Preparation of Stable Copper(I) Derivatives of the Octahydropentaborate(1−) and Nonahydrohexaborate(1−) Ions

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Summary Compounds $(Ph_3P)_2CuB_5H_8$ and $(Ph_3P)_2CuB_6H_9$, the first air-stable derivatives of pentaborane(9) and hexaborane(10), have been prepared and studied for possible insertion of the metal into the bridge position.

IN recent years a number of metal complexes of various borane anions have been reported.[1,2] Particular interest has centred around $(Ph_3P)_2M$ and $(Ph_3P)_3M$ derivatives where M is Cu, Ag, or Au. Bisphosphinecopper derivatives of borohydride, BH_4^-, and triborohydride, $B_3H_8^-$, have been prepared and studied. In the solid state the boron unit is attached to the metal through hydrogen bridges, as shown by single crystal *X*-ray studies.[3] The analogous derivative of the decaborane anion, $B_{10}H_{13}^-$, also appears to involve some form of covalent bonding.[1] On the other hand, $B_9H_{14}^-$ and $B_{11}H_{14}^-$ form trisphosphine derivatives with metals and are apparently ionic.[1]

Recently, the $B_5H_8^-$ and $B_6H_9^-$ anions have been prepared.[4-6] Studies of the reactions of $B_5H_8^-$ with silicon, germanium, tin, and lead moieties indicate that insertion of these elements into the bridge position takes place between two boron atoms.[7] We have studied reactions of these anions with $(Ph_3P)_3CuCl$ because of the interesting possibility that Cu^I may insert into the B–B bond of the B_5 and B_6 frameworks rather than form M–H–B bridge bonds.

We report the preparation of $(Ph_3)_2CuB_5H_8$ (**A**) and $(Ph_3P)_2CuB_6H_9$(**B**). Compound (**A**) is a white air-stable crystalline solid which shows no sign of decomposition at room temperature over a period of months. Compound

(**B**) is also a white crystalline solid but stable at room temperature in air for only about four days.

In a typical reaction, $(Ph_3P)_3CuCl$ was mixed with an equivalent quantity of the potassium salt of the appropriate anion in the mixed solvent methylene chloride–tetrahydrofuran at −78°. The mixture was allowed to warm slowly until complete solution occurred. Ether was added at −78° to precipitate the product which was filtered off and isolated. The product was purified by washing it first with water, then with ethanol, and finally it was recrystallized from methylene chloride–diethyl ether.

I.r. spectra of the pentaborane(9) derivative (KBr pellet or Nujol mull) showed B–H terminal absorptions at 2570, 2535, 2510, and 2455 cm^{-1}. For the hexaborane(10) adduct, B–H terminal absorptions occurred at 2560, 2530, 2510, 2425, and 2360 cm^{-1}. The area in which B–H–B absorptions normally occur, 1700—2000 cm^{-1}, was masked by phenylphosphine absorptions.

Treatment of these derivatives with HCl in solution regenerated pentaborane(9) and hexaborane(10) in 75% yields indicating that the parent structures, obtained from deprotonation of the bridge position, remain intact in the metal derivatives since B_5H_9 and B_6H_{10} are similarly regenerated when $B_5H_8^-$ and $B_6H_9^-$ are treated with HCl.[5,6]

The ^{11}B n.m.r. spectrum at 32·1 MHz of the pentaborane species in methylene chloride at ambient temperature consists of a broad singlet and a doublet occurring at 15·0 and 47·8 p.p.m. (*J* 140 Hz), respectively, relative to $BF_3 \cdot Et_2O$. The relative ratio of the areas of the singlet to doublet at room temperature is 3·8 : 1.

The absorptions and chemical shifts recorded for the hexaborane complex in methylene chloride at room temperature consist of a broad singlet at −9·1 and a doublet at 49·0 p.p.m. (*J* 140 Hz).

The basal resonances of (**A**) and (**B**) at ambient temperature show no apparent multiplet character whereas for the free anions multiplet basal resonances collapse only at lower temperatures (−25° for LiB_5H_8 and −5° for LiB_6H_9).[6] As the temperature of solutions of (**A**) and (**B**) is lowered, the ^{11}B n.m.r. shows increased broadening of the basal peaks until at −50° for (**A**) and 0° for (**B**) the peak is no longer apparent. This would be consistent with either a slower rate of molecular motion or also a slower rate of intramolecular exchange than for the anions $B_5H_8^-$ and $B_6H_9^-$. Comparable observations in the ^1H n.m.r. spectrum of $(Ph_3P)_2CuB_3H_8$ have been accounted for in this way.[8]

Whether exchange involves copper and only terminal hydrogens in a form of pseudorotation or whether it involves the insertion of copper into the base so as to slow the rate of exchange of the bridge protons is not yet clear. It is not possible to draw direct analogies between the situation of these two anions being studied and $B_3H_8^-$ since the proton exchange seems to be different for $B_3H_8^-$ than for $B_5H_8^-$ and $B_6H_9^-$. Variable temperature ^1H n.m.r. studies of the $B_5H_8^-$ moiety, at present being conducted, indicate that at low temperature there may be an interaction between the copper and the bridge system although we have not as yet been able to interpret the spectrum completely.

Results of the insertion of the dimethylboryl group into $B_3H_8^-$ and $B_5H_8^-$ indicate that insertion of copper into the bridge may occur.[9] Dimethylboryl "inserts" between two terminal protons of $B_3H_8^-$ to form a tetraborane(10) derivative, whereas it inserts directly into the B–B bond of $B_5H_8^-$ to form a μ-substituted derivative of pentaborane(9).

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