Ruthenium Promoted Oxidation of Amines

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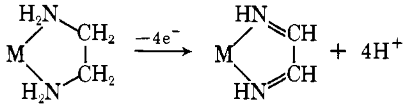
Abstract: The oxidation of benzylaminepentaammineruthenium(III) results in a high yield of the nitrile bound to the metal ion with the imine as a recognizable intermediate stage. The formal reduction potentials for the pentaammineruthenium(III)-(II) couples with the amine, imine, and nitrile as ligands are 0.120, 0.320, and 0.510 V, respectively. With cyclohexylamine as the ligand, dehydrogenation stops at the imine stage, but the ruthenium(III) imine intermediate readily hydrolyzes to hexaammine and a ketone. When the methylamine complex is oxidized, the N-bound HCN is formed as an intermediate. On rearranging to the C-bound form, the trans ammonia is labilized and a polymeric species is produced.

The dehydrogenation of amine ligands has been of interest to inorganic chemists for several years. Reactions of this type have been observed for nickel(II) macrocyclic amine ligand complexes[1-3] and ethylenediamine complexes of ruthenium(II)[4] and iron(II).[5] In these cases the oxidized lig-



and remains coordinated to the metal. Similar results have been reported involving oxidations to triple bonds. McWhinnie showed that hexakisamine complexes of ruthenium(II) react readily with molecular oxygen to give cyano and possibly nitrile complexes.[6]

Recently we found that oxidation of ruthenium(II) nitrile complexes activated the resulting ruthenium(III) species for nucleophilic attack producing amides.[7] This result coupled with the results on the oxidation of amine ligands led us to the study described herein.

Experimental Section

Chemical and Reagents. Chloropentaammineruthenium(III) chloride was prepared by refluxing hexaammineruthenium(III) chloride (obtained from Matthey Bishop, Inc.) in 6 *M* HCl for 4 hr followed by crystallization from 0.1 *M* HCl.[8] The following compounds were used without further purification: cyclohexylamine, 97% (Aldrich Chemical Co.), benzylamine (Matheson Coleman and Bell), methylamine, 40% in water (Matheson Coleman and Bell), and benzonitrile, 99% (Aldrich Chemical Co.). Solutions of 0.1 *M* hydrochloric acid were made directly from Titrisol (Brinkmann Instruments, Inc.). Silver oxide was obtained from Allied Chemical Co. Microanalyses were performed by the Stanford Microanalytical Laboratory, Stanford, Calif.

Equipment. A Cary Model 15 recording spectrophotometer was used for absorption measurements. Infrared spectra were recorded on a Perkin-Elmer Model 621 grating infrared spectrophotometer. Electrochemical studies employed a cyclic voltammetry apparatus constructed in this laboratory using a platinum inlay electrode (Beckman 39273) or a hanging mercury drop electrode (Brinkmann E410) as the indicator electrode and a standard calomel reference electrode. Analytical vapor phase chromatography was carried out with an HP-402 Model gas chromatograph using a 6 ft × 0.25 in. glass column packed with 3% OV-17 on Gas Chrom Q.

Synthesis of Complexes. Benzylaminepentaammineruthenium(II) hexafluorophosphate was prepared in the following manner. In 2 ml of hot water 75 mg of silver oxide was dissolved by dropwise addition of concentrated trifluoroacetic acid (ca. 12 drops) and 100 mg of $[(NH_3)_5RuCl]Cl_2$ was added to this solution with stirring. The silver chloride was removed by filtration and the volume was increased to 5 ml. The resulting solution was reduced with zinc amalgam for 10 min in an argon atmosphere at which time a tenfold excess of benzylamine was added (ca. 0.4 ml). After 2 hr the pH of the solution was adjusted to ca. 1 using 1 *M* trifluoroacetic acid. The solution was filtered and ammonium hexafluorophosphate (ca. 1 g) was added. The resulting yellow solid was filtered and washed with ether. Recrystallization from water yielded the desired complex. Anal. Calcd for $[(NH_3)_5RuC_7H_9N](PF_6)_2$: C, 14.4; N, 14.4; H, 4.12; Ru, 17.3. Found: C, 14.3; N, 14.6; H, 4.09; Ru, 17.3. The ruthenium(II) complexes can be readily oxidized to the ruthenium(III) amine complexes using silver trifluoroacetate or bromine water.

Methylaminepentaammineruthenium(II) hexafluorophosphate was prepared in the same manner as described above. Anal. Calcd for $[(NH_3)_5RuCH_5N](PF_6)_2$: C, 2.37; N, 16.6; H, 3.94; Ru, 19.9. Found: C, 2.53; N, 16.7; H, 3.94; Ru, 19.7.

Cyclohexylaminepentaammineruthenium(III) perchlorate was prepared in the following manner. Aquopentaammineruthenium(II) trifluoroacetate, prepared as described above, was transferred under argon into a bubble flask containing a 15-fold excess of thoroughly degassed cyclohexylamine. Zinc hydroxide immediately precipitated and the reaction proceeded for 1.5 hr at which time the solution was acidified with 6 *M* HCl. The solution containing the ruthenium(II) complex was oxidized to the ruthenium(III) amine complex using bromine water. Pyraziniumpentaammineruthenium(II) was used as an indicator in the oxidation.[9] The reaction mixture was filtered and 3 ml of concentrated perchloric acid was added to the filtrate causing immediate precipitation of a white solid. After cooling, the solid was collected on a sintered glass funnel but not dried. (Ruthenium perchlorate salts are subject to detonation when dried. Work with only milligram quantities!) The solid was dissolved in 0.1 *M* perchloric acid at 40° and filtered. Addition of concentrated perchloric acid again caused precipitation of the complex. The solid was washed with a 4:1 mixture of ether:ethanol and dried in a vacuum desiccator. With appropriate precautions the solid was removed from the filter. Anal. Calcd for $[(NH_3)_5RuC_6H_{13}N](ClO_4)_3$: C, 12.3; N, 14.4; H, 4.80. Found: C, 12.4; N, 14.2; H, 4.69.

Benzonitrilepentaammineruthenium(II) hexafluorophosphate was prepared from chloropentaammineruthenium(III) chloride by a procedure very similar to that reported in the literature.[10] Anal. Calcd for $[(NH_3)_5RuC_7H_5N](PF_6)_2$: C, 14.5; N, 14.5; H, 3.45. Found: C, 14.4; N, 14.7; H, 3.61. In addition, the infrared and electronic spectra corresponded to those of the known complex.

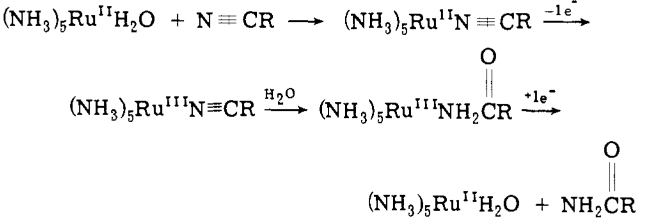
Results

Benzylamine. The benzylaminepentaammineruthenium(II) and -(III) hexafluorophosphate salts were characterized using electronic and infrared absorption spectra and cyclic voltammetry. In general, the electronic absorption spectra are the least reliable since the aminepentaammineruthenium complexes have bands of low extinction coefficients and trace impurities having much larger extinction coefficients may vitiate the absorption measurements. The infrared spectrum of the benzylamineruthenium(III) complex agrees with that expected for a saturated amineruthenium complex. The spectra of these species are similar to those of known hexaammineruthenium complexes.[11] The cyclic voltammogram in 0.1 *M* HCl shows one electrochemically reversible couple at 120 mV (Table I).[12] This agrees well with ammineruthenium(III)-(II) couples quoted in the literature.[13]

As mentioned in the Experimental Section, oxidation to the ruthenium(III) complex occurred readily with a variety of oxidizing agents. However, further facile oxidation of the complex proceeded only in nonacidic media (pH >5). In a typical experiment the benzylamineruthenium(II) product solution was extracted with ether to remove the excess benzylamine. The pH of this yellow solution was adjusted to ca. 7 using 1 *M* trifluoracetic acid. A continuous stream of oxygen was passed through the solution causing a gradual color change to deep red. By the end of 1 hr the solution was again yellow. The pH was adjusted to ca. 1 using 1 *M* trifluoroacetic acid and excess ammonium hexafluorophosphate produced a yellow precipitate which was washed with ether and dried. The solid was recrystallized from water at 40–50°. The infrared spectrum of this solid shows a strong band at 2190 $\mathrm{cm^{-1}}$ corresponding to that of benzonitrilepentaammineruthenium(II) perchlorate reported in the literature.[10] The electronic absorption spectrum also conforms to that of the known complex. The cyclic voltammogram of this complex in 0.1 *M* HCl shows a reversible couple at 510 mV in agreement with the value for benzonitrilepentaammineruthenium(II) hexafluorophosphate prepared from benzonitrile and aquopentaammineruthenium(II) trifluoroacetate shown in Table I. Microanalytical data led to the formulation of this species as $\mathrm{[(NH_3)_5RuNCC_6H_5](PF_6)_2}$. A blank experiment with an aqueous solution of benzylamine was run which showed no benzonitrile to be present after oxidation. It was determined that the oxidation also occurs using a 5% aqueous sodium hypochlorite solution. The overall oxidation reaction is

$$\mathrm{(NH_3)_5RuNH_2CH_2C_6H_5{}^{2+} + O_2 \longrightarrow (NH_3)_5RuNCC_6H_5{}^{2+} + 2H_2O}$$

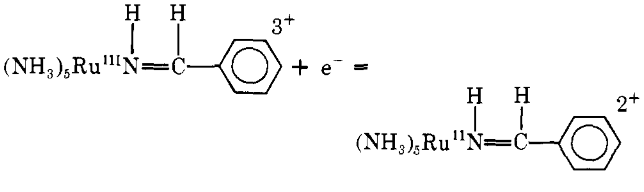
This oxidation was coupled to the sequence of reactions reported earlier.[7] In this scheme a nitrile can be converted to an amide using aquopentaammineruthenium(II) trifluoroacetate. The reaction sequence is



$$\mathrm{(NH_3)_5Ru^{II}H_2O + N{\equiv}CR \longrightarrow (NH_3)_5Ru^{II}N{\equiv}CR \xrightarrow{-1e^-} (NH_3)_5Ru^{III}N{\equiv}CR \xrightarrow{H_2O} (NH_3)_5Ru^{III}NH_2\overset{O}{\overset{\|}{C}}R \xrightarrow{+1e^-} (NH_3)_5Ru^{II}H_2O + NH_2\overset{O}{\overset{\|}{C}}R}$$

In analogy to the work referred to it was possible to oxidize the benzonitrileruthenium(II) complex further to the benzonitrileruthenium(III) complex finally producing benzamide.

The last series of experiments performed on this system was devoted to identifying the red species initially produced in the oxidation. Electronic absorption spectra of the amine complex in oxygenated water show peaks corresponding to the nitrile plus one additional peak at 450 nm (Figure 1). This is close to those observed for the diimine complexes of ruthenium(II).[5] When the oxidation is complete this peak disappears. The cyclic voltammogram of a partially oxidized solution of the amine shows that peaks attributable to the amine and nitrile are present and also a new one at 320 mV (in 0.1 *M* HCl). The couple responsible for the peak is present in only a small amount and is believed to be the imine couple



As the oxidation nears completion the intensity of this peak decreases and the solution changes color. It should be emphasized that each step in the reaction sequence amine → imine → nitrile is irreversible.

Table I. Formal Reduction Potentials of Ruthenium Complexes[a]

Redox couple	E,[b] mV vs. NHE
$\mathrm{Ru(NH_3)_6{}^{3+,2+}}$	51,[c] 60[d]
$\mathrm{Ru(NH_3)_5Cl^{2+,+}}$	−42[c]
$\mathrm{Ru(NH_3)_5NH_2CH_2C_6H_5{}^{3+,2+}}$	120[d]
$\mathrm{Ru(NH_3)_5NHCHC_6H_5{}^{3+,2+}}$	320[d]
$\mathrm{Ru(NH_3)_5NCC_6H_5{}^{3+,2+}}$	510,[d] 510[e]
$\mathrm{Ru(NH_3)_5NH_2CH_3{}^{3+,2+}}$	100[d]
$\mathrm{Ru(NH_3)_5NH_2C_6H_{11}{}^{3+,2+}}$	110[d]
$\mathrm{Ru(NH_3)_5NHC_6H_{10}{}^{3+,2+}}$	190[d,f]

[a] All measurements done using 0.1 *M* HCl as a supporting electrolyte unless otherwise indicated. [b] All the couples have approximately the same peak separation and are therefore taken to be reversible. [c] Measured in 0.2 *M* $\mathrm{CF_3COONa}$ or $\mathrm{NaClO_4}$ as reported in ref 12. [d] This work. [e] Measured on an authentic solid prepared independently from the nitrile. [f] Measured in 0.1 *M* $\mathrm{NaHCO_3}$.

Experiments to determine the yield of the benzonitrileruthenium(II) complex produced by the oxidation were done. The values of the extinction coefficients in the literature for the known complex were used to determine the concentration of the product complex. The yields ranged between 70 and 85% depending on the conditions of the oxidation. The lower yields corresponded to runs done at lower pH, thus extending over a longer period of time.

Methylamine. Oxidation of the methylamineruthenium(II) complex at pH 7 using oxygen produced a blue-green complex which had previously been identified in this laboratory as the polymeric species $\mathrm{-Ru^{II}CNRu^{II}CN-}$ or a similar polymer, partially oxidized to ruthenium(III).[14] This species has a broad absorption in the ir at 1940 $\mathrm{cm^{-1}}$ which was used for characterization. A sample which had been only partially oxidized in 0.1 *M* acid using bromine water was prepared and the infrared spectrum of the solid was measured. The band characteristic of the N-bound form of the HCN complex $\lambda_{\max}$ 2085 $\mathrm{cm^{-1}}$, was observed, although present in only a small amount.

Cyclohexylamine. Cyclohexylamine was chosen as a substrate because dehydrogenation does not proceed beyond the imine stage. Characterization as before confirmed the identity of the cyclohexylamineruthenium(III) salt (see Table I). The oxidation could be carried out using a 5% aqueous solution of sodium hypochlorite or oxygen, but for this system the best results were obtained using 30% hydrogen peroxide in a sodium bicarbonate buffer.

In a typical experiment 2 equiv of hydrogen peroxide was added per mole of the ruthenium(III) amine complex in solution at pH 8 (bicarbonate buffer) and left for 1.5 hr. After this time, cyclic voltammetry showed the major ruthenium containing species, in scanning the potential range which covers the imine complex to hydroxopentaammineruthenium, to be ruthenium hexaammine, with a trace (<5%) of the hydroxopentaammineruthenium ion present. In one experiment the pH was raised to 11 (carbonate buffer) and even though 2 equiv of hydrogen peroxide was added, the oxidation was not complete; ruthenium imine, ruthenium hexaammine, and hydroxopentaammineruthenium were all present. In this case, using blanks the concentrations of the ruthenium species were determined and more than 90% of the ruthenium was accounted for by these products. The hexaammine was again the dominant product. The rest potential of the product solution was such as to ensure that ruthenium imine was present as ruthenium(II) rather than ruthenium(III). The cyclic voltammogram after 2 hr for this solution is shown in Figure 2.

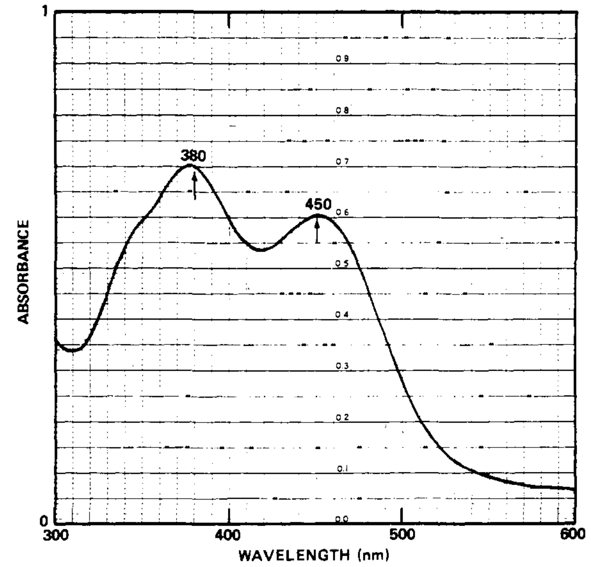


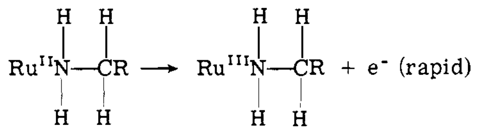
Figure 1. Visible spectra of a partially oxidized benzylamine complex.

Attempts were made to identify the organic product. After the oxidation was complete reaction solutions were extracted with dichloromethane. Removal of the solvent yielded cyclohexanone as the exclusive product. It was identified by gas chromatographic and infrared techniques using authentic samples of the ketone for comparison.

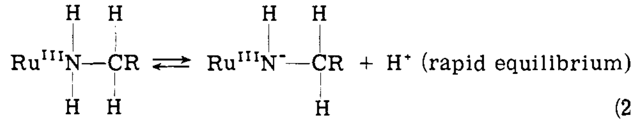
Discussion

The three ligands benzylamine, methylamine, and cyclohexylamine lead to different products on oxidation, but it seems likely that they have as a common first step the formation of an imine intermediate. For cyclohexylamine, the imine is the terminal oxidation state, though a subsequent hydrolysis reaction does occur. For benzylamine, the cyclic voltammetric experiments, as well as color changes, show that an intermediate is formed. On the basis of its properties, this intermediate is almost certainly the imine complex of ruthenium(II). Further oxidation is rapid, so that the intermediate is not formed in a high steady state concentration. By changing pH, the temperature, and the nature of the oxidizing agent, it is likely that the steady state concentration can be increased, but the extensive systematic work which this calls for has not been done. There is no direct evidence for the imine state when methylamine as ligand is oxidized, and we infer that further oxidation is particularly facile in this instance.

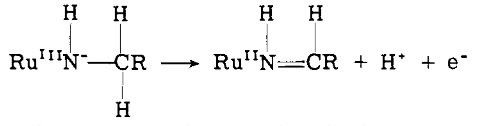
In view of the readiness with which ruthenium(II) is oxidized to ruthenium(III), and the fact that the rate of ligand oxidation increase with the pH, the reaction sequence leading to the imine state is likely the following



$$\mathrm{Ru^{II}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{R} \longrightarrow \mathrm{Ru^{III}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{R} + e^- \text{ (rapid)} \tag{1}$$



$$\mathrm{Ru^{III}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{R} \rightleftharpoons \mathrm{Ru^{III}}\overset{\mathrm{H}}{\mathrm{N}}^{-}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{R} + \mathrm{H^+} \text{ (rapid equilibrium)} \tag{2}$$



$$\mathrm{Ru^{III}}\overset{\mathrm{H}}{\mathrm{N}}^{-}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{R} \longrightarrow \mathrm{Ru^{II}}\overset{\mathrm{H}}{\mathrm{N}}=\overset{\mathrm{H}}{\mathrm{C}}\mathrm{R} + \mathrm{H^+} + e^- \tag{3}$$

Particular interest attaches to the third step in this sequence, where presumably the explanation for the difference between ruthenium(III), on the one hand, and cobalt(III) or chromium(III), on the other, in facilitating oxidation of the ligand is to be found. The step may involve hydride transfer from carbon to ruthenium(IV), Ru(IV)-(H^-) being equivalent to Ru(II)-(H^+), so that on proton loss the oxidation is consummated. This formulation implies involvement of the πd electrons of ruthenium, an involvement which has been suggested in other systems as well.[15,16] The stabilization of ruthenium(II) by the π acid product ligand, and vice versa, through back-donation, is presumably another factor which facilitates the reaction.

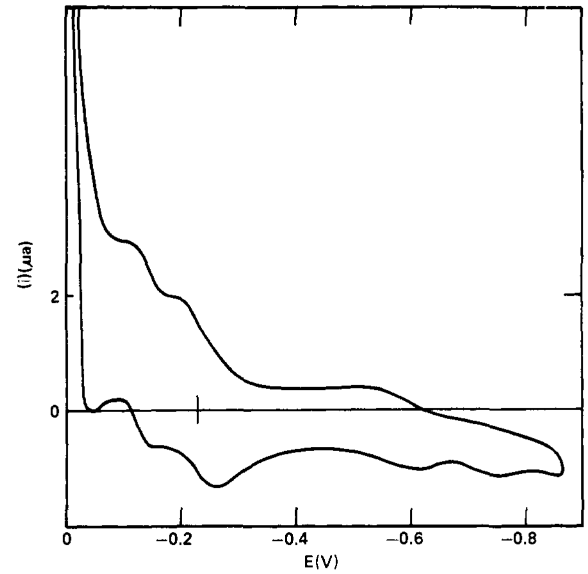


Figure 2. Cyclic voltammogram of a partially oxidized cyclohexylamine complex. Vertical tick on the zero line indicates position of the standard hexaammineruthenium(III)-(II) couple.

In considering the subsequent reactions of the imine intermediate, the cyclohexylamine system will be dealt with first because its chemistry is the most straightforward. The ruthenium(III) imine intermediate is shown to be quite labile, and, on hydrolyzing, it yields mainly at carbon (forming hexaammine) rather than at ruthenium (forming hydroxopentaammine). A matter of interest is the relative lability of the ruthenium(II) compared to the ruthenium(III) imine complexes. The experiment described in the results section, in which less than the equivalent amount of oxidizing agent acted on the system, shows the ruthenium(II) imine to survive under conditions under which the ruthenium(III) would be completely hydrolyzed. The difference in lability, with ruthenium(II) stabilizing the imine, can be understood in the same terms as for ruthenium(II) stabilizing nitrile while ruthenium(III) promotes hydrolysis (vide infra).

The statements made on the mechanism of the oxidation of amine to imine, at least in general respects, may apply also to the further oxidation step, imine to nitrile. When benzylamine is the ligand, the nitrile is formed in high yield—as high as 85%. A possible side reaction which would reduce the yield is hydrolysis of the ruthenium(III) complex at the imine stage. For this supposition to be in accord with the observations, the hydrolysis reaction must increase in rate less rapidly than does the oxidation of the imine as the pH rises.

As the present and earlier results show, reaction does not necessarily stop at the nitrile stage. On oxidizing the ruthenium(II) to the ruthenium(III) complex, the stabilization of nitrile by back-bonding is lost resulting in a strong Lewis acid, ruthenium(III), being bound to nitrogen of the nitrile group. Since the metal ion is a low spin d^5 system of oxidation state 3+, the nitrile group is not readily lost by aquation, and as has been shown in other work, hydrolysis of the nitrile to amide ensues. On reducing ruthenium(III) to ruthenium(II), amide is displaced by water forming aquopentaammineruthenium(II). In principle at least, the conversion of amine to amide under mild conditions can be made catalytic with respect to the metal ion. If in fact the 15% deficit in the intermediate production of nitrile is, as suggested, really caused by N–C hydrolysis at the imine stage, in each cycle ca. 15% of the ruthenium ammine will be lost in being converted to hexaammine.

With methylamine as ligand the primary product of the oxidation of the imine is expected to be the N-bound HCN complex $[(NH_3)_5RuNCH]^{2+}$, and this species was detected by infrared spectroscopy in the solid obtained from a product solution. This species is known to rearrange to $[(NH_3)_5RuCN]^+$, more rapidly at a higher pH. The ammonia trans to the cyanide is then labilized whereupon polymer formation ensues.[14]

Little has been done on imines as ligands, and our work shows that the chemistry of the monoimine complexes in water is severely circumscribed by the ease with which hydrolysis to aldehydes or ketones takes place. The work on the benzylamine system shows there to be a stepwise increase in the stability of ruthenium(II) relative to ruthenium(III) as the ligand is taken through the changes amine–imine–nitrile. The stabilization of ruthenium(II) relative to ruthenium(III) is greater for benzylimine than for cyclohexylimine, as might be expected because the interaction of the aromatic ring with the imine group on the former case would render the ligand a better π acceptor.

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Photochemical Reaction Pathways of Ruthenium(II) Complexes.[1,2] Photoredox and Photosubstitution Reactions of the Acetonitrile Complex $Ru(NH_3)_5CH_3CN^{2+}$ and of the Dinitrogen Complex $Ru(NH_3)_5N_2{}^{2+}$

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Abstract: Quantum yields are reported for the photolysis of the ruthenium(II) complex $Ru(NH_3)_5CH_3CN^{2+}$ in aqueous solution over a wide range of the irradiation wavelength. Ligand field excitation with 366-nm light leads exclusively to substitution reactions with CH_3CN and NH_3 aquation occurring with comparable rates and with an overall quantum yield of approximately 0.26 mol/einstein. Higher energy irradiation results in the formation of both photosubstitution and photoredox products, the latter including Ru(III) complexes and molecular hydrogen. The wavelength dependent quantum yields for Ru(III) formation range from 0.008 with 313-nm irradiation to 0.51 with 213.9-nm light. Quantum yields for H_2 production were markedly enhanced by the presence of isopropyl alcohol in solution implicating the formation of hydrogen atoms as a photochemical consequence. These data are interpreted in terms of at least two competing photochemical mechanisms: ligand substitution occurring via a ligand field excited state of this $4d^6$ complex and oxidation of Ru(II) to Ru(III) resulting from charge transfer to solvent excitation. The photochemical behavior of the dinitrogen complex $Ru(NH_3)_5N_2{}^{2+}$ under the influence of 254-nm irradiation was also examined. The principal photoreaction was redox in character with a quantum yield for Ru(III) formation equaling 0.17 mol/einstein. H_2 is also a significant photolysis product.

The electronic excited state chemistry of ruthenium(II) complexes is widely varied. For example, irradiation of aqueous $Ru(bipy)_3{}^{2+}$ leads only to strong phosphorescence in the absence of other substrates[4] but to energy transfer (sensitization) processes[5] and in some cases to electron transfer reactions in their presence.[6] The closely analogous ion, *cis*-$Ru(bipy)_2(4\text{-stilbazole})_2{}^{2+}$, is only a weak emitter in ambient temperature fluid solution but undergoes relatively efficient reactions of coordinated stilbazole when irradiated at wavelengths corresponding to metal-to-ligand charge transfer (MLCT) or π–π^* internal ligand bands.[7] In contrast, the ruthenium(II) ammine complexes of the type