X-Ray Crystallographic Characterization of the Single Hydrogen Bridge Attachment of the Tetrahydroborate Group in Tris(methyldiphenylphosphine)tetrahydroboratecopper

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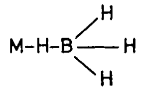
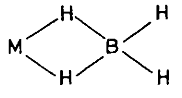
Summary The *X*-ray crystal structure of [$(MePh_2P)_3Cu$-BH_4] has revealed that the copper atom exists in a distorted tetrahedral environment consisting of the phosphorus atoms of the three phosphine ligands and a single hydrogen atom of the tetrahydroborate group.

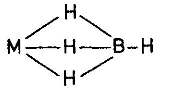
Although metal complexes containing the BH_4^- group have been characterized by diffraction methods for the double[1] (II) and triple[2] (III) hydrogen bridge, no such evidence has heretofore been presented for the single



(I)



(II)



(III)

hydrogen atom bridge (I). Recent spectroscopic studies reported by Bommer and Morse,[3] and independently conducted by us, have led to the conclusion that situation (I) obtains for [$(MePh_2P)_3CuBH_4$] in the solid state.

The i.r. spectrum of [$(MePh_2P)_3CuBH_4$] in a KBr disc is consistent with monodentate co-ordination by BH_4^-. Upon dissolving the complex in benzene, however, the spectrum changes noticeably and may now be interpreted in terms of bidentate co-ordination by BH_4^-. Formation of the second Cu–H bond presumably occurs at the expense of one of the originally co-ordinated $MePh_2P$ ligands, since a molecular weight measurement indicates that the complex is extensively dissociated in benzene. A ^{31}P n.m.r. study indeed confirms that a rapid exchange of free and co-ordinated phosphine is occurring. In order to establish with certainty the proposed novel mode of attachment of the BH_4^- group in the solid state, the *X*-ray crystal structure of [$(MePh_2P)_3CuBH_4$] has been determined. Crystals suitable for X-ray analysis were grown from chloroform–ethanol (1 : 2) at *ca.* 5 °C.

Crystal data: $C_{39}H_{43}BCuP_3$, orthorhombic, space group $Pn2_1a$, M 679·0, $a = 20·291(9)$, $b = 17·434(9)$, $c = 10.419(6)$ Å, $U = 3686·2$ Å^3, $Z = 4$, μ(Mo-K_α) 7·71 cm^{-1}. Intensity data were recorded on an Enraf–Nonius CAD-4 diffractometer employing the ω-2θ scan technique; for 3113 reflections, $R = 0·026$.†

The bonding mode of the BH_4^- group is clearly shown by both the location of the bridging hydrogen atom and by the Cu · · · B separation. The positions of the hydrogen atoms of the tetrahydroborate ion have been unambiguously determined from a difference Fourier map. For the co-ordinated hydrogen atom, the Cu–H bond length is 1·47 Å, the B–H distance is 1·19 Å and the Cu–H–B bond angle is 170°. The bond distances agree well with those predicted from a sum of covalent radii.[4] The Cu · · · B separation, 2·650-(5) Å, is substantially greater than the 2·184(9) Å value for bidentate BH_4^- in [$(Ph_3P)_2CuBH_4$][1a] and the Co · · · B approach of 2·21 Å for bidentate BH_4^- in Co(P_3)BH_4.[5]

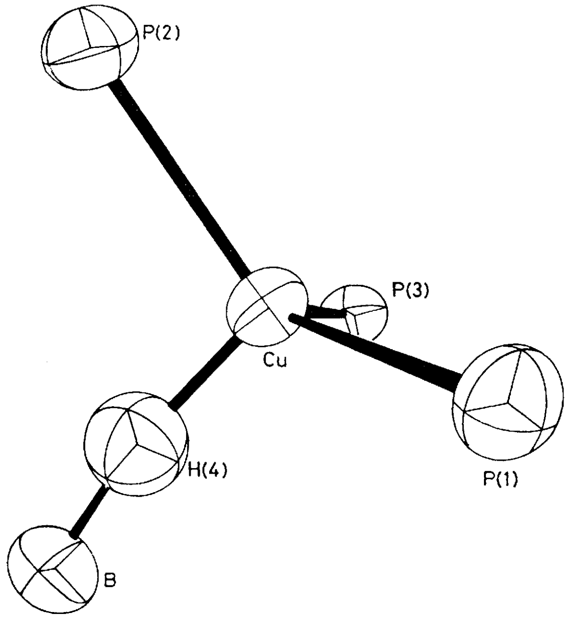


Figure. Co-ordination sphere of Cu in [$(MePPh_2)_3CuBH_4$] with the non-hydrogen atoms represented by their 50% probability ellipsoids for thermal motion.

The co-ordination sphere of the Cu atom is shown in the Figure. The three Cu–P distances of 2·276(2), 2·290(2), and 2·293(2) Å agree well with the Cu–P bond length of 2·276(1) Å in [$(Ph_3P)_2CuBH_4$]. The P–Cu–P bond angles are 108·9(1), 117·8(1), and 118·0(1)°, while the B · · · Cu–P angles are 101·0(4), 101·7(4), and 106·9(3)°.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] (a) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223; (b) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *ibid.*, 1968, **7**, 1575; D. S. Marynick and W. N. Lipscomb, *ibid.*, 1972, **11**, 820.

[2] P. H. Bird and M. R. Churchill, *Chem. Comm.*, 1967, 403; A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, 1968, **22**, 328; V. Plato and K. Hedberg, *Inorg. Chem.*, 1971, **10**, 590.

[3] J. C. Bommer and K. W. Morse, *J.C.S. Chem. Comm.*, 1977, 137.

[4] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, ch. 7.

[5] P. Dapporto, S. Midollini, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 2768.