

In the case of the bromo systems the values of the equilibrium constants are always smaller than 1 and also decreases with decreasing ligand basicity and increasing bulkiness. The 3-methyl-substituted pyridine complexes are marginally more stable than the 4-substituted complexes because the minor retardation seen in their displacement is not found in their formation. This fact explains why the reactions of the 2,6-dimethylpyridines and of the nucleophiles having $pK_a < 5$ with $[\text{AuBr}_4]^-$ could not be kinetically studied under our experimental conditions.

The larger stability of the chloro systems as compared to that of the bromo is mainly due to the fact that the affinity of Au(III) for pyridines lies between that for chloride and bromide and the variation of the other ligands in the complex has a minor effect, except insofar as the response to ligand bulkiness is affected.

Conclusions. As was pointed out when the study was first made, the lack of steric hindrance effects in the displacement of am from $[\text{AuCl}_3(\text{am})]$ by chloride (and other nucleophiles) indicates that the steric hindrance in the rate-determining transition state is not significantly greater than that in the final product, and it was suggested that the Au-N bond was fully developed in the rate-determining transition state and that the main source of repulsion was between the 2(6)-methyl groups and the *cis* ligands (which become axial in the transition state). The observation of strong steric effects in the reactions of $[\text{AuBr}_3(\text{am})]$ with Br^- (albeit less marked than in those of the reverse reactions) tells us that the

transition state is more crowded than both the reagents ground state and the products state. In order to avoid the paradoxical conclusion that there is less steric repulsion in $[\text{AuBr}_3(\text{am})]$ than in $[\text{AuCl}_3(\text{am})]$, we conclude that the 2(6)-methyl groups can no longer lie in the plane of the former complexes and therefore interfere with the two bromides in the trigonal plane of the transition state. A number of studies to examine this question in detail have suggested themselves, and these are now in progress.

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Registry No. $[\text{AuBr}_3(2,4,6\text{-trimethylpyridine})]$, 97374-28-2; $[\text{AuBr}_3(2,3,6\text{-trimethylpyridine})]$, 97374-29-3; $[\text{AuBr}_3(2,6\text{-dimethylpyridine})]$, 21113-12-2; $[\text{AuBr}_3(2,4\text{-dimethylpyridine})]$, 21113-14-4; $[\text{AuBr}_3(2,3\text{-dimethylpyridine})]$, 97374-30-6; $[\text{AuBr}_3(3,4\text{-dimethylpyridine})]$, 97374-31-7; $[\text{AuBr}_3(3,5\text{-dimethylpyridine})]$, 21113-13-3; $[\text{AuBr}_3(2\text{-methylpyridine})]$, 21113-09-7; $[\text{AuBr}_3(4\text{-methylpyridine})]$, 21113-11-1; $[\text{AuBr}_3(\text{pyridine})]$, 21524-04-9; $[\text{AuBr}_3(3\text{-chloropyridine})]$, 97374-32-8; $[\text{AuBr}_3(4\text{-cyanopyridine})]$, 21113-16-6; $[\text{AuBr}_4]^-$, 14337-14-5; HAuBr_4 , 17083-68-0; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 3,5-dimethylpyridine, 591-22-0; 3,4-dimethylpyridine, 583-58-4; 2-methylpyridine, 109-06-8; 2,3-dimethylpyridine, 583-61-9; 2,4-dimethylpyridine, 108-47-4; 2,6-dimethylpyridine, 108-48-5; 2,3,6-trimethylpyridine, 1462-84-6; 2,4,6-trimethylpyridine, 108-75-8; bromine, 7726-95-6.

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Phosphine-Ligated Copper(I) Derivatives of Dicarbahexaborane(8) and 2,3-Dimethyldicarbahexaborane(8)

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The reactions of $\text{K}[\text{R}_2\text{C}_2\text{B}_4\text{H}_5]$, where $\text{R}_2 = (\text{H})_2$ or $(\text{CH}_3)_2$, with $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuBr} \cdot 1/2\text{C}_6\text{H}_6$ or $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{CuI}$ afford respectively $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuC}_2\text{B}_4\text{H}_7$ (I), $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5$ (II), $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{CuC}_2\text{B}_4\text{H}_7 \cdot \text{CH}_2\text{Cl}_2$ (III), and $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{Cu}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5 \cdot 1/2\text{CH}_2\text{Cl}_2$ (IV). The species were characterized by boron-11 and proton NMR spectroscopies. Complexes I-IV exist as the nido-pentagonal-pyramidal cupriocarboranes in which the phosphine-ligated copper(I) electrophile has replaced a bridging proton in the parent carborane and thus occupies a bridging position between two basal boron atoms. Infrared spectral data may be interpreted to suggest the presence of copper-hydrogen-boron bridge bonds between the copper atom and the adjacent terminal hydrogens on basal boron atoms. Studies of the solution properties of the complexes I-IV in CD_2Cl_2 by ^{31}P NMR spectroscopy indicate that extensive phosphine ligand-exchange processes occur at temperatures down to -100°C .

Introduction

The Brønsted acidity of bridging hydrogen atoms in boron hydrides^{1,2} and the related carboranes^{3,4} is now well established. The resulting conjugate bases each possess at least one boron-boron bond that is susceptible to insertion of Lewis acids.⁵ The Lewis acids range from simple species such as H^+ and BH_3 ^{6,7} through more complex main-group^{5,8} and transition-metal moieties.^{1,9}

Since the first transition-metal-borane complex, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8$, was prepared from B_5H_9 ,¹⁰ many systems involving the insertion of transition-metal moieties into a basal boron-boron bond of the square-pyramidal nido-borane have been reported. Examples for the related nido-pentagonal-pyramidal species are not so well-known. The metalloboranes $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_6\text{H}_9$,^{10a} prepared from the $[\text{B}_6\text{H}_9]^-$ anion, and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8\text{Fe}(\text{CO})_3$,¹¹ prepared from the $[\text{B}_5\text{H}_8\text{Fe}(\text{CO})_3]^-$ ion, have been reported. For both species, infrared spectra^{10a,11,12} suggest the presence of a copper-hydrogen-boron bridge bond and, in the case of the latter, the presence of this bridge bond is indicated by the crystal structure. The carborane anion $[\text{C}_2\text{B}_4\text{H}_7]^-$, which is isostructural and isoelectronic with $[\text{B}_6\text{H}_9]^-$ and $[\text{B}_5\text{H}_8\text{Fe}(\text{CO})_3]^-$ in terms of the polyhedral skeletal electron pair theory,¹³ forms

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complexes in which the metal atoms of $[(C_6H_5)_3P]_2Rh^+$, $[(C_6H_5)_3PAu]^+$, $[C_6H_5Hg]^+$,¹⁴ and $[\eta^5-C_5H_5]Fe(CO)_2^+$ ¹⁵ insert into the boron-boron bond. None of these nido species exhibits evidence for metal-hydrogen-boron bonds.

In this paper we describe the synthesis and characterization of a series of new compounds with the formula $L_2CuR_2C_2B_4H_5$, where $L_2 = [(C_6H_5)_3P]_2$, $[(C_6H_5)_2PCH]_2$ and $R = H, CH_3$. We also discuss their solution behavior as indicated by ³¹P NMR spectrometry. Finally we discuss the interaction between the borane cage and the Cu atom and present some evidence that these species possess copper-hydrogen-boron bridge bonds.

Experimental Section

Reagents. Pentaborane(9) was obtained from Callery Chemical Co. and was distilled before use, 2,3-dicarbohexaborane(8) was prepared from B_2H_9 and C_2H_2 according to published methods,^{16,17} and 2,3-dimethyl-dicarbohexaborane(8) was prepared from 2-butyne and B_2H_6 in the presence of $(C_2H_5)_3N$ as recently reported.¹⁸ 1,2-Bis(diphenylphosphino)ethane (dppe) was obtained from Strem Chemicals Inc. and triphenylphosphine from Matheson Coleman and Bell. The compounds $[(C_6H_5)_3P]_2CuBr \cdot 1/2 C_6H_6$, (dppe)NiX₂, X = Cl, Br, and (dppe)CuI were prepared by literature methods.¹⁹⁻²² Solvents were refluxed for 2 days over LiAlH₄, KH, or P₄O₁₀ and distilled on a vacuum line into Pyrex storage vessels fitted with Teflon stopcocks. KH, obtained as a mineral oil suspension from Alfa Products, was washed repeatedly with anhydrous C₂H₁₂ before use. The activity of the powder was 94-98% as determined by reaction with methanol.

Apparatus. Standard high-vacuum-line and drybox techniques were employed in this work.²³ NMR spectra were obtained routinely on a Nicolet NT-300 high-resolution spectrometer operating at 300.1, 96.3, and 121.5 MHz to observe ¹H, ¹¹B, and ³¹P resonances, respectively. Some spectra were obtained on a JEOL FX-100 operating at 99.5 and 32.1 MHz for the observation of ¹H and ¹¹B resonances. All ¹¹B chemical shifts are reported in ppm, positive signs denoting a shift at a lower field than the standard BF₃O(C₂H₅)₂, and ¹H and ³¹P chemical shifts were measured relative to Si(CH₃)₄ and H₃PO₄, respectively, again positive shifts representing deshielding. IR spectra were run as Nujol mulls prepared in the drybox, or as KBr pellets, on Perkin-Elmer 337 and 457 spectrometers and also on a Perkin-Elmer MX 10 Fourier transform spectrometer. X-ray powder diffraction patterns were recorded on a General Electric XRD-5 system using Cu K α radiation.

Synthesis of 4,5-[μ -Bis(triphenylphosphine)copper(I)]-2,3-dicarbohexaborane(8), $[(C_6H_5)_3P]_2CuC_2B_4H_7$ (I). With use of a vacuum extractor attached to a reaction vessel with a side arm, 0.65 g (0.92 mmol) of $[(C_6H_5)_3P]_2CuBr \cdot 1/2 C_6H_6$ was tipped into a solution of $K[C_2B_4H_7]$ (0.95 mmol) in 1.2 mL of (CH₃)₂O at -196 °C. The $K[C_2B_4H_7]$ was prepared by deprotonation of C₂B₄H₈ at -78 °C with KH in (CH₃)₂O. Onto the reaction mixture at -196 °C was distilled 7.5 mL of CH₂Cl₂, and the system was allowed to warm to -35 °C and stirred for 2 h at this temperature and at -78 °C for a further 12 h. The resulting solution, which had a pale brown tint to it, was filtered slowly at -35 °C and the residue washed with 2 \times 5 mL portions of CH₂Cl₂. The copper(I)-carborane complex is only very sparingly soluble at -78 °C in CH₂Cl₂. The volatiles were then completely removed, and the off-white solid was transferred to another extractor under N₂. Five milliliters of CH₂Cl₂ was condensed in, and the mixture was stirred at -35 °C for 2 h when approximately 70% of the solid went into solution. A 9-mL portion of (C₂H₅)₂O was condensed in, and the mixture was stirred for 4 h at -78 °C. The white slurry was filtered slowly at -78 °C and washed with 3 \times 3 mL portions of (C₂H₅)₂O and 2 \times 5 mL portions of C₂H₁₂. The pure white solid, which was dried in vacuo, was obtained in a yield of >60% and melted at 137-140 °C with decomposition. Anal. Calcd for C₃₈H₃₇B₄CuP₂: C, 68.89; H, 5.63; P, 9.35; Cu, 9.58; B, 6.52. Found: C, 68.52; H, 5.65;

P, 9.18; Cu, 9.04; B, 6.77. The IR run as a Nujol mull showed the following absorptions in the ν_{B-H} stretching region: 2601 (sh), 2592 (m), 2557 (sh), 2548 (m), 2521 (m), 2388 (w, br) cm⁻¹. Several attempts to grow crystals at low temperatures were unsuccessful.

Synthesis of 4,5-[μ -Bis(triphenylphosphine)copper(I)]-2,3-dimethyl-dicarbohexaborane(8), $[(C_6H_5)_3P]_2CuC_2(CH_3)_2B_4H_5$ (II). In a typical reaction, in the drybox a two-neck reaction vessel was charged with KH (0.025 g, 0.62 mmol) and sealed with a rotatable solid addition tube containing $[(C_6H_5)_3P]_2CuBr \cdot 1/2 C_6H_6$ (0.40 g, 0.56 mmol). After evacuation on the vacuum line, 2 mL of THF and 0.74 mmol of C₂-(CH₃)₂B₄H₆ were condensed into the reaction vessel at -196 °C. Deprotonation under continual stirring proceeded in 15 min at -35 °C when 0.60 mmol of H₂ was evolved and the solution became clear. The use of THF rather than (CH₃)₂O facilitated dissolution of the copper ligand although ultimate removal of solvent is much easier when (CH₃)₂O is used. After deprotonation was complete, the H₂ was removed, 5-mL portions each of THF and CH₂Cl₂ were condensed in at -196 °C, the solution was warmed to -35 °C, and the $[(C_6H_5)_3P]_2CuBr \cdot 1/2 C_6H_6$ was added slowly from the tipper tube arm while the solution was stirred vigorously. The mixture was stirred at -35 °C for 4 h, at room temperature for 0.5 h, and overnight at -78 °C under a blanket of dry nitrogen. It was filtered at -78 °C to remove KBr and unreacted $[(C_6H_5)_3P]_2CuBr$, the solvent was distilled from the filtrate, and the extractor was taken into the drybox, where the residue was extracted with dry benzene and filtered. The benzene was removed by distillation on the vacuum line, and the product was dissolved in a minimum amount of CH₂Cl₂. Slow removal of the solvent resulted in the formation of pale yellow amorphous glasslike product. The yield was 0.10 g (0.14 mmol, 22%). No CH₂Cl₂ resonance of appreciable intensity was present in the proton NMR spectrum of the purified product. Anal. Calc for C₄₀H₄₁B₄CuP₂: C, 69.58; H, 5.98. Found: C, 66.89; H, 5.99. The IR spectrum, run as a KBr pellet, showed the following absorbances (cm⁻¹): 3080 (m), 2290 (m), 2950 (m), 2890 (m), 2560 (s), 2420 (m), 1490 (s), 1270 (m), 1100 (s), 1030 (m), 1000 (m), 800 (m), 740 (s), 695 (s). Several attempts to grow crystals at low temperatures were unsuccessful.

Synthesis of 4,5-[μ -[1,2-Bis(diphenylphosphino)ethane]copper(I)]-2,3-dicarbohexaborane(8), $[(C_6H_5)_2PCH_2]_2CuC_2B_4H_7$ (III). In a typical reaction, in the drybox, a two-neck reaction flask attached to an extractor was charged with KH (0.0485 g, 0.93 mmol) and sealed with a rotatable solid addition tube containing (dppe)CuI (0.5420 g, 0.921 mmol). After evacuation on the vacuum line, 1.1 mmol of C₂B₄H₈ and 5 mL of (C₂H₅)₂O were condensed in at -196 °C. Stirring at -78 and -45 °C for 15 min each afforded 0.95 mmol of H₂. Hydrogen gas, the (CH₃)₂O solvent, and excess C₂B₄H₈ were removed at -45 °C, leaving the white solid $K[C_2B_4H_7]$. Methylene chloride, 10 mL, was condensed in at -196 °C, the (dppe)CuI was tipped in, and additional CH₂Cl₂ was distilled in on top of the solid. The mixture was allowed to warm and stirred vigorously for 2 h at -78 °C, for 4 h at -45 °C and overnight at -78 °C under a blanket of dry N₂. The mixture was filtered at -78 °C, and the isolated solid remaining on the glass frit was identified as KI by its X-ray powder pattern. The amount of KI obtained was 0.15 g (0.90 mmol).

The pale yellow filtrate was frozen at -196 °C, and under positive flow of N₂ the flask was transferred to a clean extractor on the vacuum line. The solution was warmed to -45 °C and concentrated to 3 mL by removal of CH₂Cl₂ in vacuo. Diethyl ether, 5 mL, was distilled in at -196 °C, and the solution was allowed to warm to -78 °C without stirring. Standing overnight at -78 °C under a blanket of nitrogen resulted in precipitation of the product, which was isolated by filtration at -78 °C and repeatedly washed with cold (C₂H₅)₂O and C₂H₁₂ to give 0.05 g (10% yield) of yellow amorphous glasslike solid, which melted with decomposition at 74-77 °C. The presence of a resonance at 5.32 ppm in the proton NMR spectrum of the purified product suggested a CH₂Cl₂ adduct. Analysis suggested the presence of one methylene chloride molecule of solvation. Anal. Calcd for C₂₇H₃₃B₄Cl₂CuP₂: C, 56.07; H, 5.35; B, 6.96. Found: C, 55.66; H, 5.81; B, 6.42. The IR spectrum, run as a KBr pellet, shows absorbances (cm⁻¹) at 3060 (m), 3030 (m), 2925 (m), 2570 (s), 2510 (s), 2465 (m), 1733 (m), 1483 (m), 1435 (s), 1415 (m), 1100 (s), 740 (s), and 700 (s).

Attempts to obtain crystals by diffusion of C₂H₁₂ or (C₂H₅)₂O into a solution of copper-carborane product in CH₂Cl₂ at low temperature resulted in the formation of oils or brown solids.

Synthesis of 4,5-[μ -[1,2-Bis(diphenylphosphino)ethane]copper(I)]-2,3-dimethyl-dicarbohexaborane(8), $[(C_6H_5)_2PCH_2]_2CuC_2(CH_3)_2B_4H_5$ (IV). In a typical reaction, in the drybox, a two-neck reaction flask attached to an extractor was charged with KH (0.0562 g, 1.37 mmol) and sealed with a rotatable solid addition tube containing (dppe)CuI (0.806 g, 1.37 mmol). After evacuation on the vacuum line, 1.5 mmol of C₂-(CH₃)₂B₄H₆ and 2 mL of THF were condensed in at -196 °C. Stirring at -78 °C for 0.25 h afforded 1.25 mmol of H₂. Additional 10-mL amounts each of THF and CH₂Cl₂ were condensed in at -196 °C, the solution was

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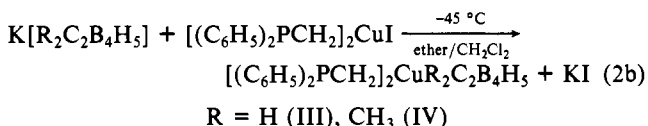
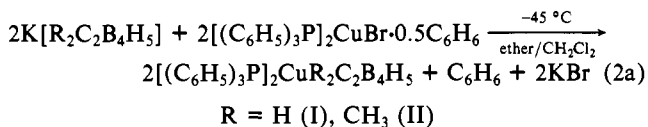
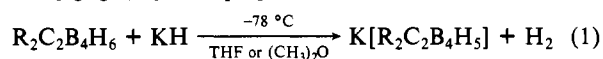
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warmed to $-78\text{ }^{\circ}\text{C}$, and the (dppe)CuI was added while the solution was stirred vigorously. Slow warming to $0\text{ }^{\circ}\text{C}$ was necessary to effect nearly complete dissolution of the (dppe)CuI ligand. The solution was stirred at $0\text{ }^{\circ}\text{C}$ for 0.25 h, during which time it turned pale yellow, at $-35\text{ }^{\circ}\text{C}$ for 4 h, and overnight at $-78\text{ }^{\circ}\text{C}$ under a blanket of N_2 . The mixture was filtered at $-78\text{ }^{\circ}\text{C}$, and the isolated solids remaining on the glass frit were identified as KI and unreacted (dppe)CuI by the X-ray powder pattern and infrared spectrum, respectively.

Reduction of the volume by half at $-35\text{ }^{\circ}\text{C}$ followed by introduction of 10 mL of $(\text{C}_2\text{H}_5)_2\text{O}$ at $-78\text{ }^{\circ}\text{C}$ failed to effect precipitation of the product after standing overnight at $-78\text{ }^{\circ}\text{C}$. The solvent was removed at $-35\text{ }^{\circ}\text{C}$ from the filtered solution, leaving behind a gummy yellow residue as the last traces were removed. Elemental analysis of the unpurified residue suggested that it was mainly (dppe)Cu $\text{C}_2(\text{CH}_2)_2\text{B}_4\text{H}_5$ contaminated with a few percent of $\text{K}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5$. The residue was extracted with C_6H_6 in a glovebox to remove the product from insoluble $\text{K}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5$, the solution was filtered, and the C_6H_6 was distilled off at room temperature under vacuum. The extracted product was dissolved in CH_2Cl_2 and was purified by slowly removing the CH_2Cl_2 solvent at $-35\text{ }^{\circ}\text{C}$ until crystallization of the product occurred. The final yield was 0.2 g (32% based on H_2 evolved) of pale yellow amorphous glasslike product, which decomposed to an orange gum at $60\text{ }^{\circ}\text{C}$. The presence of a resonance at 5.32 ppm in the proton NMR spectrum of the purified product suggested a CH_2Cl_2 adduct. Analysis suggested the presence of a half CH_2Cl_2 molecule of solvation. Anal. Calcd for $\text{C}_{31.5}\text{H}_{36}\text{B}_4\text{ClCuP}_2$: C, 60.40; H, 5.98; B, 7.13. Found: C, 60.23; H, 6.51; B, 6.84. The IR spectrum, run as a KBr pellet, shows absorbances (cm^{-1}) at 3080 (m), 2980 (m), 2930 (m), 2550 (s), 2500 (m), 2450 (m), 2380 (m), 1480 (m), 1430 (s), 1410 (m), 1260 (s), 1100 (s), 1020 (s), 880 (s), 730 (s), and 675 (s). Again attempts to grow crystals for structural analysis were unsuccessful.

Results and Discussion

Preparation and Properties. Copper(I) derivatives of $\text{C}_2\text{B}_4\text{H}_8$ and $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$ were prepared according to



Species I was isolated in 60% yield as a white powder that melted at $137\text{--}140\text{ }^{\circ}\text{C}$. The species is stable in the pure state at $25\text{ }^{\circ}\text{C}$ for several months and also possesses air stability. It is sparingly soluble in CH_2Cl_2 at $-78\text{ }^{\circ}\text{C}$, but at $-35\text{ }^{\circ}\text{C}$ solutions of the order of 0.05 M may be prepared. These solutions are stable at $-35\text{ }^{\circ}\text{C}$ but decompose slowly at temperatures above this. Solutions maintained at $25\text{ }^{\circ}\text{C}$ for 30 min turned pale brown and contained black particles, presumably of $\text{Cu}(0)$. Isolation of the dimethyl derivative II proved more difficult. The species was much more soluble in CH_2Cl_2 and had to be isolated by extraction with benzene. Species II was obtained as a pale yellow amorphous glasslike solid in 22% yield. It exhibited greater stability in solution than I.

The (dppe)Cu^I derivatives were isolated as the CH_2Cl_2 adducts. It is not unusual for phosphine-ligated copper(I) borane complexes or indeed (dppe)Cu^I halides²² to form solvates with CHCl_3 ²⁴ or CH_2Cl_2 .^{25,26} III was obtained in 10% yield as a pale yellow amorphous glasslike solid that melted between 74 and $77\text{ }^{\circ}\text{C}$. Chemical analysis suggested the formula (dppe)Cu $\text{C}_2\text{B}_4\text{H}_7 \cdot \text{CH}_2\text{Cl}_2$. IV was more difficult to isolate from CH_2Cl_2 solutions. Removal of CH_2Cl_2 afforded product contaminated with $\text{K}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5$. Final purification involved extraction with C_6H_6

Table I. Boron-11 NMR Data^a

atom	δ^b (J_{BH}^c)	
	$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuC}_2\text{B}_4\text{H}_7^d$	$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5$
basal B's	-0.41 (180)	-3.54 (152), -0.9 br
Apical B	-50.5 (165)	-46.5 (191)
atom	δ^b (J_{BH}^c)	
	$[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{CuC}_2\text{B}_4\text{H}_7$	$[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{Cu}(\text{CH}_3)_2\text{B}_4\text{H}_5$
B ⁴ , B ⁵	2.4 br	3.15 (163), -0.2 (177)
B ⁶	-5.67 (180)	-7.49 (133)
B ¹	-56.4 (173)	-46.8 (145)

^a For numbering scheme, see Figure 1. ^b Chemical shifts are expressed relative to $\delta(\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2) = 0$; deviations are ± 0.3 ppm. ^c J_{BH} values are in Hz; apical borons ± 5 Hz, basal borons ± 20 Hz. ^d Spectrum of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuC}_2\text{B}_4\text{H}_7$ recorded at 28.87 MHz; all others recorded at 96.3 MHz.

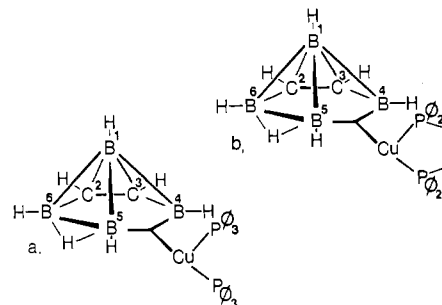


Figure 1. Proposed structures of (a) $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuC}_2\text{B}_4\text{H}_7$ and (b) $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{CuC}_2\text{B}_4\text{H}_7$.

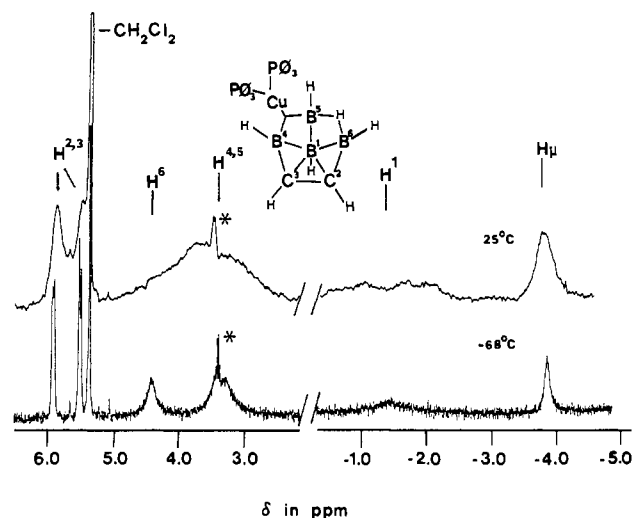


Figure 2. 300-MHz ^1H NMR spectra of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuC}_2\text{B}_4\text{H}_7$ (I) in CD_2Cl_2 at 25 and $-68\text{ }^{\circ}\text{C}$ in the borane cage region. Missing are the resonances due to C_6H_5 groups on P (see Table II). The asterisk indicates $(\text{C}_2\text{H}_5)_2\text{O}$ impurity.

followed by crystallization from CH_2Cl_2 to afford 32% yields of pale yellow solid (dppe)Cu $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5 \cdot 1/2\text{CH}_2\text{Cl}_2$, which melted at $60\text{ }^{\circ}\text{C}$ with decomposition. The species II, III, and IV were more soluble than I and more stable than I, and the lower yields reflect the fact that they were isolated with difficulty and work up took much longer. Attempts to grow crystals suitable for X-ray diffraction studies were unsuccessful.

Nuclear Magnetic Resonance Spectra. Proton and ^{11}B spectral data are listed in Tables I and II.

$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuC}_2\text{B}_4\text{H}_7$ (I). The 28.87-MHz boron-11 spectrum run at $-80\text{ }^{\circ}\text{C}$ is indicative of a pyramidal species and shows a diffuse low-field doublet and a sharper doublet at high field, both of which afford broad singlets on decoupling. The basal resonances are significantly overlapping, and the similarity in $^{11}\text{B}\text{--}^1\text{H}$ coupling constants gives the appearance of a single doublet. The peak width at half height ($W_{1/2}$) of the proton-decoupled basal resonance is

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Table II. 300-MHz Proton NMR Data^{a-c}

atom	δ	
	$[(C_6H_5)_3P]_2^-$ $CuC_2B_4H_7$	$[(C_6H_5)_3P]_2^-$ $Cu(CH_3)_2C_2B_4H_5$
phenyl H	7.17	7.13, 7.30
H ⁴ , H ⁵ (overlap)	3.3	2.94
H ⁶	4.38	3.9
H ² or H ³	5.86 ($J = 8.4$ Hz)	
H ³ or H ²	5.45 ($J = 7.2$ Hz)	
CH ₃		2.01, 1.94
H ¹	-1.48	-1.25
μ -H	-3.9	-3.5

atom	δ	
	$[(C_6H_5)_2PCH_2]_2^-$ $CuC_2B_4H_7$	$[(C_6H_5)_2PCH_2]^-$ $Cu(CH_3)_2C_2B_4H_5$
phenyl H	7.21	7.25
methylene	2.5	2.46
H ⁴ , H ⁵ (overlap)	3.2	} 1.5-3.5 obscured by CH ₂ and CH ₃ peaks
H ⁶	2.3	
H ² or H ³	5.55	
H ³ or H ²	6.04	
CH ₃		1.90, 1.94
H ¹	-1.74	-1.74
μ -H	-3.46	-3.2

^aChemical shifts expressed relative to $\delta(\text{Me}_4\text{Si}) = 0$, in CD_2Cl_2 .
^bValues are accurate to $\delta = \pm 0.04$, except for protons on B, which overlap. ^cFor numbering schemes, see Figure 1.

~ 80 Hz. The proton NMR spectrum is more informative, and it is shown in Figure 2 along with the proposed structure of I. The coupled spectra are shown at 25 and at -68°C . The boron quadrupole moment leads to decoupling of the $^1\text{H}-^{11}\text{B}$ spin-spin interaction, due to the availability of additional relaxation processes.²⁷ This effect is enhanced at lower temperatures and increasing solution viscosity. For pyramidal boranes, the apical boron nuclei have the longest relaxation times²⁸ and thus the observed decoupling is the least obvious. The resonance labeled H¹ at $\delta = -1.48$ is assigned as a partially collapsed 1:1:1:1 quartet arising from the proton on the apical boron atom. This general line shape is predicted for a partially decoupled 1:1:1:1 quartet.^{27,29,30} At -68°C a single broad resonance is observed presumably due to more effective thermal decoupling. In these copper(I) complexes the effects of thermal decoupling are enhanced by the quadrupole moment of the copper nuclei. These spectra are simpler than those for previously reported complexes of $\text{C}_2\text{B}_4\text{H}_8$. Thus the species $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_2\text{B}_4\text{H}_7$ ¹⁵ and $\mu\text{-5,6-MR}_3\text{C}_2\text{B}_4\text{H}_7$ complexes, where M = Si, Ge,³¹ Sn, Pb,³² all exhibit proton spectra in which the protons on basal boron atoms are observed as 1:1:1:1 quartets. On the other hand, I exhibits a spectrum in which the resonances for H⁶ and H⁴, H⁵ are single broad peaks. These assignments are made on the basis of their chemical shifts, relative peak areas and the expectation that the protons adjacent to the Cu atom would have chemical shifts similar to each other and different from that of the hydrogen bonded to B⁶. Again these resonances are partially decoupled from ^{11}B at 25°C and at -68°C this decoupling is essentially complete. The single bridging proton is assigned to the resonance at -3.9 ppm and falls in the expected region for such resonances. The hydrogens at positions 2 and 3, bonded to carbon, appear as sharp doublets at -68°C and as broad singlets at 25°C . The broadening of these resonances at 25°C is probably due to long-range coupling of these hydrogens to boron. The sharpening of these resonances to doublets ($J = 8.4, 7.2$ Hz) at -68°C suggests thermal decoupling of this interaction. Resonances due to the phenyl protons

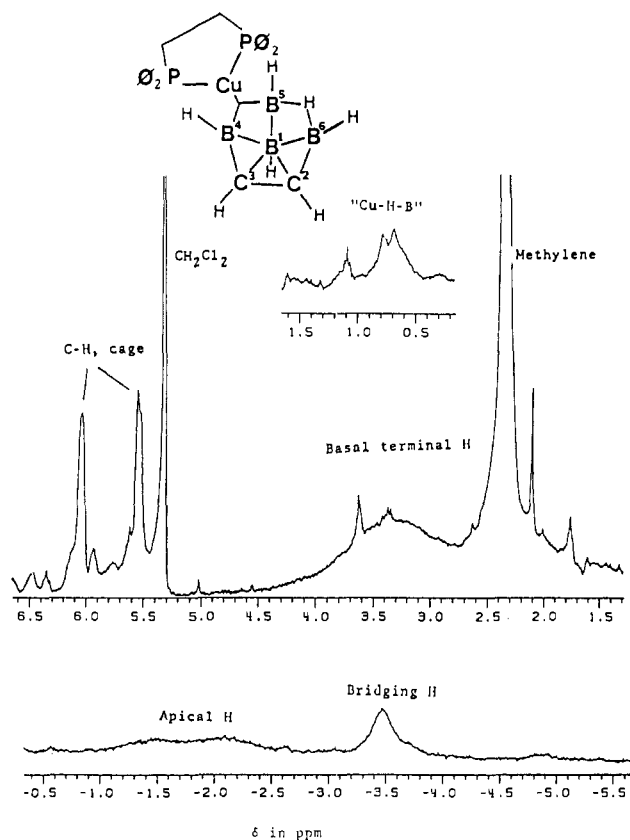


Figure 3. 300-MHz ^1H NMR spectrum of $[(C_6H_5)_2PCH_2]_2CuC_2B_4H_7 \cdot CH_2Cl_2$ in CD_2Cl_2 at -78°C . Omitted are resonances due to the phenyl H's on P (see Table II). The unlabeled spikes are due to traces of impurity protio solvents.

appear as a complex multiplet at $\delta = 7.11$. Boron-11 decoupling of this spectrum only slightly sharpens the resonances of the hydrogens bonded to boron, suggesting that the spectrum is thermally decoupled.³³ The spectra suggest that the system is not fluxional, and this observation is not surprising since the molecule does not contain a boron-boron bond and thus there are no sites into which either the bridging hydrogen or the copper moiety can move. This absence of fluxionality is noted for other $\text{C}_2\text{B}_4\text{H}_7^-$ derivatives; the spectra are similar to those obtained for the related species 5,6- $[(C_5H_5)Fe(\text{CO})_2]C_2B_4H_7^-$ and 5,6-(μ -metalloid) $\text{C}_2\text{B}_4\text{H}_7^-$ derivatives^{15,31,32}.

$[(C_6H_5)_3P]_2Cu(CH_3)_2C_2B_4H_5$ (II). The 96.3-MHz boron-11 spectrum exhibits two resonances in the region where basal borons are expected to appear. A doublet, $\delta = -3.54$ ($J = 152$ Hz), overlaps with another doublet at $\delta = -0.9$; relative areas are $\sim 2:1$. The apical boron appears as a doublet at $\delta = -46.5$ ($J = 191$ Hz). The 300-MHz proton spectrum is similar to that for the related species I, and the data are listed in Table II. The two methyl resonances appear as singlets, and a very low intensity peak due to $[(CH_3)_2C_2B_4H_5]^-$ is observed presumably due to some dissociation in solution. The basal terminal H's appear as well-separated broad resonances ($W_{1/2} = 20$ Hz) in area ratio 1:2 at 3.9 and 2.94 ppm, respectively. The other data listed in Table II are similar to these listed for I.

$[(C_6H_5)_2PCH_2]_2CuC_2B_4H_7$ (III). Boron-11 spectra, listed in Table I, distinguish the B⁴, B⁵ and B⁶ and B¹ environments, and the spectra are typical for $\text{C}_2\text{B}_4\text{H}_8$ derivatives. The 300-MHz proton spectrum at -78°C that is tabulated in Table II is displayed in Figure 3. This species, which crystallizes out as a CH_2Cl_2 solvate, exhibits a strong resonance due to CH_2Cl_2 , at $\delta = 5.32$; however, this does not obscure the well-resolved resonances for

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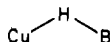
(33) Some preliminary spectral data were obtained for I at 90 MHz. Decoupling to ^{11}B was possible for these spectra only. We acknowledge the assistance of Dr. C. Cottrell of Ohio State University for these spectra. All other spectra were obtained at 300 MHz.

Table III. Proton-Decoupled 121.5-MHz Phosphorus-31 NMR Data^a

temp, °C	[(C ₆ H ₅) ₃ P] ₂ CuCu ₂ B ₄ H ₇		[(C ₆ H ₅) ₃ P] ₂ - Cu(CH ₃) ₂ C ₂ B ₄ H ₅		[(C ₆ H ₅) ₂ PCH ₂] ₂ - CuCu ₂ B ₄ H ₇		[(C ₆ H ₅) ₂ PCH ₂] ₂ - Cu(CH ₃) ₂ C ₂ B ₄ H ₅	
	δ	W _{1/2} , Hz	δ	W _{1/2} , Hz	δ	W _{1/2} , Hz	δ	W _{1/2} , Hz
-20			-1.79	63				
-40	-2.94	53	-1.89	27	7.72	865	7.78	581
-60	-3.08	53	-1.94	18	7.73	600	7.78	422
-94	-3.50	31	-2.89	12			7.78	338

^a Chemical shifts relative to H₃PO₄; solvent CD₂Cl₂. At 0 °C, δ(dppe) = -12.6 and δ(Ph₃P) = -5.9.

the protons bonded to cage C atoms at 5.55 and 6.04 ppm. The resonance arising from the methylene protons on the ligand (δ = 2.5) overlaps with the region in which the basal hydrogens appear; however, two broad resonances are discernible at δ = 3.2 (H⁴, H⁵) and δ = ~2.3 (H⁶). The apical hydrogen appears as a partially collapsed quartet at δ = -1.74, and the bridge hydrogen is seen at δ = -3.46. The methylene protons appear as a single resonance with multiplet structure at δ = 2.33. On the basis of the predicted static structure shown in Figure 1, equivalent environments for the methylene protons on the dppe ligand would not be expected. A broad resonance exhibiting some fine structure has also been reported for the methylene protons of the previously reported³⁴ dppe-ligated Ni(II), Pt(II), and Pd(II) derivatives of [B₅H₅]⁻. Therefore, either the resonances of the expected AA'BB' pattern are too broad to be resolved or there exists a process that exchanges the ends of the dppe ligand such as a bidentate-unidentate equilibrium. This possibility is discussed later. Although complete dissociation of the dppe ligand may occur, it need not be invoked to explain the NMR spectrum. Additional support for this type of equilibrium is provided by the ³¹P NMR spectrum which comprises only one resonance. The protons on the phenyl rings of the dppe ligand appear as two multiplets, area ratio 3:2, at 7.13 and 7.30 ppm. A weak, relatively narrow (W_{1/2} = 50 Hz) resonance is observed at 0.7 ppm in the proton spectrum. This is in the region where a



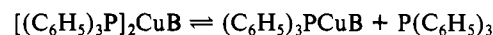
bridge bond (hereafter referred to as a bent Cu-H-B bridge bond) would occur, and this is discussed later.

[(C₆H₅)₂PCH₂]₂Cu(CH₃)₂C₂B₄H₅ (IV). Data for the boron-11 NMR spectrum are given in Table I. This spectrum also exhibits resonances assigned to traces of carborane anion in solution, but the spectrum is easily recognized. Three doublets assigned to the three basal borons at δ = 3.15, -0.2 (B⁴, B⁵) and δ = -7.49 (B⁶) collapse to singlets on decoupling, and the single upfield resonance δ = -46.8 ppm (B¹) decouples to a singlet. This spectrum is indicative of a relatively unperturbed pyramidal arrangement, and this is confirmed by the proton spectrum, which resembles that for III except the spectrum is dominated by the methyl resonances on the cage carbon atoms. These occur as two sharp singlets at δ = 1.90 and 1.94. The hydrogens H⁴, H⁵, and H⁶, which are not assigned, are seen as two broad resonances in the region δ = 1.5-3.5 and are further obscured by the intense ligand methylene resonance at δ = 2.46. The apex and bridge hydrogens are clearly seen at δ = -1.74 and δ = -3.2 as a partially collapsed multiplet and a broad singlet, respectively. The protons on the phenyl rings of the dppe ligand give rise to a multiplet centered at 7.25 ppm, and a resonance at 5.32 ppm indicates the presence of solvated methylene chloride.

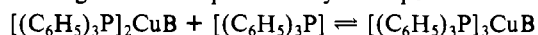
Phosphorus-31 Spectra. As indicated in Table III, the ³¹P NMR spectra in CD₂Cl₂ all exhibit only one major resonance over a range of temperatures and this falls downfield of that for pure ligand. Assuming the proposed structures are correct, two resonances are expected. This observation of one resonance from a structure with two inequivalent P atoms is best interpreted in terms of a rapid equilibrium of low activation energy that exchanges P environments. It is well established that the phosphine

ligands on copper or other coinage metal halides or borane complexes are labile.^{25,35-37} Indeed, phosphine ligands may be removed from borane complexes by titration with BH₃ in solution³⁶ to generate R₃PBH₃ and the ligands in [(C₆H₅)₃P]₂CuB₅H₈ may be replaced by stirring with excess³⁷ dppe at 40 °C.

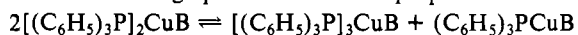
Spectra of the (C₆H₅)₃P complexes, I and II, exhibit temperature dependence; the single resonance moves about 1 ppm upfield as the solution is cooled from -20 to 94 °C. I exhibits only a single resonance whereas II shows an intense peak surrounded by small shoulders and peaks. The positions and half-widths of the small resonances are temperature dependent. This observation suggests the presence of several minor species. It is known that, for copper(I) phosphine complexes, discrete crystalline materials often dissolve to afford several solution species,³⁸⁻⁴⁰ including coordinatively unsaturated complexes, uncomplexed metal moieties, and polynuclear species. In our study the presence of only one resonance for I suggests that ligand exchange is more rapid for this species. Also the line width for I shows much less dependence on temperature than that for II. At low temperature the resonance for I narrows slightly whereas that for II narrows significantly. Equimolar mixtures of II and (C₆H₅)₃P exhibit only one resonance between +20 and -100 °C. The position of this single resonance is temperature dependent. At 20 °C the single sharp resonance is observed at δ = -4.38 (W_{1/2} = 43 Hz) but on cooling it shifts upfield so that, at -100 °C, a much broader resonance is seen at δ = -6.95 (W_{1/2} = 183 Hz). Addition of incremental quantities of free (C₆H₅)₃P to the solution at room temperature causes the single resonance to move upfield to a limiting value of δ = -4.83, still downfield of the resonance for pure ligand (δ = -5.09). These data suggest that an equilibrium exists between complex and free ligand in solution for both I and II as indicated:



(B = borane anion). In the case of II, above -40 °C, the single resonance seen for a solution containing equal amounts of II and (C₆H₅)₃P falls between those of the complex and free ligand, which is where the averaged resonance is expected; however, at temperatures below -40 °C, the solution exhibits a ³¹P resonance at fields increasingly higher than that of free ligand as the temperature is lowered. The reason for this is uncertain; however, ring current effects, known for pyramidal boranes, may be responsible for this shielding effect at lower temperatures. Important processes that exchange ³¹P environments for these species must include both dissociative and associative processes. Thus in addition to the monodentate/bidentate equilibrium proposed above, the following associative process may be important:



Coordination of a third mole of phosphine allows the Cu atom to achieve the desired 18e configuration. Furthermore, both L₂CuX and L₃CuX (when X = halide or borane anion) species are well established.⁴⁰ Another process that may contribute to the solution-exchange processes is the disproportionation



Solutions of I and II exhibit reversible color changes upon warming

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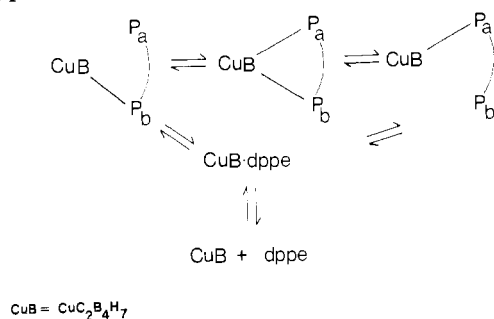
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Scheme I



and cooling. At $-50\text{ }^\circ\text{C}$ solutions are almost colorless to faint yellow in hue whereas on warming the solutions turn bright yellow. Whether these are charge-transfer bands due to formation of carborane ion and L_2Cu^+ ion or some other species is not clear; however, similar effects are observed for $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_{10}\text{H}_{13}$, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{AgB}_{10}\text{H}_{13}$, and $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{CuB}_{10}\text{H}_{13}$, which are known to undergo ligand exchange in solution.⁴¹

The ^{31}P NMR spectra of the dppe derivatives of $\text{C}_2\text{B}_4\text{H}_6$ and $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$, i.e. III and IV, are understandably more complex since ligand dissociation leads to many more possible solution species. Thus the spectrum of III includes low-intensity resonances at approximately -14 , -11 , and -7.5 ppm in addition to the broad principal resonance at $\delta = 7.73$ ($W_{1/2} = 865$ Hz). The minor species comprise about 30% of the total intensity. The resonances sharpen at lower temperatures. At $0\text{ }^\circ\text{C}$ an approximately equimolar mixture of III and dppe in CDCl_2 exhibits no observable resonance, suggesting a rapid exchange between coordinated and free dppe. When excess dppe is added, the ligand is observed at its normal position ($\delta = -12.6$). At $-110\text{ }^\circ\text{C}$ this solution exhibits the free ligand resonance, slightly shifted upfield, as a sharp peak ($\delta = -14.5$), a broad resonance at 8.66 ppm ($W_{1/2} = 486$ Hz) presumably due to the complex III, and a very weak one at -7.8 ppm. Warming the solution causes the free ligand resonance to move downfield, and at $-60\text{ }^\circ\text{C}$, the resonance that appeared at -7.8 ppm had disappeared and the resonance due to the complex had broadened significantly. As temperatures are raised above $-60\text{ }^\circ\text{C}$, only the resonance due to free dppe is seen and this continues to move downfield. Again the observation of one major ^{31}P resonance for the complex III suggests that the two P environments are exchanged averaged and the data obtained in the presence of free ligand support this proposal. For the bidentate ligand, excluding polynuclear species that undoubtedly are present in solution⁴⁰ Scheme I, which shows exchanging P environments, is proposed. The ^{31}P NMR spectra for IV behave similarly; several minor species corresponding to $\sim 20\%$ of the total intensity are observed upfield from the resonance observed for IV ($\delta = 7.83$). The temperature dependence of the ^{31}P NMR spectrum of an equimolar mixture of IV and dppe in CDCl_2 is shown in Figure 4. At $-100\text{ }^\circ\text{C}$ the most prominent peak is observed at $\delta = 8.55$ ($W_{1/2} = 268$ Hz) along with very weak broad resonances at ~ 0 , -3.42 , and -9.26 ppm and sharp resonances at -13.35 and -14.6 ppm. Raising the temperature to $-60\text{ }^\circ\text{C}$ causes coalescence of the small resonances into a single broad one at $\delta = -7.76$ ppm ($W_{1/2} = 729$ Hz). Further warming causes this resonance to sharpen and shift upfield slightly while the resonance that appears at $\delta = 8.55$ at $-100\text{ }^\circ\text{C}$ broadens, shifts slightly upfield, and eventually at $\sim 30\text{ }^\circ\text{C}$, merges with the baseline. At temperatures above $-10\text{ }^\circ\text{C}$, essentially only one sharp resonance at $\delta = -9.11$ is observed.

With use of the ^{31}P NMR data, estimates of the energy barriers for the exchange processes may be made. Thus from Figure 4, assuming that the low-field resonance at $-100\text{ }^\circ\text{C}$ is due to complex and the high-field resonance is free dppe, the two major resonances between these two, i.e. at -9.26 and -3.42 ppm, may arise from the two inequivalent P atoms of the monodentate complex, P_a and

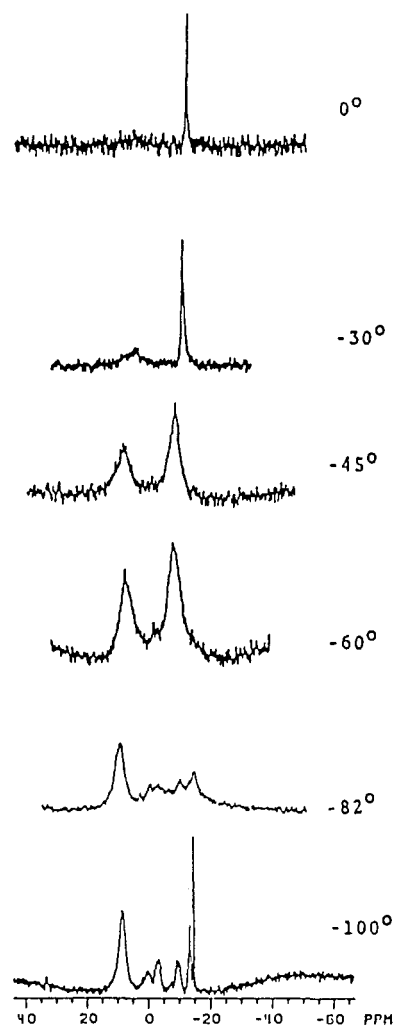


Figure 4. Temperature dependence of the 121.5-MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of an approximately equimolar mixture of dppe and $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{CuC}_2(\text{CH}_3)_2\text{B}_4\text{H}_5$ in CD_2Cl_2 .

P_a , respectively, from Scheme I. A value of 9.3 kcal/mol is estimated for the energy barrier for exchange of monodentate and free dppe by using approximate methods.⁴² This assumes a coalescence temperature of $-60\text{ }^\circ\text{C}$ and a $\delta\nu$ value of 588 Hz. The energy barrier exchange of bidentate and uncomplexed dppe for III and IV may also be estimated from the data. Thus if the coalescence temperatures for dppe exchange are assumed to be -45 and $0\text{ }^\circ\text{C}$ and the difference between the resonance frequencies of the coalescing nuclei is 2794 Hz, then the approximate energy barriers are 9 and 11 kcal/mol, respectively. This confirms that ligand exchange for $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{CuC}_2\text{B}_4\text{H}_7$ is more rapid than that of $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{CuC}_2(\text{CH}_3)_2\text{B}_4\text{H}_5$. Assuming that the electron density on the anion in I and III is higher than that for II and IV, this trend is the opposite of that suggested previously.³⁹ In the series $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{CuX}$, dissociation decreases in the order $\text{X} = \text{Cl} > \text{X} = \text{Br} > \text{X} = \text{I}$ and the authors conclude that this is due to the higher electron density on the anion. On the basis of the greater electron-releasing inductive effect of the CH_3 group compared to that of H , it could be the case here that ionic size and the charge dispersion effects are more important in these systems.

Infrared Spectra. The spectra, obtained as Nujol mulls or KBr disks, are tabulated in the Experimental Section. The B-H

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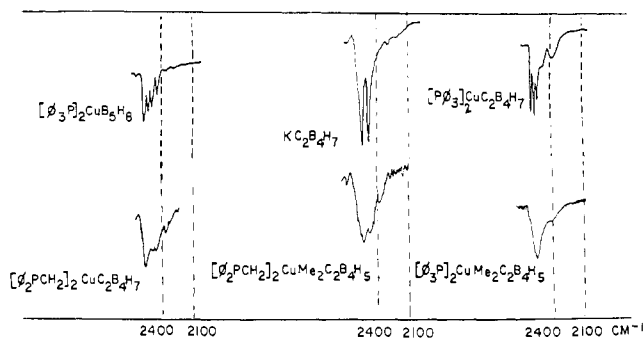
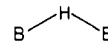


Figure 5. Infrared spectra of the species I–IV along with those for $[\text{Ph}_3\text{P}]_2\text{CuB}_5\text{H}_8$ and $\text{KC}_2\text{B}_4\text{H}_7$. The upper spectra were run as Nujol mulls and the lower ones as KBr disks. The spectrum of $[\text{Ph}_3\text{P}]_2\text{CuB}_5\text{H}_8$ was reproduced with permission from ref 44.

stretching regions of the infrared spectra, i.e. the range 2100–2600 cm^{-1} , are displayed in Figure 5 for species I–IV along with those for $\text{K}[\text{C}_2\text{B}_4\text{H}_7]$ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8$. NMR spectra¹⁰ of the last complex indicated that the $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}^+$ electrophile replaces a proton and occupies a basal bridge bonding site. The more recent crystal structure determination⁴³ confirms this and provides no evidence for interaction of the Cu atom with the terminal hydrogens on the adjacent boron atoms. The structure indicates the Cu atom lies well below the basal plane of the square pyramid. The infrared spectrum of this species⁴⁴ shows no absorptions in the region 2100–2400 cm^{-1} . This region is where absorptions due to bent Cu–H–B bridge stretching modes have been assigned.²⁴ There is now a series of cuprioboranes in which the presence of a bent Cu–H–B bridge bond is confirmed by crystal structure data and which show absorption bands^{44,45} in the region 2100–2400 cm^{-1} . It is now generally accepted that this region in the infrared is diagnostic for the presence of bent Cu–H–B bridge bonds. Thus the following species, all of which possess bent Cu–H–B bridges, exhibit bands in this region as indicated: $\text{Cu}^1\text{B}_{10}\text{H}_{10}$, 2100–2300 br ;⁴⁵ $\text{Cu}^1\text{B}_3\text{H}_8$, 2250;³⁶ $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuBH}_4$, 2240–2290;⁴⁶ $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_3\text{H}_8$, 2000–2200;⁴⁶ $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_{10}\text{H}_{10}\cdot\text{CHCl}_3$, 2150–2400;²⁴ $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}(\text{CNBH}_3)\}_2$, 2207–2200;⁴⁷ $[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P}]_3\text{CuBH}_4$, 2045 cm^{-1} .⁴⁸ In view of the fact that, in many BH_4^- derivatives, absorption bands due to B–H stretching modes typically fall 100–200 cm^{-1} lower in frequency than those of other boranes, all of the above data lend support to the infrared criteria for the presence of bent Cu–H–B bridge bonds. There are two pentagonal-pyramidal cuprioboranes that are considered to possess such bridging bonds. The copper(I) derivatives of the ferrapentaborane $\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3$, in which a $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}^+$ moiety replaces a bridging proton,¹¹ contains a single bent Cu–H–B bridge bond. This is demonstrated by the crystal structure of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_9\text{Fe}(\text{CO})_3$ and is further supported by the presence of a weak, but distinctive, infrared band at 2292 cm^{-1} . The species $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_9$, isoelectronic¹³ with $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_9\text{Fe}(\text{CO})_3$ and I, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuC}_2\text{B}_4\text{H}_7$, contains a band in the infrared^{10a,12} at 2360 cm^{-1} . Although the crystal structure of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_6\text{H}_9$ has not been determined, the presence of the infrared band and the fact that the species only differs from the ferraborane derivative described above in that an $\text{Fe}(\text{CO})_3$ moiety is subrogated by the isolobal BH group suggests that it also possesses a bent Cu–H–B bridge bond. We see from Figure 5 that each of the species I–IV contain either weak absorptions or shoulder absorptions in the diagnostic region. Since $\text{C}_2\text{B}_4\text{H}_8$ is formally related to B_6H_{10} and $(\text{CO})_3\text{FeB}_5\text{H}_9$, by virtue

of the fact that the polyhedral electron counts for CH, BH_2 , and $(\text{CO})_3\text{Fe-H}$ are equal,¹³ it is not surprising that species in which a $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cu}^+$ electrophile replaces a proton behaves similarly to the other pentagonal-pyramidal boranes. Clearly the infrared data suggest that a bent Cu–H–B bridge bond may also exist in the $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$ derivatives. All of the examples where it appears that bonding between the copper atom and the terminal hydrogen on adjacent basal boron atoms occurs are pentagonal-pyramidal species. It has been suggested¹¹ that the exo hydrogens on adjacent borons of a pentagonal-pyramidal base are more accessible than those in a square pyramid. In $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_9\text{Fe}(\text{CO})_3$ the Cu atom occupies an elevated position, only 12° below the basal plane of the pentagonal pyramid; however, for $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8$, the Cu atom is 52° from coplanarity with the basal plane.⁴³ In the former, where exo hydrogens are more accessible, the Cu atom is able to achieve the 18-electron configuration via formation of a bent Cu–H–B bond; however, in the cases where these exo hydrogens are not so accessible, the Cu atom retains the 16-electron configuration. Thus we suggest that the pentagonal-pyramidal species reported herein, I–IV, for which the infrared spectra exhibit bands in the diagnostic region, do indeed contain the bent Cu–H–B bridge bonds. There is no precedent for such bonding in *nido*-metalloboranes; however, there is evidence for a weak Hg–bridge hydrogen interaction⁴⁹ in $(\mu\text{-Hg})[(\eta^2\text{-C}_2\text{H}_5)_2\text{Co}(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_4]_2$. This example is quite different from what we are suggesting herein. The metal–hydrogen–boron interaction involves a bridge hydrogen rather than a terminal hydrogen, and the mercury atom, which replaces protons and bridges a pair of pentagonal-pyramidal cobaltacarboranes, forms a plane with the adjacent borons that lies at an angle of 67.27° to the basal planes of the pentagonal-pyramidal cobaltacarboranes.

If indeed there is a bent Cu–H–B bridge bond in the complexes I–IV, then there should appear in the ¹H NMR spectrum a resonance corresponding to this proton. Resonances falling in the region $\delta = 0.8\text{--}1.0$ have been assigned in the spectra^{44,50} of copper(I) borane complexes to such Cu–H–B bridge bonds. This region is obscured by resonances from protio solvents in samples of I and IV although in each case a broad weak resonance is observed at about 0.8 ppm. For III, a distinct weak resonance is seen at 0.7 ppm (see Figure 3) which may arise from such a bond; however, no such resonance is observed for II. Many systems containing bent Cu–H–B bridge bonds have been observed to be fluxional.^{44,51} The data presented herein do not suggest any fluxional motion involving positions of hydrogens in the pentagonal base nor of the metal moiety relative to the positions of the basal atom vertices of the pentagonal pyramid. Fluxionality for these systems is not expected nor is rotation around the Cu–carborane cage axis, except at high temperatures. This latter effect would not be observed since the species are unstable in solutions at high temperatures. The lability of the phosphine ligands is the best explanation for the observation of only one ³¹P resonance for I–IV. The interaction between the Cu atom and the deprotonated

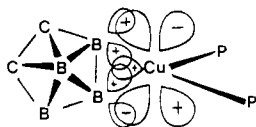


moiety may be considered to be analogous to that between a transition metal and an olefin. This point has been given much attention^{9c,51} in the case of the interaction between an $\text{Fe}(\text{CO})_4$ fragment and B–B bonds. Indeed there are many similarities between η^2 metal–olefin bonds and bridging metalloboranes. The geometries of the two classes of compounds are similar, and in the case of Zeise's salt, the C_2H_4 may be replaced⁵² by the B–B bond of B_6H_{10} . Furthermore, it has been pointed out that the σ -donation, π -back-donation model of Dewar, Chatt, and Duncan could be used to describe the bonding^{9c,51} between the $\text{Fe}(\text{CO})_4$ or Cl_2Pt fragments and the basal B–B bond in B_6H_{10} .

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The B-B bond in B_6H_{10} is ~ 0.22 Å shorter⁵² than in the complex $(B_6H_{10})_2PtCl_2$. This can be explained in terms of back-donation of electron density from nonbonding d orbitals on the metal fragment to an antibonding B-B orbital. Theoretical calculations on B_6H_{10} suggest that there is a low-lying empty orbital analogous to the π^* orbital of ethylene.⁵³ Bonding between the carborane anion cage and L_2Cu in the species I-IV may be described similarly. Donation of a pair of electrons from the B-B bond in the anion into an empty sp^2 type orbital on the Cu may be accomplished by back-bonding from a filled d orbital on the Cu into the antibonding orbital of the B-B bond. Thus the structure shown below assumes the perpendicular mode of attachment, found for similar systems, and may be compared with metal-olefin interactions in organometallic systems:



This back-bonding argument was not mentioned in the theoretical discussion⁵⁴ of $(CO)_4FeB_6H_{10}$, and the same workers suggested that the bonding in $(CO)_4FeB_6H_{10}$ is different from that in the

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hypothetical species⁵⁵ $(\mu-(H_3P)_2Cu)B_5H_8$, which might be expected to resemble the compounds I-IV prepared in this study.

The proposed structures shown in Figure 1 for species I-IV have been drawn purposely to suggest that the Cu lies close to the basal plane of the carborane. This would be expected if the Cu does interact with a terminal H on an adjacent B atom to form a bridge bond. If this is the case, the L_2Cu fragment becomes a pseudo-vertex as it does in the species $(CO)_3FeB_5H_8Cu[P(C_6H_5)_3]_2$, where there is a bent Cu-H-B bridge bond.¹¹ According to the polyhedral skeletal electron pair theory,¹³ the L_2Cu moiety contributes two electrons to the cluster, which is thus best described as a nido-hexagonal-pyramidal species. The alternative way to consider this system is assume that the L_2Cu moiety replaces a proton and thus does not contribute to the polyhedral skeletal electron count. X-ray structural determinations for these species would help resolve this question.

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Registry No. I, 97921-24-9; II, 97921-25-0; III, 97921-26-1; IV, 97921-27-2; $[(C_6H_5)_3P]_2CuBr$, 47814-88-0; (dppe)CuI, 15228-76-9.

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Diastereotopic Exchange in the Square-Planar Platinum(II) Complex (*N,N'*-Dimethylethylenediamine)bis(guanosine)platinum(II)¹

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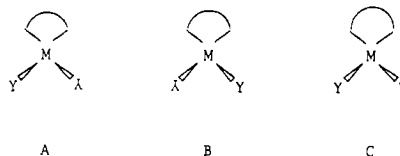
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A total of six diastereomeric configurations of the chiral square-planar platinum(II) complex (*N,N'*-dimethylethylenediamine)-bis(guanosine)platinum(II), $[Pt(N,N'-Me_2en)(Guo)_2]^{2+}$, are detected. Three sets of stereoisomers result from the configuration of the two coordinated ethylenediamine nitrogens, and these are designated *RR*, *SS*, and *SR*. In addition, the ribose moieties of the guanosines break all mirror symmetry in and between the stereoisomers, producing pairs of diastereomers possessing different physical and chemical properties. Rotation about the Pt-guanosine bond, which is rapid at 103 °C on the NMR time scale, causes exchange within each pair of diastereomers producing a sharp, four-line, ¹H NMR spectrum in the guanosine H(8) region. A complex set of ¹H NMR resonances is observed at -32 °C due to slow exchange in the *SR* set of diastereomers and in one of the *RR* or *SS* sets of diastereomers while the fast-exchange peak from the remaining set of diastereomers is only approaching coalescence. The concentration-dependent activation free energy for exchange between the *SR* diastereomers is about 65 kJ mol⁻¹ while that for the higher energy exchange process between the *RR* or *SS* diastereomers is about 55 kJ mol⁻¹.

Introduction

It has been recognized for over 20 years that sufficiently bulky ligands can block rotation about the metal-ligand bond in square-planar complexes.^{2,3} Observation of isomers, which can result from such restricted rotation, has been reported for complexes such as $[Pt(L)(olefin)Cl_2]$ ⁴ and *trans*- $[Pd(hydrazone)_2Cl_2]$,^{5,6} but such isomers have not been widely studied.

Square-planar complexes having two cis ligands with C_s local symmetry can exist in three stereoisomeric configurations, A-C, where Y represents the bulky ligand and the remaining coordination positions are occupied, for example, by a chelate. The



head to tail, H-T, isomers A and B are nonsuperimposable mirror

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