2,3-μ-Bis(triphenylphosphine)cuprio-pentaborane(9), -1-methylpentaborane(9), and -4-methylpentaborane(9)

By **Vincent T. Brice** and **Sheldon G. Shore,*** Evans Chemical Laboratories, Ohio State University, Columbus, Ohio 43210, U.S.A.

The title compounds have been prepared and isolated as crystalline solids. They appear to be more stable in air at room temperature than previously reported bridge-substituted derivatives of pentaborane(9). ^1H N.m.r. spectra are consistent with a structure in which Cu^I is inserted into the B–B bond of the B_5 framework. The compounds do not appear to be fluxional on the n.m.r. time scale.

THE deprotonation of pentaborane(9) [1-3] and its methyl derivatives [4] by removal of a bridging proton has been established. The resulting anions $[B_5H_8]^-$, $[1\text{-}MeB_5H_7]^-$, and $[2\text{-}MeB_5H_7]^-$ produce n.m.r. spectra which are consistent with fluxional systems in which the remaining bridge hydrogen atoms undergo rapid migration on the n.m.r. time scale while terminal hydrogens remain static. These anions are structurally analogous to B_6H_{10} which has been shown to display such dynamic behaviour.[5]

The availability of the basal boron–boron bond to chemical reaction in $[B_5H_8]^-$ has been demonstrated by the insertion of BH_3,[2,3] Me_3Si,[6] Me_3Ge,[7] Me_3Sn,[7] Me_2B,[8] and $F_3C(Me)P$ [9] into this site. The n.m.r. spectra of these bridge-substituted derivatives are consistent with static non-fluxional systems on the n.m.r. time scale. We have reported[10] the preparation of $\mu\text{-}(Ph_3P)_2Cu\text{-}B_5H_8$. However, the ^{11}B n.m.r. spectrum presents a question as to whether the bridge system is static or whether an exchange process occurs as opposed to the examples cited above.[2,3,6-9] In this paper we give further details concerning $2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}B_5H_8$ and the preparation and properties of $2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}1\text{-}MeB_5H_7$ and $2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}4\text{-}MeB_5H_7$.

RESULTS AND DISCUSSION

Preparation and Properties.—The compounds were prepared according to the general reaction (1), where

$$[CuCl(PPh_3)_3] + K[RB_5H_7] \longrightarrow 2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}RB_5H_7 + KCl + PPh_3 \quad (1)$$

R = H, and 1- or 4-Me. In the pure state the solid compounds are cream white and appear to exhibit greater stability in air at room temperature than previously reported bridge-substituted derivatives of pentaborane(9). After 2—3 weeks of exposure to air they were noticeably yellow; however, even after months of exposure to air their i.r. and n.m.r. spectra and *X*-ray powder patterns were principally those of the original compounds. In solution [CH_2Cl_2, $CHCl_3$, or tetrahydrofuran (thf) is the solvent] at ambient temperature they decompose slowly in the absence of air, but rapidly in the presence of air. Treatment of the compounds with HCl in Me_2O yielded the parent neutral borane (B_5H_9, $1\text{-}MeB_5H_8$, or $2\text{-}MeB_5H_8$) in *ca.* 80% yield.

^1H *N.m.r. Spectra.*—Over the temperature range studied, 24 (ambient)—60 °C, ^1H n.m.r. spectra were essentially unchanged. Table 1 contains a summary of the data. While spin coupling of terminal hydrogen atoms with boron is observed for the parent anions ($[B_5H_8]^-$, $[1\text{-}MeB_5H_7]^-$, and $[2\text{-}MeB_5H_7]^-$),[4] there was no apparent spin coupling of basal boron atoms with protons in the Cu^I derivatives. However, the spectra sharpened somewhat with decreasing temperature. This situation resembles that of $\mu\text{-}(Ph_3P)_2Cu\text{-}B_3H_8$ compared to $[B_3H_8]^-$ in which the effect of copper, due to quadrupolar relaxation, causes apparent decoupling of boron atoms from protons in the ^1H n.m.r. spectra.[11,12] The result is that singlets are observed where normally there would be quartets.

TABLE 1

^1H N.m.r. chemical shifts [a]

Compound	τ_t [b]	τ_a [b]	τ_μ [b]	CH_3
$2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}B_5H_8$	7·72 8·02	9·72	12·89 13·09	
$2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}1\text{-}MeB_5H_7$	7·64 7·98		12·35 12·68	9·75
$2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}4\text{-}MeB_5H_7$	7·92	9·7 [c]	12·15 12·45 13·01	9·71

[a] Relative to $SiMe_4$ (τ 10·00), in CH_2Cl_2 (τ 4·67); τ given in p.p.m. with an estimated precision of ±0·05 p.p.m., except as noted for *c*. [b] t = Terminal basal protons, a = apical terminal proton, and μ = bridge protons. Assignments are based on values given in ref. 5. [c] The apical proton resonance was broad and covered by the methyl resonance; τ_a is estimated to a precision of ±0·1 p.p.m.

The apical boron atom was spin coupled to the apical proton in $2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}B_5H_8$ and $2,3\text{-}\mu\text{-}(Ph_3P)_2Cu\text{-}4\text{-}MeB_5H_7$. However, it was necessary to irradiate each of these compounds at the resonance frequency of its apical ^{11}B atom in order to observe the apical proton resonance, since the undecoupled quartet was small and merged into the base line. In the case of 2,3-μ-

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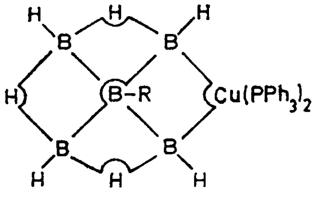
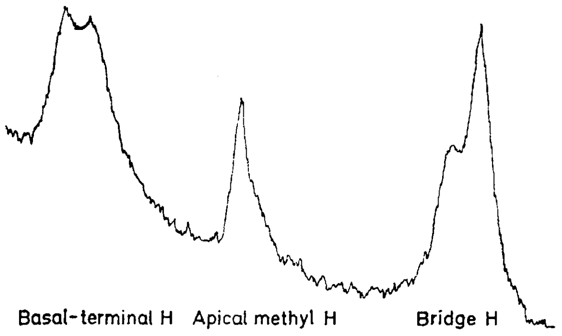
$(Ph_3P)_2Cu$-4-MeB_5H_7 the methyl and apical proton resonances overlapped. The chemical shift of the methyl resonance was determined from a spectrum in which the apical proton resonance was not spin decoupled from the apical boron and was thus not observed. The methyl resonance was markedly attenuated at high radio-frequency (r.f.) power, thus making possible observation of the apical proton resonance when it is decoupled from the apical boron.

^1H N.m.r. spectra of 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 and 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 were similar. The presence of two resonances from bridging hydrogen atoms and two resonances from terminal hydrogens in these spectra minimize the possibility of fluxional behaviour on the ^1H n.m.r. time scale over the temperature range studied. The spectra are consistent with static structure (I) in which Cu^I is inserted into a bridge site. The possibility of copper being joined to the boron framework through terminal hydrogens serving as bridging hydrogen atoms is remote since such arrangements have been shown to be fluxional.[12-14] Furthermore, bridging hydrogen atoms which are bonded to Cu have much broader resonances [12-14] than the proton resonances observed in the present study.* A typical ^1H n.m.r. spectrum of 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 is shown in the Figure. The base line is not level because of the high r.f. power required to distinguish the two separate bridge resonances. The high r.f. power has also caused attenuation of the methyl and basal-terminal resonances which saturate more readily than the bridge-proton resonances.

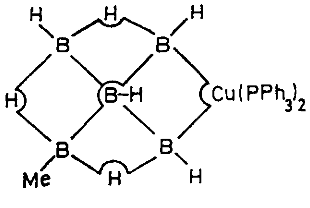


(I) R=H or Me

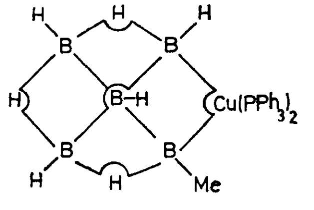


^1H N.m.r. spectrum of 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 at −60 °C in CH_2Cl_2

The ^1H n.m.r. spectrum of 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7 irradiated at the apical ^{11}B resonance frequency consisted of a broad peak assigned to unresolved basal-terminal proton resonances, three broad bridge-proton resonances of equal area, a single resonance from the methyl protons, and a resonance from the apical proton. The presence of three bridge resonances is consistent with the formation (as the predominant product) of one of two possible geometric isomers (II) and (III) (including their enantiomers). Based on studies of insertion of metals into boron–boron bonds of 2-MeB_6H_9 and $[2\text{-}MeB_6H_8]^-$ [15] and studies of the position of the boron–boron bond in static structures of $[2\text{-}MeB_5H_7]^-$ and $[2\text{-}MeB_6H_8]^-$,[15] we favour isomer (II) as the predominant product.



(II)



(III)

^{11}B *N.m.r. Spectra.*—Table 2 contains a summary of chemical shifts and assignments for the ^{11}B n.m.r. spectra of 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8, 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7, and 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7. Variable-temperature ^{11}B n.m.r. spectra of 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 are typical for members of this series. The apical resonance was a relatively sharp peak while basal resonances were unresolved, giving a broad peak which became markedly broader with decreasing temperature. In the case of 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7 the resonance of basal boron B_4 (the atom to which the methyl group is bound) appeared as a distinct peak from the unresolved resonances of the remaining basal boron atoms at 25 °C. However, with decreasing temperature, broadening of

TABLE 2

^{11}B N.m.r. chemical shifts [a]

Compound	δ(apex) [b]	*J*(apex) [c]	δ(base) [b]
2,3-μ-$(Ph_3P)_2Cu$-B_5H_8	47·8	140	15·0
2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7	38·9		14·3
2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7	45·5	142	0·0 (B_4) 17·4 ($B_{2,3,5}$)

[a] Relative to F_3B,OEt_2, $\delta = 0$. [b] Values are given in p.p.m. with an estimated precision of ±0·2 p.p.m. [c] Coupling constants, *J*, are given in Hz with an estimated precision of ±5 Hz.

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* *Note added in proof.* Recently, the presence of two broad bands at 2230 and 2325 cm^{-1} in the i.r. spectrum of $(Ph_3P)_2Cu$-$B_{10}H_{10}$ was cited as evidence for Cu–H–B interaction (T. E. Paxon, M. F. Hawthorne, L. D. Brown, and W. N. Lipscomb, *Inorg. Chem.*, 1974 **13**, 2772). We observe two very weak absorptions at *ca.* 2280 and 2340 cm^{-1} in the i.r. spectrum of 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 in Nujol mull. In KBr pellet a single slightly stronger band is observed at 2380 cm^{-1}. In CH_2Cl_2 solution this single band is observable for only *ca.* 15 min after sample preparation. While these observations might reflect some Cu–H–B interaction in the present case, the proton n.m.r. spectra strongly favour B–Cu–B interaction as the predominant interaction of Cu with the B_5H_8 moiety in solution.

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basal resonances was so severe that at 0 °C B_4 was no longer discernible as a separate resonance. In spectra of all the Cu^I derivatives, basal-boron resonances became so broad at *ca.* −50 °C that they merged with the base lines. In the light of the fact that n.m.r. spectra of bridge-inserted Group 4 derivatives of $[B_5H_8]^-$ show clearly resolved basal resonances, the broad basal resonances observed in the Cu^I derivatives and the marked broadening observed with decreased temperature probably arises mainly from the influence of quadrupolar relaxation of the copper nuclei.

EXPERIMENTAL

Reagents.—Pentaborane(9) was obtained from the Callery Chemical Company. 1-Methyl-[16] and 2-methyl-pentaborane(9)[17] were prepared according to the literature. The anions were prepared as described elsewhere.[2-4] Triphenylphosphine was purchased from Matheson, Coleman, and Bell. Chlorotris(triphenylphosphine)copper(I) was prepared according to the literature.[18] Solvents were dried over $LiAlH_4$ and stored in glass vessels with Teflon stopcocks.

Apparatus.—Standard vacuum-line techniques were employed. ^1H N.m.r. spectra were obtained at 100 MHz and ^{11}B spectra at 32·1 MHz using a Varian HA-100 high-resolution spectrometer. Heteronuclear decoupling was accomplished with a General Radio Co. 1164A coherent-decade frequency synthesiser and an Electronic Navigation Instrument Co. model 320LRF power amplifier. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer. *X*-Ray powder patterns were obtained on a North American Philips Co. *X*-ray machine using Cu-K_α radiation. Analyses were made by Schwartzkopf Microanalytical Laboratories.

Synthesis of 2,3-μ-*Bis*(*triphenylphosphine*)*cuprio-pentaborane*(9), -1-*methylpentaborane*(9), *and* -4-*methylpentaborane*(9).—Potassium hydride (0·200 g, 5·00 mmol) was weighed into a round-bottom flask (100 cm³) containing a Teflon-covered stirring bar in a dry-box. To a tip-tube side arm was added $[CuCl(PPh_3)_3]$ (3·54 g, 4·00 mmol). The side arm was attached to the flask. An adapter containing a Fischer–Porter Teflon stopcock was attached to the vessel which was then removed from the box to the vacuum line and evacuated. Into the vessel was condensed B_5H_9 (5·0 mmol) and tetrahydrofuran (thf, 10 cm³) at −196 °C. The vessel was then warmed to −78 °C at which temperature $[B_5H_8]^-$ is formed. After the evolution of hydrogen had stopped, the solution was frozen at −196 °C, the hydrogen pumped away, and methylene chloride (*ca.* 20—30 cm³) condensed in. The $[CuCl(PPh_3)_3]$ was tipped in and the vessel warmed until all the material was in solution (*ca.* −20 to −30 °C, but not above 0 °C). The mixture was stirred for 2 h at −45 °C and then overnight at −78 °C. Diethyl ether was added (*ca.* 30—40 cm³) until a heavy white precipitate appeared. On some occasions precipitation was slow, requiring the solution to remain stirring at −78 °C overnight. The mixture was frozen at −196 °C and, under nitrogen, the vessel was removed to an extractor. The mixture was then filtered at −78 °C on the vacuum line. After all solvent had been removed from the precipitate, the extractor was opened to the air. The *precipitate* of 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 was washed with water followed by diethyl ether and then pumped overnight on the vacuum line. Another method of purification was to extract the precipitate with CH_2Cl_2 at low temperature on the vacuum line, reprecipitate it with diethyl ether, and filter again as before. The compounds 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 and 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7 were prepared in the same manner. Yields of the compounds were 50, 53, and 65% respectively. All three compounds decompose between 95 and 100 °C [Found: C, 65·95; H, 6·00; B, 7·95; Cu, 9·70; P, 9·30. 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 requires C, 66·5; H, 5·85; B, 8·30; Cu, 9·80; P, 9·55. Found: C, 65·9; H, 6·05; B, 7·85; Cu, 9·35; P, 9·25. 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 requires C, 66·9; H, 6·05; B, 8·15; Cu, 9·55; P, 9·35. Found: C, 64·35; H, 5·50; B, 8·40; Cu, 9·50; P, 9·25. 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7 requires C, 66·9; H, 6·05; B, 8·15; Cu, 9·55; P, 9·35%]. The i.r. spectra showed B–H terminal stretches at: 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 2 570s, 2 535s, 2 510s, and 2 455s; 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 2 550s, 2 500s, and 2 450s; and 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7 2 570m, 2 540s, 2 480s, and 2 460m (sh) cm⁻¹. There were no B–H–B bridging stretches visible. They are apparently very weak and are covered by triphenylphosphine absorptions. The remainder of the spectra were characteristic of triphenylphosphine derivatives. *X*-Ray powder patterns, *d*/Å (strongest lines): 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 9·06 (vs), 7·40 (m), 6·90 (w), 6·51(m), 5·87 (w), 5·60 (m), 4·60 (s), 4·31 (m), and 3·94 (s); 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 10·65 (w), 9·23 (vs), 8·34 (m), 7·54 (m), 6·58 (m), 6·14 (m), 4·91 (m), 4·71 (s), 4·32 (m), and 4·06 (s); and 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7 12·41 (s), 10·54 (vs), 9·41 (s), 8·34 (m), 7·87 (m), 7·53 (m), 6·58 (m), 6·30 (m), 5·57 (w), 5·37 (s), 4·88 (m), 4·45 (s), and 4·00 (w).

Reaction of the Compounds with HCl.—In a typical reaction 2,3-μ-$(Ph_3P)_2Cu$-B_5H_8 (0·500 mmol) was weighed into a reaction vessel (50 cm³). Dimethyl ether (*ca.* 10 cm³) and an excess of HCl were then condensed into the tube. The mixture was stirred at −35 °C for 5 h. Fractionation of the solution yielded B_5H_9 (0·401 mmol, 80%). Similar reactions with 2,3-μ-$(Ph_3P)_2Cu$-1-MeB_5H_7 and 2,3-μ-$(Ph_3P)_2Cu$-4-MeB_5H_7 yielded 75% 1-MeB_5H_8 and 82% 2-MeB_5H_8, respectively.

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