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### From activation to stabilization

*Different applications of a frustrated Lewis pair*

Boom, D.H.A.

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# Chapter 6

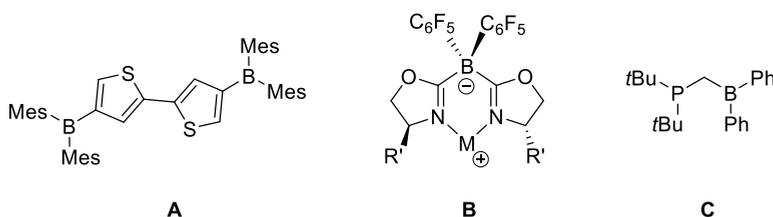
## Facile Synthesis of Diarylchloroboranes

**Abstract:** In this chapter, we describe a high yielding two-step synthesis for diphenylchloroborane, dimesitylchloroborane and bis(pentafluorophenyl)chloroborane starting from commercially available materials. Additionally, we introduce a new methodology for the synthesis of highly Lewis acidic diarylchloroboranes by applying a protection–deprotection strategy using (diethylamino)dichloroborane. Following this new strategy, four highly Lewis acidic chloroboranes were successfully synthesized, of which three were isolated spectroscopically pure and in high yield (85–99%).

**Manuscript:** In preparation

## 6.1 Introduction

Diarylchloroboranes are versatile, Lewis acidic boron building blocks that are incorporated in a large variety of compounds, which find their use as luminescent materials (**A**, Figure 1),<sup>[1]</sup> transition metal ligands (**B**),<sup>[2]</sup> and frustrated Lewis pairs (FLPs) (**C**).<sup>[3]</sup> Generally, installation of the Lewis acidic borane moiety proceeds via salt metathesis by reaction of a haloborane, often chloroborane, and, e.g., an organolithium or Grignard reagent. Alternatively, hydridoboranes, often synthesized from the corresponding chloroboranes, are applied in hydroboration reactions with, e.g., alkenes and alkynes.<sup>[4,11]</sup>

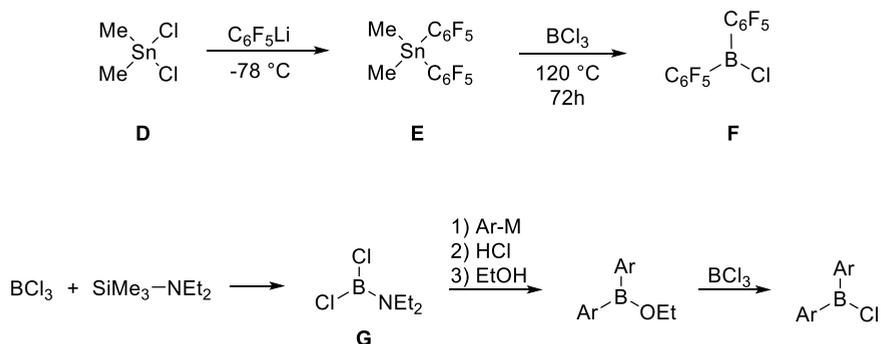


**Figure 1.** Examples of compounds containing a diarylborane moiety.

The synthesis of these widely used Lewis acidic chloroboranes is thus of key importance. (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BCl, for example, can be obtained directly from BX<sub>3</sub> and an organozinc,<sup>[5]</sup> Grignard,<sup>[6]</sup> organolithium,<sup>[7]</sup> or organocopper arylating agent.<sup>[8]</sup> Generally these strategies are, however, unselective and result in formation of complex product mixtures containing starting material, mono-, bis-, and tris-addition products that are very difficult to separate. Alternatively, Haly and co-workers investigated the use of the less reactive borates B(OR)<sub>3</sub> (R = Me, Et, *n*Pr, *i*Pr, *n*Bu, *s*Bu, *i*Bu, *t*Bu, Bz) as starting material for selective bis-substitution,<sup>[9]</sup> yet they also observed poor selectivity when using Grignard reagents; only for selected cases, such as the synthesis of Ph<sub>2</sub>BO*i*Pr and (*p*-CH<sub>3</sub>OPh)<sub>2</sub>BO*i*Pr, the reaction conditions could be optimized for full selectivity towards the bis-substituted product.

To overcome these selectivity issues, Chivers<sup>[10]</sup> and Piers<sup>[11]</sup> developed a synthetic route for (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BCl starting from dimethyltin dichloride (**D**; Scheme 1). They reported that **D** can be functionalized using C<sub>6</sub>F<sub>5</sub>Li to form organotin intermediate **E**, which, subsequently,

can be utilized for bis-substitution of  $\text{BCl}_3$  to afford  $(\text{C}_6\text{F}_5)_2\text{BCl}$  (**F**) in good selectivity and yield (68%) compared to the previously described methods. Although this method is a major step forward, it also presents drawbacks. The dimethyltin dichloride byproduct is difficult to remove, often requiring repeated sublimation or distillation of the product, and is highly toxic. Additionally, a few specific methods are reported for  $(\text{C}_6\text{F}_4\text{H})_2\text{BCl}$  and  $(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_2\text{BCl}$ ,<sup>[12,13]</sup> however, no general protocol for the synthesis of diarylchloroboranes is known to date.

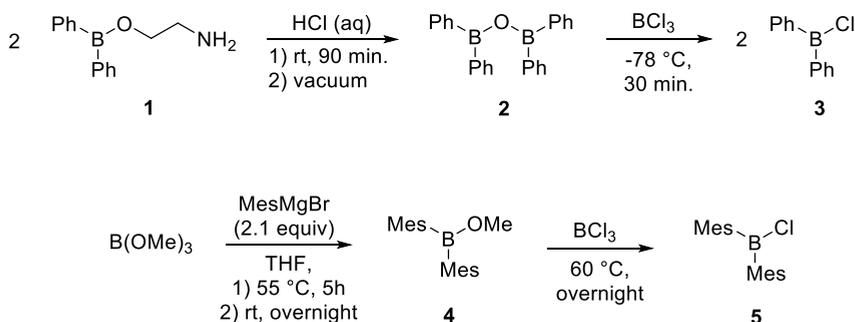


**Scheme 1.** Synthesis of  $(\text{C}_6\text{F}_5)_2\text{BCl}$  using organotin reagents (top), and a protection–deprotection strategy (bottom).

In our group, we optimized the synthesis of diphenylchloroborane using commercially available materials and just two reaction steps that were separately reported in the literature. This finding inspired us to design a selective and straightforward synthesis of a variety of commonly used highly Lewis acidic chloroboranes. Herein, we describe our protection–deprotection strategy using (diethylamino)dichloroborane **G** (Scheme 1) as starting material, which can be easily functionalized using the appropriate Grignard or organolithium reagent and converted into the corresponding chloroborane in a few simple, high yielding steps with easy workup protocols.

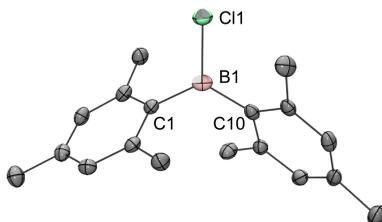
## 6.2 Results and Discussion

As an alternative to the organotin mediated synthesis of diphenylchloroborane (**3**),<sup>[14]</sup> we found a simple two-step procedure that starts with the commercially available borinic ester **1**.<sup>[15,16]</sup> Namely, treatment of **1** with HCl (aq) and subsequent dehydration cleanly afforded boronic anhydride **2** as a beige powder in 85% yield. Subsequent treatment of anhydride **2** with 1 equivalent of boron trichloride generated diphenylchloroborane **3** ( $\delta^{11}\text{B}\{\text{H}\} = 62.7$  ppm), which was isolated as a colorless solid in 94% yield (85% overall), simply after extraction of the crude product into *n*-pentane and removal of all volatiles *in vacuo*.



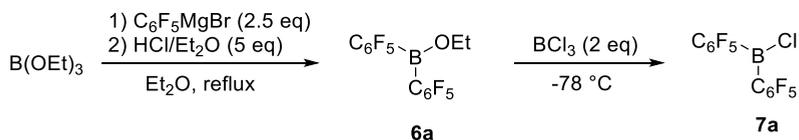
**Scheme 2.** Synthesis of diphenylchloroborane and dimesitylchloroborane.

Encouraged by the facile B–O to B–Cl transformation for diphenylchloroborane (**3**), we envisioned that the bulkier dimesitylchloroborane (**5**) should also be easily accessible from dimesitylborinic esters by treatment with  $\text{BCl}_3$  (Scheme 2, bottom). As the mesityl analogue of **2**,  $\text{Mes}_2\text{BOBMes}_2$ , is much more difficult to prepare<sup>[17]</sup> and bis-arylation of trimethylborate using  $\text{MesMgBr}$  offers a facile route to  $\text{Mes}_2\text{BOMe}$  (**4**; 82%), we decided to investigate this methyl ester for the synthesis of  $\text{Mes}_2\text{BCl}$  (**5**). Satisfyingly, conversion of **4** to  $\text{Mes}_2\text{BCl}$  (**5**) was achieved by heating a mixture of **4** and  $\text{BCl}_3$  at 60 °C overnight, which cleanly afforded **5** ( $\delta^{11}\text{B}\{\text{H}\} = 69.9$  ppm) after workup as a colorless solid in 92% yield (78% overall starting from  $\text{B(OMe)}_3$ ). Single-crystal X-ray diffraction analysis revealed a typical B–Cl single bond (1.783(3) Å) and a flat geometry around the boron atom ( $\Sigma(\text{CBC}) = 360.0$ ; Figure 2).



**Figure 2.** Molecular structures of **5** (ellipsoids at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: B1–Cl1 1.783(3), B1–C1 1.559(4), B1–C10 1.1567(4),  $\Sigma(\text{CBC})$  360.0.

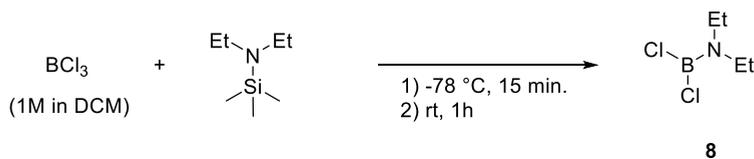
A similar methodology as for the synthesis of **5** can be applied for the preparation of bis(pentafluorophenyl)chloroborane **7a**. We found that changing the boron precursor to triethylborate results in the highest selectivity for bis-substitution, and the reaction between 2.5 equivalents of  $\text{C}_6\text{F}_5\text{MgBr}$  and  $\text{B}(\text{OEt})_3$  resulted in conversion to borinic ester **6a** and the corresponding mono-substituted boronic ester in a 85:15 ratio, respectively. Subsequently, borinic ester **6a** ( $\delta^{11}\text{B}\{\text{H}\} = 42.9$  ppm) was isolated in 56% yield as a colorless liquid after distillation under reduced pressure. Conversion of **6a** to  $(\text{C}_6\text{F}_5)_2\text{BCl}$  (**7a**, general procedure C) was achieved by the reaction of **6a** with 1.2 equivalents of  $\text{BCl}_3$  at 0 °C, which afforded **7a** ( $\delta^{11}\text{B}\{\text{H}\} = 58.6$  ppm) after workup as a colorless solid in 96% yield (54% overall yield,).



**Scheme 3.** Synthesis of bis(pentafluorophenyl)chloroborane **7a** from triethylborate.

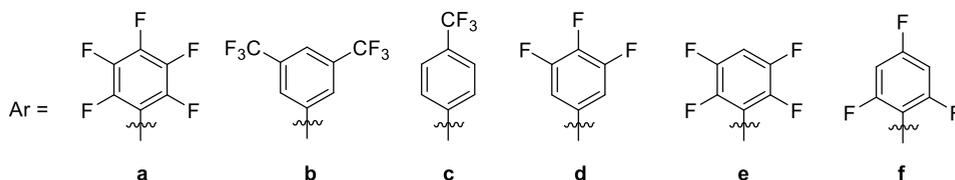
The synthetic strategy towards chloroborane **5** only works well with bulky, *ortho*-substituted substituents, while reduced steric bulk on the aryl group results in selectivity problems towards bis-addition,<sup>[9]</sup> which leads to difficult workup procedures and significantly reduced yields (as was also observed for **6a**). We envisioned that (diethylamino)dichloroborane **8** could serve as a mono-protected boron building block

promoting selective bis-arylation. **8** was easily prepared following a procedure from Abel and co-workers,<sup>[18]</sup> which we slightly modified. The reaction between diethyltrimethylsilylamine and boron trichloride (Scheme 4) was performed at  $-78\text{ }^{\circ}\text{C}$  and the reaction mixture was subsequently warmed to room temperature, after which  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy revealed full conversion to the product. Vacuum distillation of the crude product under nitrogen atmosphere afforded the mono-protected product **8** as a colorless liquid in 75% yield ( $\delta^{11}\text{B}\{^1\text{H}\} = 30.5\text{ ppm}$ ).



**Scheme 4.** Synthesis of (diethylamino)dichloroborane **8**.

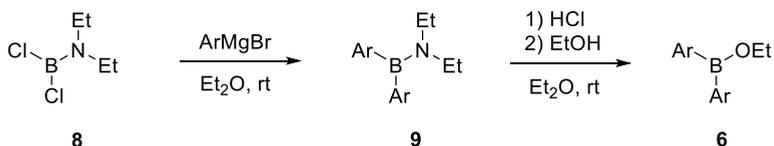
With **8** as mono-protected starting material in hand, we selected a series of commonly used fluorinated aryl groups (Figure 3), which could give access to a variety of borinic esters and subsequently highly Lewis acidic chloroboranes.



**Figure 3.** Selected aryl substituents.

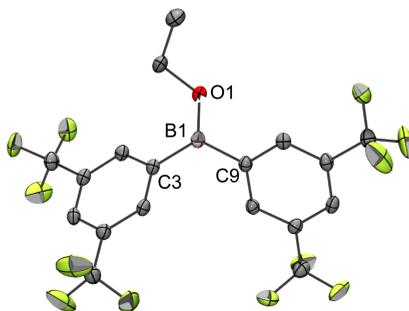
To functionalize the starting material, **8** was reacted with 2.5 equivalents of the corresponding Grignard reagent to yield diarylaminoborane **9** (Scheme 5) that, subsequently, was converted *in situ* to the desired borinic ester **6** by reaction with HCl/Et<sub>2</sub>O and ethanol. Following this strategy (general procedure A), aryl groups **b–d** were successfully introduced by using the corresponding Grignard reagent at room temperature;  $^{11}\text{B}\{^1\text{H}\}$  NMR

spectroscopy showed full conversion to aminoboranes **9b–d** ( $\delta^{11}\text{B}\{\text{H}\} = 40.4$  ppm (**9b**), 41.5 ppm (**9c**), 44.2 ppm (**9d**)). Unfortunately, the installation of sterically more demanding aryl groups bearing *ortho*-fluorine atoms (**a,e,f**) was unsuccessful via this method, for which an alternative procedure was developed (see page 164).



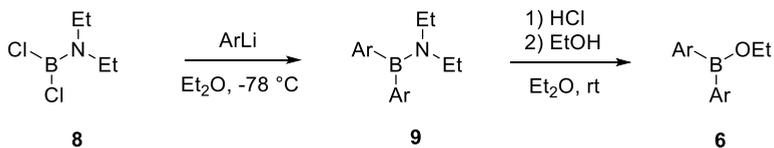
**Scheme 5.** Synthesis of borinic esters **6b–d**.

The conversion of **9b–d** into **6b–d** proceeds smoothly by the addition of 3 equivalents HCl/Et<sub>2</sub>O followed by 3 equivalents ethanol at room temperature and after extraction into *n*-pentane the borinic esters **6b–d** were obtained as analytically pure brown solids in good yield (80–85%) ( $\delta^{11}\text{B}\{\text{H}\} = 43.2$  ppm (**6b**), 44.5 ppm (**6c**), 41.2 ppm (**6d**)). When desired, the brown color could be removed by stirring a solution of **6** together with active charcoal in pentane overnight. Subsequent filtration and removal of the solvent *in vacuo* afforded **6b** as a pale beige solid and **6c–d** as colorless oils. Single-crystal X-ray diffraction analysis confirmed the formation of **6b** and the molecular structure shows a typical B–O bond length for a borinic ester (1.342(3) Å),<sup>[19]</sup> as well as an expected planar geometry around the boron center ( $\Sigma(\text{CBC}) = 360.0$ ; Figure 4).



**Figure 4.** Molecular structures of **6b** (ellipsoids at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: B1–O1 1.342(3), B1–C3 1.587(3), B1–C9 1.575(3),  $\Sigma(\text{CBC})$  360.0.

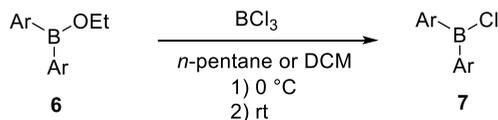
In order to solve the unproductive arylation for substituents **a,e,f** when using Grignard reagents, we switched to the more reactive aryllithium salts (Scheme 6), which were generated at  $-78\text{ }^{\circ}\text{C}$  and kept at low temperatures at all times to avoid exothermic decomposition.



**Scheme 6.** Synthetic approach towards borinic esters **6a,e-f**.

Slow addition of the aryllithium reagent to **8** in  $\text{Et}_2\text{O}$  at  $-78\text{ }^{\circ}\text{C}$  and subsequent warm-up to room temperature resulted in full conversion to aminoboranes **9a,e,f** according to  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy (general procedure **B**). Subsequent ethanolysis of **9a**, in analogy to **9b-d**, works well and **6a** was isolated after workup as a colorless solid in 79% yield ( $\delta^{11}\text{B}\{^1\text{H}\} = 42.9\text{ ppm}$ ). Interestingly, ethanolysis of **9e,f** was unsuccessful and no reaction with HCl or ethanol was observed at room temperature nor under refluxing conditions, which we ascribe to the reduced electron-withdrawing properties of the aryl substituents. Thus in these two cases, the aminoborane intermediates **9e,f** were isolated as white solids in 67 and 95% yield, respectively ( $\delta^{11}\text{B}\{^1\text{H}\} = 41.1\text{ ppm}$  (**9e**),  $39.2\text{ ppm}$  (**9f**)).

Next, we focused on the conversion of the obtained borinic esters **6a-d** to the desired diarylchloroboranes **6a-d** by the reaction with one equivalent of boron trichloride (general procedure **C**, Scheme 7). The elegance of this step is that the only byproduct formed is  $\text{Cl}_2\text{BOEt}$ , which can easily be removed *in vacuo*. Following this strategy, quantitative conversion to **7a-d** was observed by  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy after addition of  $\text{BCl}_3$ , and after workup diarylchloroboranes **7a-c** were obtained in high yield and purity (85–99%), and only product **7d** was not analytically pure yet. Thus far, we found that when crude product **7a** was washed with small portions of *n*-pentane at  $-78\text{ }^{\circ}\text{C}$ , drying of the remaining solid *in vacuo* afforded chloroborane **7a** in high yield (96%) and purity. Motivated by this success, we are currently developing a general purification method for **7a-d**.



**Scheme 7.** Synthesis of diarylchloroboranes **7a–d**.

## 6.3 Conclusion

In summary, we have developed an improved method for the synthesis of diphenylchloroborane **3**, dimesitylchloroborane **5** and bis(pentafluorophenyl)chloroborane **7a** using two-step procedure starting from commercially available materials. We also introduced a new methodology for the synthesis of highly Lewis acidic diarylchloroboranes following a protection–deprotection strategy using (diethylamino)dichloroborane **8** as common building block. **8** can be functionalized with aryl groups **a–f** using Grignard or organolithium reagents and we found that **9a–d** can be subsequently converted to the borinic esters **6a–d** via ethanolysis. The reaction of **6a–d** with  $\text{BCl}_3$  results in quantitative conversion into the corresponding chloroboranes **7a–d**. To date, chloroboranes **7a–c** were isolated in high yield (85–99%) and purity. Currently, we are finalizing this general procedure for the synthesis of highly Lewis acidic chloroboranes using **8** as mono-protected starting material, which enables a straightforward preparation of these important building blocks.

## 6.4 Experimental Details

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and drybox techniques, with exception for the synthesis of **2** that was performed in normal atmosphere until. After dehydration, **2** was stored under nitrogen atmosphere. Solvents were purified, dried, and degassed according to standard procedures.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance 500, Bruker Avance 400 or Bruker AV300-II spectrometer and internally referenced to the residual solvent resonances ( $\text{CDCl}_3$ :  $^1\text{H}$   $\delta$  7.26,  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  77.2).  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance 500, Bruker Avance 400 or Bruker AV300-II spectrometer and externally referenced

(BF<sub>3</sub>·OEt<sub>2</sub>). <sup>19</sup>F spectra were recorded on a Bruker AV300-II and externally referenced (CFCl<sub>3</sub>). Melting points were measured in sealed capillaries and are uncorrected. Diphenylboric acid 2-aminoethyl ester (**1**), BCl<sub>3</sub> (1 M) solutions (in heptane or DCM), *n*-butyllithium (1.6 M in hexanes), HCl/Et<sub>2</sub>O solutions (1 or 2 M), 2-mesitylmagnesium bromide (1 M in THF), B(OMe)<sub>3</sub>, diethyltrimethylsilylamine and the used arylbromides were purchased from commercial resources and used without further purification. EtOH was dried using 3Å molecular sieves prior to use.

#### **Preparation of Ph<sub>2</sub>BOBPh<sub>2</sub> (**2**):**<sup>[15]</sup>

A solution of aqueous hydrochloric acid (3.5 M, 67 mL, 235 mmol, 3.5 equiv) was added to diphenylboric acid 2-aminoethyl ester (**1**; 67.1 mmol, 15.1 g, 1.0 equiv) at room temperature. The formed suspension was stirred for 90 minutes after which the suspension turned into a sludge. The crude product was extracted into ethyl acetate (3 x 50 mL) and the combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and the solvent was removed *in vacuo*. The obtained yellow oil was put under vacuum and slowly heated to 50 °C, after which the oil turned into a beige solid. Subsequent heating under vacuum at 90 °C overnight afforded the product as a lightly beige solid (9.88 g, 85.1%). *Note that the resulting solid should be a very fine powder. Any remaining chunks should be grind into a fine powder in order to fully convert the borinic acid to the anhydride.*

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, 290 K): δ 7.89 (d, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz, 8H; *o*-PhH), 7.51 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 4H; *p*-PhH), 7.42 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 8H; *m*-PhH).

<sup>11</sup>B{<sup>1</sup>H} NMR (128.38 MHz, CDCl<sub>3</sub>, 290 K): δ 43.6 (br. s).

#### **Preparation of Ph<sub>2</sub>BCl (**3**):**<sup>[16]</sup>

A solution of BCl<sub>3</sub> (1 M in heptane, 11.6 mL, 11.6 mmol, 1.0 equiv) was added dropwise to a suspension of diphenylboronic anhydride (**2**; 4.01 g, 11.6 mmol, 1.0 equiv) in DCM (25 mL) at -78 °C and was kept at -78 °C for 30 minutes, after which the reaction mixture was warmed to room temperature. After 1 hour of stirring at room temperature, brown solids were formed and all volatiles were removed *in vacuo* and the product was extracted into *n*-pentane (3 x 20 mL). The combined extracts were dried *in vacuo* yielding Ph<sub>2</sub>BCl (**3**) as a thick oil,

which turned into a colorless solid after storage in a  $-20\text{ }^{\circ}\text{C}$  freezer overnight (4.33 g, 94%). The product can be recrystallized by cooling a saturated solution in *n*-pentane to  $-20\text{ }^{\circ}\text{C}$ .

$^1\text{H NMR}$  (400.13 MHz,  $\text{CDCl}_3$ , 290 K):  $\delta$  8.01 (d,  $^3J_{\text{H,H}} = 7.0\text{ Hz}$ , 4H; *o*-PhH), 7.62 (t,  $^3J_{\text{H,H}} = 7.4\text{ Hz}$ , 2H; *p*-PhH), 7.51 (t,  $^3J_{\text{H,H}} = 7.5\text{ Hz}$ , 4H; *m*-PhH).

$^{11}\text{B}\{^1\text{H}\}$  NMR (128.38 MHz,  $\text{CDCl}_3$ , 290 K):  $\delta$  62.7 (br. s).

#### Preparation of Mes<sub>2</sub>BOMe (4):<sup>[20]</sup>

A solution of MesMgBr (1 M in THF, 27 mL, 27 mmol, 2.1 equiv) was added dropwise to a solution of B(OMe)<sub>3</sub> (1.45 mL, 1.35 g, 13.0 mmol, 1.0 equiv) in THF (15 mL), which resulted in a grey suspension that turned into a brown solution after heating to  $55\text{ }^{\circ}\text{C}$  for 5h and subsequent stirring at room temperature overnight. The volatiles were removed *in vacuo* and the mixture was extracted into *n*-pentane (40 + 18 mL). The combined extracts were dried *in vacuo* to yield Mes<sub>2</sub>BOMe (4) as a colorless solid (2.98 g, 82%). Crystallization of this compound was possible from hot methanol (10 mL/g product) to afford colorless crystals upon cooling.

$^1\text{H NMR}$  (500.23 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  6.79 (s, 4H; MesH), 3.75 (s, 3H; OCH<sub>3</sub>), 2.27 (s, 6H; *p*-MesCH<sub>3</sub>), 2.22 (s, 12H; *o*-MesCH<sub>3</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.80 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  128.3 (br. s; *m*-MesC), 54.3 (s; OCH<sub>3</sub>), 22.4 (s; *o*-MesCH<sub>3</sub>), 21.3 (s; *p*-MesCH<sub>3</sub>), the signals for *ipso*-MesC, *o*-MesC and *p*-MesC are unresolved.

$^{11}\text{B}\{^1\text{H}\}$  NMR (128.38 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  45.0 (br. s).

#### Preparation of Mes<sub>2</sub>BCl (5):<sup>[21]</sup>

A solution of BCl<sub>3</sub> (1 M in heptane, 19 mL, 19 mmol, 1.3 equiv) was added dropwise to a solution of Mes<sub>2</sub>BOMe (4; 4.13 g, 14.8 mmol, 1.0 equiv) in heptane (20 mL) at room temperature, after which the mixture was heated overnight at  $60\text{ }^{\circ}\text{C}$ . The reaction mixture was cooled to room temperature and the volatiles were removed *in vacuo* to afford pinkish solids that were extracted into *n*-pentane (12 + 20 mL). The combined extracts were dried *in vacuo*, which afforded Mes<sub>2</sub>BCl (5) as a colorless solid (3.86 g, 92%). X-ray quality colorless crystals were obtained by recrystallization from hot pentane (2.6 mL/g crude Mes<sub>2</sub>BCl) and subsequent washing with pentane (0.5 mL/g crude) at  $-80\text{ }^{\circ}\text{C}$ .

**Melting point (nitrogen, sealed capillary):** 80–84 °C (trajectory).

**<sup>1</sup>H NMR (500.23 MHz, CDCl<sub>3</sub>, 293 K):** δ 6.83 (s, 4H; Mes*H*), 2.30 (s, 12H; *o*-MesCH<sub>3</sub>), 2.28 (s, 6H; *p*-MesCH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR (125.80 MHz, CDCl<sub>3</sub>, 293 K):** δ 140.9 (s; *o*-MesC), 140.5 (s; *p*-MesC), 129.0 (s; *m*-MesC), 23.4 (s; *o*-MesCH<sub>3</sub>), 21.4 (s; *p*-MesCH<sub>3</sub>), the signal for *ipso*-MesC is unresolved.

**<sup>11</sup>B{<sup>1</sup>H} NMR (128.38 MHz, CDCl<sub>3</sub>, 293 K):** δ 69.9 (br. s).

### **Preparation of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BOEt from B(OEt)<sub>3</sub> (6a):**

Bromopentafluorobenzene (6.7 mL, 13.27 g, 53.7 mmol, 2.9 equiv) was added to a mixture of magnesium turnings (1.5 g, 61.7 mmol, 3.3 equiv) in Et<sub>2</sub>O (55 mL), after which the mixture was stirred overnight. The formed Grignard solution was added via a thin cannula to a solution of triethylborate (3.2 mL, 2.75 g, 18.8 mmol, 1 equiv) in Et<sub>2</sub>O (25 mL) and the resulting mixture was refluxed overnight. Next, the mixture was cooled to 0 °C and a solution of HCl (2 M in Et<sub>2</sub>O, 50 mL, 100 mmol, 5.3 equiv) was added after which the mixture was allowed to warm to room temperature and stirred for 1 hour. All volatiles were removed *in vacuo* and the product was subsequently extracted into *n*-pentane (3x30 mL). The combined extracts were evaporated to dryness to yield the crude product as a brown liquid, which was distilled under reduced pressure (0.5 mbar, 130 °C) to afford the product as a colorless liquid (4.76 g, 65% yield).

**<sup>1</sup>H NMR (499.91 MHz, CDCl<sub>3</sub>, 299 K):** δ 4.26 (q, <sup>3</sup>*J*<sub>H,H</sub> = 6.4 Hz, 2H; CH<sub>2</sub>), 1.40 (t, <sup>3</sup>*J*<sub>H,H</sub> = 6.9 Hz, 3H; CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR (125.70 MHz, CDCl<sub>3</sub>, 298 K):** δ 147.7 (dm, <sup>1</sup>*J*<sub>C,F</sub> = 246.8 Hz; *o*-PhC), 143.1 (dm, <sup>1</sup>*J*<sub>C,F</sub> = 257.1 Hz; *p*-PhC), 137.6 (dm, <sup>1</sup>*J*<sub>C,F</sub> = 253.1 Hz; *m*-PhC), 109.2 (br. s; *ipso*-PhC), 66.7 (s; CH<sub>2</sub>), 17.0 (s; CH<sub>3</sub>).

**<sup>11</sup>B{<sup>1</sup>H} NMR (96.28 MHz, CDCl<sub>3</sub>, 298 K):** δ 42.9 (s).

**<sup>19</sup>F NMR (282.36 MHz, CDCl<sub>3</sub>, 299 K):** δ -132.0 (dd, <sup>3</sup>*J*<sub>F,F</sub> = 27.7 Hz, <sup>4</sup>*J*<sub>F,F</sub> = 8.8 Hz; *o*-PhF), -149.5 (t, <sup>3</sup>*J*<sub>F,F</sub> = 19.3 Hz; *p*-PhF), -160.8–-161.4 (m; *m*-PhF).

**Preparation of Et<sub>2</sub>NBCl<sub>2</sub> (8):**<sup>[18]</sup>

Diethyltrimethylsilylamine (17.05 mL, 13.09 g, 90 mmol, 1.0 equiv) was added dropwise to a solution of boron trichloride (1 M in DCM, 100 mL, 100 mmol, 1.1 equiv) at -78 °C after which a white suspension was formed. The reaction mixture was kept for 15 minutes at -78 °C and was subsequently warmed to room temperature resulting in a transparent yellow reaction mixture. After stirring for 1 hour at room temperature, the mixture was carefully concentrated *in vacuo*. The crude product was distilled under reduced pressure at 40 mbar and 56 °C with a micro short-path distillation apparatus and Et<sub>2</sub>NBCl<sub>2</sub> (8) was obtained as a colorless liquid (10.4 g, 75%).

**Boiling point:** 56 °C / 40 mbar.

**<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, 296 K):** δ 3.27 (q, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 4H; CH<sub>2</sub>), 1.13 (t, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 4H; CH<sub>2</sub>).

**<sup>11</sup>B{<sup>1</sup>H} NMR (128.38 MHz, CDCl<sub>3</sub>, 296 K):** δ 30.5 (s).

**General procedure A, synthesis of 6 with a Grignard reagent:**

The corresponding arylbromide (2.5 equiv) was added at once to a suspension of magnesium turnings (2.8 equiv) in Et<sub>2</sub>O (0.5 M aryl bromide concentration) and the reaction mixture was refluxed without external heating for 30 minutes and stirred at room temperature overnight. Subsequently, the resulting ArMgBr reagent (0.5 M in Et<sub>2</sub>O, 2.5 equiv) was added dropwise via a thin cannula to a solution of Cl<sub>2</sub>BNET<sub>2</sub> (8; 0.25 M in Et<sub>2</sub>O, 1.0 equiv), which gave a white suspension that turned into a brown solution after stirring overnight at room temperature. Next, HCl (1 M in Et<sub>2</sub>O, 3.0 equiv) was added at 0 °C after which the mixture was warmed to room temperature and stirred for 2 hours. Subsequently, EtOH (3 equiv) was slowly added and the mixture was stirred for an additional 2 hours. The solvent was removed *in vacuo* and the crude product was extracted into *n*-pentane. The combined extracts were evaporated to dryness *in vacuo* to yield the product, which could be decolorized by stirring it in *n*-pentane in the presence of active charcoal overnight with subsequent filtration and removal of the solvent *in vacuo*.

### Preparation of bis(3,5-bis(trifluoromethyl)phenyl)ethoxyborane (6b):

Following general procedure A: 3,5-bis(trifluoromethyl)bromobenzene (25 mmol) was used as starting material, which gave after extraction and removal of the solvent **6b** as a brown solid (4.26 g, 85%). Overnight stirring of the product in *n*-pentane in the presence of active charcoal and subsequent filtration and removal of the solvent *in vacuo* gave the product as light beige solid (3.51 g, 70%). Colorless X-ray quality crystals were grown at  $-20\text{ }^{\circ}\text{C}$  from a saturated solution in *n*-pentane.

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  8.08–8.00 (m, 6H; *o,p*-PhH), 4.23 (q,  $^3J_{\text{H,H}} = 6.7$  Hz, 2H;  $\text{CH}_2$ ), 1.42 (t,  $^3J_{\text{H,H}} = 7.0$  Hz, 3H;  $\text{CH}_3$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.72 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  138.2 (br. s; *ipso*-PhC), 133.7 (s; *o*-PhC), 131.5 (q,  $^2J_{\text{C,F}} = 33.2$  Hz; *m*-PhC), 124.7 (m; *p*-PhC), 123.5 (q,  $^1J_{\text{C,F}} = 272.4$  Hz;  $\text{PhCF}_3$ ), 65.1 (s;  $\text{CH}_2$ ), 17.5 (s;  $\text{CH}_3$ ).

$^{11}\text{B}\{^1\text{H}\}$  NMR (128.38 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  43.2 (s).

$^{19}\text{F}$  NMR (282.36 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$   $-64.3$  (s).

### Preparation of bis(4-(trifluoromethyl)phenyl)ethoxyborane (6c):

Following general procedure A: 1-Bromo-4-(trifluoromethyl)benzene (25 mmol) was used as starting material, which gave after extraction and removal of the solvent **6c** as a yellow oil (2.83 g, 82%). Overnight stirring of the product in *n*-pentane in the presence of active charcoal and subsequent filtration and removal of the solvent *in vacuo* gave the product as colorless oil (2.24 g, 65%).

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.74–7.64 (m, 8H; *o,m*-PhH), 4.18 (q,  $^3J_{\text{H,H}} = 7.0$  Hz, 2H;  $\text{CH}_2$ ), 1.35 (t,  $^3J_{\text{H,H}} = 7.0$  Hz, 3H;  $\text{CH}_3$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.70 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  140.8 (br. s; *ipso*-PhC), 134.2 (s; *o*-PhC), 132.2 (q,  $^2J_{\text{C,F}} = 32.3$  Hz; *p*-PhC), 124.6 (q,  $^3J_{\text{C,F}} = 3.6$  Hz; *m*-PhC), 124.3 (q,  $^1J_{\text{C,F}} = 272.2$  Hz;  $\text{PhCF}_3$ ), 64.4 (s;  $\text{CH}_2$ ), 17.7 (s;  $\text{CH}_3$ ).

$^{11}\text{B}\{^1\text{H}\}$  NMR (128.38 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  44.5 (s).

$^{19}\text{F}$  NMR (282.36 MHz,  $\text{CDCl}_3$ , 299 K):  $\delta$   $-63.0$  (s).

### Preparation of bis(3,4,5-trifluorophenyl)ethoxyborane (**6d**):

Following general procedure **A**: 1-bromo-3,4,5-trifluorobenzene (25 mmol) was used as starting material, which after extraction and removal of the solvent afforded **6d** as a pale white oil (2.70 g, 85%). No treatment with active charcoal was required.

<sup>1</sup>H NMR (499.91 MHz, CDCl<sub>3</sub>, 298 K): δ 7.18–7.09 (m, 4H; *o*-PhH), 4.15 (q, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2H; CH<sub>2</sub>), 1.34 (t, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 3H; CH<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.70 MHz, CDCl<sub>3</sub>, 298 K): δ 151.5 (dd, <sup>1</sup>J<sub>C,F</sub> = 252.7 Hz, <sup>2</sup>J<sub>C,F</sub> = 9.8 Hz; *m*-PhC), 141.5 (dt, <sup>1</sup>J<sub>C,F</sub> = 255.6 Hz, <sup>2</sup>J<sub>C,F</sub> = 14.5 Hz; *p*-PhC), 117.6 (dd, <sup>2</sup>J<sub>C,F</sub> = 14.5 Hz, <sup>3</sup>J<sub>C,F</sub> = 3.8 Hz; *o*-PhC), 64.6 (s; CH<sub>2</sub>), 17.5 (s; CH<sub>3</sub>). The signal for *ipso*-PhC is unresolved.

<sup>11</sup>B{<sup>1</sup>H} NMR (96.28 MHz, CDCl<sub>3</sub>, 294 K): δ 41.2 (s).

<sup>19</sup>F NMR (282.36 MHz, CDCl<sub>3</sub>, 294 K): δ -134.4 (dd, <sup>3</sup>J<sub>F,F</sub> = 20.1 Hz, <sup>4</sup>J<sub>F,F</sub> = 7.1 Hz; *m*-PhF), -156.8 (br. s; *p*-PhF).

### General procedure B, synthesis of **6** with an organolithium reagent:

*n*-Butyllithium (1.6 M in hexanes, 2.0 equiv) was added dropwise to a solution of the corresponding arylbromide (2.0 equiv) in Et<sub>2</sub>O (0.5 M aryl bromide concentration) at -78 °C and after addition the reaction mixture was stirred for 30 minutes at -78 °C. Next, a solution of Cl<sub>2</sub>BNEt<sub>2</sub> (**8**; 0.33 M in Et<sub>2</sub>O, 1.0 equiv) was added to the mixture at -78 °C and the reaction mixture was stirred for 1 hour at -78 °C with subsequent warm up to room temperature overnight. HCl (2 M in Et<sub>2</sub>O, 3.0 equiv) was added at room temperature and the mixture was stirred for 1 hour. Next, EtOH (3.0 equiv) was added at room temperature and the mixture was stirred overnight. The solvent was removed *in vacuo* and the crude product was extracted into *n*-pentane. The combined extracts were evaporated to dryness *in vacuo* to yield the product.

### Preparation of bis(pentafluorophenyl)ethoxyborane (**6a**):<sup>[6]</sup>

Following general procedure **B**: bromopentafluorobenzene (10 mmol) was used as starting material, which after extraction and removal of the solvent afforded **6a** as a colorless solid (1.64 g, 79%).

<sup>1</sup>H NMR (499.91 MHz, CDCl<sub>3</sub>, 299 K): δ 4.26 (q, <sup>3</sup>J<sub>H,H</sub> = 6.4 Hz, 2H; CH<sub>2</sub>), 1.40 (t, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 3H; CH<sub>3</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.70 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  147.7 (dm,  $^1J_{\text{C,F}} = 246.8$  Hz; *o*-PhC), 143.1 (dm,  $^1J_{\text{C,F}} = 257.1$  Hz; *p*-PhC), 137.6 (dm,  $^1J_{\text{C,F}} = 253.1$  Hz; *m*-PhC) 109.2 (br. s; *ipso*-PhC), 66.7 (s;  $\text{CH}_2$ ), 17.0 (s;  $\text{CH}_3$ ).

$^{11}\text{B}\{^1\text{H}\}$  NMR (96.28 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  42.9 (s).

$^{19}\text{F}$  NMR (282.36 MHz,  $\text{CDCl}_3$ , 299 K):  $\delta$  -132.0 (dd,  $^3J_{\text{F,F}} = 27.7$  Hz,  $^4J_{\text{F,F}} = 8.8$  Hz; *o*-PhF), -149.5 (t,  $^3J_{\text{F,F}} = 19.3$  Hz; *p*-PhF), -160.8–-161.4 (m; *m*-PhF).

#### Preparation of bis(2,3,5,6-tetrafluorophenyl)diethylaminoborane (9e):

Following general procedure **B**: 1-bromo-2,3,5,6-tetrafluorobenzene (2.48 mmol) was used as starting material. This procedure did not yield the desired borinic ester and after extraction and removal of the solvent aminoborane **9e** was obtained as a colorless solid (0.32 g, 67%).

$^1\text{H}$  NMR (300.10 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  7.20–7.06 (m, 2H; *p*-PhH), 4.27 (q,  $^3J_{\text{H,H}} = 7.1$  Hz, 4H;  $\text{CH}_2$ ), 1.40 (t,  $^3J_{\text{H,H}} = 7.1$  Hz, 6H;  $\text{CH}_3$ ).

$^{11}\text{B}\{^1\text{H}\}$  NMR (96.28 MHz,  $\text{CDCl}_3$ , 294 K):  $\delta$  41.1 (s).

$^{19}\text{F}$  NMR (282.36 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  -133.0 (m; PhF), -138.6 (m; PhF).

#### Preparation of bis(2,4,6-trifluorophenyl)diethylaminoborane (9f):

Following general procedure **B**: 1-bromo-2,4,6-trifluorobenzene (10 mmol) was used as starting material. This procedure did not yield the desired borinic ester and after extraction and removal of the solvent aminoborane **9f** was obtained as a colorless solid (1.61 g, 95%).

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ , 303 K):  $\delta$  6.65–6.48 (m, 4H; *m*-PhH), 3.22 (q,  $^3J_{\text{H,H}} = 7.1$  Hz, 4H;  $\text{CH}_2$ ), 1.13 (t,  $^3J_{\text{H,H}} = 7.2$  Hz, 6H;  $\text{CH}_3$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.70 MHz,  $\text{CDCl}_3$ , 303 K):  $\delta$  163.9 (dm,  $^1J_{\text{C,F}} = 240.8$  Hz; PhCF), 100.3–99.5 (m; *m*-PhC), 111.9 (br. s; *ipso*-PhC), 43.9 (s;  $\text{CH}_2$ ), 15.1 (s;  $\text{CH}_3$ ). One PhCF signal remains unresolved.

$^{11}\text{B}\{^1\text{H}\}$  NMR (96.28 MHz,  $\text{CDCl}_3$ , 295 K):  $\delta$  39.2 (s)

$^{19}\text{F}$  NMR (282.36 MHz,  $\text{CDCl}_3$ , 294 K):  $\delta$  -100.4 (s; *o*-PhF), -109.0 (s; *p*-PhF).

### General procedure C, synthesis of 7:

To a solution of the corresponding borinic ester **6** (1.0 equiv) in *n*-pentane a solution of BCl<sub>3</sub> (1 M in heptane, 1.2 equiv) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 hours after which all volatiles were removed *in vacuo* to afford the product **7**. If necessary, the product can be washed with portions of *n*-pentane at –78 °C.

### Preparation of bis(pentafluorophenyl)chloroborane (**7a**):<sup>[11]</sup>

Following general procedure C borinic ester **6a** (6.10 mmol) was used as starting material as a 0.15 M *n*-pentane solution. After stirring for 5 hours at room temperature, the mixture was cooled to –78 °C to afford a suspension, which was filtered and washed with *n*-pentane (2x 10 mL) at –78 °C. Drying of the remaining solids *in vacuo* afforded product **7a** as a colorless solid (2.21 g, 96%).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.70 MHz, CDCl<sub>3</sub>, 298 K): δ 148.5 (dm, <sup>1</sup>J<sub>C,F</sub> = 253.8 Hz; PhC), 145.0 (dm, <sup>1</sup>J<sub>C,F</sub> = 262.1 Hz; *p*-PhC), 137.7 (dm, <sup>1</sup>J<sub>C,F</sub> = 254.4 Hz; PhC), 112.0 (br. s; *ipso*-PhC).

<sup>11</sup>B{<sup>1</sup>H} NMR (160.38 MHz, CDCl<sub>3</sub>, 298 K): δ 58.6 (br. s).

<sup>19</sup>F NMR (282.36 MHz, CDCl<sub>3</sub>, 293 K): δ –128.3––128.7 (m; PhF), –143.5––143.7 (m; *p*-PhF), –159.8––160.2 (m; PhF).

### Preparation of bis(3,5-bis(trifluoromethyl)phenyl)chloroborane (**7b**):<sup>[13]</sup>

Following general procedure C borinic ester **6b** (5.3 mmol) was used as starting material. As solvent DCM (15 mL) was used instead of *n*-pentane, as well as a solution of BCl<sub>3</sub> in DCM (1 M). After removal of all volatiles chloroborane **7b** was obtained as a white solid (2.46 g, 99%).

<sup>1</sup>H NMR (499.91 MHz, CDCl<sub>3</sub>, 298 K): δ 8.35 (s; 4H; *o*-PhH), 8.18 (s, 2H; *p*-PhH).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.70 MHz, CDCl<sub>3</sub>, 298 K): δ 138.6 (br. s; *ipso*-PhC), 136.4 (br. s; *o*-PhC), 132.2 (q, <sup>2</sup>J<sub>C,F</sub> = 33.7 Hz; *m*-PhC), 127.5–127.2 (m, *p*-PhC), 123.2 (q, <sup>1</sup>J<sub>C,F</sub> = 272.9 Hz; PhCF<sub>3</sub>).

<sup>11</sup>B{<sup>1</sup>H} NMR (160.39 MHz, CDCl<sub>3</sub>, 293 K): δ 63.2 (br. s).

<sup>19</sup>F NMR (282.36 MHz, CDCl<sub>3</sub>, 298 K): δ –63.1 (s).

### Preparation of bis(4-(trifluoromethyl)phenyl)chloroborane (7c):<sup>[14d]</sup>

Following general procedure C borinic ester **6c** (0.32 mmol) was used as starting material as a 0.06 M *n*-pentane solution. In this case, the BCl<sub>3</sub> solution was added at room temperature. After removal of all volatiles a white oil was obtained. Due to the presence of impurities, the yield was not determined.

<sup>1</sup>H NMR (499.91 MHz, CDCl<sub>3</sub>, 299 K): δ 8.07 (d, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 4H; PhH), 7.77 (d, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, 4H; PhH).

<sup>11</sup>B{<sup>1</sup>H} NMR (160.39 MHz, CDCl<sub>3</sub>, 300 K): δ 63.8 (br. s).

<sup>19</sup>F NMR (282.36 MHz, CDCl<sub>3</sub>, 298 K): δ -65.3 (s).

### Preparation of bis(3,4,5-trifluorophenyl)chloroborane (7d):

Following general procedure C borinic ester **6d** (0.74 mmol) was used as starting material as a 0.15 M *n*-pentane solution. After removal of all volatiles, **7d** was obtained as a pale yellow oil (0.20 g, 85%).

<sup>1</sup>H NMR (499.91 MHz, CDCl<sub>3</sub>, 299 K): δ 7.60–7.51 (m, 4H; *o*-PhH).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.70 MHz, CDCl<sub>3</sub>, 298 K): δ 151.3 (ddd, <sup>1</sup>J<sub>C,F</sub> = 253.8 Hz, <sup>2</sup>J<sub>C,F</sub> = 9.8 Hz, <sup>3</sup>J<sub>C,F</sub> = 2.7 Hz; *m*-PhC), 143.7 (dt, <sup>1</sup>J<sub>C,F</sub> = 261.9 Hz, <sup>2</sup>J<sub>C,F</sub> = 15.3 Hz; *p*-PhC), 132.7 (br. s; *ipso*-PhC), 128.8 (dd, <sup>2</sup>J<sub>C,F</sub> = 14.8 Hz, <sup>3</sup>J<sub>C,F</sub> = 4.8 Hz; *o*-PhC).

<sup>11</sup>B{<sup>1</sup>H} NMR (96.28 MHz, CDCl<sub>3</sub>, 295 K): δ 63.1 (br. s).

<sup>19</sup>F NMR (282.36 MHz, CDCl<sub>3</sub>, 294 K): δ -134.8 (dd, <sup>3</sup>J<sub>F,F</sub> = 20.2 Hz, <sup>4</sup>J<sub>F,F</sub> = 7.3 Hz; *m*-PhF), -152.7–-153.1 (m; *p*-PhF).

### X-ray structure determination for **5** and **6b**:

The single-crystal X-ray diffraction studies were carried out on a Bruker-Nonius KappaCCD diffractometer at 123(2) K using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) (**5**) or Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) (**6b**). Direct Methods (SHELXS-97)<sup>[22]</sup> (for **5**) and Dual space methods (SHELXT)<sup>[23]</sup> (for **6b**) were used for structure solution and refinement was carried out using SHELXT-2013/2014 (full-matrix least-squares on  $F^2$ ).<sup>[24]</sup> Hydrogen atoms were localized by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied.

**5:** colorless crystals,  $C_{18}H_{22}BCl$ ,  $M_r = 284.61$ , crystal size 0.27 x 0.09 x 0.03 mm, monoclinic, space group  $P2_1/c$  (no.14),  $a = 8.279(1) \text{ \AA}$ ,  $b = 7.855(1) \text{ \AA}$ ,  $c = 24.218(3) \text{ \AA}$ ,  $\beta = 92.03(1)^\circ$ ,  $V = 1573.9(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 1.201 \text{ Mg/m}^3$ ,  $\mu(\text{Mo-K}\alpha) = 0.23 \text{ mm}^{-1}$ ,  $F(000) = 608$ ,  $2\theta_{\text{max}} = 50.6^\circ$ , 12556 reflections, of which 2840 were independent ( $R_{\text{int}} = 0.054$ ), 187 parameters,  $R_1 = 0.051$  (for 2190  $I > 2\sigma(I)$ ),  $wR_2 = 0.129$  (all data),  $S = 1.04$ , largest diff. peak / hole = 0.34 / -0.25  $e \text{ \AA}^{-3}$ .

**6b:** colorless crystals,  $C_{18}H_{11}BF_{12}O$ ,  $M_r = 482.08$ , crystal size 0.30 x 0.20 x 0.16 mm, monoclinic, space group  $P2_1/c$  (no.14),  $a = 14.2305(6) \text{ \AA}$ ,  $b = 9.2703(4) \text{ \AA}$ ,  $c = 16.1406(6) \text{ \AA}$ ,  $\beta = 115.983(1)^\circ$ ,  $V = 1914.06(14) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 1.673 \text{ Mg/m}^3$ ,  $\mu(\text{Mo-K}\alpha) = 1.66 \text{ mm}^{-1}$ ,  $F(000) = 960$ ,  $2\theta_{\text{max}} = 144.4^\circ$ , 3739 reflections, of which 3739 were independent, 290 parameters,  $R_1 = 0.045$  (for 3510  $I > 2\sigma(I)$ ),  $wR_2 = 0.122$  (all data),  $S = 1.03$ , largest diff. peak / hole = 0.51 / -0.47  $e \text{ \AA}^{-3}$ .

## 6.5 References

- [1] T. Noda, Y. Shirota, *J. Am. Chem. Soc.* **1998**, *120*, 9714–9715.
- [2] C. Mazet, V. Köhler, A. Pfaltz, *Angew. Chem. Int. Ed.* **2005**, *44*, 4888–4891.
- [3] a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76. b) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316. c) D. W. Stephan, *Science* **2016**, *354*, 1248.
- [4] a) H. C. Brown, G. Zweifel, *J. Am. Chem. Soc.* **1959**, *81*, 247–247. b) H. C. Brown, *Tetrahedron* **1961**, *12*, 117–138.
- [5] Y. Sun, W. E. Piers, M. Parvez, *Can. J. Chem.* **1998**, *76*, 513–517.
- [6] R. Duchateau, S. J. Lancaster, M. Thornton-Pett, M. Bochmann, *Organometallics* **1997**, *16*, 4995–5005.
- [7] M. Schlögl, S. Riethmueller, C. Troll, M. Möller, B. Rieger, *Macromolecules* **2004**, *37*, 4004–4007.
- [8] A. Sundararaman, F. Jäkle, *J. Organomet. Chem.* **2003**, *681*, 134–142.
- [9] T. E. Cole, B. D. Haly, *Organometallics* **1992**, *11*, 652–657.
- [10] R. D. Chambers, T. Chivers, *J. Chem. Soc.* **1965**, 3933–3939.
- [11] D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics*, **1998**, *17*, 5492–5503.
- [12] D. Winkelhaus, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Dalton Trans.* **2012**, *41*, 8609–8614.
- [13] K. Samigullin, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2014**, *33*, 3564–3569.

- [14] a) K. Niedenzu, H. Beyer, J. W. Dawson *Inorg. Chem.* **1962**, *1*, 738–742. b) P. M. Treichel, J. Benedict, R. G. Haines, B. Gassenheimer, T. Wartik, *Inorg. Synth.* **1972**, *13*, 32–41. c) K. B. Dillon, G. F. Hewitson, *Polyhedron* **1984**, *3*, 957–962. d) J. C. Thomas, J. C. Peters, *Inorg. Chem.* **2003**, *42*, 5055–5073.
- [15] For synthesis procedures of **2**, see: a) T. Hosoya, H. Uekusa, Y. Ohashi, T. Ohhara, R. Kuroki, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 692–701. b) X. Chen, H. Ke, Y. Chen, C. Guan, G. Zou, *J. Org. Chem.* **2012**, *77*, 7572–7578.
- [16] For a synthesis procedure of **3**, see: E.W. Abel, S. H. Dandegaonker, W. Gerrard, M. F. Lappert, *J. Chem. Soc.* **1956**, 4697–4699.
- [17] R. T. Hawkins, W. J. Lennarz, H. R. Snyder, *J. Am. Chem. Soc.* **1960**, *82*, 3052–3059.
- [18] E. W. Abel, D. A. Armitage, R. P. Bush, G. R. Willey, *J. Chem. Soc.* **1965**, 62–64.
- [19] A. Schnurr, H. Vitze, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics*, **2010**, *29*, 6012–6019.
- [20] N. M. D. Brown, F. Davidson, R. McMullan, J. W. Wilson, *J. Organomet. Chem.* **1980**, *193*, 271–282.
- [21] A. Sundaraman, F. Jäkle, *J. Organomet. Chem.* **2003**, *681*, 134–142.
- [22] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.
- [23] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8.
- [24] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8.