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Ferrocenylboranes. I. The Preparation and Properties of Ferrocenyldichloroborane[1]

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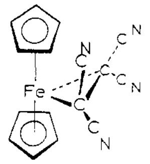
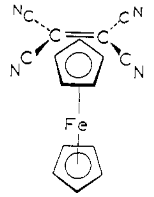
Ferrocene reacts with diboron tetrachloride to produce ferrocenyldichloroborane, $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4BCl_2)$. Other products of this reaction include H_2, $HBCl_2$, BCl_3, and HCl. An examination of the volatile products suggests the following reaction path. First, B_2Cl_4 reacts with ferrocene to give ferrocenyldichloroborane and $HBCl_2$. Dichloroborane then reacts with ferrocene to give more of the ferrocenylborane and H_2; this latter reaction is cyclic since more $HBCl_2$ may be produced by the reaction of H_2 with B_2Cl_4. Ferrocenylboranes are isoelectronic with α-ferrocenylcarbonium ions; as these carbonium ions are notably more stable than their phenyl analogs, this suggests that ferrocenyldichloroborane should be a weaker Lewis acid than its phenyl analog, $C_6H_5BCl_2$. Although ferrocenyldichloroborane forms 1:1 adducts with $N(CH_3)_3$, pyridine, and tetrahydrofuran, infrared and nmr methods indicate that it is a weaker acid than phenyldichloroborane. The title compound may also be prepared more efficiently from BCl_3 and ferrocenyl mercurichloride in hexane. Other properties of ferrocenyldichloroborane are discussed.

Introduction

When ferrocene is dissolved in strong protonic acids, there is evidence for a direct interaction between the proton and the iron atom of ferrocene.[2] The e_{2g} orbitals, which are involved to only a small extent in metal–ring bonding, are thought to be utilized in bonding the proton.[3] Ferrocene also interacts with the π acid tetracyanoethylene (TCNE).[4] Because of the interaction of the proton with the ferrocene nonbonding orbitals, it was thought that the TCNE may be bonded to the iron atom through these orbitals in a manner similar to that proposed for olefin–metal bonding (I). An alternative explanation, subsequently confirmed by crystallographic studies,[5] was that TCNE is bonded through the π orbitals of the cyclopentadienyl ring (II).



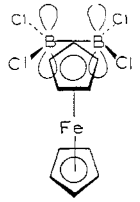
I



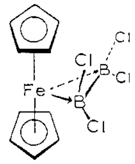
II

Diboron tetrachloride might also be considered a π acid.[6] The addition of B_2Cl_4 to olefins is thought to proceed through a π complex, followed by concerted *cis* addition to the olefin.[7,8] Another reaction in which B_2Cl_4 may function as a π acid is its reaction with naphthalene.[9]

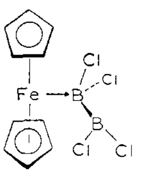
It is possible, then, that B_2Cl_4 might interact with ferrocene in a variety of ways. Since our work was begun before the elucidation of the ferrocene–TCNE crystal structure, both structures III and IV were considered possible. In addition, the protonation of ferrocene suggests V as a possibility. As reported earlier,[10] the actual reaction product is ferrocenyldichloroborane $(FcBCl_2)$[11] (VI), a compound which may have resulted from the initial formation of a π complex such as III. This paper describes the B_2Cl_4–ferrocene reaction in greater detail and our additional work on the properties of $FcBCl_2$.



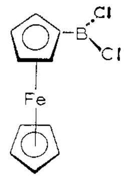
III



IV



V



VI

Experimental Section

Equipment and General Techniques.—Air-sensitive, volatile materials were handled in a preparative vacuum line equipped with mercury float valves.[12] Nonvolatile air-sensitive substances were handled in a HE-43 Vac-Atmosphere drybox equipped with a drying and deoxygenating train.[13]

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[1] (a) Abstracted from the Ph.D. thesis of E. W. P., Kansas State University, 1969. (b) Parts of this research were presented at the 4th Midwest Regional Meeting of the American Chemical Society, Manhattan, Kan., Oct 1968, and the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; see Abstract No. INOR 103.

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

[3] (a) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, Wiley, New York, N. Y., 1965; (b) J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev., Sect. A*, **4**, 479 (1969).

[4] M. Rosenblum, R. W. Fish, and C. Bennett, *J. Amer. Chem. Soc.*, **86**, 5166 (1964).

[5] E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *ibid.*, **89**, 4540 (1967).

[6] G. Urry in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 351.

[7] R. W. Rudolph, *J. Amer. Chem. Soc.*, **89**, 4216 (1967).

[8] M. Zeldin, A. R. Gatti, and T. Wartik, *ibid.*, **89**, 4217 (1967); for a report of *trans* addition see H. K. Saha, L. J. Glicenstein, and G. Urry, *J. Organometal. Chem.*, **8**, 37 (1967).

[9] W. B. Fox and T. Wartik, *J. Amer. Chem. Soc.*, **83**, 498 (1961).

[10] J. C. Kotz and E. W. Post, *ibid.*, **90**, 4503 (1968).

[11] The ferrocenyl group, $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4\text{–})$, will be abbreviated as Fc throughout this paper.

[12] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[13] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).

Many of the reactions described in this paper were done in a sealed, evacuated, all-glass *zweikügel* (double Schlenk tube).[12] This apparatus is essentially an H tube having glass break-seals through which volatile materials may be returned to the vacuum line. The reaction is carried out in one side of the tube, and solvent and soluble materials are decanted to the other side after completion of the reaction; further extraction of the reaction product is accomplished by distilling the solvent back to the reaction side and washing the insoluble reaction residue before again decanting.

Proton nmr spectra were obtained with a Varian A-60 spectrometer; TMS was used as an internal standard and the sideband technique was used for chart calibration. Sample tubes were filled in the drybox or when attached to the vacuum line in the case of volatile materials. The 32-MHz ^{11}B spectra were obtained with a Varian HA-100 and referenced to $BF_3 \cdot O(C_2H_5)_2$.[14]

Infrared spectra were obtained using a Perkin-Elmer 337 or 457. Solids were run as Nujol mulls, and gases in a 10-cm cell; KBr windows were used throughout. When BCl_3, HCl, B_2H_6, and $HBCl_2$ were used or obtained as mixtures, quantitative determinations of the amount of each gas in the mixture were done spectrophotometrically. A measured aliquot of the gas mixture was distilled into the infrared gas cell, and the amount of each gas was determined using the extinction coefficients listed in Table I. Since the bands for B_2H_6 are pressure sensitive, the ϵ value for this gas was determined at a cell pressure of 25 mm; mixtures containing small amounts of B_2H_6 were run at 25 mm. The value for $HBCl_2$ was taken from the literature[15] and found to be correct by independent checks. Values for other gases were determined at the indicated frequencies; to calculate ϵ for HCl, the average absorbance of the second, third, and fourth lowest frequency bands in the R branch was used.

TABLE I

EXTINCTION COEFFICIENTS FOR BCl_3, $HBCl_2$, B_2H_6, AND HCl

Compound	Obsd freq, cm^{-1}	Extinction coeff
BCl_3	996	0.0166
$HBCl_2$	1114	0.0206
B_2H_6	1626	0.0073
	996	0.00038
HCl	2950	0.00025

Solvents and Reagents.—All solvents were reagent grade; they were dried over appropriate agents and then distilled under nitrogen. The solvents were stored over molecular sieves in stoppered bottles in the drybox or in evacuated bulbs on the vacuum line.

Diboron tetrachloride was prepared using an apparatus very similar to one previously described.[16] Immediately before use, the halide was repeatedly fractionated through traps at −45, −78, and −196° to give a B_2Cl_4 fraction having a vapor pressure of 42.2–42.5 mm at 0° (lit.[12] vapor pressure 44 mm at 0°). Diboron tetrafluoride was prepared from B_2Cl_4 and SbF_3 according to the method of Finch and Schlesinger.[17]

Dichloroborane was prepared by treating B_2Cl_4 with H_2 in the gas phase in a 1-l. bulb.[18] (Carrying out the reaction in the gas phase rather than with liquid B_2Cl_4 gave higher yields of $HBCl_2$ and fewer unwanted by-products.) Maximum yields of $HBCl_2$ were obtained after 15 min of reaction time. The reaction mixture was fractionated through traps at −78, −112, and −196°. A mixture of $HBCl_2$ and BCl_3 was found at −112°, and a small quantity of B_2H_6 was trapped at −196°. $HBCl_2$ is known to disproportionate to BCl_3 and B_2H_6 according to eq 5.[19] Therefore, in order to ensure the presence of $HBCl_2$ in its subsequent reaction with ferrocene, a mixture of $HBCl_2$ and BCl_3 was used. Difluoroborane (HBF_2) and B_2H_6 were prepared according to literature methods.[20]

Trimethylamine was prepared on the vacuum line by the action of aqueous KOH on $(CH_3)_3N \cdot HCl$. It was fractionated to a constant vapor pressure of 680 mm at 0° (lit.[12] vapor pressure 680 mm at 0°). Dimethylamine (Matheson, anhydrous) was dried over CaH_2 at −78° before use; the vapor pressure at 0° (564 mm) agreed with the literature.[12]

Ferrocene (Alfa Inorganics) was recrystallized from hexane or sublimed before use. Ferrocenyl mercurichloride (FcHgCl)[21] was prepared by first mixing 18.60 g (100 mmol) of FcH and 6.41 g (20.1 mmol) of mercuric acetate in 400 ml of 1:1 diethyl ether–methanol. (Drying the solvent mixture overnight with Drierite minimized the amount of green by-product and improved the yield.) After stirring for 3 hr, 2 g of powdered KCl was added. An orange precipitate formed which was filtered off after 1 hr. This solid was washed with hot CH_3OH, and the washings and original filtrate were combined; solvent was removed under reduced pressure to give an orange solid. After removing most of the ferrocene by prolonged vacuum sublimation, the residue was washed with hot CH_3OH to remove the last traces of FcH. The remainder was extracted with hot xylene-1-butanol; on evaporation of the filtrate, 5.28 g of FcHgCl (62.4% yield) was obtained. The melting point agreed with the literature,[21] and the infrared spectrum was identical with that of an authentic sample (Alfa Inorganics).

The Reaction of B_2Cl_4 with Ferrocene.—In a typical experiment 6.035 mmol of sublimed ferrocene was placed in one arm of an oven-dried *zweikügel* before it was evacuated at −5° for 2 hr to remove any traces of moisture. About 15 ml of dry hexane and 6.028 mmol of B_2Cl_4 were distilled into the vessel at −196° before it was sealed off with a torch.

Upon warming to 0°, with shaking, the contents turned dark red almost immediately. Some red-brown solid appeared to form throughout the tube, but disappeared after 1 or 2 hr. The vessel was shaken often for the first hour, but only occasionally thereafter. Bubbles of a gas were observed to escape from the solution when the tube was disturbed. Formation of a flocculent green precipitate was observed as the reaction progressed. Most of the ferrocene had been taken into solution after 60 hr. The vessel was then cooled to −196° and opened to a Toepler pump. Hydrogen (1.18 mmol, identified by its mass spectrometric ionization potential[22]) was collected. The vessel was again sealed, and, after warming to 0°, the solution was decanted from the green solid. (The insoluble solid turned to a yellow-black intractable tar at room temperature.) Extraction of the insoluble residue was continued until the hexane washings were no longer colored. All of the condensable materials were held in the side containing the product, and the two sides of the *zweikügel* were separated by sealing with a torch.

The tube containing the product was opened to the vacuum line, and the volatiles were distilled out while the vessel was held at −23°. After the hexane had been removed, the vessel was opened to another trap at −196°, and evacuation was continued for 2 days at room temperature. Ferrocene and a small amount of solid product were collected in this trap. A red solid, ferrocenyldichloroborane, remained in the *zweikügel*. This tube was transferred to the drybox where it was warmed to liquefy the product; the red viscous liquid was then transferred with a syringe to preweighed thin glass bulbs which were then sealed off with a

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[14] We wish to thank Dr. R. Middaugh and his students at Kansas University for their assistance in obtaining these spectra.

[15] H. G. Nadeau and D. M. Oaks, Jr., *Anal. Chem.*, **38**, 1480 (1960).

[16] A. G. Massey, D. S. Urch, and A. K. Holliday, *J. Inorg. Nucl. Chem.*, **28**, 365 (1966).

[17] A. Finch and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **80**, 3573 (1958).

[18] G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).

[19] (a) L. Lynds and C. D. Bass, *Inorg. Chem.*, **3**, 1147 (1964); (b) H. W. Myers and R. F. Putnam, *ibid.*, **2**, 655 (1963).

[20] T. D. Coyle, J. Cooper, and J. J. Ritter, *ibid.*, **7**, 1014 (1968).

[21] M. R. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957). Although the preparation of FcHgCl is described in this paper, few details are given. Furthermore, since we have made some modifications and have obtained better yields, we describe our method in detail.

[22] We wish to thank Drs. R. W. Kiser and D. Dugger for this determination.

TABLE II

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR FERROCENYLDICHLOROBORANE

Property	Data
Color	Deep red-orange
Mp, °C	33° *in vacuo*
Elemental analysis	Calcd: Cl, 26.6 Found: Cl, 25.7
Mol wt (fp depression in benzene)	Calcd: 267 Found: 254
Ir spectrum (main bands in cm^{-1}; neat)[a]	1285 vs, 1192 m, 1107 s (antisym ring breathe), 1055 s, 1032 m, 1000 s (C–H bend), 922 s (^{10}B–Cl str), 887 vs (^{11}B–Cl), 825 s (C–H bend), 787 s, 650 s, 510 m, 498 s (antisym ring tilt), 475 s (antisym ring–Fe str), 445 s (B–Cl bend?)
Nmr spectrum (in $CDCl_3$)	
^{1}H	τ 5.80 (singlet, rel intens 5), τ 5.47 (triplet, J = 2 Hz, rel intens 2), τ 5.20 (triplet, J = 2 Hz, rel intens 2)
^{11}B[b]	−50.87 ppm
Ultraviolet spectrum (in hexane)	450 mμ (ϵ 430), 342 mμ (sh; ϵ 303)

[a] Assignments of bands characteristic of the ferrocenyl group are according to ref 3a. [b] Referenced to external $BF_3 \cdot O(C_2H_5)_2$. Compare with −54.68 ppm for $C_6H_5BCl_2$.

torch. A 3.697-mmol sample of $FcBCl_2$ was isolated for a 61% yield based on ferrocene. The physical properties of $FcBCl_2$ are summarized in Table II.

The volatiles from the reaction were fractionated through a series of traps at −78, −126, and −196°. The −196° trap contained 0.151 mmol of a material which was a mixture of HCl and a trace of $HBCl_2$; both gases were identified by their characteristic infrared spectra.[15] The −126° fraction contained BCl_3 and a trace of $HBCl_2$. The −78° (hexane) and the −126° fractions were combined and titrated tensimetrically with $N(CH_3)_3$ at 0°. An end point of 4.38 mmol was found; since only a trace of $HBCl_2$ was contained in this sample, this is essentially equal to the amount of BCl_3. The infrared spectrum of the white solid from the titration confirmed that it was $(CH_3)_3N \cdot BCl_3$; no $B_2Cl_4 \cdot 2N(CH_3)_3$ was detected.

Reaction of BCl_3 with Ferrocene.—About 10 ml of dry hexane and 3.43 mmol of BCl_3 were distilled into a *zweikügel* containing 1.01 mmol of ferrocene. The tube was sealed off and maintained at 0° for 1 week. A small amount of green solid formed, and the solution had a red tint. Unreacted ferrocene was separated from the green solid by decantation and repeated extraction. The volatiles, including ferrocene, were removed under vacuum over a 36-hr period. A small amount of red solid remained in the vessel; this was confirmed as $FcBCl_2$ by infrared spectroscopy. Unchanged ferrocene (0.683 mmol) was recovered from a removable trap. The volatiles were separated by fractionation through a series of traps at −78, −112, −126, and −196°. The −196° fraction was identified as a mixture of HCl (0.213 mmol) and BCl_3 (0.05 mmol). Since the −126° fraction was only BCl_3, this fraction was combined with the −78 and −112° fractions (hexane and BCl_3) and tensimetrically titrated with $N(CH_3)_3$. The titration endpoint indicated that 3.0 mmol of BCl_3 had been recovered.

Reaction of Dichloroborane with Ferrocene.—Ferrocene (1.04 mmol) was allowed to react with $HBCl_2$ (0.42 mmol) and BCl_3 (1.70 mmol) in 7 ml of hexane in a *zweikügel*. Within 5 min of warming the vessel to 0°, bubbles of H_2 were observed. After 24 hr, the solution was red-orange, and gas evolution had virtually ceased. The solution was still red-orange after 60 hr when it was opened to a Toepler pump; 0.256 mmol of H_2 was collected. The other volatiles, including ferrocene, were removed under vacuum with the vessel at room temperature for 12 hr. The infrared spectrum of the red paste remaining in the reaction vessel confirmed the presence of $FcBCl_2$ (0.206 mmol). Unreacted ferrocene (0.573 mmol) and a trace of $FcBCl_2$ were collected in a removable trap. The volatiles were fractionated through a series of traps at −78, −126, and −196°. Diborane (0.025 mmol) and HCl (0.085 mmol) were present in the −196° fraction. The −126° fraction contained only hexane and BCl_3; no $HBCl_2$, which would appear in this fraction if present, was detected. Tensimetric titration of the combined −126 and −78° fractions with $N(CH_3)_3$ at 0° indicated that 1.78 mmol of BCl_3 was recovered. Although more BCl_3 (0.08 mmol) was recovered than was originally placed in the reaction vessel, the difference agrees with the amount of B_2H_6 observed (eq 1; see also eq 5 and ref 19).

$$0.12HBCl_2 \longrightarrow 0.02B_2H_6 + 0.08BCl_3 \qquad (1)$$

Reaction of Ferrocenyl Mercurichloride with BCl_3.—The apparatus used was a modified *zweikügel*. The two sides were 50-ml flasks rather than the glass tubes previously used; a coarse-porosity glass filter separated the two sides. In a typical preparation, 6.34 mmol of FcHgCl, 12.9 mmol of BCl_3, and 15 ml of dry hexane were placed in one bulb. The temperature was maintained at 0°, and the contents were magnetically stirred; a red color was noted 15 min after starting the reaction. Formation of a dark, blue-green insoluble solid (identified as a ferrocenium salt by its infrared spectrum[23]) accompanied the reaction. The solution was decanted through the filter into the other bulb at 0°, and the solvent distilled back. This extraction process was repeated every 3 hr for 30 hr, after which product formation had apparently ceased. The volatiles were distilled into the vacuum line and discarded. The vessel containing the $FcBCl_2$ was opened in the drybox where the product was washed out with hexane and filtered through a medium-porosity glass filter. After removing the hexane, 4.48 mmol of $FcBCl_2$ (71% yield) was collected.

Reactions of Ferrocenyldichloroborane. (i) With Trimethylamine.—A tensimetric titration of 2.44 mmol of $FcBCl_2$ in 15 ml of xylene at 0° with $N(CH_3)_3$ indicated the formation of a 1:1 complex. The yellow-orange complex sublimed at 110–120° *in vacuo;* it was not sensitive to moist air over short periods of time. Physical data are summarized in Table III. The phenyl analog, $(C_6H_5)BCl_2 \cdot N(CH_3)_3$, was synthesized in an identical manner (see also Table III).

(ii) **With Pyridine.**—Careful addition of pyridine to $FcBCl_2$ in hexane in the drybox gave the yellow-orange adduct. The adduct sublimed without decomposition at 100–105° *in vacuo* and was air sensitive. Physical data are summarized in Table III.

(iii) **With Tetrahydrofuran.**—The THF adduct of $FcBCl_2$ was prepared in the same manner as the pyridine adduct. Physical data for the air-sensitive orange solid are in Table III. In the course of the Lewis acidity experiments, we attempted to obtain the spectrum of $FcBCl_2$ in THF. A 10:1 to 12:1 base: acid mole ratio was necessary to dissolve the adduct. The nmr spectrum of an 11:1 solution at room temperature [τ 5.80 (doublet, C_5H_4); 5.19 (singlet, C_5H_5); 6.36 (α-CH_2 of THF); 8.23 (β-CH_2 of THF)] did not have separate peaks for free and coordinated THF. The same solution at −56 to −68° gave broad peaks due to THF but none assignable to coordinated THF.

(iv) **With Dimethylamine.**—A thin-wall bulb containing $FcBCl_2$ (1.50 mmol) was broken in an evacuated *zweikügel*. About 5 ml of dry hexane and 7.54 mmol of $HN(CH_3)_2$ were distilled into the vessel before sealing it off. Upon warming to −96° and shaking for 30 min, some yellow-orange solid formed; additional solid formed at −78°. Repeated extraction was carried out at room temperature until only a white solid (presumably $(CH_3)_2NH \cdot HCl$) was left in the reaction side. A dark orange

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(23) I. J. Spilners, *J. Organometal. Chem.*, **11**, 381 (1968); see also ref 3a.

TABLE III

PHYSICAL PROPERTIES OF DERIVATIVES OF FERROCENYLDICHLOROBORANE AND PHENYLDICHLOROBORANE

Property	$FcBCl_2 \cdot N(CH_3)_3$[a]	$FcBCl_2 \cdot py$	$FcBCl_2 \cdot THF$	$FcB[N(CH_3)_2]_2$
Mp, °C	200–203	162–165	78–96	Liq
Analysis				
Element	C H N	C H N		
Calcd	47.9 5.57 4.30	52.1 4.08 4.05	...	...
Found	47.4 5.66 4.33	52.4 4.24 4.15		
Nmr spectra[b]				
^1H (τ)	7.29 (s, 9.4); 5.80, 5.76, and 5.74 (all singlets; total rel intens 9)	5.68 (s, 5), 5.63 (s, 3.9), 1.82–2.67 (multiplet, 5)	7.92 (coord β-CH_2), 5.72 (coord α-CH_2), 5.72 (s, C_5H_4), 5.8 (s, C_5H_5)[c]	7.22 (s, 10.5), 5.99 (s, 5.0), 5.8 (s, 3.9)
^{11}B (ppm)	−10.98	...	...	−32.7
Ir spectra[d] (main bands in cm^{-1})				
Antisym ring breathe	1105 s	1102 m	1103 s	1105 s
C–H bend (||)	1000 m	998 w	995 s	1000 m
C–H bend (⊥)	812 s	822 m	830 s	815 s
B–Cl str	740 vs	715 vs	725 vs	...
B–N or B–O	715 s	1090 vs	660 or 560 (?)	1505 (?)
Antisym ring tilt	502 s	497 s	495 s	495 s
Ring–Fe str	485 s	475 m	475 s	475 s
Others	1245 m, 1220 s, 1195 m, 1042 s, 1032 m, 975 s, 760 s	1625 m, 1222 s, 1213 s, 1098 s, 1038 s, 762 s, 745 s, 735 s	1220 s, 1040 s, 990 s, 860 s	1235 s, 1205 s, 1180 m, 1145 m, 1120 s, 1077 s, 1065 m, 1025 s, 895 m, 830 s, 680 m, 505 s
	$C_6H_5BCl_2 \cdot N(CH_3)_3$	$C_6H_5BCl_2 \cdot py$	$C_6H_5BCl_2 \cdot THF$	$C_6H_5B[N(CH_3)_2]_2$
Nmr spectra				
^1H (τ)	7.26 (s, 8.5) 2.5 (multiplet, 5)	See Table V	8.28 (free β-CH_2),[e] 6.45 (free α-CH_2), 8.00 (coord β-CH_2), 5.78 (coord α-CH_2), 2.78, 2.36 (multiplets, phenyl group)	7.39 (s, 11.5), 2.75 (multiplet, 5)
^{11}B (ppm)	−10.94	...	...	−32.25
Ir spectra (selected bands, cm^{-1})				
B–Cl str	710 vs	725 vs[f]	730 vs	...
Others	1240 m, 1172 s, 1113 m, 972 s, 843 s, 818 s, 773 m, 745 s, 720 s, 697 s		1185 s, 990 m, 860 m, 830 m, 700 vs, 622 m, 582 m	1505 s, 1235 s, 1190 m, 1145 m, 1127 s, 1060 s, 1025 m, 750 m, 700 s

[a] Molecular weight by boiling point elevation: calcd, 326; found, 333. Uv spectrum: 442 mμ (ϵ 12); 340 mμ (sh, ϵ 17). [b] Spectra of the three adducts were obtained in $CDCl_3$; $FcB[N(CH_3)_2]_2$ was run as a pure liquid. Multiplicity of the band and its relative intensity are given in parentheses. Boron-11 spectra referenced to $BF_3 \cdot O(C_2H_5)_2$. [c] At −11°. Data are given for the 1:1 complex dissolved in $CDCl_3$. [d] Assignments for vibrations of ferrocenyl group based on ref 3a. Symbols for intensity have their usual significance. [e] At −47°. Compound dissolved in THF. [f] Spectrum agrees with that given in ref 25.

liquid remained after removing the solvent and excess amine. Infrared and nmr data for the air-sensitive product, $FcB[N(CH_3)_2]_2$, are summarized in Table III. The phenyl analog (see also Table III) was synthesized in an identical manner.

Cyclic Voltammetry of Ferrocenylboranes.—Cyclic voltammograms were obtained in a dry nitrogen atmosphere using an apparatus previously described.[24] The scan rate was 5 V/min. Solutions of FcH, $FcBCl_2$, and $FcBCl_2 \cdot N(CH_3)_3$ in acetonitrile were prepared in the drybox. In each case, the solution was 4.5–6.5 m*M* in solute and 0.1 *M* in tetraethylammonium perchlorate. No color changes were observed at the electrodes throughout the scans.

Infrared Techniques in the Lewis Acidity Study.—The coordination frequency shift of the carbonyl group of complexed ethyl acetate ($CH_3COOC_2H_5$) has been used as a measure of relative Lewis acidities.[25,26] Dry CCl_4 was used as the solvent in our studies. The ν_{CO} frequency for free $CH_3COOC_2H_5$ was determined using a 0.05 *M* solution in a demountable cell having a 0.5-mm path length. Using the same path length, ν_{CO} was observed for $(C_6H_5)BCl_2 \cdot CH_3COOC_2H_5$ when a 1:6.5 acid:base ratio was used (0.00516 *M* in $(C_6H_5)BCl_2$ and 0.0335 *M* $CH_3COOC_2H_5$); a 0.45-mm cell filled with CCl_4 was used in the reference beam. With the weaker acid n-$C_4H_9SnCl_3$, a 7:1 acid:base ratio was used (0.23 *M* n-$C_4H_9SnCl_3$ and 0.0335 *M* $CH_3COOC_2H_5$) in a 0.5-mm cell in the sample beam and a 0.475-mm cell filled with a 0.0168 *M* $CH_3COOC_2H_5$ solution in the reference beam. In the study of $FcBCl_2$, acid:base ratios of 2:1 (0.07 *M* $FcBCl_2$ and 0.0335 *M* $CH_3COOC_2H_5$) to 23:1 (0.247 *M* $FcBCl_2$ and 0.0105 *M* $CH_3COOC_2H_5$) were used in a 0.50-mm cell; for the lower concentration study a cell filled with a CCl_4 solution of $CH_3COOC_2H_5$ was in the reference beam.

Molecular Weight Techniques. (i) Molecular Weight of $FcBCl_2$ by Cryoscopy.—The apparatus and technique have been

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(24) M. F. Marcus and M. D. Hawley, *J. Electroanal. Chem.*, **18**, 175 (1968); we wish to thank Drs. J. Lawless and M. D. Hawley for performing the electrochemical experiments.

(25) M. F. Lappert and H. Pyrzora, *J. Chem. Soc., A*, 1024 (1968).

(26) D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, **90**, 5706 (1968).

described previously.[27] A sample of 0.01701 g of $\mathrm{FcBCl_2}$ in 21.4665 g of benzene gave freezing point depressions of 0.181, 0.181, and 0.182° in three successive runs. Since the molal freezing point depression constant for benzene in our apparatus was 5.81, the observed depressions give an average molecular weight of 254 (calcd 267).

(ii) **Molecular Weight of $\mathrm{FcBCl_2 \cdot N(CH_3)_3}$ by Ebulliometry.**—The differential ebulliometer used in this study has been described previously.[27] The boiling point elevation constant for benzene in our apparatus was 2.97. A sample of 0.0754 g of $\mathrm{FcBCl_2 \cdot N(CH_3)_3}$ in 30.6321 g of benzene gave boiling point elevations of 0.0223, 0.0233, and 0.0205° in three successive runs. Another sample of 0.2933 g in 30.6250 g of benzene gave elevations of 0.0840 and 0.0870° in two successive runs. These results give an average molecular weight of 333 (calcd 326).

Results and Discussion

The Diboron Tetrachloride–Ferrocene Reaction. Probable Reaction Path.—The solid product of interest from the $\mathrm{B_2Cl_4}$–ferrocene reaction (eq 2) is ferrocenyldichloroborane (VI) ($\mathrm{FcBCl_2}$), the properties of which are discussed below. However, the seemingly complex mixture of other products is also of interest for the information which these products provide concerning the details of the reaction path.

$$\mathrm{FcH} + \mathrm{B_2Cl_4} \xrightarrow[\text{60 hr}]{\text{hexane, 0°}} 0.61\mathrm{FcBCl_2} + 0.73\mathrm{BCl_3} + 0.20\mathrm{H_2} + 0.03\mathrm{HCl} + \mathrm{HBCl_2}\ (\text{trace}) + \text{unreacted FcH and intractable solids} \tag{2}$$

The volatile product of greatest importance is hydrogen. The evolution of $\mathrm{H_2}$ was observed soon after warming the reaction mixture to 0°. Since it seems clear that the $\mathrm{H_2}$ arises from the ferrocene–$\mathrm{B_2Cl_4}$ reaction,[28] an explanation of its source is of importance in rationalizing the overall reaction sequence.[29] In addition, an explanation for the fact that $\mathrm{H_2}$ is observed at all, particularly in view of its known rapid reaction with $\mathrm{B_2Cl_4}$ (eq 3),[18,30] is important.

$$\mathrm{H_2} + \mathrm{B_2Cl_4} \longrightarrow 2\mathrm{HBCl_2} \tag{3}$$

A clue to the source of the $\mathrm{H_2}$ was found in the observation of a trace of dichloroborane ($\mathrm{HBCl_2}$). Since $\mathrm{HBCl_2}$ might be expected to be a major by-product of ring substitution by $\mathrm{B_2Cl_4}$ (eq 4), it must be consumed by another reaction. There are at least two possibilities: disproportionation (eq 5)[19] and reaction with ferrocene (eq 6).

$$\mathrm{B_2Cl_4} + \mathrm{FcH} \longrightarrow \mathrm{FcBCl_2} + \mathrm{HBCl_2} \tag{4}$$

$$\mathrm{HBCl_2} \longrightarrow {}^{1}\!/_{6}\mathrm{B_2H_6} + {}^{2}\!/_{3}\mathrm{BCl_3} \tag{5}$$

$$\mathrm{HBCl_2} + \mathrm{FcH} \longrightarrow \mathrm{H_2} + \mathrm{FcBCl_2} \tag{6}$$

If $\mathrm{HBCl_2}$ disproportionated according to eq 5, $\mathrm{B_2H_6}$ should have been observed. Although $\mathrm{B_2H_6}$ was not observed in the ferrocene–$\mathrm{B_2Cl_4}$ reaction system, this does not necessarily rule out $\mathrm{HBCl_2}$ disproportionation. The diborane could have been consumed by reaction with $\mathrm{B_2Cl_4}$;[31] we have found that $\mathrm{B_2H_6}$ does not react with ferrocene or $\mathrm{FcBCl_2}$.

That $\mathrm{HBCl_2}$ may be consumed by reaction with ferrocene was conclusively shown (eq 7). Most importantly we found that $\mathrm{H_2}$ and $\mathrm{FcBCl_2}$ are products of this reaction and that $\mathrm{H_2}$ is isolated in a quantity comparable with the amount of $\mathrm{FcBCl_2}$ isolated.[32] It should also be noted that $\mathrm{B_2H_6}$ was observed in reaction 7, its source presumably being the disproportionation of $\mathrm{HBCl_2}$ (*cf.* eq 1). This again suggests that any $\mathrm{B_2H_6}$ which may have been produced in the $\mathrm{B_2Cl_4}$–ferrocene reaction *via* $\mathrm{HBCl_2}$ disproportionation may have been consumed by reaction with $\mathrm{B_2Cl_4}$, the only compound present in reaction 2 which was not present in (7).

$$1.04\mathrm{FcH} + 1.70\mathrm{BCl_3} + 0.42\mathrm{HBCl_2} \xrightarrow[\text{60 hr}]{\text{hexane, 0°}} 0.26\mathrm{H_2} + {>}0.2\mathrm{FcBCl_2} + 0.025\mathrm{B_2H_6} + 0.085\mathrm{HCl} + 1.78\mathrm{BCl_3} + \text{unreacted FcH} \tag{7}$$

No $\mathrm{B_2Cl_4}$ was recovered from its reaction with ferrocene. This is understandable in view of the fact that it may be consumed by reactions with ferrocene (eq 2), $\mathrm{H_2}$ (eq 3),[18] and $\mathrm{B_2H_6}$[31] or by thermal decomposition (eq 8).[18] The latter reaction may account for some of the yellow-black tar observed in (2).[33] If it is assumed that a large fraction of the $\mathrm{BCl_3}$ observed in (2) arises from reaction 8, and if the intractable solid is composed partly of $\mathrm{(BCl)}_n$, all of the boron introduced in the form of $\mathrm{B_2Cl_4}$ in reaction 2 is accounted for by $\mathrm{BCl_3}$, $\mathrm{FcBCl_2}$, and $\mathrm{(BCl)}_n$.

$$n\mathrm{B_2Cl_4} \longrightarrow n\mathrm{BCl_3} + \mathrm{(BCl)}_n \tag{8}$$

Although it may be argued that most of the $\mathrm{BCl_3}$ arises from reaction 8, the disproportionation of $\mathrm{HBCl_2}$ (eq 5) remains a possibility. No matter what its source, $\mathrm{BCl_3}$ has been found to react very slowly with ferrocene (eq 9). While this reaction produces very little $\mathrm{FcBCl_2}$,

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[27] A. W. Laubengayer and G. F. Lengnick, *Inorg. Chem.*, **5**, 503 (1966).

[28] The hydrolysis of boron–boron bonds at high temperatures or under alkaline conditions is known to give $\mathrm{H_2}$: T. Wartik and E. F. Apple, *J. Amer. Chem. Soc.*, **80**, 6155 (1958); ref 18. However, neither of these conditions obtained in our experiments. Furthermore, every attempt was made to ensure the absence of water, and approximately the same relative amount of $\mathrm{H_2}$ was evolved in all 14 attempts at the reaction. Therefore, we can only conclude that $\mathrm{H_2}$ does indeed arise directly from the ferrocene–$\mathrm{B_2Cl_4}$ reaction.

[29] The evolution of $\mathrm{H_2}$ in an electrophilic aromatic substitution reaction seems unusual. However, $\mathrm{H_2}$ was observed when $\mathrm{BCl_3}$ was treated with aromatic hydrocarbons in the presence of $\mathrm{AlCl_3}$ and Al: E. L. Muetterties, *J. Amer. Chem. Soc.*, **82**, 4163 (1960); E. L. Muetterties and F. N. Tebbe, *Inorg. Chem.*, **7**, 2663 (1968). The following reaction sequence was proposed to account for this

$$\mathrm{ArH} + \mathrm{BCl_3} \longrightarrow \mathrm{ArHBCl_3} \xrightarrow{\mathrm{AlCl_3}} \mathrm{ArHBCl_2{}^+AlCl_4{}^-}$$

$$\mathrm{ArHBCl_2{}^+AlCl_4{}^-} \longrightarrow \mathrm{ArBCl_2} + \mathrm{H^+AlCl_4{}^-}$$

$$3\mathrm{H^+AlCl_4{}^-} + \mathrm{Al} \longrightarrow {}^{3}\!/_{2}\mathrm{H_2} + 4\mathrm{AlCl_3}$$

Although $\mathrm{H_2}$ could arise in our system due to the reaction

$$2\mathrm{H^+BCl_4{}^-} + \mathrm{B_2Cl_4} \longrightarrow \mathrm{H_2} + 4\mathrm{BCl_3}$$

this seems unlikely in view of the fact that $\mathrm{BCl_3}$ does not react with HCl: W. Graff, *C. R. Acad. Sci.*, **197**, 754 (1933).

[30] In our earlier communication[10] we suggested that $\mathrm{B_2Cl_4}$ may be stabilized toward reaction with $\mathrm{H_2}$ by forming a π complex with ferrocene (III). To test this proposal we treated $\mathrm{B_2Cl_4}$ with $\mathrm{H_2}$ in the presence of trichloroethylene: J. Kotz and E. Post, unpublished work. TCE is known to prevent the thermal decomposition of $\mathrm{B_2Cl_4}$, presumably through the formation of a π complex: T. D. Coyle and J. J. Ritter, *J. Organometal. Chem.*, **12**, 269 (1968). We found that TCE does indeed inhibit the $\mathrm{H_2}$–$\mathrm{B_2Cl_4}$ reaction, but not to an extent sufficient to allow us to ignore the potential importance of reaction 3.

[31] S. B. Rietti and J. Lombardo, *J. Inorg. Nucl. Chem.*, **28**, 365 (1966).

[32] It should be noted that an attempt to prepare $\mathrm{FcBF_2}$ by treating ferrocene with $\mathrm{HBF_2}$ was not successful; the reactants were recovered quantitatively.

[33] Due to its intractable nature, the tar was not completely investigated; however, qualitative analysis indicated that it contained at least boron and chlorine. It probably also contained a ferrocenium salt, as suggested by the formation of a green, insoluble solid in the course of the reaction; ferrocenium salts are often green or blue-green.[23] The salt is apparently due to the reaction of $\mathrm{FcBCl_2}$ with HCl; a green, intractable solid was formed when these two compounds were allowed to react in a separate experiment.

it does account for the presence of HCl in reactions 2 and 7.[34]

$$1.01FcH + 3.43BCl_3 \xrightarrow[\text{7 days}]{\text{hexane, 0°}} 0.21HCl + 3.05BCl_3 + 0.68FcH + \text{isolable amount of } FcBCl_2 + \text{green solid} \quad (9)$$

On the basis of the evidence presented above, we believe that the B_2Cl_4–ferrocene system may represent a competitive situation wherein both H_2 and ferrocene react with B_2Cl_4 to produce $HBCl_2$ which in turn reacts with ferrocene. To a very large extent, then, the system involves reactions 4 and 10. In fact, reaction 4 need occur to only a small extent; for example, if, on a relative basis, 0.1 mol of B_2Cl_4 reacts with ferrocene to produce 0.1 mol of $HBCl_2$ and this amount of $HBCl_2$ cycles through sequence 10 five times,[35] the observed relative amounts of H_2 and $FcBCl_2$ may be accounted for.

$$\begin{tikzcd} HBCl_2 + FcH \arrow[r] & FcBCl_2 + {}^1/_2H_2 + {}^1/_2H_2 \arrow[l, bend left, "{}^1/_2B_2Cl_4"] \end{tikzcd} \quad (10)$$

Fox and Wartik have reported that B_2Cl_4 reacts very slowly with benzene to give phenyldichloroborane; apparently BCl_3 was the only volatile product isolated.[9] The following reaction path was suggested. In light of

$$2B_2Cl_4 + C_6H_6 \xrightarrow{\text{slow}} C_6H_6 \cdot 2B_2Cl_4$$
$$C_6H_6 \cdot 2B_2Cl_4 \xrightarrow{\text{fast}} C_6H_6 \cdot 2BCl + 2BCl_3 \quad (11)$$
$$C_6H_6 \cdot 2BCl \xrightarrow{\text{slow}} C_6H_5BCl_2 + \text{other products}$$

our observations on the B_2Cl_4–ferrocene system, this proposal should probably be reexamined.

Several ways in which B_2Cl_4 could interact with ferrocene were discussed in the Introduction. The TCNE–ferrocene complex and the recent report of a π interaction between ferrocene and triphenyliodosilane[36] suggest III as the most reasonable intermediate in the formation of $FcBCl_2$. In an attempt to obtain evidence for such a complex, we examined nmr spectra of ferrocene with B_2Cl_4 or B_2F_4 in methylcyclohexane.[37] However, in the temperature range −100° to room temperature, there was no change in the chemical shift or line width of the ferrocene resonance.

One of the interesting features of the B_2Cl_4–ferrocene reaction is its apparently greater rate compared with that of the uncatalyzed BCl_3–ferrocene reaction.[38] This could be due to at least three factors. (1) Ferrocene may form an intermediate π complex with B_2Cl_4 more readily than with BCl_3. (2) The reaction may be thermodynamically controlled. That is, in the B_2Cl_4–ferrocene reaction the B–B bond breaks ($\Delta H = 87.6$ kcal/mol)[39] and $HBCl_2$ is formed ($\Delta H = -60.4$ kcal/mol),[19a] whereas in the BCl_3–ferrocene reaction a B–Cl bond breaks ($\Delta H = 110.2$ kcal/mol)[39] and HCl is formed ($\Delta H = -22.1$ kcal/mol).[40] (3) The predominant reaction in the B_2Cl_4–ferrocene system may actually be that of $HBCl_2$ with ferrocene; no such reaction is possible in the BCl_3–ferrocene system.

The relative reactivity of B_2Cl_4 and BCl_3 toward ferrocene is paralleled by the reactions of these boron halides with benzene; whereas B_2Cl_4 reacts very slowly with benzene,[9] BCl_3 does not react at all in the absence of catalysts.[29,41] Finally, the fact that both boron halides react more readily with ferrocene than with benzene is yet another example of the great ability of ferrocene to undergo electrophilic substitution reactions.[3a]

General Chemical and Physical Properties of Ferrocenyldichloroborane.—The red solid product of the B_2Cl_4–ferrocene reaction, $FcBCl_2$, formed long, flat, needlelike crystals when solvent and excess ferrocene were removed by prolonged evacuation. Handling the low-melting solid was somewhat difficult. On opening the material in a drybox, it formed a viscous liquid which could be transferred with a syringe if warmed slightly. The material crystallized again when placed under vacuum.

The evidence which formed the basis for characterizing the reaction product as ferrocenyldichloroborane was summarized in our previous communication.[10] The infrared spectrum is given in Table II, and the main bands are assigned. The 60-MHz pmr spectrum of $FcBCl_2$ in benzene showed a multiplet of five lines (τ 5.61, relative intensity 4) and a singlet (τ 6.08, relative intensity 5). However, in $CDCl_3$, the 60-MHz spectrum was more clearly that of a monosubstituted ferrocene where the substituent is an electron-withdrawing group;[42] two well-defined, well-separated triplets and a singlet to higher field were observed (Table II). The observation of a poorly defined spectrum in benzene can be attributed to solvent effects; similar observations have been made for other substituted ferrocenes.[43]

Rosenblum has noted that the 440-mμ (ϵ 91) and 325-mμ (ϵ 52) bands in the uv-visible spectrum of ferrocene usually exhibit a bathochromic shift when electron-withdrawing substituents are placed on the rings.[44] Such an observation was made for $FcBCl_2$ (Table II), the shift being comparable to that induced by a carboxylic acid group (FcCOOH has bands at

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[34] The amount of HCl produced is not equal to the quantity of BCl_3 consumed due to a reaction of HCl with $FcBCl_2$ to produce the insoluble green solid; see ref 33.

[35] The sequence begins and ends with $HBCl_2$; therefore, 0.1 mol of $FcBCl_2$ and 0.05 mol of "free" H_2 are produced in each of the five cycles.

[36] G. P. Sollott and W. R. Peterson, Jr., *J. Amer. Chem. Soc.*, **89**, 5054 (1967).

[37] Diboron tetrafluoride was used since it did not give $FcBF_2$. However, on attempting to separate ferrocene and B_2F_4 on the vacuum line, we noticed that separation was more difficult than anticipated; this suggested that a weak interaction may occur between these two compounds at low temperatures: unpublished work, W. J. Painter, this laboratory.

[38] BCl_3 reacts much more rapidly with ferrocene in the presence of $AlCl_3$: S. McVey, I. G. Morrison, and P. L. Pauson, *J. Chem. Soc., C*, 1847 (1967).

[39] V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 50 (1969).

[40] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., Jan 1968, p 25.

[41] In this connection, it is worthwhile to note that BF_3 does not react with ferrocene in the absence of catalysts, paralleling B_2F_4 in this respect;[37] furthermore, BF_3 does not react with benzene even in the presence of catalysts.[29]

[42] See ref 3a, p 88.

[43] K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *J. Amer. Chem. Soc.*, **85**, 970 (1963).

[44] See ref 3a, p 42.

445 mμ (ε 223) and 340 mμ (sh, ε 361)[45]). Both $FcBCl_2$ and FcCOOH also show an increase in band intensity relative to ferrocene. The spectrum of the trimethylamine adduct (Table III), on the other hand, more closely resembles ferrocene in having weaker bands at somewhat shorter wavelengths.

Attempts to prepare $FcBF_2$ by halogen exchange between $FcBCl_2$ and B_2F_4[46] or SbF_3 were not successful. Although $FcBCl_2$ reacted with $LiAlH_4$ in diethyl ether, neither $FcBH_2$ nor Fc_3B could be isolated.[47]

As expected, $FcBCl_2$ is readily hydrolyzed to the known boronic acid, $FcB(OH)_2$,[38] which subsequently dehydrates to triferrocenylboroxine. We have studied the boronic acid with regard to the possibility of intramolecular hydrogen bonding between a –BOH group and the iron atom. This investigation, as well as a mass spectral study of $FcB(OH)_2$ and other boronic acids and their boroxines, is discussed in the following paper.[48]

Several other groups have found a direct correlation between the oxidation potentials of substituted ferrocenes and the electron-withdrawing properties of the substituents.[49] In order to obtain such information for the $-BCl_2$ and $-BCl_2 \cdot N(CH_3)_3$ groups, cyclic voltammetry studies were initiated.[24] A reversible one-electron oxidation was observed for FcH, $FcBCl_2$, and $FcBCl_2 \cdot N(CH_3)_3$. The oxidation potential for the amine adduct ($E_{1/2}$ = 0.45 V *vs.* sce) was quite close to that of ferrocene ($E_{1/2}$ = 0.42 V *vs.* sce), thereby indicating that $-BCl_2 \cdot N(CH_3)_3$ differs little from –H in its electron-withdrawing ability, a not unexpected result. Since these experiments had to be done in a basic solvent (in order to dissolve the supporting electrolyte), coordination of the boron atom in $FcBCl_2$ occurs; the oxidation potential of $FcBCl_2$ ($E_{1/2}$ = 0.45 V *vs.* sce) is also almost the same as that for ferrocene. Of most interest in this study was the observation of two partially reversible reduction waves for the ferrocenylboranes.[50] No reduction of ferrocene was observed down to −2.0 *vs.* sce. We tentatively suggested that the substituent was the site of the reduction.[10] Since the first reduction wave for $FcBCl_2 \cdot N(CH_3)_3$ was partially reversible, this suggested that the reduced species did not decompose too readily. Therefore, an attempt was made to determine the site of reduction by electrochemically reducing the compound in the cavity of an esr spectrometer.[51] A variety of potentials from −0.3 to −1.2 V (*vs.* sce) were used while slowly sweeping the field. However, no signal was observed.

Other Methods for Preparing Ferrocenyldichloroborane.—Good yields of $FcBCl_2$ are obtained from the B_2Cl_4–ferrocene reaction; however, the method is tedious and a supply of B_2Cl_4 is required, a major disadvantage. Therefore, alternative methods for preparing $FcBCl_2$ were sought.

Pauson and his coworkers[38] have obtained $FcB(OH)_2$ after hydrolyzing the products from the reaction of BCl_3 and ferrocene under Friedel–Crafts conditions; $FcBCl_2$ is obviously the intermediate. However, other ferrocenylboranes are formed in this reaction, and separation of $FcBCl_2$ would be virtually impossible.

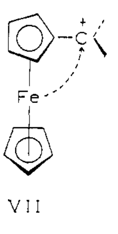
Therefore, a transmetalation reaction appear to be the most promising. Of the many available methods, the reaction of FcHgCl with BCl_3 (eq 12) was chosen.

$$FcHgCl + BCl_3 \xrightarrow[0°]{\text{hexane}} FcBCl_2 + HgCl_2 \qquad (12)$$

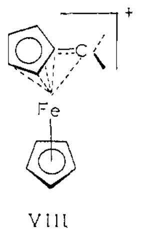
When toluene was used as a solvent, the color of $FcBCl_2$ appeared very soon after mixing the reagents. However, before the product could be separated, it turned to a blue solid, presumably a ferrocenium salt.[23] When the reaction was run in hexane, however, approximately 70% yields of $FcBCl_2$ were realized in a number of attempts.[52]

The Lewis Acidity of Ferrocenyldichloroborane.—As anticipated, ferrocenyldichloroborane forms adducts with a variety of strong Lewis bases (Table III). No adduct was formed, however, with diethyl ether, and, although some reaction was apparent, no adduct with triphenylphosphine could be isolated.

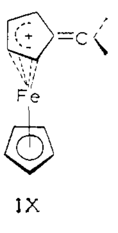
Ferrocenylboranes are isoelectronic with α-ferrocenylcarbonium ions, a class of carbonium ions that has been the subject of some controversy.[53] Such carbonium ions are particularly stable species, the ferrocenyl group being as effective in stabilizing the positive charge as three phenyl groups. Several suggestions have been made to account for this unusual stability. Structure VII involves a direct interaction of the metal e_{2g} nonbonding electrons with the empty carbon orbital.[54] Structures VIII and IX depict different modes of charge delocalization.[55,56]



VII



VIII



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(45) R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

(46) A. K. Holliday, G. N. Jessop, and R. P. Ottley, *J. Organometal. Chem.*, **14**, 211 (1968).

(47) E. Wiberg, J. E. F. Evans, and H. Noth, *Z. Naturforsch.*, *B*, **13**, 263 (1958); these authors reported that $(C_6H_5BH_2)_2$ was the product of the reduction of $C_6H_5BCl_2$ with $LiBH_4$ in ether at room temperature. D. R. Nielsen, W. E. McEwen, and C. A. Vanderwerf [*Chem. Ind.* (London), 1069 (1957)] reported that triphenylborane was obtained from $C_6H_5BCl_2$ and $LiAlH_4$ in boiling dioxane.

(48) E. W. Post, R. G. Cooks, and J. C. Kotz, *Inorg. Chem.*, **9**, 1970 (1970).

(49) D. W. Hall and C. D. Russell, *J. Amer. Chem. Soc.*, **89**, 2316 (1967); W. F. Little, C. N. Reilley, J. D. Johnson, and A. P. Sanders, *ibid.*, **86**, 1382 (1964).

(50) Reduction waves for $FcBCl_2$ were observed at −0.16 and −0.33 V; those for $FcBCl_2 \cdot N(CH_3)_3$ were at −0.25 and −0.93 V ($E_{1/2}$ values are in volts *vs.* sce).

(51) We wish to thank Dr. W. C. Danen for assistance in performing this experiment.

(52) The failure of the reaction when run in toluene must be related to the solubility of $HgCl_2$ in toluene relative to hexane; $HgCl_2$ is known to react with ferrocene and may also react with $FcBCl_2$.[23] Others have experienced similar problems on treating inorganic halides with FcHgCl in toluene.[21]

(53) M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966).

(54) J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, **81**, 3484 (1959).

(55) E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961).

(56) J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Lett.*, **12**, 1299 (1966).

Whatever stabilizing mechanism operates for the carbonium ions, it is reasonable to expect that the same mechanism would lower the Lewis acidity of the ferrocenylboranes. Therefore, this aspect of ferrocenyldichloroborane was investigated by nmr and infrared methods, an aromatic analog, phenyldichloroborane, being used for comparison.

The most firmly established nmr method for determining relative Lewis acidities is the observation of the coordination chemical shift for protons of coordinated THF.[57-59] When $FcBCl_2$ was dissolved in THF, rapid intermolecular exchange of base was evident at room temperature and below (see Experimental Section). Therefore, the isolated adduct was dissolved in $CDCl_3$; at room temperature one peak for the α-CH_2 protons was observed 27 Hz below the α-CH_2 multiplet of pure THF in $CDCl_3$. On lowering the temperature to $-11°$, the α-CH_2 resonance shifted to 34 Hz below the position in pure THF (Tables III and IV); further reduction of the temperature did not change the position or shape of the peak. The coordination chemical shift for the α-CH_2 protons of THF in its adduct with $C_6H_5BCl_2$ was determined from a solution of the Lewis acid in THF.[60] Sharp signals for free and coordinated THF that did not change position or shape were observed at -57 to $-47°$. The coordinated and free THF multiplets coalesced at $-27°$. The THF coordination chemical shift data (Table IV) indicate that $FcBCl_2$ is definitely a weaker acid than $C_6H_5BCl_2$, the latter being comparable to BF_3 in coordinating strength. Using the acidity scale of Deters, *et al.*,[57] $FcBCl_2$ is 55% as acidic as BCl_3, whereas the phenyl analog is 65% as acidic.

TABLE IV

COORDINATION CHEMICAL SHIFTS FOR THE α-CH_2 PROTONS IN THF COMPLEXES

Borane	$\Delta\delta(\alpha\text{-}CH_2)$,[a] Hz	Acidity[b]	Temp, °C	Ref
BH_3	20.1[c]	33	-45	59
$(i\text{-}C_4H_9)_2BCl$	25.5	41	Ambient	57
$(n\text{-}C_4H_9)_2BCl$	33.0	54	Ambient	58
$FcBCl_2$	34[d]	55	-11	This work
$C_6H_5BCl_2$	40[d]	65	-47	This work
BF_3	40.5[c]	66	-80	59
H_2BCl	40.7	66	-33	58
$HBCl_2$	47.3	77	$+28$	58
$i\text{-}C_4H_9BCl_2$	50.2	82	Ambient	57
$n\text{-}C_4H_9BCl_2$	51	83	Ambient	58
BCl_3	61.5	100	-20	59

[a] All shifts are to lower field than free THF. THF in $CDCl_3$: β-CH_2, τ 8.17; α-CH_2, τ 6.29. [b] Relative acidity scale based on BCl_3; see ref 57. [c] These determinations were repeated in our laboratory and good agreement was found. [d] Shift data in Table III.

As mentioned above, when $FcBCl_2$ was dissolved in THF, base exchange could not be slowed even at temperatures as low as $-80°$. On the other hand, the isolated adduct in $CDCl_3$ underwent only slow exchange at $-11°$. The large difference in temperatures at which exchange could be slowed in these experiments suggests that different mechanisms for exchange are responsible. A similar observation has been made for other borane–ether systems.[61] The fact that base exchange with $C_6H_5BCl_2$ could be slowed at a higher temperature than for $FcBCl_2$ (when both are dissolved in excess THF) also suggests that the phenyl compound is a stronger acid. Of course the reasonable assumptions must be made that the same mechanism is responsible in both cases, that steric problems are minor, and that the rate-determining factor is the relative B–O bond strength in the two adducts.

The most reliable spectroscopic method for determining relative Lewis acidities is a comparison of coordination frequency shifts for ethyl acetate adducts of Lewis acids.[25,26] Under conditions described in the Experimental Section, coordination frequency shifts were observed for $C_6H_5BCl_2$ ($\Delta\nu_{CO}$ = 149 cm^{-1}) and n-$C_4H_9SnCl_3$ ($\Delta\nu_{CO}$ = 41 cm^{-1}).[62] We anticipated that the acidity of $FcBCl_2$ would fall between these two compounds. However, under a variety of conditions designed to ensure the maximum concentration of adduct in solution, no coordination frequency shift could be observed for ethyl acetate–CCl_4 solutions of $FcBCl_2$. While this is negative evidence, it does suggest that $FcBCl_2$ is a considerably weaker acid toward ethyl acetate than either the tin compound or $C_6H_5BCl_2$. Another indication of the low acidity of $FcBCl_2$ is the fact that, although the solid adduct $C_6H_5BCl_2 \cdot CH_3COOC_2H_5$ may be isolated with ease, no adduct could be isolated with $FcBCl_2$ under the same conditions useful for the phenyl compound; both $FcBCl_2$ and the ester were completely recovered after mixing in hexane.

Three other nmr methods were investigated as a means of determining the relative acidity of $FcBCl_2$. The first of these was a determination of the coordination chemical shift for the 2,6 protons of coordinated pyridine.[63] Although the difference between the shifts for the ferrocenyl and phenyl compounds is small (Table V), $FcBCl_2$ is apparently the weaker acid. Unlike the THF experiment, the pyridine data suggest that both the ferrocenyl and phenyl compounds are stronger Lewis acids than BF_3.

TABLE V

COORDINATION CHEMICAL SHIFTS FOR PYRIDINE 2,6 PROTONS IN PYRIDINE COMPLEXES[a]

Adduct	Base:acid mole ratio	$\Delta\delta$, Hz	Adduct	Base:acid mole ratio	$\Delta\delta$, Hz
$py \cdot BF_3$	10:1	13	$py \cdot C_6H_5BCl_2$	5:1 or 25:1	30
$py \cdot FcBCl_2$	16:1	23	$py \cdot BCl_3$	10:1	48

[a] BF_3 and BCl_3 values from ref 63. All coordination chemical shifts are downfield.

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(57) J. F. Deters, P. A. McCusker, and R. C. Pilger, *J. Amer. Chem. Soc.*, **90**, 4583 (1968).

(58) D. J. Pasto and P. Balasubramaniyan, *ibid.*, **89**, 295 (1967).

(59) A. Fratiello, T. P. Onak, and R. E. Schuster, *ibid.*, **90**, 1194 (1968).

(60) This solution was prepared by condensing the reagents from the vacuum line into an nmr tube at $-196°$ and allowing the contents to warm slowly in the spectrometer. $C_6H_5BCl_2$ apparently cleaved THF when the solutions were allowed to stand at room temperature; the solution became viscous and new signals appeared in the nmr spectrum after several hours.

(61) A. C. Rutenberg, A. A. Palko, and J. S. Drury, *ibid.*, **85**, 2702 (1963); see also J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, **4**, 1741 (1965).

(62) The shift for $C_6H_5BCl_2$ was about 10 cm^{-1} smaller than that observed by Lappert in ethyl acetate as the solvent;[25] however, since we used CCl_4, the difference is very likely due to solvent effects. The value for n-$C_4H_9SnCl_3$ is in good agreement with the literature.[26]

(63) A. Fratiello and R. E. Schuster, *Inorg. Chem.*, **7**, 1581 (1968).

The coordination chemical shift of the methyl protons of trimethylamine adducts has been used to measure relative Lewis acidities for a number of boron compounds.[64] The spectra of $FcBCl_2 \cdot N(CH_3)_3$ and $C_6H_5BCl_2 \cdot N(CH_3)_3$ were obtained in $CDCl_3$ at room temperature; there was no evidence for dissociation or exchange. The coordination shifts (Table VI) for these compounds again place them between BF_3 and BCl_3 and suggest that the ferrocenyl and phenyl compounds have almost identical Lewis acidities.

TABLE VI

COORDINATION CHEMICAL SHIFTS FOR THE N-METHYL PROTONS IN TRIMETHYLAMINE COMPLEXES[a]

Adduct	$\Delta\delta$,[b] Hz	Adduct	$\Delta\delta$,[b] Hz
$(CH_3)_3N \cdot B(CH_3)_3$	16.2[c]	$(CH_3)_3N \cdot C_6H_5BCl_2$	31[d]
$(CH_3)_3N \cdot BH_3$	22	$(CH_3)_3N \cdot BCl_3$	49
$(CH_3)_3N \cdot BF_3$	23	$(CH_3)_3N \cdot BBr_3$	56
$(CH_3)_3N \cdot B(C_6H_5)_3$	23	$(CH_3)_3N \cdot BI_3$	68
$(CH_3)_3N \cdot FcBCl_2$	30[d]		

[a] Except as noted, all data from ref 64. [b] All shifts downfield from $N(CH_3)_3$; the free amine was taken to be 133 Hz below TMS. [c] A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.*, **91,** 2911 (1969). [d] This work.

The mechanisms for α-ferrocenylcarbonium ion stabilization suggest that the acidity of $FcBCl_2$ can be reduced by π-electron donation from the cyclopentadienyl ring or donation of e_{2g} electrons from the metal. A method which measures the extent of involvement of the empty boron orbital with the metal or the ring π electrons should also provide information on the acidity of ferrocenylboranes. Mack and Yoder recently reported that the N-methyl ^{13}C–H coupling constants for a series of compounds of the general formula $(CH_3)_3M–N(CH_3)_2$ (where M = C, Si, Ge, Sn) varied with the extent of π donation from the nitrogen atom to the empty d orbitals of the atom M.[65] Therefore, the amount of pπ–pπ overlap in the B–N bond of aminoboranes might be reflected by the N-methyl ^{13}C–H coupling constant. In a series of analogous compounds of the type $RB[N(CH_3)_2]_2$ or $R_2B–N(CH_3)_2$, the magnitude of $J(^{13}C–H)$ should also reflect the π-bonding ability of the R group. That is, the greater the amount of R–B π bonding, the less electron deficient the boron atom will be; less extensive B–N π interaction and a smaller $J(^{13}C–H)$ should result. A comparison of the coupling constants for $FcB[N(CH_3)_2]_2$ and $C_6H_5B[H(CH_3)_2]_2$ (Table VII) suggests that the ferrocenyl and phenyl groups are almost identical in their interaction with the empty boron orbital. However, this conclusion must be viewed with some caution until a more extensive series of both mono- and bis(dimethylaminoboranes) can be investigated. Less doubtful at the moment is the conclusion that FcB– and C_6H_5B– are more π-electron withdrawing than the group IV $(CH_3)_3M$– groups, the latter compounds having smaller N-methyl ^{13}C–H coupling constants. This result is not unexpected, since N–B pπ–pπ overlap should be more favorable than pπ–dπ bonding in group IV compounds.

TABLE VII

N-METHYL ^{13}C–H COUPLING CONSTANTS IN DIMETHYLAMINO COMPOUNDS[a]

Compound	$J(^{13}C–H)$, Hz	Compound	$J(^{13}C–H)$, Hz
$(CH_3)_3C–N(CH_3)_2$	131.4	$(CH_3)_3Sn–N(CH_3)_2$	130.2
$(CH_3)_3Si–N(CH_3)_2$	132.2	$FcB[N(CH_3)_2]_2$	133.1
$(CH_3)_3Ge–N(CH_3)_2$	131.4	$C_6H_5B[N(CH_3)_2]_2$	132.9

[a] The values for the group IV compounds are from ref 65.

In summarizing the Lewis acidity experiments, we can best conclude that $FcBCl_2$ is a somewhat weaker acid than its phenyl analog. This conclusion is suggested by the THF and ethyl acetate methods, the two most reliable methods used. Although the steric bulk of the ferrocenyl group may be partly responsible, electronic factors are suggested as the primary cause. Therefore, there does indeed seem to be a parallel between the ferrocenylboranes and their isoelectronic analogs, the α-ferrocenylcarbonium ions.

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(64) A. G. Massey and A. J. Park, *J. Organometal. Chem.*, **5**, 218 (1966).

(65) J. Mack and C. H. Yoder, *Inorg. Chem.*, **8**, 278 (1969).