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Structural Characterization of the Single Hydrogen Bridge Attachment of the Tetrahydroborate Group in Tris(methyldiphenylphosphine)(tetrahydroborato)copper

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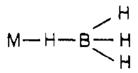
The crystal and molecular structure of $Cu[PPh_2Me]_3BH_4$ has been determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group $Pn2_1a$ with unit cell dimensions a = 20.292 (8) Å, b = 17.435 (7) Å, and c = 10.419 (5) Å, Z = 4. The copper atom resides in a quasi-tetrahedral environment consisting of the phosphorus atoms of the three PPh_2Me ligands and a single hydrogen atom of the tetrahydroborate group. This novel attachment of BH_4^- has a bridging Cu–H distance of 1.47 Å and a Cu–H–B angle of 170°. Upon dissolution of the compound in benzene, a phosphine dissociates and its coordination site is occupied by a second hydrogen atom from BH_4^-. This monodentate–bidentate conversion is readily discernible from a comparison of the solid-state and solution infrared spectra. The factors which influence the preferred coordination mode of the tetrahydroborate group in copper(I)–phosphine compounds are discussed.

Introduction

Covalent complexes containing the tetrahydroborate group, BH_4^-, have been reported for the majority of d and f transition metals.[2] Of the three possible modes of attachment, the double (II) and triple (III) hydrogen bridge structures have been characterized definitively by X-ray and neutron diffraction techniques.[2b] In contrast, evidence for the single hydrogen atom bridge (I) has been sparse and comprised entirely of spectroscopic observations. Holah and co-workers, for example, proposed that structure I obtains in $Co(PPh_3)_3BH_4$[3] and some five- and six-coordinate Ru(II) complexes[4] on the basis of electronic, infrared, and NMR data. More recently, Bommer and Morse presented infrared and NMR evidence in support of a singly bridged BH_4^- in $Cu[PPh_2Me]_3BH_4$.[5] Independent studies (vide infra) of this Cu(I) complex conducted by us resulted in a similar conclusion.[6]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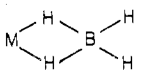
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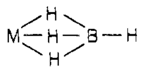
III

The novel structural features associated with the single-bridge attachment of BH_4^-, coupled with the considerable interest in the stereochemistry of tetracoordinate copper(I)–phosphine complexes,[7-10] prompted us to determine the detailed structure of $Cu[PPh_2Me]_3BH_4$ by single-crystal X-ray diffraction. Our results, which have been summarized in a preliminary communication,[6] are reported in full here.

Table I. Crystal Data

compd	$Cu[P(C_6H_5)_2CH_3]_3BH_4$
mol wt	679.0
linear abs coeff, cm^{-1}	7.71
calcd density,[a] g cm^{-3}	1.22
max crystal dimensions, mm	0.20 × 0.20 × 0.20
space group	$Pn2_1a$
molecules/unit cell	4
cell constants,[b] Å	
a	20.292 (8)
b	17.435 (7)
c	10.419 (5)
cell vol, $Å^3$	3686.2

[a] Experimental density was not determined. [b] Mo Kα radiation, λ 0.710 69 Å. Ambient temperature of 22 °C.

Experimental Section

A. Preparation and Characterization of $Cu[PPh_2Me]_3BH_4$. Cuprous chloride[11] and diphenylmethylphosphine[12] were obtained by literature methods. $Cu[PPh_2Me]_3BH_4$ was prepared by the general method of Lippard and Ucko,[13] using either a 2:1 or the recommended 4:1 mole ratio of phosphine to CuCl. Anal. Calcd: C, 68.98; H, 6.38; P, 13.68; Cu, 9.36; mol wt 679. Found: C, 68.70; H, 6.17; P, 13.84; Cu, 8.95; mol wt (0.011–0.016 M complex in benzene) 381; mp 123–123.5 °C (uncorrected). Analyses were performed by Galbraith

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Laboratories, Knoxville, Tenn. Infrared spectra were obtained with a Perkin-Elmer 621 grating spectrophotometer, while ^{31}P NMR spectra were run on a JEOL PFT-100 spectrometer.

B. Collection and Reduction of X-ray Data. Crystals suitable for X-ray analysis were grown from a chloroform–ethanol (1:2) solution at ~5 °C. One of approximately cubic slope was sealed in a thin-walled capillary and subjected to X-ray structural analysis. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was determined as *Pnma* or $Pn2_1a$ from systematic absences.

Data were taken on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.3° min^{-1}. Moving-crystal, moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B\tan\theta$$

where $A = 0.70°$ and $B = 0.35$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters have been described previously.[14] As a check on the stability of the instrument and the crystal, two reflections, (080) and (800), were measured after every 45 reflections; in no case was a variation of greater than ±2% noted.

The integrated intensity of a reflection, I, and its estimated standard deviation, $\sigma(I)$, were calculated with the equations

$$I = [C - 2(B_1 + B_2)]/S$$

$$\sigma(I) = [C + B_1 + B_2 + 0.03^2(C + B_1 + B_2)^2]^{1/2}$$

where C is the number of counts collected during the scan and B_1 and B_2 are the background counts. S is an integer which is proportional to the total scan time.

One independent octant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 3105 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 15 was obtained in the prescan. Based on these considerations, the data set of 3105 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[15] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors for Cu, P, and B were taken from Cromer and Waber,[16] and the scattering for Cu was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[17] Scattering factors for hydrogen were taken from ref 18.

The position of the copper atom was revealed by inspection of a Patterson map. A Fourier map phased on the copper atom in the centric space group *Pnma* produced five peaks which could reasonably be assigned to phosphorus atom positions. Since this result is chemically unreasonable, the acentric space group $Pn2_1a$ was chosen, and an electron density map afforded the coordinates of all three of the phosphorus atoms. All nonhydrogen atoms were found from a subsequent Fourier map. Isotropic least-squares refinement led to a discrepancy factor of $R_1 = \sum(|F_o| - |F_c|)/|F_o| = 0.14$. The hydrogen atoms of the phenyl rings were then placed at calculated positions of 0.98 Å from the bonded carbon atoms, and the methyl and tetrahydroborate hydrogen atoms were located on a three-dimensional difference Fourier map (at values of ~0.6 e/Å^3). Subsequent anisotropic refinement of all nonhydrogen atoms[19] led to final values of $R_1 = 0.025$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2\}^{1/2} = 0.025$. (For the inverse absolute configuration the values were $R_1 = 0.026$ and $R_2 = 0.027$.) The largest parameter shifts in the final cycle of refinement were less than 0.02 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.2 e/Å^3. The standard deviation for an observation of unit weight was 0.53. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Table II.

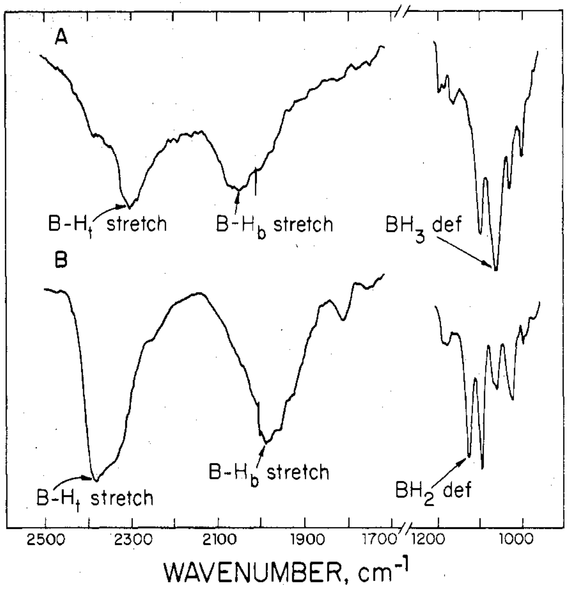


Figure 1. Infrared spectra of $Cu[PPh_2Me]_3BH_4$ in (A) a KBr disk and (B) a benzene solution (~0.05 M). The spike observed at 2000 cm^{-1} is an instrumental artifact.

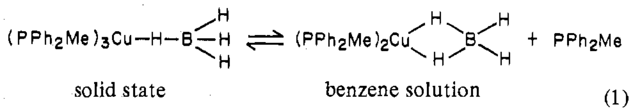
Results and Discussion

A. Physical Studies of $Cu[PPh_2Me]_3BH_4$. Several observations may be cited as evidence that the white solid which analyzes as $Cu[PPh_2Me]_3BH_4$ is, in fact, a pure compound rather than a mixture. Thus, (1) samples with essentially identical composition result from preparations with different initial copper/phosphine ratios, (2) the melting point is sharp,[20] and (3) repeated recrystallization or washing does not alter the composition.

Infrared spectroscopy has proven to be a valuable technique for delineating the mode of BH_4^- coordination.[21] The solid-state spectrum (reproduced in Figure 1A) is consistent with the single hydrogen bridge attachment (I) in that the bands assigned as B–H (terminal) stretching, B–H (bridge) stretching, and BH_3 deformation fall within the frequency regions suggested by Marks[2b] for this structure. Upon dissolution in benzene, however, the spectrum (Figure 1B) changes discernibly and may now be interpreted in terms of bidentate coordination by BH_4^-. Specifically, the bands in the B–H stretching region shift, a band assigned to BH_2 deformation appears, and the BH_3 deformation band experiences a drastic reduction in intensity. The latter two features are especially diagnostic of a fundamental change in BH_4^- coordination.

The low molecular weight measured in benzene indicates that $Cu[PPh_2Me]_3BH_4$ undergoes extensive dissociation in this solvent. Evidence for phosphine lability is provided by ^{31}P NMR studies. Thus a 0.1 M solution of PPh_2Me exhibits a peak at 27.7 ppm (all chemial shifts relative to external H_3PO_4), while a 0.05 M solution of $Cu[PPh_2Me]_3BH_4$ shows a single peak at 22.1 ppm. As a consequence of rapid exchange, a solution mixture of 0.1 M ligand and 0.05 M complex exhibits a single resonance at an intermediate value of 24.1 ppm.

The behavior of $Cu[PPh_2Me]_3BH_4$ noted above can be interpreted in terms of the equilibrium shown in eq 1. In the



$$(PPh_2Me)_3Cu{-}H{-}BH_3 \rightleftharpoons (PPh_2Me)_2Cu(\mu{-}H)_2BH_2 + PPh_2Me \quad (1)$$

solid state the copper atom is bound to the P atoms of three

Table II. Final Fractional Coordinates and Anisotropic Thermal Parameters[a] for $Cu[P(C_6H_5)_2CH_3]_3BH_4$

atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.3807 (1)	0.2475	0.2941 (1)	0.0018 (1)	0.0028 (1)	0.0072 (1)	0.0001 (1)	−0.0001 (1)	−0.0003 (1)
B	0.3129 (3)	0.1290 (3)	0.3821 (4)	0.0037 (2)	0.0031 (2)	0.0080 (4)	−0.0010 (1)	−0.0005 (2)	0.0010 (2)
P(1)	0.4741 (1)	0.2570 (1)	0.4170 (1)	0.0016 (1)	0.0037 (1)	0.0071 (1)	−0.0002 (1)	−0.0001 (1)	−0.0004 (1)
P(2)	0.3050 (1)	0.3436 (1)	0.3075 (1)	0.0018 (1)	0.0026 (1)	0.0091 (1)	0.0003 (1)	−0.0003 (1)	−0.0004 (1)
P(3)	0.4091 (1)	0.2045 (1)	0.0941 (1)	0.0025 (1)	0.0027 (1)	0.0066 (1)	0.0002 (1)	0.0001 (1)	−0.0005 (1)
C(1)	0.4596 (2)	0.2496 (4)	0.5896 (3)	0.0029 (1)	0.0078 (2)	0.0081 (4)	−0.0005 (2)	0.0000 (2)	−0.0002 (4)
C(2)	0.5277 (2)	0.3403 (2)	0.4003 (4)	0.0018 (1)	0.0033 (1)	0.0103 (4)	−0.0000 (1)	0.0001 (2)	−0.0017 (2)
C(3)	0.5681 (2)	0.3668 (3)	0.4982 (5)	0.0030 (1)	0.0054 (2)	0.0137 (6)	−0.0005 (1)	−0.0007 (2)	−0.0023 (3)
C(4)	0.6058 (2)	0.4322 (3)	0.4801 (6)	0.0031 (1)	0.0053 (2)	0.0231 (9)	−0.0009 (2)	−0.0012 (3)	−0.0046 (4)
C(5)	0.6052 (2)	0.4704 (3)	0.3679 (7)	0.0025 (1)	0.0034 (2)	0.0299 (11)	−0.0002 (1)	0.0002 (3)	−0.0032 (4)
C(6)	0.5668 (2)	0.4444 (3)	0.2692 (6)	0.0034 (1)	0.0037 (2)	0.0208 (8)	−0.0004 (1)	0.0009 (3)	0.0007 (3)
C(7)	0.5275 (2)	0.3797 (2)	0.2874 (4)	0.0027 (1)	0.0035 (2)	0.0143 (6)	−0.0003 (1)	−0.0002 (2)	−0.0004 (3)
C(8)	0.5283 (2)	0.1751 (2)	0.3894 (4)	0.0017 (1)	0.0036 (1)	0.0082 (4)	−0.0002 (1)	−0.0006 (2)	0.0007 (2)
C(9)	0.5077 (2)	0.1021 (3)	0.4282 (4)	0.0026 (1)	0.0043 (2)	0.0145 (6)	0.0002 (1)	−0.0002 (2)	0.0019 (3)
C(10)	0.5448 (3)	0.0384 (3)	0.4017 (5)	0.0038 (2)	0.0038 (2)	0.0190 (7)	0.0004 (1)	−0.0013 (3)	0.0026 (3)
C(11)	0.6031 (2)	0.0449 (3)	0.3357 (5)	0.0031 (2)	0.0044 (2)	0.0190 (7)	0.0011 (1)	−0.0018 (2)	−0.0011 (3)
C(12)	0.6243 (2)	0.1162 (3)	0.2955 (5)	0.0020 (1)	0.0053 (2)	0.0172 (6)	0.0002 (1)	0.0000 (2)	−0.0023 (3)
C(13)	0.5869 (2)	0.1812 (2)	0.3217 (4)	0.0020 (1)	0.0037 (2)	0.0119 (5)	−0.0002 (1)	−0.0001 (2)	−0.0008 (2)
C(14)	0.2237 (2)	0.3180 (2)	0.2474 (5)	0.0023 (1)	0.0044 (2)	0.0177 (6)	0.0001 (1)	−0.0018 (2)	−0.0006 (3)
C(15)	0.3282 (2)	0.4292 (2)	0.2201 (4)	0.0021 (1)	0.0032 (1)	0.0098 (4)	0.0006 (1)	0.0006 (2)	0.0006 (2)
C(16)	0.2987 (2)	0.4496 (3)	0.1040 (4)	0.0035 (1)	0.0050 (2)	0.0118 (5)	0.0007 (1)	−0.0002 (2)	0.0017 (3)
C(17)	0.3218 (3)	0.5103 (3)	0.0336 (5)	0.0042 (2)	0.0063 (3)	0.0150 (7)	0.0009 (2)	0.0012 (3)	0.0034 (4)
C(18)	0.3727 (3)	0.5516 (3)	0.0757 (5)	0.0042 (2)	0.0048 (2)	0.0176 (7)	0.0011 (2)	0.0029 (3)	0.0041 (3)
C(19)	0.4028 (2)	0.5354 (3)	0.1926 (6)	0.0032 (1)	0.0052 (2)	0.0233 (9)	−0.0006 (2)	0.0015 (3)	0.0016 (4)
C(20)	0.3795 (2)	0.4724 (2)	0.2637 (5)	0.0030 (1)	0.0038 (2)	0.0163 (6)	−0.0000 (1)	0.0004 (2)	0.0013 (3)
C(21)	0.2823 (2)	0.3793 (2)	0.4664 (4)	0.0019 (1)	0.0027 (1)	0.0110 (4)	0.0001 (1)	0.0006 (2)	−0.0000 (2)
C(22)	0.2909 (2)	0.3330 (2)	0.5726 (4)	0.0036 (1)	0.0033 (2)	0.0114 (5)	0.0006 (1)	0.0014 (2)	0.0003 (2)
C(23)	0.2699 (2)	0.3559 (3)	0.6938 (4)	0.0048 (2)	0.0050 (2)	0.0107 (5)	0.0004 (2)	0.0022 (3)	−0.0001 (3)
C(24)	0.2402 (2)	0.4262 (3)	0.7077 (4)	0.0035 (1)	0.0051 (2)	0.0128 (6)	−0.0005 (1)	0.0024 (2)	−0.0027 (3)
C(25)	0.2309 (2)	0.4732 (3)	0.6035 (5)	0.0034 (1)	0.0039 (2)	0.0158 (6)	0.0004 (1)	0.0021 (2)	−0.0021 (3)
C(26)	0.2519 (2)	0.4500 (2)	0.4823 (4)	0.0030 (1)	0.0032 (2)	0.0135 (5)	0.0005 (1)	0.0012 (2)	0.0003 (2)
C(27)	0.4506 (2)	0.1114 (2)	0.0953 (4)	0.0037 (1)	0.0033 (2)	0.0111 (5)	0.0008 (1)	−0.0008 (2)	−0.0007 (2)
C(28)	0.4649 (2)	0.2673 (2)	0.0056 (3)	0.0025 (1)	0.0035 (2)	0.0077 (3)	−0.0002 (1)	0.0003 (2)	−0.0010 (2)
C(29)	0.5318 (2)	0.2515 (4)	−0.0084 (4)	0.0030 (1)	0.0057 (2)	0.0164 (6)	0.0002 (2)	0.0014 (2)	0.0003 (4)
C(30)	0.5731 (2)	0.3046 (4)	−0.0673 (6)	0.0028 (1)	0.0084 (3)	0.0213 (9)	−0.0008 (2)	0.0023 (3)	−0.0002 (5)
C(31)	0.5488 (3)	0.3727 (4)	−0.1122 (5)	0.0046 (2)	0.0070 (3)	0.0159 (7)	−0.0019 (2)	0.0018 (3)	−0.0001 (4)
C(32)	0.4832 (3)	0.3886 (3)	−0.0985 (5)	−0.0055 (2)	0.0043 (2)	0.0146 (6)	−0.0013 (2)	0.0006 (3)	0.0010 (3)
C(33)	0.4420 (2)	0.3366 (3)	−0.0388 (4)	0.0034 (1)	0.0041 (2)	0.0126 (5)	−0.0004 (1)	0.0004 (2)	0.0006 (3)
C(34)	0.3442 (2)	0.1856 (2)	−0.0240 (3)	0.0029 (1)	0.0029 (1)	0.0063 (1)	−0.0001 (1)	−0.0000 (2)	−0.0001 (2)
C(35)	0.3588 (2)	0.1709 (3)	−0.1521 (4)	0.0038 (1)	0.0048 (2)	0.0072 (4)	−0.0000 (1)	0.0002 (2)	−0.0005 (2)
C(36)	0.3088 (3)	0.1541 (3)	−0.2381 (4)	0.0056 (2)	0.0044 (2)	0.0069 (4)	−0.0004 (2)	−0.0010 (2)	−0.0003 (2)
C(37)	0.2447 (2)	0.1512 (3)	−0.1984 (5)	0.0046 (2)	0.0049 (2)	0.0117 (5)	−0.0016 (2)	−0.0026 (3)	0.0003 (3)
C(38)	0.2300	0.1638 (3)	−0.0710 (5)	0.0034 (2)	0.0072 (3)	0.0122 (6)	−0.0017 (2)	−0.0006 (2)	−0.0004 (3)
C(39)	0.2793 (2)	0.1804 (3)	0.0154 (4)	0.0034 (1)	0.0046 (2)	−0.0085 (1)	−0.0011 (2)	−0.0000 (2)	−0.0003 (2)

atom	x/a	y/b	z/c	B, Å^2	atom	x/a	y/b	z/c	B, Å^2
H(1)[B]	0.347	0.181	0.350	6.2	H(23)[C(18)]	0.388	0.597	0.030	6.2
H(2)[B]	0.312	0.088	0.313	5.7	H(24)[C(19)]	0.441	0.563	0.228	5.6
H(3)[B]	0.277	0.151	0.457	6.4	H(25)[C(20)]	0.401	0.459	0.347	4.1
H(4)[B]	0.332	0.103	0.456	6.3	H(26)[C(22)]	0.313	0.283	0.562	5.1
H(5)[C(1)]	0.432	0.207	0.604	5.1	H(27)[C(23)]	0.274	0.322	0.768	5.2
H(6)[C(1)]	0.434	0.295	0.612	5.8	H(28)[C(24)]	0.225	0.444	0.793	4.8
H(7)[C(1)]	0.496	0.247	0.369	4.9	H(29)[C(25)]	0.211	0.524	0.612	5.3
H(8)[C(3)]	0.568	0.342	0.583	5.2	H(30)[C(26)]	0.245	0.484	0.407	5.3
H(9)[C(4)]	0.633	0.454	0.551	5.7	H(31)[C(27)]	0.466	0.096	0.010	4.8
H(10)[C(5)]	0.631	0.518	0.362	5.3	H(32)[C(27)]	0.415	0.071	0.131	5.0
H(11)[C(6)]	0.567	0.472	0.188	5.6	H(33)[C(27)]	0.483	0.110	0.147	5.0
H(12)[C(7)]	0.498	0.364	0.218	4.6	H(34)[C(29)]	0.550	0.203	0.023	5.1
H(13)[C(9)]	0.466	0.098	0.477	5.3	H(35)[C(30)]	0.619	0.287	−0.074	6.0
H(14)[C(10)]	0.529	−0.013	0.430	5.3	H(36)[C(31)]	0.578	0.411	−0.161	5.4
H(15)[C(11)]	0.630	−0.007	0.321	4.9	H(37)[C(32)]	0.462	0.436	−0.124	5.6
H(16)[C(12)]	0.667	0.122	0.249	4.6	H(38)[C(33)]	0.395	0.349	−0.025	4.1
H(17)[C(13)]	0.602	0.230	0.293	4.1	H(39)[C(35)]	0.406	0.169	−0.181	5.2
H(18)[C(14)]	0.223	0.305	0.156	4.6	H(40)[C(36)]	0.319	0.147	−0.327	5.5
H(19)[C(14)]	0.196	0.355	0.258	5.5	H(41)[C(37)]	0.209	0.140	−0.258	5.0
H(20)[C(14)]	0.208	0.271	0.302	5.3	H(42)[C(38)]	0.183	0.160	−0.042	5.6
H(21)[C(16)]	0.262	0.417	0.070	6.0	H(43)[C(39)]	0.267	0.185	0.112	3.4
H(22)[C(17)]	0.300	0.521	−0.050	6.6					

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

PPh_2Me ligands and a single H atom of the tetrahydroborate group. Upon dissolution of the complex in benzene, a phosphine dissociates and its coordination site is occupied by a second H atom from BH_4^-. The ready reversibility of this process suggests that a delicate balance exists between the single and double hydrogen bridge structures in $Cu[PPh_2Me]_3BH_4$.

B. X-Ray Structure of $Cu[PPh_2Me]_3BH_4$. $Cu[PPh_2Me]_3BH_4$ crystallizes as monomeric units with the structure shown in Figure 2. Pertinent intramolecular dis-

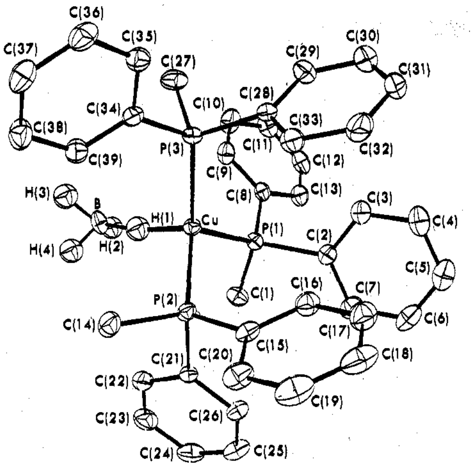


Figure 2. Molecular structure and atom numbering scheme for $Cu[PPh_2Me]_3BH_4$. Nonhydrogen atoms are represented by their 30% probability ellipsoids for thermal motion, while the hydrogen atoms of the BH_4^- group are shown as isotropic spheres.

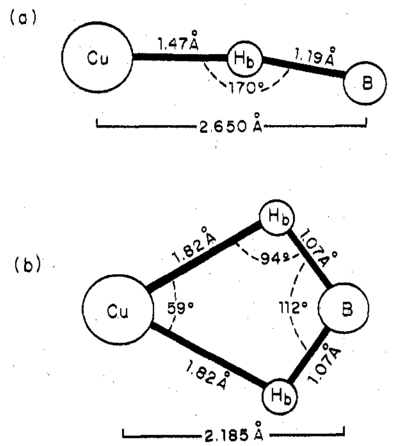


Figure 3. Schematic comparison of the different modes of BH_4^- attachment in (a) $Cu[PPh_2Me]_3BH_4$ and (b) $Cu[PPh_3]_2BH_4$.

tances and angles are summarized in Table III. The copper atom resides in a distorted tetrahedral environment consisting of the phosphorus atoms of the three phosphine ligands and a single hydrogen atom of the tetrahydroborate group. The structural features associated with this novel single hydrogen bridge attachment are depicted more prominently in Figure 3. The Cu–H–B moiety is nearly linear with a Cu–H_b bond length of 1.47 Å.[22] This distance is significantly shorter than the corresponding metal–hydrogen distances in $Cu[PPh_3]_2BH_4$[23] or in other transition-metal tetrahydroborate complexes containing double or triple hydrogen bridges.[2b] We attribute this result to the particularly favorable metal–hydrogen overlap which arises from monodentate BH_4^- coordination. In contrast, the constraint imposed by the formation of a four-membered chelate ring[24] (note small H_b–Cu–H_b angle for $Cu[PPh_3]_2BH_4$ in Figure 3) reduces this overlap for bidentate and tridentate coordination with a consequent lengthening of the metal–hydrogen bridge bond.

Table III. Intramolecular Distances (Å) and Angles (deg) for Tris(methyldiphenylphosphine)(tetrahydroborato)copper

Cu-P(1)	2.293 (1)	C(11)-C(12)	1.382 (7)
Cu-P(2)	2.276 (1)	C(12)-C(13)	1.390 (6)
Cu-P(3)	2.289 (1)	C(13)-C(8)	1.386 (5)
Cu-H(1)	1.47	C(15)-C(16)	1.396 (5)
Cu-B	2.650 (5)	C(16)-C(17)	1.370 (6)
B-H(1)	1.19	C(17)-C(18)	1.332 (7)
B-H(2)	1.02	C(18)-C(19)	1.391 (7)
B-H(3)	1.14	C(19)-C(20)	1.408 (6)
B-H(4)	0.97	C(20)-C(15)	1.362 (5)
P(1)-C(1)	1.827 (4)	C(21)-C(22)	1.380 (5)
P(1)-C(2)	1.823 (4)	C(22)-C(23)	1.391 (6)
P(1)-C(8)	1.827 (4)	C(23)-C(24)	1.374 (6)
P(2)-C(14)	1.821 (4)	C(24)-C(25)	1.373 (6)
P(2)-C(15)	1.809 (4)	C(25)-C(26)	1.392 (6)
P(2)-C(21)	1.828 (4)	C(26)-C(21)	1.388 (5)
P(3)-C(27)	1.829 (4)	C(28)-C(29)	1.393 (5)
P(3)-C(28)	1.825 (4)	C(29)-C(30)	1.391 (7)
P(3)-C(34)	1.832 (4)	C(30)-C(31)	1.368 (8)
C(2)-C(3)	1.387 (5)	C(31)-C(32)	1.367 (7)
C(3)-C(4)	1.387 (7)	C(32)-C(33)	1.380 (6)
C(4)-C(5)	1.345 (8)	C(33)-C(28)	1.376 (6)
C(5)-C(6)	1.367 (7)	C(34)-C(35)	1.390 (5)
C(6)-C(7)	1.395 (6)	C(35)-C(36)	1.385 (6)
C(7)-C(2)	1.362 (6)	C(36)-C(37)	1.365 (7)
C(8)-C(9)	1.400 (5)	C(37)-C(38)	1.378 (7)
C(9)-C(10)	1.370 (6)	C(38)-C(39)	1.377 (6)
C(10)-C(11)	1.372 (7)	C(39)-C(34)	1.384 (6)

P(1)-Cu-P(2)	118.0 (1)	C(12)-C(11)-C(10)	119.6 (4)
P(1)-Cu-P(3)	108.9 (1)	C(13)-C(12)-C(11)	120.3 (4)
P(2)-Cu-P(3)	117.8 (1)	C(8)-C(13)-C(12)	120.3 (4)
H(1)-Cu-P(1)	102.4	P(2)-C(15)-C(16)	122.4 (3)
H(1)-Cu-P(2)	104.6	P(2)-C(15)-C(20)	119.1 (3)
H(1)-Cu-P(3)	102.5	C(16)-C(15)-C(20)	118.3 (4)
Cu-H(1)-B	170	C(17)-C(16)-C(15)	121.0 (5)
H(1)-B-H(2)	110	C(18)-C(17)-C(16)	120.4 (5)
H(1)-B-H(3)	108	C(19)-C(18)-C(17)	121.3 (5)
H(1)-B-H(4)	110	C(20)-C(19)-C(18)	118.0 (5)
H(2)-B-H(3)	136	C(15)-C(20)-C(19)	120.9 (4)
H(2)-B-H(4)	104	P(2)-C(21)-C(22)	119.7 (3)
H(3)-B-H(4)	82	P(2)-C(21)-C(26)	121.5 (3)
Cu-P(1)-C(1)	114.3 (1)	C(22)-C(21)-C(26)	118.6 (4)
Cu-P(1)-C(2)	119.9 (1)	C(23)-C(22)-C(21)	121.5 (4)
Cu-P(1)-C(8)	110.7 (1)	C(24)-C(23)-C(22)	119.0 (5)
Cu-P(2)-C(14)	114.1 (1)	C(25)-C(24)-C(23)	120.6 (4)
Cu-P(2)-C(15)	113.6 (1)	C(26)-C(25)-C(24)	120.1 (4)
Cu-P(2)-C(21)	118.5 (1)	C(21)-C(26)-C(25)	120.2 (4)
Cu-P(3)-C(27)	113.6 (1)	P(3)-C(28)-C(29)	122.7 (4)
Cu-P(3)-C(28)	114.8 (1)	P(3)-C(28)-C(33)	119.1 (3)
Cu-P(3)-C(34)	119.3 (1)	C(29)-C(28)-C(33)	117.9 (4)
P(1)-C(2)-C(3)	123.2 (3)	C(30)-C(29)-C(28)	120.1 (5)
P(1)-C(2)-C(7)	118.8 (3)	C(31)-C(30)-C(29)	120.7 (5)
C(3)-C(2)-C(7)	118.0 (4)	C(32)-C(31)-C(30)	119.5 (5)
C(4)-C(3)-C(2)	120.0 (5)	C(33)-C(32)-C(31)	120.1 (5)
C(5)-C(4)-C(3)	121.3 (5)	C(28)-C(33)-C(32)	121.6 (4)
C(6)-C(5)-C(4)	119.7 (5)	P(3)-C(34)-C(35)	121.7 (3)
C(7)-C(6)-C(5)	119.4 (5)	P(3)-C(34)-C(39)	119.8 (3)
C(2)-C(7)-C(6)	121.6 (4)	C(35)-C(34)-C(39)	118.4 (4)
P(1)-C(8)-C(9)	119.0 (3)	C(36)-C(35)-C(34)	120.3 (4)
P(1)-C(8)-C(13)	122.4 (3)	C(37)-C(36)-C(35)	120.6 (4)
C(9)-C(8)-C(13)	118.3 (4)	C(38)-C(37)-C(36)	119.5 (4)
C(10)-C(9)-C(8)	120.9 (4)	C(39)-C(38)-C(37)	120.4 (4)
C(11)-C(10)-C(9)	120.5 (4)	C(34)-C(39)-C(38)	120.8 (4)

Even in the absence of hydrogen atom locations, the long Cu···B separation in $Cu[PPh_2Me]_3BH_4$ is diagnostic of the single hydrogen bridge attachment of BH_4^-. Thus the observed distance of 2.650 (5) Å is close to the value predicted[25] for a linear Cu–H–B linkage. The double hydrogen bridge structure found in $Cu[PPh_3]_2BH_4$, on the other hand, brings the B atom into considerably closer proximity to the metal. On the basis of structural data from the present study and the earlier work of Hamilton et al.,[26] we note the useful generalization that for a given metal M, the M···B separation should vary with the mode of BH_4^- coordination in the order monodentate > bidentate > tridentate.

$Cu[PPh_2Me]_3BH_4$ is isostructural with $Cu[PPh_2Me]_3Cl$,[10] and the parameters associated with the phosphine ligands in the two complexes are in close agreement. Somewhat unexpected, however, is the near identity of the mean Cu–P bond length in $Cu[PPh_2Me]_3BH_4$ (2.286 Å) with that in the structurally dissimilar $Cu[PPh_3]_2BH_4$ (2.280 Å).[23] We attribute this latter result to the confluence of two opposing effects. Thus PPh_2Me, having smaller steric size and being a stronger base than PPh_3, should exhibit a shorter attachment (~0.06 Å) to copper. This difference is compensated,

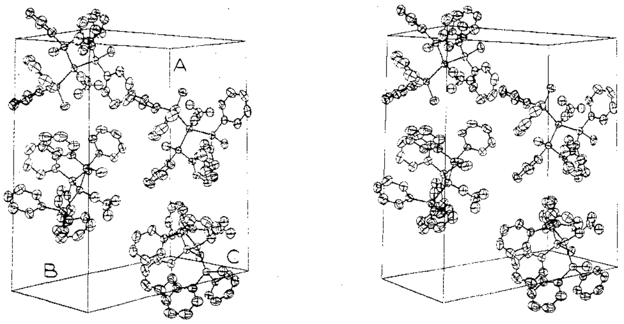


Figure 4. Stereoscopic view of the unit cell packing in Cu[PPh$_2$Me]$_3$BH$_4$.

however, by the expected increase in the Cu–P bond length (~0.07–0.09 Å) resulting from the change in the number of bound phosphines from two to three.[10]

The unit cell packing of Cu[PPh$_2$Me]$_3$BH$_4$ is typical of this kind of molecular compound[10] and is depicted in Figure 4.

Concluding Remarks

The present investigation of Cu[PPh$_2$Me]$_3$BH$_4$ provides the first definitive structural characterization of the single hydrogen bridge attachment of the tetrahydroborate group. Clearly, the preferred mode of coordination by BH$_4^-$ is strongly influenced by its immediate environment in the first coordination sphere of the metal. Thus the replacement of a phenyl group by methyl sufficiently reduces the steric requirements of PPh$_2$Me (relative to PPh$_3$) to permit three of the phosphine ligands to bind to copper. This effectively reduces to one the number of vacant coordination sites available to BH$_4^-$ and facilitates formation of the single hydrogen bridge structure.[27] More generally, we might expect such behavior to be paradigmatic of Cu(P)$_3$BH$_4$ type complexes. An interesting test of this premise would be provided by a complete structural determination of [1,1,1-tris(diphenylphosphinomethyl)ethane](tetrahydroborato)copper, a compound containing a tripod phosphine ligand.[28] Although it has been suggested that the BH$_4^-$ coordination is bidentate, the reported infrared spectrum can be interpreted equally well in terms of a monodentate attachment.

The structural change (eq 1) which obtains upon dissolving solid Cu[PPh$_2$Me]$_3$BH$_4$ in benzene illustrates that the nature of the surrounding medium also influences the mode of BH$_4^-$ coordination. The increase in entropy accompanying the release of a molecule of PPh$_2$Me in solution presumably provides the driving force for this process.[29]

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Registry No. Cu[PPh$_2$Me]$_3$BH$_4$, 63371-86-8.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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(19) Attempted refinement of the hydrogen atoms of the BH$_4^-$ group did not result in convergence with reasonable parameters. Consequently, the coordinates of these atoms were fixed at the values obtained after two cycles of refinement at a damping of 0.2.
(20) The once-melted solid exhibits the same melting point upon reheating, although the brownish coloration of the resulting liquid signals that some decomposition has occurred.
(21) Since our results are in essential agreement with those of Bommer and Morse,[5] we present an abbreviated interpretation of the infrared spectra.
(22) Since the hydrogen atom coordinates were not refined to convergence,[19] it is not possible to calculate standard deviations for the distances or angles involved. However, on the basis of the well-defined peak for H(1) on the difference Fourier map, the accuracy of the Cu–H distance is estimated to be ±0.05 Å. The peaks for the remaining hydrogen atoms of the BH$_4^-$ group were not as well resolved, and thus no significance should be attached to the differences of the parameters listed in Table III from those expected for perfect tetrahedral geometry.
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