

The First *hypho*-Carbaborane $\text{Me}_3\text{N-CB}_5\text{H}_{11}$

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Summary Alkaline methanolysis of 6- NMe_3 -6- CB_5H_{11} affords, in 75% yield, *hypho*-3,4- μ -(trimethylaminocarba)-hexaborane(11), an analogue of B_5H_{11} , in which the 3,4-H-bridge is replaced by the $-\text{CHNMe}_3$ -bridge; existence of this structural building-element indicates the possibility of the preparation of a large series of new carbaboranes.

DURING the last fifteen years a large number of *closo*- and *nido*-carbaboranes,^{1,2} but only four *arachno*-carbaboranes, namely $\text{C}_2\text{B}_5\text{H}_{13}$,³ $\text{C}_2\text{B}_8\text{H}_{14}$,⁴ CB_8H_{14} ,⁵ and $\text{L-CB}_5\text{H}_{13}$,⁶ have been described.

We now report on the first *hypho*-carbaborane which originated from stepwise degradation of four boron atoms in the ten-vertex skeleton of the 6- NMe_3 -6- CB_5H_{11} carbaborane (I). The degradation was performed by treatment of (I) with concentrated MeOH-KOH solution at 60 °C, followed by neutralization of the reaction mixture with carbon dioxide.

The resulting *hypho*-3,4- μ -(trimethylaminocarba)hexaborane(11) (II) which was obtained in 75% yield was recrystallized from $\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_{14}$ to give a white crystalline compound, m.p. 139–140 °C, R_F 0.46 (CH_2Cl_2 on Silufol⁷). The carbaborane (II) is moderately air-stable and can be stored under nitrogen without noticeable change. The mass spectrum of (II) exhibited a molecular cut-off at m/e 137, corresponding to the $(^{12}\text{C}_4^{14}\text{N}^{11}\text{B}_5^{1}\text{H}_{20})^+$ ion. The 100 MHz ^1H n.m.r. spectrum in $(\text{CD}_3)_2\text{CO}$ (relative to Me_4Si) exhibited peaks at δ 3.15 (9H, s, NMe_3), 1.32 (1H, s, carbaborane CH), 0.65 (1H, s br, μ -H), and -1.87 (2H, s br, μ -H). The 32.1 MHz ^{11}B n.m.r. spectrum (relative to $\text{BF}_3\text{-OEt}_2$) (shown in Figure 1), very similar to that of

arachno- B_5H_{11} borane,⁸ consisted of one triplet (12.4 p.p.m.) and two doublets (23.2 and 60.2 p.p.m.), both split by ^{11}B - μ -H coupling. The i.r. spectrum exhibited the terminal and B- μ -H absorptions at 2500 and 1400–1500 cm^{-1} , respectively. The i.r. spectrum of (II) is very similar to that of crystalline solid 'A' which was isolated as an unidentified by-product in the preparation of the $1\text{-CB}_5\text{H}_{10}^-$ anion.⁹

The data obtained are consistent with the unique *hypho*- $\text{B}_6\text{H}_{12}^{2-}$ -type structure shown in Figure 2. The bridging

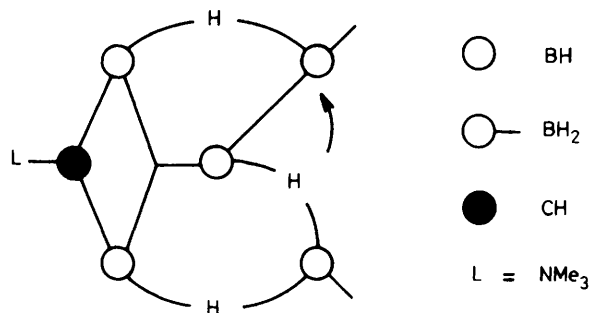


FIGURE 2. Proposed topological structure for $\text{Me}_3\text{N-CB}_5\text{H}_{11}$.

$-\text{NMe}_3\text{CH}-$ group is symmetrically attached to both B(3) and B(4) atoms by two two-centre two-electron C-B bonds. The n.m.r. data of (II) clearly indicate the presence of two equivalent BH_2 groups and two bridging hydrogens as well as one unique hydrogen bridge alternating between both B(1)-B(2) and B(1)-B(5) atoms. A similar unusual hydrogen bridge was also believed to exist in the *arachno*- B_5H_{11} borane.⁸

A salient characteristic of the new carbaborane-type is the $-\text{CHR}-$ bridge between two boron atoms in the open face of the skeleton. A similar $-\text{CHR}-$ bridge was previously found in the *nido*-series in the $\text{Ph}_2\text{C}_2\text{B}_{10}\text{H}_{11}^-$ anion.¹⁰ The existence of this type of bridge in the *nido*- as well as in the *hypho*-series indicates that this arrangement may be general and demonstrates the possibility of the existence of many other carbaboranes derived from boranes or heteroboranes by the substitution of a hydrogen bridge by the $-\text{CR}^1\text{R}^2-$ group.

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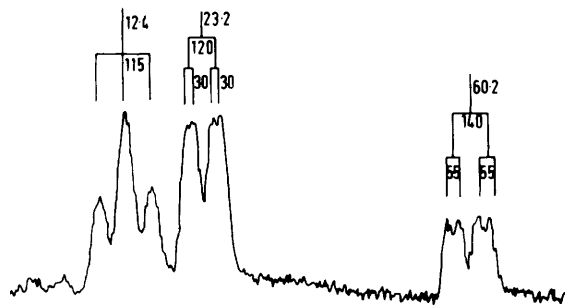


FIGURE 1. The 32.1 MHz ^{11}B n.m.r. spectrum of $\text{Me}_3\text{N-CB}_5\text{H}_{11}$ in $(\text{CD}_3)_2\text{CO}$ solution.

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