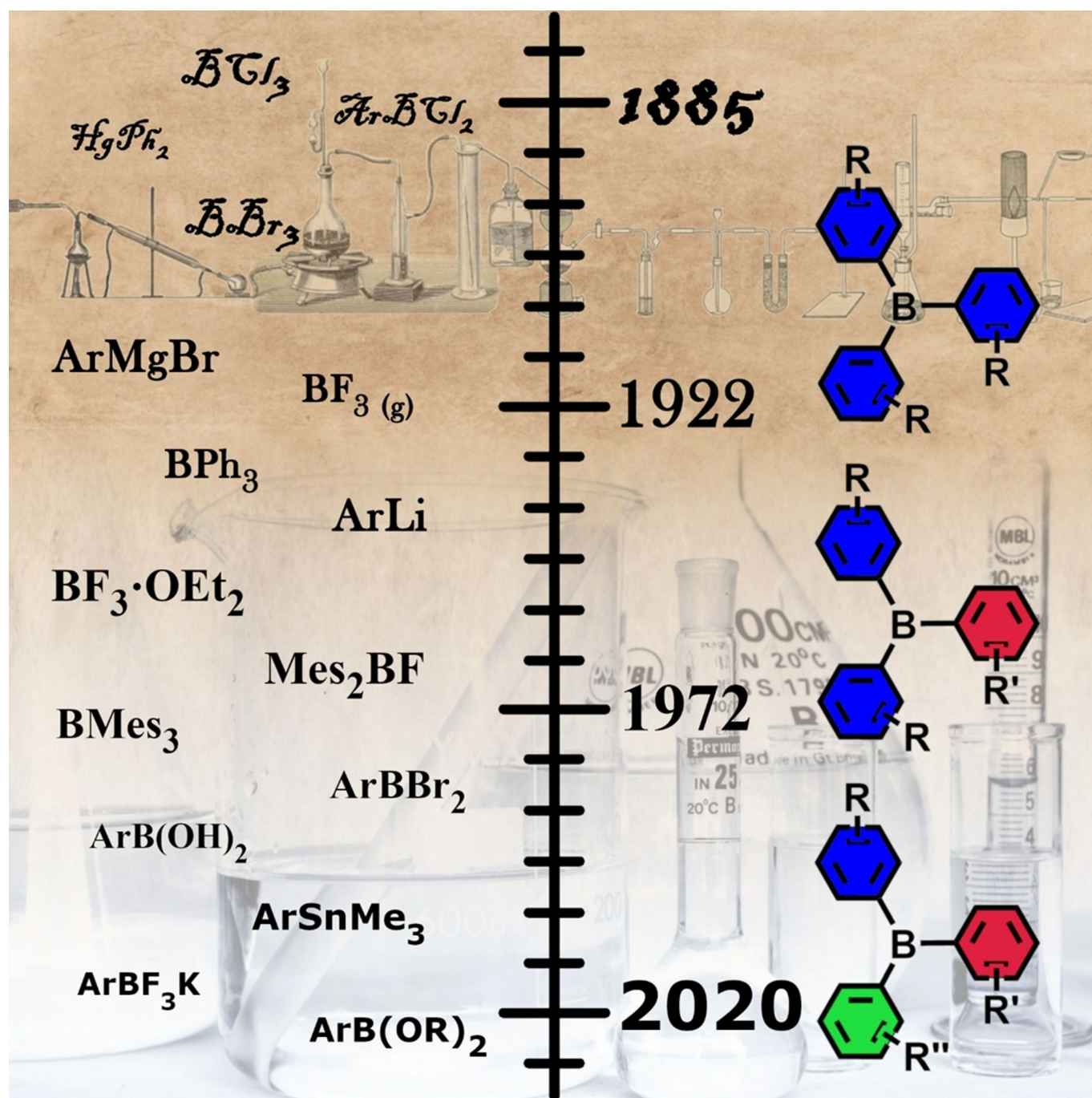


■ Boranes | *Reviews Showcase*

## 🏆 Synthetic Approaches to Triarylboranes from 1885 to 2020

Sarina M. Berger<sup>†</sup>, Matthias Ferger<sup>†</sup>, and Todd B. Marder<sup>\*[a]</sup>*Dedicated to the memory of Professor Suning Wang, a good friend and outstanding boron chemist*

**Abstract:** In recent years, research in the fields of optoelectronics, anion sensors and bioimaging agents have been greatly influenced by novel compounds containing triarylborane motifs. Such compounds possess an empty p-orbital at boron which results in useful optical and electronic properties. Such a diversity of applications was not expected when the first triarylborane was reported in 1885. Synthetic approaches to triarylboranes underwent various changes over the following century, some of which are still used in

the present day, such as the generally applicable routes developed by Krause et al. in 1922, or by Grisdale et al. in 1972 at Eastman Kodak. Some other developments were not pursued further after their initial reports, such as the synthesis of two triarylboranes bearing three different aromatic groups by Mikhailov et al. in 1958. This review summarizes the development of synthetic approaches to triarylboranes from their first report nearly 135 years ago to the present.

## Introduction

Within the last few decades, compounds containing three-coordinate boron motifs have found increasing applicability in various fields including optoelectronics,<sup>[1–3]</sup> selective sensors for anions<sup>[4–6]</sup> or small molecules,<sup>[7,8]</sup> and bioimaging agents<sup>[9–15]</sup> due to the empty p-orbital at the boron center. Whereas numerous compounds and their potential applications have been reviewed by several groups,<sup>[16–23]</sup> synthetic methodology for the preparation of triarylboranes has been reviewed only rarely. In 1956, a summary by Lappert et al. gave a very general overview of the syntheses of many different types of organoboron compounds.<sup>[24]</sup> Very recently, Melen and co-workers summarized synthetic pathways to halogenated triarylboranes as well as their use in catalysis and frustrated Lewis pair (FLP) chemistry.<sup>[25]</sup> This review presents developments in the synthesis of triarylboranes since their first report in 1885.<sup>[26]</sup>

In theory, it is possible to synthesize 3-fold symmetric triarylboranes bearing one type of aromatic system ( $\text{BAr}_3$ ) as well as those containing two or three different aromatic systems ( $\text{BAr}_2\text{Ar}'$  or  $\text{BArAr}'\text{Ar}''$ ). Furthermore, their synthesis should be possible from all known boron trihalides. Recently, the synthesis of triarylboranes from potassium aryltrifluoroborates<sup>[27–31]</sup> and boronic esters<sup>[32]</sup> was reported. We do not discuss dibenzoboroles<sup>[33]</sup> or boron-containing polyaromatic hydrocarbons (B-PAHs)<sup>[34–36]</sup> in our review as both topics have been reviewed recently.

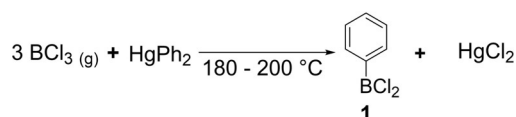
This review is divided into sections based on symmetrically ( $\text{BAr}_3$ ,  $\text{BAr}_2\text{Ar}'$ ) and unsymmetrically substituted ( $\text{BArAr}'\text{Ar}''$ ) triarylboranes depending on the starting material used as the boron source. In this context, the term unsymmetrically substi-

tuted triarylboranes means that the boron center is bound to three different aromatic systems. Symmetrically substituted triarylboranes bear one or two different types of aromatic groups as indicated in parentheses (vide infra) and, thus, have either (exact or approximate) 3-fold or 2-fold symmetry, respectively.

## 1. Synthesis of Symmetrically Substituted Triarylboranes

### 1.1. Boron trichloride, tribromide and boronic esters as boron sources

In 1880, Michaelis and co-workers began to investigate arylboranes to determine the valency of boron which was, at the time, debated to be three or five.<sup>[37]</sup> They reacted gaseous  $\text{BCl}_3$  with diphenylmercury at elevated temperatures in a sealed tube and observed the formation of dichlorophenylborane **1** and  $\text{HgCl}_2$  (Scheme 1). Compound **1** was isolated via distillation and was characterized by elemental analysis and conclusive follow-up chemistry.




Scheme 1. Synthesis of dichlorophenylborane **1** from  $\text{BCl}_3$ .<sup>[37]</sup>


After addition of different aqueous solutions, they obtained phenylboronic acid, the respective ethyl ester and the sodium, calcium and silver salts of the acid, as well as their *p*-tolyl analogues.<sup>[38]</sup> On an interesting side note, phenylboronic acid, as well as its sodium salt, were also investigated for their antiseptic behavior, and were consumed by humans on a gram scale without causing any considerable complaints.<sup>[38]</sup> In 2015,<sup>[39]</sup> a series of boronic acids and esters were tested using the Ames assay,<sup>[40,41]</sup> and most of them were found to be mutagenic. Thus, this class of compounds should be treated with appropriate care and due testing should be performed prior to use in humans, although several boronic acids or related compounds have been approved for use as drugs.<sup>[39]</sup>


In a different approach, Michaelis and co-workers developed a procedure to generate triphenyl derivatives of various main

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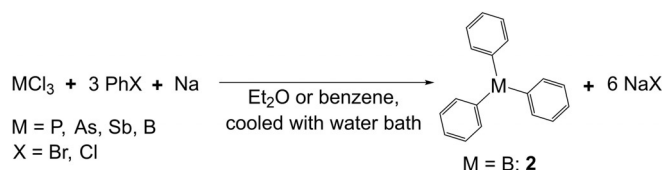
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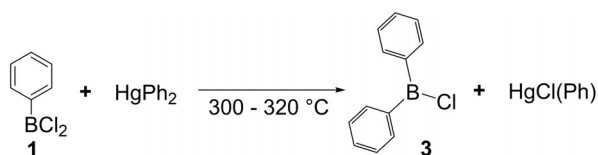
group elements (M), namely phosphorus, arsenic, antimony, and boron.<sup>[42,43]</sup> The respective  $MCl_3$  compound was reacted with a phenylhalide and elemental sodium at low temperature to generate the corresponding triphenyl compound according to Scheme 2.



Scheme 2. Synthesis of triphenyl derivatives of main group elements.<sup>[26,42,43]</sup>

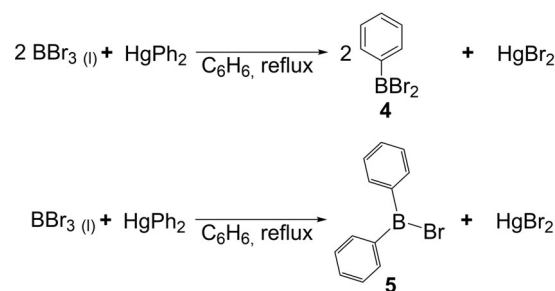
In 1885, Michaelis and co-workers mentioned that, via this general route, a small amount of triphenylborane **2** was obtained, but it was not discussed further.<sup>[26]</sup> To the best of our knowledge, this was the first literature report of the synthesis of a triarylborane. Four years later, the synthesis of **2** was improved by reacting dichlorophenylborane **1** with chlorobenzene and sodium.<sup>[44]</sup> This time, compound **2** was characterized by elemental analysis and the appearance of a green flame characteristic of boron<sup>[45]</sup> when burning the compound.

In 1889, Gattermann and co-workers reported a convenient method for the synthesis of  $BCl_3$ .<sup>[46]</sup> Thus, access to the starting material was facilitated. Therefore, Michaelis et al. synthesized more dichloroarylboranes and their respective boronic acids, namely the *o*-tolyl,  $\alpha$ -naphthyl,  $\beta$ -naphthyl, *p*-methoxyphenyl, *o*-methoxyphenyl and *p*-ethoxyphenyl derivatives.<sup>[47]</sup> For the latter three compounds, the reaction proceeded smoothly at room temperature. Furthermore, chlorodiphenylborane **3** and its borinic acid derivative were reported and characterized. Compound **3** was formed by reacting dichlorophenylborane with diphenylmercury at ca. 300 °C in a sealed tube (Scheme 3). It was noted that triphenylborane **2** was not obtained this way.



Scheme 3. Synthesis of chlorodiphenylborane **3** under harsh conditions.<sup>[47]</sup>

In 1901, Michaelis and co-workers reported an improved method for the synthesis of mono- and diarylboranes in which they replaced gaseous  $BCl_3$  with liquid and, thus, easier to handle  $BBr_3$  as the boron source.<sup>[48]</sup> For this purpose, they developed a convenient and large-scale synthesis of  $BBr_3$  from elemental boron and bromine.  $BBr_3$  was then reacted with diphenylmercury in dry benzene. The reaction was performed in a flask with a reflux condenser at 80 °C. Depending on the stoichiometry, dibromophenylborane **4** and bromodiphenylborane **5** were synthesized and isolated via distillation (Scheme 4).



Scheme 4. Synthesis of mono- and diarylboranes, starting from  $BBr_3$ .<sup>[48]</sup>

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Matthias Feger studied chemistry at the Julius-Maximilians-University of Würzburg. He completed his Bachelor's thesis in the group of Prof. Dr. Udo Radius on anionic  $sp^2$ - $sp^3$  adducts of diboron(4) compounds and received his BSc degree in 2014. He then joined Prof. Dr. Todd B. Marder's group, completed his Master's thesis in 2016 and is currently carrying out his PhD research on the development of methodology for the synthesis of triarylboranes, and on the synthesis and photophysical properties of triarylborane chromophores for DNA and RNA sensing.

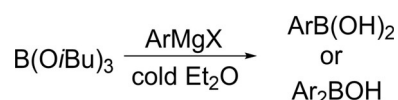


Todd Marder obtained his BSc from M.I.T. and his PhD from UCLA (Regents Intern Fellow). He was a postdoc at the University of Bristol (UK), and a Visiting Research Scientist at DuPont Central Research before joining the faculty at the University of Waterloo, Canada. He moved to the University of Durham (UK) in 1997 as Chair of Inorganic Chemistry and then to the University of Würzburg, Germany in 2012, also as Chair of Inorganic Chemistry. Honors include: the Rutherford Memorial Medal for Chemistry (Royal Society of Canada), RSC (UK) Awards in Main Group Element Chemistry and in Organometallic Chemistry, JSPS Fellowship, Humboldt Research Award, Royal Society Wolfson Research Merit Award, elected member of the Bavarian Academy of Sciences, fellow of the Royal Society of Chemistry (FRSC), the American Association for the Advancement of Science (AAAS), and the European Academy of Science (EurAsc), Visiting/Honorary/Distinguished/Guest Professorships in the UK, France, Hong Kong, mainland China, Japan, India and the Craig Lectureship in Australia.



Some derivatives, namely dibromo-*p*-tolylborane, dibromo-2,4-dimethylphenylborane, and dibromo-2,4,5-trimethylphenylborane were synthesized and characterized, accordingly. The respective boronic and borinic acids were obtained and characterized after hydrolysis. Again, it was mentioned that, despite extensive studies in this direction, triphenylborane could not be isolated. They assumed that triphenylborane had been formed, but complete separation from diphenyl impurities could not be achieved.

Another difficulty of arylborane syntheses were the often laborious and multistep syntheses of the required diarylmercury compounds. With the discovery of the Grignard reagent in 1900, a powerful tool for the transfer of aryl groups became available.<sup>[49]</sup> The first to utilize this in arylborane chemistry, were Khotinsky and Melamed.<sup>[50]</sup> They treated various alkylborate esters with an aryl Grignard reagent in a cold Et<sub>2</sub>O solution. The best results were obtained for the *iso*-butylborate ester. Furthermore, Khotinsky and Melamed characterized the phenylboronic *iso*-butyl ester and the *m*-tolylboronic *iso*-butyl ester, as well as the respective boronic acids after saponification. In an attempt to attach two arenes to the boron using Grignard reagents, Strecker reacted an excess of phenyl magnesium bromide with BCl<sub>3</sub>, but obtained only phenylboronic acid after aqueous work up.<sup>[51]</sup> A more extensive study of the reactions of aryl Grignard reagents with the *iso*-butylborate ester was carried out by König and Scharnbeck in 1915. The results were reported in 1930.<sup>[52]</sup> They characterized several novel arylboronic acids and diarylborinic acids which were synthesized according to Scheme 5 and isolated after aqueous work-up indicating that the organometallic reagent used was too unreactive to form the corresponding triarylborane. More than 70 years later, it was demonstrated by several groups that triarylboranes can also be synthesized using boronic esters as starting materials and more reactive organometallic reagents (*vide infra*).<sup>[39,53–58]</sup>



**Scheme 5.** Synthesis of boronic acids and borinic acids, starting from *iso*-butylborate ester.<sup>[52]</sup>

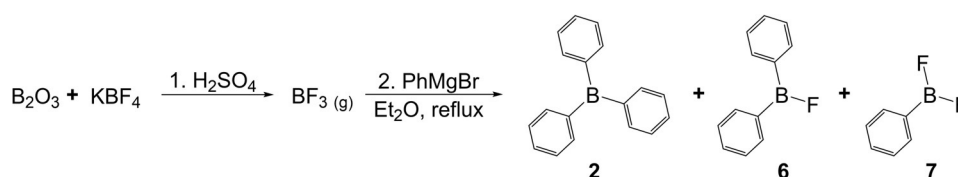
## 1.2. Boron trifluoride as the boron source

Despite reports of the synthesis of triphenylborane,<sup>[26,44]</sup> reproducible synthetic access was only available for mono- and diarylboranes in the beginning of the 20th century. This changed with the studies of Krause, who made use of the synthesis of

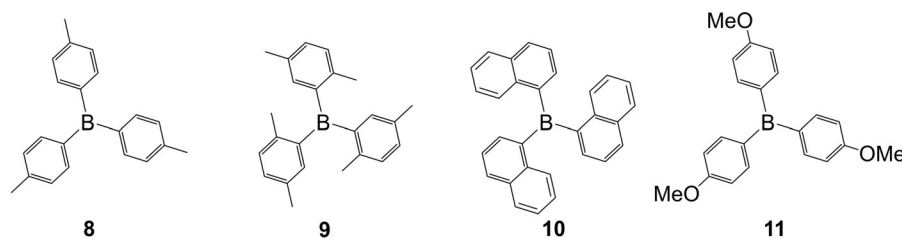
gaseous boron trifluoride (BF<sub>3</sub>) from boric anhydride (B<sub>2</sub>O<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and potassium tetrafluoroborate (KBF<sub>4</sub>), reported by Schiff et al.<sup>[59]</sup> In 1921, Krause and co-workers used gaseous BF<sub>3</sub> in combination with Grignard reagents to yield triarylboranes as well as alkylboronic acids.<sup>[60]</sup> Subsequently, Krause et al. applied this method for the synthesis of triphenylborane **2** (Scheme 6).<sup>[61]</sup>

They isolated BPh<sub>3</sub> **2** by distillation of the crude reaction mixture in ca. 50% yield. The product crystallized easily, but it was also mentioned that **2** decomposes in air. Furthermore, Krause and co-workers observed the formation of phenyldifluoroborane **6** as well as diphenyldifluoroborane **7**, but isolation of these two compounds was not possible by distillation. This indicates that the reactivity of the Grignard reagent is insufficient to generate only BPh<sub>3</sub>, as byproducts **6** and **7** were observed. However, with BPh<sub>3</sub> **2** in hand, the group investigated its reactivity with neat sodium<sup>[62]</sup> and the other alkali metals potassium, lithium, rubidium and cesium.<sup>[63]</sup> Krause and co-workers observed the formation of intensely colored solutions as well as the formation of, mostly, yellow crystals. Both solutions and solids were reported to be highly air sensitive, as the solutions turned colorless when exposed to air. The colorless solution was converted into the colored solution again if neat metal was still present in the solution. After Krause and co-workers had isolated the reaction product of BPh<sub>3</sub> **2** with neat sodium,<sup>[63]</sup> they titrated the reaction product under a nitrogen atmosphere with elemental iodine which regenerated BPh<sub>3</sub> and sodium iodide. In the same study, the synthesis of tri-*p*-tolylborane **8** was mentioned. Its final synthesis and full characterization were reported two years later.<sup>[64]</sup> Again, the reactivity of **8** with sodium and potassium was investigated as well as its reaction with nitrogenous bases such as ammonia, pyridine, and piperidine. The reaction of **8** with neat sodium was described to be the same as for **2**. During the reactions of **8** with nitrogenous bases, the group observed a temperature increase of the reaction mixture as well as the formation of crystalline and more air-stable products which were assigned to be addition products of the nitrogenous bases with **8** (Scheme 7). This assumption was confirmed by elemental analysis of the reaction products. In 1930, Krause and co-workers also reported the synthesis of tri-*p*-xylylborane **9** and tri- $\alpha$ -naphthylborane **10**, which were investigated similarly to the previous compounds **2** and **8**.<sup>[65]</sup> For the isolation of **9** and **10**, the work up was slightly modified. Thus, to quench the remaining Grignard reagent, water was added and the resulting crude mixture was distilled with exclusion of air, as none of the previously synthesized triarylboranes are stable to air.

Nevertheless, what they refer to as an “oxidation process” of compound **10** starts only after two weeks in air. Furthermore,



**Scheme 6.** Synthesis of the first reported triarylborane **2** according to Krause et al.<sup>[61]</sup>

Scheme 7. Structures of compounds 8–11.<sup>[64–66]</sup>

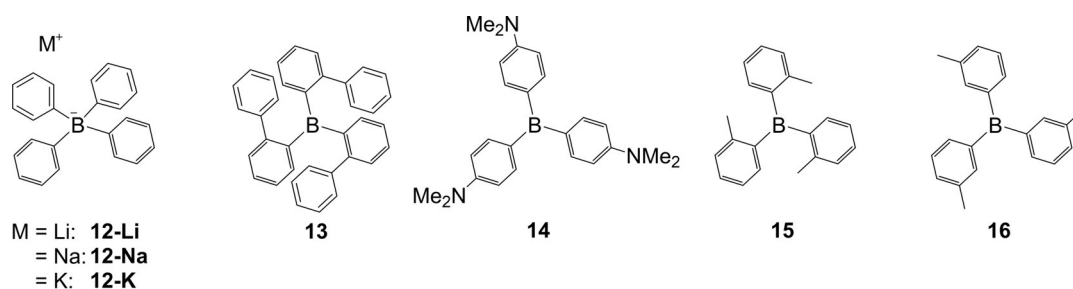
Krause et al. reported that solutions of **10** in benzene, chloroform, tetrachloromethane, carbon disulfide, and diethyl ether show a light blueish fluorescence that was more clearly visible with a quartz lamp. They did not provide any further information regarding what kind of lamp or which wavelength they used for excitation. Furthermore, the observed fluorescence was not investigated in detail. In 1931, the same group reported another triarylborane, namely tri-*p*-anisylborane **11**, which was found to be as air-sensitive as triphenylborane **2**.<sup>[66]</sup> In addition, Krause et al. had to change their work up once again, as they could not isolate **11** in pure form from the crude reaction mixture. Therefore, they reacted a crude mixture of **11** with gaseous ammonia to form the corresponding tetra-coordinate Lewis acid-base adduct which was then purified and subsequently reacted with sulfuric acid with exclusion of air to yield compound **11**. Similarly, 20 years later, the same group described the formation of BPh<sub>3</sub> upon heating different tetraarylborate salts to at least 200 °C.<sup>[67]</sup> Tetraarylborates are used on rare occasions to this day as valuable, alternative precursors to triarylboranes.<sup>[68–70]</sup>

Based on this work, Brown et al. re-synthesized tri- $\alpha$ -naphthylborane **10** as a reference Lewis acid to estimate the Lewis base strength of primary, secondary, and tertiary amines,<sup>[71]</sup> having slightly modified the synthesis of the triarylborane. To make the synthesis safer, Brown and co-workers used boron trifluoride etherate (BF<sub>3</sub>·OEt<sub>2</sub>) instead of gaseous boron trifluoride. Furthermore, they found that the triarylborane they synthesized was stable to air for more than one year. As this finding was in contrast with the reports of Krause et al.,<sup>[65]</sup> Brown et al. had a closer look into the geometry of the compound. They assigned the discrepancy between their and the earlier results to the existence of two possible rotational conformers, i.e., steric hindrance resulted in restricted rotation around the B–C bonds.

In 1947, Wittig et al. investigated the possible application of triphenylborane **2** as a catalyst for the lithiation of hydrocarbons.<sup>[72]</sup> Instead of successful catalysis of the reaction, they found the formation of a stable complex which was later identified as lithium tetraphenylborate **12-Li**.<sup>[73]</sup> Further investigations of such compounds, especially the reaction of sodium tetraphenylborate **12-Na** with various mono-cationic elements in aqueous solution, led to the discovery of an almost insoluble complex **12-K** formed after addition of potassium salts. Later on, compound **12-Na** became commercially available as Kalignost® for the quantitative analysis of potassium in aqueous solution (Scheme 8).<sup>[74]</sup>

Wittig and co-workers found that triarylboranes such as **2** can also be synthesized from the corresponding, more reactive lithiated species instead of the Grignard reagent.<sup>[73]</sup> As long as it was possible to synthesize the desired compounds from Grignard reagents and BF<sub>3</sub> etherate, they did so. However, for tri(*o*-diphenyl)- **13** and tri(4-(*N,N*-dimethylamino)phenyl)borane **14**, Wittig et al. used the corresponding aryllithium reagent.<sup>[74]</sup> Nevertheless, the synthesis of **14** was still challenging, as the amine formed complexes with excess BF<sub>3</sub>. Furthermore, this group reported a yellowish fluorescence from **14** in the solid state as well as a blue fluorescence in acetone upon irradiation with UV light. Compounds **15** and **16** were described as having a yellowish-white fluorescence upon UV-irradiation. None of these observations were further explained or investigated by Wittig et al. Very recently, Marder and co-workers reported that a sample of pure **16** showed only blue fluorescence, with no phosphorescence being observed at room temperature.<sup>[75]</sup>

In 1956, Lappert summarized the preparation, chemical and physical properties, reactivities, etc. of almost all organoboranes that had been synthesized up to that date.<sup>[24]</sup> In this summary, several methods to synthesize monohaloboranes as

Scheme 8. Structures of compounds 12–16.<sup>[73,74]</sup>

well as unsymmetrically substituted diaryl borinic esters were described. However, almost none of these syntheses were utilized for the formation of triarylboranes, especially not for the formation of boranes bearing three different aromatic systems.

One year later, Brown et al. reported the synthesis of the sterically demanding trimesitylborane **17** from the corresponding Grignard reagent and  $\text{BF}_3$  etherate.<sup>[76]</sup> The group heated the reagents in toluene under reflux for 4 h which they described as forcing conditions. If the reaction was stopped after 2 h, only fluorodimesitylborane **18** was isolated showing once again that the formation of triarylboranes from Grignard reagents is possible, but requires heat to achieve completion due to the lower reactivity of arylmagnesium reagents compared to, e.g., aryllithium reagents (Scheme 9). Furthermore, Brown and co-workers examined the reactivity of **17** with amines as well as its decomposition with water and oxygen. It was found that **17** was less reactive than tri- $\alpha$ -naphthyl- **10** or triphenylborane **2** due to its greater steric hindrance.

Subsequently, the syntheses of compounds **17** and **18** were further improved by Hawkins et al.<sup>[77]</sup> who changed the solvent for the formation of the Grignard reagent from diethyl ether to THF according to a general procedure reported by Ramsden et al.<sup>[78]</sup> This change resulted in a shorter reaction time for the formation, as well as an increased yield, of the Grignard reagent. In addition, this led to the isolation of fluorodimesitylborane **18** in 96% yield. Due to its steric hindrance, the reaction of excess mesityl Grignard reagent with  $\text{BF}_3$  etherate at 55 °C stops at the fluorodimesitylborane stage as long as the reaction time is shorter than 2 h. Furthermore, Hawkins and co-workers were able to nitrate **17** to yield compound **19**.

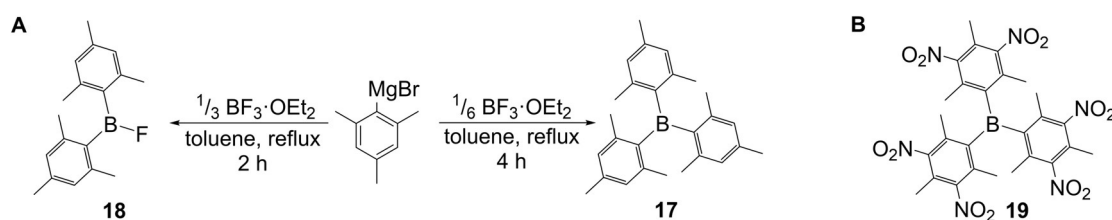
In 1967, at Eastman Kodak, Grisdale and co-workers began to investigate the photophysical reactions of tetraarylborates and triarylboranes in solution.<sup>[79]</sup> They again found trimesitylborane **17** to be more stable than triphenylborane **2**. To investigate further the influence of different substituents on the sta-

bility of triarylboranes, Grisdale et al. had a closer look at the influence of the *para*-substituent in various dimesitylphenylboranes.<sup>[80]</sup> To synthesize a variety of these new triarylboranes **20**, this group was the first to combine the methods previously developed by different groups. First, Grisdale and co-workers isolated fluorodimesitylborane **18** as reported by Brown.<sup>[76]</sup> This fluoroborane was then added to a lithiated species prepared from the corresponding halogenated aromatics yielding **20 a–e** in 40–90%, as Wittig et al. had found lithium reagents to be suitable to react with boronhalides.<sup>[73]</sup> This reaction sequence reflects the different reactivities of Grignard and organolithium reagents. Grisdale et al. also conducted one of the first systematic investigations of the photophysical properties of the new triarylboranes in various solvents, observing emission solvatochromism, suggesting the stabilization of charge transfer excited states in polar solvents.

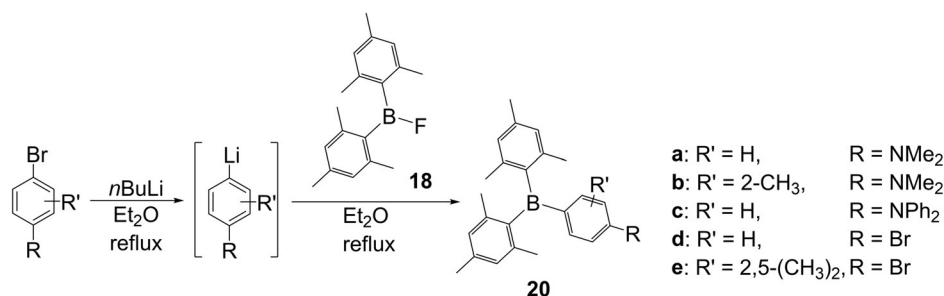
### 1.3. Metal-boron exchange reactions for the synthesis of triarylboranes

To date, the most widely used method for the synthesis of triarylboranes is the procedure developed by Grisdale and co-workers (Scheme 10)<sup>[80]</sup> i.e., reaction of  $\text{BF}_3$  with either Grignard reagents or lithium reagents as discovered by Krause et al.<sup>[61]</sup> and Wittig et al.,<sup>[73]</sup> respectively. However, mercury, zinc, copper, silicon, and tin reagents have also been employed in the synthesis of triarylboranes with different reactivities, solvent compatibilities, stabilities, and accessibilities of these organometallic reagents. Furthermore, while mercury and tin reagents are not widely used currently due to their toxicities, other safety aspects may dominate the choice of organometallic reagent, depending on the organic group to be transferred.

Arylmercury compounds were the first ArM reagents to be used for the synthesis of arylboranes (vide supra), but apart from a few reports on arylboronic acid syntheses,<sup>[81,82]</sup> they



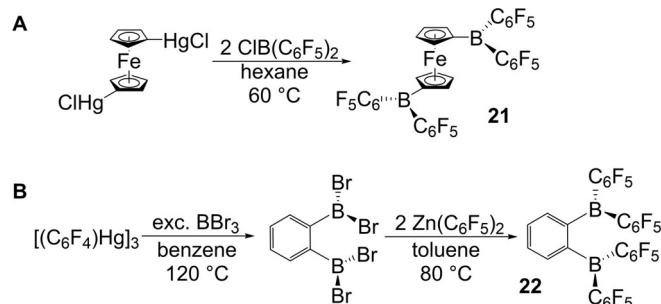
Scheme 9. A) Reaction sequences for the synthesis of compounds **17** and **18**.<sup>[76]</sup> B) Structure of compound **19**.<sup>[77]</sup>



Scheme 10. Synthetic route to symmetrically substituted triarylboranes **20 a–e** reported by Grisdale et al.<sup>[80]</sup>

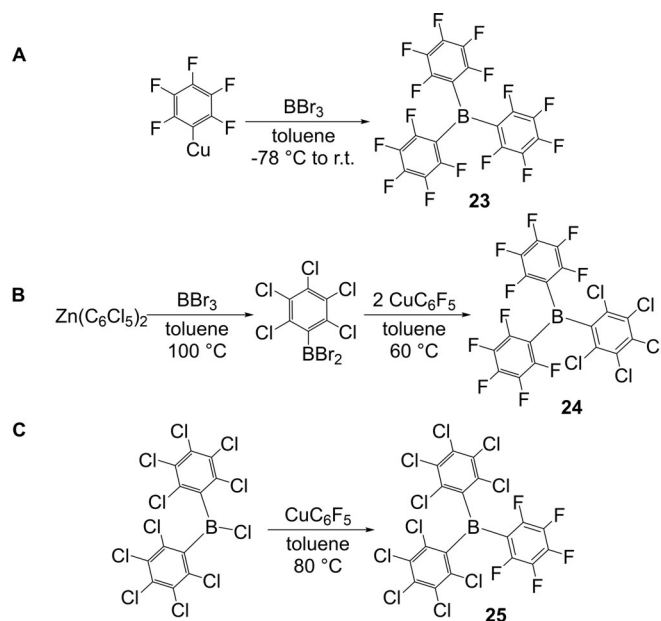


have generally been replaced by Grignard or organolithium reagents. However, in 2001, Piers and co-workers obtained the diborylated ferrocene compound **21** by reacting 1,1'-F(HgCl)<sub>2</sub> with ClB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (Scheme 11 A).<sup>[83]</sup> The same group made use of Hg-B exchange to generate the diborylated compound **22**, which was then converted into a triarylborane via Zn-B exchange (Scheme 11 B).<sup>[84]</sup> A year before, they reported Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> as a potential C<sub>6</sub>F<sub>5</sub> transfer agent, which reacted with BCl<sub>3</sub> to generate inseparable mixtures of mono-, di- and triarylboranes.<sup>[85]</sup>



**Scheme 11.** A) Hg-B exchange reaction by Piers and co-workers.<sup>[83]</sup> B) Sequential Hg-B and Zn-B exchange reaction by Piers, Collins, Marder and co-workers.<sup>[84]</sup>

In 2003, Jäkle et al. demonstrated the applicability of arylcopper reagents in Cu-B exchange reactions.<sup>[86]</sup> Using mesitylcopper, a maximum of two arenes were attached even when the reaction with BX<sub>3</sub> (X = Cl, Br) was heated to 100 °C, or when dichlorophenylborane **1** was used as the starting material to decrease the steric demand around the boron. Reaction of C<sub>6</sub>F<sub>5</sub>Cu with BX<sub>3</sub> at room temperature gave B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> **23** irrespective of stoichiometry (Scheme 12 A). Pentafluorophenylcopper was also employed by Ashley, O'Hare and co-workers

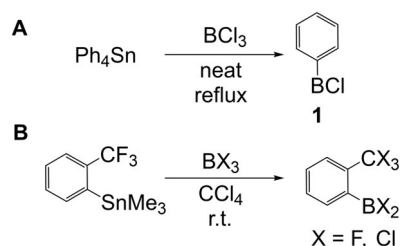


**Scheme 12.** Triarylborane formation using CuC<sub>6</sub>F<sub>5</sub> as an aryl transfer reagent by Jäkle and co-workers and O'Hare and co-workers, respectively.<sup>[86,87]</sup>

as an aryl transfer reagent for the synthesis of triarylboranes **24** and **25** (Scheme 12 B, C) and, in one case, they made use of a Zn-B exchange to form the dibromoarylborane precursor (Scheme 12 B).<sup>[87]</sup>

Later, Jäkle and co-workers demonstrated that 2,4,6-tri-*iso*-propylphenylcopper (CuTip) could also be employed in Cu-B exchange reactions. Thus, CuTip was reacted with sterically unhindered bromodiarylboranes to add the third arene to the boron center,<sup>[88,89]</sup> and these triarylborane precursors were used in the formation of organoborane macrocycles and borazine oligomers.

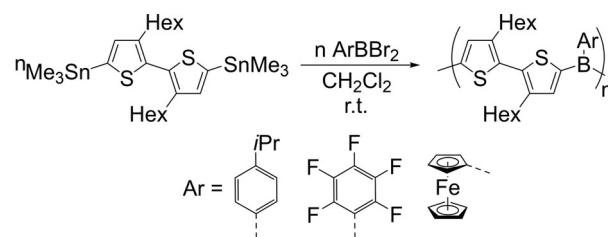
Apart from Grignard and lithium reagents, the most widely used substrates for exchange reactions with boron are organosilanes and organotin reagents. Aryltin reagents were used in Sn-B exchange reactions in the 1960s. In a first approach by Burch et al., the phenyl groups of SnPh<sub>4</sub> were transferred to BCl<sub>3</sub> to give compound **1**.<sup>[90]</sup> Reaction of SnPh<sub>4</sub> with BCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> transferred one of the four phenyl rings from tin to boron. Without the use of solvent, and under reflux conditions, all four rings were transferred (Scheme 13 A). In 1970, a more selective method was reported by Chivers, who synthesized *ortho*-substituted monoarylboranes from the corresponding monoaryltrimethylsilanes according to Scheme 13 B.<sup>[91]</sup> Halogen exchange between BCl<sub>3</sub> and the *ortho*-trifluoromethyl group was observed.



**Scheme 13.** Formation of monoarylboranes via Sn-B exchange by Burch et al. and Chivers, respectively.<sup>[90,91]</sup>

In 2005, Jäkle and co-workers reported the synthesis of triarylborane-containing polymers via Sn-B exchange,<sup>[92]</sup> reacting a distannylated bithiophene precursor with different dibromoarylboranes to obtain the respective polymers (Scheme 14).

Based on this procedure, many different triarylborane-containing polymers and triarylborane model compounds were also synthesized.<sup>[93,94]</sup>

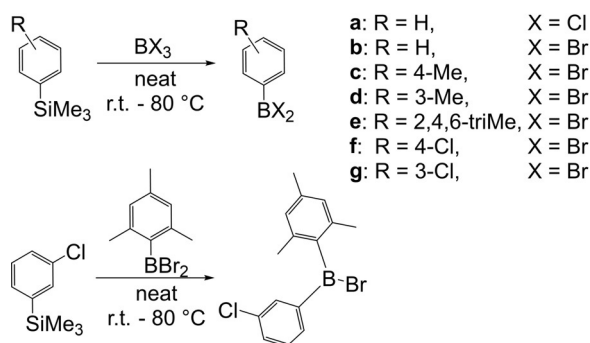


**Scheme 14.** Formation of triarylborane-containing polymers via Sn-B exchange.<sup>[92]</sup>

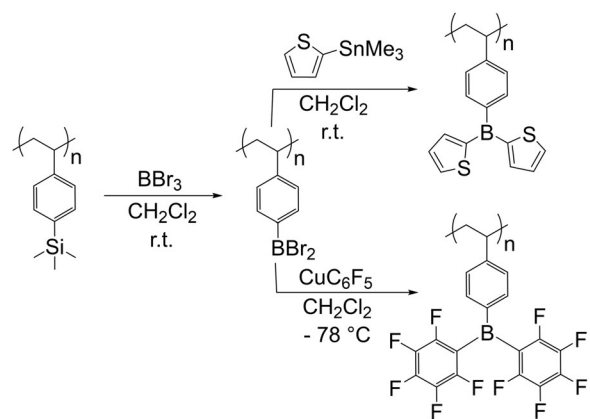
In 1986, Haubold and co-workers reported the synthesis of several mono- and diarylboranes via Si–B exchange.<sup>[95]</sup> The exchange reaction was tolerant to some functional groups, and even an unsymmetrically substituted ArAr'BBr compound was generated (Scheme 15). Starting from BBr<sub>3</sub>, 35% of triphenylborane **2** was formed under harsh reaction conditions, whereas starting from BCl<sub>3</sub> gave the monoarylboranes exclusively.

Further studies as well as potential applications were reported one year later by Kaufmann et al.<sup>[96,97]</sup> and Snieckus et al.<sup>[98]</sup> Jäkle and co-workers reported an efficient method for the introduction of a triarylborane moiety into the side chain of polystyrene.<sup>[99,100]</sup> The first step involved Si–B exchange and, in the next step, the triarylborane was formed via Sn–B and Cu–B exchanges, respectively (Scheme 16).

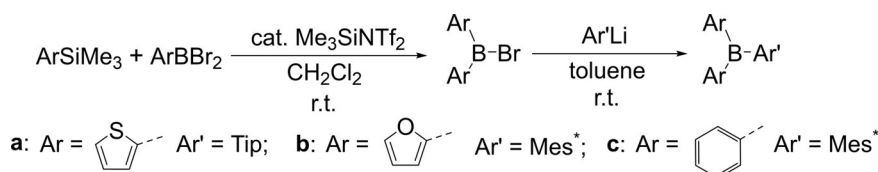
More recently, Helten and co-workers improved the Si–B exchange reaction significantly by employing a catalytic amount of Me<sub>3</sub>SiNTf<sub>2</sub>,<sup>[101]</sup> synthesizing three triarylboranes via Si–B ex-



**Scheme 15.** Si–B exchange reactions reported by Haubold and co-workers.<sup>[95]</sup>



**Scheme 16.** Si–B exchange reaction followed by Sn–B or Cu–B exchange for triarylborane formation by Jäkle and co-workers.<sup>[99,100]</sup>

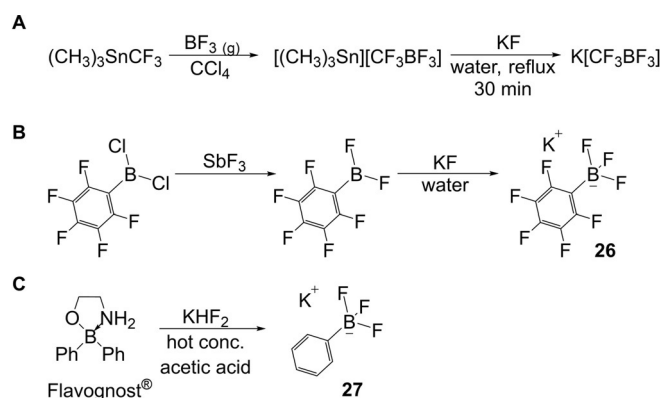


**Scheme 17.** Catalyzed Si–B exchange followed by Li–B exchange for triarylborane formation.<sup>[101]</sup>

change and subsequent Li–B exchange reactions (Scheme 17). Helten and co-workers employed this method for the synthesis of triarylborane-containing macromolecules and polymers. In each case, the third arene was attached to the boron using an aryl lithium reagent.<sup>[102,103]</sup>

#### 1.4. Potassium aryltrifluoroborates as boron sources

Potassium aryltrifluoroborates (ArBF<sub>3</sub>K salts) have been known since 1960.<sup>[104]</sup> Chambers et al. reported the synthesis of potassium (trifluoromethyl)trifluoroborate from a boiling, aqueous solution of trimethyltin (trifluoromethyl)trifluoroborate and potassium fluoride (Scheme 18A). In 1963, Stafford reported the synthesis of a potassium vinyltrifluoroborate that was isolated in a similar way to that previously described by Chambers.<sup>[105]</sup> Two years later, Chambers reported the synthesis of an aromatic potassium trifluoroborate **26** which was obtained from reaction of (pentafluorophenyl)difluoroborane and potassium fluoride (Scheme 18B).<sup>[106]</sup> In 1967, Thierig and Umland reported the synthesis of potassium phenyltrifluoroborate **27** from Flavognost® and potassium bifluoride (Scheme 18C).<sup>[107]</sup>

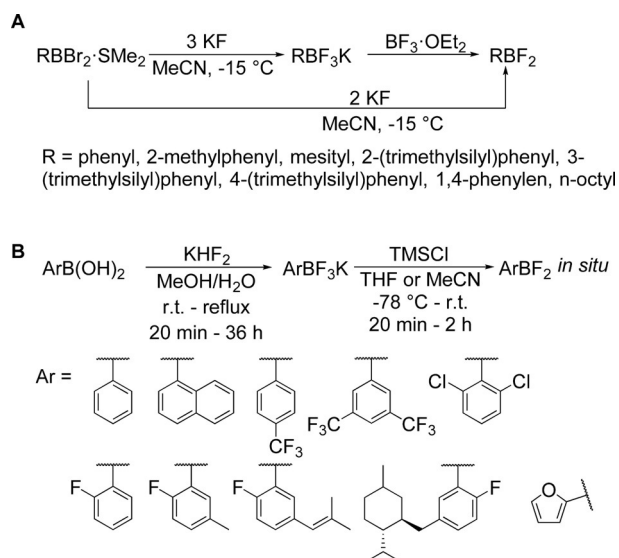


**Scheme 18.** Synthetic pathways to potassium trifluoroborates by Chambers, Stafford, and Thierig, respectively.<sup>[104,105,107]</sup>

About 20 years later, Kaufmann and co-workers made use of the solubility of potassium fluoride in acetonitrile to convert RBBR<sub>2</sub> compounds into their RBF<sub>2</sub> analogues or the corresponding potassium trifluoroborates (Scheme 19A).<sup>[108]</sup> They also found BF<sub>3</sub>·OEt<sub>2</sub> to be a suitable reagent to convert the latter salts in situ into RBF<sub>2</sub> compounds.

Another way to activate potassium aryltrifluoroborates was reported by Vedejs in 1995,<sup>[109]</sup> who showed that potassium aryltrifluoroborates can be activated in situ to form aryldifluoro-





**Scheme 19.** A) Conversion of aryl dibromoboranes to potassium aryltrifluoroborates or aryl difluoroborates.<sup>[108]</sup> B) A convenient route to potassium aryltrifluoroborates and their activation reactions.<sup>[109]</sup>

boranes by addition of trimethylsilyl chloride (TMSCl). Furthermore, they provided a convenient route to potassium aryltrifluoroborates from the corresponding boronic acids and potassium bifluoride,  $\text{KHF}_2$  (Scheme 19B).

To date,  $\text{BF}_3\text{K}$  salts are mostly employed in reactions in which the boron motif is lost, for example, in coupling reactions.<sup>[110]</sup> However, such compounds can also be used as the boron source for the syntheses of triarylboranes.

In 2004, Morrison et al. were the first to synthesize triarylboranes **28** from potassium aryltrifluoroborate reagents which were activated with  $\text{BF}_3$  etherate and then reacted with the Grignard reagent  $\text{C}_6\text{F}_5\text{MgBr}$  (Scheme 20).<sup>[27]</sup>

Since then, a few other groups reported the synthesis of triarylboranes from these bench-stable boron precursors. Especially for applications in frustrated Lewis pairs, this approach was used for the synthesis of triarylboranes bearing aromatic systems in which multiple fluoro- and chloro-substituents are desired. Soós and co-workers<sup>[28,111,112]</sup> and Hoshimoto et al.<sup>[113]</sup> synthesized triarylboranes **29–35** from potassium aryltrifluoroborates and Grignard reagents without prior activation of the

$\text{BF}_3\text{K}$  salt. The Grignard reagents in these cases were each prepared from the corresponding brominated precursor in combination with the so called “Turbo-Grignard” *iso*-propyl magnesium chloride lithium chloride (*i*PrMgCl·LiCl) as summarized in Scheme 21 A. A very similar strategy, without the use of the Turbo-Grignard, was used by Marder and co-workers to synthesize a push-pull system with a pyrene core **36** (Scheme 22 A).<sup>[30]</sup>

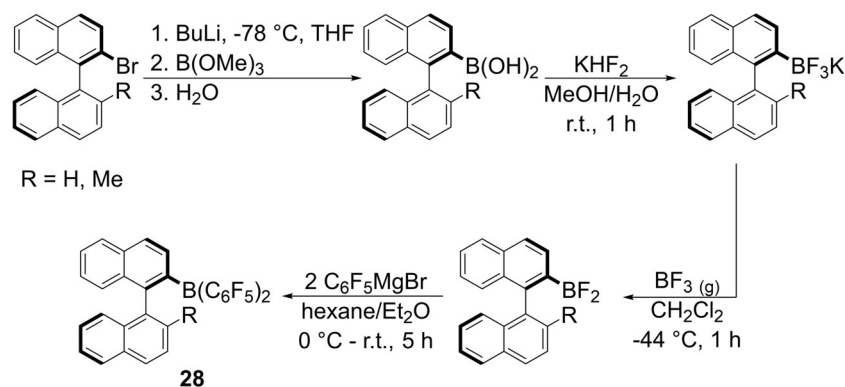
In contrast, Wagner and co-workers synthesized triarylboranes as precursors to polycyclic aromatic hydrocarbons<sup>[29]</sup> or quadruply annulated borepins.<sup>[114]</sup> In both cases, the required triarylboranes were synthesized from potassium aryltrifluoroborates which were reacted with various aryl lithium reagents yielding compounds **37–40** (Scheme 22 B, C).

### 1.5. Direct dimesitylborylation

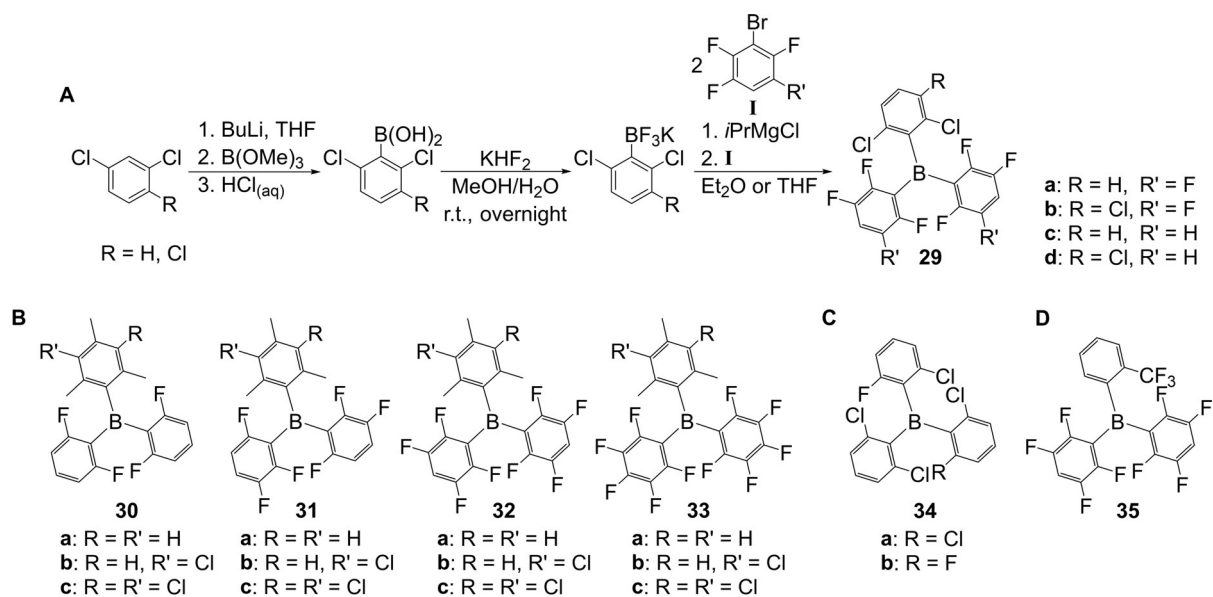
Ito and co-workers reported the direct dimesitylborylation of various aryl halides<sup>[115]</sup> by reaction of (diphenylmethylsilyl)dimesitylborene with aryl halides in the presence of a base (Scheme 23 A). The halide was replaced by boron or silicon in a ratio of ca. 9 to 1. Furthermore, the reaction was tolerant to several functional groups, and the resulting triarylboranes were isolated in moderate to good yields. In 2019, the same group reported an iridium-catalyzed C–H dimesitylborylation of benzofuran using a silyldimesitylborene reagent (Scheme 23 B),<sup>[116]</sup> preparing several derivatives and isolating the triarylboranes in moderate to good yields. Under optimized conditions, they reported the formation of the silylated side product in ca. 29% yield.

## 2. Synthesis of Unsymmetrically Substituted Triarylboranes

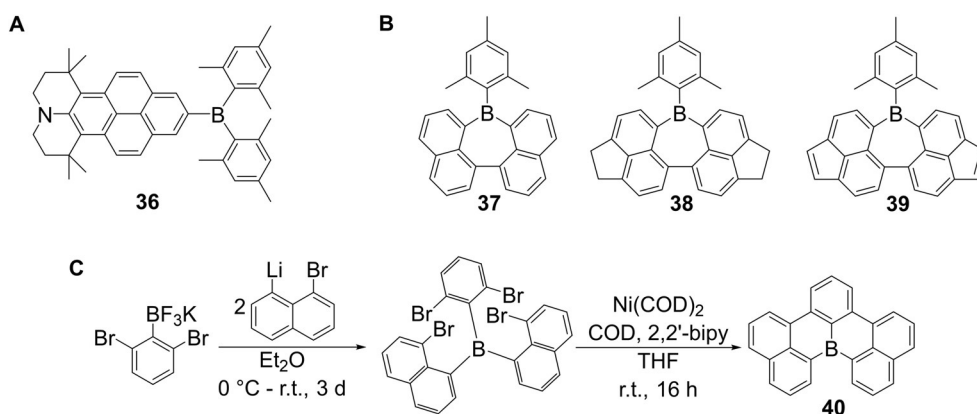
Thus far, we have summarized the syntheses of symmetrically substituted  $\text{BAR}_3$  and  $\text{BAR}_2\text{Ar}'$  triarylboranes. The synthesis of unsymmetrically substituted  $\text{BARAr}'\text{Ar}''$  triarylboranes bearing three different aromatic rings bound to the boron center can be achieved by different routes, most of which use the same approaches used for the syntheses of symmetrically substituted triarylboranes. However, other routes employed symmetrically substituted triarylboranes as precursors.



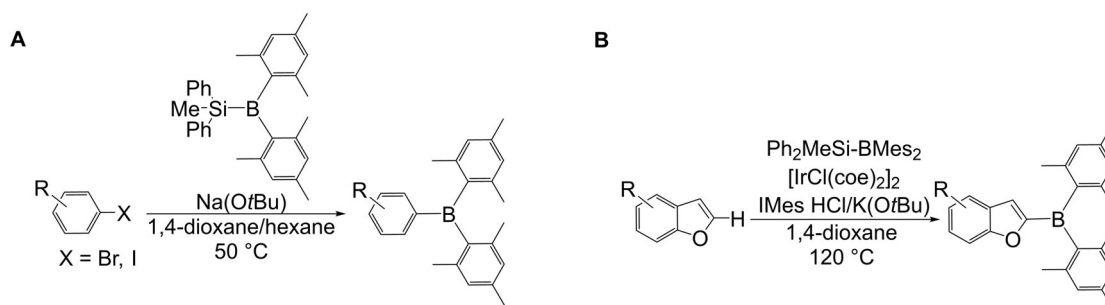
**Scheme 20.** First reported synthesis of triarylboranes from potassium aryltrifluoroborates.<sup>[27]</sup>



**Scheme 21.** A) General reaction sequence for the synthesis of multi-halogenated triarylboranes.<sup>[28]</sup> B,<sup>[111]</sup> C,<sup>[112]</sup> D)<sup>[113]</sup> Structures of compounds 29–35 synthesized according to Scheme 21 A.



**Scheme 22.** A) Structure of compound 36.<sup>[30]</sup> B) Structures of compounds 37–39.<sup>[114]</sup> C) Synthetic route to planarized triarylboranes.<sup>[29]</sup>



**Scheme 23.** A) Dimesitylborylation of aryl halides.<sup>[115]</sup> B) Dimesitylborylation of benzofuran derivatives.<sup>[116]</sup>

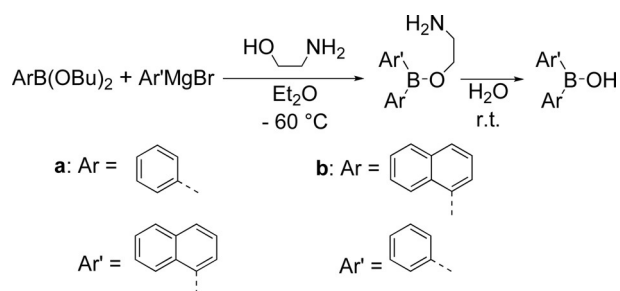
One of the first unsymmetrically substituted triarylboranes was reported in 1971 by Grisdale et al. at Eastman Kodak.<sup>[117]</sup> As mentioned above, this group investigated the photolysis of triarylboranes and tetraarylborates. During these studies, they observed an organoboron compound, formed after irradiation

of potassium dimesityldiphenylborate, which contained three different aromatic systems bound to the boron center.

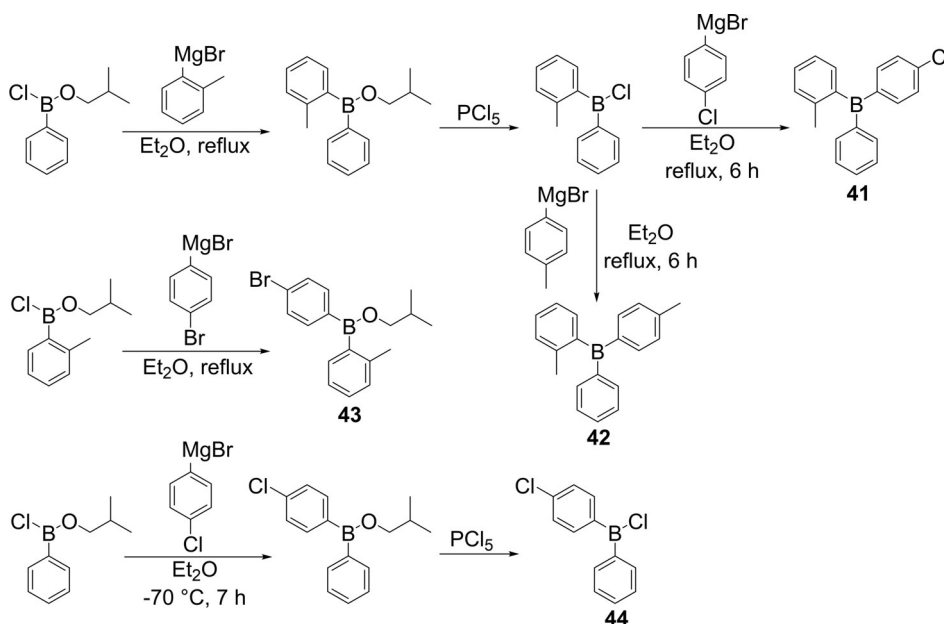
## 2.1. Boronic esters as boron sources

In 1955, Letsinger and co-workers reported the synthesis of the first unsymmetrically substituted borinic acid starting from a boronic ester.<sup>[118]</sup> They reacted phenylboronic acid butyl ester with  $\alpha$ -naphthylmagnesium bromide and isolated the borinic acid as its  $\beta$ -aminoethyl ester, which was readily hydrolyzed to the borinic acid (Scheme 24). They also demonstrated that the synthesis works when the aryl starting materials are switched to  $\alpha$ -naphthylboronic acid butyl ester and phenylmagnesium bromide, respectively, but the product was not used for the synthesis of a  $\text{BArAr}'\text{Ar}''$  triarylborane.

In 1958, Mikhailov et al. reported the sequential synthesis of unsymmetrically substituted triarylboranes<sup>[119]</sup> (Scheme 25) starting from an *iso*-butyl boronic ester wherein the boron atom is additionally bound to one phenyl and one chlorine atom, respectively. In the first step, the chlorine atom was substituted by an *o*-tolyl group introduced from a Grignard reagent. In the second step, the *iso*-butyl substituent was converted to a chloride via reaction with  $\text{PCl}_5$ . The chlorine atom was subsequently substituted by other arenes introduced from



**Scheme 24.** Synthesis of an unsymmetrical borinic acid by Letsinger and co-workers.<sup>[118]</sup>



**Scheme 25.** Syntheses of unsymmetrically substituted triarylboranes **41** and **42**.<sup>[119]</sup>

Grignard reagents yielding two different unsymmetrically substituted triarylboranes (**41** and **42**). Mikhailov and co-workers reported the synthesis of two other borinic acids (**43** and **44**), but their conversion to unsymmetrically substituted triarylboranes was not described.

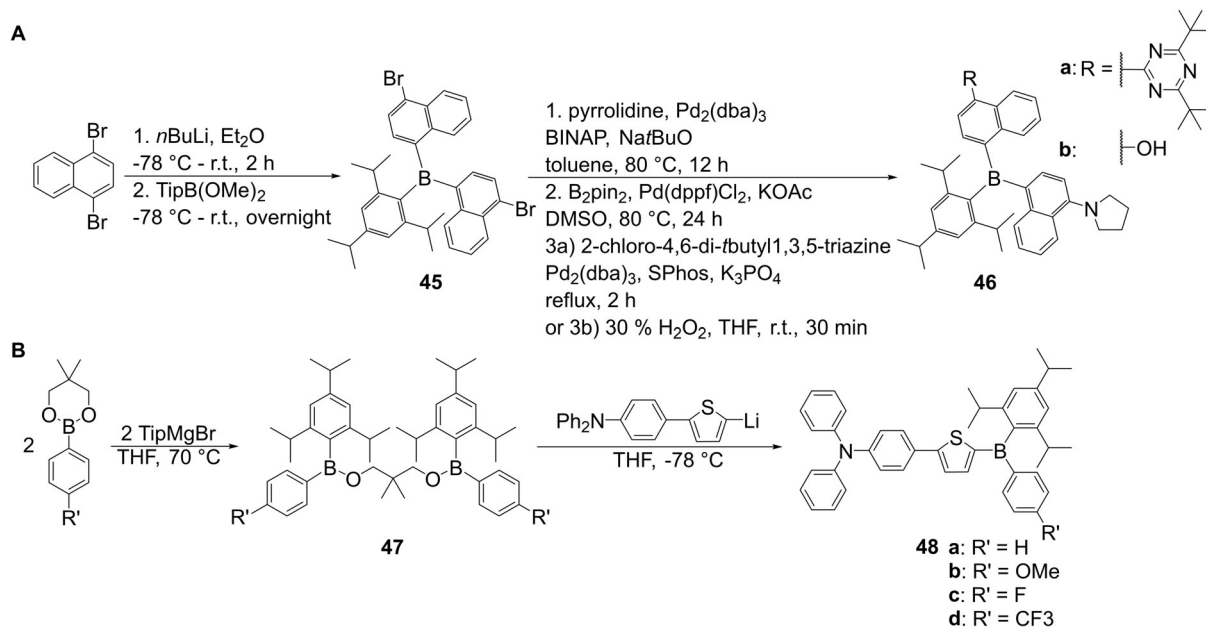
Recently, Liu et al.<sup>[7,120]</sup> synthesized the unsymmetrically substituted triarylboranes **46 a, b** from  $\text{BAr}_2\text{Ar}'$  **45**. Compound **45** was synthesized from the boronic ester  $\text{TipB}(\text{OMe})_2$  (Tip = Tri-*iso*-propyl) which was obtained from reaction of trimethoxyborane ( $\text{B}(\text{OMe})_3$ ) with 2,4,6-tri-*iso*-propylphenyl magnesium bromide ( $\text{TipMgBr}$ ).<sup>[121]</sup> This boronic ester was then converted to the symmetrically substituted triarylborane **45** by reaction with a lithiated species (Scheme 26 A). Stepwise substitution of the bromides then yielded the unsymmetrically substituted triarylboranes **46 a, b** (Scheme 26 A).

Yamaguchi and co-workers reported the synthesis of a series of unsymmetrically substituted triarylboranes **48 a–d** from a boronic ester precursor (Scheme 26 B).<sup>[32]</sup> This was then converted with  $\text{TipMgBr}$  to a dimeric intermediate **47**, which was cleaved by the addition of a lithiated species yielding compounds **48 a–d** (Scheme 26 B). In the same paper, Yamaguchi and co-workers reported the synthesis of a derivative of compound **48** bearing *tert*-butyl groups instead of the *iso*-propyl groups, but it was not possible to synthesize **48 e** according to Scheme 26 B. Therefore, they used a different approach starting from boron tribromide (vide infra, Scheme 30 B).

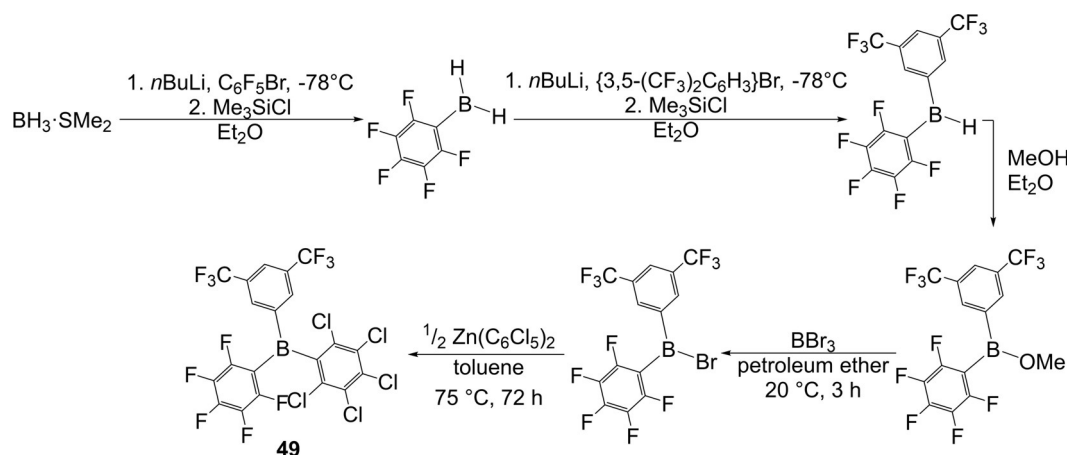
## 2.2. Borane dimethyl sulfide as the boron source

In 2016, Blagg et al. reported the synthesis of the “first 1:1:1 hetero-tri(aryl)borane”, by their own account.<sup>[122]</sup> In terms of investigating the Lewis acidity of such “hetero-tri(aryl)boranes”, they substituted the hydrogen atoms of a borane dimethyl sulfide complex stepwise with arenes (Scheme 27). The first aro-





**Scheme 26.** A) Synthesis of unsymmetrically substituted triarylborane **46** from a symmetrically substituted precursor.<sup>[7,120]</sup> B) Synthesis of unsymmetrically substituted triarylboranes **48a–d** from a boronic ester.<sup>[32]</sup>



**Scheme 27.** Synthesis of unsymmetrically substituted triarylborane **49** from borane dimethyl sulfide.<sup>[122]</sup>

matic groups were introduced using aryl lithium reagents. The resulting intermediate was converted to a boronic ester with methanol and was then activated with BBr<sub>3</sub> for reaction with an organozinc reagent yielding the unsymmetrically substituted triarylborane **49**.

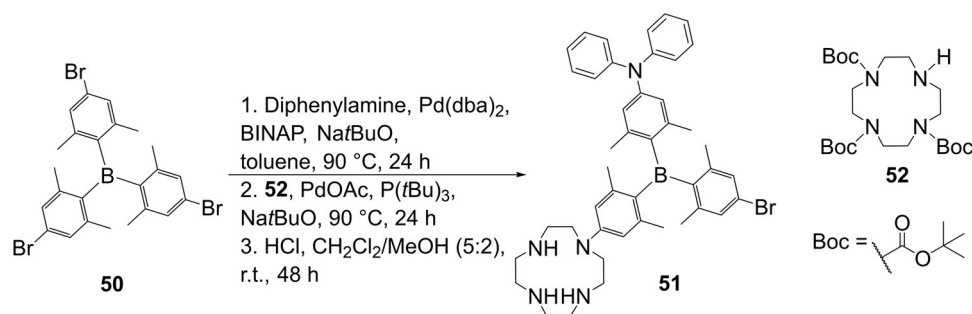
### 2.3. Boron trifluoride as the boron source

Liu et al. used the symmetrically substituted compound **50**, which was prepared from BF<sub>3</sub>·OEt<sub>2</sub> and the respective aryl lithium reagent, to prepare unsymmetrically substituted triarylborane **51** via sequential cross-coupling reactions (Scheme 28).<sup>[123]</sup>

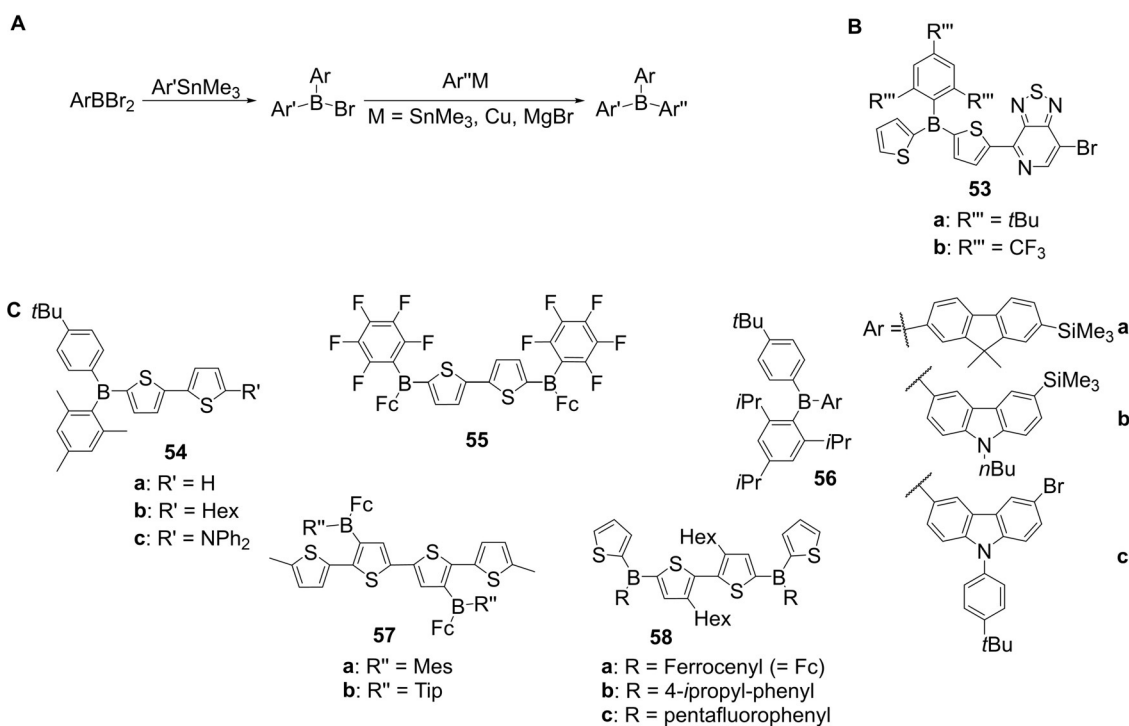
### 2.4. Boron tribromide as the boron source

In 2005, Jäkle and co-workers reported the synthesis of different unsymmetrically substituted triarylboranes as reference compounds for their polymers.<sup>[92]</sup> Both monomeric and polymeric boron-containing systems were synthesized from aryl-dibromoboranes and organotin reagents (vide supra, Scheme 14; vide infra, Scheme 29). They subsequently used this strategy for similar applications with slight modifications of the synthetic procedure, the third aryl group being added via a tin,<sup>[92]</sup> a copper<sup>[124–126]</sup> or a Grignard reagent<sup>[127]</sup> (Scheme 29).

The same group then reported the synthesis of an unsymmetrically substituted triarylborane **53** (Scheme 29B) via stoichiometric Stille coupling of a symmetric precursor<sup>[128]</sup> which



**Scheme 28.** Synthesis of unsymmetrically substituted triarylborane **51** by stepwise modification of a symmetrically substituted precursor.<sup>[123]</sup>



**Scheme 29.** A) Synthetic route to unsymmetrically substituted triarylboranes developed by Jäkle and co-workers.<sup>[92]</sup> B) Structure of compound **53**.<sup>[128]</sup> C) Compounds **54–58** synthesized according to Scheme 29 A.<sup>[92, 124–128]</sup>

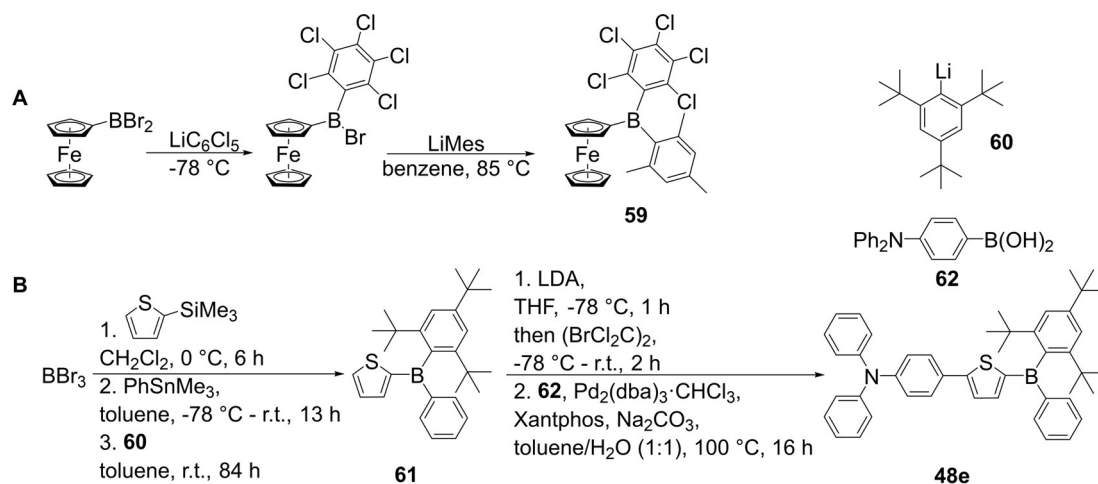
had been obtained from boron tribromide and an excess of a tin reagent.<sup>[129]</sup>

In 2014, Kelly et al. reported the synthesis of a ferrocene-containing triarylborane bearing three different aromatic systems by stepwise reaction of dibromoferrocenylborane with two different aryl lithium reagents (Scheme 30 A).<sup>[130]</sup>

As shown in Scheme 26 B, Yamaguchi and co-workers reported a route to unsymmetrically substituted triarylboranes from boronic esters,<sup>[32]</sup> but for **48 e**, the route was not successful as the incorporated arene was sterically too demanding. Therefore, they used a route established by Jäkle and co-workers: after a boron–silicon exchange at the thiophene, the ArBBR<sub>2</sub> system was reacted with a tin reagent followed by 2,4,6-*tert*-butylphenyllithium to give **48 e** (Scheme 30 B).

## Summary and Outlook

Over the years, the synthetic approaches to triarylboranes presented herein has led to the generation of countless compounds containing triarylborane motifs. Initially, examination of their properties was limited to their reactivity with other metals or as Lewis acids. Some of the early reaction sequences, such as those developed by Krause et al. and Grisdale et al., are still used. Today, the applications of these compounds are no longer limited to their reactivity. The photophysical and electronic properties of triarylboranes and compounds containing this structural motif remain under increasingly active investigation as such properties lead to numerous applications, for example, in OLEDs,<sup>[2]</sup> optoelectronics,<sup>[1, 3, 23]</sup> sensors for anions<sup>[4–6]</sup> or small molecules,<sup>[7, 8]</sup> as catalysts, for example, for hydrogenation or amination of carbonyls,<sup>[28, 111, 112]</sup> or bioimaging agents.<sup>[9, 10, 12, 14, 15]</sup> With the further exploration of more gen-



**Scheme 30.** A) Synthesis of unsymmetrically substituted triarylborane **59** by Kelly et al.<sup>[130]</sup> B) Synthesis of sterically more demanding, unsymmetrically substituted triarylborane **48e** by Yamaguchi and co-workers.<sup>[32]</sup>

eral routes to unsymmetrically substituted triarylboranes, the applicability of these compounds can be expected to continue to increase as this structural motif provides the possibility for fine tuning of the photophysical and electronical properties of the resulting small molecules and, therefore, also of potential macromolecules and polymers.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** arylmetalate · boranes · chromophore · Lewis acid · synthetic methods

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