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THE PREPARATION AND CHARACTERIZATION OF METHYL(PERFLUOROVINYL)BORANES *

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Summary

The methyl(perfluorovinyl)boranes $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ and $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ were prepared by reaction of $(\text{CH}_3)_2\text{Sn}(\text{C}_2\text{F}_3)_2$ with $(\text{CH}_3)_2\text{BBr}$ and CH_3BBr_2 , respectively. The methyl(perfluorovinyl)boranes were found to be thermally stable at temperatures to 100°C , but decompose rapidly above 200°C . Spectroscopic data is presented which indicates that B—C π -bonding may be more significant in the perfluorovinylboranes than in the analogous vinylboranes.

Introduction

An interesting feature of perfluorovinylhaloboranes and tris(perfluorovinyl)borane is their apparent stability towards fluorine atom migration from carbon to boron. Experimentally it has been found that the majority of organoboranes with fluorine bonded to a carbon atom α or β to boron, decompose rapidly via a fluorine migration to yield boron fluorides [1,2]. Another apparent exception is CF_3BF_2 which has been shown to be stable indefinitely in vacuo, but quantitatively decomposes by loss of difluorocarbene when catalyzed [3]. Several salts of the $[\text{CF}_3\text{BF}_3]^-$ anion have also been reported [4]. Stability of the anion is due, at least in part, to all boron valence orbitals being involved in σ -bonding thereby eliminating the acceptor ability of boron.

A reduction of the Lewis acidity of boron was recognized as the key in preparing α or β -fluorine substituted organoboranes. For example, no hexafluoropropene is formed in the thermal decomposition of $[(\text{CH}_3)_2\text{N}]_2\text{BC}_3\text{F}_7$, apparently as a result of B—N multiple bonding which prevents internal nucleophilic

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attack of fluorine on boron [5]. Moderately stable perfluorovinylhaloboranes were first reported by Stafford and Stone [6]. These authors concluded that decomposition by a fluorine atom shift mechanism to yield boron fluorides is inhibited by delocalization of the perfluorovinyl π -electrons into the boron p_{π} -orbital. It was further postulated that the perfluorovinylboron compounds might be more stable than their as yet unknown perfluoroethyl analogs since the boron p_{π} -orbital would be less satisfied in the latter.

Delocalization of the perfluorovinyl π -electrons into the available boron p_{π} -orbital has been postulated to cause a shift in the C=C stretching frequency [7] in the infrared as well as a deshielding of the β -fluorines [8] in the ^{19}F NMR spectra of these compounds. Thermal stability of the perfluorovinylboranes has also been rationalized as being due to B—C π -bonding. Ritter et al. [9] first compared the stability of mixed alkylboranes (i.e., methylethylboranes) with the analogous unsaturated methylvinylboranes. In this study they reported only a transient existence for the mixed alkylboranes which rearranged to the symmetrical $\text{B}(\text{CH}_3)_3$ and $\text{B}(\text{C}_2\text{H}_5)_3$. In contrast, mixed methylvinylboranes could be prepared and isolated. This suggested a mesomeric B—C interaction which could stabilize the vinylboranes. This conclusion was based on the inability to isolate the mixed alkylboranes; however, more recent studies [2,10-12] indicate that these compounds can be isolated and disproportionate only slowly.

In our efforts to elucidate the nature of the boron—carbon bond in vinylboranes [13-15], we have prepared and characterized the new compounds, methylbis(perfluorovinyl)borane and dimethyl(perfluorovinyl)borane. We were particularly interested in the thermal stability of these compounds relative to the methylvinylboranes because of the implications regarding the ability of the perfluorovinyl group to engage in a mesomeric interaction when bonded to an electron-deficient center such as boron. Additionally, since there are no halogens directly bonded to boron, any mesomeric interaction arises from delocalization of π -electron density of the perfluorovinyl group into the boron p_{π} orbital (neglecting the possibility of hyperconjugation) thereby simplifying an interpretation of the source of the mesomeric interaction.

Experimental

Methods

Standard high-vacuum techniques were employed wherever possible throughout this investigation. All starting materials were checked for purity by vapor pressure measurement and/or NMR, IR or mass spectrometry. Purification was achieved by trap-to-trap fractionation or by a low temperature, vacuum fractionation column [16].

Materials

Bis(perfluorovinyl)dimethyltin was prepared according to a published procedure from $(\text{CH}_3)_2\text{SnCl}_2$ (Alfa), Mg powder (Alfa) and $\text{C}_2\text{F}_3\text{Br}$ (PCR) [17]. Bromodimethylborane and dibromomethylborane were obtained commercially (Alfa) and used without further purification. Trimethylamine was obtained commercially (Matheson) and was purified until it exhibited a vapor pressure of 685 torr at 0° (lit. 680 torr at 0° [18]).

Spectroscopic techniques

Nuclear magnetic resonance spectra were obtained on Varian Associates XL-100-15 (^1H , 100.1 MHz; ^{11}B , 32.1 MHz; ^{19}F , 94.1 MHz) or A-60 (^1H , 60 MHz) spectrometers. Standard variable temperature techniques were employed. Field/frequency stabilization was provided by locking externally to the ^{19}F resonance of C_6F_6 or internally to the ^2H resonance of the methyl deuteriums of $\text{C}_6\text{D}_5\text{CD}_3$. All ^1H chemical shifts were referenced to external TMS. All ^{11}B chemical shifts were referenced to external neat $\text{B}(\text{OCH}_3)_3$ and were subsequently converted to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ reference by a factor of -18.1 ppm [19]. Fluorine-19 chemical shifts were referenced to an external sample of 10% CF_2Br_2 in toluene- d_8 and were adjusted to CFCl_3 reference by a conversion factor of -7 ppm [20]. Integrations were obtained directly from the spectrometer.

Gas phase infrared spectra were recorded on Perkin-Elmer 621 or 337 grating spectrophotometers in a 10 cm cell equipped with KBr optics. All spectra obtained on the Perkin-Elmer 337 spectrophotometer were calibrated immediately against known peaks in the spectrum of polystyrene film. Mass spectra were obtained on a Perkin-Elmer RMU-6 using the heated gas-inlet and were recorded at 70 and 15 eV. Exact mass measurements were obtained on an AEI MS 902.

Synthesis of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$

In a typical preparation, 6.9 mmol of $(\text{CH}_3)_2\text{BBr}$ were condensed into an evacuated and thoroughly dried glass reaction vessel. To this, 4.1 mmol of $(\text{CH}_3)_2\text{Sn}(\text{C}_2\text{F}_3)_2$ were measured and condensed into the reaction vessel which was then sealed from the system under dynamic vacuum. The reaction vessel was placed in a -112°C bath (CS_2 slush) which was allowed to warm slowly. Reaction began below -100°C as evidenced by the formation of a white precipitate. After the slush had warmed to -50°C (approximately 2 h), the vessel was agitated in an ice bath for an additional 30 min. The vessel was opened to the line under vacuum and all volatile material pumped onto a low temperature vacuum fractionation column for purification. Only one major volatile fraction was obtained, yielding 6.8 mmol of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ which represents a 98% yield based on $(\text{CH}_3)_2\text{BBr}$ consumed.

Synthesis of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$

The preparation of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ was basically the same as described above. If the reaction vessel is allowed to warm rapidly to room temperature from -196°C , formation of a brown, non-volatile oil was observed and yields of only 35% were obtained. By slowly warming the reaction vessel in a -112°C slush, the yield of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ was improved to 95.3% based on the amount of CH_3BBr_2 consumed.

Synthesis of $(\text{CH}_3)_2(\text{C}_2\text{F}_3)\text{B} \cdot \text{N}(\text{CH}_3)_3$ and $(\text{CH}_3)(\text{C}_2\text{F}_3)_2\text{B} \cdot \text{N}(\text{CH}_3)_3$

Adducts were prepared in evacuated 5 mm NMR tubes due to their low volatility. Equimolar quantities of the Lewis acid and base were condensed into the tube at -196°C and then allowed to warm slowly to 0°C . After pumping on the mixture to remove any excess acid or base, toluene- d_8 was condensed into the tube which was sealed under dynamic vacuum. Integration of the 60 MHz ^1H spectrum resulted in the following $(\text{CH}_3)\text{B}/(\text{CH}_3)_3\text{N}$ ratio for $(\text{CH}_3)_2(\text{C}_2\text{F}_3)\text{B} \cdot$

$N(CH_3)_3$: found, 1.00:1.56 (calcd., 1.00:1.50); for $(CH_3)(C_2F_3)_2B \cdot N(CH_3)_3$: found, 1.00:2.96 (calcd., 1.00:3.00).

Hydrolysis studies

Neutral hydrolysis of $(CH_3)_2BC_2F_3$ and $CH_3B(C_2F_3)_2$ results in the cleavage of the perfluorovinyl group with formation of HC_2F_3 which can be identified by IR and/or mass spectrometry. In one experiment, 1.06 mmol of $(CH_3)_2BC_2F_3$ were condensed into a reaction vessel containing 5 ml of degassed, distilled H_2O . The vessel was sealed under vacuum and placed in an oven at $120^\circ C$ for 24 h. Fractionation of the recovered volatile materials through traps held at -78° , -130° and $-196^\circ C$, yielded 1.04 mmol HC_2F_3 (calcd., 1.06 mmol) which condensed at $-196^\circ C$.

Employing the same experimental conditions, hydrolysis of 0.53 mmol of $CH_3B(C_2F_3)_2$ resulted in the formation of 1.03 mmol of HC_2F_3 (calcd., 1.06 mmol).

Vapor pressure data

$(CH_3)_2B(C_2F_3)$. Vapor pressures were measured in the temperature range -45.0 to $+12.0^\circ C$ using standard techniques and the data analyzed by least squares. The observed vapor pressures ($+12.0^\circ C$, 326 torr; $+5.5^\circ C$, 248 torr; $0.0^\circ C$, 180 torr; $-23.0^\circ C$, 54 torr; $-45.0^\circ C$, 13 torr) are expressed by the equation

$$\log p_{\text{torr}} = 8.07 - 1590/T$$

The melting point determined by the Stock plunger technique is $-137^\circ C$ and the extrapolated boiling point is $+33^\circ C$. The ΔH_{vap} and Trouton constant are $7.28 \text{ kcal mol}^{-1}$ and $23.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$ respectively.

$CH_3B(C_2F_3)_2$. Use of a conventional mercury manometer for vapor pressure measurements was precluded since it appears that Hg catalyzes the decomposition of $CH_3B(C_2F_3)_2$. Vapor pressures were measured using a U-tube of mineral oil in which vapor pressure of the compound could be nulled by adjusting the pressure on the other leg of the U-tube. The pressure necessary to null the ambient vapor pressure could then be read from a Hg manometer. Solubility in the mineral oil appeared minimal and the plot of $\log p$ vs $1/T$ was linear. The observed vapor pressures ($-5.0^\circ C$, 13 torr; $0.0^\circ C$, 17 torr; $+10.0^\circ C$, 29 torr; $+20.0^\circ C$, 48 torr; $+23.0^\circ C$, 54 torr; $+20.0^\circ C$, 48.5 torr; $0.0^\circ C$, 17 torr) are expressed by the equation

$$\log p_{\text{torr}} = 7.72 - 1770/T$$

The last two vapor pressure measurements were obtained on decreasing the temperature and indicate little decomposition occurred during data acquisition. The melting point determined by the Stock plunger technique is $-56^\circ C$ and the extrapolated boiling point is $+93^\circ C$. The ΔH_{vap} and Trouton constant are $8.10 \text{ kcal mol}^{-1}$ and $22.1 \text{ cal deg}^{-1} \text{ mol}^{-1}$ respectively.

Decomposition studies

Known quantities of sample were condensed into break-seal tubes and were sealed under dynamic vacuum. The samples were left at room-temperature or placed in an oven for measured lengths of time after which the tube was reopen-

TABLE 1
RESULTS OF THERMAL DECOMPOSITION STUDIES

Molecule	Experimental conditions	Dec. (%)
$(\text{CH}_3)_2\text{BC}_2\text{F}_3$	5 days at 27°C	0.0
$(\text{CH}_3)_2\text{BC}_2\text{F}_3$	16 days at 27°C	3.7
$(\text{CH}_3)_2\text{BC}_2\text{F}_3$	36 h at 100°C	3.6
$(\text{CH}_3)_2\text{BC}_2\text{F}_3$	1 h at 230°C	83.9
$\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$	5 days at 27°C	2.0
$\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$	2 h at 100°C	0.0
$\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$	36 h at 100°C	34.8
$\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$	1 h at 250°C	100.0

ed and the samples purified on the low temperature column. Results of these studies are shown in Table 1.

Results

Hydrolysis studies. Previous studies [17] have shown that perfluorovinyl groups can be quantitatively cleaved from tin compounds by protonic acids and by warm water with the formation of HC_2F_3 . Neutral hydrolysis experiments on methyl(perfluorovinyl)boranes demonstrated a cleavage of 0.98 and 1.94 perfluorovinyl groups per boron atom in $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ and $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$, respectively.

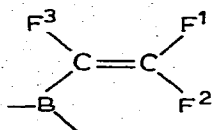
Mass spectral studies. The fragmentation patterns in the mass spectra (70 eV) of the methyl(perfluorovinyl)boranes is complex. However, molecular ions are observed for both compounds. The fragments $((\text{CH}_3)_2^{11}\text{B}^+)$ m/e 41 and $((\text{CH}_3)_2^{10}\text{B}^+)$ m/e 40 were intense in the spectrum of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ and absent in the spectrum of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$. Ions which were common to both spectra were: m/e 82 (HC_2F_3^+), m/e 49 ($^{11}\text{BF}_2^+$), m/e 45 ($\text{H}_2\text{C}_2\text{F}_3^+$), m/e 44 (HC_2F^+), m/e 43 (C_2F^+), m/e 42 ($^{11}\text{BCF}^+$ and/or $\text{H}^{10}\text{BCF}^+$) and m/e 31 (CF^+). High resolution mass spectra of the compounds contained the parent ion peaks: ($^{11}\text{B}^{12}\text{C}_4^{19}\text{F}_3^1\text{H}_6$), found 122.0513, calcd. 122.0515; $^{11}\text{B}^{12}\text{C}_5^{19}\text{F}_6^1\text{H}_3$, found 188.0230, calcd. 188.0232).

Infrared studies. Previous studies of compounds containing the perfluorovinyl group indicate several intense stretching frequencies which are diagnostic of the presence of the C_2F_3 group [7]. These are: C=C stretch, 1695–1732 cm^{-1} ; =CF₂

asymmetric stretch, 1274–1327 cm^{-1} ; $\begin{array}{c} \text{F} \\ \diagdown \\ \text{C} \\ \diagup \end{array}$ stretch, 1121–1178 cm^{-1} and =CF₂ symmetric stretch, 1004–1049 cm^{-1} . While several stretching frequencies of the methyl(perfluorovinyl)boranes are not within these ranges, four intense absorptions at frequencies very near the reported ranges were observed in the spectrum of both compounds. In the 4000–600 cm^{-1} range, the following absorption maxima were recorded (cm^{-1}) at 10 torr for $(\text{CH}_3)_2\text{BC}_2\text{F}_3$: 2995w, 2918vw, 2354vww, 1684vs, 1327s, 1261m, 1222w, 1108s, 997s, 904w, 801w; for $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ at 10 torr: 3007vw, 2940vw, 2550vw, 2457vw, 1677vs(br), 1346s, 1308s(sh), 1256m, 1233m(sh), 1131s, 1108m(sh), 1058w, 1003m, 950s, 844w, 758m, 663vw, 625vw, 600w.

NMR studies. The 32.1 MHz ^{11}B NMR spectra of both methyl(perfluorovinyl)-

boranes consisted of a single, broad resonance line with chemical shifts of 72.7 and 57.8 ppm deshielded with respect to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ for $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ and $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$, respectively. The 100.1 MHz ^1H NMR of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ consisted of a doublet ($^5J(\text{H}-\text{F})$ 2.4 Hz) at τ 9.94 ppm. The ^1H NMR of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ consists of a triplet ($^5J(\text{H}-\text{F})$ 3.5 Hz) at τ 9.40 ppm. The doublet and triplet arise from spin-spin coupling of the methyl protons to the F_2 fluorines using the numbering system shown below:



Irradiation at the F_2 fluorine frequency caused the multiplet to collapse to a single line in both cases.

Previous studies of the ^{19}F NMR spectra of perfluorovinyl compounds have established that $J(\text{FF})(\text{trans}) > J(\text{FF})(\text{cis}) > J(\text{FF})(\text{geminal})$ [8]. Fluorine-19 chemical shifts have also been assigned and our assignments are based on these investigations as well as coupling constant patterns. The 94.1 MHz ^{19}F NMR spectrum (Fig. 1) of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ consists of three separate fluorine resonances, all more shielded than external CFCl_3 : (1) a doublet of doublets assigned to $\text{F}(1)$

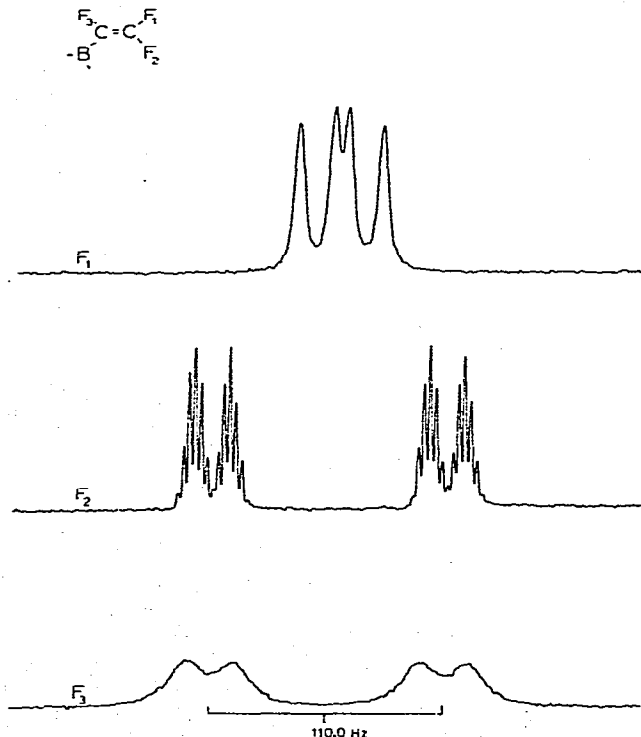


Fig. 1. The 94.1 MHz ^{19}F NMR spectrum of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ in toluene- d_8 . Chemical shifts and coupling constants are given in Results section.

(δ 79.6 ppm; $^3J(\text{F}(1)\text{F}(3))$ 23.0 Hz, $^2J(\text{F}(1)\text{F}(2))$ 16.3 Hz), (2) a doublet of doublets of septets assigned to F(2) (δ 94.6 ppm; $^3J(\text{F}(2)\text{F}(3))$ 110.0 Hz, $^2J(\text{F}(1)\text{F}(2))$ 16.3 Hz, $^5J(\text{H}-\text{F})$ 2.5 Hz) and (3) a doublet of doublets assigned to F(3) (δ 184.5 ppm; $^3J(\text{F}(2)\text{F}(3))$ 110.0 Hz, $^3J(\text{F}(1)\text{F}(3))$ 23.0 Hz).

Three separate resonances were also observed in the ^{19}F spectrum of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ (Fig. 2). However, the spectrum is very complex and resisted all attempts at a first-order analysis. Hence, coupling constants and chemical shifts are not known and we are able to report only the location of the center of each resonance which are all more shielded than CFCl_3 : F(1) (δ 75.7 ppm), F(2) (δ 90.7 ppm) and F(3) (δ 184.5 ppm). This multiplicity of lines has been previously observed by Coyle et al. in the ^{19}F NMR spectra of perfluorovinyl derivatives of Si, Ge, Sn, As and Hg [8]. Non-first order spectra were observed for those molecules which contained two or more perfluorovinyl groups on the central atom. This was rationalized in terms of long-range spin coupling between fluorine atoms in different perfluorovinyl groups. The ^{19}F NMR spectrum of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ shown in Fig. 1, can be satisfactorily interpreted on a first order basis. Introduction of a second perfluorovinyl group, as in $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$, results in the non-first order spectrum shown in Fig. 2.

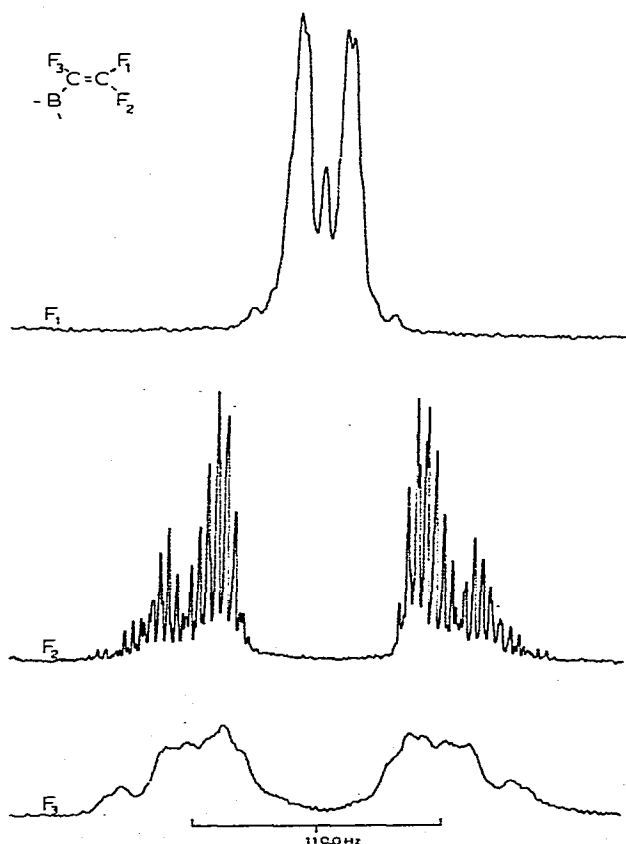


Fig. 2. The 94.1 MHz ^{19}F NMR spectrum of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ in toluene- d_8 . Chemical shifts are given in Results section.

Discussion

While there is extensive data to support a small mesomeric B—C π -interaction in vinylboranes [15], there is very little data available for the analogous perfluorovinylboranes. A priori, one might expect that substitution of hydrogen by fluorine should substantially alter the bonding characteristics of the vinyl group and it would seem unlikely that the perfluorovinyl and vinyl groups should interact similarly with the boron p_{π} -orbital. However, it has been found that the first ionization potential of C_2H_4 (10.6 eV) is almost identical with the value of 10.52 eV for C_2F_4 as measured by photoelectron spectroscopy [21]. This suggests that while the σ -electron density is fluorine atom based, the π -MO is localized on the vinyl carbon framework. Stabilization of the π -MO by mixing of the σ -AO's of fluorine with the ethylene group orbitals is countered by a C—F antibonding overlap [21]. As a result, ionization from the π -MO is effectively unaltered by fluorine substitution. Since delocalization of the perfluorovinyl electron density would be expected to occur through the π -framework, it might then not be unreasonable to expect that the C_2F_3 and the C_2H_3 groups will interact in a similar fashion mesomerically when bonded to boron.

It is important to point out that the magnitude of the mesomeric interaction in vinylboranes is apparently relatively small. In a microwave, Raman and infrared study [14] of vinyldifluoroborane, a planar conformer was the only one found in both the solid and fluid phases and the barrier to internal rotation about the boron—carbon bond was found to be $4.17 \text{ kcal mol}^{-1}$. Although maximum π -delocalization would be expected to take place when the molecule is in a planar conformation, the barrier is not unusually large for a two-fold rotation. Carbon-13 NMR spectroscopy has demonstrated [15] that a mesomeric interaction occurs in vinylboranes and appears to be the most sensitive technique used thus far to investigate π -electron delocalization in these systems.

At this time there are no structural studies reported nor are there any barriers to rotation known for any (perfluorovinyl)borane systems. Also, it does not appear that ^{13}C NMR studies will be as fruitful because of experimental difficulties and time considerations. Carbon—fluorine spin coupling in these systems is quite large and to observe a ^{13}C resonance in a reasonable amount of time requires ^{19}F "noise decoupling". Unfortunately, the fluorine chemical shifts cover a wide range and it was found experimentally impossible to completely decouple all fluorines as can be done for hydrogens in the vinylboranes.

As mentioned previously, decoupling of the F(2) resonance resulted in collapse of the triplet observed in the ^1H NMR spectrum of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ to a single line. There are two sets of circumstances that could give rise to this triplet. It could actually be an overlapping doublet of doublets. This necessitates magnetic non-equivalence of the two F(2) fluorines and also requires that both fluorines couple equally (or nearly so) to the methyl protons. Due to the complexity of the ^{19}F NMR spectrum, it is possible that the two F(2) resonances have nearly identical chemical shifts and can not, therefore, be resolved.

Alternatively, the triplet could arise from spin coupling of the methyl protons to two magnetically equivalent fluorines. The F(2) fluorines can be rendered magnetically equivalent by rapid rotation on the NMR time scale about the B—C bond. We observed no change in the ^1H NMR spectrum over the temperature

range -80 to $+75^\circ\text{C}$. However, failure to stop any rotational motion that would average both F(2) environments at -80°C only implies a low barrier to interconversion.

In the discussion of the ^{19}F NMR spectrum of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$, the non-first order spectrum was rationalized in terms of magnetic non-equivalence of corresponding fluorine atoms on the different perfluorovinyl groups. In no static structure which can be envisioned for methylbis(perfluorovinyl)borane are both F(2) fluorines magnetically equivalent. Consequently, no definitive statement can be made regarding solution structure. It does seem unlikely, however, that the triplet observed in the ^1H NMR spectrum results from spin coupling of the methyl protons to two magnetically equivalent fluorine atoms.

A comparison of the ^{11}B chemical shifts in Table 2 reflects an interesting trend. In every case, the resonances are more shielded in the order perfluorovinyl $>$ vinyl $>$ ethyl. While this trend is qualitatively consistent with increased electron density at the boron atom in question, conclusions regarding B—C π -bonding are restricted by the inability to separate σ - and π -contributions to the boron chemical shift.

If the shielding of the boron nucleus in the (perfluorovinyl)boranes is a result of a mesomeric π -interaction, this could result in a reduced tendency for an internal nucleophilic attack of fluorine on boron, since the Lewis acidity of boron would be reduced. Also, a mesomeric π -interaction would raise the activation energy necessary to achieve a four-coordinate transition state through which a simple group redistribution mechanism most likely passes. Delocalization would, therefore, remove or reduce the two most likely modes of decomposition and thereby exert a stabilizing influence on the molecule.

In an investigation of the thermal stability of the new molecules, we found the compounds to be very stable to prolonged periods of heating at moderate temperatures, which sharply contrasts with the behavior of the analogous methylvinylboranes. After 36 h at 100°C , only a trace of HC_2F_3 was formed from the decomposition of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$. Decomposition of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ under identical conditions resulted in the formation of small amounts of HC_2F_3 and $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ the major product from the decomposition being a non-volatile, air-stable solid. At temperatures of 200°C and higher, severe decomposition occurs for both com-

TABLE 2

 ^{11}B CHEMICAL SHIFTS OF ETHYLBORANES, VINYLBORANES AND PERFLUOROVINYLBORANES ^a

Molecule	Chemical shift	Molecule	Chemical shift	Molecule	Chemical shift
$\text{F}_2\text{BC}_2\text{H}_5$	-28.6 ± 0.2 ^b	$\text{F}_2\text{BC}_2\text{H}_3$	-22.6 ^f	$\text{F}_2\text{BC}_2\text{F}_3$	-21.8
$\text{FB}(\text{C}_2\text{H}_5)_2$	-59.6 ± 0.2 ^b	$\text{FB}(\text{C}_2\text{H}_3)_2$	-42.4 ^f	$\text{FB}(\text{C}_2\text{F}_3)_2$	—
$\text{Cl}_2\text{BC}_2\text{H}_5$	-63.4 ± 0.2 ^b	$\text{Cl}_2\text{BC}_2\text{H}_3$	-53.5 ^f	$\text{Cl}_2\text{BC}_2\text{F}_3$	-31.3
$\text{ClB}(\text{C}_2\text{H}_5)_2$	-78.0 ± 0.2 ^b	$\text{ClB}(\text{C}_2\text{H}_3)_2$	-56.7 ^f	$\text{ClB}(\text{C}_2\text{F}_3)_2$	-49.9
$\text{Br}_2\text{BC}_2\text{H}_5$	-65.6 ^c	$\text{Br}_2\text{BC}_2\text{H}_3$	-54.7 ^f	$\text{Br}_2\text{BC}_2\text{F}_3$	-49.6
$\text{BrB}(\text{C}_2\text{H}_5)_2$	-81.9 ^c	$\text{BrB}(\text{C}_2\text{H}_3)_2$	-60.1 ^f	$\text{BrB}(\text{C}_2\text{F}_3)_2$	-57.0
$\text{B}(\text{C}_2\text{H}_5)_3$	-85 ± 1 ^d	$\text{B}(\text{C}_2\text{H}_3)_3$	-56.4 ^f	$\text{B}(\text{C}_2\text{F}_3)_3$	-46.1
$(\text{CH}_3)_2\text{BC}_2\text{H}_5$	-86.1 ^e	$(\text{CH}_3)_2\text{BC}_2\text{H}_3$	-74.5 ^d	$(\text{CH}_3)_2\text{BC}_2\text{F}_3$	-72.7
$\text{CH}_3\text{B}(\text{C}_2\text{H}_5)_2$	-86.2 ^e	$\text{CH}_3\text{B}(\text{C}_2\text{H}_3)_2$	-64.4 ^d	$\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$	-57.8

^a Shifts are reported in ppm relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. Negative sign denotes decreased shielding. Shifts reported for the perfluorovinylboranes were measured as 20% by volume solutions in toluene- d_8 and are accurate to ± 0.2 ppm. ^b Ref. 22. ^c Ref. 23. ^d Ref. 24. ^e Ref. 10. ^f Ref. 13.

pounds. Formation of a brown polymeric material was observed from the decomposition of both compounds. This material was previously observed in the decomposition of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ at lower temperatures. The polymeric material formed in each experiment appeared similar but the compound defied characterization. The compound is suspected to be a difluoroacetylene $(\text{C}_2\text{F}_2)_n$ type polymer. Formation of C_2F_2 could occur through an internal nucleophilic attack of a β -fluorine on boron. Since most of the boron present in the original methylperfluorovinylborane is recovered in volatile products, the boron content of the polymer must be low. In addition to the polymeric material, SiF_4 , HC_2F_3 , $(\text{CH}_3)_2\text{BF}$ and CH_3BF_2 were identified by IR and mass spectroscopy as products from the decomposition of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ at 230°C . From the decomposition of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ at 250°C , SiF_4 , HC_2F_3 , $(\text{CH}_3)_3\text{B}$ and BF_3 were identified. Formation of SiF_4 in both experiments indicates that secondary reactions are occurring at these high temperatures.

Formation of compounds that contain B—F bonds indicates that decomposition by a fluorine shift occurs at high temperatures. How important is the available boron p_π -orbital in the decomposition of these molecules? An insight into the answer could be gained from a decomposition study of perfluorovinyl derivatives of Si, Ge and Sn which, unfortunately, is beyond the scope of this investigation. If decomposition by fluorine migration occurs in these molecules, then perhaps the presence of the boron p_π -orbital is not significant in the decomposition of the perfluorovinylboranes. There is currently little information available regarding the behavior of perfluorovinyl derivatives of Si, Ge and Sn at high temperature. However, it has been reported [17] that $\text{Sn}(\text{C}_2\text{F}_3)_4$ was recovered unchanged after being heated at 150°C for 6 h. Further studies might elucidate the importance of the boron p_π -orbital in the thermal decomposition of the methylperfluorovinylboranes.

As was found for the vinylboranes, experimental evidence supports a mesomeric B—C π -interaction in the perfluorovinylboranes also. The trend to a more shielded ^{11}B resonance (Table 2) suggests that delocalization may be more significant in the perfluorovinylboranes than in the vinylboranes. It has been reported that $(\text{CH}_3)_2\text{BC}_2\text{H}_3$ decomposes 33% in 5 days at 27°C [9] whereas $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ decomposes only 3.7% after 16 days at 27°C . Decomposition by halogen migration will, of course, only occur in the perfluorovinylboranes, and since this mode of decomposition has been found to occur readily in other systems, this makes the relative thermal stability of $(\text{CH}_3)_2\text{BC}_2\text{F}_3$ even more striking. A comparison of the relative thermal stabilities of $\text{CH}_3\text{B}(\text{C}_2\text{H}_3)_2$ and $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ is hampered by a lack of experimental details reported for the vinyl compound. While the thermal stability of $\text{CH}_3\text{B}(\text{C}_2\text{F}_3)_2$ is reduced relative to $(\text{CH}_3)_2\text{BC}_2\text{F}_3$, it compares favorably with the data reported for $\text{CH}_3\text{B}(\text{C}_2\text{H}_3)_2$. The stability of the methylperfluorovinylboranes to halogen migration or disproportionation suggests a small but significant B—C mesomeric interaction and further investigations into the nature and magnitude of the interaction would be desirable.

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