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Aminoethynyl-silanes, -germanes and -stannanes: novel organometallic-substituted enamines via 1,1-organoboration

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The reactions of diethylaminoethynyl(trimethyl)silane (1), bis(diethylaminoethynyl)methylsilane (2), diethylaminoethynyl(trimethyl)germane (3), dimethylaminoethynyl(triethyl)germane (4), diethylaminoethynyl(trimethyl)stannane (5) and methyl(phenyl)aminoethynyl(trimethyl)stannane (6) with trialkylboranes [BEt_3 (7b), BPr_3 (7c), B^iPr_3 (7d) and 9-alkyl-9-borabicyclo[3.3.1]nonanes 9-Me-9-BBN (8a) and 9-Et-9-BBN (8b)] were studied. The alkynes 1 and 2 did not react even with boiling BEt_3, whereas the reactions of 3–6 afforded mainly novel enamines [(*E*)-1-amino-1-trialkylgermyl-2-dialkylboryl-alkenes (9, 10), (*E*)-1-diethylamino-1-trimethylstannyl-2-dialkylboryl-alkenes (11, 12), (*E*)-1-methyl(phenyl)amino-1-trimethylstannyl-2-dialkylboryl-alkenes (13, 14)]. This particular stereochemistry is unusual for products from 1,1-organoboration reactions, indicating a special influence of the amino group. The starting materials and products were characterized by multinuclear magnetic resonance spectroscopy (^1H, ^{11}B, ^{13}C, ^{15}N, ^{29}Si, ^{119}Sn NMR). Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: alkynes; boron; silicon; germanium; tin; heterocycles; Organoboration; multinuclear magnetic resonance

INTRODUCTION

Organometallic-substituted alkenes are attractive synthons for further transformations.[1–4] This potential in synthesis can be enhanced if an amino group is present, in addition to the organometallic substituents. We have found that 1,1-organoboration[5] is a convenient method for converting organometallic-substituted alkynes ($R^1 = H$, alkyl, aryl), in high yield, regio- and stereo-specifically into alkenes. In general, such reactions proceed by cleavage of the M–C≡bond to give a zwitterionic alkynyl-borate like intermediate **A** with the fragment containing M coordinated side-on to the C≡C bond.[5,6] In the next step, an organyl group migrates from boron to carbon and the fragment containing M and the boryl group in **B** are in cis-positions at the C=C bond (Scheme 1).

The stereochemistry may be less well defined if R^1 contains a functional group or is itself a functional group. Previously, it was observed that in most cases for $R^1 = CH_2OMe$[7] or CH_2NMe_2[8–10] the stereochemistry is the same as in **B**. Recently, we have studied the 1,1-organoboration for R^1 = OMe or OEt and M=Si, Ge, Sn, and again the same stereochemistry as in **B** was observed.[11] If R^1 is an amino group, however, the nature of the intermediate **A** could be markedly changed, and, therefore, the result of the 1,1-organoboration might be different from type **B**. Here, we have studied the reactivity of various aminoethynyl-Group-14 derivatives with Si–C≡(**1, 2**), Ge–C≡(**3, 4**) and Sn–C≡bonds (**5, 6**) with respect to their reactivity towards different trialkylboranes (Scheme 2).

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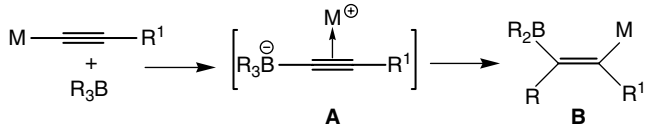
RESULTS AND DISCUSSION

Aminoethynyl-group-14 compounds 1–6 and their NMR spectroscopic properties

All compounds **1–6** were prepared following literature procedures.[12,13] The aminoethynyl derivative **2** has not been described so far. ^{13}C, ^{29}Si, ^{119}Sn and some ^{15}N NMR data are



Scheme 1.

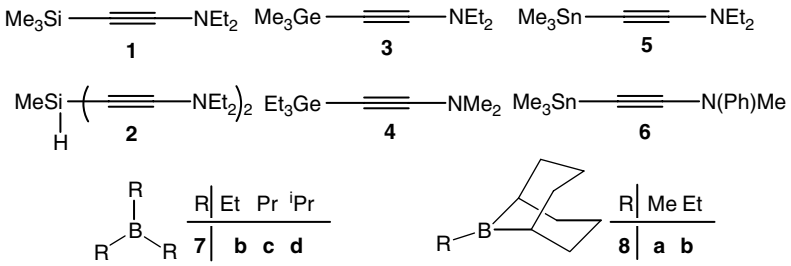
given in Table 1. The δ^{13}C(alkyne)[14] and the δ^{15}N NMR data indicate that the bonding situation at the alkynyl carbon atoms and at the nitrogen atoms hardly changes with different MMe_3 groups. The change in δ^{15}N in compound **4** is fully consistent with the effect of methyl in comparison to ethyl groups.[15] Therefore, it was of interest to find out whether the magnitude of the coupling constants $^1J(^{13}C{\equiv}^{13}C)$ responds to the nature of M in MMe_3. These data could be measured reasonably fast by application of polarization transfer experiments (Fig. 1) in order to circumvent the problem of notoriously long relaxation times of alkynyl ^{13}C nuclei. The data for M═Si and M═Ge are almost identical and the value for M═Sn is smaller by *ca* 10 Hz, which is also the effect usually observed for other alkyn-1-yl-silanes and -stannanes.[17] The presence of the diethylamino group causes an increase in the magnitude of $^1J(^{13}C{\equiv}^{13}C)$ [e.g. $Me_3Si{-}C{\equiv}C{-}^tBu$: $^1J(^{13}C{\equiv}^{13}C) = 130.6$ Hz and $Me_3Ge{-}C{\equiv}C{-}^tBu$: $^1J(^{13}C{\equiv}^{13}C) = 131.5$ Hz[17]], and also of $^1J(M,^{13}C{\equiv})$ (M═Si, Sn) when compared with corresponding alkyn-1-yl-silanes [e.g. $Me_3Si{-}C{\equiv}C{-}Me$: $^1J(^{29}Si,^{13}C{\equiv}) = 80.9$ Hz[18]] or stannanes (e.g. $Me_3Sn{-}C{\equiv}C{-}Me$: $^1J(^{119}Sn, ^{13}C{\equiv}) = 502.9$ Hz[19]), in which the NEt_2 group is replaced by an alkyl group.

Reaction of the aminoethynyl derivatives 1–6 with the trialkylboranes 7 and 8

The silicon compounds **1** and **2** did not react with triethylborane (**7b**), even after heating **1** or **2** in BEt_3 as the solvent for 5 days at 100 °C. In contrast, the germanes **3** and **4**, and, much more readily, the tin compounds **5** and **6**, reacted with the trialkylboranes.

In the cases of the germanes **3** and **4**, after heating in toluene at 105 °C (with BEt_3, **7b**) or in benzene at 75 °C (with BPr_3, **7c**) for 3 to 5 days in the presence of an excess of the borane **7b** or **7c**, the alkenes **9** and **10** were obtained in almost quantitative yield (Scheme 3). They are air- and moisture-sensitive yellowish oils, which can be further purified by distillation (**9b** and **10b**) under reduced pressure, and they can be stored in solution or in the pure state in the refrigerator for prolonged periods without decomposition.

The stereochemistry in **9** and **10** follows from the ^{13}C NMR data (one broad and one sharp signal in the olefinic region; see Fig. 2 for the tin compound **11c**, and the data given in



Scheme 2.

Table 1. ^{13}C, ^{15}N, ^{29}Si and ^{119}Sn NMR data[a] of the aminoethynyl-Group-14 compounds **1**–**6**

	1	2	3	4	5	6
δ^{13}C(M–C≡)	64.6 (96.5)	61.3 (110.0)	64.0	56.8	61.3 [557.7]	66.2 [513.3]
δ^{13}C(N–C≡)	108.4 (20.2)	109.1 (24.4)	107.3	112.3	111.6 [130.7]	105.9 [122.1]
$^1J(^{13}C{\equiv}^{13}C)$	152.1	n.m.	152.3	n.m.	142.0	n.m.
δ^{13}C(MMe/MEt)	1.3 (55.9)	0.4 (61.0)	0.8	6.5, 9.2	−7.5 [402.7]	−7.5 [404.4]
δ^{13}C(NEt_2/ NMe_2/N(Ph)Me)	47.9, 12.9	47.8, 12.9	47.4, 12.9	43.6	48.3, 12.9	145.0, 114.3, 129.2, 120.4 (Ph); 38.8 (Me)
δ^{15}N	−332.1	−331.1	−332.5	−360.9	−331.2	n.m.
δ^{29}Si/δ^{119}Sn	−19.7[b]	−63.0[c]	—	—	−67.6[d]	−63.0

[a] Measured in C_6D_6 at 23 °C; coupling constants $J(^{29}Si,^{13}C)$ are given in parentheses (±0.1 Hz), $J(^{119}Sn,^{13}C)$ in brackets [±0.1 Hz], both measured from ^{29}Si or ^{119}Sn NMR spectra respectively; n.m. means not measured.
[b] Isotope-induced chemical shifts: $^1\Delta^{12/13}C_{Me}(^{29}Si) = -1.5$ ppb; $^1\Delta^{12/13}C_{C\equiv}(^{29}Si) = -13.5$ ppb; $^2\Delta^{12/13}C_{C\equiv}(^{29}Si) = -2.5$ ppb.
[c] Isotope-induced chemical shifts $^1\Delta^{12/13}C_{Me}(^{29}Si) = +2.0$ ppb; $^1\Delta^{12/13}C_{C\equiv}(^{29}Si) = -9.5$ ppb; $^2\Delta^{12/13}C_{C\equiv}(^{29}Si) = -2.2$ ppb.
[d] Isotope-induced chemical shifts $^1\Delta^{12/13}C_{Me}(^{119}Sn) = \pm 0$ ppb; $^1\Delta^{12/13}C_{C\equiv}(^{119}Sn) = -48$ ppb; $^2\Delta^{12/13}C_{C\equiv}(^{119}Sn) = -6$ ppb.

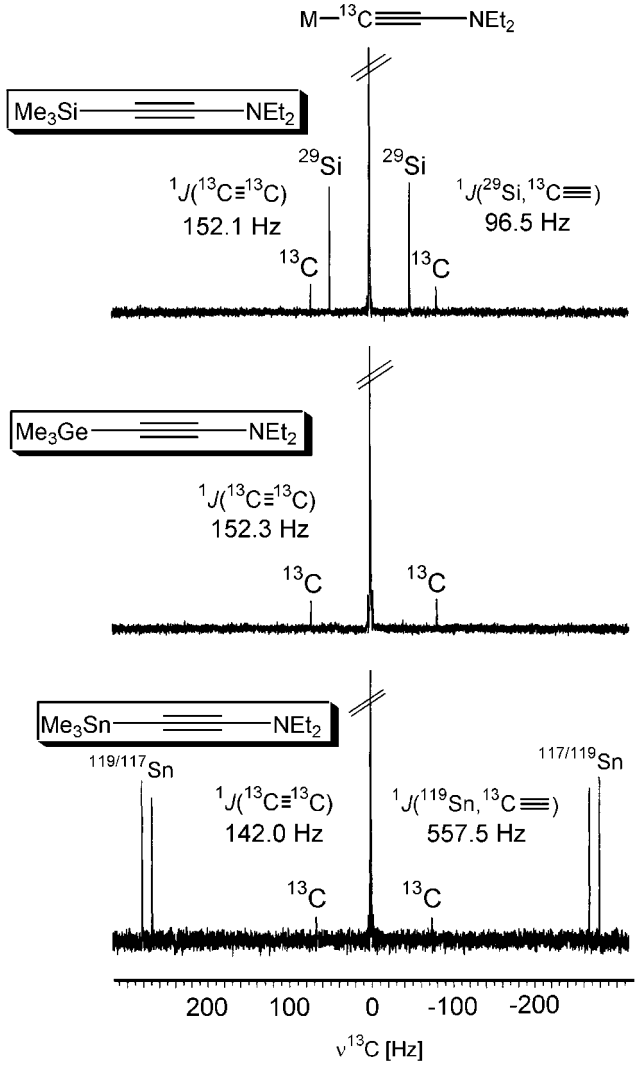
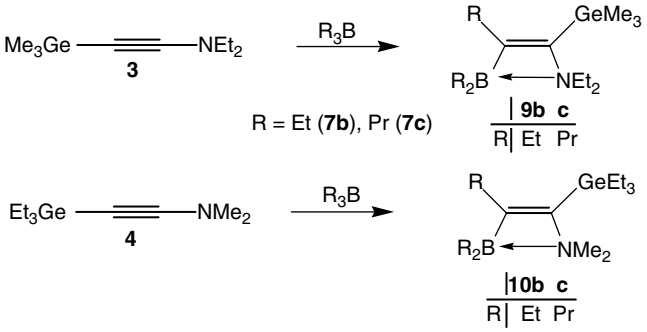


Figure 1. The 125.8 MHz $^{13}C\{^1H\}$ NMR spectra of the diethylaminoethynyl derivatives **1**, **3**, and **5**, recorded using the refocused INEPT pulse sequence based on $^3J(\equiv{}^{13}C,M,C,^1H) = 3.5$ Hz.[16] Shown is the $^{13}C(M-C\equiv)$ NMR signal in each case, and the respective satellite signals are indicated.

Table 2), typical of this substituent pattern, and also from the ^{11}B chemical shifts which are indicative of an intramolecular coordinative N–B bond.[21] Measurement of ^{11}B NMR spectra of strongly diluted or concentrated samples gave identical $\delta^{11}B$ values, which means that intermolecular (e.g. dimer-type interactions) do not play an important role. Usually, the 1,1-organoboration leads to alkenes of type **B**, in which the boryl group and the organometallic substituent are in cis positions at the C=C bond.[5] Apparently, the presence of the amino group changes this situation completely.

It is well known[5,22] that the Sn–C≡bond is much more labile than Si–C≡ or the Ge–C≡ bonds, and, in general, the 1,1-organoboration of most alkyn-1-yl-stannanes is complete



Scheme 3.

after warming the respective reaction mixture from −78 °C to room temperature.[5] Exactly this behaviour was observed for the reactions of **6** with the trialkylboranes **7b**, **7d** and **8b**, and almost quantitative formation of the alkenes **13** and **14** was observed. In contrast, the reactions of **5** with the boranes **7b,c** and **8a,b** were not complete under these conditions. Heating of the reaction mixtures mainly caused decomposition. However, when the reaction solutions were kept for 24–72 h at room temperature, defined products could be identified in the mixtures, which contained mainly (>60%) the alkenes **11** and **12**. Monitoring of the reactions by ^{119}Sn NMR spectroscopy did not reveal the formation of appreciable amounts of isomers of **11** or **12**. Side products were tetralkylstannanes, such as $SnMe_4$, Me_3SnEt or Me_2SnEt_2, along with numerous products (due to exchange of B-alkyl/SnMe groups) in minor quantities, for which the structures could not be assigned. The results for **5** and **6** are summarized in the Schemes 4 and 5.

The stereochemistry of all 1,1-organoboration products **11**–**14** is again unusual,[5] in analogy to the findings for the germanium derivatives **9** and **10**. The boryl and the stannyl groups are in trans positions at the C=C bond, irrespective of fairly strong (**11**) or rather weak coordinative N–B bonds (**12**–**14**). ^{13}C and ^{11}B NMR data (Table 2), and $^1H/^1H$ NOE difference experiments[23] [irradiation of $^1H(SnMe_3)$ and response of $^1H(R-C=)$ transitions] provide convincing evidence for the proposed structures. Molecular models supported by semi-empirical AM1 calculations[24,25] and low-level *ab initio* molecular orbital calculations (RHF/STO-3G[24,26]) suggest that the bicyclic frameworks containing the boron atom in **12** and **14** prevent significant intramolecular coordinative N–B bonding for steric reasons. In addition, the Lewis basicity of the N(Ph)Me group is low; therefore, N–B bonding is rather weak, even in **13b**, where steric conditions at the boron atoms (the plane of CCB is perpendicular on average to the B–C=C plane) would, in principle, be favourable (see **11**) for intramolecular coordinative N–B bonding. Both $\delta^{11}B$ and $\delta^{119}Sn$ NMR data of the compounds **11**–**14** are independent of the concentration (within experimental error). Therefore, as in the case of the germanium compounds, intermolecular interactions appear to be extremely weak and can be neglected for the structural assignment in solution.

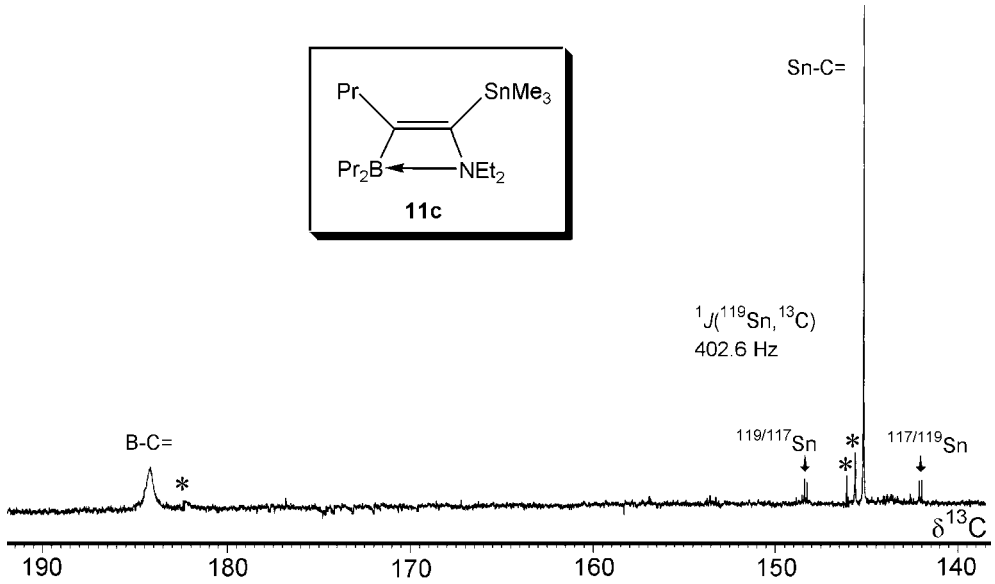


Figure 2. The 62.9 MHz $^{13}C\{^1H\}$ NMR spectrum of the 1,1-propylboration product **11c**, showing the region for olefinic carbon atoms. The broad signal is typical for a ^{13}C nucleus linked to boron,[20] and the sharp signal is accompanied by $^{117/119}Sn$ satellites (arrows) corresponding to $^1J(^{117/119}Sn,^{13}C)$. Signals arising from impurities are marked by asterisks.

The magnitude of the coupling constants $|J(^{119}Sn,^{13}C)|$[27–29] in the alkenes **11**–**14** deserve a brief comment. In the compounds with coordinative N–B bonding, the values $|^1J(^{119}Sn,^{13}C{=})|$ are small (400.0 and 402.6 Hz in **11b**, **11c**), in contrast to those where N–B bonding is weak or absent (512.0, 462.1, 462.5, 505.7 Hz in **12b**, **13b**, **13d**, **14b**). On the other hand, the values $|^1J(^{119}Sn,^{13}C(Me))|$ are significantly smaller, particularly in the cases of **12a** and **12b** (285.5 and 284.3 Hz), than in **11b** or **11c** (332.5 and 332.6 Hz). These effects could be explained by the assumption of weak intramolecular coordinative N–Sn interactions if the lone pair of electrons at the nitrogen atom is not engaged in coordinative N–B bonding. In agreement with the data, such effects for the $SnMe_3$ groups are more pronounced in compounds with the NEt_2 (**12a**, **12b**) rather than with the N(Ph)Me group (**14b**: $|^1J(^{119}Sn,^{13}C(Me))| = 307.4$ Hz), since the nitrogen atom in the latter amino group is less basic. A coordinative N–Sn bond would lead to distorted trigonal bipyramidal surroundings of the tin atom by which the olefinic carbon atom always occupies an equatorial position (larger values of $|^1J(^{119}Sn,^{13}C{=})|$!), and the methyl groups change between equatorial and axial positions. The contribution of the axial position to $|^1J(^{119}Sn,^{13}C(Me))|$ is small, as is known for the anion $[SnMe_5]^-$[30] and other penta-coordinate methyltin compounds;[31,32] therefore, the averaged values for $|^1J(^{119}Sn,^{13}C(Me))|$ become smaller. The magnitude of $|^3J(^{119}Sn,^{13}C)|$ is rather small in the compounds **11** to **14**. This is due to the presence of the electronegative nitrogen atom at the C=C bond and to the cis-position of the carbon atom with respect to ^{119}Sn. Scheme 6 shows relevant NMR data for two 1-boryl-2-stannyl-1-alkenes with (*E*)- and (*Z*)-configuration for comparison.[33]

Proposed mechanism of the 1,1-organoboration

In the cases of aminoethynyl-Group-14 derivatives, it is tempting to assume that the reaction with trialkylboranes starts with the formation of an amine–borane adduct, especially in the diethylamino derivatives **1**–**5**. However, the NMR spectra (^1H, ^{13}C, ^{29}Si NMR) of the silanes **1** and **2** did not change in the presence of BEt_3 (**7**), and the same is true for the germanes **3** and **4** (^1H, ^{13}C NMR). In the ^{11}B NMR spectra of these mixtures, the ^{11}B NMR signal is exactly in the position for free BEt_3 in C_6D_6 ($\delta^{11}B$ 85.5 ppm); this indicates negligible N–B donor–acceptor interactions between the silanes or germanes and BEt_3. There was also no appreciable change in the NMR data in mixtures of the germane **3** and 9-Me-9-BBN (**8a**), which is the most Lewis-acidic trialkylborane used in this study.

In the cases of mixtures containing **5** and any of the boranes **7b,c** or **8a,b**, the positions of the ^1H and $^{13}C(SnMe_3, NEt_2)$ NMR signals of **5** change slightly. The magnitude of the coupling constant $|^1J(^{119}Sn,^{13}C_{Me})|$ becomes smaller, particularly in the presence of **8a** or **8b** (*ca* 375 Hz instead of 402.7 Hz); the ^{13}C NMR signals for the alkynyl carbon atoms are no longer in the place for **5**, and they are difficult to detect (assignment uncertain!). The ^{11}B NMR signal is shifted significantly to low frequencies (up to 60 ppm, e.g. $\delta^{11}B$ 26.4 ppm in the case of **5** and **8a** in a molar ratio of approximately 1 : 1) with respect to that of the free borane, depending on the borane/**5** ratio. ^{119}Sn NMR spectroscopy[27] provides another powerful probe for studying potential interactions of **5** with the trialkylboranes. The ^{119}Sn NMR signal for mixtures of **5** with **7b** or **7c** is shifted to high frequencies (up to 20 ppm), dependent on the excess of the borane and on temperature. The change in the ^{119}Sn resonance

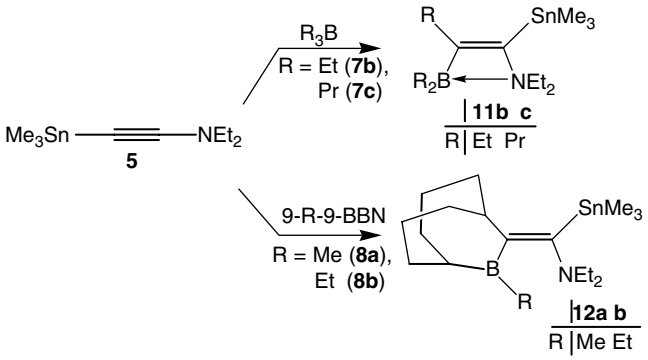
Table 2. ^{11}B, ^{13}C, ^{29}Si NMR data of the alkenes **9**–**14**

Compound	$\delta^{13}C$(MC=)	$\delta^{13}C$(BC=)	$\delta^{13}C$(MMe/Et)	$\delta^{13}C$(BR_2)	$\delta^{13}C$(R)	$\delta^{13}C$(NEt_2/NMe_2/N(Ph)Me)	$\delta^{119}Sn$	$\delta^{11}B$
9b	144.0	182.0 (br)	1.3	10.5 (br), 10.3	23.6, 14.0	46.7, 10.3	—	15.3
9c	145.2	181.0 (br)	1.8	24.0(br), 20.7, 17.9	33.2, 23.2, 14.8	47.2, 11.1	—	15.9
10b	143.5	182.6 (br)		12.0 (br), 13.0	23.8, 14.1	45.2	—	13.5
10c	144.4	181.4 (br)	6.5, 9.2	23.2 (br), 20.7, 18.0	33.2, 22.9, 15.1	45.7	—	13.3
11b	144.3 [400.0]	185.7 (br)	−6.6 [332.5]	12.0 (br), 10.8	25.0 [17.3], 15.1 [6.4]	46.2 [3.5], 9.9	−87.0	16.5
11c	145.2 [402.6]	184.2 (br)	−6.4 [332.6]	25.6 (br), 19.3, 17.7	34.2 [16.2], 22.9 [6.0], 14.8	46.4 [3.5], 10.1	−87.4	15.8
12a	171.5 [n. m.]	157.5 (br)	−3.7 [285.5]	15.5 (br) (Me)[b]	43.6 [41.0] (CH), 34.9 [4.1] (CH_2)	50.7 [16.0], 14.4 [6.0]	−80.1	75.3
12b	169.9 [512.0]	159.0 (br)	−3.6 [284.3]	21.3 (br) (BCH_2), 34.2 (br) (BCH), 29.1, 23.5 (CH_2)	43.7 [40.1] (CH), 35.2 [4.4] (CH_2)	50.7 [16.1], 14.2 [5.7]	−81.4	79.8
13b	146.8 [462.1]	171.9 (br)	−7.1 [319.4]	18.3 (br), 9.0	26.5 [27.2], 15.0 [6.6]	149.7, 116.3, 128.9, 119.9 (Ph); 41.1 [4.0] (Me)	−57.1	72.4
13d	146.0 [462.5]	174.8 (br)	−6.3 [312.0]	24.6 (br), 19.3	34.7 [30.3], 24.3	150.5, 115.8, 129.1, 119.3 (Ph); −41.1 (Me)	−53.3	81.6
14b	166.1 [505.7]	163.8 (br)	−5.7 (307.4)	19.6 (br) (BCH_2), 29.4 (br) (BCH), 28.6, 23.1 (CH_2)	44.8 [34.9] (CH) 34.8 [4.0] (CH_2)	148.2, 114.3, 129.4, 117.9 (Ph); 41.6 (Me)	−44.0	87.0

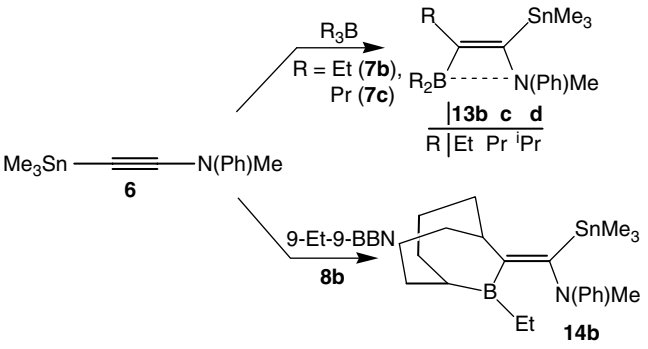
[a] Measured in C_6D_6 at 23 °C; n.m. means not measured; coupling constants $J(^{119}Sn,^{13}C)$ are given in brackets [±0.2 Hz]; (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{13}C–^{11}B coupling.
[b] Not assigned due to overlap with other signals.

frequency is more dramatic for mixtures containing **5** and **8a** or **8b**: in the presence of a slight excess of the boranes, the ^{119}Sn resonance is observed as a broad signal at δ^{119}Sn −4.0 ppm, shifted by >60 ppm to high frequency with respect to pure **5**.

Considering the similarity of the NMR data of **1**, **3** and **5** (Table 1), especially of the ^{15}N chemical shifts, it is unlikely that interactions between the boron atom in the boranes and the NEt_2 group in **5** are particularly strong. Therefore, it is suggested that the special property of alkyn-1-yl-stannanes, the labile Sn–C≡bond, is responsible for the observed behaviour of **5** in the presence of trialkylboranes (Scheme 7). The adduct formation (Scheme 7(a)) appears to be unimportant. For M = Sn, cleavage of the Sn–C≡bond takes place (Scheme 7c), leading to zwitterionic intermediates of the type $\mathbf{A}^1$, in which either the stannyl group and BR_3 are linked to the same carbon atom (the structure corresponds to that of a keteniminium cation[34]) or the stannyl group is coordinated to the nitrogen atom of the amino group (rather than to the C≡C bond as in **A**; Scheme 1): The equilibrium between $\mathbf{A}^1$ and **5** and the boranes could involve the unstable borane adduct (Scheme 7b). The intermediacy of fairly long-lived species $\mathbf{A}^1$ (M═Sn) helps to explain at least two important observations: (i) the 1,1-organoboration of **5** proceeds much more slowly compared with most other alkyn-1-yl-stannanes; (ii) side reactions (Scheme 7e,f) take place, which usually are not observed. These side reactions are most prominent for the more reactive boranes, such as **7b**, **8b** and in particular **8a**, and they are of minor importance for the less reactive



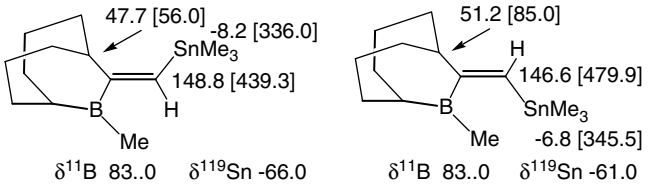
Scheme 4.



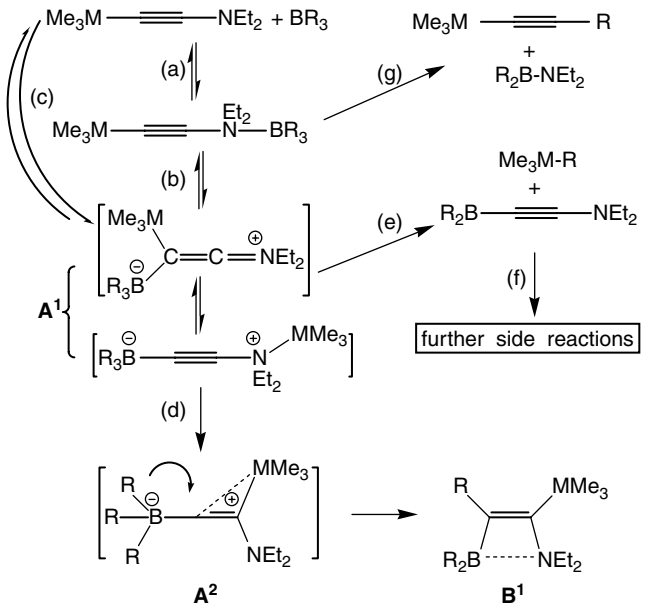
Scheme 5.

BPr_3 (**7c**). Since these side reactions are not observed in the course of the reactions of **6** with the boranes, the lifetime of the intermediates corresponding to $\mathbf{A}^1$ may be shorter as a result of the reduced π donor properties and lower basicity of the N(Ph)Me group. Aminoboranes $R_2B–NEt_2$ (Scheme 7g) could be detected only in trace quantities in the ^{11}B NMR spectra by their characteristic signals in the range of δ^{11}B 44 to 46 ppm.[21] In the case of M═Ge, the harsh reaction conditions, required to induce the intermolecular reaction with boranes, will reduce the lifetime of any intermediate, including $\mathbf{A}^1$ (M═Ge); therefore, the reaction proceeds immediately towards $\mathbf{B}^1$, and side reactions are of minor importance. For M═Si, the cleavage of the Si–C≡bond, necessary for the formation of $\mathbf{A}^1$ (M═Si), cannot be induced.

The final rearrangement of $\mathbf{A}^1$ into $\mathbf{B}^1$ by a 1,2-shift of the group R from boron to carbon may proceed via the intermediate $\mathbf{A}^2$, related to **A** (Scheme 1). $\mathbf{A}^2$ represents a structure in which the MMe_3 group migrates between the carbon atom bearing the BR_3 unit and the amino nitrogen atom, and the unsymmetrical bridging of the C≡C bond in $\mathbf{A}^2$ will favour a stereochemistry such as in $\mathbf{B}^1$, in contrast to that in **B** (Scheme 1).



Scheme 6.



Scheme 7.

CONCLUSIONS

1,1-Organoboration of aminoethynyl-germanium and -tin compounds leads to novel enamines, in which the boryl and the germyl or stannyl groups are in trans positions, an unusual stereochemistry of 1,1-organoboration products. This stereochemistry allows for an intramolecular coordinative N–B bond if the bulkiness of the borane and the basicity of the amino group are favourable. In the absence of such a bond, NMR data, in particular coupling constants $^1J(^{119}Sn,^{13}C)$, indicate weak intramolecular N–Sn interactions between the diethylamino and the trimethylstannyl group, which are in geminal positions at the C=C bond.

EXPERIMENTAL

Starting materials and measurements

All synthetic work and the handling of samples was carried out under an inert atmosphere (Argon or Nitrogen), and carefully oven-dried glassware and dry solvents were used. The organometal halides, amines, trichloroalkenes, BuLi in hexane (1.6 M), triethylborane (**7b**) and tripropylborane (**7c**) were commercial products. The aminoethynyl derivatives **1**, **3**–**5**,[12,13] triisopropylborane (**7d**),[35] 9-Me-9-BBN (**8a**)[36] and 9-Et-9-BBN (**8b**)[37] were prepared following literature procedures. Routine mass spectra (EI, 70 eV; Finnigan MAT 8500 with direct inlet) did not give conclusive results for the 1,1-organoboration products. IR spectra: Perkin Elmer, Spectrum 2000 FTIR. NMR measurements in C_6D_6 (concentration *ca* 10–15%) with samples in 5 mm tubes at 23 ± 1 °C: Bruker ARX 250, Bruker AC 300, and Bruker DRX 500 spectrometers for ^1H, ^{11}B, ^{13}C,^{15}N, ^{29}Si and ^{119}Sn NMR; chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15 ppm; $\delta^{13}C$ (C_6D_6) = 128.0 ppm; $\delta^{29}Si$ = 0 ppm for $\Xi(^{29}Si)$ = 19.867 184 MHz], external BF_3–OEt_2 [$\delta^{11}B$ = 0 ppm for $\Xi(^{11}B)$ = 32.083 971 MHz], external $MeNO_2$ [$\delta^{15}N$ = 0 ppm for $\Xi(^{15}N)$ = 10.136 767 MHz], and external $SnMe_4$ [$\delta^{119}Sn$ = 0 ppm for $\Xi(^{119}Sn)$ = 37.290 665 MHz]. $^{15}N\{^1H\}$, $^{29}Si\{^1H\}$ and some ^{13}C (see Fig. 1) NMR spectra were measured using the refocused INEPT pulse sequence.[38,39] The $^{119}Sn\{^1H\}$ NMR spectra[27] were recorded both by inverse gated ^1H decoupling and by the INEPT pulse sequence. Chemical shifts are given to ±0.1 ppm, coupling constants to ±0.1 to 0.3 Hz in most cases (excluding satellites belonging to broad signals). Isotope-induced chemical shifts $\Delta^{12/13}C(^{29}Si)$[40] and $\Delta^{12/13}C(^{119}Sn)$[30] [Table 1; given in ppb (±1); a negative sign indicates a shift of the NMR signal of the heavier isotopomer to lower frequencies] are found in the usual ranges.

Bis(diethylaminoethynyl)methylsilane (2)

Diethylaminotrichloroethene (5.7 g, 28 mmol) dissolved in diethyl ether (5 ml) was added dropwise at −10 °C to a solution of BuLi in hexane (1.6 M, 35 ml; 56 mmol), and the mixture was kept stirring for 2 h at room temperature. After addition of a solution of $MeSi(H)Cl_2$ (1.35 ml, 13 mmol) in diethyl ether (8 ml), stirring was continued for 12 h at room temperature. Insoluble materials were filtered off and the product was obtained by fractional distillation (1.23 g; 40%; b.p. 80–85 °C/5 × 10^{-2} Torr). IR: 2142 cm^{-1} [ν(Si–H) and ν(C≡C)]. ^1H NMR (250.1 MHz): δ = 0.44 (d, 3H, SiMe, $^3J(^1H,Si,C^1H)$ = 3.5 Hz), 2.55, 0.95 (q, t, 8H, 12H, NEt_2), 5.01 (q, 1H, SiH, $^3J(^1H,Si,C^1H)$ = 3.5 Hz).

Attempts at the 1,1-ethylboration of the silanes 1 and 2

Samples of the silanes **1** or **2** (*ca* 0.08 to 0.1 g) were placed in an NMR tube and triethylborane (1.2 ml) was added. The tubes were heated in an oil bath (105 °C) for 3–5 days, and ^{29}Si NMR spectra were measured every 24 h. In the case of **1**, there was no reaction at all. In the case of **2**, there was also no indication of 1,1-ethylboration after 2 days. However, decomposition of **2** became noticeable; after 3 days only a small amount of the starting material **2** was left, and, according to numerous signals of low intensity in the ^{29}Si NMR spectra, defined products from 1,1-organoboration were not formed.

1,1-Organoboration of the germanes 3 and 4: (*E*)-1-amino-1-trialkylgermyl-2-dialkylboryl-alkenes (9, 10)

Triethylborane (**7a**, 1.35 g, 13.8 mmol) was added in one portion to a solution of **3** (1 g, 4.6 mmol) in toluene (4.5 ml), and the mixture was heated at 110 °C for 65 h. After that, IR spectra did not show the absorption for ν(C≡C). All volatile materials were removed *in vacuo*, and the fractional distillation of the residue gave 0.92 g (64%) of **9b** as an oily, slightly yellowish liquid (b.p. 75–77 °C/5 × 10^{-2} Torr). Compound **10b** was obtained in the same way (reaction time 110 h) in a yield of 50% (b.p. 80–85 °C/10^{-2} Torr). The reactions of **3** and **4** with tripropylborane (**7c**), leading to **9c** and **10c** respectively, were carried out in benzene as the solvent, and heating at 75 °C for 160 h was necessary to complete the reaction (monitored by IR spectroscopy). Heating at higher temperatures induces slow decomposition of BPr_3 (dehydroboration). Distillation of **9c** or **10c** led to decomposition.

9b: ^1H NMR (250.1 MHz): δ = 0.27 (s, 9H, $GeMe_3$), 1.11, 0.90 (m, m 10H, BEt_2), 2.29, 0.80 (q, t, 2H, 3H, =C–Et), 2.64, 0.80 (q, t, 4H, 6H, NEt_2). **9c**: ^1H NMR (250.1 MHz) δ = 0.28 (s, 9H, $GeMe_3$), 1.4, 1.2 (m, t, 8H, 6H, BPr_2), 2.26, 1.53, 0.95 (m, m, t, 2H, 2H, 3H, =C–Pr), 2.64, 0.80 (q, t, 4H, 6H, NEt_2).

10b: ^1H NMR (250.1 MHz): δ = 1.0–0.7 (m, m, m, 28H, $GeEt_3$, BEt_2, CH_3 of =C–Et), 2.13 (s, 6H, NMe_2), 2.21 (q, 2H, =C–CH_2). **10c**: ^1H NMR (250.1 MHz): δ = 1.6–0.7 (m, m, m, m, m, 34H, Et_3Ge, BPr_2, CH_2CH_3 of =C–Pr), 2.14 (s, 6H, NMe_2), 2.15 (m, 2H, =C–CH_2).

1,1-Organoboration of diethylaminoethynyl (trimethyl)stannane 5: (*E*)-1-diethylamino-1-trimethylstannyl-2-dialkylboryl-alkenes (11, 12)

The stannane **5** (0.105 g, 0.8 mmol) was placed in an NMR tube and dissolved in C_6D_6 (0.7 ml). The solution was cooled

until it became solid. Then the particular borane (**7b**, **7c**, **8a**, **8b**) was added in one portion (0.9 to 1 mmol in each case), and the two phases were allowed to mix slowly. NMR spectroscopic measurements (^{1}H, ^{11}B, ^{13}C, ^{119}Sn NMR) of the mixtures showed that a reaction had taken place, although the products of 1,1-organoboration were not formed after 4 h at room temperature. Heating of these mixtures caused extensive decomposition. When the mixtures were kept for 2 or 3 days at room temperature, NMR spectra indicated the presence of the 1,1-organoboration products **11b,c** and **12a,b** (60–80%), along with numerous side products, most of which were not identified. Attempts at purification of these mixtures led to decomposition.

11b: ^{1}H NMR (250.1 MHz): $\delta[^2J(^{119}\mathrm{Sn},^1\mathrm{H})] = 0.19$ [53.4] (s, 9H, $SnMe_3$), 1.0, 0.86 (m, m, 10H, BEt_2), 2.22, 0.80 (q, t, 2H, 3H, =C–Et), 2.63, 0.80 (q, t, 4H, 6H, NEt_2). **11c**: ^{1}H NMR (250.1 MHz): $\delta[^2J(^{119}\mathrm{Sn},^1\mathrm{H})] = 0.20$ [53.5] (s, 9H, $SnMe_3$), 1.40, 1.12, 0.9 (m, m, t, 14H, BPr_2), 2.17, 1.55, 0.9 (m, m, t, =C–Pr), 2.64, 0.74 (q, t, 4H, 6H, NEt_2).

12a: ^{1}H NMR (250.1 MHz): $\delta[^2J(^{119}\mathrm{Sn},^1\mathrm{H})] = 0.28$ [50.3] (s, 9H, $SnMe_3$); other signals not assigned because of overlap with signals from other compounds. **12b**: ^{1}H NMR (250.1 MHz): $\delta[^2J(^{119}\mathrm{Sn},^1\mathrm{H})] = 0.30$ [50.0] (s, 9H, $SnMe_3$), 1.19, 0.9 (m, m, 5H, BEt), 2.0–1.4 (m, 13H, BCH and six CH_2 groups), 2.62, 0.93 (q, t, 4H, 6H, NEt_2), 2.85 (m, 1H, =C–CH).

1,1-Organoboration of methyl(phenyl)amino-ethynyl(trimethyl)stannane 6: (*E*)-1-methyl-(phenyl)amino-1-trimethylstannyl-2-dialkylboryl-alkenes (13, 14)

A solution of **6** (0.081 g, 3 mmol) in hexane (10 ml) was cooled to −78 °C, and an excess of the particular borane (**7b**, **7d**, **8b**; *ca* 10 mmol each) was added in one portion. When the mixtures were warmed to room temperature, a dark colour developed. ^{119}Sn NMR spectra indicated that the reaction was complete. Then, all volatile materials were removed *in vacuo*, and a brown-coloured oily residue was left in all cases. Attempts at crystallization failed; chromatography on alumina or silica led to decomposition, and this was also observed for attempts at distillation at reduced pressure. However, the compounds **13b,c** and **14b** were present in the raw material in high purity (^{1}H NMR: >95%).

13b: ^{1}H NMR (300 MHz): $\delta[J(^{119}\mathrm{Sn},^1\mathrm{H})] = 0.06$ [53.6] (s, 9H, $SnMe_3$), 1.15–1.10 (m, 10H, BEt_2), 2.23 [8.1], 0.97 (q, t, 2H, 3H, =C–Et), 2.70 [3.0], (s, 3H, NMe), 6.78, 6.81, 7.12 (m, m, m, 1H, 2H, 2H, NPh). **13d**: ^{1}H NMR (300 MHz): $\delta[^2J(^{119}\mathrm{Sn},^1\mathrm{H})] = 0.08$ [52.3] (s, 9H, $SnMe_3$), 1.48, 1.00 (m, d, 2H, 12H, B^iPr_2), 2.56, 1.12 (sp, d, 1H, 6H, =C–^{i}Pr), 2.70 (s, 3H, NMe), 6.27, 6.80, 7.12 (m, m, m, 1H, 2H, 2H, NPh).

14b: ^{1}H NMR (300 MHz): $\delta[J(^{119}\mathrm{Sn},^1\mathrm{H})] = 0.04$ [52.3] (s, 9H, $SnMe_3$), 1.35, 0.92 (m, m, 5H, BEt), 2.08 (m, 1H, BCH), 1.85–1.20 (m, 12H, six CH_2 groups), 2.80 [m, 1H, =C–CH), 2.82 [4.5] (s, 3H, NMe), 6.71, 6.60, 6.71, 7.15 (m, m, m, 2H, 1H, 2H, NPh).

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