see K. Mislow and M. Raban, *Top. Stereochem.*, 1, 1 (1967).
(11) For a discussion of the relative importance of through-space and through-bond contributions in analogous five-bond fluorine–fluorine couplings see K. L. Servis and K.-N. Fang, *J. Am. Chem. Soc.*, 90, 6712 (1968).
(12) M. Fild and O. Glemser, *Fluorine Chem. Rev.*, 3, 129 (1969).
(13) M. G. Hogben and W. A. G. Graham, *J. Am. Chem. Soc.*, 91, 283 (1969).
(14) For a recent review see (a) W. B. Jennings, *Chem. Rev.*, 75, 307 (1975); (b) K. Mislow and M. Raban, *Top. Stereochem.*, 1, 1 (1967); (c) T. H. Siddall and W. E. Stewart, *Prog. Nucl. Magn. Reson. Spectrosc.*, 5, 33 (1969); (d) M. van Gorkom and G. E. Hall, *Q. Rev., Chem. Soc.*, 22, 14 (1968).

(15) (a) W. McFarlane, *Chem. Commun.*, 229 (1968); (b) D. G. Rowsell, *J. Mol. Spectrosc.*, 23, 32 (1967); (c) H. Goldwhite and D. G. Rowsell, *ibid.*, 27, 364 (1968); (d) R. V. Jardine, A. H. Gray, and J. B. Reesor, *Can. J. Chem.*, 47, 35 (1969); (e) R. V. Jardine, J. B. Reesor, A. H. Gray, and L. R. Provost, *Spectrochim. Acta, Part A*, 28, 1751 (1972); (f) P. E. Clark, K. D. Berlin, J. Mosbo, and J. G. Verkade, *Phosphorus*, 2, 265 (1973).
(16) J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, 91, 5927 (1969).
(17) J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *Tetrahedron Lett.*, 4919 (1973).
(18) (a) M. Fild and W. Althoff, *J. Chem. Soc., Chem. Commun.*, 933 (1973); (b) M. Fild and J. A. Gibson, unpublished results.

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Synthesis of Novel Fluorine-Containing Small Carboranes and Bis(difluoroboryl)methane

N. J. MARASCHIN and R. J. LAGOW*[1]

The first fluorine-containing smaller carboranes and bis(difluoroboryl)methane have been prepared. The controlled reaction of $C_2B_5H_7$ with elemental fluorine yields the new compounds $BF_2CH_2BF_2$ (I), $3\text{-}FC_2B_5H_6$ (II), $1\text{-}FC_2B_5H_6$ (III), $5\text{-}FC_2B_5H_6$ (IV), $1,5\text{-}F_2C_2B_5H_5$ (V), $1,3\text{-}F_2C_2B_5H_5$ (VI), and $5,6\text{-}F_2C_2B_5H_5$ (VII). These new carboranes were characterized by ^{11}B NMR spectroscopy, mass spectroscopy, and infrared spectroscopy.

Introduction

Electrophilic and photochemical halogenations of $o\text{-}C_2H_2B_{10}H_{10}$ have been reported.[2] In the electrophilic chlorination, only four boron atoms of the cage are substituted. These four positions (boron atoms 8, 9, 10, 12) correspond to the most negative atoms in the cage as predicted by nonempirical molecular orbital theory. The monochloro derivative has been found to be mainly $9\text{-}Cl\text{-}o\text{-}C_2H_2B_{10}H_9$ with a small amount of $8\text{-}Cl\text{-}o\text{-}C_2H_2B_{10}H_9$.[2b] Electrophilic bromination and iodination appear to give similar results.[3] Photochemical chlorinations and brominations are much less selective. Exhaustive photochemical chlorination of o-carborane yields $o\text{-}C_2H_2B_{10}Cl_{10}$. The monofluorinated compounds $3\text{-}F\text{-}o\text{-}C_2H_2B_{10}H_9$ and $2\text{-}F\text{-}m\text{-}C_2H_2B_{10}H_9$ have been prepared from $o\text{-}C_2H_2B_{10}H_{10}$[4a] and the lithiated carboranes,[4b] respectively. Direct fluorination of $o\text{-}$, $m\text{-}$, and $p\text{-}C_2H_2B_{10}H_{10}$ in liquid HF gave $o\text{-}$, $m\text{-}$, and $p\text{-}C_2H_2B_{10}F_{10}$.[5] Perfluoro-$m$-carborane, $C_2F_2B_{10}F_{10}$, was prepared by the fluorination of $m\text{-}C_2F_2B_{10}H_{10}$.[5] In the earlier work with this direct fluorination technique, Lagow and Margrave fluorinated $m\text{-}C_2H_2B_{10}H_{10}$ to $m\text{-}C_2F_2B_{10}F_{10}$ directly.[6]

Much less work has been done on the halogenation of the small carboranes. 2,4-Dicarba-*closo*-heptaborane(7) has been chlorinated with and without an $AlCl_3$ catalyst.[7] With the catalyst, only $5\text{-}ClC_2B_5H_6$ was found, while without the catalyst, the chlorination gave 1-, 3-, and $5\text{-}ClC_2B_5H_6$, results reminiscent of the halogenations of the large carboranes.

In view of the results of the direct fluorination of $m\text{-}C_2H_2B_{10}H_{10}$, it was of interest to examine the fluorination of the smaller carboranes to see if the perfluoro analogs could be prepared. Using the conditions described in the Experimental Section, only partially fluorinated derivatives of $C_2B_5H_7$ were found, along with unreacted $C_2B_5H_7$, $BF_2CH_2BF_2$, and BF_3.

Experimental Section

The direct fluorination apparatus has been described previously.[8] Mass spectra were measured on a Hitachi RMU 6D mass spectrometer at 70 eV. ^{19}F and ^1H NMR spectra were taken on a Perkin-Elmer R20-B spectrometer (60 MHz for protons and 56.4 MHz for fluorine) which could be coupled to a Digilab Fourier transform system. Chemical shifts and coupling constants were

Table I

Zone no. (T, °C)	He flow, cm³/min	F_2 flow, cm³/min	Time, hr
2 (−120)	60	0.5	20
3 (−120)	60	0.5	4
3 (−120)	30	0.5	6.5
3 (−80)	60	0	10
3 (room temp)	60	0	12

calculated using frequencies counted on a Takeda Riken-TR-3824X frequency counter. ^{11}B spectra were taken on a Bruker HFX-90 spectrometer at 28.8 MHz. The Bruker HFX-90 spectrometer was interfaced with a Digilab FTS/NMR Fourier transform data system. Typical parameters used were 2048-point transform, 5-kHz bandwidth, 35° nutation angle, 0.5 sec between repetitive pulses, 10–6000 pulses, and ^1H broad-band decoupling. The sample (in Et₂O) was contained in a 4-mm tube inserted concentrically into a 10-mm tube. The field/frequency lock was provided by C_6F_6 contained in the 10-mm tube. Chemical shifts are given with reference to TMS for protons, $CFCl_3$, CF_3COOH, or C_6F_6 for fluorine, and $BF_3 \cdot O(C_2H_5)_2$ for boron. Positive chemical shifts refer to absorbances at higher field with respect to the reference. Gas chromatography was done using either a Varian or Bendix gas chromatograph equipped with thermal conductivity detectors and cryogenic temperature controllers. Columns were made of 10% SE-30 on Chromosorb P and 13% fluorosilicone on Chromosorb P. Both columns were 10 ft × 1/4 in. Infrared data were recorded on a Beckman IR 20A instrument. Gas-phase spectra were run in a 10-cm cell with $AgNO_3$ windows. Mulls (Nujol and fluorocarbon) were run between KBr plates. X-Ray powder patterns were run on a Norelco X-ray diffractometer. 2,4-Dicarba-*closo*-heptaborane(7) (Chemical Systems Co.) was condensed into a glass tube equipped with a vacuum stopcock and ground-glass joint. This tube could then be attached to the fluorination system by way of a Swaglok T joint placed just before the cold box. In order to condense the $C_2B_5H_7$ into the cold box, the fluorination system was evacuated to a pressure of about 25 Torr.

Reaction I. $C_2B_5H_7$ (0.59814 g, 7.07 mmol) was condensed into the second trap of the cold reactor which was held at −120°. The fluorination conditions are given in Table I. The glass products trap was kept at −196° for the entire reaction and contained a quantity of white material at the end of the reaction. The trap was taken to the vacuum line and evacuated while kept at −196°. Then the material was transferred into the vacuum line and fractionated. The compounds which passed a −126° trap were shown to be SiF_4 and BF_3 by ^{19}F NMR,[9] mass, and ir spectroscopy.[10]

Table II. ^{11}B Chemical Shifts of Some Substituted $C_2B_5H_7$ Derivatives

	B(1)		B(3)		B(5)		B(6)		B(7)		
Compd	δ^a	J^b	δ	J	δ	J	δ	J	δ	J	Ref
$C_2B_5H_7$	24.04	180	−4.84	190	−2.07	170	−2.07	170	24.04	180	12
1-FC$_2$B$_5$H$_6$	11.42	70^c	−7.96	190	−2.07	155	−2.07	155	42.83	185	This work
1-ClC$_2$B$_5$H$_6$	13.7		−9.6	179	−4.2	160	−4.2	160	31.0	184	7
1-CH$_3$C$_2$B$_5$H$_6$	10.5		−9.2	188	−5.3	177	−5.3	177	25.7	185	12b
3-FC$_2$B$_5$H$_6$	18.39	177	−18.17	37.5^c	−1.73	183.5	−1.73	183.5	18.39	177	This work
3-ClC$_2$B$_5$H$_6$	18.7	177	−15.1		−3.0	172	−3.0	172	18.7	177	7
3-CH$_3$C$_2$B$_5$H$_6$	20.4	178	−13.8		−3.1	175	−3.1	175	20.4	178	12b
5-FC$_2$B$_5$H$_6$	23.27	180	−1.03	180	−16.20	c	6.65	144	23.27	180	This work
5-ClC$_2$B$_5$H$_6$	21.1	181	−4.1	185	−12.4		−0.15	184	21.1	181	7
5-CH$_3$C$_2$B$_5$H$_6$	21.0	174	−6.1	182	−9.2		−2.4	184	21.0	174	12b
1,5-F$_2$C$_2$B$_5$H$_5$	12.05	72^c	−3.53	148	−15.79	c	6.44	204	42.80	198	This work
1,3-F$_2$C$_2$B$_5$H$_5$	10.47	63.5^c	−16.05	37.5^c	1.29	175	1.29	175	40.68	187	This work
5,6-F$_2$C$_2$B$_5$H$_5$	20.56	181	−3.25	180	10.82	c	−10.82	c	20.56	181	This work

^{a} Chemical shifts referred to external BF$_3$·OEt$_2$ and are in ppm. ^{b} Coupling constants in Hz. ^{c} Not affected by proton decoupling.

The fraction that stayed at −126° and passed −95° contained a little C$_2$B$_5$H$_7$, a few fluorocarbons, and BF$_2$CH$_2$BF$_2$ (I). *Caution!* Bis(difluoroboryl)methane, BF$_2$CH$_2$BF$_2$, is highly reactive and explodes when exposed to air or water. Several purification techniques were attempted on this mixture, but with all methods trace quantities of C$_2$B$_5$H$_7$ and fluorocarbons remained. Gas chromatography was precluded by the danger of explosion. Consequently, the material was characterized while approximately 90% pure. The low-resolution mass spectrum showed an isotope pattern corresponding to two boron atoms at m/e 90–93 (m/e 93 corresponds to ^{11}B$_2$^{19}F$_4$^{12}CH$_2$$^+$). The next isotope pattern occurred at m/e 70–73 (m/e 73 corresponds to ^{11}B$_2$^{19}F$_2$^{12}CH$^+$). The high-resolution mass spectrum showed a weak parent minus hydrogen at m/e 111.02055 (calcd for ^{11}B$_2$^{19}F$_4$^{12}CH 111.02005) and 110.02327 (calcd for ^{11}B^{10}B^{19}F$_4$^{12}CH 110.02388). The most intense peaks occurred for the fragments due to the parent minus fluorine at m/e 93.02907 (calcd for ^{11}B$_2$^{19}F$_3$^{12}CH$_2$ 93.02947) and 92.03325 (calcd for ^{11}B^{10}B^{19}F$_3$^{12}CH$_2$ 92.03310). The vapor-phase molecular weight of the impure compound was found to be 118 (calcd for B$_2$F$_4$CH$_2$ 111.6). The gas-phase ir showed absorptions at 1370 (vvs), 1300 (vs), 1160 (w), 800 (s), and 490 (m) cm^{-1}. The ^{11}B NMR spectrum consisted of a triplet (J = 69.025 Hz) at −27.8 ppm from external BF$_3$·OEt$_2$. The triplet was unchanged when proton decoupling was applied. The ^{19}F NMR spectrum consisted of a quartet (J = 69 Hz) which collapsed to a singlet when boron decoupled. The singlet was at −4.5 ppm from external trifluoroacetic acid. The ^{1}H NMR spectrum consisted of a very broad signal at 0.29 ppm from TMS. The yield of BF$_2$CH$_2$BF$_2$ was about 4%. BF$_2$CH$_2$BF$_2$ decomposes slowly at room temperature, leaving a brown, viscous oil.

BF$_2$CH$_2$BF$_2$ was also derivatized to (HO)$_2$BCH$_2$B(OH)$_2$ following the literature method. (HO)$_2$BCH$_2$B(OH)$_2$ was recrystallized from acetone several times; mp 154–155°; lit.^{11a} mp 155–155.5°. The ^{1}H NMR (H$_2$O) signal was at 0.35 ppm from external TMS; lit.^{11b} 0.4 ppm.

The fraction which stayed at −95° on the vacuum line contained peaks in the mass spectrum indicating the presence of C$_2$B$_5$H$_7$, C$_2$B$_5$H$_6$F, and C$_2$B$_5$H$_5$F$_2$. It was dissolved in diethyl ether (dried over LiAlH$_4$) and separated by gas chromatography (fluorosilicon column). The major component was C$_2$B$_2$H$_7$ (7.34%). C$_2$B$_5$H$_7$ was identified by mass spectroscopy (parent peak cutoff at m/e 86 for ^{12}C$_2$^{11}B$_5$H$_7$), ir spectroscopy (2600 (vs), 1200 (vs), 1050 (vs), 900 (br,w), 790 (w), 670 (w) cm^{-1}) and ^{11}B NMR spectroscopy (Table II). The ^{11}B NMR spectrum was in agreement with the reported spectrum.^{12} There were three other large peaks in the gas chromatogram which were collected and identified as 3-FC$_2$B$_5$H$_6$ (II), 1-FC$_2$B$_5$H$_6$ (III), and 5-FC$_2$B$_5$H$_6$ (IV).

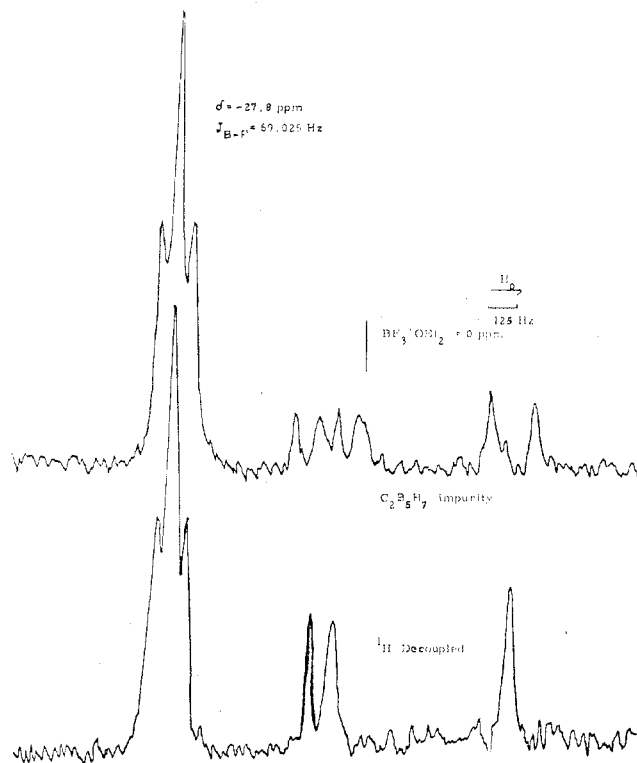**3-FC$_2$B$_5$H$_6$.** The yield was 0.43%. The mass spectrum showed a strong five-boron pattern with a cutoff at m/e 104 (^{12}C$_2$^{11}B$_5$H$_6$^{19}F). There were weak fragments corresponding to the loss of CH and BF. The gas-phase ir spectrum showed absorbances at 2630 (s), 1390 (m), 1350 (vs), 1200 (m), 1160 (w), 1060 (br,w), 1030 (w), 880 (vs), 720 (vw), and 650 (vw) cm^{-1}. The ^{11}B NMR in diethyl ether is shown in Table II.

1-FC$_2$B$_5$H$_6$. The yield was 0.69%. The mass and ir spectra were the same as those for 3-FC$_2$B$_5$H$_6$. The ^{11}B NMR spectrum is shown in Table II.

5-FC$_2$B$_5$H$_6$. The yield was 0.71%. The mass spectrum was the

Table III

Zone no. (T, °C)	He flow, cm^3/min	F$_2$ flow, cm^3/min	Time, hr
2 (−120)	30	0.5	23.5
3 (−120)	30	0.5	1.5
3 (−120)	15	0.5	2
3 (−120)	0	0.5	1
3 (−120)	15	0.5	5
3 (−120)	30	0	3
3 (−80)	30	0	8
3 (room temp)	30	0	5

Figure 1. ^{11}B NMR of BF$_2$CH$_2$BF$_2$.

same as that for 3-FC$_2$B$_5$H$_6$. The gas-phase ir spectrum showed absorbances at 2620 (vs), 1410 (w), 1360 (vs), 1155 (s), 1050 (s), 880 (w), 690 (vw), and 665 (vw) cm^{-1}. The ^{11}B NMR spectrum is shown in Table II.

Reaction II. A 0.56814-g sample of C$_2$B$_5$H$_7$ (6.67 mmol) was condensed into the second trap of the cold reactor (at −120°) as was done in reaction I. The following conditions in Table III were used for the fluorination. The products were worked up in the same way as the products from reaction I. The yield of compound I was 0.50%. The mass spectrum of the unseparated mixture that stayed at −95° under vacuum indicated the presence of C$_2$B$_5$H$_7$, C$_2$B$_5$H$_6$F, C$_2$B$_5$H$_5$F$_2$, C$_2$B$_5$H$_4$F$_3$, and C$_2$B$_5$H$_3$F$_4$. The mixture was separated by gas

J(B-F) = 69.4 Hz

δ = -4.5 ppm

CF₃COOH
0 ppm

H₀→
60 Hz

¹¹B Decoupled

Impurity
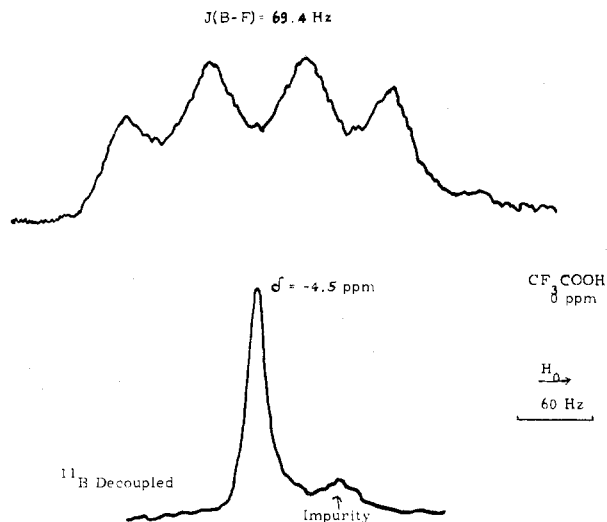
Figure 2. ¹⁹F NMR of BF₂CH₂BF₂.

H₀→
125 Hz

¹H Decoupled

B(3)
J=37.5 Hz

B(5,6)
J=183.75 Hz

B(1,7)
J=177.5 Hz

*Impurity of 1-FC₂B₅H₈
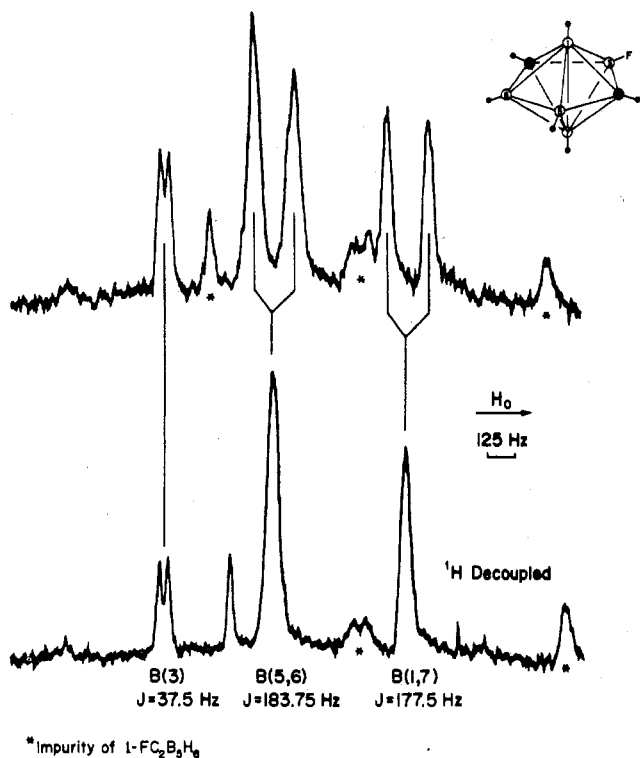
Figure 3. ¹¹B NMR of 3-FC₂B₅H₆.

Table IV

Zone no. (T, °C)	He flow, cm³/min	F₂ flow, cm³/min	Time, hr
1 (−120), 2 (−180)	30	0.5	12
2 (−120), 3 (−180)	30	0.5	12
3 (−120), 4 (−180)	15	0.5	4
4 (−180)	15	0.5	3.5
4 (−120)	15	0	3
4 (room temp)	15	0	12

H₀→
120 Hz

impurity

¹H Decoupled

B(3)   B(5,6)   B(1)
J=190 Hz J=155 Hz

B(7)
J = 185 Hz
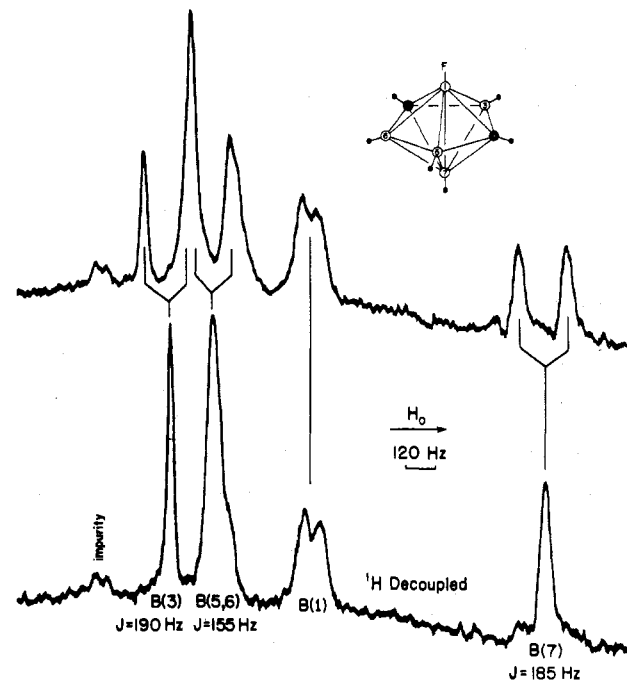
Figure 4. ¹¹B NMR of 1-FC₂B₅H₆.

H₀→
120 Hz

B(6)
J=144 Hz

B(3)
J=180 Hz

B(1,7)
J=180 Hz

B(5)

¹H Decoupled
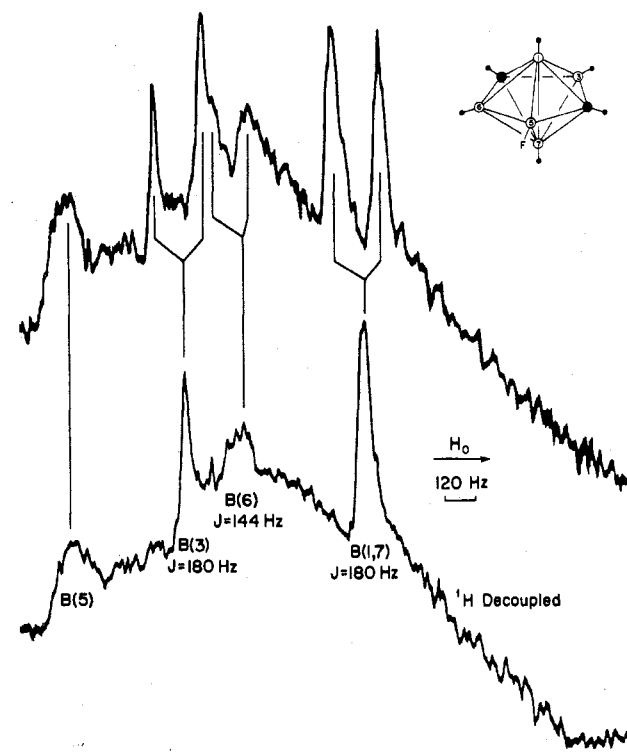
Figure 5. ¹¹B NMR of 5-FC₂B₅H₆.

chromatography and gave a 0.07% yield of C₂B₅H₇, 0.03% yield of II, 1.6% yield of III, 2.39% yield of IV, and 1.08% yield of 1,5-F₂C₂B₅H₅ (V).

1,5-F₂C₂B₅H₅. The mass spectrum of V consisted of an intense group of peaks with a cutoff at m/e 122 (^{12}C₂^{11}B₅H₅^{19}F₂). There were weak patterns at lower m/e values, corresponding to the loss of CF and BF₂ from the parent compound. The gas-phase ir spectrum showed absorptions at 2630 (s), 1370, and 1340 (vs, br), 1275 (vw), 1160 (m), 1080 (br, vw), 1030 (w), 940 (vw), 900 (vw), 810 (m), 630 (w), and 560 (w) cm⁻¹. The ¹¹B NMR spectrum of V is shown in Table II.

Reaction III. A 1.01663-g sample of C₂B₅H₇ (11.94 mmol) was condensed into the first zone of the cryogenic reactor (at −120°). The following fluorination conditions of Table IV were used. The products were vacuum fractionated as described above. The yield of I was 8.7%. The mass spectrum of the crude mixture which stayed at −95° showed peaks corresponding to C₂B₅H₇⁺, C₂B₅H₇F⁺, C₂B₅H₅F₂⁺, C₂B₅H₄F₃⁺, and C₂B₅H₃F₄⁺. The mixture was separated by gas chromatography and gave a 16.4% yield of C₂B₅H₇, 0.75% yield of II, 1.37% yield of III, 1.86% yield of IV, 0.55% yield of V, 0.41% yield

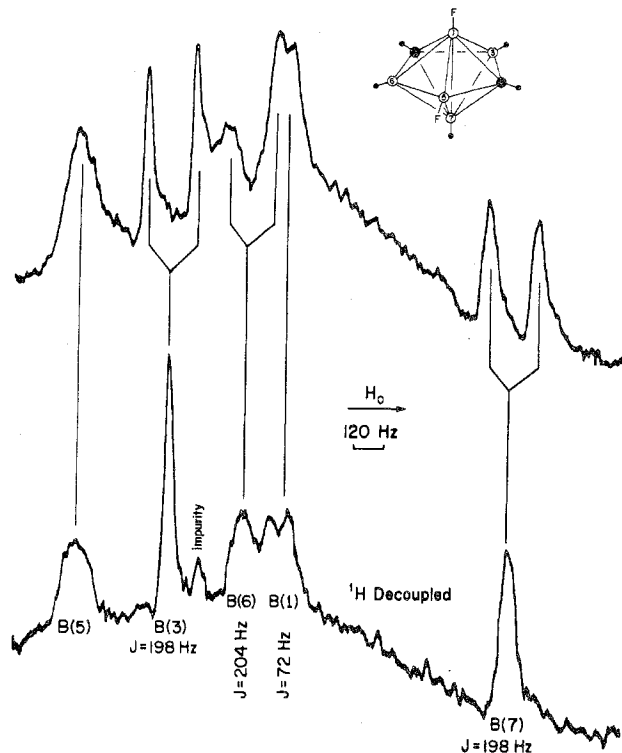of 1,3-F₂C₂B₅H₅ (VI), and 0.28% yield of 5,6-F₂C₂B₅H₅ (VII).

1,3-F₂C₂B₅H₅. The mass and ir spectra of VI were identical with those for V. The ¹¹B NMR spectrum is shown in Table II.

The ir spectrum of VII was identical with that for V. The ¹¹B

Figure 6. ^{11}B NMR of 1,5-$F_2C_2B_5H_5$.

NMR spectrum is shown in Table II.

^{1}H and ^{19}F NMR spectra of these compounds were not possible to obtain because of concentration problems. The compounds were volatile liquids which decomposed on standing at room temperature or 0°, leaving a white powder. The white powder had an ir spectrum identical with that of boric acid.

Results and Discussion

$BF_2CH_2BF_2$ (I) has not been previously prepared. It is a volatile, explosive liquid which decomposes at room temperature. In the description of the preparation of $(BF_2)_4C$, Stone mentioned that other difluoroboryl compounds were made but that they were heat-sensitive and brown viscous oils were deposited at room temperature.[13] The ^{11}B NMR spectrum of I is shown in Figure 1. The ^{11}B chemical shift of I was −27.8 ppm (external $BF_3 \cdot OEt_2$) and the B–F coupling was 69 Hz. This is in excellent agreement with Stone's values of −23 ppm and 58 Hz for $(BF_2)_4C$.[13] The ^{19}F NMR spectrum of I is shown in Figure 2. The chemical shift was −4.5 ppm (external CF_3COOH). Stone did not report the ^{19}F shift of $(BF_2)_4C$, but $CH_3CH_2BF_2$, n-$C_3H_7BF_2$, and CH_3BF_2 have ^{19}F chemical shifts in the range of −1 to −6 ppm.[14] The mass spectrum of bis(difluoroboryl)methane did not contain a parent peak, but the parent minus fluorine fragment was the most prominent feature of the spectrum. That fragment then lost HF.

Several fluorinated derivatives of 2,4-dicarba-*closo*-heptaborane(7) were isolated and characterized. They include 3-fluoro-2,4-dicarba-*closo*-heptaborane(7) (II), 1-fluoro-2,4-dicarba-*closo*-heptaborane(7) (III), 5-fluoro-2,4-dicarba-*closo*-heptaborane(7) (IV), 1,5-difluoro-2,4-dicarba-*closo*-heptaborane(7) (V), 1,3-difluoro-2,4-dicarba-*closo*-heptaborane(7) (VI), and 5,6-difluoro-2,4-dicarba-*closo*-heptaborane(7) (VII). The ^{11}B NMR spectra for these compounds are shown in Figures 3–8. A ^{11}B NMR spectrum of $C_2B_5H_7$ is shown in Figure 9.

Unambiguous structural assignments could be made from the ^{11}B NMR. Table I shows the results of this work as well as other reported ^{11}B NMR shifts for substituted $C_2B_5H_7$. For the three monochlorinated isomers, Spielman found evidence
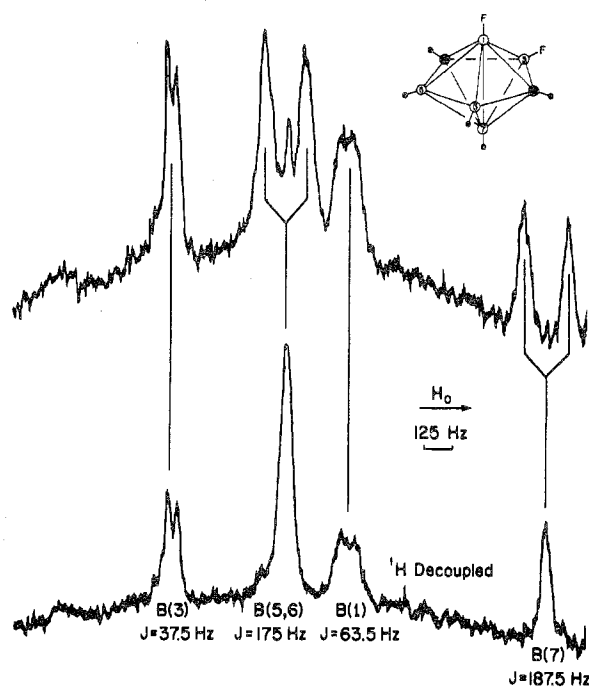
Figure 7. ^{11}B NMR of 1,3-$F_2C_2B_5H_5$.
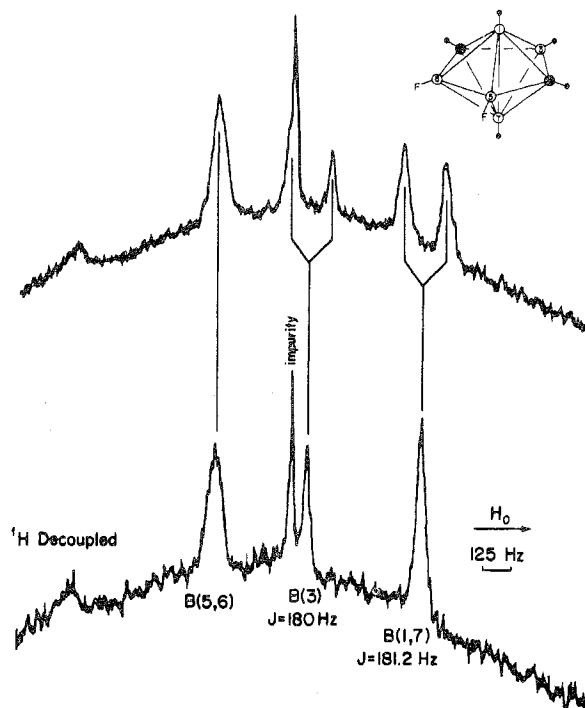
Figure 8. ^{11}B NMR of 5,6-$F_2C_2B_5H_5$.

of a "trans" effect and reciprocal effects in the ^{11}B NMR spectra.[7] By the trans effect he referred to the large upfield shift (7–8 ppm) of boron 7 when boron 1 was substituted with chlorine. A larger trans effect (16–18 ppm) is seen for the fluorinated compounds 1-$FC_2B_5H_6$, 1,3-$F_2C_2B_5H_5$, and 1,5-$F_2C_2B_5H_5$. Spielman also made the observation that the resonance for the substituted boron atom was shifted downfield by about 10 ppm relative to its unsubstituted position. In the fluorinated compounds, this downfield shift varies from 13 to 14 ppm except in the 5,6-$F_2C_2B_5H_5$ isomer, where it is only 8 ppm. By the reciprocal effect, Spielman was referring to the observation that if substitution in the 3 position shifted the boron 1 resonance by 5 ppm, then substitution in the 1 position shifted the resonance of boron 3 by 5 ppm. The
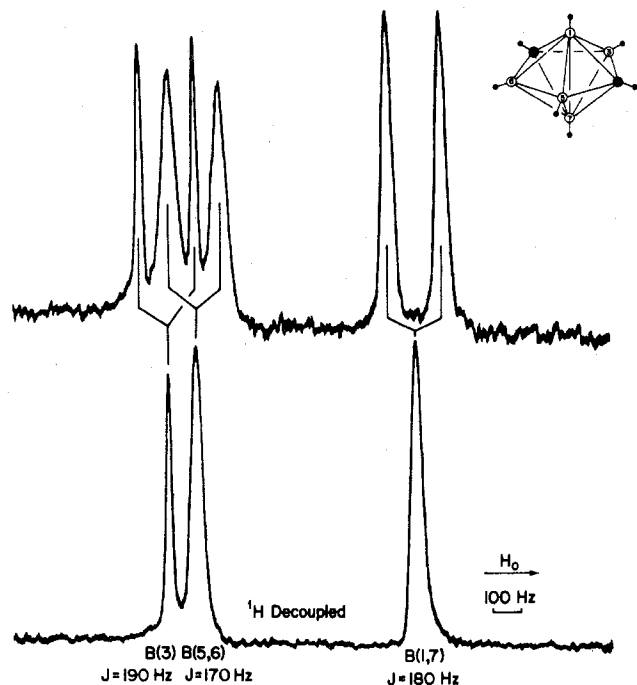
Figure 9. ^{11}B NMR of $C_2B_5H_7$.

B(3) B(5,6)
J=190 Hz J=170 Hz
B(1,7)
J=180 Hz

^{1}H Decoupled

H_0
100 Hz

presence of the reciprocal effect is ambiguous in the fluorinated carboranes. It seems that the general trend of substituent effects for ^{11}B NMR resonances is followed when fluorine is substituted on the cage.

Only isomers with one and two fluorines on the cage were isolated and identified. (There were other peaks in the gas chromatogram of the crude mixture which probably were the other isomers of $F_2C_2B_5H_5$, but they were not abundant enough to collect and characterize). However, mass spectral evidence indicated that in the mixture species with three or four fluorines on the cage were present. If large quantities of material were fluorinated, it would probably be possible to isolate some of the other isomers. The fact that each reaction yielded some $C_2B_5H_7$ as well as BF_3 and $BF_2CH_2BF_2$ might

indicate that the fluorination proceeded to a certain extent and then decomposition of the fluorinated product occurred. Whether the last stable fluorinated carborane was $C_2B_5H_3F_4$ and adding one more fluorine destabilized the cage so much that it decomposed or whether something in the fluorination technique itself caused the decomposition of the cage is not clear.

The isomers with one, two, three, and four fluorines present were not pyrophoric as was $BF_2CH_2BF_2$, but they were definitely moisture sensitive and possibly thermally unstable. Even at 0° in an evacuated, flame-dried tube, substantial decomposition occurred. Spectroscopic studies of organometallic compounds prepared from these partially fluorinated lower carboranes may be a valuable source of structural information.

References and Notes

(1) Alfred P. Sloan Fellow.
(2) (a) R. N. Grimes, "Carboranes", Academic Press, New York, N.Y., 1970, pp 134–137; (b) L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, **170**, 92 (1966).
(3) V. I. Stanko and A. I. Klimova, *Zh. Obshch. Khim.*, **38**, 1194 (1968).
(4) (a) L. I. Zakharkin, V. N. Kalinin, and V. V. Gedymin, *J. Organomet. Chem.*, **16**, 371 (1969); (b) J. S. Roscoe, S. Kongpricha, and S. Papetti, *Inorg. Chem.*, **9**, 1561 (1970).
(5) S. Kongpricha and H. Schroeder, *Inorg. Chem.*, **8**, 2449 (1969).
(6) R. J. Lagow and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **35**, 2084 (1973).
(7) R. Warren, D. Paquin, T. Onak, G. Dunks, and J. R. Spielman, *Inorg. Chem.*, **9**, 2285 (1970).
(8) N. J. Maraschin and R. J. Lagow, *J. Am. Chem. Soc.*, **94**, 8601 (1972).
(9) C. H. Dungen and J. R. Van Wazer, "Compilation of Reported F^{19} NMR Chemical Shifts", Wiley, New York, N.Y., 1970, pp 3–5.
(10) D. M. Gage and E. F. Barber, *J. Chem. Phys.*, **7**, 455 (1959).
(11) (a) D. S. Matteson and T. C. Cheng, *J. Organomet. Chem.*, **6**, 100 (1966); (b) R. S. Castle and D. S. Matteson, *ibid.*, **20**, 19 (1969).
(12) (a) T. P. Onak, F. J. Gelhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963); (b) R. N. Grimes, *ibid.*, **88**, 1895 (1966).
(13) J. E. Dobson, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc.*, 1882 (1969).
(14) T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960).

Contribution from the Department of Chemistry and the Materials Science Center, Cornell University, Ithaca, New York 14853

Gas-Phase Molecular Structure of Trifluoromethyliminosulfur Difluoride [F3CNSF2]

R. R. KARL, Jr. and S. H. BAUER*

Structural and dynamic parameters for trifluoromethyliminosulfur difluoride [F3CNSF2] were found by least-squares fitting of the calculated to the experimental molecular–electron scattering function, over the range $q = 10$–125 Å^{-1}. The r_g parameters are C—F = 1.332 ± 0.005 Å, [S=N] = 1.447 ± 0.006 Å, N—C = 1.469 ± 0.010 Å, S—F = 1.583 ± 0.004 Å, ∠CNS = 130.4 ± 0.7°, ∠NSF = 112.6 ± 0.5°, ∠FSF = 81.1 ± 1.6°, and ∠NCF = 110.3 ± 0.4°. A wide range of models were tested, covering many positional isomers about the S=N and N—C bonds. The bisector of the SF2 angle is essentially cis to the N—C bond; the thermal average position of the CF3 group is approximately gauche with respect to the N—S bond.

Introduction

Investigation of the physical and chemical properties of sulfur tetrafluoride led to a new class of compounds, the iminosulfur difluorides. Glemser and Schröder[1] reported the synthesis of a compound with the empirical formula NSF3; it was assigned the structural formula FN=SF2. Reactions of alkyl isocyanates with SF4 generate compounds of the type RN=SF2.[2] Of these, F3CNSF2 is of special interest, since

its structure is representative of a uniquely bonded collection of atoms which heretofore had not been quantitatively investigated. One presumes that the nonbonding electron pair associated with the nitrogen atom induces a nonlinear configuration to CNS. Furthermore, the double-bonded N=S, plus the nonbonding electron pair on the sulfur atom, places the terminal fluorine atoms in a unique charge distribution. To resolve the question of the cis–trans conformation about