Palladium-Catalyzed Insertion of Alkynes into the Sn−B Bond of a 2-Stannyl-2,3-dihydro-1*H*-1,3,2-diazaborole and X-ray Structure Analyses of 1,3-Di-*tert*-butyl-2[(*Z*)-2-phenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole and 1,3-Di-*tert*-butyl-2[(*Z*)-1-ethyl-2-phenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole

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Reaction of equimolar amounts of 1,3-di-*tert*-butyl-2-trimethylstannyl-2,3-dihydro-1*H*-1,3,2-diazaborole (**1**) with a series of alkynes $R^1-C\equiv C-R^2$ (**2**) (**a**: $R^1 = H$, $R^2 = Ph$; **b**: H, 4-ClC_6H_4; **c**: H, 4-BrC_6H_4; **d**: Ph, Ph; **e**: Me, Ph; **f**: Et, Ph; **g**: H, *n*-C_4H_9; **h**: Et, Et; **i**: H, *n*-C_6H_{13}) in the presence of a catalytic amount of $[Pd(PPh_3)_4]$ (2 mol %) regioselectively afforded high yields of the alkenes (*Z*)-R^1[B]C=C(R^2)$SnMe_3$ (**3a**−**h**) ([B] = *t*BuNCH=CHN(*t*Bu)B] as the result of a cis-addition of the BSn bond of **1** to the acetylenic triple bond of **2**. Spectroscopic evidence and X-ray structural analyses of **3a** and **3f** revealed that the bulky borolyl unit was added to the least sterically hindered end of the CC multiple bond.

Introduction

The synthesis of the first 2,3-dihydro-1*H*-1,3,2-diazaboroles dates back to the early 1970s,[1,2] and since then a number of papers dedicated to the synthesis, structure, and bonding of such compounds have been published.[3−6] Besides the preparation of a few tricarbonyl chromium complexes[7] and the cleavage of an N−Si bond in some N−$SiMe_3$-substituted 2,3-dihydro-1*H*-1,3,2-diazaboroles by sodium amide or potassium *tert*-butoxide,[8] the chemistry of this ring system is relatively undeveloped. A thorough investigation of the chemical reactivity of 2,3-dihydro-1*H*-1,3,2-diazaboroles was hampered mainly by the lack of functional substituents in the molecules.

Recently we launched a program for the synthesis of the 2-halo-2,3-dihydro-1*H*-1,3,2-diazaboroles[9,10] as starting materials for further chemical transformations. In these studies it was demonstrated that these compounds can easily be converted into 2-cyano-, 2-isocyanato-, 2-isothiocyanato,[10] 2-hydro-, 2-alkyl-, 2-alkynyl-, and 2-stannyl-2,3-dihydro-1*H*-1,3,2-diazaboroles by halide replacement with the respective nucleophile.

The aim of the work described herein was to provide an efficient synthesis for 2-alkenyl-2,3-dihydro-1*H*-1,3,2-diazaboroles which are highly functionalized at the organic substituent at the boron center.

Results and Discussions

For the synthesis of 2-alkenyl-2,3-dihydro-1*H*-1,3,2-diazaboroles **III** generally two strategies may be envisaged. A first approach involves sodium amalgam reduction of the corresponding borolium salt **I**, which should be available by treatment of a 1,4-diazabutadiene with an alkenylboron dihalide. A second route is based upon the reaction of a 2-halo-1,3,2-diazaborole **II** with an alkenyllithium or an alkenyl Grignard reagent.

A serious limitation of these synthetic pathways is given in the fact that most functional groups (in the alkenyl part) are reactive toward a Grignard or an organolithium reagent.

Recently it was disclosed by Japanese scientists that this problem to some extent can be circumvented by the palladium-catalyzed borylsilylation of alkynes and borylsilylative carbocyclization of diynes, enynes, and allenes.[12−15] Similarly, the borylstannylation of alkynes

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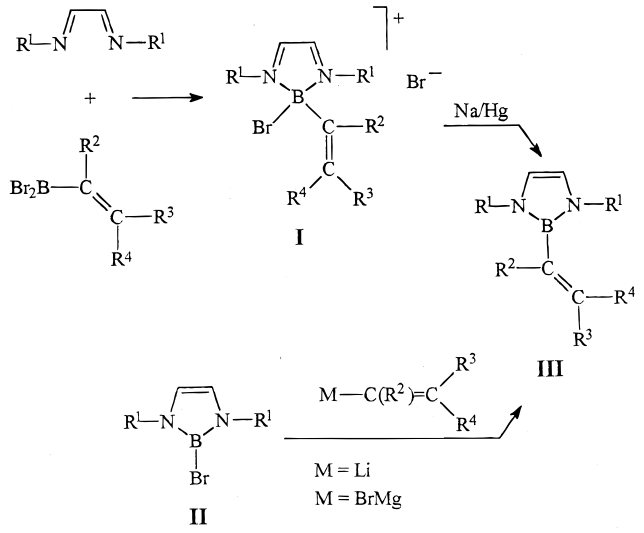
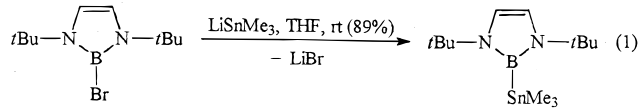
Scheme 1



and borylstannylative carbocyclization reactions of diynes and enynes were achieved using boron−tin compounds such as $Me_3SnBN(Me)CH_2CH_2NMe$ and $Me_3SnB(NEt_2)_2$.[15−17]

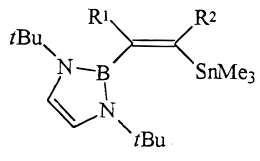
These reports motivated us to synthesize 2-alkenyl-2,3-dihydro-1*H*-diazaboroles via the palladium-assisted borylstannylation of alkynes using 2-trimethylstannyl-2,3-dihydro-1*H*-1,3,2-diazaborole **1**. The latter reagent is easily available in excellent yield from the reaction of 1,3-di-*tert*-butyl-2-bromo-2,3-dihydro-1*H*-diazaborole with an equimolar amount of in situ-generated $LiSnMe_3$ (eq 1).[11]



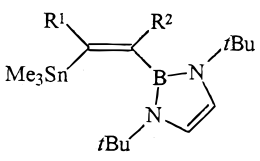
1

Reaction of **1** and equimolar amounts of alkynes **2a**−**i** in the presence of a catalytic amount (2 mol %) of $[Pd(PPh_3)_4]$ in refluxing benzene led to the regio- and stereoselective formation of alkenes **3a**−**i**. Products **3a**−**f** were obtained as colorless crystals from *n*-pentane, whereas **3g**−**i** were isolated as colorless oils by vacuum distillation (Scheme 2). It is obvious that this addition reaction proceeds equally well with terminal and internal alkynes.

However, the attempted borylstannylation of *tert*-butylacetylene, phenyl(trimethylsilyl)acetylene, propargylic alcohol, and dimethyl acetylenedicarboxylate with **1** failed. Basicly, the reaction of unsymmetrically substituted alkynes such as **2a**, **2b**, **2c**, **2e**, **2f**, **2g**, and **2i** could result in formation of regioisomers such as **A** and **B**.

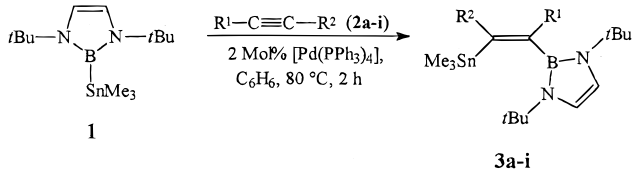


A



B

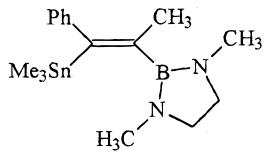
Scheme 2



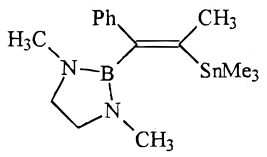
1 **3a-i**

2,3	R¹	R²	Yield (%)
a	H	C_6H_5	84
b	H	4-ClC_6H_4	78
c	H	4-BrC_6H_4	52
d	C_6H_5	C_6H_5	74
e	CH_3	C_6H_5	84
f	C_2H_5	C_6H_5	89
g	H	*n*-C_4H_9	77
h	C_2H_5	C_2H_5	66
i	H	*n*-C_6H_{13}	82

NMR spectroscopic evidence of the compounds **3a**, **3b**, **3c**, **3e**, **3f**, **3g**, and **3i**, however, indicated the selective formation of a single product. This contrasts to some extent with Tanaka's work in which the cis-addition of $MeNCH_2CH_2N(Me)BSnMe_3$ to PhC≡CMe (**2e**) furnished an 85:15 mixture of the regioisomers **C** and **D**.[16]



C



D

The $^{119}Sn\{^1H\}$ NMR spectra of the products **3** display singlet resonances in the region δ −45.6 to −58.0. In the $^{11}B\{^1H\}$ NMR spectra of **3a**−**i** the ^{11}B nuclei give rise to singlets in the narrow range δ 21.1−24.1, which is typical for 2,3-dihydro-1*H*-1,3,2-diazaboroles with organic substituents on the boron atom.[1,5,6] The boron atoms in **3** are markedly shielded when compared with Tanaka's borylstannylation products, in which the boron is incorporated in a saturated $MeNCH_2-CH_2N(Me)-B$ ring (δ 30.5−30.8).[16] The vinylic protons in the ^1H NMR spectra of **3a**−**c**, **3g**, and **3i** appear as singlets at δ 6.97−7.28. Coupling with the tin atoms was not detectable. We therefore assume, in line with Tanaka's results, that the 1,3,2-diazaborolyl unit of **1** is attached to the sterically less hindered end of the alkyne reactant. This is confirmed by the X-ray analyses of **3a** and **3f**. The ^{13}C NMR signals of the borylated carbon atoms of the C=C double bond of **3a**−**i** appear as broad singlets at δ 132.4−147.2 and are slightly shielded with respect to the stannylated carbon atoms of the alkenes (δ 150.5−156.3).

The regiochemistry of **3f** was unambigiously revealed by X-ray crystallography, showing that the borolyl unit was attached to the alkylated carbon of the C=C bond, and the same obviously holds true for **3e**.

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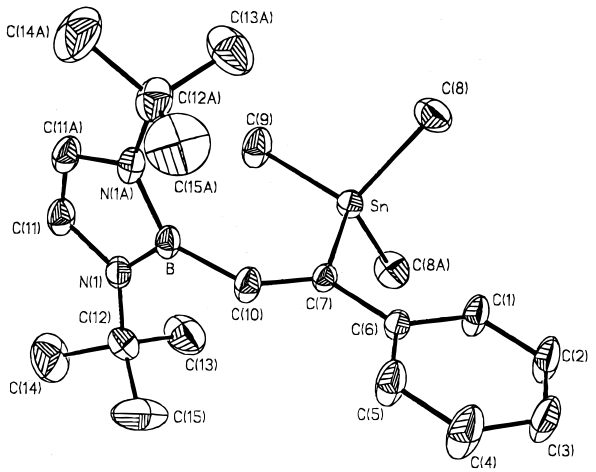
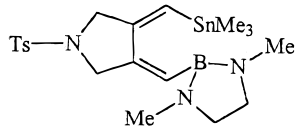


Figure 1. Molecular structure of **3a** in the crystal. Selected bond lengths (Å) and angles (deg): B−N(1) 1.438(3), N(1)−C(11) 1.401(3), N(1)−C(12) 1.491(3), C(11)−C(11A) 1.341(5), B−C(10) 1.581(5), C(7)−C(10) 1.345(4), Sn−C(7) 2.179(3), C(6)−C(7) 1.500(4), Sn−C(8) 2.146(3), Sn−C(9) 2.147(4), N(1)−B−N(1A) 105.9(3), B−N(1)−C(11) 107.1(2), N(1)−C(11)−C(11A) 109.9(1), B−N(1)−C(12) 130.8(2), C(11)−N(1)−C(12) 122.1(2), N(1)−B−C(10) 127.0(1), B−C(10)−C(7) 129.5(3), Sn−C(7)−C(10) 121.7(2), C(6)−C(7)−C(10) 121.5(3), Sn−C(7)−C(6)116.8(2), C(8)−Sn−C(8A) 110.1(2), C(8)−Sn−C(9) 105.7(1), C(8)−Sn−C(7) 109.8(1), C(7)−Sn−C(9) 115.6(1).

X-ray Structural Analysis of 3a. No X-ray structural information on simple borylstannylation products of monoalkynes has been published to date, although the molecular structure of the borylstannylative carbocyclization product **4** (obtained from 4-$MeC_6H_4S(O)_2N[CH_2{-}C{\equiv}CH]_2$ and $MeNCH_2CH_2N(Me)BSnMe_3$) was elucidated by X-ray analysis.[17]



4

Single crystals of **3a** were grown from *n*-pentane at −30 °C and were structurally investigated. The molecular structure of **3a** (Figure 1) features a planar 1,3,2-diazaborole ring with a (2-phenyl-2-trimethylstannyl)-ethenyl substituent which is linked to the boron atom via a B−C single bond of 1.581(5) Å. The plane defined by the atoms of the phenyl ring, B, Sn, C(7), C(10), and C(9) bisects the plane of the heterocycle. Clearly, the Me_3Sn group and the heterocycle are located in a cis-disposition at the double bond C(7)−C(10) [1.345(4) Å], whereby the tin atom and the ipso carbon atom of the phenyl ring are attached to C(7). The bond Sn−C(7) of 2.179(3) Å is elongated when compared with the bond lengths Sn−C(8) [2.146(3) Å] and Sn−C(9) [2.147(4) Å]. Due to steric congestion, the valence angles B−C(10)−C(7) [129.5(3)°] and C(7)−Sn−C(9) [115.6(1)°] are markedly opened in comparison to the angles at C(7) [116.8(2)−121.7(2)°] and C(8)−Sn−C(9) [105.7(1)°], C(8)−Sn−C(7) [109.8(1)°], and C(8)−Sn−C(8A) [110.1(2)°]. Inter-

(17) Onozawa, S.; Hatanaka, Y.; Choi, N.; Tanaka, M. *Organometallics* **1997**, *16*, 5389.

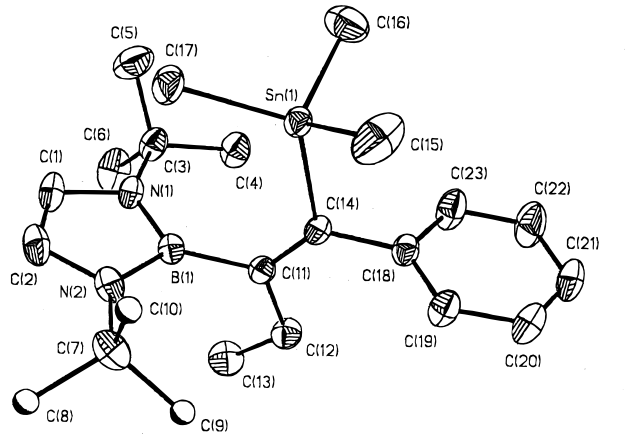


Figure 2. Molecular structure of **3f** in the crystal. Selected bond lengths (Å) and angles (deg): B−N(1) 1.444(3), B−N(2) 1.443(3), C(11)−C(14) 1.349(3), N(1)−C(3) 1.484(3), N(2)−C(7) 1.488(3), Sn(1)−C(14) 2.164(2), N(1)−C(1) 1.400(3), N(2)−C(2) 1.399(3), C(14)−C(18) 1.495(3), C(1)−C(2) 1.336(4), B−C(11) 1.577(3), C(11)−C(12) 1.529(3), Sn−C(15) 2.133(3), Sn−C(14) 2.138(3), Sn−C(17) 2.145(2), N(1)−B−N(2) 105.27(17), B−N(1)−C(1) 107.32(18), N(1)−C(1)−C(2) 110.0(2), C(1)−C(2)−N(2) 110.03(19), C(2)−N(2)−B 107.33(18), B−N(1)−C(3) 134.71(17), B−N(2)−C(7) 134.42(19), C(2)−N(2)−C(7) 119.92(18), C(1)−N(1)−C(3) 117.92(18), N(1)−B−C(11) 128.08(19), N(2)−B−C(11) 126.64(19), B−C(11)−C(14) 120.78(18), B−C(11)−C(12) 119.37(18), C(12)−C(11)−C(14) 119.84(18), C(11)−C(14)−Sn 126.83(15), Sn−C(14)−C(18) 110.41(14), C(11)−C(14)−C(18) 122.75(18), C(14)−Sn−C(15) 105.66(10), C(14)−Sn−C(16) 107.13(10), C(14)−Sn−C(17) 119.24(9), C(15)−Sn−C(16) 108.83(15), C(16)−Sn−C(17) 106.14(12), C(15)−Sn−C(17) 109.53(13).

nuclear distances and valence angles within the diazaborolyl ring are in good agreement with the respective data for **1** and merit no further discussion.[6,11]

X-ray Structural Analysis of 3f. To unambigiously determine the regiochemistry of the borylstannylation product of an unsymmetrical CC triple bond, an X-ray structural analysis of **3f** was performed. Single crystals were grown from *n*-pentane at −30 °C. The molecular structure of **3f** (Figure 2) displays a planar 1,3,2-diazaborole ring which is attached to a (1-ethyl-2-phenyl-2-trimethylstannyl)ethenyl group via a B−C single bond of 1.577(3) Å. Again the borolyl group prefers the lesser congested end of the CC multiple bond. Bonding parameters within the heterocyclic unit of **3f** are comparable with the situation in **3a**. The difference between the two structures arises from the orientation of the phenyl rings at the heavily substituted alkenyl group with respect to the plane of the 1,3,2-diazaborolyl ring.

In both structures the plane defined by the boron atom, the tin atom, and the two carbon atoms of the CC double bond is oriented perpendicularly to the plane of the heterocycle. In **3a** the phenyl ring is included in the plane of the substituent, whereas in **3f** the phenyl group is orthogonal to the plane with the atoms B(1), C(11), C(14), and Sn(1) and is parallel to the plane of the heterocycle (Figure 3). Relevant torsion angles are N(1)−B(1)−C(11)−C(14) = 86.7°, N(2)−B(1)−C(11)−C(14) = −92.0°, B(1)−C(11)−C(14)−Sn(1) = −3.5°, B(1)−C(11)−C(14)−C(18) = 178.0°, C(11)−C(14)−C(18)−C(19) = −86.7°, and C(11)−C(14)−C(18)−C(23) = 96.7°.

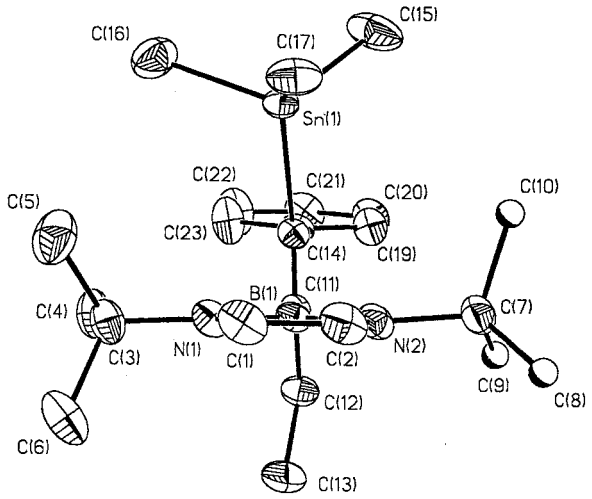


Figure 3. Molecular structure of **3f** with a view in the plane of the 1,3,2-diazaborole ring.

Experimental Section

All operations were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen prior to use. ^{1}H, ^{11}B, ^{13}C, and ^{119}Sn NMR spectra were recorded in C_6D_6 at 22 °C using Bruker AC 100 (^{1}H, 100.13 MHz, ^{11}B, 32.13 MHz) and Bruker Avance DRX 500 (^{1}H, 500.13 MHz, ^{11}B, 160.46 MHz, ^{13}C, 125.75 MHz, ^{119}Sn, 186.51 MHz) spectrometers. References: $SiMe_4$ (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), $SnMe_4$ (^{119}Sn). Elemental analyses were performed at the Microanalytical Laboratory of the University of Bielefeld. Compounds *t*BuNCH=CHN(*t*Bu)BSnMe$_3$ (**1**),[11] *p*-chlorophenylacetylene,[18] and [Pd(PPh$_3$)$_4$][19] were synthesized according to literature procedures. All other alkynes employed in this work were purchased from Aldrich.

General Procedure for the Syntheses of 2-(*β*-Stannylalkenyl)-1,3,2-diazaboroles (3a−i). A sample of the 1,3,2-diazaborole *t*BuNCH=CHN(*t*Bu)BSnMe$_3$ (**1**) (0.450 g, 1.30 mmol) and 2 mol % of the catalyst [Pd(PPh$_3$)$_4$] (0.030 g, 0.026 mmol) were dissolved in benzene (5 mL) at room temperature. An equimolar amount of the respective alkyne was added, and the mixture was heated at 80 °C for 2 h. After cooling to ambient temperature, solvent and volatile components were removed in vacuo. The residue was dissolved in 20 mL of *n*-pentane and filtered. The concentrated filtrate (ca. 5 mL) was stored at −30 °C to afford the crude products **3a**−**f** as black crystals. Recrystallization from *n*-pentane gave analytically pure materials. In the case of **3g**−**i** the pentane extracts were freed from solvent and the oily residues were purified by vacuum distillation to yield **3g**−**i** as colorless oils. The distillation flask was heated by the air stream (ca. 400 °C) of a hot air gun.

1,3-Di-*tert*-butyl-2[(*Z*)-2-phenyl-2-trimethylstannylethenyl]2,3-dihydro-1*H*-1,3,2-diazaborole (3a). Yield: 84%, mp 79 °C. ^{1}H NMR: δ 0.15 [s, J_{SnH} = 52.7 Hz, 9H, Sn(CH$_3$)$_3$], 1.35 [s, 18H, C(CH$_3$)$_3$], 6.32 (s, 2H, NCH), 7.08 (t, J_{HH} = 7.3 Hz, 1H, Ph), 7.23 (t, J_{HH} = 7.8 Hz, 2H, Ph), 7.28 (s, 1H, BCH), 7.38 (d, J_{HH} = 7.5 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ −7.7 (s, $^{1}J_{SnC}$ = 319.6 Hz, SnCH$_3$), 32.6 [s, C(*C*H$_3$)$_3$], 53.1 [s, *C*(CH$_3$)$_3$], 113.1 (s, NCH), 126.2 (s, Ph), 127.8 (s, Ph), 128.8 (s, Ph), 146.1 (s, br, BCH), 150.2 (s, J_{SnC} = 49.4 Hz, *i*C−Ph), 155.9 (d, $^{1}J_{SnC}$ = 469.2 Hz, SnC=). ^{11}B{^{1}H} NMR: δ 23.6 s. ^{119}Sn{^{1}H} NMR: δ −48.9 s. MS/EI: *m*/*z* (relative intensity) 446 (100) [M$^+$], 180 (98) [*t*BuNCH=CHN(*t*Bu)BH$^+$]. Anal. Calcd for $C_{21}H_{35}BN_2Sn$ (445.04): C, 56.80; H, 7.72; N, 6.31. Found: C, 56.81; H, 7.87; N, 6.31.

1,3-Di-*tert*-butyl-2[(*Z*)-2-*p*-chlorophenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (3b). Yield: 78%, mp 106 °C. ^{1}H NMR: δ 0.12 [s, 9H, J_{SnH} = 52.1 Hz, Sn(CH$_3$)$_3$], 1.36 [s, 18H, C(CH$_3$)$_3$], 6.34 (s, 2H, NCH), 7.17 (s, 1H, BCH), 7.24 (m, 4H, Ph). ^{13}C{^{1}H} NMR: δ −8.1 (s, $^{1}J_{SnC}$ = 321.4 Hz, SnCH$_3$), 32.3 [s, C(*C*H$_3$)$_3$], 52.9 [s, *C*(CH$_3$)$_3$], 112.9 (s, NCH), 127.2 (s, Ph), 128.7 (s, Ph), 131.8 (s, Ph), 146.8 (s, br, BCH), 148.4 (s, $^{3}J_{SnC}$ = 50.6 Hz, *i*C−Ph), 154.5 (s, SnC=). ^{11}B{^{1}H] NMR: δ 21.1 s. ^{119}Sn{^{1}H} NMR: δ −47.4 s. MS/EI: *m*/*z* (relative intensity) 480 (9) [M$^+$], 180 (100) [*t*BuNCH=CHN(*t*Bu)BH$^+$]. Anal. Calcd for $C_{21}H_{34}BClN_2Sn$ (479.49): C, 52.60; H, 7.15; N, 5.84. Found: C, 52.79; H, 6.95; N, 5.88.

1,3-Di-*tert*-butyl-2[(*Z*)-2-*p*-bromophenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (3c). Yield: 52% after 3× recrystallization (crude yield 93%), mp 123 °C. ^{1}H NMR: δ 0.10 [s, 9H, $^{2}J_{SnH}$ = 52.1 Hz, Sn(CH$_3$)$_3$], 1.31 [s, 18H, C(CH$_3$)$_3$], 6.31 (s, 2H, NCH), 7.05 (d, J_{HH} = 8.8 Hz, 2H, Ph), 7.17 (s, 1H, BCH), 7.31 (d, J_{HH} = 8.3 Hz, 2H, Ph). ^{13}C {^{1}H} NMR: δ −7.9 (s, $^{1}J_{SnC}$ = 337.8 Hz, SnCH$_3$), 32.5 [s, C(*C*H$_3$)$_3$], 53.1 [s, *C*(CH$_3$)$_3$], 113.2 (s, NCH), 120.1 (s, Ph), 127.8 (s, Ph), 128.3 (s, Ph), 131.9 (s, Ph), 147.2 (s, br, BCH) 149.1 (s, Ph), 154.7 (s, SnC=). ^{11}B{^{1}H} NMR: δ 23.4 s. ^{119}Sn-{^{1}H} NMR: δ −47.5 s. MS/EI: *m*/*z* (relative intensity) 524 (8) [M$^+$], 453 (6) [M$^+$ − Br], 180 (100) [*t*BuNCH=CHN(*t*Bu)BH$^+$]. Anal. Calcd for $C_{21}H_{34}BBrN_2Sn$ (523.94): C, 48.14; H, 6.54; N, 5.35. Found C, 48.22; H, 6.35; N, 5.31.

1,3-Di-*tert*-butyl-2[(*Z*)-1,2-diphenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (3d). Yield: 74%, mp 114 °C. ^{1}H NMR: δ 0.12 [s, $^{2}J_{SnH}$ = 50.9 Hz, 9H, Sn(CH$_3$)$_3$], 1.40 [s, 18H, C(CH$_3$)$_3$], 6.37 (s, 2H, NCH), 6.94 (m, 4H, Ph), 7.14 (m, 4H, Ph), 7.31 (d, $^{3}J_{HH}$ = 7.6 Hz, 6H, Ph). ^{13}C{^{1}H} NMR: δ −7.9 [s, $^{1}J_{SnC}$ = 331.0 Hz, SnCH$_3$], 32.1 [s, C(*C*H$_3$)$_3$], 53.9 [s, *C*(CH$_3$)$_3$], 114.1 (s, NCH), 125.4 (s, Ph), 126.0 (s, Ph), 126.6 (s, Ph), 128.9 (s, Ph), 131.6 (s, Ph), 143.4 (s, BC=), 148.2 (s, $^{3}J_{SnC}$ = 57.5 Hz, *i*C−Ph), 155.2 (s, SnC=). ^{11}B{^{1}H} NMR: δ 24.1 s. ^{119}Sn{^{1}H} NMR: δ −45.6 s. MS/EI: *m*/*z* (relative intensity) 522 (9) [M$^+$], 357 (100) [M$^+$ − ^{120}SnMe$_3$], 178 (69) [*t*BuNCH=CHN(*t*Bu)BH$^+$]. Anal. Calcd for $C_{27}H_{39}N_2Sn$ (521.09): C, 62.23; H, 7.54; N, 5.38. Found: C, 62.54; H, 7.55; N, 5.33.

1,3-Di-*tert*-butyl-2-[(*Z*)-1-methyl-2-phenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (3e). Yield: 84%, mp 68 °C. ^{1}H NMR: δ 0.04 [s, $^{2}J_{SnH}$ = 52.1 Hz, 9H, Sn(CH$_3$)$_3$], 1.34 [s, 18H, C(CH$_3$)$_3$], 1.92 (s, $^{3}J_{SnH}$ = 63.1 Hz, 3H, C−CH$_3$), 6.29 (s, 2H, NCH), 7.00−7.25 (m, 5H, Ph). ^{13}C-{^{1}H} NMR: δ −8.8 (s, $^{1}J_{SnC}$ = 316.4 Hz, SnCH$_3$), 23.3 (s, $^{3}J_{SnC}$ = 69.0 Hz, C-*C*H$_3$), 32.1 [s, C(*C*H$_3$)$_3$], 53.5 [s, *C*(CH$_3$)$_3$], 113.4 (s, NCH), 125.2 (s, Ph), 126.3 (s, Ph), 134.2 (s, Ph), 138.1 (s, br, BC), 147.3 (s, $^{3}J_{SnC}$ = 46.0 Hz, *i*C−Ph), 152.3 (s, SnC=). ^{11}B{^{1}H} NMR: δ 24.0 s. ^{119}Sn{^{1}H} NMR: δ −51.9 s. MS/EI: *m*/*z* (relative intensity) 460 (9) [M$^+$]. Anal. Calcd for $C_{22}H_{37}BN_2Sn$ (459.07): C, 57.56; H, 8.12; N, 6.10. Found: C, 57.76; H, 8.38; N, 5.89.

1,3-Di-*tert*-butyl-2-[(*Z*)-1-ethyl-2-phenyl-2-trimethylstannylethenyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (3f). Yield: 89%, mp 72 °C. ^{1}H NMR: δ 0.04 [s, $^{3}J_{SnH}$ = 50.7 Hz, Sn(CH$_3$)$_3$], 0.98 (t, $^{3}J_{HH}$ = 7.7 Hz, 3H, CH$_2$C*H*$_3$), 1.41 [s, 18H, C(CH$_3$)$_3$], 2.35 (q, $^{3}J_{HH}$ = 7.7 Hz, 2H, C*H*$_2$CH$_3$), 6.31 (s, 2H, NCH), 7.00−7.25 (m, 5H, Ph). ^{13}C{^{1}H} NMR: δ −8.9 (s, $^{1}J_{SnC}$ = 329.9 Hz, SnCH$_3$), 14.3 (s, CH$_2$*C*H$_3$), 29.4 (s, $^{3}J_{SnC}$ = 66.7 Hz, *C*H$_2$CH$_3$), 32.2 [s, C(*C*H$_3$)$_3$], 53.6 [s, *C*(CH$_3$)$_3$], 113.9 (s, NCH), 125.1 (s, Ph), 125.9 (s, Ph), 134.2 (s, Ph), 138.0 (s, br, BC=), 147.7 (s, $^{3}J_{SnC}$ = 46.0 Hz, *i*C−Ph), 151.3 (s, $^{1}J_{SnC}$ = 498.6 Hz, SnC=). ^{11}B{^{1}H} NMR: δ 23.4 s. ^{119}Sn{^{1}H} NMR: δ −54.2 s. MS/EI: *m*/*z* (relative intensity) 474 (14) [M$^+$], 309 (100) [M$^+$

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− $SnMe_3$]. Anal. Calcd for $C_{23}H_{39}BN_2Sn$ (473.10): C, 58.39; H, 8.31; N, 5.92. Found: C, 58.47; H, 8.28; N, 6.04.

1,3-Di-*tert*-butyl-2-[(*Z*)-2-trimethylstannylhex-1-enyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (3g). Yield: 77%, bp ca. 350 °C/5·10^{-5} bar. ^{1}H NMR: δ 0.12 [s, $^2J_{SnH}$ = 50.9 Hz, 9H, $Sn(CH_3)_3$], 0.94 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3CH_2), 1.33 [s, 18H, $C(CH_3)_3$], 1.35 (m, 2H, CH_2), 1.54 (q, 2H, $^3J_{HH}$ = 5.0 Hz, CH_2), 2.46 (t, $^3J_{HH}$ = 6.9 Hz, =C−CH_2), 6.30 (s, 2H, NCH), 6.95 (s, 1H, BCH). ^{13}C{^{1}H} NMR: δ −8.4 (s, $^1J_{SnC}$ = 323.2 Hz, $SnCH_3$), 14.2 (s, CH_3), 23.1 (s, CH_2), 32.5 [s, $C(CH_3)_3$], 44.7 (s, CH_2), 53.0 [s, $C(CH_3)_3$], 112.7 (s, NCH), 143.1 (s, br, BC), 156.3 (s, SnC=). ^{11}B{^{1}H} NMR: δ 23.6 s. ^{119}Sn{^{1}H} NMR: δ −53.1 s. MS/EI: *m*/*z* (relative intensity) 426 (100) [M^+]. Anal. Calcd for $C_{19}H_{39}BN_2Sn$ (425.05): C, 53.69; H, 9.25; N, 6.59. Found: C, 53.64; H, 9.15; N, 6.53.

1,3-Di-*tert*-butyl-2-[(*Z*)-2-ethyl-2-trimethylstannylbut-1-enyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (3h). Yield: 66%, bp ca. 350 °C/5·10^{-5} bar. ^{1}H NMR: δ 0.12 [s, $^2J_{SnH}$ = 50.9 Hz, 9H, $Sn(CH_3)_3$], 1.04 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_2CH_3), 1.08 (t, $^3J_{HH}$ = 7.7 Hz, 3H, CH_2CH_3), 1.31 [s, 18H, $C(CH_3)_3$], 2.40 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2CH_3), 2.48 (q, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2-CH_3), 6.26 (s, 2H, NCH. ^{13}C{^{1}H} NMR: δ −8.2 (s, $^1J_{SnC}$ = 316.0 Hz, $SnCH_3$), 12.2 (s, CH_3), 14.2 (s CH_3), 26.0 (s, CH_2), 28.2 (s, CH_2), 32.2 [s, $C(CH_3)_3$], 53.4 [s, $C(CH_3)_3$], 114.1 (s, NCH), 132.4 (s, BC), 150.5 (s, SnC=). ^{11}B{^{1}H} NMR: δ 23.3 s. ^{119}Sn{^{1}H} NMR: δ −58.0 s. MS/EI: *m*/*z* (relative intensity) 426 (14) [M^+]. Anal. Calcd for $C_{19}H_{39}BN_2Sn$ (425.05): C, 53.69; H, 9.25; N, 6.59. Found: C, 53.56; H, 9.21; N, 6.24.

1,3-Di-*tert*-butyl-2-[(*Z*)-2-trimethylstannyloct-1-enyl]-2,3-dihydro-1*H*-diazaborole (3i). Yield: 82%, bp ca. 400 °C/5·10^{-5} bar. ^{1}H NMR: δ 0.15 [s, $^2J_{SnH}$ = 52.1 Hz, 9H, $Sn(CH_3)_3$], 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_2CH_3), 1.32 (m, 6H, CH_2), 1.34 [s, 18H, $C(CH_3)_3$], 1.59 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 2.48 (t, $^3J_{HH}$ = 7.2 Hz, =C−CH_2), 6.30 (s, 2H, NCH), 6.97 (s, 1H, BCH). ^{13}C{^{1}H} NMR: δ −8.4 (s, $^1J_{SnC}$ = 263.2 Hz, $SnCH_3$), 14.4 (s, CH_3), 23.1 (s, CH_2), 23.2 (s, CH_2), 29.2 (s, CH_2), 29.8 (s, CH_2), 32.1 [s, $C(CH_3)_3$], 45.0 (s, =C−CH_2), 53.0 [s, $C(CH_3)_3$], 112.7 (s, NCH), 142.8 (s, br, BC), 156.3 (s, =CSn), 157.5 (s, BCH). ^{11}B{^{1}H} NMR: δ 23.6 s. ^{119}Sn{^{1}H} NMR: δ −53.2 s. MS/EI: *m*/*z* (relative intensity) 455 (18) [M^+], 180 (100) [*t*BuNCH$_2$-CH_2N(*t*Bu)BH^+]. Anal. Calcd for $C_{21}H_{43}BN_2Sn$ (453.10): C, 55.67; H, 9.57; N, 6.18. Found: C, 55.90; H, 9.69; N, 5.99.

X-ray Structural Analysis of 3a. Single crystals of **3a** were grown from *n*-pentane at −30 °C. A colorless crystal with the approximate dimensions of 1.1 × 1.0 × 0.9 mm^3 was measured on a Siemens $P(2)_1$ diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 173 K. Crystal data and refinement details (refined from the diffractometer angles of 50 centered reflections): a = 14.374(5) Å, b = 12.352(4) Å, c = 25.628(7) Å, V = 4550(2) $Å^3$, Z = 8, d_{calcd} = 1.299 g cm^{-3}, μ = 1.129 mm^{-1}, space group *Cmca*, data collection of 3430 unique intensities ($2\theta_{max}$ = 60°), structure solution by direct methods and anisotropic refinement with full-matrix least-squares methods on F^2 for all non hydrogen atoms (program used Siemens SHELXTL plus/SHELXL-97, riding model for hydrogen atoms, 134 parameters, maximum residual electron density 0.9 e/$Å^3$, R_F = 0.031 based on 2940 reflections with ($I > 2\sigma(I)$), wR_{F^2} = 0.079.

X-ray Structural Analysis of 3f. Single crystals of **3f** were grown from *n*-pentane at −30 °C. A colorless crystal with the approximate dimensions of 0.9 × 0.6 × 0.5 mm^3 was measured on a Siemens $P(2)_1$ diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 173 K. Crystal data and refinement details (refined from the diffractometer angles of 50 centered reflections): a = 15.006(6) Å, b = 10.376(6) Å, c = 16.364(8) Å, β = 105.68(4)°, V = 2453(2) $Å^3$, Z = 4, d_{calcd} = 1.281 g cm^{-3}, μ = 1.051 mm^{-1}, space group $P2_1/n$, data collection of 7141 unique intensities ($2\theta_{max}$ = 60°), structure solution by direct methods and anisotropic refinement with full-matrix least-squares methods on F^2 for all non hydrogen atoms (program used Siemens SHELXTL plus/SHELXL-97, riding model for hydrogen atoms, 266 parameters, maximum residual electron density 0.812 e/$Å^3$; R_F = 0.0325 based on 6209 reflections with ($I > 2\sigma(I)$), wR_{F^2} = 0.0830 for all data. Disorder of *tert*-butyl group C(8)−C(10) on three positions (42:32:26).

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Supporting Information Available: Table of X-ray data, atomic coordinates, thermal parameters, and complete bond distances and angles and thermal ellipsoid plots for compound **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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