

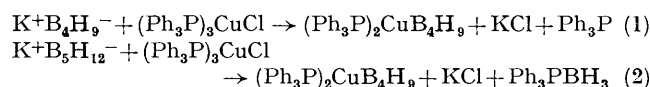
## Bistriphenylphosphinecuprapentaborane, an Unusual Copper-borane

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**Summary** The metallaborane  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  is the first metalla-derivative of the  $\text{B}_4\text{H}_9^-$  ion and is a unique copperborane in that the copper atom serves as a vertex of the cluster framework with no evidence for Cu-H-B bridge bonding.

THE  $\text{B}_4\text{H}_9^-$  ion,<sup>1</sup> the conjugate base of  $\text{B}_4\text{H}_{10}$ , is an *arachno* species, and the chemistry of its derivatives has received relatively little study. The addition of an electrophilic metal group to this anion poses interesting possibilities as to how the polyhedral structure might be expanded. With this thought in mind we have prepared the first metalla-derivative<sup>2</sup> of  $\text{B}_4\text{H}_9^-$ ,  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$ . This copperborane was obtained by two routes [reactions (1) and (2)], one of which involved abstraction of  $\text{BH}_3$  from the  $\text{B}_5\text{H}_{12}^-$  ion.<sup>1</sup>



Using high-vacuum apparatus, a typical reaction involved stirring an equimolar amount of the borane anion with  $(\text{Ph}_3\text{P})_3\text{CuCl}$  for 3 h at  $-45^\circ\text{C}$  in tetrahydrofuran- $\text{CH}_2\text{Cl}_2$ . The mixture was filtered to remove KCl and concentrated, and  $\text{Et}_2\text{O}$  added to precipitate the cream-white product. In contrast to free  $\text{B}_4\text{H}_9^-$  salts,  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  is remarkably stable in the air in the solid state, with no appreciable signs of decomposition after long times at ambient temperature. In solution  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  quickly decomposes above  $0^\circ\text{C}$ ; below  $-25^\circ\text{C}$  its solubility is 0.1 M in  $\text{CH}_2\text{Cl}_2$ . It shows B-H i.r. stretching vibrations at (Nujol mull) 2528s, 2499s,sh, 2466s,sh, 2449vs, and 2440s  $\text{cm}^{-1}$  but, significantly, no bands in the range (2400—2100  $\text{cm}^{-1}$ ) normally assigned to Cu-H-B stretching modes.<sup>3</sup> All copper(I) boranes<sup>4</sup> which have been shown to have Cu-H-B bridges by X-ray crystallography show some absorption in this range: 2,3- $\mu$ - $(\text{Ph}_3\text{P})_2\text{CuB}_5\text{H}_5$ ,<sup>5</sup> does not absorb in this range and an X-ray study<sup>6</sup> does not support the presence of Cu-H-B bridges.

The  $^{11}\text{B}$  n.m.r. spectrum ( $0^\circ\text{C}$ ) of  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  at 28.8 MHz provides evidence for a pyramidal structure. A broad asymmetric resonance at  $\delta +3.2$  p.p.m. (positive shifts downfield of  $\text{BF}_3\cdot\text{OEt}_2$ ) of area 3 is assigned to basal boron atoms while a triplet at  $-55.2$  p.p.m. ( $J_{\text{B-H}}$  98 Hz) of area 1 is assigned to the apex, indicating that two hydrogens are bound to the apical boron. This triplet collapses to a sharp singlet upon  $^1\text{H}$  spin-decoupling.

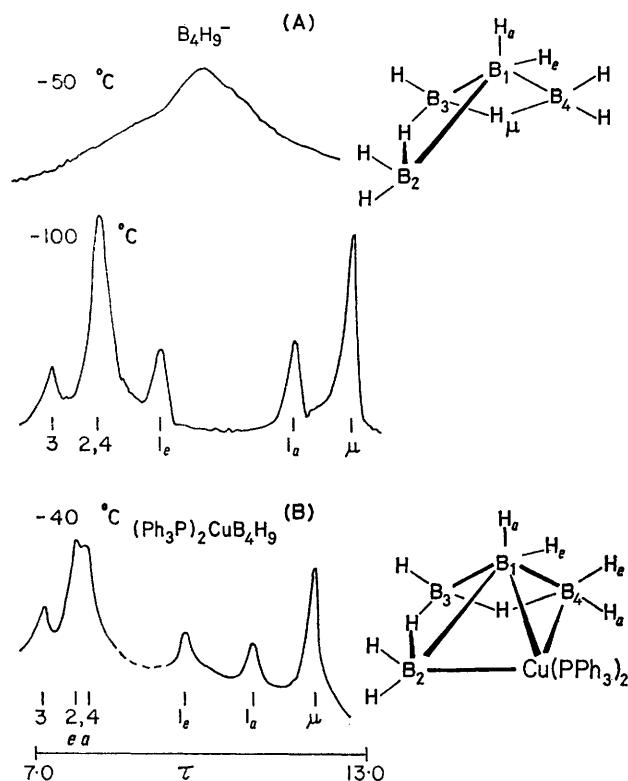


FIGURE. Comparison of the 100 MHz  $^{11}\text{B}$  decoupled  $^1\text{H}$  n.m.r. spectra of  $\text{K}[\text{B}_4\text{H}_9]$  in  $(\text{CD}_3)_2\text{O}$  (A) with the  $^{11}\text{B}$  decoupled  $^1\text{H}$  n.m.r. spectrum of  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  in  $\text{CD}_2\text{Cl}_2$  (B). The dashed line denotes an impurity peak due to  $\text{Ph}_3\text{PBH}_3$ .

The 100 MHz  $^1\text{H}$  n.m.r. spectrum at  $-40^\circ\text{C}$  of  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  is shown in the Figure. Assignments have been made in part from selective  $^{11}\text{B}$  spin-decoupling experiments [ $\tau$  7.16, 3-H; 7.68, 2-, 4e(a)-H; 7.86, 2-, 4a(e)-H;

9.69, 1e-H; 10.92, 1a-H; 12.00,  $\mu$ -H] and in part from the limiting (slow exchange)  $^1\text{H}$  n.m.r. spectrum<sup>1</sup> of  $\text{B}_4\text{H}_9^-$  at  $-100^\circ\text{C}$  (Figure). The two spectra are strikingly similar, suggesting that the hydrogen configuration of the borane fragment in the copper complex is approximately the same as that in the free ion which has  $C_s$  symmetry. Line widths at half-peak height are comparable in both spectra (ca. 30 Hz), which are appreciably sharper than resonances observed in copperboranes (ca. 100 Hz) containing Cu-H-B bridges.<sup>7</sup> The  $^1\text{H}$  n.m.r. spectrum of  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  is independent of temperature in the available range ( $-66$  to  $0^\circ\text{C}$ ), giving no evidence for dynamic character. This contrasts markedly with the highly fluxional character of the  $\text{B}_4\text{H}_9^-$  ion on the  $^1\text{H}$  n.m.r. time scale; see the Figure and the spectra of  $\text{B}_4\text{H}_9^-$  at  $-100$  and  $-50^\circ\text{C}$ . Only a single exchange-averaged resonance is observed at  $-20^\circ\text{C}$ .

The spectral data are consistent with the structure shown in the Figure. The copper vertex is on a mirror plane. The implied  $\eta^3$ -interaction of the borane framework with copper is reminiscent of that observed in many 'slipped sandwich' metalla-carboranes<sup>8</sup> and metal complexes with carborane clusters.<sup>9</sup>

An alternative structure of  $C_s$  symmetry with Cu-H-B bonding through axial H atoms of B-2 and B-4 seems less likely. Typically, such an arrangement gives fluxional systems with  $^1\text{H}$  n.m.r. spectra which are single broad resonances.<sup>7</sup> Furthermore, the i.r. spectrum of  $(\text{Ph}_3\text{P})_2\text{CuB}_4\text{H}_9$  provides no support for Cu-H-B bonding.<sup>3</sup>

Another structural arrangement which has been considered and discarded contains copper at a bridging site between B-1 and B-2 or B-2 and B-4. Oscillation of the boron framework with respect to the  $(\text{Ph}_3)_2\text{Cu}$  group such that copper alternates between these two sites could produce a  $^1\text{H}$  n.m.r. spectrum which would suggest  $C_s$  symmetry. However, this supposes that no concomitant proton exchange occurs. Such a supposition is hardly justified, especially at the highest temperature ( $0^\circ\text{C}$ ) of the  $^1\text{H}$  n.m.r. study. The apparent absence of proton exchange averaging at this temperature and the absence of evidence for loss of apparent  $C_s$  symmetry (retardation of Cu-borane oscillation) at lower temperatures leads us to consider that this third structural possibility is not likely. It would be of interest to examine the solid state structure of this compound, but we have not yet managed to obtain single crystals.

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