CONTRIBUTION NO. 2788 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Deuteration and Spectroscopic Studies of (3)-1,2- and (3)-1,7-Dicarba-*nido*-dodecahydroundecaborate(1−) and (3)-1,2-Dicarba-*nido*-undecaborane(13)

BY D. V. HOWE,[1] C. J. JONES,[2] R. J. WIERSEMA, AND M. F. HAWTHORNE*

Received May 14, 1971

The deuterium-exchange reactions of (3)-1,2-$B_9C_2H_{12}^-$, (3)-1,7-$B_9C_2H_{12}^-$, and (3)-1,2-$B_9C_2H_{13}$ have been studied using ^{11}B nmr and infrared spectroscopy. On the basis of these measurements and ^{13}C nmr spectral measurements probable structures for these compounds are proposed. It has been found that some terminal hydrogen exchange takes place under acidic but not basic conditions. A total assignment of the ^{11}B nmr spectrum (80.5 MHz) of (3)-1,2-$B_9C_2H_{12}^-$ is proposed on the basis of the deuteration studies and ^{11}B nmr data obtained from 6-C_6H_5-(3)-1,2-$B_9C_2H_{11}^-$ and 9,12-Br_2-(3)-1,2-$B_9C_2H_{10}^-$. An assignment of the ^{11}B nmr spectrum of (3)-1,2-$B_9C_2H_{13}$ is also proposed.

The monoanions (3)-1,2-dicarba-*nido*-dodecahydroundecaborate(1−),[3] (3)-1,2-$B_9C_2H_{12}^-$, and (3)-1,7-dicarba-*nido*-dodecahydroundecaborate(1−),[3] (3)-1,7-$B_9C_2H_{12}^-$, are the products of the base degradation of 1,2-$B_{10}C_2H_{12}$ and 1,7-$B_{10}C_2H_{12}$, respectively.[4,5] Both (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$ have one acidic hydrogen atom (Ha) which can be reversibly removed with strong base.[6] In addition (3)-1,2-$B_9C_2H_{12}^-$ can be reversibly protonated to yield (3)-1,2-dicarba-*nido*-undecaborane(13), (3)-1,2-$B_9C_2H_{13}$.[4] These three compounds, (3)-1,2$B_9C_2H_{12}^-$, (3)-1,7-$B_9C_2H_{12}^-$, and (3)-1,2-$B_9C_2H_{13}$, are the stable precursors to a large number of smaller carboranes,[7-9] metal-substituted carboranes,[10-13] and transition metal complexes.[6,14,15] Despite the importance of these compounds, there are a number of unanswered questions concerning details of their structures.

It is reasonably well established that these species are 11-particle, icosahedral fragments with one terminal hydrogen on each of the 11 heavy atoms. (Figure 1 shows the proposed basic heavy-atom structure of these compounds along with the numbering system.) The exact nature of the acidic hydrogen (Ha) has, however, been the subject of considerable discussion.[4,5] The only spectral evidence, which has so far been reported,[5] for Ha in (3)-1,2-$B_9C_2H_{12}^-$ is found in the 60-MHz ^{11}B nmr spectrum of this compound (Figure 2). In this spectrum the doublet centered at +32.1 ppm[16] is observed to have fine structure which has been attributed[5] to coupling between Ha and the unique boron atom in the open face of the molecule [B(8)]. In addition, the infrared spectrum of (3)-1,2-$B_9C_2H_{13}$ shows a weak band at 1965 cm^{-1} which was tentatively assigned to a B–H–B stretching mode by Hawthorne and Weisboeck.[4] However, no detailed spectroscopic studies have been carried out on these compounds. We wish to report the results of deuteration studies and additional spectroscopic data which permit more definite conclusions to be drawn as to the exact nature of the acidic hydrogen atoms in these three compounds.

Deuteration Studies on (3)-1,2-$B_9C_2H_{12}^-$.—The preparation of monodeuterated (3)-1,2-$B_9C_2H_{12}^-$ was achieved by reaction of (3)-1,2-$B_9C_2H_{11}^{2-}$ [5] with D_2O to give (3)-1,2-$B_9C_2H_{11}D^-$ which was isolated as its tetramethylammonium salt. The ^{11}B nmr spectrum of this compound (Figure 3b) is quite similar to that of the undeuterated material (Figure 3a). However, the fine structure on the resonance of area 1 centered at +32.4 ppm has been removed by deuteration, thus establishing that this fine structure is indeed due to Ha. There is no evidence from these spectra that any of the terminal hydrogens have been exchanged with deuterium during the reaction. Figures 3c, 3d and 3e show the effect, on the ^{11}B nmr spectrum of (3)-1,2-$B_9C_2H_{12}^-$, of substituting terminal hydrogens in known positions. These results will be discussed in detail later (*vide infra*).

In order to investigate further the hydrogen-exchange reactions of (3)-1,2-$B_9C_2H_{12}^-$, ^{11}B nmr spectra of solutions of the potassium salt in D_2O, D_2O 2 *M* in K_2CO_3, and D_2O 5 *M* in DCl were recorded. The spectra of solutions in D_2O and D_2O 2 *M* in K_2CO_3 showed that Ha could be exchanged under basic conditions, since the addition of K_2CO_3 resulted in the collapse of the fine structure in the resonance centered at +32.8 ppm in D_2O solution. Also, there was no evidence for the exchange of terminal hydrogen with deuterium under these conditions. Under acidic conditions, however, the spectrum showed that not only was Ha exchanged for deuterium but the terminal hydrogen had also exchanged (Figure 4). The resonances at +32.8 (area 1),

---

[1] National Science Foundation Trainee, 1965–1969.

[2] NATO Research Fellow, 1970–1972.

[3] The system of numbering used in this paper is that described by M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

[4] R. A. Weisboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1642 (1964).

[5] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

[6] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

[7] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **90**, 869 (1968).

[8] D. A. Owen, P. M. Garrett, and M. F. Hawthorne, submitted for publication in *Inorg. Syn.*

[9] P. M. Garrett, T. A. George, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2008 (1969).

[10] G. Popp and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 6553 (1968).

[11] B. M. Mikhailov and T. V. Potopova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **5**, 1153 (1968).

[12] R. L. Voorhees and R. W. Rudolph, *J. Amer. Chem. Soc.*, **91**, 2174 (1969).

[13] D. A. T. Young and M. F. Hawthorne, submitted for publication in *J. Amer. Chem. Soc.*

[14] H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968).

[15] L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 4823 (1968).

[16] All ^{11}B nmr chemical shifts are in ppm relative to an external reference sample of $BF_3 \cdot O(C_2H_5)_2$. Coupling constants are in Hz and, unless otherwise stated, the spectra were recorded at 80.53 MHz.

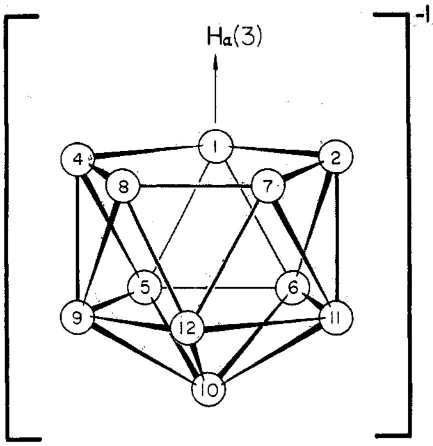

Figure 1.—The proposed heavy-atom structure of the $B_9C_2H_{11}$ fragment and the numbering system used in this paper.

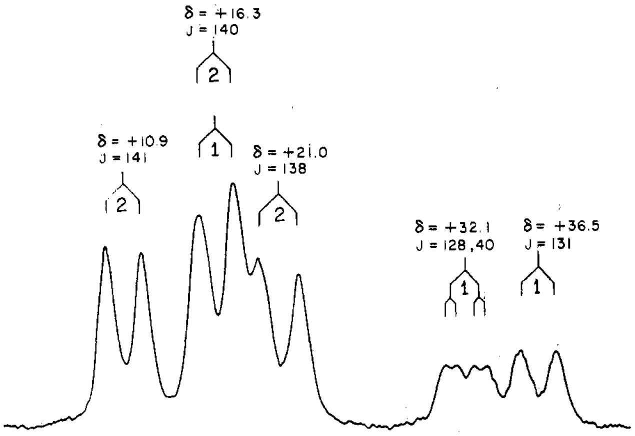

Figure 2.—The 60-MHz ^{11}B nmr spectrum of $(CH_3)_3NH$-(3)-1,2-$B_9C_2H_{12}$ in acetone.

+18.7 (area 3), and +12.2 (area 2) ppm in D_2O all collapse, indicating that the terminal hydrogen on the boron atoms responsible for these signals exchanges with deuterium under acidic conditions. The ^{11}B nmr spectra of a solution of K-(3)-1,2-$B_9C_2H_{12}$ in aqueous HCl showed no changes. Exchange, even of Ha, was found to be slow in the absence of acid or base since spectra of D_2O solutions of the monoanion showed little change even after a period of weeks.

Infrared spectral studies also provide evidence for the exchange of terminal hydrogen under acidic conditions. The infrared spectra of (3)-1,2-$B_9C_2H_{12}^-$ which had been treated with 1 *M* DCl in D_2O for extended periods of time exhibited a band at 1880 cm^{-1} which increased in relative intensity with time (Figure 5). Bands in this region of the infrared spectrum have been assigned to terminal B–D stretching vibrations.[17] The infrared spectrum of material treated with aqueous HCl, on the other hand, showed no changes. No bands attributable to B–H–B bridge vibrations were observed.[5]

Structure of (3)-1,2-$B_9C_2H_{12}^-$.—The coupling constant of *ca.* 40 Hz observed in the spectrum of (3)-1,2-$B_9C_2H_{12}^-$ and assigned to coupling between Ha and B(8) is inconsistent with the presence of a BH_2 group in the monoanion (terminal B–H coupling constants are

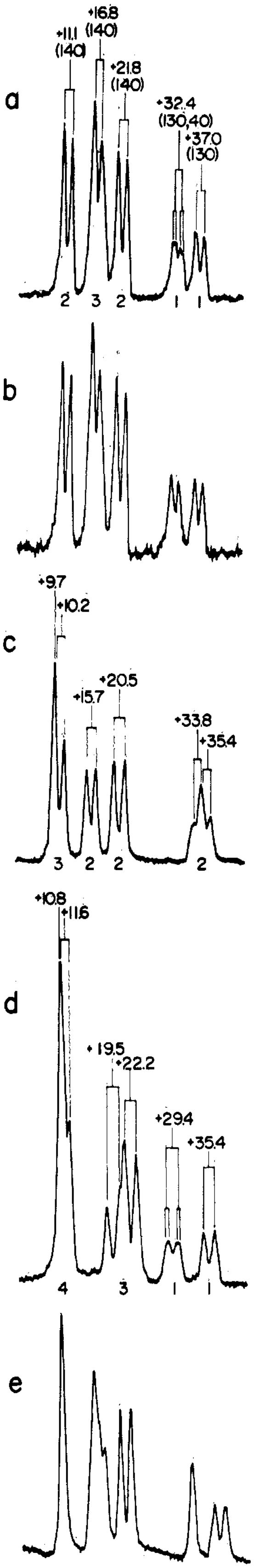

Figure 3.—The 80.5-MHz ^{11}B nmr spectra of (3)-1,2-$B_9C_2H_{12}^-$ and substituted analogs in CH_3CN: (a) $(CH_3)_3NH$-(3)-1,2-$B_9C_2H_{12}$; (b) $(CH_3)_4N$-(3)-1,2-$B_9C_2H_{11}D$; (c) $(CH_3)_4N$-6-C_6H_5-(3)-1,2-$B_9C_2H_{11}$; (d) $(CH_3)_4N$-9,12-Br_2-(3)-1,2-$B_9C_2H_{10}$; (e) deuterated $(CH_3)_4N$-(3)-1,2-$B_9C_2H_{12}$ from the hydrolysis of deuterated (3)-1,2-$B_9C_2H_{13}$.

[17] W. J. Lehmann, C. O. Wilson, J. F. Ditter, and I. Shapiro, *Advan. Chem. Ser.*, **No. 32**, 139–150 (1961).

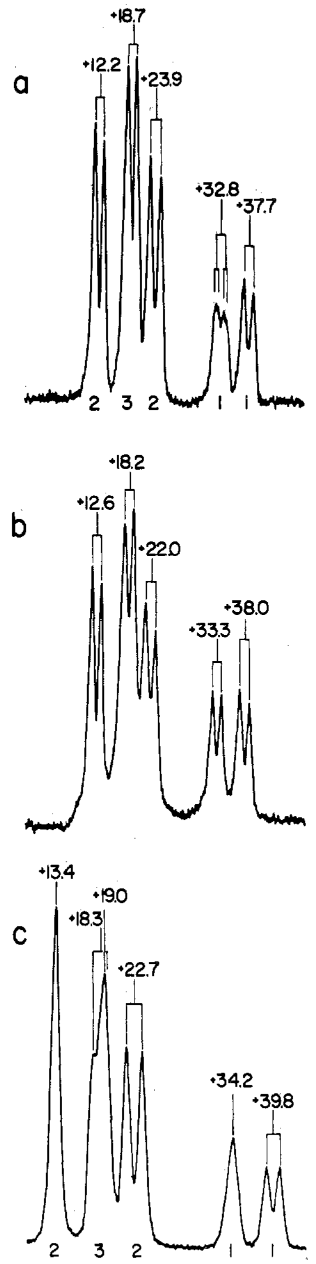

Figure 4.—The 80.5 MHz ^{11}B nmr spectra of K-(3)-1,2-$B_9C_2H_{12}$ in (a) neutral D_2O, (b) D_2O 2 *M* in K_2CO_3, and (c) D_2O 5 *M* in DCl.

typically of the order of 140 Hz). Also, the infrared spectrum of (3)-1,2-$B_9C_2H_{11}D^-$ shows no absorption bands which could be attributed to a terminal B–D stretching vibration. Consequently Ha is assumed to occupy a bridging position.

Three types of static B–H–B bridges are conceivable. First, the bridge may be either between B(4) and B(8) or between B(7) and B(8); in either case the plane of symmetry of the 1,2-$B_9C_2H_{11}$ unit would be destroyed.[18] Such a structure seems unlikely since the ^{11}B nmr spectrum[5] of 1-C_6H_5-(3)-1,2-$B_9C_2H_{11}^-$, which also has no plane of symmetry, is complex and quite unlike that of (3)-1,2-$B_9C_2H_{12}^-$.

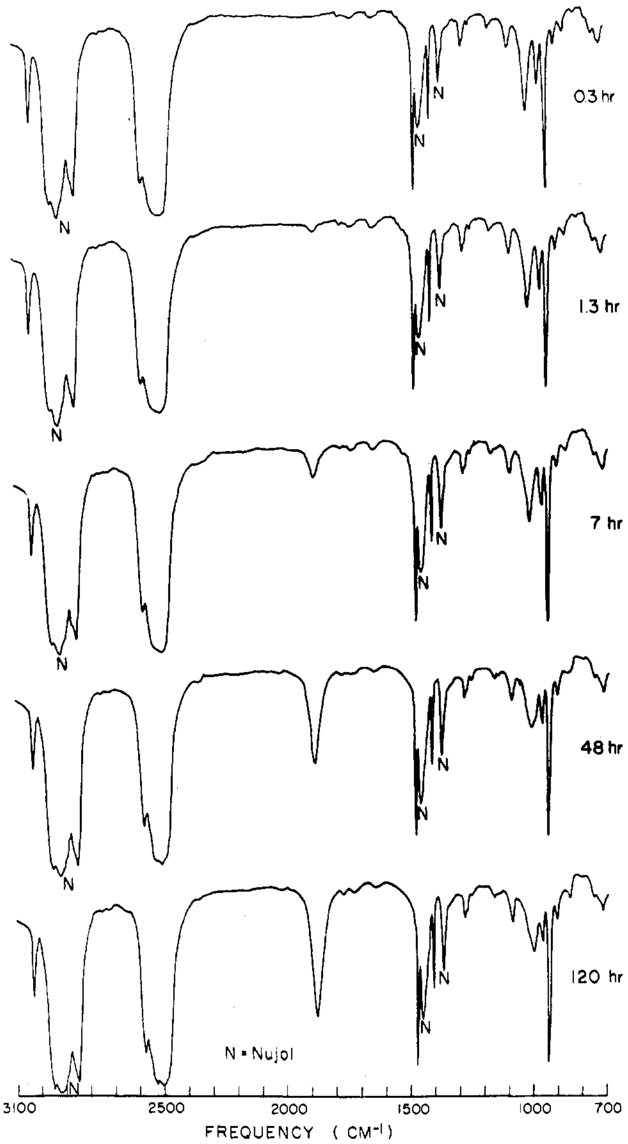

Figure 5.—Changes in the infrared spectra (Nujol mulls) of $(CH_3)_4N$-(3)-1,2-$B_9C_2H_{12}$ during the D_2O–DCl exchange experiments.

The second and third types of bridging structure involve either a three-center bridge between B(4), B(8), and B(7) or a five-center bridge between all five atoms in the pentagonal face. The ^{13}C nmr spectrum of K-(3)-1,2-$B_9C_2H_{12}$ in H_2O consists of a doublet at +145 ppm,[19] J_{CH} = 160 Hz, which shows no evidence of coupling between Ha and the carbon atoms (proton decoupling of this spectrum effected the collapse of this doublet to a singlet). Since no coupling was observed between Ha and the carbon atoms, the five-center bridge structure would seem unlikely. An asymmetric three-center bridge in which Ha is more closely associated with B(8) than with B(4) and B(7) would be consistent with the observed spectrum if the Ha–B(4) or –B(7) coupling were too small to be observed.

An alternative structure, which also agrees with the observed spectrum, involves a dynamic B–H–B bridge in which Ha is rapidly tautomerizing between a B(4)–B(8) and a B(7)–B(8) bridging position. Such a structure

---

[18] The structure shown in Figure 1 has a plane of symmetry passing through B(6), B(8), and B(10) and bisecting the C(1)–C(2) bond. This gives rise to six types of boron atoms in the ratio 2:2:2:1:1:1, *i.e.*, B(4), B(7):B(5), B(11):B(9), B(12):B(6):B(8):B(10).

[19] The ^{13}C nmr spectra were recorded at 63.1 MHz using a computer accumulation of 2000 scans for K-(3)-1,2-$B_9C_2H_{12}$ and K-(3)-1,7-$B_9C_2H_{12}$ and of 500 scans for (3)-1,2-$B_9C_2H_{13}$. Shifts are quoted relative to carbon disulfide.

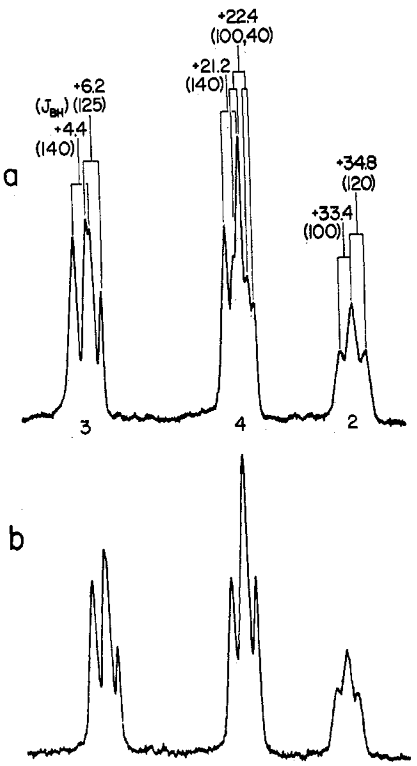

Figure 6.—The 80.5-MHz ^{11}B nmr spectra (CH_3CN solution) of (a) $(CH_3)_3NH$-(3)-1,7-$B_9C_2H_{12}$ and (b) $(CH_3)_4N$-(3)-1,7-$B_9C_2H_{11}D$.

would account for the observation of coupling between Ha and B(8) and the unobserved coupling between Ha and B(4) and B(7) since Ha is bonded to B(8) at all times but is only transiently bonded to B(4) and B(7).

Deuteration Studies on (3)-1,7-$B_9C_2H_{12}^-$.—The preparation of monodeuterated (3)-1,7-$B_9C_2H_{12}^-$ was achieved by reaction of Na_2-(3)-1,7-$B_9C_2H_{11}$[5] with D_2O to give (3)-1,7-$B_9C_2H_{11}D^-$ which was isolated as its tetramethylammonium salt. The ^{11}B nmr spectrum of the corresponding undeuterated material (Figure 6a) consisted of three signals of which the resonance of area 2, at +22.4 ppm, exhibits a splitting of *ca.* 40 Hz attributable to coupling with Ha. In the spectrum of the deuterated compound (Figure 6b) the fine structure is no longer present and this signal appears as a doublet which overlaps with another doublet at +21.2 ppm to give a signal whose overall appearance is that of a triplet. As was the case with (3)-1,2-$B_9C_2H_{12}^-$, there are no other significant differences between the spectra of the undeuterated and monodeuterated materials.

The infrared spectrum of (3)-1,7-$B_9C_2H_{12}^-$ contains a number of weak bands in the region generally assigned to B–H–B bridge hydrogen stretching modes[17] (*i.e.*, 1600–1900 cm $^{-1}$) (Figure 7a). The infrared spectrum of (3)-1,7-$B_9C_2H_{11}D^-$ by comparison shows no bands in this region but instead bands are present at 1305, 1250, and 1205 cm^{-1} (Figure 7b) which are not present in the spectrum of the undeuterated material. These bands may be assigned to B–D–B bridging deuterium vibrations which have previously been observed in the region 1100–1500 cm^{-1}.[17]

To study the deuterium-exchange reactions of (3)-1,7-$B_9C_2H_{12}^-$ further, ^{11}B nmr spectra of K-(3)-1,7-$B_9C_2H_{12}$ dissolved in D_2O, D_2O 2 *M* in K_2CO_3, and D_2O 5 *M* in DCl were recorded. As was found with (3)-1,2-$B_9C_2H_{12}^-$, Ha exchanged with deuterium under basic conditions resulting in the collapse of the fine structure on the resonance centered at 23.9 ppm in D_2O. The resulting signal in D_2O–K_2CO_3 solution appeared as a quartet due to the overlap of two doublets centered at +23.3 and +24.2 ppm (Figure 8). Again there was no evidence of terminal hydrogen exchange under basic conditions.

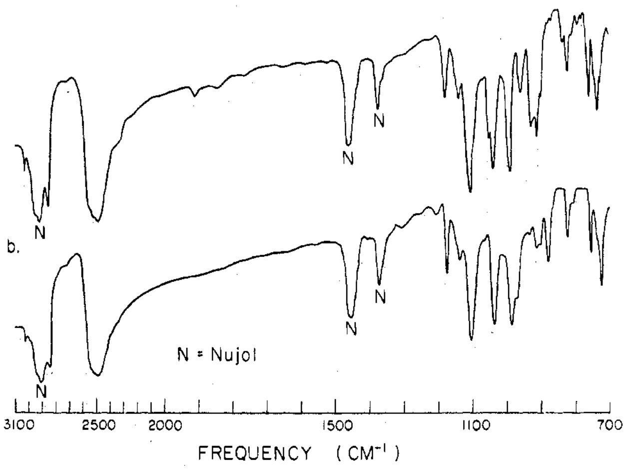

Figure 7.—The infrared spectra (Nujol mulls) of (a) Cs-(3)-1,7-$B_9C_2H_{12}$ and (b) Cs-(3)-1,7-$B_9C_2H_{11}D$.

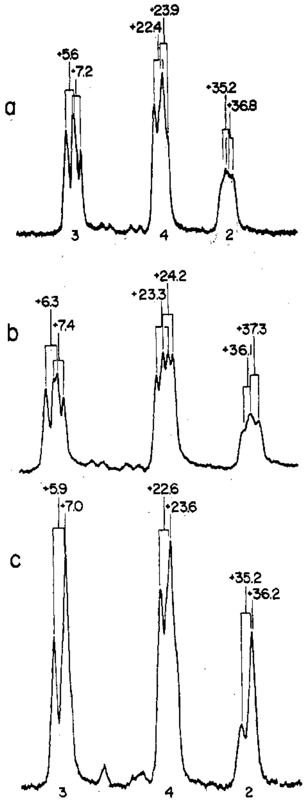

Figure 8.—The 80.5-MHz ^{11}B spectra of K-(3)-1,7-$B_9C_2H_{12}$ in (a) neutral D_2O, (b) D_2O 2 *M* in K_2CO_3, and (c) D_2O 5 *M* in DCl.

Under acidic conditions the ^{11}B nmr spectrum of (3)-1,7-$B_9C_2H_{12}^-$ shows evidence of terminal hydrogen exchange. The resonance of area 1 at +36.8 ppm in D_2O was collapsed to a singlet as was the resonance of area 1 at +7.2 ppm. However, the resonance at +23.9 ppm shows no significant change showing that the terminal hydrogen on the boron atoms coupled with Ha does not exchange under acidic conditions. Further, there does not appear to be any change in this resonance which could be due to exchange of Ha under these conditions.

Structure of (3)-1,7-$B_9C_2H_{12}^-$.—The ^{11}B nmr spectrum of (3)-1,7-$B_9C_2H_{12}^-$ (Figure 6a) can be rationalized in terms of a symmetric structure for this molecule.[20] The low-field signal comprised of a doublet of area 2 at +4.4 ppm and a doublet of area 1 at +6.2 ppm. The central signal arises from the overlap of two resonances of area 2 at +21.2 and +22.4 ppm of which the latter exhibits coupling with Ha. The remaining signal results from the overlap of two doublets of area 1 at +33.4 and +34.8 ppm. Thus Ha occupies a time-averaged position which does not destroy the plane of symmetry of the 1,7-$B_9C_2H_{11}$ unit. In addition, the deuteration studies (Figure 6b) establish that Ha is bonded to the pair of equivalent boron atoms which give rise to the signal at +22.4 ppm. The presence of bands attributed to B–H–B stretching vibrations[17] in the infrared spectrum of (3)-1,7-$B_9C_2H_{12}^-$ (Figure 7) also suggests that Ha occupies a bridging position between two boron atoms.

The observed B–Ha coupling constant of 40 Hz is similar to that observed in (3)-1,2-$B_9C_2H_{12}^-$ suggesting that Ha is bonded to the same pair of boron atoms at all times, as is thought to be the case for Ha and B(8) in (3)-1,2-$B_9C_2H_{12}^-$. Also, the ^{13}C nmr spectrum of K-(3)-1,7-$B_9C_2H_{12}$ consists of a doublet at +164 ppm,[19] J_{CH} = 150 Hz, which shows no evidence of coupling between Ha and the carbon atoms. Proton decoupling of the spectrum effects the collapse of this doublet to a singlet.

On the basis of the above data the most plausible structure for (3)-1,7-$B_9C_2H_{12}^-$ is one in which Ha occupies a static bridging position between B(4) and B(8) (Figure 1).

Deuteration Studies on (3)-1,2-$B_9C_2H_{13}$.—A sample of (3)-1,2-$B_9C_2H_{13}$ may be conveniently prepared by the reaction of K-(3)-1,2-$B_9C_2H_{12}$ with 85% aqueous phosphoric acid.[13] The ^{11}B nmr spectrum of material prepared by this method exhibited four resonances of relative area 2:2:2:3 (Figure 9a).

This spectrum can be rationalized in terms of a symmetric structure for (3)-1,2-$B_9C_2H_{13}$.[18] The two doublets of area 2 at −3.0 and +5.3 ppm can be assigned to two pairs of equivalent boron atoms. The asymmetric doublet of area 2 at +17.6 ppm is then assigned to the overlap of two resonances of area 1, due to two unique boron atoms. The remaining signal at +28.1 ppm, of area 3, is assigned to the overlap of resonances due to the remaining unique boron and pair of equivalent borons.

The ^{11}B nmr spectrum of deuterated (3)-1,2-$B_9C_2H_{13}$ prepared using D_3PO_4 (85% solution in D_2O) confirms this rationalization. In this spectrum (Figure 9b) one of the resonances at +17.6 ppm has collapsed to a singlet while the other has remained unchanged, thus establishing that this signal is due to two overlapping resonances. Also, the signal at +28.1 ppm has collapsed and appears to consist of a singlet of area 2 overlapping a doublet of area 1 at slightly lower field. The resonance at −3.0 ppm remains unchanged but the doublet at +5.3 ppm is partially collapsed, showing that the terminal hydrogens on the boron atoms producing this signal have been partially exchanged with deuterium.

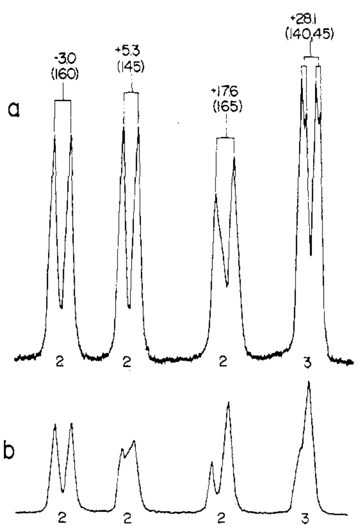

Figure 9.—The 80.5-MHz ^{11}B nmr spectra (benzene solution) of (a) (3)-1,2-$B_9C_2H_{13}$ and (b) (3)-1,2-$B_9C_2H_{13}$ deuterated using D_3PO_4.

A sample of deuterated (3)-1,2-$B_9C_2H_{13}$ was also prepared by the reaction of K-(3)-1,2-$B_9C_2H_{12}$ with a large excess of DCl in diethyl ether. In the ^{11}B nmr spectrum (32.1 MHz) of this material all the signals except one appear as singlets (Figure 10b). The resonance of area 1 at +17.1 ppm is the only doublet observed in this spectrum, indicating that all but one of the terminal B–H hydrogens have exchanged with deuterium.

The infrared spectrum of this material confirms that there has been extensive exchange of the terminal hydrogens on boron. A very intense, complex band, which can be assigned to terminal B–D stretching vibrations,[17] is present at 1923 cm^{-1}. Also, the band at 2580 cm^{-1}, which has been assigned to terminal B–H stretching vibrations in the spectrum of the undeuterated material, is of much lower relative intensity in the spectrum of the deuterated material. No bands attributable to B–H–B bridge vibrations were observed.[4]

Structure of (3)-1,2-$B_9C_2H_{13}$.—The ^{11}B nmr spectrum of (3)-1,2-$B_9C_2H_{13}$ exhibits no signals which could be assigned to a BH_2 group. Further, this spectrum is consistent with the presence of a plane of symmetry in the (3)-1,2-$B_9C_2H_{13}$ molecule (*vide supra*). The ^{13}C nmr spectrum of this compound in benzene solution consists of a doublet at +126 ppm,[19] J_{CH} = 170 Hz, which shows no evidence of coupling between the labile hydrogen atoms and the carbon atoms. Proton decoupling of the spectrum effects the collapse of this doublet to a singlet. In the light of these data the most reasonable structure for (3)-1,2-$B_9C_2H_{13}$ is one in which the labile hydrogen atoms occupy two equivalent, static bridging positions: one between B(4) and B(8) and the other between B(7) and B(8).

Further support for this proposed structure is provided by ^{11}B nmr and X-ray diffraction studies with 4,5-dicarba-*nido*-hexaborane(8). The structure of this compound has been shown to consist of a pentagonal pyramid with two adjacent carbon atoms in the pentag-

---

[20] The basic 1,7-$B_9C_2H_{11}$ unit contains a plane of symmetry passing through B(2), B(9), and B(10) and bisecting the B(4)–B(8) bond (Figure 1). Thus the molecule contains six types of boron atoms in the ratio 2:2:2:1:1:1, (*i.e.*, B(4), B8):B(5), B(12):B(6), B(11):B(2):B(9):B(10).

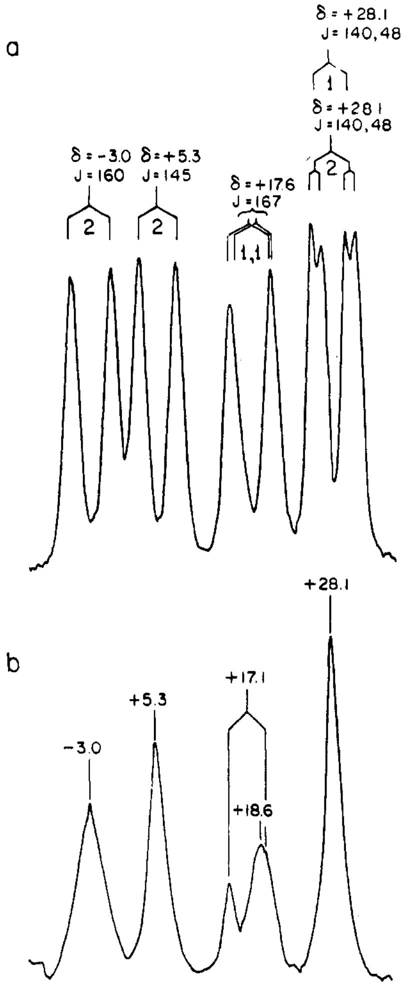

Figure 10.—The 32.1-MHz ^{11}B nmr spectra (benzene solution) of (a) (3)-1,2-$B_9C_2H_{13}$ and (b) (3)-1,2-$B_9C_2H_{13}$ deuterated using DCl in diethyl ether.

onal base.[21] Each of the heavy atoms carries a terminal hydrogen atom; the remaining two hydrogen atoms occupy equivalent B–H–B bridging positions in the pentagonal face, in exactly the same manner as postulated for (3)-1,2-$B_9C_2H_{13}$. The ^{11}B nmr spectrum (32.1 MHz) of 4,5-$B_4C_2H_8$[22,23] contains a signal which is very similar in appearance to that observed in the spectrum of (3)-1,2-$B_9C_2H_{13}$ at +28.1 ppm (Figure 10b). In the case of 4,5-$B_4C_2H_8$ this signal is assigned[22] to the pair of equivalent boron atoms in the pentagonal face, and the larger coupling of 154 Hz is attributed to terminal B–H coupling. The fine splitting of 44 Hz, which is effectively the same as the fine coupling observed in the spectrum of (3)-1,2-$B_9C_2H_{13}$, is attributed to coupling between the pair of boron atoms and the bridging hydrogens. In addition, the infrared spectrum of 4,5-$B_4C_2H_8$ contains bands at 1940 and 1520 cm^{-1} which have been assigned to B–H–B stretching vibrations.[22] Bands at 1965 and 1520 cm^{-1} are also observed in the infrared spectrum of (3)-1,2-$B_9C_2H_{13}$ and may be similarly assigned to B–H–B stretching vibrations.

The fine splitting of 45 Hz observed in the signal at +28.1 ppm in the ^{11}B nmr spectrum of (3)-1,2-$B_9C_2H_{13}$ (Figure 9a) can be attributed to coupling[24] between the bridging hydrogen and the pair of equivalent boron atoms in the open face [*i.e.*, B(4) and B(7)].

If this splitting were due to coupling between the bridging hydrogen atoms and B(8), a triplet would be expected instead of the observed doublet since B(8) would be coupled with two bridging hydrogen atoms. Thus the resonance of area 2, which comprises part of the signal at +28.1 ppm, can be assigned to B(4) and B(7).

The spectrum of deuterated (3)-1,2-$B_9C_2H_{13}$ (Figure 9b) shows that, of the pairs of equivalent boron atoms, B(4) and B(7) exchange terminal hydrogen most readily. (The signal assigned to B(4) and B(7) at +28.1 ppm is completely collapsed, whereas, of the other resonances of area 2, one has only partially collapsed and the other remains unchanged after deuteration.)

Assignment of the 80.5-MHz Spectrum of (3)-1,2-$B_9C_2H_{12}^-$.—Using the information obtained in the deuteration experiments described earlier, along with ^{11}B nmr spectral data for (3)-1,2-$B_9C_2H_{12}^-$ substituted in known positions, it has been possible to assign all the resonances in the 80.5-MHz ^{11}B nmr spectrum of (3)-1,2-$B_9C_2H_{12}^-$.

The signal of area 1 at +32.4 ppm can be assigned to the unique boron atom in the open pentagonal face, B(8), since this signal exhibits fine coupling with Ha (Figure 3a).

Comparison of the ^{11}B nmr spectrum of the previously reported[25] compound 6-C_6H_5-(3)-1,2-$B_9C_2H_{11}^-$ with that of (3)-1,2-$B_9C_2H_{12}^-$ allows the resonance due to B(6) to be assigned (Figure 3c). In the spectrum of the substituted material the doublet of area 1, which appeared at +16.8 ppm in the spectrum of (3)-1,2-$B_9C_2H_{12}^-$, has collapsed to a singlet and moved downfield to +9.7 ppm. The rest of the spectrum remains largely unchanged on substitution, establishing that the resonance of area 1 at +16.8 ppm in the spectrum of (3)-1,2-$B_9C_2H_{12}^-$ is due to the unique boron atom B(6). The doublet of area 1 at +37.0 ppm must, therefore, be due to the remaining unique boron atom B(10).[18]

X-Ray diffraction studies[26] have established that bromination of 1,2-$B_{10}C_2H_{12}$ with 2 equiv of bromine results in the formation of 9,12-Br_2-1,2-$B_{10}C_2H_{10}$. Base degradation of this compound results in the formation of the monoanion 9,12-Br_2-(3)-1,2-$B_9C_2H_{10}^-$ (irrespective of whether B(3) or B(6) is removed during the degradation the stereochemistry of the final product is the same). Comparison of the spectrum of this material (Figure 3d) with that of the unsubstituted material shows that bromination of B(9) and B(12) has caused the resonance of area 2, which comprises part of the signal at +16.8 ppm in the spectrum of the unsubstituted compound, to collapse to a singlet and move downfield to +10.8 ppm. The remainder of the spectrum remains largely unchanged except for small chemical shift changes in some of the signals. Consequently, the resonance of area 2 at +16.8 ppm in the spectrum of (3)-1,2-$B_9C_2H_{12}^-$ can be assigned to the pair of equivalent boron atoms B(9) and B(12).

---

[21] F. P. Boer, W. E. Streib, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1666 (1964).

[22] R. E. Williams and T. Onak, *J. Amer. Chem. Soc.*, **86**, 3159 (1964).

[23] T. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

[24] Comparison of spectra at 32.1 and 80.5 MHz establishes that this splitting is due to genuine spin–spin coupling and not due to the overlap of signals of slightly different chemical shift.

[25] M. F. Hawthorne and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 896 (1968).

[26] J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1471 (1966).

Earlier, it was established that the terminal hydrogens on the pair of boron atoms in the pentagonal face of (3)-1,2-$B_9C_2H_{13}$ could be exchanged for deuterium, while the other pairs of boron atoms, at most, only partially exchanged terminal hydrogen (*vide supra*). Hydrolysis of deuterated (3)-1,2-$B_9C_2H_{13}$ with D_2O affords (3)-1,2-$B_9C_2H_{12}^-$ in which some of the terminal hydrogen atoms have been exchanged with deuterium. The ^{11}B nmr spectrum of this compound (Figure 3e) shows that, of the doublets of area 2 observed in the spectrum of the undeuterated monoanion, that at +11.1 ppm has collapsed to a singlet in the spectrum of the deuterated compound. The signal at +16.8 ppm has partially collapsed and that at +21.8 ppm remains unchanged. Since the resonance at +16.8 ppm in the spectrum of (3)-1,2-$B_9C_2H_{12}^-$ has already been assigned to B(6), B(9), and B(12), the signal at +11.1 ppm must be due to the pair of equivalent boron atoms in the pentagonal face of the molecule, *i.e.*, B(4) and B(7). The doublet of area 2 at +21.8 ppm must, therefore, be due to the remaining pair of equivalent boron atoms, B(5) and B(11) (Figure 1).

Assignment of the 80.5-MHz Spectrum of (3)-1,2-$B_9C_2H_{13}$.—Using the above assignments in conjunction with the results of the deuteration studies it is possible to tentatively asign the 80.5-MHz ^{11}B nmr spectrum of (3)-1,2-$B_9C_2H_{13}$. It was established earlier, on the basis of coupling with the labile protons, that the resonance of area 2 at +28.1 ppm is due to B(4) and B(7). Of the remaining two pairs of equivalent boron atoms, that giving rise to the signal at −3.0 ppm shows no evidence of deuterium exchange (Figure 9). In the spectrum of the hydrolyzed material (Figure 3e) the resonance assigned to B(5) and B(11) remains as a doublet due to terminal B–H coupling and establishes that the doublet at −3.0 ppm in the spectrum of (3)-$B_9C_2H_{13}$ is due to B(5) and B(11). The doublet of area 2 at +5.3 ppm must therefore be due to the unassigned pair of equivalent borons B(9) and B(12).

The ^{11}B nmr spectrum of 6-C_6H_5-(3)-1,2-$B_9C_2H_{12}$, prepared by reaction of Cs-6-C_6H_5-(3)-1,2-$B_9C_2H_{11}$ with H_3PO_4 (Figure 11), is similar to that of (3)-1,2-$B_9C_2H_{13}$ (Figure 9a) except that one of the resonances of area 1 at +17.6 ppm has collapsed to a singlet and moved downfield to +8.1 ppm. This establishes that one of the resonances of area 1 at +17.6 ppm in the spectrum of (3)-1,2-$B_9C_2H_{13}$ is due to the unique boron atom B(6).

In order to assign the signals due to the remaining unique boron atoms in (3)-1,2-$B_9C_2H_{13}$, a sample of deuterated 6-C_6H_5-(3)-1,2-$B_9C_2H_{12}$ was prepared by the reaction between D_3PO_4 and $(CH_3)_4N$-6-C_6H_5-(3)-1,2-$B_9C_2H_{11}$. The ^{11}B nmr spectrum of this compound was similar to that of the undeuterated material (Figure 11) except that the signals at +4.5 and +27.3 ppm had partially collapsed and the resonance of area 1 at +19.6 ppm had completely collapsed to a singlet. Since the resonance of area 1 at +19.6 ppm collapses to a singlet on deuteration, the doublet of area 1 at +17.6 ppm in the spectrum of deuterated (3)-1,2-$B_9C_2H_{13}$ (Figure 9b) can be assigned to B(6). The spectrum of deuterated (3)-1,2-$B_9C_2H_{12}^-$ obtained by hydrolysis of deuterated (3)-1,2-$B_9C_2H_{13}$ (Figure 3e) shows that, of the unique boron atoms B(8) and B(10), B(8) exchanges terminal hydrogen for deuterium whereas B(10) does not. Thus the resonance of area 1 at +17.6 ppm in the spectrum of (3)-1,2-$B_9C_2H_{13}$ which collapses to a singlet on deuteration can be assigned to B(8). The resonance of area 1 at +28.1 ppm can therefore be assigned to the remaining unique boron atom B(10).

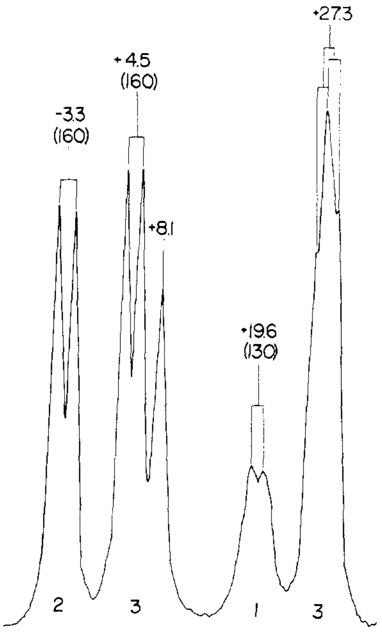

Figure 11.—The 80.5-MHz ^{11}B nmr spectrum (benzene solution) of 6-C_6H_5-(3)-1,2-$B_9C_2H_{12}$.

In the spectrum of 6-C_6H_5-(3)-1,2-$B_9C_2H_{12}$ (Figure 11) the signal of area 1 at +19.6 ppm is broadened. Since the other signals in the spectrum are well resolved, this broadening would appear to be the result of unresolved coupling and not the conditions under which the spectrum was recorded. Such a coupling is consistent with the previous assignment of this signal to B(8) which might be expected to exhibit coupling with the two bridging hydrogen atoms.

Experimental Section

Physical Measurements.—The ^{11}B nmr spectra at 80.5 MHz and ^{13}C nmr spectra at 63.1 MHz were recorded using an instrument designed and constructed by Professor F. A. L. Anet and Dr. C. H. Bradley. The ^{11}B nmr spectra at 32.1 MHz were recorded using a Varian HA-100 spectrometer. Infrared spectra were obtained using a Perkin-Elmer Model 421 infrared spectrophotometer.

Materials.—Deuterium oxide (99.8% isotopic purity) was obtained from Bio-Rad Laboratories. Deuterium chloride (38% solution in D_2O, 99% isotopic purity) and deuteriophosphoric acid (85% solution in D_2O, 99% isotopic purity) were obtained from Research Organic/Inorganic Chemical Corp. Anhydrous deuterium chloride was prepared by treating benzoyl chloride with D_2O and purified by fractional condensation *in vacuo*. Diethyl ether and tetrahydrofuran were redistilled from lithium aluminum hydride; benzene and acetonitrile were redistilled from calcium hydride. The compounds (3)-1,2-$B_9C_2H_{11}^{2-}$,[5] (3)-1,7-$B_9C_2H_{11}^{2-}$,[5] 6-C_6H_5-(3)-1,2-$B_9C_2H_{11}^-$,[24] and 9,12-Br_2-1,2-$B_{10}C_2H_{10}$[27] were prepared by previously reported methods. Tetramethylammonium chloride used to precipitate deuterated anions was dried *in vacuo* over P_2O_5 before use.

Preparation of Monodeuterated Tetramethylammonium (3)-1,2-Dicarba-*nido*-undecahydroundecaborate(1−).—A solution of Na_2-(3)-1,2-$B_9C_2H_{11}$ (13 mmol) in tetrahydrofuran was prepared by the method of Hawthorne, *et al.*,[5] and filtered under an atmosphere of nitrogen. The solution was then treated with D_2O (25 ml) and stirred under nitrogen for 15 min. After this time

---

[27] H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

the bulk of the tetrahydrofuran was evaporated under reduced pressure and tetramethylammonium chloride (2.2 g, 20 mmol) dissolved in D_2O (20 ml) was added to the residual solution. The white precipitate of $(CH_3)_4N$-(3)-1,2-$B_9C_2H_{11}D$ was isolated by filtration, washed with D_2O, and recrystallized from acetone–D_2O to give 2.4 g (89%) of product.

Preparation of Monodeuterated Tetramethylammonium (3)-1,7-Dicarba-*nido*-undecahydroundecaborate(1−).—This compound was prepared in exactly the same manner as $(CH_3)_4N$-(3)-1,2-$B_9C_2H_{11}D$ using Na_2-(3)-1,7-$B_9C_2H_{11}$[5] in place of Na_2-(3)-1,2-$B_9C_2H_{11}$. The yield of $(CH_3)_4N$-(3)-1,7-$B_8C_2H_{11}D$ was 2.4 g (89%).

Infrared Study on the Acid-Catalyzed Exchange Reactions of Potassium (3)-1,2-Dicarba-*nido*-dodecahydroundecaborate(1−).—K-(3)-1,2-$B_9C_2H_{12}$ (2.0 g, 11.6 mmol) was dissolved in 1 *M* DCl in D_2O (15 ml). Samples (0.5 ml) of this solution were removed after 0.1, 0.3, 1.3, 4.0, 7.0, 24, 48, and 120 hr, diluted to *ca.* 5 ml with D_2O, and treated with excess tetramethylammonium chloride dissolved in D_2O. The resulting precipitates were isolated by filtration, washed with D_2O, and dried *in vacuo* at 70°. The infrared spectra (Nujol mulls) of these samples were then recorded.

Preparation of Deuterated (3)-1,2-Dicarba-*nido*-undecaborane(13).—Samples of this material were prepared by two different methods which, on the basis of the ^{11}B nmr data, displayed different degrees of deuteration.

a. K-(3)-1,2-$B_9C_2H_{12}$ (0.5 g, 3 mmol) was added to D_3PO_4 (5 ml of an 85% solution in D_2O) and the mixture stirred under nitrogen in a sealed flask for 2 hr at room temperature. At the end of this time the reaction mixture was extracted with four 10-ml portions of benzene. The combined benzene extracts were then evaporated to dryness under reduced pressure at 30°, and the product was obtained by sublimation of the residual solid at 40° under high vacuum onto a Dry Ice–acetone cooled probe. To obtain a sample for ^{11}B nmr spectral measurements the product was washed directly off the probe with a small quantity of benzene under a stream of nitrogen. The resulting solution was collected, under nitrogen, in a clean, dry flask and was suitable for nmr measurements. This method of preparation affords a material in which the terminal hydrogens on only four of the boron atoms have been completely exchanged with deuterium.

b. (The operations described in this preparation were carried out using standard vacuum techniques or under an atmosphere of nitrogen). K-(3)-1,2-$B_9C_2H_{12}$ (1.0 g, 5.5 mmol) suspended in diethyl ether (30 ml) was stirred with DCl (12 mmol) at room temperature for 2 hr *in vacuo*. The solvent was then distilled off *in vacuo* at −40° and the product was sublimed at 35° onto a −77° cold finger condenser. This product was dissolved in diethyl ether (30 ml) and stirred with DCl (12 mmol) at room temperature for 12 hr *in vacuo*. The DCl, HCl, and solvent were then distilled off *in vacuo* at −40°. This process was repeated three additional times. The final product was sublimed under high vacuum at 35° onto a −77° cold finger condenser to give a white solid which melted to an oil at room temperature. This material was resublimed three times *in vacuo* at 25° in a closed system onto a 0° cold finger condenser. The sublimation apparatus was occasionally reevacuated to remove any more volatile impurities. The yield of colorless, crystalline deuterated (3)-1,2-$B_9C_2H_{13}$ was 0.2 g (1.4 mmol, 25%). The ^{11}B nmr spectrum of this compound showed that all but one of the terminal hydrogens had exchanged with deuterium.

Preparation of Tetramethylammonium 9,12-Dibromo-(3)-1,2-dicarba-*nido*-decahydroundecaborate(1−).—1,2-$B_{10}C_2H_{10}Br_2$ (5.8 g, 19 mmol) was dissolved in a solution of potassium hydroxide (2.0 g, 36 mmol) in absolute ethanol (30 ml) under a nitrogen atmosphere. The mixture was stirred at room temperature for 3 hr then refluxed for 0.5 hr. After this time the solution was allowed to cool and a stream of carbon dioxide was passed through the reaction mixture to precipitate the excess potassium hydroxide as potassium carbonate. The mixture was then filtered and the residue washed with two 50-ml portions of ethanol. The combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was dissolved in water and added to a solution of tetramethylammonium chloride (3.0 g, 27 mmol) in water. The precipitated product was isolated by filtration, washed with water, and recrystallized from either ethanol or ethanol–water. The yield of $(CH_3)_4N$-9,12-Br_2-(3)-1,2-$B_8C_2H_{10}$ was 5.5 g (88%).

Hydrolysis of Deuterated (3)-1,2-Dicarba-*nido*-undecaborane(13).—A sample of deuterated (3)-1,2-$B_9C_2H_{13}$ was prepared from K-(3)-1,2-$B_9C_2H_{13}$ and D_3PO_4 as described previously (*vide supra*). The material obtained by sublimation was dissolved in D_2O and treated with a solution of tetramethylammonium chloride in D_2O. The resulting precipitate was isolated by filtration, washed with D_2O, and recrystallized from acetone–D_2O.

Preparation of a Benzene Solution of 6-C_6H_5-(3)-1,2-$B_9C_2H_{12}$.—Cs-6-C_6H_5-(3)-1,2-$B_9C_2H_{11}$ (0.5 g, 1.5 mmol) was stirred under nitrogen in a sealed flask with H_3PO_4 (5 ml of an 85% aqueous solution) for 2 hr at room temperature. After this time the mixture was extracted with three 10-ml portions of benzene. The benzene extracts were combined, filtered through magnesium sulfate, and evaporated to *ca.* 1 ml at 30° under reduced pressure. The concentrated solution obtained by this means was suitable for ^{11}B nmr measurements.

Preparation of a Benzene Solution of Deuterated 6-C_6H_5-(3)-1,2-$B_9C_2H_{12}$.—$(CH_3)_4N$-6-C_6H-(3)-1,2-$B_9C_2H_{11}$ (0.5 g) was stirred with D_3PO_4 (5 ml of an 85% solution in D_2O) and benzene (10 ml) for 10 hr in a sealed flask containing a nitrogen atmosphere. The benzene layer was separated and the residue extracted with two 10-ml portions of benzene. The combined benzene extracts were then filtered through dry magnesium sulfate powder. The benzene solution so obtained was evaporated to *ca.* 1 ml at 30° under reduced pressure and was suitable for ^{11}B nmr spectral measurements.

Acknowledgments.—The authors are greatly indebted to Professor F. A. L. Anet and Dr. Craig Bradley of this department for the ^{11}B and ^{13}C nmr spectra. The award of a NATO fellowship (to C. J. J.) is gratefully acknowledged. This work was also supported, in part, by the Institute of Geophysics and Planetary Physics and the Office of Naval Research.