

Scheme I. Reaction Sequence for the Synthesis of Thioiridium(I) Complexes

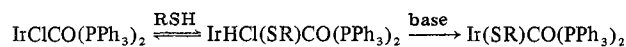


Table I. Infrared Spectral Data for Compounds $\text{IrHCl}(\text{SR})\text{CO}(\text{PPh}_3)_2^a$

R	ν_{IrH} , cm^{-1}	ν_{CO} , cm^{-1}	R	ν_{IrH} , cm^{-1}	ν_{CO} , cm^{-1}
Et	2240	2045	Cy	2260	2045
<i>i</i> -Pr	2250	2040	Ph ⁶	2263	2029
<i>n</i> -Bu	2240	2045	<i>p</i> -tol	2259	2030

^a The values are accurate to within $\pm 5 \text{ cm}^{-1}$.

Table II. Analytical Data for Compounds $\text{Ir}(\text{SR})\text{CO}(\text{PPh}_3)_2$

R	% C		% H		Mol wt (C_6H_6)	
	Calcd	Found	Calcd	Found	Calcd	Found
Et	58.1	57.9	4.38	4.27	805	794
<i>i</i> -Pr	58.6	57.9	4.55	4.49	819	823
<i>n</i> -Bu	59.0	58.3	4.71	4.86	833	835
Cy	60.1	59.3	4.81	4.83	859	840
Ph	60.5	59.6	4.13	4.13		
<i>p</i> -tol	60.9	60.3	4.30	4.19	867	840

Table III. Spectral Data for Compounds $\text{Ir}(\text{SR})\text{CO}(\text{PPh}_3)_2$

R	ν_{CO} , cm^{-1}	τ , ppm	J , Hz
Et	1945	9.48 (Me), 7.97 (CH_2)	7.0
<i>i</i> -Pr	1940	9.55 (Me)	6.5
<i>n</i> -Bu	1952	7.9, 9.2 (multiplets)	
Cy	1955	9.0 (multiplets)	
Ph	1950		
<i>p</i> -tol	1950		

dition of RSH to $\text{IrClCO}(\text{PPh}_3)_2$, followed by strong base elimination of HCl. The intermediate hydro complexes $\text{IrHCl}(\text{SR})\text{CO}(\text{PPh}_3)_2$, which are unstable to spontaneous reductive elimination of RSH, have been characterized by ir spectroscopy (Table I). However, when these compounds are suspended in methanol and treated with excess of a methanolic solution of NaOMe, reductive elimination of HCl occurs and the compounds $\text{Ir}(\text{SR})\text{CO}(\text{PPh}_3)_2$ are formed. The reaction proceeds readily with other strong bases, and NaOH, 1,5-diazabicyclo[4.3.0]non-5-ene, and potassium 2,6-di-*tert*-butyl phenoxide have been successfully used. The reduction of $\text{IrHCl}(\text{SPh})\text{CO}(\text{PPh}_3)_2$ to $\text{Ir}(\text{SR})\text{CO}(\text{PPh}_3)_2$ fails with ammonia, triethylamine, pyridine, and 1,8-bis(dimethylamino)naphthalene. The synthetic procedure with strong bases can be carried out without the isolation of hydroiridium(III) intermediates, since the preparation of $\text{Ir}(\text{SR})\text{CO}(\text{PPh}_3)_2$ can be accomplished from $\text{IrClCO}(\text{PPh}_3)_2$ by initial treatment with PhSH followed by NaOMe. Our procedure was unsuccessful for the synthesis of $\text{Ir}(\text{S-}i\text{-Bu})\text{CO}(\text{PPh}_3)_2$ probably because of the failure of the initial oxidative addition step to proceed to any significant extent.

These compounds irreversibly add oxygen to form $\text{Ir}(\text{SR})\text{CO}(\text{O}_2)(\text{PPh}_3)_2$, which show diagnostic bands in the ir spectrum in the region of 1990 and 840 cm^{-1} . The spectra of the dioxygen complexes show no new bands at 1050, 1300–1350, or 1140 cm^{-1} for the oxidation of sulfur to a coordinated sulfoxide or sulfone. The sulfur ligand is removed with strong acid since treating $\text{Ir}(\text{SPh})\text{CO}(\text{PPh}_3)_2$ with HCl gives $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$.

The reaction sequence for the formation of these iridium(I) complexes is shown in Scheme I. The stereochemistry of $\text{IrHCl}(\text{SPh})\text{CO}(\text{PPh}_3)_2$ is reported to have a geometry with H and Cl mutually trans,⁶ which suggests that the reductive elimination of the strong acid must occur from this stereochemical arrangement. It is probable that in the basic medi-

um there is also removal of RSH; however this would form NaSR which would undergo metathetical replacement with $\text{IrClCO}(\text{PPh}_3)_2$ in the time duration of the reaction. The proportion of each acid eliminated cannot be estimated since the final product is solely $\text{Ir}(\text{SR})\text{CO}(\text{PPh}_3)_2$, and the ir spectra show no bands in the region of 315 cm^{-1} for the Ir–Cl stretch.

In conclusion it may be stated that this synthetic procedure is a useful general method for the preparation of monomeric alkyl- and arylthioiridium(I) complexes in good yield.

Experimental Section

Microanalyses were carried out by Chemalytics Inc., Tempe, Ariz. Molecular weights were measured on a Hitachi Perkin-Elmer Model 115 vapor phase osmometer as solutions in benzene. The benzene solutions were prepared with the careful exclusion of air. The syringe system of the osmometer was purged with nitrogen in order to maintain the solutions in an oxygen-free atmosphere. At the completion of the measurements the solutions were the original bright yellow color and not the orange color of the oxygen complex. The equilibration time of the thermistor system is 2 min, and the solutions are air stable for significantly longer periods than this. As a further check on the validity of the molecular weight measurements we determined the value for $\text{Ir}(\text{S-}p\text{-tol})\text{CO}(\text{O}_2)(\text{PPh}_3)_2$. The found value was 871 which shows an increase of 31 over the value for $\text{Ir}(\text{S-}p\text{-tol})\text{CO}(\text{PPh}_3)_2$. Infrared spectra were obtained on a Perkin-Elmer Model 700 spectrometer as Nujol mulls and all operations were carried out in an inert atmosphere.

Method of Preparation of the Complexes. To a suspension of $\text{IrClCO}(\text{PPh}_3)_2$ in benzene was added an excess of the appropriate thiol. The reaction mixture became homogeneous and then $\text{IrHCl}(\text{SR})\text{CO}(\text{PPh}_3)_2$ slowly precipitated. The solid was filtered and quickly transferred into dry methanol, and a solution of NaOMe was added. After 48 hr the bright yellow complex was filtered with the careful exclusion of air. The complex was washed with dry methanol and ether, dried *in vacuo*, and stored in evacuated ampoules. The yield was essentially quantitative. As a representative example, the *p*-tol derivative was prepared using $\text{IrClCO}(\text{PPh}_3)_2$ (1.00 g) and *p*-toluenethiol (0.162 g) in benzene (20 ml). After 24 hr the complex obtained was reduced with sodium (0.35 g) in methanol (10 ml) by the addition of this solution to $\text{IrHCl}(\text{S-}p\text{-tol})\text{CO}(\text{PPh}_3)_2$ in methanol (10 ml). The analytical and spectral data for the complexes are shown in Tables II and III, respectively.

The complexes $\text{Ir}(\text{SR})\text{CO}(\text{O}_2)(\text{PPh}_3)_2$ were obtained by allowing a solution of the iridium(I) compound in oxygen-saturated benzene to stand for 24 hr at room temperature.

Acknowledgments. We wish to thank Mr. T. B. Rauchfuss for helpful discussions and for carrying out the molecular weight determinations. This work was supported by the National Science Foundation under Grant No. GP 38775.

Registry No. $\text{IrClCO}(\text{PPh}_3)_2$, 14871-41-1; $\text{IrHCl}(\text{SEt})\text{CO}(\text{PPh}_3)_2$, 51935-87-6; $\text{IrHCl}(\text{S-}i\text{-Pr})\text{CO}(\text{PPh}_3)_2$, 51935-88-7; $\text{IrHCl}(\text{S-}n\text{-Bu})\text{CO}(\text{PPh}_3)_2$, 51935-89-8; $\text{IrHCl}(\text{SCy})\text{CO}(\text{PPh}_3)_2$, 51935-90-1; $\text{IrHCl}(\text{S-}p\text{-tol})\text{CO}(\text{PPh}_3)_2$, 52019-99-5; $\text{Ir}(\text{SEt})\text{CO}(\text{PPh}_3)_2$, 51935-91-2; $\text{Ir}(\text{S-}i\text{-Pr})\text{CO}(\text{PPh}_3)_2$, 51935-92-3; $\text{Ir}(\text{S-}n\text{-Bu})\text{CO}(\text{PPh}_3)_2$, 51935-93-4; $\text{Ir}(\text{SCy})\text{CO}(\text{PPh}_3)_2$, 51935-94-5; $\text{Ir}(\text{SPh})\text{CO}(\text{PPh}_3)_2$, 51935-95-6; $\text{Ir}(\text{S-}p\text{-tol})\text{CO}(\text{PPh}_3)_2$, 51935-96-7.

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Nucleophilic Substitution on Sulfur. Reactions of *S*-Methyl-*S*-phenylsulfiminium Ion with Iodide and Thiourea

James H. Krueger* and Richard J. Kiyokane

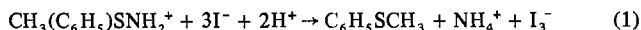
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Several reactions involving nucleophilic substitution at sul-

(6) C. V. Senoff, *Can. J. Chem.*, **48**, 2444 (1970).

fonium sulfur centers have been described.¹ The kinetics and mechanisms of reaction of the *S,S*-dimethylsulfiminium ion, $(\text{CH}_3)_2\text{SNH}_2^+$, with iodide and thiourea have been reported,² and we now report results for the related $\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+$ species. Reaction 1 presumably involves substi-



tution on sulfur and it was of interest to examine the influence of solvent and of the phenyl group on the rate of this reaction, in addition to identifying other nucleophiles that possess reactivity toward $\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+$.

Experimental Section

Solvent and Reagents. Dimethyl sulfoxide (DMSO, Crown-Zellerbach commercial grade) was distilled and aqueous mixtures were prepared as described previously.³ The solvents were purged with pre-purified nitrogen for runs involving higher hydrogen ion concentrations. Reagent grade solids were used as received, after drying at 110°.

$\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2\text{ClO}_4$. This compound was prepared using procedures reported for dimethylsulfiminium salts.^{2,4} A solution of 11.4 g (0.20 mol) of NaOCH_3 in 140 ml of dry methanol and 21.3 g (0.19 mol) of hydroxylamine-*O*-sulfonic acid⁵ in 150 ml of dry methanol (S°) were simultaneously added in portions to 24 ml (0.20 mol) of methyl phenyl sulfide (Aldrich, 99%) over a period of 3 hr at 5°. After 1 additional hr of stirring, Na_2SO_4 was removed and the solution (pH ~7) concentrated under vacuum to ca. 40 ml. To 10 ml of the resulting yellow solution was added an equivalent amount of sodium perchlorate in methanol. After 24 hr the Na_2SO_4 was removed and a tenfold excess of anhydrous ether was added slowly. The crude product was purified by dissolving a 1.5-g quantity in 1 ml of dry methanol, followed by 10 ml of chloroform. After storage for 24 hr at 0°, the Na_2SO_4 that had separated was removed and the product was precipitated by addition of ether. After repeating the recrystallization, the resulting white, powdery product was washed with ether and stored *in vacuo* over P_2O_5 . Although no difficulty was experienced, this perchlorate is potentially hazardous and should be prepared in small quantities and handled with care.

The product (mp 61°) was 95–98% pure based on iodometric analysis. *Anal.* Calcd for $\text{C}_7\text{H}_{10}\text{ClNO}_4\text{S}$: C, 35.08; H, 4.21; N, 5.85. Found: C, 34.84; H, 4.33; N, 5.94. Ir (Nujol or Kel-F) (cm^{-1}): 3360 (s), 3240 (s), 3020 (w), 2930 (w), 1580 (w), 1560 (w), 1475 (w), 1440 (s), 1420 (m), 1170–1040 (s) (ClO_4^-), 750 (s), 680 (s). ¹H nmr (Varian HA-100, in D_2O ; vs. DSS, internal): δ 3.4 (CH_3), 7.9 (C_6H_5); relative areas 0.61:1.00. Uv spectrum: ϵ 800 $M^{-1} \text{cm}^{-1}$ at λ_{max} 265 nm.

Kinetics. Increases in absorbance were measured using a Cary 16K spectrophotometer at 265 nm or, in the case of the initial-rate studies in 0.50–1.00 mole fraction of DMSO, at 365 nm (ϵ_{365} 25,800 $M^{-1} \text{cm}^{-1}$ for I_3^-). Blank corrections (1–3%) arising from oxidation of iodide by DMSO were applied in DMSO-containing solvents.³

Results

Reactions in Water. The stoichiometry in eq 1 was verified by titrimetric analysis of hydrogen ion consumed and total iodine produced and by comparison of infinite-time absorbances with values expected for the products. Reactions with iodide in water were carried out with H^+ and I^- in large excess. Plots of $\log(A_\infty - A)$ vs. time were linear for the extent of reaction examined, ca. 2–4 half-lives. Observed first-order rate constants were obtained over the range of initial concentrations shown in Table I, leading to rate law (2). At 20.0° and 0.120 *M* ionic strength, $k_1 = 0.96 \pm 0.02$

$$d[\text{I}_3^-]/dt = k_1 [\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+][\text{I}^-][\text{H}^+] \quad (2)$$

$M^{-2} \text{sec}^{-1}$. Values at 10.4, 29.7, and 40.2° were 0.45, 1.90, and 4.0 $M^{-2} \text{sec}^{-1}$, respectively, giving $\Delta H^\ddagger = 12.3 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -16.6 \pm 0.4$ eu. In several runs Br^- , Cl^- ,

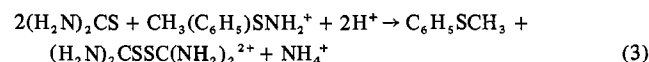
Table I. Kinetics of the *S*-Methyl-*S*-phenylsulfiminium-Iodide Reaction in Water at 20.0° and 0.120 *M* Ionic Strength^a

$10^2[\text{I}^-]_0, M$	$10^2[\text{H}^+]_0, M$	$10^5[\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+]_0, M$	$k_1, M^{-2} \text{sec}^{-1}$
0.53	10.0	4.4	0.98
1.31	2.08	1.33	0.97
2.13	2.08	4.6	0.97
3.01	2.08	2.84	0.96
3.02	2.08	4.6	0.98
3.02	2.08	4.4	0.96
3.04	1.04	4.6	0.94
4.03	2.08	4.4	0.97
4.13	3.93	4.9	0.96
4.17	3.93	4.8	0.96
4.22	3.93	4.8	0.93
4.22	2.08	2.84	0.97
4.24	2.08	4.8	0.95
6.08	0.42	2.39	0.96
6.08	1.96	2.19	0.94
8.06	0.98	2.19	0.95
8.07	0.98	2.19	0.97

^a Maintained using NaClO_4 . ^b Added HClO_4 .

or SCN^- was added at the 0.1 *M* level. No rate increases were observed, indicating that these potential nucleophiles are far less reactive than iodide.

Thiourea reacted with $\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+$ according to (3) as judged by analysis of infinite-time absorbances. The kinetics of (3) were measured with initial concentrations in

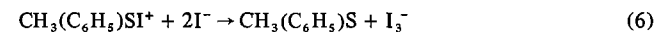
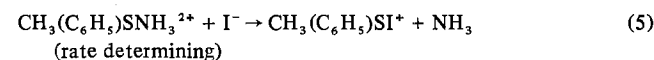
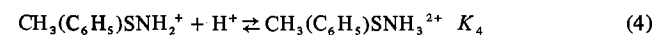


the ranges $[\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+]_0 = (8.5\text{--}10.0) \times 10^{-5} M$, $[(\text{H}_2\text{N})_2\text{CS}]_0 = (2.0\text{--}4.7) \times 10^{-3} M$, and $[\text{H}^+]_0 = 0.039\text{--}0.20 M$. Plots of $\log(A_\infty - A)$ vs. time were linear and the resulting data, analyzed assuming the rate law $-d[(\text{H}_2\text{N})_2\text{CS}]/dt = k_{\text{tu}}[\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+][(\text{H}_2\text{N})_2\text{CS}][\text{H}^+]$, yielded $k_{\text{tu}} = 17.9 \pm 0.4 M^{-2} \text{sec}^{-1}$ at 20.0° and $\mu = 0.12 M$.

Reactions in DMSO-Water Solvents. Reaction 1 was studied in several DMSO-water mixtures. Initial rates, obtained from plots of absorbance vs. time with a precision of $\pm 2\%$, were measured as a function of initial concentrations shown in Table II. Rate law (2) was assumed to be valid in DMSO-H₂O (as supported by the more extensive studies in 0.70 mole fraction of DMSO) and analysis of the data using eq 2 gave the third-order rate constants listed in Table II. Addition of Cl^- or Br^- did not catalyze the reaction. Added thiourea catalyzes reaction 1, reacting with $\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+$ to yield an intermediate that is in turn reduced by iodide. In 0.70 mole fraction of DMSO with $[\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+]_0 = 3.69 \times 10^{-4} M$, $[\text{I}^-]_0 = 4.28 \times 10^{-2} M$, $[\text{H}^+]_0 = 3.14 \times 10^{-3} M$, and $[(\text{H}_2\text{N})_2\text{CS}]_0 = 3.99 \times 10^{-3} M$, the initial rate was $3.73 \times 10^{-9} M \text{sec}^{-1}$ compared with $1.74 \times 10^{-9} M \text{sec}^{-1}$ in the absence of thiourea. These results give $k_{\text{tu}} = 0.43 M^{-2} \text{sec}^{-1}$ using $k_1 = 0.034 M^{-2} \text{sec}^{-1}$ and the rate law $d[\text{I}_3^-]/dt = \{[\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+][\text{H}^+]\} \{k_1[\text{I}^-] + k_{\text{tu}}[(\text{H}_2\text{N})_2\text{CS}]\}$, analogous to that found for the reaction of $(\text{CH}_3)_2\text{SNH}_2^+$ with thiourea.²

Discussion

The results support the mechanism given by eq 4–7 for re-



- (1) J. L. Kice, *Progr. Inorg. Chem.*, **17**, 147 (1972).
- (2) J. H. Krueger, *J. Amer. Chem. Soc.*, **91**, 4974 (1969).
- (3) J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).
- (4) R. Appel and W. Buchner, *Chem. Ber.*, **95**, 849 (1962).

Table II. Kinetics of the *S*-Methyl-*S*-phenylsulfiminium-Iodide Reaction in DMSO-Water Solvents at 20.0° and 0.120 *M* Ionic Strength

$10^2 [I^-]_0, M$	$10^2 [H^+]_0, M$	$10^4 [CH_3-(C_6H_5)SNH_2^+]_0, M$	$k_I, M^{-2} \text{ sec}^{-1}$
0.50 Mole Fraction of DMSO			
1.01	7.86	3.73	0.0218
2.10	7.86	3.73	0.0227
			Av 0.022
0.70 Mole Fraction of DMSO			
0.60	3.93	3.84	0.038
0.60	1.96	3.84	0.035
3.13	0.393	3.84	0.038
5.61	0.393	4.29	0.034
6.04	0.393	3.85	0.032
6.04	0.393	7.7	0.034
6.26	0.393	3.84	0.035
7.00	0.393	2.03	0.036
			Av 0.035
6.03	0.393	3.85	0.032 ^a
0.00	0.393	2.03	0 ^b
5.61	0.393	4.29	0.034 ^c
1.00 Mole Fraction of DMSO			
5.15	0.314	1.91	0.014

^a 0.010 *M* KBr added. ^b 0.30 *M* NaBr, λ 265 nm. ^c 0.016 *M* KCl added.

action 1. Substitution takes place at the sulfur center (eq 5). Substitution on nitrogen, which would lead to the same products, can be eliminated by a comparison of the results with those obtained for reactions of $H_2\ddot{N}OSO_3^-$. The hydroxylamine-*O*-sulfonate anion is known to undergo substitution on nitrogen.^{5,6} Protonation to give $H_3N^+-OSO_3^-$ does not, in general, lead to an increase in reactivity. In contrast, incorporation of a proton in the activated complex⁷⁻⁹ is crucial for the reaction of $CH_3(C_6H_5)SNH_2^+$ with iodide. Furthermore, in neutral solution, thiosulfate ion is highly

(5) J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, **12**, 2714 (1973).

(6) P. F. Blanchet and J. H. Krueger, *Inorg. Chem.*, **13**, 719 (1974).

(7) Presumably as in eq 4, although the timing of inclusion of the proton is open to question. For analogous reactions of sulfoxides it has been suggested^{5,9} that addition of the halide ion nucleophile to form $R(Ar)S(X)OH$ occurs prior to inclusion of the second proton required.

(8) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).

(9) G. Scorrano, *Accounts Chem. Res.*, **6**, 132 (1973).

reactive toward $H_2\ddot{N}OSO_3^-$ yet shows no significant reactivity toward $CH_3(C_6H_5)SNH_2^+$ under the same conditions.

The largest k_I values were observed in aqueous solution; in solvents of increasing DMSO content, k_I values decrease, go through a minimum near 0.50 mole fraction of DMSO, and then increase with further increases in DMSO content. The results closely resemble those observed² for $(CH_3)_2SNH_2^+$ in which $\log k_I$ paralleled pK_a for the *m*-nitroanilinium ion (an indicator of the proton-donating ability of the solvent mixture) over the entire solvent range. This behavior arises from the importance of equilibrium 4 in determining the rate.

In water at 20°, the ratio of third-order rate constants for reaction of $CH_3(C_6H_5)SNH_2^+$ and of $(CH_3)_2SNH_2^+$, $k_{(CH_3)(C_6H_5)}/k_{(CH_3)_2}$, is 2.6 with iodide and 1.2 with thiourea. Extensive studies have been made of analogous acid-catalyzed reactions of alkyl aryl sulfoxides with halide ions, which proceed *via* substitution at sulfur with an H_2O molecule as the leaving group. The results indicate that the dominant influence of the R group and Ar group is to alter the basicity of the substrate sulfoxide.⁹⁻¹¹ Electron-withdrawing groups decrease the basicity of sulfoxides and, by analogy, $CH_3(C_6H_5)SNH_2^+$ would be expected to react less rapidly than $(CH_3)_2SNH_2^+$, due to a decrease in K_4 . The somewhat greater steric requirements of the phenyl group would also lead to a decrease in substitution rate on sulfur. The slightly greater reactivity observed for $CH_3(C_6H_5)SNH_2^+$ suggests that the phenyl group provides a net stabilizing influence on going to the transition state, possibly by delocalization of the increased positive charge that develops on sulfur in the transition state.

Sulfonium sulfur in $CH_3(C_6H_5)SNH_2^+$, with its three bond pairs and one lone pair of electrons, is a predominantly soft electrophilic center as evidenced by the substantial reactivity of iodide (>bromide, chloride) and thiourea.

Acknowledgment. This work was supported by the National Science Foundation under Grant GP-7981.

Registry No. $CH_3(C_6H_5)SNH_2ClO_4$, 51934-47-5; methyl phenyl sulfide, 100-68-5; iodide, 20461-54-5; thiourea, 62-56-6; hydroxylamine-*O*-sulfonic acid, 2950-43-8.

(10) For example, $\rho = -0.90$ for HI reduction of para-substituted aryl methyl sulfoxides,⁸ but this largely reflects the influence of substitution on the protonation equilibrium $CH_3(Ar)SO + H^+ \rightleftharpoons CH_3(Ar)SOH^+$.¹¹

(11) Reference 1, p 185.

Correspondence

Mechanism of Hydroxo-Bridge Cleavage in Dicobalt(III) Complexes

AIC401587

Sir:

Octahedral divalent transition metal ions have been shown to undergo substitution by an $SN1$ process,^{1,2} and more

(1) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, for a definition of terms $SN1$ etc. and examples. C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, have introduced alternative terminology.

(2) K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

recently interest has reverted to reactions of trivalent metal ions. Substantial evidence has been obtained for an $SN1$ mechanism in the acid hydrolysis of pentaamminecobalt(III) complexes $[Co(NH_3)_5X]^{(3-n)+}$.³ Varying degrees of associative character have however been proposed for reactions of other trivalent ions, including the d^6 complexes $[Rh(NH_3)_5H_2O]^{3+}$ and $[Ir(NH_3)_5H_2O]^{3+}$,⁴ as well as coordinatively unsaturated octahedral complexes with low d-electron populations.⁵⁻⁷

(3) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965); A. Haim, *ibid.*, **9**, 429 (1970).

(4) D. Gattegno and F. Monacelli, *Inorg. Chim. Acta*, **7**, 370 (1973), and references therein.

(5) H. Diebler, *Z. Phys. Chem. (Frankfurt am Main)*, **68**, 64 (1969).