A STUDY OF THE BORON-11 NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE (3)-1,2-$B_9C_2H_{12}^-$ AND [(3)-1,2-$B_9C_2H_{11}]_2Co^-$ IONS*

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SUMMARY

The 70.6 MHz ^{11}B NMR spectrum of (3)-1,2-$B_9C_2H_{12}^-$ consists of five doublets of relative intensities 2/3/2/1/1 reading upfield. The proposed assignment of these doublet resonances is B(4, 7); B(6) and B(9, 12); B(5, 11); B(8) and B(10) respectively. The ^{11}B NMR spectrum of [(3)-1,2-$B_9C_2H_{11}]_2Co^-$ contains five doublets of relative intensities 1/1/4/2/1 reading upfield. The proposed assignment of these doublets is B(8); B(10); B(9, 12) and B(4, 7); B(5, 11) and B(6) respectively.

INTRODUCTION

Degradation of 1,2-$B_{10}C_2H_{12}$ by basic reagents produces the (3)-1,2-$B_9C_2H_{12}^-$ ion[1]. A proton can be removed from this carborane anion with sodium hydride to generate (3)-1,2-$B_9C_2H_{11}^{2-}$ which reacts with cobalt(II) chloride to form the [(3)-1,2-$B_9C_2H_{11}]_2Co^-$ ion[2]. We have studied the 70.6 MHz ^{11}B NMR spectra of a series of specifically labeled (3)-1,2-$B_9C_2H_{12}^-$ and [(3)-1,2-$B_9C_2H_{11}]_2Co^-$ derivatives. This has provided a complete assignment of the boron resonances in these ions. These results will allow the structural elucidation of many of the products of substitution reactions of these ions which as yet are largely unexplored.

EXPERIMENTAL

General comments

The 70.6 MHz ^{11}B NMR spectra were obtained on a Varian HR-220 spectrometer with digitized frequency sweep. The ^{11}B chemical shifts were measured relative to an external capillary of $BF_3 \cdot O(C_2H_5)_2$ and have an error of ± 0.15 ppm.

The ^{13}C NMR spectra were measured at 15.086 MHz employing a Fourier transform instrument built by Adam Allerhand and A.O. Clouse of this department. Chemical shifts are reported relative to $CS_2 = 0$ ppm.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Starting materials

The $1,2,3,4,-B_{10}D_4H_{10}$ was prepared by the aluminum chloride catalyzed deuteration of decaborane[3] and converted to $8,9,10,12-B_{10}D_4H_6C_2H_2$ by a previously developed procedure[4]. Literature methods were used to prepare $9,12-Br_2-1,2-B_{10}C_2H_{10}$[5], $(CH_3)_4N[6-C_6H_5-(3)-1,2-B_9C_2H_{11}]$[6], $(CH_3)_4N[4-I-(3)-1,2-B_9C_2H_{11}]$[7], $(CH_3)_4N[8,9,10,12-D_4-(3)-1,2-B_9C_2H_8]$[1], $(CH_3)_4N[(6-C_6H_5-(3)-1,2-B_9C_2H_{10})_2-Co]$[6], $[(3)-1,2-B_9C_2H_{10}]_2CoS_2CH$[8] and $(CH_3)_4N[8-SH-(3)-1,2-B_9C_2H_{10}]_2Co$[12].

(CH$_3$)$_3$NH$[9,12-Br_2-(3)-1,2-B_9C_2H_{10}]$. A mixture of 1.2 g of $9,12-Br_2-1,2-B_{10}C_2H_{10}$, 15 ml absolute ethanol and 2 ml hydrazine hydrate were stirred in a nitrogen atmosphere under gentle reflux until hydrogen evolution ceased. Water and ethanol were removed on a rotary evaporator and the syrupy residue taken up in water and this solution filtered. Addition of trimethylammonium chloride gave a white precipitate which was collected on a filter and recrystallized from acetone/water to afford 0.7 g (50% yield) of white crystals which were dried *in vacuo*. (Found: C, 17.27; H, 5.75; Br, 45.74. $C_5H_{20}NBr_2B_9$ calcd.: C, 17.09; H, 5.70; Br, 45.58%.)

(CH$_3$)$_4$N$[(3)-1,2-B_9C_2H_{11}D]$. A 0.5 g sample of $(CH_3)_3NH[(3)-1,2-B_9C_2H_{12}]$ was converted to $Na_2B_9C_2H_{11}$ with excess sodium hydride in tetrahydrofuran[2]. The solution was Schlenk filtered to remove unreacted sodium hydride and then treated with 5 ml D_2O. The resulting solution was rotary evaporated to remove the tetrahydrofuran and then treated with a solution of tetramethylammonium chloride in D_2O whereupon a white solid separated. This was collected on a filter and recrystallized from acetone/D_2O. The yield of the salt was nearly quantitative. The infrared spectrum showed no bands due to B–D terminal stretching.

4-(3-Bromopyridine)-(3)-1,2-B$_9$C$_2$H$_{11}$. This compound was prepared from $K[(3)-1,2-B_9C_2H_{12}]$, 3-bromopyridine and ferric chloride by literature methods[9]. The product was purified by recrystallization from benzene/heptane and obtained as small yellow crystals, m.p. 196–198° (uncorr.) (evacuated sealed capillary). (Found: C, 28.96; H, 5.17; N, 4.83. $C_7H_{15}NBrB_9$ calcd.: C, 29.29; H, 5.32; N, 4.80%.)

Deuterated B$_9$C$_2$H$_{13}$ and B$_9$C$_2$H$_{12}^-$. Deuterated phosphoric acid was prepared from phosphorous oxychloride and D_2O. Unreacted starting materials were removed by pumping under high vacuum. One gram of $K[(3)-1,2-B_9C_2H_{12}]$ was added under nitrogen to a stirred mixture of 25 mmole D_3PO_4 and 10 ml dry benzene. The mixture was stirred for five hours and then the benzene layer separated and solvent removed *in vacuo*. The residue was sublimed onto a $-80°$ probe under high vacuum at room temperature without heating. The deuterated $B_9C_2H_{13}$ was removed from the sublimator and handled in a dry box. A sample was taken for NMR analysis. The remainder was dissolved in D_2O to which solid trimethylammonium chloride was added. The white precipitate was collected on a filter and washed with a small amount of ice cold D_2O and dried *in vacuo* to give 0.75 g (70% yield) of deuterated $(CH_3)_3NH[(3)-1,2-B_9C_2H_{12}]$.

RESULTS AND DISCUSSION

Studies of $(3)-1,2-B_9C_2H_{12}^-$ and its derivatives

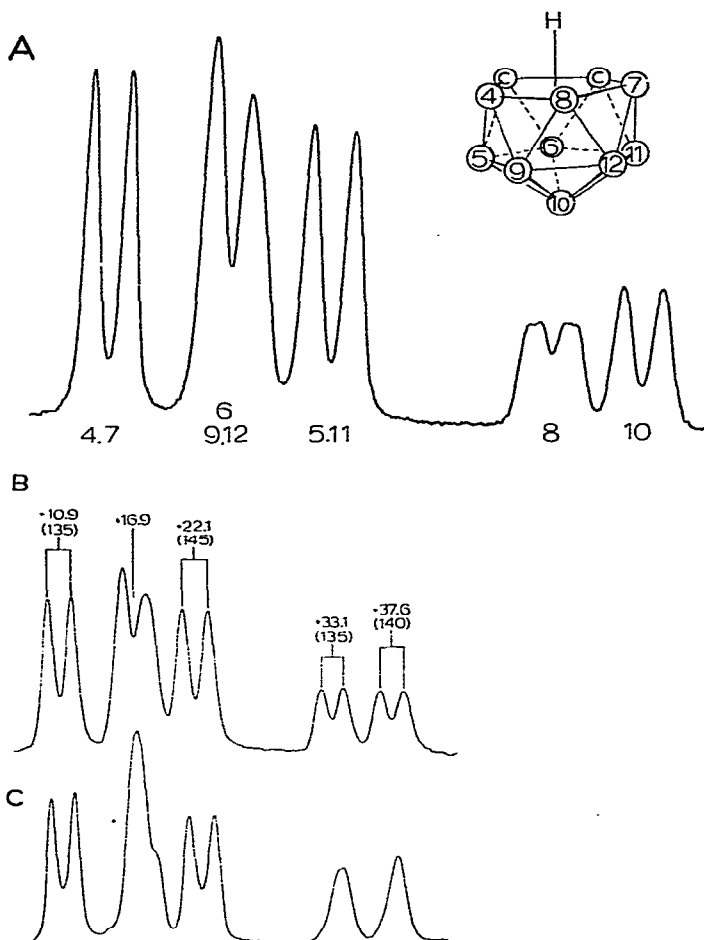The 70.6 MHz ^{11}B NMR spectrum of $(CH_3)_4N[(3)-1,2-B_9C_2H_{12}]$ in acetone

Fig. 1. The 70.6 MHz ^{11}B NMR spectra of (3)-$1,2$-B$_9$C$_2$H$_{12}^-$ and deuterated derivatives in acetonitrile: a, $(CH_3)_3NH[(3)$-$1,2$-B$_9$C$_2$H$_{12}]$, proposed structure of the carborane and numbering system; b, $(CH_3)_4$-N$[(3)$-$1,2$-B$_9$C$_2$H$_{11}$D$]$; c, $(CH_3)_4$N$[8,9,10,12$-D$_4$-(3)-$1,2$-B$_9$C$_2$H$_8]$.

solution is shown in Fig. 1a along with the proposed structure for this carborane anion*. The (3)-$1,2$-B$_9$C$_2$H$_{12}^-$ ion in the proposed structure consists of six nonequivalent boron atom environments. These are B$(4, 7)$; B$(5, 11)$; B(6); B(8); B$(9, 12)$; and B(10). This should give rise to a ^{11}B NMR spectrum containing six doublets of areas $1/1/1/2/2/2$. The unique twelfth proton is probably associated with atoms in the open face and could give rise to additional spin coupling. The spectrum of (3)-$1,2$-B$_9$C$_2$H$_{12}^-$ consists of five doublets of relative areas $2/3/2/1/1$ reading upfield respectively. Deprotonation of (3)-$1,2$-B$_9$C$_2$H$_{12}^-$ with sodium hydride and treatment of the resulting dianion with D$_2$O formed (3)-$1,2$-B$_9$C$_2$H$_{11}$D$^-$. There was no evidence in the infrared spectrum of the tetramethylammonium salt of this deuterated product that the ter-

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* The numbering systems used in this article follow the nomenclature rules which were recently adopted for boron compounds[10].
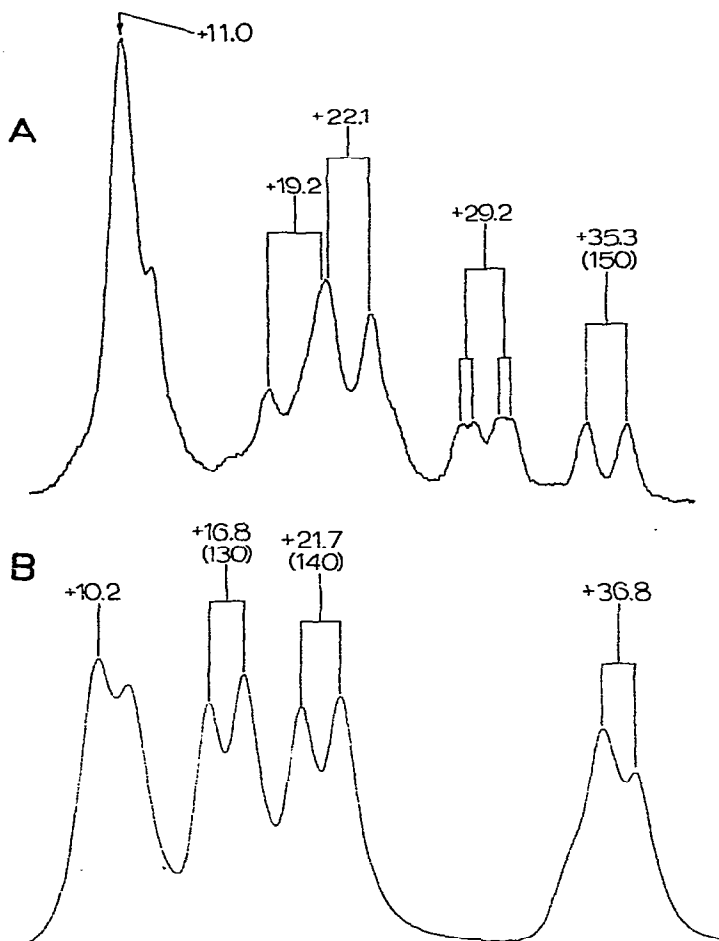
Fig. 2. The 70.6 MHz ^{11}B NMR spectra of some substituted derivatives of (3)-1,2-B$_9$C$_2$H$_{12}^-$ in acetonitrile: a, (CH$_3$)$_4$N[9,12-Br$_2$-(3)-1,2-B$_9$C$_2$H$_{10}$]; b, (CH$_3$)$_4$N[6-C$_6$H$_5$-(3)-1,2-B$_9$C$_2$H$_{11}$]; c, 4-(3-bromopyridine)-(3)-1,2-B$_9$C$_2$H$_{11}$; d, (CH$_3$)$_4$N[4-I-(3)-1,2-B$_9$C$_2$H$_{11}$]; e, proton decoupled spectrum of (CH$_3$)$_4$N-[4-I-(3)-1,2-B$_9$C$_2$H$_{11}$].

minal B–H protons had exchanged for deuterium. Examination of the ^{11}B NMR spectrum of (3)-1,2-B$_9$C$_2$H$_{11}$D$^-$ (Fig. 1b) indicates that the fine structure on the doublet at 33.1 ppm has disappeared. Identical results were obtained by decoupling the bridge proton region while observing the ^{11}B spectrum of (3)-1,2-B$_9$C$_2$H$_{12}^-$. This information indicates that the doublet of unit area at 33.1 is associated with B(8). The coupling between the unique proton and B(8) is about 50 Hz. This unique proton has not been observed to couple with any other boron or carbon nucleus in (3)-1,2-B$_9$C$_2$H$_{12}^-$*.

The spectrum of (CH$_3$)$_4$N[8,9,10,12-D$_4$-(3)-1,2-B$_9$C$_2$H$_8$] shown in Fig. 1c contains two singlets of area 1 at 33.1 and 37.6 ppm. The resonance at 33.1 ppm has

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* The ^{13}C NMR spectrum of (CH$_3$)$_4$N[(3)-1,2-B$_9$C$_2$H$_{12}$] in acetone contained a doublet at 147.9 ppm [J(CH) 142 Hz] assigned to the carborane carbon atoms.
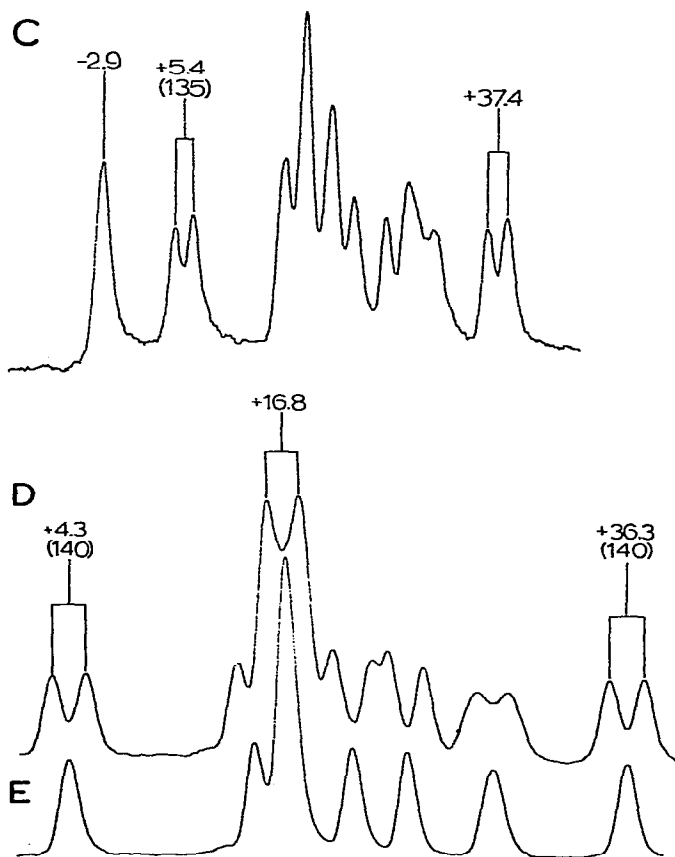
already been assigned to B(8) and therefore the resonance at 37.6 ppm must be due to B(10). There is a singlet of area 2 at 16.9 ppm in Fig. 1c which is due to B(9, 12). The assignment of B(9, 12) is further confirmed by the ^{11}B NMR spectrum of 9,12-Br$_2$-(3)-1,2-B$_9$C$_2$H$_{10}^-$ (Fig. 2a)*. The unsymmetrical doublet of area 3 at 16.9 ppm in Fig. 1b has been reduced to a doublet of area 1 in the spectrum of the dibromo derivative. As expected the singlet due to the brominated boron atoms is found at lower field (11.0 ppm).

Since the resonances associated with B(8) and B(10) have been assigned, the remaining doublet of area 1 at appro: mately +16.9 ppm in Fig. 1b must be due to B(6). The ^{11}B NMR spectrum of 6-C$_6$H$_5$-(3)-1,2-B$_9$C$_2$H$_{11}^-$ shown in Fig. 2b further confirms this assignment. Replacement of a hydrogen atom by a phenyl group at B(6) reduces the doublet at 16.8 ppm from area 3 to area 2. The phenyl-substituted boron resonance appears downfield at about 10.2 ppm.

Oxidative substitution of (3)-1,2-B$_9$C$_2$H$_{12}^-$ with 3-bromopyridine and ferric
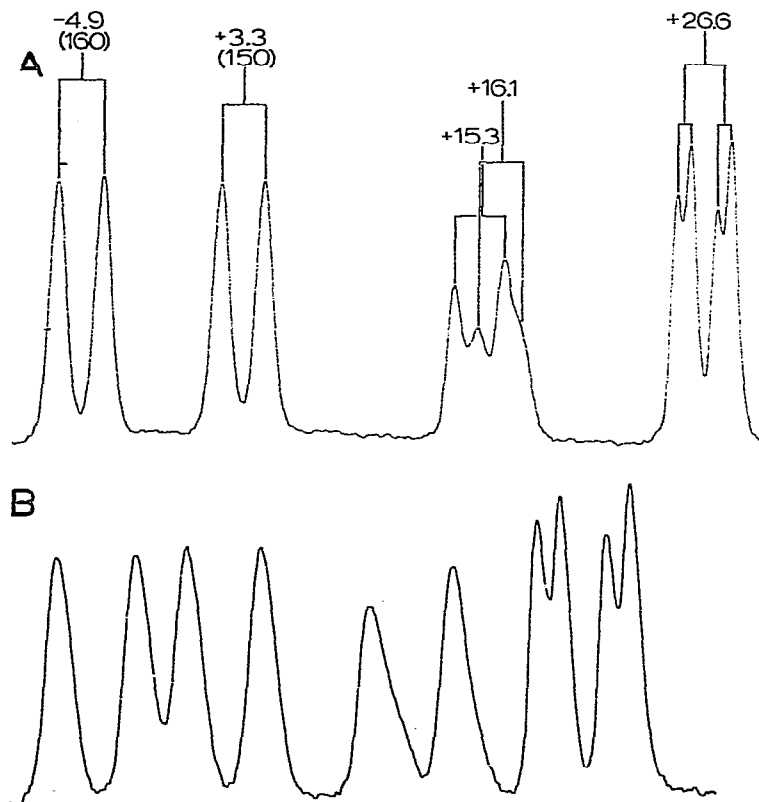
Fig. 3. The ^{11}B NMR spectrum of; a, (3)-1,2-$B_9C_2H_{13}$ in pentane at 70.6 MHz; b, (3)-1,2-$B_9C_2H_{13}$ in pentane at 32 MHz; c, (3)-1,2-$B_9C_2H_{13}$ deuterated with D_3PO_4 in pentane at 70.6 MHz; d, (CH$_3$)$_3$NH-[(3)-1,2-$B_9C_2H_{12}$] from deuterated (3)-1,2-$B_9C_2H_{13}$ in acetonitrile at 70.6 MHz.

chloride formed (3)-1,2-$B_9C_2H_{11}$(3-bromopyridine)[9]. The proton* and 70.6 MHz boron (Fig. 2c) NMR spectra of this derivative suggest that substitution has occurred off the mirror plane defined by B(6, 8 and 10). The same results were obtained previously for the position of substitution in (3)-1,2-$B_9C_2H_{11}$(pyridine)[9]. It is expected that substitution will occur on the open face of the $B_9C_2H_{12}^-$ ion. Apparently upon substitution the boron resonance is shifted downfield relative to its position in the parent molecule. Treatment of (3)-1,2-$B_9C_2H_{12}^-$ with iodine[7] produced (3)-1,2-$B_9C_2H_{11}I^-$. The 70.6 MHz boron spectrum and the proton-decoupled spectrum are shown in Figs. 2d and 2e respectively**. The appearance of six doublets of unit area clearly indicates that substitution is off the mirror plane. This iodination reaction is probably best considered as an electrophilic substitution by iodine which would be expected to occur on the open face of the $B_9C_2H_{12}^-$ ion. Earlier work suggests that attack does not occur at carbon[7]. Thus substitution at B(4) or B(7) is most probable.

* The proton NMR spectrum of (3)-1,2-$B_9C_2H_{11}$(3-bromopyridine) in CDCl$_3$ solution contained two broad peaks assigned to the carborane CH protons at 2.85 and 2.14 ppm downfield relative to tetramethyl-silane.
** A referee pointed out that the caption to Fig. 1 of reference 7 was apparently reversed.
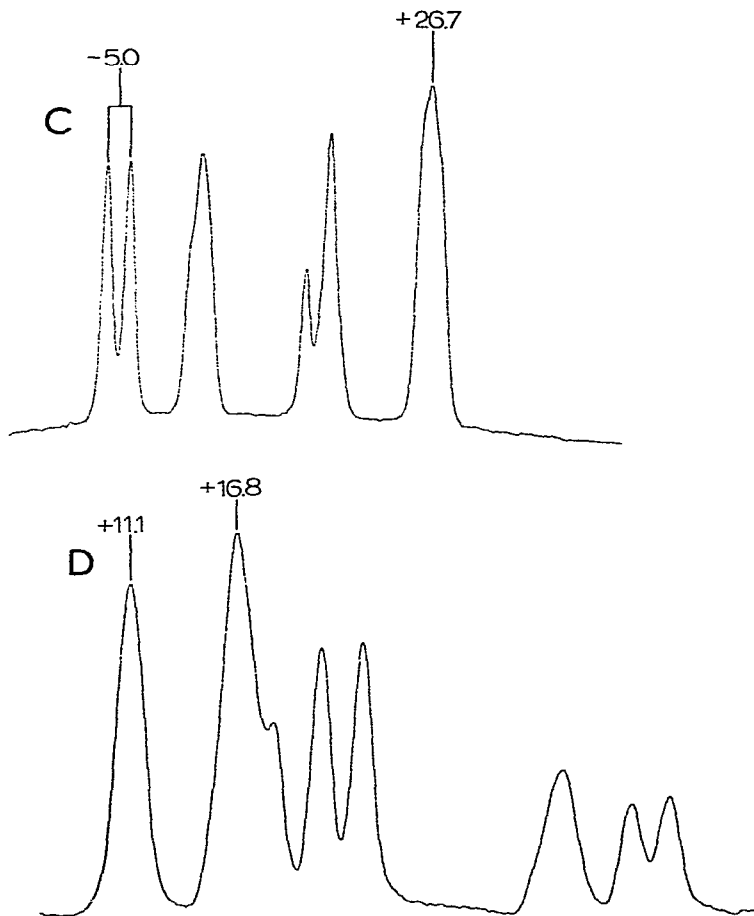
The expected singlet due to the iodo-substituted boron atom is not apparent in Fig. 2d. Integration of the proton decoupled spectrum (Fig. 2e) indicated that the large peak at 16.8 ppm was of relative area three and contained the hidden singlet. The doublet of area two at lowest field in the spectrum of (3)1,2-B$_9$C$_2$H$_{12}^-$ is reduced to area one in the spectrum of (3)-1,2-B$_9$C$_2$H$_{11}$I$^-$ and as expected the resonance of the iodo-substituted boron atom has moved upfield. The spectra of these two substituted derivatives suggest that the low field doublet in the boron spectrum of (3)-1,2-B$_9$C$_2$H$_{12}^-$ is due to B(4, 7).

Further evidence concerning the B(4, 7) assignment was obtained from the boron spectrum of (3)-1,2-B$_9$C$_2$H$_{13}$[13] shown in Fig. 3a. This spectrum can be divided into a 2/2/1/1/2/1 pattern of doublets reading upfield. This pattern suggests that the neutral carborane maintains a plane of symmetry and has the same basic structure as the (3)-1,2-B$_9$C$_2$H$_{12}^-$ ion*. The two acidic hydrogens probably occupy bridging positions on the open face between B(4) and B(8) and between B(7) and B(8). There

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* The ^{13}C NMR spectrum of (3)-1,2-B$_9$C$_2$H$_{13}$ in *pentane* solution indicates that the carbon atoms are equivalent with a chemical shift of 128.2 ppm.

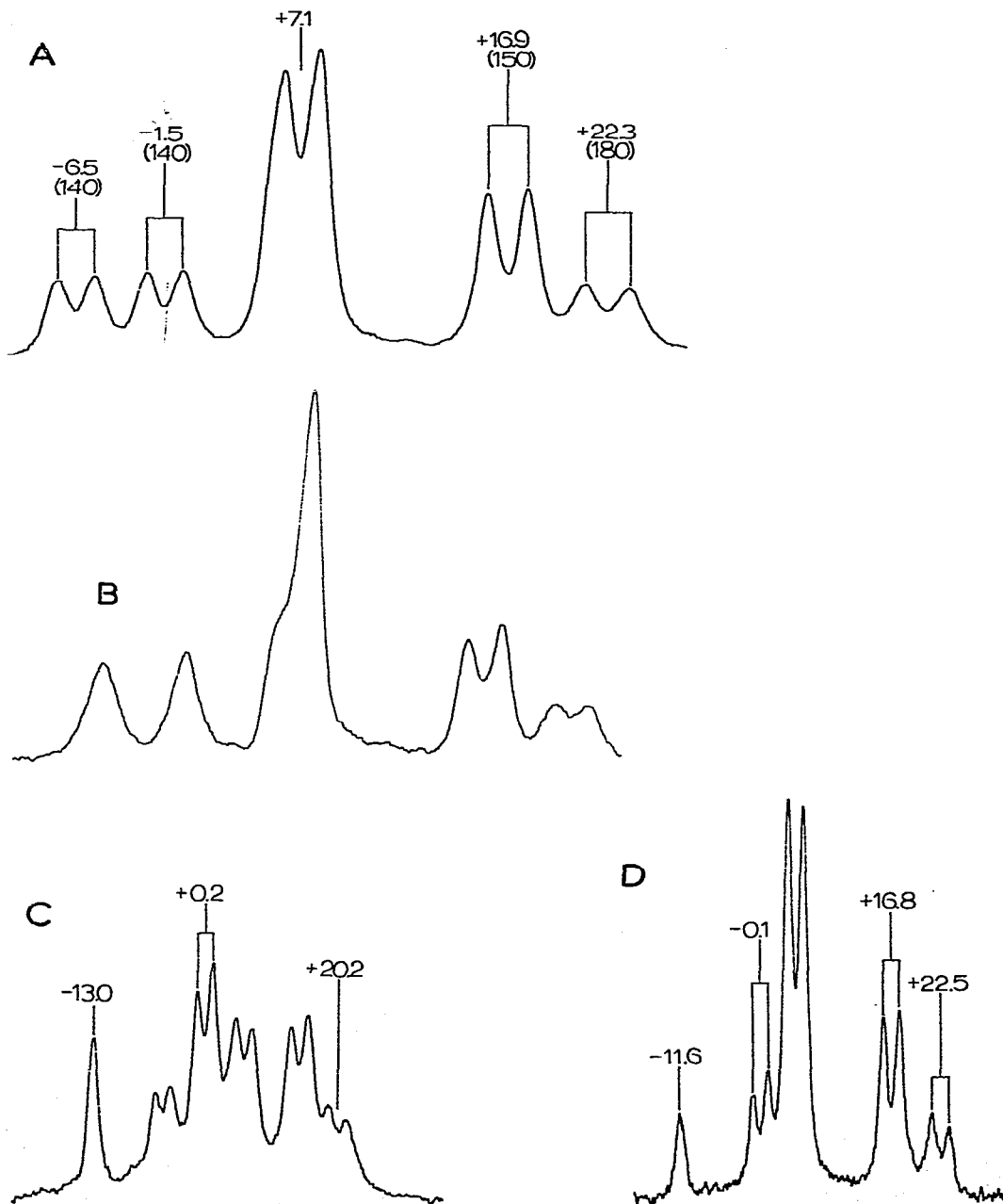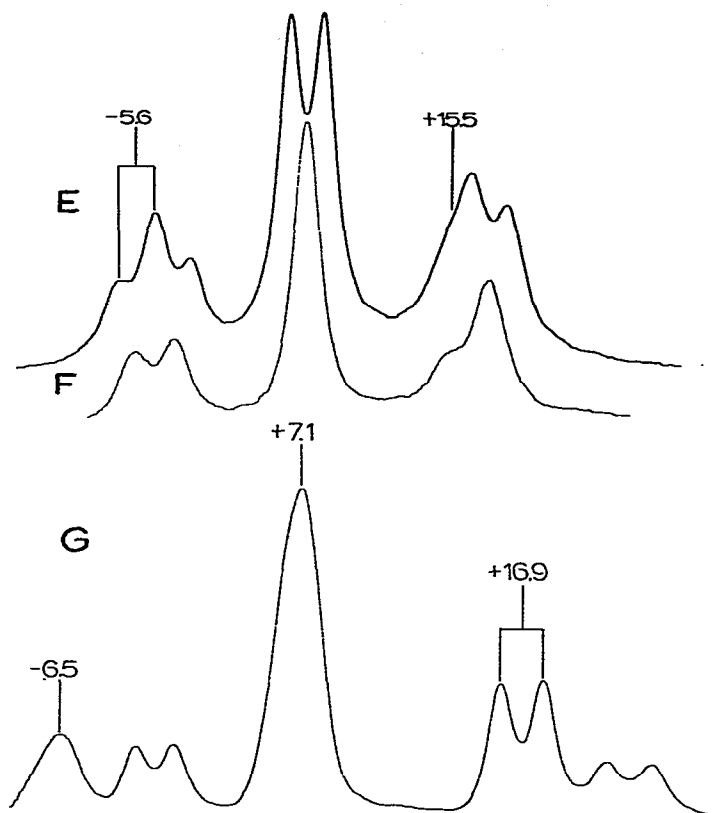Fig. 4. The 70.6 MHz ^{11}B NMR spectra of; a, $(CH_3)_4N[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co$ (acetone solution); b, $(CH_3)_4N[8,9,10,12\text{-}D_4\text{-}(3)\text{-}1,2\text{-}B_9C_2H_7]_2Co^\star$; c, $[(3)\text{-}1,2\text{-}B_9C_2H_{10}]_2CoS_2CH$; d, $(CH_3)_4N[8\text{-}SH\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}]_2Co$; e, $(CH_3)_4N[6\text{-}C_6H_5\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}]_2Co$; f, $(CH_3)_4N[6\text{-}C_6H_5\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}]_2Co$ (proton decoupled); g, $(CH_3)_4N[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co$ obtained from D_3PO_4 deuterated $(3)\text{-}1,2\text{-}B_9C_2H_{13}$.

$\star$ Spectra 4b through 4g were obtained in acetonitrile solution.

is secondary splitting (about 55 Hz in the 70.6 MHz spectrum) of the doublet of area two at 26.6 ppm. The 32 MHz spectrum of (3)-1,2-B$_9$C$_2$H$_{13}$ (Fig. 3b) also shows this fine splitting (about 50 Hz) suggesting that the bridge hydrogens are spin coupling with B(4) and B(7). Bridge hydrogen coupling to B(8), the unique boron atom in the open face, would give triplet fine coupling on one of the unit area doublets. This has not been observed. Deuterated (3)-1,2-B$_9$C$_2$H$_{13}$ obtained by reaction of (3)-1,2-B$_9$C$_2$H$_{12}^-$ with D$_3$PO$_4$ has the spectrum shown in Fig. 3c. The resonance attributed to B(4, 7) at 26.7 ppm has undergone extensive hydrogen/deuterium exchange. Some but not all of the other terminal hydrogens have exchanged. The neutral deuterated carborane was converted to the corresponding deuterated (3)-1,2-B$_9$C$_2$H$_{12}^-$ in D$_2$O and its boron spectrum is shown in Fig. 3d. The partly collapsed signal at 16.8 ppm has already been assigned to B(6) and B(9, 12). The singlet at 11.1 ppm must therefore be due to B(4, 7) in agreement with the results with the iodo and 3-bromopyridine derivatives (*vide supra*). The doublet of area two at 22.1 ppm in Fig. 1b must therefore be due to the remaining unassigned pair of boron atoms, B(5, 11).

Studies of [(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Co$^-$ *and its derivatives*

The (3)-1,2-B$_9$C$_2$H$_{12}^-$ ion or the labeled derivatives described in the previous section can be deprotonated with bases and reacted with cobalt(II) chloride to insert the cobalt atom in the open face of the cage to form [(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Co$^-$ or labeled derivatives. The boron spectrum of (CH$_3$)$_4$N[(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Co in acetone solu-

tion is shown in Fig. 4a. The number of nonequivalent boron atom environments and the numbering system for the boron atoms are identical to those described for the (3)-1,2-$B_9C_2H_{12}^-$ ion (*vide supra*). The spectrum of the cobalt complex consists of five doublets of relative areas 1/1/4/2/1 reading upfield. The doublet at 7.1 ppm is due to the accidental superposition of two doublets of area two each.

The boron spectrum of $[8,9,10,12-D_4-(3)-1,2-B_9C_2H_7]_2Co^-$ given in Fig. 4b shows partial collapse of the doublet character of the resonance at 7.1 ppm. Thus half of the resonance at 7.1 ppm can be assigned to B(9, 12). Deuteration has also resulted in collapse to singlets of the unit area resonances at -6.5 and -1.5 ppm which can be assigned to B(8) and B(10) in an indefinite manner.

Reaction of $[(3)-1,2-B_9C_2H_{11}]_2Co^-$ with carbon disulfide, aluminum chloride and hydrogen chloride produced $[(3)-1,2-B_9C_2H_{10}]_2CoS_2CH^8$. The S_2CH bridging unit has been shown by an X-ray study[8] to be attached to B(8) in both dicarbollyl ligands. Under acidic conditions[12], the bridged complex hydrolyzed to $[8-SH-(3)-1,2-B_9C_2H_{10}]_2Co^-$. The ^{11}B NMR spectra of these two derivatives are shown in Figs. 4c and 4d. In both spectra a low field singlet has replaced the lowest field doublet of unit area in the spectrum of the parent compound. On this basis the doublet at -6.5 ppm in Fig. 4a is assigned to B(8). The study of the deuterated derivative (*vide supra*) then pinpoints the resonance at -1.5 ppm as due to B(10). The remaining unassigned doublet of unit area at 22.3 ppm in Fig. 4a must then be due to B(6). Confirmation of this latter assignment is obtained from the boron NMR spectrum of $(6-C_6H_5-(3)-1,2-B_9C_2H_{10})_2Co^-$ given in Fig. 4e and 4f. The substituted boron atom resonance appears as a singlet at approximately 15.5 ppm. A downfield shift of this resonance would be expected upon phenyl substitution.

Treatment of $(3)-1,2-B_9C_2H_{12}^-$ with D_3PO_4 followed by deprotonation with water led to terminal hydrogen–deuterium exchange at B(4, 7), B(9, 12) and B(8).

The boron spectrum of the cobalt complex made from this deuterated carborane is shown in Fig. 4g. The appearance of a singlet at 7.1 ppm indicates that B(4, 7) as well as B(9, 12) can be assigned to this multiplet of area four. The one remaining unassigned resonance at 16.9 ppm (see Fig. 4a) must then be due to B(5,11).

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