Table I. Dependence of the Preparation Yield of $TMPH_2$ on the Quantities of *p*-Chloranil Used in the Oxidation Step[a]

mg of *p*-chloranil (mmol; equiv with respect to pyrrole)	$TMPH_2$ yield, %
200 (8.3; 0.17)	15
400 (1.67; 0.33)	20
600 (2.5; 0.5)	15
1200[b] (5; 1)	2–8

[a] The reagent quantities used are the ones indicated in the Experimental Section. [b] This amount of *p*-chloranil is the one used by Lindsey et al. in a preliminary communication: Lindsay, J. S.; et al. *Tetrahedron Lett.* **1986**, *27*, 4969.

which contains the pure mesitylporphyrin. The second pink-yellow band, already containing small amounts of *p*-chloranil, was also collected and combined with the crude reaction mixture of other preparations of $TMPH_2$. The first pink band was evaporated to dryness, recrystallized from distilled CH_2Cl_2 and dried under vacuum. One obtained 200 mg (yield: 20%) of the pure mesitylporphyrin. Purity of the sample has been checked by elemental analysis,[17] and the UV-visible spectrum was identical with that previously reported.[14] The IR spectrum did not show any traces of *p*-chloranil.

Discussion

Lindsey's preparation[16] was modified by using the methanol adduct of borontrifluoride and 2,2-dimethoxypropane to scavenge all possible traces of water during the reaction. We found that the reproducibility of the preparation described above is highly dependent on several factors.

(i) The first factor is the age of purchase and time of opening of the bottle of BF_3 catalyst. Three months after opening the $BF_3{\cdot}CH_3OH$ bottle, 50% of its catalytic activity is already lost. The reported quantity of $BF_3{\cdot}CH_3OH$ corresponds to that one of a freshly opened bottle.

(ii) The second factor is the amount of *p*-chloranil used in the second step (Table I). The best yield is obtained for 0.33 equiv of quinone oxidant with respect to pyrrole. When a large quantity of *p*-chloranil is employed, the formed porphyrin is partially destroyed by overoxidation, and furthermore the removal of all the quinone is difficult, even after two chromatography columns.

(iii) Third, the porphyrinogen equilibration is obtained within 45 min. The prolongation of that period usually leads to a reduced yield in $TMPH_2$.

(iv) Finally, overheating in the oxidation step must be avoided. A gentle reflux reduced the oxidative degradation of the formed porphyrin. The temperature control is even more crucial when a larger amount of *p*-chloranil is used.

However the yield of the reaction does not seemed to be influenced by shielding the reaction solution from ambient lighting.

In conclusion, the present synthesis of $TMPH_2$ leads to a respectable yield (20%) for such a sterically hindered porphyrin which is one of the favorite ligands used in metalloporphyrin-mediated catalytic oxygenations of hydrocarbons. The same procedure can be extended to the synthesis of tetrakis(2,6-dichlorophenyl)porphyrin.

Acknowledgment. M.K.-B. is grateful to the CNRS for a 9-month fellowship.

Note Added in Proof. During the submission procedure for the present note, a similar preparation has been reported by Lindsey et al. using the same modifications presented here.[18]

Registry No. $TMPH_2$, 56396-12-4; pyrrole, 109-97-7; mesitaldehyde, 487-68-3.

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(17) Anal. Calcd for $C_{56}H_{54}N_4$ (mol wt 782.62): C, 85.90; H, 6.95; N, 7.16. Found: C, 85.69; H, 7.24; N, 6.88.

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Anion Effects on the Hydrolysis of the (μ-Oxo)bis(pentaamminechromium(III)) Ion in Basic Solution

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Although the electronic structures of the (μ-oxo)bis(pentaamminechromium(III)) ion and related linear, oxo-bridged dimers have been probed extensively through spectroscopic and magnetic measurements,[1-3] the reaction chemistry of rhodo and erythro chromium dimer species is not well understood. In particular, the thermodynamic and mechanistic basis for the most characteristic reaction of the basic rhodo dimer, hydrolysis to the hydroxo erythro ion (eq 1) in alkaline media, is not fully revealed in the

$$[(NH_3)_5Cr]_2O^{4+} + H_2O \rightarrow (NH_3)_5Cr(OH)Cr(NH_3)_4(OH)^{4+} + NH_3 \quad (1)$$

several mechanistic studies of this process reported to date.[4-6] Having established the stoichiometry of reaction 1, Wilmarth and co-workers[4] suggested that negative charge buildup on chromium owing to $p\pi(O)-d\pi(Cr)$ bonding is responsible for the weakening of a Cr–N bond and ultimately displacement of NH_3. Similarly, Schwarzenbach and Magyar attribute the first-order decay of the basic rhodo cation ($k = 1.6 \times 10^{-2}\ s^{-1}$, 20 °C) to a trans effect of the bridging oxide ion.[6] A weak inhibitory effect of hydroxide ion was reported in an earlier study of the basic rhodo decay rate,[5] leaving the existence of a OH^--dependent term in the rate law uncertain.

Our group has explored the acid hydrolysis mechanism of the (μ-oxo)bis(pentaaquachromium(III)) cation (aqua dimer), a close relative to the basic rhodo ion, and documented unexpected sensitivity of the rate to the presence of reducing agents and anions.[7,8] We report here studies of anion and temperature effects on the rate of reaction 1. Of particular interest is the possibility that the Jahn–Teller effect may account for the intrinsic instability of the basic rhodo ion toward loss of ammonia, coupled with protonation of the bridging oxygen atom and bending of the Cr–O–Cr structural unit. A kinetic trans effect is ruled out by the finding[9] that *cis*-$[Cr(NH_3)_5(OH)Cr(NH_3)_4(OH)]^{4+}$ is the sole chromium-containing hydrolysis product of the basic rhodo cation.

Experimental Section

The acid rhodo bromide salt $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Br_5{\cdot}2H_2O$ was prepared through the aerobic oxidation of chromous bromide in concentrated aqueous ammonia, followed by acidification of the product mixture with HBr.[10] A 1 M chromous bromide stock solution was prepared by the addition of Aldrich Gold Label chromium chunks to anaerobic (N_2-purged) 2 M HBr. The crude acid rhodo product was recrystallized twice by dissolving in cold, 1 mM HBr and slowly adding cold, 1 M HBr. Anal. Calcd for $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Br_5{\cdot}2H_2O$: Cr, 14.3; N, 19.27; H, 4.85. Found: Cr, 14.9; N, 19.33; H, 4.96.

Reagent grade chemicals were used throughout, and solutions were prepared with triply distilled water. Kinetic measurements were made on a Durrum D-110 stopped flow apparatus, interfaced to an Apple II

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Table I. Observed Rate Constants for Decay of the Basic Rhodo Ion[a]

anion	[anion], M	$[OH^-]$, M	$10^2 k_{obsd}$, s^{-1}
ClO_4^- ($LiClO_4$)	0.00	1.00 (LiOH)	1.88
	0.180	0.820	2.07
	0.360	0.640	2.19
	0.540	0.460	2.34
	0.720	0.280	2.62
	0.900	0.100	2.78
	0.00	0.050	2.13
	0.205	0.050	2.38
	0.410	0.050	2.43
	0.615	0.050	2.55
	0.820	0.050	2.63
	1.030	0.050	2.69
Cl^- (KCl)	0.00	0.050 (KOH)	2.14
	0.200	0.050	2.06
	0.400	0.050	2.09
	0.600	0.050	2.15
	0.800	0.050	2.13
	1.00	0.050	2.17
	0.950	0.050	2.10
	0.760	0.240	2.08
	0.570	0.430	2.13
	0.380	0.620	2.15
	0.190	0.810	2.13
	0.00	1.00	2.08
F^- (NaF)	0.00	0.050 (LiOH)	2.18
	0.0953	0.050	2.09
	0.191	0.050	2.08
	0.286	0.050	2.09
	0.381	0.050	2.13
	0.472	0.050	2.17
BF_4^- ($NaBF_4$)	0.119	0.050 (LiOH)	3.02
	0.238	0.050	2.83
	0.356	0.050	2.77
	0.512	0.050	2.57

[a] 25.0 °C. Estimated uncertainty in k_{obsd} = ±5%.

Table II. Temperature Dependence of the Basic Rhodo Ion Decay Rate[a]

T, K	k_{obsd}, s^{-1}	*T*, K	k_{obsd}, s^{-1}
313.15	0.109	293.15	0.0154
303.15	0.0487	283.15	0.0061

[a] Conditions: 1.0 M $NH_3(aq)$, I = 0.5 M ($LiClO_4$). Estimated uncertainty in k_{obsd} = ±5%.

Plus computer for data acquisition and quantitative interpretation.[7] Reaction 1 was initiated by mixing a solution containing 1.00 mM acid rhodo bromide, 1.00 mM HBr, and a salt to maintain constant ionic strength with a solution of known, excess hydroxide concentration; ionization of the acid rhodo hydroxo bridge (faster than the stopped-flow time scale) occurs with a pK_a of 7.63.[6] Decay of the basic rhodo cation was monitored at 393 nm. Observed first-order rate constants (k_{obsd}) were calculated as the linear least-squares slopes of ln $(A_t - A_\infty)$ vs time plots that covered over 90% of the total absorbance change and exhibited correlation coefficients of ≥0.999. Reported rate constants are the mean of at least three trials.

Results and Discussion

Several experiments were carried out at 25.0 °C to determine whether hydroxide ion enters into the rate law for release of ammonia from the basic rhodo ion (Table I). Mori et al. attribute a slight retardation of the rate in concentrated alkaline media to an increase in solution viscosity.[5] In our experiment at a constant ionic strength of 1.0 M ($LiOH/LiClO_4$), this apparent retardation by OH^- was more pronounced than that cited by either of the previous two groups that examined the kinetics of basic rhodo ion decay.[5,6] Thus, k_{obsd} at $[OH^-]$ = 1.00 M (1.88×10^{-2} s^{-1}) is 33% smaller than the corresponding rate constant at a hydroxide concentration of 0.100 M. Considering the uncharacteristically large influence of perchlorate ion on the aqua dimer acid hydrolysis rate,[8] catalysis by perchlorate ion should be considered along with retardation by hydroxide ion in evaluating the results of the constant ionic strength experiment. Indeed, when $[OH^-]$ was held constant at 0.050 M, k_{obsd} increased from 2.13×10^{-2} to 2.69×10^{-2} s^{-1} within the ClO_4^- concentration interval 0–1.030 M.

In order to determine whether the influence of perchlorate ion on the basic rhodo decay rate is a specific anion effect or simply an ionic strength dependence, kinetic experiments with other anions were carried out at constant $[OH^-]$ (Table I). Unfortunately, sulfate, phosphate, nitrate, bromide, and iodide ions induced the precipitation of the acid rhodo precursor and therefore were not amenable to kinetic investigation. However, solutions of KCl, NaF, and $NaBF_4$ were compatible with both acid and basic rhodo cations on the time scale of the substitution reaction of interest (30 min). While [KOH] was held constant at 0.050 M, k_{obsd} was found to be independent (($2.12 \pm 0.06) \times 10^{-2}$ s^{-1}) of chloride ion in the concentration range 0–1.00 M, suggesting that reaction 1 exhibits a negligible ionic strength dependence. Similarly, NaF does not appreciably affect the rate up to a concentration of 0.472 M. In contrast, the addition of 0.119 M $NaBF_4$ to a 0.050 M LiOH solution raises k_{obsd} from 2.18×10^{-2} to 3.02×10^{-2} s^{-1}, while further increases in tetrafluoroborate concentration *decrease* the basic rhodo decay rate slightly.

With the negligible effect of KCl on k_{obsd} at constant hydroxide concentration established, the dependence of the basic rhodo decay rate on OH^- was again examined at constant ionic strength, this time by employing KOH as the base and KCl to maintain the total ionic strength at 1.0 M (Table I). This experiment conclusively ruled out the existence of an authentic OH^--dependent term in the rate law, as k_{obsd} was found to be independent of hydroxide ion concentration (($2.11 \pm 0.04) \times 10^{-2}$ s^{-1}) betwen 0.050 and 1.00 M. It is clear, therefore, that hydroxide ion does not activate a conjugate base mechanism or function as an incoming group prior to the rate-determining step in the loss of NH_3 from the basic rhodo ion.

The temperature dependence of the basic rhodo–hydroxo erythro transformation (Table II) was examined in 1.00 M $NH_3(aq)$ at I = 0.5 M ($LiClO_4$), covering a 30 °C interval. Least-squares activation parameters derived from a linear Eyring plot of ln (k_{obsd}/T) vs $1/T$ are $\Delta H^{\ddagger} = 16.7 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -10 \pm 1$ eu. These values are in only fair agreement with parameters reported previously:[5] E_a = 21 kcal/mol; $\Delta S^{\ddagger}$ = +2 eu. By comparison, the enthalpy and entropy of activation that govern the acid hydrolysis of $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ to give $[(NH_3)_5Cr(OH_2)]^{3+}$ are 27.1 kcal/mol and +9.6 eu, respectively.[9,11]

Of the anions treated in this study, only the tetrahedral species ClO_4^- and BF_4^- appreciably influence the transformation rate of $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ into *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+}$. Pathways following first-order chloride and bromide dependences have been linked to anation intermediates in the acid hydrolysis of *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]^{5+}$[9,11] but such anation by ClO_4^- or BF_4^- is highly unlikely in the base hydrolysis reaction of the basic rhodo cation, especially considering the absence of associative participation by the incoming OH^- group prior to the rate-determining step. We propose, therefore, that the modest rate enhancements associated with the perchlorate and tetrafluoroborate ions arise from ion pairing, analogous to that proposed earlier to account for the influences of Cl^-, Br^-, and ClO_4^- on the aqua dimer acid hydrolysis rate.[8] Thus, anions could provide electrostatic anion-incipient dipole stabilization of an activated complex in which substantial bending of the Cr–O–Cr unit is required; the Cr–O–Cr angle characteristic of the *cis*-aquaerythro cation is 168°.[12] Such an explanation does not readily account for the failure of Cl^- and F^- to accelerate the rate, however, or the contradictory kinetic influences of the larger ClO_4^- and BF_4^- anions at high concentrations. The specific affinity of oxyanions for ion pairing along the C_3 symmetry axes of trivalent metal ammine and amine complexes[13,14] could contribute to the

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basic rhodo hydrolysis rate enhancement by perchlorate ion.

Although constant ionic strength was not maintained in the perchlorate variation studies at fixed [OH^-], a quantitative fit of the rate data to a kinetic expression (eq 2) based on a mechanism (eq 3) that presumes 1:1 ion pairing between the basic rhodo cation

$$k_{\mathrm{obsd}} = k_2 + (k_1 - k_2)/(1 + K_{\mathrm{ip}}[\mathrm{ClO_4^-}]) \qquad (2)$$

$$\mathrm{BR^{4+} + ClO_4^- \overset{K_{ip}}{\rightleftharpoons} BR^{4+}{\cdot}ClO_4^-}$$

$$\mathrm{BR^{4+}} \xrightarrow{k_1} \text{products} \qquad (3)$$

$$\mathrm{BR^{4+}{\cdot}ClO_4^-} \xrightarrow{k_2} \text{products}$$

(BR^{4+}) and ClO_4^- is instructive. The plausibility of such an ion-pairing scheme is supported by a successful nonlinear least-squares fit[8] of the kinetic data from Table I to eq 2; parameters derived in this manner are $k_1 = (2.14 \pm 0.03) \times 10^{-2}\ \mathrm{s^{-1}}$, $k_2 = (3.1 \pm 0.2) \times 10^{-2}\ \mathrm{s^{-1}}$, and $K_{\mathrm{ip}} = 1.3 \pm 0.6\ \mathrm{M^{-1}}$.

As has been pointed out previously,[6] release of ammonia from the basic rhodo cation in alkaline media is more than 3 orders of magnitude faster than the corresponding reaction of $Cr(NH_3)_6^{3+}$ at ambient temperature. It should also be noted that only one NH_3 ligand in $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ is exceptionally labile; substitution of the remaining nine ammine ligands in the hydroxo erythro cation is not observed on the stopped-flow time scale. Since a trans effect of the bridging oxide ion cannot account for the cis stereochemistry of the hydroxo erythro product, another source of configurational instability within the basic rhodo ion must be sought. According to a semiquantitative molecular orbital treatment of linear, oxo-bridged Cr(III) dimers,[15,16] the π-electronic configuration of the basic rhodo ion should be $(e_u^b)^4[(b_{1u})(b_{2g})(e_g)]^6$, where e_u^b is strongly bonding and the remaining MO's are approximately nonbonding (derived from the Cr 3d t_{2g} set) and are in close energetic proximity to one another. Although the ground-state electronic configuration $(e_u^b)^4(b_{1u})^2(b_{2g})^2(e_g)^2$ has been suggested for the basic rhodo ion,[17] alternative distributions of the six nonbonding electrons that could generate a triplet ground term include $(b_{1u})^1(b_{2g})^1(e_g)^4$, $(b_{1u})^1(b_{2g})^2(e_g)^3$, and $(b_{1u})^2(b_{2g})^1(e_g)^3$. Considering the strong temperature dependence of the effective magnetic moment,[18] several of these electronic configurations may contribute under the conditions of our kinetic study and influence the substitution dynamics of an ammonia ligand. The latter two configurations are noteworthy in that ^3E_u and ^3E_g ground terms would be susceptible to a Jahn–Teller distortion that would necessarily involve bending of the Cr–O–Cr moiety in order to lift orbital degeneracy.[8] Although spectroscopic or magnetic proof is lacking, the hypothesis that a Jahn–Teller distortion required for symmetry reasons provides the "hidden" driving force of the basic rhodo hydrolysis reaction deserves careful consideration and is being explored further in related oxo-bridged, aminechromium(III) dimers. The activation parameters that govern this reaction are consistent with rate-limiting bending of the Cr–O–Cr unit, resulting in loss of π-bonding, coupled with stretching of the Cr–N bond to the NH_3 leaving group.

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Registry No. $[(NH_3)_5Cr]_2O^{4+}$, 28050-10-4; ClO_4^-, 14797-73-0; BF_4^-, 14874-70-5.

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Synthesis and NMR Characterization of the New Complex *trans*-Dihydridotris((2-methoxyethyl)diphenylphosphine-*P*;-*P*;*O*,*P*)ruthenium(II) with a Reactive Ru–O Bond: Observation of a Low-Energy Exchange Equilibrium[1]

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Several ruthenium hydrides containing phosphine ligands are known to be potential catalysts for homogeneous hydrogenation processes.[2] During the last few years, increasing attention has been focused on the complex chemistry of "hemilabile" ligands, for example phosphorus–nitrogen,[3] –sulfur,[4] and especially –oxygen[3–6] systems. For ruthenium, interesting results dealing with hybrid ligand halide complexes have been reported,[3,5,6] whereas little work has been done on hydride complexes. As a part of our research in homogeneous catalysis with transition-metal compounds,[6,7] here we report the synthesis and the chemical and spectroscopical properties of the dihydride *trans*-$H_2Ru(\overset{\frown}{\mathrm{PO}})(\mathrm{P{\sim}O})_2$ (**2**); $\overset{\frown}{\mathrm{PO}}$ designates the chelated, bidentate ligand, while $\mathrm{P{\sim}O}$ designates the P-coordinated, η^1 ligand, with the O functionality not coordinated.

Experimental Section

All operations were performed under dry, oxygen-free argon,[8] by employing the usual Schlenk techniques. Solvents were dried and stored under argon. IR spectra were recorded with a Bruker IFS 113c Fourier infrared spectrophotometer. Proton-decoupled ^{31}P NMR spectra were obtained at 32.391 MHz and ^1H NMR spectra at 80.132 MHz with Bruker WP 80 and AC 80 spectrometers. Chemical shifts are in parts per million downfield from 1% H_3PO_4/acetone-d_6 or from Me_4Si, respectively. FD mass spectra were recorded with a Varian MAT 711 A mass spectrometer (8 kV, 50 °C). Elemental analyses were performed with a Carlo Erba 1106 analyzer; ruthenium was determined with a Perkin-Elmer 4000 atom absorption spectrometer.

Reagents. The ruthenium source $RuCl_3{\cdot}3H_2O$ was a gift of Degussa AG. The precursor complex $Cl_2Ru(\overset{\frown}{\mathrm{PO}})_2$ (**1**)[6] and the ether phosphine ligand $Ph_2PCH_2CH_2OCH_3$[9] were prepared according to literature procedures.

Preparation of Complex 2. To a solution of *trans*-$Cl_2Ru(\overset{\frown}{\mathrm{PO}})_2$ (**1**) (330 mg, 0.5 mmol) and 1 equiv of $Ph_2PCH_2CH_2OCH_3$ in a hydrogen-saturated mixture of 20 mL of methanol and 50 mL of benzene was added $NaBH_4$ in small portions at 20 °C, until the initial red solution had turned to light yellow. The solvents were removed in vacuo at ambient temperature, leaving a yellow residue. It was suspended in 15 mL of cold (0 °C) methanol and the resulting mixture stirred for 20 min. Filtration (P3) of the suspension gave *trans*-$H_2Ru(\overset{\frown}{\mathrm{PO}})(\mathrm{P{\sim}O})_2$ (**2**) as a bright yellow powder; vacuum drying at 20 °C yielded 305 mg (73%) of **2**, mp 47 °C. IR (KBr, cm^{-1}): $\nu(RuH_2)$ 1986; $\nu_{as}(C_2O)$ 1092, 1026. ^1H NMR (acetone-d_6, 20 °C): RuH_2 −17.5 ppm (quadruplet; $^2J_{P-H}$ = 25.3 Hz; Figure 1). FD-MS: m/z 833, $[M - H_2]^+$. Anal. Calcd for $C_{45}H_{53}O_3P_3Ru$: C, 64.66; H, 6.39; Ru, 12.09. Found: C, 63.89; H, 6.28; Ru, 11.68.

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