Properties of the *C,C′*-Dimethylpentahydro-4,5-dicarba-*nido*-hexaborate-(1−) ion, $C_2Me_2B_4H_5^-$, and its Reactions with Halogen species

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The nature of the anion, $C_2Me_2B_4H_5^-$, prepared by the action of alkali metal hydrides, or alkyls, on *C,C′*-dimethyl-4,5-dicarba-*nido*-hexaborane(8) $C_2Me_2B_4H_6$, has been clarified from a study of its ^{11}B n.m.r. spectrum over the temperature range 308—373 K. The anion reacts with iodine monochloride to yield 2-$ClC_2Me_2B_4H_5$ and 3-$ClC_2Me_2B_4H_5$ (in a 3:1 ratio), while bromine yields the 3-substituted isomer, 3-$BrC_2Me_2B_4H_5$, as the major product. Bridge halogen derivatives are believed to be intermediates in these reactions. The 220 MHz ^1H n.m.r. spectrum of the parent carborane, $C_2Me_2B_4H_6$, is also described to illustrate the potential advantage of using such spectra in studies on these compounds.

THE nido-carboranes of the general formula $C_2R_2B_4H_6$, where R_2 = H,H; H, Me; or Me, Me, (I), are known to yield anions, $C_2R_2B_4H_5^-$, when treated with nucleophiles, such as the H^- ion or lithium alkyls.

It has been suggested that one of the two bridging hydrogen atoms is removed from the neutral carborane

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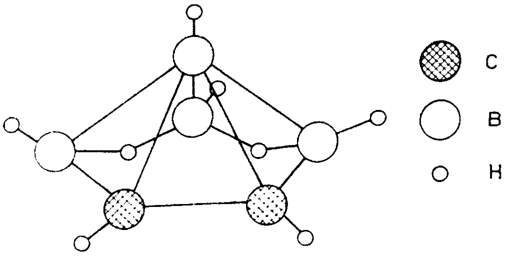
since addition of a proton donor (HCl, DCl, or $B_{10}H_{14}$) yields the original carborane, and when deuterium chloride is used it is the bridge-deuteriated species 2,3-μ-$DC_2R_2B_4H_5$, which is obtained.[1] Attempts to remove the second bridge hydrogen to yield the anion $C_2R_2B_4H_4^{2-}$ have been unsuccessful, even after treating the anion, $C_2R_2B_4H_5^-$, with an excess of sodium hydride at 200°.[1] The high thermal stability of anions of this type is in sharp contrast to the properties of the iso-electronic ion, $B_6H_9^-$, derived from hexaborane(10).[2]



(I)

However, the characterisation of these carborane anions remains incomplete because only preliminary information has been obtained previously from the ^{11}B n.m.r. spectra, and no crystalline derivatives could be prepared by the use of alkyl ammonium cations. The 12·8 MHz ^{11}B n.m.r. spectra of the $C_2R_2B_4H_5^-$ (R = H or Me) anions are reported to consist of a high field doublet, and three broad overlapping low-field signals which were assigned to three inequivalent basal boron atoms.[1] We report here the results of a study of the ^{11}B n.m.r. spectrum of the *C,C'*-dimethyl anion, $C_2Me_2B_4H_5^-$, over a temperature range 308—373 K, and experiments made to determine the relative reactivity of the anion, compared with that of the neutral carborane, by reaction with halogen species. Other results on the reaction of the anion with halogen-containing compounds such as Me_3MCl (M = Si or Ge) have shown that a bridge substituted derivative, 2,3-μ-$Me_3MC_2Me_2B_4H_5$, is formed first at ambient temperatures, and that the germanium compound slowly isomerises to the terminal isomer, 2-$Me_3GeC_2Me_2B_4H_5$ at 413 K.[3,4] However, interesting differences exist in the rate of isomerisation and reactivity of these compounds compared with the μ-$Me_3MC_2B_4H_7$ (M = Si, Ge, Sn, or Pb) analogues.[5]

RESULTS AND DISCUSSION

The lithium (or sodium) salt of the $C_2Me_2B_4H_5^-$ anion was prepared by stirring the carborane, $C_2Me_2B_4H_6$, with an excess of lithium (or sodium) hydride or lithium n-butyl in ether (diethyl ether, monoglyme, or diglyme) at ambient temperatures. One mole of hydrogen (or alkane) per mole of carborane was evolved over a two hour period. Solutions of the anion are stable at ambient temperatures, and although colourless at low concentrations they become steadily more viscous and yellow as the solvent is removed. Complete removal of the solvent is not possible, since viscous gums are obtained, whose i.r. spectra contain absorptions typical of the solvent, and, in contrast to the parent carborane, broad absorptions at 2540 and 2496 cm^{-1} with shoulders at 2600, 2580, 2460, and 2440 cm^{-1} arising from the terminal B–H bonds. The absorption at 1940 cm^{-1}, from the B–H–B bonds, is relatively weaker than in the parent carborane consonant with the removal of a bridging hydrogen atom.

The ^{11}B n.m.r. spectrum of the anion at 308 K (Figure 1) shows a high field doublet (area 1·0) and two broad overlapping signals at low-field (area 2·8), these latter two signals becoming resolved into two distinct resonances in the ratio 2 : 1 above 353 K. At 308 K no coupling can be detected in the low-field signals, but as the diglyme solution of the anion is warmed pro-pressively to 373 K (Figures 1a—d) the signals become better resolved, and B–H_t coupling is clearly observed. The changes are reversible on cooling to 308 K, and the data for the chemical shift values are summarised in Table 1. These variations in the spectra are similar to those observed for the $B_5H_8^-$ and $B_6H_9^-$ ions, although severe line broadening in these spectra only occurs at 233 and 173 K respectively.[2] However, as in these cases, the changes are probably largely related to the viscosity of the solutions since below 313 K the concentrated solutions of the $C_2Me_2B_4H_5^-$ anion, which are necessary in order to observe the resonances clearly, are almost too viscous to pour. Under these conditions the

TABLE 1

^{11}B N.m.r. spectral data for $NaC_2Me_2B_4H_5$ in diglyme solution at various temperatures

Temperature/ K	Signal multi-plicity	δ/p.p.m.[a]	J(BH)/ Hz[a]	Area[b]	Assign-ment
308	Broad singlet	−5·9			B^2, B^3, B^6
	Broad singlet	+7·4			
	Doublet	+48·0	160	1·21	B^1
333	Singlet	−5·8		1·67	B^3, B^6
	Singlet	+7·3		1·12	B^2
	Doublet	+48·0	164	1·21	B^1
363	Doublet	−5·7	90	1·69	B^3, B^6
	Doublet	+7·3	66	1·10	B^2
	Doublet	+48·0	164	1·21	B^1
373	Doublet	−5·7	109	1·86	B^3, B^6
	Doublet	+7·2	68	1·08	B^2
	Doublet	+48·2	160	1·06	B^1

[a] Small discrepancies in the chemical shifts and coupling constants are due to the broadness of the signals. Chemical shifts are relative to $BF_3,Et_2O = 0$. [b] Due to overlap of the two basal resonances these values are approximate at temperatures below 373 K

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

[2] H. D. Johnson, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 1970, **9**, 908.

[3] C. G. Savory and M. G. H. Wallbridge, *Chem. Comm.*, 1971, 622.

[4] C. G. Savory and M. G. H. Wallbridge, *J.C.S. Dalton*, 1972, 918.

[5] A. Tabereaux and R. N. Grimes, *Inorg. Chem.*, 1973, **12**, 792.

interaction of the boron nuclear quadrupoles is increased with a consequential decrease in the relaxation time. A further similarity to the $B_5H_8^-$ and $B_6H_9^-$ anions lies in the relative broadening associated with the basal and apical doublets, which is expected to be highly dependent upon the local field symmetry around the resonating nucleus.[2] The relatively greater broadening of the basal doublets (see Figure 1) probably reflects the higher charge asymmetry at those sites.

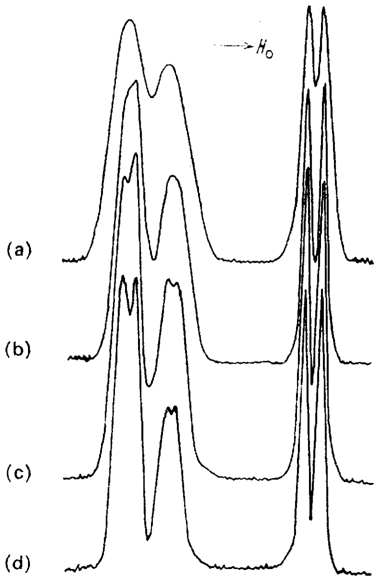
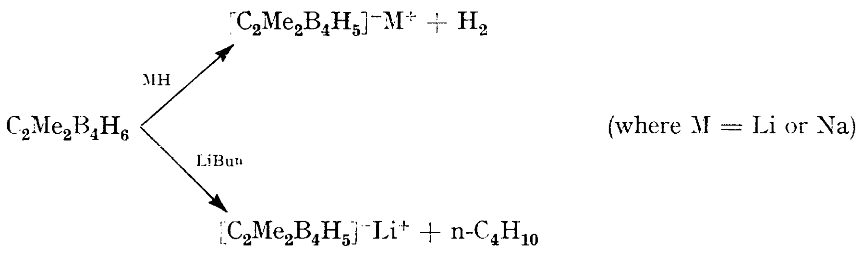


FIGURE 1 ^{11}B N.m.r. spectrum of $NaC_2Me_2B_4H_5$ in diglyme at (a) 308, (b) 333, (c) 363, and (d) 373 K



The ^{11}B n.m.r. spectra established that no exchange occurs between either the terminal hydrogen atoms themselves (on boron atoms 2, 3, and 6) or the terminal-bridge protons, since the two doublet signals observed at 373 K would appear as a quartet or quintet if such exchange was taking place. The lack of resolution of the doublet at +7·2 p.p.m., from the B^2 atom, is almost certainly due to the presence of coupling with the single bridge hydrogen atom. This situation is similar to that encountered in the (3)-1,2-$B_9C_2H_{12}^-$ ion where a single hydrogen bridge proton is rapidly exchanging into an adjacent vacant bridge site.[6] Thus in the present system the B^2 atom is coupled to the bridging proton all the time, but only transient coupling is to be expected with the 3-(6-)boron atoms due to exchange. However, unlike the ^{11}B n.m.r. spectrum of the (3)-1,2-$B_9C_2H_{12}^-$ ion which shows the smaller bridge coupling (40 Hz) superimposed upon the $B\text{-}H_t$ doublet (the spectrum was recorded at 80·5 MHz), the coupling in the present spectrum (recorded at 32·1 MHz) is not resolved and each portion of the doublet has a broadened appearance (Figure 1d). It is also unlikely that any exchange occurs between two anions in an intermolecular process since this would require the interaction of two negatively charged species. Similar arguments to those above have been used to explain the appearance of the ^{11}B n.m.r. spectra of the $B_5H_8^-$ and $B_6H_9^-$ anions, and indeed a close similarity exists between the behaviour of the present anion and those systems.

The comparison between the carborane and borane anions may be extended to the chemical shifts and coupling constants observed. Thus for the $^{11}B\text{-}^1H$ coupling constants the values of $J(BH)$ decrease in all the anions $C_2Me_2B_4H_5^-$, $B_5H_8^-$, and $B_6H_9^-$ compared with the parent compound (see Table 1). The values of $J(BH)$ for B^3 and B^6 (109 Hz) are remarkably close to the values for the basal B–H groups in the $B_6H_9^-$ anion (107 Hz),[2] but the values for B^2 are significantly lower, although in this case the signal is less well resolved (a general characteristic of the B^2 atoms in these systems), and the value can only be regarded as approximate. The general lowering of the $J(^{11}B^1H)$ values suggest less *s* character in the terminal B–H bonds,[7] and the suggestion made elsewhere that a consequential decrease in the bond order of the B–H bonds is to be expected [8] is substantiated by the fact that the terminal B–H stretching frequencies occur some 60 cm^{-1} lower in $C_2Me_2B_4H_5^-$ than in $C_2Me_2B_4H_6$. The difficulty of predicting the relative chemical shifts in such systems has been outlined,[2] and it is noteworthy that for the $C_2Me_2B_4H_5^-$ anion in the ^{11}B n.m.r. spectrum both the apical, B^1, and basal, B^2, atoms show an upfield shift while the B^3 and B^6 basal atoms show a downfield shift compared with the neutral carborane. In contrast for the $B_5H_8^-$ and $B_6H_9^-$ anions all the basal atoms are shifted upfield, while the apical boron atom is shifted downfield with respect to the values for the neutral hydrides.[2]

Our attempts to prepare a crystalline sample of the anion were unsuccessful in that, for example, reaction of $NaC_2Me_2B_4H_5$ with Me_4NX (X = Br or I) and $Bu^n{}_4NI$ did not lead to an isolable product of the corresponding alkyl ammonium salt, and only viscous

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[6] D. V. Howe, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, *Inorg. Chem.*, 1971, **10**, 2516.

[7] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

[8] A. B. Burg and H. Heinen, *Inorg. Chem.*, 1968, **7**, 1021.

residues could be obtained. In view of the facile reactions of the $C_2Me_2B_4H_5^-$ anion with deuterium chloride,[1] and halogeno-species of the Group IVB elements,[3-5] we have studied the reactions with iodine monochloride and bromine to compare the reactivity of other halogen compounds. When equimolar quantities of iodine monochloride and the $C_2Me_2B_4H_5^-$ ion are stirred in ether solution at ambient temperatures fractionation of the volatile products of the reaction yields the original carborane, $C_2Me_2B_4H_6$, ethyl iodide, iodine, and a slightly volatile liquid (vapour pressure <1 mmHg at 21°). The ^{11}B n.m.r. spectrum of this liquid (see Table 2 and Figure 2) shows a fairly complex pattern in which resonances arising from $3\text{-}ClC_2Me_2B_4H_5$ can be clearly recognised.[9] However, the major resonances in the spectrum, namely a low-field singlet, a mid-field quartet, and a high-field doublet, are consistent with halogen substitution of the B^2 atom. Since the mass spectrum shows only a molecular ion corresponding to $C_2Me_2B_4H_5Cl^{+\cdot}$ with no mono-iodo compound present the major product is clearly the $2\text{-}ClC_2Me_2B_4H_5$ isomer.

TABLE 2

^{11}B and ^1H N.m.r. spectral data for 2-Cl and $2\text{-}BrC_2Me_2B_4H_5$ compounds

$2\text{-}Cl_2Me_2B_4H_5$ Assignment	^{11}B [a]	^1H [a]	$J(BH)/Hz$
5	δ/p.p.m.	τ	
B^1	46·0	9·95	172
B^2	−19·7		
B^3, B^6	11·5	6·75	145 (Terminal) 51 (Bridge)
C^4, C^5		7·59	
Bridge H atoms		10·55	
$2\text{-}BrC_2Me_2B_4H_5$			
B^1	45·2	10·6	180
B^2	−12·7		
B^3, B^6	11·3	6·7	160 (Terminal) 46 (Bridge)
C^4, C^5		7·4	
Bridge H atoms		11·0	

[a] The ^1H and ^{11}B n.m.r. spectra were recorded at 60 and 32·1 MHz respectively

The relative proportions of this and the B^3–Cl isomer can be estimated from the ^{11}B n.m.r. spectrum.

$$\underset{}{Na^+C_2Me_2B_4H_5^-} + ICl \xrightarrow[298\text{ K}]{Et_2O} \underset{(70\%)}{2\text{-}ClC_2Me_2B_4H_5} + \underset{(30\%)}{3\text{-}ClC_2Me_2B_4H_5} + C_2Me_2B_4H_6 + EtI + I_2 + NaI\downarrow$$

A similar reaction in the presence of aluminium chloride yields the same products in about the same ratio (2-Cl : 3-Cl = 3 : 1), and in both reactions the overall yield of the chloro-carboranes (based on the amount of $C_2Me_2B_4H_5^-$ used) is *ca.* 50%. The course of the reaction under Friedel–Crafts conditions is surprising since the action of iodine monochloride on the neutral carborane, $C_2Me_2B_4H_6$, under these conditions yields only $3\text{-}IC_2Me_2B_4H_5$.[9]

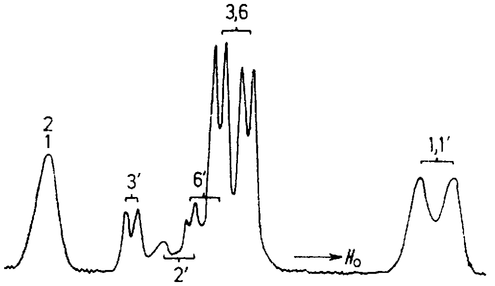

FIGURE 2 ^{11}B N.m.r. spectrum of the volatile products from the $Na^+C_2Me_2B_4H_5^-$–ICl reaction. Signals 1,2,3,6 arise from $2\text{-}ClC_2Me_2B_4H_5$ and 1', 2', 3', 6' from $3\text{-}ClC_2Me_2B_4H_5$

$$\begin{tikzcd}
 & & 2\text{-(or 3-)}YC_2Me_2B_4H_5 + X_2\text{/other products} \\
Na^+C_2Me_2B_4H_5 + X\text{–}Y \arrow[r] & {[2,3\text{-}\mu XC_2Me_2B_4H_5]} \arrow[ur, "XY"] \arrow[dr, "\text{Isomerisation}"'] & \\
 & & 2\text{-(or 3-)}XC_2Me_2B_4H_5
\end{tikzcd}$$

(X = I, Y = Cl; X = Y = Br)

When bromine is used in place of iodine monochloride the product is a colourless liquid whose ^{11}B n.m.r. spectrum contains resonances arising from $3\text{-}BrC_2Me_2B_4H_5$ [9] and also a low-field singlet, a mid-field pair of doublets, and a high-field doublet arising from $2\text{-}BrC_2Me_2B_4H_5$. However, it is now the 3-isomer which predominates, the ratio of the 3-Br to 2-Br product being *ca.* 9 : 1. The assignments for these derivatives are similar to those for the 2- and 3-Cl compounds (Table 2). The ^1H n.m.r. spectra of the 2-Cl and 2-Br derivatives are consistent with substitution at the B^2 position in that only two quartets are observed for each compound corresponding to the B^1 and equivalent B^3 (B^6) atoms. In addition resonances assignable to the bridging hydrogen atoms and the *C*-methyl groups are also observed (Table 2).

In view of both the marked change in the relative proportions of the products from the reaction of the anion, $C_2Me_2B_4H_5^-$, with bromine and iodine monochloride, and the absence of any iodo-carborane derivatives with the latter reagent, we undertook a further study of these reactions at lower temperatures. Reactions of an ether solution of the $C_2Me_2B_4H_5^-$ ion with

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[9] J. S. McAvoy, C. G. Savory, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1971, 3038.

iodine monochloride at 253 K leads to the isolation of a light red liquid (the colouration is probably due to dissolved iodine or iodine monochloride) with a vapour pressure of <1 mmHg at 293 K. On standing for a short period at room temperature the vapour pressure increases and ethyl iodide and $C_2Me_2B_4H_6$ can be recovered. The ^{11}B n.m.r. spectrum of the original liquid at 253 K is similar to that observed for the room temperature reaction in that it contains resonances due to $C_2Me_2B_4H_6$ can be seen, together with a weak low-field doublet at $\delta = -14{\cdot}0$ p.p.m. [$J(^{11}B^1H)$ 154 Hz]. As the sample is allowed to warm up in the probe the resonances attributable to $C_2Me_2B_4H_6$ increase and the low-field doublet disappears. Similarly in the ^1H n.m.r. spectrum resonances attributable to ethyl iodide and $C_2Me_2B_4H_6$ increase as the sample is warmed up. Although no signals assignable to any iodo-carboranes (*e.g.* 3-$IC_2Me_2B_4H_5$) can be observed in either the ^{11}B or ^1H n.m.r. spectra [9] a parent molecular ion of a compound of the empirical formula $C_4B_4H_{11}I$ may be detected mass spectrometrically in the mixture of reaction products indicating at least the presence of such a compound in trace quantities in the mixture.

A similar low-temperature study of the bromine reaction also shows the formation of $C_2Me_2B_4H_6$ as the reaction products are allowed to warm in the probe. Again a low-field doublet at $\delta = 13{\cdot}6$ p.p.m. (J 157 Hz) is observed in the ^{11}B n.m.r. spectrum.

Since both reactions proceed identically in the presence and absence of aluminium halides it seems reasonable that the initial reaction involves attack by I^+ and Br^+ species respectively. The experimental evidence suggests that these reactions are similar to those involving the action of other halogen species (DCl,[1] Me_3SiCl,[4] H_2SiCl_2,[10] *etc.*) where the attacking electrophile enters the bridging position. Several observations indicate the initial formation of a bridged halo-carborane, 2,3-μ-$XC_2Me_2B_4H_5$ (X = Br or I). First, the low-field doublet observed in both ^{11}B n.m.r. spectra of the reactions mixtures at 253 K is similar to that observed in the stable bridge compounds [for example, 2,3-μ-$Me_3SiC_2Me_2B_4H_5$ shows a doublet at $\delta = -10{\cdot}96$ p.p.m. (J 152 Hz) assigned to the B^3 atom [4]], and may be similarly assigned to the B^2 atom. Secondly, the detection of $C_2Me_2B_4H_6$ and smaller quantities of $C_2Me_2B_4H_5I$ resembles products obtained in the isomerisation reactions of the 2,3-μ-$YC_2Me_2B_4H_5$ (Y = Me_3Si, Me_3Ge, Me_2ClSi, *etc.*) compounds.[4] Thirdly, it is well established that reaction with deuterium chloride results in insertion of deuterium into the bridging position.[1] In the case of the reaction using iodine monochloride it is necessary that subsequent nucleophilic attack by chloride ion occurs either in a concerted process or by further attack by iodine monochloride since the major products are the chloro-substituted carboranes. The ratio of the products will thus be determined by the relative ground state electron densities of the various boron atoms, providing that the energies of activation for the alternative reaction pathways are comparable.

In the case of the Br_2–$C_2Me_2B_4H_5^-$ reaction no ethyl bromide is detected and the ratio of the product is reversed. Thus although initial formation of μ-$BrC_2Me_2B_4H_5$ seems the most reasonable postulation, nucleophilic attack by bromide ion need not occur and instead isomerisation may take place together with some decomposition. Nucleophilic attack on μ-$BrC_2Me_2B_4H_5$ by bromide ion cannot be ruled out and the reversal of reaction products (compared with the iodine monochloride reaction), may well be explicable in terms of the differing effects of bromine and iodine on the attached boron atom. This latter effect can be seen clearly by a difference in the chemical shift of 12·6 p.p.m. for the B^3 atom in 3-Br and 3-$IC_2Me_2B_4H_5$.[9]

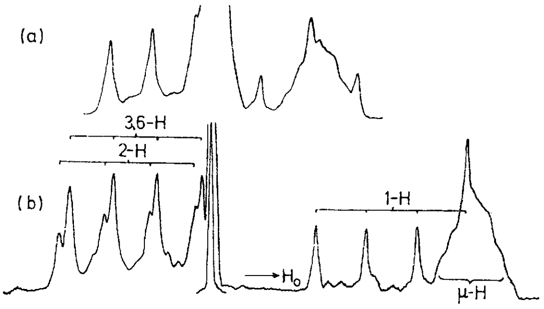

FIGURE 3 ^1H N.m.r. spectra of $C_2Me_2B_4H_6$ at (a) 100 MHz and (b) 220 MHz

Attempts to follow the entire reaction by carrying out the reaction in an n.m.r. tube and using ^{11}B n.m.r. spectroscopy were not successful due to reaction at the interface of the two components ($Na^+C_2Me_2B_4H_5^-$ and Br_2 or ICl), with the formation of sodium chloride which blocked the tube and prevented further reaction.

Finally, we wish to report a preliminary study of the 220 MHz ^1H n.m.r. spectrum of the parent carborane to illustrate the potential use of such spectra. Generally the ^1H n.m.r. spectra of carboranes are relatively little used in studies involving substitution or rearrangement reactions due to overlapping signals and coupling of the protons to the boron atoms ($I = 3/2$). Thus for $C_2Me_2B_4H_6$ the signals from the hydrogen atoms on the $B^3(B^6)$ and B^2 atoms are not resolved, and overlap of the signals from the bridge hydrogen atoms and that on the apical boron atom occurs (Figure 3) at 100 MHz. In contrast at 220 MHz all the hydrogens in the various environments are resolved, and even the coupling constant for the bridge hydrogen atoms, not previously observed, can be obtained (Figure 3 and Table 3). The spectrum shows that the J(BH) values for the proton on the B^2 atom is in fact greater than that for the protons on the $B^3(B^6)$ atoms rather than the reverse as has been suggested, and in addition several members of the expected septets arising from coupling with the ^{11}B isotope ($I = 3$) are also observed. Thus it is worthwhile noting that such spectra would be of value in deter-

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[10] W. A. Ledoux and R. N. Grimes, *J. Organometallic Chem.*, 1971, **28**, 37.

mining uniquely the changes in local environment associated with either the protons (and indirectly the boron atoms) in such compounds and their derivatives.

In conclusion the above results clarify the nature of the carborane anions, $C_2R_2B_4H_5^-$ ($R = H$ or Me), and show that not unexpectedly the charge distribution in the anion $C_2Me_2B_4H_5^-$ is significantly different from that of the neutral carborane which in turn affords a preparative method for obtaining various isomers of the substituted carboranes.

TABLE 3

^1H N.m.r. spectral data for $C_2Me_2B_4H_6$ at 220 MHz

Signal multiplicity	δ (p.p.m.)[a]	J_{B-H} (Hz)	Assignment
Quartet	-3.62	163	Terminal H (2-B)
Quartet	-3.47	160	Terminal H(3-, 6-B)
Singlet	-2.22		C-CH_3 hydrogen
Quartet	$+0.76$	183	Terminal H(1-B)
Multiplet	$+2.13$	40—45	Bridge H atoms

[a] Chemical shifts are relative to tetramethylsilane = 0.

EXPERIMENTAL

All the volatile compounds were handled by means of a standard high-vacuum line, or in a dry nitrogen-filled glove box. Sodium and lithium hydrides (Koch–Light Ltd.) were used as received and had a purity of 88% (based on an active hydrogen determination). Diglyme, monoglyme, and diethyl ether were dried by distillation from lithium aluminium hydride under a nitrogen atmosphere, and stored over molecular sieve 4A. Bromine was dried over phosphorus pentoxide and purified by distillation *in vacuo*. Aluminium chloride was purified by sublimation *in vacuo* at 403 K, and tetra-n-butylammonium iodide (B.D.H.) and anhydrous hydrogen chloride (I.C.I. Ltd.) were used as received. Deuterium chloride,[11] n-butyl-lithium,[12] iodine monochloride,[13] were prepared by the literature methods. The parent carborane, $C_2Me_2B_4H_6$, was prepared by the action of pentaborane(9) on but-2-yne at 443 K, and purified by g.l.c.[14]

The i.r. spectra were recorded using a Perkin-Elmer 457 grating spectrometer, and the ^{11}B n.m.r. spectra were recorded using a Varian HA 100 spectrometer operating at 32·1 MHz. The ^1H n.m.r. spectra were obtained on a Perkin-Elmer R12A spectrometer operating at 60 MHz. The mass spectra were obtained using an A.E.I. MS 9 spectrometer at 70 e.v., an accelerating voltage of 8 kV, a trap current of 100 μA, and a pressure of 10^{-5} to 10^{-6} mmHg with the source temperature (*ca.* 323 K) maintained by water cooling. The samples were introduced as vapours *via* a heated inlet.

Preparation of the C,C′-*Dimethylpentahydro*-4,5-*dicarba-nido-hexaborate* (1−) *Ion*, $C_2Me_2B_4H_5^-$.—Sodium hydride (0·583 g, 24·2 mmol), together with a Teflon-coated magnetic stirring bar, was placed in a 100 ml flask, fitted with a stopcock. After evacuating the flask, dry diglyme (5 ml) and the carborane, $C_2Me_2B_4H_6$ (0·540 g, 5·18 mmol), were distilled in at 77 K and the reaction mixture allowed to warm to room temperature with stirring. Gas evolution occurred rapidly at 295 K, and periodically the volume of non-condensable gas was checked using a Töepler pump. After 1 h, 110 ml of hydrogen (4·92 mmol, 95% theoretical for 1 mol of H_2 liberated per mol of carborane used) had been evolved. After another 2 h, a further 5 ml of H_2 (total 5·14 mmol, 99% theoretical) had been evolved. Further evolution of hydrogen was very slow and the reactions were usually terminated after 4 h. The solution was filtered through a sintered glass funnel (in the glove box) to yield a clear solution, which was colourless when dilute, but which took on a yellow colouration when concentrated.

Addition of anhydrous hydrogen chloride to the solution of the anion resulted in recovery of the original carborane, $C_2Me_2B_4H_6$ (0·465 g, 4·47 mmol, 86% of the carborane initially used).

The anion, $C_2Me_2B_4H_5^-$, was also prepared in monoglyme and diethyl ether by the action of both sodium and lithium hydrides on the carboranes. The reaction of $C_2Me_2B_4H_6$ with n-butyl-lithium in diethyl ether also yields the anion, but in light petroleum there is no reaction.

For comparative purposes the $C_2Me_2B_4H_5$ ion was treated with anhydrous deuterium chloride to yield mainly μ-$DC_2Me_2B_4H_5$. Treatment of the latter with sodium hydride afforded μ-$DC_2Me_2B_4H_4^-$, for an ^{11}B n.m.r. study, which on addition of anhydrous deuterium chloride yielded mainly μ-$D_2C_2Me_2B_4H_4$ as evidenced by the mass spectral cut-off at *m/e* 106.

Attempted Preparation of $Me_4NC_2Me_2B_4H_5$.—Tetra-n-butylammonium iodide (1·014 g, 2·75 mmol) in dry dichloromethane (20 ml), was added to an ether solution of the $C_2Me_2B_4H_5^-$ ion (2·75 mmol in 5 ml of diethyl ether), and stirred for 2 h at room temperature. No precipitate was observed and removal of the solvents afforded a tacky white solid whose i.r. spectrum corresponded closely to that of the $C_2Me_2B_4H_5^-$ ion. However a discrete product was not obtained.

Reaction of the $C_2Me_2B_4H_5^-$ *Ion with Iodine Monochloride.*—In a typical reaction an ether solution of the $C_2Me_2B_4H_5^-$ ion (4·83 mmol) was placed in a reaction flask and iodine monochloride (0·7653 g, 4·71 mmol) condensed in at 77 K. The flask was warmed to room temperature and the contents stirred for a 2 h period. Fractionation of the volatile components through traps at 233, 213, 193, and 77 K yielded a mixture of 2- and 3-chlorocarborane, $C_2Me_2B_4H_5Cl$ (0·244 g, 1·76 mmol, 49% yield based on the overall consumption of the carborane), condensed in the 233 K trap, ethyl iodide in the 213 K trap, $C_2Me_2B_4H_6$ (0·131 g, 1·26 mmol) in the 193 K trap, and diethyl ether in the 77 K trap. The chlorocarborane mixture possessed a slight pink colouration probably due to a trace of dissolved iodine.

When the reaction was carried out at 233 to 253 K, the 233 K trap contained a liquid with a vapour pressure of < 1 mmHg at 293 K. Upon standing at room temperature, however, the vapour pressure increased, and ethyl iodide and $C_2Me_2B_4H_6$ were produced, both identified from their i.r. and mass spectra.[9]

An identical reaction was observed in the presence of aluminium chloride. The reaction was performed at low temperature (*ca.* 233 K) to minimise the cleavage of diethyl ether by aluminium chloride. In all cases the chlorocarboranes were characterised by their ^{11}B n.m.r. and mass

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spectra. The mass spectrum of the 2- and 3-chlorocarborane mixture was identical with that of the 3-chlorocarborane [8] and the mass spectral analyses were carried out on ' head ' and ' tail ' fractions of the products and found to be identical.

Reactions of the $C_2Me_2B_4H_5^-$ *Ion with Bromine*.—The reactions were carried out in the same manner as those for iodine monochloride. In a typical reaction using an ether solution of the $C_2Me_2B_4H_5^-$ ion (5·0 mmol) and bromine (0·7936 g, 4·96 mmol) 2- and 3-bromocarboranes, $C_2Me_2B_4H_5Br$ (0·282 g, 0·54 mmol, 42% yield based on the overall consumption of the carborane), and $C_2Me_2B_4H_6$ (0·139 g, 1·34 mmol) and recovered and separated by fractionation *in vacuo* as described above, and identified from their spectroscopic and mass spectral properties.[9] No ethyl bromide was detected.

An identical reaction occurred in the presence of aluminium bromide at low temperatures (233—273 K) and $C_2Me_2B_4H_6$ was recovered together with 2- and 3-$BrC_2Me_2B_4H_5$. The bromocarboranes were again characterised by their ^{11}B n.m.r. and mass spectra.

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