Data Treatment. The experimental results gave the concentration of $B_{10}H_{10}^{-2}$ and $B_{10}H_{12}[(C_2H_5)_3N]py$ at known time intervals. The slope of plots of these concentrations *vs.* time gave values for k_s and k_e when divided by the initial substrate concentration. No significant intercepts were observed for the individual rate runs.

$$k_s = \frac{d[B_{10}H_{10}^{-2}]}{dt}\Big/[B_{10}H_{12}[(C_2H_5)_3N]_2]$$

$$k_e = \frac{d[B_{10}H_{12}[(C_2H_5)_3N](py)]}{dt}\Big/[B_{10}H_{12}[(C_2H_5)_3N]_2]$$

Product Determination. The products present after 5% reaction were determined by thin-layer chromatographic analysis. A solution containing 0.100 *M* pyridine, 0.0240 *M* triethylamine, and 7.67 × 10^{-3} *M* $B_{10}H_{12}[(C_2H_5)_3N]_2$ was placed in two tubes which were degassed and sealed under vacuum. The tubes were heated at 100° in a steam bath. The first tube was removed after 15 min and the second tube after 32 min. Samples from the two tubes were analyzed as follows. Mixtures of either 80 parts (by volume) of chloroform with 20 parts of pentane, or 60 parts of acetone with 40 parts of chloroform, were found to be good eluents. With either of these eluents, known mixtures of $B_{10}H_{12}[(C_2H_5)_3N]_2$, $B_{10}H_{10}^{-2}$ salts, $B_{10}H_{12}(py)_2$, and $B_{10}H_{12}[(C_2H_5)_3N]py$ were completely separated when silica gel was used as the stationary phase. The R_f values were in the order $B_{10}H_{12}[(C_2H_5)_3N]_2 > B_{10}H_{12}[(C_2H_5)_3N]py > B_{10}H_{12}(py)_2 > B_{10}H_{10}^{-2}$ salts = 0. Triethylammonium and pyridinium salts of $B_{10}H_{10}^{-2}$ were used. Analysis of the experimental samples was carried out by placing a spot of the unknown mixture between spots of a known synthetic mixture on the plate and eluting. After developing the plates with iodine vapor, visual inspection showed that the unknown samples contained $B_{10}H_{12}[(C_2H_5)_3N]_2$, $B_{10}H_{10}^{-2}$ salts, and $B_{10}H_{12}[(C_2H_5)_3N]py$; no spot could be seen in a position corresponding to $B_{10}H_{12}(py)_2$. Both eluents gave the same results.

A second product determination in which the sample solution contained 0.300 *M* pyridine, 0.0120 *M* triethylamine, and 7.67 × 10^{-3} *M* $B_{10}H_{12}[(C_2H_5)_3N]_2$ was heated at 100° for 40 min and then analyzed as described above. Again no spot corresponding to $B_{10}H_{12}(py)_2$ was observed; the material present was $B_{10}H_{12}[(C_2H_5)_3N]_2$ with smaller quantities of $B_{10}H_{10}^{-2}$ and $B_{10}H_{12}[(C_2H_5)_3N]py$.

A control kinetic run in which $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was used as substrate proved that, under the same conditions, no yellow products were formed from this material.

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Observation of the Chelate Effect with a Bidentate Lewis Acid, $F_2BCH_2CH_2BF_2$

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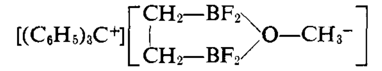
Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received October 5, 1966

Abstract: Chelate adducts appear to form when $F_2BCH_2CH_2BF_2$ reacts with triphenylmethyl ethers. These adducts involve the coordination of both boron atoms of the Lewis acid to a central oxygen donor, *e.g.*



$$[(C_6H_5)_3C^+]\left[\begin{matrix}CH_2\text{—}BF_2 \\ | \\ CH_2\text{—}BF_2\end{matrix}\!\!>O\text{—}CH_3^-\right]$$

This is the converse of the usual situation where a central metal ion serves as an acceptor toward a difunctional base. The chelate effect appears to contribute to the stability of these adducts as evidenced by the displacement of BF_3 from $[(C_6H_5)_3C^+][H_3CO\cdot 2BF_3^-]$ by $F_2BCH_2CH_2BF_2$. In the course of these studies, a number of more conventional 2:1 donor–acceptor adducts were prepared by the interaction of a variety of oxygen-containing Lewis bases with the difunctional Lewis acids $F_2BCH_2CH_2BF_2$ and $Cl_2BCH_2CH_2BCl_2$.

It has been reported that the difunctional Lewis acid, 1,2-bis(dichloroboryl)ethane,[1] reacts with bases in a straightforward manner to produce 2:1 adducts,[2,3] *e.g.*

$$Cl_2BCH_2CH_2BCl_2 + 2(CH_3)_3N \longrightarrow (CH_3)_3NBCl_2CH_2CH_2BCl_2N(CH_3)_3 \quad (1)$$

If the Lewis base contains a labile proton, however, B–Cl bond cleavage occurs,[3] *e.g.*

$$Cl_2BCH_2CH_2BCl_2 + 4MeOH \longrightarrow (H_3CO)_2BCH_2CH_2B(OCH_3)_2 + 4HCl \quad (2)$$

It is not surprising that the chloro acid reacts normally, with each boron atom acting as an electron-pair acceptor toward a monofunctional Lewis base. However, the structure of the molecule suggests that a chelate adduct (1:1 stoichiometry of acid and base) could be achieved with a proper donor atom. This would be the analog of the well-known ethylenediamine–metal ion systems found in transition metal coordination chemistry. For such systems, it is known that the complex which contains a five- or six-membered chelate ring is generally more stable than a similar complex containing monofunctional ligands.[4] To a first approximation, this chelate effect has a simple statistical explanation;[4] so the chelate effect is expected for difunctional acids as well as difunctional bases.

In order to achieve a chelate adduct with the dihaloborylethanes, a base must be employed which contains at least two nonbonding electron pairs on a single atom. Furthermore, the dibasic donor atom must be of sufficient basicity to coordinate both boron atoms, yet of

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(1) For brevity, 1,2-bis(dichloroboryl)ethane is referred to as the "chloro acid," and 1,2-bis(difluoroboryl)ethane is likewise termed "fluoro acid."

(2) G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5299 (1954).

(3) A. K. Holliday and A. G. Massey, *J. Chem. Soc.*, 43 (1960).

(4) C. G. Spike and R. W. Parry, *J. Am. Chem. Soc.*, **75**, 2726 (1953).

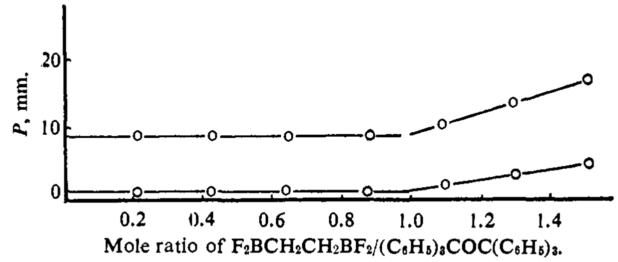

Figure 1. Tensimetric titration of triphenylmethyl ether with 1,2-bis(difluoroboryl)ethane. The solvent is toluene. Data for the upper curve were collected at 0° and for the lower curve at −23°.

insufficient basicity to cause boron–halogen bond cleavage. These basicity considerations along with steric considerations led us to concentrate on oxygen-containing bases such as ethers, ketones, and the methoxide ion.

Experimental Section

Materials. The following compounds were prepared according to procedures given in the literature: 1,2-bis(dichloroboryl)ethane, vapor pressure at 26.3° 7.0 mm (lit.[2] 6.9 mm), mp −28.5° (lit.[2] −28.9); 1,2-bis(difluoroboryl)ethane, vapor pressure at 0° 154.6 mm (lit.[5] 156 mm), mp −31.2° (lit.[5] −31°), mol wt (gas density), 128 (calcd 126); triphenylmethyl ether, mp 239–240° (lit.[6] 235–238°); methyl triphenylmethyl ether, mp 83–84° (lit.[7] 84°); diphenylcyclopropenone, mp 119° (lit.[8] 119°). Dimethyl ether and tetrahydrofuran were distilled from lithium aluminum hydride directly into the reaction vessel. Pyridine N-oxide was distilled under reduced pressure. Methylene chloride, toluene, and dimethyl sulfoxide were dried over calcium hydride and distilled. Other materials were analytical grade reagents and were used without further purification.

Techniques. Most of the compounds used in these studies were air sensitive, so manipulations were performed on a vacuum line or in a glove bag or drybox.

The initial experiment performed with each donor compound was a tensimetric titration. Tared samples of the less volatile reagent were dissolved in toluene, and incremental additions of the more volatile component were then made. After each addition the pressure above the solution was measured. Typical results are shown in Figure 1.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. Alfred Bernhardt, Mikroanalytisches Laboratorium, Mühlheim (Ruhr), West Germany.

Visible and ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer. Infrared measurements were performed on a Beckman Model IR-9 prism-grating spectrometer.

Results and Discussion

2:1 Adducts. Since the purpose of this research was to prepare "chelate" adducts, the 2:1 adducts were not investigated in as much detail as the 1:1 adducts.

Dimethyl Ether. In the tensimetric titration, a white solid precipitated from the reaction medium when dimethyl ether was treated with either acid. A break in the titration curve occurred at a ratio of 1.9 moles of ether to 1 mole of the acid. As shown by infrared spectra, the product isolated from the titration was identical with a sample of the 2:1 complex prepared by reaction of stoichiometric quantities of the ether and acid in a sealed tube. This white crystalline compound sublimes *in vacuo*. *Anal.* Calcd for $C_6H_{16}B_2Cl_4O_2$: C, 25.41; H, 5.69; B, 7.63; Cl, 50.00. Found: C, 25.17; H, 5.60; B, 7.85; Cl, 50.04. A similar product was obtained as colorless crystals (mp ~63°) from the reaction of dimethyl ether with the fluoro acid in a sealed tube. The compound had a high vapor pressure and dissociated when taken from the sealed tube.

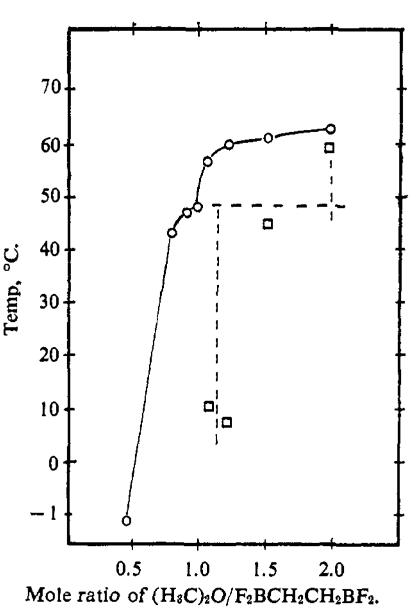

Figure 2. Phase relationships in the dimethyl ether–1,2-bis(difluoroboryl)ethane system: ○, liquidus; □, approximate solidus.

A partial phase diagram of the dimethyl ether–fluoro acid system was obtained by the visual determination of melting points for a series of samples contained in sealed tubes. A break in the melting point curve at 38° (Figure 2) indicated the presence of a new phase which melts incongruently. The visual technique used in these determinations did not allow accurate observations of the first sign of melting. Thus the stoichiometry of the incongruently melting phase could only be approximately determined as 1:1. This unstable intermediate may be the desired 1:1 chelate adduct, but other possibilities include polymers or singly coordinated $F_2BCH_2CH_2BF_2$.

Other 2:1 Adducts. As judged by tensimetric titration and weight-gain experiments, the following bases formed 2:1 adducts: tetrahydrofuran, $F_2BCH_2CH_2BF_2 \cdot 2THF$, mp 71–73°; $Cl_2BCH_2CH_2BCl_2 \cdot 2THF$, mp 81–82°; diphenylcyclopropenone, $F_2BCH_2CH_2BF_2 \cdot 2C_{15}H_{10}O$, mp 134°; pyridine N-oxide, $F_2BCH_2CH_2BF_2 \cdot 2C_5H_5NO$.

To summarize, dimethyl ether and each of the above compounds seem to react in a manner which is consistent with a normal Lewis acid–base neutralization reaction similar to that shown in eq 1.

1:1 Adducts. Since we were unsuccessful in preparing stable 1:1 chelate adducts with the oxygen-containing donors listed above, a stronger base, the methoxide ion, was tried. The preparation of pure methoxide salts with large organic cations appeared unattractive, so we investigated the possibility of cleaving triphenylmethyl ethers with the Lewis acid to provide *in situ* generation of the cation and methoxide group, in a manner analogous to the known protolytic cleavage

$$H^+ + (C_6H_5)_3COC(C_6H_5)_3 = (C_6H_5)_3C^+ + HOC(C_6H_5)_3$$

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(5) P. Ceron, A Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **81**, 6368 (1959).

(6) M. Gomberg, *ibid.*, 35, 205 (1913).

(7) W. R. B. Arthur, A. G. Evans, and E. Whittle, *J. Chem. Soc.* 1940 (1959).

(8) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965).

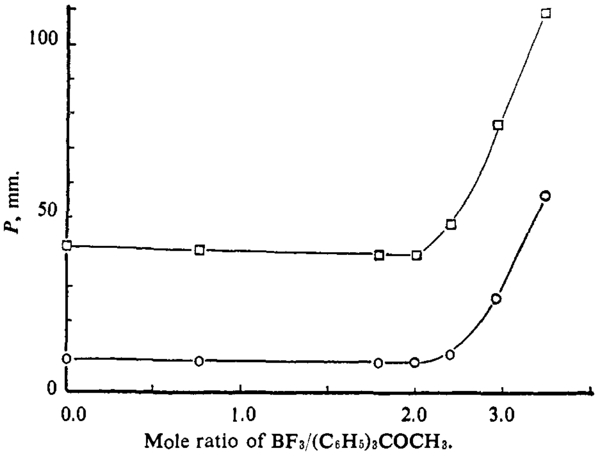


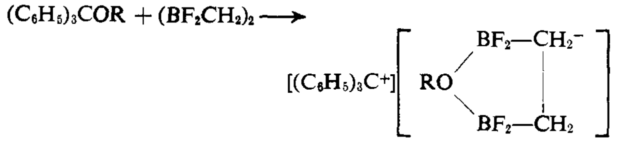
Figure 3. Tensimetric titration of methyl triphenylmethyl ether in methylene chloride solution with boron trifluoride: ○, −45°; □, −23°.

Triphenylmethyl Ether. Addition of the fluoro acid to a toluene solution of the ether produced an immediate yellow coloration. The visible spectrum of this solution showed twin absorption maxima at 410 and 430 mμ. This agrees with the published spectrum of the triphenylmethyl cation.[9] Continued addition of the fluoro acid produced a yellow precipitate. A break in the tensimetric titration curve occurred at a 1.0 mole ratio of acid to base (Figure 1). The compound isolated from the reaction tube consisted of air-sensitive, golden yellow crystals, mp 113–114°. *Anal.* Calcd for $C_{40}H_{34}B_2F_4O$: C, 76.46; H, 5.45; B, 3.44; F, 12.10. Found: C, 76.26; H, 5.65; B, 3.24; F, 11.84. A weight-gain experiment showed that 1.01 moles of the acid was absorbed for each mole of the base. The infrared spectrum revealed the complete absence of B–F stretching frequencies for trigonally bonded boron (1350–1380 cm^{-1}), while new peaks appeared which are attributable to B–F vibrations of four-coordinate boron (1045 and 1062 cm^{-1}). This indicates that both ends of the acid molecule are coordinated.

Methyl Triphenylmethyl Ether. The characteristic yellow coloration due to triphenylmethyl cation was again produced upon addition of the fluoro acid to toluene solutions of the ether. A break in the tensimetric titration curve occurred when 1.0 mole of the acid had been added per mole of the ether. The product was isolated as yellow-orange crystals, mp 72–73°. The weight gain of the product obtained from methylene chloride solution showed 0.990 mole of the acid absorbed per mole of the ether, and an infrared spectrum revealed BF_2 stretching frequencies in the vicinity of 1050 cm^{-1}.

Triphenylmethylcarbinol. When treated with the fluoro acid, this compound behaves in a manner analogous to the methyl triphenylmethyl ether. The tensimetric titration curve showed that 1.1 moles of acid had been absorbed per mole of base. The product was a lemon yellow solid, mp 68–69°. It displayed the B–F infrared absorptions around 1040 cm^{-1}.

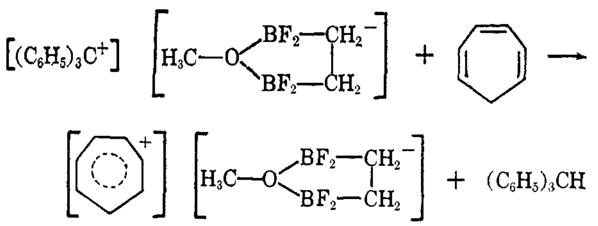
The above reactions indicate that a 1:1 complex is formed in the reaction between 1,2-bis(difluoroboryl)-ethane and triphenylmethyl ethers. The simplest equation for the reaction is


(3)

where R = $(C_6H_5)_3C$, CH_3, and H.

In order to obtain pure solids which displayed a weight gain corresponding to 1:1 stoichiometry from methylene chloride solution, it was necessary to remove most of the solvent in the presence of $F_2BCH_2CH_2BF_2$ vapor. This was accomplished by maintaining an excess of the fluoro acid in the system while the bulk of the methylene chloride was removed by distillation into a trap held at 0°. This left a deposit of crystals from which the last traces of solvent could be removed under high vacuum. When these precautions were not taken, a low weight gain was observed. Similarly, some spectrophotometric data on methylene chloride solutions indicated that an equilibrium loss of $F_2BCH_2CH_2BF_2$ occurs. We interpret the general nature of the equilibrium in terms of competition between the Lewis acids $(C_6H_5)_3C^+$ and $F_2BCH_2CH_2BF_2$ for the available coordination sites on the methoxide.

To avoid the complications which this equilibrium would introduce in molecular weight measurements, a tropenium (tropylium) derivative was prepared (eq 4).


(4)

The resonance stabilization of the tropenium ion should reduce its acidity and thus stabilize the product in solution. The details of this reaction have been presented in a previous communication, where it was also shown that freezing point depression data in a sulfolane solution of the ionic product of eq 4 agree with the formulation presented.[10] This molecular weight data along with the infrared spectra, which show that both ends of the fluoro acid are coordinated, indicate that the 1:1 salts are correctly formulated as chelate adducts.

In order to test for the chelate effect, we prepared a BF_3 adduct, $[(C_6H_5)_3C^+][H_3CO\cdot 2BF_3^-]$, and performed a competition experiment to see if this compound or the corresponding $F_2BCH_2CH_2BF_2$ adduct is the more stable. The reaction of BF_3 with a methylene chloride solution of $(C_6H_5)_3COCH_3$ was followed by tensimetric titration at 0, −23, and −45° (Figure 3). At all three temperatures the curve broke when 2.0 moles of acid had been added per mole of ether. The mixture was allowed to stand overnight at −78° after which removal of the volatiles and measurement of the BF_3 showed that 2.2 moles of BF_3 had been absorbed. A further indication of the instability of this adduct was afforded by the slow evolution of small quantities of gas, which were less volatile than BF_3, and the weight gain of the solid, which was less than expected. Presumably, $B(OCH_3)_3$ and/or methoxyfluoroboranes are produced upon standing. The competition experiments which are described below were conducted in 4

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(9) G. Branch and H. Walba, *J. Am. Chem. Soc.*, **76**, 1564 (1954).

(10) M. J. Biallas and D. F. Shriver, *ibid.*, **88**, 375 (1966).

Table I. Displacement Reactions

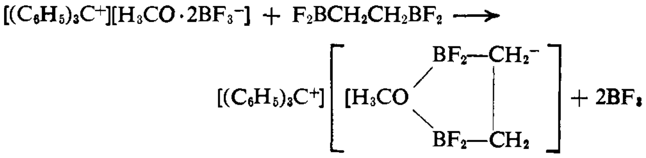
Expt	Temp, °C	$(C_6H_5)_3COCH_3$ mmole	$(C_6H_5)_3COCH_3$ M.f.	BF_3 mmole	BF_3 M.f.	$F_2BCH_2CH_2BF_2$ mmole	$F_2BCH_2CH_2BF_2$ M.f.	Recovered reagent, mmole	Ratio, ether: $(CH_2BF_2)_2$
1	25	0.420	...	0.844	...	0.435	...	0.843 (BF_3)	1.00
2	−23	0.341	...	Excess	...	3.489	...	3.138 ($(CH_2BF_2)_2$)	1.03
3	−45	0.158	0.00361	...	0.0441	1.649	0.0377	1.494 ($(CH_2BF_2)_2$)	0.98

hr or less, so they are probably not affected by fluoride–methoxide metathesis.[11]

Three displacement experiments are summarized in Table I. In the first two, an excess of BF_3 over $F_2BCH_2CH_2BF_2$ was present, but as a consequence of the greater volatility of BF_3 and the appreciable free gas volume in the system, the concentration of difunctional Lewis acid in solution exceeded that of BF_3. Thus, the preference of the ether for the difunctional Lewis acid in these two cases is not compelling evidence for a chelate effect.

The third experiment was conducted at −45° and involved a tenfold excess of $F_2BCH_2CH_2BF_2$ over the ether. The low temperature ensured that all of the difunctional Lewis acid would be retained in the methylene chloride solution, and the excess of acid ensured that its concentration would not be significantly altered by the reaction. The pressure of BF_3 over this system was 552.6 mm, and from Raoult's law this leads to a calculated concentration of BF_3 in the methylene chloride solution of 0.0441 mole fraction. This concentration exceeds that of the difunctional acid (0.0377 mole fraction) so the experiment constitutes a good check for the chelate effect.

The direct removal of volatiles from this reaction mixture will initially deplete the most volatile component, BF_3, and conceivably shift the equilibrium to favor the difunctional acid. To avoid this complication, the mixture was allowed to equilibrate for 1 hr at −45°; it was then quickly frozen with liquid nitrogen, and a large excess of pentane was distilled into the system.[12] The mixture was allowed to melt at which point the presence of pentane quenched the reaction by causing the ionic adduct to precipitate. The volatiles were then quickly removed, and BF_3 was separated from the solvent, pentane, and $F_2BCH_2CH_2BF_2$ by trap-to-trap distillation. The less volatile fraction was treated with an excess of triethylamine to produce the bis(triethylamine) adduct of $F_2BCH_2CH_2BF_2$ which was determined by weight. As shown in Table I, the difunctional acid rather than BF_3 was retained by by the ether; that is



This result demonstrates that the chelate effect contributes to the stability of the adduct formed between 1,2-bis(difluoroboryl)ethane and the methoxide ion.

Acknowledgment. This research was supported by the National Science Foundation through Grants GP-1977 and GP-3804 and also by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center. M. J. B. was the holder of an NSF predoctoral fellowship (1962–1964). We thank Dr. Judd Posner and Professor John Frey for helpful discussion.

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(11) Tensimetric titration of triphenylmethyl ether with boron trifluoride also showed the existence of a yellow 1:2 adduct. However, structures of these compounds were not established in our work. Judging from their color, they are undoubtedly ionic, but the second boron may be linked to either oxygen or a fluorine, *i.e.*, either $R{-}O(BF_3)_2^-$ or $R{-}O{-}BF_2{-}F{-}BF_3^-$. From a variety of chemical analogies we favor the former structure. In a formal sense we may test for a chelate effect irrespective of the exact structure of this anion.

(12) In the process of freezing the reaction mixture, the concentration of BF_3 in solution is undoubtedly increased above the value given in Table I.