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REACTIONS OF *cis*-2-BORYL-1-STANNYLALKENES WITH CARBODIIMIDES, THIOCYANATES, ISOTHIOCYANATES, AND ISOCYANATES*

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The reactions of (E)-2-diethylboryl-1-trimethylstannylbut-1-ene and (Z)-3-diethylboryl-2-trimethylstannylpent-2-ene with carbodiimides, methyl thiocyanate, thioisocyanates, and isocyanates were studied, and the products were characterized by multinuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR). It was found that carbodiimides bearing tert-butyl or trimethylsilyl groups at the nitrogen atoms do not react with (E)-2-boryl-1-stannylalkenes, in contrast to dicyclohexylcarbodiimide. There was also no reaction in the case of MeSCN. All other reactions proceed via a weak N→B adduct formation in the initial step, followed by different rearrangements, depending on the structure of reagents as well as on the substitution pattern at the C=C bond in alkenes. New heterocycles are formed, in which the boron atom is either tricoordinated (1,2-azaborolenes, 1,2-azaborolanes), and one ethyl group has been transferred to the neighbor olefinic carbon atom, or the boron atom is tetracoordinated (1,2-azaboratoles, 1,2-oxoniaboratoles), and the trimethylstannyl group has migrated to one of the heteroatoms of the heterocumulenes.

Keywords: (*E*)-2-diethylboryl-1-trimethylstannylbut-1-ene, (*Z*)-3-diethylboryl-2-trimethylstannylpent-2-ene, dicyclohexylcarbodiimide, methylthiocyanate, thioisocyanates, isocyanates, 1,2-azaborolenes, 1,2-azaborolanes, 1,2-azaboratoles, 1,2-oxoniaboratoles.

Alkenes substituted by organometallic groups are attractive synthons considering the reactivity of the M–C= bonds, and also the C=C bond itself. If two organometallic substituents are linked in *cis* positions to the C=C bond, further interesting aspects can arise as a result of the close proximity of the two organometallic groups. 1,1-Organoboration of 1-alkynyltin compounds [1, 2] has opened a convenient access to alkenes of type **1** and **2**, in which the trimethylstannyl and the diethylboryl groups occupy *cis* positions at the C=C bond (Scheme 1).

Previously we have shown that the Lewis acidity of the boron atom in **1** or **2** is sufficient to cause weak interactions with reagents containing a nucleophilic center [3, 4]. If such reagents contain both a nucleophilic and an electrophilic center [5, 6], intramolecular reactions are promoted once the nucleophilic center is attracted by the electron-deficient boron atom (as in **A**). These reactions may then proceed *via* cleavage of B–C and/or

* Dedicated to Professor Dr. Edmunds Lukevics on the occasion of his 65th birthday.

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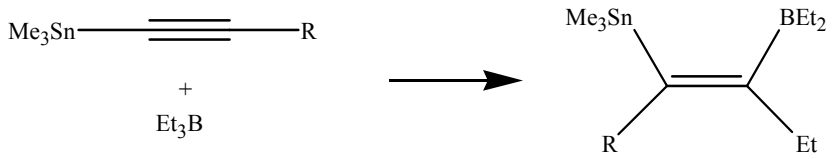
Scheme 1

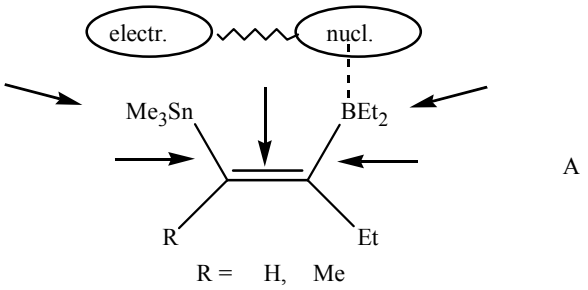


1 R = H; **2** R = Me **1**, **2**

Compounds **1** and **2** are formed quantitatively [19] and can be used without further purification.

Sn–C bonds, and/or by rearrangements (Scheme 2). In the present work, we have studied the reactivity of **1** and **2** towards carbodiimides $R^1N{=}C{=}NR^1$ [**3**: R^1 = cyclohexyl(cyl) (**a**), *t*-Bu (**b**), $SiMe_3$ (**c**)], the thiocyanate MeS–C≡N (**4**), isothiocyanates R^1–N=C=S [**5**: R = Et (**a**), Ph (**b**)], and isocyanates R^1–N=C=O [**6**: R = Et (**a**), Ph (**b**), 1-naphthyl (**c**)].

Scheme 2



A nucleophilic center is attracted (**A**) by the electron-deficient boron atom (dashed line). Further reactions may then take place if the reagent also contains an electrophilic center (reactive Sn–C and B–C bonds as well as the reactive C=C bond are indicated by arrows).

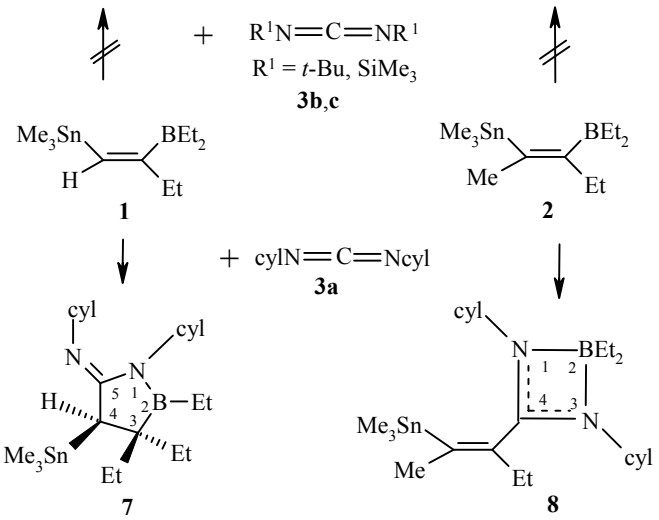
RESULTS AND DISCUSSION

Reactions of Substituted Alkenes 1a,b with Carbodiimides 3

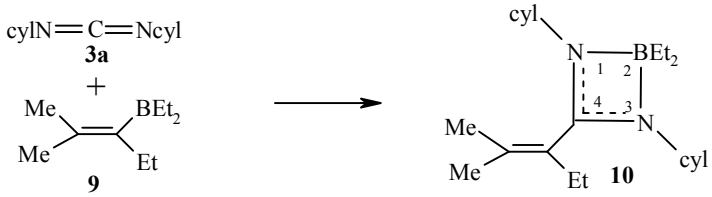
Compounds **1** or **2** did not react (70°C; 12 h) with the carbodiimides $R^1N{=}C{=}NR^1$ **3b** (R^1 = *t*-Bu) and **3c** (R^1 = $SiMe_3$). It is conceivable that the groups R^1 in **3b**, **c** are too bulky to allow an efficient interaction of the imino nitrogen atoms with the boron atom in **1** or **2**, and therefore the complex **A** is not formed, and consecutive reactions cannot be induced. In contrast, in the case of cyclohexyl substituents (**3a**, R^1 = cyl), reactions of **3a** with **1** or **2** took place (Scheme 3). However, completely different types of products were formed, depending on R = H (**1**) and R = Me (**2**), as the result of adduct formation in the first step, and either rearrangement (to give **6**) or insertion into the B–C= bond (to give **7**). In both cases, a weak complex of type **A** is likely to be the first intermediate. The following intramolecular reactions depend on R. If R = H, an electrophilic attack can take place readily at the olefinic carbon atom bearing the $SnMe_3$ group, accompanied by a 1,2-shift of the ethyl group from boron to the neighbor olefinic carbon atom, giving the heterocycle **7**. Similar 1,2-shifts have been observed frequently in the chemistry of alkenylboranes [7-9]. In the case of R = Me, the analogous reaction pathway is apparently much less favored, possibly due to steric effects, and the major final product is formed *via* electrophilic attack at the olefinic carbon atom next to boron, leading to cleavage of the B–C= bond and

formation of **8**. In the absence of a trimethylstannyl group, as in the alkenylborane **9** [10], the reaction with **3a** proceeds in the same way to give compound **10**, analogous to **8** (Scheme 4), as shown by the ^{11}B NMR signal at δ^{11}B + 8.5, typical of tetracoordinated boron [11].

Scheme 3



Scheme 4



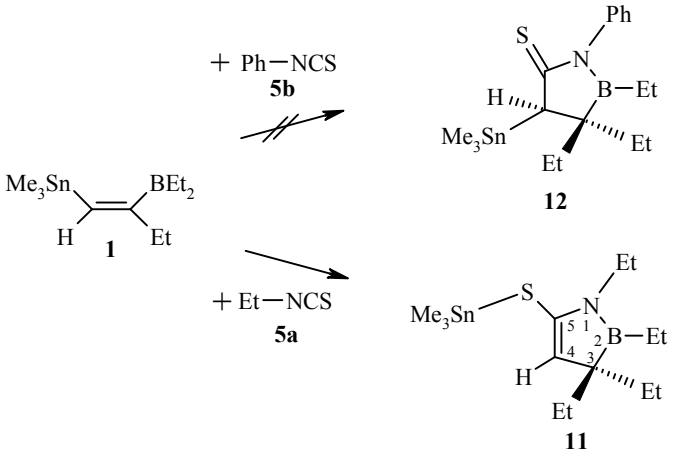
Reactions of 1 and 2 with Methyl Thiocyanate (4)

Both alkenes **1** and **2** did not react with MeS–C≡N (**4**), even after prolonged heating in boiling hexane. In contrast to the situation for other triorganoboranes [12, 13], there is also no reaction between **1** and nitriles $R^1C{\equiv}N$ (R^1 = Me, *t*-Bu, Ph, $SiMe_3$). This can be understood if the stability of the relevant complexes of type **A** is low at ambient temperature or above (the δ^{11}B values of solutions of **1** in hexane or acetonitrile are the same within the experimental error). At low temperature, complexes of type **A** may be more stable; however, further reactions do not take place under these conditions, since the adduct-induced changes in bond-polarization are small.

Reactions of 1 with Ethyl Isothiocyanate (5a), Phenyl Isothiocyanate (5b), and of 1 and 2 with Ethyl Isocyanate (6a), and Phenyl- (6b) and 1-Naphthyl Isocyanate (6c).

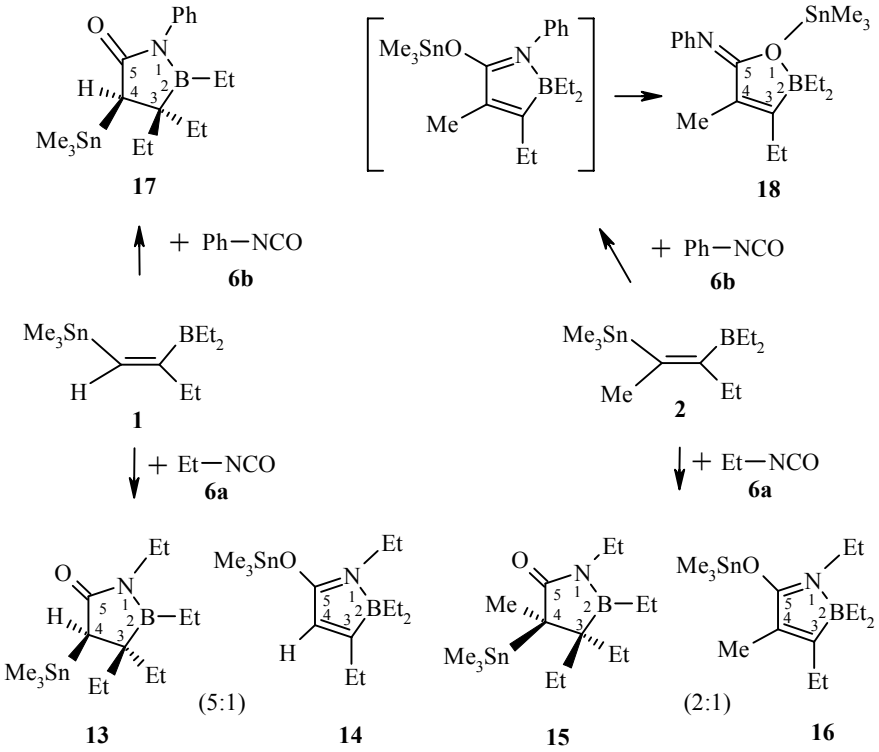
Compound **1** reacted slowly (3 days) with ethyl isothiocyanate **5a** at room temperature to give the heterocycle **11**, in which the trimethylstannyl group has migrated to the sulfur and one ethyl group has shifted from boron to the neighbor carbon atom (Scheme 5). This type of heterocycle has not been observed in any of the other reactions. Under the same conditions phenyl isothiocyanate **5b** does not react with **1** at room temperature or after short (ca. 10 min) heating at 70°C. Therefore, a compound like **12** or an analogue to **11** could not be obtained or even detected in small quantities. After prolonged heating (12 h) at 70°C, extensive decomposition was observed, leading to numerous unidentified products and to tetramethyltin which was readily detected by ^{119}Sn, ^{1}H, and ^{13}C NMR.

Scheme 5



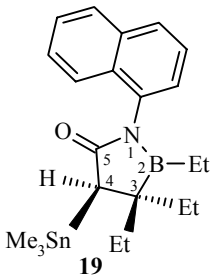
In contrast to isothiocyanates, the isocyanates **6** reacted rather fast (1 h at room temperature), except **6c**, with the alkenes **1** or **2**. The results are summarized in Scheme 6. In the case of ethyl isocyanate **6a**, mixtures of two products (**13**, **14** and **15**, **16**, respectively) were obtained from the reactions with **1** or **2**. In the case of **1**, the heterocycle **13** was formed in large excess, whereas in the case of **2**, only a small excess of the analogous product **15** was found. The products **13** and **15** correspond closely to the findings described for the reaction of **1** with the carbodiimide **3a** (compound **7** in Scheme 3). The products **14** and **16** arise from adduct formation and migration of the trimethylstannyl group from carbon to the oxygen atom. This process is not accompanied by a

Scheme 6



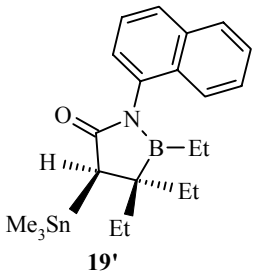
1,2-shift of one of the ethyl groups at the boron atom. The reaction of **1** with phenyl isocyanate **6b** afforded mainly the heterocycle **17** with tricoordinated boron, analogous to **13** and **15**, whereas the product of the reaction of **2** with **6b** could be identified as another new heterocycle **18**, containing a coordinative O–B bond. The structure in brackets, analogous to **16**, is a likely intermediate, which rearranges to **18**.

Compound **1** reacts very slowly with **6c** (heating leads to decomposition), and at least two products are formed together with various unidentified species. The δ^{119}Sn and other NMR data (vide infra) indicate that these compounds could be the analogues of **17**, the isomers **19** and **19'**, by assuming restricted rotation about the N-naphthyl bond. So far we failed to isolate pure products from this reaction.



19

δ^1H(SnMe$_3$) = 0.44 [53.5]
0.43 [53.5]
δ^1H(4-H) = 2.73 [84.0]
2.61 [83.5]



19'

δ^{119}Sn = 10.1, 12.6

δ^{11}B = 60 (broad)

NMR Spectroscopic Results

The ^{11}B, ^{13}C, and ^{119}Sn NMR data of the products are listed in Tables 1 (**7**, **11**, **13**, **15**, and **17**) and 2 (**8**, **14**, **16**, and **18**), and ^{1}H NMR data are given in the experimental section. The δ^1B data show clearly whether the boron atoms are tricoordinated (Table 1) or tetracoordinated (Table 2), and of course the ^{11}B NMR spectra can be used to assess the composition of mixtures (e.g., **13**/**14** or **15**/**16**). In any case, the ^{13}C NMR signals together with $^{117/119}$Sn satellites, and the characteristic broadening of the signals for ^{13}C nuclei linked to ^{11}B [14], provide complementary, consistent structural information.

In the case of compounds **7**, **13**, **15**, and **17**, the carbon atom C-4 is a chiral center which leads to different surroundings of the ^{13}C (3-Et$_2$) signals as well as to diastereotopic ^{1}H (2-CH$_2$, B–CH$_2$ and N–CH$_2$) nuclei. In contrast, the absence of a chiral center in **11** simplifies its ^{1}H and ^{13}C NMR spectra. The ^{119}Sn NMR signals for **7**, **13**, **15**, and **17** are in a typical range [15, 16] for trimethyl(organo)tin compounds; they can be observed as slightly broadenend resonances [17] together with the ^{13}C satellites (Fig. 1), confirming the assignment of the ^{13}C NMR spectra. Again, in contrast, the ^{119}Sn NMR signal for **11** is shifted to much higher frequency, in agreement with the presence of a Me$_3$Sn–S group [15, 16].

In the heterocycles **8**, **14**, **16**, and **18** the boron atoms are tetracoordinated, and the trimethylstannyl group has moved to an imino nitrogen (**8**), to a carbonyl oxygen atom (**14**, **16**), or to an oxonium center (**18**). Both, δ^{11}B and δ^{119}Sn data are indicative of the respective structures. In the case of **18**, the δ^{11}B value is similar to that of other heterocycles containing a coordination O→B bond [4, 18] at higher frequency when compared with compounds containing the =N→BR$_3$ unit (see Table 2), and the ^{119}Sn nucleus is deshielded with respect to alkoxy(trimethyl)tin compounds [15, 16, 18].

TABLE 1. ^{11}B, ^{13}C, and ^{119}Sn NMR Characteristics* of the Heterocycles **7**, **11**, **13**, **15**, and **17**, Containing Tricoordinated Boron

δ	**7**	**11**	**13**	**15**	**17**
$^{13}C(3)$	39.5 (br)	47.6 (br)	38.9 (br)	40.9 (br)	39.1 (br)
$^{13}C(4)$	41.4 [296.1]	125.6	44.3 [270.2]	50.4 [263.0] 14.7 (4-Me)	44.5 [256.0]
$^{13}C(5)$	167.8 [40.1]	139.3	188.7 [18.8]	189.2 [31.4]	187.0
$^{13}C(NR)$	58.7*[2]	38.3, 18.7	35.7, 16.5	35.5, 16.2	139.8*[3]
$^{13}C(BEt)$	8.9 (br), 9.5	7.7 (br), 8.9	7.7 (br), 8.6	7.7 (br), 9.6	7.9 (br), 8.3
$^{13}C(3\text{-}Et_2)$	34.3, 9.6 [<5] [5.8] 30.6, 10.9 [50.8] [6.2]	29.8, 11.0	29.9, 10.4 [35.0] [<5] 30.7, 11.2 [17.0] [<5]	30.6, [33.2] 25.8 [27.0]	30.3, 11.0 [34.3] [<5] 30.8. 17.4 [18.8] [6.0]
$^{13}C(Me_3Sn)$	-6.9 [317.0]	-4.5 [353.1]	-7.2 [334.8]	-7.9 [319.6]	-7.1 [336.3]
^{11}B	55.0	46.5	58.9	57.6	60.4
^{119}Sn	-1.0	90.3	9.5	44.9	13.6

* In C_6D_6 (23±1°C); coupling constants $J(^{119}Sn, ^{13}C)$ are given in brackets [±0.5 Hz]; (br) denotes broad ^{13}C NMR signals owing to partially relaxed $^{13}C–^{11}B$ coupling.

*[2] (NCH) N-cyclohexyl; =N-cyclohexyl: 54.0 (NCH); other ^{13}C resonances (without assignment): 36.0, 33.6, 32.0, 27.3, 27.2, 27.1, 26.8, 26.4, 25.3, 25.0.

*[3] C(i) N–Ph; other ^{13}C resonances: 126.7 (*o*), 128.9 (*m*), 124.8 (*p*).

TABLE 2. ^{11}B, ^{13}C, and ^{119}Sn NMR Characteristic* of the Heterocycles **8**, **14**, **16**, and **18**, Containing Tetracoordinated Boron

δ	**8**	**14**	**16**	**18**
$^{13}C(3)$	—*[2]	181.0	182.0	191.7 (br)
$^{13}C(4)$	167.3 [30.5]	125.0	125.0 14.5 (4-Me)	129.5 12.9 (4-Me)
$^{13}C(5)$	—	174.4	174.4	175.3
$^{13}C(NR)$	56.3*[3]	36.6*[5]	36.6, 13.1	143.5*[6]
$^{13}C(BEt_2)$	13.9 (br), 10.5	16.0 (br), 10.7	16.2 (br), 11.2	14.7 (br), 10.9
$^{13}C(3\text{-}Et)$	27.9, 13.6*[4]	23.1*[5]	23.1, 13.1	24.1, 10.0
$^{13}C(Me_3Sn)$	-7.5 [339.5]	0.4 [n. m.]	0.7 [458.0]	-0.4 [450]
^{11}B	11.2	0.4	-1.3	8.7
^{119}Sn	-37.2	90.5	90.0	169.3

* In C_6D_6 (23±1°C); coupling constants $J(^{119}Sn, ^{13}C)$ are given in brackets [±0.5 Hz]; (br) denotes broad ^{13}C NMR signals owing to partially relaxed $^{13}C–^{11}B$ coupling; n. m. means not measured.

*[2] **8**: alkene ^{13}C data: 150.1 [449.0], 133.5 [31.8]; $\delta^{13}C(Me)$ 18.5.

*[3] (NCH) N-cyclohexyl; other ^{13}C resonances (without assignment): 35.7, 30.0, 27.1, 26.5, 25.1.

*[4] =C–Et.

*[5] Not assigned due to overlap with other signals.

*[6] C(i) N–Ph; other ^{13}C resonances: 126.7 (*o*), 128.9 (*m*), 124.8 (*p*).

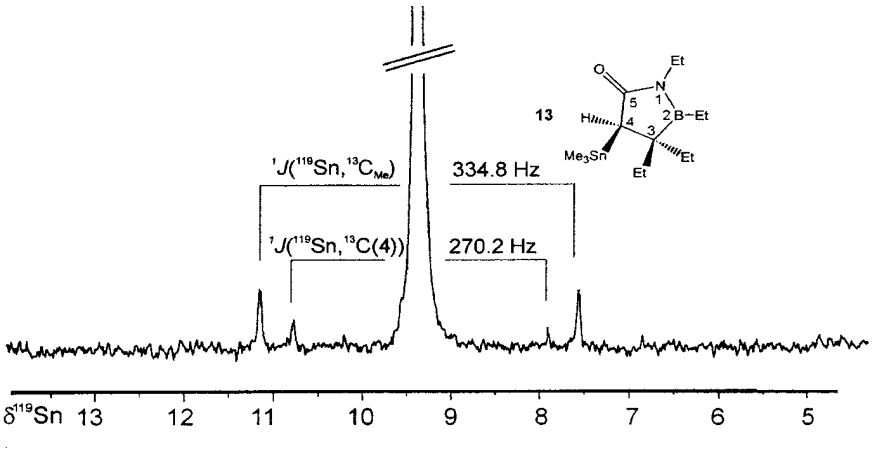


Fig. 1. 99.6 MHz ^{119}Sn NMR spectrum of the heterocycle **13**, recorded by using the refocused INEPT pulse sequence with ^{1}H decoupling [20-22] (polarization transfer was based on $^2J(^{119}Sn, ^1H_{Me}) = 52.0$ Hz). The ^{13}C satellites for $^1J(^{119}Sn, ^{13}C)$ are readily observed and assigned according to their different intensities. Other ^{13}C satellites for $^nJ(^{119}Sn, ^{13}C)$ ($n > 1$; see Table 1) are hidden in the base of the moderately broad ($h_{1/2}$ = 15 Hz) central resonance signal. The broadening is due to partially relaxed ^{119}Sn–^{11}B coupling across three bonds [17].

EXPERIMENTAL

General and Instrumentation

All preparative work was carried out under an atmosphere of pure N_2 or Ar, with all precautions to exclude traces of air and moisture, using oven-dried glassware and carefully dried solvents. The starting alkenes **1**, **2** [18] and **9** [9] were prepared as described. It is important to use the compounds **1** or **2** immediately after synthesis; otherwise these products must be distilled, and then they can be stored at -20°C for several years without decomposition or isomerization. The reagents **3** to **6** were commercial products which were distilled once and checked for purity by ^{1}H NMR before being used in the reactions with **1** and **2**.

NMR measurements (in 5 mm tubes at 23±1°C): Bruker AC 300, ARX 250 and DRX 500 spectrometers [chemical shifts are given with respect to $CHCl_3/CDCl_3$ (δ^1H = 7.24; δ^{13}C = 77.0), [D_8]toluene (δ^1H ($C_6D_5CD_2H$) 2.03; δ^{13}C ($C_6D_5CD_3$) 20.4), C_6D_6 (δ^1H (C_6D_5H) 7.14; δ^{13}C 128.0), external Et_2O–BF_3 (δ^{11}B = 0 for $\Xi(^{11}B)$ = 32.083971 MHz), external Me_4Sn (δ^{119}Sn = 0 for $\Xi(^{119}Sn)$ = 37.290665 MHz). Mass spectra: Varian MAT CH7, EI-MS (70 eV), direct inlet. IR spectra: Perkin Elmer 983 G.

Syntheses

1-Cyclohexyl-5-(cyclohexyl)imino-2,3,3-triethyl-4-trimethylstannyl-1,2-azaborolane (7) and 1,3-Dicyclohexyl-2,2-diethyl-4-(1-ethyl-2-trimethylstannylprop-2-enyl)-1-aza-3-azonia-2-boratacyclobut-3-ene (8). Dicyclohexylcarbodiimide **3a** (1.03 g, 50 mmol) was dissolved in hexane (50 ml), and the solution was cooled to -78°C. Then the respective alkenylborane **1** or **2** was injected in one portion into the stirred solution, the mixture was warmed to room temperature, and stirring was continued for 5 h. NMR control

indicated that the reaction was complete. After removing the solvent in vacuo, the product **7** was left as a colorless, highly viscous oil, which was >97% pure (^{1}H NMR). Attempts to crystallize **7** from various solvents and solvent mixtures failed. The product **8** was obtained in the same way as a yellowish oil (purity >80%) along with some unidentified impurities which could not be separated. **7**: ^{1}H NMR (300 MHz; C_6D_6): δ [J(^{119}Sn, ^{1}H)] = 0.08 [51.4] (9H, s, Me_3Sn); 0.70-3.90 (37H, m, Ncyl, =Ncyl, C(3)–Et_2, BEt); 2.46 [95.2] (1H, s, C(4)–H). **8**: ^{1}H NMR (300 MHz; C_6D_6): δ [J(^{119}Sn, ^{1}H)] = 0.21 [54.2] (9H, s, Me_3Sn); 0.50-3.20 (37H, m, Ncyl, Ncyl, CEt, BEt_2); 1.81 (3H, s, CMe).

1,3-Dicyclohexyl-2,2-diethyl-4-(1-ethyl-2-methylprop-2-enyl)-1-aza-3-azonia-2-boratacyclobut-3-ene (10) was obtained in the same way from the reaction of the alkenylborane **9** [9] with carbodiimide **3a**. **10**: ^{1}H NMR (250 MHz; C_6D_6): 3.04 (m, NCH); 2.11 (m, CH_2–C=); 1.66 (s, Me–C=); 1.51 (s, Me–C=), all other signals are overlapping multiplets; ^{13}C NMR (62.9 MHz; C_6D_6): 165.0 (CNN), 135.3 (=C–Et); 125.1 (=CMe_2); 54.5 (NCH); 24.9, 13.2 (Et–C=); 23.1. 20.4 (Me_2C=), 14.0, 15.0 (br), 10.5, 11.3 (Et_2B).

1,2,3,3-Tetraethyl-5-trimethylstannylthio-1,2-azaborol-4-ene (11). Ethyl isothiocyanate (0.43 g, 5.0 mmol) was dissolved in hexane (50 ml), cooled to -78°C, and the alkenylborane **1** (0.93 g, 5.0 mmol) was added in one portion. After stirring for 3 days at room temperature, NMR control indicated that all starting materials were consumed. Evaporation of the solvent left a colorless oil which consisted of >70% (^{1}H NMR) of **11**. Attempts to purify **11** by distillation led to decomposition, and so far, **11** could not be crystallized. ^{1}H NMR (300 MHz; C_6D_6): δ [J (^{119}Sn, ^{1}H)] = 0.30 [55.9] (9H, s, Me_3Sn); 3.41, 0.70 (5H, q, t, NEt); 0.50-1.30 (15H, m, C(3)–Et_2, BEt); 5.04 (1H, s, C(4)–H).

1,2,3,3-Tetraethyl-4-trimethylstannyl-1,2-azaborolan-5-one (13), 1,2,2,3-Tetraethyl-5-trimethylstannyloxo-2H-1,2-azoniaboratole (14), 1,2,3,3-Tetraethyl-4-methyl-4-trimethylstannyl-1,2-azaborolan-5-one (15), 1,2,2,3-Tetraethyl-4-methyl-5-trimethylstannyloxo-2H-1,2-azoniaboratole (16), 2,3,3-Triethyl-1-phenyl-4-trimethylstannyl-1,2-azaborol-5-one (17), and 2,3,3-Triethyl-4-methyl-5-(phenyl)imino-1-trimethylstannyl-2H-1,2-oxoniaboratole (18). Ethyl isocyanate **6a** (0.35 g, 5.0 mmol) was dissolved in hexane, cooled to -78°C, and the respective alkenylborane **1** or **2** was added in one portion. After warming to room temperature and strirring for 30 min, NMR control indicated complete reaction. In the case of **1**, a 5:1 mixture of **13** and **14** was left after evaporation of the solvent, whereas in the case of **2** the compounds **15** and **16** were formed in a 2:1 ratio. Treatment of **1** with phenyl isocyanate in the same way gave mainly **17** (>90%) along with minor, unidentified side products. In the same procedure, phenyl isocyanate **6b** (0.59 g, 5.0 mmol) reacted with the alkenylborane **2** to give, after stirring for 16 h at room temperature, the compound **18** almost quantitatively (>95% pure by ^{1}H NMR) as a viscous, colorless oil. The compound **18** is sensitive to traces of moisture and very soluble in all common inert solvents, and, therefore, it could not be crystallized as yet. From the reaction of the alkenylborane **1** with 1-naphthyl isocyanate **6c**, it was not possible, so far, to obtain defined products. ^{11}B and ^{119}Sn NMR spectra of the reaction mixture point towards the presence of the isomers **19** and **19'**. **13**: ^{1}H NMR (250 MHz; C_6D_6): δ [J(^{119}Sn, ^{1}H)] = 0.23 [52.0] (9H, s, Me_3Sn); 0.5-1.6 (18H, m, C(3)–Et_2, BEt, Me); 2.26 [86.8] (1H, s, C(4)–H); 3.16, 3.29 (2H, m, NCH_2). **14**: ^{1}H NMR (250 MHz; C_6D_6): δ = 0.6 (br. s, Me_3Sn); 0.5-1.6 (m, overlap with signals of **13**); 2.53 (2H, d, q, C(3)–CH_2); 5.80 (1H, s, C(4)–H). **15**: ^{1}H NMR (250 MHz; C_6D_6): δ [J(^{119}Sn, ^{1}H)] = 0.04 [52.0] (9H, s, Me_3Sn); 0.4-1.7 (18H, m, C(3)–Et_2, BEt, N–CH_2–$\underline{CH_3}$); 1.30 [83.5] (3H, s, C(4)–Me); 3.13, 3.21 (2H, m, NCH_2). **16**: ^{1}H NMR (250 MHz; C_6D_6): δ [J (^{119}Sn, ^{1}H)] = 0.65 [62.0] (9H, br. s, Me_3Sn); 0.4-1.7 (m, overlap with signals for **15**), 1.76 (3H, s, C(4)–Me); 2.47 (2H, q, C(3)–CH_2); 3.25 (2H, m, NCH_2). **17**: ^{1}H NMR (250 MHz; C_6D_6): δ [J(^{119}Sn, ^{1}H)] = 0.25 [53.6] (9H, s, Me_3Sn); 0.6-1.9 (15H, m, C(3)–Et_2, BEt); 2.42 [83.0] (1H, s, C(4)–H); 6.8-7.2 (5H, m, N–Ph). **18**: ^{1}H NMR (300 MHz; C_6D_6): δ [J(^{119}Sn, ^{1}H)] = 0.12 [55.0] (9H, s, Me_3Sn); 0.4-1.0 (10H, m, Et_2B); 1.75 (3H, s, C(4)–Me); 2.45, 1.15 (5H, q, t, C(3)–Et); 7.10-7.16 (5H, m, N–Ph).

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