

Complexes with Asymmetric Tetraamine Ligands V*. Base Hydrolysis of Rhodium(III) Complexes

MARIEL M. MUIR** and LOURDES M. TORRES

Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931 (U.S.A.)

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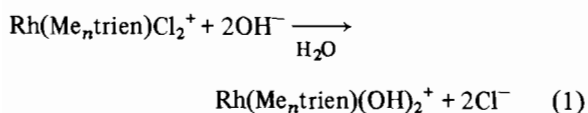
Abstract

Kinetic studies of the base hydrolysis reactions of a series of Rh(III) complexes with optically active methyl-substituted trien derivatives gave the observed rate law $-d[\text{complex}]/dt = (k_1 + k_2[\text{OH}^-])[\text{complex}]$. For the reaction of $[\text{Rh}(\text{Me}_n\text{trien})\text{Cl}_2]\text{X}$ to give the dihydroxo complex, total retention of configuration was observed for all the *cis*- α and *cis*- β dichloro complexes, but rearrangement from *trans* to *cis*- β was observed for all the *trans* dichloro complexes.

Introduction

Stereochemical studies of reactions of complexes of Rh(III) are of interest for comparison with other widely studied systems such as Co(III) [3–11]. The use of complexes with optically active ligands, although they are synthetically difficult to obtain, can provide considerable stereochemical information about the reaction under study.

The syntheses and characterization of the complexes have been reported [12] and the structure of the *cis*- β isomer of one has been determined [13]. The general formula of the complexes studied is $[\text{Rh}(\text{Me}_n\text{trien})\text{Cl}_2]\text{X}$, where $n = 0, 2, \text{ or } 3$, $\text{X} = \text{Cl}^-$ or ClO_4^- and Me_ntrien is a tetradentate ligand of general formula $\text{H}_2\text{N}-\text{CHR}-\text{CH}_2-\text{NH}-\text{CHR}'-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CHR}-\text{NH}_2$. The optically active tetraamines used in the study were the methyl-substituted triethylenetetramine (trien) derivatives: 2*S*,9*S*-dimethyltrien ($\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$) and the diastereomers 2*S*,5*R*,9*S*-trimethyltrien and 2*S*,5*S*,9*S*-trimethyltrien ($\text{R} = \text{R}' = \text{CH}_3$). The reactions were



*For Part IV, see ref. 1; presented in part previously, see ref. 2(a); taken in part from ref. 2(b).

**Author to whom correspondence should be addressed.

Experimental

Materials

Complexes were prepared and characterized as reported previously [12] by a modification of previously reported methods for $[\text{Rh}(\text{trien})\text{Cl}_2]\text{X}$ [14, 15]. All gave satisfactory elemental analyses. Water was distilled in an all-glass still. All other substances were reagent grade materials.

Kinetic Studies

In a 1.00 cm quartz cell 3.00 ml of a 2.0×10^{-3} M aqueous solution of the complex were maintained at 25.0 °C in the thermostatted cell compartment of a Hitachi-Perkin-Elmer 200 spectrophotometer. The UV-Vis spectrum was recorded and the instrument was calibrated at the wavelength selected for following the reaction.

The kinetic run was started by injection of 20 to 60 μl of a 5 M NaOH solution into the cell. The reaction was followed by recording the percent transmittance as a function of time at the wavelength of maximum absorbance of the complex. The pH of the reaction mixture was measured with a micro combination electrode and a Metrohm Herisau pH meter before and after the kinetic run. Several runs were done in which the optical rotation was measured instead of the absorbance. A Perkin-Elmer 141 polarimeter, equipped with a Bausch and Lomb grating monochromator and a Xenon source, was used to obtain ORD curves and optical rotation as a function of time. UV-Vis spectra and ORD curves of the final reaction mixtures were used to help confirm the nature of the products. Several kinetic runs were carried out at 15.0 and at 44.0 °C.

Results

The base hydrolysis reactions (1) of $[\text{Rh}(\text{Me}_n\text{trien})\text{Cl}_2]^+$ were carried out at initial pH values from 11.6 to 13.2 with $[\text{OH}^-]$ always present in at least tenfold excess relative to the concentration of complex. The reactions were followed spectrophotometrically at a wavelength where an appropriate change in absorbance

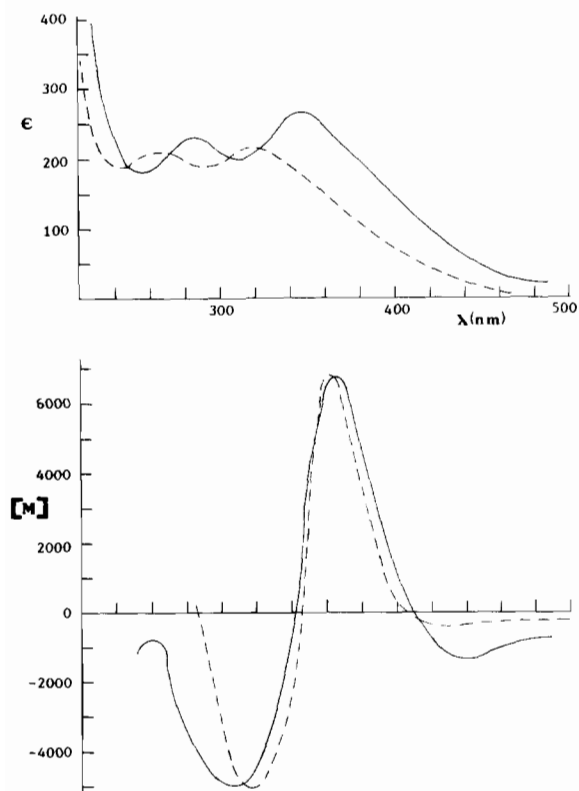


Fig. 1. Molar absorptivity ϵ (l mol⁻¹ cm⁻¹) and optical rotatory dispersion [M] (° l mol⁻¹ m⁻¹) for aqueous solutions of Λ -*cis*- α -RR-[Rh(2*S*,5*R*,9*S*-Me₃trien)XY]⁺; — X = Y = Cl; - - - solution after base hydrolysis, X = Y = OH.

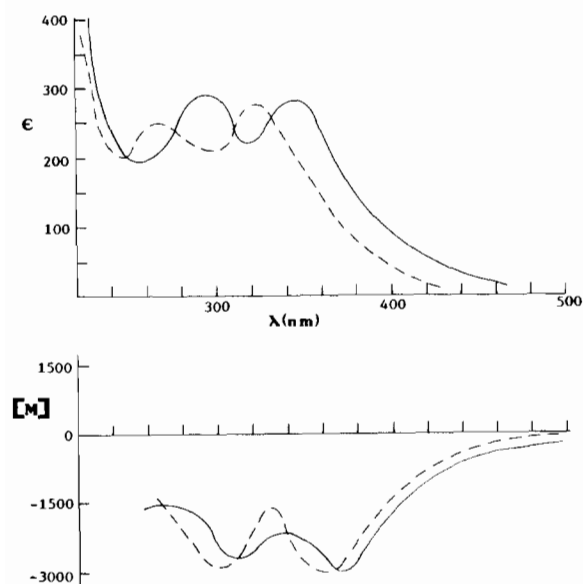


Fig. 2. Molar absorptivity ϵ (l mol⁻¹ cm⁻¹) and optical rotatory dispersion [M] (° l mol⁻¹ m⁻¹) for aqueous solutions of Λ -*cis*- β -SS-[Rh(2*S*,5*R*,9*S*-Me₃trien)XY]⁺; — X = Y = Cl; - - - solution after base hydrolysis, X = Y = OH.

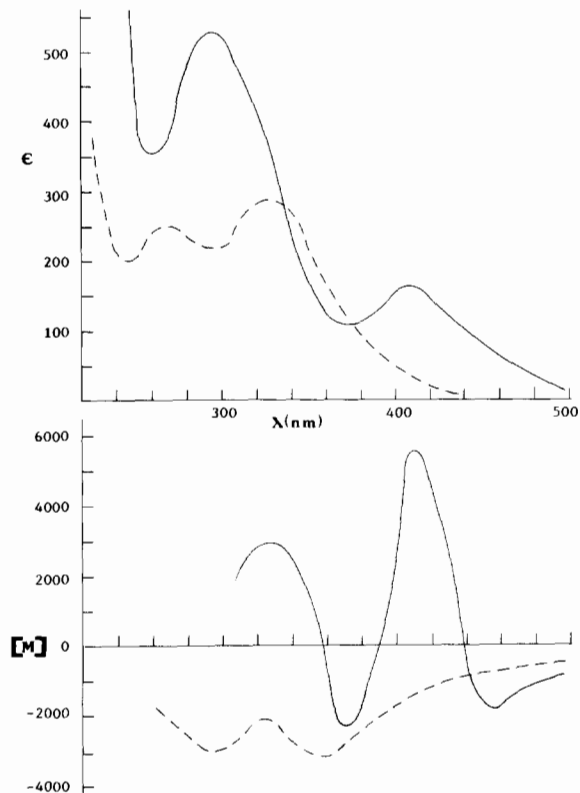


Fig. 3. Molar absorptivity ϵ (l mol⁻¹ cm⁻¹) and optical rotatory dispersion [M] (° l mol⁻¹ m⁻¹) for aqueous solutions of *trans*-SS-[Rh(2*S*,5*R*,9*S*-Me₃trien)XY]⁺; — X = Y = Cl; - - - solution after base hydrolysis, X = Y = OH.

could be seen. Figures 1 to 3 show the changes in absorption spectra and in ORD curves during the base hydrolyses of one set of isomers. All the other complexes gave very similar spectral changes. In all cases the product obtained was the dihydroxo complex, Rh(Me_{*n*}trien)(OH)₂⁺. The spectral data show retention of configuration for the *cis*- α and *cis*- β isomers, while the *trans* isomers rearrange to give the *cis*- β dihydroxo product, as summarized in Table 1. No evidence for the chlorohydroxo species could be obtained in any of the reactions, so the loss of the second chloride in strong base was assumed to be faster than loss of the first. When the base hydrolysis products were acidified, the resulting spectra were those of the corresponding diaquo ions, [Rh(Me_{*n*}trien)(OH)₂]³⁺, rather than the spectra of the chloroaquo ions, which can be prepared by a photochemical route.

Pseudo-first-order behavior was observed for all the reactions, and plots of $-\log(A - A_\infty)$ as a function of time were linear for at least two to three half-lives. Linear least-squares analysis of the observed pseudo-first-order rate constants as a function of [OH⁻] gave values for k_1 and k_2 , where k_1 is the rate constant for the base-independent path and k_2 is the

TABLE 1. Rate constants k_1 and k_2 for the base hydrolysis reactions $[\text{Rh}(\text{L})\text{Cl}_2]^+ + 2\text{OH}^- \rightarrow [\text{Rh}(\text{L})(\text{OH})_2]^+ + 2\text{Cl}^-$

L	Isomer	$10^4 \times k_1 (\text{s}^{-1})$	$10^3 \times k_2 (\text{M}^{-1} \text{s}^{-1})$	Product isomer
		$T = 25.0 \text{ }^\circ\text{C}$		
trien	<i>cis</i> - α	4.2 ± 0.4	1.4 ± 0.3	<i>cis</i> - α
	<i>cis</i> - β	9.4 ± 0.3	12.3 ± 0.1	<i>cis</i> - β
	<i>trans</i>	1.0 ± 0.7	11.0 ± 0.4	<i>cis</i> - β
SS-Me ₂ trien	Λ - <i>cis</i> - α -RR	2.2 ± 0.1	0.80 ± 0.02	Λ - <i>cis</i> - α -RR
	Λ - <i>cis</i> - β -SS	1.7 ± 0.4	8.36 ± 0.04	Λ - <i>cis</i> - β -SS
	<i>trans</i> -SS	1.3 ± 0.7	16.0 ± 1.0	Λ - <i>cis</i> - β -SS
SRS-Me ₃ trien	Λ - <i>cis</i> - α -RR	2.5 ± 0.8	22.0 ± 0.9	Λ - <i>cis</i> - α -RR
	Λ - <i>cis</i> - β -SS	36.0 ± 6.0	145.0 ± 3.0	Λ - <i>cis</i> - β -SS
	<i>trans</i> -SS	0.6 ± 0.2	13.0 ± 1.0	Λ - <i>cis</i> - β -SS
SSS-Me ₃ trien	Λ - <i>cis</i> - β -SS	0.7 ± 0.2	123.0 ± 0.9	Λ - <i>cis</i> - β -SS
	<i>trans</i> -SS	1.2 ± 0.3	9.7 ± 0.4	Λ - <i>cis</i> - β -SS
$T = 15.0 \text{ }^\circ\text{C}$				
trien	<i>cis</i> - α	0.72 ± 0.01	0.56 ± 0.013	<i>cis</i> - α
	<i>cis</i> - β	0.58 ± 0.07	0.98 ± 0.06	<i>cis</i> - β
	<i>trans</i>	0.56 ± 0.03	0.35 ± 0.02	<i>cis</i> - β
$T = 44.0 \text{ }^\circ\text{C}$				
trien	<i>cis</i> - α	12.0 ± 2.0	15.0 ± 1.0	<i>cis</i> - α
	<i>cis</i> - β	2.0 ± 1.0	106.0 ± 17.0	<i>cis</i> - β
	<i>trans</i>	15.0 ± 4.0	31.0 ± 2.0	<i>cis</i> - β

rate constant for the base-dependent reaction path. The rate law is

$$-\frac{d[\text{complex}]}{dt} = (k_1 + k_2[\text{OH}^-])[\text{complex}]$$

which is consistent with a dissociative-conjugate base (D-CB) mechanism for the base hydrolysis [3–7]. In Table 1 are shown the rate constants for each of the complexes studied. A significant variation was found in the rates as the isomer and the substituents on the ligand were changed. Complexes with trien were included in this study for comparison.

Values of k_1 , the rate constant for the base-independent path, were very small in all cases, with generally small variations among isomers for a given complex. For the *cis*- α complexes and the *trans* complexes, the variation in k_1 was only a factor of two. A larger range of k_1 values was observed for the *cis*- β complexes, which varied from 0.7×10^{-4} to $36 \times 10^{-4} \text{ s}^{-1}$.

The variations among the k_2 values for different isomers were greater, with a range of about 180. The *cis*- α complexes gave the smallest k_2 values, even smaller than for the *trans* complexes. The values of k_2 for the *trans* complexes of trien derivatives are lower than for the *cis*- β complexes, except for the Me₂trien case, and the range of variation among different ligands is not as great for the *cis*- β complexes.

Since only small amounts of the complexes with the optically active ligands were available, no activation parameters could be determined for those complexes. However, sufficient amounts of the isomers of trien complexes were obtained to permit rate studies at three temperatures, 15.0, 25.0 and 44.0 $^\circ\text{C}$. The deviations in the k_1 values, derived from the intercepts of the pseudo-first-order rate plots, were large enough that no activation parameters were calculated for the base-independent path. The values of ΔH^\ddagger in kJ/mol for the base dependent (k_2) path were 84 for *cis*- α -, 112 for *cis*- β - and 117 for *trans*-[Rh(trien)Cl₂]⁺. These values for the enthalpies of activation of the trien complexes are very similar to one another. This is consistent with values of ΔH^\ddagger determined in this laboratory for the Co(III) analogs [11] and with other values reported in the literature [4, 9, 16]. The values for the entropy of activation ΔS^\ddagger in J mol⁻¹ K⁻¹ were -12 for *cis*- α -, 100 for *cis*- β - and 92 for *trans*-[Rh(trien)Cl₂]⁺. The errors in the ΔH^\ddagger values were 10 to 15% and in ΔS^\ddagger were large, 50 to 70%, so only the relative magnitudes are significant.

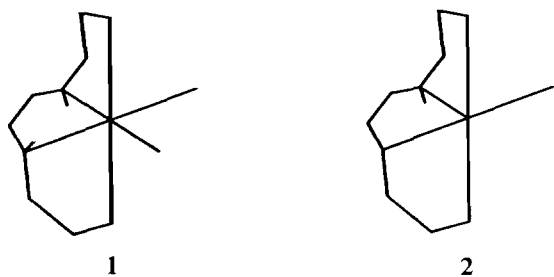
Discussion

In a dissociative-conjugate base (D-CB) mechanism, the five-coordinate intermediate can be

stabilized through π -bonding of the amido group formed by deprotonation of an amine group [3–7]. Tobe has suggested from studies on complexes of Co(III) that base hydrolysis is most effectively promoted by deprotonation of a ‘flat’ secondary N–H which is *cis* to the leaving group, which permits optimum π -overlap between the amido group and the metal ion in a *tbp* intermediate [5]. These conditions can be fulfilled for the *cis*- β and *trans* isomers, but the *cis*- α isomers have only ‘angular’ secondary N–H groups.

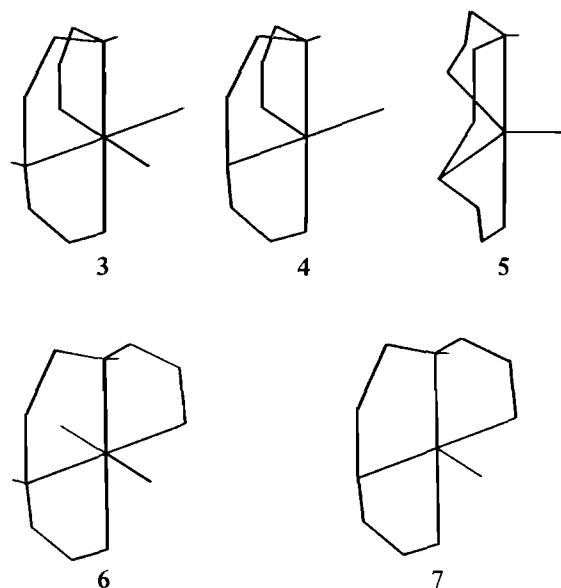
The rates of base hydrolysis of the *cis*- β isomers were faster than those of the corresponding *cis*- α isomers by factors of 6 to 10. This is a much smaller difference than that for base hydrolysis of analogous isomers of Co(III) complexes [5] where the *cis*- β isomers are faster than the *cis*- α by about 10^4 . A relative lack of reactivity of *cis*- α isomers has also been observed for the acid hydrolyses of complexes of Co(III) with the same optically active ligands [11].

All the *cis*- α -RR-[Rh(Me_ntrien)Cl₂]⁺ complexes (1) studied hydrolyzed slowly and with complete retention of configuration. A good reason for this is evident upon examination of the square-pyramidal intermediate species (2), which would be formed by a dissociative process. No possible trigonal bipyramidal (TBP) intermediate can be formed without causing enormous strain in the central chelate ring, which cannot be stretched easily to the required 120° angle. Thus, the most likely intermediate for the *cis*- α complexes is the square pyramid (SP) 2, which should be less able to lower the transition energy than a TBP. The steric hindrance to rearrangement accounts for both the lower reactivity and the retention of configuration observed in the *cis*- α isomers.



All the *cis*- β -SS-[Rh(Me_ntrien)Cl₂]⁺ complexes (3) hydrolyze with total retention of configuration, which would seem to suggest an intermediate similar to that for the *cis*- α complexes, but other factors need to be considered. First, the *cis*- β isomers do not have the same steric constraints as the *cis*- α isomers. After dissociation of a Cl[−] ligand to give SP 4, the TBP intermediate 5 can be formed readily, since no chelate ring has to span more than a 90° angle. Second, it is important to note that the *cis*- β -SS-[Rh(Me_ntrien)(OH)₂]⁺ products from base hydrolysis

of the *trans*-SS isomers (6) have the same configurations of the rings and secondary nitrogens as the products of hydrolysis of the *cis*- β dichloro isomers. Thus, it is reasonable to assume that the *trans* and *cis*- β isomers should have the same TBP intermediate 5 which can form either *trans* or *cis*- β products through the SP intermediates 7 and 4. The observation that even after base hydrolysis, the product dihydroxo isomers have the same optical configurations as the starting *cis*- α and *cis*- β dichloro isomers is further evidence for the great stereosensitivity of the systems with these ligands and suggests that the degree of stabilization of the preferred geometries must be significant. For the complexes with methyl substituents on the tetraamine ligand, inversion at the secondary nitrogen following deprotonation would give a less favorable ring conformation, with one or more new axial methyl groups.



Virtually complete *trans* to *cis* isomerization has been reported [16] for base hydrolysis reactions of *trans*-[Rh(en)₂Cl₂]⁺ (en = ethylenediamine), which is consistent with the rearrangements observed for *trans* isomers in this work. The Λ -(+)-*cis*-[Rh(en)₂Cl₂]⁺ complex gave retention of configuration during base hydrolysis [17], which is also consistent with the results of this work, although the importance of steric effects should be less in the en complexes.

The differences in *k*₂ observed for the complexes with trien derivatives are less dramatic than for the complexes with en, where the value of *k*₂ for *trans*-[Rh(en)₂Cl₂]⁺ is three orders of magnitude less than for *cis*-[Rh(en)₂Cl₂]⁺ [18]. Although the *cis*- α complexes have an amino group *trans* to each chloride, the steric hindrance in the trien framework prevents the stabilization usually produced by formation of an amido species.

Addition of a methyl group to each terminal ring of trien to give 2*S*,9*S*-Me_ntrien results in a slower reaction. This is consistent with the necessity for the motion required by these rings in which the methyl groups must shift to minimize strain energy in the new ring conformations in the TBP intermediate. However, when a methyl group is added to the central ring of trien, the reaction is considerably faster than for either the trien or the Me₂trien system. Since both diastereomeric Me₃trien systems show a similar increase, the reason might be primarily an inductive electron donating effect of the methyl group adjacent to the amino group which loses the proton. Although such an effect might reduce the acidity of the amino group, it would help stabilize the amido group formed, and thus the TBP intermediate 5.

Values for ΔS^\ddagger are generally considered to have a more direct relationship with the rearrangements that may occur in the transition state than do values of ΔH^\ddagger . Tobe [19] has proposed that higher entropies of activation are indicative of dissociative processes proceeding through TBP intermediates and that lower, or negative, entropies of activation should be associated with SP intermediates. Calculations for Co(III) complexes lend support to this idea [19]. The results obtained in this work are consistent with those predictions. For the *cis*- α isomer, the small negative value obtained, $-12 \text{ J mol}^{-1} \text{ K}^{-1}$, fits the lack of rearrangement observed for that system. The positive, larger values obtained for both *cis*- β and *trans* isomers are consistent with their ability to form TBP intermediates, which allow the *trans* to *cis* rearrangement.

Conclusions

The results of this study of complexes of Rh(III) are in agreement with the currently accepted D-CB mechanism for base hydrolysis of octahedral complexes. The retention of configuration at both secondary nitrogens during base hydrolysis can be explained by consideration of the preferred ring conformations when methyl substituents are present.

Acknowledgements

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