technique.[29] The contact of methanol with Viton O-rings which were used to separate the reaction mixture from the pressurizing fluid caused an increase in absorption at the near-ultraviolet region. Therefore, the rates for **2** and **3** were obtained by the batch method. The reaction mixture was kept in a glass hypodermic syringe with a Teflon cap for 3 to 15 h at the desired conditions and analyzed spectrophotometrically. Oxygen was not excluded during kinetic measurements. We determined the rate constants for azobenzene under anaerobic (N_2) conditions; they were in good agreement withe the aerobic rate constants within experimental error.

Acknowledgment. The authors thank Professors T. Kunitake and M. Takagi for helpful discussions and Miss M. Sato for technical assistance. They are also pleased to acknowledge helpful discussions with Professor J.-M. Lehn.

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[29] Whalley, E. *Adv. Phys. Org. Chem.* **1964**, *2*, 93.

Neutron and X-ray Diffraction Studies of Tris(methyldiphenylphosphine)[tetrahydroborato(1−)]copper, $Cu[P(C_6H_5)_2CH_3]_3(BH_4)$. The First Accurate Characterization of an Unsupported Metal–Hydrogen–Boron Bridge Bond

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Abstract: A single-crystal neutron diffraction study of tris(methyldiphenylphosphine)[tetrahydroborato(1−)]copper, $Cu(PPh_2Me)_3(BH_4)$, has been carried out at low temperature (15 ± 0.5 K) in order to examine the nature of the unidentate attachment of the tetrahydroborate group to the Cu atom. The compound crystallizes in the space group $Pna2_1$, $Z = 4$. Cell constants at 15 K are $a = 19.980$ (2) Å, $b = 10.175$ (1) Å, and $c = 17.282$ (2) Å. The structure was refined on the basis of measured intensities of 4765 reflections, and final discrepancy factors for all reflections are $R(F^2) = 0.043$ and $R(wF^2) = 0.047$. One H atom of the tetrahydroborate group participates in bonding to the Cu atom with Cu–H = 1.697 (5) Å, Cu–B = 2.518 (3) Å, and Cu–H–B = 121.7 (4)°. There is no evidence for other Cu–H bonding interactions (the second shortest CuH distance is 2.722 (7) Å). The H–Cu–P angles [86.2 (2)°, 108.5 (2)°, 115.3 (2)°] are more widely distributed than the B–Cu–P angles [101.4 (6)°, 101.7 (7)°, 108.8 (7)°], and the bridging H atom is significantly displaced off the pseudothreefold axis defined by the CuP_3 group. This bent, off-center positioning of the bridging H atom is reminiscent of similar observations found in M–H–M bridges and may provide some information about the nature of M–H–B overlap. The tetrahydroborate group is somewhat distorted from tetrahedral symmetry; three of the four B–H distances agree well with one another (1.179 ± 0.005 Å), but the fourth [1.330 (6) Å] is significantly longer. Surprisingly, however, the long distance is not the one associated with the Cu–H–B bridge. In addition to the neutron diffraction analysis, structures were determined from room-temperature X-ray data obtained from two other crystals. In general, for nonhydrogen structural parameters there is good agreement among all of the determinations including the original work of Atwood et al. However, one outstanding point of disagreement occurs in the Cu–B distances which range from 2.498 (5) to 2.650 (5) Å in the individual determinations. This variation in distance may be indicative of disorder of the (μ-H)BH_3 unit.

For the past few years we[1a,e] have been investigating compounds having unsupported[2] metal–hydrogen–metal bonds with neutron diffraction techniques, in an attempt to understand the bonding patterns in three-center/two-electron (3c, $2e^-$) bonds.[3] The results of these studies, and those of others,[4] led us to conclude that the overlap pattern in the M–H–M bridge bond is of the "closed" type[5] and also led us to suspect that the M–H–M bond is inherently bent. We have therefore sought to extend these studies to metal–hydrogen–boron systems (and, eventually, boron–hydrogen–boron systems), to see if these general conclusions also hold for other types of 3c, $2e^-$ bonds.

Unsupported[2] M–H–B bonds are very rare. The unidentate tetrahydroborate ligand is suspected to exist in a few cobalt,[6a]

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[2] We define a molecule having an unsupported 3c, $2e^-$ bond as one in which the two halves of the molecule are held together solely by one 3c, $2e^-$ bond, without other bridging groups. Thus, molecules such as B_2H_6 or $H_2Re_2(CO)_8$, which have two X–H–X bridges, are not included by this definition. An unsupported Zr–H–Al bridge, incidentally, has been reported recently [Kopf, J.; Vollmer, H. J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 985].

[3] (a) Bau, R.; Koetzle, T. F. *Pure Appl. Chem.* **1978**, *50*, 55. (b) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

[4] (a) Roziere, J.; Williams, J. M.; Stewart, R. P.; Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 4497. (b) Petersen, J. L.; Johnson, P. L.; O'Connor, J.; Dahl, L. F.; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 3460.

[5] A "closed" 3c, $2e^-$ bond is one in which all three orbitals overlap in a common region of space; in the case of the M–H–M bond this would mean that there is a significant amount of M–M bonding as well as M–H bonding.

Table I. Crystallographic Details of $Cu[P(C_6H_5)_2CH_3]_3(BH_4)$

	neutron (15 K)	X-ray (room temperature)	
		crystal 1	crystal 2
(A) Crystal Data			
mol wt		679.06	
space group		$Pna2_1$ $(Z = 4)$	
cell dimens[a]			
a, Å	19.980 (2)	20.292 (5)	20.334 (17)
b, Å	10.175 (1)	10.405 (3)	10.412 (8)
c, Å	17.282 (2)	17.403 (6)	17.420 (12)
V, Å^3	3513.2 (7)	3674 (2)	3688 (4)
linear abs coeff μ, cm^{-1}	2.58 (for λ = 1.1614 Å neutrons)	7.75 (for Mo Kα X-rays)	7.71 (for Mo Kα X-rays)
d(calcd), g cm^{-3}	1.28	1.23	1.22
(B) Details of the Neutron Diffraction Analysis			
cryst wt = 13.88 mg			
cryst vol = 10.88 mm^3 at 15 K			
no. of crystal faces = six: (100), $(\bar{1}00)$, (011), $(0\bar{2}1)$, (001), $(00\bar{1})$			
transmission range = 0.49–0.63			
no. of reflctns measd = 5168			
no. of independent reflctns (m) = 4765			
agreement factor for averaging $R_c = (\Sigma_{i=1}^{n} \lvert\langle F_o^2\rangle - F_{oi}^2\rvert)/\Sigma n\langle F_o^2\rangle = 0.018$			
no. of parameters (n) = 787			
$R_1 = \Sigma \lvert F_o^2 - k^2F_c^2\rvert/\Sigma F_o^2 = 0.043$			
$R_2 = [\Sigma w(F_o^2 - k^2F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.047$			
$S = [\Sigma w(F_o^2/k^2 - F_c^2)^2/(m - n)]^{1/2} = 1.357$			

[a] For purposes of comparison, the unit cell dimensions determined from the first neutron diffraction analysis[10] at 18 K are a = 19.986 (7) Å, b = 10.178 (5) Å, c = 17.281 (7) Å, and V = 3517 (2) Å^3. Those from the X-ray analysis of Atwood, Kutal, et al.[8] at room temperature are a = 20.292 (8) Å, b = 10.419 (5) Å, c = 17.435 (7) Å, and V = 3686.2 Å^3.

ruthenium,[6b] copper,[7] and silver[7] complexes and has been characterized crystallographically in only one case, $Cu(PPh_2Me)_3(BH_4)$.[8] In that analysis, a bridging H position was found which corresponded to a linear Cu–H–B bridge (170°) and Cu–H and B–H bond lengths of 1.47 and 1.19 Å, respectively. Although those results showed unequivocally that the BH_4 attachment was unidentate, the H position was not precisely determined by that X-ray analysis. Furthermore, independent X-ray studies in two of our laboratories[1b,c] proved to be at variance with this initial structure report and with each other. The main differences concern the Cu–B distances of 2.578 (10)[1b] and 2.498 (5) Å[1c] vs. 2.650 (5) Å reported in the earlier work.[8] Additionally, the tetrahydroborate H atoms were located in one study,[1b] giving a Cu–H–B bond angle of 126°. In order to get more accurate structural parameters for a detailed examination of the Cu–H–B bond and possibly resolve this question of variable Cu–B distances, we embarked upon a neutron diffraction study.

Experimental Section

Crystal Preparation. The procedure of Bommer and Morse[7d] was used to prepare $Cu[(C_6H_5)_2CH_3]_3BH_4$. Crystals were grown by allowing pentane to diffuse slowly into a CH_2Cl_2 solution of this compound at −78 °C.

Collection and Reduction of X-Ray Diffraction Data. Lattice constants and other pertinent crystal data from the two X-ray diffraction studies are given in Table IA.

Crystal 1[1b] was irregularly shaped of approximate dimensions 0.17 × 0.21 × 0.35 mm. It was sealed in a thin-walled glass capillary. Cell dimensions and an orientation matrix for data collection were determined by least-squares refinement of the angular settings of 15 reflections. A Syntex P$\bar{1}$ diffractometer was employed with Mo Kα radiation monochromatized by pyrolytic graphite ($2\theta_{mon}$ = 11.69°). Integrated intensities were obtained by using the θ–2θ scan mode ($2\theta_{max}$ = 60°).

Reflections were scanned over a range 1.0° below the Kα_1 peak to 1.0° above the Kα_2 peak by using a variable scan speed of 2–4°/min, depending on the intensity of the reflection. Five standard intensities ($\bar{4}0\bar{4}$, $\bar{6}00$, $\bar{2}06$, $3\bar{4}\bar{1}$, and $\bar{2}\bar{2}\bar{2}$) monitored every 100 reflections showed no significant variation with time. Of the 6292 intensity measurements, 2820 independent reflections for which $I > 3\sigma(I)$ were considered observed. The intensity data were corrected for Lorentz and polarization[9a] effects. No absorption corrections were applied.

Crystal 2[1c] was irregularly shaped of approximate dimensions 0.2 × 0.2 × 0.2 mm. It was sealed in a thin-walled glass capillary and mounted with c coincident with ϕ on a Picker FACS-I diffractometer equipped with auxiliary disk memory. Precise lattice constants were determined by least-squares refinement based on the angular settings of 12 Friedel pairs (38° < 2θ < 40°) by using Nb-filtered Mo Kα radiation. Integrated intensities were collected by the θ–2θ scan technique ($2\theta_{max}$ = 60°). Stationary backgrounds were measured at equal angles above and below the respective Kα peak of base width 1.2°. A dispersion factor allowing for α_1–α_2 splitting was applied to large 2θ values; the take-off angle was 2.5°. Twenty second background counts were used for 2θ < 55° and 40 second counts for 2θ > 55°. A total of 5208 reflections were measured, of which 5165 were independent and 3894 had $F > 3\sigma(F)$. The intensity data were corrected for Lorentz and polarization effects. Absorption corrections were not applied.

Structure Analysis from X-ray Data. This analysis was carried out prior to the publication of the atomic coordinates.[8b] The structure was solved by Patterson and Fourier techniques[9b] using the data from crystal 1. A trial position for the Cu atom was obtained from a three-dimensional Patterson summation. Least-squares refinement of the coordinates and isotropic temperature factor of this atom gave a conventional R_1 of 0.566. The positions of the three P atoms were located on a Fourier map. Least-squares refinement of the Cu and three P atoms reduced R_1 to 0.462. The locations of the remaining nonhydrogen atoms were determined from successive Fourier maps. Refinement of the positional and isotropic thermal parameters of all nonhydrogen atoms gave an R_1 of 0.070. Conversion to anisotropic temperature factors followed by least-squares refinement reduced R_1 to 0.055. Phenyl and methyl H atoms were included at their calculated positions (C–H = 0.98 Å), and tetrahydroborate H atom positions were located from a difference-Fourier map. The terminal H atoms of the BH_4^- group were refined successfully, but continued refinement of the bridging H atom caused it to shift to a position unreasonably close to the Cu atom. The bridging H atom was therefore fixed at the position found on the difference-Fourier map. The final refinement gave $R_1 = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$ and $R_2 = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$ equal to 0.044 and 0.059, respectively, with an average shift/error of 0.06. Refinement assuming the opposite Bijvoet sense of the Miller indices gave a slightly lower R index (0.043) but none of the tetrahydroborate H atoms could be located in that case.

The positional and anisotropic temperature parameters for nonhydrogen atoms determined with the data from crystal 1 were used as a starting point for refinement on the basis of the data from crystal 2. Difference maps revealed the positions of all but the four tetrahydroborate H atoms. The final R_1 index is 0.062 with an average shift/error of 0.3. A slightly higher R_1 index (0.064) resulted with indices of the opposite Bijvoet sense. In the structure analysis of crystal 2, neither the bridging nor any of the terminal hydrogens in the BH_4^- group could be clearly seen in the difference map.

In refinements for both crystals a fixed isotropic temperature factor (U = 0.063 Å^2) was used for H atoms. Atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[9c] and H scattering factors were those of Stewart, Davidson, and Simpson.[9d] Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ were applied to P (0.11, 0.12) and Cu (0.36, 1.36).[9b] The quantity minimized in least-squares calculations was $\sum w(\lvert F_o\rvert - k\lvert F_c\rvert)^2$. Positional and thermal parameters for crystal 1 and crystal 2 are available (see paragraph at the end of the paper for details).

Collection and Reduction of Neutron Diffraction Data. The initial neutron analysis[10] was carried out at 18 K on a crystal of volume 1.79

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[6] (a) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Wright, K. *Can. J. Chem.* **1974**, *52*, 2990. (b) Holah, D. G.; Hughes, A. N.; Hui, B. C. *Ibid.* **1976**, *52*, 320.

[7] (a) Bommer, J. C.; Morse, K. W. *J. Am. Chem. Soc.* **1974**, *96*, 6222. (b) *J. Chem. Soc., Chem. Commun.* **1977**, 137. (c) *Inorg. Chem.* **1979**, *18*, 531. (d) *Ibid.* **1980**, *19*, 587.

[8] (a) Atwood, J. L.; Rogers, R. D.; Kutal, C.; Grutsch, P. A. *J. Chem. Soc., Chem. Commun.* **1977**, 593. (b) Kutal, C.; Grutsch, P.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558.

[9] (a) The polarization correction was carried out by using a factor for mosaic spread of 0.5 [see: Suortti, P.; Paakkari, T. *J. Appl. Crystallogr.* **1968**, *1*, 121]. (b) Stewart, J. M.; Kruger, G. J.; Ammon, H. L.; Dickinson, C.; Hall, S. R. "The X-Ray System", Technical Report TR-192; Computer Science Center; University of Maryland: College Park, MD June 1972. (c) Cromer, D. T.; Waber, J. T. *Acta. Crystallogr.*, **1965**, *18*, 104. (d) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

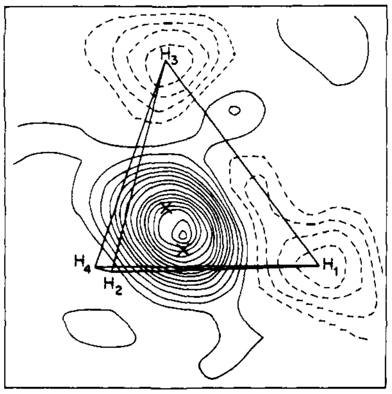

Figure 1. Section of the neutron scattering-density map (F_o map) through the borohydride group. Atoms H(1) and H(3), and the midpoint of the H(2)-H(4) bond, define the plane with contours drawn at intervals of 0.3 × 10^{-11} mm/Å^3 (negative contours are dashed and the zero level contour is omitted). The two alternate sites for boron (if B is refined as a disordered atom) are denoted by X. However, no conclusive evidence for the presence of such disorder could be extracted from the data.

mm^3. However, the results of that analysis were not entirely satisfactory, primarily because the data set was very weak. Consequently, a larger crystal was grown (volume 10.81 mm^3) and used for a second data collection. This crystal was mounted on an aluminum pin, the end of which was made hollow in order to reduce the amount of metal in the neutron beam, and was oriented with the crystallographic *a* axis approximately parallel to the pin. The sample was sealed in an aluminum can under a helium atmosphere and placed in a closed-cycle helium refrigerator[11] mounted on a four-circle diffractometer at the Brookhaven High Flux Beam Reactor.[12] A germanium (2,2,0) crystal monochromator was employed to obtain a neutron beam of wavelength 1.1614 (2) Å (based on KBr, a = 6.6000 Å at 298 K). The temperature measured during data collection was 15 ± 0.5 K.[13]

The cell dimensions were refined by a least-squares procedure on the basis of the sin θ values of 32 reflections ($52° < 2\theta < 70°$) and are listed in Table IA. Reflection intensities were measured in one octant of reciprocal space ($+h,+k,+l$) with $2\theta \leq 106°$ and an additional octant ($+h,-k,+l$) with $2\theta \leq 30°$, employing a θ–2θ step-scan technique. The scan range was varied according to the equation $\Delta 2\theta = (1.052 + 4.0 \tan \theta)°$ for high-angle data ($2\theta > 60°$) and $\Delta 2\theta = 3.6°$ for low-angle data. The step size was adjusted to give between 55 and 70 steps in each scan. At each point, counts were accumulated for approximately two seconds, with the exact time interval being determined by monitoring the incident beam intensity. As a general check on experimental stability, the intensities of two reflections were monitored every 100 measurements. These did not vary to any significant degree during the entire period of data collection. Integrated intensites of reflections were obtained by an orthodox peak-minus-background procedure, assuming 20% of the scan, at either extremity, to represent the background intensity. Lorentz and absorption corrections were applied by using the analytical method of De Meulenaer and Tompa.[14] The variance of the squared observed structure factor ($F_o^2 = I \sin 2\theta$) of each reflection was estimated by using the equation $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + AF_o^2 + B$, where $\sigma_c(F_o^2)$ is the standard deviation from counting statistics. Coefficients *A* and *B*, estimated from the discrepancies between symmetry-related reflections, are $A = 0.000\,14$ and $B = 0.31$, with F_o^2 on an absolute scale in barn units.

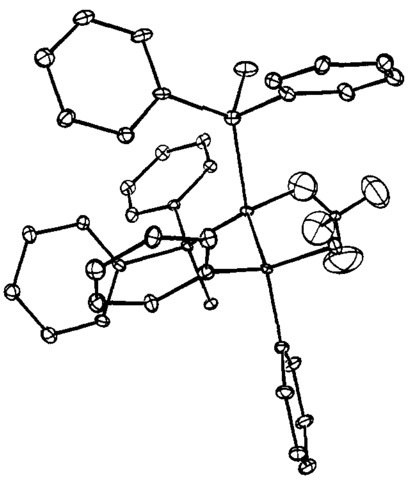

Figure 2. Molecular plot[36] of Cu(PPh$_2$Me)$_3$(BH$_4$), with the H atoms on the phenyl and methyl groups removed for clarity. Ellipsoids are shown at the 50% probability level.

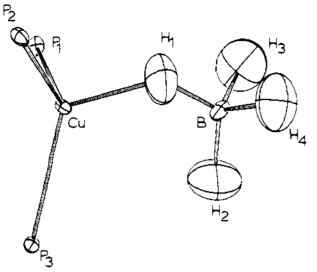

Figure 3. A plot of the P$_3$CuBH$_4$ core of the molecule, with ellipsoids drawn as in Figure 2.

Structure Analysis from Neutron Data. The atomic coordinates of the nonhydrogen atoms from the X-ray determination[8b] were used (with a slight modification[15]) as initial values for the present refinement. After a few cycles, a difference scattering-density map showed all H positions. All parameters, including a type I isotropic extinction correction factor,[16] were varied by a block-diagonal least-squares technique,[17] minimizing $\sum w(F_o^2 - k^2F_c^2)^2$. Weights were taken as $w = 1/\sigma^2(F_o^2)$. The most significant extinction correction value applied to F_c^2 was 0.83 for the reflection 1,2,1. The U_{22} and U_{33} anisotropic thermal components for the B atom initially converged to negative values. Subsequently, the B scattering length was varied together with the positional and thermal parameters, resulting in a value of $b_B = 0.627\ (6) + 0.016\ (6)i \times 10^{-12}$ cm. The thermal ellipsoid is highly anisotropic, but the tensor remains positive definite. A difference scattering-density map computed at this stage was essentially featureless. However, because of the elongated appearance of the B ellipsoid and the unusual B–H distances (vide infra), after inspection of the F_o map (Figure 1) it was decided to attempt refinement of a disordered model with two partially occupied B sites. Although this refinement did converge, provided that positional and isotropic thermal parameters of the B sites were varied in alternate cycles, there was essentially no improvement in *R* indices. Thus, the neutron diffraction data give no conclusive evidence for the presence of such disorder. The results reported in this paper are for the ordered model.

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(10) The initial neutron diffraction analysis was carried out with a data set of 2058 reflections having intensities greater than $2\sigma(I)$. The phenyl and methyl groups were treated as rigid bodies in the least-squares refinement, which converged to agreement factors (based on *F*) of $R_1 = 0.122$ and $R_2 = 0.118$. The geometrical details determined from this analysis [Cu-H = 1.77 (4) Å, Cu-B = 2.55 (2) Å, Cu-P = 2.28 (1) Å, B-H = 1.28 (5) Å, P-C(Me) = 1.82 (2) Å, P-C(Ph) = 1.84 (1) Å, B-Cu-P = 103 (5)°, Cu-H-B = 116 (3)°] agree within experimental error with those of the subsequent (more precise) analysis described in the text. It is interesting to note that, in this initial structure determination, the B-H(3) terminal distance also refined to an unusually long value [1.43 (4) Å].

(11) Air Products and Chemicals Inc., DISPLEX Model CS-202.

(12) (a) Dimmler, D. G.; Greenlaw, N.; Kelley, M. A.; Potter, D. W.; Rankowitz, S.; Stubblefield, F. W. *IEEE Trans. Nucl. Sci.* **1976**, *NS-23*, 398. (b) McMullan, R. K. and, in part, Andrews, L. C.; Koetzle, T. F.; Reidinger, F.; Thomas, R.; Williams, G. J. B. "NEXDAS", Neutron and X-Ray Data Acquisition System, unpublished work, 1976.

(13) These values were calibrated with reference to a magnetic phase transition in FeF$_2$ at $T_N = 78.38$ (1) K. With a FeF$_2$ crystal mounted in the same fashion as the sample, the platinum resistance thermometer used to monitor the temperature indicated $T_N = 76.1$ K. Thus 2 K was added to the recorded values.

(14) De Meulenaer, J.; Tompa, H. *Acta. Crystallogr.* **1965**, *19*, 1014.

(15) The coordinates used in the neutron analysis (x_N, y_N, z_N) are related to those in the X-ray structure determination[8b] (x_X, y_X, z_X) by the following equations: $x_N = x_X + {}^1/_2$; $y_N = 1 - z_X$; $z_N = y_X + 0.7525$. The (y,z) interchange was carried out in order to transform a nonstandard setting of space group number 33 ($Pn2_1a$) to the standard setting ($Pna2_1$). The shift of the *z* coordinate by 0.7525 was done in order to place the arbitrary *z* coordinate of the Cu atom at 1.0.

(16) Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A* **1975**, *A31*, 417.

(17) The scale factor, overall temperature factor, and isotropic extinction parameter were put in one block (3 × 3), while the positional and anisotropic thermal parameters of each atom were put in individual blocks (9 × 9 or 11 × 11 for B when scattering factors were varied). Refinement was continued until the largest parameter shift was less than 0.3σ.

Table II. Positional and Thermal Parameters from the Neutron Diffraction Analysis at 15 K

	fractional atomic coordinates[a]			thermal parameters[b]					
atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	0.87832 (5)	0.7037 (1)	1.000000 (0)	0.0058 (4)	0.0042 (3)	0.0090 (4)	−0.0002 (3)	−0.0000 (3)	0.0003 (3)
P(1)	0.80231 (8)	0.6916 (2)	0.90137 (9)	0.0050 (6)	0.0083 (6)	0.0080 (6)	0.0012 (5)	0.0002 (5)	0.0022 (5)
P(2)	0.97398 (8)	0.5830 (1)	0.9869 (1)	0.0073 (6)	0.0072 (6)	0.0124 (6)	−0.0017 (5)	0.0004 (6)	0.0004 (6)
P(3)	0.90538 (8)	0.9062 (1)	1.04369 (9)	0.0090 (6)	0.0047 (6)	0.0069 (6)	0.0025 (5)	0.0010 (5)	0.0017 (5)
C(11)	0.71895 (7)	0.7508 (1)	0.92669 (8)	0.0087 (5)	0.0154 (5)	0.0135 (5)	0.0053 (5)	0.0045 (4)	0.0024 (5)
C(21)	0.95979 (7)	0.4060 (1)	0.9922 (1)	0.0135 (6)	0.0080 (5)	0.0315 (7)	−0.0012 (5)	−0.0013 (6)	−0.0015 (6)
C(31)	0.94812 (7)	0.9047 (1)	1.13709 (7)	0.0125 (5)	0.0138 (5)	0.0078 (5)	0.0022 (5)	−0.0001 (4)	0.0021 (5)
C(121)	0.82575 (6)	0.7848 (1)	0.81629 (7)	0.0076 (5)	0.0086 (5)	0.0104 (5)	0.0008 (4)	0.0002 (4)	0.0029 (4)
C(122)	0.79498 (7)	0.9037 (1)	0.79863 (8)	0.0112 (5)	0.0112 (5)	0.0143 (5)	0.0044 (5)	0.0039 (4)	0.0048 (5)
C(123)	0.82009 (7)	0.9802 (1)	0.73563 (8)	0.0163 (6)	0.0119 (6)	0.0156 (6)	0.0006 (5)	0.0025 (5)	0.0038 (5)
C(124)	0.87000 (7)	0.9381 (1)	0.69447 (8)	0.0127 (6)	0.0129 (5)	0.0127 (5)	−0.0003 (5)	0.0005 (5)	0.0008 (5)
C(125)	0.90616 (7)	0.8184 (1)	0.71273 (8)	0.0131 (6)	0.0143 (6)	0.0105 (5)	−0.0013 (5)	0.0009 (4)	0.0029 (5)
C(126)	0.88129 (7)	0.7427 (1)	0.77330 (7)	0.0106 (5)	0.0128 (5)	0.0097 (5)	0.0020 (5)	0.0022 (4)	0.0023 (5)
C(131)	0.78052 (6)	0.5301 (1)	0.86228 (7)	0.0071 (5)	0.0091 (5)	0.0090 (5)	0.0015 (4)	−0.0010 (4)	−0.0006 (4)
C(132)	0.78914 (6)	0.4202 (1)	0.91233 (7)	0.0105 (5)	0.0067 (5)	0.0114 (5)	−0.0018 (4)	−0.0002 (4)	0.0004 (4)
C(133)	0.76706 (7)	0.2965 (1)	0.88847 (8)	0.0121 (6)	0.0114 (5)	0.0153 (6)	−0.0024 (5)	0.0004 (5)	−0.0005 (5)
C(134)	0.73648 (7)	0.2822 (1)	0.81637 (8)	0.0122 (6)	0.0137 (5)	0.0157 (6)	−0.0034 (5)	−0.0005 (4)	−0.0022 (5)
C(135)	0.72792 (7)	0.3910 (1)	0.76816 (8)	0.0121 (5)	0.0163 (6)	0.0153 (6)	−0.0017 (5)	−0.0023 (5)	−0.0032 (5)
C(136)	0.74951 (7)	0.5147 (1)	0.79180 (7)	0.0106 (5)	0.0160 (5)	0.0100 (5)	−0.0005 (5)	−0.0012 (4)	−0.0013 (4)
C(221)	1.02869 (6)	0.6102 (1)	1.06986 (7)	0.0085 (5)	0.0080 (5)	0.0119 (5)	−0.0003 (4)	−0.0015 (4)	0.0016 (4)
C(222)	1.00760 (7)	0.5661 (1)	1.14306 (8)	0.0101 (5)	0.0162 (6)	0.0142 (6)	0.0005 (5)	0.0016 (4)	0.0060 (5)
C(223)	1.04582 (7)	0.5938 (1)	1.20861 (8)	0.0130 (6)	0.0182 (6)	0.0164 (6)	0.0034 (5)	−0.0002 (5)	0.0046 (5)
C(224)	1.10530 (7)	0.6654 (1)	1.20228 (8)	0.0118 (6)	0.0183 (6)	0.0104 (5)	0.0034 (5)	−0.0023 (5)	−0.0015 (5)
C(225)	1.12613 (7)	0.7105 (1)	1.13002 (7)	0.0102 (5)	0.0135 (5)	0.0090 (5)	0.0008 (5)	0.0002 (4)	−0.0017 (4)
C(226)	1.08811 (6)	0.6825 (1)	1.06408 (8)	0.0079 (5)	0.0095 (5)	0.0114 (5)	−0.0005 (4)	0.0009 (4)	0.0017 (4)
C(231)	1.02836 (6)	0.6029 (1)	0.90333 (7)	0.0074 (5)	0.0086 (5)	0.0131 (5)	0.0028 (4)	−0.0018 (4)	−0.0020 (4)
C(232)	1.06794 (7)	0.5012 (1)	0.87250 (8)	0.0110 (5)	0.0122 (5)	0.0190 (6)	0.0042 (5)	−0.0001 (5)	−0.0046 (5)
C(233)	1.10574 (7)	0.5193 (1)	0.80731 (8)	0.0119 (6)	0.0149 (6)	0.0181 (6)	0.0044 (5)	0.0009 (5)	−0.0036 (5)
C(234)	1.10570 (7)	0.6406 (1)	0.76968 (8)	0.0127 (6)	0.0179 (6)	0.0142 (6)	0.0014 (5)	−0.0028 (5)	−0.0029 (5)
C(235)	1.06736 (7)	0.7434 (1)	0.79902 (8)	0.0144 (6)	0.0157 (6)	0.0123 (5)	0.0024 (5)	0.0009 (5)	−0.0030 (5)
C(236)	1.02802 (7)	0.7245 (1)	0.86517 (7)	0.0130 (5)	0.0106 (5)	0.0113 (5)	0.0016 (5)	−0.0003 (4)	−0.0005 (4)
C(321)	0.83931 (6)	1.0266 (1)	1.06238 (7)	0.0106 (5)	0.0059 (5)	0.0093 (5)	0.0010 (4)	0.0020 (4)	0.0005 (4)
C(322)	0.85499 (7)	1.1591 (1)	1.07582 (7)	0.0146 (6)	0.0059 (5)	0.0133 (6)	0.0013 (4)	−0.0009 (4)	−0.0010 (4)
C(323)	0.80472 (7)	1.2498 (1)	1.09140 (8)	0.0160 (6)	0.0073 (5)	0.0130 (5)	0.0011 (5)	0.0004 (5)	−0.0006 (4)
C(324)	0.73786 (7)	1.2098 (1)	1.09429 (8)	0.0165 (6)	0.0112 (5)	0.0138 (5)	0.0027 (5)	0.0032 (5)	−0.0021 (5)
C(325)	0.72172 (7)	1.0777 (1)	1.08200 (8)	0.0169 (6)	0.0100 (5)	0.0166 (6)	0.0030 (5)	0.0045 (5)	−0.0027 (5)
C(326)	0.77251 (7)	0.9865 (1)	1.06609 (8)	0.0130 (5)	0.0091 (5)	0.0167 (5)	−0.0006 (5)	0.0061 (5)	−0.0029 (5)
C(331)	0.96187 (6)	0.9974 (1)	0.98022 (7)	0.0104 (5)	0.0064 (4)	0.0114 (5)	−0.0005 (4)	0.0006 (4)	0.0005 (4)
C(332)	1.03043 (6)	1.0110 (1)	0.99607 (7)	0.0109 (5)	0.0124 (5)	0.0108 (5)	−0.0027 (4)	−0.0005 (4)	0.0013 (5)
C(333)	1.07360 (7)	1.0694 (1)	0.94222 (7)	0.0117 (5)	0.0145 (6)	0.0108 (5)	−0.0027 (5)	0.0030 (4)	0.0008 (5)
C(334)	1.04863 (7)	1.1155 (1)	0.87193 (8)	0.0141 (5)	0.0118 (5)	0.0137 (5)	−0.0017 (5)	0.0002 (5)	0.0005 (5)
C(335)	0.98053 (7)	1.1028 (1)	0.85565 (8)	0.0112 (5)	0.0120 (5)	0.0119 (5)	−0.0018 (5)	0.0016 (4)	0.0017 (4)
C(336)	0.93744 (7)	1.0438 (1)	0.90911 (7)	0.0129 (6)	0.0119 (5)	0.0086 (5)	−0.0002 (5)	0.0002 (4)	0.0025 (4)
H(122)	0.7519 (2)	0.9383 (3)	0.8290 (2)	0.030 (2)	0.030 (2)	0.043 (2)	0.014 (1)	0.019 (1)	0.007 (1)
H(123)	0.7948 (2)	1.0696 (4)	0.7196 (2)	0.040 (2)	0.030 (2)	0.040 (2)	0.010 (1)	0.014 (2)	0.012 (1)
H(124)	0.8949 (2)	0.9977 (3)	0.6478 (2)	0.033 (2)	0.029 (2)	0.031 (2)	−0.002 (1)	0.009 (1)	0.013 (1)
H(125)	0.9490 (2)	0.7826 (4)	0.6799 (2)	0.029 (2)	0.037 (2)	0.032 (1)	0.009 (1)	0.015 (1)	0.008 (1)
H(126)	0.9050 (2)	0.6498 (3)	0.7881 (2)	0.030 (2)	0.028 (1)	0.034 (2)	0.011 (1)	0.008 (1)	0.008 (1)
H(132)	0.8117 (2)	0.4324 (3)	0.9688 (2)	0.036 (2)	0.021 (1)	0.029 (1)	−0.003 (1)	−0.012 (1)	0.003 (1)
H(133)	0.7741 (2)	0.2123 (3)	0.9261 (2)	0.047 (2)	0.019 (1)	0.032 (1)	−0.006 (1)	−0.010 (1)	0.002 (1)
H(134)	0.7198 (2)	0.1854 (3)	0.7966 (2)	0.039 (2)	0.025 (1)	0.037 (2)	−0.007 (1)	−0.004 (1)	−0.010 (1)
H(135)	0.7054 (2)	0.3777 (4)	0.7114 (2)	0.032 (2)	0.041 (2)	0.028 (2)	−0.005 (1)	−0.010 (1)	−0.004 (1)
H(136)	0.7428 (2)	0.5983 (4)	0.7543 (2)	0.039 (2)	0.030 (2)	0.027 (1)	−0.001 (1)	−0.005 (1)	0.004 (1)
H(222)	0.9605 (2)	0.5131 (4)	1.1489 (2)	0.027 (2)	0.040 (2)	0.033 (2)	−0.009 (1)	0.003 (1)	0.007 (1)
H(223)	1.0287 (2)	0.5583 (4)	1.2634 (2)	0.030 (2)	0.054 (2)	0.023 (1)	−0.002 (2)	−0.003 (1)	0.010 (1)
H(224)	1.1350 (2)	0.6862 (4)	1.2533 (2)	0.031 (2)	0.044 (2)	0.021 (1)	0.001 (1)	−0.008 (1)	0.001 (1)
H(225)	1.1728 (2)	0.7655 (3)	1.1245 (2)	0.022 (1)	0.033 (2)	0.028 (1)	−0.007 (1)	−0.000 (1)	−0.001 (1)
H(226)	1.1046 (2)	0.7167 (3)	1.0077 (2)	0.026 (1)	0.034 (2)	0.018 (1)	−0.007 (1)	0.005 (1)	0.003 (1)
H(232)	1.0685 (2)	0.4056 (3)	0.9031 (2)	0.037 (2)	0.023 (1)	0.041 (2)	0.013 (1)	0.005 (1)	0.004 (1)
H(233)	1.1346 (2)	0.4390 (4)	0.7822 (2)	0.039 (2)	0.029 (2)	0.048 (2)	0.011 (1)	0.012 (2)	0.000 (2)
H(234)	1.1359 (2)	0.6533 (4)	0.7179 (2)	0.030 (2)	0.043 (2)	0.030 (2)	0.009 (1)	0.009 (1)	0.001 (1)
H(235)	1.0670 (2)	0.8386 (3)	0.7706 (2)	0.037 (2)	0.027 (1)	0.029 (1)	0.010 (1)	0.011 (1)	0.003 (1)
H(236)	0.9970 (2)	0.8037 (3)	0.8862 (2)	0.034 (2)	0.022 (1)	0.028 (1)	0.008 (1)	0.008 (1)	−0.000 (1)
H(322)	0.9069 (2)	1.1902 (3)	1.0730 (2)	0.029 (2)	0.020 (1)	0.041 (2)	−0.004 (1)	−0.002 (1)	−0.004 (1)
H(323)	0.8164 (2)	1.3528 (3)	1.1009 (2)	0.034 (2)	0.010 (1)	0.043 (2)	0.002 (1)	0.004 (1)	−0.006 (1)
H(324)	0.6989 (2)	1.2809 (3)	1.1070 (2)	0.033 (2)	0.026 (2)	0.039 (2)	0.008 (1)	0.002 (1)	−0.002 (1)
H(325)	0.6708 (2)	1.0457 (4)	1.0858 (3)	0.031 (2)	0.030 (2)	0.054 (2)	−0.001 (1)	0.012 (2)	−0.015 (2)
H(326)	0.7603 (2)	0.8839 (3)	1.0580 (2)	0.032 (2)	0.016 (1)	0.045 (2)	−0.007 (1)	0.007 (1)	−0.007 (1)
H(332)	1.0506 (2)	0.9746 (3)	1.0500 (2)	0.024 (1)	0.037 (2)	0.025 (1)	−0.002 (1)	−0.009 (1)	0.006 (1)
H(333)	1.1262 (2)	1.0775 (4)	0.9552 (2)	0.026 (1)	0.043 (2)	0.033 (2)	−0.006 (1)	−0.001 (1)	0.007 (1)
H(334)	1.0813 (2)	1.1600 (4)	0 8306 (2)	0.033 (2)	0.036 (2)	0.030 (2)	−0.003 (1)	0.003 (1)	0.003 (1)
H(335)	0.9602 (2)	1.1369 (4)	0.8002 (2)	0.027 (1)	0.037 (2)	0.028 (1)	−0.003 (1)	−0.001 (1)	0.013 (1)
H(336)	0.8850 (2)	1.0320 (4)	0.8945 (2)	0.025 (1)	0.038 (2)	0.023 (1)	−0.006 (1)	−0.004 (1)	0.007 (1)
H(11)	0.7197 (2)	0.8532 (3)	0.9427 (2)	0.027 (2)	0.027 (1)	0.044 (2)	0.008 (1)	0.004 (1)	−0.009 (1)
H(12)	0.6838 (2)	0.7352 (4)	0.8793 (2)	0.023 (1)	0.048 (2)	0.031 (1)	0.007 (1)	−0.007 (1)	−0.003 (2)

Table II (*Continued*)

	fractional atomic coordinates[a]			thermal parameters[b]					
atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(13)	0.7036 (2)	0.6935 (4)	0.9769 (2)	0.031 (2)	0.038 (2)	0.038 (2)	0.003 (1)	0.015 (1)	0.016 (2)
H(21)	1.0051 (2)	0.3503 (3)	1.0028 (3)	0.027 (2)	0.023 (1)	0.063 (2)	0.005 (1)	−0.004 (2)	0.003 (2)
H(22)	0.9255 (2)	0.3895 (4)	1.0396 (3)	0.033 (2)	0.029 (2)	0.060 (2)	−0.003 (1)	0.016 (2)	0.010 (2)
H(23)	0.9353 (2)	0.3722 (4)	0.9390 (3)	0.041 (2)	0.027 (2)	0.057 (2)	−0.004 (1)	−0.013 (2)	−0.014 (2)
H(31)	0.9131 (2)	0.8596 (4)	1.1786 (2)	0.030 (2)	0.044 (2)	0.023 (1)	−0.006 (1)	0.008 (1)	0.013 (1)
H(32)	0.9928 (2)	0.8429 (4)	1.1342 (2)	0.028 (2)	0.035 (2)	0.034 (2)	0.014 (1)	−0.008 (1)	−0.001 (1)
H(33)	0.9610 (2)	1.0020 (3)	1.1562 (2)	0.040 (2)	0.026 (1)	0.031 (1)	0.007 (1)	−0.008 (1)	−0.003 (1)
B	0.8120 (1)	0.6143 (1)	1.1121 (2)	0.025 (1)	0.0070 (7)	0.0084 (7)	0.0086 (6)	0.0056 (6)	0.0027 (4)
H(1)	0.8562 (2)	0.5939 (5)	1.0694 (3)	0.040 (2)	0.054 (2)	0.055 (2)	0.001 (2)	0.014 (2)	0.017 (2)
H(2)	0.7988 (4)	0.7249 (5)	1.1273 (4)	0.094 (5)	0.035 (2)	0.093 (4)	0.014 (3)	0.019 (4)	−0.008 (3)
H(3)	0.7563 (2)	0.5675 (7)	1.0802 (3)	0.039 (2)	0.084 (4)	0.066 (3)	−0.007 (2)	−0.009 (2)	−0.008 (3)
H(4)	0.8196 (3)	0.5486 (6)	1.1678 (3)	0.055 (3)	0.075 (3)	0.049 (2)	0.008 (3)	−0.003 (2)	0.025 (2)

[a] The atomic coordinates for the "disordered boron" refinement (see Figure 1 and Experimental Section) are as follows: B [0.8029 (1), 0.6107 (3), 1.1110 (2)]; B' [0.8201 (1), 0.6177 (3), 1.1140 (2)]; H(1) [0.8560 (2), 0.5939 (5), 1.0693 (3)]; H(2) [0.7897 (4), 0.7252 (5), 1.1274 (4)]; H(3) [0.7562 (2), 0.5674 (6), 1.0802 (3)]; H(4) [0.8195 (3), 0.5483 (6), 1.1679 (3)]. [b] Thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Table III. Selected Bond Distances (Å) in $Cu(PPh_2Me)_3(BH_4)$

	neutron	X-ray crystal 1	X-ray crystal 2	X-ray ref 8
		B-H		
B-H(1)	1.170 (5)	1.03 (8)		1.19
B-H(2)	1.185 (5)	0.86 (9)		1.02
B-H(3)	1.330 (6)	0.93 (8)		1.14
B-H(4)	1.182 (6)	0.85 (9)		0.97
		Cu-H		
Cu-H(1)	1.697 (5)	1.83 (8)		1.47
Cu···H(2)	2.722 (7)	2.56 (8)		3.12
		B-Cu		
B-Cu	2.518 (3)	2.578 (10)	2.498 (5)	2.650 (5)
		Cu-P		
Cu-P(1)	2.282 (2)	2.304 (2)	2.285 (2)	2.276 (1)
Cu-P(2)	2.283 (2)	2.297 (2)	2.304 (2)	2.293 (1)
Cu-P(3)	2.260 (2)	2.276 (2)	2.297 (2)	2.289 (1)
		P-C(Me)		
P(1)-C(11)	1.823 (2)	1.819 (9)	1.830 (9)	1.821 (4)
P(2)-C(21)	1.826 (2)	1.821 (8)	1.807 (8)	1.827 (4)
P(3)-C(31)	1.826 (2)	1.809 (9)	1.837 (8)	1.829 (4)
		P-C(Ph)		
P(1)-C(121)	1.815 (2)	1.824 (8)	1.822 (8)	1.809 (4)
P(1)-C(131)	1.818 (2)	1.824 (8)	1.832 (8)	1.828 (4)
P(2)-C(221)	1.823 (2)	1.829 (8)	1.839 (8)	1.823 (4)
P(2)-C(231)	1.819 (2)	1.829 (8)	1.831 (8)	1.827 (4)
P(3)-C(321)	1.830 (2)	1.822 (8)	1.854 (7)	1.832 (4)
P(3)-C(331)	1.827 (2)	1.826 (8)	1.825 (8)	1.825 (4)
		Average Values		
C-H (methyl)	1.088 (3)			
C-H (phenyl)	1.084 (1)			
C-C (phenyl)	1.398 (2)	1.373 (14)	1.384 (9)	1.379 (6)

The real part of the B scattering length [0.627 (6) × 10^{-12} cm] is larger by about 15σ than the literature value (0.535 × 10^{-12} cm)[18] for natural boron. This discrepancy is unexpected, since the published cross sections are believed to be quite accurate. However, it should be pointed out that, in another neutron diffraction analysis of a borohydride complex in which B scattering lengths were allowed to vary,[19] the "real part" refined to values of 0.49 (3) and 0.61 (4) for the two independent B atoms in that structure. In the present structure determination the neutron scattering lengths of P and Cu were also varied, but the refined values agree with literature values[18] within their standard deviations. Neutron scattering lengths used are $b_{Cu} = 0.769$, $b_P = 0.513$, $b_C = 0.665$, and $b_H = -0.374 \times 10^{-12}$ cm.[18] The final R indices are summarized in Table IB, while positional and thermal parameters for all atoms are listed in Table II. Distances and angles in the molecule are given in Tables III and IV, respectively. Listings of observed and calculated structure factors are available (see paragraph at the end of the paper for details).

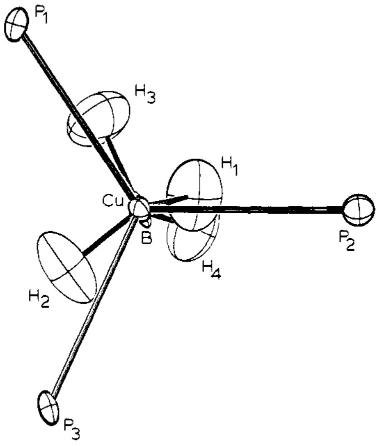

Figure 4. A plot of the P_3CuBH_4 core of the molecule viewed down the Cu-B axis, showing the approximate eclipsing of the H and P atoms. Ellipsoids are drawn as in Figure 2.

Description of the Structure

Since neutron diffraction provides the most definitive view of the Cu/BH_4 binding region, the following discussion will be largely centered on the neutron-derived results. Figure 2 shows a plot of the entire molecule, and Figures 3 and 4 show two views of the P_3CuBH_4 core. Figure 4 illustrates the approximate eclipsing of the P and H atoms around the central Cu-H-B unit. The coordination about both the Cu and B atoms is distorted tetrahedral: the P_3CuH (bridging) and $CuBH_3$ (terminal) fragments are appreciably distorted from tetrahedral symmetry, while the P_3CuB and BH_4 units are much more regular (Table IV).

Cu-H-B Core. Probably the most important result in the present structure analysis is the fact that the central Cu-H-B core is found to be distinctly bent [Cu-H-B = 121.7 (4)°], with accompanying Cu-H, B-H, and Cu-B distances of 1.697 (5), 1.170 (5), and 2.518 (3) Å, respectively. This result is in marked contrast to the nearly linear Cu-H-B bridge (170°) and the much shorter Cu-H bond length (1.47 Å) found in the earlier X-ray analysis.[8] This difference can be partly rationalized by the well-known fact that H atom positions derived from X-ray diffraction data are often biased by the effects of bonding electron density: in this case, the H atom is apparently "drawn into" the Cu-B bonding region and "toward" the Cu atom. More will be said about the bonding in the Cu-H-B core later.

B-H Distances. One puzzling feature in this structure determination is the unusual distribution of B-H distances, one of which [B-H(3) = 1.330 (6) Å] is distinctly longer than the other three

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(18) Koester, L. In "Neutron Physics", by Koester, L.; Steyerl, A.; Springer-Verlag: Berlin, Heidelberg, New York, 1977; p 36.

(19) Bernstein, E. R.; Hamilton, W. C.; Keiderling, T. A.; La Placa, S. J.; Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 3009.

Table IV. Selected Angles (Deg) in $Cu(PPh_2Me)_3(BH_4)$

(A) Bond Angles

	neutron	X-ray crystal 1	X-ray crystal 2	X-ray ref 8
		H-B-H		
H(1)-B-H(2)	118.4 (5)	96 (7)		110
H(1)-B-H(3)	107.7 (4)	118 (7)		108
H(1)-B-H(4)	108.4 (4)	106 (7)		110
H(2)-B-H(3)	104.2 (5)	110 (8)		136
H(2)-B-H(4)	112.7 (5)	118 (8)		104
H(3)-B-H(4)	104.1 (4)	109 (8)		82
		Cu-B-H		
Cu-B-H(1)	35.0 (3)	35 (4)		5
Cu-B-H(2)	86.8 (4)	79 (6)		108
Cu-B-H(3)	104.5 (3)	95 (5)		108
Cu-B-H(4)	139.7 (3)	141 (6)		116
		B-H-Cu		
B-H(1)-Cu	121.7 (4)	126 (6)		170
B-H(2)···Cu	67.4 (3)	81 (6)		54
		B-Cu-H		
B-Cu-H(1)	23.3 (2)	19 (2)		4
B-Cu···H(2)	25.8 (1)	19 (2)		18
		B-Cu-P		
B-Cu-P(1)	101.72 (7)	102.2 (2)	103.2 (1)	101.7 (2)
B-Cu-P(2)	108.82 (7)	107.3 (2)	105.1 (1)	107.0 (1)
B-Cu-P(3)	101.43 (6)	102.5 (2)	101.8 (1)	101.0 (1)
		H-Cu-H		
H(1)-Cu···H(2)	47.9 (2)	32 (3)		
		H-Cu-P		
H(1)-Cu-P(1)	108.5 (2)	109 (2)		105
H(1)-Cu-P(2)	86.2 (2)	89 (2)		102
H(1)-Cu-P(3)	115.3 (2)	112 (3)		103
H(2)···Cu-P(1)	102.6 (2)	113 (2)		111
H(2)···Cu-P(2)	127.7 (1)	113 (2)		114
H(2)···Cu-P(3)	78.3 (1)	83 (2)		83
		P-Cu-P		
P(1)-Cu-P(2)	117.03 (6)	116.68 (8)	117.6 (1)	118.0 (1)
P(1)-Cu-P(3)	117.21 (7)	117.25 (8)	118.0 (1)	117.8 (1)
P(2)-Cu-P(3)	108.85 (7)	109.17 (7)	108.8 (1)	108.9 (1)
		Average Values[a]		
Cu-P-C	115.1 (1)	115.6 (3)	115.6 (2)	115.4 (1)
C-P-C	102.9 (6)	102.6 (4)	102.7 (3)	102.9 (2)
P-C-H (methyl)	109.7 (8)		116 (3)	
H-C-H (methyl)	109.2 (4)		102 (5)	
P-C-C (phenyl)	120.4 (5)	121.1 (5)	120.7 (5)	120.8 (3)
C-C-C (phenyl)	120.0 (1)	120.2 (9)	120.0 (7)	120.0 (4)
C-C-H (phenyl)	119.9 (1)		119 (3)	

(B) Torsion Angles (Neutron Results)

P(1)-Cu-B-H(2)	−94.7	P(1)-Cu-H(1)-B	−76.4
P(1)-Cu-B-H(3)	9.2	P(2)-Cu-H(1)-B	166.4
P(1)-Cu-B-H(4)	143.2	P(3)-Cu-H(1)-B	57.3
P(2)-Cu-B-H(2)	141.2	Cu-H(1)-B-H(2)	−27.9
P(2)-Cu-B-H(3)	−114.9	Cu-H(1)-B-H(3)	90.0
P(2)-Cu-B-H(4)	19.1	Cu-H(1)-B-H(4)	−157.9
P(3)-Cu-B-H(2)	26.6		
P(3)-Cu-B-H(3)	130.4		
P(3)-Cu-B-H(4)	−95.6		

[a] The standard deviations of the average values were estimated by using the equation $\sigma = [\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$, where n is the number of observations.

[1.170 (5), 1.185 (5), 1.182 (6) Å]. Surprisingly, however, the long distance is not that associated with the Cu–H–B bridge. The situation is thus in contradiction with what is normally expected: namely, that bridging B–H distances [e.g., 1.339 (6) Å in B_2H_6[20]] are longer than terminal B–H distances [e.g., 1.196 (8) Å in B_2H_6]. We have, at present, no satisfactory explanation for the anomalous B–H(1) and B–H(3) distances in $Cu(PPh_2Me)_3(BH_4)$,[21] except to remark that the B thermal ellipsoid is elongated in the B–H(3) direction (Figure 3), possibly implying some disorder of the borohydride group (vide supra).

Cu–H Distance. The observed Cu–H (bridging) distance of 1.697 (5) Å found here represents the first Cu–H bond analyzed by single-crystal neutron diffraction techniques. It is (somewhat surprisingly) shorter than the average of 1.87 Å derived from the X-ray analyses of other copper borohydride complexes: 1.84 (5) Å in $Cu(PPh_3)_2(B_3H_8)$,[22] 1.86 (10) Å in $[Cu(PPh_3)_2(BH_3CN)]_2$,[23] 1.97 (6) Å in $[Cu(PPh_3)_2]_2(B_{10}H_{10})$,[24] and 1.82 (3) Å in $Cu(PPh_3)_2(BH_4)$.[25] It is also somewhat shorter than estimates of 1.78–1.80 Å derived from covalent radii arguments.[26] Finally, for purposes of comparison, a Cu–H distance of 1.73 Å has been reported for copper hydride (result derived from neutron diffraction data from a powdered sample),[27a] and for diatomic CuH a distance of 1.463 Å has been measured in the gas phase.[27b]

Proximity of H(2) to Cu. One other very interesting feature found in the structure of $Cu(PPh_2Me)_3(BH_4)$ is the position of H(2). This atom is definitely out of bonding range of Cu, and yet it is close enough to warrant special attention [Cu···H(2) = 2.722 (7) Å]. The title compound is known to dissociate in solution to yield PPh_2Me and $Cu(PPh_2Me)_2(BH_4)$,[7,8] which contains a bidentate BH_4 group. Thus, one can imagine H(2) to be poised for coordination to the Cu atom, ready to bond to it when one of the phosphine ligands dissociates. The Cu···H(2) interaction can therefore be described as an incipient Cu–H bonding interaction. In addition, the particular orientation of the BH_4 group found in the present complex can be considered a model for the suspected unidentate intermediate in the BH_4 scrambling process $[M(\mu\text{-}H)_2BH_2 \rightleftharpoons M(\mu\text{-}H)BH_3 \rightleftharpoons M(\mu\text{-}H)_2BH_2]$, a process which is known to take place in solution for many metal borohydride complexes.[28]

Comparisons with other Metal Borohydride Complexes. It is difficult to accurately compare the M–H–B bonding region of this compound with those of other metal borohydride complexes, for the simple reason that very few of them have been analyzed by neutron diffraction. Boron compounds are usually poorly suited for neutron diffraction analysis because of the high absorption cross section of ^{10}B for thermal neutrons. The compounds that have been analyzed by this method are either isotopically enriched in ^{11}B (as in the analysis of $B_{10}H_{14}$)[29] or contain an acceptably low amount of boron. In $Hf(BH_4)_4$[30] and $U(BH_4)_4$[19] the mole fractions of B are 0.182 and 0.145, respectively, while in the present case $[Cu(PPh_2Me)_3(BH_4)]$ the mole fraction of B is exceptionally low (0.016). Table V summarizes the structural parameters of boron-containing molecules for which accurate measurements of bridging H positions are available. From these limited results one can discern a few general trends: (a) with the exceptions of $U(BH_4)_4$ and the present compound, B–H (terminal) distances are significantly shorter than B–H (bridging) distances, as discussed earlier, (b) M–H–B angles are all distinctly bent and become smaller along the series unidentate > bidentate > tridentate BH_4 ligands, and (c) M–B distances also decrease in the above sequence when differences in covalent radii of the metal atoms are taken into account. The latter conclusion has been

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(20) Bartell, L. S.; Carroll, B. L. *J. Chem. Phys.* **1965**, *42*, 1135.

(21) Interestingly, in $U(BH_4)_4$ one also sees a wide scatter of values for B–H distances: the terminal B–H distance [1.24 (3) Å] is, in fact, no shorter than the average of bridging distances [range 1.09 (4)–1.34 (4) Å; average 1.24 Å] in that compound.[19] However, in all other compounds the usual trend is found (Table V).

(22) Lippard, S. J.; Melmed, K. M. *Inorg. Chem.* **1969**, *8*, 2755.

(23) Melmed, K. M.; Li, T. I.; Mayerle, J. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1974**, *96*, 69.

(24) Gill, J. T.; Lippard, S. J. *Inorg. Chem.* **1975**, *14*, 751.

(25) The Cu–H value for $Cu(BH_4)(PPh_3)_2$ was originally reported as 2.02 (5) Å [Lippard, S. J.; Melmed, K. M. *Inorg. Chem.* **1967**, *6*, 2223] but was later revised to 1.82 (3) Å [see ref 27 of Gill, J. T.; Lippard, S. J. *Inorg. Chem.* **1975**, *14*, 751].

(26) See Table V of ref 19.

(27) (a) Goedkoop, J. A.; Andersen, A. F. *Acta Crystallogr.* **1955**, *8*, 118. (b) Herzberg, G. "Spectra of Diatomic Molecules"; D. van Nostrand Co.: Princeton, NJ, 1950.

(28) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(29) Tippe, A.; Hamilton, W. C. *Inorg. Chem.* **1969**, *8*, 464.

(30) Marks, T. J.; Williams, J. M., private communication.

Table V. A Summary of Accurate Measurements of Bridging Hydrogen Positions in Various Boron-Containing Molecules

(A) Boron Hydrides

compd	method[a]	B-H(t), Å	B-H(b), Å	B-H-B, deg	B-B, Å	ref
B_2H_6	e	1.196 (8)	1.339 (6)	83.0 (3)	1.775 (3)	20
B_5H_9	m	1.186 (2)	1.352 (4)	83.6 (6)	1.803 (2)	33
$B_{10}H_{14}$[b]	n	1.180 (4)	1.298 (5)[c] 1.347 (7)[c]	84.3 (4)	1.775 (5)	29

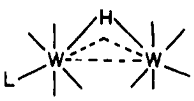
(B) Metal Borohydride Complexes

compd	method[a]	bond type[d]	B-H(t), Å	B-H(b), Å	M-H(b), Å	M-H-B, deg	M-B, Å	ref
$U(BH_4)_4$[e]	n	3	1.24 (3)	1.23 (3)	2.34 (2)	83 (1)	2.52 (1)	19
		2		1.25 (4)	2.41 (2)	98 (1)	2.86 (2)	
$Hf(BH_4)_4$	n	3	1.15 (2)	1.23 (1)	2.13 (1)	80.6 (6)	2.28 (1)	30
$Hf(C_5H_4Me)_2(BH_4)_2$	n	2	1.19 (1)	1.23 (1)	2.09 (1)	96.8 (5)	2.553 (6)	34
$Co(terpyridine)BH_4$	n	2	1.22 (1)	1.29 (1)	1.72 (2)	90.0 (8)	2.15 (1)	35
$Cu(PPh_2Me)_3(BH_4)$	n	1	1.23 (5)	1.170 (5)	1.697 (5)	121.7 (4)	2.518 (3)	this work

[a] e = electron diffraction; m = microwave spectroscopy; n = neutron diffraction. [b] Measurements were actually carried out on a sample of $^{11}B_{10}D_{14}$. [c] The bridging H atoms in $B_{10}H_{14}$ are asymmetric. [d] 1 = $M(\mu\text{-}H)BH_3$; 2 = $M(\mu\text{-}H)_2BH_2$; 3 = $M(\mu\text{-}H)_3BH$. [e] Uranium borohydride is polymeric in the solid state, i.e., $[U(BH_4)_4]_n$.

noticed before[8,19,28] and in fact is often taken as a diagnostic test to distinguish between bidentate and tridentate modes of BH_4 attachment.[31]

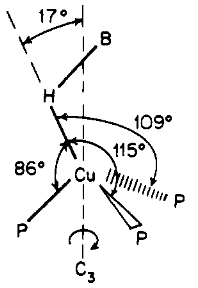
Implications on the Bonding in M-H-B Systems. As mentioned in the introduction, one of the reasons for choosing molecules with unsupported 3c, 2e⁻ bonds is to get some insight into the nature of overlap in such systems. In the case of $HW_2(CO)_9(NO)$, $[HW_2(CO)_{10}]^-$, and related compounds,[3] we showed that the M-H-M linkage is not only bend but is also off-axis, meaning that the bridging H atom is not strictly colinear with the ligand trans to it (I). This was taken as an indication that the nature of the M-H-M overlap is "closed" (II).[5]



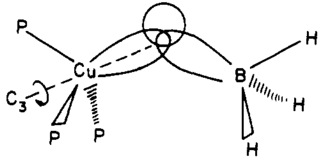
I

II

Now, in the case of $Cu(PPh_2Me)_3(BH_4)$ the essential point is seen when the angles around Cu are examined: the three P-Cu-P angles agree reasonably well with one another (109°, 117°, 117°), indicating that the CuP_3 fragment has approximate C_{3v} symmetry. However, the H-Cu-P angles (86°, 109°, 115°) show considerable deviation from threefold symmetry, indicating that the H atom is significantly displaced off the pseudothreefold axis defined by the CuP_3 group (III), and suggests that the overlap pattern in the Cu-H-B bond is also "closed"(IV).



III



IV

Comparison of Structural Parameters Obtained from Several Crystals. Variations in the Cu-B Distance. Structural parameters are now available from the analyses of five crystals of $Cu[P(C_6H_5)_2CH_3]BH_4$. The results of these analyses (two by neutrons, three by X-rays) are collected in Tables III and IV and ref 10. In the X-ray analysis of crystal 1 positions of all H atoms were determined, although the B-H distances appear short. Within limitations recognized for the location of H atoms by X-ray diffraction methods, the results point to a bent Cu-H-B bridge, 126°, in contrast to the earlier X-ray study[8] which suggested a linear arrangement. In general, bonding parameters involving nonhydrogen atoms agree well for all five structures. There is, however, one outstanding discrepancy. The Cu-B distances range from 2.498 (5) to 2.650 (5) Å. This large range is probably artifactual and may arise from disorder of the $(\mu\text{-}H)BH_3$ unit, preventing an entirely satisfactory refinement of this portion of the structure.[32]

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Supplementary Material Available: Listing of the final atomic parameters from the X-ray analyses and the observed and calculated structure factors from the neutron analysis (35 pages). Ordering information is given on any current masthead page.

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[31] (a) Edelstein, N. *Inorg. Chem.* **1981**, *20*, 297. (b) Rietz, R. R.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Ibid.* **1978**, *17*, 653. (c) Rietz, R. R.; Edelstein, N. M.; Ruben, H. W.; Templeton, D. H.; Zalkin, A. *Ibid.* **1978**, *17*, 658. (d) Zalkin, A.; Rietz, R. R.; Templeton, D. H.; Edelstein, N. M. *Ibid.* **1978**, *17*, 661.

[32] One reviewer suggests that an alternative way of viewing the bonding in this complex (other than the 3c, 2e⁻ M-H-B picture described in the text) would be to consider the Cu/BH_4 interaction as largely ionic in character and that perhaps electrostatic and packing effects are responsible for the curious BH_4^- ligation.

[33] Schwoch, D.; Burg, A.B.; Beaudet, R. A. *Inorg. Chem.* **1977**, *16*, 3219.

[34] Johnson, P. L.; Cohen, S. A.; Marks, T. J.; Williams, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2709.

[35] Corey, E. J.; Cooper, N. J.; Canning, W. M.; Lipscomb, W. N.; Koetzle, T. F. *Inorg. Chem.*, in press.

[36] Johnson, C. K. "ORTEP-II", Report ORNL-5138, Oak Ridge National Laboratory: Oak Ridge, TN, 1976.