Synthesis and Characterization of $C_3B_4H_{12}$: the First Parent *hypho* Carbaborane and the First Open Seven-vertex Carbaborane Cluster

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The first unsubstituted neutral *hypho* carbaborane, $C_3B_4H_{12}$, has been synthesised by hot–cold reaction of *arachno*-B_4H_{10} with propyne; the compound is unusual in having three skeletal carbon atoms and a unique seven-vertex structure.

Very few *hypho* polyhedral boranes (*i.e.* containing $n + 4$ framework electron pairs) are known[1] and among the thousands of known carbaboranes the only reported example that falls into this category is $Me_3N \cdot CB_5H_{11}$,[2] in which the 3,4-H-bridge of B_5H_{11} is replaced by the -CHNMe₃- linkage. Carbaboranes containing three skeletal carbon atoms are also rare; they include the alkyl derivatives of *nido*-$C_3B_3H_7$,[3] two isomeric *arachno*-$C_3B_7H_9$ compounds,[4] *arachno*-μ-6,9-RCH-9-R-5,6,9-$C_3B_7H_{11}$ (R = H or Me)[5] and *nido*-5,6,10-Me₃-5,6,10-$C_3B_7H_8$.[5] As is the case with the binary boranes themselves, seven-vertex carbaboranes are extremely rare, the only one known being *closo*-$C_2B_5H_7$.[6] We now report the synthesis of $C_3B_4H_{12}$, which is not only the first example of a parent *hypho* carbaborane, but also one which contains three carbon atoms and a novel open seven-vertex cluster framework.

The new compound was one of several products from the hot–cold reaction of *arachno*-B_4H_{10} with propyne, a technique that is not normally used to synthesise carbaboranes. Previous studies of the reaction between B_4H_{10} and propyne under normal pyrolysis conditions have not yielded the tricarbaborane.[3] The present reaction was carried out over a period of one hour in a concentric-tube reactor, similar in design to that described by Klein *et al.*,[7] with the inner surface heated to 100 °C and the outer surface cooled to −35 °C. Volatile

products were separated by cold-column fractionation,[8] monitored continuously by mass spectrometric analysis. The observed cut-off for the *hypho* product (a colourless, volatile liquid that becomes viscous and decomposes to as yet unidentified products when allowed to stand at room temperature) was at m/z 92; high-resolution measurements confirmed the assignment of this to the parent molecular ion $[^{12}C_3{}^{11}B_4{}^1H_{12}]^+$ (observed m/z 92.1306, calculated m/z 92.1311). The reaction stoichiometry is therefore B_4H_{10} + $MeC{\equiv}CH \rightarrow hypho$-$C_3B_4H_{12}$ + H_2.

The 128 MHz $^{11}B\{^1H\}$ NMR spectrum in $CDCl_3$ at 223 K consists of just two sharp signals of equal integrated intensity. In the line-narrowed, undecoupled spectrum the peak at δ −20.1 (relative to $BF_3 \cdot OEt_2$) comprises a doublet of doublets of doublets (J_{BH} 165, 63, 37 Hz), and the peak at δ 1.60 appears as a broadened doublet (J_{BH} 145.0 Hz). The 400 MHz boron-decoupled ^1H NMR spectrum in $CDCl_3$ at 223 K consists of eight signals of relative intensity 2:2:2:2:1:1:1:1 at δ values (relative to Me_4Si) of 3.25, 2.23, 1.61, 0.68, 0.24, −0.90, −1.40 and −2.16, respectively. Comparison of the proton spectra with and without boron decoupling allowed the peaks at δ 1.61, −0.90 and −1.40 to be assigned to C–H protons.

These data imply a mirror-plane symmetry and are consistent with the structure shown in Fig. 1. The complex splitting
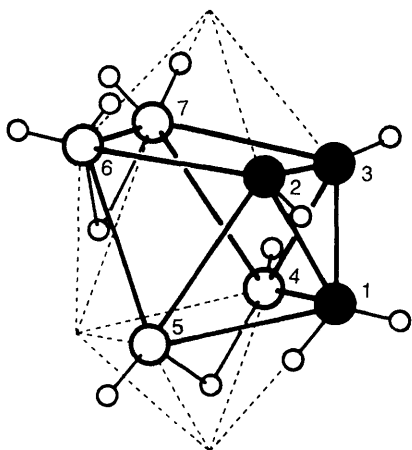
Fig. 1 Proposed structure of $hypho$-$C_3B_4H_{12}$ showing its relation to that of $closo$-$B_{10}H_{10}{}^{2-}$; large open circles B, full circles C, small open circles H

of the boron signal at δ -20.1 can be attributed to the coupling of boron atoms B(6,7) to the three sets of protons H_{exo}, H_{endo} and H_{bridge}, respectively. The other boron signal is attributed to atoms B(4,5), for which the coupling to the bridge hydrogen is unresolved. The proton signal of intensity 2 at δ 1.61 is assigned to the two equivalent C–H protons, and the two signals at δ -0.90 and -1.40, each of which features unresolved geminal coupling, are assigned to the non-equivalent methylene protons on C(1). The proposed structure is also consistent with [^{1}H-^{1}H]-$\{^{11}$B$\}$ COSY data.

The structure is a seven-atom fragment of a closed triangular ten-vertex bicapped Archimedean antiprism from which the two caps and one five-connected vertex have been removed. It has 2243 $styx$ topology, and is consistent with the Williams–Wade cluster geometry and electron-counting rules,[9] which require a contribution of eleven electron pairs to the framework bonding. Other possible structures derived from this geometry or from the alternative 1:3:3:3 stack geometry for an $isocloso$ system can be ruled out, either because they are inconsistent with the NMR data, or because it is not possible to devise topological representations that are compatible with the $hypho$ electron-count of this molecule. [A

referee has suggested that the molecule could perhaps also be viewed as a $hypho$ six-vertex trigonal prismatic C_2B_4 cluster with a μ_2-bridging CH_2 group. Further work is planned to address this point.]

The isolation of this new carbaborane from a reaction involving the previously little-exploited hot–cold technique, coupled with the possibility of extending the method to reactions of other unsaturated small molecules, presages new discoveries in the general area of small cluster heteroborane chemistry. The likelihood that $hypho$ species of this type are intermediates in the formation of the more familiar $closo$ and $nido$ systems also has important implications concerning the mechanisms of formation of carbaboranes from boranes in the gas phase, an area in which very little is known at present.[10]

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