ganometallic rings containing active hydrogens at carbon atoms.

It appears from our studies on $[Cu(acac)_2]^3$ that the reaction requires a metal-oxygen ring opening, followed by C_2N_2 attack at the vacant site and its subsequent transfer to the coordinated ligand.

The reactivity trend found here, which is a function of the nature of the β-keto enolato ligand and of the metallic center, may well be in agreement with this metal-controlled mechanism.

The insertion reaction of electrophiles into the C-H methino bonds of the copper and nickel β-keto iminato rings was discovered in 1973.[22] Strong kinetic and/or thermodynamic effects on the overall process due to the nature of the metal and of the substituents in the rings have already been noticed.[9] For the tetradentate Schiff-base complexes Cu^{II} was found to be a more reactive metal center than Ni^{II}, in full agreement with our findings. A noticeable feature of the cyanogen reactivity is the strong tendency of the organometallic Schiff-base metal rings to undergo bis(cyanogen) addition without any preparative evidence of mono(cyanogen) addition products. This result contrasts with the findings relevant to (4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dionato)copper(II), for which the stepwise synthesis of mono- and diamino derivatives was possible[22] upon reaction with a variety of organic isocyanates.

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Registry No. $Cu(dbmC_2N_2)_2$, 82677-51-8; $Cu(en(acac)_2(C_2N_2)_2)$, 86365-10-8; $Cu(en(ba)_2(C_2N_2)_2)$, 86365-11-9; $Ni(en(ba)_2(C_2N_2)_2)$, 86365-12-0; $Ni(pap)\alpha$, 82677-52-9; $Cu(eaa)_2$, 14284-06-1; $Cu(ba)_2$, 14128-84-8; $Cu(dbm)_2$, 14405-48-2; $Cu(en(acac)_2)$, 36885-37-7; $Cu(en(ba)_2)$, 15277-26-6; $Ni(en(acac)_2)$, 36802-27-4; $Ni(en(ba)_2)$, 53109-27-6; Cu(pap)Cl, 29966-36-7; Ni(pap)Cl, 29966-42-5; $Cu(acacC_2N_2)_2$, 77136-26-6; C_2N_2, 460-19-5; eaa, 141-97-9; ba, 93-91-4; dbm, 120-46-7; $en(acac)_2$, 6310-76-5; $en(ba)_2$, 16087-30-2; pap, 28484-27-7.

Supplementary Material Available: Listings of structure factor amplitudes, some least-squares planes, and final thermal parameters for non-hydrogen atoms (18 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department, Royal Veterinary and Agricultural University, Copenhagen V, Denmark,
Chemistry Department I, H. C. Ørsted Institute, University of Copenhagen, Copenhagen Ø, Denmark,
and Department of Chemistry, University of California, Santa Barbara, California 93106

Photoreactions of Rhodium(III) Complexes: The Cyanoammines $Rh(NH_3)_5CN^{2+}$ and *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$

L. H. SKIBSTED*[1] and PETER C. FORD*[2]

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The photoreactions resulting from the ligand field excitation of the rhodium(III) cyanoammine complexes $Rh(NH_3)_5CN^{2+}$ and *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ are described. In each case, the reaction product in aqueous solution is the *cis*-$Rh(NH_3)_4(H_2O)CN^{2+}$ ion. The quantum yield for NH_3 aquation from $Rh(NH_3)_5CN^{2+}$ is 0.09 mol/einstein while the quantum yield for photoisomerization of *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ is 0.52 mol/einstein. These results are discussed in terms of theoretical models for ligand field excited-state reactions. Synthesis schemes and spectral properties for $Rh(NH_3)_5CN^{2+}$, *cis*- and *trans*-$Rh(NH_3)_4(CN)Cl^{+}$, and *cis*- and *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ are described as are the pK_a values for the latter ions. The rate constant for thermal Cl^- aquation from *trans*-$Rh(NH_3)_4(CN)Cl^{+}$ is also reported (3.6×10^{-4} s^{-1} at 25 °C, a value about 500-fold larger than that for $Rh(NH_3)_5Cl^{2+}$ under analogous conditions).

Introduction

The pentaamine and tetraamine complexes of rhodium(III), RhA_5Y^{n+} and *cis*- and *trans*-RhA_4XY^{m+} (A = NH_3 or an organic amine such as ethylenediamine/2), have proved especially valuable experimental models for the investigation of the ligand field (LF) photosubstitution reactions of d^6 hexacoordinate complexes (e.g., eq 1).[3] For such complexes both

$$\begin{aligned} RhA_5^{n+} + S &\xrightarrow{h\nu} RhA_5S^{3+} + Y^{(3-n)-} \\ &\xrightarrow{h\nu} RhA_4SY^{n+} + A \qquad (1) \\ S &= \text{solvent} \end{aligned}$$

the emission spectroscopy and absorption spectroscopy can be characterized and give significant insight into the natures of the lower energy singlet and triplet excited states. Furthermore, in certain cases, not only the photosubstitution quantum yields but also the rates of the reactive deactivation processes from the ligand field excited states can be determined as functions of systemic parameters.[4,5] Such data serve as empirical tests of theoretical models for the photosubstitution reactions[6,7] and are now beginning to provide a more detailed mapping of the LF excited-state reaction mechanisms including both ligand labilization[8] and stereochemical rearrangement of the coordination sphere.[9] However, for nearly all the

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(1) RVAU.

(2) HCØI and UCSB. Address correspondence to this author at UCSB.

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published investigations of Rh(III) amine complexes, the ligands X and Y have been weak field relative to the amines. Given that the ligand field strength of Y should have profound effects on the identity of the ligands labilized, the quantum efficiency of this process, and the sterochemical nature of the reaction products, it is of interest to extend the range of ligands investigated to those with fields stronger than those of the amines. Described here are photochemical investigations of several complexes with Y as the strong-field cyanide ligand.

Experimental Section

Materials and Syntheses. Analytical grade chemicals and doubly distilled water were used for all operations. Elementary analyses were performed by the Mikroanalytisk Laboratorium at the H. C. Ørsted Institute. The cyanoamminerhodium(III) complexes used in the photochemical studies were synthesized from $[Rh(NH_3)_5H_2O](ClO_4)_3$ (prepared according to the literature)[10] by the route suggested by Baranovskii and Babaeva,[11] which utilizes the trans-labilizing effect of coordinated sulfite as outlined in eq 2–5

$$Rh(NH_3)_5H_2O^{3+} + 2SO_3^{2-} \rightarrow \textit{trans}\text{-}Rh(NH_3)_4(SO_3)_2^- + H_2O \quad (2)$$

$$\textit{trans}\text{-}Rh(NH_3)_4(SO_3)_2^- + CN^- \rightarrow \textit{trans}\text{-}Rh(NH_3)_4(SO_3)(CN) + SO_3^{2-} \quad (3)$$

$$\textit{trans}\text{-}Rh(NH_3)_4(SO_3)CN + 2HCl \rightarrow \textit{trans}\text{-}Rh(NH_3)_4(CN)Cl^+ + SO_2 + Cl^- + H_2O \quad (4)$$

$$\textit{trans}\text{-}Rh(NH_3)_4(CN)Cl^+ + NH_3 \rightarrow Rh(NH_3)_5CN^{2+} + Cl^- \quad (5)$$

The complexes were prepared and isolated as follows.

***trans*-[Rh(NH$_3$)$_4$(CN)Cl]Cl·1.5H$_2$O.** A reaction solution prepared from $[Rh(NH_3)_5H_2O](ClO_4)_3$ (1.75 g, 3.47 mmol) plus Na_2SO_3 (3.5 g, 28 mmol) in water (~25 mL) was heated for 1.5 h at 85 °C. The solution was then cooled to 25 °C and a small amount (~0.1 g) of a white precipitate noted. Ethanol (~5 mL) was then added, a process resulting in the immediate formation of a voluminous white precipitate. This material was isolated by suction filtration, washed with ethanol and then ether, and air-dried to give a yield of 1.29 g (95%) of the crude bis(sulfite) product $Na[Rh(NH_3)_4(SO_3)_2]\cdot 2H_2O$.

In the next step a solution prepared from $Na[Rh(NH_3)_4(SO_3)_2]\cdot 2H_2O$ (1.15 g, 3.0 mmol) plus KCN (0.63 g, 9.6 mmol) in water (0.5 mL) was heated near boiling on a hot plate for 1.5 h. This solution was then cooled in an ice bath to give a white precipitate. The latter was collected by filtration, washed with ethanol and then ether, and air-dried to give a crude yield of 0.70 g (76%) of the cyano sulfite product $[Rh(NH_3)_4(SO_3)CN]$. The entire 0.70 g (2.2 mmol) of this intermediate was then added to 10 mL of concentrated HCl solution and the heterogeneous mixture heated at 95 °C for 15 min. (The heating process was accompanied by gas evolution). The mixture was cooled and the white solid collected by filtration and then air-dried to give 0.62 g of product corresponding to a 94% yield, assuming the formulation $[Rh(NH_3)_4(CN)Cl]Cl\cdot 1.5H_2O$. This material was recrystallized from 4 N HCl to give 0.57 g (85% overall yield) of the white microcrystalline product. Anal. Calcd for $[Rh(NH_3)_4(CN)Cl]Cl\cdot 1.5H_2O$: C, 4.07; H, 5.13; N, 23.74; Cl, 24.04. Found: C, 4.01; H, 5.05; N, 23.62; Cl, 23.94. Attempts to determine the ionic chloride of this salt by direct titration in aqueous solutions gave high and nonreproducible values, the lowest being 13.8%. (Theoretical is 12.0% assuming one ionic chloride and one coordinated.) However, it was subsequently found that this product is thermally labile in aqueous solution, releasing the coordinated Cl^- at rates sufficient to interfere with the analysis procedure (see Results).

[Rh(NH$_3$)$_5$CN]Cl$_2$. A solution prepared from $[Rh(NH_3)_4(CN)Cl]Cl\cdot 1.5H_2O$ (250 mg, 0.85 mmol) plus NH_4Cl (250 mg) in 15 M aqueous ammonia (15 mL) was heated at ~90 °C for 1.25 h. After the solution was cooled, the resulting white precipitate was isolated by suction filtration to give a 160-mg yield of the crude product. This material was redissolved in hot 10^{-3} M HCl and the resulting solution filtered. Enough concentrated HCl was then added to the solution to give a concentration of ~1 N; the solution was reheated to clarity and allowed to cool slowly. Over a period of several hours, small shiny white crystals deposited. These were then collected by filtration and air-dried to give a 140-mg yield (58%) of the desired $[Rh(NH_3)_5CN]Cl_2$. Anal. Calcd for $[Rh(NH_3)_5CN]Cl_2$: C, 4.21; H, 5.31; N, 29.45; Cl, 24.88. Found: C, 4.04; H, 5.88; N, 29.29; Cl, 24.68.

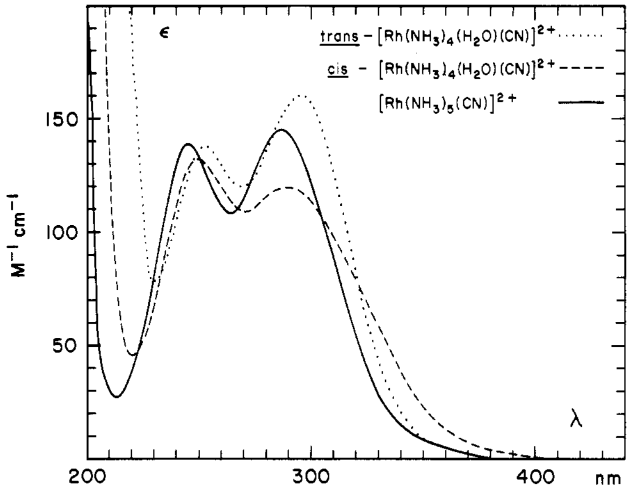

Figure 1. Electronic spectra of cyano complexes.

Photolyses. Photolyses were carried out at 25.0 ± 0.5 °C by the same methods and with the photolysis apparatus previously described.[9] Light intensities were determined by standard ferrioxalate actinometry, and quantum yields were evaluated from spectral and pH changes by numerical procedures also previously described.[12]

Absorption Spectra. Electronic spectra were recorded on a Zeiss DMR 21 or on a Cary 219 spectrophotometer.

pH Measurements. A Radiometer PHM 52 pH meter with a combination-glass electrode with 1.0 M NaCl in the reference part was used for the pH measurements. The definition $pH = -\log [H^+]$ was used throughout, and the standardized perchloric acid solutions had the same ionic strength as the samples for pH standards. pK_a values were calculated from titration curves by standard numerical procedures.[13]

Ion Exchange. Sephadex resin A25 in the perchlorate form was used in the anion-exchange experiments. Amberlite IR-120 sodium form was used as cation exchanger in the cyanide assay (~10-cm column length with ~1-cm diameter in both cases).

Cyanide Analysis. Ionic cyanide was analyzed by the colorimetric method of Lambert et al.[14] A 5.0-mL sample of photolyzed or thermally equilibrated solution was subjected to cation exchange in order to separate the complex ion from the free cyanide. Four 10.0-mL fractions were collected upon elution with water, and 2.0-mL aliquots of each were analyzed. The sensitivity of the method in the present modification[15] was found to be ~1 nmol of CN with a recovery of 90%, as determined from experiments under identical conditions with added known quantitites of NaCN.

Results

Absorption spectra in aqueous solution of the various cyanide complexes relevant to this investigation are summarized in Table I. The tetraammine complexes plus the pentaammine $Rh(NH_3)_5CN^{2+}$ each show two LF bands in the ultraviolet region (corresponding to the assignments $(^1E, ^1A_2) \leftarrow {}^1A_1$ and $(^1E, ^1B_2) \leftarrow {}^1A_1$ for those of C_{4v} symmetry). Notably for $Rh(NH_3)_5CN^{2+}$, the two band maxima (287 and 246 nm, see Figure 1) are significantly higher energy than the corresponding maxima (305 and 255 nm)[16] for the spectrum of the hexaammine $Rh(NH_3)_6^{3+}$, consistent with the greater

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Table I. Electronic Spectra in Aqueous Solutions at Room Temperature

complex ion	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	λ_{min}, nm (ϵ, M^{-1} cm^{-1})	comments
$Rh(NH_3)_5(CN)^{2+}$	287 (146), 246 (139)	264 (107), 214 (~25)	$[Rh(NH_3)_5(CN)]Cl_2$ in 0.10 M $HClO_4$
trans-$Rh(NH_3)_4(H_2O)(CN)^{2+}$	296 (160), 253 (138)	269 (123), 232 (65)	*trans*-$[Rh(NH_3)_4Cl(CN)]Cl\cdot 1.5H_2O$ thermally equilibrated in 0.01 M $NaClO_4$
trans-$Rh(NH_3)_4(OH)(CN)^{+}$	295 (184), 260 (192)	278 (174), 235 (129)	*trans*-$[Rh(NH_3)_4Cl(CN)]Cl\cdot 1.5\ H_2O$ thermally equilibrated in 0.05 M NaOH
trans-$Rh(NH_3)_4Cl(CN)^{+}$	302 (171), 259 (142)		*trans*-$[Rh(NH_3)_4Cl(CN)]Cl\cdot 1.5H_2O$ in 0.01 M NaCl/0.0001 M $HClO_4$; extrapolated to time of dissolution
cis-$Rh(NH_3)_4(H_2O)(CN)^{2+}$	291 (119), 251 (133)	272 (110), 221 (~50)	product spectrum of photolysis of $Rh(NH_3)_5(CN)^{2+}$ in 0.1 M $HClO_4$
	292 (116), 251 (132)	275 (109), 226 (~70)	product spectrum of photolysis of *trans*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$ in 0.01 M $HClO_4$
cis-$Rh(NH_3)_4(OH)(CN)^{+}$	305 (142),[a] 266 (191)	226 (104)	product solution from photolysis of $Rh(NH_3)_5CN^{2+}$ adjusted to 0.06 M NaOH
cis-$Rh(NH_3)_4Cl(CN)^{+}$	336 (~109), 262 (~166)		product solution from $Rh(NH_3)_5(CN)^{2+}$ photolysis anated in 0.3 M HCl

[a] Shoulder.

Table II. Photoreaction Quantum Yields[a]

complex	principal product	λ_{irr}, nm	Φ, mol/einstein	ref
$Rh(NH_3)_5(CN)^{2+}$	*cis*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$	313, 334	0.09	this work
trans-$Rh(NH_3)_4(H_2O)(CN)^{2+}$	*cis*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$	313, 334	0.52	this work
$Rh(NH_3)_6{}^{3+}$	$Rh(NH_3)_5(H_2O)^{3+}$	313	0.075	3b
$Rh(NH_3)_5(H_2O)^{3+}$	$Rh(NH_3)_5(H_2O)^{3+}$	313	0.43	3b
trans-$Rh(NH_3)_4(H_2O)_2{}^{3+}$	*cis*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$	350	0.012	12
cis-$Rh(NH_3)_4(H_2O)_2{}^{3+}$	*trans*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$	350	0.072	12
trans-$Rh(NH_3)_4(H_2O)(OH)^{2+}$	*cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$	350	0.59	12

[a] Photoreaction resulting from excitation with monochromatic light in aqueous solution at 25 °C.

ligand field strength of CN^- vs. that of NH_3. This difference is also reflected in the emission spectra,[16,17] which indicate the 0–0 energy gap between the ground state and the lowest energy triplet LF state to be about 1000 cm^{-1} larger for $Rh(NH_3)_5CN^{2+}$ than for $Rh(NH_3)_6{}^{3+}$. Notably on a two-dimensional scale for LF strength, CN^- is a substantially stronger σ-donor and is a π-acceptor relative to NH_3.[6,18]

There was some difficulty in obtaining the aqueous solution spectrum of the *trans*-$Rh(NH_3)_4(CN)Cl^+$ ion. This ion underwent a thermal reaction, as indicated by the spectral changes observed for acidic aqueous solutions of *trans*-$[Rh(NH_3)_4Cl(CN)]Cl\cdot 1.5H_2O$ kept in the dark. Throughout this reaction isosbestic points were maintained at 349, 296, 275, 256, and 227 nm. The reaction rate was first order in complex (concentration $\sim 10^{-3}$ M), and the rate constant calculated from spectral changes at four different wavelengths from two experiments was $(3.6 \pm 0.1) \times 10^{-4}$ s^{-1} at 25 °C in 0.010 M $NaClO_4$ adjusted to pH 4.0. The reaction was not accompanied by any significant pH change or by any detectable cyanide release. The product spectrum and the initial spectrum, calculated by extrapolation back to the time of dissolution, are presented in Table I. The reaction observed was chloride aquation (eq 6) as evidenced by lack of NH_3 or CN^-

$$trans\text{-}Rh(NH_3)_4Cl(CN)^+ + H_2O \rightleftharpoons trans\text{-}Rh(NH_3)_4(H_2O)(CN)^{2+} + Cl^- \quad (6)$$

release and by the nature of the spectral changes. Chloride ions in thermally equilibrated solutions of *trans*-$Rh(NH_3)_4Cl(CN)^+$/*trans*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$ (λ_{max} = 296 and 253 nm, $\epsilon_{max}/\epsilon_{max} = 1.14 \pm 0.01$) were exchanged with perchlorate ions via chromatography and the solutions reequilibrated at 25 °C. The spectral characteristics (λ_{max} = 296 and 253 nm, $\epsilon_{max}/\epsilon_{max} = 1.15 \pm 0.01$, five experiments) showed that no further chloride aquation took place, indicating that equilibrium 6 is almost completely shifted in favor of the *trans*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$ product under the present conditions. The $pK_a = 7.78 \pm 0.05$ of the *trans*-aquacyanotetraamminerhodium(III) ion was determined in dilute aqueous perchlorate solutions at 25 °C by titration of equilibrated and ion-exchange solutions, and the absorption spectrum of the conjugated base was recorded in 0.05 M NaOH (Table I).

Attempts to prepare the *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ complex as the solid perchlorate salts by reaction with acidic silver perchlorate proved unsuccessful owing to the tendency of these salts to polymerize to an intractable white solid, which showed only poor solubility. A similar product was obtained when the $[Rh(NH_3)_4(CN)Cl]Cl$ salt was heated in hydroxide solution followed by acidification with $HClO_4$.

Photoreactions of *trans*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$ and *trans*-$Rh(NH_3)_4(OH)(CN)^+$. Aqueous solutions of *trans*-$[Rh(NH_3)_4ClCN)]Cl\cdot 1.5H_2O$ in 10^{-3} M $HClO_4$ were equilibrated overnight, and the *trans*-$Rh(NH)_4(H_2O)(CN)^{2+}$ generated was subsequently photolyzed at 313 or 334 nm. The spectrum of an exhaustively photolyzed solution ($\sim 10^{-3}$ M, 5 mL, light path 2 cm, 313-nm monochromatic light with 8×10^{-7} einstein/min intensity over a front window of 2.3-cm diameter, 5 h of irradiation, 25 °C) had the following spectral characteristics: λ_{max} (ϵ) 292 nm (116 M^{-1} cm^{-1}), 251 (132). Isosbestic points were maintained at 322, 248, and 230 nm for ~25% of photolysis. During the photolysis, only insignificant pH changes were observed, and CN^- analysis indicated that less than 0.1% of this ligand was released into solution. Quantum yields for the photoreaction were evaluated from spectral changes (two to four characteristic wavelengths) by using the initial and final spectra as reactant and as product spectra, respectively. No wavelength dependence (313 or 334 nm) was found, and the value $\Phi = 0.52 \pm 0.03$ mol/einstein was calculated from seven experiments (Table II). Three of the experiments were performed with solutions that had first undergone equilibration and then were passed through an anion-exchange resin to exchange ClO_4^- for Cl^- (negative test for Cl^-). It was found that the presence of ionic chloride in the reaction solution had no measurable effect on the product

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(17) Frink, M.; Ford, P. C., work in progress.
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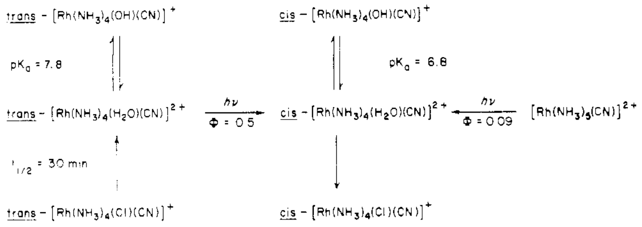
Scheme I



distribution or quantum yield.

Solutions of *trans*-$Rh(NH_3)_4(OH)(CN)^+$ generated in a similar way as the aquo complex showed no spectral changes or CN^- release after 1 h of photolysis at pH 12.7.

Photoreactions of $Rh(NH_3)_5(CN)^{2+}$. The UV–visible spectrum of an aqueous 0.10 M $HClO_4$ solution of $[Rh(NH_3)_5(CN)]Cl_2$ did not show any significant changes after 25 h at room temperature when excluded from light, and a cyanide analysis indicated that <0.05% of the coordinated cyanide was aquated during the same time period. These results demonstrate that the cyanopentaamminerhodium(III) ion is very robust and that any thermal reactions are very minor during the photolysis experiment.

A solution of $Rh(NH_3)_5(CN)^{2+}$ in 0.10 M $HClO_4$ after exhaustive photolysis (313 nm, conditions as for *trans*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$, 20 h of irradiation) had the following spectral characteristics: λ_{max} (ϵ_{max}) 291 nm (119 M^{-1} cm^{-1}), 251 (133). Throughout the photolysis, isosbestic points were maintained at 305, 267, 253, and 223 nm (the last isosbestic point, however, only to ~80% of photoreaction). An analogous experiment with 334-nm monochromatic light had, within experimental uncertainties, an identical product spectrum, and similar results were obtained in a 0.00500 M $HClO_4$/0.10 M $NaClO_4$ medium. Titration of 5.0-mL samples of exhaustively photolyzed $Rh(NH_3)_5(CN)^{2+}$ in the latter medium with 0.010 M NaOH/0.090 M $NaClO_4$ (25 °C) showed that two weak Brønsted acids were present in equal concentration, one with $pK_a = 6.79 \pm 0.02$ and the other with $pK_a \sim 9.1$. A cyanide analysis showed that less than 0.05% of the coordinated cyanide was aquated during the photolysis, thus indicating that the photoproducts were $Rh(NH_3)_4(H_2O)(CN)^{2+}$ and NH_4^+. The quantum yields, evaluated as for *trans*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$, showed no acid concentration (10^{-3} M $\leq [H^+] \leq 10^{-1}$ M in aqueous 0.10 M perchlorate solution) or wavelength (313 or 334 nm) dependence, and $\Phi = 0.086 \pm 0.004$ mol/einstein was calculated from eight experiments. The quantum yield was also estimated from pH changes during the initial stages of photolysis in a 0.0010 M $HClO_4$/0.10 M $NaClO_4$ solution, and comparable results were obtained.

When the product solution was adjusted with NaOH to pH 12.8 and then photolyzed at 313 nm, only very minor and uncharacteristic spectral changes were observed but no CN^- was detectable in the reaction solution. Thus, the conjugate base of the photoproduct appears to be photoinert.

The photochemical and thermal reaction results described here are summarized in Scheme I.

Discussion

The *trans*-$Rh(NH_3)_4(CN)Cl^+$ complex was prepared from *trans*-$Rh(NH_3)_4(SO_3)_2^-$ by the sequential substitution of one SO_3^{2-} by CN^- (eq 3) and then the other SO_3^{2-} by Cl^- (eq 4). Given the known stereoretentive thermal substitution reactions of Rh(III) ammine complexes,[19] it is concluded that the cyano chloro complex also has the trans configuration. The cation of the solid material is at least largely *trans*-$Rh(NH_3)_4(CN)Cl^+$ although the analyses for ionic chloride (see Experimental Section) were consistently higher than the theoretical value for one ionic Cl^- (but much lower than the value for two ionic Cl^-). The reason for this error lies in the thermal aquation of *trans*-$Rh(NH_3)_4(CN)Cl^+$ (eq 6), which is sufficiently rapid to interfere with the titrimetric analytical procedure. Notably, the rate constant for thermal aquation (3.6×10^{-4} s^{-1} at 25 °C) is about 500-fold larger than that for the Cl^- aquation from $Rh(NH_3)_5Cl^{2+}$ (7×10^{-7} s^{-1} at 25 °C)[20] and indicates the strongly labilizing character of the trans cyanide. In contrast, the *trans*-dichloro complex $Rh(NH_3)_2Cl_2^+$ has been shown to be only about twice as reactive as $Rh(NH_3)_5Cl^{2+}$ in thermal aquation studies carried out at 80 °C.[19] Because of its thermal lability, the photoreactions of *trans*-$Rh(NH_3)_4(CN)Cl^+$ were not studied. Instead, dilute solutions of this compound were allowed to aquate to *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$, and the photoreaction properties of this ion were investigated.

The photoproducts from LF excitation of $Rh(NH_3)_5CN^{2+}$ or of *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ have identical spectra. For the former ion, only NH_3 is aquated, and the product apparently has the formula $Rh(NH_3)_4(H_2O)CN^{2+}$. For *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$, the photolysis induces spectral changes but neither NH_3 or CN^- loss, so we conclude the photoproduct to be the isomer *cis*-$Rh(NH_3)_4(H_2O)CN^{2+}$ or a photostationary mixture of the cis and trans isomers. The latter alternative can be discounted on the basis that the same final product spectrum for the $Rh(NH_3)_5CN^{2+}$ photolysis is observed for 313- and 334-nm irradiation, despite the significantly different ratios of the extinction coefficients for the trans starting material and the product for these two wavelengths (Figure 1). In the case of a cis/trans photostationary mixture, the final cis/trans ratio would be a function of the irradiation wavelength[12] ($[cis]/[trans] = (\Phi_{t\rightarrow c}\epsilon_t)/(\Phi_{c\rightarrow t}\epsilon_c)$). Thus we may conclude a simple trans-to-cis photoisomerization with only the cis isomer present in the final product mixture (Scheme I).

That the photoaquation of $Rh(NH_3)_5CN^{2+}$ does not occur with the intermediacy of *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ is evidenced by the isosbestic points (see Results) maintained throughout the photolysis. Given the marked differences in the extinction coefficients of the cis and trans isomers at 304 nm, any significant production of the trans isomer would have degraded this isosbestic point. Thus, the primary photoproduct upon LF irradiation of $Rh(NH_3)_5CN^{2+}$ is *cis*-$Rh(NH_3)_4(H_2O)CN^{2+}$ (Scheme I).

For the $Rh(NH_3)_5CN^{2+}$ ion, the observed photochemistry is consistent with that expected from the theoretical treatments of Vanquickenborne[6a] and others,[7,21] assuming that the photolabilization principally represents a reaction of the lowest energy excited state (LEES). With the strong σ-donor CN^- as the unique ligand, the lowest LF state is $^3A_2$ (one-electron configuration: $(d_{xz}, d_{yz})^4 (d_{xy})^1 (d_{x^2-y^2})^1 (d_{z^2})^0$) and labilization is expected among the equatorial ligands, i.e. the ammonias, as observed. In agreement with this assignment of the LEES, NH_3 labilization is the only observed photoreaction; however, the *cis*-$Rh(NH_3)_4(H_2O)CN^{2+}$ product would have been expected regardless of which NH_3 (axial or equatorial) was labilized (see below). Despite this, it is notable that preliminary results from a photochemical investigation of the substrate *trans*-$Rh(NH_3)_4(^{15}NH_3)CN^{2+}$ indicate that at least 95% of the NH_3 photolabilized originates from the equatorial sites.[22]

For the *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ ion, photoisomerization is presumably coupled to ligand photolabilization, as has been

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[20] Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapter 3.

[21] (a) Wrighton, M.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 164. (b) Incorvia, M.; Zink, J. I. *Inorg. Chem.* **1974**, *13*, 2489.

[22] Skibsted, L. H.; Svendsen, J. S., studies in progress.

demonstrated in each well-documented case of the LF photoisomerization of hexacoordinate d^6 complexes.[3,9] A particularly relevant example is eq 7,[9] for which photoexchange of

$$cis\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \xrightarrow{h\nu\ (366\ nm)} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \quad (7)$$

H_2O with the aqueous solvent occurs with a quantum yield (Φ_{ex} = 0.56 mol/einstein) just slightly larger than that for isomerization (Φ_{isom} = 0.46 mol/einstein). In this content, we conclude that Φ_{ex} from *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ is ≥0.52 mol/einstein, the value of Φ_{isom}. This value is comparable to the Φ_{ex} values measured by isotope labeling procedures for $Rh(NH_3)_5H_2O^{3+}$ (0.43)[23] and *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ (0.39).[9] In addition, since labilization of OH^- from *trans*-$Rh(NH_3)_4(OH)CN^+$ should also lead to isomerization (vide infra), we also conclude that Φ_{ex} for this ion is essentially 0. Again, this value is consistent with the photoinert behavior of $Rh(NH_3)_5OH^{2+}$ studied[23] previously by isotope-exchange procedures; however, it is not certain whether the low value of Φ_{ex} is the result of the inherently low reactivity of hydroxo complexes or reflects also a contribution from a hydroxide-quenching mechanism.[12,24]

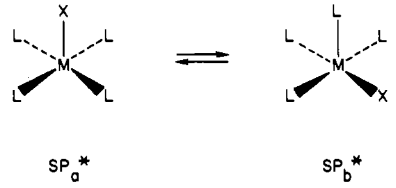
For the case of the C_{4v} ion *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$, the presence of both a strong-field CN^- and a weaker field H_2O on the unique axis leads to some ambiguity as to whether the LEES is ^3E or $^3A_2$. Certainly the H_2O labilization would suggest the reactivity of the ^3E (one-electron configuration: $(d_{xy})^2\ (d_{xz}, d_{yz})^3\ (d_{z^2})^1\ (d_{x^2-y^2})^0$), but it is likely the two states will be close in energy and thermally accessible to each other.

The Vanquickenborne model[6a] allows analysis of the relevant excited states by calculation of excited-state bond indices I^*(M–L) that constitute the contribution to the M–L bond energy from interaction with the metal d orbitals. The calculations are easily accomplished by utilizing solutions to the additive angular overlap model and spectroscopic σ and π parameters for individual ligands. However, quantitative aspects suffer from the absence of accurate spectroscopic parameters calculated for the heavier transition elements. Although the conclusion that the ligand with the smallest I^*(M–L) would be the one labilized from an excited state has been shown not to be universal, the calculated I^*(M–L) values do indicate likely trajectories for reactive deactivation of particular LF states. In this context, it is notable that I^*(M–L) values calculated for *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ suggest the Rh–H_2O bond to be by far the most susceptible to labilization in the ^3E state but to have a somewhat larger I^*(M–L) value than that for Rh–NH_3 bond for the $^3A_2$ state.[25,26] For both excited-state configurations, I^*(Rh–CN) is clearly not the weakest for *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ or $Rh(NH_3)_5CN^{2+}$, consistent with the failure to observe any CN^- photoaquation in either case. This behavior is similar to earlier reports of exclusive NH_3 photoaquation from $Cr(NH_3)_5CN^{2+}$[27] and exclusive Cl^- photoaquation from *trans*-$Co(en)_2ClCN^+$[28] but contrasts with the observation of both NH_3 and CN^- photoaquation (the former the more predominant) for $Co(NH_3)_5CN^{2+}$.[29] The latter result may reflect the role of reactions from upper excited states in cobalt(III) amine complex photochemistry.[3b]

The trans-to-cis photoisomerization of the $Rh(NH_3)_4(H_2O)CN^{2+}$ ion is consistent with the generalized model for photoisomerization of d^6 complexes.[6b,28,30] The qualitative aspects of this model are as follows. Isomerization of a species ML_4XY occurs via an electronically excited pentacoordinate species formed by the dissociation of the labilized ligand Y from the initial hexacoordinate LF state (eq 8). This species,

$$ML_4XY \xrightarrow{h\nu} ML_4XY^* \rightarrow ML_4X^* + Y \quad (8)$$

having a square-pyramidal configuration, has two isomers SP_a^* and SP_b^*, which may interconvert to each other (eq 9) in



(9)

competition with electronic deactivation and trapping by solvent (S) to give respectively the trans and cis ML_4XS products. According to the model, the relative energies of SP_a^* and SP_b^* as well as the rates of interconversion (eq 9) are strongly dependent on the natures of L and X. A dominant feature is the relative σ-donor strengths, SP_a^* being favored (therefore cis-to-trans photoisomerization) when X is a weaker σ-donor than L and SP_b^* (thus, trans-to-cis photoisomerization) being favored in the opposite case. Although the original examples upon which the model was based involved weak σ-donor X's (hence, cis-to-trans isomerization), the prediction of trans-to-cis isomerization has since been demonstrated[9b,12,31] with M = Rh(III) and X = OH^-. The present study is consistent with the model, given that CN^- is a stronger σ-donor than is NH_3.[32] Similar trans-to-cis isomerization has been noted for X = OH^- and *M* = Ir(III)[33] and for X = CN^- and M = Co(III),[28] indicating that the model has generally applicability to the photostereochemistry of d^6 complexes.

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Registry No. $Rh(NH_3)_5(CN)^{2+}$, 48031-56-7; *trans*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$, 86646-27-7; *cis*-$Rh(NH_3)_4(H_2O)(CN)^{2+}$, 86707-57-5; *trans*-$Rh(NH_3)_4Cl(CN)^+$, 86646-28-8; *cis*-$Rh(NH_3)_4Cl(CN)^+$, 86707-58-6; *trans*-$Rh(NH_3)_4(OH)(CN)^+$, 86646-29-9; *cis*-$Rh(NH_3)_4(OH)(CN)^+$, 86707-59-7.

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(25) Note that these calculations were carried out by using the σ and π parameters for Cr(III) reported in ref 6a and 18. However, the same qualitative conclusion is drawn by using the σ and π parameters recently estimated for Rh(III) complexes.[26]

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(32) Note, therefore, that since labilization of a trans NH_3 from the LF excited state of $Rh(NH_3)_5CN^{2+}$ would give the same SP_a^* intermediate as H_2O labilization from excited *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$, the observation of a *cis*-$Rh(NH_3)_4(H_2O)CN^{2+}$ product from the former cannot be cited as evidence for the predicted equatorial labilization.

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