inexpensive reagents and makes efficient use of the trifluoromethanesulfonic acid. The product may contain some $Ba(CF_3SO_3)_2$, but this has never been a problem in any of the preparative applications tried. Our experience has been that attempts to prepare $[(NH_3)_5CoOH_2](CF_3SO_3)_3$ by crystallization from a solution of CF_3SO_3H and another salt of $(NH_3)_5CoOH_2^{3+}$ lead to mixed-anion salts which must be recrystallized several times from aqueous CF_3SO_3H. This can consume large amounts of the acid and cobalt(III) before a pure product is obtained.

The benefits of using $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ (I) as a starting material have been extolled already[3] and are demonstrated further here by the preparation of two previously unattainable products,[4,5] the fumaronitrile and *p*-nitrophenoxide complexes. Only the 2,4- and 2,5-dinitrophenoxide complexes could be prepared previously, but now it seems that a range of phenoxide complexes can be made.

The observation that 2,6-dimethylpyridine can act as a noncoordinating base in the presence of I increases the scope and convenience of the preparation. This feature is illustrated here in the preparations with methyl *p*-hydroxybenzoate and *p*-toluenesulfonamide. In both cases the ligand loses a proton on coordination to $(NH_3)_5Co^{3+}$ but the proton reacts with 2,6-dimethylpyridine to allow the reaction to go to completion.

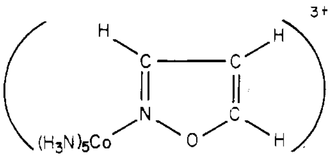
The sensitivity of phenoxide complexes to hydrolysis in aqueous acid has been mentioned by Gould et al.[5] The hydrolyses of the *p*-nitrophenoxide and methyl *p*-oxobenzoate complexes have been studied kinetically, and the reactions were both first order in $[H^+]$ with rate constants of 3.77×10^{-3} and 9.16×10^{-3} M^{-1} s^{-1}, respectively (0.05–0.500 M H^+, in 0.5 M $LiClO_4/HClO_4$, 25 °C). The smaller rate constant with the more electron-withdrawing *p*-nitro substituent is consistent with the reaction scheme

$$H^+ + (NH_3)_5CoOC_6H_4X^{2+} \underset{K_a}{\rightleftharpoons}$$

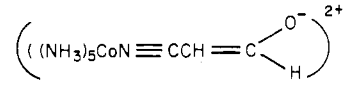
$$(NH_3)_5CoOHC_6H_4X^{3+} \xrightarrow{k_1} (NH_3)CoOH_2^{3+} + HOC_6H_4X$$

Then the measured rate constant is (k_1/K_a) and the larger K_a for *p*-nitrophenoxide would make (k_1/K_a) smaller. There was no indication of saturation in the kinetic data, which indicates that $K_a \gg [H^+]$ at least for $[H^+]$ up to 0.50 M.

The isoxazole complex is an example of a preparation of a new complex with a base sensitive ligand. Isoxazole undergoes ring opening to $NCCH_2CHO$.[9] The NMR and electronic spectra are typical of nitrogen coordination and are consistent with the structure



The isoxazole complex is very susceptible to ring opening in aqueous sodium hydroxide. Stopped-flow studies have shown that the reaction is first order in hydroxide ion with a rate constant of 467 M^{-1} s^{-1} (1.0×10^{-2}–1×10^{-3} M OH^- in 0.50 M $NaClO_4$, 25 °C). The reaction product is strongly colored and has absorption maxima at 500 and 346 nm with molar extinction coefficients of 210 and 1.00×10^3 M^{-1} cm^{-1}, respectively. The structure of the product is tentatively assigned as



$$\left((NH_3)_5CoN{\equiv}CCH{=}C\begin{smallmatrix}O^-\\H\end{smallmatrix}\right)^{2+}$$

based on the infrared absorption at 2240 cm^{-1} and known isoxazole reactions.[9] The chemistry of this system is currently under investigation.

The malononitrile complex originally reported[1] seems to have contained some impurity since the electronic spectrum does not agree with that reported here or by Creaser et al.[10] In fact, our results (Table I) even differ from those of Creaser et al.,[10] who found maximum molar extinction coefficients of 72 and 82 at 474 and 341 nm, respectively. Our experience with a number of these nitrile complexes,[8] of which succinonitrile and fumaronitrile (Table I) are typical, has always given maxima at 467–468 and 333–335 nm. The presence of carboxamido or aquo complex impurities will shift the maxima to longer wavelength.

The malononitrile complex was reported originally[1] to react rapidly with chromium(II). The complex described in the present work does not react unusually rapidly with chromium(II). The reaction rate seems to be rather typical of other nitrile complexes previously reported.[8] However, the reduction is competitive with hydrolysis to the carboxamide and aquo complexes, and no detailed studies have been undertaken.

Finally, to return to the preparative aspect of this work, $[(NH_3)_5CoOH_2](CF_3SO_3)_3$ may be dehydrated by heating it in sulfolane in the presence of molecular sieves. This appears to be a convenient in situ method of generating the reactive sulfolane or trifluoromethanesulfonato complex.

Acknowledgment. The authors wish to acknowledge financial support and fellowship support to W.C.K. from the Natural Science and Engineering Research Council of Canada.

Registry No. I, 75522-50-8; $[(NH_3)_5CoOH_2](O_3SCF_3)_3$, 69897-22-9; $[(NH_3)_5CoOH_2](SO_4)(HSO_4)$, 80679-80-7; $[(NH_3)_5Co(NC(CH)_2CN)](ClO_4)_3$, 80679-82-9; $[(NH_3)_5Co(OC_6H_4NO_2)](ClO_4)_2$, 80679-84-1; $[(NH_3)_5Co(OC_6H_4CO_2CH_3)](ClO_4)_2 \cdot 3NaClO_4$, 80679-86-3; $[(NH_3)_5Co(NCCH_2CN)](ClO_4)_3$, 15649-18-0; $[(NH_3)_5Co(NHSO_2C_6H_4CH_3)](ClO_4)_2$, 78891-47-1; $[(NH_3)_5Co(ONC_3H_3)](ClO_4)_3$, 80679-88-5.

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Contribution from Rocketdyne, a Division of Rockwell
International Corporation, Canoga Park, California 91304

Perfluoroammonium Salts of Metal Heptafluoride Anions

William W. Wilson and Karl O. Christe*

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Due to its high-energy content and unusual kinetic stability, the NF_4^+ cation is a unique oxidizer. Its salts have found numerous applications such as solid propellant NF_3–F_2 gas generators for chemical HF–DF lasers,[1] ingredients in high detonation pressure explosives,[2] and fluorinating agents for aromatic compounds.[3] Although the NF_4^+ cation has successfully been combined with a large number of different anions in the form of stable salts, all these anions were derived from relatively strong Lewis acids, and their number of ligands did not exceed six. It was therefore of interest to explore whether NF_4^+ salts containing metal heptafluoride anions can exist.

Experimental Section

Apparatus. Volatile materials used in this work were handled in a stainless-steel–Teflon FEP vacuum line. The line and other hardware

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used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry-nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution with an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.[4] Thermal decomposition measurements were carried out in a previously described[5] sapphire reactor.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and Claassen filter[6] for the elimination of plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

Elemental analyses were carried out as previously described.[7]

Materials. Literature methods were used for the syntheses of NF_4SbF_6[8] and NF_4HF_2 solutions in HF.[9] Hydrogen fluoride (Matheson) was dried by storage over BiF_5 to remove the H_2O.[10] Tungsten hexafluoride (high purity, Alfa) and UF_6 (Allied) were used as received. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox.

Preparation of NF_4WF_7. Dry CsF (15.0 mmol) and NF_4SbF_6 (15.0 mmol) were loaded in the drybox into half of a prepassivated Teflon double U metathesis apparatus. Dry HF (15 mL of liquid) was added on the vacuum line, and the mixture was stirred with a Teflon-coated magnetic stirring bar for 15 min at 25 °C. After the apparatus was cooled to −78 °C, it was inverted and the NF_4HF_2 solution was filtered into the other half of the apparatus. Tungsten hexafluoride (22.5 mmol) was condensed at −196 °C onto the NF_4HF_2. The mixture was warmed to ambient temperature, and two immiscible liquid phases were observed. After 30 min of vigorous stirring at 25 °C, the lower WF_6 layer dissolved in the upper HF phase. Most of the volatile products were pumped off at ambient temperature until the onset of NF_4HF_2 decomposition became noticeable (NF_3 evolution). An additional 8.0 mmol of WF_6 was added at −196 °C to the residue. When the mixture was warmed to ambient temperature, a white solid product appeared in the form of a slurry. All material volatile at −31 °C was pumped off for 1 h and consisted of HF and some NF_3. An additional 14.5 mmol of WF_6 was added to the residue, and the resulting mixture was kept at 25 °C for 14 h. All material volatile at −13 °C was pumped off for 2 h and consisted of HF and WF_6. The residue was kept at 22 °C for 2.5 days, and pumping was resumed at −13 °C for 2.5 h and at 22 °C for 4 h. The volatiles, collected at −210 °C, consisted of some HF and small amounts of NF_3 and WF_6. The white solid residue (5.138 g, 84% yield) was shown by vibrational and ^{19}F NMR spectroscopy to consist mainly of NF_4WF_7 with small amounts of SbF_6^- as the only detectable impurity. On the basis of its elemental analysis, the product had the following composition (weight %): NF_4WF_7, 98.39; $CsSbF_6$, 1.61. Anal. Calcd: NF_3, 17.17; W, 44.46; Cs, 0.58; Sb, 0.53. Found: NF_3, 17.13; W, 44.49; Cs, 0.54; Sb, 0.55.

Preparation of NF_4UF_7. A solution of NF_4HF_2 in anhydrous HF was prepared from CsF (14.12 mmol) and NF_4SbF_6 (14.19 mmol) in the same manner as described for NF_4WF_7. Most of the HF solvent was pumped off on warmup from −78 °C toward ambient temperature until the onset of NF_4HF_2 decomposition became noticeable. Uranium hexafluoride (14.59 mmol) was condensed at −196 °C into the reactor, and the mixture was stirred at 25 °C for 20 h. The material volatile at 25 °C was briefly pumped off and separated by fractional condensation through traps kept at −78, −126, and −210 °C. It consisted of HF (6.3 mmol), UF_6 (9.58 mmol), and a trace of NF_3. Since the NF_4HF_2 solution had taken up only about one-third of the stoichiometric amount of UF_6, the recovered UF_6 was condensed back into the reactor. The mixture was stirred at 25 °C for 12 h, and the volatile material was pumped off again and separated. It consisted of HF (12.8 mmol), UF_6 (1.7 mmol), and a trace of NF_3. Continued pumping resulted in the evolution of only a small amount of UF_6, but no NF_3 or HF, thus indicating the absence of any unreacted NF_4HF_2. The pale yellow solid residue (5.711 g, 88% yield) was shown by vibrational and ^{19}F NMR spectroscopy and elemental analysis to have the following composition (weight %): NF_4UF_7, 97.47; NF_4SbF_6, 1.50; $CsSbF_6$, 1.03. Anal. Calcd: NF_3, 15.34; U, 50.32; Sb, 0.90; Cs, 0.37. Found: NF_3, 15.31; U, 50.2; Sb, 0.90; Cs, 0.37.

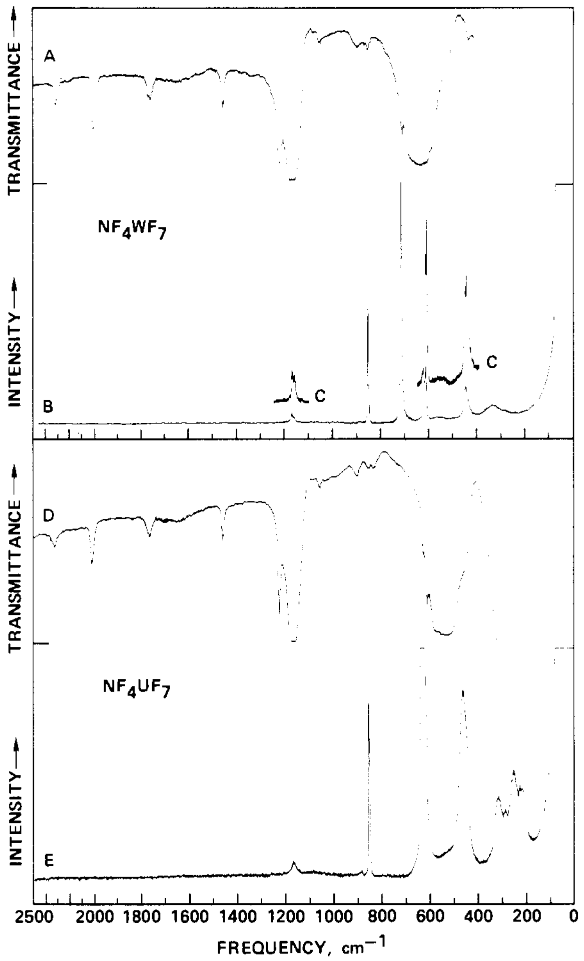

Figure 1. Vibrational spectra of solid NF_4WF_7 and NF_4UF_7: traces A and D, infrared spectra of the dry powders pressed between AgCl disks (the broken lines indicate absorption due to the AgCl window material); traces B, C, and E, Raman spectra recorded at different sensitivities and resolution.

Results and Discussion

Synthesis of NF_4XF_7 Salts. The synthesis of NF_4XF_7 salts proved rather difficult because metal hexafluorides are weak Lewis acids and exhibit only a moderate tendency to form the energetically relatively unfavorable heptafluoro anions. Consequently, neither direct synthetic methods, based on the reaction of NF_3 with F_2 and a Lewis acid in the presence of an activation energy source,[11] nor indirect methods such as displacement reactions[12] or metathesis in anhydrous HF solution[10] could be used. For example, anhydrous HF displaces UF_6 from $NOUF_7$ or $CsUF_7$.[13] However, in the course of

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Table I. Vibrational Spectra of Solid NF_4WF_7 and NF_4UF_7

obsd freq, cm^{-1} (rel intens[a])					
NF_4WF_7		NF_4UF_7		assignt (point group)[b]	
IR	Raman	IR	Raman	NF_4^+ (T_d)	WF_7^- (D_{sh})[c]
2315 vw		2315 vw		$2\nu_3(A_1 + E + F_2)$	
2000 w		2001 w		$\nu_1 + \nu_3(F_2)$	
1760 vw		1760 vw		$\nu_3 + \nu_4(A_1 + E + F_2)$	
1456 w		1458 w		$\nu_1 + \nu_4(F_2)$	
1220 mw		1222 mw		$2\nu_4(A_1 + E + F_2)$	
1165 vs	1165 (0.3) 1155 sh	1165 vs	1164 (0.1)	$\nu_3(F_2)$	
1055 vw		1052 vw		$\nu_2 + \nu_4(F_1 + F_2)$	
895 vw	890 (0+)	898 vw	885 (0+)	$2\nu_2(A_1 + A_2 + E)$	
851 vw	849 (5.0)		851 (1.1)	$\nu_1(A_1)$	
711 w	711 (10)	626 w	628 (10)		$\nu_1(A_1')$
630 vs, br		530 vs, br			$\nu_3(A_2'')$, $\nu_5(E_1')$
610 sh	614 (1.3) 609 (2.0)	610 m	613 (~1.0) sh	$\nu_4(F_2)$	
	446 (0.9) 441 (1.1)		457 (1.0)	$\nu_2(E)$	
436 w	435 sh	460 sh	457 (1.0)		$\nu_8(E_1'')$
	328 (0.3) br		311 (0.4)		$\nu_6(E_1')$
	285 sh		283 (0+)		$\nu_4(A_2'')$
			249 (0.5)		
			225 (0+)		
			214 (0.3)		

[a] Uncorrected Raman intensities. [b] Based on the splitting of the bands and the violations of the selection rules observed for some of the modes, the actual site symmetries of these ions are expected to be lower than T_d and D_{sh}. [c] Assignments based on ref 16.

a recent study in our laboratory a method for the preparation of $(NF_4)_2SiF_6$ was discovered[14] in which equilibrium 1 was

$$2NF_4HF_2{\cdot}nHF + SiF_4 \rightleftarrows (NF_4)_2SiF_6 + 2(n + 1)HF \quad (1)$$

successfully shifted to the right by repeatedly treating a highly concentrated NF_4HF_2–HF solution[9] with an excess of SiF_4 while periodically stripping off the HF. This method has now been extended to the synthesis of NF_4WF_7 and NF_4UF_7 according to (2) and provided the first known examples of NF_4^+ salts containing complex anions with more than six ligands about their central atom.

$$NF_4HF_2{\cdot}nHF + XF_6 \rightleftarrows NF_4XF_7 + (n + 1)HF \quad (X = W, U) \quad (2)$$

The purity of the NF_4XF_7 salts prepared in this manner was about 98 weight % with $CsSbF_6$ and NF_4SbF_6 as the principal impurities. Product purification by recrystallization from HF solution was not possible due to equilibrium 2, which in the presence of a large excess of HF is shifted to the left. The yields of NF_4XF_7 were about 86%, on the basis of NF_4HF_2, with most of the NF_4HF_2 values lost being due to hang up of some mother liquor on the $CsSbF_6$ filter cake during the metathetical preparation of NF_4HF_2 according to (3).

$$NF_4SbF_6 + CsHF_2 \xrightarrow{HF} CsSbF_6{\downarrow} + NF_4HF_2 \quad (3)$$

Physical Properties. NF_4WF_7 and NF_4UF_7 are white and pale yellow, respectively, and are moderately soluble in BrF_5. They are crystallinic, hygroscopic solids that are stable in a dynamic vacuum at 125 °C. At higher temperatures, both salts decompose according to (4), with no evidence for the

$$NF_4XF_7 \rightarrow NF_3 + F_2 + XF_6 \quad (4)$$

formation of stable, volatile, higher valence state florides. The ratio of NF_3 to XF_6 in the decomposition products was shown to be 1:1, and the vibrational spectra of the solid residues showed no evidence for doubly charged anions. These observations indicate that neither the stepwise (eq 5) nor re-

$$2MUF_7 \rightarrow M_2UF_8 + UF_6 \quad (5)$$

ductive (eq 6) decomposition, previously observed for the

$$M_2UF_8 \rightarrow M_2UF_7 + {}^1/_2F_2 \quad (6)$$

alkali-metal salts,[13] are significant for the NF_4^+ salts. Based on the observed decomposition rates in a dynamic vacuum at 145 °C (NF_4UF_7, 25% decomposition/h; NF_4WF_7, 1.4% decomposition/h), NF_4WF_7 is thermally somewhat more stable than NF_4UF_7.

Vibrational Spectra. The infrared and Raman spectra of NF_4WF_7 and NF_4UF_7 are shown in Figure 1, and the observed frequencies and their assignments are summarized in Table I. These spectra establish beyond doubt the presence of NF_4^+ cations[15] and WF_7^-[16] and UF_7^- anions[13] and also demonstrate that, under the given reaction conditions, no significant amounts of XF_8^{2-} salts are formed.

^{19}F NMR Spectra. The ionic nature of the NF_4XF_7 salts in BrF_5 solution was established by ^{19}F NMR spectroscopy. For NF_4WF_7 at –60 °C two signals, a triplet of equal intensity at ϕ = 222.7 with J_{NF} = 232.7 Hz and a half-line width of 2 Hz and a singlet at ϕ = 142.2 with a half-line width of 2.8 Hz and missing ^{183}W satelites were observed which are characteristic for NF_4^+[4,9] and WF_7^-,[13,17] respectively. An area integration of the two signals showed a ratio of 4:6.99, in excellent agreement with the expected ratio of 4:7. These two signals changed very little when the sample was warmed to ambient temperature; however, the solvent signals which at –60 °C were well resolved collapsed at 25 °C to a single peak. For NF_4UF_7 at –60 °C, again, well-resolved signals for the BrF_5 solvent and NF_4^+ were observed, but the UF_7^- signal could not be detected. These observations rule out a rapid

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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.

Acknowledgment. The authors gratefully acknowledge helpful discussions with Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson and financial support from the Office of Naval Research and the Army Research Office.

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.

Contribution from the Departments of Chemistry,
Chelsea College, London SW3 6LX, England,
and Brown University, Providence, Rhode Island 02912

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

P. O'Brien*[1a] and D. A. Sweigart*[1b]

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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

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

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.

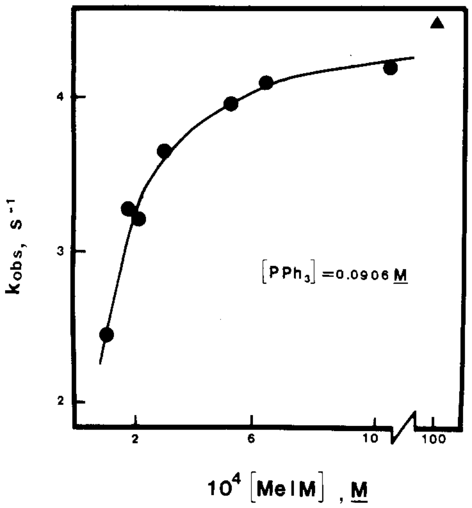

Figure 1. Rate constants at 25 °C for reaction 1 with L = PPh_3 and X = MeIm. The nucleophile concentration is varied.

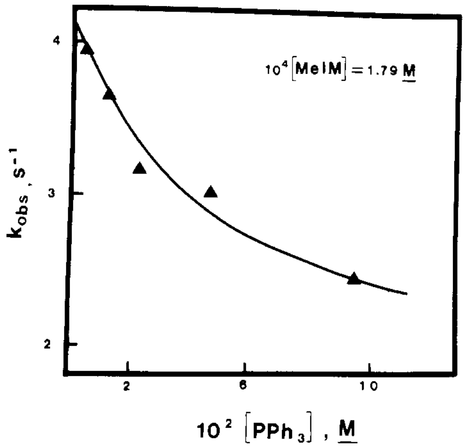

Figure 2. Rate constants at 25 °C for reaction 1 with L = PPh_3 and X = MeIm. The leaving group concentration is varied.

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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