

The vapor tensions of *n*-propyldifluoroborane (Table III) determined the equation $\log p_{\text{mm.}} = 8.478 - 1535 T^{-1}$, from which is calculated a boiling point of 1.1°, and the Trouton constant of 25.6 e.u. The compound melts at -106°.

The new compound allyldifluoroborane was prepared by heating boron trifluoride with tetraallyltin. The vapor tensions (Table IV) of allyldifluoroborane (m.p. -154.7°) determined the equation $\log p_{\text{mm.}} = 8.160 - 1462 T^{-1}$, implying a boiling point of 3.7° and a Trouton constant of 24.2 e.u.

4. Vapor Tensions of the Vinylhaloboranes.—Vapor tensions given in Table V imply the relevant physical constants summarized in Table I.

5. Infrared Spectra of the New Organohaloboranes.—These were recorded as gases using a 4 cm. cell fitted with NaCl plates. Initially a pressure of 100 mm. was used, but in order to establish the centers of the strong bands, further spectra at 20 mm. pressure were taken.^{14,21}

6. Reactions between Vinylidifluoroborane and Certain Organometallic Compounds.—Vinylidifluoroborane (101 cc., 4.5 mmoles) and *tetravinyltin* (0.643 g., 2.83 mmoles) were heated in a one-liter bulb at 120° for 15 hr., after which time 99.7 cc. of vinylidifluoroborane (identified by its infrared spectrum) and a trace of boron trifluoride (identified by

its spectrum) were recovered. The vinylidifluoroborane then was returned to the reaction vessel and heated at 150° for 17 hr., but even under these conditions 98% of the vinylboron fluoride was recovered, although the tin compound had begun to decompose, yielding ethylene and a trace of butadiene (identified by their infrared spectra).

Vinylidifluoroborane was unaffected on heating for 18 hr. with *divinylmercury* (at 120°) and *tetraethyltin* (at 120°). Similarly, the vinylboron fluoride was 96% recovered after treatment with *divinylzinc* at room temperature for 18 hr.

A 0.611 g. (4.95 mmoles) sample of *diethylzinc* was treated with 101 cc. (4.51 mmoles) of vinylidifluoroborane for 1 hr. at ambient temperature. Fractionation of the products, with identification by comparing spectra with those of the pure compounds, yielded 43.4 cc. of triethylborane held at -80°, and 52.7 cc. of vinylidifluoroborane condensed at -196°. This represents a 95% recovery of boron.

Trimethylaluminum (1.59 g., 22.1 mmoles) reacted rapidly with vinylidifluoroborane (150 cc., 6.70 mmoles) near 0° to afford 104 cc. of trimethylborane (identified by comparing its infrared spectrum with an authentic sample of Me₃B) condensing at -120° and 3.5 cc. of a trimethylborane-ethylene mixture at -196°. This corresponds to a 71% conversion of vinylidifluoroborane to trimethylborane.

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Organoboron Halides. III. Lewis Acidity and F¹⁹ Nuclear Magnetic Resonance Spectra of Some Organodifluoroboranes^{1,2}

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The trimethylamine addition compounds of methyl-, ethyl-, *n*-propyl- and vinylidifluoroborane have been prepared and their liquid saturation pressures and gas-phase dissociations measured. The enthalpies of dissociation are markedly similar. F¹⁹ nuclear magnetic resonance chemical shifts indicate that the substituent group X in X-BF₂ molecules exerts an effect on the BF₂ moiety which is different from that predicted on the basis of simple electronegativity considerations. The possible significance of these observations is discussed.

Introduction

The study of gas-phase dissociation equilibria of molecular addition compounds⁴ has demonstrated that a variety of factors may play a part in determining the relative stabilities of a series of similar adducts. The substituents bonded to any given pair of donor and acceptor atoms, *e.g.*, nitrogen and boron, are of great importance in determining their coordination behavior, and it has been amply shown that substituent effects may be inductive, steric, mesomeric or a combination of these and other factors. Unfortunately, most of the existing data which demonstrate substituent effects have been concerned with the donor. With but two exceptions, mentioned below, quantitative gas-phase dissociation studies of molecular addition compounds of boron with donor atoms of Groups V and VI have involved either boron trifluoride, borane or trimethylborane as the Lewis acid.

(1) (a) Previous paper, F. E. Brinckman and F. G. A. Stone, *THIS JOURNAL*, **82**, 6218 (1960). (b) Also Part IV of the series "Molecular Addition Compounds of Boron"; for Part III see H. D. Kaesz and F. G. A. Stone, *ibid.*, **82**, 6213 (1960).

(2) The work described in this paper was made possible by the award of a grant (G5106) from the National Science Foundation and was first presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(3) Edwin W. Rice, Jr., Fellow of the General Electric Educational and Charitable Fund, 1959-1960.

(4) For a review of molecular addition compounds of the Group III elements, see F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

The earliest systematic investigation of the effect of varying substituents on the boron atom was performed by Burg and Green⁵ who showed that successive substitution of methyl groups for the more highly electronegative fluorine led to decreasing acidity toward trimethylamine in the sequence BF₃, CH₃BF₂, (CH₃)₂BF, (CH₃)₃B. More recently, Miller⁶ has shown a similar order of acidity in the methylchloroboranes.

The relative effect of different alkyl groups on the acceptor power of boron has not been investigated heretofore. In contrast, Brown and his co-workers⁷ have shown that methyl, ethyl and *n*-propyl groups on nitrogen increase the Lewis basicity of the amines in the order NH₃ < CH₃NH₂ < C₂H₅NH₂ < *n*-C₃H₇NH₂, as would be expected on the basis of the accepted order of electron-releasing power of the substituent groups. A complementary study of the relative Lewis acidities of a series of organoboron compounds seemed, therefore, to offer an interesting area of investigation.

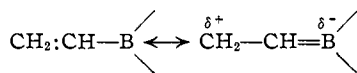
The possible effect on Lewis acidity of a vinyl group bonded to boron is particularly interesting, both intrinsically and for the sake of comparison

(5) A. B. Burg and A. A. Green, *THIS JOURNAL*, **65**, 1838 (1943).

(6) N. E. Miller, *Diss. Abstr.*, **18**, 1972 (1958).

(7) (a) H. C. Brown, H. Bartholomay and M. D. Taylor, *THIS JOURNAL*, **66**, 435 (1944); (b) H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947); (c) H. C. Brown, M. D. Taylor and S. Sujishi, *ibid.*, **73**, 2464 (1951).

with the corresponding effects of saturated groups. On theoretical grounds, the vinyl group, with sp^2 -hybridized carbon, may be expected to be more electronegative than a typical alkyl group, *e.g.*, ethyl, in which the carbon hybridization is sp^3 .⁸ Dipole moment measurements⁹ support this prediction. Accordingly one might expect substitution of a vinyl group for an ethyl group on boron to increase acceptor strength through operation of an inductive effect, leading in organodifluoroboranes, for example, to the hypothetical order of acidity: $C_2H_3BF_2 > C_2H_5BF_2$. However, trivalent boron possesses a low-lying vacant p_π -orbital, suggesting that mesomeric interactions of the type



may make a substantial contribution to the ground state of the free acceptor molecule which would be absent in the adduct, where the boron atom is tetravalent. Such an interaction in the free acid, with partial double bond character in the B-C bond, would increase the reorganizational energy⁴ necessary for addition compound formation. If this effect were dominant, the order of acidity might then be $C_2H_5BF_2 > C_2H_3BF_2$.

Qualitative evidence already has been given¹⁰ that such an effect exists in the vinylalkylboranes, and the results of dipole moment studies indicate that there may be a similar mesomeric interaction in the closely analogous $C_6H_5BF_2$.¹¹ However, no quantitative evaluation has been made of the mesomeric effect of the vinyl or similar unsaturated groups in these compounds.

An investigation¹² in this Laboratory of the effect of the vinyl group on donor power of phosphorus established the order of basicity $C_2H_3P(CH_3)_2 < P(CH_3)_3 < C_2H_5P(CH_3)_2$ relative to trimethylborane. While there is more than one possible explanation of such an order, it is clear that delocalization of π -electron density into the vacant d-orbitals of phosphorus can have no significant effect on the over-all Lewis base character of vinyl dimethylphosphine.

The qualitative evidence for delocalization of electron density from the vinyl group in vinylboranes, contrasted with the apparent absence of the somewhat analogous $d_\pi-p_\pi$ interaction in a vinylphosphine, led us to extend our proposed study of the alkyl boron compounds to include a comparable vinylboron compound. We therefore undertook to investigate the relative acceptor power of boron atoms bonded to methyl, ethyl, *n*-propyl and vinyl groups by the gas-phase dissociation technique, using a suitable reference base. For the reasons outlined below, the organodifluoroboranes were chosen as the Lewis acids to be studied. This choice had the added advantage of allowing us to extend the scope of the study to include an investigation of the F^{19} nuclear mag-

netic resonance spectra of the free acceptor molecules, providing an additional source of information on the influence of the organic substituent.

The choice of suitable boron-containing Lewis acids was performed a compromise dictated by the need to attain several desirable characteristics. Ideally, the reference acids RB_2 should be chosen to minimize the possibility of complicating steric effects, should be stable to chemical reaction other than the reversible dissociation of the adduct, should form adducts which are partially dissociated in a convenient temperature range and should be such that the groups Y, if different from R, are constant in their effect on the acceptor strength of the central atom. Naturally, the groups Y must be identical within the series. The triorganoboranes are unsuitable on steric grounds and because of the instability of trivinylborane. Mixed organoboranes, *e.g.*, $RB(CH_3)_2$, are well known to be unstable toward disproportionation, especially in the presence of base, while the same is true for organodiboranes. The easily accessible¹³ organodifluoroboranes, on the other hand, have been shown to be quite stable, have minimal steric requirements and afford trimethylamine adducts which are partially dissociated in the gas phase in the range 125–165°. Consequently, the RBF_2 series was chosen for this study. The complex $(CH_3)_3N \cdot BF_2CH_3$ was previously investigated by Burg and Green,⁵ but this study was repeated here using several experimental refinements¹² which have come into general use since the early work and in order to provide internal consistency within our series.

Experimental

1. Starting Materials and Apparatus for the Study of the Addition Compounds $(CH_3)_3N \cdot BF_2R$.—Trimethylamine (Eastman White Label) was treated with phosphorus pentoxide to remove traces of primary and secondary amines and distilled to yield a homogeneous sample with vapor pressure 680 mm. at 0° (lit.¹³ 681.7 mm.). Methyl, ethyl-, *n*-propyl- and vinyl difluoroborane were prepared by treatment of the appropriate tetra-organotin compound with boron trifluoride¹⁴ and purified by repeated fractional condensation in the vacuum line until tensimetric homogeneity was attained. The infrared spectra of the purified Lewis acids showed no bands attributable to the principal contaminant, boron trifluoride, under conditions where a few tenths of 1% would be readily apparent. Methyl difluoroborane had a vapor pressure of 78.0 mm. at -96.1° (lit.¹⁴ 78.1 mm.). The other organodifluoroboranes exhibited vapor pressures in close agreement with the values obtained by other workers in this Laboratory.¹⁵ Additional purification of propyl difluoroborane by formation of the trimethylamine adduct and displacement by boron trifluoride had no effect on the observed enthalpy of dissociation of the addition compound. The structure of the *n*-propyl difluoroborane was indicated by infrared and proton nuclear magnetic resonance spectra. Additional confirmation of the straight chain structure was given by the mass-spectrometric cracking pattern. The importance of purity factors may be judged from the fact that the undetected presence of 1% inert impurity in the Lewis acid vinyl difluoroborane would result in an enthalpy value which is about 0.2 kcal. mole⁻¹ too low.

The apparatus used for measurement of saturation pressures and gas-phase dissociations has been described pre-

(12) (a) H. C. Brown, M. D. Taylor and M. Gerstein, *ibid.*, **66**, 431 (1944); (b) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

(13) J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen and H. F. Zahr, *ibid.*, **66**, 1171 (1944).

(14) A. B. Burg, *ibid.*, **62**, 2228 (1940).

(8) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p. 207.

(9) (a) H. C. Brown, *THIS JOURNAL*, **61**, 1483 (1939); (b) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

(10) T. D. Parsons, M. Silverman and D. M. Ritter, *THIS JOURNAL*, **79**, 5091 (1957).

(11) C. Curran, P. A. McCusker and H. S. Makowski, *ibid.*, **79**, 5188 (1957).

viously,¹⁵ as have the limits of accuracy of the dissociation measurements.¹²

Samples for saturation pressure measurements were prepared by combining equivalent amounts of carefully purified acid and base in the tensimeter. Any slight excess of either component was removed by pumping briefly at low temperature after the tensimeter had been held for thirty minutes or more at a temperature at which the adducts are liquid, in order to ensure complete reaction. Sample size (54 ± 1 cc.),¹⁶ tensimeter volume (120 cc.) and pressure range were comparable for all samples. Under these conditions, saturation pressures and the "boiling points" and other constants obtained from the vapor pressure equations are comparable. Observed pressure values were corrected for density and vapor pressure of mercury.

For the gas-phase equilibrium measurements, samples were formed by combining accurately known and approximately equal volumes of acid and base in the dissociation tensimeter.¹⁵ Equilibrium constants were calculated from the equation

$$\log K_p (\text{atm.}) = \frac{(p_{\text{obsd.}} - p_{A'}) (p_{\text{obsd.}} - p_{B'})}{(p_{A'} + p_{B'} - p_{\text{obsd.}}) 760}$$

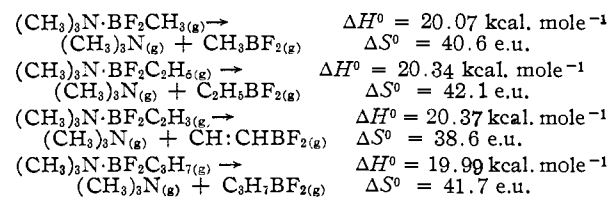
where $p_{\text{obsd.}}$ is the observed pressure, and $p_{A'}$ and $p_{B'}$, respectively, are the pressures which would be exerted by the acid and base if present alone in the tensimeter volume.

2. Saturation Pressures of the Complexes.—The observed liquid saturation pressures of the various complexes, formed by treating trimethylamine with an equal volume of the appropriate organodifluoroborane in the saturation pressure tensimeter, are recorded in Table I. In the case of $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_5$, after a saturation pressure determination a barely perceptible increase in the apparent vapor pressure of the complex was noted. Prolonged heating, *e.g.*, 7 hr. at 130° , increased the value of the saturation pressure at 84.4° by 5%, and after residual gases were removed by opening the complex to high vacuum at room temperature, the apparent vapor pressure of the material in the tensimeter was somewhat lower than had been observed previously.¹⁷ This result suggests that some disproportionation of the Lewis acid occurs at elevated temperatures. Such behavior is not unexpected in unsymmetrical boranes, especially in the presence of base and in the liquid phase. It is significant that reproducibility of observed pressures during dissociation measurements indicates that no measurable disproportionation occurs in the gas phase under the conditions of the measurements reported below.

The constants which may be derived from the saturation pressure measurements are summarized in Table VI.

3. Gas-Phase Dissociation of the Complexes.—The results for typical dissociation experiments are given in Tables II–V. During studies on $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_5$ evidence for disproportionation was obtained in some dissociation runs, as indicated by the production of traces of ethylene (identified by its infrared spectrum) and the occurrence of more or less sharp discontinuities in the $\log K_p$ versus T^{-1} curve. Constants calculated from the curves below the discontinuity agree with the results of the low pressure run recorded in Table IV in which no irreversibility was observed.

The results given in Tables II–V lead to these constants



4. Nuclear Magnetic Resonance Studies.— F^{19} Nuclear magnetic resonance spectra were obtained using a Varian V-4300B NMR Spectrometer equipped with superstabilizer, sample spinner and Sanborn 151 Recorder, and operating at 40 Mcps. at a field of approximately 10,000 gauss. Samples

(15) T. D. Coyle, H. D. Kaesz, F. G. A. Stone, *THIS JOURNAL*, **81**, 2989 (1959).

(16) Throughout this paper the abbreviation cc. refers to gases at standard conditions.

(17) Similar behavior was observed with liquid $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_5$ but not with $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{CH}_3$ or $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_3\text{H}_7$.

TABLE I

SATURATION PRESSURES OF LIQUID $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{R}$					
$t, ^\circ\text{C.}$	$P_{\text{mm.}}$ (obsd.)	$P_{\text{mm.}}$ (calcd.)	$t, ^\circ\text{C.}$	$P_{\text{mm.}}$ (obsd.)	$P_{\text{mm.}}$ (calcd.)
(a) $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{CH}_3$					
77.3	8.63	8.61	105.1	35.7	35.8
83.9	12.3	12.3	111.8	49.1	49.0
90.7	17.6	17.6	119.0	67.9	67.8
98.2	25.9	25.6			
(b) $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_5$					
77.3	5.84	5.81	105.6	27.5	27.4
84.4	8.72	8.77	111.9	37.5	37.5
91.4	13.0	12.9	118.9	52.5	52.5
98.5	19.0	19.0			
(c) $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_3$					
71.8	3.21	3.21	90.7	9.05	9.08
77.0	4.27	4.32	98.1	13.3	13.2
84.1	6.30	6.40	112.1	26.0	26.1
(d) $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_3\text{H}_7$					
70.2	2.57	2.56	104.8	19.5	19.5
77.0	3.93	3.95	111.8	28.3	28.1
83.9	5.99	6.00	118.9	40.3	40.2
91.0	9.08	9.10	126.1	57.5	57.0
97.9	13.5	13.4			

TABLE II

GAS-PHASE DISSOCIATION OF $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{CH}_3$

$t, ^\circ\text{C.}$	$P_{\text{obsd.}}$ (mm.)	$P_{\text{calcd.}}^{\text{a}}$ (mm.)		K_p (atm.)
		$P_{(\text{CH}_3)_3\text{N}}^{\text{a}}$ [$p_0 = 21.154$] ^a	$P_{\text{BF}_2\text{CH}_3}^{\text{a}}$ [$p_0 = 21.022$] ^a	
124.8	41.21	30.82	30.63	0.00715
129.8	43.09	31.21	31.01	.00987
134.9	45.05	31.60	31.41	.0134
139.9	47.02	31.99	31.79	.0180
145.1	49.29	32.39	32.19	.0249
150.0	51.29	32.77	32.57	.0325
155.1	53.43	33.17	32.96	.0430
159.9	55.48	33.54	33.33	.0561
145.1 ^b	49.29
129.8 ^b	43.14

^a $P_{\text{calcd.}}$ at 0° . ^b Check point on cooling.

TABLE III

GAS-PHASE DISSOCIATION OF $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_5$

$t, ^\circ\text{C.}$	$P_{\text{obsd.}}$ (mm.)	$P_{\text{calcd.}}^{\text{a}}$ (mm.)		K_p (atm.)
		$P_{(\text{CH}_3)_3\text{N}}^{\text{a}}$ [$p_0 = 20.940$] ^a	$P_{\text{BF}_2\text{C}_2\text{H}_5}^{\text{a}}$ [$p_0 = 21.474$] ^a	
124.9	43.26	30.51	31.29	0.0108
130.0	45.43	30.90	31.69	.0153
135.1	47.51	31.30	32.09	.0207
140.2	49.78	31.69	32.49	.0286
145.3	52.01	32.08	32.89	.0387
150.5	54.19	32.48	33.30	.0515
154.9	56.11	32.81	33.65	.0665
159.9	58.22	33.20	34.04	.0883
165.3	60.26	33.61	34.47	.116
150.5 ^b	54.17
135.1 ^b	47.51

^a $P_{\text{calcd.}}$ at 0° . ^b Check point on cooling.

were measured as pure liquids and in solution in CCl_3F . Samples for solution spectra were prepared by combining known quantities of the organodifluoroborane and CCl_3F (both measured as gases) in 5 mm. o.d. Pyrex tubes. Typically, solutions of 10, 15, 25 mole per cent. organodifluoroborane were prepared. The separations of the sample peaks from the reference peak of the solvent were measured

TABLE IV
 GAS-PHASE DISSOCIATION OF $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{CH}_2\text{CH}_3$

$t, ^\circ\text{C}.$	$P_{\text{obsd.}}$ (mm.)	$P_{\text{calcd.}}$		K_p (atm.)
		$P'_{(\text{CH}_3)_3\text{N}}$ [$p_0 = 13.463$] ^a	$P'_{\text{BF}_2\text{C}_2\text{H}_5}$ [$p_0 = 13.257$] ^a	
119.9	23.08	19.37	19.08	0.00127
124.5	23.93	19.60	19.30	.00176
129.8	24.98	19.86	19.56	.00253
135.0	26.01	20.12	19.81	.00345
140.0	27.09	20.36	20.05	.00468
145.1	28.21	20.62	20.30	.00622
150.0	29.38	20.86	20.54	.00824
155.0	30.63	21.10	20.78	.0110
145.1 ^b	28.20
135.0 ^b	26.01
124.5 ^b	23.96

^a $P_{\text{calcd.}}$ at 0° . ^b Check point on cooling.

 TABLE V
 GAS-PHASE DISSOCIATION OF $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_3\text{H}_7$

$t, ^\circ\text{C}.$	$P_{\text{obsd.}}$ (mm.)	$P_{\text{calcd.}}$ (mm.)		K_p (atm.)
		$P'_{(\text{CH}_3)_3\text{N}}$ [$p_0 = 20.275$] ^a	$P'_{\text{BF}_2\text{C}_3\text{H}_7}$ [$p_0 = 20.952$] ^a	
129.8	45.28	29.91	30.91	0.0187
134.9	47.43	30.29	31.30	.0257
140.0	49.60	30.67	31.69	.0350
145.1	51.70	31.05	32.08	.0466
150.0	53.71	31.41	32.46	.0614
155.0	55.71	31.78	32.84	.0808
159.9	57.67	32.15	33.22	.107
164.9	59.57	32.52	33.60	.141
170.0	61.21	32.90	33.99	.179
155.0 ^b	55.71
140.0 ^b	49.60

^a $P_{\text{calcd.}}$ at 0° . ^b Check point on cooling.

by the method of Filipovich and Tiers.¹⁸ By this means, averages of from ten to twenty individual measurements were obtained with a standard deviation of about 0.1 p.p.m. Extrapolation to zero mole per cent. organodifluoroborane did not change the relative orders of chemical shifts and indicated that the shift varies approximately linearly with concentration in this range. No peaks were observed which could be attributed to mixed organoboron halides or to chlorofluoromethanes other than CCl_3F , indicating no reaction of the solvent with the organodifluoroboranes. Measurements on pure liquid ethyl- and propyl-difluoroborane were obtained in 5 mm. o.d. Pyrex tubes containing CCl_3F , in a sealed capillary tube, as an external reference. Separations were measured by sweeping rapidly through the sample and reference peaks with a known modulating frequency applied to provide a calibration of the recorder trace. Results obtained by this technique are comparable to those obtained by the method used for the solution samples, although standard deviations are typically higher. Since it appeared injudicious to seal the more volatile methyl- and vinyl-difluoroborane in small sample tubes, these were measured in 5 mm. tubes to which a 75 cc. expansion bulb was sealed. The samples were condensed into the 5 mm. portion of the sample tube and the resonance observed as the sample warmed and vaporized. No bulk susceptibility corrections were applied.

The nuclear magnetic resonance spectra of the organodifluoroboranes each consist of four peaks of approximately equal intensity, as anticipated for two equivalent fluorines spin-coupled to the B^{11} nuclei (spin = 3/2). Unresolved underlying structure is evidently due to spin-coupling to the less abundant B^{10} (spin = 3), which would be expected to yield a septet. The chemical shift values listed in Table VIII are the separations in parts per million of the centers of the quartets from the single peak due to CCl_3F . The average peak-to-peak separation in the quartets yields the

(18) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 781 (1959).

$\text{B}^{11}\text{-F}^{19}$ spin coupling constants listed in the last column of Table VIII.

Discussion

Physical properties of the addition compounds are summarized in Table VI. The average values for the thermodynamic dissociation data are listed in Table VII. The dissociation data indicate that in terms of equilibrium constants the stability order: $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_5 > (\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{CH}_3 > (\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_3\text{H}_7 > (\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_3\text{H}_7$ is observed. However, this order largely reflects the variation of the entropy values. In terms of the usual criterion of strength of molecular addition compounds, *viz.*, enthalpies,⁴ the acceptor power of boron is markedly similar in all the compounds studied. While there is some indication that vinyl-difluoroborane is the strongest Lewis acid of the four and propyl-difluoroborane the weakest, it is most significant that all of the enthalpy values lie within the range 20.2 ± 0.2 kcal. mole⁻¹, the value 0.2 kcal. representing the approximate limits of experimental error in this technique.

 TABLE VI
 TRIMETHYLAMINE ADDUCTS OF ORGANODIFLUOROBORANES

Compound	M.p. ($^\circ\text{C}.$)	$\text{Log } p_{\text{v.m.}} = \frac{B}{A} - \frac{C}{T}$		B.p.^a ($^\circ\text{C}.$)	Trouw- ton con- stant ⁷ (e.u.)
		B	A		
$(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{CH}_3$	43.3-43.7	9.363	2954	183	29.7
$(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_2\text{H}_5$	23.7-24.7	9.774	3158	185	31.5
$(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_3\text{H}_7$	23.0-24.0	10.025	3302	189	32.7
$(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{C}_3\text{H}_7$	35.5-36.5	9.202	3000	201	28.9

^a By extrapolation of the vapor pressure equation.

It thus appears that the alkyl groups investigated have approximately the same effect on the acceptor power of boron in the alkyl-difluoroboranes. Comparison of our value for $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{CH}_3$ with the enthalpy of dissociation of $(\text{CH}_3)_3\text{N}\cdot\text{B}(\text{CH}_3)_3$ (17.62 kcal. mole⁻¹)^{7a} and of $(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$ (estimated^{4,19} to be 26.6-30.9 kcal. mole⁻¹) indicates that the effect of substituting methyl groups

 TABLE VII
 GAS-PHASE DISSOCIATION DATA^a FOR $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{R}$

R	$\text{Log } K_p$ (atm.) ⁻¹		$\Delta H^{\circ b}$ (kcal. mole ⁻¹)	$\Delta S^{\circ b}$ (e.u.)	$\Delta F^{\circ b}$ at 150° (kcal. mole ⁻¹)	K_p^b at 150° (atm.)	α^c at 150°
	A	B					
CH_3	8.908	4401	20.14	40.76	2.9	0.0323	0.58
C_2H_5	9.152	4426	20.25	41.88	2.5	.0494	.64
$n\text{-C}_3\text{H}_7$	9.147	4384	20.06	41.85	2.4	.0614	.68
C_3H_8	8.433	4458	20.40	38.59	4.1	.00793	.41

^a The values reported are averages. ^b ΔH° , ΔS° , ΔF° and K_p values are for the dissociation, $(\text{CH}_3)_3\text{N}\cdot\text{BF}_2\text{R}_{(g)} \rightarrow (\text{CH}_3)_3\text{N}_{(g)} + \text{RBF}_2_{(g)}$. ^c Approximate degree of dissociation at 150° under the conditions of these experiments.

for fluorine atoms is the greatest for the first such substitution. The enthalpy of dissociation of $(\text{CH}_3)_3\text{N}\cdot\text{B}(\text{C}_2\text{H}_5)_3$ is unknown, but displacement reactions have shown that triethylborane is considerably weaker than trimethylborane toward trimethylamine although the reverse is true with ammonia as the reference base.²⁰ These observations indicate that steric effects are important in

(19) S. H. Bauer and R. E. McCoy, *ibid.*, **60**, 1529 (1956).

(20) H. C. Brown, *This Journal*, **67**, 374 (1943).

determining the acidity of triethylborane toward trimethylamine, but it would appear from the results summarized in Table VII that the steric factors are unimportant when a single ethyl- or *n*-propyl group is bonded to boron, at least as far as enthalpy values are concerned.

The small effect on acid strength of changing the alkyl group is consistent with the relatively small variations in electronegativity among these simple *n*-alkyl groups. It is interesting to note that Brown and his co-workers³ obtained for the enthalpies of dissociation of the trimethylborane adducts of methyl-, ethyl and *n*-propylamines the values 17.64, 18.00 and 18.14 kcal. mole⁻¹, respectively. While these values are in the order expected from inductive effects, the differences, especially between ethylamine and propylamine, are quite small relative to the expected experimental error of 0.1–0.2 kcal. Similarly small differences may therefore be expected when the various alkyl groups are bonded to the acceptor atom in a Lewis acid-base pair, if the same effects are operating. Moreover, as will be described below, there is a possibility that factors operating within the BF₂ group may serve to oppose the effects of the organic group, making this system less sensitive to substituent changes than the alkylamine-trimethylborane system.

The enthalpy of dissociation of the vinyl-difluoroborane adduct may reflect such a lack of sensitivity to substituent changes, despite the greater electronegativity of the vinyl group. Alternatively, the possible inductive (acid-strengthening) and resonance (acid-weakening) effects noted above may approximately balance each other. Consequently, these data do not permit any clear decision as to the reality of the suggested π -delocalization in vinyl-difluoroborane.

Since Lewis acidity is a property of the molecule *per se*, the effects of the substituent group R in RBF₂ cannot be considered apart from the effects of the BF₂ group. The possibility of partial donation of lone-pair electrons from fluorine orbitals of suitable symmetry into the vacant p-orbital of boron in BF₃ has long been recognized²¹ and is invoked to explain the observed weakness of BF₃ as a Lewis acid relative to BCl₃ and BBr₃.^{22,23} Such interactions would occur equally well in RBF₂, and if the group R is less effective as a " π -donor" than is a fluorine atom, then the π -donation per fluorine atom, and B-F double bond character, may well be greater in RBF₂ than in BF₃. Similarly, the character of the B-F bonds may well differ in RBF₂ and R'BF₂ if R and R' differ in π -bonding ability. Such changes in the B-F bonds would affect the charge density at the central boron atom and hence the "reorganizational" energy required to promote the planar free acid to a tetrahedral configuration suitable for coordinate bond formation, and, therefore, could modify the acceptor power of the boron atom.

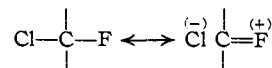
(21) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1959, p. 318.

(22) H. C. Brown and R. R. Holmes, *THIS JOURNAL*, **78**, 2173 (1956).

(23) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

If the delocalization of π -electron density from the vinyl group occurs in vinyl-difluoroborane, the effect will be to weaken the acid relative to ethyldifluoroborane, in which such mesomeric interactions cannot occur. However, if the greater degree of π -donation from the vinyl group were to be accompanied by a corresponding decrease in π -donation from the fluorine atoms, the net effect on Lewis acidity might be small.

Considerations such as these led us to investigate the response of the fluorine atoms to changes in the substituent group in the RBF₂ series by studying the F¹⁹ nuclear magnetic resonance chemical shifts of a series of fluoroboranes. The theoretical work of Saika and Schlichter,²⁴ as well as a considerable body of experimental data, indicates that F¹⁹ chemical shifts may frequently be correlated with the covalent character of the bond to the fluorine atom, *i.e.*, to the electron density at the fluorine. Thus the more ionic fluorides, in which the fluorine is more highly and symmetrically shielded, show the smaller paramagnetic shifts and exhibit resonance at higher applied field. Chemical shifts in binary fluorides, for example, are related to the electronegativity of the group bonded to fluorine. Moreover, Meyer and Gutowsky²⁵ found that in the fluoromethanes the chemical shift sequence, in terms of increasing field strength, is CF₄ < CF₃H < CF₂H₂ < CFH₃. Thus, as a result of the expected inductive effect, fluorine resonances are displaced to higher field as fluorine is replaced by the less electronegative hydrogen. In systems of this type, however, it is important to note that factors other than pure inductive effects may influence the chemical shifts. In the chlorofluoromethanes, formally analogous to the fluoromethane series, Meyer and Gutowsky²⁵ observed the order CFCl₃ < CF₂Cl₂ < CF₃Cl < CF₄, which they interpreted in terms of the increased importance of mesomeric interactions of the type



More recently, Smith and Smith²⁶ measured F¹⁹ chemical shifts in several other chlorofluorocarbons and found that here also electronegativity considerations are inadequate to explain the direction of the observed shifts.

The F¹⁹ chemical shifts and apparent B¹¹-F¹⁹ spin coupling constants obtained for the organo-difluoroboranes are summarized in Table VIII. All the resonances occur at considerably lower field than that of boron trifluoride which appears at about 127 p.p.m. on the CCl₄F scale. In terms of the present understanding²⁴ of F¹⁹ chemical shifts the data in Table VIII imply that there is a withdrawal of electron density from the remaining fluorines when one fluorine atom in boron trifluoride is replaced by an organic group, even though the latter usually is considered to be less "electronegative." This is understandable in terms of π -bonding effects in boron fluorides. Replacement of one of the fluorine atoms in boron tri-

(24) A. Saika and C. P. Schlichter, *ibid.*, **22**, 26 (1954).

(25) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(26) T. S. Smith and E. A. Smith, *ibid.*, **63**, 1701 (1959).

fluoride by an organic group with a compensatory increase in π -donation by the remaining fluorines could lead to magnetic unshielding of the fluorine nuclei with displacement of the resonance to lower applied field. It is significant that the F^{19} chemical shifts of the alkylidifluoroboranes, lying close together, appear at somewhat lower applied field than vinylidifluoroborane. This is in agreement with the idea of the presence of boron-carbon π -bonding in vinylidifluoroborane which would be expected to lead to the F^{19} resonances appearing in this compound at higher field than in ethylidifluoroborane.

TABLE VIII

F^{19} CHEMICAL SHIFTS^a AND B^{11} - F^{19} COUPLING CONSTANTS IN ORGANODIFLUOROBORANES

Compound	$\delta(\text{soln.})^b$	$\delta(\text{i.d.})^c$	$\delta(\text{liq.})^d$	$J_{(B^{11}-F^{19})}^e$
CH_3BF_2	69.3	68.8	73.6	77
$\text{C}_2\text{H}_5\text{BF}_2$	74.9	74.6	78.4	81
$\text{C}_3\text{H}_7\text{BF}_2$	73.2	72.8	75.8	81
$\text{C}_2\text{H}_3\text{BF}_2$	88.9	88.6	92.7	67

^a Parts per million relative to CCl_3F , increasing toward higher field. ^b Typical value, concentration *ca.* 15.5 mole %, in CCl_3F . ^c Extrapolated to zero concentration in CCl_3F . ^d Pure liquid, external reference CCl_3F in sealed capillary. ^e Cycles per second.

Concerning the suggestion put forward here that F^{19} chemical shifts in XBF_2 molecules may be related to the extent of F-B dative π -bonding, it has been found in studies reported elsewhere²⁷ that if X is one of a number of other atoms or groups, nominally less "electronegative" than fluorine, *e.g.*, Cl, Br, $\text{CF}_2\text{:CF}$, the F^{19} resonance appears at considerably lower field than in boron trifluoride. Moreover, the relative positions of the F^{19} resonances in a sequence of similar XBF_2 molecules are in agreement with present ideas concerning π -bonding between unlike atoms. Thus

(27) T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960).

in BrBF_2 the F^{19} resonance appears at lower applied field than in ClBF_2 . This is expected in terms of a chlorine atom's being able to partake in p_π - p_π bonding more effectively than a bromine atom but not so effectively as a fluorine atom. Moreover, in X_2BF compounds, where two fluorine atoms of boron trifluoride have been replaced, an even greater F^{19} shift to lower fields should occur because there should be greater π -bonding from fluorine to boron in X_2BF than in XBF_2 . Results are in agreement with this expectation. In dimethylfluoroborane, for example, the F^{19} resonance lies about 20 p.p.m. on the CCl_3F scale.

Among the alkylidifluoroboranes it might be expected that apart from hyperconjugative contributions if any, effects on fluorine shielding would be rather similar and inductive in nature. In fact, the order of electron attracting power, by the nuclear magnetic resonance criterion, appears to be methyl > *n*-propyl > ethyl. It should be noted that this sequence has been observed in recent nuclear magnetic resonance studies of mercury alkyls²⁸ and triorganosilanes.²⁹

Our results suggest, not surprisingly, that we cannot vary the substituent in the RBF_2 system without simultaneously inducing changes in the remainder of the molecule. It would be remarkable if this were not the case to some degree in any chemical system. The fluoroboranes, however, provide a particularly favorable situation for such interaction, having a relatively strong acceptor atom with a vacant orbital of suitable symmetry to overlap with the filled lone-pair orbitals of the adjacent atoms, with bond distances sufficiently short to permit significant overlap. This means in turn that simple substituent effects observed in other systems, *e.g.*, the alkylamines, may be wholly or partially obscured.

(28) R. E. Dessy, T. J. Flautt, H. H. Jaffé and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

(29) D. E. Webster, private communication.

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Preparation and Study of Some Perfluoroalkyl Compounds of Tin and Lead^{1,2}

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Tetraalkyllead compounds react directly with perfluoroalkyl iodides, under the influence of ultraviolet light or on heating, to give compounds of the type $\text{R}_3\text{PbC}_n\text{F}_{2n+1}$. When similar reactions were carried out with tetraalkyltin compounds most of the perfluoroalkyl groups went to produce fluorocarbons, and only small amounts of the $\text{R}_3\text{SnC}_n\text{F}_{2n+1}$ compounds were detected. However, the tin-tin bond in hexaorganoditin compounds is cleaved readily by perfluoroalkyl iodides to give the desired $\text{R}_3\text{SnC}_n\text{F}_{2n+1}$ derivatives. The perfluoroalkyl group is quantitatively removed by base from the perfluoroalkyltin and -lead compounds, but treatment with electrophilic reagents leads to preferential cleavage of alkyl or aryl groups. Important features of the infrared spectra of the new compounds are described.

In this Laboratory we have for some time been interested in preparing organoboron compounds in which the organo-group bonded to boron is

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(2) Presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, 1960. For a preliminary communication see H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *Chem. Ind. (London)*, 1409 (1959).

highly fluorinated. Therefore, a reaction between bis-(pentafluoroethyl)-mercury and boron trichloride at elevated temperatures was investigated, but the only product of significance was boron trifluoride.³ It has long been the opinion of many workers in this field that a boron compound in which a highly fluorinated organo-group is attached

(3) The same result was obtained in an independent study elsewhere. See J. J. Lagowski and P. G. Thompson, *Proc. Chem. Soc.*, 301 (1959).