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FERROCENYLBORANES
III. THE PREPARATION AND PROPERTIES OF *B*-TRIFERROCENYLBORAZINE

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SUMMARY

Orange, air-stable *B*-triferrocenylborazine, $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4BNH)]_3$, has been prepared by the reaction of ferrocenyldichloroborane with ammonia in toluene. A 90% yield of crystalline, analytically pure material is easily obtained. The most interesting aspects of the compound are its mass spectrum and electrochemistry. The 70 eV mass spectrum gave no indication of fragmentation; only the molecule ion and the doubly charged molecule ion (17% abundant compared with the molecule ion) were observed. A cyclic voltammogram of the borazine in dimethylformamide showed that it underwent a simultaneous and completely reversible loss of three electrons; oxidation occurred at +0.36 V *vs.* SCE, a potential 0.1 V lower than the oxidation potential of ferrocene under the same conditions. The extreme stability of the gaseous ion, and the lowering of the oxidation potential and stabilization of the tripositive cation in solution, are most easily ascribed to extensive π delocalization of charge throughout the molecular framework.

INTRODUCTION

Previous research on ferrocenylboranes has shown that the ferrocenyl group can impart unusual properties to the reactive boron center. For example, the Lewis acidity of ferrocenyldichloroborane was found to be less than that of phenyldichloroborane, an observation consistent with the fact that the isoelectronic α-ferrocenylcarbonium ions are more stable than analogus phenylcarbonium ions[1]. A mass spectral study also showed that fragmentation was considerably reduced upon attaching a ferrocenyl group in place of a phenyl group in organoboric acids[2]. In related research on the coordination chemistry of ferrocenylphosphines[3], the unique steric and electronic influence of the ferrocenyl group on the Lewis basicity of the phosphorus atom was indicated.

The unusual properties of these molecules prompted us to investigate the

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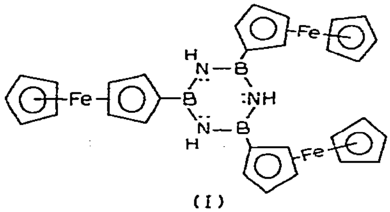
synthesis of other ferrocenylboranes, particularly those containing several ferrocenyl groups. We were interested in observing further the effect of the ferrocenyl group on the Lewis acidity of the boron atom and in examining the electrochemistry of a molecule containing both electron-rich and electron-deficient centers. We first attempted to scale-up our recently reported synthesis of triferrocenylborane, Fc_3B[2,*]. However, neither our method nor those of Sollott *et al.*[4] gave Fc_3B in sufficiently good yield and purity to carry out further studies. For this reason we turned to the synthesis and study of *B*-triferrocenylborazine, $(FcBNH)_3$(I).



(I)

RESULTS AND DISCUSSION

Synthesis and general properties

Although a variety of methods are available for the synthesis of symmetrically substituted *B*-triorganoborazines[5], reaction (1) was found to be most convenient. The

$$3\ FcBCl_2+9\ NH_3 \rightarrow (FcBNH)_3+6\ NH_4Cl \qquad (1)$$

reaction proceeds readily in toluene or hexane to give *B*-triferrocenylborazine in 80–90% yields. The compound is a yellow-orange, crystalline solid, soluble in common organic solvents, and stable to normal laboratory air for several weeks (the infrared spectrum indicated no change after the solid had stood for four weeks in air). Table 1 lists selected physical properties of the borazine, and Table 2 lists the *d*-spacings of the crystalline material.

Assuming that the hydrolysis of borazines is initiated through nucleophilic attack by water at the boron atom[6], any effect which increases the effective electron density at this site will stabilize the borazine to hydrolysis. A π interaction between the *B*-substituent and the ring can deter hydrolysis to some extent[7], but it has been found that stability is best achieved through steric shielding of the boron atom[8]. Considering both factors, it was anticipated that *B*-triferrocenylborazine would possess a greater hydrolytic stability than *B*-triphenylborazine. There are qualitative indications that this is the case. The observed and calculated[2] molecular ion envelopes in the mass spectra of these two borazines are given in Table 3. Agreement is good for molecular ions lighter than the base peak (*m/e* 633 or *m/e* 309), but experimental intensities above the base peak indicate the presence of an impurity. The most logical impurity in each borazine is the corresponding boroxine, $(RBO)_3$; a boroxine can arise by dehydration of the organoboric acid, $RB(OH)_2$, produced in the hydrolysis of the borazine. Even though $(PhBNH)_3$ and $(FcBNH)_3$ were prepared and handled

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

TABLE 1

PHYSICAL PROPERTIES FOR *B*-TRIFERROCENYLBORAZINE

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^1H NMR Spectrum in $CDCl_3$; τ(N–H) 4.91, broad singlet; $\tau(\pi\text{-}C_5H_4)$ 5.53, singlet; $\tau(\pi\text{-}C_5H_5)$ 5.86, singlet.

Ultraviolet Spectrum in $CHCl_3$; 445 nm, $\varepsilon=49.5$; 294 nm, sh, $\varepsilon=1020$.

IR Spectrum as KBr pellet (cm^{-1})[a];

3434 m N–H stretch
3084 m C–H stretch
1485 s B–N stretch
1420 s
1378 s
1337 s
1310 s
1288 s
1255 m

1186 m
1116 w
1105 s antisym. ring breathe
1070 m
1030 m
1000 m C–H bend (//)
897 w
870 w
816 s C–H bend (⊥)

728 s B–N ring deform.
722 s
707 w
676 m
608 w
492 s antisym. ring tilt
482 s antisym. ring–metal stretch

Solubility

Soluble in toluene, benzene, chloroform, methylene chloride, carbon disulfide, acetone, dimethoxyethane, dioxane, dimethylformamide.

Slightly soluble in petroleum ether (30–60°), ethanol, diethyl ether, carbon tetrachloride, acetonitrile, cyclohexane.

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[a] Assignments of bands characteristic of the ferrocenyl group are according to M. Rosenblum, ref. 11; those characteristic of the borazine are according to A. Meller, ref. 27.

TABLE 2

POWDER X-RAY DIFFRACTION DATA (Cu-*K*α RADIATION)

d Spacing	Intensity	*d* Spacing	Intensity
7.63	vvw	3.83	m
6.62	vvw	3.52	m
6.13	vvs	3.28	vvw
5.60	s	2.92	vvw
5.26	s	2.74	w
4.92	vs	2.36	vw
4.50	w	2.05	vvw
4.28	w	1.74	vvw
4.11	vvw		

in an identical manner, it would seem that the phenylborazine is more susceptible to hydrolysis since it contains the greater amount of boroxine*.

As mentioned above, solid $(FcBNH)_3$ is reasonably stable to hydrolysis in the air. However, it does hydrolyze when placed in contact with water; no borazine was detected after stirring for four days in a 10% water/dioxane solution under nitrogen. For comparison, it has been found that *B*-triphenylborazine has a half-life of only 8.5 min under similar conditions[9], while *B*-trimesityl-*N*-trimethylborazine is stable for months[8].

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* This conclusion rests on the reasonable assumption that the relative volatilities and ionization cross sections are nearly the same for each borazine–boroxine pair.

TABLE 3

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

Compound	Relative abundance (%)								
$(FcBNH)_3$	Mass	626	627	628	629	630	631		
	Calcd.	0.03	0.21	0.98	3.9	13.3	33.2		
	Found			1.0	4.1	12.1	34.0		
	Mass	632	633	634	635	636	637		
	Calcd.	68.5	100	37.1	8.1	1.2	0.1		
	Found	68.1	100	41.8	11.1	3.8	1.0		
$(PhBNH)_3$	Mass	306	307	308	309	310	311	312	313
	Calcd.	1.4	16.8	68.6	100	20.0	2.0	0.1	
	Found	2.8	17.5	70.0	100	21.4	10.0	11.0	2.0

[a] Calculations were done according to the previously described procedure; see ref. 2.

Spectroscopic properties

(*i*). *Infrared and NMR spectra.* The infrared bands for *B*-triferrocenylborazine are listed in Table 1. Bands in the 700–750 cm^{-1} region have been assigned previously to the B–N ring deformation mode. Goldstein and Mooney assigned the medium intensity 747 cm^{-1} band in *B*-triphenylborazine to this mode and suggested that its presence indicates the coplanarity of the phenyl and borazine rings[10]. *B*-triferrocenylborazine displays a strong band at 728 cm^{-1}; while it may be correct to assign this to a B–N ring deformation, we are reluctant to suggest that the C_5H_4 ring of the ferrocenyl group and the borazine ring are therefore coplanar.

The proton NMR spectrum of $(FcBNH)_3$ was obtained in $CDCl_3$ at 60 MHz (see Table 1). Rosenblum notes that the cyclopentadienyl ring of ferrocene which is singly substituted with an electron-donating group produces a singlet, whereas a ring having an electron-withdrawing group gives rise to a symmetrical pair of triplets[11]. An example of the latter is $FcBCl_2$[1]. Since the C_5H_4 ring protons of $(FcBNH)_3$ give rise to a singlet, this suggests that the borazine ring acts as an electron-donating group. As discussed below, this is not inconsistent with the electrochemical results.

(*ii*). *Mass spectrum.* Our recently reported study of the mass spectra of some ferrocenyl boric acids and their phenyl analogues indicated that the ferrocenyl group lends a special stability to the parent molecule ion and to certain daughter ions[2]. We expected to observe, therefore, the same stabilization of the parent molecule ion of *B*-triferrocenylborazine relative to *B*-triphenylborazine.

The 70 eV mass spectrum of *B*-triphenylborazine resembles those of other borazines whose spectra have been described in the literature[12]. That is, more-or-less complete fragmentation is observed. For example, the parent molecule ion loses a phenyl radical to give $Ph_2B_3N_3H_3^+$ (*m/e* 232, 38% relative abundance); this ion apparently fragments further by ring cleavage to give $PhB_2N_2H_2^+$ (*m/e* 129, rel. abund. 37%)*.

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* The complete spectrum of $(PhBNH)_3$ is not reported for several reasons. As mentioned above, it contained the boroxine, $(PhBO)_3$, as an impurity which was difficult to remove. Therefore, ion abundances could not be determined with accuracy; for ions of low abundance, it was difficult to determine whether they came from the borazine or the boroxine.

In contrast, the mass spectrum of *B*-triferrocenylborazine is striking. *The only ions observed in the 70 eV spectrum were the parent molecule ion (m/e 633, 100%) and the doubly charged molecule ion (m/e 316.5, 17%).* Our experience with the mass spectrometry of organometallic compounds includes other ferrocenylboranes (one of which, *B*-triferrocenylboroxine, $(FcBO)_3$, is isoelectronic with $(FcBNH)_3$)[2], ferrocenylphosphines[13], arenemetal carbonyls[13], and boron-containing heterocycles[14]. We have never observed the complete lack of fragmentation of a molecule at 70 eV in the course of this work. Furthermore, we are not aware of any examples in the mass spectrometry literature. [1,3,5-Triferrocenylbenzene, a molecule also isoelectronic with $(FcBNH)_3$, has been prepared; although the molecular weight of the compound was apparently determined mass spectrometrically, no details of the spectrum are given[15].]

The stability of the ferrocenylborazine may also be illustrated by a comparison of the relative abundance of its doubly charged ion with the relative abundances of doubly charged ions of other ferrocenyl- and phenylboranes (see Table 4).

More efficient π delocalization of charge was given as the explanation for the special stability of gaseous ions arising from ferroceneboronic acids when compared with their phenyl analogues[2]. It seems reasonable to extrapolate this argument to explain the incredible stability of $(FcBNH)_3^{+\cdot}$ and $(FcBNH)_3^{2+}$.

(*iii*). *Electrochemistry.* One of the main reasons for attempting the synthesis of *B*-triferrocenylborazine was to examine its electrochemistry. The electrochemical behavior of this molecule was of interest for three reasons: (*a*) the possibility that a mixed-valence compound might be obtained upon partial oxidation; (*b*) the expectation that a comparison of its reduction potential with those of other borazines would lead to further information on relative π mobility; and (*c*) the hope that an electrochemically generated radical cation or anion would give rise to an ESR spectrum.

Mixed-valence compounds are known in an almost endless variety; many have unique magnetic and/or spectroscopic properties[16]. One organometallic mixed valence salt, biferrocene(Fe^{II}, Fe^{III}) picrate, has recently been investigated thoroughly[17]. The very great stability of $(FcBNH)_3^{+\cdot}$ and $(FcBNH)_3^{2+}$ in the mass spectrometer suggested that it might be possible to prepare a stable mixed-valence salt of *B*-triferrocenylborazine.

It was anticipated that electrochemical oxidation of the borazine could proceed in at least three ways. (*a*) Each iron atom could be oxidized at a different

TABLE 4

RELATIVE ABUNDANCE OF DOUBLY CHARGED IONS[a]

Compound		Abundance relative to molecular ion (%)
Fc_3B	Triferrocenylborane	8
$(Fc_2B)_2O$	Diferrocenylborinic anhydride	6
$Ph_3B_3O_3$	Triphenylboroxine	7.4
$Fc_3B_3O_3$	Triferrocenylboroxine	11.2
$Ph_3B_3N_3H_3$	*B*-Triphenylborazine	ca. 0.5
$Fc_3B_3N_3H_3$	*B*-Triferrocenylborazine	17

[a] See ref. 2 for mass spectral details of compounds other than the borazines.

potential. As one iron atom is oxidized, the oxidation potential of the remaining two might be raised if the ferrocenyl groups have a significant electronic effect on one another. Partial oxidation in this manner would give a mixed-valence compound. (*b*) Only one iron atom might be oxidized. If sufficient electron density were to flow toward the oxidized site away from the unoxidized iron atoms, oxidation of the remaining iron atoms might be entirely prevented. (*c*) All three iron atoms might be oxidized simultaneously at the same potential.

Shriver, Smith, and Smith demonstrated that the reduction potentials of substituted borazines were related to the calculated energies of the lowest empty π molecular orbitals of the borazines[18]. Therefore, the second reason for investigating the electrochemistry of $(FcBNH)_3$ was the hope that its reduction potential could be obtained and compared with those previously reported.

The previously studied borazine radical anions decomposed very readily[18]. Just as ferrocenyl groups stabilize the borazine radical cation, it was hoped that they might lend stability to a radical anion. Such a stabilized radical anion could give rise to an ESR spectrum which might provide further information on the extent of electron delocalization in the system.

A cyclic voltammogram of a dilute solution of $(FcBNH)_3$ in dimethylformamide is shown in Fig. 1. Oxidation of the compound occurs at an $E_{\frac{1}{2}}$ of +0.37 V *vs.* SCE; the process is seen to be electrochemically reversible since the ratio of the peak anodic current to the peak cathodic current equals one[19]. Little if any reduction to a radical anion occurs in the potential range examined. Unfortunately, even though degassed and thoroughly dry solvents were used, and the experiments were conducted under dry nitrogen, cathodic potentials greater than −2.2 V could not be achieved.

Controlled potential coulometry experiments at +0.80 V *vs.* SCE indicated that the oxidation process involved the *simultaneous and reversible removal of three electrons.* From chronoamperometry experiments, the diffusion coefficient was found to be 6.1×10^{-6} cm²/sec in DMF. This is approximately one-fourth of the value for ferrocene (2.4×10^{-5} cm²/sec)[20] and is therefore considered very reasonable.

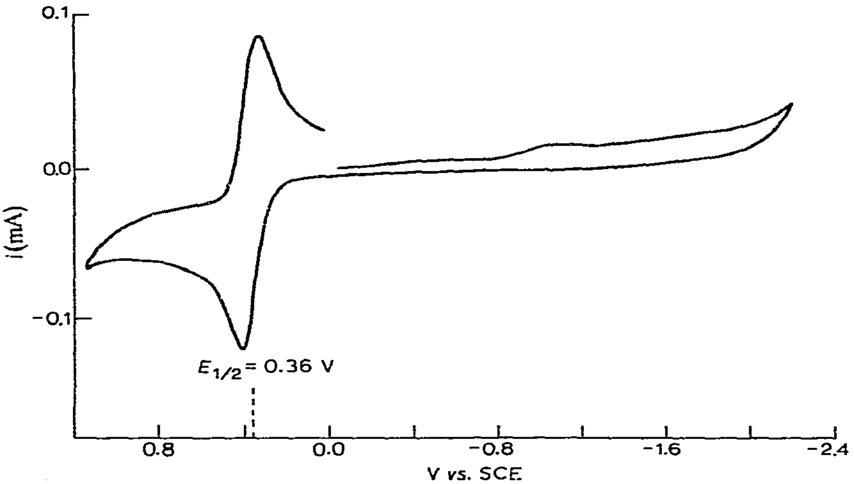

Fig. 1. Cyclic voltammogram of *B*-triferrocenylborazine (1.018×10^{-3} *M*) in dimethylformamide with 0.1 *M* tetraethylammonium perchlorate as the supporting electrolyte.

Since only very small quantities are oxidized during cyclic voltammetry experiments, no color change was apparent at the electrodes. However, the initially yellow-orange solution became deep blue-green in the course of the exhaustive coulometry experiments. This color, typical of ferrocenium salts[21], persisted for several hours, even when the solution was open to the air. No ESR signal was observed upon oxidizing the borazine directly in the cavity at potentials between +0.5 and +1.0 V *vs.* SCE; the blue-green solution generated in the coulometry experiments also did not give rise to an ESR signal.

In summary, *B*-triferrocenylborazine undergoes a reversible, three-electron oxidation at +0.37 V *vs.* SCE. Under the same conditions, ferrocene undergoes a reversible, one-electron oxidation at +0.48 V *vs.* SCE. There are a number of literature reports that electron-donating substituents increase the ease of oxidation of ferrocene derivatives relative to ferrocene[22]. The fact that $(FcBNH)_3$ forms a very stable tri-positive cation at a lowered potential leads us to conclude that a π interaction between the borazine ring and the ferrocenyl group may be extremely important. This conclusion is of course consistent with the mass spectrum of $(FcBNH)_3$ and the results of our other studies on the chemical and physical properties of ferrocenylboranes.

This work has prompted us to investigate the synthesis and properties of other organometallic compounds containing several metal atoms. We are currently developing the synthesis of metal compexes utilizing ferrocene as the backbone of a chelating ligand.

EXPERIMENTAL

Equipment and general techniques

Air sensitive, volatile materials were handled in a preparative vacuum line equipped with mercury float valves[23]. Nonvolatile, air sensitive substances were handled in a HE-43 Vac-Atmosphere drybox equipped with a drying and deoxygenating train[24].

Proton NMR spectra were obtained with a Varian A-60 spectrometer: TMS was used as an internal standard and the side-band technique was used for chart calibration. Infrared spectra were run on a Perkin–Elmer 337 or 457.

The ultraviolet spectrum reported in Table 1 was obtained using a Cary 11; the $CHCl_3$ solutions were 0.1 to 2×10^{-3} *M* in $(FcBNH)_3$. In a concentration of 0.01 *M* in hexane, $(PhBNH)_3$ did not absorb in the 300–500 nm region.

Mass spectra were determined on an AEI MS 9 instrument using 70 eV ionizing energy, 100 μA trap current, and 8 kV accelerating voltage. Samples were introduced by direct insertion at 185° into the ion source. Ion abundance is expressed as a percentage of the base peak.

Solvents and reagents

Except as noted, most chemicals were reagent grade and were used as received. Solvents were dried over appropriate drying agents (usually CaH_2) and distilled shortly before use. The dimethylformamide used in the electrochemical studies was dried over BaO and vacuum distilled before use.

Ferrocenyldichloroborane was prepared from FcHgCl (Research Organic

Chemicals, Sun Valley, Calif.) and BCl_3 in hexane according to the previously described procedure. The BCl_3 used in this preparation was purified by trap-to-trap distillation to a constant vapor pressure of 476 mm at 0°.

Preparation of B-triferrocenylborazine

A solution of $FcBCl_2$ (3.65 g, 13.65 mmole) in 50–75 ml of dry toluene was prepared in a 100 ml, three-neck flask in the drybox. After stoppering the flask and removing it from the box, it was equipped with a nitrogen inlet, a gas dispersion tube for introducing ammonia, a magnetic stirrer, and a reflux condenser. Ammonia was bubbled through the stirred solution for about 30 min at room temperature; during this time NH_4Cl began to precipitate and the solution went from deep red-orange to a yellow-orange. In order to complete the condensation of the $FcBCl_2 \cdot NH_3$ adduct to the borazine, the solution was refluxed for about one hour while ammonia addition was continued. After cooling to room temperature, the solution was filtered through a short (5 x 5 cm) cellulose column (Whatman Chromedia CF 11 cellulose) to remove NH_4Cl*. Solvent was removed from the filtrate in a rotating evaporator to give 2.56 g (4.04 moles; 89% yield) of analytically pure $(FcBNH)_3$. Orange crystals; m.p. (sealed capillary) 259°. (Found: C, 56.86; H, 4.71; B, 5.27; N, 6.24. $C_{30}H_{30}B_3Fe_3N_3$ calcd.: C, 56.87; H, 4.74; B, 5.21; N, 6.63%.) The physical properties of the borazine are given in Table 1.

Electrochemistry

All of the electrochemical work was done in a glove bag filled with dry nitrogen. The dimethylformamide solutions were usually about 1×10^{-3} *M* in borazine and 0.1 *M* in tetraethylammonium perchlorate, the supporting electrolyte. The cyclic voltammetry and chronoamperometry experiments were done using a three-electrode potentiostat-galvanostat system previously described[25]. The controlled potential coulometry experiments also used previously described instrumentation[26].

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* The solution may be passed through another cellulose column to ensure complete removal of NH_4Cl. We have found this to be a much more efficient method than the centrifugation procedure given in the literature; see ref. 5, p. 111.

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