## **ORGANOMETALLICS**

### One-Pot Synthesis of $[(C_6F_5)_2BH_2]^-$ from $C_6F_5MgBr/BH_3 \cdot SMe_2$ and Its in Situ Transformation to Piers' Borane

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Supporting Information

**ABSTRACT:** Depending on the crystallization procedure, the onepot reaction between 2  $C_6F_5MgBr$ , 1  $BH_3 \cdot SMe_2$ , and 1  $Me_3SiCl$ furnishes the hydridoborate salts  $[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]$ and  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2$ , both of which are convenient starting materials for the in situ generation of Piers' borane  $(C_6F_5)_2BH$ .



**P**erfluoroarylboranes find applications as anion sensors, as cocatalysts in metallocene-based homogeneous olefin polymerizations, and as Lewis acid catalysts in a range of organic transformations (e.g., addition of silyl enol ethers to aldehydes, alkyl chlorides, and  $\alpha_{,\beta}$ -unsaturated ketones; hydrosilylation of carbonyl functions; Diels–Alder reactions).<sup>1</sup> Together with sterically encumbered Lewis bases, they can form so-called "frustrated Lewis pairs (FLPs)", which have been employed for the activation of various small molecules, including H<sub>2</sub>.<sup>2</sup>

Even though tris(pentafluorophenyl)borane,  $(C_6F_5)_3B_7^{3,4}$  is still the most widely used perfluoroarylborane, much of the progress witnessed in the aforementioned application fields was due to the development of more sophisticated derivatives—among them bulky molecules such as tris(2,2',2''-perfluorobiphenyl)borane,<sup>5</sup> bifunctional species,<sup>6</sup> and even polymeric<sup>7</sup> and dendritic<sup>8</sup> perfluoroarylboranes.

The incorporation of boryl functionalities into molecular frameworks can conveniently be achieved via the hydroboration reaction. Thus, in the present context the secondary borane  $(C_6F_5)_2BH$ , which has been developed by Piers et al., is a key reagent for the synthesis of compounds  $(C_6F_5)_2BR$ , in which R (i) provides the set-screw for a fine tuning of the Lewis acidity at the boron center or (ii) bears an additional functional group as in the chelating Lewis acid  $(C_6F_5)_2B(Me_3Si)C(H) - C(H)_2B(C_6F_5)_2^{-5}$ or the bridged FLP  $(C_6F_5)_2BC(H)_2-C(H)_2PMes_2$  (Mes = mesityl).<sup>10</sup> Hydroboration reactions with (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BH generally occur with high rates and regio- and chemoselectivity comparable to or better than those with other reagents. Most importantly, terminal alkynes can selectively be monohydroborated to the corresponding vinylboranes  $(C_6F_5)_2BC(H)=C(H)R^{9,11}$ This offers a convenient tool to modulate the optoelectronic properties of extended conjugated  $\pi$ -electron systems and is therefore interesting for the design of novel boron-doped photoand electroluminescent organic materials.<sup>12</sup>

 $(C_6F_5)_2BH$  adopts a dimeric structure in the solid state and undergoes a monomer/dimer equilibrium in aromatic solvents.<sup>11</sup>

The currently best established synthesis protocols for  $(C_6F_5)_2BH$  and for its thioether adduct  $(C_6F_5)_2BH \cdot SMe_2$  are outlined in Scheme 1.

**Route 1.**  $(C_6F_5)_2BH$  can be prepared from  $(C_6F_5)_2BCl^{13}$  by treatment with Me<sub>2</sub>Si(H)Cl.<sup>9,11</sup> The synthesis of  $(C_6F_5)_2BCl$ , in turn, starts from  $C_6F_5Li$  and  $Cl_2SnMe_2$  and proceeds via the reaction of the resulting stannane  $(C_6F_5)_2SnMe_2^{-14}$  with BCl<sub>3</sub>.<sup>11</sup> By this method,  $(C_6F_5)_2BH$  is obtained in a very satisfactory overall yield of 62%. However, the procedure has to be regarded as experimentally demanding: (i)  $C_6F_5Li$  is a thermolabile, potentially hazardous compound, (ii)  $Cl_2SnMe_2$  and BCl<sub>3</sub> are toxic/corrosive, and (iii)  $C_6F_5$  transfer from tin to boron has to be carried out at 120 °C (thick-walled glass bomb; boiling point of BCl<sub>3</sub> at ambient pressure: 12.6 °C) and takes 48 h.

**Route 2.**  $(C_6F_5)_2$ BH is also accessible in a one-step procedure by heating commercially available  $(C_6F_5)_3$ B and Et<sub>3</sub>SiH in benzene to 60 °C for 3 days (69% yield).<sup>11</sup> In comparison to route 1, route 2 is less labor intensive but nevertheless suffers from certain disadvantages: (i)  $(C_6F_5)_3$ B is high-priced and the commercial samples tend to be contaminated with the water adduct  $(C_6F_5)_3$ B·OH<sub>2</sub>, (ii) the reaction requires a rather long time and shows a tendency to over-reduce the borane, thereby contaminating the product with the dimer  $[(C_6F_5)_2B(\mu-H)_2B-(H)(C_6F_5)]$ , and (iii) one-third of the  $C_6F_5$  rings is transferred to silicon and therefore wasted.

**Route 3.** An (in principle) more atom-economic variant of route 2 has been reported by Lancaster et al., who replaced  $Et_3SiH$  by  $BH_3 \cdot SMe_2$ , which reacts with  $(C_6F_5)_3B \cdot OEt_2$  in light petroleum at room temperature within minutes to give  $(C_6F_5)_2BH \cdot SMe_2$  in 54% yield.<sup>15</sup> In a related study, Hoshi et al. recently reported that a solution of  $(C_6F_5)_2BH \cdot SMe_2$  in hexane can be generated by substituent redistribution between

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### Scheme 1. Literature Syntheses of $(C_6F_5)_2BH$ and $(C_6F_5)_2BH \cdot SMe_2$





<sup>*a*</sup> Legend: (i) donor = THF, Et<sub>2</sub>O/THF, room temperature, 12 h; donor =  $SMe_2$ , Et<sub>2</sub>O/toluene, room temperature, 12 h. Note that the composition of the (complex) cations is unknown.

 $(C_6F_5)_3B$  and  $BH_3 \cdot SMe_2$  and that  $(C_6F_5)_2BH \cdot SMe_2$  catalyzes the hydroboration of alk-1-ynes with pinacolborane.<sup>16</sup>

Our interest in  $(C_6F_5)_2BH$  mainly arises from applications in materials sciences: i.e., from its reactivity toward terminal alkynes and from the possibility to modulate the optoelectronic properties of extended conjugated  $\pi$ -systems. Since the results of Lancaster and Hoshi indicate that there is facile exchange between hydride and  $C_6F_5$  groups in the corresponding boranes and their adducts, we decided to investigate the reaction between  $C_6F_5MgBr$  and  $BH_3 \cdot SMe_2$  in order to develop a safe time- and cost-efficient method for the synthesis of  $(C_6F_5)_2BH$  itself and of its adduct  $(C_6F_5)_2BH \cdot SMe_2$ .

#### RESULTS AND DISCUSSION

**One-Pot Synthesis of the**  $[(C_6F_5)_2BH_2]^-$  **Anion.** In all studies reported herein, the Grignard reagent  $C_6F_5MgBr$  was employed, because it is thermally much more stable than the corresponding lithium compound  $C_6F_5Li$  and can therefore conveniently be prepared and handled at room temperature and above.<sup>17</sup>

In a first exploratory experiment,  $BH_3 \cdot THF$  in THF was treated at room temperature with 1 equiv of  $C_6F_5MgBr$  in  $Et_2O$ . The mixture was stirred for 12 h and then investigated by <sup>11</sup>B NMR spectroscopy ( $C_6D_6$ ). Three signals at -30.2 ppm (triplet,  $^{1}J_{BH} = 82$  Hz), -34.1 ppm (quartet,  $^{1}J_{BH} = 79$  Hz), and -39.7 ppm (quintet,  $^{1}J_{BH} = 81$  Hz) were observed (integral ratio 1:3:1), which agree well with the reported shift values of  $[(C_6F_5)_2BH_2]^{-,18}$   $[(C_6F_5)BH_3]^{-,19}$  and  $[BH_4]^{-,20}$  We note that an increase in the amount of added  $C_6F_5MgBr$  to 2 equiv did *not* result in a significant change of the product distribution as



**Figure 1.** <sup>11</sup>B NMR spectra of mixtures of  $C_6F_5MgBr$  and  $BH_3 \cdot SMe_2$ ( $C_6D_6$ ): (a) stoichiometric ratio 2:1, Et<sub>2</sub>O/toluene, room temperature, 12 h; (b) stoichiometric ratio 3:1, benzene, 75 °C, 18 h; (c) stoichiometric ratio 1:1, Et<sub>2</sub>O/toluene, room temperature, 3 h; (d) stoichiometric ratio 2:1, +1 Me<sub>3</sub>SiCl, Et<sub>2</sub>O/toluene, room temperature, 3 h.

long as room temperature was maintained (Scheme 2). However, replacement of the solvents with benzene, addition of a third equivalent of  $C_6F_5MgBr$ ,<sup>21</sup> and the application of elevated temperatures (75 °C; 14 h) led to an increase in the relative proportion of  $[(C_6F_5)_2BH_2]^-$ . The formation of this borohydride was further confirmed by the isolation of  $[Mg_2(THF)_6Br_3][(C_6F_5)_2BH_2]$ , which was structurally characterized by X-ray crystallography (cf. the Supporting Information for details). From these results we conclude that the hydride adduct  $[(C_6F_5)_2BH_2]^-$  of the target molecule  $(C_6F_5)_2BH$  can indeed be generated by this methodology, albeit in low yields ( $\leq 10\%$ ).

In the next step, the series of experiments was repeated with  $BH_3 \cdot SMe_2$  (solution in toluene) in order to study the influence of the Lewis base on the reaction outcome. As shown in Scheme 2, the reaction with 2 equiv of  $C_6F_5MgBr$  at room temperature effected a higher proportion of  $[(C_6F_5)_2BH_2]^-$  than in the case of  $BH_3 \cdot THF$  (cf. Figure 1a for the <sup>11</sup>B NMR spectrum of the mixture). When the transformation was carried out in benzene at reflux temperature,  $[(C_6F_5)_2BH_2]^-$  became the major product; however, significant amounts of other species were still present, as was confirmed by <sup>11</sup>B (Figure 1b) and <sup>19</sup>F{<sup>1</sup>H} NMR spectroscopy.

In an attempt to achieve an exchange between hydride and  $C_6F_5$  groups under milder conditions and thereby to avoid unwanted side products, we decided to generate three-coordinate borane intermediates by means of Me<sub>3</sub>SiCl as a hydride acceptor. In a three-step sequence (Scheme 3), a mixture of  $[(C_6F_5)_2BH_2]^-$ ,  $[(C_6F_5)BH_3]^-$ , and  $[BH_4]^-$  was first generated from  $BH_3 \cdot SMe_2$  and 1 equiv of  $C_6F_5MgBr$  in Et<sub>2</sub>O/toluene at room temperature (cf. Figure 1c for the <sup>11</sup>B NMR spectrum), followed by the addition of 1 equiv of neat Me<sub>3</sub>SiCl and a further 1 equiv of the Grignard reagent (cf. the Supporting Information for the detailed synthesis protocol). According to <sup>11</sup>B (Figure 1d) and <sup>19</sup>F{<sup>1</sup>H} NMR spectroscopy, <sup>18</sup> this procedure resulted in the essentially quantitative formation of  $[(C_6F_5)_2BH_2]^-$ .

Finally, benefitting from the fact that  $C_6F_5MgBr$  does not react with Me<sub>3</sub>SiCl in Et<sub>2</sub>O at room temperature,<sup>22</sup> the aforementioned procedure could be developed into a one-step synthesis protocol: 2 equiv of  $C_6F_5MgBr$  were treated at room temperature with 1 equiv of BH<sub>3</sub> · SMe<sub>2</sub> and immediately after with 1 equiv of neat Me<sub>3</sub>SiCl. After workup, the dihydridoborate can be isolated by crystallization from either CHCl<sub>3</sub>/ Et<sub>2</sub>O or benzene.

# Scheme 3. Three-Step and One-Step Syntheses of $[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]$ and $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_a^a$



crystallization from CHCl<sub>3</sub>/Et<sub>2</sub>O: x = 1, [cation] = [Mg<sub>2</sub>(Et<sub>2</sub>O)<sub>3</sub>Br<sub>2</sub>Cl] crystallization from benzene: x = 2, [cation] = [Mg(Et<sub>2</sub>O)<sub>2</sub>]

<sup>*a*</sup> Legend: (i) Et<sub>2</sub>O/toluene, room temperature, 3 h.

From CHCl<sub>3</sub>/Et<sub>2</sub>O, the salt  $[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]$ was obtained; its composition was confirmed by elemental analysis (C, H, Cl, Br) and X-ray crystallography. Crystal data and structure refinement details for the compound are compiled in Table 1. The salt crystallizes together with 1 equiv of toluene and 2 equiv of CHCl<sub>3</sub> as a centrosymmetric dimer with a complex cationic core and two peripheral  $[(C_6F_5)_2BH_2]^-$  anions (Figure 2). The cation can be described as consisting of two face-sharing heterocubanes, two opposite corners of which are unoccupied. The positions X(2)and X(3) are shared between  $Br^-$  and  $Cl^-$  with relative occupancy factors of 0.704(5):0.296(5) and 0.681(5):0.319(5), respectively. If both ratios are artificially forced to 0.5:0.5, the R values of the structure solution become only slightly worse (i.e., R1 (all data) = 0.1209 vs 0.1124, wR2 (all data) = 0.1252 vs 0.1061 ). Given this background, we used the fully refined structure for the discussion of bond lengths and angles but find it adequate to employ the idealized formula sum of  $[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]$  to refer to the compound and for calculations of its molecular mass.

In the case of Mg(2), an octahedral coordination sphere is completed by two Et<sub>2</sub>O ligands, whereas Mg(1) bears one Et<sub>2</sub>O ligand and has one hydridoborate ion in close proximity. Using Edelstein's<sup>23</sup> correlation of metal—boron distances as a measure of the denticity of a hydridoborate group, a value of  $1.6 \pm 0.1$  Å is estimated for the ionic radius of a bidentate  $[R_2BH_2]^-$  ligand. In turn, a B···Mg distance of about 2.26 Å would be indicative for a  $R_2BH_2-\eta^2$ -Mg coordination mode (effective ionic radius of pentacoordinate Mg<sup>2+</sup>: 0.66 Å<sup>24</sup>). In  $[Mg_2(Et_2O)_3Br_2Cl]$ - $[(C_6F_5)_2BH_2]$ , the B(1)···Mg(1) distance is stretched to 2.498(7) Å, most likely as a result of steric repulsion. We refrain from a detailed discussion of the geometric parameters of the anion  $[(C_6F_5)_2BH_2]^-$ , because the crystal structure of the related compound  $[Li(Et_2O)][(C_6F_5)_2BH_2]$  has already been described and no significant differences were observed.<sup>18</sup>

From benzene, we obtained crystals of the salt  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2$ , which features two dihydridoborate ligands bonded to the Mg<sup>2+</sup> ion in an  $\eta^2$  fashion (B···Mg = 2.416(3) Å; the compound crystallizes together with 2 equiv of benzene; cf. the Supporting Information for details of the X-ray crystal structure analysis). However, EDX measurements revealed the presence of minor amounts of Cl<sup>-</sup> and Br<sup>-</sup> ( $\leq$ 3 atom %). Moreover, after the addition of water to a representative sample of the crystal crop, the signature of MgBr<sub>2</sub>·6H<sub>2</sub>O was visible in the

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formula	$C_{48}H_{64}B_2Br_{4.8}Cl_{1.2}F_{20}Mg_4O_6\boldsymbol{\cdot}$
	$C_7H_8 \cdot 2CHCl_3$
fw	1992.83
color, shape	colorless, block
temp (K)	173(2)
radiation ( $\lambda$ (Å))	Μο Κα (0.71073)
cryst syst	orthorhombic
space group	Pbca
a (Å)	17.371(2)
b (Å)	21.4852(19)
c (Å)	21.5176(18)
$\alpha$ (deg)	90
$\beta$ (deg)	90
$\gamma$ (deg)	90
$V(Å^3)$	8030.8(13)
Z	4
$D_{\rm calcd} ({\rm g \ cm^{-3}})$	1.648
F(000)	3970
$\mu \ (\mathrm{mm}^{-1})$	2.763
cryst size (mm <sup>3</sup> )	$0.35\times0.32\times0.27$
no. of rflns collected	42 315
no. of indep rflns $(R_{int})$	7552 (0.1151)
no. of data/restraints/params	7552/0/446
GOF on $F^2$	0.869
R1, wR2 $(I > 2\sigma(I))$	0.0505, 0.0893
R1, wR2 (all data)	0.1124, 0.1061
largest diff peak, hole (e $Å^{-3}$ )	0.860, -0.860

Table 1. Selected Crystallographic Data for  $\{[Mg_2(Et_2O)_3Br_{2.4}Cl_{0.6}][(C_6F_5)_2BH_2]\}_2 \cdot (toluene) \cdot 2CHCl_3$ 

X-ray powder diffractogram of the solid hydrolysate. In a subsequent purification step, we applied a static vacuum to a suspension of  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2$  in benzene (350 Torr; reflux temperature; 24 h), thereby driving off excess  $Et_2O$  and reducing the solubility of magnesium halide contaminants. After filtration, crystals of  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2$  were grown from the filtrate, which, according to EDX spectroscopy, now contained  $\leq 1$  atom % of Cl<sup>-</sup>/Br<sup>-</sup> ions.

A critical overview of our synthesis protocol to  $[(C_6F_5)_2BH_2]^$ and its suitability for the further preparation of Piers' borane has to consider the following facts: (i) The actual synthesis took an overall time of 5 h; crystallization required an additional 5 days (CHCl<sub>3</sub>/Et<sub>2</sub>O; yield: 68%) or 7 days (benzene; yield: 57%). The new access route has therefore considerable advantages over the literature-known method<sup>18</sup> based on  $(C_6F_5)_2BCl$ . (ii) The salt  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2$  contains a lower proportion of Et<sub>2</sub>O than the salt  $[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]$ . Both species proved to be suitable starting materials for the hydroboration of alk-1-ynes with in situ generated  $(C_6F_5)_2BH$  (described below are the syntheses using  $[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]$ ). (iii) The new protocol cannot be applied to the synthesis and isolation of the free borane  $(C_6F_5)_2BH$ , most likely because Et<sub>2</sub>O reacts with  $(C_6F_5)_2BH$  in the absence of more powerful trapping agents.

Synthesis of  $(C_6F_5)_2BH \cdot SMe_2$  from  $[Mg_2(Et_2O)_3Br_2CI]$ - $[(C_6F_5)_2BH_2]$ . { $[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]$ }<sub>2</sub> · (toluene) ·2CHCl<sub>3</sub> was freed from toluene and CHCl<sub>3</sub> under a dynamic vacuum, dissolved in SMe<sub>2</sub>, and treated with 1 equiv of Me<sub>3</sub>SiCl.



**Figure 2.** Molecular structure and numbering scheme of compound  $\{[Mg_2(Et_2O)_3Br_{2.4}Cl_{0.6}][(C_6F_5)_2BH_2]\}_2$  (displacement ellipsoids are drawn at the 30% probability level; H atoms except on boron and ethyl groups on coordinated  $Et_2O$  molecules are omitted for clarity; positions X are shared between Br and Cl). Selected bond lengths (Å), atom··· atom distances (Å), and angles (deg): Mg(1)-Br(1) = 2.711(2), Mg(2)-Br(1) = 2.768(2), Mg(2A)-Br(1) = 2.688(2), B(1)-C(1) = 1.625(8), B(1)-C(11) = 1.610(8), B(1)···Mg(1) = 2.498(7); Mg(1)-Br(1)-Mg(2) = 88.7(1), Mg(1)-Br(1)-Mg(2A) = 90.2(1), Mg(2)-Br(1)-Mg(2A) = 95.7(1), C(1)-B(1)-C(11) = 112.7(4). Symmetry transformation used to generate equivalent atoms: (A) -x + 1, -y + 1, -z + 1.

After 90 min, the <sup>11</sup>B NMR spectrum of the mixture revealed exclusively one doublet at -12.1 ppm; in the <sup>1</sup>H NMR spectrum, a broad multiplet at 3.58 ppm and a singlet at 1.10 ppm (integral ratio 1:6) testified to the presence of one boron-bonded H atom and one coordinated SMe<sub>2</sub> ligand, respectively. The adduct  $(C_6F_5)_2BH \cdot SMe_2$  was isolated in 90% yield as a colorless flaky solid; all NMR shift values were in full agreement with published data<sup>15</sup> for this compound.

In Situ Generation of  $(C_6F_5)_2BH$  and Hydroboration of Alk-1-ynes. *tert*-Butylacetylene or phenylacetylene in benzene (2 equiv) was added at room temperature to a suspension of { $[Mg_2(Et_2O)_3-Br_2Cl][(C_6F_5)_2BH_2]$ } in benzene/hexane (1:1). The mixture was treated with Me<sub>3</sub>SiCl (2 equiv) and stirred for 2 h. Reaction control by NMR spectroscopy (<sup>1</sup>H, <sup>11</sup>B, <sup>19</sup>F{<sup>1</sup>H}; C\_6D\_6) revealed quantitative conversion to the monohydroboration products ( $C_6F_5$ )<sub>2</sub>-BC(H)=C(H)<sup>t</sup>Bu<sup>11</sup> and ( $C_6F_5$ )\_2BC(H)=C(H)Ph;<sup>11</sup> after workup, yields of 70% and 79% were respectively obtained.

#### CONCLUSION

The hydride adduct  $[(C_6F_5)_2BH_2]^-$  of Piers' borane  $(C_6F_5)_2BH$  is conveniently accessible in a one-pot procedure from  $C_6F_5MgBr$ ,  $BH_3 \cdot SMe_2$ , and  $Me_3SiCl$ . Starting from this compound,  $(C_6F_5)_2BH$  can be generated in situ and trapped with  $SMe_2$  or *tert*-butylacetylene/phenylacetylene. We therefore suggest our method as a viable alternative to the established syntheses of  $(C_6F_5)_2BH$  whenever the hydroboration of alk-1-ynes is the focus of application.

With regard to the underlying reaction mechanism, the following results are noteworthy: (i) The electron-poor  $C_6F_5$  substituent readily takes part in aryl/hydride redistribution

reactions at a boron center. In previous work, we have shown that ferrocenylborane (FcBH<sub>2</sub>), generated in situ from Li-[FcBH<sub>3</sub>], immediately undergoes a condensation reaction to Fc<sub>2</sub>BH and B<sub>2</sub>H<sub>6</sub>,<sup>25,26</sup> whereas the corresponding cymantrenylborane dimer ((CymBH<sub>2</sub>)<sub>2</sub>) can readily be isolated and structurally characterized by X-ray crystallography.<sup>27</sup> So far, we have attributed the different reactivities to differences in the electron densities on the organometallic fragments. The observations described in this paper now suggest that other factors are also likely to play a role. (ii) In our one-pot protocol, the C<sub>6</sub>F<sub>5</sub>/hydride scrambling reaction does not lead to a statistical mixture of all conceivable products  $[(C_6F_5)_xBH_{4-x}]^-$  (x = 0-4) but selectively gives  $[(C_6F_5)_2BH_2]^-$  in preparatively useful yields.

#### EXPERIMENTAL SECTION

**General Remarks.** All manipulations were carried out under a nitrogen atmosphere using Schlenk tube techniques and rigorously dried solvents. NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts are referenced to residual solvent signals (<sup>1</sup>H), external BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B, <sup>11</sup>B{<sup>1</sup>H}), or external CFCl<sub>3</sub> (<sup>19</sup>F{<sup>1</sup>H}). Abbreviations: s = singlet, d = doublet, tr = triplet, q = quartet, quin = quintet, br = broad, n.r. = multiplet expected in the <sup>1</sup>H NMR spectrum but not resolved. Me<sub>3</sub>SiCl was stirred with CaH<sub>2</sub> (30 min) and vacuum-transferred into a Schlenk storage vessel. SMe<sub>2</sub> was dried over LiAlH<sub>4</sub> (12 h at room temperature) and vacuum-transferred into a Schlenk storage vessel. BH<sub>3</sub>·SMe<sub>2</sub> (2.0 M in toluene; Aldrich), and C<sub>6</sub>F<sub>5</sub>Br (fluorochem) are commercially available and were used as received.

Synthesis of  $\{[Mg_2(Et_2O)_3Br_2CI][(C_6F_5)_2BH_2]\}_2$ . At room temperature, a stirred solution of freshly prepared  $C_6F_5MgBr$ (8.0 mmol) in Et<sub>2</sub>O (10 mL) was treated first with a solution of BH<sub>3</sub>·SMe<sub>2</sub> in toluene (2.0 M; 2.0 mL, 4.0 mmol) and then with neat Me<sub>3</sub>SiCl (0.52 mL, 4.1 mmol). The mixture was stirred for 3 h, the volatiles were driven off in vacuo, and the solid pale brown residue was dissolved in CHCl<sub>3</sub> (40 mL) and Et<sub>2</sub>O (5 mL). After filtration from a small amount of insoluble material (mainly unconsumed Mg turnings), the light yellow filtrate was concentrated under reduced pressure until it turned slightly turbid and then stored at 5 °C. Crystallization of  $\{[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]\}_2 \cdot (toluene) \cdot 2CHCl_3 \text{ started after}$ several hours and continued for another 5 days. Crystals suitable for X-ray diffraction were isolated by decantation; concentration of the mother liquor in vacuo and further storage at 5 °C yielded a second crop. Samples used for reactions were washed with a mixture of benzene (2 mL) and hexane (4 mL) and dried in vacuo over a period of 2 h to remove cocrystallized toluene and CHCl<sub>3</sub>. Yield of {[Mg<sub>2</sub>(Et<sub>2</sub>O)<sub>3</sub>- $Br_2Cl][(C_6F_5)_2BH_2]$   $\geq 2.21$  g (68%). For the three-step synthesis of  $\{[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]\}_2$  and for the synthesis of  $[Mg(Et_2 O_{2}][(C_{6}F_{5})_{2}BH_{2}]_{2}$ , see the Supporting Information.

<sup>1</sup>H NMR (300.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.25 (tr, 18H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz; OCH<sub>2</sub>CH<sub>3</sub>), 2.03 (br q, 2H, <sup>1</sup>J<sub>BH</sub> = 70 Hz; BH<sub>2</sub>), 3.81 (q, 12H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz; OCH<sub>2</sub>CH<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (96.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -30.5 ( $h_{1/2}$  = 40 Hz). <sup>11</sup>B NMR (96.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -30.5 (tr, <sup>1</sup>J<sub>BH</sub> = 70 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (282.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -164.8 (br, 4F; F<sub>m</sub>), -159.6 (br, 2F; F<sub>p</sub>), -133.1 (br, 4F; F<sub>o</sub>). MS (ESI<sup>-</sup>): m/z (%) 347.3 (100) [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BH<sub>2</sub>]<sup>-</sup>. Anal. Calcd for C<sub>24</sub>H<sub>32</sub>BBr<sub>2</sub>ClF<sub>10</sub>Mg<sub>2</sub>O<sub>3</sub> [813.18]: C, 35.45; H, 3.97; Br, 19.65; Cl, 4.36. Found: C, 35.07; H, 3.58; Br, 19.7; Cl, 4.87.

**Synthesis of**  $(C_6F_5)_2BH \cdot SMe_2$ . Me<sub>3</sub>SiCl in SMe<sub>2</sub> (0.75 M; 0.50 mL, 0.38 mmol) was added at room temperature via syringe to a stirred solution of  $\{[Mg_2(Et_2O)_3Br_2Cl]]((C_6F_5)_2BH_2]\}_2$  (0.28 g, 0.17 mmol) in SMe<sub>2</sub> (5 mL), whereupon a colorless precipitate immediately formed. The reaction mixture was stirred for 90 min, all volatiles were

removed under reduced pressure, and the colorless solid residue was suspended in benzene (5 mL). After filtration, the insoluble material was extracted with benzene (2  $\times$  5 mL) and the combined organic phases were freeze-dried in vacuo to obtain (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BH·SMe<sub>2</sub> as a colorless flaky solid. Yield: 0.13 g (90%). All <sup>1</sup>H, <sup>11</sup>B, and <sup>19</sup>F{<sup>1</sup>H} NMR shift values are in full agreement with

All <sup>1</sup>H, <sup>11</sup>B, and <sup>19</sup>F{<sup>1</sup>H} NMR shift values are in full agreement with the published data for  $(C_6F_5)_2BH \cdot SMe_2$  (cf. the Supporting Information for details).<sup>15</sup>

General Procedure for the Hydroboration of Alk-1-ynes.  $\{[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]\}_2$  was suspended in a mixture of benzene (2 mL) and hexane (2 mL). The alk-1-yne (solution in benzene) and Me<sub>3</sub>SiCl (solution in hexane) were added at room temperature via syringe. After the mixture was stirred for 2 h, the conversion was complete (NMR spectroscopic control). The reaction mixture was filtered, the insoluble material was extracted with benzene (2 × 1 mL), and the combined organic phases were evaporated to dryness under reduced pressure to obtain the hydroboration product in pure form.

 $(C_6F_5)_2BC(H)=C(H)^{t}Bu: {[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]]_2}$ (0.10 g, 0.06 mmol), *tert*-butylacetylene (0.13 M in benzene; 0.95 mL, 0.12 mmol), and Me\_3SiCl (0.27 M in hexane; 0.50 mL, 0.14 mmol); yield: 0.036 g (70%).  $(C_6F_5)_2BC(H)=C(H)Ph: {[Mg_2(Et_2O)_3Br_2Cl]-[(C_6F_5)_2BH_2]]_2}$  (0.027 g, 0.017 mmol), phenylacetylene (0.17 M in benzene; 0.20 mL, 0.033 mmol), and Me\_3SiCl (0.18 M in hexane; 0.20 mL, 0.037 mmol); yield: 0.012 g (79%). All <sup>1</sup>H, <sup>11</sup>B, and <sup>19</sup>F{<sup>1</sup>H} NMR shift values are in full agreement with the published data for these compounds (cf. the Supporting Information for details).<sup>11</sup>

X-ray Crystal Structure Analysis of [Mg2(THF)6Br3]- $[(C_6F_5)_2BH_2], \{[Mg_2(Et_2O)_3Br_{2,4}Cl_{0,6}][(C_6F_5)_2BH_2]\}_2 \cdot (toluene) \cdot$ 2CHCl<sub>3</sub>, and  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2 \cdot 2(benzene)$ . Data were collected on a STOE IPDS II two-circle diffractometer with graphitemonochromated Mo Ka radiation. Empirical absorption corrections were performed using the MULABS<sup>28</sup> option in PLATON.<sup>29</sup> The structures were solved by direct methods using the program SHELXS<sup>30</sup> and refined against  $F^2$  with full-matrix least-squares techniques using the program SHELXL-97.31 Five of the six coordinating THF molecules in  $[Mg_2(THF)_6Br_3][(C_6F_5)_2BH_2]$  are disordered over two positions with occupancy factors of 0.51(1), 0.53(3), 0.54(2), 0.60(4), and 0.53(2) for the major occupied sites. The C atoms of the disordered THF molecules were isotropically refined. Bond lengths and angles of the disordered THF molecules were restrained to be equal to those of the nondisordered THF molecule. In  $\{[Mg_2(Et_2O)_3Br_{2.4}Cl_{0.6}][(C_6F_5)_2BH_2]\}_2 \cdot (toluene) \cdot 2CHCl_3,$ the toluene molecule is disordered over two equally occupied positions. One of the Br atoms (Br(1)) was refined as being fully occupied, the remaining two halogen positions were refined as being disordered with Cl but sharing the same coordinates and the same displacement parameters. The respective site occupation factors refined to 0.704(5) for Br(2) and 0.681(5) for Br(3). If both ratios are artificially forced to 0.5:0.5, several peaks appear in the residual electron density map slightly below 1 e  $Å^{-3}$  at distances of ca. 0.5 Å from X(2) and X(3) (cf. Figure 2). If the ratio Br<sup>-</sup>:Cl<sup>-</sup> is refined freely, no significant peak arises close to X(2) and X(3). In  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2 \cdot 2(benzene), the H atoms bonded to B were$ freely refined.

 $\begin{array}{l} CCDC \ reference \ numbers: \ 813324 \ ([Mg_2(THF)_6Br_3][(C_6F_5)_2BH_2]), \\ 813325 \ (\{[Mg_2(Et_2O)_3Br_{2.4}Cl_{0.6}][(C_6F_5)_2BH_2]\}_2 \cdot (toluene) \cdot 2CHCl_3), \\ and \ 813326 \ ([Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2 \cdot 2(benzene)). \end{array}$ 

#### ASSOCIATED CONTENT

**Supporting Information.** Synthesis and crystallization of  $[Mg_2(THF)_6Br_3][(C_6F_5)_2BH_2]$ , three-step synthesis of  $\{[Mg_2(Et_2O)_3Br_2Cl][(C_6F_5)_2BH_2]\}_2$ , and synthesis of  $[Mg(Et_2O)_2]-[(C_6F_5)_2BH_2]_2$ .<sup>1</sup>H, <sup>11</sup>B, and <sup>19</sup>F $\{^{1}H\}$  NMR spectra of  $(C_6F_5)_2BH \cdot SMe_2$ ,  $(C_6F_5)_2BC(H)=C(H)^{t}Bu$ , and  $(C_6F_5)_2BC(H)=C(H)Ph$ .

Selected crystallographic data, plots of the molecular structures, and selected geometric parameters of  $[Mg_2(THF)_6Br_3][(C_6F_5)_2BH_2]$  and  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2 \cdot 2(benzene)$  and ORTEP plot of  $\{[Mg_2(Et_2O)_3Br_2_4Cl_{0.6}][(C_6F_5)_2BH_2]\}_2$ . CIF files for  $[Mg_2(THF)_6Br_3][(C_6F_5)_2BH_2]$ ,  $\{[Mg_2(Et_2O)_3Br_2_4Cl_{0.6}]](C_6F_5)_2BH_2]\}_2 \cdot (toluene) \cdot 2CHCl_3$ , and  $[Mg(Et_2O)_2][(C_6F_5)_2BH_2]_2 \cdot 2(benzene)$ . This material is available free of charge via the Internet at http://pubs.acs.org.

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