Evon Martins and Peter S. Sheridan

Ligand Field Photochemistry of the Dichloro(β,β',β''-triaminotriethylamine)rhodium(III) Cation, [Rh(tren)Cl$_2$]$^+$:[1] A Stereospecific Photolysis

EVON MARTINS and PETER S. SHERIDAN*

Ligand field photolysis of [Rh(tren)Cl$_2$]$^+$ leads to chloride loss (ϕ_{Cl^-} = 0.090) with negligible amine aquation (ϕ_{H^+} = 0.0035). The photoproduct [Rh(tren)Cl(OH$_2$)]$^{2+}$ differs from the ion produced upon thermal aquation of the dichloro ion in acidic aqueous solution. On the basis of differences in the electronic spectra and mechanisms for the formation of [Rh(tren)Cl(OH$_2$)]$^{2+}$, the photoproduct is assigned as β-[Rh(tren)Cl(OH$_2$)]$^{2+}$ (coordinated water cis to the tertiary amine), while the predominant thermal aquation product is assigned as the α isomer. The photoproduct has an isomeric purity of at least 98%, is photoinert, but thermally aquates to the diaquo ion. The α-[Rh(tren)Cl(OH$_2$)]$^{2+}$ product is thermally inert but photosensitive to ligand field photolysis. A model, involving the photolabilization of the coordination site cis to the tertiary amine and the formation of a trigonal-bipyramid intermediate, is proposed to account for the stereospecific chloride aquation upon ligand field photolysis.

Introduction

The stereochemical course of a photoinduced chemical reaction is controlled, to a large extent, by the stereochemistry of the thermally equilibrated excited (thexi) state. Little is known of the detailed structure of thexi states, for under the fluid conditions generally encountered in photochemical studies, they are the transient intermediates in the photochemical reaction. Insight into the structure and stereochemical requirements of the thexi state can be gained, however, through analysis of the effects of minor stereochemical changes upon a photochemical reaction.

That stereochemical changes in the ground state can affect the reactivity of the thexi state has been demonstrated in several systems,[2] although in several of these studies the number of chelate rings, and hence the number of aliphatic carbon chains, differs from one complex to another within a given series. This variation in aliphatic character could result in significant changes in the rate of collision-induced radiationless deactivation of the thexi state. The observed changes in photochemical quantum yield may thus reflect major changes in deactivation pathways, rather than any significant change in the chemical reactivity of the thexi state.

An attractive system (which avoids this problem) for the study of the effects of stereochemical changes upon excited-state reactivity centers around the quadridentate amines trien and tren.[1] In octahedral complexes, three geometric isomers of the trien complex and one isomer of the tren complex are theoretically possible. When the metal center is Rh(III) and X is chloride ion, all four of these complexes have been reported,[3] and they provide an attractive system for photochemical investigation. As with most rhodium(III) amines, the complexes are thermally robust;[4] yet recent studies[5] have shown that Rh(III) complexes are generally photosensitive. An earlier investigation[6] of the photochemistry of the cis-α and cis-β trien as well as the tren complexes of Co(III) revealed that the stereochemistry of the quadridentate amine had a pronounced effect upon the photoinduced reactions of these cations. The analogous cis-[Rh(NH$_3$)$_4$Cl$_2$]$^+$[7] and cis-[Rh(en)$_2$Cl$_2$]$^+$[8] complexes isomerize to the trans configuration upon photolysis, suggesting that stereochemical change may also play an important role in the photochemistry of Rh(III) complexes.

With these considerations in mind, we have investigated the photochemistry of Rh(III) complexes with both cis configurations of the trien ligand, as well as Rh(III)–tren complexes. We report here on the photochemistry of [Rh(tren)Cl$_2$]$^+$ and [Rh(tren)Cl(H$_2$O)]$^{2+}$; a subsequent paper will discuss the trien system.

Experimental Section

Preparation of Compounds. Dichloro(β,β',β''-triaminotriethylamine)rhodium(III) Chloride. With minor adaptations, the method of Johnson and Basolo[9] was used. Solid RhCl$_3$·3H$_2$O (1.0 g, 0.0038 mol) and tren·3HCl (0.99 g, 0.0038 mol) were dissolved in 50 mL of LiOH solution (0.11 M) and refluxed for ca. 5 min or until the solution cleared. Aliquots of LiOH solution (5 mL, 0.11 M) were added at 2-min intervals to the refluxing solution until a total volume of ca. 95 mL was reached. The LiOH solution was then added, a drop at a time, until the solution was neutral, as determined by multirange pH paper (Alkacid test paper—Fisher Scientific Co.). Careful control of pH reduces the interference from the formation of metallic Rh and an uncharacterized pale yellow precipitate–colloid which is often difficult to remove from the solution.

The procedure of Johnson and Basolo was followed to isolate a solid salt, which was then carefully washed (to remove LiCl) at least eight times with small (3-mL) amounts of warm (30 °C) ethanol. The resulting solid was recrystallized from 5 M HCl or 5 M HClO$_4$ to give the chloride or perchlorate salt. Anal. Calcd for [Rh(tren)Cl$_2$]ClO$_4$: C, 17.2; H, 4.3; N, 13.3. Found: C, 17.2; H, 4.6; N, 13.2. (Elemental analysis was done by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.)

Chloroaquo(β,β',β''-triaminotriethylamine)rhodium(III) Cation. Thermally Prepared Isomer. A solution of [Rh(tren)Cl$_2$]Cl in 0.1 N H$_2$SO$_4$ was heated to 60 °C for ca. 5 h. The resulting solution was cooled and passed down an SP Sephadex (C-25) cationic exchange column in the H$^+$ form, with 0.2 N H$_2$SO$_4$ as the eluent. Minor amounts of the unreacted dichloro cation were eluted quickly, and the chloroaquo product then came off as a single band. A solid was not isolated, but the electronic spectrum and the elution characteristics indicated the product was [Rh(tren)Cl(OH$_2$)]$^{2+}$ as observed by Madan.[10]

Photochemically Prepared Isomer. A solution of [Rh(tren)Cl$_2$]Cl in 0.1 N H$_2$SO$_4$ at 1 °C was placed in a 10-cm photolysis cell (29 mL) and exposed to 405-nm irradiation. The sample was kept at 1 °C with a water-jacketed cell holder and irradiated with light from a short-arc Hg lamp, which had passed through a hot mirror and an interference filter. After photolysis was complete (ca. 4 h), the product was separated from any unreacted dichloro cation by ion-exchange chromatography. No solid was isolated.

Attempts to separate the two aquochloro isomers by ion-exchange chromatography were unsuccessful.

Photolyses. Irradiation at 405 nm was done with a 200-W Hg short-arc lamp (Illumination Industries Inc.) with a hot mirror (Baird Atomic) to reflect infrared radiation and an interference filter (Baird Atomic) for wavelength selection. Solutions of 2.5 (±0.5) × 10^{-3} M were photolyzed in 5- and 10-cm cells with continuous mixing by a magnetic stirrer. Aliquots of the photolyzed solution were transferred to 1.0-cm cells for spectral analysis. Light intensities were measured with ferrioxalate actinometry and averaged about 7 × 10^{-8} einstein/s at 405 nm in a cell with a front window area of 2.9 cm^2.

Instrumentation. Electronic spectra were recorded on a Beckman Acta M IV spectrophotometer in the absorbance mode. A Radiometer
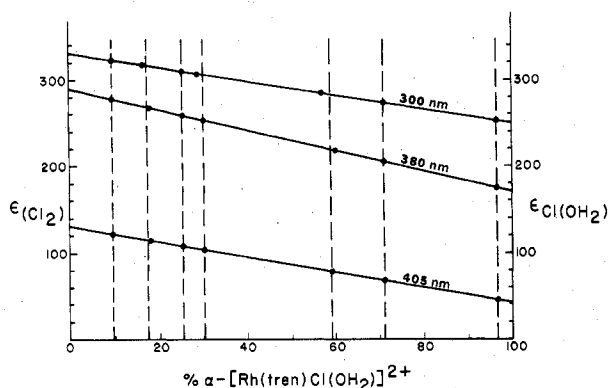
Figure 1. Analysis of the spectral changes upon photolysis of [Rh(tren)Cl₂]⁺. See ref 11 for details.

PHM 64 pH meter with a GK2320C combined electrode (Radiometer) was used for pH measurements, and a F1012C1 Selectrode and K701 calomel reference were used for chloride determinations.

Product Analysis. The spectral changes upon photolysis of [Rh(tren)Cl₂]⁺ were analyzed by a graphical method,[11] in which the absorbances of the starting material and final product at various wavelengths were noted on the two vertical axes (Figure 1). Solid lines connect the absorbance values, and the composition of any intermediate solution could be determined by noting the absorbance of the solution at the wavelengths being monitored. The dotted lines connect the points from a given photolysis, and vertical dotted lines which do not deviate significantly from the individual data points (Figure 1) not only give the composition of the solution but also show that the intermediate spectra can be generated as linear combinations of the spectra of the initial and final products.

Quantum Yields. Quantum yields for amine loss were determined by pH changes, and chloride release was measured with a chloride-sensitive electrode. Each reported yield is the average of at least three separate experiments, and conversion to photoproduct was held under 15% to reduce inner filter effects. The precision of these measurements was 8–10%. The photolysis of [Rh(tren)Cl₂]⁺ offered an unusual situation, as only one photoproduct formed, and there was no measurable interference from secondary thermal or photochemical processes. As discussed elsewhere,[11] this allows a more accurate determination of the quantum yield, based on spectral changes throughout the photolysis. In a two-component system, we can write

$$\frac{-d[A]}{dt} = \phi_A I_a \left[\frac{\epsilon_A[A]}{\epsilon_A[A] + \epsilon_B[B]} \right] \quad (1)$$

where A represents [Rh(tren)Cl₂]⁺ and B represents the photoproduct [Rh(tren)Cl(OH₂)]²⁺. With only two Rh(III) species in solution, $[A] + [B] = [A]_{init}$, eq 1 can be expanded to

$$(\epsilon_A - \epsilon_B)([A] - [A]_{init}) + \epsilon_B[A]_{init} \ln\left(\frac{[A]}{[A]_{init}}\right) =$$
$$\frac{\epsilon_A \phi_A I_0'}{V}(1 - 10^{-D})t \quad (2)$$

where I_0' is the incident light intensity (einsteins/s), V is the solution volume (L), D is the average optical density (absorbance) at the photolysis wavelength, and t is the time of photolysis (s). A graph of the term on the left of eq 2 as a function of $(1 - 10^{-D})t$ yields a line of slope $\epsilon_A(I_0')\phi/V$ from which the quantum yield was determined.

Base Hydrolyses. Solutions of the thermally prepared and photochemically prepared chloroaquo ions in 0.10 N H₂SO₄ at 35 °C were added to two volumes of 0.10 N NaOH also at 35 °C. The change in absorbance at 360 nm was monitored as a function of time. The reactions were clean, and real (experimentally determined) A_∞ values were used.

Results

Thermal Aquation of [Rh(tren)Cl₂]⁺. In acidic aqueous solution [Rh(tren)Cl₂]⁺ releases 1.0 mol of Cl⁻/mol of Rh complex initially present, with negligible pH changes (less than 0.5% of the amine ligands are released). A kinetic study of the aquation,[10] based upon spectral changes, has been reported,
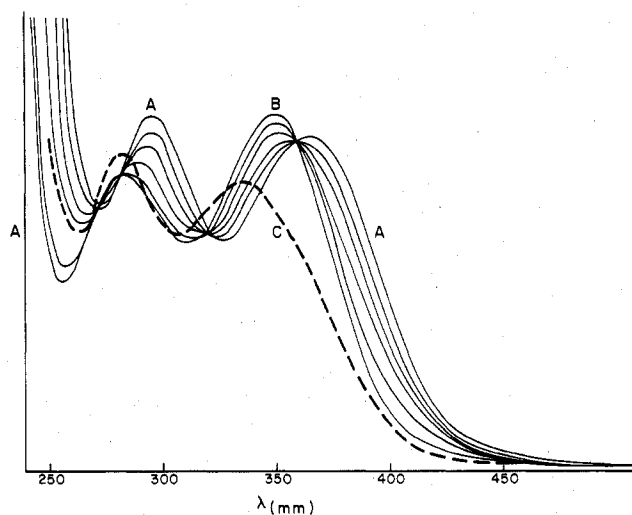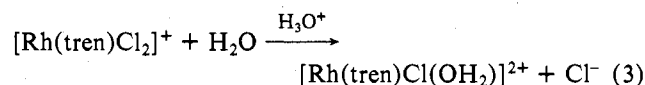

Figure 2. Spectral changes upon photolysis of [Rh(tren)Cl₂]⁺ (A) to yield the photoproduct [Rh(tren)Cl(OH₂)]²⁺ (B). Under identical conditions, thermally produced [Rh(tren)Cl(OH₂)]²⁺ gives spectrum C (---).

Table I. Absolute Quantum Yields upon Ligand Field Photolysis of Some Rhᴵᴵᴵ-tren Complexes

complex	ϕ_{Cl^-}	ϕ_{H^+}
[Rh(tren)Cl₂]⁺	0.090 ± 0.002	0.0035 ± 0.0004
α-[Rh(tren)Cl(OH₂)]²⁺ ᵃ	0.10 ± 0.002	0.0035 ± 0.0004
β-[Rh(tren)Cl(OH₂)]²⁺ ᵇ	<10⁻⁴	<10⁻⁴

ᵃ Produced upon aquation of [Rh(tren)Cl₂]⁺. ᵇ Produced upon photolysis of [Rh(tren)Cl₂]⁺.

and in acidic solution the predominant reaction is chloride aquation (eq 3). The electronic absorption spectrum of the starting material and aquation product are given in Figure 2.

$$[Rh(tren)Cl_2]^+ + H_2O \xrightarrow{H_3O^+} [Rh(tren)Cl(OH_2)]^{2+} + Cl^- \quad (3)$$

Photolysis of [Rh(tren)Cl₂]⁺. Excitation of the lowest energy ligand field band of [Rh(tren)Cl₂]⁺ in acidic aqueous solution leads to the spectral changes observed in Figure 2. Isosbestic points are maintained throughout the photolysis, and despite the absorption of incident radiation by the photoproduct, no secondary photolysis was detected. Chloride-release measurements show that 1.0 mol of chloride is released/mol of Rh complex initially present and that the pH changes are minor. The quantum yield for chloride release was 0.090, while proton uptake (amine labilization) was less efficient (ϕ_{H^+} = 0.0036). Thus, [Rh(tren)Cl(OH₂)]²⁺ is also the predominant photoproduct, despite the differences in the electronic spectra of the photoproducts and thermal products.

Photolyses were done at temperatures between 0 and 25 °C, in solutions with pH values of 1.0, 2.9, and 4.0, and in degassed as well as air-saturated solutions, and none of these variables had a measurable effect upon the photolysis.

Quantum yields for the formation of [Rh(tren)Cl(OH₂)]²⁺ were calculated by a graphical method which accounts for the constantly decreasing amount of light absorbed by the starting material as the photolysis proceeds (Experimental Section). The isosbestic points (Figure 2) suggest the photolysis is a clean, two-component system, and a more thorough analysis of the spectra confirms that all of the intermediate spectra are linear combinations of the initial and final products. The quantum yield for chloride loss from [Rh(tren)Cl₂]⁺ was constant through at least 95% reaction (Table I).

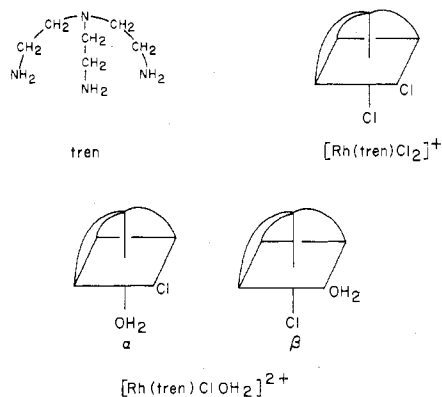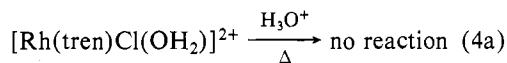Two geometric isomers of [Rh(tren)Cl(OH₂)]²⁺ are possible (Figure 3), which have been labeled the α and β isomers,

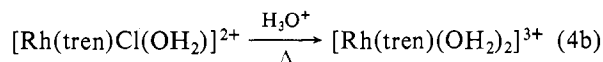**Figure 3.** Geometric isomers possible for $[Rh(tren)Cl(OH_2)]^{2+}$.

following the standard convention. The differences in the electronic spectra and rates of hydrolysis in alkaline solution (vide supra), coupled with the identical analytical results for the formation of these species, imply that photolysis and aquation lead to different isomers of $[Rh(tren)Cl(OH_2)]^{2+}$. In order to assign these isomers, their behaviors in acidic solution, in alkaline solution, and upon photolysis in acidic solution were studied.

Thermally produced $[Rh(tren)Cl(OH_2)]^{2+}$ is thermally inert.[10] No change in the electronic spectrum was detected when the sample was held at 60 °C for several days. The photoproduced isomer of $[Rh(tren)Cl(OH_2)]^{2+}$ aquates smoothly at 60 °C, however. Spectral changes occur with four isosbestic points between 250 and 400 nm, and the final spectrum has λ_{max}'s at 325 and 272 nm. Chloride is lost during the aquation, the pH remains constant (±0.005 pH unit), and the final electronic spectrum is virtually identical with that observed upon acidification of the base-hydrolysis products of both aquochloro isomers (vide infra). Unlike the thermally produced isomer, photochemically produced $[Rh(tren)Cl(OH_2)]^{2+}$ aquates to the diaquo ion (eq 4).

thermal

$$[Rh(tren)Cl(OH_2)]^{2+} \xrightarrow[\Delta]{H_3O^+} \text{no reaction} \quad (4a)$$

photo

$$[Rh(tren)Cl(OH_2)]^{2+} \xrightarrow[\Delta]{H_3O^+} [Rh(tren)(OH_2)_2]^{3+} \quad (4b)$$

The photochemical behavior of the two $[Rh(tren)Cl(OH_2)]^{2+}$ ions is the reverse of their thermal behavior. Photolysis of $[Rh(tren)Cl_2]^+$ leads to a thermally reactive but photoinert isomer of $[Rh(tren)Cl(H_2O)]^{2+}$, as prolonged photolysis of the photoproduct solution caused no further spectral, pH, or chloride-concentration changes. In contrast, thermally produced (and thermally inert) chloroaquo ion has a photochemical behavior reminiscent of the dichloro ion (Table I). Photoinduced chloride loss is efficient ($\phi_{Cl^-} = 0.10$) with only minor amine aquation occurring. Extensive photolysis leads to an electronic spectrum consistent with $[Rh(tren)(OH_2)_2]^{3+}$, which is assumed to be the predominant photoproduct.

Both isomers of $[Rh(tren)Cl(OH_2)]^{2+}$ undergo hydrolysis in alkaline solutions, and both isomers give products with identical electronic spectra (λ_{max} 332, 274 nm) consistent with the formation of $[Rh(tren)(OH)_2]^+$. Upon acidification with sulfuric acid, both base-hydrolysis products generate a species with an electronic spectrum identical with that previously identified as $[Rh(tren)(OH_2)_2]^{3+}$.

A thorough kinetic study of the base hydrolysis of the two isomers of $[Rh(tren)Cl(OH_2)]^{2+}$ will be reported separately, but preliminary results confirm that the two isomers differ in

Scheme I
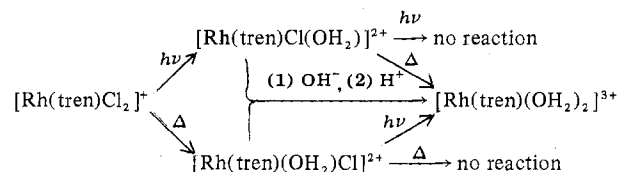
their reactivity toward the hydroxide ion. In the presence of excess OH$^-$ ion (Experimental Section), both isomers react in a pseudo-first-order manner with the thermally produced isomer having a second-order rate constant of 7.6×10^{-3} M^{-1} s^{-1} at 35 °C and the photoproduct reacting at a rate of 1.0×10^{-3} M^{-1} s^{-1} (35 °C).

These reactions are summarized in reaction Scheme I.

Discussion

The stereospecificity of the photolysis of $[Rh(tren)Cl_2]^+$ allows insight into the mechanism of the ligand field photolysis of Rh(III) complexes. Identification of the α and β chloroaquo ions is of prime concern, and lacking a single-crystal X-ray structure, the available kinetic and spectroscopic information, as outlined below, implies that photolysis leads to pure β-$[Rh(tren)Cl(OH_2)]^{2+}$, while aquation in the dark leads to the α isomer as the principal product. After isomer assignment, a photolysis model, which accounts for the stereospecific loss of chloride, will be discussed.

Isomer Composition. The kinetic studies of the base hydrolysis of the two isomers give a measure of isomeric purity. The photoproduced isomer (the more slowly reacting) displayed clean, pseudo-first-order kinetics throughout the reaction period (at least 5 half-lives). An impurity of 2% of the more rapidly reacting isomer would have been detected by deviation from linearity of the ln $(A - A_\infty)$ vs. time graphs. No deviation was observed, so the photoproduced $[Rh(tren)Cl(OH_2)]^{2+}$ has an isomeric purity of at least 98%.

Reaction of the thermally produced isomer was more complex and was shown to undergo two consecutive pseudo-first-order hydrolyses in alkaline solution. After completion of the faster reaction (about 10^4 s) a second pseudo-first-order reaction occurred with a rate constant identical (±2%) with that observed upon hydrolysis of the photoproduct. When the contributions to the spectral changes from the slower reaction were subtracted, it was shown that the initial spectral changes are also due to a pseudo-first-order reaction.[12] We conclude that aquation of $[Rh(tren)Cl_2]^+$ (in the dark) leads to both isomers of $[Rh(tren)Cl(OH_2)]^{2+}$. Extrapolation of the two pseudo-first-order graphs to the beginning of the reaction gives the relative absorbances (at 360 nm) of the two isomers present in the initial solution. When combined with the known molar absorptivity coefficients for the two isomers, it can be calculated that thermally prepared $[Rh(tren)Cl(OH_2)]^{2+}$ contains 8% (±2%) of the same species produced upon photolysis of the dichloro ion, while the predominant product (92%, ±2%) is the other, more rapidly hydrolyzing isomer.

Electronic Absorption Spectra. The UV–visible spectrum of $[Rh(tren)Cl_2]^+$ is typical of d^6 cationic haloamine complexes, with two broad, relatively weak ligand field bands at energies below the intense ligand-to-metal charge-transfer transitions. The lowest energy band (366 nm) may be assigned as $(^1A', ^1A'', ^1A'') \leftarrow {}^1A_1$ with A' and 2 A'' being derived from T_1 upon descent from O_h to C_s site symmetry.[13] Typically, no resolution of these three transitions was observed in room-temperature solutions. The second ligand field band (298 nm) may be assigned as $(^1A', ^1A', ^1A'') \leftarrow {}^1A_1$ with 2 A' + A'' derived from T_2; no resolution of these transitions was observed. The lack of resolution implies that the spectra of these complexes may be discussed in terms of an "average-environment" octahedral field model.

The electronic spectra of the two isomers of [Rh(tren)-Cl(OH$_2$)]$^{2+}$ are readily assigned by analogy with the dichloro spectra, but the spectra of the aquochloro ions are surprisingly different for two complexes with identical *cis*-[RhN$_4$ClO] chromophores. While the second ligand field bands are almost isoenergetic, the photoproduct has a significantly lower energy (but higher intensity) $^1T_1 \leftarrow {}^1A_1$ transition.

Ligand field (d–d) transitions are not strictly forbidden unless the atomic orbitals used in the formation of the metal-centered frontier orbitals are pure d oribitals and hence have a center of symmetry. Neither isomer of [Rh(tren)-Cl(OH$_2$)]$^{2+}$ can have an inversion center, so a relaxation of the LaPorte selection rule ($\Delta l = \pm 1$) is expected. In fact, the intensity of d–d transitions in such similar complexes can be roughly correlated to the extent of distortion away from O_h symmetry; by this model, the photoproduct [Rh(tren)Cl-(OH$_2$)]$^{2+}$ would be the more distorted chloroaquo isomer. Such distortion would hinder effective metal–ligand interaction, reducing the average ligand field strength of the ligands, consistent with the lower energy $^1T_1 \leftarrow {}^1A_1$ transition for the photoproduct.

Isomer Assignment. In the absence of translabilization by chloride[14] current models for the aquation of Rh(III) complexes involve an associative interchange (I$_a$) process, with cis water attack and stereoretentive aquation.[15] The environments around the two chlorides in [Rh(tren)Cl$_2$]$^+$ differ significantly, as the chloride trans to the tertiary amine is in a hydrophilic pocket, surrounded by amine-bonded protons, capable of attractive interactions with the aqueous solvent shell. The chloride cis to the tertiary amine, on the other hand, is in a more hydrophobic region, as several methylene protons are forced into close proximity to that coordination site. (These considerations are supported by an NMR study of α- and β-[Co(tren)ClNH$_3$]$^{2+}$.[16])

It is reasonable that an I$_a$ reaction would favor replacement of a ligand in a hydrophilic region rather than one in a hydrophobic region. Substitution of the chloride trans to the tertiary amine would lead to α-[Rh(tren)Cl(H$_2$O)]$^{2+}$ as the predominant aquation product. On the basis of this assignment, the photoproduct must be β-[Rh(tren)Cl(H$_2$O)]$^{2+}$.

Assignment of the photoproduct as β-[Rh(tren)Cl(OH$_2$)]$^{2+}$ is consistent with the considerations of the electronic spectra (vide supra). In β-[Rh(tren)Cl(OH$_2$)]$^{2+}$ the water molecule is in a hydrophobic region, so that the Rh–O attractions would be hindered by the repulsive ineractions between the water and the aliphatic chains of the tren ligand. These repulsions would reduce the ligand field strength of the water molecule and would distort the tren ligand from its normal coordinated geometry. The observable consequences would be a lower energy, but more intense $^1T_1 \leftarrow {}^1A_1$ band for β-[Rh(tren)-Cl(H$_2$O)]$^{2+}$, supporting the assignment of the β isomer as the photoproduct.

Photolysis. The photoinduced loss of chloride from [Rh-(tren)Cl$_2$] (ϕ_{Cl^-} = 0.09) upon irradiation of the $^1T_1 \leftarrow {}^1A_1$ ligand field absorption is consistent with previous studies on cationic haloamine complexes of Rh(III).[5] The formation of the thermally inaccessible isomer of [Rh(tren)Cl(OH$_2$)]$^{2+}$ upon photolysis clearly indicates that the photochemistry results from the chemical reactivity of the photoproduced excited state and is not merely a hot ground-state process.

Application of ligand field models to such asymmetric complexes is difficult, but most models would predict photoinduced labilization in the plane of the cis chloride ligands. Cleavage of a specific Rh–Cl bond (presumably of the chloride cis to the tertiary amine) with instantaneous water coordination would account for the observed stereospecificity, but an explanation of why a specific chloride is labilized is not straightforward.

The semiempirical photolysis rules of Adamson[17] have not generally been applicable to Rh(III) complexes,[18] and they predict the axis of labilization in [Rh(tren)Cl$_2$]$^+$ to be the tertiary amine–chloride axis. With tertiary amine loss prevented by the ligand structure, chloride labilization along that axis would lead to α-[Rh(tren)Cl(H$_2$O)]$^{2+}$. This is not in agreement with the assignment of the photoproduct as β-[Rh(tren)Cl(H$_2$O)]$^{2+}$. Both chlorides in [Rh(tren)Cl$_2$]$^+$ are trans to amines of similar ligand field strength, so any such labilization scheme cannot convincingly deal with the stereospecific chloride loss. An assumption in this analysis is that formation of only one geometric isomer implies the photoinduced labilization of a specific chloride. Without labeling experiments which would distinguish the two chlorides, irrefutable proof of stereospecific chloride loss is not possible, but the stereochemical constraints inherent in the tren ligand allow only certain molecular distortions. It is difficult to envision a distortion which would result in the formation of β-[Rh(trien)Cl(H$_2$O)]$^{2+}$ upon loss of the chloride trans to the tertiary amine.

The edge-displacement model,[6] proposed for quadridentate amine complexes of Co(III), predicts amine rather than chloride labilization. In the Co(III) system, the strain induced by the tren ligand was thought to be responsible for the abnormal photochemical (and thermal) behavior of [Co-(tren)Cl$^-$]$^+$.[11,19] Some strain is undoubtedly introduced by the tren ligand in the Rh complexes, but their thermal and photochemical reaction rates are not atypical for Rh(III) complexes, so the effect of any strain is not pronounced in the Rh(III) ions.

A successful model for the photochemistry of these complexes must account for the photoproduced formation of only one isomer of [Rh(tren)Cl(H$_2$O)]$^{2+}$ and for the different photosensitivities of α- and β-[Rh(tren)Cl(H$_2$O)]$^{2+}$. These results can be explained through a model based upon the intraligand repulsions inherent in the tren ligand. Photoinduced labilization of the ligand cis to the tertiary amine would occur if cleavage of the rhodium–chloride bond is considered to be only one component of a distortion of the entire complex toward a trigonal-bipyramid (TBP) geometry. A TBP structure has been proposed for other tren (and substituted tren) complexes,[20] as the intraligand repulsions present in the octahedral complexes[21] are reduced in the TBP geometry. Water attack along any equatorial edge of the TBP structure would give the observed β-[Rh(tren)Cl(OH$_2$)]$^{2+}$ isomer.

The TBP model also accounts for the differing photosensitivities of the two chloroaquo ions. The thermally prepared (α) isomer has a chloride in a coordination site cis to the tertiary amine, which would be lost upon formation of a TBP structure. The similarity of the chloride-release efficiency of the dichloro and the α-chloroaquo ions indicates that cleavage of the Rh–Cl bond is not the efficiency-determining step in the photolysis, as separation of charge considerations would suggest lower efficiency for chloride release from a dipositive ion than from the monopositive dichloro ion. The similar yields do suggest that the photolysis efficiencies may be determined by some other process common to both ions—distortion toward a common TBP geometry is one possibility.

In contrast, photochemically prepared β-[Rh(tren)Cl-(OH$_2$)]$^{2+}$ is insensitive toward further photoinduced chloride loss, as the chloride cis to the tertiary amine is lost in the primary photolysis. Water exchange would be predicted upon photolysis of β-[Rh(tren)Cl(OH$_2$)]$^{2+}$, but we have no evidence to support or refute such a proposition. The TBP model therefore nicely accounts for the observation that formation of [Rh(tren)(OH$_2$)$_2$]$^{3+}$ from the dichloro ion requires two steps: thermal aquation to replace the chloride trans to the tertiary amine and photolysis to labilize the chloride cis to the
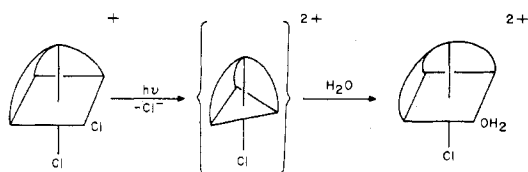
Figure 4. Model for the photochemical behavior of $[Rh(tren)Cl_2]^+$ based upon the formation of a trigonal-bipyramid intermediate.

tertiary amine. The ordering of these two steps is not important (Scheme I).

In summary, the distortions represented in Figure 4 account for the stereospecific photochemistry of $[Rh(tren)Cl_2]^+$. The resulting conclusion that the ligands cis to the tertiary amine are photolabile, while those trans to the tertiary amine are photoinert, readily accounts for the photochemical behavior of α- and β-$[Rh(tren)Cl(OH_2)]^{2+}$. Population of the antibonding e_g-derived orbitals would inhibit σ donation to the metal, so that Rh–Cl and Rh–N bond lengthening would result. Relief of intraligand repulsions within the tren ligand would be possible if Rh–Cl bond lengthening is accompanied by an opening of the amine–Rh–amine angles from ca. 90° (ground state) toward 120° (TBP). Such a concerted process would favor exclusion of the chlorine cis to the tertiary amine, for loss of the trans chloride would not significantly reduce intraligand repulsions. Work is currently in progress to determine whether a TBP model is useful in other, non-tren complexes.

References and Notes

(1) Abbreviations used throughout: trien = triethylenetetramine, $(H_2N-CH_2CH_2NHCH_2)_2$; tren = β,β',β''-triaminotriethylamine, $N(CH_2C-H_2NH_2)_3$.
(2) C. Kutal and A. Adamson, *Inorg. Chem.*, **12**, 1454 (1973); **12**, 1990 (1973); M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **94**, 7152 (1972); *Inorg. Chem.*, **13**, 1342 (1974).
(3) P. M. Gidney, R. D. Gillard, B. T. Heaton, P. S. Sheridan, and D. H. Vaughn, *J. Chem. Soc., Dalton Trans.*, 1462 (1973).
(4) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967.
(5) P. C. Ford, R. E. Hintze, and J. D. Petersen, in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter 5.
(6) P. S. Sheridan and A. W. Adamson, *Inorg. Chem.*, **13**, 2482 (1974).
(7) D. Strauss and P. C. Ford, *J. Chem. Soc., Chem. Commun.*, 194 (1977).
(8) M. M. Muir and W. L. Huang, *Inorg. Chem.*, **12**, 1831 (1973).
(9) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).
(10) S. Zipp and S. Madan, *J. Inorg. Nucl. Chem.*, **37**, 181 (1975).
(11) P. S. Sheridan and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 3032 (1974).
(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, N.Y., 1965.
(13) E. D. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.
(14) M. J. Pavelich and G. M. Harris, *Inorg. Chem.*, **12**, 423 (1973).
(15) S. B. Tung and T. W. Swaddle, *Inorg. Chem.*, **13**, 1538 (1974).
(16) C.-H. Liu Yang and Merland W. Grieb, *J. Chem. Soc., Chem. Commun.*, 656 (1972).
(17) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).
(18) P. C. Ford, *Inorg. Chem.*, **14**, 1440 (1975).
(19) S. K. Madan, W. M. Reiff, and J. C. Bailar, Jr., *Inorg. Chem.*, **4**, 1366 (1965).
(20) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967).
(21) P. Paoletti and L. Fabbrizzi, *Coord. Chem. Rev.*, **15**, 435 (1975).

Contribution from the Department of Chemistry
University of Missouri-St. Louis, St. Louis, Missouri 63121

Photochemistry of Cyclopentadienyliron Dicarbonyl Halide Complexes[1]

DONNA G. ALWAY and KENNETH W. BARNETT*

The primary photochemical process (366 or 436 nm) for η^5-$C_5H_5Fe(CO)_2Br$ and η^5-$C_5H_5Fe(CO)_2I$ is dissociation of carbon monoxide. Photolysis of η^5-$C_5H_5Fe(CO)_2X$ (X = Cl, Br, I) in benzene solutions saturated with ^{13}CO yields η^5-$C_5H_5Fe(CO)(^{13}CO)X$. Irradiation of the bromo or iodo derivatives in the presence of triphenylphosphine leads to the formation of the covalent complexes η^5-$C_5H_5Fe(CO)(PPh_3)X$ (X = Br, I) with a high quantum efficiency. Quantum yields for the substitution processes increase with increasing triphenylphosphine concentration and decrease with increasing concentration of carbon monoxide. The linkage isomers η^5-$C_5H_5Fe(CO)_2NCS$ and η^5-$C_5H_5Fe(CO)_2SCN$ interconvert upon 366- or 436-nm irradiation in tetrahydrofuran. They undergo thermal and photochemical substitution reactions with triphenylphosphine to produce the new compounds η^5-$C_5H_5Fe(CO)(PPh_3)NCS$ and η^5-$C_5H_5Fe(CO)(PPh_3)SCN$. η^5-$C_5H_5Fe(CO)_2NCS$ reacts with triphenylarsine under photochemical conditions to yield η^5-$C_5H_5Fe(CO)(AsPh_3)NCS$.

Introduction

A variety of photochemical deactivation pathways are available to cyclopentadienylmetal carbonyl complexes containing one-electron-donor ligands (X). These include dissociation of carbon monoxide,[2–5] homolytic[6–10] or heterolytic[11,12] cleavage of the metal–X bond, intramolecular isomerization[1,2] and intraligand rearrangements.[13,14] The photochemistry of the dinuclear compounds $[CpMo(CO)_3]_2$,[6,9] $[CpW(CO)_3]_2$,[6,8] and $(CO)_3CpMo-WCp(CO)_3$[15] (Cp = η^5-C_5H_5) is dominated by homolytic cleavage of the metal–metal bond yielding the reactive radical species $CpM(CO)_3\cdot$ (M = Mo, W). The

tetranuclear complex $[CpFe(CO)]_4$ undergoes photooxidation in the presence of halocarbons to $[CpFe(CO)]_4^+$.[16]

Although the synthetic utility of irradiation of the mononuclear complexes $CpM(CO)_3X$[3,17–20] (M = Mo, W) and $CpFe(CO)_2X$[3,18,19,21,22] has been recognized for some time, information regarding mechanistic aspects of their photochemical reactions is severely limited. Photolysis of $CpM(CO)_3CH_3$ (M = Cr, W) in the presence of triphenylphosphine or trimethyl phosphite yields a mixture of the mono- and disubstituted methyl compounds $CpM(CO)_2(L)CH_3$ and $CpM(CO)(L)_2CH_3$ as well as the acetyl complexes CpM-