55.0 (J = 157 Hz, area 1), and 29.4 (J = 117 Hz, area 2), all of which collapsed to singlets on <sup>1</sup>H decoupling.

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Since I and II formally contain 20 and 22 skeletal valence electrons (based on a donation<sup>11</sup> of 3 from each  $(C_5H_5)Ni$  and 2 from each BH unit), both species are [2n + 4]-electron systems (n = the number of vertices) and thus were expected to adopt nido12 structures. However, x-ray diffraction data14 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  $(\eta^5 - C_5H_5)_4Co_4B_4H_4$  (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  $(\eta^5 C_5H_5)_4Ni_4B_4H_4$ ,  $B_8H_8^{2-}$ ,  $C_2B_6H_8$ , and  $(\eta^5-C_5H_5)_4Co_4B_4H_4$ , which are assigned, respectively, 20, 18, 18, and 16 skeletal valence electrons, all exhibit the same (closo) polyhedral geometry. The structure of  $(CH_3)_4C_4B_4H_4$ ,<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.19 Indeed, a recent MO study<sup>21</sup> indicates that  $B_8H_8^{2-}$  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 <sup>11</sup>B and <sup>1</sup>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 II  $\rightarrow$  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>  $(\eta^5-C_5H_5)_3Ni_3CB_5H_6$ , 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  $B_5H_8^-$  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  $B_5H_8^$ with FeCl<sub>2</sub> and  $C_5H_5^-$  produces monoferraboranes<sup>22</sup> such as  $2-(\eta^5-C_5H_5)$ FeB<sub>5</sub>H<sub>10</sub> rather than metal-rich species. Investigations in this area are continuing.

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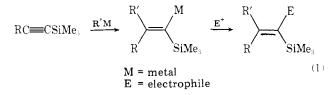
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## Nickel-Catalyzed Addition of Grignard Reagents to Silylacetylenes. Synthesis of Tetrasubstituted Alkenes

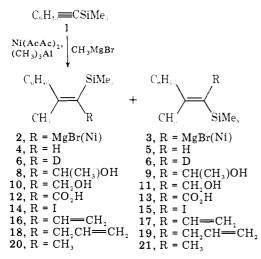
Sir:

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 silvlacetylenes 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 ( $RCu \cdot MgX_2$ ) to terminal acetylenes is the one general carbometalation reaction of acetylenes.<sup>5,6</sup> However, with the exception of ethynylsilanes,<sup>7</sup> the addition of organocoppers or organocuprates does not take place to silylacetylenes.<sup>8,9</sup> Furthermore, addition of a methyl group is difficult since methylcopper does not add to acetylenes, although 5 equiv of Me<sub>2</sub>CuMgCl·LiBr adds slowly to 1-oct-yne.<sup>5</sup> Recently, the carbometalation of terminal acetylenes by trialkylaluminum and zirconocene dichloride was reported.<sup>10</sup>

We wish to report that methylmagnesium bromide (4 equiv, 3 M in THF-benzene) adds to 1-trimethylsilyl-1-octyne (1) in the presence of 10 mol % 1:1 nickel acetylacetonate-trimethylaluminum<sup>11</sup> in THF to give the vinylorganometallic **2** in good yield. On standing, **2** slowly isomerizes to a mixture of **2** and **3**, probably catalyzed by nickel.<sup>12</sup> Quenching the reaction with water after 24 h gives a 9:1 mixture of **4** and **5** in 80% yield.<sup>13,14</sup> Small amounts of recovered **1** (2-5%) and dimer or oligomer (10-15%) are also obtained. At shorter reaction times more **1** is still present, while at longer times isomerization to **3** has progressed further.

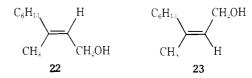


The organometallics 2 and 3 are highly reactive as expected for Grignard reagents. Quenching with  $D_2O$  leads to a 9:1 mixture of 6 and 7 in 75% yield, indicating that an organometallic is present in solution. Quenching with acetaldehyde gives an 85:15 mixture of 8 and 9 in 70% yield while formaldehyde gives a 9:1 mixture of 10 and 11 in 66% yield. The cis and trans isomers 8 and 9 and 10 and 11 are easily separable on silica gel.<sup>15</sup> This is apparently due to steric constraints on binding to the adsorbent imposed by the trimethylsilyl group, since the desilylated alcohols are inseparable on silica. This ease of separation will allow this procedure to be used for the stereoselective synthesis of tetrasubstituted alkenes. Quenching with carbon dioxide gives the acids 12 and 13 as a 4:1 mixture in 61% yield. Addition of a mixture of 2 and 3 to excess iodine gives a 9:1 mixture of the vinyl iodides 14 and 15 in 71% yield. These vinyl iodides should be very useful in synthesis since treatment of the 14-15 mixture with 2 equiv of tert-butyllithium gives a clean solution of the vinyllithiums. Protonation gives a 9:1 mixture of 4 and 5 in quantitative yield.

The vinylorganometallics 2 and 3 also undergo reactions which are probably nickel catalyzed. Addition of 2 and 3 to vinyl bromide<sup>16</sup> gives a 85:15 mixture of dienes 16 and 17 in 48% yield. In addition a 15% yield of dimer is also obtained. Coupling with allyl bromide proceeds normally giving an 88:12 mixture of coupling products 18 and 19 in 63% yield, and reaction with methyl iodide gives a 4:1 mixture of 20 and 21 in 50% yield.

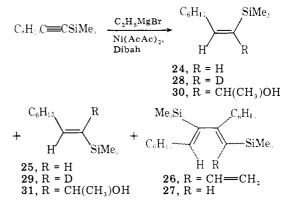
This nickel-catalyzed addition of methylmagnesium bromide is sensitive to the conditions employed. With methylmagnesium bromide in ether, rather than in THF-benzene, the mixture is heterogeneous and the reaction rate is slower, while isomerization proceeds at the same rate. With methylmagnesium chloride in THF, isomerization of 2 to 3 is much faster. In the previously reported nickel-catalyzed additions of methylmagnesium bromide to diphenylacetylene, bis(triphenylphosphine)nickel chloride was used as a catalyst.<sup>17,18</sup> Under these conditions methylmagnesium bromide does not add to 3-hexyne.<sup>17,18</sup> Using a variety of phosphine nickel chloride catalysts we have been unable to add methylmagnesium bromide to trimethylsilyloctyne. Nickel bromide or nickel acetylacetonate do catalyze this addition but at slower rates leading to more severe isomerization problems. Some of the methyl groups transferred may arise from trimethylaluminum since use of Ni(AcAc)2.diisobutylaluminum hydride as catalyst leads to small amounts of hydrometalation. However,  $Ni(AcAc)_2$  and 1.5 equiv of trimethylaluminum do not react with 1;<sup>19</sup> methylmagnesium bromide is necessary.<sup>20</sup> The steric bulk of the trimethylsilyl group may prevent the oligomerization of the acetylene with the reactive nickel catalyst used.

The cis stereochemistry of this carbometalation reaction is expected on mechanistic grounds. This was confirmed by examination of the <sup>1</sup>H NMR spectra of **10** and **11** in the presence of Eu(THD)<sub>3</sub>. In the major isomer **10** the methyl group shifts 8.8 (parts per million/equivalent of Eu(THD)<sub>3</sub>), while the methylene group shifts 5.2. In the minor isomer **11** these shifts are almost exactly reversed. The methylene group shifts 8.3 and the methyl group shifts 4.8.<sup>21</sup> Desilylation of **10** and **11** with fluoride in Me<sub>2</sub>SO<sup>22</sup> at 70 °C gives stereospecific desilylation with retention of configuration to the alcohols **22** and **23**.<sup>23</sup>



The NMR absorptions of the allylic methyls of 4 and 5 are consistent with this assignment. The methyl group of 4 absorbs at  $\delta$  1.78 as a doublet (J = 1.5 Hz), while the methyl group of 5 absorbs at  $\delta$  1.74 as a doublet (J = 0.6 Hz). The trimethylsilyl group is known to shield a *cis*-methyl more than a *trans*-methyl.<sup>24-26</sup> Furthermore, cis allylic coupling constants in similar trisubstituted vinylsilanes are larger than the trans coupling constants,<sup>25</sup> although the opposite is the case in disubstituted silanes.<sup>26</sup>

The nickel-catalyzed reaction of ethylmagnesium bromide with trimethylsilyloctyne takes an entirely different course. Treatment of 1 in THF with 2 equiv of ethylmagnesium bromide in ether in the presence of 10 mol % 1:1 nickel acetylacetonate-diisobutylaluminum hydride for 2 h at 0 °C, followed by quenching with water, gives a 50% yield of a 95:5



mixture of *cis*- and *trans*-trimethylsilyloctenes (24 and 25) and a 30% yield of 26. This is consistent with formation of an

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  $\sim$ 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 vield.

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<sub>2</sub>S 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-SB9H11 has the same framework structure<sup>3</sup> as  $nido-B_{10}H_{14}$  and since  $6-SB_9H_{11}$  is isoelectronic 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<sub>9</sub>H<sub>11</sub> 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 2alkyl-B<sub>5</sub>H<sub>8</sub> 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<sub>9</sub>H<sub>11</sub> 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 <sup>32</sup>S:<sup>34</sup>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 <sup>11</sup>B NMR. All of the alkene and alkyne hydroboration products investigated here gave very similar <sup>11</sup>B NMR spectra. These spectra all are reminiscent of that of 6-SB9H113 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<sup>-1</sup> range; those for 6-SB<sub>9</sub>H<sub>11</sub> are at 1920-1950 cm<sup>-1</sup>. Unfortunately, <sup>1</sup>H and <sup>13</sup>C NMR data were not so useful for characterization as might be anticipated. The <sup>13</sup>C spectra were consistent with hydroboration even though of the six investigated only two spectra (those with the  $B-C_5H_8$  and  $B-C_2H_5$  moieties) showed signals which could be attributed to carbon bound to <sup>11</sup>B. Similar difficulties have been encountered for other organoboranes.9