Boron Compounds. XIII.[1]
C-Methyl-B-pentaethyl-2-carbahexaborane(9)

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Abstract: Unique structural qualification can be obtained for the recently prepared C-methyl-B-pentaethyl derivative of 2-carbahexaborane(9) on the basis of its ^1H and ^{11}B nmr and infrared spectra. The chemical properties of this compound in some reactions have been examined. No H/D exchange is observed when the compound is heated with tetraethyldideuteriodiborane. With sodium triethylborohydride a sodium salt of the carborane is obtained. Above 180° decomposition with formation of closed-cage carboranes and benzene-insoluble solid occurs.

The compound 2-carbahexaborane(9) belongs to a group of isosteric boron compounds (I–V) (Figure 1) which are derived from hexaborane(10) (I) by stepwise replacement of B–H_b groups by carbon atoms. Although hexaborane(10)[2] as well as 2,3-dicarbahexaborane(8) (III)[3] have been known for some time, derivatives of monocarbahexaborane(9) (II),[4,5] tricarbahexaborane(7) (IV),[5,6] and tetracarbahexaborane(6) (V)[7] have only recently been described. In the reaction of ethyldiborane with acetylene[8] or the dehalogenation of alkylhaloboranes[9] and also in the reaction of ethyldiborane with sodium,[10] one obtains, among other products, a compound with a molecular weight of 230,[11] the formula of which has been determined by high-resolution mass spectrometry[12] as $C_{12}H_{31}B_5$. This compound has now been identified as the C-methyl-B-pentaethyl derivative of 2-carbahexaborane(9).

Experimental Section

1. **Preparation.** A freshly prepared solution of 62.4 g (0.8 mole) of ethyldifluoroborane in 150 ml of THF was dropped over 3 hr into a well-stirred suspension of 11.2 g (1.6 g-atoms) of finely divided lithium in 300 ml of THF. The reaction mixture, cooled to 0 to −5°, was stirred for 7 hr, and for a further 8 hr at 15°, until all the metal was consumed. The LiF (62.6 g, containing 1.9% of boron) was centrifuged off and washed with hexane. The yellow THF solution was concentrated by distillation at 12 torr, 340 g (95% THF, 4% triethylborane) being collected. The residual 70 ml, together with the hexane-washed liquor, was treated with ethylene at *ca.* 50 atm for about 1 hr at room temperature. Subsequent distillation afforded 54 g of a colorless fraction of bp 68–72° (glpc analysis: 92% THF and hexane, 5% triethylborane, 3% unidentified compounds), 18.7 g of a yellow fraction of bp 41–91° (20 torr), which contained mainly compounds with B–O bonds and 10.5 g of a colorless liquid, bp 65–106° (10^{-2} torr) having the compositions (glpc analysis) shown in Table I.

Table I

Compound	%
$C_{12}H_{31}B_5$ (VI)	26
$C_{12}H_{27}B_5$ C,C′-dimethyl-B-tetraethyl-2,4-dicarbaclovo-heptaborane(7) (three isomers, VIIa–c)	12
$C_{10}H_{27}B_5$ C-methyl-B-tetraethyl-2-carbahexaborane(9) (three isomers VIIIa–c)	5
$C_{14}H_{31}B_5$ C,C′-dimethyl-B-pentaethyl-2,4-dicarbaclovo-heptaborane(7) (IX)	24
Other carboranes	33

Spinning-band fractional distillation of 8.1 g of this carborane mixture afforded 1 ml of a fraction, bp 83° (10^{-3} torr), containing 61% VI, as well as 1 ml of a fraction, bp 84° (10^{-3} torr), containing 80% VI, from which the pure compound was obtained by preparative gas chromatography.

In a second experiment from 2.0 mole of ethyldifluoroborane, 16.8 g of a fraction, bp 45–110° (10^{-2} torr), was obtained, fractional distillation of which afforded 2.5 ml of a fraction, bp 86° (10^{-3} torr), containing 30% VI and 2.0 ml of a fraction, bp 88° (10^{-3} torr), containing 72.7% VI.

2. **Reactions. a. Oxidation.** A carborane mixture (2.5 ml), containing 15% VI, was heated with 10 ml of 2 *N* sulfuric acid and 10 ml of 30% aqueous hydrogen peroxide at 100° for 8 hr. The reaction mixture was then extracted twice with diethyl ether and the ether solution dried with calcium chloride. After evaporating the ether, there remained 0.4 ml of a carborane mixture, containing 21% of VI. Thus 22.4% of the original amount of VI was unchanged. When stirred in the same oxidative medium at room temperature for 30 min, VI can be recovered in nearly quantitative yield. Oxidation by air is evident only after several months of contact.

b. Protonolysis. Pure VI (54.5 mg, 0.236 mmole) was heated at 140° with 1.0 ml of propionic acid and a Pd catalyst. After 20 hr 52.0 ml (STP) of gas (45.0% H_2, 55.0% ethane) had been evolved. Thus 4.43 moles of H_2 and 5.41 moles of ethane per mole of VI were obtained.

c. Reaction with Tetraethyldideuteriodiborane. A carborane mixture, 400 mg (80% VI, 17% IX), was heated at 120° for 8 hr with 3.0 g of tetraethyldideuteriodiborane. After removal of the ethyldiborane by distillation, the reaction mixture was analyzed by mass spectrometry. It was shown that neither VI nor IX had undergone H–D exchange.

Under the same conditions (4 hr of heating) in a mixture of 28.6% VI, 1.9% VIIa–c, 8.7% VIIIa–c, and 51.7% IX, all three isomers VIIa–c and at least one isomer of VIII take up one deuterium, as indicated by the shift of parent peaks in mass spectrum from *m/e* 226 to 227 and from 202 to 203, respectively.

d. Reaction with Sodium Triethylborohydride. A mixture of carboranes, 620 mg (46% VI, 6% VIIIa–c, 34% IX), was heated for 8 hr at 100° with 3.4 g of sodium triethylborohydride. In this period 49.5 ml (2.2 mmoles) of H_2 was evolved. Distillation gave aside from triethylborane *ca.* 100 mg of a carborane mixture, bp 48–56° (10^{-3} torr), with the composition 5% VI, 20% VIIa–c, 67% IX, and 8% other carboranes of the closed-cage type. The distillation residue was dissolved in diethyl ether, and dry HCl gas was passed

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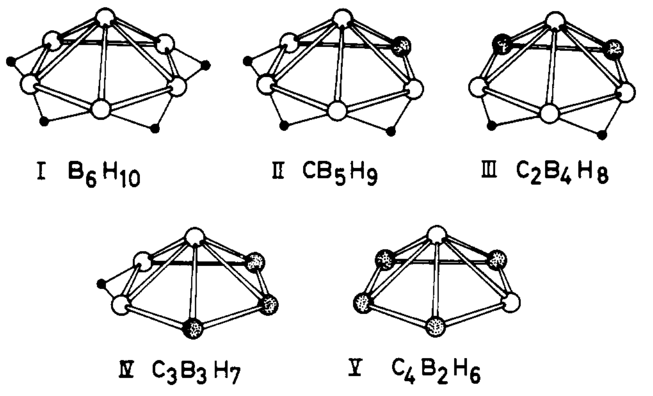

Figure 1. The isosteric compounds $C_xB_{6-x}H_{10-x}$ (x = 0–4).

through this solution to the neutral point. The solution was filtered to remove sodium chloride, and the ether and triethylborane were removed by distillation. There remained *ca.* 150 mg of a carborane mixture containing 79% VI and 6% IX. Neutralization with DCl in place of HCl gave material in which *ca.* one-fourth of the VI was monodeuterated.

e. Pyrolysis. A carborane mixture, 165.3 mg (72.7% VI, 1.1% VIIa–c, 1.0% VIIIa–c, 24.0% IX, 1.2% unidentified compounds), was heated at 250° for 6 hr. Gas (33 ml) was evolved (36.2% H_2, 20.3% methane, 43.5% ethane). The reaction mixture had become brown, and dark solid particles were evident. After cooling, the mixture was digested with warm benzene, and the benzene solution was separated from the insoluble material and evaporated. There resulted 70.4 mg consisting of 20% benzene, 1.6% triethylborane, 11.6% C,C′-dimethyl-B-triethyl-1,5-dicarbaclovo-pentaborane(5) (X), 7.4% VI, 11.0% VIIa–c, and 26.7% IX. The benzene-insoluble portion weighed 60.6 mg. Analysis, using the method of Rittner and Culmo,[13] indicated that it contained 27.4% B. The same carborane mixture (44.2 mg) was heated for 10 hr at 190°; 36 ml of gas was evolved. The reaction mixture was yellow and viscous but remained homogeneous. It contained 1.7% triethylborane, 66% VI, 2.0% VIIa–c, 0.6% VIIIa–c, 29% IX, and 3.0% X.

3. Gas Chromatography. a. Analysis. A Carlo Erba instrument was used with an open tubular 50-m stainless steel 0.25-mm i.d. column, liquid phase squalene, carrier gas argon, 22.5 psig, detector FID, sample 0.2 μl split 1:200; retention indices I^s_{120} (Kovats[14]) were VI, 1504.8; VIIa, 1247.4; VIIb, 1265.8; VIIc, 1292.8; IX, 1427.2; X, 1234.2.[15]

b. Preparative. An F & M 720 instrument equipped with a 2-m (4-mm i.d.) column, 15% Apiezon L with 0.1% Atpet on Embacel, was used with a double thermal conductivity detector, temperature programming from 60 to 300° with a heating rate of 7.5°/min, and a heated exit with low dead volume. The temperature of the exit was measured with a thermocouple to ensure that condensation did not occur in the exit. The entire operation was carried out under an inert atmosphere. Three passes on the chromatogram afforded 20 mg of VI.

4. Infrared Spectrum. The infrared spectrum of VI (Table II) was taken on a solution of 20 mg in 100 μl of carbon tetrachloride, using a Perkin-Elmer 125 grating spectrometer.

Table II. Infrared Absorption Spectrum of C-Methyl-B-pentaethyl-2-carbahexaborane(9)

2960–2860 vs	1456 vs	1138 m
2720 w	1435 sh	1037 s
	1375 s	1019 s
		959 s
1845 s	1311 s	897 w
1800 m		819 s
1750 m	1250 sh	764 s
1665 sh	1232 m	750 s

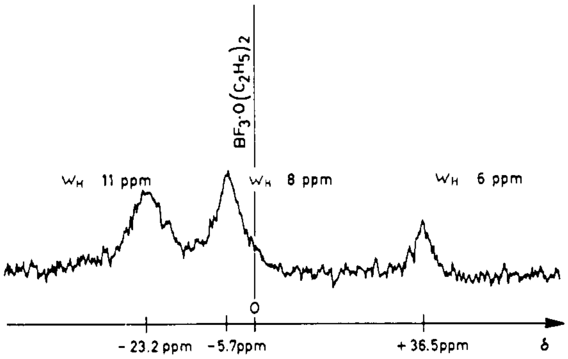

Figure 2. ^{11}B nmr spectrum of C-methyl-B-pentaethyl-2-carbahexaborane(9).

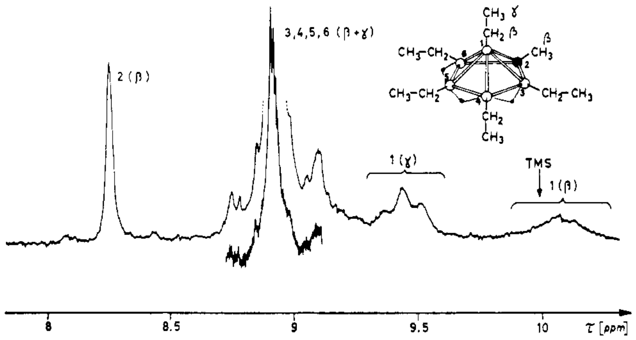

Figure 3. ^1H nmr spectrum of C-methyl-B-pentaethyl-2-carbahexaborane(9).

5. Nmr Spectra. A solution of 20 mg of VI in 100 μl of carbon tetrachloride was prepared. The ^{11}B nmr spectrum (Figure 2) was obtained at 19.3 MHz using a Varian DP-60 instrument. The ^1H nmr spectrum (Figure 3) was measured on a Varian HA-100 instrument with TMS as an internal standard.

Results and Discussion

Infrared Spectrum. Mass spectral analyses of carborane mixtures, prepared either from the reaction of acetylene with ethyldiborane[8] or the dehalogenation of ethylhaloboranes,[9] showed the molecular weight series 174, 202, 230. Pure VI, collected by glpc, showed a parent peak at *m/e* 230, corresponding to the fully alkylated carborane, without terminal B–H bonds. The infrared spectrum of VI (Table II) is in agreement with this observation, as no absorption is detected in the region (2500–2600 cm^{-1}) characteristic of terminal B–H groups. On the other hand, bands at 1750, 1800, and 1845 cm^{-1}, which can be attributed to $B–H_b–B$ bridging vibrations, are observed. The infrared spectrum of the next lower homolog, VIIIa–c with molecular weight 202, shows besides the $B–H_b–B$ bridging vibration intense absorptions around 2540 cm^{-1} due to terminal B–H stretching vibrations.

^{11}B Nmr Spectrum. The spectrum (Figure 2) consists of three structureless signals with δ_1 −23.3 (half-width, W_H = 11 ppm), δ_2 −5.7 (W_H = 8 ppm), and δ_3 +36.5 ppm (W_H = 6 ppm), shifts referred to boron trifluoride etherate, with intensities of 2:2:1. This may be interpreted by a pentagonal pyramidal CB_5 skeleton with one B atom in the apex. The high-field signal δ_3 can be assigned to an apical boron atom. The chemical shift may be compared with that of the apical boron atom in the hexaethyl derivative of tetracarbahexaborane(6)

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[13] R. C. Rittner and R. Culmo, *Anal. Chem.*, **35**, 1268 (1963).

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[15] A discussion of the I and ΔI values of the carboranes will be presented elsewhere.

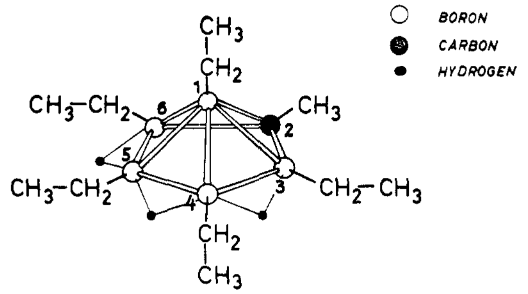

Figure 4. Molecular structure of C-methyl-B-pentaethyl-2-carbahexaborane (9).

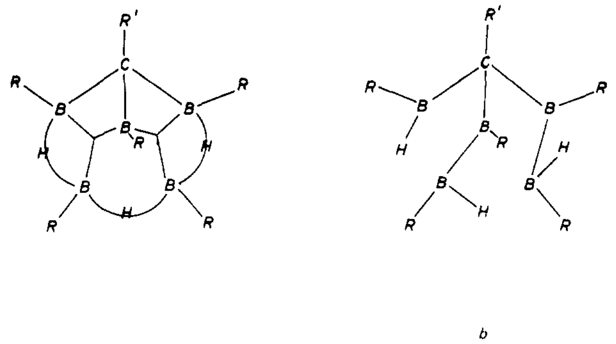

Figure 5. Bonding in the CB_5H_9 system: "resonance structures" with (a) and without (b) three-center bonds.

(V, δ +41 ppm).[7] In the unsubstituted compounds $C_xB_{6-x}H_{10-x}$ (x = 0, 1, 2), the signals of the apical B atoms are found at somewhat higher fields (around +50 ppm).[16] The signals δ_1 and δ_2 are within the range where absorption of boron atoms in the base of a pyramidal or bipyramidal B or BC skeleton usually occurs.

^{1}H Nmr Spectrum (Figure 3). A strong unresolved signal at τ 8.9 ppm can be assigned to the four ethyl groups attached to the boron atoms which form part of the pyramidal base. The δ_3 peak of the ^{11}B nmr spectrum corresponds in the ^{1}H nmr spectrum to a "triplet" at τ 9.44 ppm, together with an unresolved signal (quartet?) at τ 10.10 ppm, which can respectively be assigned to the methyl and methylene protons of the B-ethyl group at the apex of the pentagonal pyramid. The sharp singlet absorption at τ 8.25 ppm suggests the presence of one C–CH_3 group in the pyramidal base. Signals for the B–H_b–B bridging atoms are not observed, presumably because of multiple splitting through B–H spin coupling.

Structure. On the basis of the formula $C_{12}H_{31}B_5$, one may expect three bridging hydrogen atoms. By analogy with the structures of hexaborane(10) (I) and 2,3-dicarbahexaborane(8) (III), these are assigned to the boron atoms at the base of the pyramid, leading to the structure shown in Figure 4.

Bonding. By using three-center bond formalism to describe the bonding of VI (Figure 5a), one can draw two central 2e3c bonds[17] joining the five B atoms. Three of the maximal five 2e3c bonds are needed for the hydrogen bridges. In two-center formalism (Figure 5b), two B–B bonds can be accounted for.

Protonolysis. On protonolysis one may expect a maximum of 5 moles of hydrogen and 6 moles of ethane per mole of VI; 4.43 moles of hydrogen and 5.41 moles of ethane were found (89 and 90% of the theoretical amount, respectively). This is in fair agreement with the proposed structure.

Deuteration. When a mixture of the three isomers VIIIa–c is heated at 120° for 4 hr with tetraethyldideuteriodiborane, at least one isomer exchanges one hydrogen for a deuterium. In contrast, VI, even with longer heating, does not take up any deuterium. This indicates that in the CB_5H_9 system, as Onak and Dunks[18] have already shown with 2,3-dicarbahexaborane(8), only terminal B–H hydrogens are exchangeable.

Salt Formation. VI reacts with sodium triethylborohydride with evolution of hydrogen to form a sodium salt. This can be used to separate VI and alkyl derivatives of the clovocarboranes (VII, IX, X). From a mixture of 46% VI and 34% IX, a fraction containing 5% VI and 67% IX and another fraction with 79% VI and 6% IX were obtained. It is not yet clear if VI is converted completely in $CB_5R_5H_2^-$ (eq 1) isoelectronic with dicarbahexaborane(8), or if salts are also formed by addition of NaH without H_2 evolution (eq 2).

$$\mathrm{VI} + \mathrm{Na^+[B(C_2H_5)_3H]^-} \longrightarrow \mathrm{Na^+[CB_5R_5H_2]^-} + \mathrm{H_2} + \mathrm{B(C_2H_5)_3} \quad (1)$$

$$\mathrm{VI} + \mathrm{Na^+[B(C_2H_5)_3H]^-} \longrightarrow \mathrm{Na^+[CB_5R_5H_4]^-} + \mathrm{B(C_2H_5)_3} \quad (2)$$

Pyrolysis. VI is stable to a temperature of about 180°. Above this temperature decomposition occurs. Aside from hydrogen, methane, ethane, and polymeric products, triethylborane and alkyl derivatives of clovocarboranes, mainly of the 1,5-$C_2B_3H_5$ system (X), are formed. The observed tendency of the $C_3B_3H_7$ (IV) derivatives to rearrange from open-cage carboranes to closed-cage carboranes[5] is therefore also evident in the CB_5H_9 system. However, the stability of VI, compared to the unsubstituted compound II, is probably significantly increased by alkyl substitution.

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(16) T. P. Onak, *Advan. Organometal. Chem.*, 3, 312 (1965).

(17) 2e3c means two-electron three center and 2e2c two-electron two center.

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