

Proof of the Triphosphine Formula.—The vapor densities of three samples of the presumed P₃(CF₃)₅ were measured in the usual mercury-containing immersible tensimeter⁹ at 35, 43, and 51°, with no difficulty when the immersion was done suddenly and the readings taken quickly. The resulting mol. wt. values were 438, 441, and 443 (calcd. 438.0).

Elementary analyses were performed by decomposition of the triphosphine to known CF₃-phosphines, which were isolated, identified, and measured as vapors or weighed. A 29.0-mg. sample (0.0662 mmole) gave 0.197 mg.-atom of P (calcd. 0.199) and 0.329 mmole of CF₃ groups (calcd. 0.331). A 50.5-mg. sample (0.115 mmole) gave 0.115 mmole of PCF₃ units as tetramer and pentamer and 0.230 mmole of P(CF₃)₂ units as P₂(CF₃)₄, quite in accord with the formula P₃(CF₃)₅.

Volatility of the Triphosphine.—The colorless liquid triphosphine P₃(CF₃)₅ could be separated easily from the less volatile PCF₃ tetramer and pentamer by passage slowly under high vacuum through a trap at -35°, and P₂(CF₃)₄ was removed by repeated passage through a trap at -50°. The vapor-tension values shown in Table I were obtained partly with the sample in a small vertical tube with adjacent wide-bore mercury manometer, and partly by means of the immersible tensimeter, with re-purification before each elevated-temperature reading, and with fast establishment of the temperature. The equation was determined partly by assuming a normal Trouton constant of 21.0 cal./deg. mole, and fits the data as well as could be expected in view of the difficulty of the measurements. It indicates the normal b.p. as 140 ± 5°.

The m.p. of P₃(CF₃)₅ could not be observed because it never formed crystals—only a glass or viscous liquid.

TABLE I

VAPOR TENSIONS OF P₃(CF₃)₅

log P _{mm} = 7.1080 + 1.75 log T - 0.00600T - 2616/T							
t, °C.	0.00	8.4	14.6	19.3	23.9	46.1	71.3
P _{mm} (obsd.)	1.43	2.63	3.87	5.34	7.01	24.2	77.2
P _{mm} (calcd.)	1.43	2.60	3.92	5.30	7.03	24.0	77.1

Spectroscopy.—The ultraviolet spectrum of P₃(CF₃)₅ showed a strong maximum at 2210 Å. Such absorption seems to be characteristic of all P-P bonded polyphosphines.

The infrared spectrum of P₃(CF₃)₅ was recorded for the vapor at pressures no higher than 17 mm. (saturated vapor at the 40° constant temperature of the Beckman IR7 instrument), in cells with 100-mm. path length. After each run the sample was investigated for decomposition products, and in order to allow for their possible effects, the spectra of these—namely, P₂(CF₃)₄ and the mixture of PCF₃ tetramer and pentamer—were recorded

(9) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937).

separately. For most of the pertinent range the cell windows were potassium bromide, but for the lowest frequencies the windows were of polyethylene, as described elsewhere.³

The fundamental frequencies (cm.⁻¹) for P₃(CF₃)₅ and its immediate decomposition products are listed with the probable assignments in Table II. The relative intensities were calculated by the equation $k = (100/P \times L) \log I_0/I$ for pressures and path length in cm., using the values for per cent transmission I at each observed band maximum. The frequencies were corrected by calibration of the instrument at the frequencies of known bands, and are believed to be accurate to 1 cm.⁻¹. Table II omits some ragged and uncertain absorption in the range 530–545 cm.⁻¹ ($k = 0.3$ or less), for both P₃(CF₃)₅ and P₂(CF₃)₄, but not found for the PCF₃ tetramer-pentamer mixture. However, the pressures of the vapor of that mixture never were very high, and the effect might have been missed.

TABLE II

INFRARED SPECTRA OF P₃(CF₃)₅ AND ITS DECOMPOSITION PRODUCTS^a

Probable assignment	—P ₃ (CF ₃) ₅ —		—P ₂ (CF ₃) ₄ —		—(PCF ₃) _{4,5} —	
	Freq.	k	Freq.	k	Freq.	k
C-F stretching	1194	82	1193	74
	1172	113	1169	151	1173	13
	1152	114	1154	64	1154	60
	1133.5	70	1141	84	1135	26
	1119	90	1120	70
CF ₃ , δ-e	747	4.7	749	5.5	742	4
CF ₃ , δ-a	562	1.0	560	1.2	553	0.3
P-C stretching	480	0.16
	455	2.0
	443	2.1	442	6.7	434	1.4
CF ₃ rocking	388	1.2	363	0.4	353?	?
	350	1.5	342	0.6

^a Abbreviations: δ = deformation; e = symmetric; a = asymmetric.

A Probable New Diphosphine.—The initial syntheses of P₃(CF₃)₅ usually gave small yields (*e.g.*, 10%) of a by-product which was not fully characterized but probably was the new diphosphine CF₃HP-P(CF₃)₂. Its vapor tension at 0° was 61 mm. and its vapor-phase mol. wt. was 269.6 *vs.* calcd. 270.0. Its infrared spectrum did not distinctly show P-H stretching, possibly because the ragged group of C-F stretching overtones covered the expected sharp peak. However, a medium-strong band at 1070 cm.⁻¹ seems assignable to P-H bending. The compound seemed unstable, for repeated high-vacuum fractional condensation always yielded small amounts of the expected decomposition products (CF₃)₂PH and the PCF₃ tetramer and pentamer.

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Synthesis and Chemistry of SF₅Cl

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Sulfur chloride pentafluoride, SF₅Cl, has been prepared in high yield from the reaction of sulfur tetrafluoride, chlorine, and cesium fluoride. Evidence is presented for the intermediate formation of CsSF₅ in this synthesis. Through the ultraviolet light-catalyzed addition of SF₅Cl to nitriles and subsequent substitution or replacement reactions, a wide range of novel SF₅N< derivatives has been prepared.

Synthesis of SF₅Cl.—Sulfur chloride pentafluoride has been prepared by electrolysis of sulfur dichloride-hydrogen fluoride mixtures,¹ by chlorination of disulfur decafluoride,² by reaction of sulfur dichloride and fluorine,³ and by addition of chlorine fluoride to sulfur tetrafluoride.⁴ Only the last method has given good conversions to SF₅Cl.

We have now found a simple, high-yield synthesis of SF₅Cl in a novel chlorofluorination of sulfur tetrafluoride.



- (1) E. L. Muetterties, U. S. Patent 2,937,123 (1960).
- (2) J. W. George and F. A. Cotton, *Proc. Chem. Soc.*, 317 (1959).
- (3) H. L. Roberts and N. H. Ray, *J. Chem. Soc.*, 665 (1960).
- (4) F. Nyman and H. L. Roberts, *ibid.*, 3180 (1962).

Other metal fluorides, *e.g.*, potassium fluoride and silver(I) fluoride, have been successfully substituted for cesium fluoride. However, the conversions to SF₅Cl were substantially lower, 5–22% as compared to 70–80% with cesium fluoride.

We have demonstrated that cesium fluoride absorbs sulfur tetrafluoride beginning at about 110° in a sealed reactor to yield the cesium salt of the novel SF₅⁻ anion

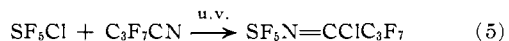
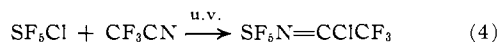
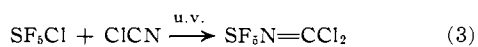


This anion presumably is isostructural with bromine pentafluoride and iodine pentafluoride. Since this salt is significantly dissociated at about 150°, it is necessary to maintain a high sulfur tetrafluoride pressure in

the reactor to ensure isolation of a solid that approaches the theoretical 1:1 CsF to SF₄ ratio.

Chlorine converts CsSF₅ to SF₅Cl and CsCl at 60° in good yields. This temperature is much lower than that required for practical rates in reaction 1 above. Temperatures at which reaction 1 proceeds at reasonable rates are comparable to minimum temperatures for attainment of equilibrium in reaction 2. We therefore suggest that CsSF₅ is an intermediate in the SF₅Cl synthesis and that the rate-controlling step is reaction 2. The lower conversions observed with other fluorides, such as potassium fluoride, are attributed to the greater activation they require in reaction 2. The pentafluorosulfur anion is considered to have marginal stability, existing perhaps only in solid lattices. The marked effectiveness of the cesium cation over smaller cations in SF₅⁻ formation is similar to the behavior observed for other anions of low stability, *e.g.*, TeF₈^{-2,5}, AsF₄^{-6,7} and IF₆^{-8,9}.

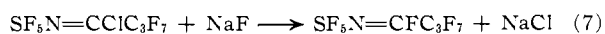
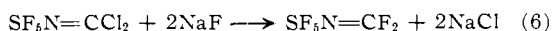
Addition of SF₅Cl to the CN Triple Bond.—Irradiation¹⁰ of mixtures of SF₅Cl and compounds that have the —C≡N function has yielded F₅SN=C< structures. Addition of SF₅Cl to cyanogen chloride and perfluoronitriles is illustrated in reactions 3–5



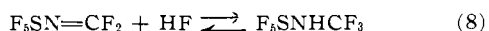
Conversions to these novel perhaloazomethines ranged from 30 to 40%. A common by-product in these additions is S₂F₁₀. Cyanogen undergoes double addition of SF₅Cl to give F₅SN=CCICCl=NSF₅.

Chemistry of the Azomethines.—All of the above perhaloazomethines are stable to storage in glass and are moderately resistant to hydrolysis at 25°. Aqueous alkali, however, quickly degrades these compounds, and all the fluorine atoms attached to sulfur appear as fluoride ions.

The chlorine atoms in the azomethines readily undergo exchange with fluoride ion. In the case of sodium fluoride, the products are perfluoroazomethines



Conversions as high as 80% were obtained. In reaction 6 an isomer of SF₅N=CF₂, described below, is formed in low yield. Hydrogen fluoride as the exchange reagent yields perfluoroazomethines, but it tends to add¹¹ to the azomethines to give amines, *e.g.*



The conversion to SF₅NHCF₃ is 75%. This amine appears thermally stable; it does not attack glass and is completely hydrolyzed by aqueous alkali. Higher homologs of this amine, *e.g.*, F₅SNHCF₂CF₃ and F₅SNHCF₂CF₂CF₂CF₃, tend to dissociate on heating, and the latter compound on attempted distillation was decomposed to the azomethine.

(5) E. L. Muettterties, *J. Am. Chem. Soc.*, **79**, 1004 (1957).

(6) A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.*, 2200 (1950).

(7) E. L. Muettterties and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 3686 (1957).

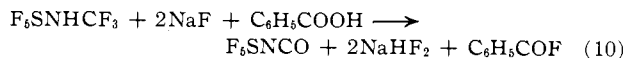
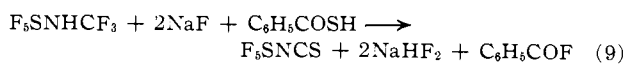
(8) H. J. Emelús and A. G. Sharpe, *J. Chem. Soc.*, 2206 (1949).

(9) E. L. Muettterties in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p. 506.

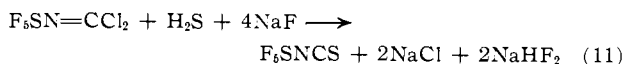
(10) Ultraviolet-catalyzed addition of SF₅Cl to olefins and acetylenes has been described by H. L. Roberts, *Quart. Rev. (London)*, **15**, 42 (1961), and J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 2066, 2070 (1961).

(11) Addition is probably the major exchange mechanism, *i.e.*, hydrogen fluoride first adds to —N=CCl₂ and hydrogen chloride is then eliminated.

The first isothiocyanate and isocyanate derivatives of sulfur hexafluoride were prepared by reaction of the amine F₅SNHCF₃ and sodium fluoride with thiobenzoic and benzoic acids, respectively.

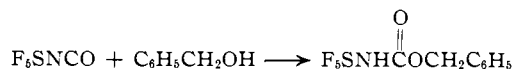


An alternative preparation of the isothiocyanato derivative involves thiolysis of F₅SN=CCl₂ with hydrogen sulfide in the presence of sodium fluoride as a hydrogen chloride acceptor



Another reaction occurs under these conditions, and a considerable amount of carbon disulfide is formed. Isothiocyanatosulfur pentafluoride, free of carbon disulfide, was obtained in the absence of sodium fluoride, but the conversion was low. Properly controlled hydrolysis of F₅SN=CCl₂ should yield SF₅NCO in good yield. We have observed formation of SF₅NCO from F₅SN=CCl₂ when traces of water were present.

The isocyanate and isothiocyanate derivatives are rapidly decomposed by aqueous alkali. Benzyl alcohol converts the isocyanate to the corresponding urethan



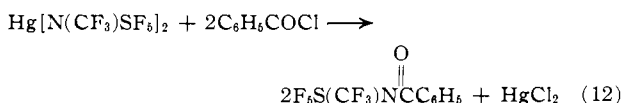
which is also decomposed by alkali.

Dimerization and Isomerization of F₅SN=CF₂.—Pyridine catalyzes the dimerization of F₅SN=CF₂ to F₅SN=CFN(CF₃)SF₅ below room temperature. The dimer is also formed when the azomethine is heated to 225° in the presence of potassium fluoride. Perfluoro-2-azapropene is similarly dimerized by ultraviolet irradiation to an open chain derivative.¹²

In addition to the monomer and the dimer, an isomer of the azomethine, F₄S=NCF₃, is formed on heating the amine F₅SNHCF₃ and potassium fluoride at 225°. This isomer is believed to be a slightly distorted trigonal bipyramid with the —NCF₃ ligand at an equatorial position. The spectroscopic data and the structure for this analog of F₄S=O will be discussed in a separate paper on five-coordinate stereochemistry. The barrier to rotation about the SN bond is 21 kcal./mole.¹³



F₅S-N- Derivatives.—Mercuric fluoride adds to the azomethine F₅SN=CF₂ at 125° to give the mercurial Hg[N(CF₃)SF₅]₂, a colorless liquid that freezes at about 20° and is rather volatile (*p*_{43°} ≅ 3 mm.) The mercurial is quite reactive; it hydrolyzes rapidly in moist air to mercuric oxide and undergoes metathesis with benzoyl chloride.



The amide is resistant to 10% aqueous sodium hydroxide at 25° but is slowly degraded at 100° by this reagent. The addition of mercuric fluoride to the azomethine and formation of an amide from reaction of the mercurial with benzoyl chloride parallels the chem-

(12) M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Org. Chem.*, **23**, 323 (1958).

(13) E. L. Muettterties, W. Mahler, K. J. Packer, and R. Schmutzler, to be submitted to *Inorg. Chem.*

istry of perfluoro-2-azapropene and its derived mercurial.^{14,15}

Silver(II) fluoride converts the amine F₅SNHCF₃ to the hydrazine at 100°. ¹⁶



This novel hydrazine is the most hydrolytically stable of the SF₅N< derivatives described in this article; it is not attacked by aqueous alkali at 100°. Addition of chlorine to the AgF₂-F₅SNHCF₃ reaction mixture yields the chloramine, ClN(CF₃)SF₅. This chloride adds to perfluoropropylene similarly to the previously described BrN(CF₃)₂.¹⁴

Experimental

Apparatus.—The F¹⁹ n.m.r. spectra were obtained on a Varian high resolution spectrometer Model V4300 and associated magnet at 56.4 Mc. Calibration of spectra was effected by superposition of an audiofrequency on the sweep field to produce side band peaks. The external reference was Freon 112.

Synthesis of Sulfur Chloride Pentafluoride.—Finely divided cesium fluoride (172 g., 1.13 moles), sulfur tetrafluoride (108 g., 1.00 mole), and chlorine (71 g., 1.00 mole) were heated with agitation for 1 hr. at 100°, for 1 hr. at 150°, and for 2 hr. at 175° in a 500-ml. Hastelloy C steel pressure vessel. The volatile product recovered (160 g.) was distilled through a low-temperature still (still head cooled to -60° since SF₅Cl freezes at -64°). The colorless fraction distilling at -23 to -21° (lit.⁴ reports -21°) amounted to 125 g.; infrared,¹⁷ F¹⁹ n.m.r.,¹⁸ and mass spectrometric analyses, by comparison with those of a pure standard, indicated the distillate contained at least 95% SF₅Cl. The conversion was about 75%. The same reactants in a similar type experiment at 125° for 2 hr. yielded SF₅Cl in about a 60% conversion.

A similar experiment with 127 g. of silver(I) fluoride in place of cesium fluoride gave SF₅Cl in a 21.5% yield based on product distilling at -25 to -21°. The reaction of molar amounts of sulfur tetrafluoride, chlorine, and potassium fluoride for 1 hr. at 175°, 1 hr. at 250°, and for 2 hr. at 300° gave SF₅Cl in 5-10% yields based on infrared analysis of the crude product.

Synthesis of CsSF₅.—The 1:1 adduct of cesium fluoride and sulfur tetrafluoride, SF₄CsF, was prepared by heating cesium fluoride (46 g., 0.30 mole) and sulfur tetrafluoride (324 g., 3.00 moles; for 1 hr. at 150°, for 1 hr. at 200°, and for 2 hr. at 250° with agitation in a 1-l. Hastelloy C pressure reactor, followed by slow cooling to room temperature. The adduct (74.1 g., 94% yield), a white, extremely moisture-sensitive solid, was recovered in a drybox. The dissociation pressure of CsF₅S is more than 1 atm. at 150°. The X-ray powder pattern showed no lines attributable to cesium fluoride.

Anal. Calcd. for CsF₅S: F, 36.5; S, 12.3. Found: F, 35.0; S, 11.4.

The adduct on being warmed with excess chlorine for 1 hr. at 60° in a pressure reactor was completely converted to SF₅Cl.

Addition of SF₅Cl to CN-Containing Compounds.—All of the ultraviolet-light catalyzed reactions were carried out in a similar manner. The reactor, either a 12- or 22-l. Pyrex flask, was provided with a quartz well, 1.5 in. in diameter and 16 in. deep, which extended from the neck into the center of the flask. A low-pressure mercury vapor resonance lamp, in the form of a tightly wound 10-in. quartz spiral, 6 mm. in diameter, which was inserted into the well, was the ultraviolet light source. The lamp was powered by a 5000 v., 60-millamp. transformer. The reactor flask was evacuated behind a protective shield and the gaseous reactants were added in sufficient quantities so that their initial pressure ranged from 600 to 730 mm. pressure. Since the products were liquids, the extent of reaction could be estimated by the decrease in pressure as reaction proceeded. When reaction stopped or slowed considerably, the reactants were removed and were purified by distillation either through a packed, low-temperature column or a spinning-band column.

A. Preparation of SF₅N=CCl₂.—A 12-l., round-bottomed flask containing cyanogen chloride (14 g., 0.23 mole) and SF₅Cl (37 g., 0.23 mole) was irradiated for 6.5 hr., after which the con-

tents were transferred to a liquid nitrogen cooled, evacuated trap and then allowed to warm up gradually to room temperature. The liquids from two such experiments were combined to give 37 g., amounting to a 36% conversion, of colorless SF₅N=CCl₂, b.p. 86-88°.

Anal. Calcd. for CCl₂F₅NS: Cl, 31.7; F, 42.4; S, 14.3. Found: Cl, 32.4; F, 42.4; S, 13.6.

The F¹⁹ n.m.r. spectrum showed a typical AB₄ pattern with J_{AB} = 157 c.p.s. and δ_A-δ_B 4.67 p.p.m. The AB₄ pattern was centered around -135 p.p.m. The infrared spectrum (gaseous) showed C=N absorption at 1653 cm.⁻¹. Mass spectrometric analysis did not detect the parent peak; peaks corresponding to the parent minus a fluorine or chlorine atom were present.

B. Preparation of SF₅N=CClCF₃.—A 22-l., round-bottomed flask containing trifluoroacetonitrile (38 g., 0.40 mole) and SF₅Cl (67 g., 0.41 mole) was irradiated for 14.5 hr. Distillation of the liquid remaining after removal of unreacted CF₃CN and SF₅Cl yielded 33 g. (32% conversion) of colorless SF₅N=CClCF₃, b.p. 58-61°.

Anal. Calcd. for C₂ClF₅NS: Cl, 13.8; F, 59.0. Found: Cl, 14.3; F, 58.7.

The F¹⁹ n.m.r. spectrum was an AB₄X₃ pattern with small δ_A-δ_B. The CF₃ multiplet was at -3.55 p.p.m. and the AB₄ peaks were centered at ~-130 p.p.m. The infrared spectrum (gaseous) showed C=N absorption at 1695 cm.⁻¹. Mass spectrometric analysis showed peaks corresponding to the parent, to the parent minus fluorine, chlorine, or CF₃, in addition to other smaller fragments.

C. Preparation of SF₅N=CClC₂F₇.—A 22-l., round-bottomed flask containing C₂F₇CN (59 g., 0.30 mole) and SF₅Cl (59 g., 0.36 mole) was irradiated for 18 hr., after which the contents were removed to a liquid nitrogen-cooled, evacuated trap and then allowed to warm up gradually to room temperature. The liquid recovered yielded on distillation 44.5 g. (41% conversion) of SF₅N=CClC₂F₇, b.p. 99-101°.

Anal. Calcd. for C₂ClF₁₂NS: Cl, 9.93; F, 63.8; S, 8.95. Found: Cl, 9.91; F, 62.6; S, 8.66.

The F¹⁹ n.m.r. spectrum had the AB₄ SF₅ pattern at -130 p.p.m. with J_{AB} = 157 c.p.s. There was a triplet CF₃ at +13.3 p.p.m., a quadruplet CF₂ at +42.3, and a singlet CF₂ at +57.2 p.p.m. The infrared spectrum (gaseous) showed C=N absorption at 1690 cm.⁻¹; mass spectrometric analysis showed peaks corresponding to the parent minus a fluorine or chlorine atom, a large peak corresponding to SF₅, and smaller fragments.

D. Preparation of SF₅N=CClCF=NSF₅.—A 22-l., round-bottomed flask containing cyanogen (23 g., 0.44 mole) and SF₅Cl (60 g., 0.37 mole) was irradiated for 22 hr. The liquid products from two such experiments were combined and distilled to give the following fractions: cut 1, b.p. 27-29°, 10 g., was chiefly S₂F₁₀; cut 2, b.p. 42-80°, 1.5 g., was not analyzed; cut 3, b.p. 80-85°, 1.4 g., comprised 30 mole % SF₅N=CCl₂ and the remainder may have been SF₅N=CClCN, based on mass spectrometric analysis which showed peaks corresponding to the parent minus a fluorine or chlorine atom; cut 4, b.p. 47-64° (32 mm.), 4.0 g., comprised 75% compound B and 25% compound A; cut 5, b.p. 65-69° (29 mm.), 6.5 g., comprised 10% compound B and 90% compound A; and cut 6, b.p. 69° (29 mm.), 6.5 g., was 100% compound A. Compound A was SF₅N=CClCF=NSF₅. The percentage compositions were derived from F¹⁹ n.m.r. data.

Anal. Calcd. for C₂Cl₂F₁₆N₂S₂: F, 50.4; S, 17.0. Found: F, 49.8; S, 16.5.

The F¹⁹ AB₄ n.m.r. spectrum was centered around -130 p.p.m. with J_{AB} = 154 c.p.s. and δ_A-δ_B 3.36 p.p.m. The infrared spectrum showed C=N absorption at 1640 cm.⁻¹. Mass spectrometric analysis showed the presence of peaks corresponding to the parent minus a chlorine atom, to SF₅, and other smaller fragments. Compound B was not isolated in a pure state but is believed to be SF₅N=CClCF=NSF₅, based on infrared absorption at 1710 (>CF=N-) and at 1652 cm.⁻¹ (>CCl=N-) and on mass spectrometric analysis which showed peaks corresponding to the parent minus a chlorine atom and to SF₅N=CClCF=N-.

Reactions of SF₅N=CCl-Containing Compounds. A. Preparation of SF₅NHCF₃.—Hydrogen fluoride (23 g., 1.15 moles) and SF₅N=CCl₂ (23 g., 0.10 mole) were heated at 70-80° (2 hr.) in a 300-ml. stainless steel pressure vessel. The crude product was transferred to a second stainless steel vessel and stored over 75 g. of sodium fluoride overnight. Distillation of the liquid remaining yielded 16.5 g. (76% conversion) of SF₅NHCF₃, b.p. 28.5-31°.

Anal. Calcd. for CHF₃NS: F, 72.0; S, 15.2. Found: F, 71.8; S, 15.9.

Mass spectrometric analysis showed a peak corresponding to the parent together with lower mass fragments, including large peaks for SF₅ and for CF₃. The infrared spectrum (gaseous) showed NH absorption at 3410 cm.⁻¹. The F¹⁹ n.m.r. spectrum was an AB₄X₃ pattern with the AB₄ pattern centered around

(14) J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Am. Chem. Soc.*, **80**, 3604 (1958).

(15) J. A. Young, W. S. Durrell, and R. D. Dresdner, *ibid.*, **84**, 2105 (1962).

(16) J. A. Young, W. S. Durrell, and R. D. Dresdner, *ibid.*, **82**, 4553 (1960), describe a similar reaction with bis-(trifluoromethyl)-amine.

(17) L. H. Cross, H. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 945 (1960).

(18) E. I. Merrill, S. M. Williamson, G. H. Cady, and D. E. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

—131 p.p.m. and the CF_3 multiplet at —10.3 p.p.m. The proton n.m.r. spectrum consisted of a single broad peak.

The amine SF_5NHCF_3 was recovered in 60% conversion from the reaction of hydrogen fluoride (15 g., 0.75 mole) and $\text{SF}_5\text{N}=\text{CF}_2$ (44 g., 0.23 mole) under conditions similar to those above.

B. Reaction of Hydrogen Fluoride with $\text{SF}_5\text{N}=\text{CClCF}_3$.—In a manner analogous to (A) above, hydrogen fluoride (20 g., 1.00 mole) and $\text{SF}_5\text{N}=\text{CClCF}_3$ (26 g., 0.10 mole) were allowed to react at 100–150° for 2 hr. Distillation of the liquid remaining after storage of the crude product over sodium fluoride yielded the following fractions: cut 1, b.p. 30–33.5°, 2.5 g., contained 10 mole % of compound B and 90 mole % compound A; cut 2, b.p. 33.5–45.5°, 7.1 g., contained approximately equal amounts of compounds A and B; and cut 3, b.p. 45.5–47°, 8.4 g., was compound B. The percentage compositions were derived from F^{19} n.m.r. data. Compound B was $\text{SF}_5\text{NH}-\text{C}_2\text{F}_5$.

Anal. Calcd. for $\text{C}_2\text{HF}_{10}\text{NS}$: F, 72.7. Found: F, 70.8.

Mass spectrometric analysis showed peaks corresponding to the parent minus a fluorine atom and other prominent peaks corresponding to SF_5 , to C_2F_5 , and to CF_3 . The F^{19} n.m.r. spectrum indicated that an SF_5 and a C_2F_5 group were present; the proton n.m.r. spectrum consisted of a single broad peak. The infrared spectrum (gaseous) showed NH absorption at about 3450 cm^{-1} . Compound A, based on F^{19} n.m.r. and infrared analysis, was $\text{SF}_5\text{N}=\text{CFCF}_3$.

C. Preparation of $\text{SF}_5\text{N}=\text{CFC}_3\text{F}_7$.—A mixture of sodium fluoride (20 g., 0.48 mole), $\text{SF}_5\text{N}=\text{CClC}_3\text{F}_7$ (42 g., 0.12 mole), and tetramethylene sulfone (83 g.) was warmed at reflux for 1.17 hr.; with the pot contents at 75°, the crude product (38 g.) was removed by reducing the pressure to 1–2 mm. Distillation of the product yielded 31.6 g. (79% conversion) of $\text{SF}_5\text{N}=\text{CFC}_3\text{F}_7$, b.p. 72–73°.

Anal. Calcd. for $\text{C}_3\text{F}_{13}\text{NS}$: F, 72.4; S, 9.38. Found: F, 72.5; S, 9.55.

Gas chromatography showed that only one compound was present. Mass spectrometric analysis showed a peak which could be attributed to the parent minus a fluorine atom and lower mass fragments which supported the structure. The infrared spectrum showed $\text{C}=\text{N}$ absorption at 1752 cm^{-1} . The F^{19} n.m.r. spectrum was an AB_4X pattern at —135 p.p.m. with $\delta_A - \delta_B$ very small. The CF multiplet was at —46.2 p.p.m., the CF_3 triplet at +13.5 p.p.m., the CF_2 multiplet at +50.4 p.p.m., and the CF_2 doublet at 59.6 p.p.m.

Hydrogen fluoride (40 g., 2.00 moles) and $\text{SF}_5\text{N}=\text{CClC}_3\text{F}_7$ (46 g., 0.13 mole) were allowed to react for 2 hr. at 150–200° in a sealed container. After storage over sodium fluoride the crude product (36 g.) was distilled to yield 27 g. (62% conversion) of $\text{SF}_5\text{N}=\text{CFC}_3\text{F}_7$, b.p. 72–73°, which was characterized by its infrared spectrum.

D. Preparation of $\text{SF}_5\text{N}=\text{CF}_2$ and $\text{SF}_4=\text{NCF}_3$.—Sodium fluoride (168 g., 4.00 moles), $\text{SF}_5\text{N}=\text{CCl}_2$ (218 g., 0.97 mole), and tetramethylene sulfone (620 g.) were heated with stirring up to 50° over a period of 0.3 hr., at 50–74° for 1.7 hr., and at 74–162° for 1.2 hr. in a 1-l. flask provided with a water-cooled condenser. The volatiles which collected in a cold trap at —77° were distilled.

A fraction distilling at 7–12.5° (136 g.) was combined with 49 g. of a similar cut from another experiment and subjected to gas chromatographic separation which yielded 19 g. of $\text{SF}_4=\text{NCF}_3$ (b.p. 0.5–1.0°) and 108 g. of $\text{SF}_5\text{N}=\text{CF}_2$ (b.p. 11–13°) containing very small amounts of SF_5NCO .

Anal. Calcd. for $\text{SF}_5\text{N}=\text{CF}_2$: F, 69.6; S, 16.8. Found: F, 68.5; S, 17.0.

The F^{19} n.m.r. spectrum consisted of a complex SF_5 resonance around —135 p.p.m. and broad AB CF_2 resonance at —24.8 p.p.m. Mass spectrometric analysis showed a peak corresponding to the parent and lower mass fragments which supported this structure, including a very large SF_5 peak. The infrared spectrum showed $\text{C}=\text{N}$ absorption at 1785 cm^{-1} .

Anal. Calcd. for $\text{SF}_4=\text{NCF}_3$: F, 69.6; S, 16.8. Found: F, 68.5; S, 17.0.

Mass spectrometric analysis supported the $\text{SF}_4=\text{NCF}_3$ structure, with a peak corresponding to the parent together with a large CF_3 mass. The infrared spectrum showed absorption at 1343 cm^{-1} (tentatively assigned to $\text{S}=\text{N}$) and no absorption in the $\text{C}=\text{N}$ region. The F^{19} n.m.r. spectrum was consistent with this structure.¹³

A sample of $\text{SF}_5\text{N}=\text{CF}_2$ (15 g.) was purified by gas chromatography and then heated for 6 hr. at 250° in a 100-ml. Hastelloy C pressure reactor. Infrared analysis showed that approximately equal amounts of $\text{SF}_4=\text{NCF}_3$ and $\text{SF}_5\text{N}=\text{CF}_2$, together with 5% SF_5NHCF_3 and a trace of SF_5NCO , were present.

E. Preparation of $\text{SF}_5\text{N}=\text{CF}_2$.—Hydrogen sulfide (59 g., 1.73 moles) and $\text{SF}_5\text{N}=\text{CCl}_2$ (59 g., 0.26 mole) were heated in a 500-ml. Hastelloy C pressure reactor for 2 hr. at 80° and autogenous pressure. After storage over sodium fluoride at room temperature and autogenous pressure, the product was distilled to give 3.4 g. of SF_5NCS , b.p. 47–48°.

Anal. Calcd. for CF_5NS_2 : F, 51.4; S, 34.6. Found: F, 51.1; S, 34.3.

The F^{19} n.m.r. spectrum was an AB_4 pattern centered around —140 p.p.m. with $J_{\text{AB}} = 156$ c.p.s. and $\delta_A - \delta_B$ 14.8 p.p.m. The mass spectrum contained peaks corresponding to the parent and lower mass fragments which supported the structure. The infrared spectrum (gaseous) showed NCS absorption at 1955 cm^{-1} .

Hydrogen sulfide (25 g., 0.74 mole), $\text{SF}_5\text{N}=\text{CCl}_2$ (45 g., 0.20 mole), and sodium fluoride (50 g., 1.19 moles) were heated for 1 hr. at 75° and for 2 hr. at 125° in a 500-ml. Hastelloy C pressure reactor. Distillation of the liquid product yielded 8.4 g., b.p. 37–40°, which infrared analysis showed to contain 50 mole % SF_5NCS and 50 mole % CS_2 , and 5.4 g., b.p. 42–44.3°, which infrared showed was 80% SF_5NCS and 20% CS_2 .

Sodium fluoride (20 g., 0.48 mole), thiobenzoic acid (19 g., 0.14 mole), and SF_5NHCF_3 (34 g., 0.16 mole) were heated for 1 hr. at 75° and for 1 hr. at 150° with agitation in a 300-ml. Hastelloy C pressure reactor. The following fractions were recovered on distillation: 9.5 g., b.p. 24.5–35°, which infrared analysis showed to contain, on a molar basis, 40% SF_5NCS , 10% SF_5NCO , and 50% SF_5NHCF_3 ; 1.8 g., b.p. 35–45°, which infrared analysis showed was 30% SF_5NHCF_3 and 70% SF_5NCS ; and 5.4 g., b.p. 45–50°, which infrared analysis showed was 95% SF_5NCS and 5% SF_5NHCF_3 .

Reactions of SF_5NHCF_3 . A. Preparation of SF_5NCO .—Benzoic acid (88 g., 0.72 mole), sodium fluoride (103 g., 2.45 moles), and SF_5NHCF_3 (129 g., 0.61 mole) were heated for 1 hr. at 100° and for 1 hr. at 200° with rocking in a 500-ml. Hastelloy C pressure reactor. The 81 g. of gaseous product recovered was distilled to yield 61 g. (59% conversion) of SF_5NCO , b.p. 5 to 5.5°.

Anal. Calcd. for CF_5NOS : F, 56.1; S, 18.9. Found: F, 55.4; S, 19.0.

The infrared spectrum showed strong NCO absorption at 2276 cm^{-1} . Mass spectrometric analysis showed a peak corresponding to the parent, to the parent minus a fluorine atom, and a large peak attributed to the SF_5 group. The F^{19} n.m.r. spectrum consisted of an AB_4 pattern centered around —140 p.p.m. with $J_{\text{AB}} = 149$ c.p.s. and $\delta_A - \delta_B$ 17.3 p.p.m.

Benzyl alcohol (9.6 g., 0.09 mole), SF_5NCO (15.0 g., 0.09 mole), and carbon tetrachloride (20 ml.) were allowed to stand at room temperature in a 125-ml. stainless steel pressure reactor for 2.5 days and then warmed for 2 hr. at 90°. Filtration yielded 20 g. of crude product which was recrystallized from carbon tetrachloride to give 12 g. of $\text{SF}_5\text{NHCO}_2\text{CH}_2\text{C}_6\text{H}_5$, m.p. 101–102°.

Anal. Calcd. for $\text{C}_7\text{H}_9\text{F}_5\text{N}_2\text{O}_2\text{S}$: C, 34.6; H, 2.89; F, 34.3. Found: C, 34.8; H, 2.61; F, 34.0.

B. Preparation of $\text{SF}_3(\text{CF}_3)\text{N}(\text{CF}_3)\text{SF}_3$.—Silver(II) fluoride (50 g., 0.34 mole) and SF_5NHCF_3 (21 g., 0.10 mole) were heated with shaking for 1 hr. at 50°, for 1 hr. at 75°, and for 1 hr. at 100° in a 200-ml. stainless steel pressure reactor. The liquid product (21 g.) was distilled through a spinning-band column to give 13 g. (62% conversion) of $\text{SF}_3(\text{CF}_3)\text{N}(\text{CF}_3)\text{SF}_3$, b.p. 103–104°.

Anal. Calcd. for $\text{C}_2\text{F}_{16}\text{N}_2\text{S}_2$: F, 72.4; S, 15.2. Found: F, 71.8; S, 15.4.

F^{19} n.m.r. spectrum was a complex $\text{AB}_4\text{X}_3-\text{X}_3\text{B}_4\text{A}$ pattern with the AB_4 pattern centered around —133 p.p.m. and the CF_3 multiplet at —10.5 p.p.m. Mass spectrometric analysis showed a peak corresponding to the parent minus SF_5 and lower mass fragments which supported the structure, including large peaks attributed to the SF_5 and CF_3 groups.

C. Preparation of $\text{SF}_5\text{N}(\text{Cl})\text{CF}_3$.—Silver(II) fluoride (60 g., 0.41 mole), chlorine (11 g., 0.16 mole), and SF_5NHCF_3 (30 g., 0.14 mole) were heated with rocking for 1 hr. at 50°, for 1 hr. at 75°, and for 1 hr. at 100° in a 300-ml. Hastelloy C pressure reactor. The gaseous and liquid volatiles (26 g.) recovered, after overnight storage over sodium fluoride, were distilled to give 13.4 g. (38% conversion) of $\text{SF}_5\text{N}(\text{Cl})\text{CF}_3$, b.p. 41–43°. The positive chlorine was determined by adding the N-chloro compound to aqueous potassium iodide and titrating the iodine liberated.

Anal. Calcd. for CClF_5NS : Cl, 14.5; positive Cl, 14.5; F, 61.9. Found: Cl, 13.9; positive Cl, 14.1; F, 61.6.

The F^{19} n.m.r. spectrum was an AB_4X_3 pattern with $\delta_A - \delta_B$ very small. The CF_3 multiplet was at —3.55 p.p.m. and the AB_4 pattern was centered around —130 p.p.m. Mass spectrometric analysis showed a peak corresponding to the parent, and large peaks corresponding to the SF_5 and CF_3 groups.

Hexafluoropropylene (12 g., 0.08 mole) and $\text{SF}_5\text{N}(\text{Cl})\text{CF}_3$ (9.9 g., 0.04 mole) were heated for 1 hr. at 75° and for 1 hr. at 150° with rocking in an 80-ml. Hastelloy C pressure reactor. The 9 g. of liquids recovered was distilled through a small spinning-band column to yield 2.5 g., b.p. 99–105°, and 3.5 g., b.p. 105–107°. The infrared and F^{19} n.m.r. analyses showed that both fractions were essentially the same and indicated that a 37% conversion to the 1:1 adduct had been obtained. The higher boiling fraction was analyzed. Available data do not distinguish

between the two possible structures $\text{SF}_5\text{N}(\text{CF}_3)\text{CF}_2\text{CFCICF}_3$ and $\text{SF}_5\text{N}(\text{CF}_3)\text{CF}(\text{CF}_2\text{Cl})\text{CF}_3$.

Anal. Calcd. for $\text{C}_4\text{ClF}_4\text{NS}$: Cl, 8.95; F, 67.2. Found: Cl, 8.73; F, 66.6.

Reactions of $\text{SF}_5\text{N}=\text{CF}_2$. A. **Preparation of $\text{SF}_5\text{N}=\text{CFN}(\text{CF}_3)\text{SF}_3$.**—Potassium fluoride (50 g., 0.86 mole) and $\text{SF}_5\text{N}=\text{CF}_2$ containing about 15% $\text{SF}_4=\text{NCF}_3$ (40 g., 0.21 mole total) were heated for 3 hr. at 225° with agitation in a 500-ml., Hastelloy C pressure reactor. The gaseous product (32 g.) was shown by infrared analysis to contain, on a molar basis, 70% $\text{SF}_5\text{N}=\text{CF}_2$, 20% $\text{SF}_4=\text{NCF}_3$, and 10% SF_5NCO . The 4.5 g. of liquid product was purified by preparative gas chromatography.

Anal. Calcd. for $\text{C}_2\text{F}_{14}\text{N}_2\text{S}_2$: F, 69.6; S, 16.8. Found: F, 69.5; S, 17.3.

The infrared spectrum (liquid) showed $\text{C}=\text{N}$ absorption at 1725 cm^{-1} . The F^{19} n.m.r. spectrum revealed the presence of two SF_3 groups, a CF_3 group, and CF in about the proper 5:5:3:1 intensity ratio. The spectrum was a composite of an AB_4X_3 and an AB_4X pattern with the CF multiplet at -66.3 p.p.m., the CF_3 multiplet at -11.5 p.p.m., the AB_4X_3 pattern centered around -142 p.p.m., and the AB_4X pattern around -131 p.p.m.

Potassium fluoride (70 g., 1.21 moles) and SF_5NHCf_3 (49 g., 0.23 mole) were heated with agitation for 1 hr. at 100° and for 2 hr. at 225° in a 300-ml. Hastelloy C pressure reactor. The crude gaseous and liquid product (38 g.) yielded 23 g. of volatiles which infrared analysis showed was 40% $\text{SF}_5\text{N}=\text{CF}_2$, 20% $\text{SF}_4=\text{NCF}_3$, 15% SF_5NHCf_3 , and 10% SF_5NCO , as well as 6.8 g., b.p. 88–92°, of $\text{SF}_5\text{N}=\text{CFN}(\text{CF}_3)\text{SF}_3$.

B. **Preparation of $\text{Hg}[\text{N}(\text{CF}_3)\text{SF}_3]_2$.**—The liquid products (212 g.) from two experiments, each involving the reaction of mercuric fluoride (53.3 g., 0.22 mole) and $\text{SF}_5\text{N}=\text{CF}_2$ (68.5 g.,

0.36 mole) at 100° for 3 hr. and at 125° for 3 hr. in a 300-ml. Hastelloy C reactor, were combined. Distillation yielded 169 g. (76% conversion) of the colorless mercurial, b.p. 43–44° (3 mm.).

Anal. Calcd. for $\text{C}_2\text{F}_{16}\text{HgN}_2\text{S}_2$: F, 49.0; Hg, 32.3. Found: F, 49.0; Hg, 31.9.

The F^{19} n.m.r. spectrum was an AB_4X_3 pattern with the CF_3 multiplet at -20.4 p.p.m. and the AB_4 pattern centered around -148 p.p.m. The liquid mercurial was rapidly hydrolyzed by moist air with the formation of yellow mercuric oxide.

Benzoyl chloride (10 g., 0.07 mole) was added with stirring to $\text{Hg}[\text{N}(\text{CF}_3)\text{SF}_3]_2$ (20 g., 0.03 mole) over a period of 0.30 hr. during which the temperature rose from 25 to 35° and large amounts of a white solid formed. Reaction was completed by warming gradually to 88° over a period of 0.80 hr. The liquid product (16 g.) was decanted from the solid mercuric chloride and distilled at 46–47° (2.2 mm.). Since the product contained unreacted benzoyl chloride, the sample was stirred with 50 ml. of 10% aqueous sodium hydroxide for 5 hr. Redistillation yielded 5.8 g. of colorless $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{N}(\text{CF}_3)\text{SF}_3$, b.p. 56–57° (4.35 mm.).

Anal. Calcd. for $\text{C}_8\text{H}_5\text{F}_8\text{NOS}$: C, 30.4; H, 1.59; F, 48.2; S, 10.2. Found: C, 31.3; H, 1.89; F, 48.0; S, 9.9.

The F^{19} n.m.r. spectrum was an AB_4X_3 pattern with the CF_3 multiplet at -13.3 p.p.m. and the AB_4 pattern centered around -143 p.p.m. Mass spectrometric analysis was satisfactory with peaks present which corresponded to the parent, and lower mass fragments which supported the structure, including large SF_5 , CF_3 , and $\text{C}_6\text{H}_5\text{C}=\text{O}$ peaks. The infrared carbonyl stretching frequency was 1740 cm^{-1} .

NOTE ADDED IN PROOF.—R. Tunder and B. Siegel, *J. Inorg. Nucl. Chem.*, **25**, 1097 (1963), report the synthesis of $(\text{CH}_3)_4\text{N}^+\text{SF}_5^-$ from SF_4 and $(\text{CH}_3)_3\text{NF}$.

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Borane Complexes of Transition Metals

BY G. W. PARSHALL

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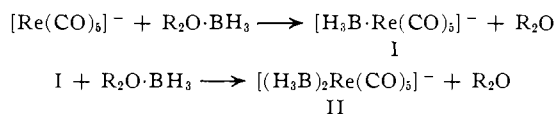
Crystalline complexes containing BH_3 as an electron-accepting ligand have been obtained by reaction of diborane with group VII metal carbonyl anions. Salts of $[\text{Re}(\text{CO})_5]^-$, $[\text{Mn}(\text{CO})_5]^-$, and $\{(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4\}^-$ give monoborane complexes in which the BH_3 is coordinated to the metal. Salts of a bis(borane) complex, $[(\text{H}_3\text{B})_2\text{Re}(\text{CO})_5]^-$, have also been isolated.

One of the dominating aspects of boron hydride chemistry is the electron deficiency of the lower boranes. Borane (BH_3), the simplest boron hydride, seems incapable of independent existence. Many stable derivatives of borane have been obtained by complex formation with molecules or ions which can supply an electron pair to the boron. Neutral ligands, such as amines, phosphines, and ethers, and anions ranging from hydride to fluoride have given isolable borane complexes. Recently Shriver¹ has reported the isolation of complexes in which BF_3 and BH_3 are coordinated to the cyanides of dicyanobis(1,10-phenanthroline)iron. To date, however, no compounds in which borane is coordinated to a transition metal have been described.

In the present work, such borane complexes have been obtained by treating borane etherates with relatively basic transition metal anions. Crystalline complexes containing BH_3 as a ligand have been isolated by reaction with salts of $[\text{Re}(\text{CO})_5]^-$, $[\text{Mn}(\text{CO})_5]^-$, and $\{(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4\}^-$. In addition, some reaction has been noted with $[\text{Co}(\text{CO})_4]^-$.

Rhenium Complexes.—The reaction of $\text{NaRe}(\text{CO})_5^2$ with an equivalent amount of a borane etherate gave the simple complex I. Treatment with an excess of borane etherate gave II which contains two borane moieties per rhenium atom. The course of complex

formation was followed by the change of diborane pressure over a solution of $\text{NaRe}(\text{CO})_5$ in bis(2-methoxyethyl) ether. No further absorption beyond two boranes per rhenium was noted.



The sodium salts of the complexes crystallize as solvates containing several molecules of the ether, but crystalline, nonsolvated tetraethylammonium and tetrabutylphosphonium salts of both borane complexes have been isolated by metathetical reactions in tetrahydrofuran. Both of the borane complexes hydrolyze readily in water or dilute acid to give boric acid and $\text{HRe}(\text{CO})_5$. They are very mild reducing agents in tetrahydrofuran solution. At room temperature, they readily reduce quinones but do not reduce acetone or benzaldehyde.

The spectral properties of the two borane complexes of the pentacarbonylrhenate anion are somewhat similar. The infrared spectra (Table I) in tetrahydrofuran solution show three similar, strong metal carbonyl stretching frequencies. The additional bands noted in the mull spectra may be due to coupling with crystal lattice vibrations. Both spectra show B–H stretching absorption at 2400–2408 cm^{-1} . The mull spectrum of the bis(borane) complex (II) also shows an equally strong absorption at 2453 cm^{-1} . If the two bands are assigned to nonequivalent BH_3 groups,

(1) D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963). Shriver recently has reported that BF_3 and $(\text{C}_6\text{H}_5)_2\text{WH}_2$ give a complex which is believed to contain a W–B coordinate bond (*ibid.*, **85**, 3509 (1963)).

(2) W. Beck, W. Hieber, and G. Braun, *Z. anorg. allgem. Chem.*, **308**, 23 (1961).