

of the metal and that the concentration of the complex is essentially constant. The last assumption will be true if the complex ion is relatively stable, since, under this condition, virtually all of the reduced metal ion will be in the form of complex ions. The assumption that a stable complex is formed with only the reduced form of the metal was made since, in practically all cases,<sup>1,2</sup> the stable complexes isolated have been complexes of the reduced form of the metal.

**Titanium Chloride System.**—Figure 1 shows the

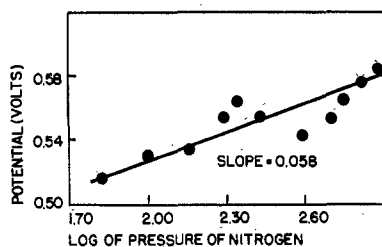


Figure 1.—The relationship between potential (compared to the saturated calomel electrode) and nitrogen pressure in the dimethyl sulfoxide-titanium(III) chloride-titanium(IV) chloride system.

results of a typical run obtained in dimethyl sulfoxide solutions for the titanium(III) chloride-titanium(IV) chloride system. As can be seen, the slope of the graph is 0.058 which indicates that  $r/q$  is equal to 1 or that there is one metal atom for each nitrogen molecule in the complex. This indicates that the formula of the complex in this solvent is probably similar to the formulas of known nitrogen complexes with rhodium, iridium, ruthenium, cobalt, and osmium.

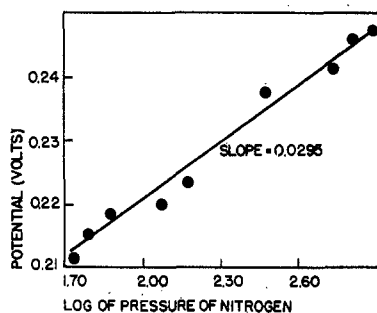


Figure 2.—The relationship between potential (compared to the saturated calomel electrode) and nitrogen pressure in the propylene carbonate-titanium(III) chloride-titanium(IV) chloride system.

Figure 2 shows typical results obtained in propylene carbonate solutions. The slope in this case (0.0295) corresponds to an  $r/q$  value of  $1/2$  which corresponds to a ratio of two metal atoms to one nitrogen molecule. This indicates that the formula of the complex in this solvent is similar to that of the ruthenium complex identified by Taube,<sup>5</sup> in that the nitrogen acts as a bridge between two metal atoms. In both of these experiments, the data shown on the graph were obtained in a random fashion in that some measurements

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were made as the pressure was increased and others were made as the pressure was decreased.

In summary, the potentiometric study has indicated that in dimethyl sulfoxide titanium(III) chloride forms a 1:1 complex with nitrogen. On the other hand, in propylene carbonate titanium(III) chloride forms a complex in which one nitrogen molecule acts as a bridge between two titanium atoms.

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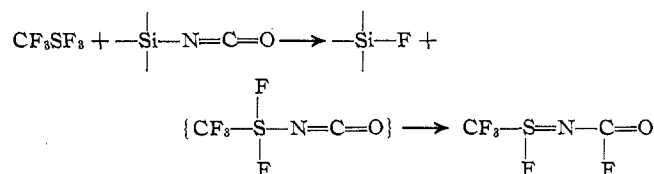
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### The Preparation of N-Fluoroformyliminotrifluoromethylsulfur Fluoride, $\text{CF}_3\text{SF}=\text{NCFO}$

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Trifluoromethylsulfur trifluoride<sup>1</sup> reacts with silicon tetracyanate forming the colorless liquid N-fluoroformyliminotrifluoromethylsulfur fluoride ( $\text{CF}_3\text{SF}=\text{NCFO}$ ) and silicon tetrafluoride:  $4\text{CF}_3\text{SF}_3 + \text{Si}(\text{NCO})_4 \rightarrow 4\text{CF}_3\text{SFNCFO} + \text{SiF}_4$ . This reaction is analogous to that of sulfur tetrafluoride and silicon tetracyanate reported by Clifford and Kobayashi<sup>2</sup> and to the reaction of thionyl tetrafluoride and silicon tetracyanate reported by Ruff.<sup>3</sup> A plausible route to the product involves  $\text{CF}_3\text{SF}_3$  addition with silicon-nitrogen cleavage and then rearrangement of the resulting species to product



#### Experimental Section

**Materials.**—Silicon tetracyanate<sup>4</sup> was prepared through the reaction of silver cyanate with silicon tetrachloride. Trifluoromethylsulfur trifluoride was obtained using a modification of the procedure suggested by Lawless and Harman.<sup>10</sup> Bistrifluoromethyl disulfide (Peninsular ChemResearch, 20 mmol) was condensed into a 100-ml Monel cylinder which had previously been charged with 28.9 g (194 mmol) of  $\text{AgF}_2$  (Harshaw). The cylinder was rapidly warmed to  $0^\circ$  and then was allowed to warm to room temperature overnight. An infrared spectrum of the gaseous product mixture after this reaction indicated the presence of  $\text{CF}_3\text{SF}_3$ ,  $\text{CF}_3\text{SF}_5$ , and  $\text{CF}_3\text{SSCF}_3$ . The desired trifluoromethylsulfur trifluoride was then isolated as a solid  $\text{CF}_3\text{SF}_3 \cdot \text{BF}_3$  ad-

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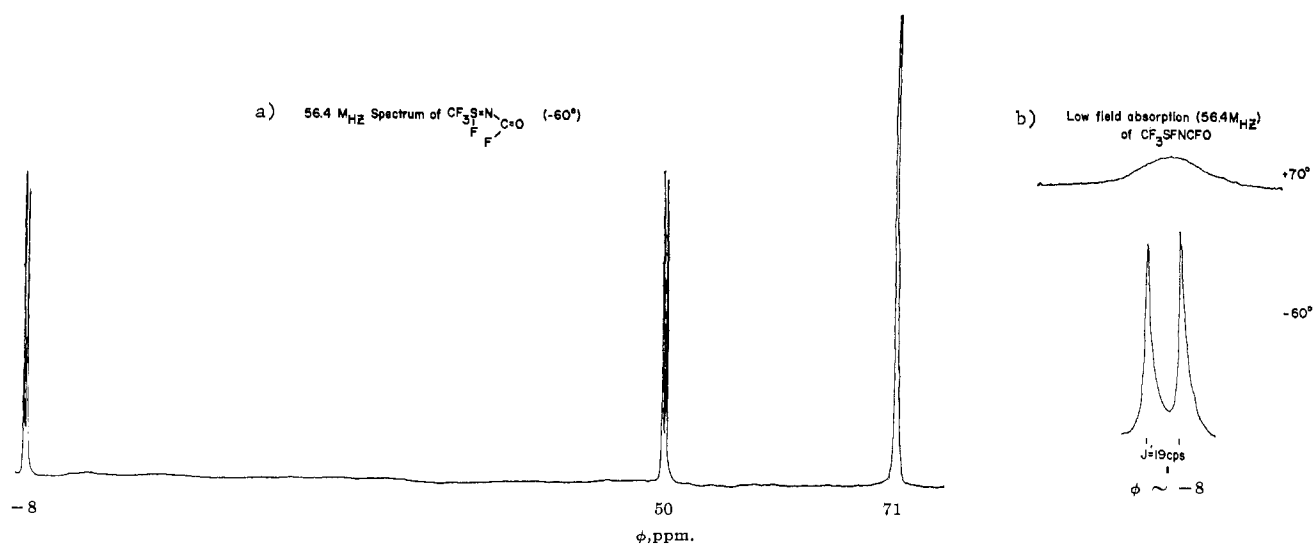


Figure 1.

duct<sup>5</sup> (at  $-65^\circ$ ) by contacting the volatile products with an equivalent molar quantity of  $\text{BF}_3$ , cooling to  $-65^\circ$ , and then removing the other materials readily volatile at that temperature. Trifluoromethylsulfur trifluoride (20 mmol) was obtained for use by treating the  $\text{BF}_3$  adduct with an excess of anhydrous potassium fluoride in a 75-ml stainless steel Hoke cylinder at  $100^\circ$  for several hours.

**Reaction.**—Trifluoromethylsulfur trifluoride (20 mmol) was vacuum transferred to a 100-ml Hoke Monel cylinder to which 0.98 g (5 mmol) of silicon tetracyanate had been added. The mixture was held at  $100^\circ$  for 24 hr and then was cooled to room temperature, and the volatile contents were passed through traps in series at  $-65$  and  $-195^\circ$ . Infrared analysis of the materials in the  $-195^\circ$  trap indicated the presence of  $\text{SiF}_4$ ,  $\text{CF}_3\text{SF}_3$ ,  $\text{CF}_3\text{SOF}$ , and a trace of  $\text{COF}_2$ . The  $-65^\circ$  trap contained the desired colorless liquid  $\text{CF}_3\text{SFNCFO}$ . The yield of  $\text{CF}_3\text{SFNCFO}$  obtained after several fractional condensation passes was 2.13 g, representing at least a 58% conversion based on  $\text{Si}(\text{NCO})_4$  used.

**Analytical Data.**—The chemical analysis of  $\text{CF}_3\text{SFNCFO}$  was carried out on a sample by Swarczkopf Microanalytical Laboratory. *Anal.* Calcd for  $\text{C}_2\text{F}_5\text{NOS}$ : C, 13.27; F, 52.46; N, 7.74; S, 17.70. Found: C, 13.34; F, 52.20; N, 7.84; S, 17.84. The molecular weight determined by gas density measurements in a calibrated bulb at room temperature yielded an average value of 182.2 (calcd for  $\text{CF}_3\text{SFNCFO}$ , 181.1). Vapor pressures were determined as a series of boiling points at different pressures using a method previously described.<sup>6</sup> Vapor pressures in the range  $+3$  to  $+50^\circ$  yielded an extrapolated normal boiling point of  $74.9^\circ$ , a heat of vaporization of 9.30 kcal/mol, and a Trouton constant of 26.7 eu. The data fit the expression  $\log P_{\text{Tot}} = [(-2.033/T) \times 10^3] + 8.720$ .

## Results

**Mass and Infrared Spectra.**—The mass spectrum was obtained at an ionization potential of 70 V. The spectrum included, in order of decreasing intensity, peaks assigned to  $\text{CF}_3^+$ ,  $\text{SN}^+$ ,  $\text{FSCOF}^+$ ,<sup>7</sup>  $\text{FSNCO}^+$ ,  $\text{COF}^+$ ,  $\text{F}_2\text{SNCOF}^+$ ,<sup>7</sup>  $\text{SF}^+$ ,  $\text{SF}_2^+$ ,  $^{-13}\text{CF}_3^+$ ,  $\text{SO}^+$ ,  $^{-34}\text{SN}^+$ ,  $\text{SNCO}^+$ ,  $\text{CF}_3\text{SNCO}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}_3\text{SN}^+$ , ? ( $m/e$  90),  $\text{F}_2\text{CS}^+$ , and  $\text{CFS}^+$ . Infrared spectra were studied using a Perkin-Elmer 521 spectrometer. The gaseous

samples were contained in a 10-cm glass cell with NaCl windows. The infrared spectra of  $\text{CF}_3\text{SFNCFO}$  showed absorptions ( $\text{cm}^{-1}$ ) at 1855 (w, sh),<sup>7</sup> 1800 (s), 1320 (w, sh),<sup>7</sup> 1250 (vs), 1132 (vs), 900 (m), 848 (m), 771 (m), 712 (s), and 668 (w). The absorption at  $1800\text{ cm}^{-1}$  is assigned to the  $\text{C}=\text{O}$ <sup>8</sup> group. The intense broad absorptions centered at 1132 and  $1250\text{ cm}^{-1}$  are attributed to  $\text{CF}^9$  and/or  $\text{S}=\text{N}^{2,10,11}$  stretching vibrations. The strong bands at 771 and  $712\text{ cm}^{-1}$  are in the region expected for  $\text{S}-\text{F}$  stretching<sup>2</sup> vibrations.

**Fluorine-19 nmr spectra** were made with a Varian Associates HA-100-IL spectrometer at 94.1 MHz and with a Varian HA-60-IL spectrometer at 56.4 MHz. Trichlorofluoromethane or 1,1,2-trichloro-1,2,2-trifluoroethane was used as an internal standard. Chemical shifts are expressed in ppm with reference to trichlorofluoromethane. Spectra of neat material at 56.4 MHz are shown in Figure 1. The resonance pattern is consistent with the formulation  $\text{CF}_3\text{SF}=\text{NCFO}$ ; three chemically shifted absorptions of relative area 3:1:1 are observed. The  $\phi$  71 ppm peak is assigned to the  $\text{CF}_3$  group<sup>1d</sup> and under high resolution appears as two doublets,  $J = 1.48$  cps and  $J = 0.54$  cps, due to coupling with the SF and CFO fluorine. The two other peaks, both doublets,  $J = 19$  cps ( $-60^\circ$ ) at  $\phi -8$  ppm and  $\phi +50$  ppm, arise from fluorine bound to sulfur and to the carbonyl group. Chemical shifts for fluorine in both CFO and SF environments have been reported in this region hence further assignment was not attempted. For example, reported CF chemical shifts ( $\phi$ ) in this region are:  $\text{F}_2\text{SNCF}_2$ ,  $-18.2$ ;<sup>2</sup>  $(\text{FSO}_2)(\text{OSO}_2\text{F})\text{NCFO}$ ,  $+6.6$ ;<sup>12</sup>  $\text{SF}_5\text{OOCFO}$ ,  $+34.4$ ;<sup>13</sup> reported SF chemical shifts in this region

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(7) The peaks assigned to  $\text{FSCOF}^+$  and  $\text{F}_2\text{SNCF}_2^+$  in the mass spectrum and the infrared absorptions at 1855 and  $1320\text{ cm}^{-1}$  indicate a trace of  $\text{F}_2\text{SNCF}_2$  was contained in the  $\text{CF}_3\text{SFNCFO}$  sample used. This impurity is believed to have resulted from contamination of the initial  $\text{CF}_3\text{SF}_3$  sample with  $\text{SF}_4$  and the subsequent reaction<sup>2</sup> of the  $\text{SF}_4$  with  $\text{Si}(\text{NCO})_4$ .

are:  $F_2SNCF_2$ ,  $-39.7$ ;<sup>2</sup>  $SF_5NSF_2$ ,  $-54.8$ ;<sup>14</sup>  $C_2F_5NSFCF(CF_3)_2$ ,  $26.2$ .<sup>10</sup> The spectra were found to show temperature dependence (see Figure 1). A neat sample yielded sharp doublet structure ( $J = 19$  cps) at  $-60^\circ$  for both the *CFO* and *SF* fluorine signals. This fine structure disappeared, the peaks broadened, and the chemical shift between the *CFO* and *SF* signals decreased as the sample temperature was raised ( $\delta$  58 ppm at  $-60^\circ$  and  $\delta$  55 ppm at  $+70^\circ$ ). The temperature dependence is believed to be the result of an exchange process with a rate at room temperature of the same order of magnitude as the spin coupling.<sup>15</sup> The exchange rate was lowered when the sample was diluted with 1,1,2-trichloro-1,2,2-trifluoromethane; hence the process may be intermolecular. The high Trouton constant (26.7) also suggests association.

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## Stereochemical Course of Addition of Hydrogen Halides to Iridium(I) Complexes. The Effect of Solvents

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Convincing evidence for kinetically controlled *trans* addition of halogens, alkyl halides, acetyl halides, and hydrogen halides to *trans*- $[(C_6H_5)_2CH_3P]_2Ir(CO)Cl$ <sup>1</sup> has been augmented by recent studies<sup>2</sup> which indicate that the addition of methyl bromide or methyl iodide to *trans*- $[(C_6H_5)(CH_3)_2P]_2IrCOCl$  is stereospecifically *trans*. In contrast to these reports is the generalized *cis* addition of diatomic molecules (X-Y) to planar *trans*- $[(C_6H_5)_3P]_2Ir(CO)Cl$  discussed by Vaska.<sup>3</sup> *cis*-Addition products were also reported by others.<sup>4</sup>

Gaseous hydrogen halides (HX) and crystalline *trans*- $[(C_6H_5)_3P]_2Ir(CO)Y$  (Y is a halogen) react to give octahedral *cis*-addition products (*i.e.*, H and X *cis*).<sup>5</sup> The addition of a diethyl ether solution of HBr to a benzene solution of *trans*- $[(C_6H_5)_2CH_3P]_2Ir(CO)Cl$  was reported to give a mixture of products with H and Br

in *trans* as well as *cis* positions.<sup>1</sup> This same mixture was obtained in a similar reaction between HCl and *trans*- $[(C_6H_5)_2CH_3P]_2Ir(CO)Br$ . Similar results, that is the formation of a single product (mixture), have been reported for the reaction of HCl and *trans*- $[(C_6H_5)_3P]_2Ir(CO)Br$  and the reaction of *trans*- $[(C_6H_5)_3P]_2Ir(CO)Cl$  and HBr.<sup>6</sup> Although it would seem from these results that the hydrogen halide addition reaction may not be stereospecific, it has been suggested that the observed mixtures of *cis* and *trans* products may result from stereoselectivity in the original oxidative-addition reaction, followed by subsequent isomerization reactions.<sup>1</sup> This proposal remains to be investigated. The effect of solvents on the stereochemical course of oxidative-addition reactions has not been carefully examined as yet. That the solvent can play a significant role in determining the stereochemistry of certain oxidative-addition reactions has been recently reported.<sup>7</sup> Herein we report experiments which indicate that the addition of hydrogen halide (HX) to square-planar iridium(I) complexes is stereospecifically *cis* in benzene solution. Mixtures of *cis* and *trans* products are obtained in benzene-methanol solution. The stereochemical course of HX addition in other solvents has also been investigated. Experiments designed to determine the origin of the mixtures of *cis*-*trans* products are described.

### Experimental Section

**Reagents.**—Reagent grade benzene was distilled and stored over molecular sieve. Reagent grade chloroform was passed through an alumina column just prior to use. All other solvents which were of reagent grade quality were stored over molecular sieve and used without any further treatment. Matheson anhydrous halogen halides were used without further treatment. Anhydrous hydrogen chloride which was passed through concentrated sulfuric acid gave the same results as the untreated anhydrous hydrogen chloride. The iridium complexes were prepared as previously described.<sup>1,8</sup>

**General Method.**—Approximately 100 mg of iridium complex was placed in a flask which was purged with nitrogen or argon. Sufficient solvent (*e.g.*, 15 ml of dry benzene, 15 ml of benzene-5 ml methanol, 15 ml of benzene-5 ml of acetonitrile, 60 ml of dichloromethane, 15 ml of dimethylformamide, or 30 ml of chloroform) was added to dissolve the iridium complex completely. Special precautions were taken to avoid exposure of these solutions to atmospheric oxygen. Solutions of the anhydrous hydrogen halide in the respective solvents were added dropwise to the yellow solution of the iridium(I) complex, with efficient stirring, until the solution became colorless or until no further color change was observed. At this point argon or nitrogen was immediately bubbled into the solution and the solvent was then stripped on a rotary evaporator. The solid was washed with ether and dried. Similar products were obtained when the volume of solvent was reduced, and diethyl ether, hexane, or methanol was added to precipitate the white solids. Recrystallization of the white solids from benzene-methanol, benzene-hexane, or dichloromethane-ethanol gave decomposition products which were generally yellow. Attempted recrystallization of  $[(CH_3C_6H_4)_3P]_2ClIrCO \cdot HBr$  from benzene-methanol, for example, gave a product with no detectable  $\nu_{Ir-Cl}$ . Thin layer chromatography was conducted on precoated silica gel plates (Brinkmann Instruments,

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