# Organoboranes. 55. Improved Procedure for the Conversion of Representative Achiral and Chiral Alkyl-, (*E*)-1-Alkenyl, (*Z*)-1-Alkenyl-, and Arylboronates into the Corresponding Organyldichloroboranes

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Diethyl alkylboronates, $R^*B(OEt)_2$, of essentially 100% enantiomeric purity, prepared by asymmetric hydroboration of readily available prochiral alkenes, were effectively converted into the corresponding chiral alkyldichloroboranes, $R^*BCl_2$, by treatment with boron trichloride (1 M solution in dichloromethane) in the presence of a catalytic amount of anhydrous ferric chloride (3 mol %). This reaction is quite general, proceeds well without detectable racemization, and is applicable to essentially optically pure boronic esters of widely varied structural requirements. The reaction is also applicable to achiral boronates, such as 1-hexyl, and hindered alkyl, such as *tert*-butyl. It is also applicable to the conversion of (*E*)- and (*Z*)-1-hexenylboronates, representative of the 1-alkenyl derivatives, and to phenylboronates, representative of aryl derivatives. Consequently, this procedure appears to be broadly applicable to the conversion of organylboronates, $RB(OR')_2$, into the corresponding organyldichloroboranes, $RBCl_2$.

## Introduction

Organoboranes have proven to be highly valuable intermediates for organic syntheses, due to their high reactivity, ease of preparation, and exceptional synthetic utility.[2] Among these organoboranes, the organyldichloroboranes, $RBCl_2$, are especially valuable because of easy accessibility, exceptionally high reactivity, and the especially economical utilization of the organic group introduced.[3] The utility of organyldichloroboranes is well-documented in the literature.[3,4] The chiral organyldichloroboranes $R^*BCl_2$, derived from chiral alkylboronic esters, are assuming a major importance in our efforts to develop a general synthesis of enantiomerically pure compounds.[5] Recently, chiral alkyldichloroboranes have been used as a catalyst in asymmetric Diels–Alder reactions.[6] Chiral alkylboronic esters are exceptionally promising intermediates for carbon–carbon bond-forming reactions.[7] These reactions are especially valuable for chiral syntheses proceeding through organoborane intermediates. However, it is often highly desirable to convert the comparatively unreactive boron–oxygen bonds in these intermediates to the highly reactive boron–hydrogen or boron–chlorine bonds.[5] The successful achievement of this objective would greatly extend both the range of the versatility and the diversity of chiral organoborane chemistry. We have already achieved the quantitative conversion of the boron–oxygen bonds in chiral boronic esters to boron–hydrogen bonds in chiral alkylborohydrides.[8]

Several methods have been reported in the literature for the preparation of various organyldichloroboranes.[9-15] Many of them involve the preparation of arylhaloboranes. In general, these compounds have been prepared by the interaction of either gaseous boron trichloride or boron trifluoride with alumina[9] in the form of its slurry with aromatic hydrocarbons or with organometallic compounds, such as boronic esters,[10a] boronic anhydrides[10b] triarylboroxines,[10c] diarylmercury,[11] tetraaryltin,[12] and vinyltin.[12d] The high-temperature reaction of boron trichloride with benzene catalyzed by palladium[13] is known to give phenyldichloroborane. Grignard reagents,[14] zinc aryls,[15] and phosphorus pentachloride[15b-d] have been utilized for the preparation of aryldichloroboranes. Among these methods, some involve the use of either gaseous boron trichloride or boron trifluoride condensed at −78 °C, and some involve the use of gaseous boron trifluoride in boiling carbon tetrachloride,[12a] dichloromethane,[12a] or benzene.[12b]

Several methods are available in the literature for proceeding from boronic esters.[5,10a,15b-d] The first method reported in 1956 by Lappert et al.[10a] involves the interaction of neat boronic esters, $RB(OR')_2$, with gaseous boron trichloride at −78 °C in the presence of a catalytic amount of ferric chloride to give the corresponding organyldichloroboranes, $RBCl_2$, in good yields (eqs 1 and 2). In this

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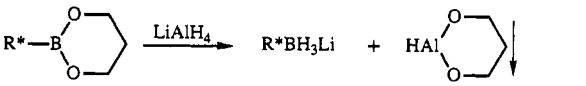
$$RB(OR')_2 + 2BCl_3 \longrightarrow RBCl_2 + 2BCl_2OR' \quad (1)$$

$$3BCl_2OR' \xrightarrow{FeCl_3} 3R'Cl + BCl_3 + B_2O_3 \quad (2)$$

reference only two examples were studied under neat conditions. The second method recently reported from our group[5] involves treatment of boronic esters with LAH to give alkylborohydrides (eq 3).[8] These, upon treatment with 3 equiv of HCl in dimethyl sulfide, yield the organyldichloroborane–dimethyl sulfide complexes in excellent yields (eq 4). This two-step procedure involves the separation of dialkoxyalane, which in some instances does not precipitate cleanly, especially in the case of acyclic boronic esters.



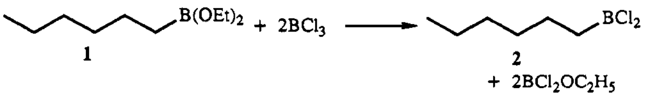
(3)

$$R^*BH_3Li \xrightarrow{3HCl\ in\ SMe_2} R^*BCl_2 \cdot SMe_2 + LiCl + 3H_2\uparrow \quad (4)$$

Therefore, as a part of our ongoing program in this area and the nonavailability of a convenient general procedure, we undertook to develop such a general procedure, applicable to the preparation of a wide variety of organyldichloroboranes from the corresponding boronic esters. Here we report an improved procedure for the conversion of chiral alkylboronic esters to highly reactive chiral alkyldichloroboranes in very high enantiomeric purities. This procedure has advantages over currently available procedures. Its applicability has also been demonstrated for the preparation of (*E*)- and (*Z*)-1-alkenyldichloroborane, and phenyldichloroborane as a representative aryl derivative, from the respective boronic esters. This procedure is also effective for the conversion of the sterically hindered *tert*-butylboronic ester to the corresponding *tert*-butyldichloroborane. The reaction appears to be general and provides a simple economical approach for the synthesis of various types of organyldichloroboranes in satisfactory yields.

## Results and Discussion

The earlier procedure[10a] for the preparation of organyldichloroboranes involves the interaction of neat boronic esters with 2 equiv of gaseous boron trichloride in the presence of a catalytic amount of ferric chloride at low temperature (−78 °C). Under these conditions, only $PhB(OBu^n)_2$ and $n$-$BuB(OBu^n)_2$ have been converted to the corresponding $PhBCl_2$ and $n$-$BuBCl_2$, respectively. In order to simplify this promising reaction to obtain clean organyldichloroboranes, we first examined the reaction of diethyl *n*-hexylboronate[16] (1) with commercially available boron trichloride in the presence of a catalytic amount of ferric chloride at 0 °C, monitoring the reaction progress by $^{11}B$ NMR. The $^{11}B$ NMR study of the reaction mixture, after it was stirred at 0 and 25 °C for 1 h each, showed the complete disappearance of the boronic ester peak at $\delta$ 30 and the appearance of the *n*-hexyldichloroborane[17] peak at $\delta$ 63, along with peaks at $\delta$ 46 and 26, indicative of $BCl_3$ and $B_2O_3$, respectively (eq 5; for decomposition[18] of $B$-



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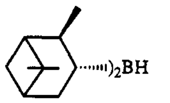
(5)

$Cl_2OC_2H_5$, see eq 2). The decomposition of dichloroborinate, $Cl_2BOR'$, to $R'Cl$, $BCl_3$, and $B_2O_3$ under the influence of catalytic quantities of ferric chloride is known.[18] After removal of volatile matter under reduced pressure (20 mmHg), the resulting residue was extracted with dichloromethane. Removal of solvent under reduced pressure yields *n*-hexyldichloroborane[17] in 80% yield. It was purified by distillation under reduced pressure, bp 100 °C/100 mmHg (lit.[17] bp 102–104 °C/100 mmHg). This yield is comparable to that realized by the earlier procedure.[10a] After establishing the most suitable reaction conditions, we examined various cyclic and acyclic ester derivatives of boronic acids, such as dimethyl, diethyl, and ethylene glycol, in order to find out the most suitable ester derivative under these reaction conditions. Among these, dimethyl and diethyl derivatives of the boronic acid gave comparable favorable results, whereas in the case of the cyclic ester derivatives the separation of product becomes difficult. Hence, for our study, we adopted the diethyl ester derivatives of boronic acids readily prepared from the corresponding boronic acids and absolute alcohol.[16]

Having established both suitable reaction conditions and a favorable ester derivative, we turned our attention toward extending the applicability of this improved procedure to the conversion of chiral alkylboronic esters to the corresponding chiral alkyldichloroboranes. Similarly, we applied this procedure to the conversion of (*E*)- and (*Z*)-1-alkenylboronic esters to the (*E*)- and (*Z*)-1-alkenyldichloroboranes, respectively, and also to the conversion of phenylboronic ester (as a representative aryl derivative) to phenyldichloroborane. Conversion of *tert*-butylboronic ester (as a representative hindered derivative) to *tert*-butyldichloroborane was also examined.

**Preparation of Chiral Alkyl-, (*E*)-1-Alkenyl-, (*Z*)-1-Alkenyl-, Phenyl-, and *tert*-Butylboronic Esters.** The optically active organoborane intermediates, chiral alkylboronic esters $R^*B(OEt)_2$, required for this study were prepared by asymmetric hydroboration of an appropriate prochiral olefin with either (+)-diisopinocampheylborane, $^dIpc_2BH$ (3) (≥99% ee),[19] or (+)-isopinocampheylborane, $^dIpcBH_2$ (4) (≥99% ee),[20] both easily



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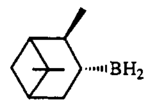

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prepared from (+)-$\alpha$-pinene. Thus, asymmetric hydroboration of *cis*-2-butene with $^dIPc_2BH$ (3) gave trialkylborane,[21] which upon treatment with 1.8 equiv of benzaldehyde resulted in selective facile elimination of the chiral auxiliary, providing the corresponding boronic ester. This on extraction with 3 N NaOH followed by acidification with 3 N HCl provided (*R*)-2-butylboronic acid in very high enantiomeric purity.[21d] The chiral diethyl (*R*)-2-butylboronate (5) was then prepared by esterification of (*R*)-2-butylboronic acid with absolute alcohol.[16] Similarly, the asymmetric hydroboration of prochiral olefins with $^dIpcBH_2$ (4), followed by crystallization of the intermediates, gave optically pure isopinocampheylalkylborane (≥99% ee).[20,21] This on treatment with acetaldehyde under mild conditions yielded the corresponding boronic esters in very high enantiomeric purity after the elimination of

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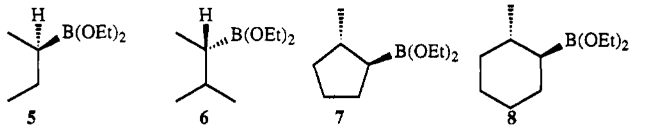
chiral auxiliary. Optically active diethyl boronates (6–8) were then prepared by esterification of the corresponding boronic acids with absolute alcohol.[16] By employment of this procedure (*S*)-diethyl (3-methyl-2-butyl)boronate (6), (1*S*,2*S*)-diethyl *trans*-(2-methylcyclopentyl)boronate (7), and (1*S*,2*S*)-diethyl *trans*-(2-methylcyclohexyl)boronate (8) have been obtained in high enantiomeric purities.[22]



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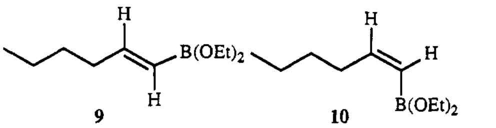

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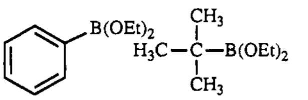


11 12

Diethyl (*E*)-1-hexenylboronate (9) was prepared as previously described, in high chemical yield and high stereochemical purity, by the hydroboration of 1-hexyne with $BHBr_2{\cdot}SMe_2$[23] followed by treatment with absolute alcohol.

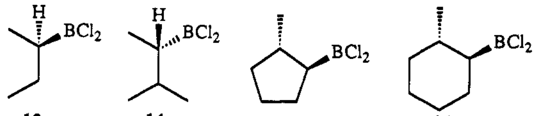
Diethyl (*Z*)-1-hexenylboronate (10) was prepared in high stereochemical purity according to the reported procedure.[24] The hydroboration of 1-bromo-1-hexyne with $BHBr_2{\cdot}SMe_2$, followed by treatment with 2-propanol, gave diisopropyl (*Z*)-(1-bromo-1-hexenyl)boronate, which upon treatment with potassium triisopropoxylborohydride (KIPBH), afforded diisopropyl (*Z*)-1-hexenylboronate. This compound was then converted into diethyl (*Z*)-1-hexenylboronate (10) by trans esterification with ethanol. Diethyl phenylboronate (11) was prepared by esterification of readily available phenylboronic acid with absolute alcohol.[16] Similarly, diethyl *tert*-butylboronate (12) was prepared according to the known procedure.[25]

**Preparation of Chiral Alkyldichloroboranes, (*E*)- and (*Z*)-1-Alkenyldichloroboranes, and Phenyldichloroborane.** After studying the conversion of *n*-hexylboronic ester 1 to *n*-hexyldichloroborane (2) (eq 5), and having all requisite boronic esters 5–12 in hand, we examined their conversion to the respective dichloroboranes 13–20 as follows. The reaction of chiral alkylboronic esters 5–8 with 2 equiv of a 1 M solution of boron trichloride in dichloromethane (available from Aldrich Chemical Co.), in the presence of a catalytic amount of anhydrous ferric chloride (3 mol %) at 0 and 25 °C for 1 h each, showed the formation of the corresponding chiral alkyldichloroboranes, $R^*BCl_2$, based on the observation made by $^{11}B$ NMR study. The $^{11}B$ NMR spectrum of the reaction mixture showed the disappearance of the boronic ester peak at $\delta$ 30 and the appearance of peaks at $\delta$ 46 and 26, indicative of $BCl_3$ and $B_2O_3$, respectively (eq 6; for

$$\underset{5\text{-}8}{R^*B(OEt)_2} + 2BCl_3 \longrightarrow \underset{13\text{-}16}{R^*BCl_2} + 2BCl_2OC_2H_5 \quad (6)$$

decomposition[18] of $BCl_2OC_2H_5$, see eq 2). The volatile matter was removed under reduced pressure, and the resulting residue was extracted with fresh dichloromethane. Removal of the solvent gave the desired alkyldichloroborane, which was purified by distillation under vacuum.

By using this procedure, the efficient conversions of (*R*)-diethyl 2-butylboronate (5) to (*R*)-2-butyldichloroborane (13), (*S*)-diethyl (3-methyl-2-butyl)boronate (6) to (*S*)-(3-methyl-2-butyl)dichloroborane (14), (1*S*,2*S*)-diethyl *trans*-(2-methylcyclopentyl)boronate (7) to (1*S*,2*S*)-*trans*-(2-methylcyclopentyl)dichloroborane (15), and (1*S*,2*S*)-diethyl *trans*-(2-methylcyclohexyl)boronate (8) to (1*S*,2*S*)-*trans*-(2-methylcyclohexyl)dichloroborane (16) have been successfully achieved. The isolated yields re-



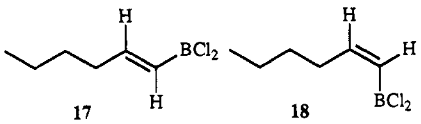
13 14 15 16

alized are in the range of 60–65% (Table I). Under these experimental conditions the conversion of chiral alkylboronic esters to the corresponding chiral alkyldichloroboranes occurred with the complete maintenance of stereochemical integrity. All chiral alkyldichloroboranes 13–16 were obtained in very high enantiomeric purity.[22]

Further, in order to explore the utility of this procedure, diethyl (*E*)-1-hexenylboronate (9) and diethyl (*Z*)-1-hexenylboronate (10) were subjected to these improved reaction conditions and the reaction results examined. Thus, (*E*)-1-hexenylboronic ester 9 was regioselectively converted to (*E*)-1-hexenyldichloroborane (17) in 75% isolated yield, bp 104 °C (100 mmHg) (lit.[26] bp 66–68 °C/18 mmHg) (eq 7; for decomposition[18] of $BCl_2OC_2H_5$ see eq 2).

$$\underset{9\text{-}12}{RB(OEt)_2} + 2BCl_3 \longrightarrow \underset{17\text{-}20}{RBCl_2} + 2BCl_2OC_2H_5 \quad (7)$$

Since the literature survey reveals that there is no method for the preparation of (*Z*)-1-alkenyldichloroboranes, we decided to test our improved procedure for this application. Thus, diethyl (*Z*)-1-hexenylboronate (10) was effectively and successfully converted to (*Z*)-1-hexenyldichloroborane (18) in 72% isolated yield, bp 100 °C (103 mmHg) (eq 7). The stereochemical purities of 17 and 18 were checked by high-resolution $^1H$ NMR. To the best of our knowledge, this is the first, simple and efficient procedure for the preparation of (*Z*)-alkenyldichloroboranes.



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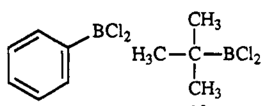

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Further, this procedure works equally well for the conversion of phenylboronic ester 11 to phenyldichloroborane (19) in 67% isolated yield, bp 66 °C/11 mmHg (lit.[10b] bp 66–66.5 °C/11 mmHg) (eq 5). Additionally, the successful exploitation of this procedure was shown for the conversion of the bulky *tert*-butyl boronic ester 12 to *tert*-butyldichloroborane (20) in 65% isolated yield, bp 86 °C/744 mmHg, (lit.[27] bp 88 °C/744 mmHg) (Table II).

We decided to examine the applicability of this reaction for the conversion of boronic acids into the desired boron dichlorides. However, when phenylboronic acid, PhB-

(22) The enantiomeric purities of chiral $R^*B(OEt)_2$ and $R^*BCl_2$ have been determined by capillary GC analysis of MTPA and MCF derivatives of alcohols derived by alkaline peroxide oxidation.
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**Table I. Conversion of Representative Chiral Alkylboronates into the Chiral Alkyldichloroboranes[a]**

| R* in R*BCl$_2$[b] | yield, %[c] | bp, °C (mmHg) | $^{11}$B NMR δ, ppm | config | % ee[f] |
|---|---|---|---|---|---|
| (*R*)-2-butyl (**13**) | 65 | 54 (32) | 64 | 2*R*[d] | ≥99 |
| (*S*)-3-methyl-2-butyl (**14**) | 60 | 44 (20) | 64 | 2*S*[e] | ≥99 |
| (1*S*,2*S*)-*trans*-2-methylcyclopentyl (**15**) | 64 | 95 (100) | 64 | 1*S*,2*S*[e] | ≥99 |
| (1*S*,2*S*)-*trans*-2-methylcyclohexyl (**16**) | 65 | 90 (20) | 63 | 1*S*,2*S*[e] | ≥99 |

[a] All reactions were carried out on a 20-mmol scale. [b] The purity of R*BCl$_2$ was checked by ethanolysis and analyzing the resulting boronic esters by $^1$H NMR.[20b] [c] The isolated yields of the distilled products. [d] Reference 21d. [e] Reference 20b. [f] Enantiomeric and stereochemical purities were determined by capillary GC analysis of MTPA derivatives of alcohols derived by alkaline peroxide oxidation.

**Table II. Conversion of Representative Alkyl-, (*E*)-1-Alkenyl, (*Z*)-1-Alkenyl-, and Arylboronates into the Corresponding Organyldichloroboranes[a]**

| R in RBCl$_2$[b] | yield, %[c] | bp, °C (mmHg) | $^{11}$B NMR[d] δ, ppm |
|---|---|---|---|
| *n*-hexyl (**2**) | 83 | 100 (100) | 63 |
| *tert*-butyl (**20**) | 65 | 86 (744) | 64 |
| (*E*)-1-hexenyl (**17**) | 75 | 104 (100) | 52 |
| (*Z*)-1-hexenyl (**18**) | 72 | 100 (103) | 52 |
| phenyl (**19**) | 67 | 66 (11) | 55 |

[a] All reactions were carried out on a 20-mmol scale. [b] The purity of RBCl$_2$ was checked by ethanolysis and analyzing the resulting boronic esters by $^1$H NMR. [c] The isolation yields of the distilled products. [d] $^{11}$B NMR spectra were recorded in CDCl$_3$.

(OH)$_2$, was allowed to react with boron trichloride under such reaction conditions, only 16% of the desired product, PhBCl$_2$, was formed, with the recovery of 84‰ of the starting boronic acid. This result reveals that this procedure is not suitable for the conversion of boronic acids to dichloroboranes, even though the procedure works very well for converting boronic esters to the corresponding dichloroboranes. The structures of these dichloroboranes **13–20** were confirmed on the basis of $^{11}$B NMR, $^1$H NMR, $^{13}$C NMR, and literature data. The chemical purity of these dichloroboranes **13–20** was checked by ethanolysis and analysis of the resulting boronic esters by $^1$H NMR.[20b]

## Conclusions

The procedure developed in this study provides a simple, convenient, and efficient approach for the preparation of chiral alkyldichloroboranes, R*BCl$_2$, from the respective chiral alkylboronic esters, R*B(OEt)$_2$, in very high enantiomeric purity. Previously there has been no procedure available for the preparation of (*Z*)-alkenyldichloroboranes. Now their preparation is readily achievable by this procedure. Similarly, this procedure makes possible the ready preparation of aryldichloroboranes from the corresponding boronic esters. From the above results and discussion, it is clear that this procedure works well for the conversion of essentially all types of boronic esters to give the corresponding organyldichloroboranes. In view of the growing utility of RBCl$_2$ compounds in organic synthesis, the present study should encourage further research in this area, using the RBX$_2$ compounds as a synthon.

## Experimental Section

All glassware used for the experiments were dried in an oven at 140 °C for several hours, assembled hot, and cooled under a stream of nitrogen. All operations were carried out under an inert atmosphere (N$_2$). $^{11}$B NMR, $^1$H NMR, and $^{13}$C NMR spectra were recorded on a Varian Gemini-300 spectrometer. The $^{11}$B NMR chemical shifts are with reference to BF$_3$·OEt$_2$ (δ 0), and the resonance values upfield from the standard are assigned negative signs. For $^1$H NMR and $^{13}$C NMR the chemical shifts are in δ values relative to that of TMS. Capillary GC analyses were carried out with a Hewlett-Packard 5890 chromatograph fitted with 15-m Supelcowax/30-m SPB-5 columns.

**Materials.** Anhydrous ethyl ether (EE) was purchased from Mallinkrodt Inc. and was used directly. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. BCl$_3$ (1 M solution in CH$_2$Cl$_2$), *t*-BuLi (1 M solution in hexane), and triisopropyl borate were obtained from Aldrich Chemical Co. Anhydrous FeCl$_3$ purchased from Fisher Scientific Co. was used under N$_2$. Absolute ethanol obtained from Midwest Grain Products Co. was used without purification. The chiral alkylboronic esters **5–8** used in this study were prepared in high enantiomeric purity according to the reported procedures.[19–21] Diethyl (*E*)-1-hexenylboronate (**9**)[23] and diethyl (*Z*)-1-hexenylboronate (**10**)[24] were prepared according to the reported procedures. Phenylboronic acid from Aldrich Chemical Co. was used as such and also converted into diethyl phenylboronate (**11**).

**Preparation of Chiral Alkyl-, (*E*)-1-Hexenyl-, (*Z*)-1-Hexenyl-, Phenyl-, and *tert*-Butyldichloroboranes.** The following procedure for the preparation of *n*-hexyldichloroborane is representative. In a dry 100-mL reaction flask, equipped with a rubber septum and a magnetic stirring bar, was placed 100 mg (3 mol %) of anhydrous FeCl$_3$ and 40 mL (40 mmol) of a 1 M solution of BCl$_3$ in CH$_2$Cl$_2$ under static pressure of N$_2$. The reaction flask was cooled to 0 °C, and 3.72 g (20 mmol) of diethyl *n*-hexylboronate[16] was slowly added over 10 min. The reaction mixture was stirred at 0 and 25 °C for 1 h each. The progress of the reaction was monitored by $^{11}$B NMR. After 2 h the solvent was removed under reduced pressure (20 mmHg) and the resulting residue was extracted with CH$_2$Cl$_2$ (3 × 40 mL). The extracts were combined together by means of a double-ended needle, and the solvent was removed under reduced pressure. The residual liquid on distillation under reduced pressure yielded a colorless liquid, 2.65 g (16 mmol, 80%) of *n*-hexyldichloroborane (**2**): bp 100 °C/100 mmHg (lit.[17] bp 102–104 °C/102 mmHg); $^{11}$B NMR (CDCl$_3$) δ 63; $^1$H NMR (CDCl$_3$) δ 0.90 (t, 3 H), 1.20–1.45 (m, 8 H), 1.50–1.60 (m, 2 H).

**(2*R*)-2-Butyldichloroborane (13)**: yield 65%; bp 54 °C/32 mmHg (lit.[27] bp 99 °C/748 mmHg); $^{11}$B NMR (CDCl$_3$) δ 64; $^1$H NMR (CDCl$_3$) δ 0.95 (t, 3 H), 1.10 (d, 3 H), 1.20–1.35 (m, 1 H), 1.45–1.75 (2 m, 2 H).

**[(2*S*)-3-Methyl-2-butyl]dichloroborane (14)**: yield 60%; bp 44 °C/20 mmHg (lit.[26] bp 110–112 °C/746 mmHg); $^{11}$B NMR (CDCl$_3$) δ 64; $^1$H NMR (CDCl$_3$) δ 0.95 (2 d, 6 H), 1.05 (d, 3 H), 1.50 (m, 1 H), 1.95 (m, 1 H).

**[(1*S*,2*S*)-*trans*-2-Methylcyclopentyl]dichloroborane (15)**: yield 64%; bp 95 °C/110 mmHg (lit.[17] bp 94–96 °C/110 mmHg); $^{11}$B NMR (CDCl$_3$) δ 64; $^1$H NMR (CDCl$_3$) δ 1.10 (d, 3 H), 1.22 (m, 1 H), 1.50–2.00 (2 m, 6 H), 2.10 (m, 1 H); $^{13}$C NMR (CDCl$_3$) δ 20.8, 26.0, 30.6, 36.3, 39.6.

**[(1*S*,2*S*)-*trans*-2-Methylcyclohexyl]dichloroborane (16)**: yield 65%; bp 90 °C/20 mmHg; $^{11}$B NMR (CDCl$_3$) δ 63; $^1$H NMR (CDCl$_3$) δ 0.90 (d, 3 H), 0.95 (m, 1 H), 1.10–1.40 and 1.65–1.85 (2 m, 9 H), 1.60 (m, 1 H); $^{13}$C NMR (CDCl$_3$) δ 23.0, 26.2, 28.0, 34.3, 35.2, 41.6.

**(*E*)-1-Hexenyldichloroborane (17)**: yield 75%; bp 104 °C 100/mmHg (lit.[26] bp 66–68 °C/18 mmHg); $^{11}$B NMR (CDCl$_3$) δ 52; $^1$H NMR (CDCl$_3$) δ 0.90 (t, 3 H), 1.35 (m, 2 H), 1.45 (m, 2 H), 2.30 (m, 2 H), 6.10 (d, 1 H, *J* = 17 Hz), 7.20 (m, 1 H); $^{13}$C NMR (CDCl$_3$) δ 13.8, 22.3, 29.8, 35.4, 165.5.

**(*Z*)-1-Hexenyldichloroborane (18)**: yield 72%; bp 100 °C/103 mmHg; $^{11}$B NMR (CDCl$_3$) δ 52; $^1$H NMR (CDCl$_3$) δ 0.90 (t, 3 H), 1.25–1.55 (m, 4 H), 2.60 (m, 2 H), 6.00 (d, 1 H, *J* = 14 Hz), 6.77 (m, 1 H); $^{13}$C NMR (CDCl$_3$) δ 13.9, 22.4, 31.5, 33.5, 163.7.

**Phenyldichloroborane (19)**: yield 67%; bp 66 °C/11 mmHg (lit.[10b] bp 66–66.5 °C/11 mmHg): $^{11}$B NMR (CDCl$_3$) δ 55; $^1$H NMR (CDCl$_3$) δ 7.50 (dd, 2 H, *o*-H), 7.70 (dd, 1 H, *p*-H), 8.20 (d, 2 H, *m*-H); $^{13}$C NMR (CDCl$_3$) δ 128.1, 135.2, 137.0.

***tert*-Butyldichloroborane (20)**: yield 65%; bp 86 °C/744 mmHg (lit.[27] bp 88 °C/744 mmHg); $^{11}$B NMR (CDCl$_3$) δ 64; $^1$H NMR (CDCl$_3$) δ 1.10 (s, 9 H).

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