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[11] Thiophene failed to react with **1a** to furnish **3**. Instead, 4-vinyl-4-oxazolin-2-one (product of a 1,3-hydrogen shift) was provided in 88% yield (**1a**/thiophene = 1/100 mol/mol, 80 °C, 11 h).

[12] No trace of **5** was detected when run 8 of Table 1 was monitored by ^{1}H NMR spectroscopy and HPLC. There were only very small amounts of impurities; 20, 29, and 51% conversions after 2, 4, and 9 h at 70 °C, respectively.

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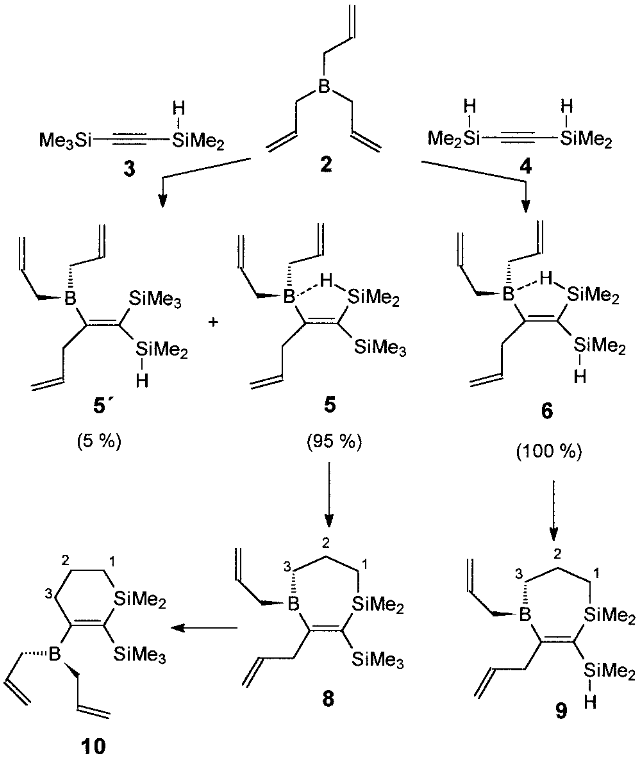
The First Si-H-B Bridge: Combination of 1,1-Organoboration and Hydrosilylation[**]

Bernd Wrackmeyer,* Oleg L. Tok, and Yuri N. Bubnov

The enormous synthetic potential of organoboron[1] and organosilicon compounds[2] is well documented. However, the combination of reactive species from both areas has not been studied extensively.[3–6] 1-Alkynylsilanes are known to react with diorganoboron hydrides by 1,2-hydroboration[4] and also by cleavage of the Si–C_{sp} bond, depending on the reaction conditions.[5] 1,1-Organoboration of 1-alkynylsilanes takes place if they are treated with triorganoboranes such as triethylborane (**1**) and heated up to 100 °C.[3c, 6] Boron compounds containing silyl groups with Si–H functionalities have received even less attention so far.

We have now observed that the reaction conditions for 1,1-organoboration can be much milder (room temperature, 0.5–1 h) if triallylborane (**2**), instead of **1**, and 1-alkynylsilanes with Si–H bonds, for example dimethylsilyl(trimethylsilyl)ethyne (**3**) and bis(dimethylsilyl)ethyne (**4**), are used. In the reaction products, the mutual positions of silyl and boryl groups at the C=C bond rouses in particular two questions: 1) Does the presence of the neighboring three-coordinate boron atom induce Si–H bond activation, or in other words, is there a Si-H-B bridge? 2) Are there further reactions between the Si–H functionalities and the C=C double bonds of the allyl groups? The answer to both questions is yes, as shown in Scheme 1.



Scheme 1. Reactions of triallylborane **2** with the 1-alykynylsilanes **3** and **4**.

The spectroscopic data of all compounds discussed here are summarized in Table 1. The presence of a Si-H-B bridge in **5** and **6** is reflected unequivocally by ^{1}H, ^{11}B, and ^{29}Si NMR and IR spectroscopic data. The ^{1}H NMR signal of the hydrogen atom in the bridge is broad, it is shifted to high field by about 1.5 ppm with respect to resonances for "normal" Si–H groups (for example, the second Me_2SiH group in **6**), and it is shifted further to high field at lower temperature (−30 °C; $\Delta\delta = -0.3$). The ^{11}B nuclear shielding is increased by about 20 (**6**) or 30 ppm (**5**) when compared with derivatives without a Si-H-B bridge. The ^{29}Si nuclear shielding is decreased by 34 (**6**; Figure 1) or 44 ppm (**5**) already at room temperature, and it decreases further at lower temperature (**5** (−30 °C): δ^{29}Si =

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Table 1. ^1H (500 MHz, $CDCl_3$, J(H,H)/Hz), ^{13}C (125.8 MHz, $CDCl_3$, J(Si,C)/Hz), ^{29}Si (99.4 MHz, $CDCl_3$, J(Si,Si)/Hz), and ^{11}B NMR data (160.5 MHz, $CDCl_3$) for compounds **5**–**10**.

5: $\delta(^1H) = 0.17$ (s, 9H, Me_3Si, 6.5{Si}), 0.32 (d, 6H, Me_2Si, 6.5{Si}, 3.0), 1.82 (dd, 2H, CH_2B, 15.3, 6.8), 2.00 (dd, 2H, CH_2B, 15.3, 8.4), 2.76 (br, 1H, SiH, 129.1{Si}), 3.03 (dt, 2H, CH_2, 7.2, 1.3(t)), 4.82 (ddt, 2H, *cis*-CH_2=, 10.2, 2.3, 1.2), 4.84 (ddt, 2H, *trans*-CH_2=, 16.9, 2.3, 1.5), 5.01 (ddt, 1H, *cis*-CH_2=, 9.9, 1.8, 1.2), 5.04 (ddd, 1H, *trans*-CH_2=, 17.1, 3.4, 1.7), 5.74 (ddt 1H, −CH=, 17.1, 9.9, 7.2), 5.91 (dddd, 2H, −CH=, 16.9, 10.2, 8.4, 6.8); $\delta(^{13}C) = -0.4$ (Me_2Si, 49.3), 1.4 (Me_3Si, 50.8), 32.6 (br, CH_2B), 42.9 (CH_2), 112.3 (CH_2={B}), 116.1 (CH_2=), 136.1 (−CH=), 136.7 (56.5), 138.9 (−CH={B}), 186.5 (br, =C−B); $\delta(^{29}Si) = -12.1$ (Me_3Si, 10.0), 12.6 (Me_2HSi, 10.0, $^2\Delta^{10/11}B(^{29}Si) = -46$ ppb); $\delta(^{11}B) = 51.6$

6: $\delta(^1H) = 0.22$ (d, 6H, Me_2Si, 6.7{Si}, 3.8), 0.27 (d, 6H, Me_2Si, 6.4{Si}, 3.4), 2.05 (br, 4H, CH_2B), 3.08 (dt, 2H, CH_2, 7.2, 1.4 (t)), 3.18 (br, 1H, *cis*-SiH, 146.0{Si}), 4.37 (sept, 1H, *trans*-SiH, 186.0{Si}, 3.8), 4.85 (ddd, 2H, *cis*-CH_2=, 10.1, 1.4, 1.4), 4.88 (ddd, 2H, *trans*-CH_2=, 17.4, 1.4, 1.4), 5.02 (ddd, 1H, *cis*-CH_2=, 9.8, 1.8, 1.2), 5.06 (ddd, 1H, *trans*-CH_2=, 16.9, 3.5, 1.7), 5.75 (ddd, 1H, −CH=, 16.9, 9.8, 7.2), 5.92 (m, 2H, −CH=); $\delta(^{13}C) = -2.1$ (Me_2Si, 50.4), −1.3 (Me_2Si, 49.6), 33.8 (br, CH_2B), 42.2 (CH_2), 112.9 (CH_2=), 116.3 (CH_2={B}), 134.1 (56.1), 135.8 (CH=), 137.8 (CH={B}), 185.5 (br, =C−B); $\delta(^{29}Si) = -31.0$ (Me_2HSi, 11.0), 3.2 (Me_3Si, 11.0, $^2\Delta^{10/11}B(^{29}Si) = -75$ ppb); $\delta(^{11}B) = 64.3$

7: $\delta(^1H) = 0.16$ (s, 9H, Me_3Si), 0.25 (d, 6H, Me_2Si), 0.95 (m, 9H, CH_3), 1.21 (q, 4H, CH_2, 7.8), 2.23 (q, 2H, CH_2, 7.6), 3.21 (br, 1H, SiH, 150.9); $\delta(^{13}C) = -1.1$ (Me_2Si, 49.7), 1.8 (Me_3Si, 50.2), 10.2 (CH_3), 13.5 (CH_3), 19.1 (br, CH_2), 30.7 (CH_2), 133.8 (=C−Si, 56.5), 191.5 (br, =C−B); $\delta(^{29}Si) = -1.1$ (Me_2Si, 10.8, $^2\Delta^{10/11}B(^{29}Si) = -50$ ppb), −12.2 (Me_3Si, 10.8); $\delta(^{11}B) = 69.4$

8: $\delta(^1H) = 0.14$ (s, 9H, Me_3Si, 7.0{Si}), 0.18 (s, 6H, Me_2Si), 0.60 (dd, 2H, H-1, 6.7{Si}), 1.39 (dd, 2H, H-3, 6.6), 1.77 (m, 2H, H-2), 2.23 (d, 2H, CH_2B, 7.5), 3.26 (dt, 2H, CH_2, 6.6, 1.5), 4.80–5.07 (m, 4H, =CH_2), 5.65–6.00 (m, 2H, =CH−); $\delta(^{13}C) = 0.6$ (Me_3Si, 49.7), 3.0 (Me_2Si, 50.2), 18.2 (C-2), 19.5 (C-1, 49.8), 29.6 (br, C-3), 36.3 (br, CH_2B), 42.9 (CH_2), 112.3 (=CH_2), 113.9 (=CH_2), 136.0 (=CH−), 136.6 (=CH−), 154.9 (=C−Si), 179.8 (br, =C−B); $\delta(^{29}Si) = -9.4$ (Me_3Si, 8.2), −4.3 (Me_2Si, 8.2); $\delta(^{11}B) = 80.5$

9: $\delta(^1H) = 0.10$ (s, 6H, Me_2Si), 0.28 (d, 6H, Me_2HSi, 4.1), 0.65 (dd, 2H, CH_2-1, 7.3, 6.7), 1.41 (t, 2H, CH_2-3, 6.6), 1.79 (m, 2H, CH_2-2), 2.24 (d, 2H, CH_2B, 7.8), 3.31 (dt, 2H, CH_2, 6.7, 1.4), 4.39 (sept, 1H, SiH, 4.1), 4.90–5.05 (m, 6H, CH_2=), 5.72 (ddt, 1H, −CH=, 16.9, 10.4, 6.6), 5.95 (m, 1H, −CH={B}); $\delta(^{13}C) = -1.5$ ($SiMe_2H$, 49.7), 0.9 ($SiMe_2$, 50.6), 18.7 (C-2), 18.7 (C-1, 49.8), 30.3 (br, C-3), 36.0 (br, CH_2B), 42.8 (CH_2), 114.1 (=CH_2{B}), 116.3 (=CH_2), 135.7 (=CH−), 136.5 (=CH−), 143.6 (=C−Si, 51.9), 180.4 (br, =C−B); $\delta(^{29}Si) = -28.4$ (Me_2HSi, 7.7), −5.00 (Me_2Si, 7.7); $\delta(^{11}B) = 81.7$

10: $\delta(^1H) = 0.03$ (s, 9H, Me_3Si), 0.23 (s, 6H, Me_2Si), 0.69 (dd, 2H, H-1, 6.7), 1.70 (m, 2H, H-2), 1.80 (dd, 2H, H-3, 6.7, 5.2), 2.23 (d, 4H, CH_2B, 7.5), 4.89–5.00 (m, 4H, =CH_2), 5.91 (ddt, 2H, =CH−, 17.8, 9.6, 7.5); $\delta(^{13}C) = 1.4$ (Me_2Si, 50.3), 1.5 (Me_3Si, 49.6), 13.6 (C-1, 50.4), 21.1 (C-2), 31.4 (C-3), 34.0 (br, CH_2B), 113.9 (=CH_2), 136.1 (=CH−), 145.1 (=C−Si, 51.9), 181.7 (br, =C−B); $\delta(^{29}Si) = -16.2$ (Me_3Si, 7.0), −6.0 (Me_2Si, 7.0); $\delta(^{11}B) = 76.9$

+18.0). This is in contrast to the finding for Zr-H-Si interactions,[7d] where the ^{29}Si shielding increases significantly, possibly as a result of Si−Zr bonding. The magnitude of the coupling constant $|^1J(^{29}Si,^1H)|$ is significantly reduced (by ca. 40 to 55 Hz; e.g. **6**: $^1J(^{29}Si,^1H) = 146$ Hz for the Si-H-B bridge and 186 Hz for the Me_2SiH group in *trans* position with respect to the boryl group), which is typical of Si−H activation and has been found for many transition metal complexes of silanes.[7] ^{11}B decoupling does not significantly sharpen the ^1H(Si-H-B) resonance since scalar $^{11}B-^1H$ coupling is averaged by fast ^{11}B quadrupolar relaxation (the line widths of the ^{11}B NMR signals exceed 300 Hz). There is an unprecedented isotope-induced shift $^2\Delta^{10/11}B(^{29}Si)$ in the ^{29}Si NMR spectra (**5**: −46 ppb, **6**: −75 ppb; confirmed by measurement at two different field strengths), transmitted through the Si-H-B bridge (Figure 1). In the IR spectrum of **5**, the band observed at 1905 cm^{-1} for ν(Si−H) is at markedly lower wavenumber than for the stretching vibrations of terminal Si−H groups (e.g. **3**: $\tilde{\nu}(Si{-}H) = 2146\ cm^{-1}$).

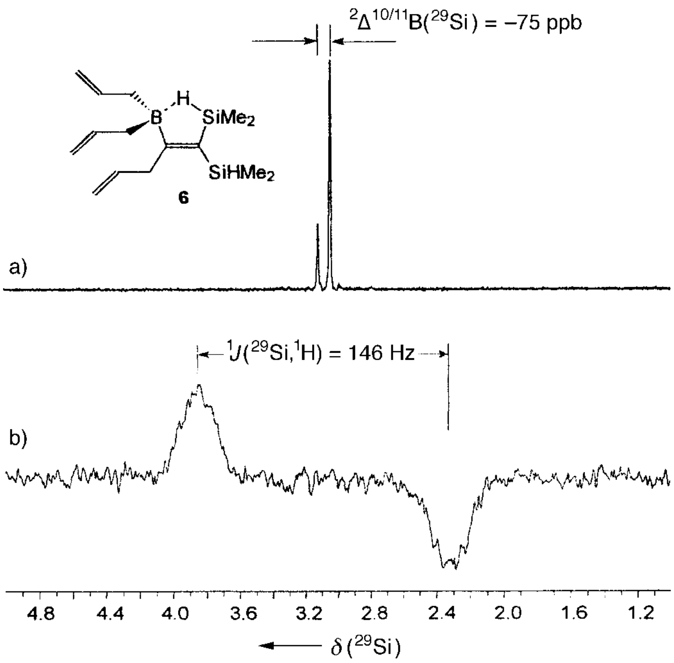
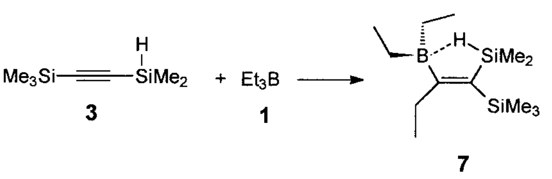


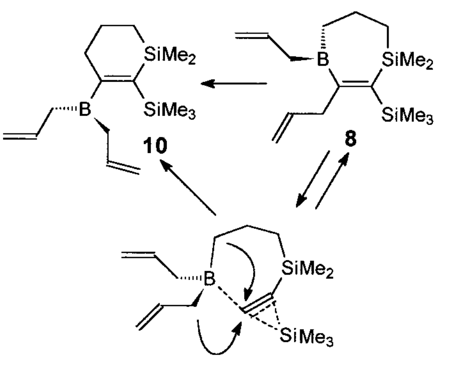
Figure 1. Sections of the ^{29}Si NMR spectra of **6** (99.4 MHz, the portions shown contain the signals for silicon atoms involved in the Si-H-B bridge). a) INEPT spectrum based on $^1J(^{29}Si,^1H) = 150$ Hz, refocused, ^1H-decoupled; the isotope-induced chemical shift $^2\Delta^{10/11}B(^{29}Si)$ is shown. b) INEPT spectrum based on $^1J(^{29}Si,^1H) = 150$ Hz, ^1H-coupled.

The product **7** obtained from the reaction of an excess of **1** with **3** [Eq. (1); no reaction at room temperature; heating for 10 h in boiling chloroform is required] has the same stereochemistry as **5**. The NMR spectroscopic properties of **7** (Table 1) are similar to those of **5** and **6**. This means that there is also a Si-H-B bridge in **7**, although the ^{11}B and ^{29}Si NMR data as well as the value of 2055 cm^{-1} for the $\tilde{\nu}$(Si−H) suggest that the bridge is somewhat weaker. Interestingly, all physical data of a comparable tin compound indicate negligible Sn-H-B interactions.[8]



(1)

After 24–48 h at room temperature in $CDCl_3$, compounds **5** and **6** have undergone further transformations. Thus, the new seven-membered heterocycles **8** and **9** (Table 1) are formed as the result of intramolecular hydrosilylation. These are rare examples of hydrosilylation taking place under extremely mild conditions without a catalyst. It is conceivable that the Si-H-B bridge is a prerequisite for this process (it should be noted that hydrosilylation of the C-allyl substituent does not take place in **6**). Compound **9** can be distilled and isolated as a colorless, extremely air-sensitive liquid. In contrast, **8** undergoes further rearrangement to give the six-membered heterocycle **10**. This can be explained as the result of 1,1-deorganoboration[3c] followed by 1,1-organoboration after which both allyl groups remain at the boron atom (Scheme 2). Intermediates of the type **11** are rather short-lived, whereas comparable derivatives with tin[9] or lead[10] instead of silicon have been isolated and fully characterized.



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Scheme 2. Proposed mechanism for the 1,1-deorganoboration and 1,1-organoboration of **8** to **10** via the short-lived intermediate **11**.

In summary, firm evidence for the presence of the Si-H-B bridge in **5** and **6** has been found. This kind of interaction will explain in particular intramolecular reactions of boron compounds which contain silyl groups with Si-H functionalities, and it will stimulate investigations in this field. First examples of novel routes to heterocycles have already been observed here in the attempt to combine 1,1-allylboration and hydrosilylation.

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Synthesis of Mono- and Di(oxopyri)porphyrins: A New Approach through Ring Enlargement with Diazomethane**

Andrei N. Kozyrev, James L. Alderfer, Thomas J. Dougherty, and Ravindra K. Pandey*

The past decade has seen increasing attention being paid to the synthesis of novel porphyrinoid aromatic compounds. A large number of these macrocyclic structures, including "expanded porphyrins", has been reported recently.[1] The interest in cyclic polypyrrole systems and their heteroanalogues is based on their potential application as photosensitizers in the treatment of cancer by photodynamic therapy, and as highly selective catalysts and organic electrical conductors.[1]

The simplest expanded porphyrins known are homoporphyrins containing an extra carbon atom in their structure. This class of porphyrins was first reported by Callot and coworkers.[2] Homoporphyrins that are expanded at *meso* positions are nonaromatic and unstable, although the related metal complexes were found to be quite stable.[3] The insertion of a carbonyl group between the α- and β-pyrrole

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