Characterisation of Degradation Products in the Oxidation of the Dodecahydro-7,8-dicarba-*nido*-undecaborate(1−) Ion: A New Synthesis of 4,5-Dicarba-*nido*-nonaborane(11)

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Degradation of aqueous 1 mol dm^{-3} K[$B_9C_2{}^{7,8}H_{12}$] by aqueous $FeCl_3$ (1.25 mol dm^{-3}) yields $B_8C_2{}^{5,6}H_{12}$ (33%) as previously reported, together with $B_8C_2{}^{5,6}H_{11}(OH)$ (1.6%), $B_8C_2{}^{5,6}ClH_{11}$ (0.9%), and $B_7C_2{}^{4,5}H_{11}$ (4.2%). The yield of $B_7C_2{}^{4,5}H_{11}$ may be increased substantially by using lower concentrations of reactants (0.1—0.2 mol dm^{-3}), and this reaction thus provides a simple synthesis of this otherwise highly inaccessible carbaborane. The mass spectrum of $B_7C_2{}^{4,5}H_{11}$ has been obtained. The ^{11}B n.m.r. spectrum of $B_8C_2{}^{5,6}ClH_{11}$, when compared with spectra of the four isomers of $B_{10}ClH_{13}$, suggests that substitution has occurred at the 10 position, but the position of substitution of the hydroxy-group in $B_8C_2{}^{5,6}H_{11}(OH)$ remains uncertain.

THE oxidation of the dodecahydro-7,8-dicarba-*nido*-undecaborate(1−) anion, $[B_9C_2{}^{7,8}H_{12}]^-$, by aqueous iron(III) chloride has previously been shown to yield 5,6-dicarba-*nido*-decaborane $B_8C_2{}^{5,6}H_{12}$ as the major product,[1] together with at least four other volatile compounds which were not identified. We have re-investigated the reaction in an attempt to identify these by-products, and thereby obtain a clearer understanding of the processes occurring in such degradation reactions.

RESULTS AND DISCUSSION

When aqueous 1 mol dm^{-3} K[$B_9C_2{}^{7,8}H_{12}$] is treated with a seven-fold molar excess of acidic aqueous $FeCl_3$ (1.25 mol dm^{-3}), and the reaction mixture extracted with pentane, three compounds may be obtained by column chromatography on silica gel with pentane as eluant. Under these conditions the products eluted successively are $B_8C_2{}^{5,6}H_{12}$ (33% yield), $B_8C_2{}^{5,6}ClH_{11}$ (0.9%), and $B_7C_2{}^{4,5}H_{11}$ (4.2%), despite a previous report[2] that $B_8C_2{}^{5,6}H_{12}$ and $B_7C_2{}^{4,5}H_{11}$ cannot be separated in this way due to hydrolysis of the latter. Although we obtained a separation it is therefore possible that some $B_7C_2{}^{4,5}H_{11}$ was lost on the column. Another product can also be separated from the original pentane extract by cooling to 0 °C for 12 h, when crystals of a *B*-hydroxy-derivative, $B_8C_2{}^{5,6}H_{11}(OH)$, are obtained in low yield (1.6%). This compound has an R_F value of *ca.* 0 (silica gel–pentane), and consequently was not detected during column chromatography. Only one other hydroxy-*nido*-carbaborane is available for comparison, namely $B_{10}Me_3(CN)H_{11}(OH)$,[3,4] although various derivatives of the *closo*-boranes $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, *e.g.* $[B_{10}H_9(OH)]^{2-}$, are known.[5]

Subsequent experiments revealed the novel feature that the yield of $B_7C_2{}^{4,5}H_{11}$ can be substantially increased by using lower concentrations of reactants (0.1—0.2 mol dm^{-3}), so that, for example, the oxidation of 0.2 mol dm^{-3} K[$B_9C_2{}^{7,8}H_{12}$] by a five-fold molar excess of 0.2 mol dm^{-3} $FeCl_3$ gave a mixture of products (16.1% based on the $[B_9C_2H_{12}]^-$ consumed), containing over 90% $B_7C_2{}^{4,5}H_{11}$ with the remainder being $B_8C_2{}^{5,6}H_{12}$ and the final yield of pure $B_7C_2{}^{4,5}H_{11}$, after sublimation and column chromatography, was 13.5%. The purified sample was much more reactive than the crude material and inflamed on contact with the atmosphere. The compound was identified from its ^{11}B n.m.r. spectrum [C_6D_6 solution, chemical shift relative to $OEt_2{\cdot}BF_3$ (0 p.p.m.)] which showed doublets centred at −10.1 (integrated intensity 1B), −4.1 (1B), 4.4 (3B), and 55.6 p.p.m. (1B), and a triplet (relative intensity 1 : 2 : 1) centred at 29.3 p.p.m. (1B). On proton decoupling all the resonances collapsed to singlets with shifts identical to those given above. This spectrum is identical, apart from slight solvent effects, with that previously reported for $B_7C_2{}^{4,5}H_{11}$ which had been obtained from the reaction of octaborane(12) (itself prepared from i-B_9H_{15}) with acetylene.[3] Oxidation of the $[B_9C_2{}^{7,8}H_{12}]^-$ ion thus provides a convenient and simple synthesis, in moderate yield, of $B_7C_2{}^{4,5}H_{11}$, an otherwise very inaccessible carbaborane.

The position of chloro-substitution in $B_8C_2{}^{5,6}ClH_{11}$ was determined by a comparison of the influence of the Cl substituent on the ^{11}B n.m.r. chemical shifts of the cage boron atoms with the corresponding effects in the four isomers of $B_{10}ClH_{13}$,[6] on the basis that, in isostructural skeletons, a given substituent should cause analogous chemical-shift changes ($\Delta\delta$) of corresponding skeletal atoms. The ^{11}B n.m.r. resonance due to the substituted atom in $B_8C_2{}^{5,6}ClH_{11}$ is readily identified as a singlet at $\delta = -0.17$ p.p.m., and since substitution of Cl for H in borane skeletons usually shifts the ^{11}B resonance of the substituted B atom some 8—15 p.p.m. downfield[6] only substitution at the 10 position (δ 8.7 p.p.m. in $B_8C_2{}^{5,6}H_{12}$) could cause a shift of the correct sign and

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[1] J. Plešek and S. Heřmánek, *Coll. Czech. Chem. Comm.*, 1974, **39**, 821.

[2] R. R. Reitz and R. Schaeffer, *J. Amer. Chem. Soc.*, 1973, **95**, 6254.

[3] W. H. Knoth, *J. Amer. Chem. Soc.*, 1967, **89**, 1274.

[4] F. R. Scholer and L. J. Todd, *J. Organometallic Chem.*, 1968, **14**, 261.

[5] W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1964, **86**, 3973.

[6] R. F. Sprecher, B. E. Aufderheide, G. W. Luther III, and J. C. Carter, *J. Amer. Chem. Soc.*, 1974, **96**, 4404.

magnitude. Furthermore, when the Δδ values of individual boron atoms in the pairs of compounds 10-$ClB_{10}H_{13}$ – $B_{10}H_{14}$ and 10-$ClB_8C_2{}^{5,6}H_{11}$ – $B_8C_2{}^{5,6}H_{12}$ are compared a relatively good correlation is obtained (Table 1).

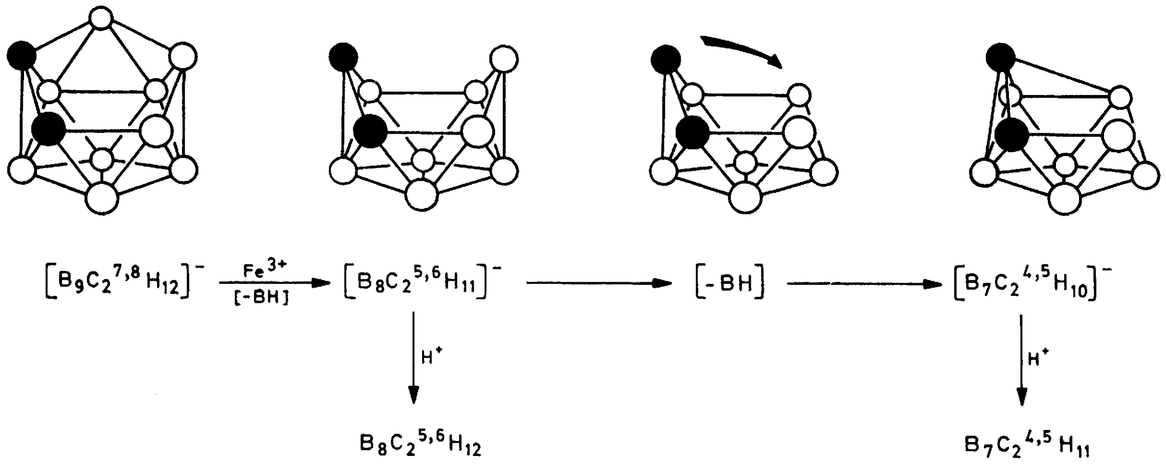
TABLE 1

Boron-11 chemical shifts [a] in $B_{10}H_{14}$ – 10-$ClB_{10}H_{13}$ and $B_8C_2{}^{5,6}H_{12}$ – 10-$ClB_8C_2{}^{5,6}H_{11}$

	B^1	B^2	B^3	B^4	B^5	B^6	B^7	B^8	B^9	B^{10}
δ($B_{10}H_{14}$) [b]	−11.9	36.1	−11.9	36.1	−0.4	−10.3	−0.4	−0.4	−10.3	−0.4
δ(10-$ClB_{10}H_{13}$) [b]	−12.0	36.6	−12.8	34.7	−4.0	−11.1	1.1	4.3	−7.9	−11.0
Δδ [c]	−0.1	0.5	−0.9	−1.4	−3.6	−0.8	1.5	4.7	2.4	−10.6
δ($B_8C_2{}^{5,6}H_{12}$) [d]	2.0 [e] (−7.6)	26.1	−6.0	38.3			−7.6 [e] (2.0)	−4.3	2.5	9.2
δ(10-$ClB_8C_2{}^{5,6}H_{11}$)	−6.8 [e]	26.4	−6.8	37.4			0.2 [e]	0.2	6.4	0.2
Δδ [c]	−1.8 (0.8)	0.3	−0.8	−0.9			0.8 (−1.8)	4.5	3.9	−9.0

[a] δ(OEt_2·BF_3) 0, upfield shifts quoted as positive. [b] Ref. 6. [c] Difference in chemical shift for each boron atom as for example δ(10-$ClB_{10}H_{13}$) − δ($B_{10}H_{14}$). [d] Ref. 8. [e] A better correlation of Δδ with 10-$ClB_{10}H_{13}$, and a better relation between positions of chemical bonds and chemical shifts (S. Heřmánek and J. Plešek, *Z. anorg. Chem.*, 1974, **409**, 115; S. Heřmánek, J. Plešek, and B. Stibr, *Abs. 3rd Internat. Meeting Boron Chem.*, 5th—9th July, 1976, München and Ettal, no. 52) in the parent $B_8C_2{}^{5,6}H_{12}$, favours this assignment rather than that in parentheses, which could be derived by a simple analogy with chemical shifts in $B_{10}H_{14}$.

The ^{11}B n.m.r. spectrum of $B_8C_2{}^{5,6}H_{11}(OH)$ shows a low-field singlet at −20.0 p.p.m. (OEt_2·BF_3 0 p.p.m.) which may be assigned to the B–OH group since other results have shown that an appreciable shift to low field occurs when the hydrogen of a B–H group is substituted by a hydroxyl group.[4,5] The overall integration and resolution of the spectrum (B–OH, 1.0; remainder of boron atoms, 7.25) indicates that only one isomer is present, but the lack of corresponding B–OH derivatives of decaborane prevents a definite assignment of the position of substitution in $B_8C_2{}^{5,6}H_{11}(OH)$, although it seems unlikely that substitution has occurred at positions 2 or 4 (doublets at δ 24.7 and 40.7 p.p.m. respectively), or at position 9, since the Δδ values of B^2 (−0.9) and B^4 (2.8) are of the wrong sign for 9 substitution. In addition the doublet at 12.1 p.p.m. in the ^{11}B n.m.r. spectrum of $B_8C_2{}^{5,6}H_{11}(OH)$ exhibits bridge-proton coupling and can be assigned as B^{10}, so that the possible positions of substitution remain as 1, 3, 7, or 8.



SCHEME Possible mode of formation of $B_7C_2{}^{4,5}H_{11}$

Although a structure based on an icosahedral fragment was originally suggested for $B_7C_2{}^{4,5}H_{11}$ [Figure 1(*i*)],[2] an alternative structure analogous to that found for the dimethyl derivative 4,9-$Me_2B_7C_2{}^{4,9}H_9$ [Figure 1(*ii*)] [7] is perhaps more likely [Figure 1(*iii*)].[8] The structures of both dicarbanonaboranes may be derived from a bicapped Archimedean antiprism, by removal of a single ' beltline ' vertex, but they differ in the positions of the carbon atoms relative to the open five-membered face. In Figures 1(*ii*) and (*iii*) one half of the antiprism is described by atom 7 (capping) and atoms 2, 3, 8, and 6 in the ' beltline '; the other half is described by atom 4 (distorted capping) with one atom missing from the ' beltline ' defined by atoms 1, 9, and 5. The formation of a pair of B–H–B hydrogen bridges at a common four-connected vertex, observed in 4,9-$Me_2B_7C_2{}^{4,5}H_9$ [Figure 1(*ii*)] is no longer possible in $B_7C_2{}^{4,5}H_{11}$ [Figure 1(*iii*)], which may well account for the presence of a non-tautomeric BH_2 group in the latter molecule as indicated by the triplet in the ^{11}B n.m.r. spectrum at room temperature.

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[7] J. C. Huffman and R. W. Streib, *J.C.S. Chem. Comm.*, 1972, 665.

[8] J. Plešek and S. Heřmánek, *Pure Appl. Chem.*, 1974, **39** ,431.

While $B_7C_2^{4,5}H_{11}$ has not hitherto been obtained by direct degradation of a higher carbaborane, a possible molecular mechanism for the formation of both $B_8C_2^{5,6}H_{12}$ and $B_7C_2^{4,5}H_{11}$ is shown in the Scheme. Since $B_8C_2^{5,6}H_{12}$ is unaffected by either aqueous $FeCl_3$ or by anhydrous $FeCl_3$ in toluene,[9] the formation of $B_7C_2^{4,5}H_{11}$ may well be due to hydrolysis, rather than oxidation, of a B_8C_2 intermediate, an idea supported by the *increased* yield of $B_7C_2^{4,5}H_{11}$ on *dilution* of the oxidising agent. Certainly, hydrolysis of $[B_8C_2^{5,6}H_{11}]^-$ in aqueous Na[OH], followed by acidification, yields small amounts of $B_7C_2^{4,5}H_{11}$ (identified by t.l.c.),[9] although these conditions are rather far removed from those used in the degradation reaction.

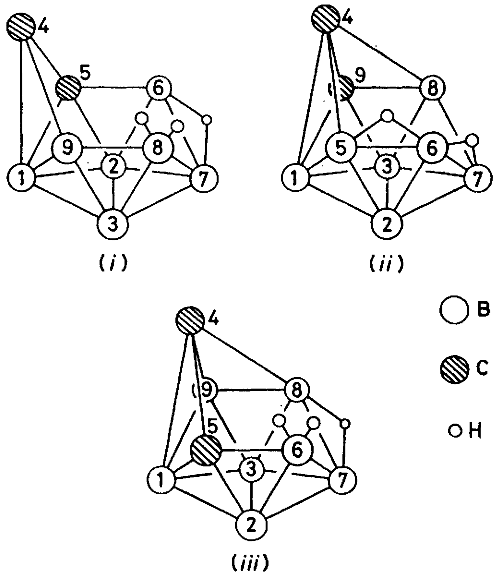

FIGURE 1 (*i*) Structure previously suggested [2] for $B_7C_2^{4,5}H_{11}$. (*ii*) Structure of 4,9-$Me_2B_7C_2^{4,9}H_9$ (ref. 7). (*iii*) Proposed structure of $B_7C_2^{4,5}H_{11}$. Terminal hydrogens (except BH_2) and methyl groups are omitted for clarity. Since both structures (*i*) and (*iii*) have the same numbering, we propose the prefix *cyclo* for structures with a restricted open face, preceded by the numbers of the atoms connected by the additional bond, *i.e.* 4,8-*cyclo*-$B_7C_2^{4,5}H_{11}$

TABLE 2

Calculated fragmentation of $B_7C_2^{4,5}H_{11}$ (by loss of hydrogen)

Fragment	Fraction of total B_7C_2 abundance (%)
$[B_7C_2H_{11}]^+$	12.81
$[B_7C_2H_{10}]^+$	5.85
$[B_7C_2H_9]^+$	32.39
$[B_7C_2H_8]^+$	16.75
$[B_7C_2H_7]^+$	12.66
$[B_7C_2H_6]^+$	13.29
$[B_7C_2H_5]^+$	−0.40
$[B_7C_2H_4]^+$	9.44
	Total 102.79%

Mass Spectra.—The mass spectra of all three by-products, $B_8C_2ClH_{11}$, $B_8C_2H_{11}(OH)$, and $B_7C_2H_{11}$ show molecular ions (M^+) together with fragments due to loss of hydrogen, as well as less-abundant ions corresponding to loss of boron from M^+. The relative abundances of the ions $[M - nH]^+$ ($n = 0$—10) may be obtained by means of a computer program,[*] and values for $B_7C_2^{4,5}H_{11}$ are shown in Table 2. Given a possible molecular formula and the relative intensities

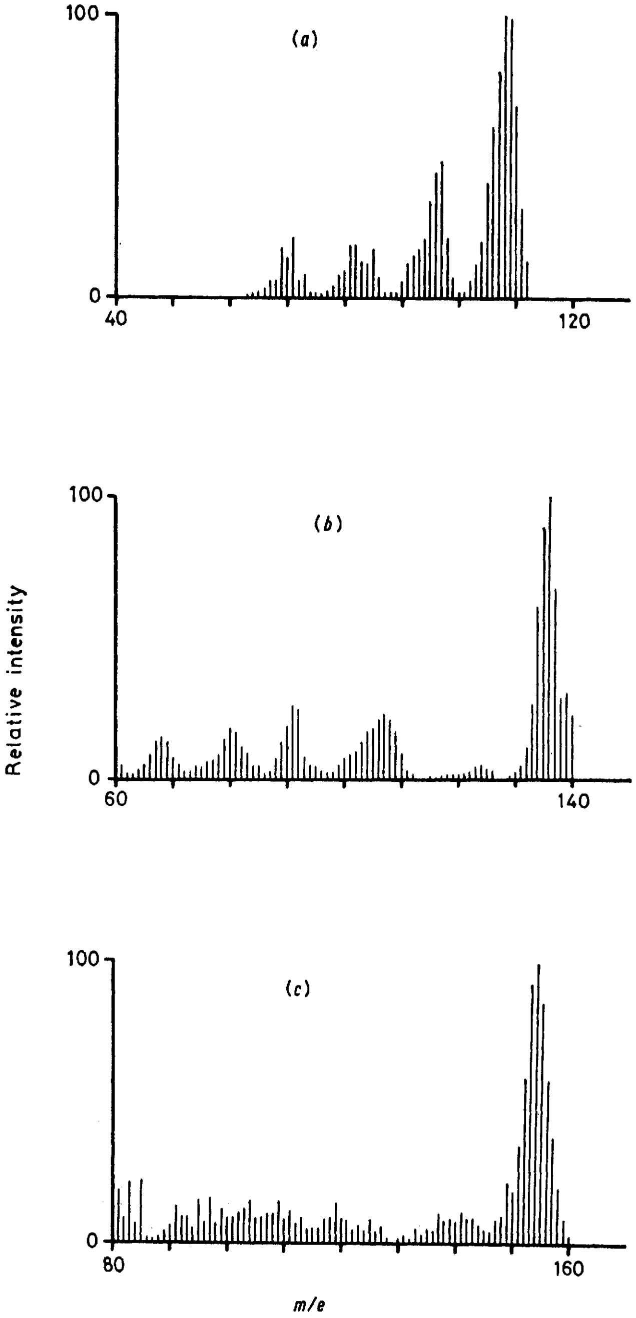

FIGURE 2 Mass spectra at 70 eV and 25 °C of (*a*) $B_7C_2H_{11}$, (*b*) $B_8C_2H_{11}(OH)$, and (*c*) $B_8C_2ClH_{11}$

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[*] Program MASPEC (Fortran IV), T. Blair and T. J. Greenhough, 1976.

[9] H. M. Colquhoun and M. G. H. Wallbridge, unpublished work.

of peaks in the parent-ion, this program first calculates the isotope pattern of the parent ion, then the relative abundance of ions produced by hydrogen loss, and finally a theoretical mass spectrum in the parent-ion region (using these calculated abundances) for comparison with the experimental spectrum. Realistic (*i.e.* positive) values for ion abundances (which should total *ca.* 100%), and a close correspondence between those parts of the theoretical and experimental spectra which are not constrained by the program to be equal, are strong indications that the proposed molecular formula is correct, *e.g.* Tables 2 and 3 which give results for $B_7C_2{}^{4,5}H_{11}$. The mass spectrum of the material could not be obtained previously, perhaps due to the presence of trace amounts of a destabilising impurity, and only the spectra of pyrolysis products were observed.[2] The mass spectra of the products $B_7C_2H_{11}$, $B_8C_2H_{11}(OH)$, and $B_8C_2ClH_{11}$ are shown in Figure 2(*a*), (*b*), and (*c*) respectively.

TABLE 3

Calculated and observed mass spectra of $B_7C_2{}^{4,5}H_{11}$ in the parent-ion region

m/e	Relative abundance	
	calc.	obs.
112	2.80	2.80
111	6.00	6.00
110	12.70	12.70
109	18.60	18.60
108	18.70	18.70
107	15.90	15.90
106	11.00	11.00
105	7.50	7.50
104	5.26	4.30
103	2.93	2.50

EXPERIMENTAL

Mass spectra were obtained at 70 eV * on a V.G. Micromass 12 instrument, i.r. spectra on a Perkin-Elmer 457 spectrophotometer, and ^{11}B n.m.r. spectra at 28.9 MHz using a Bruker W.H.90 Fourier-transform spectrometer [$\delta(OEt_2{\cdot}BF_3)$ 0, upfield shifts quoted as positive]. Thin-layer chromatography was performed on silica gel (Merck $60F_{254}$ pre-coated aluminium sheet), and R_F values are given relative to $B_{10}C_2{}^{1,2}H_{12}$ (R_F 100). Although crude $B_7C_2{}^{4,5}H_{11}$ could be exposed briefly to the air without undue decomposition, the purified sublimed material was spontaneously flammable, and was therefore handled under dry nitrogen.

By-products from the Oxidation of $K[B_9C_2H_{12}]$.—An aqueous solution of iron(III) chloride (1.25 mol dm^{-3}, 300 cm^3, containing 10 cm^3 concentrated HCl) was added dropwise over 30 min, with vigorous mechanical stirring, to an aqueous solution of $K[B_9C_2H_{12}]$ (1 mol dm^{-3}, 50 cm^3) under pentane (250 cm^3). The reaction mixture was stirred for 2 h and the organic layer separated, washed with water (2 × 50 cm^3), and evaporated to small volume. Column chromatography on silica gel with pentane as eluant afforded $B_8C_2{}^{5,6}H_{12}$ (2.02 g, 33%, R_F 260), 10-$ClB_8C_2{}^{5,6}H_{11}$ (0.07 g, 0.9%, R_F 25), and $B_7C_2{}^{4,5}H_{11}$ (0.23 g, 4.2%, R_F 100). The mass spectrum of 10-$ClB_8C_2{}^{5,6}H_{11}$ showed a strong parent-ion envelope with cut-off at *m/e* 160 (calc. for $^{11}B_8{}^{12}C_2{}^{37}Cl^1H_{11}$: *m/e* 160).

In another experiment the pentane extract was separated, dried over $Na_2[CO_3]$, filtered, and cooled to 0 °C for 12 h. The white crystalline precipitate of $B_8C_2{}^{5,6}H_{11}(OH)$ was filtered off, washed with a little cold pentane, and dried. The yield was 0.11 g (1.6%), R_F 0, m.p. 119 °C. The mass spectrum had a sharp cut-off at *m/e* 140 (calc. for $^{11}B_8{}^{12}C_2{}^1H_{12}{}^{16}O$: *m/e* 140). The i.r. spectrum contained bands at 3 110s,br [ν(OH)], 2 560s [ν(BH)(terminal)], 1 955vw and 1 880w [ν(BH)(bridging)], and the ^{11}B n.m.r. spectrum contained a singlet at δ −20 (B–OH), and doublets at −8.5 [2 B, J(B–H) 154], 1.4 (1 B, 174), 5.3 (1 B, –), 12.1 [1 B, 138, $J(B\text{–}H_\mu)$ 24 Hz], 24.7 (1 B, 171), and 40.5 p.p.m. (1 B, 152 Hz).

Preparation of $B_7C_2{}^{4,5}H_{11}$.—An aqueous solution of $K[B_9C_2H_{12}]$ (0.2 mol dm^{-3}, 250 cm^3) was added rapidly with stirring to an aqueous solution of $FeCl_3$ (0.2 mol dm^{-3}, 1 250 cm^3, containing 20 cm^3 of concentrated HCl) under pentane (400 cm^3). After stirring for 30 min the pentane layer was separated, washed with water (3 × 150 cm^3), and dried over $Mg[SO_4]$. Evaporation to dryness gave a pale yellow solid which, after sublimation at 60 °C and 10^{-2} mmHg, afforded 0.68 g of crude (>90%) $B_7C_2{}^{4,5}H_{11}$. Pure product (0.57 g) was obtained by column chromatography, as described above, and unchanged $[B_9C_2{}^{7,8}H_{12}]^-$ (12.1 mmol) was recovered by precipitation with $[NEt_3H]Cl$, giving an overall yield of 13.5% $B_7C_2{}^{4,5}H_{11}$, based on $[B_9C_2{}^{7,8}H_{12}]^-$ consumed.

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 mmHg ≈ 13.6 × 9.8 Pa.