ferences in the anisotropy of neighboring atoms are probably negligible.

Changes in relative Lewis acidities with different reference bases appear to be due almost entirely to steric factors. Marked effects may be noted for several examples which include both planar and tetrahedral Lewis acids. With tetrahydrofuran as reference base, the acidity of isobutyldichloroborane is 72, but, with the sterically less open bases *n*-butyl and ethyl ethers as reference bases, the acidity drops to 68. The branched alkyl group on boron apparently offers greater interference to interaction with *n*-butyl and ethyl ethers than with the sterically more accessible tetrahydrofuran. The steric effect of two isobutyl groups on boron is more extreme. With tetrahydrofuran, diisobutylchloroborane has an acidity of 25 relative to boron chloride, but with *n*-butyl and ethyl ethers as reference bases the acidity drops to a value which cannot be distinguished from zero. Similarly, stannic bromide has a significant acidity (25) toward tetrahydrofuran but an apparent zero acidity toward *n*-butyl ether. A further example of steric interference with complex formation is afforded by a comparison of the relative acidities of stannic bromide (25) and stannic iodide (0.0) toward tetrahydrofuran. The larger iodide atoms apparently completely block the oxygen atom of tetrahydrofuran from approaching near enough for complex formation to occur, but the smaller bromine atoms do not. A somewhat decreased acidity might be expected for stannic iodide for electronegativity reasons, but the observed extreme difference can hardly be due to electronic factors alone.

While the data are not available for gallium trichloride, a definite trend of decreasing acidity is shown for the trichlorides of boron, aluminum, and indium. This trend suggests that, when empty p orbitals are involved in the bonding, Lewis acidities toward ethers decrease with increasing size of the central atom in a periodic group. In periodic groups in which d orbitals are involved in complex formation, the opposite trend is noted. The acidity increases from silicon tetrachloride to tin tetrachloride and from arsenic trichloride to antimony trichloride. For the trichlorides of group III the sterically open planar structure makes the empty p orbital readily accessible to the donor molecule, and thus electronic factors are dominant in determining relative Lewis acidities. On the other hand the tetrahedral structure of the group V halides results in dominance of steric factors in relative Lewis acidities.

The relative basicities of ethers can also be conveniently determined from proton magnetic resonance data on solutions of different ethers and less than an equivalent amount of Lewis acid. The field positions of the α-proton resonances give directly the ratio of complexed to free ether in solution. The results of such a study will be reported in a later communication.

Boron–Fluorine Chemistry. II. The Reaction of Boron Monofluoride with Acetylenes

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Abstract: The cocondensation of boron monofluoride and acetylene at −190° yields a polymer and several volatile compounds. The most abundant of these volatiles has been shown by its proton and fluorine nmr spectrum to be $(F_2BCH{=}CH)_2BF$. This compound loses boron trifluoride in the vapor phase above room temperature to give quantitative yields of the compound $C_4H_4B_2F_2$, 1,4-difluoro-1,4-diboracyclohexadiene, which is isoelectronic and structurally similar to *p*-benzoquinone. The reaction of boron monofluoride with methylacetylenes yields $C_4(CH_3)_2H_2B_2F_2$ and $C_4(CH_3)_4B_2F_4$. These compounds of type $C_4R_4B_2F_2$ are all destroyed by air or water, and some polymerize in the condensed phase at room temperature.

It has been shown that boron monofluoride can be formed in preparative amounts by the action of boron trifluoride on boron at 1800–2000° at low pressure. Reaction of boron monofluoride has occurred with volatile inorganic and organic compounds by cocondensation at −196°.[2]

The present work was undertaken to find if a stable three-membered ring would result from the addition of boron monofluoride to an acetylenic bond, although caged carboranes also seemed likely products from such a reaction.

Only a few unsaturated organic compounds containing boron and fluorine have been reported previously. Brinckmann, Coyle, and Stone[3] studied the vinylfluoroboranes, and Schlesinger, *et al.*,[4] obtained the compound $C_2H_2B_2F_4$ from acetylene and diboron tetrafluoride. Relatively little has been published about the chemistry and spectroscopic properties of these compounds.

The Reaction of BF and C_2H_2

The initial product of cocondensation of BF and C_2H_2 at −196° was a yellow solid. On warming this

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[2] P. L. Timms, *J. Am. Chem. Soc.*, **89**, 1629 (1967).

[3] (a) F. E. Brinckmann and F. G. A. Stone, *ibid.*, **82**, 6218 (1960); (b) T. D. Coyle and F. G. A. Stone, *ibid.*, **82**, 6223 (1960).

[4] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 6389 (1959).

to room temperature, it melted and part of it volatilized leaving a yellow viscous liquid.

The volatile fraction contained C_2H_2, BF_3, B_2F_4, and a group of compounds all containing the elements C, H, B, and F. This last group was separated on a low-temperature vacuum distillation column into two minor and two major components.

The two minor components were obtained in amounts only sufficient for mass spectrometric study. The spectra indicated them to be $C_2H_3BF_2$ and $C_2H_2B_2F_4$, probably vinyldifluoroborane described by Brinckmann and Stone,[3a] and the reaction product of acetylene and B_2F_4 described by Schlesinger.[4]

The two less volatile, major components were respectively a solid and a liquid at room temperature, the latter being much the more abundant. The solid was found by its vapor density, mass spectrum, and chemical analysis to have the formula $C_4H_4B_2F_2$, while the liquid had the formula $C_4H_4B_3F_5$. Under optimum conditions, about 8% of the BF formed could be recovered as $C_4H_4B_3F_5$ and $C_4H_4B_2F_2$.

At room temperature, or preferably at 70–100°, the vapor of $C_4H_4B_3F_5$ was observed to change quantitatively into the vapor of $C_4H_4B_2F_2$ with liberation of 1 mole of boron trifluoride. Although this change was easily detected by infrared spectroscopy after a few minutes at room temperature, it took several hours to go to completion even at 100°. The reaction could not be carried out in the condensed phase as only solid polymers were formed.

The Structure of $C_4H_4B_3F_5$

The mass spectrum of $C_4H_4B_3F_5$ is shown in Table I. No parent ion, $C_4H_4B_3F_5^+$, was observed. Two groups of ions at *m/e* 103–105 and 110–112 corresponding respectively to $C_2H_2B_2F_3^+$ and $C_4H_4B_2F_2^+$ were by far the most prominent in the spectrum below 15 eV. These groups of ions were probably formed by the processes

Table I. Principal Ions in the Mass Spectra of $C_4H_4B_3F_5$ and $C_4H_4B_2F_2$ at 50 eV

Mass	Probable identity	Relative abundance $C_4H_4B_3F_5$	$C_4H_4B_2F_2$
180	$C_4H_4{}^{11}B_3F_5^+$	...	..
112	$C_4H_4{}^{11}B_2F_2^+$	47	61
105	$C_2H_2{}^{11}B_2F_3^+$	12	...
56	$C_2H_2{}^{11}BF^+$	29	28
55	$C_2H{}^{11}BF^+ + C_2H_2{}^{10}BF^+$	100	100
49	${}^{11}BF_2^+$	25	Trace
38	$C_2H_3{}^{11}B^+$	5	22
37	$C_2H_2{}^{10}B^+ + C_2H_3{}^{11}B^+$	15	41

$$\begin{tikzcd}
 & C_2H_2B_2F_3^+ + C_2H_2BF_2 + 2e^- \\
e^- + C_4H_4B_3F_5 \arrow[ur] \arrow[dr] & \\
 & C_4H_4B_2F_2^+ + BF_3 + 2e^-
\end{tikzcd}$$

No BF_3^+ or $C_2H_2BF_2^+$ was seen in the spectrum of the compound. Elimination of neutral BF_3 on electron impact has been observed with other compounds containing two or more $-BF_2$ groups.[2]

The vapor-phase infrared spectra of $C_4H_4B_3F_5$ (Table II) showed a medium-strong absorption at 1595 cm^{-1}, the position of which changed only slightly (to 1580 cm^{-1}) in the deuterated molecule, $C_4D_4B_3F_5$. This absorption is in the range of C=C stretching frequencies reported by Brinckmann and Stone[3a] for vinylboron halides. The absorptions observed at 3036 and 3002 cm^{-1} are also in a similar position to the C–H stretching frequency of the =CH– group in the vinylhaloboranes. The absence of any but very weak bands in the region 900–1000 cm^{-1} makes it unlikely that $C_4H_4B_3F_5$ contains a *trans* –CH=CH– group. Either of the strong bands at 763 or 823 cm^{-1} could be associated with the out-of-plane C–H deformation in a *cis* –HC=CH– group.

Table II. Infrared Spectra (cm^{-1}) of Compounds I, III, V, and VI

I $C_4H_4B_3F_5$	III $C_4H_4B_2F_2$	V $C_4(CH_3)_2$-$H_2B_2F_2$	VI $C_4(CH_3)_2$-$H_2B_2F_2$
3036 mw	3012 w	2990 mw	2989 mw
3002 mw	3000 w	2890 w	2880 w
2955 w	2975 w		
1595 m	1552 m[a]	1578 m	1574 m
1405 vs	1393–1420 s	1450 s	1449 s
1360 vs	1239–1255 s	1360 s	1355 s
1225–1250 vs	1073 m[a]	1285 m	1275 m
1080–1100 m	1027 w	1240 m	1235 m
823 m	833 ms[b]	1100 m	1099 m
766 m		898 m[b]	896 m[b]

[a] Showing P and R branches. [b] Showing P, Q, and R branches.

The most important structural information was obtained from the proton and fluorine nmr spectra of the compound (Table III). The proton spectrum was taken on the neat liquid containing 5% of tetramethylsilane (TMS) as internal standard. The spectrum has been interpreted as a simple four-line, AB, spectrum with further splitting of the two types of protons by fluorine

Table III. Nmr Spectra of Compounds I, III, V, VI, and VII

Compound	Chemical shift, ppm	Coupling constants, Hz	Description of spectrum
	Proton Spectra (TMS as reference)		
I, $C_4H_4B_3F_5$	-6.50 -7.06	J_{H-C-BF_2}? 7 J_{H-C-BF} 11 J_{H-H} 18	AB pattern with coupling to fluorine giving a doublet of doublets and a high-field doublet of triplets
III, $C_4H_4B_2F_2$	-6.82		Broad singlet
V, $C_4(CH_3)_2$-$H_2B_2F_2$	-6.39	J_{H-C-BF}? 7	Broad doublet
	-1.88		Sharp singlet, $-CH_3$ group
VI, $C_4(CH_3)_2$-$H_2B_2F_2$	-6.30	J_{H-C-BF}? 8	Broad doublet
	-1.89		Sharp singlet, $-CH_3$ group
VII, $C_4(CH_3)_4$-B_2F_2	-1.80		Sharp singlet, $-CH_3$ group
	Fluorine Spectra (CCl_3F as reference)		
I	+46		Broad resonance, –BF– group
	+82		Broad, collapsed quartet, $-BF_2$ group
III	+81		Broad, collapsed quartet, –BF– group
V, VI	+70		Broad, collapsed quartet, –BF– group
VII	+67		Broad resonance, –BF– group

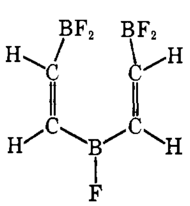
atoms to give a high-field doublet of triplets and a low-field doublet of doublets. The form of the high-field doublet of triplets is very similar to that observed by Coyle[5] in the spectrum of β-chlorovinyldifluoroborane. For this molecule, he measured a H–C–BF_2 coupling constant of about 6 cps. The low-field doublet of doublets in the spectrum of $C_4H_4B_3F_5$ suggests a coupling of a proton with a single fluorine atom.

Two broad resonances were observed in the ^{19}F nmr spectrum of $C_4H_4B_3F_5$. These had chemical shift values of 46 and 81 ppm on the high-field side of the reference CCl_3F and an area ratio of between 1:4 and 1:5. The high-field resonance could be clearly assigned to the fluorine atoms of –BF_2 groups as found in vinyldifluoroborane. The low-field resonance was at a somewhat higher field than for fluorine atoms in saturated C–BF–C groups. However, if the –BF– group was attached to carbon–carbon double bonds, this could move the position of resonance upfield.[3b]

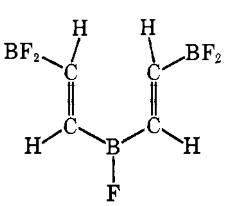
The ^{11}B nmr spectrum of the compound at 32 MHz showed only one very broad resonance centered at −23 ppm relative to boron trifluoride etherate. The position of the resonance is very similar to that found in triboron pentafluoride (−24 ppm) which only gives one broad resonance although it contains –BF_2 and –BF– groups. Thus the ^{11}B nmr spectrum of $C_4H_4B_3F_5$ merely indicates the presence of boron joined to fluorine in the molecule, but does not distinguish between –BF– and –BF_2 groups.

When $C_4H_4B_3F_5$ was hydrolyzed at room temperature, using water free from dissolved oxygen, about 10% of the carbon in the molecule was recovered as 1-butene. On heating the resulting solution to 120° in a sealed tube, the rest of the carbon was recovered as ethylene. Brinckmann and Stone[3a] observed that vinylboron halides gave ethylene on hydrolysis at 120°, but they did not report the formation of any 1-butene. As ethylene is the main product of hydrolysis of $C_4H_4B_3F_5$, the molecule must contain two C_2 units rather than one C_4 unit. Some polymerization of $C_4H_4B_3F_5$ presumably accompanies hydrolysis giving the C_4 units in the product.

The combination of the above chemical and physical studies on $C_4H_4B_3F_5$ suggests it may have one of two possible structures, I or II. Although the H–H coupling constant in the proton nmr spectrum would favor II, this is not favored by the infrared spectra or by the observed ease of elimination of BF_3 to form $C_4H_4B_2F_2$ (see below). Thus I seems more probable. A mixture of the two compounds is almost certainly not present, as this would give a much more complicated proton nmr spectrum than that observed.



I



II

The compound $C_4H_4B_3F_5$ melts at −68° and has a vapor pressure of 20 mm at 0°. It is unstable in the liquid phase at room temperature, quickly polymerizing to a viscous yellow liquid. Its conversion to $C_4H_4B_2F_2$ in the vapor phase has been mentioned above. The compound is pyrophoric and is very rapidly hydrolyzed.

The Structure of $C_4H_4B_2F_2$

The fairly rapid formation of $C_4H_4B_2F_2$ from $C_4H_4B_3F_5$ by quantitative loss of BF_3 strongly suggested the elimination was accompanied by ring closure and that $C_4H_4B_2F_2$ was a heterocycle.

In the mass spectrum of $C_4H_4B_2F_2$ (Table I), the parent ion at *m/e* 110–112 was prominent. However, the main fragmentation process split the molecule in two to give $C_2H_2BF^+$ and C_2HBF^+ ions. Mass spectra, which have been reported on other compounds containing –BF_2 groups, contain the BF_2^+ ion.[2] The absence of this ion in the spectrum of $C_4H_4B_2F_2$ indicated it contained no –BF_2 group.

On hydrolysis $C_4H_4B_2F_2$ yielded precisely the same mixture of ethylene and 1-butene as that obtained by hydrolysis of $C_4H_4B_3F_5$. Thus the molecule must also contain C_2 units, not a C_4 unit.

The most concrete evidence for the structure of $C_4H_4B_2F_2$ came from its infrared spectrum (Table II). There is a remarkable similarity in the general form of the infrared spectrum of the compound with that of *p*-benzoquinone. The spectrum of the latter has been analyzed in detail and reported in a series of papers by Anno, Becker, *et al.*[6]

p-Benzoquinone shows five main bands in its gas-phase infrared spectrum in the region 600–2000 cm^{-1}, while the fully deuterated molecule *p*-$C_6D_4O_2$ shows four bands in the same region. The compounds $C_4H_4B_2F_2$ and $C_4D_4B_2F_2$ also show five and four bands, respectively. The isotopic shifts and structure of the bands allow some fairly positive assignments to be made based on the benzoquinone model.

The strong bands showing P, Q, and R branches centered at 880 and 795 cm^{-1} for *p*-$C_6H_4O_2$ and *p*-$C_6D_4O_2$, respectively, are assigned to the C–H out-of-plane deformation. Strong bands with similar P, Q, and R branches are found for $C_4H_4B_2F_2$ and $C_4D_4B_2F_2$ at 833 and 742 cm^{-1}, respectively. The medium intensity band with P and R branches centered at 1063 cm^{-1} in *p*-$C_6H_4O_2$ is assigned to the C–H in-plane deformation, but no band of equivalent intensity is observed in *p*-$C_6D_4O_2$. A similar medium intensity doublet is observed for $C_4H_4B_2F_2$ at 1074 cm^{-1} but not in the spectrum of $C_4D_4B_2F_2$. The C=C stretching frequency is assigned to the doublet at 1591 cm^{-1} in *p*-$C_6H_4O_2$ and 1560 cm^{-1} in *p*-$C_6D_4O_2$. A doublet of comparable intensity is seen for $C_4H_4B_2F_2$ at 1552 cm^{-1} and for $C_4D_4B_2F_2$ at 1533 cm^{-1}. Further direct comparisons in this region are complicated by the difference in the C=O and B—F stretching frequencies.

Absorptions due to C–H or C–D stretches appear at lower frequency with $C_4H_4B_2F_2$ or $C_4D_4B_2F_2$ than for the benzoquinones. Thus the doublet at 3006 cm^{-1} in $C_4H_4B_2F_2$ is probably equivalent to the band at 3067 cm^{-1} in *p*-benzoquinone, while the weaker absorption at 2975 cm^{-1} may match the weak band at 3012 cm^{-1} assigned by Davies and Pritchard[7] to a C–H stretch of *p*-benzoquinone. Similar bands in $C_4D_4B_2F_2$ and *p*-

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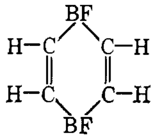
[5] T. D. Coyle, private communication.

[6] T. Anno, E. D. Becker, E. Charney, H. Stammreich, T. T. Sana, and H. Ziffer, *J. Chem. Phys.*, 42, 910 (1965).

[7] M. Davies and F. E. Pritchard, *Trans. Faraday Soc.*, **59**, 1248 (1963).

$C_6D_4O_2$ are centered at 2228 and 2277 cm^{-1}, respectively.

The proton nmr spectrum of $C_4H_4B_2F_2$ dissolved in TMS showed only a rather broad singlet at -6.8 ppm, indicating that all the protons are equivalent. The structure most consistent with the above data is III.



III

The fluorine nmr spectrum of $C_4H_4B_2F_2$ showed only one resonance, a broad, poorly resolved quartet, at $+81$ ppm relative to CCl_3F. This is at a much higher field than normally associated with $-BF-$ groups, and is in almost the same position as the resonance for the $-BF_2$ groups in $C_4H_4B_3F_5$. However, the resonance cannot be due to a $-BF_2$ group as this would imply that $C_4H_4B_2F_2$ contained either a $C-BF_2$ group or a $B-BF_2$ group. Neither of these groups could be contained in structures with equivalent protons, and the $B-BF_2$ grouping would result in the evolution of hydrogen on hydrolysis.

The white solid $C_4H_4B_2F_2$ decomposes without melting at about 35°, forming an involatile yellow solid. Even at 0°, solid $C_4H_4B_2F_2$ polymerizes quite rapidly. It is much more stable in the gas phase and can be kept at a few centimeters pressure at 100° for several hours with little decomposition. The vapor pressure of $C_4H_4B_2F_2$ is 32 mm at 0°.

The Reaction of BF with Other Acetylenes

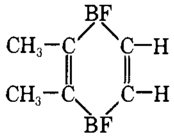
When propyne was cocondensed with BF under conditions identical with those used for the reaction with acetylene, three new volatile compounds were obtained. The most volatile of these (IV) was only present in trace amounts and was very difficult to separate from the less volatile, more abundant compound V. Each of the compounds was shown from its mass spectrum to contain only C, H, B, and F. All the compounds gave a well-defined parent ion of considerable intensity at *m/e* 140 corresponding to $C_6H_8B_2F_2^+$. The remainder of the mass spectrum of each of the compounds was almost the same. The first fragment ion was at mass 125 corresponding to loss of a methyl group from the parent. Ions of mass 69, thought to be $C_3H_3BF^+$, *i.e.*, half the molecule less one hydrogen, were prominent but less dominant than equivalent ions in the spectrum of $C_4H_4B_3F_5$ and $C_4H_4B_2F_2$.

The infrared spectra of the three isomers were also similar. Each showed a medium intensity absorption at 1574–1578 cm^{-1} which is reasonably assigned to a C=C stretch.

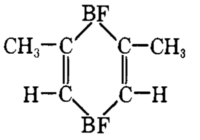
The proton nmr spectra of compounds V and VI were alike with broad doublets at -6.39 and -6.30 ppm, respectively, relative to TMS, and a singlet due to the protons of the methyl groups at -1.88 ppm. The area ratio of the doublet to singlet was 1:2.95. The single broad resonance obtained for each compound in the fluorine nmr was at 70 ppm on the high-field side of the reference CCl_3F.

Hydrolysis of compounds V and VI at 120° with water gave a very complex mixture of hexenes with only about 10% of propylene. No pentenes were found among the hydrolysis products.

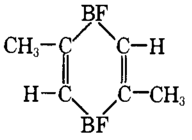
The three isomers of $C_6H_8B_2F_2$ appear to have the same skeleton as that in $C_4H_4B_2F_2$. The similarities in the nmr and mass spectra, and the position of the C=C stretch in the infrared, strongly indicate this. Their formula should thus be written $C_4(CH_3)_2H_2B_2F_2$. However, it is not possible from present evidence to give a definite assignment of the relative positions of the methyl groups around the ring. If the volatility of the compounds follows the same order as that observed in disubstituted xylenes and *p*-benzoquinones, then the structures will be as shown below.



IV



V



VI

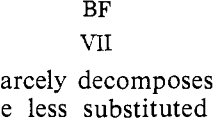
Compound IV was not obtained sufficiently pure to allow its melting point to be determined. Compound V melted at 5°. Compound VI melted with decomposition at 55–56° and had a vapor pressure of about 3 mm at 0°.

Cocondensation of 2-butyne with BF gave a yellow polymer which evolved small amounts of volatile material on warming to room temperature. The main volatile product was a white solid which could be moved only with difficulty in a vacuum system at room temperature.

The mass spectrum of the white solid indicated a molecular formula $C_8H_{12}B_2F_2$ as the ion at *m/e* 168 ($C_8H_{12}B_2F_2^+$) was dominant at all electron voltages. The main fragment ions corresponded to the loss of one of two methyl groups from the parent. No appreciable amount of the ion corresponding to half the molecule was observed. The proton nmr of the solid dissolved in benzene gave a single sharp resonance at -1.80 ppm relative to TMS. The ^{19}F nmr, taken on a 10% solution in hexafluorobenzene, gave a rather broad quartet centered at $+67.0$ ppm relative to CCl_3F. The infrared spectrum of the vapor taken at 40° showed a medium intensity band at 1580 cm^{-1} which can be assigned to a C=C stretching frequency.

Hydrolysis of $C_8H_{12}B_2F_2$ at room temperature gave mainly 3,4-dimethyl-2-hexene, but, on heating the solution in a sealed tube to 120° with water, a little *cis*-2-butene was also formed.

The similarity of the nmr spectral behavior of $C_8H_{12}B_2F_2$ to that of the dimethyl compounds IV and VI and to $C_4H_4B_2F_2$ suggests that the compound is the tetramethyl derivative of $C_4H_4B_2F_2$ with the structure VII shown below. The observed C=C stretching frequency and the relatively high intensity of the $C_8H_{12}B_2F_2^+$ ion in the mass spectrum support this.



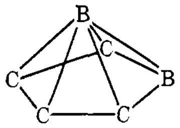
VII

The compound scarcely decomposes at room temperature, but, like the less substituted compounds, it is highly reactive toward air and water.

Discussion

A molecule with the C_4B_3 skeleton was isolated only in the reaction of BF with acetylene, and not in the reactions with methyl-substituted acetylenes. It is possible that the mechanism for the formation of the C_4B_3 skeleton is in all cases *via* the C_4B_3 species, but that $C_4H_4B_3F_5$ was the only molecule sufficiently stable to be isolated without loss of BF_3. The initial attack on the acetylene must be by monomeric BF, as other reactive boron fluorides such as B_2F_4 or B_8F_{12} do not give the observed products.[2,4] A species C_2R_2BF (where R = H or Me) could be formed, and this may be a three-membered ring or a diradical. Dimerization of this species would apparently lead directly to the C_4B_2 ring, but the mechanism is less obvious if there is an intermediate $C_4B_3F_5$ species formed. It was observed experimentally that the presence of a little BF_3 mixed with the BF was important in the formation of $C_4H_4B_3F_5$, but it is not clear what role this BF_3 plays in the over-all reaction scheme. Attempts to cocondense BF with equimolar mixtures of BF_3 and C_2H_2, or B_2F_4 and C_2H_2, have not given significantly improved yields of $C_4H_4B_3F_5$.

The compounds $C_4R_4B_2F_2$ are the first reported to contain a 1,4-diboracyclohexadiene ring. Binger[8] attempted to make the same ring system with alkyl or hydrogen substituents on the boron. The resulting compounds were C_4B_2 caged carboranes with the skeleton shown below. These carboranes were characterized by the very different electronic environment of the apical and basal boron atoms and of two pairs of basal carbon atoms. Thus the proton nmr of a fully methylated C_4B_2 carborane showed four resonances: two 0.2 ppm apart corresponding to the two types of $C-CH_3$ protons, and two widely separated corresponding to the $B-CH_3$ protons. The absence of similar effects in the proton and fluorine nmr of the $C_4R_4B_2F_2$ compounds shows that they do not have a cage structure.



When fluorine is joined to boron, there is the possibility of overlap of the filled p_z orbitals on the fluorine with the vacant p_z orbitals on boron. This reduces the tendency of boron to take part in multicenter bonding and must make a caged carborane structure of $C_4R_4B_2F_2$ less favored than a planar structure. However, two facts suggest an additional form of electron delocalization in the compounds. The first is the low C=C stretching frequency, and the second the position of the ^{19}F resonance which is at a higher field than in known -BF- compounds. Both can be explained by assuming there is some overlap of the carbon π electrons with the vacant p_z orbital on the boron. This would weaken the carbon-carbon bond and, by slightly reducing the extent of p-pπ bonding from fluorine to boron, increase the shielding of the fluorine compared with other -BF- compounds. This effect was also assumed by Coyle and Stone[3b] to explain the difference in ^{19}F chemical shift between alkyl- and vinyldifluoroborane.

Attempts to form the ion $C_4R_4B_2F_2^{2-}$ by reduction with sodium amalgam have led only to polymeric products. The $C_4B_2^{2-}$ nucleus is isoelectronic with the benzene nucleus. However, the additional charge on the ring may be too concentrated about the electronegative fluorine atoms in a $C_4B_2F_2$ structure for the ring system to be very stable.

There are at present insufficient experimental data to explain the observed change in hydrolysis products in going from $C_4H_4B_2F_2$ to $C_4(CH_3)_4B_2F_2$. The C_4B_2 ring of the former splits yielding mainly ethylene, but the latter yields mainly a C_8 olefin. It is not known if the C_8 unit is formed by an inter- or intramolecular process.

Experimental Section

The formation of boron monofluoride and the methods used for cocondensation reactions have been described elsewhere.[2] In a typical experiment, 0.04 mole of BF_3 was passed over boron at about 1880° during a 30-min period, giving 80% conversion to BF. The mixture of BF and unchanged BF_3 was cocondensed at $-196°$ with 0.1 mole of C_2H_2 (Matheson, 99.8% pure). The furnace was then cooled and the condensate allowed to warm to room temperature, any liberated volatiles being pumped into a cold trap.

The mixture in the cold trap was fractionated partly by conventional trap-to-trap distillation, mainly on a 3-ft, low-pressure, low-temperature distillation column.

Vapor density measurements were performed in a 100-ml constant volume apparatus at 25°. The pressure of vapor was measured with a mercury manometer, and the weight of sample by condensation in weighed capillaries. The method was found accurate to $\pm 1\%$ using 10–15 mg of sample.

Hydrolysis of the compounds was carried out on 5–50 mg of the compounds distilled into small glass ampoules containing a little oxygen-free water. The ampoules were sealed and heated to 120°. The volatiles formed were analyzed by mass and infrared spectroscopy.

The Stock ring method was used to obtain the melting point of $C_4H_4B_2F_2$, and the temperature was measured with a calibrated pentane thermometer.

Mass spectra were taken on a Bendix time-of-flight machine using an all-glass inlet system. Samples unstable at room temperature were vaporized directly from the condensed phase into the ion source of the mass spectrometer.

Proton nmr spectra were run at 60 and 100 MHz, fluorine spectra at 56.6 MHz, and boron spectra at 32 Mcps using Varian machines. To avoid decomposition, spectra of the compounds were taken below room temperature, and the spectra of $C_4H_4B_3F_5$ were measured at $-50°$.

Infrared spectra were obtained with either a Perkin-Elmer 411 spectrophotometer or with Infracords. Silver chloride windows were found most satisfactory with the vapors of $C_4H_4B_2F_2$ and $C_4H_4B_3F_5$. Sodium chloride or potassium bromide windows could be used but gave a slight increase in the rate of decomposition of the compounds. Adequate spectra were normally obtained with pressures of 5–20 mm in a 10-cm gas cell.

$C_4H_4B_3F_5$. The vapor density was found to be 179 ± 2 (calcd 179.5. *Anal.* Calcd: C, 26,7; H, 2.23. Found: C, 25.2; H, 2.20.

$C_4H_4B_2F_2$. The vapor density was found to be 112 ± 1 (calcd 111.6). *Anal.* Calcd: C, 43.0; H, 3.59. Found: C, 42.4; H, 3.70. $C_4D_4B_2F_2$ was made from C_2D_2 and BF. The C_2D_2 was prepared by the action of 99.8% D_2O on calcium carbide. The compound $C_4D_4B_3F_5$ was formed first, and then this was converted at 70° in the vapor state to $C_4D_4B_2F_2$.

$C_4(CH_3)_2H_2B_2F_2$ (V). The vapor density was found to be 138 ± 2 (calcd 139.6). *Anal.* Calcd: C, 51.6; H, 5.72. Found: C, 50.8; H, 5.50.

Assignments of formulas and structures to compounds IV and VI ($C_4(CH_3)_2H_2B_2F_2$) and VII ($C_4(CH_3)_4B_2F_2$) were based on the mass spectral evidence and other data discussed above. The propyne and 2-butyne used in their preparation were of greater than 98% purity.

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