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THE CHEMISTRY OF SOME METALLOBORANE DERIVATIVES HAVING IRON—BORON SINGLE BONDS

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Summary

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{cyclohexene})]PF_6$ with $B_{10}H_{13}^-$ and $7,8\text{-}B_9C_2H_{12}^-$ forms $6\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_{10}H_{13}$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}(7,8\text{-}B_9C_2H_{12})$ respectively which have iron—boron single bonds. The reactions of these compounds with bromine and with Lewis bases such as trialkylamines, CH_3CN and Ph_3P are described.

Introduction

We have recently reported the syntheses of a number of new heteroatom borane metal complexes formed by reaction of cationic transition metal complexes of molydenum and iron with heteroatom borane anions [1]. This paper describes the syntheses and some chemistry of the complexes $6\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_{10}H_{13}$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2B_9H_{10}C_2R_2$ (R=H, CH_3).

Experimental

General comments

Boron (^{11}B) NMR (Table 3, at 70.6 MHz) and ^1H NMR spectra (Table 2) were obtained with a Varian HR-220 spectrometer. The boron spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$. The ^{13}C NMR spectrum was obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.1 MHz. The ^{13}C chemical shifts were measured relative to internal acetone and reported relative to tetramethylsilane using the conversion factor $\delta(TMS) = \delta[(CH_3)_2CO] + 30.43$ ppm.

Elemental analyses (Table 1) were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York or Midwest Microanalytical Laboratories, Indianapolis, Indiana. Infrared spectra (Table 4) were recorded

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TABLE 1

CHEMICAL ANALYSES

Compound	Analysis found (calcd.) (%)	
	C	H
6-[(η^5-C_5H_5)Fe(CO)$_2$]$B_{10}H_{13}$ (I)	28.0 (28.2)	5.9 (6.0)
(η^5-$C_5H_4B_{10}H_{13}$)Fe(CO)$_2$Br (II)	22.8 (22.3)	4.6 (4.5)
(η^5-C_5H_5)Fe(CO)$_2$[7,8-$B_9H_{10}C_2(CH_3)_2$] (IV)	35.2 (34.8)	6.0 (5.5)
(η^5-C_5H_5)Fe(CO)$_2$[7,8-$B_9H_{10}C_2(CH_3)_2$] (IV)	39.1 (39.3)	6.2 (6.3)
$(CH_3)_4N$[(η^5-C_5H_5)Fe(CO)$_2$(7,8-$B_9C_2H_{11}$)] (V)	39.9 (40.7)	7.9 (7.3)
[(η^5-C_5H_5)Fe(CO)$_2CH_3CN$](7,8-$B_9C_2H_{12}$) (VI)	37.2 (37.3)	5.9 (5.7)
[(η^5-C_5H_5)Fe(CO)($CNC_6H_{11})_2$](7,8-$B_9C_2H_{12}$) (VII)	51.9 (52.8)	7.4 (7.8)

as KBr disks using a Perkin–Elmer 137-G instrument. Low resolution mass spectra were obtained with an Atlas CH-7 instrument.

Starting materials

Dicarbonyl(cyclohexene)cyclopentadienyliron hexafluorophosphate was prepared by the method of Fischer and Moser [2]. The synthesis of [(η^5-C_5H_5)-Fe(CO)$_2CH_3CN$]PF_6 was accomplished employing the procedure of Williams and Lalor [3]. The procedure of Hawthorne and coworkers was used to prepare $(CH_3)_3NH[7,8\text{-}B_9C_2H_{12}]$ [4].

TABLE 2

^1H NMR SPECTRA

Compound	Chemical shift τ (ppm)	Assignment
I	4.94, singlet	C_5H_5 group
	11.60, broad singlet	B—H—B bridge hydrogens
II	4.33, triplet	substituted C_5H_5 group
	5.45, triplet	
III	4.42, singlet	C_5H_5 group
	7.78, broad singlet	carborane CH groups
	8.05, broad singlet	
	13.42, broad singlet	B—H—B bridge hydrogens
IV	4.40, singlet	C_5H_5 group
	8.49, singlet	CH_3 groups
	8.84, singlet	
	12.92, broad singlet	B—H—B bridge hydrogens
V	5.35, singlet	C_5H_5 group
	6.63, singlet	$N(CH_3)_4$ group
	10.28, broad singlet	B—H—B bridge hydrogen

TABLE 3

^{11}B NMR SPECTRA (70.6 MHz)

Compound	Feature	Chemical shift (ppm (*J*, Hz))	Relative area
I[a]	singlet	−40.8	1
	doublet	−11.9 (150)	2
	doublet	−7.2 (160)	1
	doublet	−0.7 (150)	4
	doublet	30.5 (150)	1
	doublet	38.2 (150)	1
II[b]	singlet	−22.7	1
	doublet	−11.8 (140)	3
	doublet	−3.3 (150)	2
	doublet	1.7 (150)	2
	doublet	29.3 (150)	1
	doublet	35.1 (151)	1
III[a]	doublet	1.8 (150)	1
	doublet	9.8 (150)	1
	doublet	17.4[c]	2
	doublet	21.4[c]	1
	doublet	24.0 (150)	2
	doublet	33.6[c]	1
	singlet	34.8	1
IV[a]	doublet	3.8[c]	1
	doublet	6.0[c]	1
	doublet	9.6 (170)	1
	doublet	15.1[c]	1
	doublet	16.6[c]	1
	doublet	23.6 (140)	2
	singlet	32.0	1
	doublet	33.3[c]	1
V[b]	singlet	−1.4	1
	doublet	11.2 (130)	2
	doublet	15.1[c]	1
	doublet	17.1[c]	1
	doublet	20.3[c]	1
	doublet	22.4[c]	1
	doublet of doublets	28.9 (130)	1
	doublet	36.0 (140)	1
VI[a]	doublet	10.5 (135)	2
	doublet	16.4 (115)	3
	doublet	21.5 (140)	2
	doublet of doublets	32.4 (115)	1
	doublet	37.4 (130)	1

[a] Methylene chloride solvent. [b] Acetone solvent. [c] Coupling constant could not be obtained due to overlap of resonances.

TABLE 4

INFRARED SPECTRA

Compound	Wave number (cm^{-1})[a]
I	3100w, 2900w, 2590vs, 2545vs, 2000vs, 1955vs, 1450w, 1090w, 1020m, 950w, 892m, 850s, 818m, 775w
II	3080w, 2980w, 2595vs, 2550vs, 2050vs, 2000vs, 1465w, 1390m, 1250m, 1000w, 850s, 808m
III	3110w, 2985w, 2550vs, 2520vs, 2060vs, 2000vs, 1440s, 1400(sh), 1085w, 1060w, 1035(sh), 1020s, 1000(sh), 990w, 853s, 800m
IV	3100w, 2980w, 2550vs, 2060vs, 2005vs, 1450w, 1420w, 1260w, 1018s, 865s, 800m
V	3150w, 2900w, 2515vs, 1965vs, 1900vs, 1498s, 1425m, 1270w, 1108w, 1080m, 1045m, 1008m, 960s, 830s, 750m
VI	3085w, 2980w, 2950w, 2510vs, 2080vs, 2040vs, 1420s, 1080m, 1025s, 855s, 800m
VII	3100w, 2970w, 2850s, 2800m, 2510vs, 2200vs, 2180vs, 2150s, 2005vs, 1465s, 1440m, 1370s, 1360m, 1340s, 1330m, 1025s, 865s

[a] Obtained as KBr disk.

(η^5-C_5H_5)Fe(CO)$_2$$B_{10}H_{13}$ (I)

Treatment of $B_{10}H_{14}$ (0.134 g, 1.1 mmole) with sodium hydride (0.024 g, 1.0 mmole) in 30 ml diethyl ether at room temperature generated $NaB_{10}H_{13}$ after stirring for 0.5 h. To this solution was added [(η^5-C_5H_5)Fe(CO)$_2$(cyclohexene)]PF_6 (0.33 g, 0.82 mmole) and the mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum and the residue chromatographed on a silica gel column with CH_2Cl_2 as eluent yielding a fast moving yellow band. This material was crystallized from CH_2Cl_2/hexane to give 0.098 g (40% yield) of (η^5-C_5H_5)Fe(CO)$_2$$B_{10}H_{13}$ which decomposed above 153°C. The elemental analysis of this compound is given in Table 1 and the infrared spectral data in Table 4.

(η^5-$C_5H_4B_{10}H_{13}$)Fe(CO)$_2$Br (II)

A solution of bromine (0.04 g, 0.25 mmole) in 5 ml of CH_2Cl_2 was added dropwise to a solution of (η^5-C_5H_5)Fe(CO)$_2$$B_{10}H_{13}$ (0.067 g, 0.22 mmole) in 45 ml CH_2Cl_2 maintained at about −20°C. After addition, the mixture was stirred at 0°C for 20 minutes and then at room temperature for another 0.5 h. The solvent was removed under vacuum and the residue crystallized from CH_2Cl_2/hexane to give 0.081 g (96% yield) of red-brown (η^5-$C_5H_4B_{10}H_{13}$)Fe(CO)$_2$Br, m.p. 144-145°C (dec.).

$(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{12})$ (III)

A solution containing $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{cyclohexene})]PF_6$ (0.40 g, 1 mmole) and $(CH_3)_3NH[7,8\text{-}B_9C_2H_{12}]$ (0.25 g, 1.29 mmole) in 50 ml acetone was stirred at reflux for 1 h. The solution was evaporated to dryness under vacuum and the residue chromatographed on a silica gel column. Elution with CH_2Cl_2 gave a fast moving red-orange band which was evaporated to dryness and crystallized from CH_2Cl_2/hexane to give 0.28 g (90% yield) of red-brown $(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{12})$ which decomposed above 155°C.

Using the same procedure red $(\eta^5\text{-}C_5H_5)Fe(CO)_2[7,8\text{-}B_9H_{10}C_2(CH_3)_2]$ (IV) was obtained in 85% yield. This compound decomposed above 170°C.

$(CH_3)_4N[(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{11})]$ (V)

Trimethylamine was bubbled into a solution of III (0.20 g, 0.65 mmole) in 20 ml of CH_2Cl_2 at room temperature. The color of the solution changed rapidly from red to yellow. The solvent was removed under vacuum and the residue was washed with water and this gave 0.21 g (88% yield) of impure $(CH_3)_3NH[(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{11})]$. The trimethylammonium salt (0.15 g, 0.41 mmole) was dissolved in 20 ml of methanolic 0.045 *N* KOH solution and the mixture was allowed to stand at room temperature for 1 h. The solvent was removed under vacuum. The residue was dissolved in 80 ml of water and this solution added thru a filter to 20 ml of saturated aqueous tetramethylammonium chloride solution. This gave a yellow precipitate which was collected and crystallized from acetone/H_2O to give 0.138 g (88% yield) of yellow $(CH_3)_4N[(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{11})]$ which decomposed above 170°C.

Reaction of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2(B_9C_2H_{11})]$ and HCl

Treatment of $(CH_3)_3NH[(\eta^5\text{-}C_5H_5)Fe(CO)_2B_9C_2H_{11}]$ (0.10 g, 0.27 mmole) with KOH (0.045 g, 0.80 mmole) in 20 ml of methanol generated the potassium salt which was isolated by removing the solvent under vacuum. The salt was dissolved in 30 ml of H_2O and 20 ml of CH_2Cl_2 added to the solution. This two layer system was treated with 10 ml of 1 *N* aqueous HCl and shaken. Very rapidly the CH_2Cl_2 layer became red. The CH_2Cl_2 layer was separated and the solvent removed under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2 as eluent and crystallized from CH_2Cl_2/hexane to give 0.05 g (59% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{12})$ which shows the same infrared and ^{11}B NMR spectra as the authentic sample.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3CN](7,8\text{-}B_9C_2H_{12})$ (VI)

(Method a). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{12})$ (0.14 g, 0.45 mmole) in 30 ml of CH_3CN was refluxed for 1 h at which point the solution was green-yellow in color. The solvent was removed under vacuum and the residue crystallized from CH_2Cl_2/hexane to give 0.151 g (96% yield) of yellow $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3CN](7,8\text{-}B_9C_2H_{12})$, m.p. 134-136°C (dec.).

In a similar manner III was treated with PPh_3 in benzene at reflux for 1 h to form $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3](7,8\text{-}B_9C_2H_{12})$ in 94% yield.

(Method b). A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3CN]PF_6$ (0.32 g, 0.88 mmole) and $[HN(CH_3)_3](7,8\text{-}B_9C_2H_{12})$ (0.23 g, 1.2 mmole) in 50 ml of acetone was refluxed for 3 h. The solvent was removed under vacuum and the residue crystallized from CH_2Cl_2/hexane to give 0.284 g (92% yield) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3CN](7,8\text{-}B_9C_2H_{12})$.

$[(\eta^5\text{-}C_5H_5)Fe(CO)(CNC_6H_{11})_2](7,8\text{-}B_9C_2H_{12})$ *(VII)*

A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(7,8\text{-}B_9C_2H_{12})$ (0.200 g, 0.65 mmole) and CNC_6H_{11} (1 g, 9.2 mmole) in 30 ml of benzene was refluxed for 1 h. The solvent was removed under vacuum and the residue crystallized from CH_2Cl_2/hexane to give 0.29 g (89% yield) of yellow $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNC_6H_{11})_2](7,8\text{-}B_9C_2H_{12})$ m.p. 150-152°C. The ^{13}C NMR (acetone solvent) δ 212.6 (CO), 148.8 [$\underline{C}$N(cyclohexyl)], 85.8 (C_5H_5), 56.7 (C(1) of cyclohexyl group), 41.8 (carborane carbons, broad), 32.7, 25.3 and 23.1 ppm (C(2), C(3), C(4) of cyclohexyl group).

Results and discussion

Chemistry of the $B_{10}H_{13}^-$ *ligand*

In a previous report of the reaction of the cationic complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]BPh_4$ with sodium borohydride the final product of the reaction was found to be $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ [5]. It was assumed that the product was formed by the sequence of reactions 1 and 2. It was therefore interesting to find that

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_3]BPh_4 + NaBH_4 \rightarrow$$
$$(\eta^5\text{-}C_5H_5)Fe(CO)_2H + CO + NaBPh_4 + BH_3 \quad (1)$$

$$2(\eta^5\text{-}C_5H_5)Fe(CO)_2H \rightarrow H_2 + [(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \quad (2)$$

treatment of an ether solution of $NaB_{10}H_{13}$ with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{cyclohexene})]PF_6$ at room temperature formed yellow $6\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_{10}H_{13}$ (I) in 40% yield. In addition to the elemental analysis (Table 1) which supports this formula, the low resolution mass spectrum cuts off at *m/e* 301 corresponding to the $[^{12}C_6{}^{13}C_1{}^{1}H_{18}{}^{11}B_{10}{}^{16}O_2{}^{56}Fe_1]^+$ parent ion. The ^1H NMR spectrum of I contains a singlet at τ 4.94 ppm and a broad peak at τ 11.6 ppm which can be assigned to the cyclopentadienyl and B—H—B bridge protons respectively. The 70.6 MHz ^{11}B NMR spectrum of I exhibits a 1/2/1/4/1/1 pattern of resonances reading from low to high field (see Table 3). The chemical shift pattern of I is quite similar to that of 6-isothiocyanodecaborane [6], 6-benzyldecaborane [7] and 6-phenyldecaborane [7]. The very low field position of the iron-substituted boron resonance (−40.8 ppm) is noteworthy. Thus the available data are consistent with our proposal that an iron—boron single bond has been formed at B(6) of the decaborane cage as illustrated in Fig. 1.

In an attempt to break the iron—boron bond and form $6\text{-}BrB_{10}H_{13}$, I was treated with bromine at −20°C which formed $(\eta\text{-}C_5H_4B_{10}H_{13})Fe(CO)_2Br$ (II) in high yield. This formula was supported by the elemental analysis and the low resolution mass spectrum which cut off at *m/e* 381 corresponding to the $[^{12}C_6{}^{13}C_1{}^{1}H_{17}{}^{11}B_{10}{}^{16}O_2{}^{81}Br_1{}^{56}Fe_1]^+$ parent ion. This interesting type of rearrangement has been observed previously in reaction 3, where the substitution is at B(3) of the carboranyl group [8]. The ^1H NMR spectrum of II contained two triplet signals of equal intensity at τ 4.33 and 5.45 ppm which is characteristic

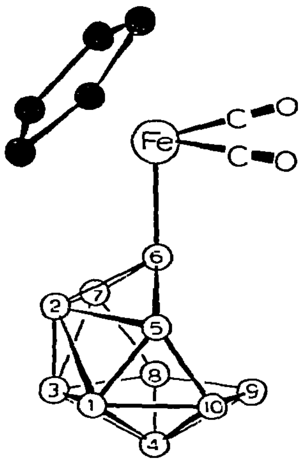
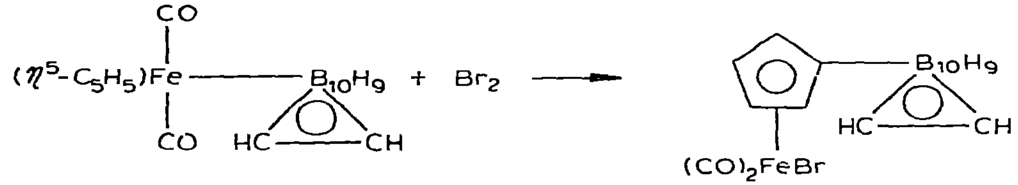


Fig. 1. Proposed structure for 6-[(η^5-C_5H_5)Fe(CO)$_2$]$B_{10}H_{13}$ (terminal and bridge hydrogen atoms have been omitted for clarity).

of a monosubstituted-*pentahapto*-cyclopentadienyl ring. The ^{11}B NMR spectrum of II exhibited a 1/3/2/2/1/1 pattern, reading from low to high field, which is similar to that of compound I. In this case the singlet resonance attributed to the cyclopentadienyl-substituted boron atom is at −22.7 ppm. We suggest that the carbon—boron single bond in II has been formed at B(6) of the decaborane cage which is consistent with the available data.



(3)

Treatment of compound I in benzene with triethylamine at room temperature rapidly forms dimeric [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ in high yield. The only boron compound we could isolate was [$(C_2H_5)_3NH$)]$_2B_{10}H_{10}$ which was obtained in about 10% yield.

Chemistry of the 7,8-$B_9H_{10}C_2R_2^-$ ligand (R = H or CH_3)

There have been several previous reports concerning the synthesis of (η^5-C_5H_5)Fe(CO)$_2$(carborane) derivatives. Treatment of (η^5-C_5H_5)Fe(CO)$_2$I with 1-Li-2-CH_3-1,2-$C_2B_{10}H_{10}$ or 1-Li-10-CH_3-1,10-$C_2B_8H_8$ afforded 1-[(η^5-C_5H_5)Fe(CO)$_2$]-2-CH_3-1,2-$C_2B_{10}H_{10}$ or 1-[(η^5-C_5H_5)Fe(CO)$_2$]-10-CH_3-1,10-$C_2B_8H_8$ respectively [9]. These are derivatives containing an iron—carbon single bond. Treatment of (η^5-C_5H_5)Fe(CO)$_2$I with the [2,3-$C_2B_4H_7$]$^-$ ion generated (η^5-C_5H_5)Fe(CO)$_2$(2,3-$C_2B_4H_7$) in which a B—Fe—B three-center two-electron bond was proposed based on available ^{1}H and ^{11}B NMR data [10].

We have found that treatment of $(CH_3)_3NH$[7,8-$B_9H_{10}C_2R_2$] (R = H or CH_3) at reflux in acetone solution with [(η^5-C_5H_5)Fe(CO)$_2$(cyclohexene)]PF_6 forms (η^5-C_5H_5)Fe(CO)$_2$(7,8-$B_9H_{10}C_2H_2$) (III) and (η^5-C_5H_5)Fe(CO)$_2$[7,8-$B_9H_{10}C_2(CH_3)_2$] (IV) in 90 and 85% yields respectively. The low resolution

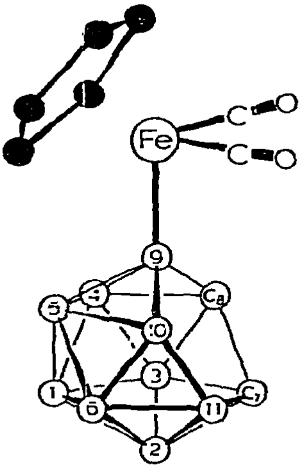


Fig. 2. Proposed structures for 9-[(η^5-C_5H_5)Fe(CO)$_2$]-7,8-$B_9C_2H_{12}$ and {9-[(η^5-C_5H_5)Fe(CO)$_2$]-7,8-$B_9C_2H_{11}$}$^-$ (terminal and bridge hydrogen atoms have been omitted for clarity).

mass spectrum of III cut off at *m/e* 313 which corresponds to the $[^{12}C_8{}^{13}C_1{}^1H_{17}{}^{11}B_9{}^{16}O_2{}^{56}Fe_1]^+$ parent ion. The presence of two broad singlet resonances in the ^{1}H NMR spectrum for the carborane CH protons of III and two CH_3 signals in the ^{1}H NMR spectrum of IV suggests that the η^5-C_5H_5Fe(CO)$_2$ moiety is attached to the carborane framework in these molecules at a position which is off the mirror plane of the cage. The ^{11}B NMR spectra of III and IV exhibit high field singlets which can be attributed to the iron-bonded boron atoms. The ^{11}B NMR spectra of III and IV appear to be like the ^{11}B NMR spectrum of $B_9C_2H_{13}$ which has been reported previously [11]. The ^{11}B NMR spectrum of 7,8-$B_9C_2H_{13}$ exhibits secondary splitting of a doublet at high field due to spin coupling with the bridge hydrogens [11]. This resonance can be assigned to the boron atoms in the open face of the carborane cage which are adjacent to the carbon atoms [B(9), B(11) in Fig. 2]. Application of proton bridge decoupling to the ^{11}B NMR spectrum of III indicated that the singlet resonance at 34.8 ppm experiences proton spin—spin splitting due to the proximity of a bridge hydrogen. Thus it is seen that the ^{11}B NMR spectra of 7,8-$B_9C_2H_{13}$, III and IV have certain interesting similarities.

Like 7,8-$B_9C_2H_{13}$ which can be readily deprotonated, we have found that III upon treatment with trimethylamine readily forms the trimethylammonium salt of {[(η^5-C_5H_5)Fe(CO)$_2$]-7,8-$B_9C_2H_{11}$}$^-$. This salt was converted to $(CH_3)_4N$[(η^5-C_5H_5)Fe(CO)$_2$(7,8-$B_9C_2H_{11}$)] (V) because it was easier to characterize by elemental analysis (see Table 1). In addition we found that treatment of K[(η^5-C_5H_5)Fe(CO)$_2$(7,8-$B_9C_2H_{11}$)] with aqueous HCl in an H_2O/CH_2Cl_2 two-layer medium rapidly reformed red III in the CH_2Cl_2 layer.

The ^{11}B NMR spectrum of V has the characteristic pattern of a boron-substituted 7,8-$B_9C_2H_{12}^-$ ion. The doublet of doublets resonance centered at 28.9 ppm is due to the boron atom on the open face of the carborane cage which is not adjacent to a carbon atom as has been determined by a previous ^{11}B NMR study [11]. The presence of eight observable resonances in the ^{11}B NMR spectrum of V indicates that substitution of the (η^5-C_5H_5)Fe(CO)$_2$ group is at a position off the mirror plane of the carborane cage. Thus analysis of the ^{11}B NMR spectra of both III and its deprotonation product V lead us to propose that these complexes are best described as substituted 7,8-$B_9C_2H_{13}$ and 7,8-$B_9C_2H_{12}^-$ derivatives respectively in which the iron—boron single bond is located at B(9) as illustrated in Fig. 2. To date only one other metal derivative of this type has been reported. Mikhailov and Potapova reported the synthesis of $(CH_3)_4N[7,8\text{-}B_9C_2H_{11})HgC_6H_5]$ by reaction of C_6H_5HgCl with $Na_2[7,8\text{-}B_9C_2H_{11}]$ [12]. They proposed that a mercury—carbon single bond was formed in this reaction but little structural data was presented in their report to substantiate this postulate.

During the course of our study we found that certain neutral Lewis bases are capable of displacing the 7,8-$B_9C_2H_{12}^-$ ion from the coordination sphere of the iron atom. Treatment of III with acetonitrile at reflux forms $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3CN](7,8\text{-}B_9C_2H_{12})$ (VI) in high yield. This product was obtained alternately by heating a mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3CN]PF_6$ and $(CH_3)_3NH[7,8\text{-}B_9C_2H_{12}]$ in refluxing acetone. The 70.6 MHz ^{11}B NMR spectrum of VI was nearly identical to the ^{11}B NMR spectrum of $(CH_3)_3NH[7,8\text{-}B_9C_2H_{12}]$ reported previously [11]. Similar carborane displacement reactions were observed with other Lewis bases (eqns. 4, 5).

$$\text{III} + PPh_3 \xrightarrow[\text{reflux}]{C_6H_6} [(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3](7,8\text{-}B_9C_2H_{12}) \quad (4)$$

$$\text{III} + C_6H_{11}NC \xrightarrow[\text{reflux}]{C_6H_6} [(\eta^5\text{-}C_5H_5)Fe(CO)(C_6H_{11}NC)_2](7,8\text{-}B_9C_2H_{12}) \quad (5)$$

Further chemical studies of these interesting metalloborane derivatives are underway and will be reported in the near future.

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