Table II. Imidazole Group Fits for Metalloproteins

protein	Cu-N_3 distance, Å	no.	ref
plastocyanin (*Phaseolus vulgaris*)			
oxidized	1.98	2.0	14
reduced	2.05	1.8	14
hemocyanin (*Megathura crenulata*)			
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-N_3 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 complex[12] 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-N_3 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 $Cu(NH_3)_4^{2+}$]. 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 results[17]) 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 B_4H_{10} and B_5H_{11}. A Practical Conversion of B_5H_9 to $B_{10}H_{14}$

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One of the principal handicaps in the investigation of the chemistry of the intermediate boron hydrides B_4H_{10} and B_5H_{11} 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 B_4H_{10} and B_5H_{11} but has also been extended to the preparation of 2-BrB_4H_9 and produced a simple conversion of B_5H_9 to $B_{10}H_{14}$.

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

$$BX_3 + [N(n\text{-}C_4H_9)_4][BH_4] \xrightarrow[CH_2Cl_2]{\text{room temperature}} [N(n\text{-}C_4H_9)_4][HBX_3] + {}^1/_2B_2H_6 \quad (1)$$

X = Cl, Br

$[N(n\text{-}C_4H_9)_4][BH_4]$[3] and appears to be quantitative. The tetra-*n*-butylammonium salts of the previously unreported anions $HBBr_3^-$ and $HBCl_3^-$ are stable, free-flowing solids under a dry atmosphere at room temperature [NMR data:[4] $HBBr_3^-$, $\delta_{^{11}B}$ = −13.0 ($J_{^{11}B-^1H}$ = 176 Hz); $HBCl_3^-$, $\delta_{^{11}B}$ = 3.1 ($J_{^{11}B-^1H}$ = 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)

$$[N(n\text{-}C_4H_9)_4][B_3H_8] + BBr_3 \xrightarrow[1\text{ h}]{0\ ^\circ C} B_4H_{10} + [N(n\text{-}C_4H_9)_4][HBBr_3] + \text{solid BH residue} \quad (2)$$

$$K[B_4H_9] + BCl_3 \xrightarrow[2.5\text{ h}]{-35\ ^\circ C} B_5H_{11} + K[HBCl_3] + \text{solid BH residue} \quad (3)$$

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, $[N(n\text{-}C_4H_9)_4][B_3H_8]$ and KB_4H_9, for these reactions

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are obtained from high-yield syntheses,[5-8] and B_4H_{10} and B_5H_{11} are routinely prepared in 20- and 10-mmol quantities, respectively, in the time frames cited above. Scaleup to larger quantities is practical.

Traditionally, B_4H_{10} and B_5H_{11} have been prepared by hot–cold reactor techniques[9,10] and more recently from the protonation of $B_3H_8^-$ salts.[11-13] In addition, B_5H_{11} has been prepared[6] from the protonation of $B_5H_{12}^-$. 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 $B_3H_8^-$ salts.[11-13] When carried out under conditions indicated, the presence of volatile impurities (trace quantities of B_2H_6 and B_5H_9 from reaction 2 and trace quantities of n-B_9H_{15} from reaction 3) present no problems in purifying B_4H_{10} and B_5H_{11}. Our present method for preparing B_5H_{11} is also superior to the earlier reported[6] protonation of $B_5H_{12}^-$, since it gives comparable yields but requires one less step in the preparative procedure.

Reaction 1 can be viewed as hydride abstraction from BH_4^- ions to give BH_3 units which combine to form B_2H_6. This reaction differs from the traditional syntheses of B_2H_6 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 B_3H_7 and B_4H_8, respectively. In view of the products obtained, it is reasonable to assume that subsequent reactions involve, effectively, transfer of BH_3 from one B_3H_7 to another B_3H_7 to produce B_4H_{10} and transfer of BH_3 from one B_4H_8 to another B_4H_8 to produce B_5H_{11}. Viewing reactions 2 and 3 in this light suggests the following stoichiometries.

$$B_3H_8^- + BBr_3 \rightarrow {}^1/_2B_4H_{10} + HBBr_3^- + (1/x)(BH_2)_x \quad (2')$$

$$B_4H_9^- + BCl_3 \rightarrow {}^1/_2B_5H_{11} + HBCl_3^- + (1/2x)(B_3H_5)_x \quad (3')$$

In these reactions 67% of the available boron in $B_3H_8^-$ is converted to B_4H_{10} and 63% of the available boron in $B_4H_9^-$ is converted to B_5H_{11}. 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 B_4H_{10} and B_5H_{11}. Residues of empirical compositions $(BH_2)_x$ and $(B_3H_5)_x$ decompose at room temperature to give small amounts of B_5H_9 and n-B_9H_{15}, respectively.

Treatment of 20 mmol of $[N(n\text{-}C_4H_9)_4][B_3H_7Br]$[17] with an equal amount of BBr_3 in 10 mL of CH_2Cl_2 at −78 °C for 12 h results in the formation of equal amounts of 2-BrB_4H_9 and B_4H_{10}, 2 mmol each. Although the yield of 2-BrB_4H_9 is relatively low, this preparation is an attractive alternative to an earlier procedure in which 10–15% yields of 2-BrB_4H_9 were obtained from the reaction of excess B_4H_{10} with Br_2 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 $[N(CH_3)_4]B_9H_{14}$ with BCl_3 gave $B_{10}H_{14}$ in a yield of 50% based on $B_9H_{14}^-$ (reaction 4).

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

$$[N(CH_3)_4][B_9H_{14}] + BCl_3 \xrightarrow[\text{6 h, followed by sublimation of } B_{10}H_{14} \text{ at 90 °C}]{\text{room temperature}} B_{10}H_{14} + [N(CH_3)_4][HBCl_3] + H_2 + \text{solid BH residue} \quad (4)$$

(reaction 4′). In this stoichiometry 56% of the boron in $B_9H_{14}^-$

$$B_9H_{14}^- + BCl_3 \rightarrow {}^1/_2B_{10}H_{14} + HBCl_3^- + {}^1/_2H_2 + (1/2x)(B_8H_{10})_x \quad (4')$$

is converted to $B_{10}H_{14}$, which corresponds well with our results and is consistent with reaction 4 being close to quantitative.

Although $B_9H_{14}^-$ is generally prepared through the degradation of $B_{10}H_{14}$ by base,[19] it is also possible to prepare this ion through the thermal decomposition of $B_5H_8^-$ which is generated by deprotonating B_5H_9. However, the yields of $B_9H_{14}^-$ prepared this way from B_5H_9 do not exceed 60%.[20-23] By allowing $B_5H_8^-$ to react with an equimolar amount of B_5H_9 in THF at room temperature, we have been able to obtain good quality $B_9H_{14}^-$ in 90% yield.[24] This is achieved by treating B_5H_9 with an alkali metal hydride (KH or NaH) in a 2:1 molar ratio. This preparation of $B_9H_{14}^-$ from B_5H_9 coupled with reaction 4 provides a practical route to $B_{10}H_{14}$ from B_5H_9, employing a single reactor for the entire procedure.

In a typical preparation of $B_{10}H_{14}$ from B_5H_9, 21.6 mmol of NaH, 43.2 mmol of B_5H_9, and 22 mmol of $[N(CH_3)_4]Cl$ 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 $[N(CH_3)_4][B_9H_{14}]$ and NaCl. Then 22 mmol of BCl_3 is condensed onto the solid reaction products, and this mixture is stirred vigorously for 6 h at 25 °C. The $B_{10}H_{14}$ is then sublimed from the flask under dynamic vacuum. A 9.57-mmol quantity of $B_{10}H_{14}$ representing a 45% conversion of B_5H_9 to $B_{10}H_{14}$ is obtained. This percent conversion of starting material to $B_{10}H_{14}$ is comparable to that reported for the conversion of $NaBH_4$ to $B_{10}H_{14}$ by a nonpyrolytic method.[25] The present procedure, however, requires fewer steps and it, also, can be scaledup.

Work is continuing on the further development of this systematic approach to boron hydride syntheses and the further development of the preparation of $B_{10}H_{14}$ from B_5H_9.

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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

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