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Ferrocenylboranes. II. Ferrocenyl Boric Acids and Related Compounds. Mass Spectral and Hydrogen-Bonding Studies[1]

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Diferrocenylborinic acid, diferrocenylborinic acid anhydride, and triferrocenylborane have been identified by mass spectrometry as products of the reaction of lithioferrocene with BF_3. Hydrolysis of ferrocenyldichloroborane gives ferrocenylboronic acid which readily dehydrates to triferrocenylboroxine. A comparison of the mass spectra of the ferrocenyl boric acids and their anhydrides with those of the analogous phenyl compounds indicates the greater stability of the ferrocenyl–B–O system. π delocalization in this system is suggested as the stabilizing factor. Several mass spectral rearrangements were observed, but these did not include Fe–O bond formation, a process which occurs in the spectra of ferrocenyl alcohols. Intramolecular hydrogen bonding between a B–OH group and the iron atom or ring π electrons was not observed for the ferrocenyl boric acids, in contrast with ferrocenyl alcohols. Although such bonding may be prevented by the geometry of the ferrocenyl boric acids, π delocalization in the ferrocenyl–B–O system may again be a factor.

Introduction

A topic of some interest in ferrocene chemistry concerns interactions of the iron atom with substituent groups. Examples include the observation of intramolecular hydrogen bonding between the hydroxyl group and the iron atom in ferrocenyl alcohols[2] and mass spectral rearrangements leading to Fe–OH bond formation in these alcohols[3] and to Fe–X bond formation in compounds of the type FcCOX (where X = C_6H_5, OH, OCH_3, and $NHCH_3$).[4,5] The lower Lewis acid strength of ferrocenyldichloroborane ($FcBCl_2$) relative to its phenyl analog may be due to either extensive π bonding between the ring and the boron or a specific Fe–B electronic interaction.[6] It was the study of this latter phenomenon that led to our interest in other ferrocenylboranes, particularly the boronic (FcB(OH)₂) and borinic acids (Fc₂BOH). Evidence was sought in these latter compounds for hydrogen bonding of the type observed in ferrocenyl alcohols and for mass spectral fragments containing Fe–O bonds. The juxtaposition of the strongly donating ferrocenyl group with an electron-accepting atom directed attention to the possibility that unusually stable molecular ions could be a feature of the mass spectrum of this type of molecule. Triferrocenylboroxine ($Fc_3B_3O_3$) was formed by dehydration of the boronic acid in the spectrometer; the effect of the ferrocenyl group vis-à-vis the phenyl group in directing the fragmentation of boroxines was also investigated.

Mass Spectral Studies

Identification of the Lithioferrocene–BF₃ Reaction

Products.—The title reaction has been reported[7] to yield triferrocenylborane (Fc_3B) and diferrocenylborinic acid, but no detailed product characterization has been published. In our hands, the reaction yielded a number of products, some of which could be isolated by chromatography on alumina and identified by spectroscopic methods. All of the chromatographed fractions contained traces of ferrocene as a contaminant which was difficult to remove completely.

Benzene eluted a red solid which was shown to be mainly triferrocenylborane. The solid exhibited, in addition to the molecular ion cluster for Fc_3B (centered at m/e 566), a second intense ion cluster of which m/e 778 was the major ion. That both of these clusters represented molecular ions was evident from variations in relative abundance with rate of insertion of sample and time in the source; furthermore, low-energy spectra showed sharp increases in these two species relative to all other ions. Exact mass measurements[8] established the formulas of these two molecular ions as $C_{30}H_{27}BFe_3$ and $C_{40}H_{36}B_2Fe_4O$. The same assignments were made by comparing the observed and calculated relative peak intensities in each molecular ion cluster (Table I).[9] Thus, triferrocenylborane is indeed formed in this reaction, and the higher molecular weight product must be diferrocenylborinic anhydride (Fc₂B–O–BFc₂).

The mass spectra of Fc_3B and Fc_4B_2O were dominated by their stable molecular ions which were accompanied by doubly charged ions of unusually high relative abundance (8 and 6%, respectively). A satisfactory

(1) (a) Abstracted from the Ph.D. thesis of E. W. P., Kansas State University, 1969. (b) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; see Abstract No. INOR 103.

(2) A. W. Baker and D. E. Bublitz, *Spectrochim. Acta*, **22**, 1787 (1966); for a complete review of this topic see J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev.*, **4**, 479 (1969).

(3) H. Egger, *Monatsh. Chem.*, **97**, 602 (1966).

(4) A. Mandelbaum and M. Cais, *Tetrahedron Lett.*, 3847 (1964); see also N. Moaz, A. Mandelbaum, and M. Cais, *ibid.*, 2087 (1965).

(5) The abbreviation Fc will be used for the ferrocenyl group.

(6) J. C. Kotz and E. W. Post, *Inorg. Chem.*, **9**, 1661 (1970).

(7) H. Rosenberg and F. L. Hedberg, Abstracts, 3rd International Symposium on Organometallic Chemistry, Munich, Germany, 1967, p 108. See also G. P. Sollott, W. R. Peterson, and J. L. Snead, Report AD634641, U. S. Department of Commerce, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va.

(8) All elemental compositions given in the text were substantiated by exact mass measurements. A resolution of at least 10,000 was employed and measurements were accurate to 10 ppm or better. The ion containing the most abundant isotope of each element present was mass measured.

(9) In molecules which contain elements having more than one abundant isotope this method provides an accurate alternative to exact mass measurements provided overlap of clusters does not occur; e.g., M·⁺ − 1 ions must be absent. A computer program (PL-1 language for IBM 360-50) was employed to calculate peak intensity distributions. Copies are available on request. See also A. Carrick and F. Glockling, *J. Chem. Soc.*, A, 40 (1967).

TABLE I

COMPUTED AND OBSERVED RELATIVE ION ABUNDANCES FOR MOLECULAR ION CLUSTERS[a]

Compound and ion						Rel abund, %				
Fc_3B	Mass:	562	563	564	565	566	567	568	569	
$C_{30}H_{27}BFe_3$	Calcd:	1.18	4.72	18.8	29.6	100	39.2	8.67	1.32	
	Obsd:	1.1	4.4	19.0	28.5	100	39.2	7.6	1.1	
$(Fc_2B)_2O$	Mass:	774	775	776	777	778	779	780	781	
$C_{40}H_{36}B_2Fe_4O$	Calcd:	3.53	11.8	29.4	52.3	100	48.4	13.8	2.75	
	Obsd:	3	10	31	50	100	49	12	2	
$FcB(OH)_2$	Mass:	227	228	229	230	231	232			
$C_{10}H_{11}BFeO_2$	Calcd:	1.55	6.31	25.2	100	13.8	1.62			
	Obsd:	1.6	8.1	25.0	100	13.7	2.0			
Fc_2BOH	Mass:	394	395	396	397	398	399	400	401	
$C_{20}H_{19}BFe_2O$	Calcd:	0.39	3.08	12.6	26.6	100	26.8	4.36	0.50	
	Obsd:	0.4	2.7	11.5	26.5	100	25.5	4.0	0.5	
$(FcBO)_3$	Mass:	631	632	633	634	635	636	637	638	639
$C_{30}H_{27}B_3Fe_3O_3$	Calcd:	0.98	3.95	13.4	33.3	68.6	100	36.7	78.4	1.4
	Obsd:	1.2	4.3	13.3	32.9	67	100	35.3	8.1	1.6
$(C_6H_5BO)_3$	Mass:	309	310	311	312	313	314			
$C_{18}H_{15}B_3O_3$	Calcd:	1.40	16.8	68.8	100	19.5	2.41			
	Obsd:	2.0	18.1	70.5	100	21.1	2.8			

[a] The $^{10}B^{11}B$ isotope ratio was taken from R. L. Middaugh, *Inorg. Chem.*, **7**, 1011 (1968). Isotope distributions for other elements were obtained from R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, pp 290-297. See ref 9.

spectrum of the anhydride was obtained by slow sublimation of Fc_3B from the sample probe. This fractional sublimation technique also gave a fair spectrum of triferrocenylborane, although it was not always possible to assign unambiguously fragment ions of less than 1% relative abundance. Triferrocenylborane showed only three daughter ions of appreciable abundance in the region above m/e 200; they resulted from loss of C_5H_5 (11% relative abundance; a commonly observed fragmentation in ferrocene derivatives), loss of a ferrocene molecule (8% relative abundance), and loss of both of these neutral fragments to give an ion of approximately 10% relative abundance.

The anhydride (Fc_4B_2O) spectrum had only one ion, m/e 527, above mass 190 with a relative abundance greater than 10% of m/e 778. This ion, $C_{25}H_{21}B_2Fe_3O$ (11% relative abundance), formally arises by loss of a ferrocenyl radical and a cyclopentadiene molecule, while simple loss of a ferrocenyl radical gives an ion of less than 1% relative abundance. m/e 267 ($C_{10}H_8$-BFe_2O, 2%) and m/e 315 ($C_{15}H_{12}BFe_2$, 1%) must arise by B-O cleavage, but their low abundances merely serve to emphasize the remarkable strength of the B-O bonds in the anhydride. The recently reported mass spectrum of dimethylborinic anhydride provides[10] an instructive contrast to the ferrocene analog in that B-O cleavage is necessary for formation of several of the more abundant daughter ions and in the fact that the molecular ion is of negligible abundance.

Elution of the reaction products with diethyl ether yielded an orange-red solid, the infrared spectrum of which suggested the presence of an -OH group (3590 cm^{-1}); the nmr spectrum indicated two ferrocene groups associated with the -OH group. The mass spectrum, discussed below with that of ferrocenylboronic acid, confirmed that this compound was diferrocenylborinic acid. Yet another compound, bi-

ferrocenyl, was also formed in small amounts; its molecular ion, m/e 370 ($C_{20}H_{18}Fe_2$), was present in variable abundance in the spectra of several samples of the borinic acid.

Ferrocenyl Boric Acids and Related Compounds.— Both ferrocenylboronic acid[11] and diferrocenylborinic acid gave mass spectra which showed very abundant molecular ions. Exact mass and isotope abundance measurements (Table I) confirmed the assigned molecular formulas. No difficulty was experienced in obtaining the spectrum of the borinic acid (Figure 1), but, at a
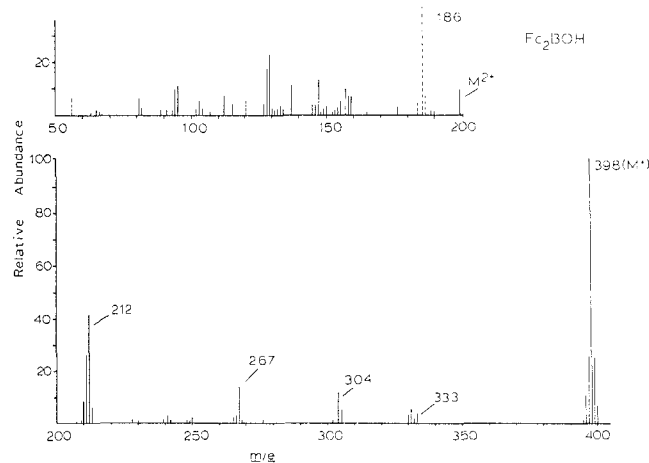

Figure 1.—Mass spectrum (70 eV, source temperature 150°) of diferrocenylborinic acid. Ferrocene impurity contributed to the ion at m/e 186 and the ferrocene fragment ions at m/e 121 and 56.

source temperature of *ca.* 150°, the boronic acid evidenced its expected facile decomposition to the corresponding boroxine. However, when the borinic acid

(10) F. Lanthier and W. A. G. Graham, *Can. J. Chem.*, **47**, 569 (1969).

(11) A previously reported attempt to obtain the spectrum of this compound was not successful: D. J. Clancy and I. J. Spilners, *Anal. Chem.*, **34**, 1839 (1962).

SCHEME I
FRAGMENTATION OF DIFERROCENYLBORINIC ACID
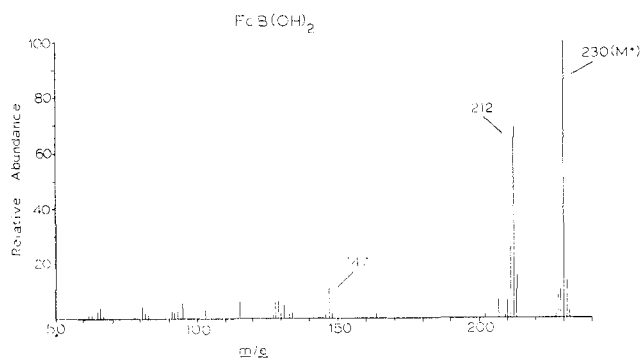

SCHEME II
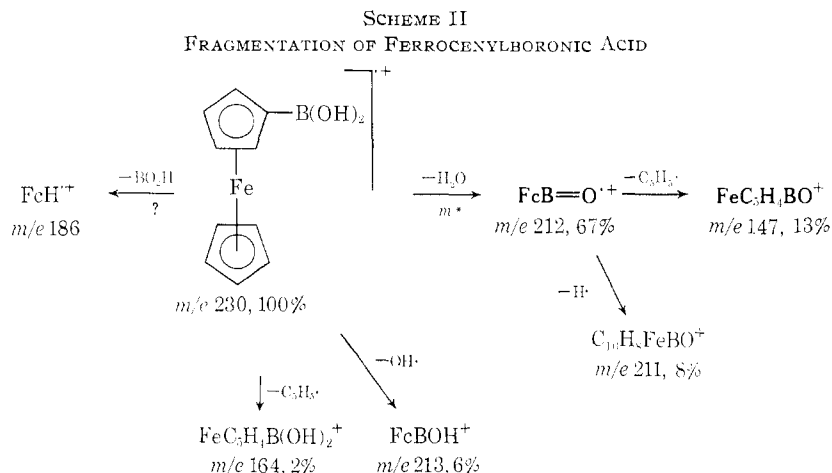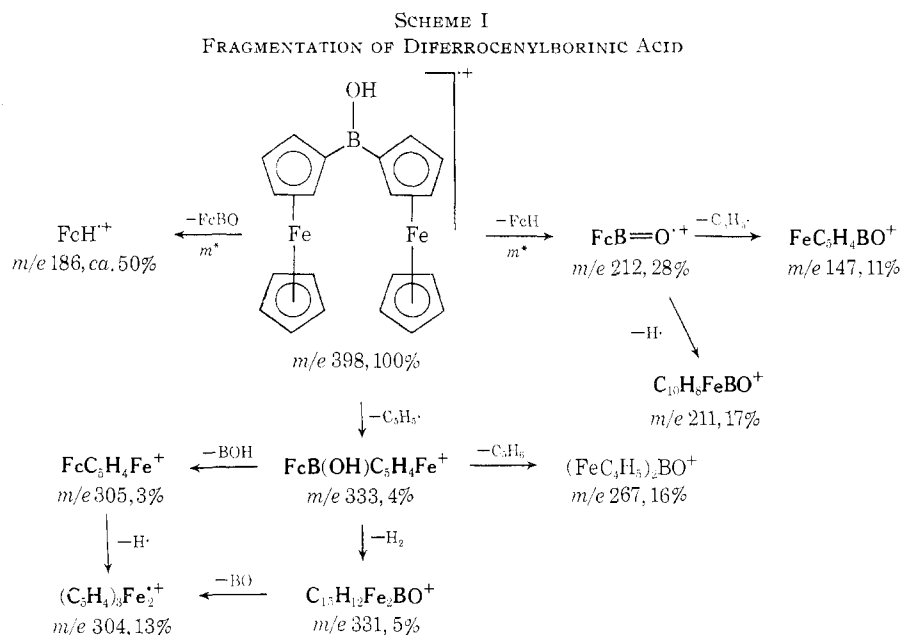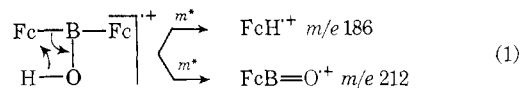FRAGMENTATION OF FERROCENYLBORONIC ACID

Figure 2.—Mass spectrum (70 eV, source temperature 50°) of ferrocenylboronic acid. Peaks at m/e 186, 121, and 56 and isotope peaks in each group were omitted because of some ferrocene impurity.

was introduced into the source at 50° by direct insertion, a good spectrum was obtained (Figure 2).

None of the more abundant fragment ions in either spectrum arose by processes involving Fe–O bond formation. This constrast with the behavior of ferrocenyl carbinols is explicable in terms of the new fragmentation pathways opened by the presence of the Fc–B–O

moiety. Thus, the main reaction evident in the borinic acid Fc₂BOH is a rearrangement, presumably four-centered, which gives either the ferrocene molecular ion (m/e 186) or FcB=O·⁺ (m/e 212) depending on the location of the charge. The occurrence of both of these processes was substantiated by the observation of metastable ions, although the ferrocene impurity present in the sample inflates the abundances of m/e 186, 121, 65, and 56 relative to the molecular ion. The abundance of FcB=O·⁺ (m/e 212) and its daughter ions may also be higher than the electron impact values as thermal decomposition was also found to lead to this species. Evidence for the proposed four-centered rearrangement (eq 1) was found by labeling the hydroxyl group. A 60% incorporation of deuterium was achieved; m/e 212 (FcBO·⁺) showed

$$\text{Fc}\!-\!\text{B}\!-\!\overline{\text{Fc}}\Big]^{\cdot+} \overset{m^*}{\underset{m^*}{\rightrightarrows}} \begin{array}{l}\text{FcH}^{\cdot+}\ m/e\ 186 \\ \text{FcB}{=}\text{O}^{\cdot+}\ m/e\ 212\end{array}$$

(1)

no shift at all while m/e 186 showed somewhat less than the expected 60% shift to m/e 187 due to the presence of some ferrocene impurity. The abun-

dant ion m/e 304 ($C_{15}H_{12}Fe_2$) and the m/e 305 ion ($C_{15}H_{13}Fe_2$) appear to be formed by BOH elimination[12] (ABC·+ → AC·+ + B type of skeletal rearrangement).[13] The m/e 129 ion was shown to have the composition $C_{10}H_9$; it presumably arises from m/e 185 or some other even-electron ion by loss of Fe, a previously documented skeletal rearrangement.[4,14] Scheme I shows the major processes which occur in Fc_2BOH. *In this scheme and those which follow the compositions of daughter ions given in bold type have been established by exact mass measurements.*[8] Relative abundances shown have been corrected for isotopic contributions.

Mentioned above are two fragment ions which result from the elimination of cyclopentadienyl hydrogen atoms. Structures I and II may be considered as possibilities for ions at m/e 315 ($C_{15}H_{12}BFe_2$), which arises from diferrocenylborinic acid anhydride, and m/e 304 ($C_{15}H_{12}Fe_2$), which occurs in the spectrum of diferrocenylborinic acid. Somewhat similar ion structures have been suggested previously.[15]
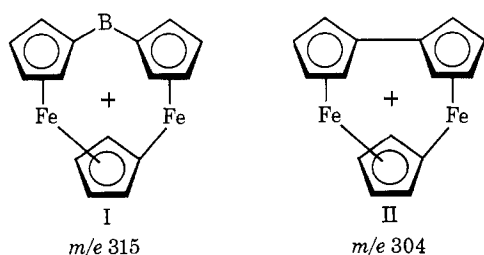
The spectrum of $FcB(OH)_2$ was notable for an abundant ion at m/e 212, due in part to electron impact induced dehydration as proved by an abundant metastable ion at m/e 195.4. The genesis of this ion probably again involves a four-centered hydrogen rearrangement. Facile thermal dehydration contributed to the species m/e 212, since it had a greater abundance than the molecular ion at higher temperatures (70°) and was present even in the absence of a detectable molecular ion at still higher temperatures. Other processes are summarized in Scheme II. The formation of the ferrocene ion (m/e 186) could not be rigorously established due to the presence of a ferrocene impurity; however, the process is considered likely, because the corresponding reaction is of major significance for phenylboronic acid (*vide infra*). The presence of ions at m/e 211 and 213 was discovered when the peak envelope calculated for m/e 212 ($C_{10}H_9BFeO$·+) was found to be in poor agreement with experiment.

Although the monomethyl ester of ferrocenylboronic acid was not isolated as such, its spectrum[16] (Table II), obtained after dissolving the acid in methanol and evaporating to dryness in air, is of some

(12) The traces of biferrocenyl impurity cannot account for these ions, which therefore appear to be genuine daughter ions.

(13) R. G. Cooks, *Org. Mass Spectrom.*, **2**, 481 (1969).

(14) D. T. Roberts, W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **89**, 6156 (1967).

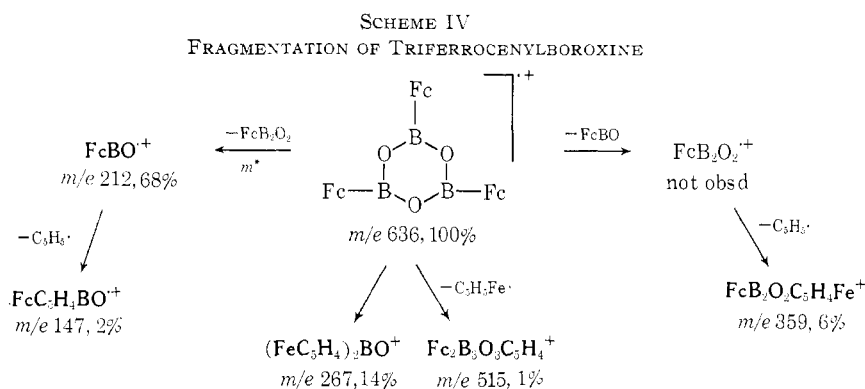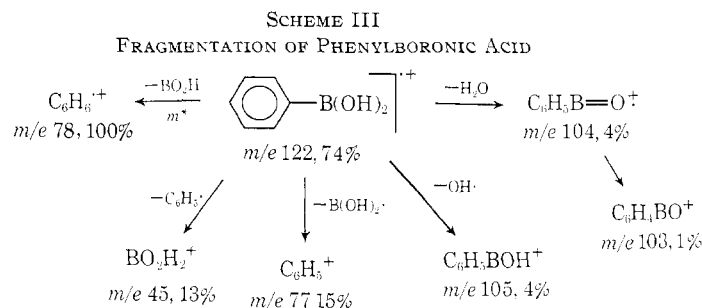(15) M. I. Bruce, *Advan. Organometal. Chem.*, **6**, 305 (1968).

(16) The spectrum showed a small amount of unconverted acid and a very small amount of the dimethyl ester.

TABLE II
MASS SPECTRA[a] OF METHYL FERROCENYLBORONATE, PHENYLBORONIC ACID, TRIFERROCENYLBOROXINE, AND TRIPHENYLBOROXINE

Methyl Ferrocenylboronate[b] [FcB(OH)(OCH₃)] (30°)	243 (1), 242 (16), 241 (3), 214 (2), 213 (15), 212 (46), 211 (11), 210 (2), 200 (0.6), 199 (1.5), 186 (6), 185 (8), 184 (4), 183 (1), 159 (2), 158 (1), 157 (1), 155 (1), 148 (3), 147 (28), 146 (6), 145 (2), 134 (2), 133 (5), 132 (1), 131 (2), 130 (6), 129 (52), 128 (20), 127 (5), 122 (7), 121 (83), 120 (15), 119 (7), 118 (2), 115 (1), 108 (1), 107 (2), 106 (1), 105 (2), 103 (6), 102 (2), 100 (1), 95 (15), 94 (25), 93 (6), 92 (4), 91 (4), 90 (2), 89 (1), 82 (2), 81 (21), 79 (3), 77 (6), 73 (8), 69 (2), 67 (4), 66 (7), 65 (8), 64 (1), 63 (5), 62 (1), 59 (7), 58 (2), 57 (7), 56 (100), 54 (6)
Phenylboronic Acid (30°)	123 (5), 122 (74), 121 (18), 105 (5), 104 (5), 103 (2), 79 (6), 78 (100), 77 (15), 76 (2), 74 (2), 63 (1), 53 (1), 52 (8), 51 (14), 50 (7), 45 (13), 44 (3), 39 (4)
Triferrocenylboroxine[c] (175°)	639 (1), 638 (8), 637 (35), 636 (100), 635 (67), 634 (33), 633 (13), 632 (4), 631 (1), 515 (1), 385 (2), 384 (1), 359 (6), 358 (3), 357 (2), 356 (1), 333 (1), 331 (2), 330 (2), 329 (1), 305 (2), 303 (1), 295 (1), 294 (2), 268 (2), 267 (14), 265 (2), 241 (1), 237 (1), 214 (1), 213 (9), 212 (68), 211 (20), 210 (5), 209 (1), 147 (2), 129 (1), 128 (1), 95 (1), 94 (1)
Triphenylboroxine (80°)	314 (3), 313 (21), 312 (100), 311 (71), 310 (18), 309 (2), 267 (1), 235 (5), 234 (4), 233 (2), 208 (7), 207 (4), 206 (1), 180 (1), 166 (1), 165 (9), 164 (19), 163 (10), 162 (2), 131 (7), 130 (3), 105 (8), 104 (20), 103 (7), 87 (3), 77 (3), 76 (4), 63 (1), 52 (1), 51 (1), 50 (1)

[a] All spectra were recorded at 70 eV, the source temperature is given for each compound, and mass numbers are followed by relative abundances given in parentheses. Multiply charged ions have been omitted. [b] Lower mass ions have enhanced abundances in this spectrum as the ion current decreased rapidly after sample insertion. [c] Ions m/e 186, 121, and 56 and associated isotope ions are not reported due to ferrocene impurity.

interest. The major process, methanol elimination, was accompanied by an abundant metastable ion and is analogous to loss of water from the acid. Loss of a methoxyl radical and a four-centered skeletal rearrangement leading to $Fc-CH_3$·+ in low abundance are also related to processes observed in the acid. The significant difference was the presence of an abundant m/e 129 ion in the ester. This was the only occasion we encountered where Fe elimination led to an abundant fragment ion, although low-abundance m/e 129 ions ($C_{10}H_9$) were present in several of the compounds

SCHEME III
FRAGMENTATION OF PHENYLBORONIC ACID

SCHEME IV
FRAGMENTATION OF TRIFERROCENYLBOROXINE

and have been reported by others.[17] Bursey and co-workers have reported an unusual rearrangement in a variety of ferrocenyl derivatives containing methoxyl groups[14,17] in which loss of C_5H_5 is followed by form-aldehyde elimination. Interestingly, this process did not occur at all in the monomethyl ester and provides yet another example of the difficulty of B–O cleavage.

Phenylboronic acid was of interest because its mass spectrum (Table II) can be compared with that of the ferrocenyl acid and the effects of the different aromatic groups can be assessed. The spectrum of the phenyl compound (Scheme III) was surprisingly different from that of the ferrocene compound; in particular, the benzene molecular ion (m/e 78) was the base peak. A metastable ion showed that it must have arisen from the molecular ion (m/e 122) by a four-centered hydrogen rearrangement. Elimination of water was correspondingly less important than in ferrocenylboronic acid. Hydroxyl radical loss, a minor process in the ferrocenyl acid, was of more importance in the phenyl analog. Phenyl–boron cleavage with the charge being retained by either C_6H_5 or the BO_2H_2 fragment was also observed. All of these results are in accord with the supposition that the phenyl–boron bond is weaker than the ferrocenyl–boron bond, possibly due to more extensive π bonding in the Fc–B–O system.

Boroxines.—The stability of the boroxine ring to mass spectral fragmentation has been discussed previously. Boroxine[18] and trimethylboroxine[19] give only a few fragment ions, most of which arise by

ring cleavage; significantly, the base peak in both cases is not the molecular ion but is due to loss of the substituent.

The spectra of triferrocenylboroxine and triphenyl-boroxine (Table II) were obtained by dehydration of the boronic acids in the hot ion source. In contrast to boroxine and trimethylboroxine, but in analogy with trifluoroboroxine,[20] the molecular ion was the base peak in both compounds.[20a] More effective π delocalization of the charge over the aromatic substituent as well as the boroxine nucleus may account for this observation.

A further indication of the stability of the phenyl and ferrocenylboroxine molecular ions was the high relative abundance (7.4 and 11.2%, respectively) of doubly charged species. Those ring cleavage processes which were observed are outlined in Schemes IV and V. The substantial increase (Table III) in the relative

TABLE III
MASS SPECTRA OF BOROXINES, $(RBO)_3$

R	M·²⁺	M·⁺ − R	M·⁺ − RBO	RBO·⁺	Ref
		Rel ion abund, %			
CH_3	12	100	1	3	19
F	100	10	31	9	20
C_6H_5	100	5	7	18	This work
Fc	100	0	0	68	This work

abundance of the RBO·⁺ ion as R is changed from CH_3 or F to C_6H_5 and then to Fc may reflect, at least crudely, the increasing ability of the substituent to

(17) D. T. Roberts, W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **89**, 4917 (1967).
(18) W. P. Sholette and R. F. Porter, *J. Phys. Chem.*, **67**, 177 (1963).
(19) W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Inorg. Nucl. Chem.*, **21**, 25 (1961).
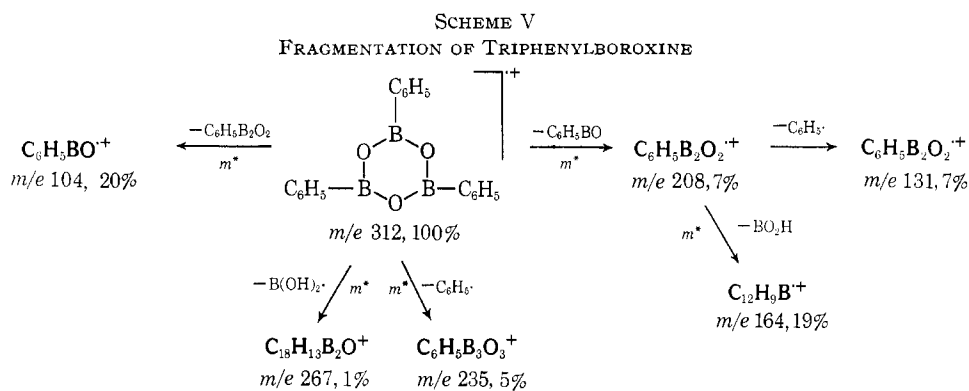
(20) R. F. Porter, D. R. Bidinosti, and K. F. Watterson, *J. Chem. Phys.*, **36**, 2104 (1962).
(20a) NOTE ADDED IN PROOF.—The mass spectra of triphenylboroxine, tricyclohexylboroxine, tri-*t*-butylboroxine, and tri-*n*-butylboroxine were reported recently. Only in the case of triphenylboroxine was the molecular ion the base peak: C. J. W. Brooks, D. J. Harvey, and B. S. Middleditch, *Org. Mass Spectrom.*, **3**, 231 (1970).

SCHEME V
FRAGMENTATION OF TRIPHENYLBOROXINE

stabilize the charge in the $RBO \cdot^+$ moiety. The $FcBO \cdot^+$ ion ($C_{10}H_9BFeO$) must certainly be very stable as it also occurs in significant abundance in the boric acid spectra (*vide supra*); its only important fragmentation is by C_5H_5 loss to give m/e 147.

Hydrogen-Bonding Studies

Some years ago Rosenblum and his coworkers found that the iron atom in ferrocene may function as a Lewis base toward the proton.[21] More recently, it was discovered that intramolecular hydrogen bonding may occur in ferrocenyl alcohols.[2] That is, the OH group has been found to interact both with the π electrons of the cyclopentadienyl ring and with the iron atom. This suggests that hydrogen bonding of a similar nature may occur in compounds such as ferrocenylboronic acid and diferrocenylborinic acid.

The investigation of this possibility was undertaken for three reasons. (1) Any bonding between a B–OH group and iron must occur at the expense of $p\pi$–$p\pi$ overlap between the cyclopentadienyl ring and the boron atom. Such overlap has been noted as a possibility in the mass spectral studies discussed above and in our study of the Lewis acidity of ferrocenyldichloroborane.[6] If such overlap does occur, then the –B(OH)R group (R = OH or Fc) must be planar, and hydrogen bonding between the OH group and either the iron or the cyclopentadienyl ring is not possible. Therefore, observation of intramolecular hydrogen bonding would strongly suggest that ring–boron π bonding is relatively weak. (2) While hydrogen bonding in alcohols has been extensively studied, there is only one brief report of such a study on an organoboric acid.[22] (3) We could find in the literature no careful determination of the band structure and frequencies for O–H vibrations of an organoboronic acid.

Diferrocenylborinic Acid.—Only one well-defined band (3641 cm^{-1}, half-width 24 cm^{-1}) was observed in the O–H stretching region for a dilute solution of Fc_2BOH in CCl_4. This compares favorably with dimethylboric acid ($\nu_{OH} = 3635$ cm^{-1}; half-width 27 cm^{-1}),[22] a molecule in which intramolecular hydrogen bonding is impossible. Therefore, the 3541-cm^{-1} band is assigned to the free O–H stretch in Fc_2BOH.

(21) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5249 (1960).

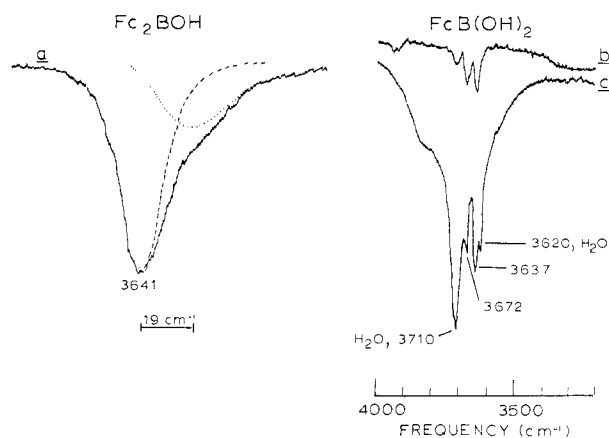(22) G. F. Lanthier and W. A. G. Graham, *Inorg. Chem.*, **8**, 172 (1969).

Figure 3.—Infrared spectra of diferrocenylborinic acid (a) and ferrocenylboronic acid (b, dried sample; c, after adding a trace of H_2O) as saturated solutions (*ca.* 0.0005 M) in CCl_4.

Under high-resolution conditions, however, the 3641-cm^{-1} band was found to be slightly asymmetric (Figure 3a) indicating that two or more bands may contribute. Although the asymmetry may arise from an OH group hydrogen bonded to the iron atom, this seems unlikely in view of the fact that the frequency shift for the second band is only 19 cm^{-1}; a much larger shift was observed for a somewhat analogous compound, ferrocenylmethanol (Table IV). Furthermore,

TABLE IV
INFRARED STRETCHING FREQUENCIES IN THE
O–H REGION (CM^{-1})

Compound	Free OH		π-Bonded OH		Iron-bonded OH		
	Asym	Sym	ν_{OH}	$\Delta\nu_\pi$	ν_{OH}	$\Delta\nu_{Fe}$	Ref
FcCH$_2$OH	3635		3620.1	15	3579.2	56	2
C$_6$H$_5$CH$_2$OH	3634		3617.4	16.6	...	...	2
FcCH$_2$CH$_2$OH	3635.9		3607.0	28.9	3537.6	98.3	2
C$_6$H$_5$CH$_2$CH$_2$OH	3634.9		3606.0	28.9	...	...	2
(CH$_3$)$_2$BOH	3635		...	...	...	...	22
Fc$_2$BOH	3641		...	...	...	...	a
FcB(OH)$_2$	3672	3637	...	...	...	...	a
FcB(OD)$_2$	2711	2685	...	...	...	...	a
C$_6$H$_5$B(OH)$_2$	3673	3637	...	...	...	...	a
C$_6$H$_5$B(OD)$_2$	2713	2686	...	...	...	...	a

a This work.

it is unlikely that it arises from a π-bonded OH group. In every case of the ferrocenyl alcohols, hydrogen bonding to the iron atom was seen if π bonding to the ring was observed;[2] this is obviously not the case here. The most reasonable explanation is that the asymmetry is caused by a small amount of another conformer of the molecule. It rotational isomers exist,

the amount of ring–B π bonding may not be the same in different configurations, thereby causing a small change in B–O π overlap and a change in ν_{OH}.

Ferrocenylboronic Acid.—When $FcB(OH)_2$ was vacuum dried, elemental and mass spectrometric analysis indicated that it had largely dehydrated to form triferrocenylboroxine. Therefore, when a dried sample of the acid was dissolved in CCl_4, only weak bands were observed in the O–H stretching region (Figure 3b). On adding a trace of water to the CCl_4 solution, it was found that the 3710-cm^{-1} band could be assigned to the asymmetric O–H stretch for water. However, the assignment of the other two bands (3672 and 3637 cm^{-1}) was not immediately straightforward. Although it seemed reasonable that the –B(OH)$_2$ group would display symmetric and asymmetric O–H stretching bands, this could not be assumed. One of the bands could be a combination band, or it could arise from a material such as $FcB(OH)–O–(HO)BFc$. In order to prove that both bands arise from the –B(OH)$_2$ group, the ferrocenyl boric acid was treated with H_2O and D_2O, and the spectrum of the analogous phenylboronic acid was investigated.

Treatment with water gave the spectrum shown in Figure 3c. The increase in intensity of the 3672- and 3637-cm^{-1} bands indicates that both arise from O–H stretching modes. Further evidence for this was found on treating the acid with D_2O. The two bands at 3672 and 3637 cm^{-1} disappeared and were replaced by bands at 2711 and 2685 cm^{-1}. The ratios of the frequencies (3672/2711 = 1.35 and 3637/2685 = 1.35) were within the range (1.3–1.4) expected for the OH to OD frequency ratio.

Although these experiments do indicate that both bands are due to O–H stretching modes, they do not necessarily prove that the bands arise from a –B(OH)$_2$ group. To obtain some evidence for this, we examined the spectrum of phenylboronic acid. The dehydration of this acid has been studied;[23] there is no evidence for the formation of intermediate dehydration products on going from the acid to the boroxine. The spectrum of a dilute CCl_4 solution of $C_6H_5B(OH)_2$ showed absorptions at 3673 and 3637 cm^{-1} in addition to those for water. Treatment of this solution with D_2O decreased the intensity of the bands in the OH region and new bands appeared at 2713 and 2686 cm^{-1} in addition to those for D_2O. Again the ratios of frequencies are in the range expected for the OH to OD ratio. Therefore, the 3673- and 3637-cm^{-1} bands were assigned to the OH stretching modes of the –B(OH)$_2$ groups in $C_6H_5B(OH)_2$. Further evidence for this was seen from the fact that the relative intensities of the bands did not change on treatment with successively greater amounts of water. If the boroxine reacted with water to form linear trimers or dimers before giving the boronic acid and if one band were due to the boronic acid and another due to a trimer or dimer, a change in the relative intensities of the bands would be expected as more water was added.

Although it is clear that two bands arise from the –B(OH)$_2$ group in $C_6H_5B(OH)_2$, the possibility that one of these absorptions may arise from free OH and the other from an OH group hydrogen bonded to the π electrons of the phenyl group must now be discussed. In benzyl alcohol, for example, two bands were observed at 3634.9 and 3617.4 cm^{-1} which were assigned to free and π-bonded OH, respectively.[2] Comparison of these bands with the data in Table IV indicates that the separation between free and π-bonded OH is around 16 cm^{-1} for both benzyl alcohol and ferrocenylmethanol; for β-phenylethanol and β-ferrocenylethanol, molecules in which steric factors allow the OH group to move closer to the ring, $\Delta\nu_{OH}$ for the π interaction is about 29 cm^{-1}. Considering the geometrical changes which occur when a boron atom is introduced in place of a carbon atom, the OH group should be further from the π cloud in $C_6H_5B(OH)_2$ than in $C_6H_5CH_2OH$; the separation between free and π-bonded OH bonds might be expected to be smaller in the boronic acid than in benzyl alcohol. Since the two bands in $C_6H_5B(OH)_2$ are separated by 36 cm^{-1}, it is considered unlikely that the 3637-cm^{-1} band arises from an OH hydrogen bonded to the π system; rather, it should be assigned to the symmetric stretch of the OH groups in the –B(OH)$_2$ moiety. The bands observed for $FcB(OH)_2$ were nearly identical in frequency with those observed for phenylboronic acid, suggesting that they also arise from the asymmetric and symmetric stretches of a –B(OH)$_2$ group. This coincidence of bands also strongly suggests that the lower frequency band in the ferrocenyl acid is not due to OH hydrogen bonded to iron.

Summary and Conclusions

The stability of Fc–B and B–O bonds in the ferrocenyl boric acids and their anhydrides was evident from the mass spectral studies, especially where comparison with their phenyl analogs was possible. Strong π interactions in the Fc–B–O moiety may account for these observations[24] and for the fact that no fragment ions which demand Fe–O bond formation could be found. By way of contrast, Fe–O bond formation does occur during fragmentation of many ferrocenyl alcohols.[3]

Also in contrast with the ferrocenyl alcohols is our finding that intramolecular hydrogen bonding does not occur in the ferrocenyl boric acids. However, this does not necessarily imply that hydrogen bonding is prevented by strong π bonding in the Fc–B–O system. On the contrary, hydrogen bonding may be prevented by the geometry of the boric acids, or the B–OH group may be an intrinsically weak hydrogen-bonding group. A thorough study of *inter*molecular hydrogen bonding involving borinic acids should be made. The stability of diferrocenylborinic acid suggests it as a good candidate for such studies; consequently, we are investigating more thoroughly its preparation and properties.

(23) L. Santucci and C. Triboulet, *J. Chem. Soc., A*, 392 (1969).

(24) Evidence for B–O π bonding was reported recently by G. F. Lanthier and W. A. G. Graham, *Chem. Commun.*, 715 (1968).

Experimental Section

Reaction of Lithioferrocene with BF₃.—The procedure for the preparation of FcLi was similar to that of Benkeser, Goggin, and Schroll.[25] A 21.3-ml aliquot of a 1.6 M hexane solution of butyllithium (34 mmol) was added in the drybox over a 15-min period to a solution of 5.01 g of ferrocene (26.9 mmol; Alfa Inorganics; recrystallized from hexane) in dry diethyl ether. A change to a darker red color accompanied the addition. After stirring for 1 hr, the solution was allowed to stand for 24 hr. Next, 1.1 ml of a 1.5 M solution of BF₃·O(C₂H₅)₂ (1.65 mmol of BF₃; prepared from the pure reagents on a vacuum line) was added dropwise with stirring over a 10-min period. After 30 min of vigorous stirring, some orange solid appeared. After 4.5 hr, solid formation had apparently ceased. The vessel was then removed from the drybox and the contents quickly poured onto ice. After warming the hydrolyzed solution to room temperature, the layers were separated, and the water layer was washed with ether. The ether fractions were then evaporated to dryness under reduced pressure to give an orange-red solid. This solid was slurried with hexane and placed on a 20 × 2 cm alumina column. Ferrocene was eluted with hexane. A second band (red) was eluted with benzene to yield 0.12 g of a red crystalline solid which was shown by mass spectrometry to consist of Fc₃B and Fc₄B₂O. A third band (yellow) was eluted with diethyl ether to give 0.26 g of an orange-red crystalline solid, Fc₂BOH. Pink and yellow bands were removed with CHCl₃, but both fractions turned to sticky red-black oils when the solvent was removed under reduced pressure.[26]

Orange-red diferrocenylborinic acid was apparently air stable as was triferrocenylborane. The pmr spectrum of the borinic acid in CDCl₃ displayed the following bands: τ 5.86 (singlet, relative intensity 9.4, unsubstituted rings); τ 5.81 (broad singlet, relative intensity 8, substituted rings); τ 5.47 (singlet, relative intensity 1.4, OH group). The main bands of its infrared spectrum were (cm⁻¹, Nujol mull): 3590 m (ν_{OH}), 1283 vs, 1150 m, 1100 m, 1081 m, 1067 w, 1043 s, 1014 m, 998 m, 924 s, 817 vs, 761 m, 752 s, 700 m, 689 s, 642 m, 595 w, 569 s, 537 s, 485 vs, 473 s, 462 s. The melting point of the borinic acid was found to be 159–161° (lit.[7] mp 172°).

Ferrocenyldichloroborane was prepared as previously described.[6] The boronic acid, FcB(OH)₂, was prepared by the following procedure. A thin-walled bulb containing 1.65 mmol of FcBCl₂ was broken in 40 ml of dry hexane under a blanket of nitrogen. While the solution was stirred vigorously, water was added dropwise until formation of an insoluble yellow solid ceased. (The water was approximately 0.20 M in SnCl₂ to pre-

vent oxidation to a ferrocenium salt.[27]) The solid hydrolysis product was washed with hexane to remove any ferrocene formed in the reaction. The remaining solid was next washed with water to remove the green tint (presumably a trace of ferrocenium salt) and then extracted with ether. Yellow FcB(OH)₂ was isolated upon evaporation of the ether under reduced pressure. The solid decomposed at 143–148° in agreement with the literature.[28] However, after drying *in vacuo* for several days, elemental analysis indicated that partial dehydration to triferrocenylboroxine had occurred. *Anal.* Calcd for C₁₀H₁₁BFeO₂: C, 52.25; H, 4.82. Calcd for C₃₀H₂₇B₃Fe₃O₃: C, 56.70; H, 4.28. Found: C, 54.06; H, 4.58.

Phenylboronic acid, C₆H₅B(OH)₂, was prepared from C₆H₅BCl₂ (Alfa Inorganics) by a procedure similar to that used for the ferrocenyl compound. The purity of the sample was checked mass spectrometrically.

Mass Spectrometric and Infrared Techniques.—Mass spectra were determined on an AEI-MS9 instrument using 70-eV ionizing energy, 100-μA trap current, and 8-kV accelerating voltage. The samples were introduced by direct insertion into the ion source. Exact mass measurements were made using perfluorotributylamine as the reference compound. Ion abundances are expressed as a percentage of the base peak; in every spectrum examined, except for that of phenylboronic acid, the base peak was the molecular ion.

Diferrocenylborinic acid-O-d_1 was formed by cointroduction of D₂O and diferrocenylborinic acid into the ion source. The degree of deuterium incorporation was found from the peak distribution in the molecular ion at low electron energy.

The solvent for the hydrogen-bonding studies, CCl₄, was dried by refluxing over P₂O₅ and then distilled under dry N₂. The absence of water in the CCl₄ was continuously checked by infrared spectroscopy. A 25-mm cell having NaCl windows was used, and the spectra were recorded on a Perkin-Elmer 457. Nearly saturated solutions (approximately 0.0005 M) of the organoboric acids were prepared in the drybox. In all studies, the spectrum of the compound was obtained as soon as possible after filling the cell. Solutions were treated with H₂O or D₂O by placing 2 or 3 drops of water in a stoppered flask where it was shaken for 2 or 3 min with the solution from the cell.

(25) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Amer. Chem. Soc.*, **76**, 4025 (1954).

(26) Our procedure for the separation of Fc₃B and Fc₂BOH differs considerably from that given by Sollott and coworkers; a more thorough investigation of this reaction and the properties of these new compounds is currently underway.

(27) S. McVey, I. G. Morrison, and P. L. Pauson, *J. Chem. Soc., C*, 1847 (1967).

(28) A. N. Nesmeyanov, W. A. Ssasonova, and V. N. Drosd, *Chem. Ber.*, **93**, 2717 (1960).