The halogen atoms in vinyl Group V halides may be replaced by hydric or organic groups, thereby giving mixed vinyl derivatives, each having its own chemical characteristics, e.g. vinylid-n-butyllarsine (b.p. 52° at 1.5 mm.; analysis: required, C 55.55, H 9.79; found, C 55.47, H 9.58). Furthermore we have found that vinyl derivatives of some of the Group V elements may be prepared from other vinyl metal compounds by means of mixed redistribution reactions:

\[
\text{(n-C}_2\text{H}_5\text{)}_2\text{Sn(CH} \cdot \text{CH}_2\text{)}_2 + 2 \text{AsBr}_3 \rightarrow 2 \text{CH}_2 \cdot \text{CH}_2 \cdot \text{AsBr}_3 + (\text{n-C}_2\text{H}_5\text{)}_2\text{SnBr}_2
\]

and

\[
\text{(n-C}_2\text{H}_5\text{)}_2\text{Sn(CH} \cdot \text{CH}_2\text{)}_3 + \text{AsBr}_3 \rightarrow (\text{CH}_2 \cdot \text{CH}_2 \cdot \text{AsBr}) + (\text{n-C}_2\text{H}_5\text{)}_2\text{SnBr}_2
\]

Vinyl Group V iodides could also be prepared by thermal decomposition of the trivinyl diiodides:

\[
(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{AsI})_2 \rightarrow (\text{CH}_2 \cdot \text{CH}_2 \cdot \text{AsI}) + \text{CH}_2 \cdot \text{CH}_2
\]

The electronic and steric effect of attaching vinyl groups to both donor and acceptor atoms is currently being investigated in this Laboratory. Thus with metals possessing electron-deficient alkyls it is perhaps possible that their vinyl analogs will have a somewhat less tendency to polymerize and a weaker acceptor power towards electron pair donors. This might occur as a consequence of a conjugation effect involving the π-electrons of the vinyl group and the vacant metal orbital. On the other hand preliminary experiments with the lone-pair donor atoms of Group V indicate that the inductive, as well as the resonance, effect of the vinyl group is likely to be important. Trivinylarsine does not form a stable addition compound with boron trifluoride even at low temperatures. Borine, which is a stronger Lewis acid towards ligand atoms below the first row of the Periodic Table, was found in preliminary experiments to undergo a violent reaction with trivinylarsine instead of forming a stable adduct. The possibility of using vinyl derivatives of Group V as ligands to transition metals is also being investigated by us. Complex compounds are readily obtained; thus we have prepared cis- [(CH\text{2} : CH\text{2})\text{3As}]\text{PtCl}_2, m.p. 90° (C, required, 24.92; C, found, 24.90; H, required, 3.14; H, found, 3.42).

It is hoped to describe in detail elsewhere the new compounds and reactions mentioned in this communication.

Aminoalcohol — Boron Trifluoride Complexes

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(Z. Naturforsch. 12 b, 264—265 [1957]; eingeg. am 18. Februar 1957)

Few complexes of boron trifluoride with polyfunctional organic bases have been characterized and these bases are restricted to polyamines. This present study was concerned with the nature of the complexes obtained from aminoalcohols. It was found that 2-aminoethanol and 3-aminopropanol added one and one-half moles of boron trifluoride to give reactive adducts that dissolved only in the more polar solvents and then with decomposition. No good evidence was obtained for the addition of two moles of boron trifluoride to one mole of the aminoalcohol. The structure of the adducts is formulated as

\[
\text{R}\text{F}_{2}\text{B} \cdot \text{O} \cdot \text{O} \cdot \text{R} \text{(where R} = -(\text{CH}_2\text{)}_3\text{NH}_2\text{BF}_3)\]

since this structure provides a simple mechanism for exchange of ROH groups. The complexes were readily


2 A. B. BURG and L. L. MARTIN, J. Amer. chem. Soc. 65, 1635 [1943].
converted to the amine fluoborates by heat or protonic solvents. Reaction of excess boron trifluoride with the aminoalcohols in tetrahydrofuran also resulted in the formation of the fluoborates.

No inert solvent for the aminoalcohol-boron trifluoride system was found, and therefore, a solution preparation was not achieved. To establish the stoichiometry of the reactions, boron trifluoride was added to a weighed sample of the aminoalcohol in a vacuum system. When no further decrease in the pressure of the system occurred, the reaction tube was evacuated and weighed. The molar ratio of boron trifluoride to base ranged from 1.44 to 1.50 which established the 3 : 2 stoichiometry of the complex. The complexes obtained in this manner were very hygroscopic, white solids. These dissolved in water and alcohols to give the amine fluoborates described below.

An attempt was made to detect the existence of a two-to-one (acid-to-base) adduct by following the stoichiometry of the solid product resulting from the stepwise addition of 2-aminoethanol to boron trifluoride. The experimental procedure of Brown and Osthoff was followed and when pressure was plotted against mole fraction, a nearly straight line intersecting the composition axis at 1.40 was obtained. Within experimental error, a three-to-two complex was indicated. There was no good evidence for a two-to-one complex.

The dropwise addition of 40 cc. of a 0.5 molar tetrahydrofuran solution of aminoalcohol to a 20 cc. tetrahydrofuran solution of $F_2BO(CH_2)_4$ resulted in a clear solution. After an induction period of from 5—10 minutes, a copious white precipitate formed. The precipitates thus obtained were filtered, washed with tetrahydrofuran and then dried in vacuum. These white polycrystalline solids were extremely hygroscopic; analysis showed them to be amine fluoborate salts.

\[ \text{Anal. Calc.'d. for } C_4H_8ONBF}_4 : \]
\[ C, 16.11; H, 5.41; N, 9.40; HBF}_4, 59.00; \text{ M.W., 74.48.} \]

\[ \text{Found: } C, 15.99; H, 5.28; N, 9.28; HBF}_4, 56.50; \text{ M.W. (F. pt., water), 68.9.} \]

\[ \text{Anal. Calc.'d. for } C_4H_8ONBF}_4 : \]
\[ C, 22.11; H, 6.18; N, 8.59; HBF}_4, 53.92; \text{ M.W., 81.49.} \]

\[ \text{Found: } C, 22.20; H, 5.90; N, 8.49; HBF}_4, 50.50, 51.10; \text{ M.W., 79.3.} \]

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**Reactions of Amine Hydrochlorides with Boron Trifluoride-Etherates**

By E. L. Muetteerties


In a search for good routes to boron trifluoride complexes of polyamines, the reactions of boron trifluoride-etherates with amine hydrochlorides were investigated. The hydrochloride salts of ethylenediamine, hexamethylenediamine and hydrazine reacted at 60—100°C with BF$_3$·(C$_5$H$_5$)$_2$O to give ethyl borate, ether, ethyl chloride and amine fluoborates. Minor amounts of hydrogen chloride were initially evolved. However, when the BF$_3$ complex with tetrahydrofuran was employed, no hydrogen chloride was detected. The organic diamines yielded the diacid salts whereas hydrazine formed the monoaacid salt.

**Anal. for HBF$_4$:**

\[ (CH$_2$)$_2$·(NH$_2$)$_2$ · 2 HBF$_4$, Theory, 60.2; Found, 58—61, \]
\[ (CH$_2$)$_2$·(NH$_2$)$_2$ · 2 HBF$_4$, Theory, 73.2; Found, 73.24, \]
\[ N$_2$H$_4$ · HBF$_4$, Theory, 73.5; Found, 73.92. \]

The results can be explained by the following sequence of reactions:

1. In part taken from a Ph.D. thesis submitted by E. L. Muetteerties to the Graduate School of Art and Sciences, Harvard University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.