The $[6\text{-}CB_9H_{14}]^-$ Anion: the Missing Link between Parent Ten-Vertex *arachno*-Boranes and Dicarbaboranes

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Reduction of the *nido*-$[6\text{-}CB_9H_{12}]^-[NMe_3H]^+$ salt with sodium metal in refluxing liquid ammonia produced in high yield a new *arachno*-$[6\text{-}CB_9H_{14}]^-$ anion which was characterized using ^1H, ^{13}C, ^{11}B, and two-dimensional (2-D) ^{11}B–^{11}B n.m.r. spectroscopy.

Two parent 10-vertex *arachno*-boranes and dicarbaboranes, the $[B_{10}H_{14}]^{2-}$ anion[1] and $6,9\text{-}C_2B_8H_{14}$[2—4] are well known and have been fully characterized. Although isoelectronic analogues of *arachno*-$[6\text{-}CB_9H_{14}]^-$, $9\text{-L-}6\text{-}CB_9H_{13}$ compounds (L = Me_2S, MeCN, PPh_3), were prepared in our laboratory[5] in 1976, all attempts at isolating the former missing parent monocarbaborane congener have so far been unsuccessful. We now report the development of an efficient preparative method for obtaining salts of the *arachno*-$[6\text{-}CB_9H_{14}]^-$ anion.

Treatment of the *nido*-$[6\text{-}CB_9H_{12}]^-$ anion (**1**)[6] ($[NMe_3H]^+$ salt) with sodium metal in refluxing liquid ammonia for 8 h, followed by decomposition of the mixture with 5% aqueous NaOH and precipitation with CsCl, led to the isolation of pure *arachno*-$[6\text{-}CB_9H_{14}]^-$ anion (**2**) (Cs^+ salt, 60%). The second crop of (**2**) was obtained on precipitation of the mother liquor with NMe_4Cl to give $[6\text{-}CB_9H_{14}]^-[NMe_4]^+$ (30%, total yield 90%) after recrystallization from aqueous acetone. The latter salt was also converted into $[BH_2(PPh_3)_2]^+[6\text{-}CB_9H_{14}]^-$ by treatment with $[BH_2(PPh_3)_2]^+I^-$ in acetone–chloroform (1:2). The former boronium salt was then purified by column chromatography on aluminium oxide in dichloromethane. Evaporation of the fraction of R_F 0.15 (checked by t.l.c. on

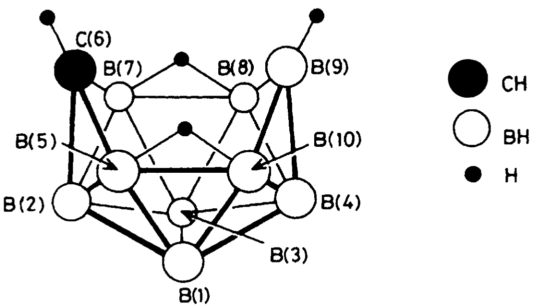

Figure 1. Gross geometry of the *arachno*-$[6\text{-}CB_9H_{14}]^-$ anion (**2**).

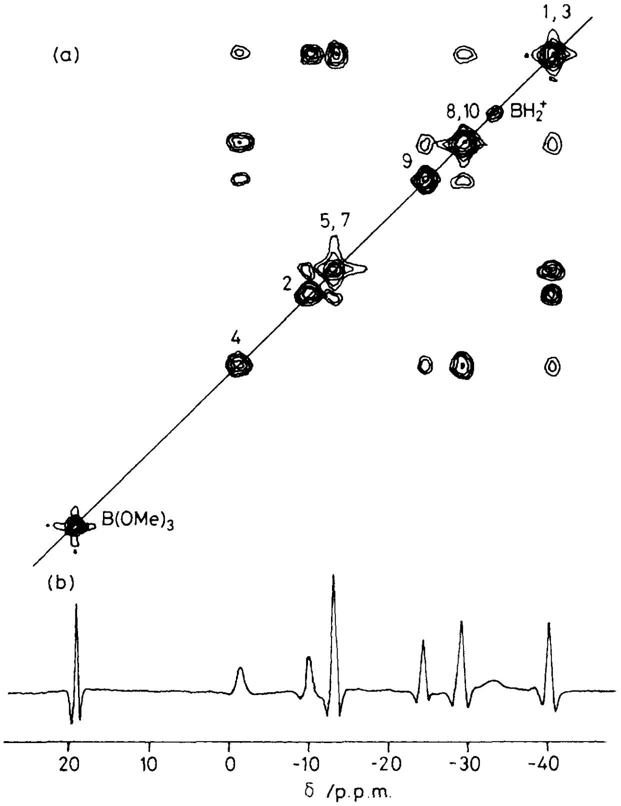

Figure 2. (a) Two dimensional (2-D) proton decoupled ^{11}B–^{11}B n.m.r. spectrum of $[BH_2(PPh_3)_2]^+[6\text{-}CB_9H_{14}]^-$ at 64.18 MHz in $CDCl_3$. Labelled peaks on diagonal correspond to (b) the conventional 1-D spectrum; off diagonal cross peaks reveal scalar coupling between specific boron nuclei.

Al_2O_3) and crystallization of the residue from chloroform–toluene (1 : 1) afforded large crystals of the boronium salt of (**2**).

Apart from the overlapping resonances of terminal BH units in the range δ −1.8—4.0, the ^1H n.m.r. spectrum of (**2**)† consists of three singlets of relative intensities 1 : 1 : 2 assigned to equatorial (*exo*) and axial (*endo*) protons of the skeletal CH_2 group and to two equivalent bridging protons. The corresponding ^{13}C n.m.r. spectrum† shows one triplet due to the resonance of the cage CH_2 group. The proton coupled ^{11}B n.m.r. spectrum of (**2**)† exhibits one triplet (intensity 1B) (cage BH_2 group) and five doublets of relative intensities 1 : 1 : 2 : 2 : 2. From the known cage geometry of the 10-vertex *arachno*-family of borane compounds[1—4] we can interpret the 2-D ^{11}B–^{11}B n.m.r. spectrum [Figure 2(a)] and assign the resonances in the 1-D spectrum [Figure 2(b)] to specific boron nuclei. In this scheme, all adjacent borons gave rise to the observed cross peaks expected for structure (**2**) (Figure 1) except for those between the B(5)–B(10) and B(7)–B(8) nuclei which are bound by hydrogen bridges.

These data unambiguously suggest for structure (**2**) a 26 cage-electron 10-vertex *arachno*-cluster with a pair of equivalent hydrogen bridges symmetrically arranged about the rim of the open hexagonal face.

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† *Fourier transform n.m.r. data* for (**2**): ^1H n.m.r. (NMe_4 salt, 100 MHz, rel. Me_4Si, CD_3COCD_3), δ 3.44 (s, 12H, NMe_4^+), −0.22 [s, 1H, *exo*-H(6)], −2.00 [s, 1H, *endo*-H(6)], −3.92 [br. s, 2H, μ-H]; ^{13}C n.m.r. (Cs^+ salt, 50.31 MHz, rel. Me_4Si, CD_3COCD_3), δ_C −3.90 [t, *J*(CH) 146 Hz, C(6)]; ^{11}B n.m.r. (NMe_4^+ salt, 64.18 MHz, CD_3COCD_3), δ_B −1.32 [d, 1B, *J*(BH) 142 Hz, B(4)], −10.21 [d, 1B, *J*(BH) 162 Hz, B(2)], −12.80 [d, 2B, *J*(BH) 147, 143 Hz, B(5,7)], −22.57 [t, 1B, *J*(BH) 112 Hz, B(9)], −28.47 [d, 2B, *J*(BH) 137 Hz, B(8,10)], −39.51 [d, 2B, *J*(BH) 141 Hz, B(1,3)]; ^{11}B n.m.r. [$BH_2(PPh_3)_2,^+$ salt, 64.18 MHz, $CDCl_3$], δ_B −2.04 [d, 1B, *J*(BH) 131 Hz, B(4)], −10.66 [d, 1B, *J*(BH) 166 Hz, B(2)], −13.64 [d, 2B, *J*(BH) 141/143 Hz, B(5,7)], −24.75 [t, 1B, *J*(BH) 110 Hz, B(9)], −29.23 [d, 2B, *J*(BH) 144 Hz, B(8,10)], −33.25 [br. s, 1B, $BH_2(PPh_3)_2^+$], −40.30 [d, 2B, *J*(BH) 138 Hz, B(1,3)].