Corresponding to the intense (ϵ 5000–12,000), structured charge-transfer band in the visible region (Table II) are found several distinct CD bands, interpreted, following Bosnich,[3] as originating in transitions from d orbitals to the azomethine π^* (a_2, b_1, in the coordinate scheme of Belford[19]) orbitals. For the benzenoid complexes, a consistent assignment of these bands can be proposed. Bands IV and V (see Table III), whose signs are positive and negative, respectively, in the complexes derived from (−)pn, and the opposite in the (−)chxn chelates, are attributed to transitions from the $d_{x^2-y^2}$ and d_{z^2} orbitals to a_2, b_1 (π^*) ($^1A_1 \rightarrow {}^1A_2$, $^1B_1$), although, as for the d–d transitions, it is not possible to say which is which. Band VI (positive in the (−)pn chelates, negative in the (−)chxn chelates) is assigned to the transitions d_{xz} and/or $d_{yz} \rightarrow a_2$, b_1 (π^*) ($^1A_1 \rightarrow {}^1B_1$, $^1A_2$, $^1B_1$, $^1A_2$). The superior resolution of the CD spectrum of $Ni(sal)_2$(−)chxn, compared to that of $Ni(sal)_2$(−)pn, has made necessary a slight modification of the assignments of Bosnich[3] for the latter compound.

At still higher energies the CD spectra reveal little more detail than the absorption spectra. It is clear however, that in the uv further new bands appear on complexation, which probably have their origin in change-transfer transitions of the ligand (σ or π) to metal type.

Acknowledgment. This research was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and by an Institutional Grant from Case Western Reserve University sponsored by the American Cancer Society.

Azidoruthenium(III) Complexes as Precursors for Molecular Nitrogen and Nitrene Complexes

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Abstract: The generality of the reaction whereby azidoruthenium(III) complexes are converted into nitrogen–ruthenium(II) complexes has been studied. Several new azidoruthenium(III) complexes have been prepared, and their ease of conversion into molecular nitrogen complexes has been studied, kinetically and otherwise. In the presence of acid, the reaction is more rapid; the products include ruthenium(II) nitrogen-bridged dimers and nitrogen–ruthenium(II) monomeric compounds. The products of the reaction are interpreted in terms of a reactive intermediate which is nitrene, NH, coordinated to the ruthenium ion.

Recent studies[1,2] have shown the azidopentaammineruthenium(III) species to be unstable toward decomposition to nitrogenpentaammineruthenium(II).

$$[Ru(NH_3)_5N_3]^{2+} \longrightarrow [Ru(NH_3)_5N_2]^{2+} + {}^1/_2N_2 \qquad (1)$$

This reaction was found to occur for several other azidoruthenium(III) complexes, in solution and in the solid state, and was investigated as a possible source of new nitrogen–ruthenium(II) compounds. Kinetic data for the solution reaction are reported in a variety of organic solvents. In the presence of acid, the reaction becomes more rapid and the products are more complex, yielding dimeric nitrogen-bridged complexes in addition to the monomeric nitrogenruthenium species of eq 1. Kinetic data were also collected for the acid reaction, and a qualitative interpretation of these is given.

The mechanism was investigated and is postulated to involve cleavage of a N–N bond in the azide ligand as the rate-determining step. This cleavage releases nitrogen gas and results in the formation of a metalated nitrene intermediate. While the production of nitrene species *via* the action of ultraviolet light or acid on organic azides is well established,[3,4] no similar reaction has been previously described for metal azide complexes. The stabilization of nitrenes by coordination to transition metals has been hypothesized,[5] but little evidence is available for the existence of such species. A copper–nitrene intermediate has been proposed in the copper-catalyzed decomposition of benzenesulfonylazide,[6] and recent studies indicate that nitrenes may be trapped as ligands in metal carbonyl complexes.[7,8] The ruthenium–nitrene species reported here are reactive and are attacked by a variety of Lewis bases. The reactivity of the ruthenium nitrene is dependent upon the nature of the inert ligands coordinated to the metal, the oxidation state of the ruthenium, and the initial concentration of acid used and of the azide complex.

Experimental Section

Preparation of Compounds. ***cis*-Diazidobis(ethylenediamine)ruthenium(III) Hexafluorophosphate.** *cis*-$[Ru(en)_2Cl_2]Cl \cdot H_2O$[9] (0.200

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[1] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

[2] (a) T. Studer, unpublished results; (b) L. Kane-Maguire, P. Sheridan, F. Basolo, and R. G. Pearson, *ibid.*, **90**, 5295 (1968).

[3] L. Horner and A. Christman, *Angew. Chem., Int. Ed. Engl.*, **2**, 599 (1963).

[4] W. Lwowski, *ibid.*, **6**, 5899 (1968).

[5] R. Gleiter and R. Hoffman, *Tetrahedron*, **24**, 5899 (1969).

[6] H. Kwart and A. Kahn, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).

[7] M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

[8] C. D. Campbell and C. W. Rees, *ibid.*, 537 (1969).

g, 0.00058 mol) was mixed with silver toluene-*p*-sulfonate (0.483 g, 0.00174 mol) and 5 ml of water was added. The suspension was stirred near the boiling point until no further silver chloride precipitated, leaving a clear red supernatant solution. This generally required 5–6 min of heating. The silver chloride was washed with water (1 ml); the washings were combined with the filtrate. The filtrate contains *cis*-$[Ru(en)_2(H_2O)_2]^{3+}$. The red color is thought to be due to a small amount of intensely colored impurity, since *cis*-$[Ru(en)_2(H_2O)_2]^{3+}$ is almost colorless. The red solution was cooled and added to solid sodium azide (0.72 g, 0.011 mol) and the mixture stirred in an ice bath. Slow gas evolution was observed. After 5 min an ice-cold filtered aqueous solution of sodium hexafluorophosphate (saturated, 6 ml) was added. Deep purple-red microcrystals of *cis*-$[Ru(en)_2(N_3)_2]PF_6$ slowly formed. The product was collected by filtration after 30 min and washed twice with small volumes of ice-cold ethanol and air-dried (0.095 g). A further crop of the product was obtained from the filtrate after a further 40 min at ice bath temperatures; the total yield was 0.14 g (54%). *Anal.* Calcd for $C_4H_{16}N_{10}PF_6Ru$: C, 10.7; H, 3.6; N, 31.1. Found: C, 10.7; H, 3.6; N, 30.0.

***cis*-(−)-Diazidobis(ethylenediamine)ruthenium(III) Hexafluorophosphate.** *cis*-(−)-$[Ru(en)_2Cl_2]I$[9] (0.15 g, 0.00035 mol) was mixed with silver toluene-*p*-sulfonate (0.10 g, 0.00035 mol). The mixture was stirred in 4 ml of water for 5 min. The silver iodide precipitate was then separated by filtration and washed with 1 ml of water. The combined filtrate and washings were added to solid sodium azide (0.61 g, 0.093 mol) and stirred at room temperature. An original orange precipitate of (−)-$[Ru(en)_2Cl_2]N_3$ dissolved within 30 min. After 50 min the solution was cooled in an ice bath and an ice-cold filtered aqueous solution of sodium hexafluorophosphate (saturated, 5 ml) was added. Purple-red microcrystals of *cis*-(−)-$[Ru(en)_2(N_3)_2]PF_6$ separated and were collected by filtration, washed with ethanol, and air-dried. The yield was 0.10 g (62%).

***cis*-Diazidotriethylenetetramineruthenium(III) Hexafluorophosphate.** *cis*-$[Ru(trien)(N_3)_2]PF_6$ was prepared from *cis*-$[Ru(trien)Cl_2]Cl\cdot H_2O$[9] by a procedure analogous to that described above for *cis*-$[Ru(en)_2(N_3)_2]PF_6$. The yield was 65%. *Anal.* Calcd for $C_6H_{18}N_{10}PF_6Ru$: C, 15.1; H, 3.8; N, 29.4. Found: C, 15.0; H, 3.8; N, 27.6.

Azidopentaammineruthenium(III) Azide. The salt $[Ru(NH_3)_5N_3](N_3)_2$ was prepared by a modification of the method of Allen, *et al.*[1] Solid $[Ru(NH_3)_5Cl]Cl_2$ (0.10 g, 0.00034 mol) was mixed with silver methanesulfonate (0.204 g, 0.00102 mol) in water (3 ml). The mixture was stirred near the boiling point for 30 min and then filtered. The silver chloride precipitate was washed with water (1 ml), and the filtrate and washings were combined and cooled. The solution was poured on solid sodium azide (1.1 g, 0.017 mol) and the mixture stirred in an ice bath for 5 min. Any silver azide was then removed on a filter and the filtrate scratched and cooled in an ice bath. After 10 min deep orange crystals of the product were isolated by filtration and washed with ethanol. The yield was 0.03 g (30%). The product was used immediately, since conversion of $[Ru(NH_3)_5N_3](N_3)_2$ to the nitrogen compound is relatively fast in the solid state at room temperature. The composition of the product was determined from its ultraviolet spectrum. For example, the sample used to obtain the data in Table VI was found to be 60% $[Ru(NH_3)_5N_3](N_3)_2$, 27% $[Ru(NH_3)_5N_2](N_3)_2$, and 13% $[Ru(NH_3)_5OH](N_3)_2$.

Azidonitrogenbis(ethylenediamine)ruthenium(II) Hexafluorophosphate. Solid *cis*-$[Ru(en)_2(N_3)_2]PF_6$ (0.10 g, 0.00022 mol) was placed in a test tube, which was partially immersed in a water bath at 65° and maintained at this temperature for 25 min. This completed the redox process, producing almost pure *cis*-$[Ru(en)_2N_2N_3]PF_6$ in a quantitative yield. *Anal.* Calcd for $C_4H_{16}N_9PF_6Ru$: C, 11.0; H, 3.6; N, 28.8. Found: C, 11.0; H, 3.6; N, 27.4. On a microscale (0.010 g) the conversion of *cis*-$[Ru(en)_2(N_3)_2]PF_6$ to *cis*-$[Ru(en)_2N_2N_3]PF_6$ was performed conveniently on a Faraday magnetic balance. The sample was kept at 65° by passing a stream of hot air through a jacket surrounding the sample pan. Heating was stopped as soon as the sample became diamagnetic (about 30 min). The weight loss at zero magnetic field during the reaction corresponded closely (±5%) to the calculated weight loss for the release of one atom of nitrogen per molecule of original *cis*-$[Ru(en)_2(N_3)_2]PF_6$. Mass spectral analysis of the gas released showed it to be greater than 99% nitrogen.

***cis*-(+)-Azidonitrogenbis(ethylenediamine)ruthenium(II) Hexafluorophosphate.** *cis*-(+)-$[Ru(en)_2N_2N_3]PF_6$ was prepared from *cis*-(−)-$[Ru(en)_2(N_3)_2]PF_6$ in an analogous manner to that described above for *racemic cis*-$[Ru(en)_2N_2N_3]PF_6$.

***cis*-Azidonitrogentriethylenetetramineruthenium(III) Cation.** Heating *cis*-$[Ru(trien)(N_3)_2]PF_6$ in the solid state at 65° until the sample was diamagnetic gave very poor yields of *cis*-$[Ru(trien)N_2N_3]PF_6$. A mixture of products was obtained, including large amounts of unknown ruthenium–nitrosyl species. However, pure *cis*-$[Ru(trien)N_2N_3]^+$ was obtained *in situ* by heating an acetone solution of *cis*-$[Ru(trien)(N_3)_2]PF_6$ for 3 hr at 45°. No solid samples have been isolated from solution.

***cis*-Aquonitrogenbis(ethylenediamine)ruthenium(II) Tetraphenylborate.** An ice-cold aqueous solution (2 ml, 0.000038 mol) of *cis*-$[Ru(en)_2N_2N_3]PF_6$ was mixed with a freshly prepared solution (5 ml, 0.000038 mol) of HNO_2. Immediate vigorous gas evolution occurred, and the solution color changed from red-brown to pale yellow. An ice-cold solution (4 ml, 0.00012 mol) of $NaB(C_6H_5)_4$ was then added after 90 sec. An immediate yellow precipitate was formed which was rapidly collected on a suction filter. The product was washed with a 50:50 water–methanol mixture and dried (15 min). It was stored in a desiccator in a refrigerator. *Anal.* Calcd for $[Ru(en)_2H_2O(N_2)][B(C_6H_5)_4]_2$: C, 68.9; H, 6.5; N, 9.3. Found: C, 68.0; H, 6.6; N, 9.1. Samples isolated after short reaction times (*e.g.*, 7 sec) were mixtures of the salts *cis*-$[Ru(en)_2H_2O(N_2)][B(C_6H_5)_4]_2$ and *cis*-$[Ru(en)_2(N_2)_2][B(C_6H_5)_4]_2$.

Aquo(iminothiourea)bis(ethylenediamine)ruthenium(III) Tetraphenylborate. A solution of thiourea (0.012 g, 0.00016 mol) in aqueous sulfuric acid (4 ml, 0.8 *M*) was added to solid *cis*-$[Ru(en)_2(N_3)_2]PF_6$ (0.016 g, 0.000036 mol). Vigorous gas evolution occurrred. After 30 min a solution of sodium tetraphenylborate (0.045 g) in water (2 ml) was added. The resulting yellow precipitate was collected on a filter within 1 min. It was washed twice with water and air-dried. *Anal.* Calcd for $[Ru(en)_2(H_2O)(NSCN_2H_4)][B(C_6H_5)_4]_3$: C, 71.8; H, 6.8; N, 7.6. Found: C, 72.5; H, 6.4; N, 7.4.

Quantitative Determination of Released Gas. Both thermal and chemical methods were used to evolve gas from samples of the metal complexes. A small Schlenk tube was used as the sample holder for the thermal reactions, and the gas was released by heating the tube to 65° for 20 min with a hot water bath. The Schlenk tube was connected to a vacuum system which contained a manometer and an adjustable mercury column which moved in a graduated cylinder. After evacuating the system, argon was introduced (150–200 mm) and the internal pressure noted, using the manometer. After releasing the gas, the pressure was returned to its original value by moving the mercury column down the graduated cylinder. The volume of released gas is measured directly from this cylinder.

The chemical methods involved either oxidation with Ce^{4+} solution or reaction with 2 *M* H_2SO_4. The same procedure was followed, except a two-bulbed sample holder was used, with the degassed oxidizing solution (or acid) placed in the bulb directly above the bulb containing the solid sample and a magnetic stirring bar. A cathetometer was used to read the mercury level of the manometer, giving internal pressure readings accurate to 0.1 mm.

Measurements of Other Properties. Conductivity data were obtained for both aqueous and dimethyl sulfoxide (Matheson Coleman and Bell, reagent grade) solutions. All measurements were made at 25° using an Industrial Instruments, Inc. conductivity bridge, Model RC-16B1. Infrared spectra in the region 4000–400 cm^{-1} were recorded on a Perkin-Elmer 337 grating spectrophotometer calibrated against polystyrene in this region. Ultraviolet and visible spectra were measured on a Cary 14 spectrophotometer using matched 1-cm silica cells. Magnetic susceptibilities of solid samples were measured on a Faraday balance. Mass spectral measurements were made on a Consolidated Electrodynamics Corp. 21-104 mass spectrograph.

Kinetic Studies of Neutral Reactions. Kinetic data were obtained in several solvents for the following redox reactions.

$$[Ru(NH_3)_5N_3]^{2+} \longrightarrow [Ru(NH_3)_5N_2]^{2+} + {}^1/_2N_2 \qquad (1)$$

$$cis\text{-}[Ru(en)_2(N_3)_2]^+ \longrightarrow cis\text{-}[Ru(en)_2N_2N_3]^+ + {}^1/_2N_2 \qquad (2)$$

$$cis\text{-}[Ru(trien)(N_3)_2]^+ \longrightarrow cis\text{-}(Ru(trien)N_2N_3]^+ + {}^1/_2N_2 \qquad (3)$$

$$[Ru(EDTA)N_3]^{2+} \longrightarrow [Ru(EDTA)N_2]^{2-} + {}^1/_2N_2 \qquad (4)$$

cis-$[Ru(en)_2(N_3)_2]^+$ and *cis*-$[Ru(trien)(N_3)_2]^+$ were used as their hexafluorophosphate salts. The complex $[Ru(NH_3)_5N_3]^{2+}$ was used as the hexafluorophosphate or azide salt, and $[Ru(EDTA)N_3]^{2-}$ was prepared *in situ via* the action of sodium azide (7.5 × 10^{-2} *M*) on K[Ru(HEDTA)Cl] (2–5 × 10^{-4} *M*). The acetone employed as solvent was spectroquality grade from Matheson Coleman and

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[9] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 546 (1967).

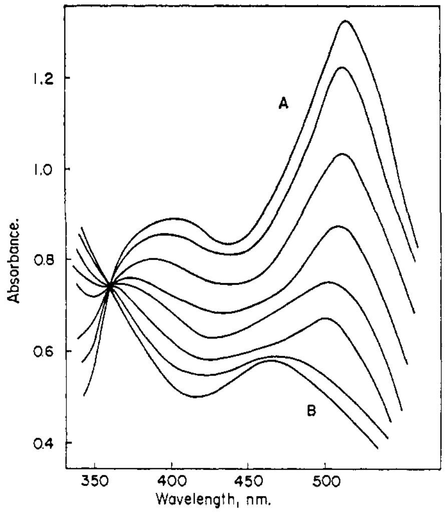

Figure 1. Spectral changes during the decompositon of *cis*-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ in acetone at 40°. A is the initial spectrum and B is final spectrum after 2 hr.

Bell. The acetonitrile was a Fischer certified reagent. Reagent grade absolute methyl alcohol was purchased from Baker and Adamson and distilled over magnesium before use.

All reactions were followed spectrophotometrically with a Beckman DU-2 spectrophotometer. The solvents were thermostated at the desired temperature (±0.1°) in the DU-2 cell compartment for at least 20 min prior to reaction. Solid azidoruthenium(III) complex was added and the solution quickly shaken and returned to the cell compartment. Complex concentrations were estimated by extrapolation of spectral data to zero time. The reactions were studied by following the decrease of absorption at a visible absorption maximum of the original azidoruthenium(III) complex. Good isosbestic points were observed over several half-lives for reactions 1-3. Typical spectral traces during the decomposition of *cis*-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ are shown in Figure 1. First-order rate constants were calculated from plots of log $(A_\infty - A_t)$ *vs.* time, where A_∞ is absorbancy at infinite reaction time and A_t is the absorbance at time t.

Kinetic Study of Acid Reaction of *cis*-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$. Reagent grade toluene-*p*-sulfonic acid was generally employed. The reaction was studied by following the decrease of absorption at the 485-nm maximum of *cis*-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$. The technique used was essentially the same as that described above for the neutral reaction. First-order rate constants, k_{obsd}, were obtained from plots of log A_t *vs.* time.

Optical Activity Experiments. Solid *cis*-(−)-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ was converted to (+)-[Ru(en)$_2$N$_2$N$_3$]PF$_6$ by heating (see above). The ORD spectra of both complexes in water were recorded using a Cary 60 ORD/CD instrument (Figure 2). The ORD spectrum was recorded for a solution of (+)-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ (0.012 g) in acetone (6 ml). The solution was allowed to stand at room temperature for 38 hr, at which stage the visible spectrum showed reaction to *cis*-[Ru(en)$_2$N$_2$N$_3$]PF$_6$ to be complete. An attempt to resolve *cis*-[Ru(en)$_3$N$_2$N$_3$]$^+$ into its optical enantiomorphs using (−)-Na[Co(en)(ox)$_2$]·H$_2$O[10] as resolving agent was unsuccessful.

Results and Discussion

Azido Complexes. Freshly prepared *cis*-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ and *cis*-[Ru(trien)(N$_3$)$_2$]PF are paramagnetic (Table I) as expected for spin-paired d^5 systems. Their ir spectra show characteristic coordinated azide ion bands in the wavelength region between 2000 and 2050 cm^{-1} (Table II), and their visible and ultraviolet spectra are recorded in Table III. They are readily soluble in water and dimethyl sulfoxide, in which they are initially 1:1 electrolytes (Table IV). They can be stored in the dark at −15° for several weeks without significant change.

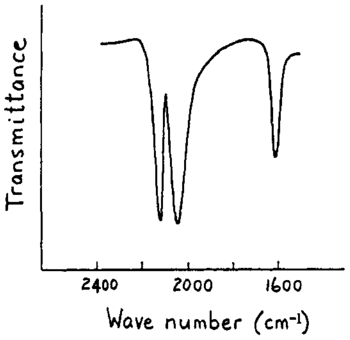

Figure 2. Infrared spectrum of [Ru(en)$_2$N$_2$N$_3$]PF$_6$ in Nujol mull.

Nitrogen Complexes. *cis*-[Ru(en)$_2$N$_2$N$_3$]PF$_6$ is a brown diamagnetic solid. It loses molecular nitrogen slowly at room temperature, and it may also be stored at −15° for long periods without change. It is characterized by its ir spectrum, which contains a strong sharp band at 2130 cm^{-1} attributed to the coordinated molecular nitrogen, and a strong band at 2050 cm^{-1} associated with the coordinated azide group (Table II, Figure 2). It is readily soluble in water and dimethyl sulfoxide, in which it is initially a 1:1 electrolyte (Table IV). The compound undergoes further reaction (*e.g.*, ligand substitution) in these solvents. Solutions

Table I. Magnetic Moments (BM per Ru atom) of Ruthenium Azido and Nitrogen Complexes

Compound	μ_{eff}	Temp, °K
cis-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$	2.0	298
cis-[Ru(trien)(N$_3$)$_2$]PF$_6$	1.9	297
cis-[Ru(en)$_2$(N$_2$)(N$_3$)]PF$_6$	Diamagnetic	294
cis-[Ru(en)$_2$(N$_2$)(H$_2$O)][B(C$_6$H$_5$)$_4$]$_2$	Diamagnetic	294

Table II. The Infrared Spectra of Some Ruthenium Azido and Nitrogen Complexes (in the 2300–1900-cm^{-1} Region)

Compound	$\nu_{\text{N-N}}$ (coordinated N$_2$), cm^{-1}	$\nu_{\text{N-N}}$ (coordinated N$_3^-$), cm^{-1}
cis-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$		2050
cis-[Ru(en)$_2$(N$_2$)(N$_3$)]PF$_6$	2130	2050
cis-[Ru(trien)(N$_3$)$_2$]PF$_6$		2030, 2050
cis-[Ru(trien)(N$_2$)(N$_3$)]PF$_6$	2120	2050
cis-[Ru(en)$_2$(N$_2$)(H$_2$O)][B(C$_6$H$_5$)$_4$]$_2$	2130	
cis-[Ru(en)$_2$(N$_2$)$_2$][B(C$_6$H$_5$)$_4$]$_2$	2220, 2190	

Table III. Visible and Ultraviolet Spectra of Ruthenium Azido and Nitrogen Complexes

Compound	Solvent	$\lambda_{\max}$, nm (ϵ, cm^{-1} l. mol^{-1})
Ru(EDTA)N$_3^{2-}$	H$_2$O	448 (2000)
cis-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$	H$_2$O	484 (2280), 382 (1560)
	Acetone	507 (2350), 385 (1550)
cis-[Ru(en)$_2$(N$_2$)(N$_3$)]PF$_6$	Acetone	465 (1100)
	Acetonitrile	465 (830)
	H$_2$O	460 (500), 225 (15,200)
cis-[Ru(trien)(N$_3$)$_2$PF$_6$	H$_2$O	482 (2410), 379 (1870)
	Acetone	500 (2800), 375 (2050)
cis-[Ru(trien)(N$_2$)(N$_3$)]PF$_6$	Acetone	460 (1750)
cis-[Ru(en)$_2$(N$_2$)(H$_2$O)]$^{2+}$	0.1 *M* H$_2$SO$_4$	220 (14,000)

[10] F. P. Dwyer, F. L. Garvan, and I. Reid, *J. Amer. Chem. Soc.*, **83**, 1285 (1961).

Table IV. Molar Conductivities ($ohm^{-1}\ cm^2\ mol^{-1}$) for Ruthenium Ethylenediamine Compounds

Compound	Concn, M ($\times 10^3$)	Λ
cis-$[Ru(en)_2Cl_2]Cl\cdot H_2O$	1.0^a	110
	0.36^b	26
cis-$[Ru(en)_2(N_3)_2]PF_6$	0.73^a	103
	0.78^b	27
cis-$[Ru(trien)(N_3)_2]PF_6$	0.65^a	126
cis-$[Ru(en)_2(N_2)(N_3)]PF_6$	1.08^a	101
	1.15^b	28
$NaB(C_6H_5)_4$	1.0^b	20
cis-$[Ru(en)_2(H_2O)(N_2)][B(C_6H_5)_4]_2$	1.0^b	35

[a] In water. [b] In dimethyl sulfoxide.

in acetone and methanol are relatively stable for several hours. Aqueous solutions of *cis*-$[Ru(en)_2N_2N_3]PF_6$ show and intense absorption band at 225 nm (ϵ 15,200) which is characteristic of ruthenium(II)-nitrogen complexes (Table III).[11] Reaction of solid *cis*-$[Ru(en)_2N_2N_3]PF_6$ with a saturated sulfuric acid solution of ceric ion releases both coordinated nitrogen and coordinated azide ion as nitrogen gas. Gas evolution experiments show 2.5 mol of nitrogen released/mol of original complex (Table V). By comparison, *cis*-$[Ru(en)_2(N_3)_2]PF_6$ releases 3.0 mol of nitrogen gas.

Table V. Gas Evolution Results

Compound	Method	Mol of N_2 released/ mol of compound: Theoretical	Mol of N_2 released/ mol of compound: Found
NaN_3	Ce^{4+}	1.50	1.55
cis-$[Ru(en)_2(N_3)_2]PF_6$	Ce^{4+}	3.00	3.02
cis-$[Ru(en)_2(N_2)(N_3)]PF_6$	Ce^{4+}	2.50	2.42
cis-$[Ru(en)_2(N_3)_2]PF_6$	65° for 20 min	0.50	0.49
cis-$[Ru(en)_2(N_3)_2]PF_6$	0.1 M H_2SO_4	Variable[a]	1.5
	2.0 M H_2SO_4	Variable	2.0
cis-$[Ru(en)_2(N_2)(N_3)]PF_6$	2.0 M H_2SO_4	?	1.02
	0.1 M H_2SO_4	?	1.03

[a] This theoretical variation (between 1.5 and 2.5 mol) results from the two possible reacton paths for *cis*-$[Ru(en)_2(N_3)_2]PF_6$ with acid (*vide infra*).

cis-$[Ru(en)_2N_2N_3]PF_6$ is a useful starting material for the preparation of other nitrogen-ruthenium(II) complexes. Reaction with nitrous acid[2b] leads to the formation of unstable *cis*-$[Ru(en)_2(N_2)_2]^{2+}$.

$$\textit{cis}\text{-}[Ru(en)_2N_2N_3]^+ + HNO_2 + H^+ \xrightarrow{\text{cold}} \textit{cis}\text{-}[Ru(en)_2(N_2)_2]^{2+} + N_2O + H_2O \quad (5)$$

Previous attempts to prepare metal-nitrogen complexes by the reaction of metal azido compounds with nitrous acids were not successful.[2a,12]

Reaction 5 is extremely rapid even at 0°. The immediate (~7 sec) addition of a cold solution of $NaB(C_6H_5)_4$ to the reaction mixture results in the coprecipitation of the salts *cis*-$[Ru(en)_2(N_2)_2][B(C_6H_5)_4]_2$ and *cis*-$[Ru(en)_2H_2O(N_2)][B(C_6H_5)_4]_2$. The two salts are identified by the N-N stretching region of the ir spectra from mixtures collected at various times. The bands at 2220 and 2190 cm^{-1} are assigned to the *cis*-dinitrogen complex, in accord with the two bands reported for *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$.[13] This assignment also agrees with the observation that the bands at 2220 and 2190 cm^{-1} decrease in intensity with increasing isolation time. In the solid state at room temperature, the bands gradually disappear in about 30 min. These results show that a metal-nitrogen compound is formed by the reaction of a metal-azido complex with nitrous acid and that the dinitrogen complex *cis*-$[Ru(en)_2(N_2)_2]^{2+}$ is not very stable. If π bonding of the type $Ru{=}N{=}N$ is important in these systems, then it is reasonable that two nitrogens would have to share in such bonding and be held less firmly than in a corresponding system containing only one nitrogen. This agrees with the observation that the N-N stretching frequencies for the dinitrogen complex *cis*-$[Ru(en)_2(N_2)_2]^{2+}$ (2220 and 2190 cm^{-1}) are higher than for the mononitrogen cation *cis*-$[Ru(en)_2H_2O(N_2)]^{2+}$ (2130 cm^{-1}). The latter complex in aqueous solution does not react with N_2 to give the dinitrogen compound, while $[Ru(NH_3)_5H_2O]^{2+}$ does react with nitrogen to yield the mononitrogen compound.[14]

The product obtained from reaction 5 after 90 sec is entirely the aquonitrogen salt. The salt $[Ru(en)_2H_2O(N_2)][B(C_6H_5)_4]_2$ has a molar conductivity in dimethyl sulfoxide at 25° of 35 $ohm^{-1}\ cm^2\ mol^{-1}$, which is consistent with the 2:1 electrolyte formulation (Table IV). It is diamagnetic, confirming the absence of any ruthenium(III). Its ir spectrum shows a single strong band in the N-N stretch region at 2130 cm^{-1}, and also supports the presence of coordinated water (bands at 1610 and 3500 cm^{-1}). In addition, its ultraviolet spectrum has a sharp band at 220 nm (ϵ 13,000). This corresponds with the band at 221 nm (ϵ 16,000) reported for $[Ru(NH_3)_5N_2]^{2+}$.[11]

Preliminary studies indicate that the reaction of *cis*-$[Ru(en)_2N_2N_3]^+$ with nitrous acid in the presence of a large excess of NaX ($X = Cl^-, I^-$) leads to the production of *cis*-$[Ru(en)_2N_2X]^+$ species. In contrast, *trans*-$[Ru(NH_3)_4H_2O(N_2)]^{2+}$ does not react with X^- to yield *trans*-$[Ru(NH_3)_4(N_2)X]^+$.[15] These observations suggest that coordinated nitrogen exerts a strong *trans*-labilizing influence.

Reaction of Acid with $[Ru(NH_3)_5N_3]^{2+}$.[16] The addition of aqueous acid to $[Ru(NH_3)_5N_3]^{2+}$ causes the vigorous evolution of gas. Mass spectral analysis showed this to be greater than 99% nitrogen. This behavior is markedly different from that of most transition metal azides in acid. In general, acid merely catalyzes the displacement of coordinated azide ion as hydrazoic acid. For the action of H_2SO_4 on $[Ru(NH_3)_5N_3](N_3)_2$, the products have been characterized by their ultraviolet spectra. Two intense bands were produced at 220 and 262 nm.[16] Their wavelengths and intensities agree well with those reported for $[Ru(NH_3)_5N_2]^{2+}$ and the dimer $[(NH_3)_5Ru{-}N{\equiv}N{-}Ru(NH_3)_5]^{4+}$ (A), respectively.[11] When reaction solutions were made slightly basic, the band at 220 nm increased. A sharp isosbestic point was observed at 240 nm. This latter behavior confirms the assignment

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(11) D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

(12) R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

(13) H. A. Scheidegger, J. N. Armor, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 3263 (1968).

(14) D. E. Harrison and H. Taube, *ibid.*, **89**, 5706 (1967).

(15) H. Taube, presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(16) L. Kane-Maguire, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4609 (1969).

of products, since it was previously shown that $[(NH_3)_5Ru-N{\equiv}N-Ru(NH_3)_5]^{4+}$ dissociates in weakly basic media into $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5OH]^{+}$.[11] Samples isolated (as tetraphenylborate salts) at the conclusion of gas evolution were invariably diamagnetic and exhibited strong infrared bands in the region (2100–2200 cm^{-1}) associated with ruthenium(II)–nitrogen complexes. The analyses of these solids corresponded to mixtures of $[Ru(NH_3)_5N_2]^{2+}$ and A.

The results of product composition studies on the acid reaction of $[Ru(NH_3)_5N_3](N_3)_2$ are summarized in Table VI. The most significant features from Table VI are: (1) the production of large amounts of nitrogen dimer A, (2) the absence of dimer A formation unless acid is present, and (3) the marked decrease of dimer A with increasing concentrations of $[Ru(NH_3)_5N_3]^{2+}$. In 0.80 *M* H_2SO_4, reaction is complete at room temperature within 5 min. This rapid appearance of nitrogen dimer A eliminates the possibility that it is produced by the combination of $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5H_2O]^{2+}$. The rate of the latter reaction has been measured by Itzkovitch and Page.[17] Under the conditions employed here, such combination would require several hours.

Table VI. Acid Reaction of $[Ru(NH_3)_5N_3](N_3)_2$ at Room Temperature in H_2O

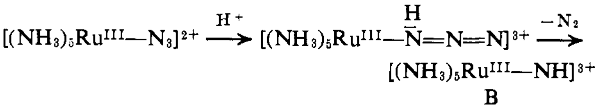
Complex concn, *M*	H_2SO_4 concn, *M*	% yield $Ru(NH_3)_5N_2^+$	% yield Dimer A	Total % yield
9.5×10^{-5}	Water	85	0	85
9.5×10^{-5}	0.05	102	8	110
9.5×10^{-6}	0.15	53	45	98
9.5×10^{-5}	0.40	47	52	99
9.5×10^{-5}	0.80	40	67	107
9.5×10^{-5}	4.0	30	65	95
9.5×10^{-5}	0.80	40	67	107
9.9×10^{-4}	0.80	45	50	95
1.1×10^{-2}	0.80	93	8	101
6.5×10^{-2}	0.80	95	<1	95

The vigorous evolution of nitrogen and the rapid formation of a nitrogen-bridged dimer is reminiscent of the behavior of organic azides when treated with acid or ultraviolet radiation.[18]

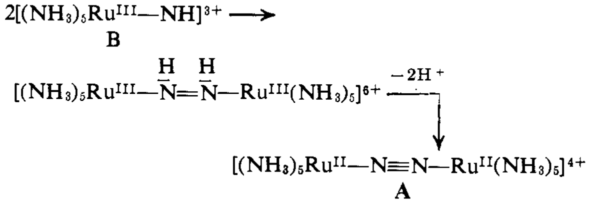
$$Ph-N_3 \xrightarrow{h\nu} Ph-N + N_2$$

$$Ph-N + Ph-N \longrightarrow Ph-N{=}N-Ph$$

A similar reaction pathway, involving a metalated nitrene (B), is proposed for the acid reaction of $[Ru(NH_3)_5N_3]^{2+}$.



$$[(NH_3)_5Ru^{III}-N_3]^{2+} \xrightarrow{H^+} [(NH_3)_5Ru^{III}-\overset{H}{\bar{N}}{=}N{=}N]^{3+} \xrightarrow{-N_2} \underset{B}{[(NH_3)_5Ru^{III}-NH]^{3+}} \quad (6)$$



$$2\underset{B}{[(NH_3)_5Ru^{III}-NH]^{3+}} \longrightarrow [(NH_3)_5Ru^{III}-\overset{H}{\bar{N}}{=}\overset{H}{\bar{N}}-Ru^{III}(NH_3)_5]^{6+} \xrightarrow{-2H^+} \underset{A}{[(NH_3)_5Ru^{II}-N{\equiv}N-Ru^{II}(NH_3)_5]^{4+}} \quad (7)$$

Strong support for the presence of the nitrene intermediate (B) was obtained from trapping experiments. In the presence of small amounts of thiourea, diethyl sulfide, or iodide ion, the reaction of acid on $[Ru(NH_3)_5N_3](N_3)_2$ generated no dimer A.[16] This behavior may be rationalized in terms of the Lewis acid character of the nitrene B. Coordinated nitrene, like the similar carbene, is expected to be a soft acid.[19] Combination of $[(NH_3)_5Ru-NH]^{3+}$ with itself to produce the dimer A is quenched by the more rapid reaction of the nitrene with the soft bases thiourea, diethyl sulfide, or I^-. On the other hand, reagents such as Cl^-, PF_6,$^-$ CH_3CN, or dimethyl sulfoxide had no observable effect on the course of the acid reaction.

The decrease in yield of the dimer A with increasing initial concentration of $[Ru(NH_3)_5N_3](N_3)_2$ (Table VI) suggests that $[Ru(NH_3)_5N_3]^{2+}$ may also function as an effective trap for the nitrene B.

$$[(NH_3)_5Ru^{III}N_3]^{2+} + [HN-Ru^{III}(NH_3)_5]^{3+} \xrightarrow{-H^+} 2[Ru^{II}(NH_3)_5N_2]^{2+} \quad (8)$$

A combination of reactions 7 and 8 explains the production of both $[Ru^{II}(NH_3)_5N_2]^{2+}$ and $[(NH_3)_5Ru^{II}-N{\equiv}N-Ru^{II}(NH_3)_5]^{4+}$ in the acid reaction of $(Ru^{III}(NH_3)_5N_3]^{2+}$.

Reaction of Acid on *cis*-$[Ru^{II}(en)_2N_2N_3]^+$. Addition of sulfuric acid to *cis*-$[Ru(en)_2N_2N_3]^+$ leads to the evolution of gas, the growth of a peak at 322 nm in the uv spectrum, and the formation of a new ruthenium(II)–nitrogen complex (D). The presence of this new species (D) is indicated by the intense peak at 220 nm in the uv spectrum. This peak, present in the original complex and characteristic of ruthenium(II)–nitrogen species, decreases only slightly during the reaction, indicating that the reaction product contains a terminally coordinated nitrogen molecule.

An electron spin resonance spectrum of the reaction solution also indicated the presence of some paramagnetic ruthenium(III) species. Mass spectral analysis of the released gas showed it to be nitrogen, 1 mol/mol of original complex (Table V). This reaction and the nature of the nitrogen complex (D) are presently under investigation and will be discussed elsewhere.[20]

Reaction of Acid with *cis*-$[Ru^{III}(en_2)(N_3)_2]^+$. The two reactions previously discussed are both involved in the acidic decomposition of *cis*-$[Ru^{III}(en)_2(N_3)_2]^+$. When this diazide complex is dissolved in acid, nitrogen gas is released (as shown by mass spectral analysis) and a large peak appears in the uv spectrum at 264 nm, with a shoulder near 320 nm. The amount of nitrogen released, and the relative intensities of the two peaks, is dependent upon the initial concentrations of both the acid and the azide complex. The spectral peaks at 264 and 320 nm are assigned to the formation of the triply bonded nitrogen dimer (E), $[N_3(en)_2Ru^{II}-N{\equiv}N-Ru^{II}(en)_2N_3]^{2+}$, and the species D observed in the previous section.

The mechanism of the acid reaction with *cis*-$[Ru(en)_2(N_3)_2]^+$, which leads to the formation of both products, is consistent with the mechanisms already discussed. Acidification leads to N–N bond cleavage with

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[17] I. J. Iszkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968).

[18] E. Lieber, J. S. Curtice, and C. N. R. Rao, *Chem. Ind.* (*London*), 586 (1966).

[19] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

[20] P. S. Sheridan, Ph.D. Thesis, Northwestern University, 1970.

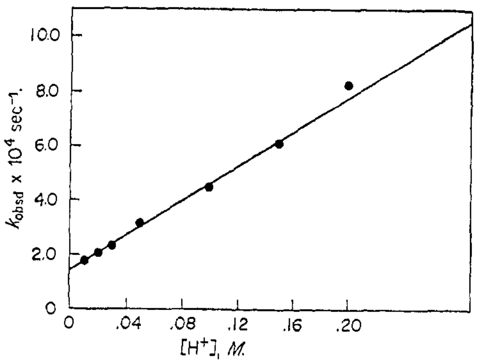

Figure 3. Plot of k_{obsd} *vs.* $[H^+]$ for the reaction of *cis*-$[Ru(en)_2(N_3)_2]PF_6$ with *p*-toluenesulfonic acid in acetone at 24.8°.

the release of nitrogen gas and the formation of a ruthenium(III)-coordinated nitrene (F).

$$[Ru^{III}(en)_2(N_3)_2]^+ \xrightarrow[-N_2]{H^+} \underset{\text{F}}{[N_3(en)_2Ru^{III}—NH]^{2+}} \qquad (9)$$

As was observed for the pentaammineruthenium(III) system, this nitrene intermediate (F) will either react with another nitrene to form a dimer (E in eq 10), or it will react with an azide ligand to form two monomeric nitrogen complexes (eq 11). This monomeric ruthenium(II) complex will react in acid to form the species D.

$$2[N_3(en)_2Ru^{III}—\overset{H}{\bar{N}}]^{2+} \xrightarrow{-2H^+} \underset{\text{E}}{[N_3(en)_2Ru^{II}—N{\equiv}N—Ru^{II}(en)_2N_3]^{2+}} \qquad (10)$$

$$[N_3(en)_2Ru^{III}—\overset{H}{\bar{N}}]^{2+} + [Ru^{III}(en)_2(N_3)_2]^+ \xrightarrow{-H^+} 2[Ru^{II}(en)_2N_2N_3]^+ \qquad (11)$$

The presence of the nitrene intermediate is strongly indicated by the effect of added Lewis bases on the acid reaction solutions. Coordinated azide is a base and is an effective trap for the ruthenium(III) nitrene. Therefore, the nitrene reaction with azide (eq 11) should be favored over the dimerization of the nitrene (eq 10) as the initial concentration of the azide complex is increased. This is observed, for as the initial complex concentration is increased, the uv spectra indicate an increased concentration of the species D and a corresponding decrease in the concentration of the nitrogen dimer E (Table VII).

In dilute solutions, where the dimerization reaction (eq 10) is the dominant reaction pathway, the presence of slight amounts of iodide ion, thiourea, or diethyl sulfide completely stopped this dimerization. These soft Lewis bases react rapidly with the nitrene, preventing dimerization. The thiourea trapped product has been isolated as the tetraphenylborate salt, and analysis points closely to $[Ru(en)_2(H_2O)(N\text{-}SCN_2H_4)][B(C_6H_5)_4]_3$ (see Experimental Section). The ir spectrum of the product differs markedly from that of the analogous thiourea complex.

Essentially first-order kinetics were observed for the rate of loss of starting material in acid solutions. The rate law for the loss of starting material has the general form

$$k_{obsd} = k_0 + k_H[H^+]$$

Table VII. Reaction of Acid on *cis*-$[Ru(en)_2(N_3)_2]PF_6$ at Room Temperature

Complex concn, *M*	H_2SO_4 concn, *M*	% yield Species D^a	% yield Species E^b	Total % yield^c
9.5×10^{-5}	Water	High	0	
9.5×10^{-5}	0.08	67	27	94
9.5×10^{-5}	0.15	54	38	92
9.5×10^{-5}	0.40	34	63	97
9.5×10^{-5}	0.80	30	67	97
9.5×10^{-5}	4.0	39	44	83
9.5×10^{-5}	8.5	43	28	71
2.3×10^{-5}	0.80	30	63	93
9.5×10^{-5}	0.80	30	67	97
9.3×10^{-4}	0.80	39	60	99
5.3×10^{-2}	0.80	75	19	94

[a] Measured at 220 nm. [b] Measured at 264 nm. [c] The total yield is decreased in high acid concentrations. This is due to the acid-catalyzed hydrolysis of the azide complex, which increases in high concentrations of acid.

Table VIII. Rate Data for the Reaction of Acid on *cis*-$[Ru(en)_2(N_3)_2]PF_6$

Temp, °C	$k_0 \times 10^4$ sec^{-1}	$k_H \times 10^3$ M^{-1} sec^{-1}
15.4	0.469	1.16
20.5	0.90	2.13
24.8	1.43	3.18
30.3	2.81	4.83
35.0	4.45	5.85
40.2	7.75	9.88

A typical plot of k_{obsd} *vs.* $[H^+]$ is shown in Figure 3, and values for k_0 and k_H are given in Table VIII. Because of the several reaction pathways available to *cis*-$[Ru(en)_2(N_3)_2]^+$ in acid solution, the rate of its decrease is not directly related to the formation of a single product. The diazidoruthenium(III) complex is consumed in several reactions, the formation of a metalated nitrene (eq 9) and the reaction of the diazido complex with a nitrene to form nitrogen–ruthenium(II) complexes (eq 11). Also contributing to the loss of the starting material is the acid-catalyzed aquation of the coordinated azide ion, and a neutral decomposition reaction, which will be discussed in the next section. Thus, k_0 and k_H are a combination of several rate constants and cannot be precisely interpreted. However, k_0 is closely related to the first-order rate constant for the neutral reaction described below, and k_H is closely related to the rate constant for reaction 9.

Neutral Reaction of Azidoruthenium(III) Complexes. The neutral decomposition of ruthenium(III) azides was observed for several compounds, in both the solid state and in solution. Our experience with $[Ru(NH_3)_5N_3](N_3)_2$ confirms the results of Allen, *et al.*,[1] that the azide complex readily reacts in the solid state to give $[Ru(NH_3)_5N_2](N_3)_2$. We also have found that *cis*-$[Ru(en)_2(N_3)_2]PF_6$ yields almost pure *cis*-$[Ru(en)_2N_2N_3]PF_6$ when heated (see Experimental Section). Mass spectral analysis of the released gas, quantitative gas evolution measurements, and weight loss upon heating all confirm the stoichiometry of the reaction

$$[Ru(en)_2(N_3)_2]PF_6 \xrightarrow{\Delta} [Ru(en)_2N_2N_3]PF_6 + {}^1/_2N_2 \qquad (12)$$

The decomposition of the corresponding triethylenetetramine complex is slower, being incomplete after 3 hr at 65°. The ir spectrum of a sample heated for only 1 hr at 65° shows a strong coordinated nitrogen band at 2120 cm^{-1} (Table II), indicating the presence of $[Ru(trien)N_2N_3]PF_6$. Continued heating causes the loss of coordinated nitrogen, and the final product contains a ruthenium–nitrosyl species.

The kinetic data of the neutral reaction in solution (Tables IX and X) reveal the same trend in the reaction rates as observed in the ease of the solid-state reaction, *i.e.*, $[Ru(NH_3)_5N_3]^{2+} > [Ru(EDTA)N_3]^{2-} >$ *cis*-$[Ru(en)_2(N_3)_2]^+ >$ *cis*-$[Ru(trien)(N_3)_2]^+$.

Table IX. Rate Data for Neutral Decomposition of *cis*-$[Ru(en)_2(N_3)_2]PF_6$ in Acetone

Temp, °C	10^4(azido complex), *M*	$k_{obsd} \times 10^5$ sec^{-1}
19.5	1.26	3.35
	2.61	3.41
	6.71	3.57
24.5	0.91	7.02
	2.52	7.42
	3.14	6.98
	4.49	7.49
30.8	1.31	17.7
	2.59	16.6
	3.44	16.5
	4.81	17.7
34.9	2.32	29.3
	3.09	30.0
	3.40	29.0
	4.01	29.6
40.5	1.46	54.4
	2.75	57.5
45.1	2.84	90.0
	3.72	92.8

Table X. Arrhenius Parameters and Rate Constants for Redox Decomposition of Ruthenium(III) Azido Complexes in Acetone at 20.8°

Complex	$k_{obsd} \times 10^5$ sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$[Ru(EDTA)N_3]^{2-}$ [a]	9.73[b]	18.9	−13
cis-$[Ru(en)_2(N_3)_2]PF_6$	4.22[b]	23.8	−2
cis-$[Ru(trien)(N_3)_2]PF_6$	1.87[b]	22.9	−2
$[Ru(NH_3)_5(N_3)](PF_6)_2$	99.0		

[a] In water. [b] Extrapolated from Arrhenius plot.

The proposed mechanism for this neutral reaction is similar to the proposed acid reaction pathway. The first step requires breaking a N–N bond in the azide ligand, which releases nitrogen gas and causes the formation of a metalated, deprotonated nitrene (H).

$$[L_5Ru^{III}N_3]^{2+} \xrightarrow{k_1} \underset{\mathbf{H}}{[L_5Ru^{III}\underline{\overline{N}}]^{2+}} + N_2 \tag{13}$$

This intermediate (H) reacts immediately with coordinated azide ligands to form two monomeric nitrogen–ruthenium(II) complexes

$$\underset{\mathbf{H}}{[L_5Ru^{III}\underline{\overline{N}}]^{2+}} + [Ru^{III}L_5N_3]^{2+} \xrightarrow{k_2} 2[L_5Ru^{II}N_2]^{2+} \tag{14}$$

This corresponds with the behavior observed in acid for azidoruthenium(III) complexes (eq 6 and 8). The dimerization of two nitrene intermediates observed in the acid reaction (eq 7), however, does not occur in the neutral reaction. Even with dilute complex concentrations, when dimerization is the dominant pathway in the acid reaction, the neutral reaction intermediate H reacts immediately with the coordinated azide ligand. In acid, the proton stabilizes the intermediate so that dimerization can occur, but in neutral solutions the inprotonated intermediate H reacts rapidly with the most prevalent Lewis base—the coordinated azide ligand.

Without the complication of the dimerization reaction, the rate of loss of the starting material is directly related to the rate of formation of the monomeric nitrogen–ruthenium(II) complex. The rate law has the simple interpretation

$$k_{obsd} = 2k_1$$

Values for k_{obsd} obtained in several solvents are given in Tables IX–XI. The reaction is first order in complex concentration and is independent of the initial complex concentration, so the proposed mechanism is consistent with the kinetic results. The rate-controlling step is the cleavage of the N–N bond in the azide ligand (k_1 in eq 13), and is followed by the rapid reaction k_2, leading to the final nitrogen–ruthenium(II) complex.

Table XI. Effect of Solvent on Rate of Redox Decomposition of Ruthenium(III) Azido Complexes

Complex ion	Temp, °C	Solvent	$k_{obsd} \times 10^3$ sec^{-1}
cis-$[Ru(en)_2(N_3)_2]^+$	34.9	Acetone	29.3
		Acetonitrile	31.4
		Methanol	50.9
$[Ru(NH_3)_5N_3]^{2+}$	20.8	Water	1.17
		Acetone	0.99
		Methanol	1.85

Trapping experiments lend further support to the proposed mechanism and to the presence of the intermediate H. The formation of *cis*-$[Ru^{II}(en)_2N_2N_3]^+$ from *cis*-$[Ru^{III}(en)_2(N_3)_2]^+$ was blocked in acetone and methanol by a tenfold excess of thiourea. The ir spectra in Figure 4 illustrate the effect of thiourea upon the neutral decomposition reaction. The initial spectra show the split azide peaks at 2050 cm^{-1}, and a weaker peak at 2130 cm^{-1} due to the presence of some azidonitrogen compound. The top series of spectra in Figure 4 shows the change in the ir spectra of the neutral reaction in acetone. One of the azide peaks disappears with the growth of the peak at 2130 cm^{-1} due to the coordinated nitrogen ligand. The bottom spectra show the effect of a tenfold excess of thiourea upon the reaction. The nature of the final products is unknown, but the azide peak disappears and the peak at 2130 cm^{-1} does not increase, indicating that the thiourea blocks the formation of the nitrogen complex.

There is little experimental evidence to prove that the nitrene mechanism is involved in the solid-state reaction. However, when solid *cis*-$[Ru^{III}(en)_2(N_3)_2]PF_6$ is heated to yield *cis*-$[Ru^{II}(en)_2N_2N_3]PF_6$, the uv spectrum of the solid product has a weak peak at 264 nm. Such a peak indicates the presence of the nitrogen-bridged dimer E which would result from

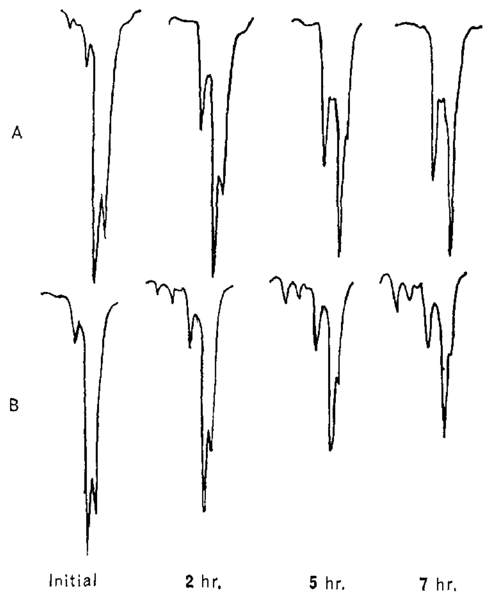

Figure 4. Infrared spectral changes during the decomposition reaction of *cis*-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ in acetone at 25° (2200–1900 cm). Series A shows the spectral change under normal conditions. Series B shows the spectral change in the presence of a tenfold excess of thiourea.

the dimerization of two intermediates (H) in the solid. The formation of slight amounts of this dimer, the positive correlation between the ease of decomposition in the solid state, and the rates of decomposition in solution indicate that nitrene formation is the probable reaction pathway, even in the solid-state reaction.

Optical Activity Measurements. The proposed mechanism is consistent with the stereospecificity observed for the neutral decomposition reaction. When solid *cis*-(−)-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ was heated to form *cis*-[Ru(en)$_2$N$_2$N$_3$]PF$_6$, it also was optically active. Similarly, when the reaction was done in solution, the product was optically active *cis* (+)-[Ru(en)$_2$N$_2$N$_3$]PF$_6$. The mechanism proposed above predicts that none of the metal–ligand bonds would be broken during the reaction, so the nitrogen complex should retain optical activity.

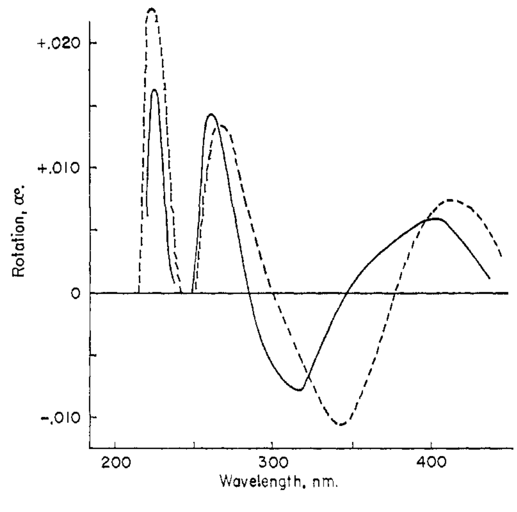

Figure 5. ORD spectra of (−)-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$ (- - -) and (+)-[Ru(en)$_2$N$_2$N$_3$]PF$_6$ (—) in water. Below 250 nm [Ru(en)$_2$(N$_3$)$_2$]PF$_6$ and [Ru(en)$_2$N$_2$N$_3$]PF$_6$ are both 0.008%. Above 250 nm [Ru(en)$_2$(N$_3$)]PF$_6$ is 0.01%, and [Ru(en)$_2$N$_2$N$_3$]PF$_6$ is 0.04%.

The ORD spectrum of *cis*-(+)-[Ru(en)$_2$N$_2$N$_3$]PF$_6$ is similar to, and a great deal weaker than, the spectrum of *cis*-(−)-[Ru(en)$_2$(N$_3$)$_2$]PF$_6$. It could be argued that the activity observed for the nitrogen complex was really due to a small percentage of the unreacted diazidoruthenium(III) complex. The spectra are sufficiently different, however, so that they represent two different compounds. The gross similarity of the two spectra (Figure 5) suggests that the compounds have the same absolute configuration. This, again, is consistent with the proposed nitrene mechanism.

A search has been made for similar acid reactions among other transition metal azide complexes. Azide complexes of Co(III), Rh(III), Pt(II), Pd(II), and Au(II) generated no gas when dissolved in 4 *M* H$_2$SO$_4$ at room temperature. Similar behavior has been found in these laboratories, however, for the Ir(III) complex, *trans*-[Ir(en)$_2$(N$_3$)$_2$]PF$_6$.[21]

Acknowledgment. This work was supported by grants from the National Science Foundation and the National Institutes of Health. We thank Mr. D. L. Diemente for the esr measurements.

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[21] R. Bauer, unpublished results.