40 °C, 60%). ^{19}F NMR spectrum: ϕ −73.3 (s). The mass spectrum showed a molecular ion peak at m/e 318 and loss of CF_3– and CF_3SO– groups. Anal. Calcd for $C_6H_8N_2S_2O_2F_6$: C, 22.64; H, 2.51; S, 20.16. Found: C, 22.50; H, 2.40; S, 17.32.

1,3,5-Tris((trifluoromethyl)sulfinyl)hexamethylcyclotrisilazane (2B) (Method II). Hexane was used as solvent. Although most of the salt was insoluble in hexane, the liquid product obtained after the decanted solvent was evaporated was contaminated with traces of the salt; yield 50%. ^{19}F NMR spectrum: ϕ −78.58. The mass spectrum contains peaks at m/e 498, $(M - CF_3)^+$, and peaks assigned to fragments resulting from subsequent loss of $CF_3S(O)$– groups.

1,4,8,11-Tris((trifluoromethyl)sulfinyl)-1,4,8,11-tetraazacyclotetradecane (2C) (Method II). After the solvent was concentrated to 5 mL, the solution was placed into a sublimation apparatus and sublimed under vacuum at 65 °C for 24 h. After the Et_3NHCl sublimed onto the cold finger, a brown solid (mp 113 °C) remained. ^{19}F NMR spectrum: ϕ −72.4 (s). The mass spectrum contains peaks at m/e 595, $(M - CF_3)^+$, and peaks assigned to fragments resulting from stepwise loss of four $CF_3S(O)$– groups.

1,4-Bis((trifluoromethyl)sulfonyl)piperazine (3A) (Method I). Piperazine was dissolved in benzene. The white crystalline product was obtained after Kugelrohring at 53 °C (1 torr) (mp 53 °C, 60%). ^{19}F NMR spectrum: ϕ −85.2 (s). The mass spectrum showed a molecular ion at m/e 350 and peaks that were assigned to stepwise loss of two CF_3SO_2– groups. Anal. Calcd for $C_6H_8N_2S_2O_4F_6$: N, 8.00; S, 18.28; F, 32.57. Found: N, 7.90; S, 18.00; F, 31.50.

1,4,8,11-Tetrakis((trifluoromethyl)sulfonyl)-1,4,8,11-tetraazacyclotetradecane (3B) (Method II). Both the product and the ammonium salt are insoluble in hexane. The brown product (mp 135 °C) has a ^{19}F NMR resonance peak at ϕ −85.82. The mass spectrum gave a molecular ion at m/e 728 and peaks that reflect the stepwise loss of three CF_3SO_2– groups.

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Equilibria between Monohydroxo- and Dihydroxo-Bridged Binuclear Amminerhodium(III) Complexes

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The binuclear ion $(NH_3)_4Rh(OH)_2Rh(NH_3)_4{}^{4+}$ (diol) equilibrates in acidic solution according to Scheme I. The kinetics and equilibria have been studied in 1 M (Na,H)ClO_4 at 25 and 34.5 °C and in the hydrogen ion concentration range 10^{-5}–0.1 M. The results at 25 °C are as follows: $k_1 = 4.26 \times 10^{-5}$ s^{-1}, $\Delta H^* = 91$ kJ mol^{-1}; $k_{-1} = 1.41 \times 10^{-5}$ s^{-1}, $\Delta H^* = 89$ kJ mol^{-1}; $k_{-2} = 9.6 \times 10^{-6}$ s^{-1}; $\Delta H^* = 109$ kJ mol^{-1}; $k_2/K_{a3} = 7.4 \times 10^{-2}$ s^{-1} M^{-1}, $\Delta H^*(k_2) - \Delta H^\circ(K_{a3}) = 58$ kJ mol^{-1}; $k_1 = k_1/k_{-1} = 3.03$, $\Delta H^\circ = 1.6$ kJ mol^{-1}. The acid dissociation constants for the diaqua monool, *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$, at 25 °C are p$K_{a1} = 3.41$ and p$K_{a2} = 8.80$. The aqua hydroxo monool has been isolated as a solid salt, *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$.

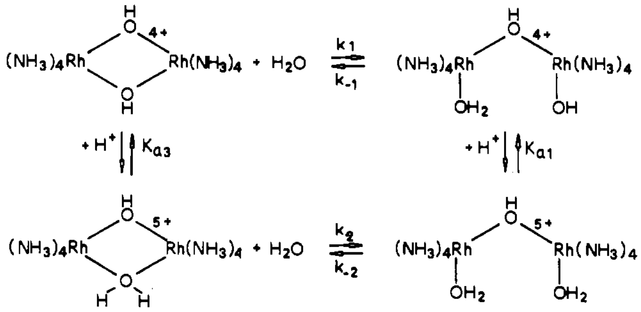
Introduction

Salts of the dihydroxo-bridged cations, diols, $(NH_3)_4Rh(OH)_2Rh(NH_3)_4{}^{4+}$ and Δ,Λ-$(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$ have been synthesized recently at this laboratory.[1-3] In analogy with the corresponding Cr(III) complexes[4-6] these Rh(III) diols equilibrate comparatively fast with their parent monohydroxo-bridged cations (monools). The thermodynamics and kinetics for the equilibration reaction between monools and diol in the Δ,Λ-ethylenediaminerhodium(III) system were published recently,[2] and we now report here our results for the tetraammine system.

Results

Synthesis and Properties of the Complexes. The diol, $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$, dissolves rapidly in strongly acidic solution and gives nearly quantitatively the acid form of the monool, *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$ (diaqua monool). The latter ion was obtained only in solution, but addition of the appropriate amount of base leads to the precipitation of pure aqua hydroxo monool salt, *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$.

Scheme I



Absorption spectra of the monool salt were measured in the $[H^+]$ region $1.0 \geq [H^+] \geq 10^{-14}$ M. All the spectral measurements could be interpreted in terms of the following two consecutive acid–base equilibria:

$$\textit{cis,cis}\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+} \overset{K_{a1}}{\rightleftharpoons} \textit{cis,cis}\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+} + H^+ \quad (1)$$

$$\textit{cis,cis}\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+} \overset{K_{a2}}{\rightleftharpoons} \textit{cis,cis}\text{-}(OH)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{3+} + H^+ \quad (2)$$

Spectral data for the three monool cations are reported in Table I. The results show that deprotonation of the hydroxo bridge to form an oxo-bridged species is unimportant for pH ≤14. The

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Table I. Ligand Field Spectra at 25 °C[a]

cation	medium	$(\epsilon, \lambda)_{max}$		$(\epsilon, \lambda)_{min}$	ref
$[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]^{4+}$	1 M $NaClO_4$	(305, 336)		(198, 304)	*b, c*
cis,cis-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH_2)]^{5+}$	1 M $HClO_4$	(464, 338)	(426, 274)	(303, 305)	*b, d*
cis,cis-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)]^{4+}$	1 M $NaClO_4$	(379, 338)	(432, 275) sh	(259, 308)	*b*
cis,cis-$[(HO)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)]^{3+}$	1 M NaOH	(392, 339)	(459, 285)	(348, 317)	*b, e*

[a] Extrapolated to the time of dissolution. [b] Perchlorate salt. [c] Identical values obtained for this medium and for 0.1 M $HClO_4$, 0.9 M $NaClO_4$ and 0.01 M NaOH, 0.99 M $NaClO_4$. [d] Identical values obtained for this medium and for 0.1 M $HClO_4$, 0.9 M $NaClO_4$. [e] Identical values obtained for this medium and for 0.1 M NaOH, 0.9 M $NaClO_4$ and 0.005 M NaOH, 1 M $NaClO_4$.

Table II. Kinetic and Thermodynamic Data for the Amminerhodium(III) Monools and Diol[a]

reaction	10^5k, s^{-1}	ΔH^{*}, kJ mol^{-1}	ΔS^{*}, J mol^{-1} K^{-1}
k_1	4.26 (18)	91 (5)	−24 (16)
k_{-1}	1.41 (6)	89 (5)	−39 (16)
k_{-2}	0.96 (3)	109 (3)	24 (11)
reaction	k, s^{-1} M^{-1}	$\Delta H^{*}-\Delta H^{\circ}$, kJ mol^{-1}	$\Delta S^{*}-\Delta S^{\circ}$, J mol^{-1} K^{-1}
k_2/K_{a3}	0.074 (2)	58 (3)	−72 (9)
reaction	K	ΔH°, kJ mol^{-1}	ΔS°, J mol^{-1} K^{-1}
K_{a1}	$10^{-3.406(8)}$	52.6 (16)	111 (5)
K_{a2}	$10^{-8.797(14)}$		
K_1	3.03 (4)	1.6 (12)	15 (4)

[a] At 25 °C and unit ionic strength $(Na,H)ClO_4$.

two acid dissociation constants K_{a1} and K_{a2} for the diaqua monool were determined by glass-electrode measurements, and the results are given in Table II.

The hydroxo-bridged structure of the monool species follows clearly from the properties mentioned above and is also strongly supported by the thermodynamic and kinetic results discussed below. The monools can exist as the three isomers cis,cis, trans,trans, and cis,trans where cis and trans refer to the position of H_2O or OH^- relative to the bridge. The proposed assignment cis,cis is derived from the geometry of the diol and the well-known tendency of rhodium(III) mainly to undergo thermal substitution without steric change.

Spectral data for the diol, $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$, in different media are reported in Table I, and it should be noted that identical spectra are obtained for $[H^+]$ varying from 0.1 to $\sim 10^{-12}$ M. This implies that protonation of the diol to give μ-aqua μ-hydroxo species must be negligible for solutions with $[H^+] \leq 0.1$ M, and therefore $K_{a3} \gg 0.1$ (Scheme I). Furthermore, deprotonation to an oxo-bridged species must be negligible for solutions with pH ≤12.

Kinetics and Thermodynamics of the Equilibrium between Monool and Diol. The absorption spectra of aqueous solutions of salts of monool or diol change with time, and these changes are interpreted on the basis of an equilibration reaction between monool and diol.

$$(NH_3)_4Rh(OH)_2Rh(NH_3)_4{}^{4+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis,cis\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+} \quad (3)$$

The kinetics and thermodynamics of this equilibrium were studied spectrophotometrically in the $[H^+]$ region $0.1 \geq [H^+] \geq 10^{-5}$ M and at 25 and 34.5 °C. Under these conditions the rate of equilibration is very pH dependent, as is also that of the subsequent hydrolysis of the monool to give monomeric *cis*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$. However, at a given $[H^+]$ the latter reaction is always much slower, by a factor of at least 100, than the former reaction. Furthermore, both monool and diol are very robust in acidic solution with respect to hydrolysis of the ammine ligands, and the equilibration reaction (eq 3) could therefore be studied without interference from such reactions.

The spectra of solutions initially containing either diol or monool became constant within a period varying from minutes (pH 1) to hours (pH 5) at 25 °C. For a given $[H^+]$ these final spectra were indentical and are therefore the spectra of equilibrium mixtures of monool (diaqua and aqua hydroxo) and diol (eq 1 and 3). The equilibrium constant $K_1 = k_1/k_{-1}$ was determined from measurements made on solutions with $[HClO_4] = 10^{-3}$, 5×10^{-4}, and 10^{-4} M, respectively (see also Experimental Section). From measurements at the two temperatures 25.0 and 34.5 °C the parameters quoted in Table II were calculated.

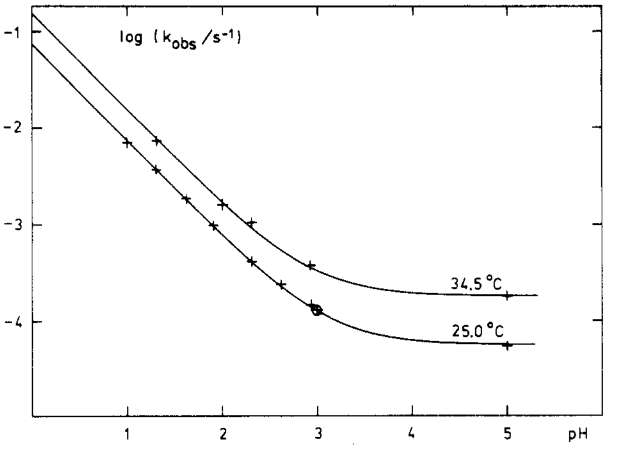

Figure 1. Observed pseudo-first-order rate constants, k_{obsd}, obtained for solutions initially containing diol (×) or monool (○) as a function of pH = −log $[H^+]$. The solid lines represent values of k calculated by eq 4, using the parameters given in Table II.

Kinetic data were obtained from spectrophotometric measurements, and pseudo-first-order rate constants, k_{obsd}, measured for solutions initially containing pure diol were calculated by using nonlinear regression analysis (Figure 1). A single experiment in which the solution initially contained pure monool was also made and gave a k_{obsd} value identical with that obtained under the same conditions (25 °C and $[H^+] = 9.9 \times 10^{-4}$ M), but starting with pure diol.

The stoichiometry of the equilibrium mixture can be described by eq 1 and 3. However, the kinetic interpretation requires an additional, acid-catalyzed reaction path as shown in Scheme I, which since $K_{a3} \gg [H^+]$, yields eq 4.

$$k_{calcd} = k_1 + \frac{[H^+]K_1k_{-2}}{K_{a1}} + \frac{K_{a1}K_1^{-1}k_1 + [H^+]k_{-2}}{K_{a1} + [H^+]} \quad (4)$$

Two of the parameters, K_1 and K_{a1}, in this equation have been determined in separate experiments as described above. Using these values, the two rate cosntants, k_1 and k_{-2}, were determined by the method of nonlinear regression analysis and gave the parameter values shown in Table II.

Discussion

The present amminerhodium(III) system shows many properties in common with the (ethylenediamine)rhodium(III) system and the corresponding chromium(III) systems.[2,4-6] Comparison of the acid strength of the monools $(H_2O)N_4M(OH)MN_4(H_2O)^{5+}$ (M = Cr(III), Rh(III); N_4 = $(en)_2$, $(NH_3)_4$) shows that $K_{a1}(en) > K_{a1}(NH_3)$ for both metal ions and that $K_{a1}(Cr) > K_{a1}(Rh)$ for both nitrogen ligands, and this trend follows that observed in the corresponding monomeric systems.[2,7] In the present system, the

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Table III. Kinetic Parameters for Bridge-Formation Reactions and Water-Exchange Reactions in Tetraammine Complexes[a]

	rhodium(III)			chromium(III)		
	10^6k, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	10^6k, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
k^{-1}	14.1[b]	89	−39	380[d]	81	−40
k_{ex}	7.5[c]	105	+11	59[e]	95	−7
k_{-2}	9.6[b]	109	+24	2.7[d]	123	+64

[a] k_{-1} and k_{-2} as defined in Scheme I. k_{ex} is the statistically corrected rate constants for exchange of *one* water in *cis*-$M(NH_3)_4(H_2O)_2^{3+}$ for M = Rh(III) or Cr(III). All values are for 25 °C and at unit ionic strength, $(Na,H)ClO_4$. [b] This work. [c] Reference 14. [d] Reference 4. [e] Reference 13.

difference between the two pK_a values for the diaqua monool, *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$, is 5.4 units, which is much greater than the difference of 1.92 units between the two pK_a values[7] of the monomeric complex *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$. This large separation between the pK_a values in the monools can be explained on the basis of intramolecular hydrogen-bond formation in the aqua hydroxo monool.[2,4-6]

The equilibration reactions between monools and diol in the present Rh(III) system occur via an acid-catalyzed and an uncatalyzed reaction path as shown in Scheme I. The acid-catalyzed path is proposed to involve protonation of one hydroxo bridge to give a labile aqua-bridged intermediate. The aqua-bridged complex was not identified, but spectroscopic results indicate that this species is a very strong acid with $K_{a3} \gg 0.1$. Similar properties have been reported for the bridge cleavage of other hydroxo-bridged binuclear complexes of Rh(III), Co(III), and Cr(III).[2,4-6,8-12]

The quantity $(k_2/K_{a3})/k_1$ gives the ratio between the rate of acid-catalyzed bridge cleavage at $[H^+] = 1$ M and the rate of uncatalyzed bridge cleavage. This ratio is approximately 2000 in the present ammonia system but only 300 in the ethylenediamine system.[2] This corresponds quantitatively with results for the analogous Cr(III) systems. In the Cr(III) ammine[4] system $(k_2/K_{a3})/k_1$ has a value of 0.40, which is larger than the upper limit value of 0.05 in the meso[5] and the racemic[6] Cr(III) ethylenediamine systems, for which the acid-catalyzed path could not be determined.

The uncatalyzed brige-cleavage reactions of the rhodium(III) diols with ammonia or ethylenediamine (Δ,Λ isomer) may be compared with those of chromium(III), and it is found that $k_1(\mathrm{en}) > k_1(\mathrm{NH_3})$ for both metal ions and also that $k_1(\mathrm{Cr}) > k_1(\mathrm{Rh})$ for both nigrogen ligands, which is in keeping with the data for substitution reactions of the corresponding monomeric cis complexes.[14-20]

In Table III the kinetic parameters for the uncatalyzed (k_{-1}) and the acid-catalyzed (k_{-2}) bridge-formation reactions in the Rh(III) ammine system are compared with those for the corresponding Cr(III) system, together with the kinetic data for water exchange (k_{ex}) of the corresponding monomeric diaqua complexes. The sequences $\Delta H^{\ddagger}(k_{-1}) < \Delta H^{\ddagger}(k_{ex}) < \Delta H^{\ddagger}(k_{-2})$ and $\Delta S^{\ddagger}(k_{-1}) < \Delta S^{\ddagger}(k_{ex}) < \Delta S^{\ddagger}(k_{-2})$ are found for both of the two metal centers. The large separation between the $\Delta H^{\ddagger}$ values of the chromium(III) reactions is evidence of a high degree of associative behavior and is in keeping with the properties of the mononuclear tetraamminechromium(III) complexes.[19,20] The sequence further illustrates the expected order, $Cr{-}OH > H_2O > Cr{-}OH_2$, of decreasing nucleophilic character.

The observation that the $\Delta H^{\ddagger}$ values for rhodium(III) are much less separated indicates that these reactions are less associative than those of chromium(III), which is in agreement with the results for the mononuclear ammine systems.[19,20] The present data for the amminerhodium(III) system also correspond well to those reported for the (ethylenediamine)rhodium(III) system for which the observation that $\Delta H^{\ddagger}(k_{-1}) \sim \Delta H^{\ddagger}(k_{-2}) \sim 100$ kcal mol^{-1} has been taken as evidence for a large degree of dissociative character.[2]

In summary, it is concluded that the variations in thermodynamic and kinetic parameters due to the nonbridging nitrogen-donor ligands are similar for Cr(III) and Rh(III). The nature of the nonbridging ligands appears to be as important a factor as the nature of the metal center, and the trends observed in the bridged systems are similar to those observed in the corresponding mononuclear systems.

Experimental Section

Materials. The complex $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4{\cdot}4H_2O$ was prepared as described previously.[1,3] All chemicals were of analytical grade.

Instruments. A Zeiss DMR 21 spectrophotometer was used for all spectrophotometric measurements. Data are given with the molar extinction coefficient ε in L mol^{-1} cm^{-1} and the wavelength λ in nm. The pH measurements were made with a Radiometer GK 2301 C combined glass and calomel electrode (modified to contain 1.0 M NaCl in the reference part) in conjunction with a Radiometer PHM 61 digital pH meter.

Analyses. H, N, and Cl analyses were performed by the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

Preparations. Bis(μ-hydroxo)bis[tetraamminerhodium(III)] Perchlorate, $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4{\cdot}2H_2O$. A mixture of a saturated solution of $NaClO_4$ (30 mL) and water (20 mL) was added to $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4{\cdot}4H_2O$ (4.28 g, 0.0055 mol). The suspension was cooled in ice and stirred vigorously for 1 h. The precipitate was isolated by filtration, washed with 96% ethanol, and dried in the air. The crude product was extracted on the filter with water (ca. 15 °C) in small portions (ca. 15 mL) within a total of 2 min (total extraction volume ca. 60 mL), and each successive portion of solution was immediately filtered into a single ice-cooled flask. When all the salt was extracted, 50 mL of a saturated solution of sodium perchlorate was added to the filtrate and the solution was stirred for 5 min with cooling ice. The crystalline pale yellow product was isolated as above; yield 4.18 g (93%) of a pure salt. Anal. Calcd. for $Rh_2H_{30}N_8Cl_4O_{20}$: H, 3.73; N, 13.83; Cl, 17.51. Found: H, 3.40; N, 13.37; Cl, 17.52.

***cis*-Tetraammineaquarhodium(III)(μ-hydroxo)-*cis*-tetraamminehydroxorhodium(III) Perchlorate. *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4{\cdot}H_2O$.** To a suspension of $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4{\cdot}2H_2O$ (5.00 g, 6.2 mmol) in water (25 mL) was added 1.000 M $HClO_4$ (15.00 mL). The mixture was stirred and kept at 25 (±0.5) °C. All complex salt dissolved within 2 min, and after a further 10 min the yellow solution was cooled in ice. To the cold solution was then added a saturated solution of $NaClO_4$ (25 mL). The solution was filtered, and addition of 1.000 M NaOH (15.00 mL) to the cold solution caused precipitation of aqua hydroxo monool perchlorate salt. The precipitate was filtered off and washed thoroughly with 96% ethanol and then diethyl ether. The product was dried in the air for 0.5 h and then kept at −15 °C. The yield was 3.75 g (75%) of pure *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4{\cdot}H_2O$. Anal. Calcd for $Rh_2H_{30}N_8Cl_4O_{20}$: H, 3.73; N, 13.84; Cl, 17.51. Found: H, 3.64; N, 13.76; Cl, 17.60.

This product (0.75 g) was reprecipitated by dissolution in 0.500 M $HClO_4$ (4.00 mL) and precipitation as above by cooling and addition of a saturated solution of $NaClO_4$ (3 mL) and 1.000 M NaOH (2.000 mL); yield 0.55 g. The absorption spectra of this sample and that above measured in 1 M $NaClO_4$ were identical for the entire region λ =

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350–220 nm. The solid salt is stable for months when stored at −15 °C, and at room temperature it is stable for at least a few days.

Potentiometric Measurements. At 25 °C normal titrations of aqueous solutions of *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$ with base (or acid) could be made. At 34.5 °C the equilibration reactions between the monools and the diol made such a procedure unreliable, and each pH measurement was made on freshly prepared solutions. Thermostated ca. 10^{-2} M solutions of *cis,cis*-$[(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)](ClO_4)_4 \cdot H_2O$ in 1 M $NaClO_4$ and the appropriate amount of 0.1 M $HClO_4$, 0.9 M $NaClO_4$ or 0.1 M NaOH, 0.9 M $NaClO_4$ were prepared as quickly as possible. Reliable readings on the pH meter could be obtained about 30 s after the time of mixing. The measurements were continued over a period of 10 min, and the pH at the time of mixing was determined by linear extrapolation that typically showed $\Delta(\mathrm{pH})/\Delta(\mathrm{min}) \approx 0.02$. The definition $\mathrm{pH} = -\log [H^+]$ was employed throughout, and concentration pH standards were made in the salt medium in question. The parameters given in Table II were calculated from measurements at 25 and 34.5 °C.

Spectra and Treatment of Spectral Data. Pseudo-first-order rate constants, k_{obsd}, and activation parameters were calculated as described previously.[2,4–6] The k_{obsd} values were calculated from absorbances measured at two or three of the wavelengths: λ = 300, 250, and 240 nm.

In all kinetic runs the hydrogen ion concentration changed slightly. These changes were generally about 1–3%, although in experiments with low initial $[H^+]$ changes of up to 8% were calculated (eq 1 and 3). However, the error introduced by this variation is very small, since at low $[H^+]$ the dependence of k_{obsd} on $[H^+]$ is small. For each experiment, the hydrogen ion concentrations at t_0, $[H^+]_0$, and equilibrium, $[H^+]_\infty$, were calculated and the values $[H^+] = {}^1/_2([H^+]_0 + [H^+]_\infty)$ were then used in the subsequent calculations.

The calculations of K_1 were based on molar absorbances of solutions of pure diol, ϵ_D, pure monool, ϵ_M, and the equilibrium solution, ϵ_∞, measured at 10 wavelengths in the wavelength region λ = 240–280 nm and using the equation $K_1 = (\epsilon_D - \epsilon_\infty)K_{a1}/(\epsilon_\infty - \epsilon_M)([H^+] + K_{a1})$.

Using the values for K_{a1} determined potentiometrically (Table II), values of K_1 at 25 and 34.5 °C were then calculated from measurements made on solutions with $[HClO_4] = 10^{-3}$, 5×10^{-4}, and 10^{-4} M, respectively.

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Optical Resolution of "Weakly Chiral" $P(OPh)(OC_6H_4\text{-}p\text{-}Cl)(OC_6H_4\text{-}p\text{-}Me)$

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The first resolution of an enantiomeric phosphorus triester, namely $P(OPh)(OC_6H_4\text{-}p\text{-}Cl)(OC_6H_4\text{-}p\text{-}Me)$ (**1**), is reported. Compound **1** is remarkably stable to substituent exchange when pure. The unusually distant seat of chirality from the phosphorus appears to have interesting consequences on some chirality-dependent phenomena at this atom.

Whereas enantiomers of PRR′R″ molecules tend to be stable to racemization via substituent exchange, those of the type RPhPER (E = S, O, NH),[2] PhP(OEt)($OZMe_3$) (Z = Si, Sn),[3] and MeP(OMe)(O-*i*-Pr)[4] are not. In view of the importance of a variety of chiral phosphorus compounds as ligands in transition-metal catalysts in asymmetric syntheses[5] and the potentially strong role of phosphorus chirality in the cyclophosphamide class of antitumor drugs[6] and in membrane phospholipids,[7] the separation of enantiomers of esters of the type P(OR)(OR′)(OR″)[8,9] is a worthy goal. Herein is reported for the first time the enantiomeric resolution of such a system, namely $P(OPh)(OC_6H_4\text{-}p\text{-}Cl)(OC_6H_4\text{-}p\text{-}Me)$ (**1**).

Compound **1** is interesting in several respects. Although syntheses of compounds of the type P(OPh)(OAr′)(OAr″) have been reported before,[8] these procedures in our hands produced only mixtures of up to nine of the possible ten esters attainable by the exchange of OAr groups, as shown by ^{31}P NMR spectroscopy. As seen in reaction 1, the 51% yield of (±)-**1** formed

$$PhOPCl_2 \xrightarrow[2NEt_3]{\substack{HOC_6H_4\text{-}p\text{-}Me \\ HOC_6H_4\text{-}p\text{-}Cl}} \underset{(\pm)\text{-}\mathbf{1},\ 51\%}{P(OPh)(OC_6H_4\text{-}p\text{-}Cl)(OC_6H_4\text{-}p\text{-}Me)} + \underset{28\%}{P(OPh)(OC_6H_4\text{-}p\text{-}Cl)_2} + \underset{21\%}{P(OPh)(OC_6H_4\text{-}p\text{-}Me)_2} \quad (1)$$

under the mild conditions employed here is approximately that expected from random attack of $PhOPCl_2$ by addition of a mixture of two phenols in the first step. Similar yields are obtained when (±)-**1** is made by treating *p*-$MeC_6H_4OPCl_2$ or *p*-Cl-$C_6H_4OPCl_2$ with an equimolar mixture of the other two phenols. By contrast, when sequential addition of the phenols in either order to $PhOPCl_2$ was carried out (as per literature reports[8]), ^{31}P NMR analysis indicated only 12–15% yields of (±)-**1** in the reaction mixture and correspondingly higher yields of the other two products shown in reaction 1. Interestingly, however, rapid flame distillation of such a mixture of esters brought the yield of (±)-**1** up to ca. 50%. It is interesting that sequential addition of the phenols to *cis*-$I_2Pt[P(OPh)Cl_2]_2$, which is presumably formed as an intermediate in the one-pot synthesis of *cis*-$Cl_2Pt(\mathbf{1})_2$ in reaction 2, does lead

$$PhOPCl_2 \xrightarrow[3.\ HOC_6H_4\text{-}p\text{-}Cl]{\substack{1.\ cis\text{-}Cl_2Pt(NCPh)_2 \\ 2.\ HOC_6H_4\text{-}p\text{-}Me}} cis\text{-}Cl_2Pt[(\pm)\text{-}\mathbf{1}]_2 \qquad (2)$$

to a 51% yield of this complex (as an *R,R*, an *R,S*, and an *S,S* mixture) in which **1** is coordinated. A second remarkable property of triester (±)-**1** is that it is quite stable when pure,[10] showing evidence of exchange in the ^{31}P NMR spectrum only after 3 days in $(CD_3)_2CO$ at room temperature. Even after a neat sample is heated for 1.5 h at 100 °C, 88% of (±)-**1** remains. Third, in the enantiomers (+)-**1** and (−)-**1** obtained via Scheme I, the seat of

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