min. Ethanol (1 ml) was added, followed by excess diethyl ether to yield yellow-orange crystals which were filtered off, washed with diethyl ether, and air-dried: yield 279 mg (90%); $^1H$ nmr ($CDCl_3$) 6.22 (4, olefin), 6.50 (2, methine), 8.75 (2, methylene), 8.18 (m, 6, $P-CH_3$); ir (Nujol) 2028 (s, $C\equiv O$), ($CH_2Cl_2$) 2019 (s, $C\equiv O$). *Anal.* Calcd for $RhC_{34}H_{34}ClO_5P_2$: C, 56.49; H, 4.74; Cl, 4.90. Found: C, 57.02; H, 4.88; Cl, 5.32; $\Lambda$ = 72.

(45) **Preparation of $[Rh(1,3\text{-butadiene})\{P(C_6H_5)_2CH_3\}_2(CO)]^+ClO_4^-$.** $[Rh(NBD)\{P(C_6H_5)_2CH_3\}_2]^+ClO_4^-$ (500 mg) was placed in 3 ml of acetone and treated with CO until a light yellow solution was obtained. Ethanol (2 ml) was added and butadiene was bubbled through the solution for 10 min. Slow addition of diethyl ether produced pale yellow crystals of the product which were filtered off, washed with diethyl ether, and air-dried: yield 438 mg (89%); $^1H$ nmr ($CH_2Cl_2$) 3.98 (2), 7.36 (2), and 9.42 (2), all br, 8.08 (d, 6, $J$ = 8.0 Hz, $P-CH_3$); $^{31}P$ ($CH_2Cl_2$) $-12.1$ ppm (d, $J_{Rh-H}$ = 133 Hz); ir (Nujol) 2031 (s, $C\equiv O$) and 1986 (m, $C\equiv O$), ($CH_2Cl_2$) 2048 (s, $C\equiv O$) and 1993 (m, $C\equiv O$). *Anal.* Calcd for $RhC_{31}H_{32}ClO_5P_2$: C, 54.36; H, 4.71; P, 9.04. Found: C, 54.48; H, 5.05; P, 8.91.

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# Chemistry of Bis[π-(3)-1,2-dicarbollyl]metalates. Protonation and Boron Substitution

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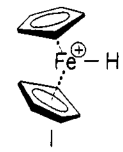
**Abstract:** The "sandwich"-bonded $\{bis[\pi\text{-}(3)\text{-}1,2\text{-dicarbollyl}]iron(II)\}^{2-}$ ion is protonated in strongly acidic media to form what may prove to be the analog of protonated ferrocene. This species readily reacts with dialkyl sulfides to form B-substituted bis(dicarbollyl)iron(II) and -(III) species. Analogous reactions have been carried out employing bis(dicarbollyl)iron(III) and -cobalt(III) anions. The preparation, characterization, and structures of these complexes are discussed.

The synthesis and properties of transition metal complexes analogous to metallocenes and employing the ligands $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$ and $(3)\text{-}1,7\text{-}B_9C_2H_{11}^{2-}$ have been reported previously.[1-3] Certain aspects of the chemistry of some of these novel compounds have also appeared, *e.g.*, bromination,[1] Lewis acid–base reactions,[2] and electrophilic substitution.[4] We now wish to report further studies which deal with the protonation and B substitution of some metalates of the $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$ ion.

## The Protonation of Ferrocene and Its Bis(dicarbollyl) Analog

Bis(cyclopentadienyl)iron(II), ferrocene, is protonated in strongly acidic media such as sulfuric acid, boron trifluoride hydrate, or hydrogen chloride–aluminum chloride. The $^1H$ nmr spectrum of this species[5] contains a broad high-field resonance at +2.09 ppm (relative to tetramethylsilane = 0.00) which Rosenblum, *et al.*,[5] have assigned to a proton bonded to the iron atom. From Ballhausen and Dahl's theoretical model of the isoelectronic molecule $(\pi\text{-}C_5H_5)_2ReH$[6] and related compounds, it was suggested that the cyclopentadienyl ring planes in protonated ferrocene are inclined, and that the unique proton is coordinated to the central of three hybrid metal orbitals as indicated in structure **1**.



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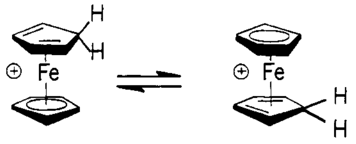

2

In this light, recent work[7] with a ring-tilted ferrocene, 1,1′-dimethyleneferrocene, indicates that ring-tilt distortion of the ferrocene nucleus is accompanied by an increase in Lewis basicity.

Ware and Traylor,[8] on the other hand, have suggested that the high-field resonance in the $^1H$ nmr spectrum of ferrocene in strong acid solution is consistent with a rapidly equilibrating σ complex, **2**. Such a structure as **2**, or its equivalent, is indeed required to explain the rapid acid-catalyzed deuteration of ferrocene.[9] It ap-

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[1] M. F. Hawthorne, *et al.*, *J. Amer. Chem. Soc.*, 90, 879 (1968).

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[6] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 15, 1333 (1961).

[7] H. L. Lentzner and W. E. Watts, *Chem. Commun.*, 26 (1970).

[8] J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965).

[9] M. Rosenblum and F. W. Abbate, *Advan. Chem. Ser.*, No. 62, 532 (1967).

**Table I.** Elemental Analyses[a]

| Compound | | % C | % H | % B | % P | % metal | % S |
|---|---|---|---|---|---|---|---|
| $(C_6H_5)_3PCH_3[(B_9C_2H_{11})_2Fe^{II}H]$ | Calcd | 46.12 | 6.90 | 32.49 | 5.17 | 9.32 | |
| | Found | 46.36 | 6.96 | 32.55 | 5.21 | 9.63 | |
| $(C_6H_5)_3PCH_3\{[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Fe^{II}\}$ | Calcd | 47.19 | 7.19 | 28.32 | 4.51 | 8.13 | 4.67 |
| | Found | 47.48 | 7.28 | 28.06 | 4.45 | 8.50 | 4.67 |
| $[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Fe^{III}$ | Calcd | 18.87 | 7.13 | 50.96 | | 14.63 | 8.40 |
| | Found | 18.83 | 6.98 | 51.39 | | 14.98 | 8.38 |
| $[B_9C_2H_{10}S(C_2H_5)_2]_2Fe^{II}$ | Calcd | 28.88 | 8.08 | 38.99 | | 11.19 | 12.85 |
| | Found | 28.96 | 8.35 | 39.25 | | 10.91 | 12.93 |
| $[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Co^{III}$ | Calcd | 23.27 | 7.57 | 47.12 | | 14.27 | 7.76 |
| | Found | 22.97 | 7.42 | 44.79 | | 13.25 | 7.57 |

[a] Performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

**Table II.** Infrared Spectra[a,b]

| | |
|---|---|
| $(C_6H_5)_3PCH_3[(B_9C_2H_{11})_2Fe^{II}H]$ | 2582 (m, sh), 2545 (s, sh), 2486 (s), 2440 (m, sh), 1885 (m), 1490 (m), 1435 (s), 1410 (w), 1390 (w), 1325 (w), 1302 (w), 1184 (w), 1157 (w), 1135 (m), 1110 (s), 1100 (m), 1017 (m), 995 (m, sh), 982 (m), 930 (w), 896 (s), 848 (w), 785 (m), 755 (m, sh), 743 (s), 716 (s), 687 (s) |
| $(C_6H_5)_3PCH_3\{[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Fe^{II}\}$ | 2610 (m, sh), 2575 (s), 2525 (s), 1475 (m, sh), 1430 (s), 1405 (w), 1338 (w), 1320 (w), 1264 (w), 1200 (w), 1169 (m), 1110 (s), 1092 (m), 1057 (w), 1023 (m), 995 (m, sh), 983 (s), 975 (sh), 940 (w), 929 (w), 915 (w), 904 (s), 880 (m), 852 (m), 827 (m), 791 (m), 776 (m), 755 (s), 719 (s), 692 (s) |
| $[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Fe^{III}$ | 2613 (m, sh), 2563 (s), 1288 (w), 1238 (vw), 1213 (m), 1148 (m), 1118 (m), 1098 (s), 1088 (w), 1078 (w), 1068 (w), 1058 (w), 1025 (m), 983 (s), 933 (m), 873 (w), 853 (w), 838 (m), 813 (w), 788 (m), 768 (m, sh), 754 (m), 723 (w) |
| $[B_9C_2H_{10}S(C_2H_5)_2]_2Fe^{II}$ | 2650 (m), 2580 (s), 1420 (m), 1305 (w), 1280 (w), 1255 (m), 1238 (w), 1160 (br, w), 1135 (w), 1115 (m, sh), 1105 (m), 1070 (w), 1055 (m), 1035 (m), 988 (m, sh), 977 (s), 958 (m, sh), 932 (w), 912 (m), 875 (m), 860 (w), 838 (m), 819 (s), 780 (m), 734 (s), 717 (s), 703 (m, sh) |
| $[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Co^{III}$ | 2630 (m), 2560 (s), 1415 (m), 1275 (w), 1260 (m), 1230 (w), 1197 (m), 1139 (m), 1112 (m), 1097 (s), 1078 (m), 1045 (w), 1015 (s), 978 (s), 922 (m), 883 (m), 868 (w), 843 (w), 822 (m), 787 (w, sh), 773 (m), 750 (m, sh), 740 (s), 720 (s) |

[a] Nujol mulls, all values in reciprocal centimeters. [b] s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder.

pears that further work in this area (low-temperature, high-resolution nmr studies) will be required to fully elucidate this problem.

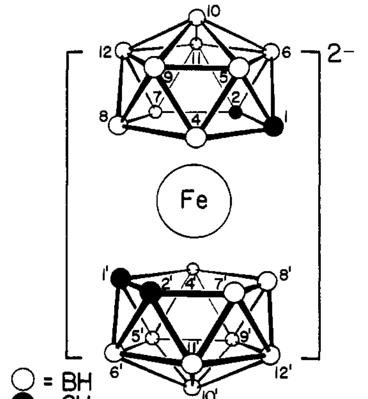

Figure 1. The structure and numbering system of the $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe^{2-}$ ion.

**Table III.** Electronic Spectral Data

| Compound | Solvent | $\lambda_{max}$, mμ (ε) |
|---|---|---|
| $(C_6H_5)_3PCH_3\{[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Fe^{II}\}$ | $CH_2Cl_2$ | 264 (15,500)[a]<br>273 (13,800)<br>388 (101)<br>512 (196) |
| $[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Fe^{III}$ | $CH_2Cl_2$ | 281 (17,900)<br>438 (555)[a]<br>505 (356)[a]<br>552 (289)[a] |
| $[B_9C_2H_{10}S(C_2H_5)_2]_2Fe^{II}$ | $CH_2Cl_2$ | 242 (13,100)<br>394 (77)<br>525 (165) |
| $Cs_2(B_9C_2H_{11})_2Fe^{II}$ | $CH_3CN$ | 240 (25,800)<br>272 (11,600)[a]<br>304 (5,580)[a]<br>380 (92)<br>508 (201) |
| $(C_6H_5)_3PCH_3[(B_9C_2H_{11})_2Fe^{II}H]$ | KBr pellet | 225 (1.0)[b]<br>268 (0.91)<br>375 (0.58)<br>462 (0.41)[a] |

[a] Shoulder. [b] Relative absorbances from KBr disk spectrum.

**Table IV.** Electrochemical Data

| Compound | Solvent | $E_{p/2}$ *vs.* sce |
|---|---|---|
| $[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Fe^{III}$ | $CH_2Cl_2$[a] | +0.13 |
| $[B_9C_2H_{10}S(C_2H_5)_2]_2Fe^{II}$ | $CH_3CN$[b] | +0.48 |
| $Cs(B_9C_2H_{11})_2Fe^{II}H$ | 10% $HClO_4$ in $CH_3OH$[c] | −0.44 |
| $Cs_2(B_9C_2H_{11})_2Fe^{II}$ | $CH_3CN$[b] | −0.42 |

[a] 0.5 *N* $(n\text{-}C_4H_9)_4NClO_4$ supporting electrolyte; reversible $Fe^{III}|Fe^{II}$ couple. [b] 0.1 *N* $(C_2H_5)_4NClO_4$ supporting electrolyte; reversible $Fe^{II}|Fe^{III}$ couple. [c] Mercury pool electrode; quasi-reversible $Fe^{II}|Fe^{III}$ couple.

The addition of concentrated hydrochloric acid to an aqueous solution containing the pink bis(dicarbollyl)-iron(II) ion,[2] $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe^{2-}$ (Figure 1), an isoelectronic dicarbollide analog of ferrocene, turns the solution an orange color which reverts to pink upon dilution with water or addition of base. Isolation of this orange species was affected by cooling a 10% (v/v) perchloric acid–methanol solution containing the $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe^{2-}$ ion and adding a stoichiometric amount of triphenylmethylphosphonium bromide. Air-sensitive crystals of $(C_6H_5)_3PCH_3\ \{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2FeH\}$ (I) were obtained as large orange needles. Elemental analysis of this material (Table I) supported the above formulation. Spectral and electrochemical data are presented in Tables II–IV. The presence of a unique proton was indicated by a medium-intensity infrared band at $1885\ cm^{-1}$, which would be consistent with an iron-bonded hydrogen atom; however, bridge

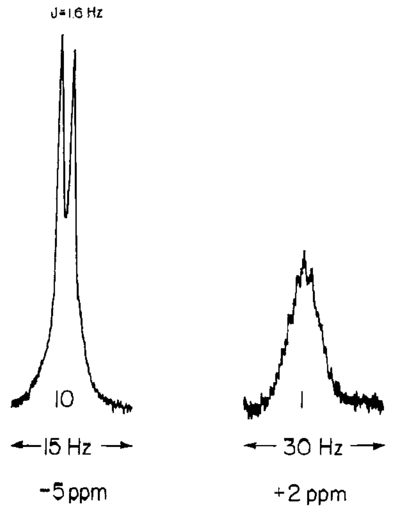

Figure 2. $^{1}H$ nmr spectrum (250 MHz) of ferrocene in $BF_3 \cdot H_2O$; not to scale; reference internal tetramethylsilane = 0.00 ppm.

B–H–B stretching frequencies also occur in this region of the infrared spectrum and hence cannot be ruled out. (The impure solid salt, $(\pi\text{-}C_5H_5)_2FeH^+AlCl_4^-$, prepared by passing HCl through a dichloromethane solution of ferrocene and $AlCl_3$, contained an infrared band at 1645 $cm^{-1}$ assigned to $\nu_{Fe-H}$.[10,11]) Chemical reactions of I (*vide infra*) give additional support to the formulation of this species as a protonated Fe(II) complex.

No high-field proton resonances were observed in the room-temperature $^{1}H$ nmr spectrum of the protonated $(B_9C_2H_{11})_2Fe^{2-}$ ion in 10% $HClO_4$-methanol solution, possibly because of very rapid proton exchange with the solvent or paramagnetic broadening due to a trace amount of the Fe(III) derivative (produced by the facile oxidation of the Fe(II) species[1]). The use of boron trifluoride hydrate as a solvent was attempted, but lack of solubility rendered this approach impossible. Spectra were also recorded in various acidic media at low temperatures, but no signal attributable to the unique proton could be detected. In contrast, the nmr spectrum of protonated ferrocene was readily reproduced (Figure 2) and found to be identical with that previously reported.[5]

The structure of the anion of I is, at present, unknown, although an X-ray crystal structure is in progress. The presently available data do not allow us to distinguish between the two immediately attractive structures, one with a proton bound to the iron atom, as in I, or one involving a rapidly exchanging $-BH_2$ or B–H–B group on one ligand. The $^{11}B$ nmr spectrum of I is significantly different from that of its parent, the $(B_9C_2H_{11})_2Fe^{2-}$ ion (Figure 3), but the extensive overlap of the observed resonances, even at 80 MHz, prevents definitive structural interpretation.

## B-Substitution Reactions of Some Bis(dicarbollyl)metalates

The presence of a proton in close proximity to hydridic hydrogens, a situation apparently present in the protonated bis(dicarbollyl)iron(II) anion, suggested the possibility of performing ligand substitution reactions upon a dicarbollide ligand with simultaneous generation of one molecule of hydrogen.[4,12] The reactions of the anion of I with various dialkyl sulfides have been found to proceed smoothly to liberate stoichiometric amounts of hydrogen and afford crystalline, air-sensitive B-substituted bis(dicarbollyl)iron(II) complexes II, according to

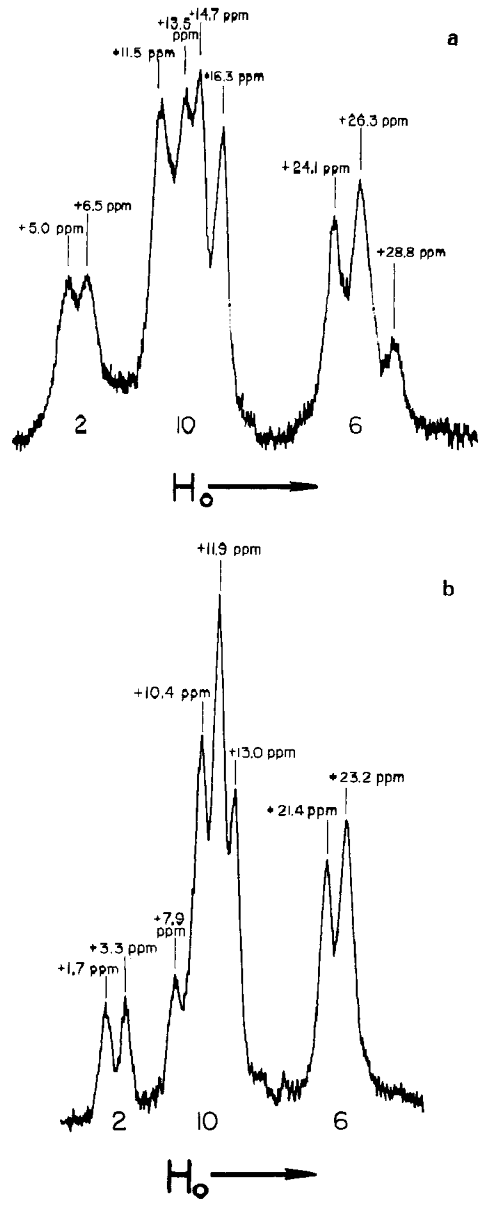

Figure 3. (a) $^{11}B$ nmr spectrum (80 MHz) of $Cs_2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe^{II}$ in acetonitrile solution; reference $BF_3 \cdot OEt_2$ = 0.00 ppm. (b) $^{11}B$ spectrum (80 MHz) of $Cs[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe^{II}H$ in 20% perchloric acid–methanol solution; reference $BF_3 \cdot OEt_2$ = 0.00 ppm.

$$\underset{}{R_2S} + \underset{\text{I}}{[HFe^{II}(B_9C_2H_{11})_2]^-} \longrightarrow H_2 + \underset{\text{II}}{[Fe^{II}(B_9C_2H_{11})(B_9C_2H_{10}SR_2)]^-} \quad (1)$$

$$R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7$$

Reaction conditions and yields of products obtained from eq 1 are reported in Table VI. Analytical data are presented in Table I and spectroscopic and electrochemical properties in Tables II–V.

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[10] M. Rosenblum, J. O. Santer, and W. G. Howells, *J. Amer. Chem. Soc.*, **85**, 1450 (1963).

[11] I. Pavlík and J. Šubrt, *Collect. Czech. Chem. Commun.*, **32**, 76 (1967).

[12] (a) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964); (b) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 3973 (1964).

Table V. $^{1}H$ Nmr Data (60 MHz)

| Compound | Resonance,[a] ppm (rel area) | Solvent | Assignment |
|---|---|---|---|
| $(C_6H_5)_3PCH_3\{[B_9C_2H_{10}S(C_2H_5)_2]$-$(B_9C_2H_{11})Fe^{II}\}$ | Multiplet, $-7.85$ (14.3) | Acetone-$d_6$ | Phenyl protons of cation |
| | Broad multiplet, $-3.0$ (11.5) | | Carborane CH, methylene protons of ethyl groups, methyl protons of cation |
| | Triplet, $-1.33$ (6.1) | | Methyl protons of ethyl groups |
| $[B_9C_2H_{10}S(C_2H_5)_2]_2Fe^{II}$ | Broad singlet, $-3.48$ (4.1) | $CH_2Cl_2$ | Carborane CH |
| | Multiplet,[b] $-2.79$ (7.8) | | Methylene protons of ethyl groups |
| | Triplet, $-1.37$ (12.0) | | Methyl protons of ethyl groups |
| $[B_9C_2H_{10}S(C_2H_5)_2](B_9C_2H_{11})Co^{III}$ | Broad singlets, $-3.17$ (2.4), $-2.74$ (2.4) | $C_6H_6$ | Carborane CH |
| | Multiplet,[b] $-2.17$ (3.6) | | Methylene protons of ethyl groups |
| | Triplet, $-0.73$ (6.0) | | Methyl protons of ethyl groups |

[a] Resonances reported in parts per million relative to internal tetramethylsilane (0.00 ppm). [b] See text.

Table VI. Conditions and Product Yields for Reaction 1

| Dialkyl sulfide ($R_2S$) | Conditions | Moles of hydrogen[a] | Moles of product (II)[a] | % yield, product (II) |
|---|---|---|---|---|
| $(CH_3)_2S$ | 1.5 hr at 65–70° | 2.68 | 2.70 | 80 |
| $(C_2H_5)_2S$ | 10 min at 90–100° | 0.41 | 0.43 | 83 |
| | 10 min at 90–100° | 1.56 | 1.72 | 80 |
| $(n\text{-}C_3H_7)_2S$ | 10 min at 125–130° | 0.49 | 0.45 | 88 |

[a] $\times 10^3$.

The dialkyl sulfide substituted complexes of Fe(II) were oxidized, slowly in solution by atmospheric oxygen, or more rapidly by $I_2$ or $FeCl_3$,

$$\underset{\text{II}}{[Fe^{II}(B_9C_2H_{11})(B_9C_2H_{10}SR_2)]^-} \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} \underset{\text{III}}{[Fe^{III}(B_9C_2H_{11})(B_9C_2H_{10}SR_2)]^0} \quad (2)$$

The neutral $d^5$ Fe(III) compounds thus formed were dark red, paramagnetic, crystalline, air- and water-stable substances. These compounds, $Fe(B_9C_2H_{11})(B_9C_2H_{10}SR_2)$, R = $CH_3$, $C_2H_5$, $n$-$C_3H_7$, could be reduced to the original Fe(II) complexes upon treatment with sodium amalgam in acetonitrile solution. The analytical, spectroscopic, and electrochemical data on a representative $Fe^{III}$ compound, $Fe(B_9C_2H_{11})[B_9C_2H_{10}S(C_2H_5)_2]$ (III) are presented in Tables I–V.

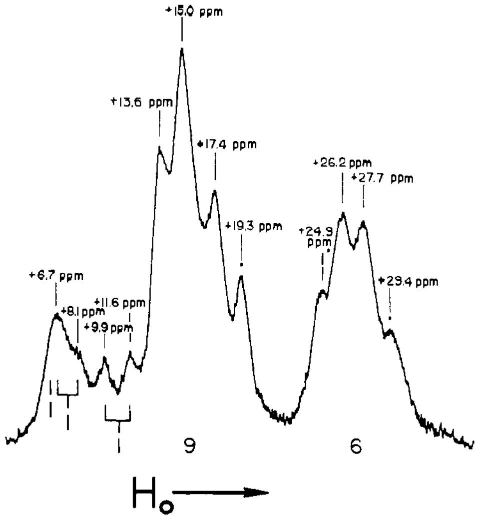

Figure 4. $^{11}B$ nmr spectrum (80 MHz) of $(C_6H_5)_3PCH_3[\pi$-(3)-1,2-$B_9C_2H_{11}][\pi$-(3)-1,2-$B_9C_2H_{10}S(C_2H_5)_2]Fe^{II}$ in acetone solution; reference $BF_3 \cdot OEt_2$ = 0.00 ppm.

No color change was observed upon acidification of solutions containing the bis(dicarbollyl)cobalt(III) anion, and numerous attempts to prepare and isolate the isoelectronic $Co^{III}$ analog of protonated bis(dicarbollyl)iron(II) have been fruitless. We have, however, found it possible to carry out substitution reactions on the cobalt complex under the strongly acidic conditions in which the protonated iron(II) derivative is formed. Thus, the neutral species $Co(B_9C_2H_{11})[B_9C_2H_{10}S(C_2H_5)_2]$ (IV) was prepared by passing anhydrous hydrogen chloride into a diethyl sulfide suspension of the $Co(B_9C_2H_{11})_2^-$ ion, eq 3. Analytical and spectroscopic data obtained for this substance are presented in Tables I–V. Similar treatment of bis(dicarbollyl)iron(III) salts produced a mixture of products. When a suspension of $CsFe(B_9C_2H_{11})_2$ in diethyl sulfide was heated in the presence of anhydrous hydrogen chloride, the major product recovered upon column chromatography was the monosubstituted $Fe^{III}$ compound mentioned above, $Fe(B_9C_2H_{11})[B_9C_2H_{10}S(C_2H_5)_2]$ (III). In addition, a small amount of an uncharged $Fe^{II}$ complex, $Fe[B_9C_2H_{10}S(C_2H_5)_2]_2$ (V), was also isolated from the reaction mixture as bright purple, air- and water-stable rhombs. Several other crystalline compounds have been isolated as well, but in yields too small to adequately characterize.

$$[Co(B_9C_2H_{11})_2]^- + HCl + (C_2H_5)_2S \longrightarrow \{Co(B_9C_2H_{11})[B_9C_2H_{10}S(C_2H_5)_2]\}^0 + H_2 + Cl^- \quad (3)$$

The disubstituted $Fe^{II}$ complex, V, was electrochemically oxidized in acetonitrile solution to afford what appears to be the first cationic bis(dicarbollyl)metalate, the $\{[B_9C_2H_{10}S(C_2H_5)_2]_2Fe^{III}\}^+$ ion (VI), which could be isolated as the perchlorate salt. This compound was a shock-sensitive red solid and gave poor elemental analyses. Attempts to purify this salt, or to isolate different salts by use of other supporting electrolytes, resulted in severe decomposition of the cation. Owing to the small amount of starting material available, this work was not pursued further.

The structural conclusions which can be drawn with regard to this series of B-substituted compounds are primarily derived from their nmr spectra. The 80-MHz $^{11}B$ nmr spectrum of the monosubstituted $Fe^{II}$ derivative, $\{Fe(B_9C_2H_{11})[B_9C_2H_{10}S(C_2H_5)_2]\}^-$ (II) (R = $C_2H_5$), is shown in Figure 4 and exhibits a low-field singlet resonance of relative area one (+6.7 ppm relative to $BF_3 \cdot OEt_2$), confirming that substitution had occurred on a boron atom of the ligand. The 60-MHz $^{1}H$ nmr spectrum of the triphenylmethylphosphonium salt of II (R = $C_2H_5$) in acetone solution was

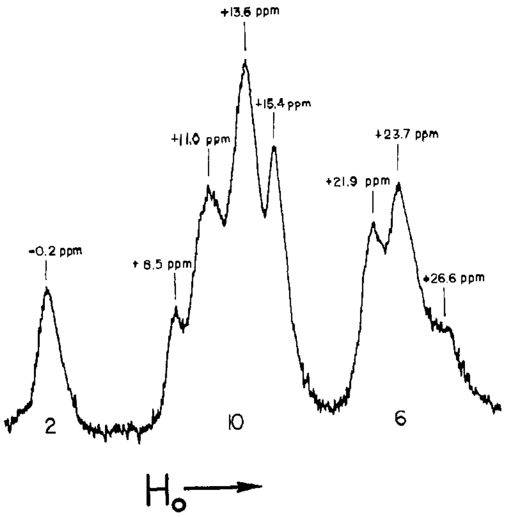

Figure 5. $^{11}$B nmr spectrum (80 MHz) of [π-(3)-1,2-$B_9H_{10}S(C_2H_5)_2]_2Fe^{II}$ in dichloromethane solution; reference $BF_3 \cdot OEt_2$ = 0.00 ppm.

complicated by overlap of ligand and cation resonances, but integral ratios indicated the presence of four carborane CH units in this compound.

The neutral, diamagnetic, air-stable $Co(B_9C_2H_{11})[B_9C_2H_{10}S(C_2H_5)_2]$ (IV) was much more structurally informative, for its $^1$H nmr spectrum was not complicated by overlapping resonances. At 60 MHz in benzene solution, this complex exhibited two equal-intensity (weight two each) broad singlet resonances at −3.17 and −2.74 ppm (relative to internal tetramethylsilane), which were assigned to carborane CH groups on the substituted and unsubstituted ligands. The observation of only a single carborane CH resonance for the substituted ligand indicated that the diethyl sulfide is substituted on one of the unique boron atoms in the ligand, for the equivalence of the CH groups is maintained after substitution. Other signals observed included a sharp triplet resonance at −0.73 ppm of relative intensity 6, assigned to the methyl group of the diethyl sulfide, and a complex multiplet centered at −2.17 ppm, relative area 4, attributed to the methylene protons of the ethyl groups. The methylene protons were magnetically nonequivalent and were further split by the three methyl protons, thereby generating an $ABC_3$ multiplet.[13,14] Confirmation of this assignment was effected by decoupling the methyl protons at 100 MHz; the multiplet collapsed into a typical four-line AB pattern. A low-field singlet resonance of relative intensity 1 (∼−5.7 ppm) was observed in the $^{11}$B nmr spectrum of IV in benzene solution and was assigned to the alkyl sulfide substituted boron atom.

The $^{11}$B nmr spectrum of $Fe^{II}[B_9C_2H_{10}S(C_2H_5)_2]_2$ (V) in dichloromethane solution at 80 MHz (Figure 5) contained a low-field singlet resonance at −0.2 ppm of relative intensity 2, assigned to the diethyl sulfide substituted boron atoms of each ligand. The remainder of the spectrum consisted of overlapping doublet resonances of total relative intensity 16 and was structurally uninformative. The 60-MHz $^1$H nmr spectrum of V in dichloromethane solution exhibited one broad singlet at −3.48 ppm of relative intensity 4, assigned to the equivalent carborane CH resonances. The observation of only one signal for these protons indicated symmetrical and identical substitution on each of the dicarbollide ligands. A multiplet, relative intensity 8, and a well-resolved triplet, relative intensity 12, were respectively assigned to the methylene and methyl protons of the coordinated diethyl sulfides. Spin decoupling at 100 MHz confirmed this assignment; the multiplet collapsed to a normal AB pattern upon irradiation of the methyl triplet.

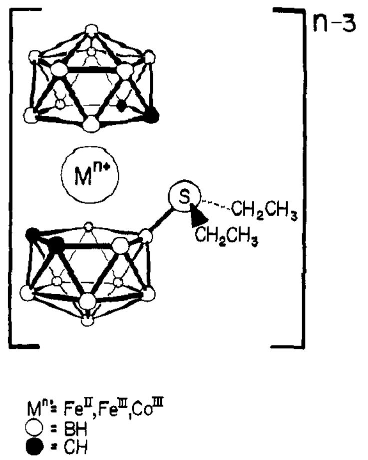

Figure 6. Proposed structures of {[π-(3)-1,2-$B_9C_2H_{11}$][π-(3)-1,2-$B_9C_2H_{10}S(C_2H_5)_2]M^{n+}\}^{n-3}$; M = $Fe^{II}$, $Fe^{III}$, $Co^{III}$.

The mechanism of formation of these B-substituted derivatives may best be described as an acid-catalyzed nucleophilic substitution[12] in which H$^+$ effects removal of a hydride ion, generating a position for nucleophilic attack. However, the nature of the intermediate in the reaction is unknown. Not only could compound I function as the intermediate, whether the proton be bound to boron or metal, but there could also be an equilibrium set up between I and dialkyl sulfide, as in eq 4, in which the dialkyl sulfide is protonated by I

$$\begin{array}{l} R_2S + [HFe^{II}(B_9C_2H_{11})_2]^- \rightleftharpoons R_2S^+H + [Fe^{II}(B_9C_2H_{11})_2]^{2-} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad H_2 + [Fe^{II}(B_9C_2H_{11})(B_9C_2H_{10}SR_2)] \end{array} \quad (4)$$

and the protonated sulfide attacks and substitutes on the cage electrophilically. This latter mechanism is similar to that proposed[4a] for the reaction of $CS_2$ with $[(B_9C_2H_{11})_2Co]^-$, in which substitution occurs[4b] on boron atom 8 (Figure 1).

We tentatively suggest that these new B-substituted compounds have the structure shown in Figure 6, in which substitution has occurred at boron atom 8. In all cases reported here, nmr data indicated that substitution takes place on ligand boron atoms while the carborane CH groups on the substituted ligands remain equivalent; boron atoms 6, 8, or 10 (Figure 1) are the only ones which can fulfill this condition. Position 6 is adjacent to the relatively electron-deficient carbon atoms and would not be expected to be the site of electrophilic substitution, if that is the correct mechanism. Position 10 was considered unlikely since bromination of the $(B_9C_2H_{11})_2Co^-$ ion[1] in glacial acetic acid has been shown to form a hexabromo deriv-

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(14) M. van Gorkom and G. E. Hall, *Quart. Rev., Chem. Soc.*, **22**, 14 (1968).

ative in which substitution occurred in the 8, 9, and 12 positions of each ligand.[15] The possibility of metal participation in electrophilic reactions of these bis(dicarbollyl)metalates, as proposed in Friedel–Crafts acetylation of ferrocene,[16] lends support to substitution at boron atom 8, which lies adjacent to the metal atom in the bonding $B_3C_2$ face of the dicarbollide ligand. Studies on the similarities between the chemistry of ferrocenes and of bis(dicarbollyl)metalates are in progress and will be reported in a subsequent communication.

## Experimental Section

**Physical Measurements.** Ultraviolet–visible spectra were measured with either a Cary Model 14 or a Beckman Model DB spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Routine proton nmr spectra were obtained by means of Varian A-60 or A-60D spectrometers, and $^{11}B$ nmr spectra were obtained at 32.1 MHz on a Varian HA-100 spectrometer and at 80.5 MHz on a spectrometer constructed by Professor F. A. L. Anet of this department. Controlled-potential cyclic voltammetry was carried out using an instrument based on the design of Lawless and Hawley.[17] Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

**Preparation of $(C_6H_5)_3PCH_3[(B_9C_2H_{11})_2FeH]$. (a) Perchloric Acid Method.** $Cs_2Fe^{II}(B_9C_2H_{11})_2$[2] (1.0 g, 1.71 mmol) was added to a solution of degassed perchloric acid (70%, 5.5 ml) in degassed anhydrous methanol (50 ml) and cooled to 0°. The resultant reddish orange mixture was stirred at 0° for 15 min and then filtered free of $CsClO_4$ in a Schlenk-tube apparatus.[18] Solid triphenylmethylphosphonium bromide (0.60 g, 1.68 mmol) was then added, with stirring, to the cold filtrate. A deep orange crystalline solid was obtained. After several hours at 0°, the product was filtered, washed with degassed anhydrous methanol, and dried *in vacuo* to afford 0.60 g (58.5%) of pure $[(C_6H_5)_3PCH_3](B_9C_2H_{11})_2FeH$, mp 180–182° dec.

**(b) Hydrochloric Acid Method.** $Cs_2Fe^{II}(B_9C_2H_{11})_2$ (0.50 g, 0.85 mmol) was added to a solution of degassed concentrated hydrochloric acid (5 ml) in degassed anhydrous methanol (50 ml) and cooled to 0°. Nearly all of the solid dissolved to give a cherry-red solution which was stirred at 0° for 15 min. Traces of undissolved starting material were filtered off and solid triphenylmethylphosphonium bromide (0.3 g, 0.84 mmol) was added, with stirring, to the cold filtrate. The resultant orange precipitate was filtered off, washed with degassed anhydrous methanol, and dried *in vacuo;* yield 0.28 g (0.47 mmol, 55%).

This compound is stable for short periods of time in rigorously dried and degassed acetonitrile, and may be recrystallized from this solvent, if accomplished rapidly. Because of this instability, spectral measurements were conducted on freshly prepared solutions containing the $HFe(B_9C_2H_{11})_2^-$ ion in methanol–perchloric acid, which were found to exhibit significantly longer lifetimes.

**Reaction of the $(B_9C_2H_{11})_2FeH^-$ Ion with Alkyl Sulfides. Reaction with Dimethyl Sulfide.** Solid $[(C_6H_5)_3PCH_3](B_9C_2H_{11})_2FeH^{II}$ (2.02 g, 3.37 mmol) was placed in a tubular container fitted with two arms, one with a constriction and other with a breakseal. The container was attached to the vacuum line by the former arm and evacuated. Dimethyl sulfide (60 ml), which had been degassed several times *in vacuo*, was distilled onto the solid reactant, which was held at −196°. When distillation was complete, the vessel was sealed off, removed from the vacuum line, allowed to warm to room temperature, and then heated with frequent shaking in an oil bath to 65–75°. After about 30 min, deep pink crystals began to deposit from the dark red, refluxing solution. After 1.5 hr, the reaction mixture was cooled to room temperature and let stand overnight. The reaction vessel was connected to a vacuum line equipped with a toepler pump, the breakseal opened, and the pressure of evolved hydrogen measured (Table I). The reaction mixture was filtered through a Schlenk unit[18] and the deep pink crystals of $(C_6H_5)_3PCH_3Fe^{II}(B_9C_2H_{11})(B_9C_2H_{10}SMe_2)$ were washed with degassed dimethyl sulfide and dried *in vacuo* overnight; yield 1.78 g (2.70 mmol, 80%), mp 215–217° dec. Further purification was achieved by column chromatography on a 3-in. silica gel column using dichloromethane to elute the product. Addition of hexane to the pink $CH_2Cl_2$ fraction afforded pink plates, mp 219–220° dec.

Similar methods were employed in the preparations of the diethyl sulfide and di-*n*-propyl sulfide derivatives. Analytical and spectral data are presented in Tables I–V.

**Oxidation of $(C_6H_5)_3PCH_3Fe^{II}(B_9C_2H_{11})(B_9C_2H_{10}SEt_2)$ with Anhydrous Ferric Chloride.** A solution of $(C_6H_5)_3PCH_3Fe^{II}(B_9C_2H_{11})(B_9C_2H_{10}SEt_2)$ (2.50 g, 3.64 mmol) in dichloromethane (125 ml) was added, under nitrogen, to solid, anhydrous ferric chloride (0.60 g, 3.70 mmol), and the resultant dark red mixture shaken for 10 min. Hexane (100 ml) was then added and the mixture was filtered. The deep red filtrate was evaporated to dryness *in vacuo* onto silica gel, and the solid placed on a 3-in. silica gel column and eluted with 1:1 dichloromethane–hexane. The main fraction, deep red, was deposited onto silica gel by evaporation and again chromatographed, this time on a 14-in. column, using 3:1 benzene–hexane to elute the products. The main fraction, deep red, eluted first, and evaporation afforded a dark red crystalline solid. Recrystallization from dichloromethane–hexane afforded lustrous dark red crystals of $Fe^{III}(B_9C_2H_{11})(B_9C_2H_{10}SEt_2)$ (0.87 g, 58%), mp 227–228°. Recrystallization from boiling 1:1 benzene–hexane gave dark red plates, mp 238–239°. Similar techniques were employed in the preparation of the $Fe^{III}$ derivatives with dimethyl and di-*n*-propyl sulfides. Analytical and spectral data are presented in Tables I–V.

**Preparation of $Fe^{II}(B_9C_2H_{10}SEt_2)_2$.** $CsFe^{III}(B_9C_2H_{11})_2$[2] (3.5 g) was suspended in 100 ml of diethyl sulfide and HCl gas was bubbled through the suspension for 2 hr. This mixture was allowed to stand overnight and the precipitated CsCl was filtered off the next day. Extraction of the filtered material with acetone and evaporation afforded 1.5 g of unreacted starting material. The filtrate was heated on a steam bath with shaking for 1 hr, the mixture was transferred to a rotary evaporator, silica gel was added to the flask, and the products were taken to dryness *in vacuo*.

The reaction products, now deposited on silica gel, were added to a 1 × 18-in. silica gel chromatography column and elution was commenced with 3:7 benzene:hexane. The first band contained a very small amount of orange product, which was not characterized, and was closely followed by a red band, which after crystallization was identified as $Fe^{III}(B_9C_2H_{11})(B_9C_2H_{10}SEt_2)$ by comparison with an authentic sample prepared as previously described. After this band had been collected, the eluting solvent was changed to pure benzene, and another red band was eluted from the column. This fraction was stripped to dryness and dissolved in dichloromethane. A small amount of heptane was added, and the solvent was slowly removed *in vacuo* until crystallization commenced. Cooling for several hours afforded large purple rhombs of $Fe^{II}(B_9C_2H_{10}SEt_2)_2$. Analytical and spectral data are presented in Tables II–VI.

**Preparation of $Co^{III}(B_9C_2H_{11})(B_9C_2H_{10}SEt_2)$.** The method of preparation of $Co^{III}(B_9C_2H_{11})(B_9C_2H_{10}SEt_2)$ was identical with that described above for the preparation of $Fe^{II}(B_9C_2H_{10}SEt_2)_2$. The first chromatographic fraction, eluted with 50:50 hexane:benzene, contained the majority of product and was recrystallized from dichloromethane–heptane to afford pure $Co^{III}(B_9C_2H_{11})(B_9C_2H_{10}SEt_2)$. Analytical and spectroscopic data are presented in Tables II–VI.

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