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Synthesis and Crystal Structure of a New Hexahydro-*closo*-hexaborate Copper(I) Complex $Cu_2[(C_6H_5)_3P]_4B_6H_6$

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Introduction

A number of bis(diphenylphosphino)copper(I) derivatives of boron hydrides have been reported in which copper is covalently bonded to the borohydride anion. The anions $\{BH_4^-\}$,[1] $\{B_3H_8^-\}$,[2] and $\{B_{10}H_{10}^{2-}\}$[3] are bidentate ligands that bond to copper(I) through Cu−H−B, three-center two-electron bonds. Structural analysis of the complexes $[(C_6H_5)_3P]_2CuB_5H_8$ and $[(C_6H_5)_3P]_2CuB_6H_9$, on the other hand, show another mode of bonding,[4] where the copper bonds directly to two edge borons through a three-center two-electron B−Cu−B bond with no significant interaction with the terminal hydrogens. In recent years, several metal derivatives of hexahydro-*closo*-hexaborate(2-) have been reported,[5−8] but of particular interest is the structure of $[Cu_2[P(C_6H_5)_3]_2B_6H_6$.[8] Each copper atom is bonded to one triphenylphosphine group and one facet of the octahedron in an η^3 fashion. We are interested in learning how the addition of another triphenylphosphine ligand to the copper atom or its removal affects the structure and the mode of bonding of copper to the hexaborate anion, since copper(I) hydroborate complexes with naked copper, one triphenylphosphine ligand, and two triphenylphosphine ligands have been isolated or detected.[9]

We report the synthesis and X-ray crystal structural analysis of the novel compound, $Cu_2[(C_6H_5)_3P]_4B_6H_6{\cdot}2CH_3CN$(I). The copper bonds to the hexaborate anion through a B−B edge but exhibits a weak Cu−H−B interaction. Another distinctive feature of this complex is that the coordination geometry around the copper is trigonal-planar. The new compound has been further characterized by IR and ^{11}B NMR.

Table 1. Crystallographic Data for $Cu_2[(C_6H_5)_3P]_4B_6H_6{\cdot}2CH_3CN^a$

chemical formula $C_{76}H_{72}B_6Cu_2N_2P$
$a = 9.6717(19)$ Å
$b = 10.576(2)$ Å
$c = 17.653(2)$ Å
$\alpha = 80.216(13)°$
$\beta = 83.631(15)°$
$\gamma = 84.642(17)°$
$V = 1763.4(5)$ Å^3
$Z = 1$

fw 1329.18
space group $P\bar{1}$
$T = -17$ °C
$\lambda = 0.71073$ Å
ρ(calcd) $= 1.252$ g cm^{-3}
$\mu = 7.37$ cm^{-1}
$R_1{}^a = 0.0597$
$wR_2{}^a = 0.1286$

[a] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $R_1 = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

Experimental Section

Methods and Materials. All synthetic work was performed using Schlenk glassware and techniques. CH_3CN was obtained from Aldrich Chemical Co. and redistilled from CaH_2. Copper(II) acetate·H_2O was obtained from Fisher Scientific Co. and triphenylphosphine was obtained from Aldrich Chemical Co. and were used without further purification. $[Bu^n{}_4N]_2B_6H_6$ was prepared using literature methods.[10]

Infrared spectra were recorded using a Nicolet 210-FTIR. ^1H and ^{11}B NMR were recorded on a JEOL FX-90Q spectrometer. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Inc. (Woodside, NY).

Synthesis of $Cu_2[(C_6H_5)_3P]_4B_6H_6{\cdot}{}^3/_2CH_3CN$]. A 400 mg (0.72 mmol) sample of $[Bu^n{}_4N]_2B_6H_6$ was dissolved in 30 mL of CH_3CN in a 100 mL Schlenk flask while nitrogen was bubbled through. The reaction mixture was placed in an ice bath, and $Cu(C_2H_3O_2)_2{\cdot}H_2O$ (288 mg, 1.44 mmol) was added. The reaction mixture was magnetically stirred and allowed to warm to room temperature. Eventually, the color of solution changed from dark blue-green to light yellow-green. Triphenylphosphine (4 equiv, 760 mg, 2.90 mmol) was added, and within 10−15 min, a heavy yellowish-white precipitate resulted. Stirring was continued for an additional hour. The solution was cooled to ∼10 °C, and the resulting precipitate was filtered in air and washed with 5 mL of cold acetonitrile followed by diethyl ether. The solid was dried at room temperature under vacuum for 4 h. Yield: 550 mg (57%). Anal. Calcd for $Cu_2P_4C_{75}H_{71.5}B_6N_{1.5}$: C, 68.83; H, 5.43; N, 1.60; Cu, 9.71; P, 9.46; B, 4.95. Found: C, 68.60; H, 5.57; N, 1.58; Cu, 9.60; P, 9.40; B, 4.98. FT-IR (KBr, cm^{-1}): ν(B−H) 2508 (s), 2472 (m), 2302 (m); also 3054 (s), 1478 (s), 1430 (s), 1160(w), 1093(s), 1023 (w), 996(w), 732 (s), 692 (vs), 506 (vs). ^1H NMR (CD_3CN, δ): (7.3, m) and (1.99, s). $^{11}B\{H\}$ NMR (CD_3CN, δ): 25.90 [referenced to $BF_3{\cdot}(C_2H_5)_2O$].

X-ray Crystals of [$Cu_2[(C_6H_5)_3P]_4B_6H_6{\cdot}2CH_3CN$]. A 200 mg (0.36 mmol) sample of $[Bu^n{}_4N]_2B_6H_6$ was dissolved in 30 mL of CH_3CN in a 100 mL Schlenk flask. $Cu(C_2H_3O_2)_2{\cdot}H_2O$ (144 mg, 0.72 mmol) was added following the same procedure described above. On addition of the triphenylphosphine (380 mg, 1.4 mmol), the resulting yellow solution was stirred for 5 min and then gravity filtered to remove any precipitate that appeared at this stage. The filtrate was left standing under the hood for 12−24 h, which resulted in the formation of light yellow needlelike crystals, which were then filtered and washed with cold acetonitrile.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 1, and selected bond distances and angles are given in Table 2.

No evidence of symmetry higher than triclinic was observed in the diffraction data. *E*-statistics suggested the centrosymmetric space group option, *P*, which yielded chemically reasonable and computationally

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cu_2[(C_6H_5)_3P]_4B_6H_6 \cdot 2CH_3CN$[a]

Distances			
Cu(1)−H(1B)	2.10(4)	Cu(1)−B(1)	2.161(5)
Cu(1)−H(2B)	2.41(5)	Cu(1)−B(2)	2.341(5)
Cu(1)−P(1)	2.2764(14)	Cu(1)−P(2)	2.3006(14)
B(1)−B(3)	1.770(7)	B(2)−B(3)	1.756(8)
B(1)−B(3A)	1.703(8)	B(3)−B(2A)	1.721(7)
B(1)−B(2)	1.749(8)	B(3)−B(1A)	1.703(8)
B(1)−B(2A)	1.717(8)	B(1)−H(1B)	1.17(4)
B(2)−B(1A)	1.717(8)	B(2)−H(2B)	1.07(5)
B(2)−B(3A)	1.721(7)	B(3)−H(3B)	1.14(4)

Angles			
H(1B)−Cu(1)−B(1)	32.0(12)	H(1B)−Cu(1)−P(1)	117.4(12)
B(1)−Cu(1)−P(1)	124.17(15)	H(1B)−Cu(1)−P(2)	104.4(12)
B(1)−Cu(1)−P(2)	117.33(15)	P(1)−Cu(1)−P(2)	115.77(5)
H(1B)−Cu(1)−B(2)	76.1(12)	B(1)−Cu(1)−B(2)	45.5(2)
P(1)−Cu(1)−B(2)	128.28(14)	P(2)−Cu(1)−B(2)	106.80(15)
B(2)−B(3)−B(1)	59.5(5)	B(1)−B(2)−B(3)	60.7(3)
B(1a)−B(2)−B(1)	89.9(4)	H(2B)−B(2)−B(1)	135(2)

[a] Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, and $-z$.

stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. The asymmetric unit contains half of the copper complex and an acetonitrile molecule and lies on an inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the borane, H(1B), H(2B) and H(3B), were located from the difference map. The hydrogen atoms of the solvent molecule were ignored, and all other hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library. [11]

Results and Discussion

The reaction of $[Bu^n{}_4N]_2B_6H_6$ with 2 equiv of $Cu(C_2H_3O_2)_2 \cdot H_2O$ in acetonitrile followed by the addition of 4 equiv of triphenylphosphine gave the title compound, $Cu_2[(C_6H_5)_3P]_4B_6H_6 \cdot 2CH_3CN$(I) (**1**), as light yellowish crystals. On heating, **1** starts to decompose at 140 °C and turns completely black at temperatures above 220 °C. Although stable in dry form, **1** is not very stable in solution and slowly decomposes in acetonitrile to give a white solid of low boron content. **1** seems to dissolve and react with most organic solvents; dissolution in chlorinated solvents with slow diffusion of pentane results in the formation of colorless crystals. Preliminary studies show that the resulting product is another copper complex of the hexaborate cage whose identity is under investigation. The molecular structure with atom labeling for **1** is shown in Figures 1 and 2.

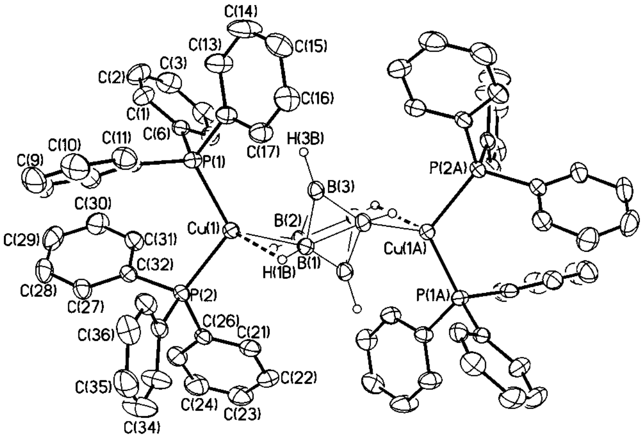

Figure 1. ORTEP diagram of $Cu_2[(C_6H_5)_3P]_4B_6H_6 \cdot 2CH_3CN$(I) showing atom labeling scheme. Thermal ellipsoids at 30% probability. Solvent molecules are omitted for clarity. Hydrogen atoms, except for those which were located on the hexaborate, are omitted for clarity.

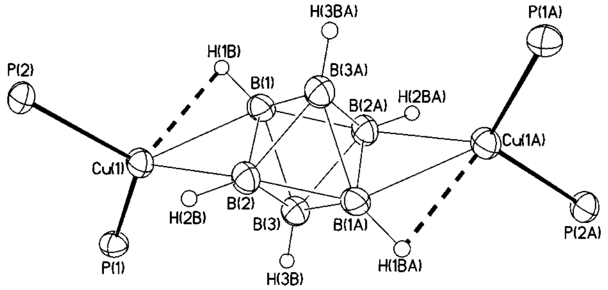

Figure 2. ORTEP diagram of $Cu_2[(C_6H_5)_3P]_4B_6H_6 \cdot 2CH_3CN$(I) focusing on the bond environment between copper atoms and hexaborate showing atom labeling scheme. Thermal ellipsoids at 30% probability.

X-ray Structure Analysis. 1 crystallizes in the $P\bar{1}$ crystallographic space group and lies on an inversion center (Figure 1). The Cu(1)−B(1) distance in **1** is 2.161(5) Å, which is comparable to that reported for $Cu_2[(C_6H_5)_3P]_2B_6H_6$ with a value of 2.178(6) Å.[8] In the latter, the copper is bonded to an octahedral facet in an η^3-fashion, using a four-centered two-electron bond, without significant interaction with the terminal hydrogens. For the complex, $Cu[(C_6H_5)_3P]_2B_5H_8$, the copper atom bonds to the boron cage through a B−B basal edge forming a B−Cu−B bond. The Cu−B distances are 2.21 and 2.24 Å, compared to Cu−H bond distances of 2.33 and 2.76 Å. The geometry around the copper was found to be trigonal-planar with angles about the copper of 114.0°, 122.3°, and 123.4°.[4a] Complexes, such as $Cu[(C_6H_5)_3P]_2BH_4$, $Cu[(C_6H_5)_3P]_2B_3H_8$, and $Cu_2[(C_6H_5)_3P]_4B_{10}H_{10}$, in which copper bonds through the terminal hydrogens forming Cu−H−B bridge bonds, show Cu−H bonds significantly shorter than Cu−B bonds. The comparative values of these distances are Cu−H(axial) [2.08(7)], Cu−H(equatorial) [1.86(6)], and Cu−B [2.30(2)] Å for the decaborate;[3a] Cu−H [1.84(5)] and Cu−B [2.30(1)] Å for the triborate;[2] Cu−H [2.02(5)] and Cu−B [2.18(1)] Å for the tetrahydroborate.[1] On the basis of the X-ray structural data, the title compound exhibits a strong interaction between Cu(1) and B(1) and a weaker interaction with both H(1B) and B(2). One can consider the copper to bond to both B(1) and B(2) through a three-center two-electron bond, where the Cu−centroid distance was found to be 2.076 Å, and the angles subtended around the copper, cent−Cu(1)−P(1), cent−Cu(1)−P(2), and P(1)−Cu(1)−P(2) have values of 129.9°, 113.7°, and 115.8°, respectively. Accordingly, the geometry around the copper is trigonal-planar, with copper being 0.100 Å out of the plane constructed from P(1), P(2), and centroid. There are no apparent stringent steric factors or crystal packing effects that might cause this asymmetric interaction between copper and the two edge borons. This asymmetry is mainly due to the weak interaction between Cu(1) and the terminal hydrogen H(1B), which is further supported by the infrared spectrum exhibiting a peak characteristic of Cu−H−B bonding at 2302 cm^{-1}.[1,3] The Cu(1)−H(2B) bond distance is relatively longer, 2.41 Å, and is comparatively considered nonbonding. A similar asymmetrical interaction of copper with a boron cluster edge in conjunction to exhibiting a weak Cu−H interaction has been reported for the complex, $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$.[12] In the latter complex, the copper−boron distances are 2.274(7) and 2.164(8) Å,

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while the Cu−H(B) is 1.96 (7) Å, values which are comparable to those of **1**.

The copper in **1** can be looked at as a coordinatively unsaturated, 16-electron center, similar to that of bis(triphenylphosphine)copper(I) complexes of the form $[(C_6H_5)_3P]_2CuX$ (X = Br, Cl, ...).[13] Unlike $[(C_6H_5)_3P]_2CuX$ compounds where the P−Cu−P angles range from 120 to 130° due to the steric effects exerted by the phenyl groups and the electronic effects of the anion,[2a] **1** shows a smaller angle with a value of 115.77°, as a consequence of the Cu−H−B interaction. The B−B distances in **1** range from 1.770(7) to 1.703(8) Å, with the bonds of the deltahedral face defined by B(1)−B(2)−B(3) opposite to the copper slightly elongated. The B(1)−H(1B) and B(3)−H(3B) bonds have lengths of 1.17(4) and 1.14(4) Å, respectively, and are slightly elongated when compared to the B(2)−H(2B) bond, which is 1.07(5) Å. The interaction of copper with H(1B) results in decreased electron density for B(1)−H(1B) and a longer bond distance, while the steric interaction of the phosphine phenyl rings with H(3B) causes elongation in the bond length.

IR Spectrum. The reaction was initially followed by FT-IR, taken at different stages of the reaction. After the addition of copper acetate to a solution of hexaborate in acetonitrile and as soon as the color of solution changed to yellow-green, an IR spectrum was taken (Figure 3a). The ν(B−H) stretching frequency which appears at 2530 cm^{-1} for B_6H_6(2-),[14] shifted to lower energy, appearing at 2482 cm^{-1}. These results indicate an interaction between the copper and the hexaborate cage at this early stage. After the addition of triphenylphosphine and within a short time, a dense cream color precipitate resulted. Analysis of the infrared spectrum (KBr pellet) shows three peaks in the ν(B−H) stretching frequency region and exhibits a shift to lower energy than that of the hexaborate(2-). The ν(B−H) peaks appear at 2508, 2472, and 2302 cm^{-1}; while the first two are assigned to the four terminal B−H with little interaction with copper, the third might be assigned to H(1B) and H(1BA), which are at a short distance from copper,[1c,3a,12,15] and fall in the region characteristic of the Cu−H−B stretching mode. A comparison of the IR spectra in the ν(B−H) region is presented in Figure 3.

NMR Spectrum. $^{11}B\{H\}$ NMR (28.69 MHz) in CD_3CN gives a single peak at δ(28.75 ppm) which shows a significant downfield shift when compared to $B_6H_6{}^{2-}$ [δ(−13.7 ppm)].[16] This is expected due to the coordination of the Lewis acid, Cu$[(C_6H_5)_3P]_2{}^+$, to the boron cage, hence deshielding the boron. The equivalence of all the boron nuclei further shows the fluxional character of the complex in a manner similar to many copper−boron hydride complexes.[17]

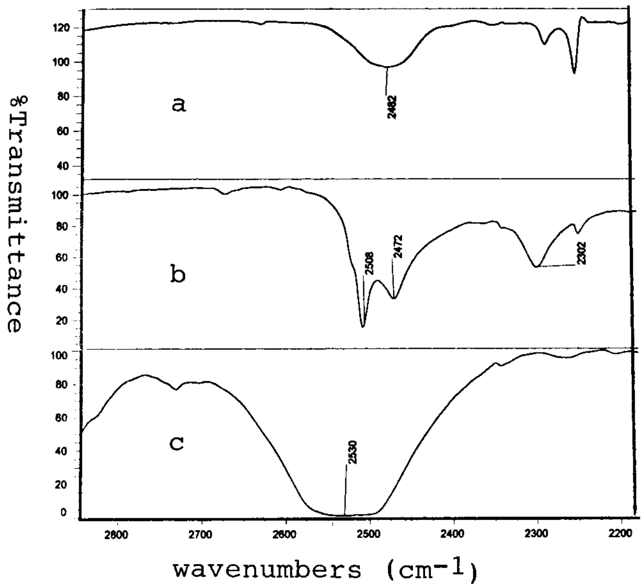

Figure 3. Infrared spectra in the ν(B−H) region of (a) reaction solution of $[Bu^n_4N]_2B_6H_6$ with $Cu(C_2H_3O_2)_2{\cdot}H_2O$ in acetonitrile, (b) $Cu_2[(C_6H_5)_3P]_4B_6H_6{\cdot}2CH_3CN$ (KBr pellet), and (c) $[Bu^n_4N]_2B_6H_6$ (KBr pellet).

We conclude by noting that the presence of two diphenylphosphines on each copper prohibits the η^3 mode of bonding, which is characteristic of metal−B_6H_6 complexes, due to steric as well as electronic factors. The title compound might be considered an intermediate in the formation of $Cu_2[(C_6H_5)_3P]_2B_6H_6$.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, complete bond lengths and bond angles, anisotropic displacement coefficients, H-atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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