

55.0 ( $J = 157$  Hz, area 1), and 29.4 ( $J = 117$  Hz, area 2), all of which collapsed to singlets on  $^1\text{H}$  decoupling.

Since I and II formally contain 20 and 22 skeletal valence electrons (based on a donation<sup>11</sup> of 3 from each  $(\text{C}_5\text{H}_5)\text{Ni}$  and 2 from each BH unit), both species are  $[2n + 4]$ -electron systems ( $n =$  the number of vertices) and thus were expected to adopt nido<sup>12</sup> structures. However, x-ray diffraction data<sup>14</sup> on I have established the closo dodecahedral ( $D_{2d}$ ) geometry shown in Figure 1a. This structure is surprising not only in that it is closo rather than nido, but also in the fact that all four metal atoms occupy low-coordinate vertices with unusually short<sup>15</sup> equivalent Ni–Ni distances of 2.354 (1) Å. Curiously, the recently reported<sup>1b,c</sup> cluster  $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$  (which has four fewer electrons than I) also adopts a closo dodecahedral shape<sup>1c,2b</sup> but with all metal atoms in high-coordinate vertices. It is remarkable that the 8-vertex species  $(\eta^5\text{-C}_5\text{H}_5)_4\text{Ni}_4\text{B}_4\text{H}_4$ ,  $\text{B}_8\text{H}_8^{2-}$ ,  $\text{C}_2\text{B}_6\text{H}_8$ , and  $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4\text{B}_4\text{H}_4$ , which are assigned, respectively, 20, 18, 18, and 16 skeletal valence electrons, all exhibit the same (closo) polyhedral geometry. The structure of  $(\text{CH}_3)_4\text{C}_4\text{B}_4\text{H}_4$ ,<sup>18</sup> a 20-electron analogue of I, has not been established although several nido geometries have been suggested.<sup>18</sup>

Clearly, 8-vertex clusters present a special case in which the cage structure is markedly affected by factors above and beyond framework electron population per se.<sup>19</sup> Indeed, a recent MO study<sup>21</sup> indicates that  $\text{B}_8\text{H}_8^{2-}$  is uncommon among the polyhedral borane anions in having very small energy differences between alternative geometries. Of significance in the present case may be the short nickel–nickel bond lengths in I, which suggest abnormally high bond orders for these interactions (there do not appear to be any particular steric constraints in this system that would produce such an effect).

The structure of II has not been established, but the geometry shown in Figure 1b is proposed on the basis of  $^{11}\text{B}$  and  $^1\text{H}$  NMR data, and on the assumption that there is a straightforward structural relationship between I and II (it is likely that I forms by net loss of a BH unit from II). Thus, a direct  $\text{II} \rightarrow \text{I}$  conversion can be effected by removing B(6)–H from II and linking B(9) to B(3) and Ni(7). In view of the fact that the 8-vertex species I is closo, in violation of the structural electron count rules,<sup>11</sup> it is possible that a similar anomaly exists in II and that a closo structure will be found here also. However, as noted above, I and other 8-vertex clusters are regarded as an exceptional group; moreover, the trinickel metallocarborane<sup>5</sup>  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{CB}_5\text{H}_6$ , an isoelectronic analogue of II, has an established nido geometry similar to that proposed here for II. Hence we expect II to adopt a nido structure as shown, in conformity with the presence of 22 skeletal electrons.<sup>11</sup>

Since cobalt and nickel can be incorporated into  $\text{B}_5\text{H}_8^-$  to give polymetallic clusters, extension to other metals and to other borane substrates seems likely; however, because the nature of the products is largely controlled by kinetic factors, the choice of reagent is crucial. Thus, the treatment of  $\text{B}_5\text{H}_8^-$  with  $\text{FeCl}_2$  and  $\text{C}_5\text{H}_5^-$  produces monoferraboranes<sup>22</sup> such as  $2\text{-}(\eta^5\text{-C}_5\text{H}_5)\text{FeB}_5\text{H}_{10}$  rather than metal-rich species. Investigations in this area are continuing.

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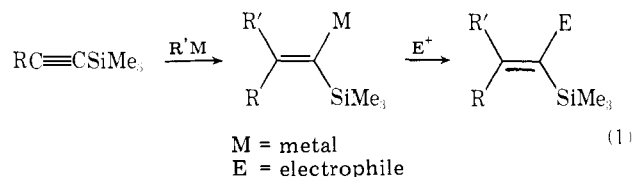
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## Nickel-Catalyzed Addition of Grignard Reagents to Silylacetylenes. Synthesis of Tetrasubstituted Alkenes

Sir:

Vinylsilanes have recently been shown to be versatile synthetic intermediates<sup>1</sup> which react with a wide variety of electrophiles, undergoing desilylation with retention of stereochemistry.<sup>1,2</sup> We are interested in developing reactions of organometallic reagents with silylacetylenes to provide new stereospecific routes to di- and trisubstituted vinylsilanes (eq 1). Although the hydroboration<sup>3</sup> and hydroalumination<sup>4</sup> of



silylacetylenes are known, there are no carbometalation reactions of silylacetylenes of general applicability. The cis addition of organocopper species  $(\text{RCu}\cdot\text{MgX}_2)$  to terminal



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 hydronickeleation 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>