suggest that halide exchange does not involve the formation of 19-electron intermediates/transition states.

Whether the mechanism is more likely to involve predissociation of an iodide ligand or ring slippage is presently not clear. Attempts to dissociate an iodide ligand by interaction of $CpMoI_2(PMe_3)_2$ with Lewis acids have been unsuccessful. No reaction takes place with $AlI_3$, whereas the interaction with $BF_3$ either in toluene or in THF involves oxidation.[22]

Analogous kinetic investigations of phosphine exchange reactions and extension to other similar systems are planned for the near future. In particular, we are interested in investigating the halide exchange kinetics in the corresponding indenyl system to probe more directly for the ring slippage mechanism.

**Supplementary Material Available:** Text giving details of the method of calculation of concentrations from EPR intensities for a generic mixture of $CpMoCl_2(PMe_3)_2$, $CpMoClI(PMe_3)_2$, and $CpMoI_2(PMe_3)_2$ and a figure showing a typical EPR spectrum of a mixture of the three complexes (3 pages). Ordering information is given on any current masthead page.

(22) The isolated product of this reaction, $[Cp^*MoI_2(PMe_3)_2]BF_4$, has been characterized crystallographically: unpublished results from this laboratory.

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# Ligand Effects on the Photoaquation of Tetrakis(amine)rhodium(III) Complexes [Rh(L)₄XY]⁺

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Photolysis at the longest wavelength absorption band of aqueous solutions of complexes of the type *trans*-[Rh(L)₄XY]⁺, where X and Y are Cl, Br, I, CN, or OH, and L is a heterocyclic amine, gave photoaquation of X, Y, and L. The quantum yield of photoaquation of the axial ligand X showed both a photochemical trans effect due to Y and a photochemical cis effect due to the heterocyclic amine ligands. The distribution of photoproducts depended strongly on the nature of X, Y, and L and significant differences were observed with the analogous [Rh(NH₃)₄XY]⁺.

## Introduction

Ligand field photolyses of complexes of Rh(III) of the type *trans*-[RhL₄Cl₂]⁺, where L is a heterocyclic amine, give photoaquation of both chloride and amine, with the distribution of photoproducts strongly dependent on the nature of the amine.[2,3] Significant differences have been noted between these complexes and analogous complexes with L = NH₃.[4–10] Both *cis*- and *trans*-[Rh(NH₃)₄XY)]⁺ isomers can be prepared,[11] and numerous examples of photoisomerization for the NH₃ complexes have been reported.[12–17] However, repeated attempts to prepare the analogous cis isomers of the tetrakis(pyridine) and other monodentate heterocyclic amine complexes of Rh(III) have been unsuccessful, and the dichloro complexes with heterocyclic amines were completely stereoretentive upon photolysis.[2,3] Thus, it seemed of interest to examine the effect of variation of the axial ligands on the photolysis products and quantum yields. In addition, complexes with derivatives of thiazole and imidazole were prepared for comparison with previously reported heterocyclic amine complexes.

## Experimental Section

**Physical Measurements.** Absorption spectra in the visible–ultraviolet region were obtained with a Perkin-Elmer 200 spectrophotometer. Measurements of absorbance at selected wavelengths for determination of molar absorptivities were made with a Hitachi Perkin-Elmer 139 spectrophotometer. A Metrohm Herisau E512 pH meter was used for all potentiometric measurements.

**Materials.** The chemicals $RhCl_3 \cdot 3H_2O$ and $RhBr_3 \cdot 2H_2O$ (Strem Chemicals), pyridine (py) (J. T. Baker Chemicals Co.), and 1-methylimidazole (mim), thiazole (tz), and 2-bromothiazole (brtz) (Aldrich Chemical Co.) were used as received.

The complexes *trans*-[Rh(L)₄Cl₂]Cl·5H₂O[18] and *trans*-[Rh(L)₄Br₂]Br·H₂O,[18] and the corresponding haloaquo complexes of the type *trans*-[Rh(L)₄(H₂O)X](ClO₄)₂,[19] where L is py, mim, tz, or brtz and X is Cl or Br, were prepared by following the literature methods. However, the yields for these and the other complexes were improved when the reaction mixtures were kept under a N₂ atmosphere.

*trans*-[Rh(py)₄Cl(OH)]ClO₄[20] was prepared from 50 mL of 2.8 mM *trans*-[Rh(py)₄(H₂O)Cl](ClO₄)₂. The pH of the solution was adjusted to 10.75 by addition of NaOH. Then 5 M NaClO₄ was added dropwise with stirring until the desired yellow product precipitated. Yield: 0.0562 g, 85%. The same method was used to prepare the analogous bromohydroxo complex, *trans*-[Rh(py)₄Br(OH)]ClO₄.

*trans*-[Rh(py)₄ClBr]ClO₄·H₂O was prepared from the chloroaquo complex. Under a N₂ atmosphere, a solution containing 0.191 g (0.284

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**Table I.** Wavelength, Molar Absorptivity, and Quantum Yields for Photoaquation for the Lowest Energy Electronic Absorption Bands for *trans*-[Rh(L)$_4$XY]$^+$

| X | Y | L | $10^2\Phi_X$, mol/einstein | $10^2\Phi_Y$, mol/einstein | $10^2\Phi_L$, mol/einstein | $\lambda_{max}$, nm | $\epsilon$, L mol$^{-1}$ cm$^{-1}$ | $\Phi_L/\Phi_{sum}{}^a$ |
|---|---|---|---|---|---|---|---|---|
| Cl | Cl | py$^b$ | 1.1$^c$ | | 4.04 | 409 | 100 | 0.77 |
| Br | Br | py | 3.5 | | 2.7 | 439 | 121 | 0.44 |
| I | I | py | 3.7 | | 3.62 | 490 sh | 569 | 0.49 |
| CN | CN | py | 12.0 | | 4.10 | 309 | 413 | 0.25 |
| Cl | Br | py | 31.5 | 2.7 | 1.47 | 422 | 102 | 0.04 |
| Cl | CN | py | 33.4 | 8.6 | 5.14 | 349 | 668 | 0.11 |
| Cl | Cl | mim | 3.42 | | 1.13 | 410 | 73 | 0.25 |
| Br | Br | mim | 3.84 | | 2.12 | 430 | 83 | 0.36 |
| Cl | Cl | tz | 0.65 | | 8.67 | 410 | 98 | 0.93 |
| Cl | Cl | brtz | 0.22 | | 10.3 | 410 | 185 | 0.98 |

$^a\Phi_{sum} = \Phi_X + \Phi_Y + \Phi_L$ when X $\neq$ Y; $\Phi_{sum} = \Phi_X + \Phi_L$ when X = Y. $^b$Values of p$K_b$ are py, 8.75; mim, 6.48; tz, 11.56; brtz, 14.6. $^c$Values for quantum yields are averages of three or more determinations. Standard deviations were within 20%.

mmol) of *trans*-[Rh(py)$_4$(H$_2$O)Cl](ClO$_4$)$_2$ in 15 mL of a 30% water–ethanol solution was refluxed until all the solid was dissolved. To the refluxing solution was added 10 mL of NaBr (0.2980 g, 2.89 mmol, pH 5.5). After 10 min of reflux the solution was cooled to room temperature and bright yellow crystals were filtered out and washed with cold acetone. Yield: 0.0741 g, 40.0%.

***trans*-[Rh(py)$_4$I$_2$]I.** Under a N$_2$ atmosphere, a solution containing 0.1425 g (0.212 mmol) of *trans*-[Rh(py)$_4$(H$_2$O)Cl](ClO$_4$)$_2$ in 15 mL of a 30% water–ethanol solution was refluxed until all the solid was dissolved. To the refluxing solution 0.324 g (2.16 mmol) of NaI were added, followed by 2 drops of concentrated HI. The solution changed from bright yellow to dark brown instantaneously and brown crystals precipitated from the solution. The brown crystals were filtered and washed with cold acetone. Yield: 0.0859 g, 55.1%.

***trans*-[Rh(py)$_4$(CN)$_2$]CN·2H$_2$O.** At 45 °C under a nitrogen atmosphere, 0.121 g (0.165 mmol) of *trans*-[Rh(py)$_4$I$_2$]I were dissolved in 25 mL of 45% water–ethanol solution. The solution was refluxed for 15 min, and NaCN (0.024 g, 0.455 mmol) was added. The pH of the solution was kept basic, greater than pH 8. The color of the solution changed from dark brown to pale yellow. Crystals of the desired product were obtained by slow evaporation of the solution to near dryness. Yield: 0.016 g, 18.2%.

***trans*-[Rh(py)$_4$(CN)Cl]ClO$_4$·H$_2$O.** To a refluxing solution of *trans*-[Rh(py)$_4$(CN)$_2$]CN (0.0876 g, 0.164 mmol, 25 mL) under a N$_2$ atmosphere was added 25 mL of 0.8 M aqueous NaCl dropwise. Also added was 10 mL of 0.5 M NaCN, in order to avoid formation of the dichloro complex. The pH of the solution was kept at 7.00 by dropwise addition of 1.5 M NaOH. After 30 min of reflux, the temperature of the solution was lowered to 5 °C. After 1 day, a bright yellow precipitate was filtered out. Yield: 0.0241 g, 25.8%.

All of the complexes were recrystallized by dissolving them in the minimum possible volume of hot methanol and allowing the solution to evaporate slowly at room temperature in the dark. All elemental analyses for C, H, and N or halogen gave satisfactory agreement with the calculated values. Wavelengths corresponding to the absorption maxima and values of molar absorptivities agreed well with values in the literature for known complexes.

**Photolyses.** The photolysis apparatus has been described previously.[2] Reineckate[21] and ferrioxalate[22] actinometers were used to measure the intensity of the incident light. The fraction of light absorbed by each sample was determined from the absorption spectrum, the concentration of the complex, and the path length of the reaction cell. No correction was made for internal filter effects. The incident intensity was determined immediately before each photolysis. The average value at 410 nm was 3.2 × 10$^{16}$ and at 340 nm was 2.0 × 10$^{16}$ photons/s.

At least three determinations of quantum yields were made for each complex. Little variation in quantum yield with variation in duration of photolysis was observed, but results were extrapolated to zero time. Photolyses of all the complexes were carried out at 25 ± 1 °C. To correct for possible thermal reactions, an aliquot of the solution was kept in the dark during photolyses. Attempts to bring about measurable reactions in the dark were made by keeping solutions at 45 °C for 24–48 h.
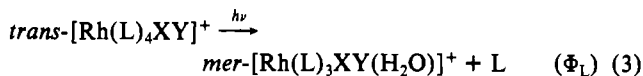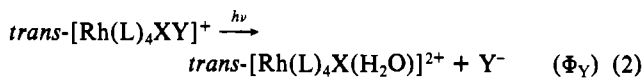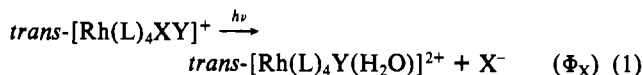
The concentration of halide or pseudohalide released during photolysis was measured with a Markson ultrasensitive ion–selective electrode and a Markson double-junction reference electrode with a Metrohm-Herisau 512 pH meter. Standard halide or pseudohalide solutions were used to prepare calibration curves. The concentration of amine released during the photolysis was measured by extracting the amine with toluene and

titrating with perchloric acid. A blank correction was made by extraction and titration of the aliquot of reaction mixture that had been kept in the dark.

Visible–UV spectra were obtained immediately after photolysis and compared with the spectrum of an aliquot kept in the dark. The sample solution concentrations were from 1 to 8 mM in complex. Thermal corrections were not significant for any of the complexes studied. Partial separation of photolyzed reaction mixtures on Sephadex columns and characterization of the product complexes have been described previously.[2]

## Results

All the photoreactions of the trans complexes in this study gave substitution with retention of geometry:

*trans*-[Rh(L)$_4$XY]$^+$ $\xrightarrow{h\nu}$

$$\text{*trans*-[Rh(L)}_4\text{Y(H}_2\text{O)]}^{2+} + \text{X}^- \qquad (\Phi_X) \quad (1)$$

*trans*-[Rh(L)$_4$XY]$^+$ $\xrightarrow{h\nu}$

$$\text{*trans*-[Rh(L)}_4\text{X(H}_2\text{O)]}^{2+} + \text{Y}^- \qquad (\Phi_Y) \quad (2)$$

*trans*-[Rh(L)$_4$XY]$^+$ $\xrightarrow{h\nu}$

$$\text{*mer*-[Rh(L)}_3\text{XY(H}_2\text{O)]}^+ + \text{L} \qquad (\Phi_L) \quad (3)$$

The wavelengths of the first electronic absorption bands, at which photolyses were carried out, for the complexes *trans*-[Rh(L)$_4$XY]$^+$ are listed in Table I, along with the quantum yields for photoaquation of X, Y, and L. Except for Y = H$_2$O or OH$^-$, for which no $\Phi$ values were obtained, the quantum yields were calculated from the concentration of free X$^-$, Y$^-$ or L in the solution. The total observed quantum yields, $\Phi_{sum} = \Phi_L + \Phi_X + \Phi_Y$, were calculated from the average values for L, X, and Y. The ratios $\Phi_L/\Phi_{sum}$ are also listed in Table I. The complexes *trans*-[Rh(py)$_4$(H$_2$O)X]$^{2+}$, where X = Cl or Br, gave no measurable photoaquation of py or of X. No attempt to measure water exchange was made. The complexes *trans*-[Rh(py)$_4$(OH)X]$^+$ for X = Cl or Br showed some change in pH and some photoaquation of X, by no change in geometry. The quantum yields were not determined because the methods used for other complexes showed larger errors at high pH. The stereochemistry of each product was determined from the spectrum and comparison with known complexes.[2] Products with hydroxo ligands were acidified to give the corresponding aquo complexes, in order to confirm the geometry. All the products had trans or *mer* geometry as indicated in eqs 1–3.

## Discussion

The improvement of the yield of product when oxygen was minimized in the solution during synthesis of the complexes is consistent with the observation by Gillard that substitution reactions in *trans*-[Rh(py)$_4$X$_2$]$^+$ are inhibited by oxygen.[23] The ligands containing both N and S (tz and brtz) were assigned as N coordination, which is consistent with the $\lambda_{max}$ values near 410

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nm for the dichloro complexes and with X-ray structural data for other complexes of thiazole derivatives.[24-26]

Various attempts were made to prepare the cis isomers of [RhL$_4$X$_2$]$^+$, but none could be isolated. The approach used by Hancock[11] to prepare cis-[Rh(NH$_3$)$_4$Cl$_2$]$^+$ via an oxalato complex gave only the trans isomer for L = py and several other heterocyclic amines. Likewise, cleavage of the binuclear complex [Rh$_2$Cl$_9$]$^{3-}$ with oxalate, followed by addition of pyridine or other heterocyclic amine, gave only the trans isomers. The difficulty in obtaining the cis complexes with any of the monodentate heterocyclic amines studied here is somewhat surprising given the existence of cis-[Rh(L-L)$_2$X$_2$]$^+$ where L-L is 2,2'-bipyridyl or related ligands.[3] In trans-[Rh(py)$_4$Br$_2$]Br·6H$_2$O the py molecules form 45° angles with the RhN$_4$ plane of coordination,[27] which could result from a combination of steric and electronic effects.

The effects of the ligands on the quantum yields are most evident in values of $\Phi_X$ and for the ratio $\Phi_L/\Phi_{sum}$. For the dichloro complexes, the value of the ratio (or of $\Phi_L$) increases as the base strength of the amine decreases, as measured by p$K_b$, which was previously reported for nitrogen heterocycle–dichloro complexes.[2] This trend suggests that the Rh–N bond strength in the excited state follows the same order as the Rh–N $\sigma$-bond strength in the ground state. For complexes with L = py and X = Y, the quantum yield for photoaquation of X increases in the order Cl < Br < I < CN. This is not the order of field strength or bond strength, but is the order which would be expected on the basis of labilization of X by the kinetic trans effect of Y in either octahedral[28] or square-planar complexes.[29] For the py complexes with X = Cl and Y = Br or CN, the importance of the trans effect of Y on $\Phi_X$ is even more evident. Since CN$^-$ has a large kinetic trans effect for ground-state reactions, solutions of the chlorocyano and dicyano complexes were kept in the dark at 45 °C for 48 h. At the end of that period, no measurable reaction had occurred. The solutions were then photolyzed and gave the same photoreactions observed for freshly prepared solutions. Thus, the trans effect observed can be considered to be a photochemical trans effect. The effect of changing X and Y is much less for L = mim, where $\Phi_X$ is only slightly greater for Br than for Cl. The effect of variations in X and Y on $\Phi_{py}$ is much smaller than the change in $\Phi_X$ and is less easily interpreted. The ratio of $\Phi_L/\Phi_{sum}$ for complexes with X

= Y decreases in the order Cl > Br > I > CN. In other words, the relative ease of amine photoaquation is opposite to the order of increasing $\Phi_X$ and of the order of the relative field strength of X. The values of $\Phi_Y$ for the chlorobromo and chlorocyano complexes show an increase as the field strength of Y increases.

The absence of trans to cis isomerization for these complexes is in contrast to the photoisomerization found for complexes of the type trans-[Rh(NH$_3$)$_4$ClY]$^+$ where Y = OH$^-$ or CN$^-$. The stereochemical behavior of the complexes with NH$_3$ has been rationalized using the Vanquickenborne–Cuelemans model[30,31] as extended by Petersen[32] and Ford and co-workers.[12] Data from a number of six-coordinate, d$^6$ systems are consistent with the formation of a five-coordinate, square-pyramidal excited-state species (SP*) by photodissociation of one ligand. The excited-state SP* species have been proposed to be triplet excited states capable of isomerization through a trigonal-bipyramidal excited species (TBP*) on a time scale competitive with deactivation and coordination of a solvent molecule.[17] The photostereochemistry has been explained on the basis of the predicted site preference for the basal position in the SP* for stronger $\sigma$-donor ligands. For dihalo complexes, in which the amine or (NH$_3$) is a stronger field ligand than the halide, the observed trans products would be predicted. When Y = a strong field ligand such as OH$^-$ or CN$^-$, concomitant labilization of X and isomerization to the cis complex would be expected and has been observed for L = NH$_3$.[13,16] This was not observed for any of the complexes with heterocyclic ligands.

Factors that might account for the significant differences between the complexes with heterocyclic ligands used in this work and those with NH$_3$ include (a) the possibility of $\pi$-bonding by the heterocyclic amines, which is not possible for NH$_3$, (b) the greater size of the heterocyclic amines, which could introduce steric hindrance to the isomerization, and (c) differences in the relative kinetics of deactivation and reaction and possible new paths for deactivation of the excited state given the greater electronic complexity of the heterocyclic amines. All three of these factors may well contribute to the observed lack of isomerization.

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