remarkably easy formation of complexes containing Pt–C$H_2$–Pt, Pt–$SO_2$–Pt, and Pt–S–Pt units along with the $Pt_2(\mu\text{-dppm})_2$ framework illustrates this effect nicely. Fortunately, the $^1H$ and $^{31}P$ NMR spectra of the complexes are very rich and allow positive structural assignments to be made. These spectra also indicate that the Pt–Pt bond in I is effectively broken when the group $CH_2$, $SO_2$, or S is added to I.

Complex V, containing the $Pt_2(\mu\text{-SMe})(\mu\text{-dppm})_2$ bridging structure, is interesting in that it shows two fluxional processes. One of these can be identified as an inversion at the bridging sulfur atom, a process which has been observed in other diplatinum complexes.[20] However, a second fluxional process which renders the $CH_2$ protons of each dppm ligand effectively equivalent on the NMR time scale is more unusual. A similar effect has been observed in the complex ion $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, but in this case exchange of bridging and terminal hydride ligands was observed.[4]

**Acknowledgment.** We express our gratitude to the Central Electricity Generating Board for the award of a Research Fellowship at St. Catherine's College, Oxford (to KRS), and to Johnson Matthey for their generous loan of potassium tetrachloroplatinate(II).

**Note Added in Proof.** Since submission of this paper, the structure of $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dpam})_2]$ has been determined and found to be similar to its palladium analogue in not containing a direct metal–metal bond. See ref 18.

**Registry No.** I, 61250-65-5; II, 68851-49-0; III, 68851-13-8; IV, 68851-48-9; V, 69215-82-3; $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$, 63911-00-2.

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# Removal of Ligands from Bis(triphenylphosphine)copper(I) Boranes: Preparation of $CuB_3H_8$ and $Cu_2B_{10}H_{10}$ and Evidence for the Existence of $P(C_6H_5)_3CuB_3H_8$ and $P(C_6H_5)_3CuBH_4$ in Solution

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Treatment of bis(triphenylphosphine)copper(I) boranes with $B_2H_6$ results in ligand removal through the formation of $P(C_6H_5)_3{\cdot}BH_3$. The complexes $CuB_3H_8$ and $Cu_2B_{10}H_{10}$ have been prepared from reactions of $[P(C_6H_5)_3]_2CuB_3H_8$ and $\{[P(C_6H_5)_3]_2Cu\}_2B_{10}H_{10}$ with $B_2H_6$ in $CH_2Cl_2$ at 0 °C. The previously unreported $CuB_3H_8$ is only slightly soluble in chlorinated hydrocarbons. Evidence for the intermediate species $P(C_6H_5)_3CuB_3H_8$ is presented. The reaction of $[P(C_6H_5)_3]_2CuBH_4$ with excess $B_2H_6$ in $CH_2Cl_2$ at −78 °C results in the removal of only 1 mol of $P(C_6H_5)_3$/mol of complex. The resulting product, $P(C_6H_5)_3CuBH_4$, decomposes rapidly above −10 °C.

## Introduction

A number of $L_2Cu^I$ boranes have been reported in which L = an organophosphine.[1-18] Examples which are pertinent to this study are $[P(C_6H_5)_3]_2CuBH_4$,[1-7] $[P(C_6H_5)_3]_2CuB_3H_8$,[6-15] and $\{[P(C_6H_5)_3]_2Cu\}_2B_{10}H_{10}$.[16-18] In these compounds the borane unit appears to be a bidentate ligand with two Cu–H–B three-center bonds per copper atom. Phosphorus-31 NMR spectra indicate that the phosphine ligands of $[P(C_6H_5)_3]_2CuB_3H_8$ are labile in solution.[8-10,19] The labile character of these phosphine ligands suggested to us the possibility of "capturing" them, thereby producing copper(I) boranes which contain less than two phosphines per molecule. To this end we have succeeded in "tying-up" labile phosphine molecules by adding $B_2H_6$ to form $P(C_6H_5)_3{\cdot}BH_3$. We describe below reactions of $B_2H_6$ with bis(triphenylphosphine)copper(I) boranes to give the isolable species $CuB_3H_8$ and $Cu_2B_{10}H_{10}$ and solutions of $P(C_6H_5)_3CuB_3H_8$ and $P(C_6H_5)_3CuBH_4$.

## Results and Discussion

**$Cu_2B_{10}H_{10}$ and $CuB_3H_8$.** The complexes $\{[P(C_6H_5)_3]_2Cu\}_2B_{10}H_{10}$ and $[P(C_6H_5)_3]_2CuB_3H_8$ react with $B_2H_6$ in $CH_2Cl_2$ at room temperature according to the following equations.

$$\{[P(C_6H_5)_3]_2Cu\}_2B_{10}H_{10} + 2B_2H_6 \rightarrow Cu_2B_{10}H_{10} + 4P(C_6H_5)_3{\cdot}BH_3 \quad (1)$$

$$[P(C_6H_5)_3]_2CuB_3H_8 + B_2H_6 \rightarrow CuB_3H_8 + 2P(C_6H_5)_3{\cdot}BH_3 \quad (2)$$

The structure of $Cu_2B_{10}H_{10}$ prepared by reaction of copper(II) salts with $B_{10}H_{10}^{2-}$ salts[16,20,21] reveals $B_{10}H_{10}$ polyhedra of $D_{4d}$ symmetry, each joined to four other polyhedra by

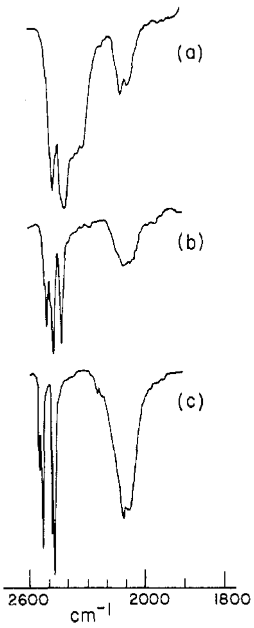



**Figure 1.** Infrared spectra of (a) $CsB_3H_8$, (b) $[P(C_6H_5)_3]_2CuB_3H_8$, and (c) $CuB_3H_8$; B–H stretching region (Nujol mulls).

bridging Cu atoms.[20] Each Cu atom is joined to one apical and one equatorial boron atom of each of the two adjacent polyhedra by Cu–H–B bridge bonds.[16]

The boron-11 NMR spectrum of an acetonitrile solution of $Cu_2B_{10}H_{10}$ prepared by displacement of ligands from $\{[P(C_6H_5)_3]Cu\}_2B_{10}H_{10}$ is identical with that of $Cu_2B_{10}H_{10}$ prepared by the literature method.[22] It should be noted that $Cu_2B_{10}H_{10}$ is probably strongly associated with solvent molecules in acetonitrile solution even though precipitation from acetonitrile with diethyl ether followed by drying under vacuum for several days yields $Cu_2B_{10}H_{10}$ free of acetonitrile.

A comparison of the infrared spectra[16] and X-ray powder diffraction patterns of $Cu_2B_{10}H_{10}$ prepared by ligand displacement and by the literature method shows the products of the two methods to be identical.

The product of reaction **2**, $CuB_3H_8$, is previously unreported. It is apparently stable at room temperature under vacuum but decomposes rapidly when it is exposed to air. It is slightly soluble in nonreacting, weakly complexing solvents such as $CH_2Cl_2$ and $CHCl_3$ and is therefore easily separated from the more soluble product $P(C_6H_5)_3{\cdot}BH_3$ which is also formed in reaction **2**. Boron-11 NMR spectra of $CuB_3H_8$ are markedly different from those of $[P(C_6H_5)_3]_2CuB_3H_8$ and $B_3H_8^-$. The boron-11 NMR spectrum of $CuB_3H_8$ at 30 °C in $CD_2Cl_2$ consists of a broad, featureless signal centered at −7 ppm (width at half-height = 1790 Hz). No significant changes in the spectrum occur as the temperature is lowered to −90 °C. In contrast, $[P(C_6H_5)_3]_2CuB_3H_8$ exhibits a sharper but still broad resonance at −32.1 ppm (width at half-height = 290 Hz). Ionic $B_3H_8^-$ exhibits a multiplet which is centered at −29.8 ppm.[23]

The infrared spectrum of $CuB_3H_8$ (Nujol mull) exhibits strong terminal B–H stretching absorptions at 2530 and 2468 cm$^{-1}$, with weak absorptions at 2542 and 2472 cm$^{-1}$. Broad overlapping bands at 2120 and 2090 cm$^{-1}$ represent B–H–B stretching modes.[24] The Cu–H–B stretching mode is generally weak. It might be masked by the B–H–B stretching modes or it might be the shoulder at 2250 cm$^{-1}$.[1,4,7,16–18] This spectrum is compared with the spectrum of $[P(C_6H_5)_3]_2CuB_3H_8$ and the infrared spectrum of $CsB_3H_8$ (Figure 1). The terminal B–H stretching region for $CuB_3H_8$ is significantly different from the corresponding regions of the spectrum of $[P(C_6H_5)_3]_2CuB_3H_8$ and ionic $CsB_3H_8$. Three strong absorptions (2500, 2465, and 2420 cm$^{-1}$) are observed in the B–H stretching region of $[P(C_6H_5)_3]_2CuB_3H_8$ whereas in the case of $CsB_3H_8$ strong absorptions are observed at 2470 and 2410 cm$^{-1}$ (broad) with a broad shoulder at 2350 cm$^{-1}$.[7]

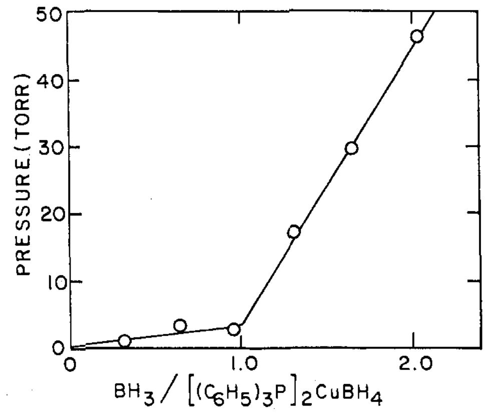



**Figure 2.** Curve representing the tensimetric titration of $[P(C_6H_5)_3]_2CuBH_4$ with $B_2H_6$ in $CH_2Cl_2$ at −78 °C.

The structure of $CuB_3H_8$ is as yet unknown. It is reasonable to assume that this compound is polymeric in the solid state with each Cu atom bound to more than one $B_3H_8$ unit through Cu–H–B bridges. The compound $Cu_2B_{10}H_{10}$ is polymeric in the solid state.[16,20]

**$P(C_6H_5)_3CuB_3H_8$.** The reaction between $B_2H_6$ and $[P(C_6H_5)_3]_2CuB_3H_8$ in $CH_2Cl_2$ at room temperature was followed tensimetrically. The titration curve showed a sharp break at $2BH_3/[P(C_6H_5)_3]_2CuB_3H_8$ which is consistent with eq 1. Formation of the intermediate species $P(C_6H_5)CuB_3H_8$ was suggested by the fact that no precipitation of $CuB_3H_8$ was noted until the ratio $BH_3/[P(C_6H_5)_3]_2CuB_3H_8$ exceeded 1/1.

$$[P(C_6H_5)_3]_2CuB_3H_8 + {}^1/_2B_2H_6 \rightarrow P(C_6H_5)_3CuB_3H_8 + P(C_6H_5)_3BH_3 \quad (3)$$

Possible formation of $P(C_6H_5)_3CuB_3H_8$ in solution is further suggested by the observation that $CuB_3H_8$, which is only slightly soluble in $CH_2Cl_2$, is solubilized upon the addition of an equimolar amount of $P(C_6H_5)_3$ or $[P(C_6H_5)_3]_2CuB_3H_8$ to a suspension of 2 mmol of $CuB_3H_8$ in 5 mL of $CH_2Cl_2$. A similar situation seems to apply in the case of $Cu_2B_{10}H_{10}$, which is sparingly soluble in $CH_2Cl_2$ but dissolves readily in this solvent in the presence of $P(C_6H_5)_3$ when molar ratios of $P(C_6H_5)_3/Cu_2B_{10}H_{10}$ exceed 2/1.

The infrared spectrum of a $CH_2Cl_2$ solution containing an equimolar amount of $P(C_6H_5)_3$ and $CuB_3H_8$ exhibits much broader absorptions in the B–H–B stretching region than do solutions containing $[P(C_6H_5)_3]_2CuB_3H_8$. The proton NMR spectra of these solutions at 0 °C reveal a broad signal (width at half-height = 74 Hz) at 0.15 ppm which is assigned to hydrogens on boron and a signal at 7.21 ppm which represents the phenyl hydrogens. Attempts to isolate solid $P(C_6H_5)_3CuB_3H_8$ from such solutions failed. Removal of solvent at room temperature yielded a mixture of solid $CuB_3H_8$ and $[P(C_6H_5)_3]_2CuB_3H_8$ which were identified from infrared spectra and X-ray powder patterns. Cooling of these solutions to −78 °C yielded precipitates believed to be $CuB_3H_8$ since the proton and phosphorus-31 NMR spectra of these systems at −78 °C revealed the presence of only $[P(C_6H_5)_3]_2CuB_3H_8$ in solution. We believe that the overall equilibrium (4) is operative. Removal of solvent or lowering of temperature shifts the equilibrium to the right.

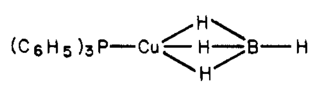
$$2P(C_6H_5)_3CuB_3H_8 \rightleftharpoons CuB_3H_8 + [P(C_6H_5)_3]_2CuB_3H_8 \quad (4)$$

**$P(C_6H_5)_3CuBH_4$.** The reaction of $[P(C_6H_5)_3]_2CuBH_4$ with $B_2H_6$ was followed by means of a tensimetric titration at −78 °C in dichloromethane. A sharp break in the titration curve at the 1/1 molar ratio of $BH_3/[P(C_6H_5)_3]_2CuBH_4$ (Figure 2) corresponds to reaction 5. The presence of $P(C_6H_5)_3\cdot BH_3$ as

$$[P(C_6H_5)_3]_2CuBH_4 + {}^1/_2B_2H_6 \rightarrow P(C_6H_5)_3CuBH_4 + P(C_6H_5)_3\cdot BH_3 \quad (5)$$

a reaction product was established from NMR spectra ($^{11}B$, $^1H$, $^{31}P$) of the solution.[25] Reaction of a second equivalent of $BH_3$ with ligand was not observed even at higher temperature (−20 °C). Further support for eq 5 is provided by the magnitude of the average molecular weight of the solute, which is discussed in the Experimental Section.

The products from eq 5 are soluble in diethyl ether as well as chlorinated hydrocarbons. Attempts to isolate $P(C_6H_5)_3CuBH_4$ failed because of its thermal instability and because of its apparently similar solubility to that of $P(C_6H_5)_3\cdot BH_3$. However, it was possible to assign proton and phosphorus-31 NMR spectra to $P(C_6H_5)_3CuBH_4$ since the $P(C_6H_5)_3\cdot BH_3$ resonance is readily identifiable.[25] The boron-11 NMR spectrum of $P(C_6H_5)_3CuBH_4$ was not discernible. It might be masked by the boron-11 signal from $P(C_6H_5)_3\cdot BH_3$, which, although a quartet, lacked resolution typical for a solution of pure $P(C_6H_5)_3\cdot BH_3$. At −43 °C the proton NMR spectrum ($^{11}B$ decoupled) consists of a signal at 1.38 ppm (B–H hydrogen) and a signal at 7.25 ppm (phenyl hydrogen). The normal B–H signal when $^{11}B$ is not decoupled is a very broad resonance (width at half-height = 210 Hz) with no apparent fine structure. At −60 °C the phosphorus-31 NMR spectrum assigned to $P(C_6H_5)_3CuBH_4$ consists of a sharp signal at 0.48 ppm. On the basis of the area ratio in the phosphorus-31 NMR spectrum, $[P(C_6H_5)_3]_2CuBH_4$ was present as an impurity in about 5 mol % of the $P(C_6H_5)_3CuBH_4$ concentration. Chemical shifts for $[P(C_6H_5)_3]_2CuBH_4$ ($\delta_{^1H} = 1.04$, $\delta_{^{31}P} = 2.82$) are upfield of those of $P(C_6H_5)_3CuBH_4$. The most probable structure, I, for $P(C_6H_5)_3CuBH_4$




I

is one in which the borohydride forms three hydrogen bridges to copper. Such bridging has been reported for the borohydrides of zirconium, hafnium, and uranium.[26]

Decomposition of $P(C_6H_5)CuBH_4$ is rapid above −20 °C. The course of decomposition was followed by allowing the NMR samples described above to come to room temperature while the phosphorus-31 signals were observed as a function of time. Within 15 min $P(C_6H_5)_3\cdot BH_3$ had increased markedly in concentration and $[P(C_6H_5)_3]_2CuBH_4$ had increased well beyond the minor impurity level. A black precipitate, believed to be CuH, was observed in the NMR tube. When maintained at room temperature for several days, this precipitate turned into metallic copper. Diborane(6) and $H_2$ were evolved during the decomposition process. On the basis of these observations, the decomposition of $P(C_6H_5)_3CuBH_4$ is believed to occur through reactions 6 and 7.

$$\begin{array}{lcl} P(C_6H_5)_3CuBH_4 \rightarrow & CuH & + P(C_6H_5)_3\cdot BH_3 \\ & \downarrow & \\ & Cu + {}^1/_2H_2 & \end{array} \qquad (6)$$

$$\begin{array}{lcl} 2P(C_6H_5)_3CuBH_4 \rightarrow [P(C_6H_5)_3]_2CuBH_4 + {}^1/_2B_2H_6 + & CuH & \\ & \downarrow & \\ & Cu + {}^1/_2H_2 & \end{array} \qquad (7)$$

## Experimental Section

**Equipment.** $^1H$ NMR spectra were obtained at 90 MHz with a Bruker HX-90 spectrometer with Fourier transform capabilities and at 100 MHz on a Varian HA-100 spectrometer. Chemical shifts are relative to $Si(CH_3)_4$ ($CHCl_3$ 7.25 ppm; $CH_2Cl_2$ 5.35 ppm). Boron-11 NMR spectra were collected at 32.1 MHz on an HA-100 spectrometer. Chemical shifts for boron-11 resonances are reported relative to $BF_3\cdot O(C_2H_5)_2$. Phosphorus-31 NMR spectra were recorded at 36.4 MHz by using a Bruker HX-90 spectrometer. Chemical shifts are relative to 85% $H_3PO_4$. For all of the NMR spectra, resonances downfield from the standard are assigned positive chemical shifts.

Infrared spectra of solids were obtained from Nujol mulls between KBr plates by using a Perkin-Elmer 457 spectrophotometer. Solution spectra were obtained by using a KBr cell with a path length of 0.1 mm.

X-ray powder diffraction patterns (Cu $K\alpha$ radiation) were obtained by using sealed capillaries in a Debye–Scherrer camera of 11.46 cm diameter.

Standard vacuum line equipment and glovebox techniques were used to handle air-sensitive and thermally unstable compounds.

**Analyses.** A several-millimole sample of a compound to be analyzed for copper was treated with a slight excess of nitric acid to convert copper(I) to copper(II). The resulting solution was analyzed for copper(II) as described in the literature.[27]

**Reagents.** The complexes $[P(C_6H_5)_3]_2CuBH_4$ and $[P(C_6H_5)_3]_2CuB_3H_8$ were prepared as described by Lippard and Ucko.[7] The method of Gill and Lippard was used to prepare $\{[P(C_6H_5)_3]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$.[17] Diborane(6) (Callery) was fractionated through a −145 °C trap, collected in a −196 °C trap, and stored under vacuum at −196 °C. A sample of $Cu_2B_{10}H_{10}$ was prepared for comparison by reaction of $CuSO_4$ with excess $K_2B_{10}H_{10}$ in aqueous solution.[21] Solvents for vacuum line use were dried over $LiAlH_4$ and distilled under vacuum. All other solvents were used as received.

**Tensimetric Titration of $[P(C_6H_5)_3]_2CuB_3H_8$ with $B_2H_6$. Synthesis of $CuB_3H_8$.** A solution of 0.819 g (1.30 mmol) of $[P(C_6H_5)_3]_2CuB_3H_8$ in dichloromethane was tensimetrically titrated with diborane(6).[28] Each portion of diborane(6) was allowed to react at 0 °C with the solution, but the solution was cooled to −78 °C for the vapor pressure readings. No visible changes were observed in the solution until after a 0.5 molar ratio of $B_2H_6$ to $[(C_6H_5)_3P]_2CuB_3H_8$ had been added. Further addition of diborane(6) resulted in the precipitation of a finely divided white solid. A break in the curve was observed at a ratio of 1.00 mol of $B_2H_6$/mol of $[P(C_6H_5)_3]_2CuB_3H_8$, which is consistent with reaction 1. The stoichiometry of this reaction was confirmed by recovery and measurement of the excess diborane.

The solid product was filtered from the solution under vacuum, washed several times with dry dichloromethane, and dried under vacuum to yield 0.1039 g (0.999 mmol, 76.8%) of $CuB_3H_8$. The dichloromethane-soluble product was isolated by evaporation of the solvent under vacuum, which gave 0.6483 g (2.348 mmol, 90.1%) of $P(C_6H_5)_3BH_3$, identified by its boron-11 NMR spectrum.

Infrared spectrum of $CuB_3H_8$ (Nujol mull) in $cm^{-1}$ (relative intensity): 2542 (m), 2530 (s), 2472 (sh), 2468 (s), 2120 (br), 2090 (br), 1332 (w), 1239 (w), 1165 (m), 1128 (m), 1090 (w), 1018 (w), 977 (m), 908 (m), 828 (w), 799 (m), 725 (w), 637 (m), 538 (w), 452 (w).

X-ray powder diffraction data for $CuB_3H_8$, in Å (relative intensity): 9.93 (m), 8.75 (w), 7.40 (w), 5.68 (s, br), 4.96 (s), 4.65 (w), 4.40 (m, br), 3.71 (m), 3.31 (w), 2.93 (w), 2.81 (w), 2.75 (m), 2.55 (w), 2.48 (vw), 2.27 (w), 2.20 (w), 2.05 (w), 1.98 (w), 1.88 (w, br), 1.63 (vw).

At room temperature, under vacuum, $CuB_3H_8$ is moderately stable, but in air it quickly decomposes to a black solid. Copper(I) octahydrotriborate is slightly soluble in dichloromethane, chloroform, benzene, dioxane, and dimethyl ether. Acetone, ethanol, acetonitrile, and water cause decomposition of the solid at room temperature.

**Preparation of $P(C_6H_5)_3CuB_3H_8$ Solutions.** To a suspension of 0.208 g (2.00 mmol) of $CuB_3H_8$ in 5 mL of solvent ($CHCl_3$ or $CD_2Cl_2$) was added 0.525 g (2.00 mmol) of $P(C_6H_5)_3$ or, alternatively, 1.256 g (2.00 mmol) of $[P(C_6H_5)_3]_2CuB_3H_8$. Agitation of the mixture resulted in rapid and complete dissolution of the $CuB_3H_8$. The resulting solution, which is thought to contain the intermediate $P(C_6H_5)_3CuB_3H_8$, decomposes over a period of several hours at room temperature.

The infrared spectrum of the $CHCl_3$ solution is almost identical with the solution spectrum of $[P(C_6H_5)_3]_2CuB_3H_8$, the only significant difference being the broadening of the B–H–B stretching absorption in $P(C_6H_5)_3CuB_3H_8$.

Attempts to isolate $P(C_6H_5)_3CuB_3H_8$ by removal of solvent or by precipitation with pentane or diethyl ether resulted in disproportionation to $[P(C_6H_5)_3]_2CuB_3H_8$ and $CuB_3H_8$, which were identified by their infrared spectra (Nujol mull) and X-ray powder diffraction patterns.

**Tensimetric Titration of $[P(C_6H_5)_3]_2CuBH_4$ wtih $B_2H_6$. Synthesis of $P(C_6H_5)_3CuBH_4$.** A solution of 0.799 g (1.32 mmol) of $[P(C_6H_5)_3]_2CuBH_4$ in 3 mL of dry dichloromethane was titrated tensimetrically with diborane(6) at −78 °C (see Figure 2). Occasional warming to −45 °C hastened the reaction. A sharp break in the titration curve was observed at a ratio of 0.50 mol of $B_2H_6$/mol of $[P(C_6H_5)_3]_2CuBH_4$. The excess $B_2H_6$ was recovered by fractionation through a −145 °C trap and measured tensimetrically to confirm the stoichiometry of the reaction.

Dry diethyl ether was distilled into the vessel in an attempt to selectively precipitate $P(C_6H_5)_3CuBH_4$. Precipitation did not occur. A similar experiment using pentane instead of diethyl ether resulted in simultaneous precipitation of both $P(C_6H_5)_3CuBH_4$ and $P(C_6H_5)_3{\cdot}BH_3$.

The average molecular weight of the product mixture was determined by freezing point depression, using a specially designed cryoscopic molecular weight apparatus which could be evacuated and used at low temperatures.[29] Solvents employed were chloroform (mp −65 °C, $K_f$ = 4.8 °C kg/mol) and chlorobenzene (mp −45 °C, $K_f$ = 7.0 °C kg/mol). Average molecular weights for the products were calculated from the freezing point depressions.

The values obtained were 300 (0.018 *m* in $C_6H_5Cl$), 303 (0.007 *m* in $C_6H_5Cl$), and 335 (0.007 *m* in $CHCl_3$), which are close to the average value expected for equimolar amounts of $P(C_6H_5)_3CuBH_4$ and $P(C_6H_5)_3{\cdot}BH_3$ (308.4).

**Synthesis of $Cu_2B_{10}H_{10}$.** A flask containing 1.49 g (1.05 mmol) of $\{[P(C_6H_5)_3]_2Cu\}_2B_{10}H_{10}{\cdot}CHCl_3$ was fitted to an extractor and evacuated, and 12 mL of dry dichloromethane was condensed into the flask. The mixture was cooled to −196 °C, and 3.05 mmol of $B_2H_6$ was condensed into the flask. The mixture was stirred for 1 h at 0 °C to give a clear solution ($Cu_2B_{10}H_{10}$ seems to be soluble in dichloromethane in the presence of $P(C_6H_5)_3{\cdot}BH_3$). The dichloromethane was distilled away and replaced with diethyl ether. The mixture was filtered, and the gummy precipitate on the frit was washed repeatedly with diethyl ether. The crude product was dissolved in acetonitrile, reprecipitated with diethyl ether, and dried under vacuum for several days to yield 0.188 g (0.767 mmol, 73.0%) of pure $Cu_2B_{10}H_{10}$. (Pure $Cu_2B_{10}H_{10}$ appears to be only slightly soluble in $CH_2Cl_2$.)

The second product of the reaction, $P(C_6H_5)_3BH_3$, was isolated by evaporation of solvent and weighed, yielding 0.872 g (3.16 mmol, 75.2%).

Infrared spectrum of $Cu_2B_{10}H_{10}$ (Nujol mull) in $cm^{-1}$ (relative intensity): 2570 (w), 2560 (s), 2540 (s), 2515 (s), 2480 (sh, br), 2280 (w, br), 2180 (m, br), 1080 (w, br), 963 (w), 713 (w).

X-ray powder diffraction data for $Cu_2B_{10}H_{10}$, in Å (relative intensity): 6.01 (s), 5.65 (m), 5.28 (s), 5.01 (vs, br), 4.70 (s), 4.13 (m), 3.89 (w), 3.76 (w), 3.62 (s), 3.47 (m), 3.34 (vw), 3.06 (m), 2.92 (s), 2.83 (w), 2.73 (m), 2.68 (m), 2.61 (vw), 2.49 (m), 2.38 (m), 2.18 (s), 2.14 (vw), 2.07 (vw), 2.04 (vw), 1.98 (vw), 1.89 (vw), 1.86 (vw), 1.84 (vw), 1.77 (vw), 1.74 (vw), 1.70 (w), 1.68 (w), 1.64 (vw), 1.60 (vw, br), 1.51 (vw), 1.48 (vw), 1.36 (vw), 1.34 (vw).

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**Registry No.** $[P(C_6H_5)_3]_2CuBH_4$, 16903-61-0; $[P(C_6H_5)_3]_2CuB_3H_8$, 12368-70-6; $\{[P(C_6H_5)_3]_2Cu\}_2B_{10}H_{10}$, 54020-26-7; $CuB_3H_8$, 71097-22-8; $P(C_6H_5)_3CuB_3H_8$, 71106-27-9; $P(C_6H_5)_3CuBH_4$, 71106-28-0; $Cu_2B_{10}H_{10}$, 52322-30-2; $B_2H_6$, 19287-45-7; $P(C_6H_5)_3BH_3$, 2049-55-0.

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