precipitate was identified as $MnBr(CO)_5$ by IR spectroscopy, and no $Mn(C(O)CH_3)(CO)_5$ could be detected in the solution.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We appreciate help from R. E. Stimson for exploratory work.

Registry No. $(CO)_5Mn(CH_3)$, 13601-24-6; CO, 630-08-0; $CClH_2COOH$, 79-11-8; CCl_2HCOOH, 79-43-6; CF_3COOH, 76-05-1; HBr, 10035-10-6.

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Direct Evidence for Rearrangement of Five-Coordinate Excited-State Fragments Generated from Ligand Field Photodissociation in d^6 Complexes of Rhodium(III)

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Received July 7, 1980

Recently, Vanquickenborne and Ceulemans[1] have used an "additive point ligand model" to explain stereochemical changes during photosubstitution reactions of d^6 complexes. Their conclusion is that the stereochemical changes that sometimes occur during the photochemical experiment are a result of rearrangement of a five-coordinate, triplet fragment which results directly from ligand loss out of the lowest triplet, ligand field excited state of the six-coordinate reactant. The five-coordinate fragment $[ML_4X]^q$ displays a thermodynamic preference for the X ligand to appear apical or basal in the square-pyramidal intermediate depending on whether $e_\sigma(L)$ is greater than or less than $e_\sigma(X)$, respectively. This thermodynamic preference, which has been observed experimentally for rhodium(III) amine complexes by our group[2] and others,[3,4] pertains only to the spin triplet and not the lower energy singlet configuration. If correct, this model is very important in deducing the mechanism of d^6 photosubstitution reactions. The presence of the five-coordinate triplet fragment not only implies a photodissociative primary process but also indicates that the reaction is occurring from an electronic excited state and not a high vibrational level in the ground-state manifold.

We have extended the theoretical work of Vanquickenborne and Ceulemans[1] to cases in which $e_\sigma(X) > e_\sigma(L)$ and have observed experimentally[5] the predicted trans to cis photoaquation reaction for *trans*-$Co(en)_2(CN)Y^{n+}$ ($Y = Cl, H_2O$) complexes. However, in a number of studies, photolysis of *cis*- and *trans*-$Rh(en)_2(NH_3)X^{2+}$ complexes ($X = Cl$,[2a] Br,[2b] I[2c]) leads to $Rh(en)_2(NH_3)(H_2O)^{3+}$ with stereoretention whenever the photolabilized ligand is X. The five-coordinate fragment which is formed, $[Rh(en)_2(NH_3)^{3+}]^*$, should not show much of a thermodynamic preference for NH_3 apical or basal ($e_\sigma(NH_3) \simeq e_\sigma(en)$), so that a cis/trans product mixture and not stereoretention should have resulted if the racemization is controlled by the thermodynamics of the square-pyramidal $[ML_4X]^q$ fragments. We have proposed[2] that the lack of rearrangement of the apical and basal $[Rh(en)_2(NH_3)^{3+}]^*$ fragments is due to a kinetic control of the rearrangement in that the barrier to NH_3 apical ↔ basal rearrangement is too large to be competitive to intersystem crossing (triplet → singlet) of the five-coordinate fragment. Since this premise is very important in assessing the applicability and correctness of the Vanquickenborne model,[1] we report here the 25 and 50 °C photochemistry of *cis*- and *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$.

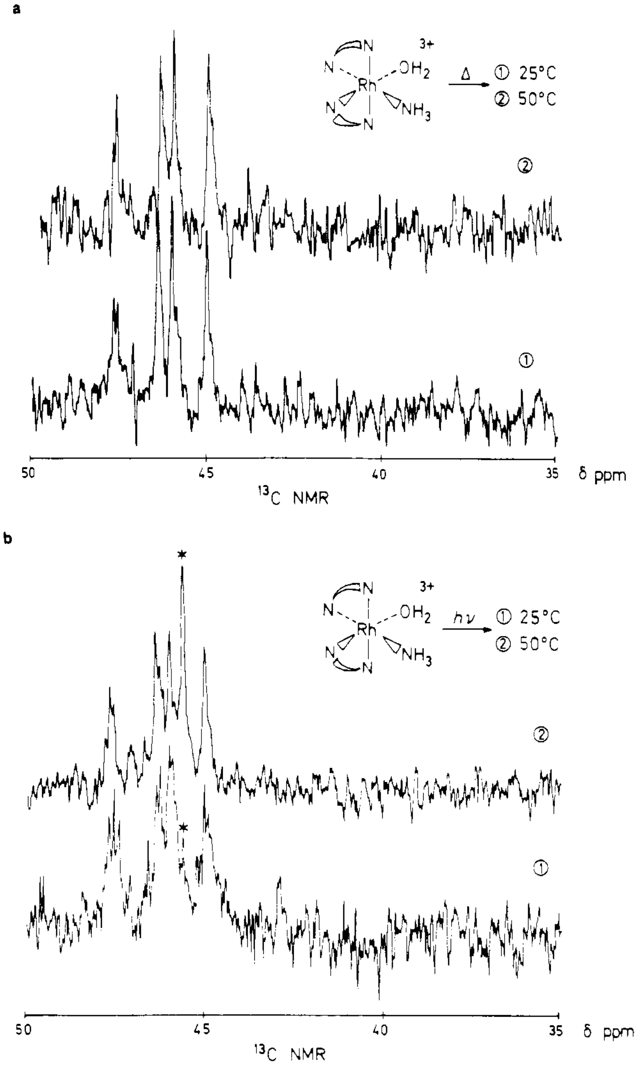

Figure 1. Proton-decoupled ^{13}C NMR spectra: (a) thermal reaction of *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ at 25 and 50 °C; (b) photochemical reaction of *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ at 25 and 50 °C with * denoting trans isomer.

Experimental Section

Materials and Syntheses. The *cis*- and *trans*-$[Rh(en)_2(NH_3)(H_2O)](ClO_4)_3$ complexes were prepared from $RhCl_3$ by previously described procedures.[2a] All reagents used in compound preparation were analytic reagent grade and used without further purification. Solvent water, used in both compound preparation and photolysis studies, was redistilled from alkaline permanganate in all glass apparatus.

Photolysis and Dark Control Reactions. All photolysis and dark control solutions were approximately 10^{-3} M in complex in pH 3.5 aqueous $HClO_4$. For photolysis solutions, the irradiation wavelength of 313 nm was used on a previously described apparatus.[6] Both photo and dark control experiments were run at both 25 and 50 °C for *cis*- and *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$. Photolyses were carried out at 50 °C until changes were minimal in the electronic spectra (8 h for the trans complex, 5 h for the cis). All other experiments—all dark

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0020-1669/81/1320-0280$01.00/0

Table I. Electronic Absorption and ^{13}C NMR Spectroscopic Data for *cis*- and *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$

complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	δ^a
trans-$Rh(en)_2(NH_3)(H_2O)^{3+}$	303	167	45.63
cis-$Rh(en)_2(NH_3)(H_2O)^{3+}$	309	227	47.68, 46.39, 45.99, 45.03^b

^{a} Chemical shifts reported vs. Me_4Si with dioxane (67.40 ppm) as an internal reference. ^{b} Reference 8.

controls and photolyses at 25 °C—were run for the corresponding length of time.

Spectroscopy. The photolysis and dark control solutions were analyzed both by electronic spectroscopy and by proton-decoupled ^{13}C NMR spectroscopy. Electronic spectroscopy utilized a Cary Model 14 UV-vis-near-IR spectrophotometer, and NMR experiments were run in 1/1 (v/v) D_2O/H_2O on a Varian XL-100 equipped with a Nicolet TT-100 data system operating at a frequency of 25.2 MHz. NMR procedures and data treatment have been described previously.[7] Table I reports the electronic absorption and ^{13}C NMR spectroscopic results on *cis*- and *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$.

Results and Discussion

Figure 1 contains proton-decoupled ^{13}C NMR spectra of solutions of *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ which were (a) thermostated at 25 or 50 °C and kept in the dark for 5 h or (b) irradiated at 25 or 50 °C for 5 h. All spectra display the four peaks which correspond to the *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$, whereas only the spectrum of the 50 °C photolysis solutions shows a significant peak at 45.63 ppm representing the trans isomer. Photoisomerization also occurred when *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$ was irradiated at 50 °C. However, under the photolysis conditions at 50 °C (8 h for trans and 5 h for cis), cis → trans photoisomerization was more pronounced than trans → cis photoisomerization. This is not surprising since the respective extinction coefficients of the cis and trans isomers at the 313-nm irradiation wavelength are 225 and 150 M^{-1} cm^{-1}, and photoaquation quantum yields for loss of X in the $RhA_4X_2^+$ systems ($A_4 = (NH_3)_4{}^3$, $(en)_2{}^2$; X = Cl, Br) are generally larger for the cis isomer.

The fact that the cis complexes generally have greater substitutional quantum yields yet are predicted to have greater M–X bond energies in the excited states[9] suggests that six-coordinate excited-state lifetimes are longer for the cis complexes. If this same trend is observed for the five-coordinate, triplet fragments, i.e., X basal longer lived than X apical, we would expect the majority of product under extensive photolysis conditions to be the trans isomer, even if the free energies of X basal and X apical are approximately equal.

Trans → cis and cis → trans photoisomerizations are predicted for $Rh(en)_2(NH_3)(H_2O)^{3+}$ by the model for five-coordinate excited-state rearrangement[1,5] and are observed in this study. The experiment also demonstrates that the photochemistry of a complex may be modified by a change in temperature. These results confirm the model proposed initially by Vanquickenborne and Ceulemans[1] and also show that the stereochemical course of a d^6 substitution reaction can be driven and controlled by light, heat, or the combination of the two.

Acknowledgment. We thank Matthey Bishop, Inc., for a loan of the rhodium used in these studies.

Registry No. *trans*-$Rh(en)_2(NH_3)(H_2O)^{3+}$, 15337-82-3; *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$, 70223-45-9.

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Synthesis and Characterization of $Cp_2Rh_2(NO)_2$ and $Cp_3Rh_3(NO)_2$

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Received April 30, 1980

Relatively few bi- or polynuclear cyclopentadienylmetal nitrosyl compounds have been prepared.[1,2] The known binuclear compounds include $Cp_2M_2(NO)_2$ (Cp = η^5-C_5H_5; M = Fe,[3,4] Co[5,6]), which contain bridging nitrosyls, and $Cp_2Cr_2(NO)_4$[7,8] and $Cp_2(\eta^1\text{-}C_5H_5)Mn_2(NO)_3$,[9,10] which have both bridging and terminal nitrosyls. The two known trinuclear compounds are $Cp_3Mn_3(NO)_4$,[7,11] which has a face-bridging nitrosyl in addition to three edge-bridging ones, and $Cp_3Co_3(NO)_2$,[12] for which two face-bridging nitrosyls have been proposed. We wish to report the rhodium congeners of the known cobalt compounds, namely, $Cp_2Rh_2(NO)_2$ and $Cp_3Rh_3(NO)_2$.

Experimental Section

The preparation of $Rh_2(CO)_4Cl_2$ was adapted from the method of McCleverty and Wilkinson.[13] $CpRh(CO)_2$ was prepared by reaction of cyclopentadienylthallium in 40% excess with $Rh_2(CO)_4Cl_2$ in an ethereal suspension, followed by chromatography on a Florisil column eluted with pentane. Nitric oxide was generated by addition of aqueous acidic $FeSO_4$ to a $NaNO_2$ solution[14] and was dried by passage through silica gel at −78 °C. All solvents were used as received without further purification, except THF, which was distilled from Na/benzophenone prior to use. Infrared spectra were recorded on Perkin-Elmer 467 and 599 spectrophotometers and calibrated with cyclohexane (2138 cm^{-1}) and polystyrene. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrophotometer. Microanalyses were performed by the School of Chemical Sciences analytical laboratory. Mass spectra were obtained on a Varian-MAT CH-5 spectrometer (electron impact) or a Varian 731 spectrometer (field desorption) by the School of Chemical Sciences mass spectroscopy laboratory.

Preparation of $Cp_2Rh_2(NO)_2$ and $Cp_3Rh_3(NO)_2$. In a nitrogen atmosphere $[Rh(CO)_2Cl]_2$ (1.46 g, 3.75 mmol) was dissolved in 75 mL of THF. The solution was stirred while nitric oxide was slowly bubbled through for 2.5 h. The solution turned from orange to dark brown within the first 15 min of nitrosylation. The reaction vessel was flushed with N_2, and freshly sublimed CpTl (3.03 g, 11.3 mmol) was added. The reaction mixture was stirred for an additional 14 h and then filtered. The solid collected was set aside for further workup (see below). The filtrate was evaporated under reduced pressure and subjected to purification by column chromatography (silica gel/benzene). The only significant product was contained in a dark brown band. The solution was evaporated to give $Cp_2Rh_2(NO)_2$ as a brown solid (108 mg, 0.27 mmol, 7.3% yield). Slightly higher yields (ca. 9%) were obtained by prolonged nitrosylation (20 h). An analytical sample was crystallized from benzene/pentane. Anal. Calcd for $C_{10}H_{10}N_2O_2Rh_2$: C, 30.33; H, 2.55; N, 7.07. Found: C, 30.60; H, 2.60; N, 6.94. IR (ν_{NO}): 1565 (m), 1516 (s) cm^{-1} (KBr); 1568 (m),

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