Synthesis and Characterization of Allylic Dihaloboranes

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Volatile allylic dihaloboranes have been prepared and characterized by ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy and mass spectrometry. The stability ($\tau_{1/2}$) of such compounds in dilute $CDCl_3$ solutions depends on the substituents and the halides and ranges from a few minutes (allylic dibromoboranes) to several days (allylic difluoroboranes). Allyldihaloborane etherates were obtained by addition of diethyl ether to the corresponding free allyldihaloborane.

In 1961, Coyle *et al.* prepared by reaction of BF_3 with tetraallylstannane the first allylic dihaloborane, $CH_2{=}CHCH_2BF_2$, which was characterized by ^{19}F NMR spectroscopy.[1] Fourteen years later, on the basis of the ^{1}H and ^{11}B NMR spectra of the crude mixture, Mikhailov *et al.* reported $CH_2{=}CHCH(Me)BCl_2$ as the product formed by redistribution of tricrotylborane with BCl_3.[2] In 1979, Haubold *et al.* described the preparation of 1,4-bis(dichloroboryl)-2-butene and 1,4-bis(difluoroboryl)-2-butene by reaction of 1,3-butadiene with B_2Cl_4 and B_2F_4, respectively.[3] Recently, allylic dichloroboranes formed by reaction of allylic tributylstannanes with BCl_3 were observed in the reaction mixture by ^{1}H NMR spectroscopy.[4] For allylic monohaloboranes, the presence of an amino[5] or phenyl[6] substituent led to kinetically stable (but also less reactive) allylic boranes. Allylic dichloro- or dibromoboranes were postulated as intermediates,[7−9] and the efficacy in carbometalation reactions of allylic dichloroboranes generated *in situ* has recently been described.[4]

During the last four years, we have reported the alkenylation, allenylation, or alkynylation of $GeCl_4$,[10] $SnCl_4$,[11] $AsCl_3$,[12] or $SbCl_3$[13] by vinylic, allenyl, and alkynyltri-*n*-butylstannane. We have recently described the formation of allylic dihalophosphines, -arsines, and -stibines by reaction of an allylic tri-*n*-butylstannane with PCl_3 or PBr_3, $AsCl_3$, or $SbCl_3$ respectively.[14] Although the low reactivity of the phosphorus and arsenic derivatives permitted their isolation and characterization, highly reactive allylation reagents are of a great interest in organic synthesis. We report here a general study devoted to volatile allylic dihaloboranes prepared by reaction of allylic stannanes with boron trihalides.

Results and Discussion

We have prepared the allylic difluoroboranes **2a**−**d** by slow addition of gaseous (≈400 mbar) BF_3 to a degassed solution of allylic tributylstannanes **1a**−**d**, respectively, in 1,1,2,2-tetrachloroethane (Scheme 1). The 2-propenyl- (**2a**[1]) and methallyldifluoroborane (**2b**) were separated from the solvent and excess BF_3 by trap-to-trap distillation and obtained in nearly quantitative yield based on the stannane **1a,b**. The versatility of the substitution is dependent on the substituents. From the crotylstannane **1c,c′** and BF_3, only the crotyldifluoroborane **2c,c′** was obtained, while (3-methyl-2-butenyl)-tributylstannane **1d** and BF_3 gave (3-methyl-2-butenyl)-difluoroborane **2d** (41% yield) and 3-methyl-1-butene (10% yield). Products **2c,c′** and **2d** probably were formed by a rearrangement of the primary γ-products,[15,16] (1-methyl-2-propenyl)- (**2e**) and (1,1-dimethyl-2-propenyl)difluoroborane (**2f**), respectively (Scheme 1). Attempts to characterize the postulated primary products by low-temperature (−80 °C) NMR spectroscopy were unsuccessful, even when the reaction was performed at −80 °C in an NMR tube with toluene-d_8 as solvent and BF_3 and stannane **1c** or **1d** as reagents.

The allylic difluoroboranes **2a**−**d** were characterized by ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopy and high-resolution mass spectrometry (HRMS). Typical of the presence of a boron atom, broad signals were observed for the allylic hydrogens (^{1}H NMR) and carbon (^{13}C NMR). The ^{11}B NMR signal of each compound was observed near 27.7 ppm (±0.1 ppm). The quadruplet (intensity 1:1:1:1, $^{1}J_{BF} \approx 80$ Hz) observed by ^{19}F NMR

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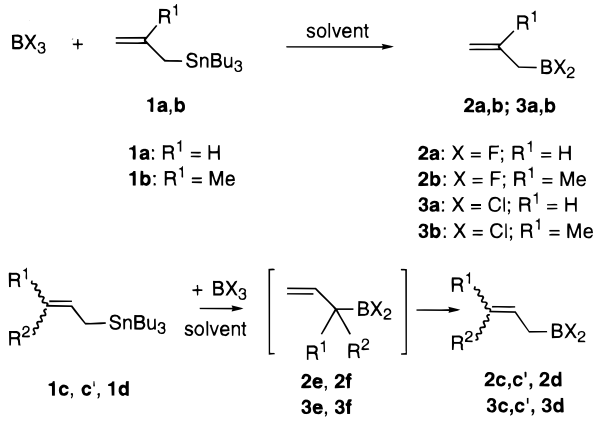
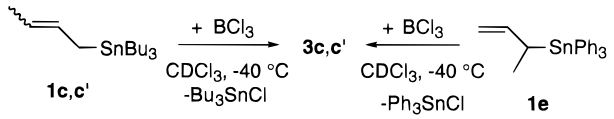
Scheme 1

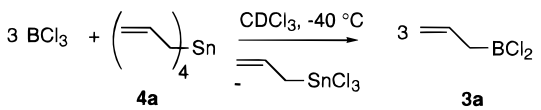


Scheme 2



spectroscopy is characteristic of the presence of a "BF" group.[17] The half-life of boranes **2a**−**d** in dilute (≈5%) solutions of $CDCl_3$ ranges from 4 h (**2b**) to several days (**2c,c′**) at room temperature; the methallyldifluoroborane (**2b**), in particular, is less stable than the other derivatives. Compounds **2a**−**d** could be condensed in pure form at low temperature and then revaporized.

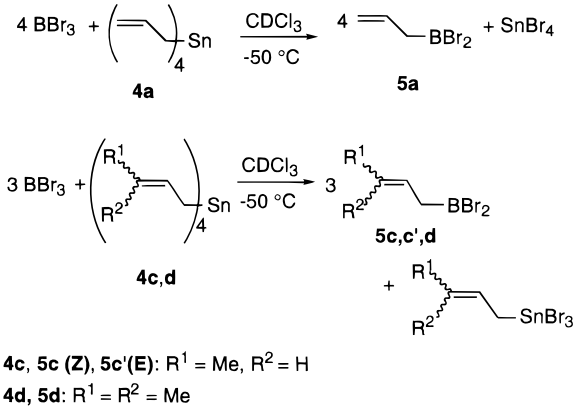
The slow addition of gaseous BCl_3 to stannane **1a** in dilute solution gave the allyldichloroborane (**3a**) in only low yield with propene as the major product of the reaction. However, good yields were obtained by addition of the stannane **1a**,**c**−**d** to a cooled (−40 °C), dilute solution of an excess of BCl_3 (Scheme 1). The formation of $BuBCl_2$ was not observed when the reaction and the distillation of the allylic boranes **3a**,**c**−**d** with $CDCl_3$ were performed at low temperature (< −10 °C). Only small amounts of 1-butene were detected in the preparation of crotylborane **3c,c′**, but 3-methyl-1-butene was formed in 20% yield in the synthesis of the (3-methyl-2-butenyl)dichloroborane (**3d**). Compound **3a** can also be prepared starting from BCl_3 and tetrallylstannane (**4a**), with the redistribution giving the allyltrichlorostannane as the organotin product (eq 1). The crotyl-



dichloroboranes **3c,c′** were obtained from BCl_3 and crotylstannanes **1c,c′** or from BCl_3 and (1-methyl-2-propenyl)triphenylstannane (**1e**). These results indicate that only the thermodynamic product (the isomer less substituted on the α-carbon) can be isolated (Scheme 2). Methallyldichloroborane (**3b**) exhibited a particular instability and was prepared from BCl_3 and stannane **1b** in a cooled (−80 °C) solution of C_7D_8.

Boranes **3a**−**d** were purified by trap-to-trap distillation. They must be trapped with a cosolvent since

Scheme 3



attempts to condense and then revaporize the pure allylic dichloroboranes **3a**−**d** were unsuccessful. Dichloroboranes **3a**−**d** were analyzed by ^1H, ^{13}C, and ^{11}B NMR spectroscopy. They exhibit typical NMR spectra: broad signals were observed for the allylic carbon and hydrogens. The ^{11}B NMR signals were observed near 61 ppm, an area characteristic of alkyldichloroboranes.[18] The presence of **3a** was confirmed by HRMS; in the ionization chamber of the mass spectrometer, the volatile borane **3a** was selectively vaporized from a mixture containing **3a** and the high-boiling solvent ($C_2H_2Cl_4$) ($M^{+\bullet}$ for $C_3H_5BCl_2$ (**3a**) calcd 121.986, found 121.986). Such dichloro derivatives are less stable than the corresponding difluoroboranes **2a**−**d**. The half-life of boranes **3a,c**−**d** in dilute (≈5%) solutions of $CDCl_3$ is about several hours at room temperature. Only the methallyldichloroborane **3b** was too unstable to be characterized at room temperature and its NMR spectra were recorded at −60 °C in toluene-d_8.

The reaction of 2-propenyltri-n-butylstannane with BBr_3 has been reported,[19] but the sole NMR signal (δ^{11}_B 39 ppm) is not consistent with a dibromoborane.[18] However, this approach effectively leads to the expected product as shown by its recently described chemical trapping.[4] We found that allylic dibromoboranes **5a,c**−**d** can be prepared by addition of a tetraallylic stannane **4a,c**,[20]**d**, respectively, to a cooled (−50 °C) solution containing boron tribromide in excess (Scheme 3). The four allylic groups of the stannane **4a** were replaced by bromine, and the sole stannane observed at the end of this reaction was tin tetrabromide (δ^{119}_{Sn} −635 ppm). From stannanes **4c,d**, the corresponding allylic dibromoboranes **5c,d** and allylic tribromostannanes were obtained (Scheme 3). Starting with BBr_3 and stannanes **1b** or **4b**, attempts to detect by low-temperature ^{11}B and ^1H NMR spectroscopy the methallyldibromoborane **5b** were unsuccessful even in toluene-d_8 at −90 °C. This result is in line with the high instability of the other methallyldihaloboranes (**2b**, **3b**) while the crotylboranes (**2c,c′**, **3c,c′**, and **5c,c′**) are, in each case, the most stable compounds. Allyldibromoboranes **5a,c,c′** were separated from stannanes by codistillation with a solvent

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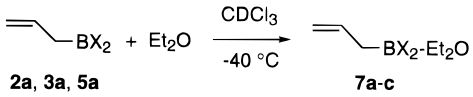
(20) Compound **4c** has been obtained by reaction of crotyl magnesium chloride with $SnCl_4$. A mixture of tetraallylic stannanes with *Z*- and *E*-crotyl- and 1-methyl-2-propenyl groups as substituents was obtained.

(C_7D_8 or $Cl_2CHCHCl_2$) but an important loss of product is observed and the presence of numerous decomposition products cannot be avoided. The half-life of boranes **5a,c**−**d** in dilute (≈5%) solutions of $CDCl_3$ is only of few minutes at room temperature. The ^{11}B NMR signals were observed near 63 ppm.

The distinctive NMR data are characteristic of the halogen substituents: the presence of the two fluorine atoms in compound **2a** shifted the signals of the allylic hydrogens ($\delta \approx 1.98$ ppm) upfield with respect to those of the chloro **3a** ($\delta \approx 2.45$ ppm) and bromo derivatives **5a** ($\delta \approx 2.55$ ppm). A similar effect was observed for the α-carbon signals in the ^{13}C NMR spectra: $\delta_{\mathbf{2a}}$ 18−21, $\delta_{\mathbf{3a}}$ 34−36, $\delta_{\mathbf{5a}}$ 48.0−48.2. The ^{11}B NMR signals were observed at 27.6 (**2a**), 61.4 (**3a**), and 63.0 ppm (**5a**), respectively.

Our results led us to reanalyze some previous reports. The reaction of tricrotylborane with BCl_3[2] cannot lead to the γ-product CH_2═$CHCH(Me)BCl_2$, since this compound rearranges to the crotyl derivatives **3c,c′** even at low temperature. The reported ^1H and ^{11}B NMR data clearly show that crotyldichloroborane **3c,c′** and 1-butene were formed. The ^1H NMR chemical shifts and coupling constants reported for 1,4-bis(difluoroboryl)-2-butene and 1,4-bis(dichloroboryl)-2-butene[3] are not consistent with those of boranes **2a**−**d** and **3a**−**d**, respectively, and especially not with those of the crotyl derivatives **2c,c′** and **3c,c′**, which have a comparable structure.

The preparation of an allylic dihaloborane complex has never been reported. The addition of stannane **1a** or **4a** on BF_3−Et_2O[21] or BCl_3−Et_2O did not give the expected product and only traces of allyldibromoborane etherate were observed by reaction of **1a** with BBr_3−Et_2O. We synthesized allylic difluoro- (**7a**), dichloro- (**7b**), and dibromoborane etherates (**7c**) by addition of diethyl ether to the corresponding free allylic dihaloborane (eq 2). The yields range from 83 (**7a**) to 63% (**7c**).



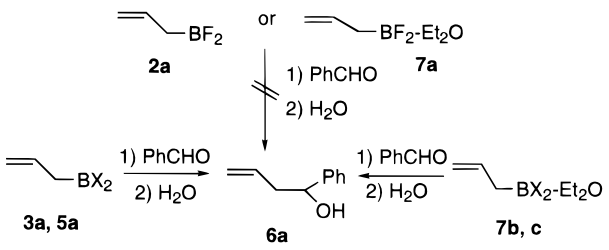
2a, **3a**, **5a** **7a-c**

2a, **7a**: X = F
3a, **7b**: X = Cl
5a, **7c**: X = Br

The ^1H and ^{13}C NMR data of compounds **7a**−**c** are similar to those of the corresponding free derivatives. Only the ^{11}B NMR signals are shifted upfield (**7a**, 15.6 ppm; **7b**, 14.6 ppm; and **7c**, 0.0 ppm). The corresponding free and complexed allyldihaloboranes exhibited a similar stability.

The mechanism of the reaction of an allylic stannane with an electrophile in the presence of a free or complexed boron halide can now be partially elucidate.[15,21] No transmetalation occurs between an allylic stannane and BF_3−Et_2O since no fluorostannane was observed in the reaction mixture.[21] However it is generally accepted that the allylation of an electrophile by an allylic stannane in the presence of BCl_3 or BBr_3 probably proceeds via a transmetalation.[4,9,21,22] We studied the reaction of free boranes **2a**, **3a**, and **5a**[23] or borane etherates **7a**−**c** with the benzaldehyde. The addition of benzaldehyde to allyldichloroboranes **3a** and **7b** or allyldibromoboranes **5a** and **7c** gave, after hydrolysis, the expected homoallyl alcohol **6a** (Scheme 4). With allyldifluoroboranes **2a** and **7a**, the alcohol **6a** was not observed. Hence, the reaction of an allylic stannane with an aldehyde in the presence of BF_3 or BF_3−Et_2O cannot proceed via a transmetalated intermediate, because this species does not react with an aldehyde to give the corresponding homoallylic alcohol. From our experiments, the mechanism is more difficult to elucidate with chloro- and bromoboranes and such reactions could be dependent on the strength of the borane−electrophile complexes, the experimental conditions, and the boron trihalide/electrophile ratio.[15a]

Scheme 4



3a, 7b: X = Cl
5a, 7c: X = Br

In conclusion, the volatile allylic difluoro-, dichloro-, and dibromoboranes were easily prepared and characterized by spectroscopy. Most of them can now be considered as isolable compounds. The allylborane etherates are synthesized by the addition of diethyl ether to the corresponding free boranes. Extension of this approach to the preparation of other highly reactive boron derivatives and the study of their chemistry currently are in progress.

Experimental Section

Materials. Boron trifluoride was prepared as described;[24] boron trichloride in *p*-xylene, boron tribromide, and 1,1,2,2-tetrachloroethane were purchased from Aldrich. All chemicals were used without further purification except BCl_3, which was separated from *p*-xylene by trap-to-trap distillation. Allylic tributylstannanes **1a**−**d**[25] and tetraallylic stannanes **4a**−**d**[26] were prepared as previously reported. A mixture of (1-methyl-2-propenyl)triphenylstannane (**1e**) and crotyltriphenylstannane was prepared as previously reported.[25b] Fractional crystallization in pentane yielded compound **1e** (33% yield) with a purity higher than 90%. 1-Phenyl-3-buten-1-ol (**6a**) was identified by comparison with an authentic sample.[27]

General. ^1H (400 MHz), ^{19}F (376 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker spectrometer ARX400 and ^{11}B (96.3 MHz) NMR on a Bruker spectrometer AC 300C. Chemical shifts are given in ppm on the scale δ relative to tetramethylsilane (^1H NMR), solvent (^{13}C NMR, $\delta = 77.7$ ppm),

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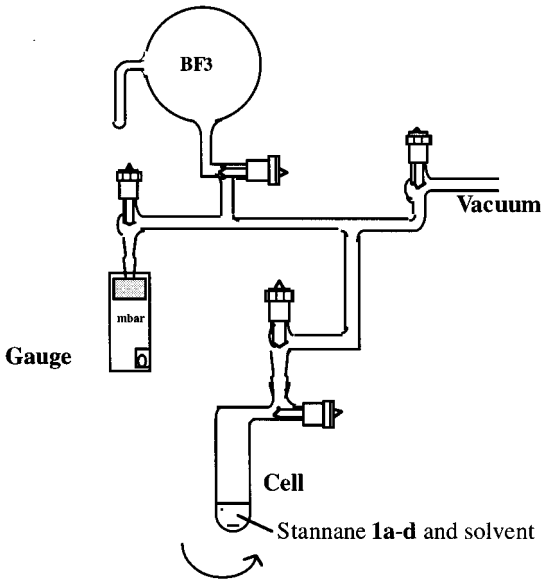

Figure 1.

external CCl_3F, (^{19}F NMR) or external BF_3-Et_2O (^{11}B NMR). The NMR spectra were recorded using $CDCl_3$ as solvent. High-resolution mass spectrometry experiments (HRMS) were performed on a Varian MAT 311 instrument. To record the mass spectra, the allylic difluoroboranes **1a**−**d** were directly introduced from a cooled cell into the ionization chamber of the spectrometer. The yields and half-lives ($\tau_{1/2}$) of the unstabilized derivatives were determined by ^1H NMR with an internal reference.

Allyldifluoroboranes 1. General Procedure. Into a 50 mL one-necked flask equipped with a magnetic stir bar and a stopcock was introduced the allylic tri-*n*-butylstannane **1a**−**d** (3.0 mmol) and 1,1,2,2-tetrachloroethane (6 mL). The flask was fitted to a vacuum line and degassed (Figure 1). The vacuum line was disconnected from the vacuum pump and filled with BF_3 at a pressure of 400 mbar. The flask was allowed to warm to room temperature and briefly opened to the BF_3 atmosphere at 5 min intervals until the pressure was unchanged. The flask then was placed on another vacuum line to perform the purification by trap-to-trap distillation. The solvent was selectively condensed in a trap cooled at −60 °C. The borane **2a**−**d** was separated from residual BF_3 by condensation at −120 °C, then revaporized and frozen on a cold finger (−196 °C) connected at the bottom to a Schlenk flask or NMR tube. If necessary, a solvent was added. The cold finger was disconnected from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen, and liquid nitrogen was subsequently removed. The product was collected in the Schlenk flask or NMR tube and kept at low temperature (< −80 °C) before analysis (NMR spectroscopy). For HRMS experiments, the cold finger containing pure boranes **2a**−**d** under vacuum was directly fitted on the mass spectrometer.

2-Propenyldifluoroborane (2a).[1] Yield: 98%. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 18 h. ^1H NMR ($CDCl_3$, RT): δ 1.98 (br s, 2H), 5.07 (d, 1H, $^3J_{HHcis}$ = 9.9 Hz), 5.11 (d, 1H, $^3J_{HHtrans}$ = 17.1 Hz), 5.82 (ddt, 1H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 9.9 Hz, $^3J_{HH}$ = 7.3 Hz). ^{11}B NMR ($CDCl_3$, RT): δ 27.6 (t, $^1J_{BF}$ = 78.8 Hz). ^{19}F NMR ($CDCl_3$, RT): δ −73.4 (q). ^{13}C NMR ($CDCl_3$, RT): δ 18−21 (very broad), 117.2 (t, $^1J_{CH}$ = 160.1 Hz), 129.8 (d, $^1J_{CH}$ = 153.9 Hz). HRMS: calcd for $(C_3H_5BF_2^{\bullet})^+$ 90.04523, found 90.0453; *m*/*z* (%) 90 (62.4), 89 (15.5), 70 (36.4), 69 (20.8), 68 (5.5), 49 (33.7), 48 (6.4), 45 (12.3), 42 (35.3), 41 (100).

(2-Methyl-2-propenyl)difluoroborane (2b). Yield: 96%. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 6 h. ^1H NMR ($CDCl_3$, RT): δ 1.82 (s, 3H), 1.96 (br s, 2H), 4.73 (s, 1H), 4.81 (s, 1H). ^{11}B NMR ($CDCl_3$, RT): δ 27.6. ^{19}F NMR ($CDCl_3$, RT): δ −72.8 (q, $^1J_{BF}$ = 80.0 Hz). ^{13}C NMR ($CDCl_3$, RT): δ 22−24 (very broad), 25.1 (q, $^1J_{CH}$ = 126.2 Hz), 112.3 (dd, $^1J_{CH}$ = 150.9 Hz, $^1J_{CH}$ = 159.6 Hz), 138.7 (s). HRMS: calcd for $(C_4H_7BF_2^{\bullet})^+$ 104.0608, found 104.061; *m*/*z* (%) 104 (48.6), 103 (10.7), 89 (22.1), 88 (5.3), 87 (5.4), 69 (31.8), 68 (6.3), 57 (6.0), 55 (13.6), 49 (13.0), 41 (100), 39 (34.7).

(*Z*)- and (*E*)-2-Butenyldifluoroboranes (2c,c′). Yield: 92% (*Z*:*E* ratio 27:73), $\tau_{1/2}$ (5% in $CDCl_3$) = 2−3 days. ***E***. ^1H NMR ($CDCl_3$, RT): δ 1.69 (d, 3H, $^1J_{HH}$ = 5.8 Hz), 1.88 (br s, 2H), 5.40−5.55 (m, 2H). ^{11}B NMR ($CDCl_3$, RT): δ 27.7 (t, $^1J_{BF}$ = 80.6 Hz). ^{19}F NMR ($CDCl_3$, RT): δ −74.2 (q). ^{13}C NMR ($CDCl_3$, RT): δ 16−19 (very broad), 19.0 (q, $^1J_{CH}$ = 125.6 Hz), 121.9 (d, $^1J_{CH}$ = 149.2 Hz), 127.6 (d, $^1J_{CH}$ = 151.6 Hz). ***Z***. ^1H NMR ($CDCl_3$, RT): δ 1.63 (d, 3H, $^1J_{HH}$ = 6.1 Hz), 1.88 (br s, 2H), 5.40−5.60 (m, 2H). ^{11}B NMR ($CDCl_3$, RT): δ 27.7. ^{19}F NMR ($CDCl_3$, RT): δ −74.2 (q, $^1J_{BF}$ = 83 Hz). ^{13}C NMR ($CDCl_3$, RT): δ 13.7 (q, $^1J_{CH}$ = 125.6 Hz), 16−19 (very broad), 120.9 (d, $^1J_{CH}$ = 158.2 Hz), 125.9 (d, $^1J_{CH}$ = 162.8 Hz). HRMS: calcd for $(C_4H_7BF_2^{\bullet})^+$ 104.0608, found 104.060; *m*/*z* (%) 104 (48.5), 103 (12.9), 89 (18.1), 81 (7.1), 69 (6.7), 68 (7.5), 56 (6.6), 56 (6.6), 55 (24.6), 54 (6.1), 49 (14.7), 41 (100), 39 (24.9).

(3-Methyl-2-butenyl)difluoroborane (2d). Yield: 41%, $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 18 h. ^1H NMR ($CDCl_3$, RT): δ 1.62 (s, 3H), 1.73 (s, 3H), 1.85 (br s, 2H), 5.18 (t, 1H, $^3J_{HH}$ = 7.3 Hz). ^{11}B NMR ($CDCl_3$, RT): δ 27.8 (t, $^1J_{BF}$ = 79.7 Hz). ^{19}F NMR ($CDCl_3$, RT): δ −74.2 (q). ^{13}C NMR ($CDCl_3$, RT): δ 13−15 (very broad), 18.6 (q, $^1J_{CH}$ = 125.1 Hz), 26.4 (q, $^1J_{CH}$ = 125.6 Hz), 114.7 (d, $^1J_{CH}$ = 155.1 Hz), 133.6 (s). HRMS: calcd for $(C_5H_9BF_2^{\bullet})^+$ 118.0765, found 118.077; *m*/*z* (%) 118 (39.0), 117 (9.9), 103 (38.7), 102 (9.8), 81 (21.9), 77 (6.0), 70 (7.8), 69 (12.5), 55 (100), 42 (20.7), 41 (30.6).

Allyldichloroboranes 3a−d. General Procedure. In a two-necked flask equipped with a nitrogen inlet and a stirring bar were introduced BCl_3 (1.3 mmol) and a solvent (1 mL of chloroform, toluene, 1,1,2,2-tetrachloroethane, etc.). The flask was cooled to −40 °C and the stannane **1a,c**−**d** (1.0 mmol) was added in about 1 min. with a microsyringe. At the end of the addition, the solution was stirred for 10 min at −40 °C and the flask then was fitted on a vacuum line. The product was purified by trap-to-trap distillation. For NMR experiments, the solvent ($CDCl_3$, C_7D_8, $C_2Cl_4D_2$, etc.) and the boranes **3a,c**−**d** were separated from chlorotributylstannane by distillation in vacuo (10^{-1} mbar) and condensation at −100 °C to remove excess BCl_3.

Pure borane **3a,c**−**d** can be obtained using 1,1,2,2-tetrachloroethane as solvent. The purification was performed by trap-to-trap distillation. The solvent was selectively condensed in a trap cooled at −50 °C and the pure boranes **3a,c**−**d** were condensed at −80 °C; a cosolvent was added at this step before revaporization to inhibit any decomposition.

The methallyldichloroborane **3b** was prepared from BCl_3 and stannane **1b** in a cooled (−80 °C) solution of C_7D_8.

2-Propenyldichloroborane (3a).[4] Yield: 62%. $\tau_{1/2}$ (5% in $CDCl_3$ or C_7D_8 at RT) ≈ 4 h. ^1H NMR ($CDCl_3$, −40 °C): δ 2.45 (br d, 2H, $^3J_{HH}$ = 7.3 Hz), 5.04 (dd, 1H, $^3J_{HHtrans}$ = 17.0 Hz, $^2J_{HH}$ = 1.5 Hz), 5.08 (dd, 1H, $^3J_{HHcis}$ = 10.3 Hz, $^2J_{HH}$ = 1.5 Hz), 5.89 (ddt, 1H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 7.3 Hz). ^{11}B NMR ($CDCl_3$, −50 °C): δ 61.4. ^{13}C NMR ($CDCl_3$, −40 °C): δ 34.5−36.5 (very broad), 117.2 (t, $^1J_{CH}$ = 155.0 Hz), 131.4 (d, $^1J_{CH}$ = 152.3 Hz). HRMS: calcd for $(C_3H_5BCl_2^{\bullet})^+$: 121.9861, found 121.986.

(2-Methyl-2-propenyl)dichloroborane (3b). Yield: 58%. $\tau_{1/2}$ (5% in $CDCl_3$ or C_7D_8) decomposed before allowed to warm to room temperature; 2 h (−60 °C). ^1H (C_7D_8, −60 °C): δ 1.52 (s, 3H), 1.87 (br s, 2H), 4.55 (s, 1H), 4.79 (s, 1H). ^{11}B NMR ($C_7H_8-C_6D_6$, −50 °C): δ 62.0. ^{13}C NMR (C_7D_8, −60 °C): δ 24.1 (q, $^1J_{CH}$ = 125.7 Hz), 38−40 (br t, $^1J_{CH}$ = 133.0 Hz), 113.2 (t, $^1J_{CH}$ = 160.0 Hz), 139.7 (s).

(*Z*)- and (*E*)-2-Butenyldichloroboranes (3c,c′).[4] (*Z*:*E* ratio 1:1) The *E*-isomer is less stable than the *Z*. Yield: 60%. $\tau_{1/2}$ (5% in $CDCl_3$ or C_7D_8 at RT) ≈ 16 h. Z. ^1H ($CDCl_3$, −40 °C): δ 1.66 (d, 3H, $^1J_{HH}$ = 6.7 Hz), 2.46 (br d, 2H, $^3J_{HH}$ = 6.2

Hz), 5.45−5.67 (m, 2H). ^{11}B NMR ($CDCl_3$, −50 °C): δ 61.0. ^{13}C NMR ($CDCl_3$, −40 °C): δ 13.0 (q, $^1J_{CH}$ = 126.2 Hz), 33.5−35.5 (very broad), 122.6 (d, $^1J_{CH}$ = 159.5 Hz), 126.2 (d, $^1J_{CH}$ = 154.7 Hz). (**E**): ^{1}H ($CDCl_3$, −40 °C): δ 1.73 (d, 3H, $^3J_{HH}$ = 4.5 Hz), 2.41 (br, 2H), 5.45−5.67 (m, 2H). ^{11}B NMR ($CDCl_3$, −50 °C): δ 61.0. ^{13}C NMR ($CDCl_3$, −40 °C): δ 18.0 (q, $^1J_{CH}$ = 125.9 Hz), 28.5−30.5 (very broad), 123.5 (d, $^1J_{CH}$ = 158.1 Hz), 127.9 (d, $^1J_{CH}$ = 158.4 Hz).

3-Methyl-2-butenyldichloroborane 3d. Yield: 32%. $\tau_{1/2}$ (5% in $CDCl_3$ or C_7D_8 at RT) ≈ 8 h. ^{1}H NMR ($CDCl_3$, −40 °C): δ 1.63 (s, 3H), 1.76 (s, 3H), 2.38 (br d, 2H, $^3J_{HH}$ = 7.6 Hz), 5.26 (t. hept, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz). ^{11}B NMR ($CDCl_3$, −40 °C): δ 60.7. ^{13}C NMR ($CDCl_3$, −40 °C): δ 18.1 (q, $^1J_{CH}$ = 126.6 Hz), 26.1 (q, $^1J_{CH}$ = 128.7 Hz), 29−31 (very broad), 116.2 (d, $^1J_{CH}$ = 154.4 Hz), 134.6 (s).

Allyldibromoboranes 5a,c−d. Into a two-necked flask (or an NMR tube) were introduced BBr_3 (1.3 mmol) and a solvent (CD_2Cl_2, $CDCl_3$, C_7D_8, $C_2D_2Cl_4$, 0.8 mL). The solution was cooled to −50 °C and the tetraallylic stannane **4a,c,d** (0.25 mmol) was added slowly with stirring. At the end of the addition, the solution was stirred for 3 min at −50 °C. To remove respectively $SnBr_4$ or (*Z*)- + (*E*)-crotyltribromostannanes from the reaction mixture, borane **5a,c,c′** and the solvent (toluene or 1,1,2,2-tetrachloroethane) were distilled *in vacuo* (10^{-1} mbar). However, this separation led to an important loss of borane, and the presence of decomposition products in the tin-free solution cannot be avoided. Attempts to distill the borane **5d** were unsuccessful.

2-Propenyldibromoborane (5a). Yield ≈ 50%. $\tau_{1/2}$ (5% in $CDCl_3$) = 3 min. ^{1}H NMR ($CDCl_3$, −50 °C): δ 2.55 (br d, 2H, $^3J_{HH}$ = 6.8 Hz), 5.10 (d, 1H, $^3J_{HHtrans}$ = 16.8 Hz), 5.14 (d, 1H, $^3J_{HHcis}$ = 11.0 Hz), 5.94 (ddt, 1H, $^3J_{HHtrans}$ = 16.8 Hz, $^3J_{HHcis}$ = 9.7 Hz, $^3J_{HH}$ = 6.8 Hz). ^{11}B NMR ($CDCl_3$, −50 °C): δ 62.6. ^{13}C NMR ($CDCl_3$, −50 °C): δ 48.1 (br t, $^1J_{CH}$ = 126.8 Hz), 117.5 (t, $^1J_{CH}$ = 154.9 Hz), 132.7 (d, $^1J_{CH}$ = 157.1 Hz).

(*Z*)- and (*E*)-2-Butenyldibromoboranes (5c,c′). Yield ≈ 60%; *E*:*Z* 4:1. $\tau_{1/2}$ (5% in $CDCl_3$) = 7 min. ***E***. ^{1}H NMR ($CDCl_3$, −40 °C): δ 1.69 (d, 3H, $^1J_{HH}$ = 4.8 Hz), 2.47 (br d, 2H, $^3J_{HH}$ = 5.5 Hz), 5.48−5.53 (m, 2H). ^{11}B NMR ($CDCl_3$, −50 °C): δ 62.5. ^{13}C NMR ($CDCl_3$, −40 °C): δ 40.8 (br t, $^1J_{CH}$ = 123.1 Hz), 19.1 (q, $^1J_{CH}$ = 126.1 Hz), 124.4 (d, $^1J_{CH}$ = 156.7 Hz), 128.3 (d, $^1J_{CH}$ = 151.8 Hz). ***Z***. ^{1}H NMR ($CDCl_3$, −40 °C): δ 1.71 (d, 3H, $^1J_{HH}$ = 6.1 Hz), 2.52 (br d, 2H, $^3J_{HH}$ = 7.4 Hz), 5.48−5.53 (m, 2H). ^{11}B NMR ($CDCl_3$, −50 °C): δ 62.5. ^{13}C NMR ($CDCl_3$, −40 °C): δ 13.1 (q, $^1J_{CH}$ = 127.0 Hz), 46.3 (br t, $^1J_{CH}$ = 120.6 Hz), 123.3 (d, $^1J_{CH}$ = 159.5 Hz), 126.8 (d, $^1J_{CH}$ = 155.4 Hz).

(3-Methyl-2-butenyl)dibromoborane (5d). Yield ≈ 50%. $\tau_{1/2}$ (5% in $CDCl_3$) = 3 min. ^{1}H NMR ($CDCl_3$, −50 °C): δ 1.73 (s, 3H), 1.61 (s, 3H), 2.49 (br d, 2H, $^3J_{HH}$ = 7.5 Hz), 5.21 (tsept, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz). ^{11}B NMR ($CDCl_3$, −50 °C): δ 61.6. ^{13}C NMR ($CDCl_3$, −50 °C): δ 18.7 (q, $^1J_{CH}$ = 125.4 Hz), 26.5 (q, $^1J_{CH}$ = 127.9 Hz), 37.6 (br t, $^1J_{CH}$ = 126.8 Hz), 116.4 (d, $^1J_{CH}$ = 156.6 Hz), 135.3 (s).

Allyldihaloborane Etherates 7a−c. General Procedure. The reactions of 2-propenyldihaloboranes **2a**, **3a**, or **5a** with diethyl ether were performed in a 25 mL two-necked flask under nitrogen. Addition with stirring of an approximately stoichiometric amount of diethyl ether to a cooled (−40 °C) solution of allyldifluoroborane (**2a**), allyldichloroborane (**3a**), or allyldibromoborane (**5a**) (1 mmol) in $CDCl_3$ (900 μL) led to a solution containing, respectively, the allyldifluoroborane diethyl etherate (**7a**), allyldichloroborane diethyl etherare (**7b**), or allyldibromoborane diethyl etherate (**7c**). This solution then was quickly transferred with a flexible needle into a cooled (−50 °C) NMR tube.

Allyldifluoroborane Diethyl Etherate (7a). Yield: 83%. $\tau_{1/2}$ (5% in $CDCl_3$ at RT) ≈ 20 h. ^{1}H NMR ($CDCl_3$, RT): δ 1.28 (t, 6H, $^3J_{HH}$ = 7.0 Hz), 1.70 (br d, 2H, $^3J_{HH}$ = 7.6 Hz), 3.77 (br q, 4H, $^3J_{HH}$ = 7.0 Hz), 4.94 (d, 1H, $^3J_{HHtrans}$ = 19.6 Hz), 4.96 (d, 1H, $^3J_{HHcis}$ = 10.2 Hz), 5.84 (ddt, 1H, $^3J_{HHtrans}$ = 19.6 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 7.6 Hz). ^{11}B NMR ($CDCl_3$, −45 °C): δ 15.6 (t, $^1J_{BF}$ ≈ 70 Hz). ^{19}F NMR ($CDCl_3$, RT): δ −89.0 (br q). ^{13}C NMR ($CDCl_3$, RT): δ 15.2 (q, $^1J_{CH}$ = 126.5 Hz), 21 (br), 68.0 (br t, $^1J_{CH}$ = 145.1 Hz), 114.6 (t, $^1J_{CH}$ = 151.5 Hz), 134.2 (d, $^1J_{CH}$ = 151.5 Hz).

Allyldichloroborane Diethyl Etherate (7b). Yield: 75%. $\tau_{1/2}$ (5% in $CDCl_3$ at RT) ≈ 5 h. ^{1}H NMR ($CDCl_3$, −40 °C): δ 1.46 (t, 6H, $^3J_{HH}$ = 7.1 Hz), 1.82 (br d, 2H, $^3J_{HH}$ = 7.1 Hz), 4.38 (br s, 4H, $^3J_{HH}$ = 7.1 Hz), 4.92 (d, 1H, $^3J_{HHtrans}$ = 19.3 Hz), 4.94 (d, 1H, $^3J_{HHcis}$ = 10.1 Hz), 5.91 (ddt, 1H, $^3J_{HHtrans}$ = 19.3 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 7.1 Hz). ^{11}B NMR ($CDCl_3$, −40 °C): δ 15.0. ^{13}C NMR ($CDCl_3$, −40 °C): δ 14.7 (q, $^1J_{CH}$ = 125.7 Hz), 33−34 (br), 74.6 (br t, $^1J_{CH}$ = 144.1 Hz), 114.3 (t, $^1J_{CH}$ = 153.5 Hz), 136.8 (d, $^1J_{CH}$ = 152.8 Hz).

Allyldibromoborane Diethyl Etherate (7c). Yield: 63%. $\tau_{1/2}$ (5% in $CDCl_3$ at RT) ≈ 10 min. ^{1}H NMR ($CDCl_3$, −50 °C): δ 1.52 (t, 6H, $^3J_{HH}$ = 6.9 Hz), 2.04 (br d, 2H, $^3J_{HH}$ = 7.1 Hz), 4.58 (br q, 4H, $^3J_{HH}$ = 6.9 Hz), 4.97 (d, 1H, $^3J_{HHcis}$ = 10.0 Hz), 5.00 (d, 1H, $^3J_{HHtrans}$ = 17.2 Hz), 5.97 (ddt, 1H, $^3J_{HHtrans}$ = 17.2 Hz, $^3J_{HHcis}$ = 10.0 Hz, $^3J_{HH}$ = 7.1 Hz). ^{11}B NMR ($CDCl_3$, −50 °C): δ 0.0. ^{13}C NMR ($CDCl_3$, −50 °C): δ 13.9 (q, $^1J_{CH}$ = 125.2 Hz), 35.1 (br t, $^1J_{CH}$ = 118.8 Hz), 68.0 (br t, $^1J_{CH}$ = 141.3 Hz), 115.3 (t, $^1J_{CH}$ = 155.5 Hz), 137.7 (d, $^1J_{CH}$ = 154.1 Hz).

Reaction of Allyldihaloboranes with Benzaldehyde. The reactions of benzaldehyde with 2-propenyldihaloboranes **2a**, **3a**, **5a**, or **7a−c** were performed under nitrogen by addition of benzaldehyde (1 mmol) to a cooled solution (−40 °C) of an allyldihaloborane (1 mmol) in CH_2Cl_2 (10 mL). After 10 min of stirring, the mixture was allowed to warm to room temperature and hydrolyzed with a saturated solution of $NaHCO_3$. The organic phase was dried on $MgSO_4$ and the volatile part was removed in vacuo. The resulting residue was chromatographed on a silica gel column to give 1-phenyl-3-butenol (**6a**). From benzaldehyde and **2a**, **3a**, and **5a**, 1-phenyl-3-butenol (**6a**) was obtained in a 0, 57, and 53% yield, respectively. The yields were 0, 67, and 38% in reactions of benzaldehyde with the corresponding borane etherates **7a**, **7b**, or **7c**.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of the allylic difluoro- (**2a−d**, **7a**) and dichloroboranes (**3a−d**, **7b**) (20 pages). Ordering information is given on any current masthead page.

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