

A comparative study of base-free arylcopper reagents for the transfer of aryl groups to boron halides

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Abstract

A comparative study on the reactivity and selectivity of arylcopper species in reactions with boron halides was performed. Mesitylcopper reacts with BX_3 ($X = Cl, Br$) in toluene at low temperature under highly selective formation of the monosubstituted boranes $MesBX_2$. The dimesitylboranes Mes_2BX are gradually formed with a twofold excess of the organocopper reagent at elevated temperature. In contrast, pentafluorophenylcopper shows a tendency for formation of $B(C_6F_5)_3$ in reactions with BX_3 irrespective of the stoichiometry used, suggesting a strong impact of electronic factors on the selectivity of the aryl transfer reaction. New procedures for the synthesis of the pentafluorophenylboron halides $C_6F_5BX_2$ ($X = Cl$: 57%; $X = Br$: 62%) and of tris(pentafluorophenyl)borane (80%) and related mixed-substituted triarylboranes from the base-free isolable pentafluorophenylcopper precursor have been developed.

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1. Introduction

The most commonly used reagents for the introduction of aryl substituents to main group metal halides are organolithium and Grignard reagents. However, these highly reactive species are often not selective enough to exclusively produce partially arylated mixed-substituted metal complexes. In addition, their preparation in ether solvents can lead to side reactions of the metal halide with the solvent. This problem is frequently encountered in reactions involving Group 13 halides [1]. Less reactive and more selective reagents such as organomercury, organozinc, organotin, or organosilicon species have therefore been developed and are now being widely used [1]. However certain limitations also restrict the general applicability of these reagents as, for example, mercury boron or zinc boron exchange reactions often require high temperatures [2] and silicon–boron exchange is

limited to very strong electrophiles such as boron tribromide or boron trichloride [3]. Furthermore, the use of silicon–boron and tin–boron exchange reactions can in certain cases be hampered by preferred transfer of the alkyl substituents in $ArSiMe_3$ or $ArSnMe_3$ over the desired reaction of the silicon–aryl bond [4]. We are currently exploring the application of arylcopper reagents for the selective transfer of aryl groups to Group 13 halides as part of our studies aimed at the development of new multifunctional and polymeric Lewis acids [4d,5]. The use of organocopper reagents may provide an interesting option in this chemistry especially in view of the high toxicity of organomercury and organotin species.

Despite extensive studies on structural aspects, the unique bonding situation in organocopper compounds, and their widespread applications in organic synthesis for carbon–carbon bond formation via organocopper intermediates [6], the use of organocopper reagents as alkyl or aryl transfer reagents in organometallic synthesis has been studied only in very few specific cases. Most notably, van Koten and coworkers have intro-

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duced organocopper reagents $[\text{ArCu}]_n$ ($\text{Ar} = 2\text{-Me}_2\text{NCH}(\text{Me})\text{C}_6\text{H}_4$) with donor substituents in *ortho*-position for the preparation of hypercoordinate organotin compounds ArRSnX_2 and Ar_2SnX_2 [7] including chiral species $\text{ArRR}'\text{SnX}$ [8]. Furthermore, formation of the trisubstituted tin halides Ph_3SnX and Me_2PhSnX from phenylcopper was found to proceed with high selectivity [7a]. Even monosubstituted organotin halides ArSnCl_3 are accessible in very high yield when the bulkier mesityl group is used [9]. However, few studies on the reactivity of organocopper species toward Group 13 halides have been undertaken [10,11].

We report in this paper on the influence of electronic characteristics of organocopper reagents on the reactivity and selectivity in metathesis reactions with boron halides. In order to account for electronic effects, we undertook a detailed comparative study of two arylcopper species, mesitylcopper [12] and pentafluorophenylcopper [13], which feature similar steric yet very different electronic properties. An impact of the electronic characteristics on the reactivity may be expected as, for example, structural aspects of organocopper species are known to strongly depend on the nature of the organic substituents [6]. Indeed, we have recently discovered that pentafluorophenylcopper displays a tetrameric structure with unique π -coordination of toluene in the solid state [14], whereas Håkansson and coworker have shown that mesitylcopper crystallizes as a pentamer from toluene without any interactions between copper and cocrystallized toluene molecules [12d].

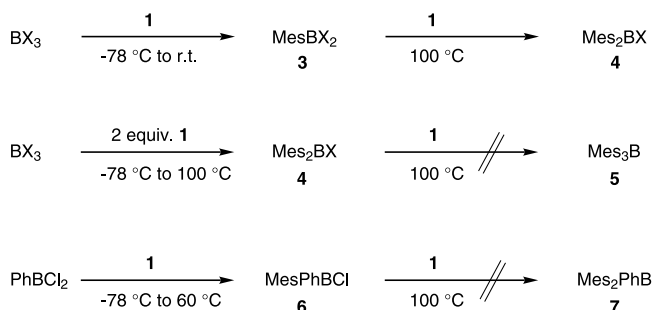
2. Results and discussion

The toluene solvate of mesitylcopper was synthesized as described by Håkansson and coworker [12d] and pentafluorophenylcopper can be prepared conveniently and in large quantities from the Grignard reagent and CuCl in diethyl ether according to a procedure reported by Cairncross and Sheppard [13]. Colorless crystals of $[\text{CuMes}]_5 \cdot \text{toluene}$ (**1**) and $[\text{Cu}(\text{C}_6\text{F}_5)]_4(\eta^2\text{-toluene})_2$ (**2**) were obtained by recrystallization from toluene at -37°C . Freshly prepared solutions of **1** and **2** were reacted in toluene with the chosen boron halide in a 1:1, 2:1, or 3:1 ratio, respectively. The crude reaction mixtures were filtered, analyzed by $^1\text{H-NMR}$ spectroscopy, and the products were subsequently isolated by recrystallization or distillation. Results for reactions of **1** and **2** with selected boron halides in toluene solution are summarized in Tables 1 and 2. Both yields as determined by $^1\text{H-NMR}$ spectroscopy and isolated yields after recrystallization or distillation of the product are given based on the limiting reagent.

2.1. Reactivity of mesitylcopper toward boron halides [15,16]

A number of different routes for the synthesis of mesityldichloroborane (**3a**) and mesityldibromoborane (**3b**) in moderate to high yields have been previously described. These include reactions of mesitylboroxin (22%) [17], mesitylmercuric bromide (49%) [18], or mesityltrimethylsilane (75–84%) [3b,3c] with BCl_3 or BBr_3 . However, in the series of dimesitylboron halides, the only thoroughly studied compound is dimesitylboron fluoride, which is obtained through reaction of mesityllithium or the Grignard reagent with $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

We found that when **1** was treated with a slight excess (1.05 equivalents) of BCl_3 or BBr_3 in toluene at -78°C and allowed to slowly warm to ambient temperature, the spectroscopically pure monoarylated boranes **3a** and **3b** were obtained in very high yields. NMR spectroscopy did not reveal formation of any diarylated by-product. The isolated yields for **3a** and **3b** after high-vacuum distillation (Scheme 1; Table 1) were 88 and 91%, respectively. Even when a twofold excess of **1** was treated with BCl_3 or BBr_3 under similar conditions, further reaction did not take place, but the monoarylated species **3a** and **3b** were observed as the major product in addition to unreacted **1**. Only after prolonged heating of the mixture to 100°C was a second aryl group transferred to the boron center to give the dimesitylboron halides **4a** and **4b** in ca. 60 and 95% spectroscopic yield, respectively (Scheme 1). Alternatively, the isolated species MesBX_2 ($\text{X} = \text{Cl}, \text{Br}$) may be treated with one equivalent **1** at ambient temperature and subsequently heated to 100°C for 12 h to give **4a** and **4b** in slightly higher spectroscopic yields of 80 and 97%, respectively. The comparatively lower yield of **4a** was traced back to formation of significant amounts of the coupled by-product dimesitylene, which was identified by comparison of the $^1\text{H-NMR}$ signals with data reported in the literature [19,20]. Compounds **4a** and **4b** were purified by recrystallization from hexanes at -37°C and isolated in 34 and 74% yield, respectively. Even though a slight excess of the organocopper reagent was employed, the trisubstituted product, trimesitylborane (**5**), was not



Scheme 1. Reactions of **1** with boron halides; $\text{X} = \text{Cl}, \text{Br}$.

Table 1
NMR spectroscopic and isolated yields for reactions of **1** with boron halides

CuAr	Borane (equivalent)	Conditions	NMR (%yield) ^a			Isolated species (%yield)
			ArBX ₂	Ar ₂ BX	Ar ₃ B	
1	BCl ₃ (1.05)	−78 °C to r.t.	> 97	0	0	3a (88)
1	BBr ₃ (1.05)	−78 °C to r.t.	> 97	0	0	3b (91)
1	BCl ₃ (0.48)	−78 to 100 °C; 24 h	15	60	0	3a , 3b , 3c , 3d
1	BBr ₃ (0.48)	−78 to 100 °C; 12 h	0	95	0	4b (72) ^d
1	PhBCl ₂ (1.05)	−78 to 60 °C; 2 h	–	95	0	6 (84) ^e
1	PhBCl ₂ (0.48)	r.t. to 100 °C; 12 h	–	50	0	3a , 3b , 3c
1	MesBCl ₂ (1.0)	r.t. to 100 °C; 12 h	15	80	0	4a (34) ^c
1	MesBBr ₂ (1.0)	r.t. to 100 °C; 12 h	–	97	0	4b (74)

^a Estimated yield from ¹H-NMR spectroscopy.

^b The product was not isolated.

^c The coupling product dimesitylene was observed as a major by-product.

^d The diarylated species was not formed at room temperature.

^e The reaction started below room temperature.

formed. Indeed, we did not observe formation of species **5** even when a larger excess of **1** (above three equivalents) was used under forcing reaction conditions (36 h at 100 °C) [21].

We anticipated that steric factors may be dominating the reactivity of the tetrameric species **1** and therefore decided to study the reactivity of dichlorophenylborane. Indeed, **1** slowly reacts with PhBCl₂ even below room temperature to give mesitylphenylchloroborane (**6**) in 95% spectroscopic yield. However, the reduction in steric bulk did not lead to placement of three aryl groups at boron. Reaction of PhBCl₂ with two equivalents of **1** did not give the expected dimesitylphenylborane (**7**), but resulted in formation of the coupling product dimesitylene in addition to monosubstituted **6**. In a similar reaction between the isolated species **6** and **1** no reaction was observed even after 36 h at 100 °C.

2.2. Reactivity of pentafluorophenylcopper toward boron halides [22,23]

Due to the strongly electron-withdrawing nature of the aryl group, pentafluorophenyltrimethylsilane and pentafluorophenyltrimethylstannane cannot readily be applied to the synthesis of (perfluoroaryl)boranes through silicon or tin–boron exchange reactions [24]. In contrast to the typically observed reactivity pattern, transfer of a methyl group occurs more readily than that of the aryl group. The pentafluorophenyl group is therefore transferred only under forcing conditions with an excess of borane [25]. The currently most widely used reagent is bis(pentafluorophenyl)dimethyltin, which has first been described by Chambers and Chivers [26] in 1963. A number of studies have since been undertaken aimed at the development of a new alternative methodology. Most notably, Bochmann and coworkers [2e] have introduced pentafluorophenylmer-

curic bromide, which gives dibromo(pentafluorophenyl)borane and bromobis(pentafluorophenyl)borane in 80 and 35% yield, respectively. Similarly, Frohn et al. [2f] have synthesized C₆F₅BBr₂ from C₆F₅HgEt and BBr₃ in 82% yield. Moreover, Piers and coworkers have recently investigated bis(pentafluorophenyl)zinc as a potential reagent [2g]. Although reaction of the organozinc reagent with boron halides does not lead to selective formation of the mono- or diarylated products, the arylzinc reagent has proven highly useful for the synthesis of triarylated boranes [2g]. Given the successful use of mesitylcopper in reactions with boron halides, we anticipated that pentafluorophenylcopper (**2**) may also serve as a selective reagent for the introduction of pentafluorophenyl groups at boron.

Pentafluorophenylcopper (**2**) was treated with boron trichloride or boron tribromide, respectively, in toluene at −78 °C; the reaction mixture was allowed to warm up to ambient temperature, and the product distribution was studied by ¹⁹F-NMR spectroscopy. The predominant species observed by NMR in equimolar reactions with either BCl₃ or BBr₃ are the monosubstituted compounds C₆F₅BCl₂ (**8a**) and C₆F₅BBr₂ (**8b**). However, the desired products are accompanied by small amounts of the diarylated boranes (C₆F₅)₂BX (**9a**, **9b**) and the triarylated tris(pentafluorophenyl)borane (**10**) (Table 2; Scheme 2). In order to maximize the yield of the aryldichloroboranes **8a** and **8b**, we decided to add the organocopper species to an excess of boron halide at low temperature. Such a reverse addition protocol indeed improves the spectroscopic yields, but does not completely eliminate formation of **9** or **10** (Table 2). However, careful fractional vacuum distillation allowed us to obtain compounds **8a** and **8b** with isolated yields of 57 and 62%, respectively.

Low-temperature reaction of BBr₃ with three equivalents of **2** gave the triarylated species tris(pentafluor-

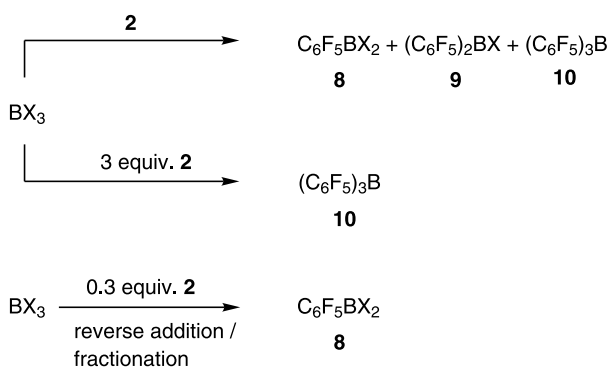
Table 2
NMR spectroscopic and isolated yields for reactions of **2** with boron halides

CuAr	Borane (equivalent)	Conditions	NMR (%yield) ^a			Isolated species (%yield)
			ArBX ₂	Ar ₂ BX	Ar ₃ B	
2	BCl ₃ (1.00)	−78 °C to r.t.	56	30	14	b
2	BCl ₃ (0.50)	−78 °C to r.t.	28	35	37	b
2	BBr ₃ (1.00)	−78 °C to r.t.	74	16	10	b
2	BBr ₃ (0.50)	−78 °C to r.t.	34	23	43	b
2	BBr ₃ (0.33)	−78 °C to r.t.	0	0	> 97	10 (80)
2	PhBCl ₂ (0.5)	−78 °C to r.t.	–	5	95	11 (56)
2	BCl ₃ (3)	−78 °C to r.t. ^c	65	27	8	8a (57)
2	BBr ₃ (3)	−78 °C to r.t. ^c	87	10	3	8b (62)

^a Estimated yield from ¹⁹F-NMR spectroscopy.

^b Separation of the individual boranes was not attempted.

^c A solution of the organocopper reagent in CH₂Cl₂ was slowly added to the borane solution.



Scheme 2. Reactions of **2** with boron halides; X = Cl, Br.

ophenyl)borane (**10**) [27] selectively and in high yield (80% after sublimation). Similarly, mixed triarylated boranes are readily accessible from arylboron halides through reaction with **2** in non-coordinating solvents. For example, the reaction of phenyldichloroborane with **2** yields PhB(C₆F₅)₂ (**11**) in ca. 95% spectroscopic yield [28,29]. Especially noteworthy is that these reactions are conveniently performed in aromatic or chlorinated solvents, in which both the organocopper species and the boron halide are highly soluble and perfectly stable. Moreover, the products are obtained in >95% purity according to ¹H- and ¹⁹F-NMR analyses and are readily isolated by filtration from the insoluble copper halides.

3. Summary and conclusions

We have performed a comparative study on the reactivity and selectivity of arylcopper species in reactions with boron halides. The reagents [CuMes]₅-toluene and [(C₆F₅)Cu]₄(η²-toluene)₂ were chosen because of their similar steric, yet very different electronic properties. Furthermore, the mesityl- and pentafluorophenylboranes obtained through reaction with boron halides

are highly useful intermediates in the development of powerful multifunctional Lewis acid catalysts and of advanced molecular and polymeric luminescent materials [15,16,22,23].

We found that mesitylcopper reacts with boron halides BX₃ (X = Cl, Br) under highly selective formation of the monosubstituted borane MesBX₂ or the disubstituted Mes₂BX depending on the molar ratio of the reagents and the temperature. To our knowledge, the unusually high selectivity for the species MesBX₂ surpasses that of any other currently available method such as the use of mercury reagents or arylsilanes. Although a preference for formation of (C₆F₅)BX₂ at low temperature was observed, overall the selectivity for monoarylated or diarylated species was considerably lower with pentafluorophenylcopper. However, use of an excess of borane BX₃ in a reverse addition protocol followed by high-vacuum fractionation gives the monoarylated boranes C₆F₅BX₂ in moderate to good yields. Moreover, pentafluorophenylcopper serves as a convenient base-free reagent for the high-yield synthesis of tris(pentafluorophenyl)borane and related mixed-substituted species such as phenylbis(pentafluorophenyl)borane.

Our observations indicate that both the steric and electronic nature of the mono- and diarylated intermediates critically effect the overall selectivity. Highly selective formation of MesBX₂ can be traced back to the lower Lewis acidity and increased steric bulk of MesBX₂ relative to BX₃. Use of the less sterically encumbered phenyldichloroborane leads to faster but still very selective formation of MesPhBCl. In contrast to the strongly reduced Lewis acidity of MesBX₂, C₆F₅BX₂ represents an organoboron halide of only slightly lower Lewis acidity than that of the boron halides BX₃ themselves [30]. Consequently, a lower selectivity is observed and steric effects rather than electronic factors are likely responsible for the preference for formation of

the monoarylated species $(C_6F_5)BX_2$ at low temperature.

In comparison to other organometallic reagents, aryl copper species show on one hand higher reactivity than arylsilanes or arylmercury species and on the other hand improved selectivity compared to highly reactive organolithium species or Grignard reagents. The ease of isolation and purification of the arylcopper compounds and their suitability for reactions in inert solvents such as hexanes, toluene, and even chlorinated solvents provide additional advantages. Organocopper reagents therefore represent an interesting alternative to currently used highly toxic organotin and organomercury species.

4. Experimental

4.1. Materials and general methods

The compounds 2-bromomesitylene, CuCl (prepurified grade), CuBr, and BCl_3 (1 M in hexanes) were purchased from Acros; $PhBCl_2$, BCl_3 (1 M in CH_2Cl_2) and BBr_3 were purchased from Aldrich and C_6F_5Br was purchased from Fluorochem. The compounds $PhBCl_2$, BBr_3 , and C_6F_5Br were distilled under vacuum prior to use, and CuBr was purified according to a literature procedure [31]. Mesitylcopper [12] and pentafluorophenylcopper [13] were prepared according to literature procedures and recrystallized from toluene. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies); chlorinated solvents were subsequently degassed via several freeze pump thaw cycles. All 500 MHz 1H -NMR spectra, 125.7 MHz ^{13}C -NMR spectra, and 470.2 MHz ^{19}F -NMR spectra were recorded on a Varian INOVA NMR spectrometer operating at 499.91 MHz. The 400 MHz 1H -NMR spectra, 100.5 MHz ^{13}C -NMR spectra, 376.2 MHz ^{19}F -NMR spectra, and 128.3 MHz ^{11}B -NMR spectra were recorded on a Varian VXR-S spectrometer. All solution's 1H - and ^{13}C -NMR spectra were referenced internally to the solvent signals. ^{11}B -NMR spectra were referenced externally to $BF_3 \cdot Et_2O$ ($\delta = 0$) and ^{19}F -NMR spectra were referenced to $\alpha, \alpha', \alpha''$ -trifluorotoluene (0.05% in C_6D_6 ; $\delta = -63.73$). All NMR spectra were recorded at ambient temperature. The abbreviations Mes and Pf are used for 2,4,6-trimethylphenyl and for pentafluorophenyl, respectively. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

Caution! BBr_3 and BCl_3 are toxic and highly corrosive and should be handled appropriately with great care.

Fluorinated grease was used for ground glass joints in reactions involving boron trihalides.

4.2. Reaction of **1** with one equivalent BCl_3 : synthesis of **3a** [17]

A solution of BCl_3 (5.2 ml, 1 M in hexanes, 5.2 mmol) was added dropwise to a suspension of **1** (1.00 g, 4.97 mmol) in toluene (25 ml) at $-78^\circ C$. The suspension immediately turned orange-red upon addition of the borane. The mixture was stirred at $-78^\circ C$ for 2 h and then allowed to slowly warm to room temperature (r.t.) overnight yielding a white precipitate in a colorless solution. After filtration from the insoluble material all volatile components were removed under high vacuum. The spectroscopic yield of **3a** was determined by 1H -NMR to be $>97\%$. The crude product was purified by distillation under reduced pressure to give 0.88 g (88%) analytically pure **3a** as a colorless liquid. For **3a**: 1H -NMR (C_6D_6 , 400 MHz): $\delta = 6.54$ (s, 2H, *meta*-Ph), 2.14 (s, 6H, *ortho*-Me), 2.01 (s, 3H, *para*-H); ^{13}C -NMR (C_6D_6 , 125.7 MHz): $\delta = 140.0$ (*para*-Mes), 137.7 (*ortho*-Mes), 136 (br, *ipso*-Mes), 128.1 (*meta*-Mes), 21.9 (*ortho*-Me), 21.1 (*para*-Me); ^{11}B -NMR (C_6D_6 , 128.3 MHz): $\delta = 60.3$ ($h_{1/2} = 250$ Hz); $C_9H_{11}BCl_2$ (200.90)—Calc.: C, 53.81; H, 5.51. Found: C, 54.54; H, 5.70%.

4.3. Reaction of **1** with one equivalent BBr_3 : synthesis of **3b** [3b,3c,18]

A solution of BBr_3 (2.63 g, 10.5 mmol) in toluene (5 ml) was added dropwise at $-78^\circ C$ to a suspension of **1** (2.01 g, 10.0 mmol) in toluene (25 ml). The suspension immediately turned orange-red upon addition of the borane. The mixture was stirred at $-78^\circ C$ for 2 h and then allowed to slowly warm to r.t. overnight yielding a white precipitate in a colorless solution. After filtration from the insoluble material all volatile components were removed under high vacuum. The spectroscopic yield of **3b** was determined by 1H -NMR to be $>97\%$. The crude product was purified by distillation under reduced pressure to give 2.64 g (91%) analytically pure **3b** as a colorless liquid. For **3b**: 1H -NMR (C_6D_6 , 500 MHz): $\delta = 6.52$ (s, 2H, *meta*-Ph), 2.14 (s, 6H, *ortho*-Me), 2.02 (s, 3H, *para*-Me); ^{13}C -NMR (C_6D_6 , 100.5 MHz): $\delta = 141.0$ (br, *ipso*-Mes), 139.9 (*para*-Mes), 136.0 (*ortho*-Mes), 128.2 (*meta*-Mes), 21.7 (*ortho*-Me), 21.0 (*para*-Me); ^{11}B -NMR (C_6D_6 , 128.3 MHz): $\delta = 62.1$ ($h_{1/2} = 230$ Hz); $C_9H_{11}BBr_2$ (289.80)—Calc.: C, 37.30; H, 3.83. Found: C, 38.05; H, 3.88%.

4.4. Reaction of **1** with 0.5 equivalent BCl_3 : attempted synthesis of **4a**

A solution of BCl_3 (4.8 ml, 1 M in xylene, 4.8 mmol) was added dropwise to a suspension of **1** (2.01 g, 10.0

mmol) in toluene (30 ml) at -78°C . The reaction mixture immediately turned orange-red and was stirred at -78°C for 4 h. The mixture was then allowed to warm to r.t. and stirred for an additional 12 h. During this period the precipitate turned light orange. $^1\text{H-NMR}$ spectroscopy of the light yellow solution showed the formation of **3a** and an unidentified species that gives rise to a set of broad peaks (δ (C_6D_6) = 6.66 (br s, 2H), 2.73 (br s, 6H), 1.98 (br s, 3H)) in addition to residual starting material **1**. The mixture was then slowly heated to 100°C and kept stirring for 12 h. The precipitate turned purple and a colorless solution was obtained. After filtration from the insoluble material all volatile components were removed under high vacuum. $^1\text{H-NMR}$ spectroscopy showed the formation of **4a** (ca. 60%), **3a** (ca. 15%), and the coupling product dimesitylene (ca. 15%). Isolation of **4a** was not attempted.

4.5. Reaction of **1** with **3a**: alternative synthesis of **4a**

A solution of **3a** (1.09 g, 5.43 mmol) in toluene (5 ml) was added to a solution of **1** (1.09 g, 5.42 mmol) in toluene (25 ml). At r.t. no reaction was observed. Upon heating of the mixture to 100°C for 36 h the solution gradually turned colorless and a white precipitate formed. After filtration from the insoluble material all volatile components were removed under high vacuum. The spectroscopic yield of **4a** was determined by $^1\text{H-NMR}$ to 80%. All volatile materials were removed first at r.t. and then at 100°C under high vacuum. The residue was purified by recrystallization from hexanes at -37°C to give 0.53 g (34%) analytically pure **4a** as a colorless crystalline solid. For **4a**: $^1\text{H-NMR}$ (C_6D_6 , 500 MHz): δ = 6.66 (s, 4H, *meta*-Ph), 2.31 (s, 12H, *ortho*-Me), 2.07 (s, 6H, *para*-Me); $^{13}\text{C-NMR}$ (C_6D_6 , 100.5 MHz): δ = 140.9 (*ortho*-Mes), 140.4 (*para*-Mes), 139 (br, *ipso*-Mes), 129.3 (*meta*-Mes), 23.2 (*ortho*-Me), 21.2 (*para*-Me); $^{11}\text{B-NMR}$ (C_6D_6 , 128.3 MHz): δ = 69.5 ($h_{1/2}$ = 650 Hz); $\text{C}_{18}\text{H}_{22}\text{BCl}$ (284.64)—Calc.: C, 75.96; H, 7.79. Found: C, 76.01; H, 7.91%.

4.6. Reaction of **1** with 0.5 equivalent BBr_3 : synthesis of **4b**

A solution of BBr_3 (0.45 ml, 4.75 mmol) in toluene (5 ml) was added dropwise at -78°C to a suspension of **1** (2.01 g, 10.0 mmol) in toluene (25 ml). The suspension immediately turned orange-red upon addition of the borane. The reaction mixture was allowed to slowly warm to r.t., which resulted in an orange suspension. $^1\text{H-NMR}$ spectroscopy of the light yellow solution indicated the formation of **3b** in addition to residual starting material **1**. Upon heating of the mixture to 100°C for 12 h the solution turned colorless and a white precipitate formed. After filtration from the insoluble material all volatile components were removed under

high vacuum. The spectroscopic yield of **4b** was determined by $^1\text{H-NMR}$ to 95%. The crude product was purified by recrystallization from hexanes at -37°C to give 1.04 g (72%) analytically pure **4b** as a colorless crystalline solid. $^1\text{H-NMR}$ (C_6D_6 , 500 MHz): δ = 6.64 (s, 4H, *meta*-Ph), 2.34 (s, 12H, *ortho*-Me), 2.05 (s, 6H, *para*-Me); $^{13}\text{C-NMR}$ (C_6D_6 , 100.5 MHz): δ = 141.0 (br, *ipso*-Mes), 140.4 (*para*-Mes), 140.3 (*ortho*-Mes), 129.4 (*meta*-Mes), 23.5 (*ortho*-Me), 21.2 (*para*-Me); $^{11}\text{B-NMR}$ (C_6D_6 , 128.3 MHz): δ = 72.1 ($h_{1/2}$ = 600 Hz); $\text{C}_{18}\text{H}_{22}\text{BBr}$ (329.09)—Calc.: C, 65.70; H, 6.74. Found: C, 65.20; H, 6.91%.

4.7. Reaction of **1** with **3b**: alternative synthesis of **4b**

A solution of **3b** (0.67 g, 2.31 mmol) in toluene (5 ml) was added to a solution of **1** (0.50 g, 2.43 mmol) in toluene (25 ml) at r.t. No reaction was observed at r.t. Upon heating of the mixture to 100°C for 3 h the solution gradually turned colorless and a white precipitate formed. After filtration from the insoluble material all volatile components were removed under high vacuum. The spectroscopic yield of **4b** was determined by $^1\text{H-NMR}$ to be 97%. The crude product was purified by recrystallization from hexanes at -37°C to give 0.56 g (74%) of analytically pure **4b** as a colorless crystalline solid.

4.8. Reaction of **1** with PhBCl_2 : synthesis of **6**

A solution of PhBCl_2 (1.36 ml, 10.5 mmol) in toluene (5 ml) was added dropwise to a solution of **1** (2.01 g, 10.0 mmol) in toluene (25 ml) at -78°C . The suspension gradually turned orange-red upon addition of the borane. The reaction mixture was allowed to slowly warm to r.t. and subsequently kept at 60°C for 2 h. A white precipitate formed in a colorless solution. After filtration from the insoluble material all volatile components were removed under high vacuum. The spectroscopic yield of **6** was determined by $^1\text{H-NMR}$ to be 95%. The crude product was purified by distillation to give 2.17 g (84%) spectroscopically pure **6** as a colorless liquid. $^1\text{H-NMR}$ (C_6D_6 , 500 MHz): δ = 8.03 (d, J = 8 Hz, 2H, *ortho*-Ph), 7.18 (t, J = 8 Hz, 1H, *para*-Ph), 7.08 (ps t, J = 8 Hz, 2H, *meta*-Ph), 6.72 (s, 2H, *meta*-Mes), 2.18 (s, 3H, *para*-Me), 2.10 (s, 6H, *ortho*-Me); $^{13}\text{C-NMR}$ (C_6D_6 , 125.7 MHz): δ = 138.5 (*para*-Mes), 138.5–138.0 (br, *ipso*-Mes, *ipso*-Ph), 137.8 (*ortho*-Mes), 137.7 (*ortho*-Ph), 134.7 (*para*-Ph), 128.5, 127.9 (*meta*-Ph, *meta*-Mes), 22.2 (*ortho*-Me), 21.2 (*para*-Me); $^{11}\text{B-NMR}$ (C_6D_6 , 128.3 MHz): δ = 67.4 ($h_{1/2}$ = 550 Hz).

4.9. Reaction of **1** with 0.5 equivalent PhBCl_2 : attempted synthesis of **7**

A solution of PhBCl_2 (96 mg, 0.61 mmol) in toluene was added dropwise to a suspension of **1** (0.25 g, 1.21 mmol) in toluene (50 ml) at -78°C . The reaction mixture immediately turned orange-red and was stirred at -78°C for 4 h. $^1\text{H-NMR}$ spectroscopy of the light yellow solution indicated the formation of **6** in addition to starting material **1**. The mixture was then slowly heated to 100°C and kept stirring for 12 h. The precipitate turned purple and a clear solution was obtained. After filtration from the insoluble material all volatile components were removed under high vacuum. $^1\text{H-NMR}$ spectroscopy indicated the formation of **6** (ca. 50%) and dimesitylene (ca. 45%).

4.10. Reactions of **1** with **4a**, **4b**, and **6**: attempted synthesis of **5** and **7**

A solution of the borane (1.0 mmol) in toluene (5 ml) was added to a solution of **1** (0.21 g, 1.0 mmol) in toluene (25 ml) at r.t. The mixture was heated to 100°C for 36 h. $^1\text{H-NMR}$ spectroscopy showed in all cases the presence of unreacted borane and **1**.

4.11. General procedure for reactions of **2** with BCl_3 and BBr_3

A solution of BCl_3 (1.0 ml, 1 M in hexanes, 1.0 mmol) or BBr_3 (0.25 g, 1.0 mmol) in toluene (3 ml) was added to a solution of **2** (0.28 g, 1.0 mmol) in toluene (25 ml) at -78°C . The reaction mixture was stirred at -78°C for 1 h and then allowed to gradually warm to r.t. With BBr_3 initially a blue-colored precipitate formed, which gradually turned off-white, whereas with BCl_3 a white precipitate is formed immediately. The product distribution in the colorless supernatant was estimated by $^{19}\text{F-NMR}$ spectroscopy (see Table 2). Preparative reactions were performed as described with toluene-free **2** in CH_2Cl_2 in order to facilitate work up of the products (Scheme 2).

4.12. Reaction of **2** with excess of BCl_3 : synthesis of **8a** [26b]

Compound **2** was repeatedly extracted with hexanes and subsequently dried under high vacuum at ambient temperature for 12 h. A solution of toluene-free **2** (3.60 g, 15.6 mmol) in CH_2Cl_2 (20 ml) was added dropwise over a period of 20 min to a solution of BCl_3 (41.4 ml, 1.13 M in CH_2Cl_2 , 46.8 mmol) at -78°C . Upon addition a white precipitate formed. The reaction mixture was stirred at -78°C for 1 h and then allowed to slowly warm to r.t. and allowed to stir for 3 h. After filtration from the insoluble material, all volatile com-

ponents were slowly removed under high vacuum first at -25°C and subsequently over a period of 3 h at 0°C . The crude product was distilled under dynamic vacuum at ca. 40°C and condensed into a trap cooled with liquid N_2 . Vacuum transfer of the crude product from the trap into a Teflon-stoppered storage flask yielded spectroscopically pure **8a** as a colorless liquid in a yield of 2.23 g (57%). $^{19}\text{F-NMR}$ (C_6D_6 , 470.2 MHz): $\delta = -129.9$ (m, 2F, *ortho*-F), -146.6 (tr, $J(\text{F}, \text{F}) = 21$ Hz, 1F, *para*-F), -162.4 (m, 2F, *meta*-F); $^{13}\text{C-NMR}$ (C_6D_6 , 125.7 MHz): $\delta = 146.5$ (d, $J(\text{F}, \text{C}) = 256$ Hz, *ortho*-F), 142.5 (d, $J(\text{F}, \text{C}) = 261$ Hz, *para*-F), 135.5 (d, $J(\text{F}, \text{C}) = 253$ Hz, *meta*-F), n.o. (*ipso*-F); $^{11}\text{B-NMR}$ (C_6D_6 , 128.3 MHz): $\delta = 52.3$ ($h_{1/2} = 130$ Hz).

4.13. Reaction of **2** with excess of BBr_3 : synthesis of **8b** [2e,2f]

Compound **2** was repeatedly extracted with hexanes and subsequently dried under high vacuum at ambient temperature for 12 h. A solution of toluene-free **2** (2.61 g, 11.3 mmol) in CH_2Cl_2 (20 ml) was added dropwise over a period of 20 min to a solution of BBr_3 (8.37 g, 34.0 mmol) in CH_2Cl_2 (30 ml) at -78°C . Upon addition a white precipitate formed. The reaction mixture was stirred at -78°C for 1 h and then slowly warmed to r.t. and allowed to stir for 3 h. After filtration from the insoluble material, all volatile components were slowly removed at -20°C under high vacuum. The crude product was distilled under dynamic vacuum at ca. 50°C and condensed into a trap cooled with liquid N_2 . The crude product was transferred under static vacuum from the trap into a Teflon-stoppered storage flask and was subsequently kept under dynamic vacuum at 0°C for 6 h in order to remove the excess boron tribromide. Spectroscopically pure **8b** was obtained as a colorless liquid in a yield of 2.40 g (62%). $^{19}\text{F-NMR}$ (C_6D_6 , 470.2 MHz): $\delta = -130.3$ (m, 2F, *ortho*-F), -147.4 (tr, $J(\text{F}, \text{F}) = 20$ Hz, 1F, *para*-F), -161.9 (m, 2F, *meta*-F); $^{13}\text{C-NMR}$ (C_6D_6 , 100.5 MHz): $\delta = 146.2$ (d, $J(\text{F}, \text{C}) = 252$ Hz, *ortho*-F), 143.7 (d, $J(\text{F}, \text{C}) = 254$ Hz, *para*-F), 137.4 (d, $J(\text{F}, \text{C}) = 253$ Hz, *meta*-F), n.o. (*ipso*-F); $^{11}\text{B-NMR}$ (C_6D_6 , 128.3 MHz): $\delta = 53.3$ ($h_{1/2} = 150$ Hz).

4.14. Reaction of three equivalents of **2** with BBr_3 : synthesis of $\text{B}(\text{C}_6\text{F}_5)_3$ (**10**) [27]

A solution of BBr_3 (0.48 g; 1.95 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of **2** (1.68 g, 6.06 mmol) in CH_2Cl_2 (20 ml) at -78°C . Upon addition a white precipitate formed. The reaction mixture was stirred at -78°C for 1 h, allowed to slowly warm to r.t., and stirred for an additional 12 h. The reaction

mixture was filtered through a fritted glass disk and washed twice with CH_2Cl_2 (10 ml). All volatile materials were removed under vacuum and the crude product was purified by high-vacuum sublimation at 80°C . Spectroscopically pure $\text{B}(\text{C}_6\text{F}_5)_3$ (**10**) was obtained as a white microcrystalline solid in a yield of 0.83 g (80%). ^{19}F -NMR (C_6D_6 , 470.2 MHz): $\delta = -130.1$ (m, 6F, *ortho*-F), -143.0 (m, 3F, *para*-F), -161.4 (m, 6F, *meta*-F); ^{13}C -NMR (C_6D_6 , 100.5 MHz): $\delta = 148.3$ (d, $J(\text{F}, \text{C}) = 251$ Hz, *ortho*-Pf), 145.2 (d, $J(\text{F}, \text{C}) = 262$ Hz, *para*-Pf), 137.6 (d, $J(\text{F}, \text{C}) = 254$ Hz, *meta*-Pf), n.o. (*ipso*-Pf); ^{11}B -NMR (C_6D_6 , 162.3 MHz): $\delta = 59.4$.

4.15. Reaction of two equivalents of **2** with PhBCl_2 : synthesis of $\text{PhB}(\text{C}_6\text{F}_5)_2$ (**11**) [28]

A solution of PhBCl_2 (0.40 g, 2.52 mmol) in toluene (5 ml) was added dropwise to a solution of **2** (1.39 g, 5.02 mmol) in toluene (30 ml) at -78°C . Upon addition a white precipitate formed. The reaction mixture was stirred at -78°C for 1 h, allowed to slowly warm to r.t., and stirred for an additional 12 h. The reaction mixture was filtered through a fritted glass disk and washed twice with toluene (10 ml). All volatile materials were removed under vacuum and the crude product was purified by crystallization from hexanes at -37°C . Spectroscopically pure $\text{PhB}(\text{C}_6\text{F}_5)_2$ (**11**) was obtained as a colorless crystalline solid in a yield of 0.59 g (56%). ^1H -NMR (C_6D_6 , 500 MHz): $\delta = 7.53$ (d, $J = 8$ Hz, 2H, *ortho*-Ph), 7.25 (t, $J = 8$ Hz, 1H, *para*-Ph), 7.11 (ps t, $J = 8$ Hz, 2H, *meta*-Ph); ^{13}C -NMR (C_6D_6 , 125.7 MHz): $\delta = 146.6$ (d, $J(\text{F}, \text{C}) = 246$ Hz, *ortho*-Pf), 143.1 (d, $J(\text{F}, \text{C}) = 258$ Hz, *para*-Pf), 139.6 (*ortho*-Ph), 137.6 (d, $J(\text{F}, \text{C}) = 253$ Hz, *meta*-Pf), 136.8 (*para*-Ph), 128.6 (*meta*-Ph), 113.8 (*ipso*-Pf), n.o. (*ipso*-Ph); ^{19}F -NMR (C_6D_6 , 376.2 MHz): $\delta = -130.9$ (m, 4F, *ortho*-F), -149.5 (m, 2F, *para*-F), -162.1 (m, 4F, *meta*-F); ^{11}B -NMR (C_6D_6 , 128.3 MHz): $\delta = 60.6$ ($h_{1/2} = 750$ Hz).

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