by means of $^1/_4$-in. Teflon nuts and compression fittings. In the case of samples containing $BrF_5$ or $SO_2ClF$ solvent, the solvent was condensed onto an appropriate quantity of solute(s) at −196 °C. Fluorosulfuric acid samples were prepared in a drybox by syringing the solvent into a sample tube containing the solute(s) cooled to −196 °C. Samples were warmed briefly to −48 °C to effect dissolution. All samples were stored at −196 °C until their spectra could be recorded.

**NMR Instrumentation and Spectra.** $^{19}F$ NMR spectra were recorded in CW mode on a JEOL PS-100 NMR spectrometer operating at 94.1 MHz and equipped with a low-temperature controller. All spectra were recorded in field-sweep mode and externally locked to $D_2O$. The pulse FT $^{129}Xe$ NMR instrumentation has been described elsewhere.[9]

The chemical shift convention is that outlined by IUPAC;[18] i.e., a positive chemical shift denotes a positive frequency and vice versa with respect to the designated reference substance. All spectra were referenced externally: $^{19}F$, neat $CFCl_3$ at the quoted sample temperature; $^{129}Xe$, neat $XeOF_4$ at 25 °C.

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**Registry No.** $WOF_4$, 13520-79-1; $MOF_4$, 14459-59-7; $XeF_2{\cdot}2WOF_4$, 56174-65-3; $XeF_2{\cdot}2MoOF_4$, 65651-37-8; $XeF_2{\cdot}WOF_4$, 55888-48-7; $XeF_2{\cdot}MoOF_4$, 74080-83-4; $XeF_2$, 13709-36-9; $XeF_2{\cdot}MoOF_4(MoOF_4)_2$, 65622-63-1; $XeF_2{\cdot}MoOF_4(MoOF_4)_3$, 74037-08-4; $XeF_2{\cdot}WOF_4(WOF_4)_2$, 65622-72-2; $FXeO{\cdot}WF_5(WOF_4)$, 74037-07-3; $FXeO{\cdot}WF_5(WOF_4)_2$, 74050-90-1; $FXeO(F)S({=}O)OMoOF_4$, 74080-82-3; $FXeOSO_2F$, 25519-01-1.

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# Photochemistry of Diacidobis(ethylenediamine)iridium(III) Complexes, *cis*- and *trans*-$Ir(en)_2XY^{n+}$. Observations Regarding the Photoisomerization of $d^6$ Complexes

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Ligand field excitation of the bis(ethylenediamine)iridium(III) complexes *cis*- and *trans*-$Ir(en)_2XY^+$ ($X = Y = Cl^-$, $Br^-$, or $I^-$; $X = OH^-$, $Y = Cl^-$) in aqueous solution leads to halide photolabilization in each case. For the *cis*- and *trans*-dichloro complexes, quantum yields were independent of solution pH, displaying the same values in acidic and basic solutions. In acidic solution, the *trans*-dihalo complexes undergo photoaquation to give *trans*-$Ir(en)_2(H_2O)X^{2+}$ with complete retention of configuration. However, the cis analogues undergo some concomitant photoisomerization to give a mixture of *trans*- and *cis*-$Ir(en)_2(H_2O)X^{2+}$ with the extent of photoisomerization following the order $Cl^- < Br^- < I^-$. In acidic solution, *trans*-$Ir(en)_2(H_2O)Cl^{2+}$ is apparently photoinert ($H_2O$ exchange excluded) while the cis analogue undergoes photoisomerization to the trans isomer with a modest quantum yield (0.03 mol/einstein). Making solutions of these ions alkaline (pH 12) gives the hydroxo analogues which demonstrate dramatically different photoreaction behavior, *cis*-$Ir(en)_2(OH)Cl^+$ undergoing $Cl^-$ labilization to give *cis*-$Ir(en)_2(OH)_2^+$ and *trans*-$Ir(en)_2(OH)Cl^+$ undergoing concomitant photohydrolysis/photoisomerization to give the same product. These results are interpreted in terms of the model proposed earlier to explain the photostereochemistry of similar rhodium(III) complexes.

## Introduction

The stereochemical properties of $d^6$ hexacoordinate complexes as the result of ligand field (LF) excitation have been the subject of much recent interest.[2-8] The photostereochemistry of rhodium(III) amine complexes has proved especially rich with recent results stimulating several related models[2a,6,7] to rationalize these. A series of observations made in these laboratories with the rhodium(III) tetraammines illustrate the types of photoreactions seen in these systems (eq 1–3). Both cis to trans and trans to cis isomerization of the

$$cis\text{-}Rh(NH_3)_4Cl_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + Cl^- \quad (1)$$

$$cis\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \quad (2)$$

$$trans\text{-}Rh(NH_3)_4(OH)Cl^+ + OH^- \xrightarrow{h\nu} cis\text{-}Rh(NH_3)_4(OH)_2^+ + Cl^- \quad (3)$$

Rh(III) tetraammines can be effected by LF excitation, depending upon the balance of the ligand field. In addition for

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[1] (a) Taken in part from the Ph.D. dissertation of M.T.-S., University of California, Santa Barbara, 1979. (b) Reported in part at the 177th National Meeting of the American Chemical Socieity, Honolulu, Hawaii, April 1979.

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eq 1 and 3 and probably for eq 2, photoisomerization occurs concomitant with ligand labilization. Notably, each of the models proposed to explain these reactions draws upon this latter point to suggest that the isomerization occurs via a five-coordinate intermediate which would be produced as the result of ligand photodissociation.

Investigations in this laboratory have also been concerned with Ir(III) photochemistry for the purpose of evaluating the generalities of the photochemical properties of $d^6$ complexes.[9–11] In this context, a close parallel has been noted between the photochemistries of the pentaammine ($Ir(NH_3)_5X^{n+}$) and *trans*-tetraammine (*trans*-$Ir(NH_3)_4X_2^{n+}$) complexes and the photochemistries of the Rh(III) homologues. However, attempts to prepare the unknown *cis*-$Ir(NH_3)_4X_2^{n+}$ species proved unsuccessful, so the present investigation of the known[12,13] *cis*- and *trans*-$Ir(en)_2X_2^{n+}$ complexes was initiated with the goal of establishing the generalities (or lack of these) for the photostereochemical properties of $d^6$ metal complexes. Notably, photostereochemical studies with the bis(ethylenediamine)rhodium(III) analogues $Rh(en)_2X_2^{n+}$ demonstrated few quantitative differences from those of the tetraammine species $Rh(NH_3)_4X_2^{n+}$. Thus, at least for those cases, one can conclude that replacing the four ammines by two ethylenediamine ligands does not introduce severe stereochemical constraints[4a,b] upon isomerization mechanisms.

## Experimental Section

**Materials.** Reagent grade materials and doubly distilled water were used throughout. The bis(ethylenediamine) complexes [*cis*-$Ir(en)_2Cl_2$]Cl, [*cis*-$Ir(en)_2Br_2$]Br, [*cis*-$Ir(en)_2I_2$]I, [*trans*-$Ir(en)_2Br_2$]Br, [*trans*-$Ir(en)_2Cl_2$]Cl, and [*trans*-$Ir(en)_2I_2$]I were prepared by published methods[12,13] and converted to their perchlorate salts by metathesis with perchloric acid. An exception was *cis*-$Ir(en)_2I_2^+$ which was isolated and recrystallized as the dithionate salt.

**Photolysis Procedures.** The photolyses in acidic aqueous solution were carried out at various radiation wavelengths ($\lambda_{irr}$) on the apparatus described earlier.[9,11,14] Reaction solutions were prepared from dilute perchloric acid (pH 3–4) with iridium complexes in the concentration range $2 \times 10^{-4}$ to $5 \times 10^{-3}$ M. Quantum yields for net release of coordinated ethylenediamine were evaluated from pH changes while quantum yields for halide aquations were evaluated from spectral changes and independently confirmed for $Cl^-$ and $Br^-$ by potentiometric titration with silver nitrate. Reaction stereochemistries were examined by heating the photoreaction solution with excess HX (where $X^-$ is the anion originally on the Ir(III) complex) to regenerate the dihalo complexes $Ir(en)_2X_2^+$. The spectra of the resulting solutions were compared quantitatively with the initial reaction solution spectra and, in the cases where the initial complex stereochemistry was cis, the solutions of the unipositive dihalo ions were treated by cation-exchange chromatography (on Bio-Rad AG 50W-X4, 200–400 mesh) to separate the cis and trans isomers.

Photolyses in alkaline solution were carried out on the same apparatus. Solutions of *cis*- and *trans*-$Ir(en)_2Cl_2^+$ were prepared by dissolving the complex in neutral solution and adjusting the pH of the resulting solution to 12 by adding 0.1 N NaOH solution. Solutions of *cis*- or *trans*-$Ir(en)_2(OH)Cl^+$ were prepared by addition of 0.1 N NaOH to solutions of *cis*- or *trans*-$Ir(en)_2(H_2O)Cl^{2+}$ prepared in situ by the stereoretentive aquations of the respective dihalo complexes (see Results).

Quantum yields from spectral changes were calculated by plotting incremental quantum yields vs. percent reaction and extrapolating to the 0% reaction intercept. The initial quantum yields thus calculated are independent of perturbations (secondary photoreactions, inner filtering, etc.) possibly introduced by products.

**Table I.** Spectra and Photochemistry of the $Ir(en)_2X_2^+$ Complexes in Acidic Aqueous Solution

| | spectra[a] | | photochemistry[a] | | | |
|---|---|---|---|---|---|---|
| $X^-$ | $\lambda_{max}$ ($\epsilon$)[b] | assignt[c] | $\lambda_{irr}$[d] | $\Phi_{X^-}$[e] | $\Phi_{H^+}$[e] | stereochemistry[f] |
| | *trans*-$Ir(en)_2X_2^+$ | | | | | |
| $Cl^-$ | 425 (13) | $^3$LF | 350 | 0.11 | <0.002 | >95% trans |
| | 345 (52) | $^1$LF | 313 | 0.12 | <0.002 | >95% trans |
| | 272 sh (58) | $^1$LF | | | | |
| $Br^-$ | 450 (13) | $^3$LF | | | | |
| | 360 (74) | $^1$LF | 366 | 0.080 | <0.002 | >95% trans |
| | 285 sh (47) | $^1$LF | | | | |
| | 230 sh ($3.0 \times 10^3$) | LMCT[g] | | | | |
| $I^-$ | 490 sh (18) | $^3$LF | 405 | 0.070 | <0.001 | >95% trans |
| | 398 (183) | $^1$LF | 366 | 0.062 | <0.001 | >95% trans |
| | 283 ($1.4 \times 10^4$) | LMCT | 313 | 0.065 | <0.001 | >95% trans |
| | | | 254 | 0.060 | <0.001 | |
| | 230 ($4.7 \times 10^4$) | LMCT | | | | |
| | *cis*-$Ir(en)_2X_2^+$ | | | | | |
| $Cl^-$ | 380 (19)[h] | $^3$LF | 313 | 0.13[i] | ⩽0.002 | 90% cis |
| | 315 (121)[h] | $^1$LF | | | | 10% trans |
| | 293 (148)[h] | $^1$LF | 254 | 0.12 | <0.002 | >85% cis |
| | 255 (162)[h] | $^1$LF | | | | <15% trans |
| $Br^-$ | 310 (205) | $^1$LF | 313 | 0.057[i] | <0.004 | 70% cis |
| | 265 sh (210) | $^1$LF | | | | 30% trans |
| | 230 sh (1730) | LMCT | | | | |
| $I^-$ | 346 (556)[h] | $^1$LF | 350 | 0.011 | <0.001 | >95% trans |
| | 283 ($3.6 \times 10^3$)[h] | LMCT | | | | |
| | 226 ($3.1 \times 10^4$)[h] | LMCT | | | | |
| | *cis*-$Ir(en)_2(H_2O)Cl^{2+}$ | | | | | |
| | 312 sh (16) | $^3$LF | 313 | 0.030 | <0.005 | >92% trans |
| | 270 (140) | $^1$LF | | | | |
| | 245 sh (154) | $^1$LF | | | | |
| | 218 (520) | | | | | |

[a] In 25 °C, dilute aqueous solution; pH 3. [b] $\lambda_{max}$ in nm; $\epsilon$ in $M^{-1}$ $cm^{-1}$.[12] [c] Assignments in analogy to those made for the acidopentaammineiridium(III) complexes: Schmidtke, H.-H. *Inorg. Chem.* 1966, *5*, 1683. [d] In nm. [e] In mol/einstein. $\Phi_{H^+}$ represents uptake of $H^+$ during course of reaction; reproducibility is better than ±10% on the basis of triplicate or more determinations. [f] Stereochemistry of $Ir(en)_2(H_2O)X^{2+}$ products; see text. [g] LMCT = ligand to metal charge transfer. [h] $\epsilon$ values somewhat higher than reported in ref 12. [i] Independent of pH between pH 2 and pH 4.

## Results

**A. Photolysis of *cis*- and *trans*-$Ir(en)_2X_2^+$ in Acidic Solution.** LF irradiation of the trans complexes in acidic aqueous solution leads to the labilization of a single halide ion as the principal reaction pathway. Solution pHs, initially in the 3.0–3.5 range, did not change, indicating that photolytic release of the Brønsted base ethylenediamine is at most a minor pathway. Given that Petersen and Jakse[15] have shown photolysis of $Rh(en)_3^{3+}$ to give the monodentate ethylenediamine complex $Rh(en)_2(enH)Cl^{3+}$ to be accompanied by stoichiometric uptake of solution acid, one can conclude that monodentate en species are not formed in the photolyses of these Ir(III) homologues. Upper limits for $H^+$ uptake during photolysis are listed in Table I. Photolyses of the trans ions did lead to spectral changes consistent with the replacement of one $X^-$ by $H_2O$. Good isosbestic points were maintained for more than 50% reaction, indicating the absence of spectrally significant secondary photoreactions. Addition of excess HX to the photoproduct solutions and heating at reflux for several hours gave solution spectra which can be analyzed in terms of the quantitative regeneration of the *trans*-$Ir(en)_2X_2^+$ species.

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Table II. Photolyses of $Ir(en)_2ClX^+$ in Alkaline Solution[a]

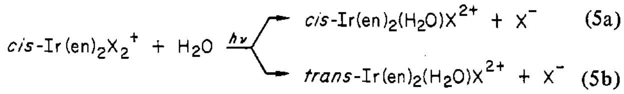
| starting material | product[b] | quantum yield[c] |
|---|---|---|
| *trans*-$Ir(en)_2Cl_2^+$ | *trans*-$Ir(en)_2(OH)Cl^+$ | 0.12<br>0.11[d] |
| *trans*-$Ir(en)_2(OH)Cl^+$ | *cis*-$Ir(en)_2(OH)_2^+$ (~90%) | 0.12<br>0.12[d] |
| *cis*-$Ir(en)_2Cl_2^+$ | *cis*-$Ir(en)_2(OH)Cl^+$ | 0.11 |
| *cis*-$Ir(en)_2(OH)Cl^+$ | *cis*-$Ir(en)_2(OH)_2^+$ (>98%) | 0.033 |

[a] Conditions: dilute aqueous solution; pH ~12; 25 °C. [b] Product stereospecificity 90% or greater in each case. [c] In mol/einstein; $\lambda_{irr} = 313$ nm except where noted. Reproducibility is ±10% or better in each case. [d] $\lambda_{irr} = 350$ nm.

Given that the thermal substitution reactions of bis(ethylenediamine) complexes of Ir(III) have been shown to be stereoretentive,[16] it is concluded that LF irradiation of *trans*-$Ir(en)_2X_2^+$ leads to stereoretentive photoaquation of $X^-$ (eq 4).

$$trans\text{-}Ir(en)_2X_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Ir(en)_2(H_2O)X^{2+} + X^- \quad (4)$$

A somewhat different result is found for the cis complexes. Again amine labilization, as characterized by pH changes in the acidic aqueous medium, was very minor leading to the conclusion that halide aquation is the principal pathway for ligand labilization. Good isosbestic points were maintained through the early stages of each photolysis. However, in these cases, isomerization to the trans product also has some importance. This is demonstrated by heating the photoproduct reaction solutions with excess HX to regenerate the dihalo ions via the stereoretentive thermal anation reactions. The spectra of the resulting solutions can be quantitatively analyzed in terms of a mixture of the cis and trans isomers for $X^- = Cl^-$ or $Br^-$ and exclusive formation of the trans isomer for $X^- = I^-$. Thus it is concluded that, for the cis isomers, photoisomerization accompanies photolabilization of $X^-$ (eq 5) with the extent of this photoisomerization being a function of the identity of $X^-$. Individual complexes are summarized below. Spectral properties and photochemical results are listed in Table I.



$$cis\text{-}Ir(en)_2X_2^+ + H_2O \xrightarrow{h\nu} cis\text{-}Ir(en)_2(H_2O)X^{2+} + X^- \quad (5a)$$

$$cis\text{-}Ir(en)_2X_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Ir(en)_2(H_2O)X^{2+} + X^- \quad (5b)$$

***trans*-Ir(en)$_2$Cl$_2^+$.** Excitation with 350-mm light leads to a decrease in the LF band at 345 nm and corresponding increased absorption by a new band at 316 nm. Good isosbestic points at 378, 329, and 253 nm persisted to more than 80% reaction. The final product after exhaustive photolysis of the solution showed the following spectrum: $\lambda_{max}$ ($\epsilon$) 316 nm (42 $M^{-1}$ $cm^{-1}$) and 270 (54). The pH of the solution, initially 3.50, showed no detectable change. When excess HCl (to give a concentration of 0.5 M) was added to the photoproduct solution, which was then heated at reflux for several hours, the result was a solution spectrum ($\lambda_{max}$ ($\epsilon$): 425 nm (12 $M^{-1}$ $cm^{-1}$), 345 (50), and 273 (55)) very close to that of the starting material (Table II). Thus, we conclude that these observations represent the transformations (6) and (7) and that the product spectrum listed above represents that of *trans*-$Ir(en)_2(H_2O)Cl^{2+}$. The quantum yield for reaction 6 calculated by the extrapolation method from the spectral change was 0.11 ± 0.01 mol/einstein while the upper limit for proton uptake was estimated as 0.002. Photolysis at 313 nm gave very similar observations (Table I).

$$trans\text{-}Ir(en)_2Cl_2^+ + H_2O \xrightarrow{h\nu} trans\text{-}Ir(en)_2(H_2O)Cl^{2+} + Cl^- \quad (6)$$

$$trans\text{-}Ir(en)_2(H_2O)Cl^{2+} + \text{excess } Cl^- \xrightarrow{\Delta} trans\text{-}Ir(en)_2Cl_2^+ + H_2O \quad (7)$$

***trans*-Ir(en)$_2$Br$_2^+$.** Observations during the photolysis of this ion were analogous to those seen for *trans*-$Ir(en)_2Cl_2^+$. Photolysis at 366 nm led to spectral changes with isosbestic points at 435 and 264 nm maintained throughout the photolysis. The product of exhaustive photolysis displayed a solution spectrum ($\lambda_{max}$ ($\epsilon$): 446 nm (sh) (5 $M^{-1}$ $cm^{-1}$) 360 (83), and 280 (43)) reasonably close to the spectrum of the species produced in situ from *trans*-$Ir(en)_2Br_2^+$ by the stereoretentive thermal substitution assisted with $Ag^+$ ion (447 nm (sh) (6 $M^{-1}$ $cm^{-1}$), 360 (78), and 280 (46)). A value of $\phi_{Br} = 0.080 \pm 0.005$ was calculated from spectral data, while the upper limit for amine labilization was 0.002 mol/einstein.

***trans*-Ir(en)$_2$I$_2^+$.** LF field photolysis ($\lambda_{irr} = 405$ nm) of the *trans*-diiodo complex in acidic aqueous solution leads to spectral changes with two clean isosbestic points at 473 and 338 nm which persisted throughout the photolysis. After exhaustive photolysis at 405 nm, the photoreaction solution spectrum displayed absorption band maxima at 385 nm (402 $M^{-1}$ $cm^{-1}$) and 226 ($1.94 \times 10^4$). To this solution was added sufficient concentrated HI to give an overall HI concentration of 0.5 M, and the mixture was refluxed for several hours. The spectrum of the resulting solution ($\lambda_{max}$ ($\epsilon$): 490 nm (sh) (17 $M^{-1}$ $cm^{-1}$) and 398 (172), higher energy peaks obscured by iodide absorption bands) was very close to that of the starting material (Table I). In addition, a solid could be isolated from this solution after concentrating by rotary evaporation, and the electronic spectrum of this material was identical with that of the starting material. Thus we conclude that the photolysis leads to stereoretentive aquation of iodide to give *trans*-$Ir(en)_2(H_2O)I^+$ (i.e., eq 4) the spectrum of which is the photoproduct solution spectrum reported above. The quantum yield based upon this conclusion and calculated by the extrapolation method was 0.070 ± 0.002 mol/einstein. There were no changes in solution pH (initially at 3.5) within experimental uncertainty leading to an upper limit of 0.001 as the quantum yield for amine labilization.

Photolysis of the *trans*-diiodo ion at 313 nm, a wavelength corresponding to the tail of the first charge-transfer band, gave spectral changes and quantum yields very similar to those observed for the longer wavelength photolysis (Table I).

***cis*-Ir(en)$_2$I$_2^+$.** LF photolysis of the *cis*-diiodo ion in aqueous solution (pH 4.00) with 350-nm light led to spectral changes with a well-defined isosbestic point at 372 nm which persisted throughout the photolysis. The solution spectrum after prolonged photolysis ($\lambda_{max}$ ($\epsilon$): 386 nm (398 $M^{-1}$ $cm^{-1}$) and 227 ($1.96 \times 10^4$)) was virtually identical with that of the species produced via the LF photolysis of *trans*-$Ir(en)_2I_2^+$ which was concluded to be *trans*-$Ir(en)_2(H_2O)I^{2+}$ (see preceding section). When the photoproduct from the cis complex was heated with excess HI, the resulting spectrum ($\lambda_{max}$ ($\epsilon$): 490 nm (sh) (17 $M^{-1}$ $cm^{-1}$) and 397 (190), higher energy bands obscured by $I^-$ absorption bands) was consistent with that of *trans*-$Ir(en)_2I_2^+$. Thus we conclude that in this case photoisomerization of the coordination sphere is concomitant with the photolabilization of one $I^-$ (eq 8). On the basis of this conclusion, the quantum yield calculations from spectral data using the extrapolation method gave a value of $\phi_{I^-} = 0.011 \pm 0.001$ for eq 8. Since the solution pH remained constant, the upper limit for amine labilization was 0.001.

$$cis\text{-}Ir(en)_2I_2^+ + H_2O \rightarrow trans\text{-}Ir(en)_2(H_2O)I^{2+} + I^- \quad (8)$$

***cis*-Ir(en)$_2$Cl$_2^+$.** LF photolysis of the *cis*-dichloro ion in aqueous solution (pH 3.5) at 313 nm gave a different type of

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result. The photolysis led to spectral changes with a reasonably well-defined isosbestic point at 273 nm which persisted for about 50% of the reaction but did not hold for longer term photolysis. Thus, we can conclude that the photoproduct(s) is (are) subject to some secondary photoreaction. When the photolyses were stopped during the early stages and treated with HCl and then heated as had been done with the trans analogue, the spectrum of the resulting solution was qualitatively that of *cis*-$Ir(en)_2Cl_2^+$. Since pH changes were minimal ($\phi_{H^+} < 0.001$), this result indicated that the photoreaction was halide aquation occurring with considerable retention of configuration (eq 5a). However, quantitative evaluation of this spectrum demonstrated a lower absorption at the 293-nm LF band $\lambda_{max}$ than expected for a pure *cis*-$Ir(en)_2Cl_2^+$ product and a correspondingly larger absorption at 345 nm, the position of the LF band $\lambda_{max}$ for *trans*-$Ir(en)_2Cl_2^+$. Thus we conclude that the largely stereoretentive $Cl^-$ photoaquation may be accompanied by some isomerization (eq 5b).

Attempts to quantify the extent of isomerization by chromatographic separation of the stereoisomeric pairs of either the $Ir(en)_2(H_2O)Cl^{2+}$ photoproducts or the $Ir(en)_2Cl_2^+$ ions produced from these via thermal anation with $Cl^-$ proved unsuccessful. Consequently, the extent of ligand photoaquation and of complex isomerization were evaluated numerically from spectral changes at two monitoring wavelengths by assuming that two products only (the ions *trans*- and *cis*-$Ir(en)_2(H_2O)Cl^{2+}$) were the result of LF photolysis at 313 nm. In this manner an overall quantum yield for $Cl^-$ photoaquation was calculated as 0.13 ± 0.01 mol/einstein with concomitant photoisomerization representing less than 11% of this process.

*cis*-**$Ir(en)_2(H_2O)Cl^{2+}$.** Exhaustive 313-nm photolysis of this ion in aqueous solution led to spectral changes consistent with the formation of the *trans*-$Ir(en)_2(H_2O)Cl^{2+}$ ion. Changes in the solution pH (initially 3.0) were undetectable, indicating that en labilization was minimal. When the product solution was heated with added HCl, the resulting solution displayed an electronic spectrum ($\lambda_{max}$ ($\epsilon$): 425 nm (13 $M^{-1}\ cm^{-1}$), 342 (52), and 276 (sh) (58)) very close to that of *trans*-$Ir(en)_2Cl_2^+$ (Table II). Numerical analysis of this spectrum assuming only the presence of *cis*- and *trans*-$Ir(en)_2Cl_2^+$ leads to the conclusion that exhaustive photolysis of *cis*-$Ir(en)_2(H_2O)Cl^+$ gives at least 92% cis → trans overall photoisomerization. Analysis of the initial spectral changes assuming only *trans*-$Ir(en)_2(H_2O)Cl^{2+}$ as the photoproduct gives a quantum yield of 0.030 mol/einstein for eq 9.

$$cis\text{-}Ir(en)_2(H_2O)Cl^{2+} \xrightarrow{h\nu} trans\text{-}Ir(en)_2(H_2O)Cl^{2+} \quad (9)$$

*cis*-**$Ir(en)_2Br_2^+$.** LF photolysis at 313 nm of this ion in aqueous solution led to results qualitatively similar to the behavior seen for the *cis*-dichloro ion. An isosbestic point at 372 nm was maintained during the early stages of the reaction; however, numerical analysis of the product spectra indicated that both *cis*- and *trans*-$Ir(en)_2(H_2O)Br^{2+}$ were products of the bromide aquation. The overall quantum yield for $Br^-$ loss was calculated as 0.057 ± 0.003 mol/einstein while concomitant isomerization ($\phi_{isom} \simeq 0.015$) occurs in no more than ~30% of the photolabilization events.

**B. Photolysis of $Ir(en)_2ClY^{n+}$ in Alkaline Solution.** Under the alkaline conditions (pH ~12) utilized here, the aquo- and diaquobis(ethylenediamine)iridium(III) complexes were assumed to be deprotonated to the hydroxo analogues. Given the $pK_a$ of $Ir(NH_3)_5H_2O^{3+}$ as 6.8,[17] virtually identical with that of the Rh(III) analogue (6.9),[17] and the recent determination that the diaquorhodium(III) tetraammines show $pK_{a_1}$ to be 4.9 (trans) and 6.4 (cis) and $pK_{a_2}$ to be 8.3 (both isomers),[18] this assumption appears valid. Thus in alkaline solution, the product of ligand photolabilization should be the hydroxo rather than the aquo complexes regardless of whether the incoming ligand in the photosubstitution is $H_2O$ or $OH^-$.

In general the behavior in alkaline solution is largely a function of whether hydroxide is in the coordination sphere *prior* to the photochemical event. Photolysis of *trans*-$Ir(en)_2Cl_2^+$ in alkaline solution leads to $Cl^-$ labilization with retention of configuration (eq 10). However, unlike the aqua

$$trans\text{-}Ir(en)_2Cl_2^+ + OH^- \xrightarrow{h\nu} trans\text{-}Ir(en)_2(OH)Cl^+ + Cl^- \quad (10)$$

analogue, which does not undergo any spectrally significant photoreaction (as evidenced by *trans*-$Ir(en)_2(H_2O)Cl^{2+}$ being the product from exhaustive photolysis of *trans*-$Ir(en)_2Cl_2^+$ in acidic solution), the *trans*-$Ir(en)_2(OH)Cl^+$ product of eq 10 undergoes secondary photolysis. In this case, the product is the result of both labilization of the remaining $Cl^-$ and of isomerization to a cis configuration (eq 11).

$$trans\text{-}Ir(en)_2(OH)Cl^+ + OH^- \xrightarrow{h\nu} cis\text{-}Ir(en)_2(OH)_2^+ + Cl^- \quad (11)$$

*trans*-**$Ir(en)_2Cl_2^+$.** LF photolysis (350 nm) of *trans*-$Ir(en)_2Cl_2^+$ in alkaline solution leads to spectral changes in the initial stages consistent with the formation of *trans*-$Ir(en)_2(OH)Cl^+$ (see Experimental Section). Isosbestic points at 387 and 330 nm were maintained during this part of the reaction. Calculation of the quantum yield via the extrapolation method assuming eq 10 as the sole photoreaction gave a quantum yield $\phi_{Cl^-} = 0.11 \pm 0.01$, essentially identical with the chloride labilization value seen in acidic solution (Table I). Longer term photolysis led to a breakdown of the isosbestic points, indicating secondary photoreactions. Exhaustive photolysis, until no further spectral changes occurred, led to a final solution spectrum (A) with absorption bands at 330 nm (sh) ($\epsilon$ 43 $M^{-1}\ cm^{-1}$), 280 (sh) (164), and 246 (533). Acidification to pH 1 with aqueous HCl gave a new spectrum (B) with bands at 360 nm (18 $M^{-1}\ cm^{-1}$), 260 (159), and 232 (150). Addition of more concentrated HCl and refluxing for 1 h gave a new solution spectrum (C) with bands at 380 nm (sh) (18 $M^{-1}\ cm^{-1}$), (sh) (103), 293 (139), and 254 nm (179) qualitatively similar to that of *cis*-$Ir(en)_2Cl_2^+$ (Table I). Thus we conclude that trans-to-cis photoisomerization is at least one consequence of the secondary photolysis. Furthermore, since spectrum B does not resemble the spectrum of the *cis*-$Ir(en)_2(H_2O)Cl^{2+}$ species prepared thermally nor does spectrum A resemble that of *cis*-$Ir(en)_2(OH)Cl^+$ (see below), we are led to the conclusion that the photoisomerization is accompanied by ligand labilization (e.g., eq 10) and that spectra B and A represent the approximate spectra of *cis*-$Ir(en)_2(H_2O)_2^{3+}$ and *cis*-$Ir(en)_2(OH)_2^+$, respectively.

*trans*-**$Ir(en)_2(OH)Cl^+$.** Solutions of this ion were prepared in situ. The *trans*-$Ir(en)_2(H_2O)Cl^{2+}$ ion ($\lambda_{max}$ ($\epsilon$): 316 nm (42 $M^{-1}\ cm^{-1}$) and 270 (54)) was first synthesized in situ by the exhaustive photolysis of *trans*-$Ir(en)_2Cl_2^+$ in pH 3 aqueous solution (see above). The solution pH was then adjusted to about 12.0 by the addition of 1 N NaOH solution dropwise. The resulting solution spectrum displayed absorption bands at 325 nm ($\epsilon$ 62 $M^{-1}\ cm^{-1}$) and 294 (92) consistent with the formation of the hydroxo analogue. Photolysis of this solution at 313 nm led to spectral changes with an isosbestic point maintained at 298 nm. The product of prolonged photolysis displayed a solution spectrum ($\lambda_{max}$ ($\epsilon$): 339 nm (sh) (45 $M^{-1}\ cm^{-1}$), 280 (sh) (164), and 246 (540)) very close to spectrum A noted above. Heating this solution with added HCl gave a solution spectrum (380 nm (sh) (18 $M^{-1}\ cm^{-1}$), 315 (106),

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(17) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965.

(18) Skibsted, L. H.; Ford, P. C. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 109.

293 (142), and 255 (sh) (180)) close to that of *cis*-$Ir(en)_2Cl_2^+$. Numerical analysis assuming this solution to consist of only *cis*- and *trans*-$Ir(en)_2Cl_2^+$ leads to the conclusion that the dichloro species are about 90 ± 2% cis. Hence we conclude that the photohydrolysis of *trans*-$Ir(en)_2(OH)Cl^+$ occurs largely with concomitant trans to cis photoisomerization (eq 11). Calculation of the quantum yield for eq 11 according to the extrapolation method gives a value of 0.12 ± 0.01 mol/einstein at 313 nm.

***cis*-$Ir(en)_2Cl_2^+$.** LF photolysis (313 nm) of this ion in alkaline solution led to spectral changes consistent with the formation of *cis*-$Ir(en)_2(OH)Cl^+$ as the principal product (eq 12). On the basis of this assumption, a quantum yield value

$$cis\text{-}Ir(en)_2Cl_2^+ + OH^- \xrightarrow{h\nu} cis\text{-}Ir(en)_2(OH)Cl^+ + Cl^- \tag{12}$$

of $\phi_{Cl^-} = 0.11 \pm 0.01$ was calculated for the disappearance of $Ir(en)_2Cl_2^+$. Prolonged photolysis of these solutions led to secondary reaction indicating the formation of *cis*-$Ir(en)_2(OH)_2^+$ (see below).

***cis*-$Ir(en)_2(OH)Cl^+$.** Solutions of this ion were prepared by heating aqueous *cis*-$Ir(en)_2Cl_2^+$ with a stoichiometric concentration of $AgClO_4$. After the AgCl(s) was removed by filtration and the solution was diluted to a known volume, the solution displayed the following spectrum: $\lambda_{max}$ ($\epsilon$) 362 nm (sh) (16 $M^{-1}$ $cm^{-1}$), 270 (140), 245 (sh) (154), and 218 (520). Adjusting the pH to 12 by addition of 1 M NaOH solution gave a new spectrum ($\lambda_{max}$ ($\epsilon$): 370 nm (sh) (18 $M^{-1}$ $cm^{-1}$), 280 (155), and 238 (sh) (617)) consistent with the formation of *cis*-$Ir(en)_2(OH)Cl^+$. Photolysis of this solution at 313 nm led to spectral changes with an isosbestic point at 280 nm persisting through the photolysis. Exhaustive photolysis gave a product solution displaying a spectrum ($\lambda_{max}$ ($\epsilon$): 330 nm (sh) (37 $M^{-1}$ $cm^{-1}$), 280 (sh) (143), and 245 (512)) similar to those noted above and suspected to consist largely of *cis*-$Ir(en)_2(OH)_2^+$. In this case, heating the solution with added HCl generated a product with a solution spectrum virtually identical ($\lambda_{max}$ ($\epsilon$): 380 nm (sh) (19 $M^{-1}$ $cm^{-1}$), 315 (sh) (121), 293 (149) and 255 (sh) (162)) with that of *cis*-$Ir(en)_2Cl_2^+$ (Table I). Thus, we conclude that LF photolysis of *cis*-$Ir(en)_2(OH)Cl^+$ leads to highly stereoretentive photohydrolysis of the remaining $Cl^-$ (eq 13). The quantum yield for eq 13 based upon initial spectral changes is 0.033 ± 0.002 mol/einstein.

$$cis\text{-}Ir(en)_2(OH)Cl^+ + OH^- \xrightarrow{h\nu} cis\text{-}Ir(en)_2(OH)_2^+ + Cl^- \tag{13}$$

Thus the overall pattern in alkaline solution emerges with LF excitation of the dichloro ions leading largely to stereoretentive photohydrolysis of one $Cl^-$ (eq 10 and 12) while for LF excitation of the hydroxochloro ions, the *cis*-dihydroxo product is formed from both isomers (eq 11 and 13). However, while eq 13 is found to occur with about 98% or better stereospecificity, the specificity of eq 11 may be no greater than about 90%. These results are summarized in Table II.

## Discussion

This discussion will focus on the following key observations: (i) LF photolysis of *cis*-$Ir(en)_2X_2^+$ in acidic aqueous solution leads to labilization only of $X^-$ accompanied by some cis to trans isomerization. The extent of the latter follows the order $I^- > Br^- > Cl^-$ for different $X^-$ (eq 5). (ii) The corresponding trans complexes each undergo stereoretentive labilization of $X^-$ under analogous conditions (eq 4). (iii) In alkaline solution, the hydroxo complex *trans*-$Ir(en)_2(OH)Cl^+$ undergoes photolabilization of $Cl^-$ concomitant with trans to cis photoisomerization (eq 11) while the cis analogue undergoes stereoretentive photohydrolysis of $Cl^-$.

For each of the dihalo complexes investigated here, amine labilization was very small, essentially below the limits of detection, in acidic solution. Since the pH method used is only applicable to weakly acidic solutions, we can make no quantitative estimate regarding the extent of amine labilization in alkaline solution. Nonetheless, the spectral changes observed under the latter conditions were fully consistent with halide hydrolysis as the principal labilization pathway.

The fact that halide aquation is the dominant photolabilization result for *trans*-$Ir(en)_2X_2^+$ is not surprising given the general agreement of various theoretical treatments that the ligand labilization from the lowest LF excited states should be largely confined to the "weak field" axis.[19] Notably, the limited wavelength dependence data (Table I) are consistent with the observation for the pentaammine complexes $Ir(NH_3)_5X^{2+}$ that photoreaction quantum yields are independent of irradiation wavelength in the LF region and with the conclusion that initial excitation is followed by efficient internal conversion/intersystem crossing to a common reactive state, the lowest energy LF excited state.[9,10] A similar conclusion has been drawn for the rhodium(III) haloamine complexes.[20] For the *cis*-$Ir(en)_2X_2^+$ species, the situation is less clear given that both the bromo- and iodopentaammines ($Ir(NH_3)_5X^{2+}$ undergo apparent trans labilization of $NH_3$ as a major photoreaction.[10] Thus one might expect some labilization of en in this case, but none is observed. In this context, however, we should note the close parallel with the *cis*-$Rh(NH_3)_4X_2^+$ complexes where halide photoaquation also predominates for $X^- = Br^-$ or $I^-$, a result rationalized in terms of the cis-labilizing effect of the second halide.[2b] The alternative explanation that en is in fact labilized and the halide is displaced by the free end of the chelating amine in a secondary thermal step seems rather unlikely in view of the results for the *cis*-$Rh(NH_3)_4X_2^+$ complexes noted above. Furthermore, any free en or monodentate en would be expected to be protonated in the acidic solutions, thus terminating any secondary thermal reactions. It is notable in this context that the quantum yields of $Cl^-$ labilization from both *trans*- and *cis*-$Ir(en)_2Cl_2^+$ proved essentially independent of the acid concentration over the pH range 2–12. A more extensive discussion of the photolabilization patterns for dihalotetraammines appears in an earlier report[2b] from this laboratory, concerning the photochemistry of *cis*- and *trans*-$Rh(NH_3)_4XY^{n+}$.

The photoisomerization patterns for the bis(ethylenediamine) complexes of iridium(III) show strong parallels to those observed for both the tetraammine-[2] and bis(ethylenediamine)rhodium(III)[3] species *cis*- and *trans*-$Rh(NH_3)_4XY^{n+}$ and $Rh(en)_2XY^{n+}$, respectively. However, for these Rh(III) complexes, where X and Y are halo, aquo, or hydroxo, photolysis of either the cis or trans isomer under similar conditions gives the identical distribution of products.[21] For example LF photolysis of *cis*- or *trans*-$Rh(NH_3)_4Cl_2^+$ in acidic aqueous solution gave *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ as the only Rh(III) photoproduct.[2b] The behavior is the same for the bis(ethylenediamine) analogues[3a] *cis*- and *trans*-$Rh(en)_2Cl_2^+$. However, this is not the case for the iridium(III) homologues reported here. Although photoaquation of *cis*-$Ir(en)_2Cl_2^+$ is accompanied by some photoisomerization, stereoretention dominates:

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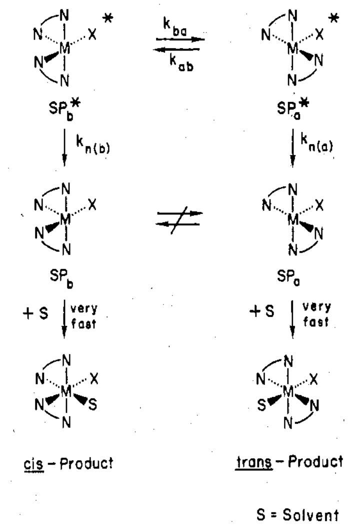
(19) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208 and references therein.

(20) Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, D. C. *J. Am. Chem. Soc.* **1979**, *101*, 4549 and references therein.

(21) An exception to this type of behavior for the $Rh^{III}(en)_2$ species is the *cis*- and *trans*-$Rh(en)_2NH_3Cl^{2+}$ ions. Under LF excitation, these undergo $Cl^-$ photoaquation to give the respective aqua complexes with little photoisomerization.

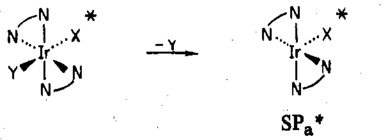
(22) (a) Glerup, J.; Mønsted, O.; Schaeffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399. (b) The ligand $\sigma$ strengths have been calculated for first-row transition elements, and we make the assumption that the qualitative order is the same for Rh(III) and Ir(III).

**Scheme I**

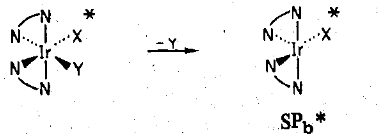


the aquo halo product is about 90% cis. In contrast the photoaquation of $Cl^-$ from *trans*-$Ir(en)_2Cl_2^+$ gives exclusively *trans*-$Ir(en)_2(H_2O)Cl^{2+}$. Similarly the *cis*- and *trans*-$Ir(en)_2Br_2^+$ ions give different distributions of photoaquation products (Table I). Thus at least for these two cases, a single, common intermediate (such as a trigonal-bipyramidal species generated by ligand dissociation)[4] cannot explain the different product distributions from *cis*- and *trans*-dihalo species.

These observations are consistent with proposed models for the photostereochemistry of $d^6$ complexes[2b,3b,6,7] which suggest that LF excited states of the hexacoordinate species undergo dissociation of one ligand to form pentacoordinate intermediates, the *trans*-dihalo complex giving an apical square pyramid (SP$_a$*, eq 14) and the *cis*-dihalo complex giving the basal square pyramid (SP$_b$*, eq 15). These models also



(14)



(15)

propose that the pentacoordinate intermediates first formed are in electronic excited states, formally "triplets", and that isomerization is the result of interconversion between these. Formulation of these species as triplets is consistent with their probable immediate predecessors being the corresponding hexacoordinate species in the lowest energy "triple" LF state (eq 14 and 15).[10] Deactivation of the pentacoordinate triplets gives the spin-paired (ground-state) intermediates (SP$_a$, SP$_b$) which are not comparably stereochemically labile and which should be trapped immediately by the solvent (Scheme I). Thus, in the context of this model, one can view net photoisomerization as the result of competition between the rates of isomerization of SP$_a$* or SP$_b$* ($k_{ab}$ or $k_{ba}$) with those for nonradiative deactivation ($k_n$(a) or $k_n$(b)). The observation of identical product distributions from the *cis*- or *trans*-$Rh(NH_3)_4XY^{n+}$ ligand photoaquations would be consistent with the SP* species being sufficiently long-lived to reach equilibrium; i.e., $k_{ba}$, $k_{ab} \gg k_n(a)$, $k_n(b)$.

The dichloro and dibromo complexes of Ir(III), which show no trans → cis isomerization accompanying ligand labilization while cis → trans isomerization occurs with smaller quantum yields than halide labilization, represent the case where deactivation and isomerization is competitive. In such a case, Scheme I would describe the ratio of isomerization to labilization for the cis isomer as

$$\frac{\phi_{\text{isom}}}{\phi_Y} = \frac{k_{ba}}{k_{ba} + k_n(b)} \tag{16}$$

Thus if $(\phi_{\text{isom}}/\phi_Y) < 0.5$, as seen for $X = Y = Br^-$ or $Cl^-$, $k_n(b) > k_{ba}$. The greater extent of isomerization as one goes down the series $Cl^-$, $Br^-$, $I^-$ for the *cis*-dihalo complexes is consistent with a decreasing kinetic barrier for the SP$_b$* → SP$_a$* isomerization ($k_{ba}$) as the $\sigma$-donor strength of the halogen decreases.[2b,7] The alternative explanation that $k_n$(b) decreases down this series seems unlikely given the larger spin–orbit coupling constants for the heavier halogens. When the effects of the metal are compared, the differenes between the Rh(III) and Ir(III) homologues should not be surprising, the isomerization rate $k_{ba}$ should be slower as the average ligand field stabilization energies increase,[2b] thus slower for M = Ir than for M = Rh, while nonradiative deactivation $k_n$(b) should be faster for the heavier Ir(III), given its larger spin–orbit coupling constant.[23]

According to these models, whether cis → trans or trans → cis photoisomerization accompanies the labilization of Y from $MA_4XY^{n+}$ ($A = NH_3$ or en/2) depends upon the nature of X and its influence on the relative energies of SP$_a$* or SP$_b$*.[2b,6,7] It is argued that SP$_a$* will be the more stable isomer if X is a significantly weaker $\sigma$ donor than A while SP$_b$* is more stable in the opposite case. Thus, given the qualitative order[22] of ligand $\sigma$-donor strengths $OH^- >$ en/2 $\sim NH_3 > H_2O > Cl^- > Br^- > I^-$, this model explains the photostereochemistry of the $Rh(NH_3)_4XY^{n+}$ series where trans → cis isomerization is observed for $X = OH^-$,[2d] cis → trans isomerization is seen with $X^- = Cl^-$ or $Br^-$ and photostationary states including significant concentrations of both isomers are the photolysis products[2d] of *cis*- or *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$. The photostereochemistry of the $Ir(en)_2XY^{n+}$ series is analogous with trans → cis isomerization found for $X = OH^-$ and cis → trans isomerization found for $X = Cl^-$, $Br^-$ or $I^-$. Notably, trans → cis photoisomerization requires the presence of $OH^-$ in the coordination sphere prior to photoexcitation, given that *trans*-$Ir(en)_2Cl_2^+$ undergoes stereoretentive photohydrolysis of $Cl^-$ in alkaline solution.

In summary, the model illustrated by Scheme I and described in more detail elsewhere[2b,2d] proposed for the photostereochemistry of rhodium(III) tetraammine complexes can rationalize the product stereochemistries of analogous Ir(III) complexes. The key feature of this model is the representation of the intermediate produced by ligand labilization from the LF excited state of the hexacoordinate starting complex as a pentacoordinate square-pyramidal species also in an electronic excited state. In the absence of strongly sterically constraining ligands, these pentacoordinated species will isomerize toward the geometry of lowest energy for this electronic configuration. Thus for the photolabilization of Y from $MA_4XY^{n+}$, the direction of potential isomerization of the coordination sphere will depend upon the relative energies of the $MA_4X^{n+}$ SP* intermediates. Strong $\sigma$-donor X's will favor the basal isomer, hence trans → cis isomerization, while weaker $\sigma$ donors will favor the apical isomer, hence cis → trans isomerization. While these considerations indicate the direction of potential isomerization, the data described here illustrate that the extent of photoisomerization accompanying labilization is determined by the competitive rates of rearrangement vs. electronic

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[23] Ford, P. C.; Petersen, J. D.; Hintze, R. E. *Coord. Chem. Rev.* **1974**, *14*, 67.

deactivation of the proposed intermediates.

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**Registry No.** *trans*-$Ir(en)_2Cl_2^+$, 25952-90-3; *trans*-$Ir(en)_2Br_2^+$, 25956-87-0; *trans*-$Ir(en)_2I_2^+$, 25952-91-4; *cis*-$Ir(en)_2Cl_2^+$, 31312-35-3; *cis*-$Ir(en)_2Br_2^+$, 45838-51-5; *cis*-$Ir(en)_2I_2^+$, 45838-65-1; *trans*-$Ir(en)_2(H_2O)Cl^{2+}$, 45838-63-9; *trans*-$Ir(en)_2(H_2O)Br^{2+}$, 73985-94-1; *trans*-$Ir(en)_2(H_2O)I^{2+}$, 73985-95-2; *cis*-$Ir(en)_2(H_2O)Cl^{2+}$, 74034-28-9; *cis*-$Ir(en)_2(H_2O)Br^{2+}$, 74034-29-0; *trans*-$Ir(en)_2(OH)Cl^+$, 73985-96-3; *cis*-$Ir(en)_2(OH)Cl^+$, 74034-30-3; *cis*-$Ir(en)_2(OH)_2^+$, 73985-97-4.

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# Photolysis of *cis*- and *trans*-Dichlorobis(ethylenediamine)ruthenium(III) and *cis*- and *trans*-Aquochlorobis(ethylenediamine)ruthenium(III) Cations in Acidic Aqueous Solution: Photoinduced Isomerizations at Ruthenium(III) Centers

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The ligand field photolysis of *cis*- and *trans*-$[Ru(en)_2Cl_2]^+$ ions causes chloride loss, aquation, and geometric isomerization, yielding mixtures of *cis*- and *trans*-$[Ru(en)_2(H_2O)Cl]^{2+}$. Photolysis of *cis*-$[Ru(en)_2Cl_2]^+$ generates 84% *cis*-$[Ru(en)_2(H_2O)Cl]^{2+}$ and 16% *trans*-$[Ru(en)_2(H_2O)Cl]^{2+}$ with $\phi_{total} = 0.0030$. Photolysis of *trans*-$[Ru(en)_2Cl_2]^+$ yields a 66/34 mixture of the cis/trans aquochloro ions with $\phi_{total} = 0.0050$. The *cis*- and *trans*-$[Ru(en)_2(H_2O)Cl]^{2+}$ ions are photoconverted to each other with similar quantum yields ($\phi_{cis} = 0.038$, $\phi_{trans} = 0.042$). An inefficient photoinduced reaction of *cis*-$[Ru(en)_2(H_2O)Cl]^{2+}$ generates a yellow species, presumably a hydroxyl-bridged Ru(III) dimer. The implications of these results, in terms of the available ligand field photolysis models, are discussed.

## Introduction

Early models[1] of the photochemical behavior of transition-metal complexes concentrated on the identification of the photolabilized ligand, without regard for the stereochemistry of the photoproduct. Only recently has any distortion other than the radial extension of the metal–ligand bond been considered in a theoretical model of ligand field (LF) photochemistry. Models for the stereochemical rearrangements of $d^3$ and $d^6$ complexes have now been presented by Vanquickenborne and Ceulemans[2] as part of their theoretical treatment of LF photochemistry. In this work, the chemical processes resulting from LF excitation are separated into three distinct steps: (1) ligand labilization, (2) intramolecular distortion of the remaining five-coordinate species, and (3) water attack of that five-coordinate species. The possibility that these steps may be concerted to some extent is recognized but is not incorporated into the model's calculations.

A controversial feature of both the $d^3$ and $d^6$ models is the requirement of a thermally equilibrated five-coordinate intermediate(s) which exists long enough to attain its stablest geometry (or a distribution between two stable forms). A consequence of this model is that, for a given combination of metal and five ligands, the same photoproduct (or mixture of photoproducts) must result. There is not yet sufficient stereochemical data to test this hypothesis, but most of the available studies have been consistent with the concept of a thermally equilibrated intermediate. For example, both *cis*-[3] and *trans*-[4] $[Rh(en)_2Cl_2]^+$ lose chloride upon ligand field photolysis, so the five-coordinate intermediate in both cases would be $\{[Rh(en)_2Cl]^{2+}\}$. Consistent with the equilibration of this species, *trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$ is the only photoproduct observed upon photolysis of either of the dichloro ions. The analogous Co(III) complexes[5,6] generate an approximately 30/70 mixture of *cis*- and *trans*-$[Co(en)_2(H_2O)Cl]^{2+}$ upon ligand field photolysis. Unfortunately, the number of such examples, where two different complexes of the same metal leave the same five ligands upon photoinduced ligand loss, is limited; stereochemical support for a thermally equilibrated five-coordinate intermediate in ligand field photochemistry is not yet established.

As part of our general interest in the stereochemical consequences of the ligand field photochemistry of transition-metal complexes, we have initiated a study of the photochemistry of Ru(III) complexes. Only a few examples of ruthenium(III)–amine complex photochemistry have been reported. Irradiation of $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5Cl]^{2+}$, between 254 (CTTM) and 321 nm (LF), causes ligand loss and aquation (or anation in the presence of other nucleophiles).[7] Stereochemical information was not available from this study, but the photolysis of aqueous solutions of *cis*-$[Ru(NH_3)_4X_2]^+$ (X = Br, I) was reported[8] to yield *cis*-$[Ru(NH_3)_4(H_2O)X]^{2+}$, although the limits of possible trans photoproduct formation were not reported.

Thus, it has not been established whether stereochemical rearrangements, so common in $d^3$ and $d^6$ photochemistry, occur about the $d^5$ Ru(III) center. In addition, it is not known whether the concept of a thermally equilibrated five-coordinate intermediate, generated upon photoinduced ligand loss, is valid. Toward that end we have studied the ligand field photolysis of *cis*- and *trans*-$[Ru(en)_2ClX]^{n+}$ (X = Cl, $H_2O$). The thermal behavior of these ions in aqueous solution has been characterized,[9,10] and the thermal reactions (aquation and anation)

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