Ligand Control of Product Stereochemistry in the Photosubstitution Reactions of Rhodium(III) Ammine Complexes. The Photoreactions of *trans*-$[Rh(NH_3)_4(OH)Cl]^+$

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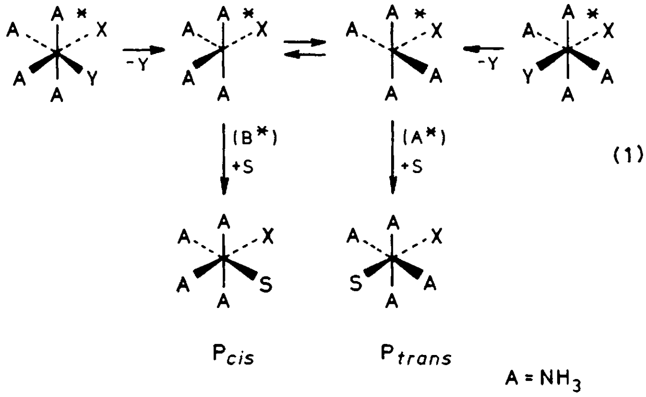
Summary Ligand field photolysis of *trans*-$[Rh(NH_3)_4(OH)Cl]^+$ results in concomitant photohydrolysis–photoisomerization (quantum yield = 0·21 mol einstein^{-1}) to give *cis*-$[Rh(NH_3)_4(OH)_2]^+$, a stereochemical result in marked contrast to the analogous aquo species, *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$, which undergo *cis* to *trans* but not *trans* to *cis* photoisomerization nor chloride photolabilization.



THE stereochemistry of ligand field (LF) photosolvolysis reactions of hexaco-ordinate d^6 transition metal complexes has recently been rationalized by a theoretical model.[1,2] This model assumes ligand dissociation from a LF triplet state to give square pyramidal (SP) intermediates also in triplet excited states (*e.g.* equation 1). Isomerization is considered the result of rapid equilibration between the basal (B*) and apical (A*) intermediates prior to deactivation and trapping by solvent with product stereochemistry determined by the relative energies of the two SP intermediates. Tests of this model in the absence of constraining polydentate ligands are few, exceptions being the rhodium(III) complexes *cis*-$[Rh(NH_3)_4XY]^{n+}$ ($X = Cl^-$ or Br^-, $Y = X$ or H_2O).[3,4] These display efficient *cis* to *trans* photoisomerization concomitant with photosolvation (equation 2) in contrast to *trans*-$[Rh(NH_3)_4XY]^{n+}$ analogues[4,5] which undergo photosolvation of Y with retention of configuration.

$$cis\text{-}[Rh(NH_3)_4XY^{n+} + H_2O \xrightarrow{h\nu} trans\text{-}[Rh(NH_3)_4(H_2O)X^{n+} + Y \qquad (2)$$

Reported here is a behavioural crossover for $X = OH^-$, the first example of stereospecific *trans* to *cis* photoisomerization of a d^6 complex, demonstrating that the stereochemical distribution of products depends on the electronic natures of the monodentate ligands.

Aqueous solutions of *trans*-$[Rh(NH_3)_4(OH)Cl]^+$ at pH 9·5—13·0 [u.v. spectrum; λ_{max} (ϵ_{max}) 372 (102 mol^{-1} cm^{-1}) and 289 nm (111)] were prepared from *trans*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$.[4] Long term irradiation at 366 nm leads to a photoproduct solution with a u.v. spectrum [335 (ϵ_{max} 116 mol^{-1} l cm^{-1}) and 283 nm (113)] very similar to that of *cis*-$[Rh(NH_3)_4(OH)_2]^+$ [335 (ϵ_{max} 122 mol^{-1} l cm^{-1}) and 281 nm (118)] prepared thermally.[6] The small spectral differences were close to those obtained by direct photolysis of *cis*-$[Rh(NH_3)_4(OH)_2]^+$, and can thus be attributed to secondary photolysis of the primary product. Isosbestic points at 359, 308, 292, and 247 nm persisted through the photolysis for more than 90% overall conversion. The identity of the primary photoproduct was further established by acidification {the resulting spectrum matched that of *cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$} and by stereoretentive thermal anation[4] by heating with added HCl. Cation exchange chromatography of the resulting solution demonstrated the principal Rh^{III} species to be *cis*-$[Rh(NH_3)_4Cl_2]^+$ (>90%) with small quantities of uncharged complexes, presumably $[Rh(NH_3)_3Cl_3]$, also present. The primary photoreaction is thus established as the concomitant hydrolysis–isomerization (3). The quantum yield evaluated from spectral changes is 0·21 ± 0·02 mol einstein^{-1} and is independent of pH between 9·5 and 13·0, indicating that

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

OH^- does not quench the photochemistry of *trans*-$[Rh(NH_3)_4(OH)Cl]^+$ in contrast to its role in the photochemistry of Cr^{III} amine complexes[7] and of the Rh^{III} species $[Rh(NH_3)_5Cl]^{2+}$.[8]

Preliminary experiments indicate that *trans*-$[Rh(NH_3)_4(OH)Br]^+$ and *trans*-$[Rh(NH_3)_4(OH)I]^+$ display analogous photolysis reactions with even higher quantum yields. In contrast, neither *trans*-$[Rh(NH_3)_4(OH)_2]^+$ nor *cis*-$[Rh(NH_3)_4(OH)Cl]^+$ display comparable photoactivity, with the quantum yield for Cl^- hydrolysis being less than 0·02 for the latter ion and there being no indication of isomerization in either case. The low photoactivities of these two exclude both as intermediates in the photolysis of *trans*-$[Rh(NH_3)_4(OH)Cl]^+$.

These results can be rationalized in terms of a site preference of the ligand X for the basal or apical coordination sites in the SP intermediates of equation (1) (B* or A*, respectively). Vanquickenborne's calculations[2] suggest the more stable triplet SP isomer to be the one with the weaker σ-donor (NH_3 *vs.* X) in the apical site of $[Rh(NH_3)_4X]^{n+}$. Thus, given the reported order of σ-donor strengths[2] $OH^- > NH_3 > H_2O > Cl^- > Br^- > I^-$, one

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can rationalize equation (2) for X = H_2O, Cl^-, or Br^- since A* should be the more stable for these. In contrast, for X = OH^-, B* should be the more stable and photodissociation of Y is accompanied by *trans* to *cis* isomerization.

These observations demonstrate that a simple change in the solution pH can lead to dramatic differences in the photostereochemical properties of aquo ammine Rh^{III} complexes. For example, *trans*-$[Rh(NH_3)_4(H_2O)Y]^{n+}$ is inert (ignoring exchange of H_2O with solvent) to LF excitation; however, raising the pH gives a species, *trans*-$[Rh(NH_3)_4(OH)Y]^{(n-1)+}$, very active toward both photosubstitution and photoisomerization. We expect that these properties may facilitate the often difficult syntheses of *cis*-disubstituted rhodium(III) and iridium(III) complexes.

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