

(Table III). These compounds decomposed on attempted recovery from solution, and their structures remain uncertain; however, the Ir species afforded the stable octahedral adducts **21** and **22** from reactions with excess CO or *t*-BuNC, respectively. That these products were formed with a new but again specific octahedral stereochemistry (**F**) was apparent from consideration of pertinent NMR data (Table III): H is coupled to equivalent P atoms with a small *J* (16 Hz) indicative of a mutually cis relationship while long-range coupling (⁴*J*) between P and each of two distinguishable types of silyl methyl proton was resolvable. Comparisons among spectroscopic data for the series of hydrido-iridium(III) complexes listed in Table III are of some further interest in that they reinforce a set of useful arguments assembled²⁴ recently by Olgemöller and Beck. Thus, while the well-established^{8,15} and concerted effect on $\nu(\text{Ir-H})$ and $\delta(\text{IrH})$ of strongly trans-influencing ligands is exemplified by values for compounds **21** and **22**, the absence of a similar systematic dependence on donor properties of ligands cis to H is confirmed since for compounds 7-9 $\nu(\text{Ir-H})$ varies as COD > diphos > dpm while $\delta(\text{IrH})$ is shifted as diphos > dpm > COD.

An unusual degree of selectivity is apparent in the formation of the octahedral (phosphinoethyl)silyl complexes **10-22** as single isomers, most of which possess structures **C** or **F**, a situation that parallels the adherence to a common geometry of enantiomeric or diastereoisomeric products⁸ of the addition to *trans*-[Ir(CO)(Cl)(PPh₃)₂] of Ph₂PCH₂CH₂SiR¹R²H (R¹, R² = Me, Ph; R¹ = Me, R² = Ph). Considered together with the regioselectivity¹ of the addition of Ph₂PCH₂CH₂SiMe₂H to IrH(CO)(PPh₃)₃ and the unexpected irregularity of the 5-coordinate arrangement around the central metal atom in compounds **1** and **2**, these observations suggest that the incipency of bidentate complexation by the P₂Si ligand exerts a powerful orientating effect at the metal center that is translated into control over ligand addition/substitution behavior at the resulting chelated M(III) site. It seems plausible that these stereochemical predilections may be a conse-

quence of the unusual electronic character of silyl ligands, which on the basis of structural and spectroscopic evidence have come to be regarded²⁵ as very strongly electron releasing.

Complexes of configurations **A**, **C**, or **E** exhibit trans P and cis Si atoms while those with structure **F** are all-cis within the planar framework. In no instance, however (here or elsewhere^{1,2,7,8}), have two silyl groups been found trans to each other at a single metal center, a situation that would be predicted if relevant arguments²⁵ regarding trans-influence are correct. Likewise in the bis(chelate) systems (**C** and **F**), a change in geometry accompanies introduction of two (rather than one) strongly trans-influencing unidentate ligands; thus, the same isomer (structure **F**) of the hydrido-carbonyliridium(III) complex **21** is isolated regardless of the order in which the required synthetic steps (NaBH₄ reduction, CO addition) are applied. A further indication of the extent to which bond weakening occurs trans to silicon is provided by recent NMR evidence²⁶ for intramolecular ligand exchange trans to SiR₃ in *cis*-[PtH(SiR₃)(PPh₃)₂] (R = Ph, *p*-ClC₆H₄, *p*-MeC₆H₄). While such a trans-labilizing effect has yet to be exploited in relation to catalytic substrate activation, stabilization by chelate incorporation of bonds from silicon to reactive transition-metal centers may allow this idea to be examined.

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Solvolysis Kinetics of Pentaammine(trifluoromethanesulfonato-*O*) Complexes of Cobalt(III), Rhodium(III), and Iridium(III)

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Rate constants for solvolysis of [M(NH₃)₅(OSO₂CF₃)](CF₃SO₃)₂ (M = Co, Rh, Ir) have been determined in a range of pure solvents where reaction proceeds smoothly to yield solvent pentaammine complexes (water, methanol, dimethyl sulfoxide, dimethylformamide, acetonitrile, and pyridine for all three metals and the additional solvents ethanol, formamide, methylformamide, and trimethyl phosphate for cobalt). Rate ratios for Co:Rh:Ir at 25 °C vary a little with solvent, but approximate 90:40:1. Activation enthalpies and entropies have been determined in each case. For all solvents except water, the progressively slower rate constant from Co to Rh to Ir arises in the activation entropy term. For water, the principal variation is in the activation enthalpy, suggesting a mechanistic uniqueness for this solvent. The activation entropies are invariably negative, consistent with an associative (I_a) mechanism or a dissociative (I_d) mechanism with appreciable charge separation in the transition state with concomitant increase in solvent electrostriction. Various relationships of rate constant and solvent properties have been probed, and no simple uniparameter relationship exists, although multiparameter relationships may apply.

Introduction

Studies of reaction mechanisms in coordination chemistry have been extensive in recent decades.¹⁻⁴ Of factors that may affect rates and mechanisms of reaction, the role of the solvent has been

one of the lesser studied, although not entirely neglected. Of those studies reported, mixed aqueous-organic solvent systems have predominated,^{1,5-10} in part as a consequence of the solubility properties of ionic complexes.

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The relationships between rate constants for solvolysis and physical properties of solvents have been extensively explored for organic systems.¹¹ Correlations between observed rate constants and "bulk" solvent properties such as dielectric constant exist in certain cases,^{12,13} while relationships with a range of empirical parameters that apparently reflect properties such as solvent polarity have been described.^{11,14-18} Multiparameter expressions have also been applied, in recognition of the fact that no single factor is likely to determine the effect exclusively.^{19,20}

Solvolysis studies of cationic complexes in pure solvents may be restricted by the limited range of solvents available with most common anions. Recently, the trifluoromethanesulfonate anion has been employed as a counterion, since it imparts good solubility to complexes in a range of solvents.²¹ Further, coordinated trifluoromethanesulfonate is a poor ligand, readily replaced by other ligands even on inert metal ions such as iridium(III).²² The properties of solubility and lability of (trifluoromethanesulfonato)metal trifluoromethanesulfonate complexes makes them obvious candidates for study of their solvolysis behavior. In this paper the rates of solvolysis of $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ ($M = Co, Rh, Ir$) in a range of pure coordinating solvents have been studied.

Experimental Section

Preparation of Complexes. The complexes $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, and $[Ir(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ were prepared as previously described.^{21,22} Care was taken to remove traces of CF_3SO_3H from the complexes by boiling the finely powdered products several times in chloroform and ether.

Solvents. Where available, AR or spectroscopic grade solvents were employed. Most solvents were dried over the appropriate molecular sieves; formamide and *N*-methylformamide were dried over sodium sulfate. Standard distillation techniques were employed to further purify and dry solvents, except for formamide and *N*-methylformamide, which were thrice subjected to freeze-melt purification.

Kinetics. The rates of solvolysis were followed at selected constant wavelengths on Hitachi 220A or Hewlett-Packard 8450A spectrophotometers at constant temperature (± 0.1 °C). All data fitted first-order kinetic plots for at least 4 half-lives, and rate constants were obtained by standard Guggenheim and/or exponential fitting programs. Triplicate independent runs were generally obtained under each set of experimental conditions. Enthalpies of activation and entropies of activation were obtained from variable-temperature data in each case via a plot of $\ln k_{obsd}$ against $1/T$. In each case solvolysis proceeds to completion, with only one species detected by cation chromatography within the error of the technique (>95%).

Results

Solvolysis reactions of $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ complexes ($M = Co, Rh, Ir$) proceed smoothly by first-order kinetics in the solvents selected for study to the $[M(NH_3)_5(solvent)](CF_3SO_3)_3$ complexes, which have been characterized previously.²¹⁻²³ The solvent- and temperature-dependent rate constants for all complexes are collected in Table I. Rate constants at 25 °C span approximately 2 orders of magnitude for each metal ion (Table II). The Co:Rh:Ir ratio of rate constants at 25 °C in each solvent varies a little, but an approximate average

Table I. Temperature Dependences of the Rate Constants for Solvolysis of Pentaammine(trifluoromethanesulfonato-*O*) Metal(III) Complexes^a

solvent	Co(NH ₃) ₅ -(OSO ₂ CF ₃) ₂ ²⁺		Rh(NH ₃) ₅ -(OSO ₂ CF ₃) ₂ ²⁺		Ir(NH ₃) ₅ -(OSO ₂ CF ₃) ₂ ²⁺	
	temp, °C	10 ⁴ k, s ⁻¹	temp, °C	10 ⁴ k, s ⁻¹	temp, °C	10 ⁴ k, s ⁻¹
water ^b	7.5	37.5	7.5	24.3	25.0	2.61
	12.0	64	12.0	42.3	32.0	6.15
	18.0	123	18.0	84.6	39.0	13.9
	25.0	268	25.0	189	46.0	29.8
methanol ^c	18.0	4.1	25.0	5.9	43.0	0.94
	25.0	9.5	32.0	12.1	50.0	1.93
	32.0	20.4	39.0	26.3	57.0	3.74
	39.0	44.8	46.0	53	62.0	6.00
ethanol ^c	18.0	2.8				
	25.0	6.65				
	32.0	15.2				
dimethyl sulfoxide	18.0	61.6	18.0	14.6	33.0	2.70
	25.0	135	25.0	31.1	40.0	5.50
	31.0	246	32.0	63.4	47.0	10.6
	36.0	430	39.0	126	54.0	20.5
formamide	12.0	69.5				
	18.0	139				
	25.0	288				
methylformamide	31.0	530				
	13.0	48.0				
	18.0	94.9				
dimethylformamide	25.0	192				
	32.0	400				
	13.0	42.0	18.0	32.6	28.0	2.50
	18.0	70.9	25.0	67.8	35.0	4.94
acetonitrile	25.0	156	32.0	131	42.0	9.65
	32.0	305	38.0	233	49.0	18.4
	18.0	2.21	28.0	2.20	47.0	0.625
	25.0	4.63	35.0	4.57	53.0	1.06
trimethyl phosphate	32.0	9.46	42.0	8.65	60.0	1.96
	39.0	19.9	49.0	16.8	67.0	3.45
	18.0	6.28				
	25.0	13.5				
pyridine	32.0	29.6				
	38.0	54				
	18.0	55	18.0	9.92	23.0	1.00
	25.0	116	25.0	20.6	30.0	2.02
	32.0	228	32.0	40.9	37.0	3.80
	37.0	370	39.0	81.4	42.0	6.36

^a Average of three independent runs; standard error $\leq 5\%$.

^b 0.1 M CF_3SO_3H . ^c Trace of CF_3SO_3H .

Table II. Rate Constants for Solvolysis at 25 °C (k_{obsd} , s⁻¹) of $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ Complexes and Rate Ratios

solvent	Co	Rh	Ir	Co:Rh:Ir
water	0.0268	0.0189	0.000261	103:72:1
methanol	0.00095	0.000591	0.0000141	67:42:1
ethanol	0.000666			
dimethyl sulfoxide	0.0135	0.00311	0.000114	118:27:1
formamide	0.0288			
<i>N</i> -methylformamide	0.0192			
<i>N,N</i> -dimethylformamide	0.0156	0.00678	0.000183	85:37:1
acetonitrile	0.000463	0.000165	0.0000075	62:22:1
trimethyl phosphate	0.00135			
pyridine	0.0116	0.00206	0.0000995	116:21:1

ratio of 90:40:1 applies. This can be compared with data for chloro pentaammine analogues in water, where Co:Rh:Ir is 17000:600:1,²⁴ and the increase in relative inertness is much greater in that case.

No simple correlation of a physical property²⁵ such as dipole moment (μ), dielectric constant (ϵ), viscosity (η), and polarizability with reactivity was evident. In particular, the correlation between

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Table III. Activation Parameters for Solvolysis of [M(NH₃)₅(OSO₂Cl₃)](CF₃SO₃)₂^a

solvent	Co		Rh		Ir	
	ΔH^\ddagger	ΔS^\ddagger	ΔH^\ddagger	ΔS^\ddagger	ΔH^\ddagger	ΔS^\ddagger
water	75.4 (±0.6)	-21	79.0 (±0.8)	-13	88.6 (±1.0)	-16
methanol	83.1 (±1.0)	-23	80.7 (±1.0)	-38	82.4 (±0.9)	-61
ethanol	87.0 (±0.6)	-14				
dimethyl sulfoxide	77.4 (±1.3)	-21	75.8 (±0.9)	-39	77.3 (±0.3)	-61
formamide	74.4 (±0.9)	-25				
N-methylformamide	74.8 (±1.2)	-27				
N,N-dimethylformamide	73.9 (±1.1)	-31	72.9 (±0.8)	-43	74.1 (±0.7)	-68
acetonitrile	76.3 (±1.3)	-51	75.1 (±1.1)	-66	74.9 (±0.2)	-92
trimethyl phosphate	78.8 (±1.0)	-34				
pyridine	72.6 (±0.8)	-38	73.0 (±0.8)	-52	72.4 (±1.1)	-77

^a ΔH^\ddagger in kJ mol⁻¹; ΔS^\ddagger in J K⁻¹ mol⁻¹.

log *k* and 1/ε or (ε - 1)/(2ε + 1) observed in several inorganic systems where dissociative mechanisms apply^{26,27} was not observed. Application of multiparameter equations²⁸ to a description of the solvent dependence is more encouraging, but analysis of this approach is deferred to the Discussion.

Activation enthalpies and entropies were determined for each system (Table III). The most obvious result is that ΔS^\ddagger is always negative, with values as large as -50 J K⁻¹ mol⁻¹ for cobalt, nearly -70 J K⁻¹ mol⁻¹ for rhodium, and over -90 J K⁻¹ mol⁻¹ for iridium. Inspection of the data yields some other important observations: (a) In water, variation from Co to Rh to Ir is principally in the ΔH^\ddagger term. For all other solvents, variation is entirely in the ΔS^\ddagger term. This implies some mechanistic uniqueness for water as a solvent and entering group. (b) Except for water, ΔS^\ddagger is constantly more negative from Co to Rh to Ir. (c) The much slower solvolysis rate in methanol compared with water is obvious. However, it arises mainly in the ΔH^\ddagger term with Co and in the ΔS^\ddagger term with Rh, while for Ir a lower ΔH^\ddagger term in the alcohol is offset by a much less favorable ΔS^\ddagger . (d) For most solvents, ΔH^\ddagger is similar or lower than the value for water, with the favorable disparity most noticeable on Ir. These effects are almost invariably offset by a less favorable (more negative) ΔS^\ddagger .

Attempts to correlate activation parameters with solvent properties also yielded no simple compelling relationships. There is some indication that ΔS^\ddagger can be correlated with solvent viscosity, but the relationship is too tenuous to sustain detailed discussion. There is a very approximate isokinetic relationship of ΔH^\ddagger and ΔS^\ddagger for each metal ion in the sense that the sets of data all follow similar slopes. The implication is that there are no abrupt mechanistic changes in any one metal ion system, and this is not expected.

Discussion

Inorganic reactions where there is no significant solvent participation have been reported; in the ligand dissociation of Rh-(P(OCH₃)₃)₃⁺, the rate constant is independent of solvent choice, for example.²⁹ However, most reactions exhibit some dependence of rate constant on choice of solvent. The effect of solvent on the rates of reactions of transition-metal complexes has been reviewed.²⁷ Previously, analysis of results has included attempts to establish relationships of rate constant with dielectric constant, viscosity, and solvent polarity. The use of bulk solvent properties such as dielectric constant and viscosity have occasionally yielded useful relationships such as the log *k* vs. 1/ε relationships for isomerization of haloalkene and haloketone complexes of low-valent platinum.²⁶ However, microscopic dielectric constants in the vicinity of ions may be very different from bulk values employed, so it may be unreasonable to expect useful relationships with ionic compounds; ε for water within 1.5 Å of an ion has been estimated to fall to ~5, rising to ~80 4 Å from the ion.³⁰

Correlations of bulk solvent properties and rate constants certainly do not exist in the present study.

With ionic species in a range of solvents of varying dielectric constant, one effect of the lowering of the dielectric constant of a solvent is to encourage ion-pair formation.^{27,31,32} In the extreme, the free energy of formation of ion pairs from the participating ions can be so large that a complex ion within the ion pair can be regarded as a species chemically different from the free complex ion.³² It is important to address this issue, since while *K*_{IP} for 1:2 electrolytes in water is small, this need not be the case in some other solvents. To limit any effects, reactions in this study were performed in the absence of any added extra electrolyte; observed rates were independent of complex concentration, albeit over a small range, suggesting no major effect. While *K*_{IP} for small coordinating anions like Cl⁻ can be high in solvents such as dimethylformamide, values for large anions of low nucleophilicity are small or not measurable. For example, *K*_{IP} for Cr-(DMF)₆³⁺, Cl⁻ is 1000 but drops to only 30 for Cr-(DMF)₆³⁺, ClO₄⁻ and is not measurable for Cr-(DMF)₆³⁺, B(C₆H₅)₄⁻.³³ Values for 2+, 1- systems will be smaller. The CF₃SO₃⁻ anion, like ClO₄⁻ and B(C₆H₅)₄⁻, is of low nucleophilicity, and the partial molar volume of CF₃SO₃⁻ (80.4 cm³ mol⁻¹) is larger than that of ClO₄⁻ (48.6 cm³ mol⁻¹).³⁴ Consequently, even in solvents where ion pairing is favored, *K*_{IP} for M²⁺, CF₃SO₃⁻ will be very small. Further, there are no clear trends in rate constants or rate ratios that can be attributed to significant ion-pairing effects. One current view is that ion pairing does not significantly affect the intrinsic reactivity of the complex cation in many reactions even if it is present.^{33,35} There are no strong grounds either to assume significant ion-pair interactions between free CF₃SO₃⁻ and M-(NH₃)₅(OSO₂CF₃)²⁺ or to support a role for them in the mechanism of solvolysis.

Apart from bulk solvent properties, considerations of a range of empirical parameters that apparently reflect microscopic solvent polarity have been reported, based on organic reactions. The Dimroth-Reichardt parameter (*E*_T)¹⁸ is a composite measure of polarity (π*) and hydrogen-bond donor acidity (α).¹⁹ It can be correlated well with other polarity parameters such as the solvatochromism *Z* parameter of Kosower¹⁴ and the χ_B parameter of Brooker.³⁶ These and other related parameters and their applications in organic reactions have been reviewed.¹¹ For the M(NH₃)₅(OSO₂CF₃)²⁺ complexes, no sensible correlation of any of these parameters with rate constant exists. Further, there is no obvious relationship with the Gutmann donor number (*D*_N),¹⁶ which reflects hydrogen-bond acceptor basicity (β).¹⁹ While relationships of *k* and *D*_N have been reported for some metal complexes,³⁷⁻³⁹ this is not a general relationship.

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The Grunwald-Winstein parameter (Y) has proved to be of value for organic solvolysis reactions.^{11,15} Its operation implies that solvolysis rates are primarily a function of the nucleophilicity and ionizing power of the solvent. Like relationships of $\log k$ and Y have been seen for certain metal complexes in mixed-solvent systems.⁴⁰⁻⁴⁴ Unfortunately, Y values for pure solvents are not extensive. Of the strictly limited values available, an acceptable correlation of $\log k$ and Y exists for $\text{Co}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)^{2+}$. Previously, coordinated CF_3SO_3^- has been shown to exhibit a very low covalent contribution to bonding in the complexes under study.²² The comparatively marked electrostatic nature of the bonding may imply that correlations with parameters reflecting ionizing power of the solvent (such as Y) may be reasonable.

Multiparameter approaches to a description of the solvent dependence of reaction rates has been applied in various organic systems,¹⁹ but only one published example of this approach has appeared for inorganic systems.²⁸ An equation of the form

$$\log k = \log k_0 + aE_T + bD_N \quad (1)$$

has been applied to isomerization of $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$ in various solvents.²⁸ The hydroxylic solvents deviate from the plot, an effect apparently related to their peculiar ability to form specific hydrogen-bonded species. Analysis of the data for the $\text{Co}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)^{2+}$ complex via eq 1 in this case yielded a moderate correlation of $\log k_{\text{obsd}}$ and $\log k_{\text{calcd}}$, again except for hydroxylic solvents, with $k_0 = 6 \times 10^{-8} \text{ s}^{-1}$, $a = 0.032$, and $b = 0.052$. Since E_T/D_N is about 2.5 for most solvents, the aE_T term is a little larger than bD_N generally, with a ratio $aE_T:bD_N$ of about 2:3. This result indicates that solvent basicity effects (reflected in D_N) make almost as significant a contribution to reactivity as do polarity and hydrogen-bond donor acidity for solvolysis of CF_3SO_3^- . This would be consistent with some association of solvent as a base with the metal ion in the transition state, an event that may accord with the negative activation entropies observed.

The consistently negative ΔS^\ddagger values for cobalt(III) in various solvents can be interpreted in two ways. An associative mechanism is usually typified by a negative ΔS^\ddagger when a neutral entering group is involved. However, reactions of cobalt(III) at least are usually asserted to be dissociative in nature,¹ although a limiting mechanism is rarely suggested, and thus some solvent participation in the transition state is required. Since we are dealing with the case of an ionic complex and an ionic leaving group, solvent electrostriction in the precursor and transition states will be markedly different if there is significant separation of the ions in the latter. There should be an increase in electrostriction from the 2+ precursor to the (3+ ... 1-) transition state; this would make a significant negative contribution to ΔS^\ddagger and offset a smaller positive contribution due solely to nuclear displacement. While electrostatic compression in the vicinity of ions will vary with solvent and may be greater for the hydroxylic solvents, it should

be a general phenomenon in the solvents studied, which are all polar.

The increasing negative ΔS^\ddagger from Co to Rh to Ir in all solvents except water implies increasing associative character down the triad but probably tied to a greater extension of the $\text{M}^{3+}-\text{OSO}_2\text{CF}_3$ bond in the transition state and concomitantly greater electrostrictive effects. The two effects are not unreasonably related since the more open character of the octahedral faces where the leaving group bond is stretched allows closer entry of the solvent molecules toward the metal ion with the larger Rh and Ir ions. In terms of the commonly cited mechanisms for reactions, there are thus two viable descriptions. An I_a mechanism, governed chiefly by the ability of a solvent molecule to associate in a nucleophilic manner with the metal ion, may operate. Alternatively, a modified I_d mechanism involving both specific Lewis base solvation of the amines with concomitant electronic effects on the $\text{M}^{3+}-\text{OSO}_2\text{CF}_3$ bond and some Lewis acid interaction of the solvent with the leaving group may apply. An interchange mechanism, with variation in the amount of dissociative and associative character for the different metal ions, would thus seem to accommodate the experimental observations.

Uniqueness of water as a solvent is strongly implied by the experimental results. Presumably the specific solvation properties of water with its three hydrogen-bonding sites on each molecule dominate its behavior. Alcohols, while still protic solvents, are bulkier and have only two effective hydrogen-bonding sites on each molecule, while aprotic solvents exert predominantly dipolar interactions. The peculiar strength of the water solvation "cage" about the complex cation, and the specific ability of a water molecule to hydrogen bond to both the leaving group and nonleaving groups in a "bridging" fashion, may determine a mechanistic constancy for all metal ions where difficulty in breaking the metal-leaving group bond is the paramount consideration, reflected in the ΔH^\ddagger term. A sharp mechanistic variation from water to other solvents is not implied; the differences are more subtle.

For the complexes studied in the chosen solvents, no simple uniparameter relationship of rate constant and solvent property seems to exist. This is not unreasonable given the various ways in which solvent molecules can interact with the leaving and nonleaving groups and the metal ion in the precursor and transition states. Multiparameter relationships appear to offer a better picture and imply that the nucleophilic and ionizing properties of the solvent may be important, at least for CF_3SO_3^- solvolysis. Clearly, more extensive studies of the role of solvent in reactions of coordination complexes need to occur; effects with traditionally associative chromium(III) complexes and the use of activation volume as a mechanistic guide are areas where extension of this research are being pursued. Systematic studies of this type should produce a greater understanding of the role of solvent in inorganic reaction mechanisms.

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Registry No. $[\text{Co}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 75522-50-8; $[\text{Rh}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 84254-57-9; $[\text{Ir}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 84254-59-1; methanol, 67-56-1; dimethyl sulfoxide, 67-68-5; dimethylformamide, 68-12-2; acetonitrile, 75-05-8; pyridine, 110-86-1; ethanol, 64-17-5; formamide, 75-12-7; methylformamide, 123-39-7; trimethyl phosphate, 512-56-1.

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