Reaction of Alkyn-1-yl(diorganyl)silanes with 1-Boraadamantane: Si-H-B Bridges Confirmed by the Molecular Structure in the Solid State and in Solution

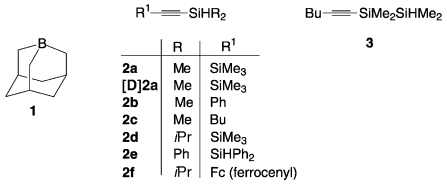
Bernd Wrackmeyer,* Wolfgang Milius, and Oleg L. Tok[a]

Abstract: 1-Boraadamantane **1** was treated with alkyn-1-ylsilanes **2** containing one or two Si–H functions. Under mild conditions, the reaction gave 4-methylene-3-borahomoadamantane derivatives **4** quantitatively and selectively by 1,1-organoboration. An electron deficient Si-H-B bridge was present in the product. The analogous reaction of **1** with an alkyn-1-yl-disilane **3** gave the corresponding alkene derivative **5**, however, without the Si-H-B bridge. Evidence for the Si-H-B bridge in **4** was given by IR data, an extensive set of NMR spectroscopical data (^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR) including various unusual isotope effects on chemical shifts and coupling constants, as well as from the molecular structure of one example, **4e**, in the solid state. The precursor of **4e**, alkyne **2e**, $Ph_2Si(H)C{\equiv}CSi(H)Ph_2$, was also studied by X-ray analysis.

Keywords: alkynes · organoboration · NMR spectroscopy · silanes · X-ray diffraction

Introduction

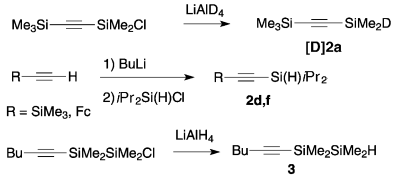
Activation of element–hydrogen bonds induced by transition metals is a well known phenomenon.[1] Main group elements with an electron-deficient center such as a trigonal planar coordinated silicon atom in a silylium cation or a boron atom in boranes can act in a similar way. Recently, convincing evidence for the first example of an electron-deficient Si-H-Si bridge has been presented.[2] We have shown in a preliminary report that an Si–H bond can be activated by a boryl group in close spatial proximity within the same molecule.[3] This may have some bearing on the mechanism of hydrosilylation catalyzed by strongly Lewis acidic boranes.[4] 1-Boraadamantane **1**[5] is probably the strongest Lewis acid among trialkylboranes, since its unique structure enforces a pyramidal environment on the three-coordinate boron atom.[6] The reaction of **1** with alkyn-1-yl(trialkyl)silanes proceeded by 1,1-organoboration.[7] This led to 4-methylene-3-bora-homoadamantane derivatives[6, 8] in which the three-coordinate boron atom still possesses pyramidal symmetry.[6] In the present work, we investigated the reactivity of **1** towards alkyn-1-yl(diorganyl)silanes, $R^1{-}C{\equiv}C{-}Si(H)R_2$ **2** and disilane **3** (Scheme 1). If these reactions follow the route of 1,1-organoboration, and if the products are formed in a stereoselective way with boryl and silyl group in *cis*-positions at the C=C bond, ideal conditions are provided to study Si-H-B bridges.



Scheme 1. Reactivity of 1-boraadamantane **1**.

Results and Discussion

Synthesis of the alkyn-1-yl(diorganyl)silanes 2 and disilane 3: With the exception of **2a**,[9] **2b**,[10] **2c**,[11] and **2e**,[12] the synthesis of alkyn-1-ylsilanes **2** and disilane **3** has not been described. The NMR data set of the known alkynes **2** was also incomplete. They are readily available by the reaction of the corresponding diorganosilicon chloride $R_2Si(H)Cl$ with the respective lithium alkynide or dilithium acetylide (Scheme 2).



Scheme 2. Generation of the alkynes **2**.

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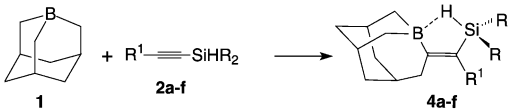
Table 1. ^{1}H, ^{13}C, and ^{29}Si NMR data[a] of the alkyn-1-ylsilanes **2** and **3**.

	$\delta^{29}Si$	$\delta^{1}H[^{1}J(^{29}Si,^{1}H)]$	$\delta^{13}C(\equiv C-Si)$ $[^{1}J(^{29}Si,^{13}C)]$	$\delta^{13}C(\equiv C-R)$ $[^{2}J(^{29}Si,^{13}C)]$
2a[b]	−38.8	4.12 [201.3]	110.3 [79.3], [12.2][c]	115.5 [76.2], [12.6][c]
[D]2a[d]	−39.0	−[30.9]	111.4 [79.8], [12.6][c]	116.4 [76.8], [12.8][c]
2b[e]	−37.2	4.29 [202.0]	91.8 [86.1]	107.6 [16.7]
2c[f]	−38.7	4.18 [199.3]	81.2 [88.7]	109.0 [17.4]
2d[g]	−16.5	3.77 [195.8]	108.2 [75.1], [11.9][c]	118.3 [76.3], [14.5][c]
2e[h]	−40.9	5.36 [215.6]	112.0 [83.9], [13.1]	–
2f[i]	−15.6	4.24 [194.3]	84.83 [84.2]	108.54 [14.9]
3[j]	−38.8	4.02 [176.6]	82.9 [78.4], [16.8][c]	110.7 [14.8], [2.2][k]

[a] In C_6D_6 at RT; coupling constants in Hz. [b] Other ^{13}C NMR data: $\delta = -3.1$ [56.1] (Me_2Si); −0.2 [56.5] (Me_3Si). Other ^{29}Si NMR data: $\delta = -18.6$ (Me_3Si, $^{3}J(^{29}Si,^{29}Si) = 1.8$ Hz). [c] ^{2}J. [d] Other ^{13}C NMR data: $\delta = -2.6$ [55.9] (Me_2Si), 0.3 [56.1] (Me_3Si), $^{2}J(^{2}H,\equiv^{13}C) = 1.2$ Hz. Other ^{29}Si NMR data: $\delta = -18.6$ (Me_3Si, $^{3}J(^{29}Si,^{29}Si) = 1.8$ Hz). Primary isotope effect $\Delta_p{}^{1}J(^{29}Si,^{2/1}H) = |{}^{1}J(^{29}Si,^{2}H)|\,(\gamma H/\gamma D) - |{}^{1}J(^{29}Si,^{1}H)| = -0.005$ Hz. [e] Other ^{13}C NMR data: $\delta = -2.4$ [55.3] (Me_2Si), 126.7 (Ph), 128.6 (Ph), 131.9 (Ph), 144.8 (5.0). [f] Other ^{13}C NMR data: $\delta = -2.8$ [56.0] (Me_2Si), 13.6 (Bu), 19.6 (Bu), 21. 9 (Bu, 3.1), 30.6 (Bu). [g] Other ^{13}C NMR data: $\delta = 0.4$ [56.3] (Me_3Si), 11.5 [57.9] (*i*Pr), 18.9 [2.2] (*i*Pr); 19.2 [2.2] (*i*Pr); other ^{29}Si NMR data: $\delta = -18.6$ (Me_3Si, $^{3}J(^{29}Si,^{29}Si) = 1.7$ Hz). [h] Other ^{13}C NMR data: $\delta = 128.2$; 130.3; 131.3 [76.3]; 135.2 [4.8]. [i] Other ^{13}C NMR data: $\delta = 11.8$ [57.8] (*i*Pr), 19.1 (*i*Pr), 19.4 (*i*Pr), 65.6 (Fc-1), 69.6, 72.7 (C-2,3,4,5), 70.9 (C_5H_5). [j] Other ^{13}C NMR data: $\delta = -6.2$ [45.0] [4.6] (Me_2SiH)); −1.5 [49.2] [5.9] (Me_2Si), 14.2 (Bu), 20.5 (Bu), 22.6 (Bu), 31.6 (Bu); other ^{29}Si NMR data: $\delta = -37.6$ (Me_2Si, $^{1}J(^{29}Si,^{29}Si) = 91.3$ Hz). [k] ^{3}J.

The deuterated compound **[D]2a** was prepared by reaction of $LiC{\equiv}CSiMe_3$ with an excess of Me_2SiCl_2 in order to obtain first $Me_2(Cl)SiC{\equiv}CSiMe_3$, which was then reduced with $LiAlD_4$. Compounds **2** and **3** were purified by distillation or crystallization, and were characterized by NMR spectrocopy (see Table 1 and Experimental Section), and in the case of **2e**, also by X-ray structural analysis (see below).

Reactions of 1-boraadamantane 1 with alkyn-1-ylsilanes 2: In contrast to other trialkylboranes, 1-boraadamantane **1** reacted readily with the alkyn-1-ylsilanes **2** at room temperature (Scheme 3). The reactions can conveniently be carried out in



Scheme 3. The reaction of **1** with alknyn-1-ylsilanes **2**.

NMR tubes, and were complete after 30 min. Products **4** were identified as 4-methylene-3-bora-homoadamantane derivatives by their characteristic NMR data (see Table 2 and Figure 1). Only one isomer was formed. The compounds **4** are oily, extremely air-sensitive liquids, and in the case of **4e**, a solid was obtained which could be recrystallized to give a material suitable for X-ray analsysis (see below).

The IR spectra of **4** show a band for $\tilde{\nu}$(Si–H) assigned to the Si-H-B bridge at significantly lower wavenumbers than expected for silicon hydrides (e.g. **4a**: $\tilde{\nu}$(Si-H-B) = 1849.0 cm^{-1}, and **2a**: $\tilde{\nu}$(Si–H) = 2139.7 cm^{-1}). This assignment was confirmed by the IR spectrum of the deuterium-labelled species **[D]4a** compared with **4a**. The Si-H-B bridge was also readily apparent in solution by NMR spectroscopy (Table 2 and Experimental Section): i) the ^{11}B NMR resonance is shifted to lower frequencies when compared with triorganoboranes;[13] this is typical of an increase in the coordination number of the boron atom; ii) the ^{29}Si nucleus in the Si-H-B bridge becomes deshielded (see for example the $\delta^{29}Si$ data for **4e**); and iii) the magnitude of the coupling constant $^{1}J(^{29}Si,^{1}H)$ becomes smaller when compared with triorganosilanes.[14] Another characteristic and rather unusual feature is the isotope-induced chemical shift $^{2}\Delta^{10/11}B(^{29}Si)$ which can be readily observed in the ^{29}Si NMR spectra (see Figures 2–4). Since this isotope effect is generally not detectable—as it is very small—in the absence of the Si-H-B bridge, it must be transmitted through the bridge and not through the C=C bond. It should be noted that this effect is larger for weak bridges (see Figure 4), and it becomes small and even changes its sign from negative to positive for strong bridges.[15] The changes in the $\delta^{11}B$ values as the result of bridge formation in **4** are much larger than in the corresponding alkenes where a diethylboryl or a diallylboryl group activates the Si–H bond.[3] This is in agreement with the enhanced Lewis acid character of the boron atom in the tricyclic framework in **4**. The ^{11}B and ^{29}Si NMR data in Table 2 indicate that the Si-H-B bridge is stronger for R^1 = silyl when compared with alkyl or aryl, in agreement with

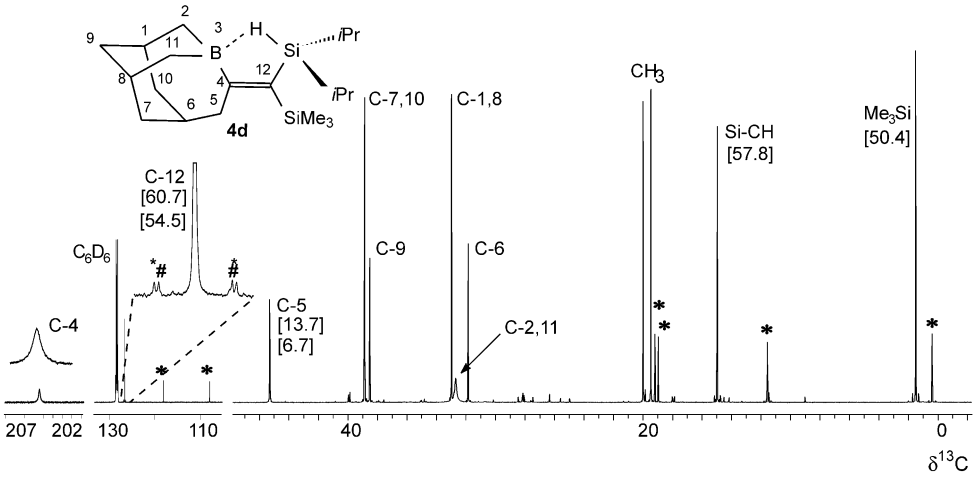


Figure 1. 125.8 MHz ^{13}C NMR spectrum of the reaction solution containing the alkene derivative **4d** (C_6D_6, 23 °C) in the presence of an excess of the alkyn-1-ylsilane **2e** (signals are marked by asterisks). Coupling constants $J(^{29}Si,^{13}C)$ are given in brackets. Note the typically broad[29] ^{13}C NMR signals of the carbon nuclei linked to boron.

Table 2. Selected ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the borahomoadamantanes **4a–f** and **5**.

	δ^{29}Si ($^{2}\Delta^{10/11}$B(^{29}Si))	δ^{11}B	δ^{1}H (Si–H)[$^{1}J(^{29}Si,^{1}H)$]	δ^{13}C(4) (B–C=)	δ^{13}C(12) (Si–C=)[$^{1}J(^{29}Si,^{13}C)$]
4a[b]	16.5 (–9.0)	37.8	3.10 [115.3]	200.9 br	129.8 [60.5, 57.8[c]]
[D]4a[d]	16.5 (–5.3)	36.9	– [17.3]	201.2 br	129.7 [60.5]
4b[e]	4.1 (–75.5)	59.5	3.54 [141.6]	174.8 br	132.3 [73.9]
4c[f]	8.7 (–62.2)	50.4	3.33 [137.0]	173.4 br	130.2 [74.9]
4d[g]	36.4 (–2.7)	36.4	2.59 [116.0]	204.5 br	126.8 [60.7, 54.5]
4e[h]	–3.0 (–33.0)	57.5	4.68 [142.3]	207.3 br	119.9 [61.7][i]
4f[j]	30.5 (–9.1)	38.2	2.65 [117.3]	178.9 br	122.5 [72.0]
5[k]	–38.5	83.4	4.14 [171.9]	164.6 br	132.1 [64.9, 4.8]

[a] In C_6D_6 at RT; coupling constants are given in Hz; br denotes ^{13}C NMR signals broadened by partially relaxed scalar $^{13}C,^{11}B$ spin–spin coupling. Isotope-induced chemical shifts $^{2}\Delta^{10/11}B(^{29}Si)$ are given in ppb (±0.5), and a negative sign indicates that the resonance signal of the heavy isotopomer is shifted to lower frequencies. [b] Other ^{13}C NMR data: $\delta = -0.3$ [47.7] (Me_2Si), 1.5 [50.3] (Me_3Si), 31.4 (br, C-2,11), 31.7 (C-6), 32.8 (C-1,8), 38.5 (C-9), 38.7 (C-7,10), 44.9 (C-5, 15.3, 6.7); other ^{29}Si NMR data: $\delta = -12.9$ (Me_3Si, $^{2}J(^{29}Si,^{29}Si) = 13.2$ Hz). [c] $^{29}Si(SiMe_3)$. [d] Other ^{13}C NMR data: $\delta = -0.4$ [47.8] (Me_2Si), 1.5 [50.4] (Me_3Si), 31.2 (br, C-2,11), 31.7 (C-6), 32.7 (C-1,8), 38.5 (C-9), 38.7 (C-7,10), 45.1 (C-5, 15.1, 5.8); other ^{29}Si NMR data: $\delta = -12.9$ (Me_3Si, $^{2}J(^{29}Si,^{29}Si) = 14.4$ Hz); primary isotope effect $\Delta_p{}^{1}J(^{29}Si,^{2/1}H) = |{}^{1}J(^{29}Si,^{2}H)|(\gamma H/\gamma D) - |{}^{1}J(^{29}Si,^{1}H)| = -2.60$ Hz. Secondary isotope effect $\Delta_s{}^{2}J(^{29}Si,^{29}Si)[^{2/1}H] = |{}^{2}J(^{29}Si,^{29}Si)[^{2}H]| - |{}^{2}J(^{29}Si,^{29}Si)[^{1}H]| = 1.2$ Hz. [e] Other ^{13}C NMR data: $\delta = -2.1$ [49.1] (Me_2Si), 31.5 (C-6), 33.8 (br, C-2,11), 33.9 (C-1,8), 38.0 (C-9), 38.2 (C-7,10), 38.3 (C-5, 9.3), 126.2, 128.7, 129.2, 142.4 [10.3] (Ph). [f] Other ^{13}C NMR data: $\delta = -1.3$ [48.0] (Me_2Si), 14.8, 23.9, 30.0 [7.7], 33.2 (Bu), 31.5 (C-6), 33.5 (br, C-2,11), 33.6 (C-1,8), 37.3 [10.3] (C-5), 38.4 (C-7,10), 38.5 (C-9). [g] Other ^{13}C NMR data: $\delta = 1.5$ [50.4] (Me_3Si), 11.6 [57.8] (Si–CH), 19.5 (*i*Pr), 19.9 (*i*Pr), 31.8 (C-6), 32.7 (br, C-2,11), 33.0 (C-1,8), 38.5 (C-9), 38.9 (C-7,10), 45.3 [13.7] [6.7] (C-5). Other ^{29}Si NMR data: $\delta = -14.2$ ($^{2}J(^{29}Si,^{29}Si) = 13.1$ Hz; Me_3Si). [h] Other ^{13}C NMR data: $\delta = 30.5$ (C-6), 32.6 (br, C-2,11), 32.9 (C-1,8), 37.3 (C-9), 37.4 (C-7,10), 43.1 [8.3] [4.7] (C-5), 127.7, 128.2 [6.1], 129.2, 130.0, 132.7 [67.8], 134.2 [68.2], 135.2 [4.9], 135.7 (Ph); other ^{29}Si NMR data: $\delta = -32.3$ ($^{2}J(^{29}Si,^{29}Si) = 12.5$ Hz; Ph_2HSi). [i] Intensities of the ^{29}Si satellites corrrespond to the presence of two ^{29}Si nuclei. [j] Other ^{13}C NMR data: $\delta = 14.3$ [50.1] (*i*Pr), 19.4 (*i*Pr), 19.8 (*i*Pr), 32.1 (C-6), 33.3 (C-1,8), 33.4 (br, C-2,11), 38.5 (C-9), 38.8 (C-7,10), 42.4 [9.8] (C-5), 68.3 (Fc), 69.5 (Fc), 70.0 (Fc), 86.4 [10.1] (Fc-1). [k] Other ^{13}C NMR data: $\delta = 2.4$ [50.5] (Me_3Si), 5.6 [54.8] (Me_2Si), 31.3 (C-6), 32.9 (C-1,8), 34.4 (br, C-2,11), 38.2 (C-7,10), 38.6 (C-9), 42.5 [13.6] [7.3] (C-5); other ^{29}Si NMR data: $\delta = -13.4$ ($^{2}J(^{29}Si,^{29}Si) = 16.2$ Hz; Me_3Si).

previous observations,[15] where a particularly weak Si-H-B bridge was found in an alkenylborane with $R^1 = Bu$. This can be interpreted as a steric effect exerted by R^1 which is required to push the $Si(H)R_2$ moiety towards the dialkylboryl group. The ^{1}H NMR signal of the Si–H bridge is shifted slightly to lower frequencies when compared with terminal Si–H units which, however, is not really of diagnostic value.

Altogether there are at least five parameters for a qualitative assessment of the strength of the Si-H-B bridge, namely the change in the Si–H stretching vibration, the shift of the ^{11}B NMR signal to lower frequencies and the shift of the ^{29}Si NMR signal to higher frequencies, the reduced magnitude of $^{1}J(^{29}Si,^{1}H)$, and the magnitude and sign of the isotope-induced chemical shift $^{2}\Delta^{10/11}B(^{29}Si)$. The latter effect is still not fully accessible by theory,[16] in particular in the case of the more heavy nuclei,[16, 17] whereas the changes in the ^{11}B and ^{29}Si nuclear shielding are in agreement with calculations of the shielding constants based on optimized geometries (see below). It is noteworthy that the isotope-induced shift $^{2}\Delta^{10/11}B(^{29}Si)$ is significantly less negative if deuterium instead of

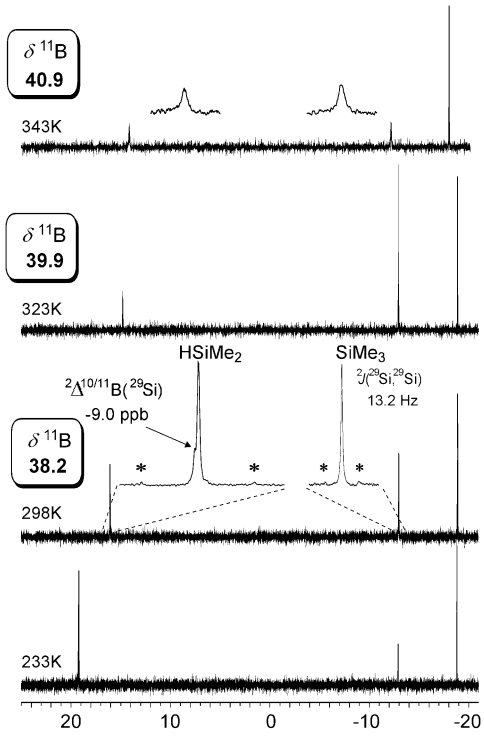


Figure 2. 99.4 MHz ^{29}Si NMR (refocused INEPT[28]) spectra of the compound **4a**, obtained from the reaction of 1-boraadamantane **1** with a slight excess of the alkyn-1-ylsilane **2a** (in C_7D_8), measured at different temperatures as indicated. The isotope-induced chemical shift $^{2}\Delta^{10/11}B(^{29}Si)$ is indicated; ^{29}Si satellites are marked by asterisks. Note the broadening of both ^{29}Si NMR signals of **4a** at elevated temperatures in contrast to the sharp signal for **2a** (only the signals of the Me_3Si group is shown, marked by an open circle).

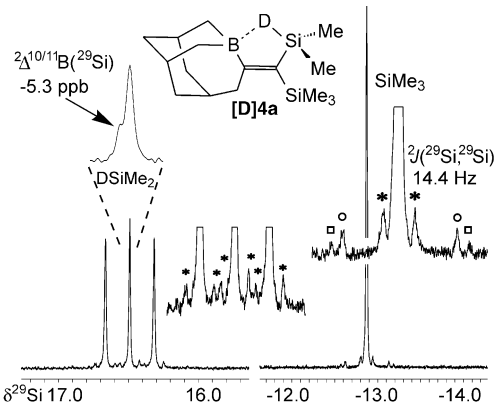


Figure 3. 99.4 MHz ^{29}Si NMR (refocused INEPT[28]) spectra of the compound **[D]4a**, obtained from the reaction of 1-boraadamantane **1** with the alkyn-1-ylsilane **[D]2a**. The isotope-induced chemical shift $^{2}\Delta^{10/11}B(^{29}Si)$ is indicated; note that this effect is smaller for the Si-D-B bridge when compared with the Si-H-B bridge in **4a** (Figure 2). There is also a small difference in the magnitude of $^{2}J(^{29}Si,^{29}Si)$ (^{29}Si satellites are marked by asterisks). ^{13}C satellites accompanying the $^{29}Si(SiMe_3)$ signal are marked by open circles (CH_3) and open squares (=C).

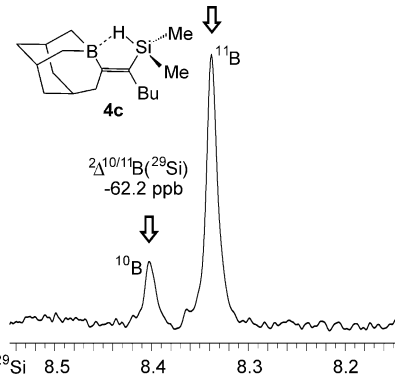
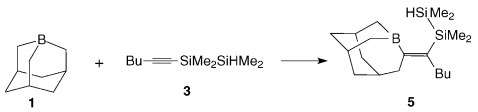


Figure 4. 99.4 MHz ^{29}Si NMR (refocused INEPT[28]) spectra of the compound **4c**, showing an example of a relatively large isotope-induced chemical shift $^{2}\Delta^{10/11}$B(^{29}Si). The other NMR data (Table 2) such as coupling constant $^{1}J(^{29}\mathrm{Si},^{1}\mathrm{H})$, δ^{29}Si and δ^{11}B indicate that the strength of this Si-H-B bridge is weaker than in most of the other compounds **4**.

hydrogen is in the bridging position (see Figures 2 and 3). Usually, the one-bond isotope-induced shift $^{1}\Delta^{1/2}\mathrm{H}(^{29}\mathrm{Si})$ in organosilanes is of the order of -200 to -250 ppb[18] (in the case of **2a/[D]2a** it is -219.5 ppb). In contrast, the value for $^{1}\Delta^{1/2}\mathrm{H}(^{29}\mathrm{Si})$ was only -25 ppb for **4a/[D]4a**; this implies the increasing influence of electronic factors rather than dynamic, solely mass-dependent factors. The unique bonding situation in the Si-H-B bridge is also reflected in the rather large primary isotope effect on the coupling constant $\Delta_{p}{}^{1}J(^{29}\mathrm{Si},^{2/1}\mathrm{H})$ in the case **4a/[D]4a** (-2.60 ± 0.03 Hz), when compared with that in the pair **2a/[D]2a**, where it is small (close to experimental error; -0.05 ± 0.03 Hz) as usual.[19] Interestingly, there is also a fairly large positive secondary isotope effect $\Delta_{s}{}^{2}J(^{29}\mathrm{Si},^{29}\mathrm{Si})[^{2/1}\mathrm{H}]$ (1.2 ± 0.03 Hz) which, however, is without precedent.

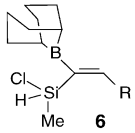
The ^{11}B and ^{29}Si chemical shifts of the nuclei involved in the Si-H-B bridge are temperature dependent (see Figure 2). With increasing temperature, the ^{11}B NMR signals were shifted slightly to higher frequencies, whereas the ^{29}Si NMR signals were shifted to lower frequencies. The magnitude of the coupling constants $^{1}J(^{29}\mathrm{Si},^{1}\mathrm{H})$ increased with increasing temperature. These findings indicate that the bridge becomes weaker at elevated temperatures, as would be expected. The accurate determination of the isotope-induced chemical shifts is difficult at variable temperature, since the ^{29}Si NMR signals become broader both on lowering or increasing the temperature. While the former effect can be explained by a reduced rate of interconversion of various conformers, the latter broadening effect is less obvious. Figure 2 shows that the linewidth of the ^{29}Si NMR signals of the alkyne **2a** is not affected by an increase in temperature, in contrast to both ^{29}Si NMR signals of the alkene **4a**. It is known that alkenes of type **4** with trialkylstannyl instead of silyl groups undergo deorganoboration quite readily.[8] Thus, it can be assumed that the observed broadening of the ^{29}Si NMR signals of **4a** at higher temperature (Figure 2) points towards the influence of an equilibrium deorganoboration/organoboration which, under these conditions, is still an intramolecular process without involving the alkyne **2a**.

Reaction of 1-boraadamantane 1 with the alkyn-1-yl-disilane 3: A smooth reaction of **1** was also observed with the disilane **3**, leading to the alkene **5**, in which the boron and disilanyl group are in *cis*-positions at the C=C bond (Scheme 4), as follows from ^{1}H/^{1}H NOE experiments.[20]



Scheme 4. The reaction of **1** with the disilane **3**.

However, there is no indication of a Si-H-B bridge. It appears that the six-membered ring which has to be formed in order to incorporate the bridge is not favorable. The same seems to be true for four-membered rings in the compounds of type **6** which have been studied both in solution and in the solid state (R = Ph).[21]



X-ray Structural analyses of bis(diphenylsilyl)ethyne 2e, and 4-methylene-3-borahomoadamantane derivative 4e:[22] The molecular structure of **2e** is shown in Figure 5, together with selected bond lengths and angles. Only few examples of

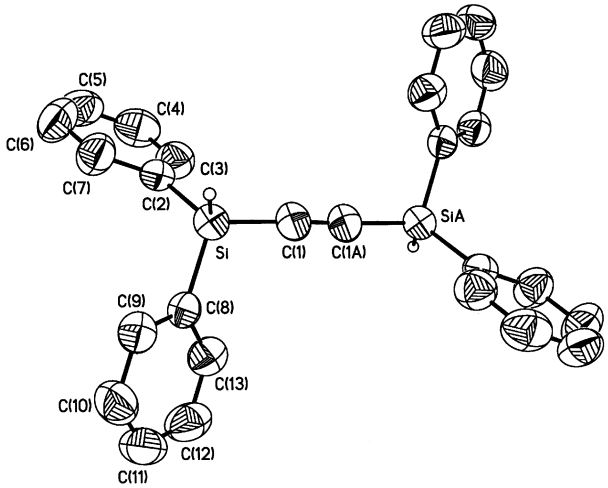


Figure 5. Molecular structure of bis(diphenylsilyl)ethyne **2e** (ORTEP plot with 50% probability; hydrogen atoms (except for Si–H) have been omitted for clarity); selected bond lengths [pm] and angles [°]: Si–C(1) 183.3(3), Si–C(2) 186.2(2), Si–C(8) 186.1(2), C(1)–C(1A) 120.8(5); C(2)-Si-C(8) 112.84(9), C(1)-Si-(C8) 108.13(10), C(1)-Si-C(2) 112.84(9).

bis(silyl)ethynes have been structurally characterized in the solid state.[23] The Si–C≡C–Si unit is linear, and the surroundings of the silicon atoms are almost tetrahedral. As expected, the bond of Si next to the ethynyl carbon atom (183.3(3) pm) is a little shorter than to the phenyl carbon atoms (186.1(2), 186.2(2) pm). The C≡C triple bond length (120.8(5) pm) is in

the range known for other C≡C bonds, though slightly longer than the average.

Although the quality of the single crystals of **4e** did not allow for a very precise structure determination (the molecular structure is shown in Figure 6), some important information can be obtained. The bridging hydrogen atom, although

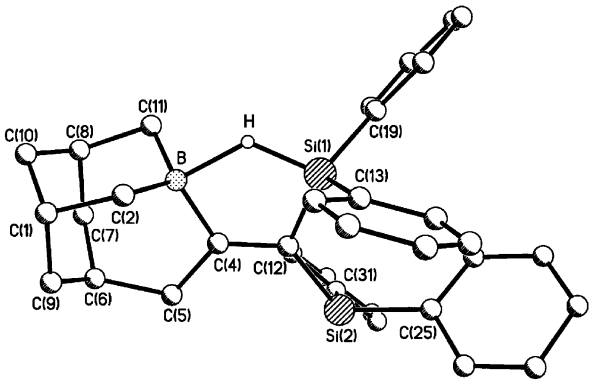


Figure 6. Molecular structure of the 3-bora-4-methylene-homoadamantane **4e** with the Si-H-B bridge (all other hydrogen atoms are omitted for clarity); selected bond lengths [pm] and angles [°]: Si(1)–H 147(10), B–H 160(10), Si(1)–C(12) 183.7(11), Si(1)–C(13) 187.9(12), Si(1)–C(19) 184.7(12), Si(2)–C(12) 186.6(11), Si(2)–C(25) 185.2(12), Si(2)–C(31) 185.5(13), C(4)–C(12) 135.1(14), BC(4) 159.8(18), B–C(2) 158.8(17), B–C(11) 154.8(18); Si(1)-H-B 126(2), C(13)-Si(1)-C(19) 112.0(5), C(25)-Si(2)-C(31) 107.5(6), Si(1)-C(12)-Si(2) 127.6(6), C(4)-C(12)-Si(1) 106.9(8), C(4)-C(12-)Si(2) 125.5(8), C(12)-C(4)-B 120.4(10), C(12)-C(4)-C(5) 125.4(10), B-C(4)-C(5) 114.2(9), C(2)-B-C(4) 118.0(11), C(2)-B-C(11) 116.0(11), C(4)-B-C(11) 115.6(11).

not accurately located, has its position half way between silicon and boron and closes a five-membered Si-H-B-C-C ring. The surroundings of the boron atom are pyramidally distorted (Σ of CBC bond angles 349.6°), significantly more than in a comparable 4-methylene-3-borahomoadamantane structure without a Si-H-B bridge (Σ of C-B-C bond angles 355.8°[6]). The sum of the C-Si-C bond angles is different for the two silyl groups (344.0 and 330.2°), with the larger sum for the silicon atom involved in the bridge; this is in agreement with the shift of the hydrogen atom towards boron. The bond angle C(12)-C(4)-B (120.4(10)°) appears to be as expected at a first glance. However, it is much more acute than the corresponding angle in the analogous structure without the Si-H-B bridge (130.6(19)°[6]), which means that the bridge in **4e** pulls the boron atom towards the silicon atom. The Si–C bond lengths are in the expected range, with the shortest bond for Si(1)–C(12) (183.7(11) pm). The C(4)=C(12) double bond (135.1(14) pm) is longer than most C=C bonds. There are also rather long C–C bonds in β-position relative to the boron atom in the tricycle (C(1)–C(2) 158.7(15) pm and C(8)–C(11) 156.2(16) pm) which indicates hyperconjugative interactions.[24]

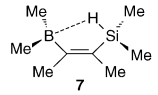
Quantum-chemical calculations of borane-silane adducts: Borane, BH_3, forms an adduct with trimethylsilane, Me_3SiH, and also with silane, SiH_4, according to the optimized geometries in the gas-phase (RB3LYP/6-311+G(d,p)[25]), when the respective molecules are combined. The analogous calculations carried out for BH_3 and the carbon analogues Me_3CH and CH_4 did not give any hint towards attractive interactions. In the case of the silanes, RB3LYP/6-311+G(d,p)-GIAO calculated ^{11}B and ^{29}Si nuclear shielding constants[26] are in agreement with the trend observed for the experimental data in the case of Si-H-B bridging: increase in the magnetic shielding of ^{11}B and decrease in the shielding of ^{29}Si (Table 3). Calculations [RB3LYP/6-311+G(d,p)] of the

Table 3. Calculated structural parameters and chemical shifts[a] of silane-BH_3 adducts and a trimethylgermane-BH_3 adduct.

	Me_3Si-H-BH_3[b]	Me_3Ge-H-BH_3	H_3Si-H-BH_3
M–H(B) [pm]	158.6	163.9	161.2
B–H(M) [pm]	132.2	136.9	131.4
M-H-B [°]	111.9	117.9	99.9
Σ angles (BH_3)	347.0	348.8	344.9
$\delta^{29}Si$[c]	22.9		– 62.4
$\delta^{11}B$[d]	– 27.1	– 19.4	– 44.7

[a] Geometries: RB3LYP/6-311+G(p,d); NMR data: RB3LYP/6-311+G(p,d)-GIAO; calculated by using the Gaussian 98 (Revision-A.9) program package.[25] [b] Calculated [R3BLYP/6-311+G(d,p) optimized geometries] stretching frequencies $\tilde{\nu}$(Si–H) = 2182.6 cm^{-1} for Me_3Si–H and 1991.1 cm^{-1} for Me_3Si-H-BH_3. [c] Calculated shielding $\sigma^{29}Si$ (Me_4Si) = 340.7 corresponding to $\delta^{29}Si = 0$; calculated shielding $\sigma^{29}Si$ (Me_3SiH) = 356.6 ($\delta^{29}Si = -15.9$; experimental: – 15.5); calculated shielding $\sigma^{29}Si$ (SiH_4) = 448.4 ($\delta^{29}Si = -107.8$; experimental: – 93.1). [d] Calculated shielding $\sigma(^{11}B)$ (B_2H_6) = 84.2 corresponds to $\delta^{11}B$ (B_2H_6) = 18.0.

geometries of molecules of type **4** (e.g. for **7**) indicated the orientation expected of the Si–H bond towards the boron atom. However, the long B – H distances (≥ 230 pm), the low degree of pyramidalization of the boron atom (sum of bond



7

Calculated geometry
[B3LYP/6-311+G(d,p)]
B ... H 271.1 pm; Si-H 149.5 pm
Σ(C-B-C) = 359.7°

angles at boron 358 – 359°), and the small increase in the calculated ^{11}B nuclear shielding (4 – 6 ppm) when compared with trigonal boranes did not provide convincing arguments. Similarly, calculations of 1-boraadamantane **1** in the presence of Me_3SiH or SiH_4 did not give useful information on Si-H-B bridging. Apparently, Si-H-B bridging depends strongly on steric constraints which are unfavorable for intermolecular interactions. In the case of intramolecular Si-H-B bridging as in **4**, it appears that the bridge is rather weak for R^1 = Bu (**4c**) and much stronger for R^1 = diorgano- or triorganosilyl. So far we have not carried out calculations on the experimental molecules such as **4a** using a large basis set.

Conclusions

1-Boraadmantane **1** is extremely reactive in 1,1-organoboration reactions when compared with other trialkylboranes. The 4-methylene-3-borahomoadamantane derivatives **4** which were formed by the 1,1-organoboration of alkyn-1-ylsilanes **2** contain the three-coordinate boron atom as a strongly

Lewis acid center which activates the neighboring Si–H bond by forming a Si-H-B bridge in **4**. The bridge is evident from the NMR data in solution, from the Si–H stretching vibration, and is also shown by the molecular structure in the solid state. The isotope effects observed both for chemical shifts and coupling constants are intriguing, since they are unusual and their successful reproduction by calculations will provide a stringent test for the models employed.

Experimental Section

General: The preparation and handling of all compounds was carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. Starting materials such as terminal alkynes, chlorosilanes and 1-boraadamantane **1** were either commercially available or were prepared following literature procedures (Fc–C≡CH,[27] **1**[5]). NMR measurements: Bruker ARX 250, Bruker DRX 500: ^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR (refocused INEPT[28] based on $^{2}J(^{29}Si,^{1}H_{Me})$ approximately 7 Hz or $^{1}J(^{29}Si,^{1}H)$ ca. 150 Hz), chemical shifts are given with respect to Me_4Si [δ^{1}H ($CHCl_3$/$CDCl_3$) = 7.24, (C_6D_5H) = 7.15; BAD indicates ^{1}H nuclei of the boraadamantane moiety; δ^{13}C ($CDCl_3$) = 77.0, (C_6D_6) = 128.0; δ^{29}Si = 0 for $\Xi(^{29}Si) = 19.867184$ MHz]; external $BF_3 \cdot OEt_2$ [δ^{11}B = 0 for $\Xi(^{11}B) = 32.083971$ MHz]. IR spectra: Perkin–Elmer, Spectrum 2000 FTIR. Melting or decomposition points: Büchi 510 melting point apparatus. All ab initio MO calculations were carried out by using the Gaussian 98 package.[25]

Synthesis of the alkyn-1-ylsilanes 2 and 3; general procedure: A suspension of freshly prepared lithium alkynide (10 mmol) in hexane/THF (20 mL; 1:1) was cooled to −78 °C, and a stoichiometric amount of the respective chloro(diorgano)silane in THF (10 mL) was added. The mixture was warmed to room temperature and stirred for 2 h. Insoluble materials were filtered off, and the solvents were removed at normal pressure. The residue was purified by fractional distillation at normal or reduced pressure, or was recrystallized. The deuterated compound **[D]2a** was prepared from chloro(dimethylsilyl)trimethylsilylethyne by reduction with $LiAlD_4$ in diethyl ether, followed by filtration and fractional distillation. Bis(silyl)ethyne **2e** was prepared from dilithioacetylene and two equivalents of Ph_2SiHCl, and was purified by recrystallization from toluene. Disilane **3** was prepared from 1-chloro-2-trimethylsilylethynyl-tetramethyldisilane by reduction with $LiAlH_4$ in diethyl ether, followed by filtration, removing of the solvent in vacuo and fractional distillation at reduced pressure.

Compound 2a: ^{1}H NMR: $\delta = 0.18$ (s, 9H; Me_3Si), 0.24 (d, 6H, $^{3}J(^{1}H,^{1}H) = 3.8$ Hz; Me_2Si); IR: $\tilde{\nu} = 2139.7$ (Si–H), 2088.3 cm^{-1} (C≡C).

Compound [D]2a: ^{1}H NMR: $\delta = 0.25$ (s, 6H; Me_2Si), 0.26 (s, 9H; Me_3Si).

Compound 2b: ^{1}H NMR: $\delta = 0.30$ (d, 6H; Me_2Si, $^{3}J(^{1}H,^{1}H) = 3.8$ Hz), 7.27 (m, 3H; Ph), 7.45 (m, 2H; Ph); IR: $\tilde{\nu} = 2139.5$ (Si–H), 2161.1 cm^{-1} (C≡C).

Compound 2c: ^{1}H NMR: $\delta = 0.27$ (d, 6H, $^{3}J(^{1}H,^{1}H) = 3.8$ Hz; Me_2Si), 0.98 (t, 3H; Bu), 1.48 (m, 2H; Bu), 1.56 (m, 2H; Bu), 2.29 (td, 2H; Bu); IR: $\tilde{\nu} =$ 2134.3 (Si–H), 2176.1 cm^{-1}(C≡C).

Compound 2d: ^{1}H NMR: $\delta = 0.26$ (s, 9H; Me_3Si), 1.1–1.2 (m, 14H; *i*Pr); IR: $\tilde{\nu} = 2120.5$ (Si–H), $\tilde{\nu}$C≡C not observed.

Compound 2e: ^{1}H NMR: $\delta = 7.4$ (m, 12H; Ph), 7.7 (m, 8H; Ph).

Compound 2f: ^{1}H NMR: $\delta = 1.17$ (m, 2H; *i*Pr), 1.28 (d, 6H; *i*Pr), 1.34 (d, 6H; *i*Pr), 4.01 (m, 2H; Fc), 4.19 (s, 5H; Fc), 4.51 (m, 2H; Fc).

Compound 3: ^{1}H NMR: $\delta = 0.27$ (d, 6H, $^{3}J(^{1}H,^{1}H) = 4.5$ Hz; Me_2Si), 0.33 (s, 6H; Me_2Si), 0.83 (m, 3H; Bu), 1.38 (m, 4H; Bu), 2.12 (m, 2H; Bu).

Reaction of 1-boraadamantane 1 with alkyn-1-ylsilanes 2 and 3; general procedure: A solution of the alkyn-1-ylsilane **2** or **3** (1.2 equivalents in the cases of volatile alkynes, and 1.0 equivalent in the case of **2e** or **2f**) in C_6D_6 (0.5 mL) was added at room temperature to a solution of 1-boraadamantane **1** (ca. 0.5 mmol) in C_6D_6 (0.5 mL). After recording of the NMR spectra, all volatile materials were removed in vacuo and a colorless oil (**4a–d**, **5**), a dark-yellow oil (**4f**) or a colorless solid (**4e**) was left, all in quantitative yield relative to **1**. The compounds were redissolved in pentane for IR measurements or in [D_8]toluene for variable temperature NMR measurements. Compound **4e** was redissolved in benzene in order to grow crystals by slow evaporation of the solvent.

Compound 4a: ^{1}H NMR: $\delta = 0.32$ (s, 9H; Me_3Si), 0.35 (d, 6H, $^{3}J(^{1}H,^{1}H) =$ 2.8; Me_2Si), 1.40 (ddd, 2H, $J(^{1}H,^{1}H) = 10.9, 3.6, 1.7$ Hz; BAD), 1.65 (m, 4H; BAD), 1.75 (ddd, 1H, $J(^{1}H,^{1}H) = 12.6, 4.9, 1.8$ Hz; BAD), 1.92 (ddd, 1H, $J(^{1}H,^{1}H) = 12.6, 5.3, 2.2$ Hz; BAD), 2.12 (m, 2H; BAD), 2.24 (m, 1H; BAD), 2.54 (br, 2H; BAD), 2.68 (d, 2H, $J(^{1}H,^{1}H) = 3.8$ Hz; BAD); IR: $\tilde{\nu} =$ 1849.0 cm^{-1} (Si–H).

Compound [D]4a: ^{1}H NMR: $\delta = 0.32$ (s, 9H; Me_3Si), 0.35 (s, 6H; Me_2Si), 1.37 (d, 2H, $J(^{1}H,^{1}H) = 11.2$ Hz; BAD), 1.63 (m, 4H; BAD), 1.76 (ddd, 1H, $J(^{1}H,^{1}H) = 12.4, 5.0, 2.0$ Hz; BAD), 1.91 (ddd, 1H, $J(^{1}H,^{1}H) = 12.4, 5.0, 2.3$ Hz; BAD), 2.13 (m, 2H; BAD), 2.24 (m, 1H; BAD), 2.53 (br, 2H; BAD), 2.68 (d, 2H, $J(^{1}H,^{1}H) = 3.8$ Hz; BAD); IR: $\tilde{\nu}$(Si–D) not assigned owing to overlap; the region around 1849 cm^{-1} (see **4a**) does not show a band of appreciable intensity.

Compound 4b: ^{1}H NMR: $\delta = 0.28$ (d, 6H, $^{3}J(^{1}H,^{1}H) = 3.2$ Hz; Me_2Si), 1.47 (d, 2H, $J(^{1}H,^{1}H) = 13.7$ H; BAD), 1.52 (d, 2H, $J(^{1}H,^{1}H) = 10.5, 1.7$ Hz; BAD), 1.59 (dtd, 1H, $J(^{1}H,^{1}H) = 12.5, 5.0, 1.9$ Hz; BAD), 1.80 (m, 3H; BAD), 1.95 (m, 2H; BAD), 2.14 (m, 1H; BAD), 2.47 (d, 2H, $J(^{1}H,^{1}H) =$ 4.2 Hz; BAD), 2.49 (br, 2H; BAD), 7.19 (m, 1H, Ph), 7.23 (m, 2H; Ph), 7.34 (m, 2H; Ph).

Compound 4c: ^{1}H NMR: $\delta = 0.34$ (d, 6H, $^{3}J(^{1}H,^{1}H) = 3.2$ Hz; Me_2Si), 1.07 (t, 3H; Bu), 1.45 (d, 2H, $J(^{1}H,^{1}H) = 12.1$ Hz; BAD), 1.50 (m, 4H; BAD, Bu), 1.58 (d, 2H, $J(^{1}H,^{1}H) = 13.9$ Hz; BAD), 1.68 (ddd, 1H, $J(^{1}H,^{1}H) =$ 12.5, 4.9, 1.8 Hz; BAD), 1.79 (dd, 2H, $J(^{1}H,^{1}H) = 10.5, 4.7$ Hz; BAD), 1.88 (ddd, 1H, $J(^{1}H,^{1}H) = 12.5, 5.3, 2.1$ Hz; BAD), 2.09 (m, 2H; BAD), 2.29 (t, 2H; Bu), 2.32 (m, 1H; BAD), 2.45 (d, 2H, $J(^{1}H,^{1}H) = 4.0$ Hz; BAD), 2.54 (m, 2H; BAD), 3.33 (m, 1H, $^{1}J(^{29}Si,^{1}H) = 137.0$ Hz; SiH); IR: $\tilde{\nu} =$ 2051 cm^{-1} (Si–H).

Compound 4d: ^{1}H NMR: $\delta = 0.35$ (s, 9H; Me_3Si), 1.15–1.25 (m, 14H; *i*Pr), 1.35 (d, 2H, $J(^{1}H,^{1}H) = 11.1$ Hz; BAD), 1.62 (d, 2H, $J(^{1}H,^{1}H) = 13.9$ Hz; BAD), 1.67 (dd, 2H, $J(^{1}H,^{1}H) = 11.3, 4.7$ Hz; BAD), 1.75 (ddd, 1H, $J(^{1}H,^{1}H) = 12.4, 5.0, 1.8$ Hz; BAD), 1.91 (ddd, 1H, $J(^{1}H,^{1}H) = 12.4, 5.2,$ 2.1 Hz; BAD), 2.12 (m, 2H; BAD), 2.26 (m, 1H; BAD), 2.49 (br, 2H; BAD), 2.59 (m, 1H; SiH, $^{1}J(^{29}Si,^{1}H) = 116.0$ Hz), 2.73 (m, 2H; BAD).

Compound 4e: M.p. 109–114 °C; ^{1}H NMR: $\delta = 1.6–1.7$ (m, 6H; BAD), 1.87 (ddd, 1H, $J(^{1}H,^{1}H) = 11.8, 4.9, 2.2$ Hz; BAD), 2.0–2.2 (m, 3H; BAD), 2.33 (m, 1H; BAD), 2.55 (br, 2H; BAD), 2.76 (d, 2H, $J(^{1}H,^{1}H) = 3.9$ Hz; BAD), 5.58 (s, 1H, $^{1}J(^{29}Si,^{1}H) = 193.7$ Hz; SiH), 7.4–8.0 (m, 20H; Ph); IR: $\tilde{\nu} = 2119, 1890$ cm^{-1} (Si–H).

Compound 4f: ^{1}H NMR: $\delta = 1.2–1.4$ (m, 14H; *i*Pr), 1.41 (m, 2H; BAD), 1.70 (d, 2H, $J(^{1}H,^{1}H) = 13.7$ Hz; BAD), 1.80 (m, 3H; BAD), 1.97 (m, 1H; BAD), 2.20 (m, 2H; BAD), 2.47 (m, 1H; BAD), 2.57 (br, 2H; BAD), 2.65 (br s, 1H; SiH, $^{1}J(^{29}Si,^{1}H) = 117.3$ Hz), 2.88 (d, 2H, $J(^{1}H,^{1}H) = 3.9$ Hz; BAD), 4.20 (m, 2H; Fc), 4.21 (s, 5H, Fc), 4.35 (m, 2H; Fc).

Compound 5: ^{1}H NMR: $\delta = 0.24$ (s, 6H; Me_2Si), 0.27 (d, 6H, $^{3}J(^{1}H,^{1}H) =$ 4.5 Hz; Me_2Si), 1.04 (t, 3H; Bu), 1.3–1.8 (m, 17H; BAD, Bu), 2.2–2.4 (m, 4H; BAD, Bu); IR: $\tilde{\nu} = 2096$ cm^{-1} (Si–H).

Acknowledgement

Support of this work by Volkswagen-Stiftung, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (B.W.) is gratefully acknowledged.

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[22] X-ray crystallographic investigations of **2e** and **4e**: The reflection intensities were collected on a Siemens P4 diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 71.073$ pm, graphite monochromated). Structure solution and refinement were carried out with the program package SHELXTL-PLUS V.5.1. Measuring temperature for the structure determinations was 296 K (no reflections were observed for **4e** at 100 K). All non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms except the hydrogen atoms at silicon are taken at calculated positions, and were refined applying the riding model with fixed isotropic temperature factors. **2e**: $C_{26}H_{22}Si_2$: a colorless crystal of irregular shape with dimensions $0.30 \times 0.18 \times 0.15$ mm crystallizes in the rhombohedral space group $R\bar{3}$ (148) with the lattice parameters $a = 31.9342(15)$, $b = 31.9342(15)$, $c = 5.8187(5)$ Å; $\alpha = \beta = 90$; $\gamma = 120°$; $V = 5138.9(6)$ Å^3; $Z = 9$; $\mu = 0.163$ mm^{-1}; 5096 reflections collected in the range $2.21 \geq \vartheta \geq 27.51°$; 2598 reflections independent; empirical absorption correction; 2598 reflections assigned to be observed [$I > \sigma(I)$], full-matrix least squares refinement against F^2 with 128 parameters converged at $R1/wR2$-values of 0.0501/0.1437; the max./min. residual electron density was 0.591/ – 0.162 e Å^{-3}. **4e**: $C_{35}H_{34}BSi_2$: a colorless, irregularly-shaped crystal with dimensions $0.18 \times 0.16 \times 0.10$ mm crystallizes in the monoclinic space group $P2(1)/n$ with the lattice parameters $a = 10.9008(18)$, $b = 8.4424(10)$, $c = 32.633(4)$ Å; $\alpha = 90$, $\beta = 96.257(8)$, $\gamma = 90°$; $V = 2985.3(7)$ Å^3; $Z = 4$; $\mu = 0.141$ mm^{-1}; 6873 reflections collected in the range $1.92 \geq \vartheta \geq 25.01°$; 5154 reflections independent; no absorption correction; 2598 reflections assigned to be observed [$I > 2\sigma(I)$]; full-matrix least squares refinement against F^2 with 343 parameters converged at $R1/wR2$ values of 0.1461/0.3882; the max./min. residual electron density was 0.772/ – 0.291 e Å^{-3}.
CCDC-206150 (**2e**) and -206151 (**4e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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