

Table II. Imidazole Group Fits for Metalloproteins

protein	Cu-N ₃ distance, Å	no.	ref
plastocyanin (<i>Phaseolus vulgaris</i>)			
oxidized	1.98	2.0	14
reduced	2.05	1.8	14
hemocyanin (<i>Megathura crenulata</i>)			
oxygenated	2.01	2.0	15
deoxygenated	1.95	2.0	16

predicts 1.7 imidazoles at 2.00 Å. The predicted distance is consistent with the crystallographic distance, but the predicted coordination number is much higher than actually occurs. However, including the contribution of backscattering by the peptide carbons at ca. 3.0 Å causes the number of imidazoles predicted to drop to 1.2, within the 20% experimental uncertainty. Application of this technique to the copper complex of the tripeptide glycylglycyl-*O*-methyl-L-histidine [Cu(GGH)] predicts 2.0 imidazoles at 1.93 Å. Again, the predicted Cu-N₃ distance is correct, but two imidazoles instead of one are suggested, even when the peptide carbons are included in the fit. The crystal structure of this complex¹² indicates that the peptide carbons, peptide nitrogens, and carboxy oxygen are arranged in such a way as to simulate an imidazole group, causing the fitting procedure to predict an additional imidazole. This type of problem may be unique to small copper-peptide complexes, since there are no known protein examples of copper coordination to peptide amides adjacent to a ligating histidine. EXAFS was also recorded on a solution of Cu(II) and histidine in a 1:2 molar ratio. Application of the group fitting technique to these data predicts the presence of 1.5 imidazoles at 1.95 Å. One explanation may be that the solution exists as a mixture of two species, with one and two imidazoles coordinated per copper atom. An alternate explanation is that two imidazoles are coordinated at slightly different distances, resulting in prediction of a lower coordination number due to static disorder. The Cu-N₃ distance obtained is consistent with the crystallographic distance in copper-histidine complexes.¹³ For further investigation of the utility of this technique in fitting imidazole ligands, fits were performed on two copper compounds where no imidazoles are present [Cu(acac)₂ and Cu(NH₃)₄²⁺]. In both cases, when fitting with imidazoles and other appropriate atoms, numbers of imidazoles significantly less than one were obtained. If imidazoles only are assumed to be present, entirely unsatisfactory fits result.

The results of application of the imidazole group fitting technique to some histidine-containing copper proteins being studied in this laboratory are summarized in Table II. Other appropriate first-shell atoms (in addition to the imidazoles) were included in the fit. Results for a blue copper protein (plastocyanin) and an oxygen-carrying protein (hemocyanin) are presented. The oxidized and reduced plastocyanin show coordination of two imidazoles (consistent with the low-resolution X-ray crystallographic results¹⁷) at 1.98 and 2.05 Å, respectively. Similar studies on hemocyanin indicate that two imidazoles are coordinated to each copper atom for both oxygenated and deoxygenated forms. The details of these metalloprotein studies will be reported in other communications.¹⁴⁻¹⁶

These results indicate that the imidazole group-fitting technique can be successfully used to reveal the structural details of histidine ligands in copper metalloproteins. The extension of the group fitting technique to other commonly occurring biological ligand structures, such as porphyrins or carbon monoxide, is currently being pursued.

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New, Systematic, Good Yield Syntheses of Boron Hydrides: Preparation of B₄H₁₀ and B₅H₁₁. A Practical Conversion of B₅H₉ to B₁₀H₁₄

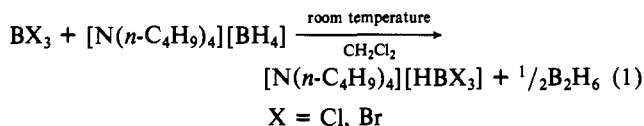
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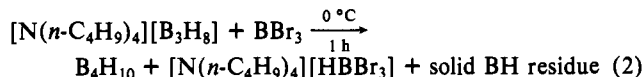
One of the principal handicaps in the investigation of the chemistry of the intermediate boron hydrides B₄H₁₀ and B₅H₁₁ has been the absence of simple preparative procedures which would provide these materials in relatively large quantities in good yield.^{1,2} We report here a new systematic approach to boron hydride syntheses which not only meets these requirements for the preparation of B₄H₁₀ and B₅H₁₁ but has also been extended to the preparation of 2-BrB₄H₉ and produced a simple conversion of B₅H₉ to B₁₀H₁₄.

The systematic nature of these syntheses relates to our observation that hydride ion can be abstracted from certain boron hydride anions to give as one of the final products a neutral boron hydride which contains one more boron atom than the anionic starting material. The simplest reaction observed (1) involves



[N(*n*-C₄H₉)₄][BH₄]³ and appears to be quantitative. The tetra-*n*-butylammonium salts of the previously unreported anions HBB₃⁻ and HBCl₃⁻ are stable, free-flowing solids under a dry atmosphere at room temperature [NMR data:⁴ HBB₃⁻, δ_{11B} = -13.0 (J_{11B-1H} = 176 Hz); HBCl₃⁻, δ_{11B} = 3.1 (J_{11B-1H} = 158 Hz)].

Tetraborane(10) and pentaborane(11) are prepared by reactions 2 and 3 in which 1:1 molar ratios of reactants are stirred vigorously in the absence of a solvent. Tetraborane(10) and pentaborane(11)



are obtained in 65% and 60% yields, respectively. These yields are based upon the amount of boron in the borane anion. In both reactions the borane anion is completely consumed. The starting materials, [N(*n*-C₄H₉)₄][B₃H₈] and KB₄H₉, for these reactions

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(4) Boron-11 NMR shifts are reported in parts per million relative to BF₃·O(C₂H₅)₂ and were obtained by use of the external standard BCl₃ (δ 46.8).

are obtained from high-yield syntheses,⁵⁻⁸ and B₄H₁₀ and B₅H₁₁ are routinely prepared in 20- and 10-mmol quantities, respectively, in the time frames cited above. Scaleup to larger quantities is practical.

Traditionally, B₄H₁₀ and B₅H₁₁ have been prepared by hot-cold reactor techniques^{9,10} and more recently from the protonation of B₃H₈⁻ salts.¹¹⁻¹³ In addition, B₅H₁₁ has been prepared⁶ from the protonation of B₅H₁₂⁻. The procedures outlined here are much safer and simpler than the classical hot-cold reactor techniques.^{9,10}

Also requirements for product purification are minimal for the present method compared to the hot-cold reactor methods^{9,10} and the method of protonation of B₃H₈⁻ salts.¹¹⁻¹³ When carried out under conditions indicated, the presence of volatile impurities (trace quantities of B₂H₆ and B₅H₉ from reaction 2 and trace quantities of *n*-B₉H₁₅ from reaction 3) present no problems in purifying B₄H₁₀ and B₅H₁₁. Our present method for preparing B₅H₁₁ is also superior to the earlier reported⁶ protonation of B₅H₁₂⁻, since it gives comparable yields but requires one less step in the preparative procedure.

Reaction 1 can be viewed as hydride abstraction from BH₄⁻ ions to give BH₃ units which combine to form B₂H₆. This reaction differs from the traditional syntheses of B₂H₆ in which diborane(6) is generated through hydride-halide exchange in reactions of metal borohydrides with group 3 halides in ethereal solvents.¹⁴⁻¹⁶

For reactions 2 and 3 hydride abstraction would yield the boranes B₃H₇ and B₄H₈, respectively. In view of the products obtained, it is reasonable to assume that subsequent reactions involve, effectively, transfer of BH₃ from one B₃H₇ to another B₃H₇ to produce B₄H₁₀ and transfer of BH₃ from one B₄H₈ to another B₄H₈ to produce B₅H₁₁. Viewing reactions 2 and 3 in this light suggests the following stoichiometries.

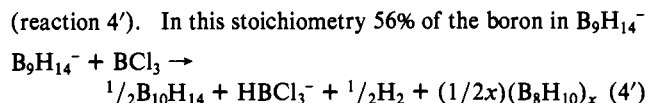
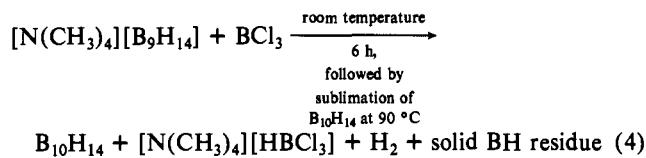


In these reactions 67% of the available boron in B₃H₈⁻ is converted to B₄H₁₀ and 63% of the available boron in B₄H₉⁻ is converted to B₅H₁₁. The close correspondence of experimental yields to these proposed stoichiometries (eq 2' and 3') suggests that within experimental error reactions 2 and 3 are quantitative with respect to yields of B₄H₁₀ and B₅H₁₁. Residues of empirical compositions (BH₂)_x and (B₃H₅)_x decompose at room temperature to give small amounts of B₃H₉ and *n*-B₉H₁₅, respectively.

Treatment of 20 mmol of [N(*n*-C₄H₉)₄][B₃H₇Br]¹⁷ with an equal amount of BBr₃ in 10 mL of CH₂Cl₂ at -78 °C for 12 h results in the formation of equal amounts of 2-BrB₄H₉ and B₄H₁₀, 2 mmol each. Although the yield of 2-BrB₄H₉ is relatively low, this preparation is an attractive alternative to an earlier procedure in which 10-15% yields of 2-BrB₄H₉ were obtained from the reaction of excess B₄H₁₀ with Br₂ over an 18-h period at -15 °C.¹⁸

The systematic nature of this procedure was further demonstrated in an extension of reactions 2 and 3. Treatment of [N(CH₃)₄][B₉H₁₄] with BCl₃ gave B₁₀H₁₄ in a yield of 50% based on B₉H₁₄⁻ (reaction 4).

A reaction stoichiometry analogous to 2' and 3' is suggested



is converted to B₁₀H₁₄, which corresponds well with our results and is consistent with reaction 4 being close to quantitative.

Although B₉H₁₄⁻ is generally prepared through the degradation of B₁₀H₁₄ by base,¹⁹ it is also possible to prepare this ion through the thermal decomposition of B₅H₈⁻ which is generated by deprotonating B₅H₉. However, the yields of B₉H₁₄⁻ prepared this way from B₅H₉ do not exceed 60%.²⁰⁻²³ By allowing B₅H₈⁻ to react with an equimolar amount of B₅H₉ in THF at room temperature, we have been able to obtain good quality B₉H₁₄⁻ in 90% yield.²⁴ This is achieved by treating B₅H₉ with an alkali metal hydride (KH or NaH) in a 2:1 molar ratio. This preparation of B₉H₁₄⁻ from B₅H₉ coupled with reaction 4 provides a practical route to B₁₀H₁₄ from B₅H₉, employing a single reactor for the entire procedure.

In a typical preparation of B₁₀H₁₄ from B₅H₉, 21.6 mmol of NaH, 43.2 mmol of B₅H₉, and 22 mmol of [N(CH₃)₄]Cl are stirred for 12 h in 16 mL of THF at room temperature. Hydrogen gas and THF are pumped away, leaving behind a dry solid which is good quality [N(CH₃)₄][B₉H₁₄] and NaCl. Then 22 mmol of BCl₃ is condensed onto the solid reaction products, and this mixture is stirred vigorously for 6 h at 25 °C. The B₁₀H₁₄ is then sublimed from the flask under dynamic vacuum. A 9.57-mmol quantity of B₁₀H₁₄ representing a 45% conversion of B₅H₉ to B₁₀H₁₄ is obtained. This percent conversion of starting material to B₁₀H₁₄ is comparable to that reported for the conversion of NaBH₄ to B₁₀H₁₄ by a nonpyrolytic method.²⁵ The present procedure, however, requires fewer steps and it, also, can be scaled up.

Work is continuing on the further development of this systematic approach to boron hydride syntheses and the further development of the preparation of B₁₀H₁₄ from B₅H₉.

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Preparation and Reactivity of the (Cyclohexadiene)manganese Tricarbonyl Anion. Potentially Useful Methods of Arene and C-H Bond Activation

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It is well established that arenes complexed to transition metals are often activated toward nucleophilic attack. Nucleophilic