistry has been emphasized by Basolo and coworkers.[9] They have pointed out experimental evidence which supports the view that the nitrene group is stabilized by $d\pi$(metal) → $p\pi$(nitrene) back-bonding. If back-bonding is important in stabilizing metal–nitrene intermediates, it would be expected that in a closely related series of reactions, the rate of decomposition should increase with the ability of the metal center to donate π-electron density.[34] The trend in rates observed here (Figure 3 and Table III) is just the opposite, and, instead, a correlation is found with the oxidizing power of the Ru(III) center. If metal–nitrene formation (reaction 9) occurs initially, the

$$Ru(bipy)_2(N_3)_2{}^+ \rightarrow Ru(bipy)_2(N_3)(N)^+ + N_2 \qquad (9)$$

Ru(III) → Ru(II) driving force is clearly a more important factor than stabilization of the nitrene by back-bonding. It is also conceivable that the rate-determining step involves intramolecular electron transfer between Ru(III) and the coordinated azide ion (reactions 10 and 11). A similar

$$(bipy)_2(N_3)Ru^{III}(N_3{}^-)^+ \rightarrow (bipy)_2(N_3)Ru^{II}(N_3{}^0)^+ \qquad (10)$$

$$(bipy)_2(L)Ru^{III}(N_3{}^-)^{2+} \rightarrow (bipy)_2(L)Ru^{II}(N_3{}^0)^{2+} \qquad (11)$$

rate-determining step may well hold for the decomposition of Mn^{III}(EDTA)(N₃)$^{2-}$.[12] Mechanisms involving the rate-determining oxidation of coordinated HN₃ have been suggested for strong, labile one-electron oxidants.[35] As will be seen in the next section, even if the Ru(III) reactions and the reactions with *strong* one-electron oxidants are similar in detail in the rate-determining step, the fate of the ligand-oxidized intermediate is apparently different.

The Overall Mechanism for the Decomposition of the Ruthenium(III)–Azide Complexes. As discussed in the previous section, the rate-determining step in the overall decomposition reactions (reactions 3 and 4) appears to be either nitrene formation (reaction 9) or intramolecular electron transfer (reaction 11). The product of an intramolecular electron-transfer process can be thought of as an intermediate which contains the azide radical bound to ruthenium(II). If the initial intermediate arises from electron transfer, its disappearance (at least for L = N₃⁻) cannot involve the formation of free azide radicals (reaction 12). No quenching of N₂ evolution

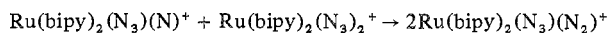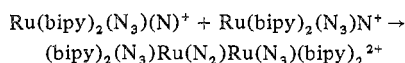$$2(bipy)_2(L)Ru^{II}(N_3{}^0)^{2+} + 2CH_3CN \rightarrow$$
$$2Ru(bipy)_2(L)(CH_3CN)^{2+} + 2N_3{}^0 \qquad (12)$$

$$2N_3{}^0 \rightarrow 3N_2 \qquad (13)$$

was observed in the thermal decomposition of Ru(bipy)₂(N₃)₂⁺ in the presence of acrylamide. The fact that free azide radicals are not formed would distinguish the Ru(III) reactions from the reactions between azide ion and strong, one-electron-transfer oxidants such as Ce(IV),[35] Co(III),[11] and Mn(III)[12] where N₃⁰ has been suggested as an intermediate.

A Ru^{II}–N₃⁰ intermediate might be stabilized (cyclic vol-

tammetry experiment on Ru(bipy)₂(N₃)₂) because spin-paired d⁶ ruthenium(II) ions are normally substitution inert, are known to stabilize reactive ligands by backbonding,[36] and might react rapidly to give the metal nitrene (reaction 14).

$$(bipy)_2(N_3)Ru^{II}(N_3{}^0)^+ \rightarrow (bipy)_2(N_3)RuN^+ + N_2 \qquad (14)$$
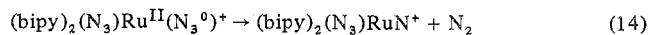
Obtaining direct evidence for intermediate nitrenes is difficult because the 2,2'-bipy complexes are less amenable to detailed mechanistic studies than are the azidoammine complexes. For example, the use of known scavengers for nitrenes[3–10] is complicated since the scavengers are commonly good reductants as well as efficient scavengers, and the azidoruthenium(III) complexes undergo rapid electron transfer. Product studies are unrevealing since in all cases the solvent complexes, Ru(bipy)₂(L)(CH₃CN)²⁺, are the ultimate products. Although dinitrogen complexes are expected to appear as products of some plausible reactions

$$Ru(bipy)_2(N_3)(N)^+ + Ru(bipy)_2(N_3)N^+ \rightarrow$$
$$(bipy)_2(N_3)Ru(N_2)Ru(N_3)(bipy)_2{}^{2+}$$

$$Ru(bipy)_2(N_3)(N)^+ + Ru(bipy)_2(N_3)_2{}^+ \rightarrow 2Ru(bipy)_2(N_3)(N_2)^+$$

we have been unable to observe them as intermediates in solution. However, an infrared study of the solid-state decomposition of Ru(bipy)₂(N₃)₂⁺ salts

$$[Ru(bipy)_2(N_3)_2]Br \rightarrow Ru(bipy)_2(N_3)Br + {}^3/_2N_2$$
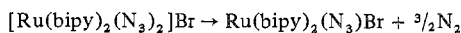
indicates that a dinitrogen complex (ν_{NN} 2150 cm⁻¹) may appear as an intermediate, presumably by the scheme,

$$2[Ru(bipy)_2(N_3)_2]Br \rightarrow 2[Ru(bipy)_2(N_3)(N_2)]Br + N_2$$

$$[Ru(bipy)_2(N_3)(N_2)]Br \rightarrow Ru(bipy)_2(N_3)Br + N_2$$
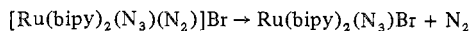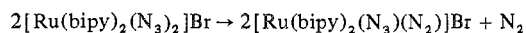
In contrast to the amine system, [Ru(en)₂(N₃)(N₂)]⁺,[6,7] the intermediate dinitrogen complex is not isolable. The band at 2150 cm⁻¹ grows as decomposition proceeds, reaches a steady-state value of probably less than 5% of the total complex present, and then disappears at the end of the net reaction. The infrared experiment indicates that the rates of formation and decomposition of the dinitrogen complex are competitive in the solid state.

The Photochemical Decomposition of Ru(bipy)₂(N₃)₂⁺. The differences in the observed photochemical behavior of the cobalt(III), rhodium(III), and iridium(III) complexes of azidopentaammine have been explained in terms of differences in the relative energies of three types of excited states: LMCT (N₃⁻ → M(III)), d–d, and a reactive, azide-localized state.[9] In this model photolysis into the d–d bands of Ir(NH₃)₅N₃²⁺ is followed by internal conversion or intersystem crossing to the relatively low-lying azide-localized state giving the nitrene complex Ir(NH₃)₅N²⁺. For Co(NH₃)₅N₃²⁺ the LMCT state is lowest lying and light-catalyzed intramolecular electron transfer (giving Co(II)) results in the production of free N₃⁰. In Rh(NH₃)₅N₃²⁺ both of the reactive excited states are accessible by ultraviolet irradiation.

The decomposition of Ru(bipy)₂(N₃)₂⁺ is clearly light induced. Although quantitative studies are difficult for the Ru(III) complexes because of the competing thermal reactions, it is clear from our qualitative work that the light-induced reaction is relatively efficient.

The light sensitivity of the complex Ru(bipy)₂(N₃)₂⁺ is almost surely the result of the existence of a LMCT (N₃⁻ → Ru(III)) excited state corresponding to the absorption band at 582 nm. For bis(2,2'-bipyridine) complexes of ruthenium(II) the existence of fairly low-lying d → π^*(bipy) and d–d excited states has been suggested to explain their luminescence[37] and photolability[29,38] properties. Complexes of bis(2,2'-bipyridine)ruthenium(III) are not noticeably light sensitive; e.g., solutions of Ru(bipy)₂Cl₂⁺ are stable to room light indefinitely in acetonitrile, nor have they been reported to luminesce. Given

Scheme I
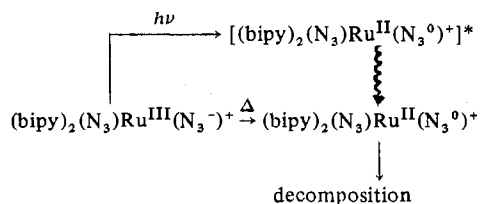
the electronic properties of bis(2,2'-bipyridine)ruthenium(III) complexes,[28] it is probable that for Ru(bipy)$_2$(N$_3$)$_2^+$, there are no low-lying CT or d–d states other than the LMCT (N$_3^-$ → Ru(III)) state. The azide-localized state, which has been suggested as the precursor excited state to metal–nitrene formation, also appears to be at an energy significantly higher than the LMCT state.[9,39] Photolysis into the LMCT band is not expected to give a nitrene directly. Rather, the light-induced decomposition of Ru(bipy)$_2$(N$_3$)$_2^+$ is expected to be similar in detail to the photochemical reactions of Co(NH$_3$)$_5$N$_3^{2+}$ and Co(CN)$_5$N$_3^{3-}$ [2,4] where light-catalyzed, intramolecular electron transfer is observed, apparently via LMCT excited states

$$Co^{III}(N_3^-) \xrightarrow{h\nu} Co^{II}(N_3^0)$$
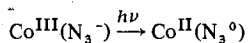
However, for the Co(III) complexes, evidence has been found for free azide radicals, e.g.

$$Co(CN)_5N_3^{3-} \xrightarrow{h\nu} N_3^0 + Co(CN)_5^{3-\ 2}$$
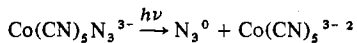
In the light-induced decomposition of Ru(bipy)$_2$(N$_3$)$_2^+$, nitrogen evolution is not quenched by acrylamide showing that free azide radicals are not a photochemical product.

For the decomposition reactions of Ru(bipy)$_2$(N$_3$)$_2^+$ it is tempting to speculate that the thermal and light-catalyzed reactions are closely related. Both reactions may involve intramolecular N$_3^-$ → Ru(III) electron transfer although initial nitrene formation cannot be ruled out for the thermal case. If electron transfer occurs, the same initial intermediate, (bipy)$_2$(N$_3$)Ru^{II}(N$_3^0$)$^+$, is formed in both cases, followed by decomposition perhaps via an intermediate nitrene (Scheme I).

Registry No. Ru(bipy)$_2$Cl$_2$, 19542-80-4; pyridine, 110-86-1; Br$_2$, 7726-95-6; CH$_3$CN, 75-05-8; Ce(IV), 16065-90-0; *cis*-Ru(bipy)$_2$-(N$_3$)$_2$, 55124-48-6; [Ru(bipy)$_2$(N$_3$)(py)](PF$_6$), 55124-50-0; [Ru(bipy)$_2$(N$_3$)(CH$_3$CN)](PF$_6$), 55124-52-2; [Ru(bipy)$_2$(CH$_3$CN)$_2$]-(PF$_6$)$_2$, 55124-54-4; [Ru(bipy)$_2$(py)(CH$_3$CN)]$^{2+}$, 55124-55-5; [Ru(bipy)$_2$(N$_3$)(py)]$^{2+}$, 55124-56-6; [Ru(bipy)$_2$(N$_3$)(CH$_3$CN)]$^{2+}$, 55124-57-7; Ru(bipy)$_2$(N$_3$)$_2^+$, 55124-58-8.

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(23) Abbreviations used here include TBAH for tetra-*n*-butylammonium hexafluorophosphate, py for pyridine, bipy for 2,2'-bipyridine, and en for ethylenediamine.
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