

ethylnickel species which rapidly undergoes  $\beta$ -hydride elimination giving ethylene and a nickel hydride. The nickel hydride can then add to **1** giving a vinylnickel species. If nitrogen is rapidly bubbled through the mixture, **24** and **25** are formed in 65% yield and the dimer **27** is formed in ~20% yield. The origin of **26** and **27** is unclear.

The vinylmagnesium species resulting from hydronickelation undergoes the expected reactions. Quenching with  $D_2O$  gives the expected alkenes- $d_1$  **28** and **29** as a 95:5 cis-trans mixture in 65% yield. Quenching with acetaldehyde gives the desired allylic alcohols **30** and **31** as a 95:5 mixture in 58% yield. Although there are other procedures for hydrometalation of acetylenes, we feel that this procedure has significant advantages since it produces a reactive organometallic directly in good yield.

We are currently exploring the scope of this hydro- and carbometalation reaction with respect to the suitability of other Grignard reagents and acetylenes and the reactivity of the resulting organometallics.

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## First Facile and Convenient Hydroboration Reaction via a Polyhedral Borane. Implications Regarding Catalysis Involving Metalloboranes

Sir:

It is well known that treatment of  $B_{10}H_{14}$  with acetylene in the presence of Lewis bases such as MeCN and  $Me_2S$  produces the dicarbaborane 1,2- $C_2B_{10}H_{12}$  where the carbon atoms are at adjacent sites in a nominally icosahedral cluster.<sup>1,2</sup> Substituted acetylenes give the corresponding C-substituted dicarbaborane. Since *nido*-6- $SB_9H_{11}$  has the same framework structure<sup>3</sup> as *nido*- $B_{10}H_{14}$  and since 6- $SB_9H_{11}$  is iso-electronic with  $B_{10}H_{14}$ , it was anticipated that treatment of 6- $SB_9H_{11}$  with acetylenes in the presence of Lewis bases would produce a new heteroborane with a 12-atom framework, a dicarbathiaborane. Contrary to these expectations, we have found that 6- $SB_9H_{11}$  undergoes a facile hydroboration reaction<sup>4</sup> when treated with alkynes and alkenes.

A facile and clean hydroboration reaction for a nonpyrophoric polyhedral borane has not been demonstrated previously. For instance, it is necessary to subject a mixture of pentaborane(9) and an olefin to 150 °C in order to form 2-alkyl- $B_5H_8$  species (alkyl = *n*-Bu, *sec*-Bu, *i*-Bu, Et).<sup>5</sup> Pentaborane(11) hydroborates ethylene,<sup>6</sup> but the reaction is not clean and  $B_5H_{11}$  is even more difficult to prepare and handle than  $B_4H_{10}$  or  $B_5H_9$ . The reactions of  $B_5H_{11}$  and  $B_4H_{10}$  with acetylenes lead to complex product mixes which include carbaboranes predominantly.<sup>7</sup> In contrast, the hydroboration described below involves the easily handled and readily prepared 6-thia-*nido*-decaborane(11). Although the reactions proceed at 25 °C for most alkenes and alkynes, they generally were run in refluxing benzene for 7-12 h to ensure completion. Typically, 224 mg (1.55 mmol) of 6- $SB_9H_{11}$  and an equivalent amount of alkene or alkyne were added under  $N_2$  to 25 mL of dry benzene in a magnetically stirred flask. The solution generally turns yellow quickly upon addition of the alkene or alkyne. Products were recovered by rotary evaporation of the benzene and sublimation of the yellow residue. Yields of sublimed product are shown in Table I. In all cases, the mass spectrum showed the expected parent ion cutoff with the correct  $^{32}S$ ,  $^{34}S$  intensity.

Hydroboration of alkenes and alkynes by 6- $SB_9H_{11}$  clearly occurs by addition of the exo BH at the 9 position across the unsaturated C-C bond as shown schematically in Figure 1. The substitution site is substantiated readily by  $^{11}B$  NMR. All of the alkene and alkyne hydroboration products investigated here gave very similar  $^{11}B$  NMR spectra. These spectra all are reminiscent of that of 6- $SB_9H_{11}$ <sup>3</sup> except for the marked downfield shift for the 9 position and its collapse from a doublet to a broad singlet due to replacement of a B-H by a B-C bond.<sup>8</sup> The IR spectra of these organothiaboranes show bridge-hydrogen absorptions in the 2040-1940- $cm^{-1}$  range; those for 6- $SB_9H_{11}$  are at 1920-1950  $cm^{-1}$ . Unfortunately,  $^1H$  and  $^{13}C$  NMR data were not so useful for characterization as might be anticipated. The  $^{13}C$  spectra were consistent with hydroboration even though of the six investigated only two spectra (those with the  $B-C_3H_8$  and  $B-C_2H_5$  moieties) showed signals which could be attributed to carbon bound to  $^{11}B$ . Similar difficulties have been encountered for other organoboranes.<sup>9</sup>

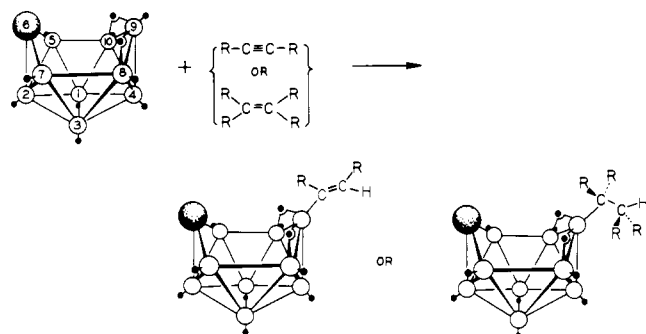
Figure 1. Hydroboration by 6-SB<sub>9</sub>H<sub>11</sub>.

Table I. Organothiaboranes and Oxidation Products

Substrate	% yield of hydroboration product <sup>a</sup>	Oxidation product <sup>b</sup>	% yield
Diphenylacetylene	85	Deoxybenzoin	90
3-Hexyne	55	3-Hexanone	80
Acetylene	69 <sup>c</sup>	<i>d</i>	
Ethylene	60	<i>d</i>	
1-Octene	55	1-Octanol	95
Cyclohexene	70	Cyclohexanol	83
Cyclopentadiene	67 <sup>e</sup>	<i>d</i>	
1-Methyl-1-cyclohexene	74	<i>trans</i> -2-Methylcyclohexanol	75

<sup>a</sup> Recovery by sublimation. <sup>b</sup> Oxidation with alkaline hydrogen peroxide. <sup>c</sup> Two moles of thiaborane consumed per mole of acetylene. <sup>d</sup> Oxidation not investigated. <sup>e</sup> Molar ratio of thiaborane/cyclopentadiene, 2/1.

The quadrupolar <sup>11</sup>B apparently gives rise to a broadening attributable to a T<sub>2</sub> scalar coupling such as that seen for <sup>14</sup>N-C bonds.<sup>10</sup> The <sup>1</sup>H NMR spectra were in many cases simpler than expected and could not be used for definitive characterization in most cases.

The stereochemistry of hydroboration was established by analysis of the alcohol or ketone which results upon alkaline peroxide oxidation of the organothiaboranes. Alkenes and alkynes and their oxidation products after hydroboration are given in Table I. A particularly definitive observation is the fact that, just as in the case of simple monoboranes,<sup>4</sup> 1-methyl-1-cyclohexene gives *trans*-2-methylcyclohexanol which indicates that the hydroboration is a regiospecific anti-Markovnikoff syn addition. The other oxidations also are consistent but not definitive for the latter stereochemistry.

Because of their stability, organothiaboranes may prove superior to monoboranes in multistep synthesis. The latter and other facets of synthetic organic chemistry via organothiaboranes currently are under investigation. Conversely, this hydroboration reaction allows for a wide modification of thiaborane properties through the easy formation of a multitude of organic derivatives.

Just as the pyrolysis of *nido*-6-SB<sub>9</sub>H<sub>11</sub> at 450 °C gives *closo*-1-SB<sub>9</sub>H<sub>9</sub>,<sup>3,11</sup> we have found that organo-substituted derivatives of *closo*-1-thiadecaborane(9) can be obtained by the 450 °C pyrolysis of the correspondingly 9-substituted *nido*-6-thiadecaborane(11). The pyrolysate typically contains a mixture of three *closo* isomers as shown by GC/MS analysis. None of the latter isomers were isolated, but the <sup>11</sup>B NMR of the mixture was distinctly similar to that of 1-SB<sub>9</sub>H<sub>9</sub><sup>3,11</sup> and is interpreted best as a mixture of the 10-, 6-, and 2-substituted isomers of 1-SB<sub>9</sub>H<sub>9</sub>.

Facile hydroboration by a heteroborane also has implications regarding the mechanism by which metalloheteroboranes catalyze reactions such as the hydrogenation and isomerization

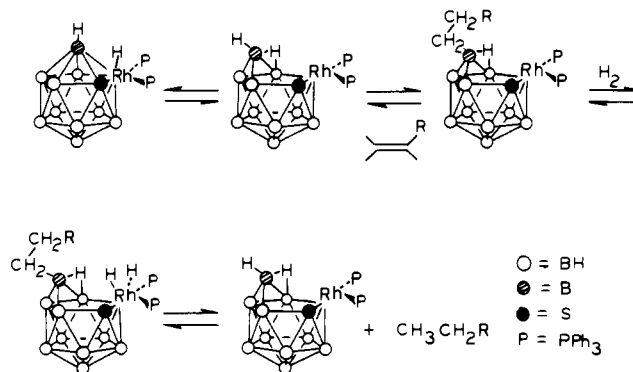


Figure 2. A possible mechanism for hydrogenation by metalloheteroboranes.

of olefins. Before demonstration of the subject facile hydroboration, the carborane ligand or the thiaborane ligand in the hydrogenation catalysts (PPh<sub>3</sub>)<sub>2</sub>Rh<sup>III</sup>H(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sup>12</sup> and (PPh<sub>3</sub>)<sub>2</sub>Rh<sup>III</sup>H(SB<sub>10</sub>H<sub>10</sub>),<sup>13</sup> respectively, need only be considered as "spectator" ligands. Activation of the catalyst by tautomerization to a rhodium(I) complex followed by metal-centered reaction steps such as oxidative addition of H<sub>2</sub> to Rh, olefin complexation, migratory insertion of the olefin into a Rh-H bond, and reductive elimination of the alkane could be envisaged. However, it is now reasonable to postulate that the heteroborane ligand is more than a "spectator" during the catalytic cycle (i.e., not all of the steps need be metal centered<sup>14</sup>) and multicenter mechanisms are also reasonable. For instance, hydrogenation might involve steps of hydroboration of the olefin by the heteroborane ligand, oxidative addition of H<sub>2</sub> to Rh, and elimination of the alkane accompanied by transfer of H from Rh to the heteroborane (Figure 2). Reaction precedents are now known for all steps of either the metal-centered mechanism or the multicenter mechanism.

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