exchange between UF_7^- and either the BrF_5 solvent or NF_4^+, but can be explained by the relatively large (400–600 Hz) half-line width previously reported[13] for UF_7^-.

Conclusion. The successful synthesis of NF_4WF_7 and NF_4UF_7 shows that even very weak Lewis acids such as metal hexafluorides are capable of forming stable NF_4^+ salts. This surprising result is a further manifestation of the unique properties of the NF_4^+ cation.

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Registry No. NF_4WF_7, 80735-93-9; NF_4UF_7, 80735-09-7; WF_6, 7783-82-6; UF_6, 7783-81-5; NF_4SbF_6, 16871-76-4.

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Kinetic Study of Axial Ligand Substitution in (Tetraphenylporphinato)chromium(III) Chloride

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Studies of axial ligand exchange or substitution in six-coordinate iron(III) and cobalt(III) metalloporphyrins have demonstrated that the axial ligands are significantly labilized compared to those of most nonporphyrin complexes. These observations raise important questions concerning the reaction mechanism, trans effects, and stability of five-coordinate metalloporphyrin intermediates.[2a] In this paper some kinetic studies of chromium(III) porphyrins are described.

Anation reactions of water-soluble tetrakis((*p*-sulfonatophenyl)porphinato)diaquochromate(III) have been reported by several groups. Fleischer[2b] first suggested an increased labilization of the axial water ligands of about 10^3. Krishnamurthy[3] recently claimed that there is no labilization compared to those of classical chromium(III) complexes. Yet more recently Ashley[4] suggested that the lability is increased by about 10^2. These anation reactions are probably dissociatively activated, although solid evidence to support a limiting dissociative mechanism (D) is not available.

Basolo et al.[5] have published a detailed study of (tetraphenylporphinato)chromium(III) chloride, Cr(TPP)Cl. In coordinating solvents, e.g., acetone, the complex (S)Cr(TPP)Cl (S = solvent) is formed. The solvent S is readily replaced by stronger ligands such as pyridine (py) and *N*-methylimidazole (MeIm) to form (L)Cr(TPP)Cl.[5] In this note the kinetics and thermodynamics of reaction 1 in toluene are reported for the

$$(L)Cr(TPP)Cl + X \rightleftharpoons (X)Cr(TPP)Cl + L \qquad (1)$$

ligands L, X including MeIm, py, triphenylphosphine (PPh_3), tris(2-cyanoethyl)phosphine ($P(C_2H_4CN)_3$), and triisopropyl phosphite ($P(OPr)_3$). This system is free of some problems inherent in the anation studies mentioned above, namely, solvent coordination and deprotonation of axially bound water at higher pH to give reactive hydroxy complexes. It is shown that reaction 1 follows a dissociative (D) mechanism and that the five-coordinate intermediate, Cr(TPP)Cl, has considerable discriminating ability. The labilizing effect of the TPP porphyrin and the importance of steric effects are also discussed.

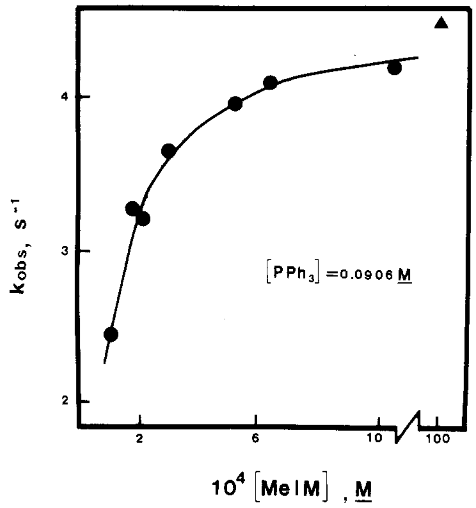

Figure 1. Rate constants at 25 °C for reaction 1 with L = PPh_3 and X = MeIm. The nucleophile concentration is varied.

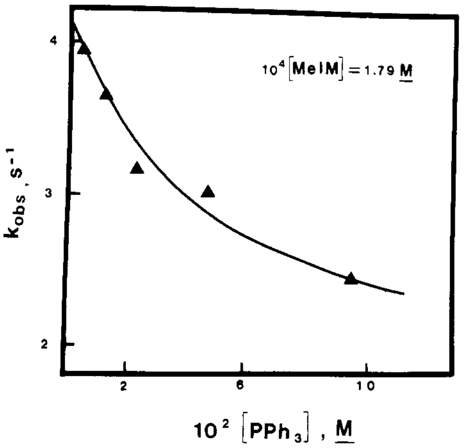

Figure 2. Rate constants at 25 °C for reaction 1 with L = PPh_3 and X = MeIm. The leaving group concentration is varied.

Experimental Section

meso-Tetraphenylporphine was used as supplied by Aldrich Chemical Co. All ligands were recrystallized or vacuum distilled prior to use. Spectroscopic grade toluene was fractionally distilled from CaH_2 and stored over 4 Å molecule sieves. Cr(TPP)Cl was prepared by the method of Basolo.[5] Cr(TPP)Cl is insoluble in dry toluene but readily dissolves in the presence of ligand, L, to form (L)Cr(TPP)Cl.

Equilibrium constants for reaction 1 were determined from static absorbance measurements on a Gilford 250 spectrophotometer thermostated at 25.0 ± 0.1 °C. Solutions contained a fixed concentration of Cr(TPP)Cl and varying ratios of leaving group (L) to nucleophile (X). Most measurements were at 410 nm, and all solutions were preequilibrated at 25 °C. The data were least-squares fit to eq 2, where Y is the fraction of the total Cr(TPP)Cl bound to the

$$\log [Y/(1 - Y)] = n \log [X] + \log (K/[L]) \qquad (2)$$

nucleophile X. The coefficient *n* was always very close to unity as required by reaction 1. Kinetic studies were done on a Dionex 110 stopped-flow spectrophotometer at 25 ± 0.2 °C. Dry toluene was the solvent for all reactions. The nucleophile and leaving group concentrations were kept in pseudo-first-order excess over the total

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(1) (a) Chelsea College. (b) Brown University.

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Table I. Kinetic and Thermodynamic Data[a] for the Reaction (L)Cr(TPP)Cl + X → (X)Cl(TPP)Cl + L

leaving group (L)	$10^2[L]/M$	nucleophile (X)	$10^2[X]/M$	k_1/s^{-1}	k_3/k_2	log K^b
PPh_3	0.46–9.5	MeIm	0.01–1.0	4.6 ± 0.3	1030 ± 200	4.8 ± 0.3
$P(OPr)_3$	9.4	MeIm	0.093–9.3	95 ± 12	24 ± 5	4.1 ± 0.6
$P(C_2H_4CN)_3$	0.10	MeIm	0.0063–0.63	80 ± 10	~200	5.3 ± 0.5[c]
py	10.0	MeIm	1.0–58	5.0 ± 0.8	1.7 ± 0.4	2.5 ± 0.1
PPh_3	9.5	py	1.0–50	3.6 ± 0.5	600[d]	2.6 ± 0.2
$P(OPr)_3$	9.5	py	1.0–40	90 ± 4	14[d]	1.9 ± 0.1
$P(C_2H_4CN)_3$	0.10	py	0.0063–0.63	90 ± 10		3.1 ± 0.3[c]
$P(C_2H_4CN)_3$	0.10	PPh_3	4.6–32	76 ± 15		0.5 ± 0.2

[a] In toluene at 25 °C; errors are at least one standard deviation. [b] Determined from eq 2. [c] Calculated from data in this table. [d] Calculated by dividing ratio with X = MeIm by 1.7.

metal concentration, which was approximately (1–2) × 10^{-5} M. Pseudo-first-order rate constants, k_{obsd}, were obtained from standard least-squares fitting of ln $(A_\infty - A)$ vs. time data.

Results and Discussion

Equilibrium constants for reaction 1 are given in Table I. The spectrophotometric measurements showed that reaction 1 accurately describes the equilibrium with only one axial position being substituted. No evidence was obtained for chloride displacement; e.g., addition of excess PPh_3 to Cr(TPP)Cl followed by addition of py gave the same spectrum as that produced by addition of Cr(TPP)Cl to a solution of py, which is known[5] to yield (py)Cr(TPP)Cl.

Rate constants are given in Table I and representative kinetic plots shown in Figures 1 and 2. The curvature in these plots suggests a simple dissociative reaction mechanism (eq 3 and 4). Applying the usual steady-state approximation to

$$(L)Cr(TPP)Cl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr(TPP)Cl + L \qquad (3)$$

$$Cr(TPP)Cl + X \xrightarrow{k_3} (X)Cr(TPP)Cl \qquad (4)$$

the Cr(TPP)Cl intermediate gives eq 5 and 6. All kinetic

$$k_{obsd} = \frac{k_1 k_3[X]}{k_2[L] + k_3[X]} \qquad (5)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{1}{k_1}\left(\frac{k_2}{k_3}\right)\left(\frac{[L]}{[X]}\right) \qquad (6)$$

results were consistent with this mechanism. With MeIm as the nucleophile, double-reciprocal plots of eq 6 gave values for k_3/k_2, which is a measure of the discriminating ability of the five-coordinate Cr(TPP)Cl intermediate. With py as the nucleophile, the observed rate constant k_{obsd} was independent of [L] and [py] at all accessible concentrations, which were constrained because of the magnitude of the equilibrium constant. This simply means that k_3[py] was much greater than k_2[L], so that $k_{obsd} = k_1$. Table I shows that k_1 is nucleophile independent as required by a dissociative mechanism.

The results show that ligands trans to chloride to (L)Cr(TPP)Cl are clearly labilized compared to those in most reactions of chromium(III).[6] The thermodynamic stability of (L)Cr(TPP)Cl follows the order MeIm > py > $P(OPr)_3$ > PPh_3 > $P(C_2H_4CN)_3$. This is also the order of decreasing proton basicity, and a Brønsted plot of log K vs. pK_a of the nucleophile conjugate acid gives a slope of 0.9 and a correlation coefficient of 0.99. Considering the diversity of nucleophile types, the correlation may be fortuitous in a quantitative sense, but qualitatively it shows that the Cr(III) center is a hard acid and that π bonding involving the ligand L is probably not important. The order of leaving group dissociation (k_1) is $P(OPr)_3 \geq P(C_2H_4CN)_3 >$ py $\geq PPh_3 >$ MeIm (90:80:5:4:0.1). The place of PPh_3 in this series is surprising in view of the stability order. As discussed below, this anomaly is probably steric in origin.

The Cr(TPP)Cl intermediate discriminates among nucleophiles according to MeIm > py > $P(OPr)_3$ > $P(C_2H_4CN)_3$ > PPh_3 (1030:600:40:5:1). Five-coordinate metalloporphyrins, in contrast to other macrocyclic complexes, possess unusual stability and, therefore, selectivity.[2a] The interesting feature here is the inability of phosphorus bases to compete effectively with nitrogen donors, a situation that does not hold[7] with the iron(III) porphyrin $Fe(TPP)(HIm)^+$. The conclusion is that the chromium(III) center is quite hard in Cr(TPP)Cl. As a nucleophile PPh_3 is relatively ineffective, yet it is slow to dissociate from $(Ph_3P)Cr(TPP)Cl$. Ineffectiveness as a nucleophile can reasonably be ascribed to a steric barrier encountered as the Cr–PPh_3 bond begins to form but before the metal has moved toward the center of the porphyrin core. Movement of the metal approximately into the porphyrin plane would relax the steric interactions. By microscopic reversibility the same steric barrier must be transversed upon PPh_3 dissociation, and this would account for the relatively small k_1.

In dry toluene displacement of chloride from (L)Cr(TPP)Cl to yield $Cr(TPP)(L_2)^+$, Cl^- was not observed for the nucleophiles in Table I. Lack of chloride dissociation could be due to thermodynamics or due to the poor solvent medium for an ionization process. In acetone, the phosphorus donors (but not the nitrogen donors) displayed biphasic kinetics that may indicate trans activation of chloride in $(R_3P)Cr(TPP)Cl$. Cyanide ion (in acetone) also gave evidence for chloride dissociation. That phosphorus donors would be expected to be much more trans labilizing than nitrogen donors is expected.[2a,7]

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Registry No. $(PPh_3)Cr(TPP)Cl$, 80822-49-7; $(P(OPr)_3)Cr(TPP)Cl$, 80822-50-0; $(P(C_2H_4CN)_3)Cr(TPP)Cl$, 80822-51-1; (py)Cr(TPP)Cl, 65013-13-0; MeIm, 616-47-7; py, 110-86-1; PPh_3, 603-35-0.

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Chemistry of Transition-Metal Phosphine and Phosphite Complexes. 2. Preparation and Properties of $XHgCo[P(OC_6H_5)_3]_3L$

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During the past 30 years there have appeared an astounding number of mercury derivatives of transition-metal carbonyls

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