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(Hetero)arene-fused boroles: a broad spectrum of applications

Jiang He, Florian Rauch, Maik Finze \mathbb{D}^* and Todd B. Marder \mathbb{D}^*

(Hetero)arene-fused boroles are a class of compounds containing a 5-membered boron diene-ring. Based on their molecular framework, the (hetero)arene-fused boroles can be considered as boron-doped polycyclic antiaromatic hydrocarbons and are thus of great interest. Due to the vacant p₂ orbital on the 3-coordinate boron atom, the antiaromaticity and strain of the 5-membered borole ring, (hetero)arene-fused boroles possess strong electron accepting abilities and Lewis acidity. By functionalization, they can be tuned to optimize different properties for specific applications. Herein, we summarize synthetic methodologies, different strategies for their functionalization, and applications of (hetero)arene-fused boroles.

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Introduction Three-coordinate boranes have been studied intensely for applications such as anion sensors,1-3 nonlinear optical materials (NLOs),4-14 live cell imaging,15-18 sensing of DNA, RNA and proteins,^{19,20} etc.²¹⁻³² Among them, boroles are distinct, being 5membered unsaturated 4π -electron heterocycles containing a 3coordinate boron center. Interest in boroles originates from

Institute for Inorganic Chemistry and Institute for Sustainable Chemistry & Catalysis with Boron (ICB), Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: maik.finze@uni-wuerzburg.de; todd.marder@ uni-wuerzburg.de

their being isoelectronic with the cyclopentadiene cation (Cp^{+})

which, in terms of Hückel's rule,³³⁻³⁶ is antiaromatic and thus highly reactive. The isolation of "free" Cp⁺ has not been achieved. Cp^+ has a triplet electronic ground state, which was confirmed by ESR spectroscopic measurements of the pentaphenylcyclopentadienyl cation at low temperature.³⁷ The C_{2y} symmetry of a borole is lower than that of Cp^+ (D_{5h} , Fig. 1), which results in a splitting of the previously degenerate halffilled molecular orbitals. The orbital with a nodal plane passing through the boron atom ("as" in Fig. 1) is lowered in energy and occupied, which leads to a singlet ground state and diamagnetic character of boroles, in contrast to the biradical character of Cp⁺. The small HOMO-LUMO gap in boroles leads to their intense color.

Jiang He obtained his bachelor's degree at Qiqihar University (Heilongjiang, China) with a major in pharmaceutical engineering. Then he moved to Xiamen University (Xiamen, China) for his Master's Thesis, under the supervision of Assoc. Prof. Dr Xiao Zheng and Prof. Dr Peiqiang Huang. From 2014 to 2016, he joined the group of Assoc. Prof. Dr Wei Lu as a research assistant at Southern

University of Science and Technology (Shenzhen, China). In 2016, he joined the groups of Prof. Dr Maik Finze and Prof. Dr Dr h.c. Todd B. Marder at the Institute of Inorganic Chemistry of the Julius-Maximilians-Universität Würzburg, where he is working towards his PhD on triarylboranes and phenylpyridyl-fused boroles.





Florian Rauch obtained his bachelor's degree at the Julius-Maximilians University of Würzburg in Chemistry. He went on to finish his Master's thesis under the supervision of Prof. Dr. Dr. h. c. Todd Marder at the Institute of Inorganic Chemistry. He stayed with the group for his PhD and completed his doctorate in 2020 on new boron materials with ortho-trifluoromethylated aryls and their

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application for thermally activated delayed fluorescence as well as their influence on borafluorenes. He is currently working as a postdoctoral researcher in the same group.





Fig. 1 Molecule orbitals of the cyclopentadiene cation (Cp^+) and borole; "as" and "s" denote the antisymmetric and symmetric orbitals, respectively, with respect to the mirror plane perpendicular to the molecule.

Similar to Cp^+ , the "free" HBC₄H₄ is inaccessible due to its high reactivity caused by its antiaromaticity³⁸⁻⁴⁰ and low lying LUMO. *Via* steric protection, monomeric pentaphenylborole (PhBC₄Ph₄, **PhB**) was first synthesized in 1969 by Eisch and coworkers,⁴¹ but its crystal structure was only determined in 2008 by Braunschweig and co-workers.⁴² Steric protection of boroles was not only achieved with phenyl groups but also with other even bulkier protecting groups, *e.g.*, ^FPh (pentafluorophenyl),⁴³



scheme 1 (Hetero)arene-fused boroles.

Mes (2,4,6-trimethylphenyl)⁴⁴ and ^FMes (2,4,6-tritrifluoromethylphenyl).⁴⁵ However, these non-fused "free" boroles are still highly reactive compounds. The chemistry of non-fused "free" boroles was previously reviewed by Eisch,⁴⁶ Marder and co-workers,⁴⁷ Braunschweig and co-workers,⁴⁸⁻⁵⁰ Wakamiya,⁵¹ Martin and co-workers⁵² and Kinjo and co-workers.^{53,54}

The stability of boroles is largely enhanced by annulation, and fused boroles are readily accessible and functionalizable (Scheme 1). In comparison to related triarylboranes, the electron accepting ability and Lewis acidity of the boron atom is largely enhanced in boroles, as a result of the antiaromaticity and strain of the 5-membered borole ring. Such fused boroles can be considered to be boron-doped polycyclic antiaromatic hydrocarbons.



Maik Finze studied chemistry at the University of Hannover and Stanford University. He conducted research at the Universities of Duisburg-Essen and Wuppertal with Prof. H. Willner and obtained his PhD in 2004 from the University of Hannover. In 2004, he started his independent research at the University of Düsseldorf. He was appointed Professor at the University of Würzburg in 2011, where he is

currently Chair of Inorganic Chemistry and Co-Head of the Institute for Sustainable Chemistry & Catalysis with Boron (ICB). His research interests focus on boron and fluorine chemistry and materials for electrochemical applications.



Todd Marder received his BSc from M.I.T. and his PhD from the UCLA (University of California Regents Intern Fellow). Following a postdoc at the University of Bristol, UK, he was a Visiting Research Scientist at DuPont Central Research. He joined the faculty at the University of Waterloo, Canada in 1985, moved to the University of Durham, UK in 1997 as Chair in Inorganic Chemistry, and to the

University of Würzburg, Germany in 2012 as Chair in Inorganic Chemistry. He received the Royal Society of Canada Rutherford Memorial Medal for Chemistry, RSC Awards in Main Group Element Chemistry and in Organometallic Chemistry, a JSPS Invitation Fellowship, a Humboldt Research Award, and a Royal Society Wolfson Research Merit Award. He was elected to the Bavarian Academy of Sciences, Fellowship of the American Association for the Advancement of Science (AAAS), and Fellowship of the European Academy of Sciences (EurASc) and received an honorary doctorate from the University of Rennes 1, France. He has held Visiting/Honorary/Distinguished Professorships in the UK, France, Hong Kong, China, Japan, India, and Australia, and served on 10 journal editorial/advisory boards. His research interests include synthesis, structure, bonding, reactivity, homogeneous catalysis, luminescence, non-linear optics, bioimaging, liquid crystals, and crystal engineering.





The first dibenzo-fused borole, namely the parent 9-borafluorene (**Bf**), was reported in the early 1960s by Köster and Benedikt,⁵⁵ but only at the start of this century, has the chemistry of **Bf**s started to attract increasing interest. (Hetero)arenefused boroles have been reviewed very briefly either as part of reviews on "free" boroles^{47,49,51,54} or on boron-doped polycyclic aromatic hydrocarbons (PAHs)^{56,57} or in the context of subvalent boranes.⁵⁸ In this review, we address the synthesis, properties and applications of (hetero)arene-fused boroles in detail, our primary focuses are: (i) the optoelectronic behavior of the compounds; and (ii) their classification based on structure property relationships. New developments in the use of the *exo*substituents on boron are also discussed. The structures of all compounds with Arabic numerals are shown in Scheme 25 at the end of the paper for the reader's convenience.

Synthetic methodology

There are three main approaches for the synthesis of 9-aryl-9borafluorenes: (1) the use of easy-to-functionalize 9-X-9borafluorenes (**XBf**, X = Cl or Br or I) as key intermediate; (2) assembling 9-aryl-9-borafluorenes in one step; and (3) stepwise substitution reactions at boron.

The first approach relies on readily available 9-X-9-borafluorenes (**XBf**, X = Cl or Br or I). Four synthetic approaches to **XBf** derivatives have been developed. In 1985, Nöth and co-workers applied a boron–mercury exchange reaction (Scheme 2, path a).⁵⁹ Analogous to the preparation of **PhB**,⁶⁰ a boron–tin exchange reaction can also be utilized for the synthesis of **XBf**s (Scheme 2, path b).^{61,62} To avoid using these highly toxic metals, a boron–silicon exchange reaction was developed (Scheme 2, path c).⁶³ **ClBf** can be obtained



Scheme 3 One-step synthesis of 9-aryl-9-borafluorenes.

directly from reaction of 2,2'-dilithiobiphenyl with BCl₃ in an aliphatic solvent (Scheme 2, path d).⁶⁴ The advantage of this approach is that once intermediate **XBf** is obtained, it is useful for subsequent derivatization.

For the one-step assembly of 9-aryl-9-borafluorenes, a borontin exchange reaction was utilized. Instead of using BX_3 (X = Cl or Br or I), PhBCl₂ was used directly (Scheme 3, path e).⁶⁵ The drawback of this methodology is that only sterically relatively unencumbered groups (e.g., phenyl and pentafluorophenyl) can be used; 61 e.g., MesBCl₂ (Mes = mesityl group) is unsuitable for this methodology. By changing the boron source from PhBCl₂ to dimethoxy aryl borates, and subsequent reaction with dilithiobiphenyl, 9-aryl-9-borafluorenes can be synthesized (Scheme 3, path f).^{66,67} There are two advantages to this approach: (1) dimethoxy aryl borates can tolerate coordinating solvents and are much more stable than their corresponding aryldihaloboranes, which makes the work up much easier; and (2) bulkier aryl groups (e.g., 2,4,6-triisopropylphenyl (Tip)) can be used. The third approach which can assemble 9-aryl-9-borafluorenes in one step was reported by Marder and co-workers,45,68 in which more stable aryltrifluoroborate salts were used as the boron source (Scheme 3, path g).⁶⁹⁻⁷⁴ The downside of this approach is the comparably low yields. Besides these three widely applied approaches, which can assemble 9-aryl-9-borafluorenes in one step, the Wehmschulte group synthesized two unsymmetric 9borafluorenes (2a and 2b, Scheme 3, path h) in one step by using H₂ClB·SMe₂ as the boron source.^{75,76} The formation of the borole ring takes place via a facile intramolecular C-H activation process, but the requirement of bulky terphenyl precursors limits its further application.



Scheme 4 Stepwise substitution reactions to synthesize fused boroles.

The third approach is a stepwise substitution reaction at boron, which was first reported in 1963 by Köster and Benedikt (Scheme 4).55 Thus, 9-alkyl-9-borafluorenes can be synthesized from B,B-dialkyl-2-biphenylborane intermediates by thermal dissociation of one alkyl-group at 180-200 °C. The compound 9phenyl-9-borafluorene (PhBf) can also be synthesized from B,Bdiphenyl-2-biphenylborane in the same way, but the temperature needs to be increased to 280-300 °C. The harsh conditions in this approach limit its further application. In 2011, the Yamaguchi group applied boronic esters as the boron source for the synthesis of heteroarene-fused boroles.77 Using the dithiophene-fused borole (3a) as an example, the boronic ester was introduced at the bithiophene via boron-lithium exchange in the first step, then the protecting group at the boron was introduced with a Grignard reagent. Finally, an intramolecular cyclization reaction completed the synthesis of 3a. More recently, Urban and co-workers applied a similar strategy, but used an intramolecular cyclization in the second step, obtaining 9-methoxy-9-borafluorene (MeOBf),78 a potential intermediate for synthesizing other 9-substituted-9-borafluorenes. In 2012, the Piers group used a reductive route with a haloborane (Precursor-4, obtained by three stepwise boron-metal exchange reactions) while attempting to synthesize the diborole 4 (Scheme 4, bottom). Instead, they initially obtained an isomer of 4 (Isomer-4) which, under irradiation with UV light (254 nm), isomerized to the desired diborole 4.79 Subsequently, the same group reported another, more efficient, thermal route to the diborole 4 from Isomer-4.80

Stability of 9-borafluorenes

The advantage of incorporating a boron atom into a 5membered diene-ring is the enhancement of electron accepting ability and Lewis acidity, but at the same time, stability is sacrificed. By fusing two phenyl rings onto a borole, the stability is greatly enhanced. The stability of the resulting 9-borafluorenes depends largely on the *exo*-substituent at boron. In this section, we compare the stability of different 9borafluorenes.



Scheme 5 Non-aryl group substituted 9-borafluorenes.



Scheme 6 9-Aryl-9-borafluorenes

When the *exo*-substituent is not a bulky aryl group, 9-borafluorenes remain highly reactive (Scheme 5). In fact, **HBf** in an unsymmetric dimer in solution and, after some time, it forms oligomers *via* a ring-opening mechanism even in dry and deoxygenated C_6D_6 .^{55,81-84} **ClBf**⁸⁵⁻⁸⁷ and ⁱ**Pr**₂**NBf** both show more than 50% decomposition within 1 hour in solution when exposed to the atmosphere.⁸⁸ '**BuOBf** is much more stable and exhibits less than 10% decomposition after 1 hour in CDCl₃ in air. This can be attributed to the steric demand of the *tert*-butyl group as the less bulky derivative **MeOBf**⁵⁹ is as sensitive to air/ moisture as ⁱ**Pr**₂**NBf** and **ClBf**.⁸⁸

An aryl group as the *exo*-substituent at 9-borafluorene increases the stability drastically (Scheme 6). **PhBf** and **MesBf** decompose only slowly in the air.⁵⁴ **PhBf** nonetheless retains high reactivity, *e.g.*, azides can insert into one of the B–C bonds of **PhBf** to generate 9,10-*B*,*N*-phenanthrenes.^{62,89} The reaction of **PhBf** with 1,2-dipolar substrates leads to the formation of the corresponding ring expansion adducts.^{90,91} By employing Tip or ^FMes as the protecting group at the boron atom of 9-bora-fluorenes, their stability is greatly enhanced, and both derivatives can be purified by column chromatography, even in air.^{66,88} Stability tests indicate that **TipBf** shows *ca*. 15% decomposition in solution in air after 24 hours and ^F**MesBf** shows only *ca*. 5% decomposition under the same conditions. Considering that the trifluoromethyl group is less bulky than the isopropyl group,⁹² this observation initially seems counterintuitive. In

fact, the higher stability of ^FMesBf is likely due to the stabilizing interaction of the vacant p_z -orbital of boron by lone pairs of the fluorine atoms of the two *ortho*-CF₃ groups of the *exo*-^FMes. This σ -donation was confirmed by the short B…F distances (2.682(6) and 2.577(5) Å) observed in the solid state (Fig. 2), which are much shorter than the sum of the van der Waals radii for boron and fluorine (3.39 Å).⁹³ The σ -donation from the fluorine atom(s) of *ortho*-CF₃ group(s) to the vacant p_z -orbital of boron was also observed in other boranes⁹⁴⁻¹⁰² and boroles.^{45,68} The 2,4,6-tri-*tert*-butylphenyl (Mes*) group is the bulkiest substituent among these protecting groups and, thus, provides the most stable 9-borafluorenes.¹⁰³ Compared to **TipBf**, which still exhibits reactivity towards the small F⁻ anion and can be applied as a F⁻ sensor, **Mes*Bf** is inert to F⁻. This demonstrates the superior stability of **Mes*Bf**.

To gain a deeper understanding of the relation between the structure and the stability, selected bond parameters of **PhBf**,¹⁰⁴ **MesBf**,¹⁰⁵ and ^F**MesBf**⁸⁸ derived from single crystal X-ray studies are listed in Table 1 and the molecular structures are depicted in Fig. 2. The free non-fused boroles, **PhB**,⁴² 1-mesityl-2,3,4,5-tetraphenylborole (**MesB**)⁴⁴ and 1-(2,4,6-tritrifluoromethylphenyl)-2,3,4,5-tetraphenylborole (^F**MesB**),⁴⁵ are included for comparison. Compared to **PhB**, the C–B bond lengths of the other five compounds are significantly longer. The short C–B bond lengths of **PhB** are a result of the strong $p_{\pi}(B)-\pi^*$ conjugation. The C1–C2 and C3–C4 bonds in **MesB** (1.356(2) and 1.351(2) Å) and ^F**MesB** (1.359(3)



Fig. 2 Molecular structures of PhB (top, left), MesB (top, middle), ^FMesB (top, right), PhBf (bottom, left), MesBf (bottom, middle) and ^FMesBf (bottom, right). For PhBF and ^FMesBf, only one of the two symmetry independent molecules is shown. Hydrogen atoms and the minor component of disordered CF₃ groups of ^FMesB are omitted for clarity. Red dashed lines in ^FMesB and ^FMesBf indicate short B-F contacts. 'Bo' and 'Ph' denote the planes of the borole and the *exo*-aryl groups, respectively.

Table 1 Selected bond lengths (Å) and angles (°) of PhB, MesB, ^FMesB, PhBf, MesBf and ^FMesBf. For PhBf and ^FMesBf, only one of the two symmetry independent molecules is listed

	PhB	MesB	^F MesB	PhBf	MesBf	^F MesBf
B1-C1	1.526(2)	1.586(2)	1.571(3)	1.573(9)	1.566(2)	1.550(6)
B1-C4	1.539(2)	1.575(2)	1.576(3)	1.59(1)	1.567(2)	1.556(5)
B1-C5	1.516(2)	1.560(2)	1.580(3)	1.58(1)	1.565(2)	1.584(5)
C1-C2	1.428(2)	1.356(2)	1.359(3)	1.431(9)	1.416(2)	1.421(5)
C3-C4	1.426(2)	1.351(2)	1.358(3)	1.421(9)	1.415(2)	1.411(5)
C2-C3	1.470(2)	1.537(2)	1.526(3)	1.51(1)	1.485(2)	1.485(5)
B1-F1			2.385(3)			2.682(6)
B1-F2			2.556(5)			2.576(5)
∠C1-B1-C4	105.4(1)	105.2(1)	106.19(17)	104.2(5)	103.7(1)	105.1(3)
∠Bo-Ph	32.71(5)	68.7(1)	82.4(3)	39.2	84.1	82.2(2)

and 1.358(3) Å) are obviously double bonds, but in the other four compounds, these bonds are significantly longer. In contrast, the remaining inner-borole C2-C3 bond is quite long in MesB (1.537(2)) and FMesB (1.526(3)) compared to those in PhB and the three fused boroles. So, similar to PhB, the Cring-Cring distances in fused boroles are indicative of some electron delocalization, which is in stark contrast to typical non-fused boroles such as MesB, resulting in significant differences in the properties of fused vs. typical non-fused boroles. The ∠C1-B1-C4 angles of the six compounds shown in Fig. 2 are quite similar. The torsion angles between the exo-aryl ring bonded to boron and the borole core are $32.71(5)^{\circ}$ (PhB), $68.7(1)^{\circ}$ (MesB), $82.4(3)^{\circ}$ (^FMesB), 32.8° and 39.2° (**PhBf**), 84.1° (**MesBf**), 80.9(12)° and 82.2 (2)° (^F**MesBf**) (the unit cell of PhBf and ^FMesBf exhibit two distinct molecules), respectively. Apparently, the bulkier the exo-aryl group is, the larger the torsion angle becomes, resulting in more efficient kinetic protection.

9-Borafluorenes with a fluorinated backbone

Inspired by the wide application of $B(C_6F_5)_3$,¹⁰⁶⁻¹⁰⁸ and the fact that 9-borafluorenes are more Lewis acidic than their corresponding boranes, Piers and co-workers synthesized a series of 9-borafluorenes with fluorinated backbones (Scheme 7). Compounds 5a and 5b are pale yellow or orange solids which exhibit lowest energy absorption maxima at 398 nm and 440 nm, respectively, in hexane.61 To explore the effect of two fluorinated 9-borafluorene centers in a molecular framework on the Lewis acidity, 5c was synthesized.¹⁰⁹ In 5c, two fluorinated 9-borafluorenes are situated ortho to one another, forming a chelating bidentate Lewis acid. Compound 5c is a deep orange solid with a lowest energy absorption maximum at 425 nm ($\varepsilon = 590 \text{ M}^{-1} \text{ cm}^{-1}$) in hexane, comparable to that of 5b, indicating that the two chromophores of the fluorinated 9-borafluorenes are not coupled. To the best of our knowledge, 5d is the only example of mono-aryl fused borole.110 Compound 5d is a red solid with its lowest energy absorption maximum at 465 nm ($\varepsilon = 900 \text{ M}^{-1} \text{ cm}^{-1}$ in toluene), and is readily soluble in most solvents.111

Compared with the corresponding fluorinated perfluoroboranes (MeB(C₆F₅)₂, B(C₆F₅)₃ and C₆F₄-1,2-[B(C₆F₅)₂]₂),^{109,112-114} fluorinated 9-borafluorenes show stronger Lewis acidities, as demonstrated by

Lewis base competition reactions, the Childs method,¹¹⁵ and semiempirical MNDO calculations.¹¹⁶ Apparently, compared with the corresponding fluorinated triarylboranes, the loss of two fluorine atoms is compensated by the antiaromaticity and strain of the 5-membered borole ring. Weak Lewis bases (LBs), *e.g.*, THF and CH₃CN, both bind to these four fluorinated 9-borafluorenes. After introduction of a Lewis base, the orange solutions of **5a** and **5c**, or lime green solution of **5b**, become colorless,¹¹⁷ and the red solution of **5d** turns pale yellow.¹¹¹ This color change is due to the interruption of $p_{\pi}(B)$ - π^* conjugation upon coordination of the Lewis base to the boron center, which results in a higher LUMO energy.⁶⁶

In a CH₃CN competition reaction between **5b** and $B(C_6F_5)_3 \cdot CH_3CN$ at 25 °C, an equilibrium constant of *ca.* 1.3 was found indicating a preference for formation of **5b** $\cdot CH_3CN$ vs. $B(C_6F_5)_3 \cdot CH_3CN$.¹¹⁷ In another competition experiment, with the bulkier THF as the base (in a ratio of 1 : 1 : 1 for **5b**, $B(C_6F_5)_3$ and THF in d_8 -toluene), only the **5b** \cdot THF adduct was observed by NMR spectroscopy. Applying the Childs method, **5a** and **5b** have a relative Lewis acidity value of 0.58 ± 0.02 and 0.70 ± 0.02 , respectively, which is only slightly higher than that of the corresponding $MeB(C_6F_5)_2$ (0.56 ± 0.02) and $B(C_6F_5)_3$ (0.68 ± 0.02) obtained by Piers.⁶¹ For the smaller Lewis base CH₃CN, **5b** and $B(C_6F_5)_3$ show comparable Lewis acidities, but for the larger Lewis base THF, **5b** shows a much stronger Lewis acidity than $B(C_6F_5)_3$. Based on these results, the authors concluded that the



Scheme 7 9-Borafluorenes with a fluorinated backbone.

relative Lewis acidities of **5b** and $B(C_6F_5)_3$ are determined by steric factors, rather than the antiaromaticity of **5b**.

Addition of $Cp_2Zr(CH_3)_2$ to 5a or 5b, leads to Me⁻ abstraction, and the corresponding ion pairs are formed rapidly.61 Both of them are remarkably more stable than their corresponding borane ion pairs in toluene (the ion pairs formed from $MeB(C_6F_5)_2$ and $Cp_2Zr(CH_3)_2$ can exchange a C_6F_5 group from $MeB(C_6F_5)_2$ with a methyl group from $Cp_2Zr(CH_3)_2$, resulting in $Me_2B(C_6F_5)$ and $Cp_2Zr(CH_3)(C_6F_5)$ under similar conditions).¹¹⁸ The combination 5a/Cp₂Zr(CH₃)₂ and 5b/Cp₂Zr(CH₃)₂ are more active and stable than their corresponding borane/ $Cp_2Zr(CH_3)_2$ ion pairs as activators for olefin polymerization. To investigate further the coordination chemistry of 5a and 5b, [Cp*Al]₄ was used.65 Surprisingly, only the thermally robust n¹ Lewis acidbase adduct was observed. Thus, the fragment of Cp*Al behaves only as a Lewis base rather than as a two-electron reducing agent. The reaction of Cp*Al with the less Lewis acidic PhBf also provides the η^1 Lewis acid–base adduct. Alternative routes to η^5 9-borafluorene aluminum complexes via reaction of PhBfLi₂ with Cp*AlCl₂(THF) were also unsuccessful. The reaction of 5b with $L^{tBu}ScR_2$ ($L^{tBu} = ((Ar)NC(^tBu)CHC(R)N(^tBu))$, $Ar = 2,6^{-i}Pr$ - C_6H_3) produced the corresponding contact ion pairs, the structures of which were thoroughly investigated both in solution and the solid state.119

Ortho-phenylene-bridged diboranes are interesting compounds and can be applied as co-initiators for olefin polymerizations.¹²⁰ Depending on the binding position of the Lewis base, ortho-phenylene-bridged diboranes (and diborole 5c) can adopt inner or outer facial coordination modes (Scheme 8).^{112-114,121} By adding a neutral Lewis base, e.g., CH₃CN or THF, coordination to the less sterically encumbered outer face of 5c was observed exclusively.¹⁰⁹ This is in contrast to the corresponding diborane C_6F_4 -1,2- $[B(C_6F_5)_2]_2$, to which CH_3CN coordinates to the inner face. The authors suggested that this is likely a result of less strain in the outer coordination mode caused by pyramidalization of the boron center in 5c; it may also be a result of the more rigid adjacent borafluorene's steric interaction which prevents the inner coordination mode in 5c. The reaction of 5c with $PhCMe_2X$ (X = Cl, OMe or N₃) gives thermally stable and isolable ion pairs which feature a weakly coordinating anion (WCA). The application of these ion pairs as initiators for isobutene polymerization were studied and the results show that the combination of C_6F_4 -1,2- $[B(C_6F_5)_2]_2$ with PhCMe₂X is more suitable than 5c with PhCMe₂X.¹²²

While perfluoropentaphenylborole reacts rapidly and irreversibly with dihydrogen (H_2) ,^{123,124} **5b** is inert to H_2 under various conditions. Therefore, **5d**, which is a structural hybrid of **5b** and perfluoropentaphenylborole, was designed and synthesized.¹¹⁰ The reaction between **5d** and H_2 was investigated experimentally and by



Fig. 3 Structure of the adduct between 5d and Et₃SiH. Only hydrogen H1 is shown, whereas other hydrogen atoms are omitted for clarity. Red dashed lines indicate the close non-bonded contacts. Selected bond lengths (Å) and angles (°): B1–C1 1.616(3), B1–C8 1.608(3), B1–C9 1.605(3), B1–H1 1.46(2), Si1–H1 1.51(2), C27–F9 3.138(3), C29–F4 3.262(2), ∠B1–H1–Si1 157, sum of ∠C–B–C 344.3(2).

theoretical calculations. Compound 5d reacts reversibly with H_{2} , but side reactions occur resulting in only limited turnover numbers of this metal-free H₂ activation reaction. Compound 5d has a comparable Lewis acidity to that of perfluoropentaphenylborole exhibits a much better solubility than but perfluoropentaphenylborole in non-coordinating solvents. Due to the better solubility of 5d, a low temperature experiment between 5d and Et₃SiH was possible.111 The borole-silane complex formation in d₈-toluene was studied by variable-temperature NMR spectroscopy. The trends of the Si-H coupling constant and the infrared stretching frequency of the Si-H bond as a function of temperature, and the molecular structure of the complex determined by X-ray diffraction (Fig. 3), clearly prove that an interaction exists between the boron atom and the silicon atom through the Si-H bond. These direct observations thus confirmed the previously proposed mechanism, i.e., that perfluoroarylboranes catalyze the hydrosilylation of C=C, C=N and C=O bonds via borane activation of the Si-H bond, not via a classical Lewis acid/base adduct process.125

Donor-acceptor 9-borafluorenes

The 9-borafluorenes exhibit a weakly allowed lowest energy absorption which extends into the visible region. This absorption was attributed to the low-lying LUMO which originates from the p_{π} - π^* conjugation through the vacant p_z orbital of boron.¹²⁶ By incorporating electron donating group(s) or electron withdrawing group(s) at different positions, the photophysical properties can be modified (Scheme 9). In this section, the 9-borafluorenes are classified according to their functional groups at different positions.



Scheme 8 A description of facial coordination modes of *ortho*-phenylene-bridged diboranes.



Scheme 9 A depiction of the different positions on a 9-borafluorene to which functional groups are attached.



Scheme 10 9-Borafluorenes with donors incorporated at the biphenyl core.

Pioneered by Yamaguchi and co-workers in 2002, three functionalized **TipBfs** (**6a–6c**) with donors (methoxy and amine groups or methoxy and thiophene groups) at the *m*- and *p*-positions were reported (Scheme 10).⁶⁶ Compared with the non-functionalized **TipBf**, both the absorption and emission of these functionalized **TipBfs** are red shifted and the quantum yields decrease (Table 2). The red shifted absorption and emission of donor-functionalized **TipBfs** were attributed to intramolecular charge transfer (ICT). Addition of F^- (or coordinating solvents) leads to a blue shift of both the absorption and emission of these functionalized **TipBfs** and, the quantum yields dramatically increase to *ca.* 0.5–0.9. Thus, these functionalized **TipBfs** can be applied as F^- sensor. In contrast to tri(9-anthryl)borane, which loses its fluorescence properties after coordination with F^- and was labeled as a "turn off" sensors, ¹ due to the increase

Table 2 Photophysical data for (hetero)arene-fused boroles

Compound	Solvent	$\lambda_{abs}/nm (log(\varepsilon))$	$\lambda_{\rm em}/{\rm nm}$	$\varPhi_{\rm F}$
1a ⁶⁸	Hexane	400 (2.48)	521	0.37
1b ⁶⁸	Hexane	386 (2.60)	510	0.30
1c ⁶⁸	Hexane	396 (2.48)	627	0.03
3a ⁷⁷	CH_2Cl_2	552 (3.05)	а	а
3b ⁷⁷	CH_2Cl_2	469 (2.93)	а	а
3c ⁷⁷	CH_2Cl_2	600 (3.04)	а	а
3 d ¹⁰⁵	CH ₂ Cl ₂	479 (3.09)	b	b
3e ¹⁰⁵	CH ₂ Cl ₂	468 (3.06)	b	b
3f ¹⁰⁵	CH ₂ Cl ₂	474 (3.05)	b	b
5a ⁶¹	Hexane	398 (-)	b	b
5 b ⁶¹	Hexane	440 (-)	b	b
5c ¹⁰⁹	Hexane	425 (2.77)	b	b
5 d ¹¹⁰	Hexane	465 (2.95)	b	b
TipBf ⁶⁶	THF	410 (2.39)	514	0.09
6a ⁶⁶	THF	480 (3.08)	561	0.03
6b ⁶⁶	THF	488 (2.95)	550	0.041
6c ⁶⁶	THF	504 (3.51)	576	0.022
6d ⁸⁸	CH_2Cl_2	398 (2.80)	499	0.10
Mes*Bf ¹⁰³	THF	397 (2.42)	501	0.35
7 a ¹⁰³	THF	470 (4.06)	608	0.24
7 b ¹⁰³	THF	457 (3.80)	600	0.48
8a ¹²⁷	Cyclohexane	430 (3.28)	529	0.21
8b ¹²⁷	Cyclohexane	430 (3.27)	527	0.36
8c ¹²⁷	Cyclohexane	451 (4.03)	567	0.13
9a ¹²⁸	Cyclohexane	380 (3.75)	519	0.55
9b ¹²⁸	Cyclohexane	411 (3.81)	513	0.42
[10a] ₄ (ref. 129)	THF	322 (4.70)	495	0.12
10b ¹²⁹	THF	375 (2.95)	520	0.27

^{*a*} Non-emissive. ^{*b*} Not reported.

of the emission intensity after adding F⁻, these functionalized 9-borafluorenes were termed fluorescence "turn on" sensors.

Six years later, the same group synthesized another two 9-Mes*-borafluorenes (7a and 7b) with donors (amine or thiophene groups) at the *m*-positions (Scheme 10).¹⁰³ Compared with the non-functionalized **Mes*Bf**, the molar extinction coefficients are much higher and a red shift was observed in both absorption and emission. Compared withtheir corresponding 9-Tip-9-borafluorenes, the fluorescence quantum yields of 9-Mes*-9-borafluorenes are higher, which is most likely due to the restricted rotation of the bulky Mes* group. The bulky Mes* group also leads to enhanced stability of these 9-Mes*-9-borafluorenes, which paves the way for their application as accepting units in organic (opto)electronics.

In 2016, Rupar and co-workers synthesized **6d** with two methoxy donors at the *p*-positions (Scheme 10). The lowest energy absorption and emission peak of **6d** appear in the same range as that of **TipBf**, and the quantum yields are also the same. The similar photophysical properties of these two compounds may be due to the weak donating ability of the methoxy groups.⁸⁸

Encouraged by the wide application of carbazole as a donating group and 9-borafluorene as an accepting group, the Zhao group synthesized three ladder-type B,N-bridged p-terphenyls, with indole fused at the p-, m-positions (8a and 8b) or o-, m-positions (8c) on one side of the borafluorene (Scheme 11).127 Later, the same group replaced the indole with benzothiophene and reported another two ladder-type B,S-bridged pterphenyls (9a and 9b).128 In these ladder-type boroles, the products of fusing at the p-, m-positions (8a, 8b and 9a), are tolerant to air and moisture, but fusing at the o-, m-positions (8c and 9b) leads to products that show slow decomposition in dilute solution in air (no specific solvent is mentioned), which is probably caused by steric congestion. Both absorption and emission show negligible solvatochromism for these laddertype boroles which indicates only a small polarity change between the ground state and the excited state. No difference of absorption and emission was observed between N-methyl 8a and N-phenyl 8b, which may be due to the large torsion angle between the phenyl group and pyrrole. Compared to 8a, 8c shows a red shift in both absorption and emission which was attributed to the lower LUMO energy as evidenced by computational studies. Compared with carbazole-fused 9-borafluorenes, the benzothiophene fused 9-borafluorenes show only slight hypochromism of both absorption and emission but



double the quantum yields. In addition to the broad use of 9borafluorenes as F^- sensors, **9a** was applied as a Hg²⁺ sensor because of its high affinity for Hg²⁺ due to the S atom. Additionally, these ladder-type boroles exhibit considerable potential for application as bipolar electron-transporting materials.

In contrast to the incorporation of donating groups at the 9borafluorene core, more recently, Marder and co-workers reported compound **1a** with four inductively withdrawing CF₃ groups attached to the *o*- and *p*-positions at the biphenyl main core (Scheme 12).⁶⁸ To investigate the effect of substitution at the *p'*-position in **1a**, **1b** with a CF₃ electron withdrawing group at the *p'*-position and **1c** with an NMe₂ electron donating group at the *p'*-position were also synthesized. Although examples appear in patents,¹³⁰ **1c** is the only example of a 3-coordinate 9borafluorene which incorporated a donor at the *exo*-aryl to have been reported in a paper.⁶⁸

Due to the strong electron withdrawing ability of the four CF₃ groups at the 9-borafluorene core, the electron accepting ability of boron was greatly enhanced, as evidenced by cyclic voltammetry (see below in the Electrochemistry section). With the extra protection of two CF₃ groups at the *o*-positions, **1a** and **1b** are more stable than ^FMesBf. Surprisingly, although 1c has a strong donor at the p'position, its absorption appears in the same region as those of 1a and 1b (this could also be caused by the weak absorption of 1c in the lower energy region), but the emission shows a large red shift (1a: $\lambda_{em} = 510$ nm; 1b: $\lambda_{em} = 521$ nm; 1c: $\lambda_{em} = 627$ nm in hexane). Both 1a ($\tau_{\rm F} = 151$ ns) and 1b ($\tau_{\rm F} = 224$ ns) exhibit very long fluorescence lifetimes in hexane, but behave differently; 1c exhibits two radiative processes ($\tau_p = 9.2$ ns and $\tau_d = 1.6 \mu s$), the latter resulting from thermally activated delayed fluorescence (TADF). Compound 1c is the first example of a borafluorene to exhibit TADF, but the rather low quantum yield ($\Phi_{\rm F} = 0.03$ in hexane) limits its further



Scheme 12 9-Borafluorenes with four CF_3 groups at the biphenyl core.

application. In contrast to the low quantum yield of **1c** in hexane, **1a** ($\Phi_{\rm F} = 0.30$) and **1b** ($\Phi_{\rm F} = 0.37$) exhibit relatively high quantum yields. Theoretical studies indicate that the LUMO of **1c** is located on the biphenyl core with a large contribution from the boron atom, whereas the HOMO is located on the *exo*-aryl moiety. Thus, the HOMO to LUMO transition is an ICT process with a small overlap coefficient (Λ) which also fits the requirement for TADF.

Heteroarene-fused boroles

In 2011, the Yamaguchi group fused electron-rich thiophene(s) onto boroles by stepwise substitution reactions and synthesized **3a–3c** (Scheme 13).⁷⁷ Surprisingly, these three Tip-protected thiophene-fused boroles are air- and moisture-sensitive. Considering that **TipBf** is stable enough to be purified in air, this instability is in opposition to an expectation that applying electron-rich thiophene would decrease the Lewis acidity of boron to form more stable compounds. The antiaromaticity of the borole rings was evaluated by DFT calculations of the nucleus-independent chemical shifts (NICS) values (Table 3).

The NICS(1)_{ZZ} (ppm) values increase in the order **TipBf** < **TipB** < **3b** < **3a** < **3c**. Thus, the biphenyl-fused borole, **TipBf** exhibits less antiaromatic character whereas the antiaromaticity of the electron-rich thiophene-fused boroles is enhanced, and is even higher than that of the non-fused "free" borole (1-Tip-1borole, **TipB**), as suggested by the NICS(1)_{ZZ} values. This result is also opposite to the conventional understanding that fusing electron-rich aromatic arenes decreases the antiaromaticity of the 5-membered borole ring.^{131,132}

To study what governs the antiaromaticity and Lewis acidity of heteroarene-fused boroles, another three heteroarene-fused boroles, **3d–3f** were synthesized (Scheme 13). NICS calculations were



Scheme 13 Electron-rich heteroarene-fused boroles.

Table 3 NICS(1)_{ZZ} (ppm) values for the 5-membered borole rings of (hetero)arene-fused boroles

	$NICS(1)_{ZZ}$		$NICS(1)_{ZZ}$		$NICS(1)_{ZZ}$
$1c^{68}$	+20.0	$1a^{68}$ Mos Pf ¹⁰⁵	+20.2	1b ⁶⁸	+20.7
4 (101. 79) TipBf ⁷⁷	+21.8 +24.5	8a ¹²⁷	+24.8	80 8b ¹²⁷	+24.2 +25.4
3e ¹⁰⁵ 3b ⁷⁷	+27.6 +30.1	MesB ¹⁰⁵ 3f ¹⁰⁵	+28.3 +30.4	TipB'' 3d ¹⁰⁵	+29.4 +31.7
3a ⁷⁷	+40.3	3c ⁷⁷	+45.3		



Fig. 4 Molecular structures of 3d (left), 3e (middle), and 3f (right). Selected bond lengths (Å): 3d: B1-C11.613(3), C1-C21.419(3), C2-C31.471(3), C3-C41.394(3), C4-B11.528(3). 3e: B1-C11.612(4), C1-C21.408(4), C2-C31.490(3), C3-C41.347(3), C4-B11.549(4). 3f: B1-C11.595(5), C1-C21.400(5), C2-C31.495(5), C3-C41.375(5), C4-B11.554(5).

conducted with the geometries derived from the crystal structures of these heteroarene-fused boroles (Fig. 4). The conclusion reached was that the smaller extent of bond alternation in the 5-membered borole ring in heteroarene-fused boroles is responsible for the high degree of antiaromaticity. Theoretical and experimental studies suggest that the LUMO energy of these heteroarene-fused boroles are relevant to the antiaromaticity, which also linearly correlates with their Lewis acidities.¹⁰⁵

In contrast to the Yamaguchi group's fused boroles with electron-rich heteroarene(s), more recently, Marder and coworkers¹²⁹ switched to the electron-poor pyridine to synthesize phenylpyridyl-fused boroles (Scheme 14). Using 4-phenylpyridine to prepare a fused borole, [10a]₄ was obtained as a white solid and adopts a unique coordination mode, forming a tetramer with a central cavity in both the solid state (X-ray diffraction, Fig. 5) and solution (¹H diffusion-ordered spectroscopy (¹H DOSY)). The coordination mode of [10a]₄ is similar to that of dimethyl(3-pyridyl) borane and diethyl(3-pyridyl)borane.133-135 The B-N bond lengths of [10a]₄ (1.644(2)-1.655(2) Å) are comparable to those of pentaphenylborole 2,6-lutidine (1.6567(3) Å)136 and sterically hindered dibenzoborole pyridine (1.638(3) Å);⁷⁵ however, in contrast to both pentaphenylborole 2,6-lutidine and the sterically hindered dibenzoborole pyridine which dissociate in solution at room temperature, $[10a]_4$ persists as a tetramer in C_6D_6 even at 50 °C (¹H DOSY). By switching 4-phenylpyridine to 2-phenylpyridine, 10b was prepared and isolated as a light yellow solid. The boron center of 10b is 3-coordinate in solution but 4-coordinate in the solid state, as evident from solid-state ¹¹B{H} RSHE/MAS NMR measurements. The difference is ascribed to the steric protection of the pyridine nitrogen by the attached phenyl group at the 2-position.

Due to the inherent electron withdrawing properties of pyridine, the electron accepting ability of **10b** is enhanced (see Electrochemical section below). The lowest energy absorption maximum of $[10a]_4$ appears at 322 nm in hexane, which is blue



Scheme 14 Electron-deficient pyridyl-fused boroles.

shifted compared to those of 10b (375 nm) and other 3-coordinate 9-borafluorenes. Compared with other Tip-protected 9borafluorenes, 10b exhibits a relatively high quantum yield (0.34 in hexane) in solution and shows an interesting dual fluorescence property. Two lifetimes are observed at the same emission wavelength of 520 nm. The authors suggested that the dual fluorescence in solution is caused by an equilibrium between the free 3-coordinate 10b and a weak intermolecular coordination adduct of 10b. This hypothesis was further supported by lifetime measurements at different concentrations, low temperature excitation spectra, low temperature ¹H NMR spectra and lifetime measurements upon addition of DMAP to a solution of **10b** to simulate the 4-coordinate **10b** species. Thus, this dual fluorescence is different from dual fluorescence induced by B-N dissociation in the excited state.137 Interestingly, the ratios of the relative percentage of the two lifetimes shows a linear relationship with temperature.



Fig. 5 Molecular structure of [10a]₄. H atoms, isopropyl groups, and C₆D₆ solvent molecules are omitted for clarity. 'Bo' and 'P' denote the planes of the phenylpyridyl-fused borole and the Tip phenyl groups, respectively. Selected bond lengths (Å) and angles (°): B_{Bo1}-N_{Bo4} 1.655(2), B_{Bo2}-N_{Bo1} 1.652(2), B_{Bo3}-N_{Bo2} 1.644(2), B_{Bo4}-N_{Bo3} 1.644(2), B_{Bo1}-B_{Bo2} 5.420(2), B_{Bo2}-B_{Bo3} 5.365(2), B_{Bo3}-B_{Bo4} 5.407(2), B_{Bo4}-B_{Bo1} 5.402(2), ∠Bo1-Bo2 89.70(2), ∠Bo2-Bo3 81.78(2), ∠Bo3-Bo4 89.22(2), ∠Bo4-Bo1 78.44(2), ∠Bo1-Bo3 33.29(3), ∠Bo2-Bo4 33.21(2).

Intramolecular dative bond in 9borafluorenes

Instead of using bulky Tip or Mes* as the protecting group at boron, Chujo and co-workers used the Mamx ligand (Mamx = 2,4-di-tert-butyl-6-[(dimethylamino)methyl]phenyl) as the steric protecting group at boron in 9-borafluorenes (Scheme 15).138 The X-ray crystal structure of MamxBf indicates that the nitrogen atom coordinates to the boron atom with a B-N bond length of 1.712 Å. The ¹¹B NMR spectrum shows a peak at 5.96 ppm, which is in the typical range for 4-coordinate boron. With the double protection of steric hindrance and nitrogen atom coordination to boron, MamxBf is stable to moisture and can be purified in air. The lowest energy absorption of MamxBf is at ca. 280 nm and it exhibits a weak emission at ca. 360 nm. Interestingly, by addition of $B(C_6F_5)_3$ to a benzene solution of **MamxBf**, phosphorescence ($\tau_p = 8.95 \ \mu s \ (69\%)$) with a peak at 597 nm was observed at room temperature, which the authors suggest is caused by triplet exciplexes. Theoretical analysis for the excited state of MamxBf suggests that this robust B-N coordination in the ground state is cleaved in the S1 state. This B-N bond cleavage in the excited state is also suggested to be responsible for the weak emission of MamxBf.

By incorporating electron withdrawing or electron donating groups at the biphenyl core, the energy of 9-Mamx-9-borafluorenes are modulated and emission from bond-cleavage-induced intramolecular charge transfer (BICT) was realized. Compound 11a has two electron withdrawing trifluoromethylphenyl groups at the biphenyl core and it shows a single emission with a peak at 373 nm, which is similar to that of MamxBf. Changing the electron withdrawing trifluoromethylphenyl groups to electron-neutral phenyl groups or electron donating methoxyphenyl groups in 11b and 11c, respectively, result in similar shaped dual emissions (ca. 330 nm and ca. 520 nm, respectively), which is in contrast to the single emission of 11a and MamxBf (Scheme 15). The authors concluded that by



Scheme 15 9-Borafluorenes with Mamx as the exo-aryl group.

incorporation of electron donating groups at the biphenyl core, the boron atom exhibits a more negative charge, and a BICT process thus occurs which results in dual emission. Theoretical calculations further support the BICT transition. The short wavelength emission was assigned to a locally-excited (LE) emission from a π - π * transition and the long wavelength emission was assigned to the BICT transition. The BICT emission is highly sensitive to the solvent viscosity and, thus, 11c can be applied as a ratiometric sensor.139

By exchanging the strongly donating dimethylamine group with the weakly donating methoxy group, Rupar and co-workers synthesized 12a (Scheme 16)140 which is a colorless powder that is air-stable in the solid state and solution. The absorption maximum appears at 284 nm and the emission maximum appears at 536 nm with a long lifetime ($\tau_{\rm F} = 122 \text{ ns}$) in CH₂Cl₂. This is an extraordinary large Stokes shift (16 500 cm⁻¹) for a small molecule; in fact, it is the largest Stoke shifts ever reported.¹⁴¹ This large Stokes shift is caused by the photodissociation of the B-O dative bond in the excited state, which is further supported by theoretical studies. By changing the methoxy groups to methylthio groups or tert-butoxy groups, 12b and 12c were synthesized, respectively, which show nearly identical structural and optical properties to that of 12a. By incorporation of two bithiophene groups as donors at the biphenyl core of 12a, the photophysical properties change significantly. The lowest energy absorption of 12d red shifts to 408 nm and the compound exhibits dual emission with peaks at 446 ($\tau_{\rm F}$ = 0.5 ns) and 639 nm ($\tau_{\rm F}$ = 4.38 ns). DFT calculations indicate that two stable structures are present in the excited state: in one, the B-O bond remains intact (4-coordinate excited state) and in the other one, the B-O bond dissociates (3-coordinate excited state). The shorter wavelength emission exhibits the shorter lifetime and is assigned to the emission from the 4coordinate S_1 state. The long wavelength emission exhibits the longer lifetime and is assigned to the 3-coordinate S1 state.

The Gabbaï group synthesized a diborane (13) with a BMes₂ group and a 9-borafluorene group at the 1- and 8-positions of a naphthalene, respectively (Scheme 17).142 Interestingly, an interaction occurs between the boron atom of the 9-borafluorene and one of the Mes groups. This interaction was confirmed by a short B-C distance (2.730(3) Å) between the boron atom of 9-borafluorene and the carbon atom of the Mes group which is connected to boron. Due to this interaction, the boron atom of the 9-borafluorene is slightly pyramidalized. By changing the BMes₂ group to a diisopropylphosphino group, Bourissou and co-workers synthesized the naphthyl-protected 9borafluorene (14)¹⁴³ which is only stable under an inert atmosphere, but is much more stable than 9-(2-diisopropylphosphinophenyl)-9-borafluorene.144,145 The 11B NMR signal appears at -8.5 ppm, confirming the presence of a P–B dative bond. The



Scheme 16 Intramolecular $O \rightarrow B$ or $S \rightarrow B$ dative bond in 9-borafluorenes.



Scheme 17 Intramolecular $C \rightarrow B$ or $P \rightarrow B$ dative bonds in 9-borafluorenes.

short P–B distance (2.011(2) Å) and the significant pyramidalization ($\sum_{C-B-C} = 338.45(5)^{\circ}$) of the boron confirmed the strong P \rightarrow B interaction. This strong P \rightarrow B interaction, even with fairly bulky substituents on the phosphine, indicates the flexibility of the system. In addition to the above mentioned intramolecular dative bonds in 9-borafluorenes, another interesting topic, namely intramolecular B–B dative bonds (one and two electron σ -bonds) in 9-borafluorenes which can be formed by one or two electron reductions, is discussed in the "Chemical reduction of fused boroles" section of this review (see below).

9-Borafluorene-based main chain polymers

By incorporating 3-coordinate boron atoms into the main chain of conjugated polymer systems, the π -systems are extended compared to the corresponding monomers, leading to different optical properties.²² It could be envisaged that incorporation of more electron-deficient 9-borafluorenes into polymers will lead to interesting properties.146 In 2008, Scherf and co-workers reported a co-polymer incorporating polyfluorenes and 9-borafluorenes in the main chain, and applied it as an anion sensor (Scheme 18).147 Interestingly, the para-cyanophenyl group surprisingly stabilizes the 9-borafluorene, supposedly providing good environmental stability. In contrast to the bulky Tip or ^FMes groups, *para*-cyanophenyl is an "unprotected" phenyl group. Unfortunately, changing the para-cyanophenyl group to other "unprotected" phenyl groups provided unstable 9-borafluorenes. Recently, Rupar and co-workers tried to reinvestigate this compound, but although different techniques were applied, they could not reproduce the reported results.88

The Rupar group adopted Yamamoto or Stille coupling reactions to synthesize two 9-Tip-9-borafluorenes based polymers (Scheme 19).¹⁴⁸ Compared with their monomeric precursor, a red shift of the absorption and emission was observed which can be ascribed to the extended conjugation in the polymers. Quantum yields of 0.50 (16a) and 0.28 (16b) in solution were obtained. 16a and 16b have a much smaller optical bandgap (calculated from the onset of lowest energy absorption) than polyfluorenes or polycarbazoles, which is mainly attributed to the lower LUMO energies of borafluorenes, and their lower LUMO energies were confirmed by measurements of their electrochemical reduction potentials and further supported by calculations. In solution, 16a and 16b are suitable F⁻ sensors. In a film, 16a can also be applied as a sensor for gaseous NH₃.

Chujo and co-workers prepared three 9-Mamx-9-borafluorenebased conjugated polymers by Suzuki–Miyaura cross-coupling reactions (Scheme 20).¹⁴⁹ These polymers are atmospherically





Scheme 18 Polymer of polyfluorenes with in-chain 9-borafluorenes.



Scheme 19 9-Tip-9-borafluorene-based polymers.

stable and contain 4-coordinate boron. Compared with the corresponding gallafluorene polymers, the borafluorene polymers show stronger electron accepting abilities and lower LUMO energies.

Electrochemistry

In this section, selected fused boroles are chosen for comparison of their electron accepting abilities as determined by electrochemical measurements. Although many fused boroles can be reduced twice, here only the first reduction potentials are compared. The reduction potentials for all known aryl group protected fused boroles range from -1.1 to -2.5 V (Table 4). **PhBf**¹¹⁷ exhibits a first reversible reduction potential at -2.16 V, which is in the same range as **TipBf** (-2.11 V (ref. 77) and -2.31 V (ref. 88) were obtained by two different groups) and **Mes*Bf** (-2.28 V).¹⁰³ After incorporation of donating groups (methoxy, amino, or thiophene) on the core of 9-borafluorene, the first reduction potentials of **6d**,⁸⁸ **7a**¹⁰³ and **7b**¹⁰³ do not change significantly, indicating that the donating groups have only a small effect on the electron accepting ability of boron in 9-borafluorenes.

By employing the electron withdrawing ^FMes group as the *exo*-aryl group on a **Bf**, the electron accepting ability of ^F**MesBf** was enhanced and the reduction potential shifts to -1.93 V.⁸⁸ The first reduction potential of phenylpyridyl-fused borole **10b** $(E_{1/2}^{\text{red}} = -1.94 \text{ V})^{129}$ is comparable to that of ^F**MesBf**, which suggests that the effect of fusing a pyridyl group onto boroles on their reducibility is comparable to that of the *exo*-^FMes group in 9-borafluorenes. Benzothiophene-fused borole **3c**⁷⁷ exhibits a first reversible reduction potential of -1.72 V, which is less negative than the electron withdrawing group-functionalized



Scheme 20 9-Mamx-9-borafluorene-based polymers.

 Table 4
 First and second reduction potentials of (hetero)arene-fused boroles

Compound	$E_{1/2}/V(1)$	$E_{\rm pc}/{\rm V}$ (2)	Conditions
PhBf ¹¹⁷	-2.16	_	0.1 M $[^{n}$ Bu ₄ N][B(C ₆ F ₅) ₄] in THF
TipBf ⁷⁷	-2.11	-3.05	$0.1 \text{ M} [^{n}\text{Bu}_{4}\text{N}][\text{PF}_{6}] \text{ in THF}$
TipBf ⁸⁸	-2.31	_	$0.1 \text{ M} \begin{bmatrix} n \text{Bu}_4 \text{ N} \end{bmatrix} \text{ PF}_6 \text{ in THF}$
Mes*Bf ¹⁰³	-2.28		$0.1 \text{ M} [^{n}\text{Bu}_{4}\text{N}][\text{ClO}_{4}] \text{ in THF}$
6d ⁸⁸	-2.36	_	$0.1 \text{ M} [^{n}\text{Bu}_{4}\text{N}][\text{PF}_{6}] \text{ in THF}$
$7a^{103}$	-2.04	-2.70(r)	$0.1 \text{ M} [^{n}\text{Bu}_{4}\text{N}][\text{ClO}_{4}] \text{ in THF}$
$7b^{103}$	-2.19	-3.00	$0.1 \text{ M} [^{n}\text{Bu}_{4}\text{N}][\text{ClO}_{4}] \text{ in THF}$
FMesBf ⁸⁸	-1.93	_	$0.1 \text{ M} [^{n}\text{Bu}_{4}\text{N}][\text{PF}_{6}] \text{ in THF}$
10b ¹²⁹	-1.94	-2.90	0.1 M $[^{n}Bu_{4}N][PF_{6}]$ in THF
3a ⁸⁸	-1.98	-2.79	$0.1 \text{ M} \begin{bmatrix} n \text{Bu}_4 \text{ N} \end{bmatrix} \text{ PF}_6 \text{ in THF}$
3 b ⁸⁸	-1.96	-2.89	0.1 M $[^{n}Bu_{4}N][PF_{6}]$ in THF
3c ⁷⁷	-1.72	-2.61	0.1 M $\begin{bmatrix} n & 1 \\ Bu_4 & N \end{bmatrix} \begin{bmatrix} PF_6 \end{bmatrix}$ in THF
3d ¹⁰⁵	-2.25	-3.04	$0.1 \text{ M} \begin{bmatrix} n \text{Bu}_4 \text{N} \end{bmatrix} \begin{bmatrix} \text{PF}_6 \end{bmatrix}$ in CH ₂ Cl ₂
3e ¹⁰⁵	-1.97	-2.85	0.1 M [^{n} Bu ₄ N][PF ₆] in CH ₂ Cl ₂
3f ¹⁰⁵	-1.89	-2.78	0.1 M $\begin{bmatrix} n Bu_4 N \end{bmatrix} \begin{bmatrix} PF_6 \end{bmatrix}$ in CH ₂ Cl ₂
4 (ref. 80)	-1.51	-2.42	0.1 M $[^{n}Bu_{4}N][PF_{6}]$ in THF
18 (ref. 150)	-1.49	-1.75	0.1 M $\begin{bmatrix} n \\ Bu_4 N \end{bmatrix} \begin{bmatrix} PF_6 \end{bmatrix}$ in THF
1a ⁶⁸	-1.21	-2.12	0.1 M $[^{n}Bu_{4}N][PF_{6}]$ in CH ₂ Cl ₂
1 b ⁶⁸	-1.13	-2.04	0.1 M $[^{n}Bu_{4}N][PF_{6}]$ in CH ₂ Cl ₂
1c ⁶⁸	-1.28	-2.15	0.1 M $\begin{bmatrix} n Bu_4 N \end{bmatrix} \begin{bmatrix} PF_6 \end{bmatrix}$ in CH ₂ Cl ₂
$5\mathbf{b} \cdot \mathrm{THF}^{117}$	-2.42 (ir)	_	0.1 M $[^{n}Bu_{4}N][B(C_{6}F_{5})_{4}]$ in THF
ⁱ Pr ₂ NBf ⁸⁸	-2.95		0.1 M $[^{n}Bu_{4}N][PF_{6}]$ in THF

^FMesBf and 10b. The strong electron accepting property of 3c is attributed to its enhanced antiaromaticity. Diborole 4 (ref. 80) and the biphenyl-linked diborole 18 (Scheme 21)^{85,150} exhibit much less negative half reduction potentials of -1.51 and -1.49 V, respectively. The strong electron accepting ability of 4 and 18 is due to the two boron centers being linked to a πconjugated unit. This enhancement is also observed in triarylboranes with two or more boron centers.^{100,151-153} By incorporation of four additional CF₃ groups at the biphenyl core, the first half reduction potentials of 1a and 1b shift to -1.21 and -1.13 V, respectively.⁶⁸ Surprisingly, although 1a and 1b exhibit extraordinarily low reduction potentials, both are stable in air.

Attempts to use noncoordinating solvents (CH_2Cl_2 and α, α, α trifluorotoluene) for the cyclic voltammetry study of perfluorinated-**PhBf**, **5b** were unsuccessful, so THF was employed.¹¹⁷ An irreversible process with a reduction potential at -2.42 V *vs.* Fc/Fc⁺ was observed. Such a negative reduction potential, which is even more negative than that of **PhBf**, was



Scheme 21 One electron reduced arene-fused boroles.

not expected. The authors suggested that the reduction process actually takes place at the fluorinated aromatic framework, not at the boron center due to the formation of **5b**·THF in THF. ⁱ**Pr₂NBf** has the most negative reversible half reduction potential of -2.95 V.⁸⁸ The weak electron accepting ability of ⁱ**Pr₂NBf** is caused by the electron-rich nitrogen atom π -backbonding to the vacant p_z-orbital of boron.

Chemical reduction of fused boroles

Boroles readily accept one electron to form a radical anion or two successive electrons to give a dianion. The chemical reduction of non-fused "free" boroles and some 9-borafluorenes was reviewed by the Braunschweig group in 2011 (ref. 48) and 2016.⁴⁹ Here we focus only on fused boroles.

One electron reduction of 9-borafluorene leads to a radical anion. In 2008, the Yamaguchi group reduced Mes*Bf with potassium in THF and the EPR signal of the reduced Mes*Bf exhibits an eleven-line signal (g = 2.002).¹⁰³ According to the simulation of the spectrum, the spin density on boron is estimated to be 0.21, indicating delocalization over the biphenylene unit of the 9-borafluorene. A similar reaction was also carried out with 7b and a spin density of 0.18 on boron was estimated by simulation. The lower spin density on boron in 7b suggested that it is delocalized over the bithiophene skeleton. The Piers group synthesized the ladder-type diborole 4 which exhibits a first reversible reduction at -1.51 V. Such a small negative reduction potential makes it possible to perform a one electron reduction with bis(pentamethylcyclopentadienyl)cobalt(II) $(E^{0'}(Cp_2^*Co) = -1.9 \text{ V}).^{154}$ Isolated [4][CoCp_2] is a deep blue solid (Scheme 21).⁸⁰ The C1–C1' distance in [4][CoCp*₂] of 1.410(3) Å is significantly longer than that of its neutral form for which d(C1-C1') = 1.367(5) Å while d(B1-C1) of $[4][CoCp*_2]$ with 1.524(3) Å is significantly shorter compared to 1.571(4) Å for 4. A detailed inspection of the structure combined with a theoretical analysis shows that there is still a high degree of delocalization of the unpaired electron throughout the whole π system.

In 2014, Wagner and co-workers linked two 9-borafluorenes by a biphenyl (18) and carried out the one electron reduction with lithium naphthalenide in toluene (Scheme 21),150 obtaining [18]Li·(THF)₄ × 0.5C₁₀H₈ as black crystals. Single crystal Xray diffraction shows that the distance between the two boron centers of [18]Li · (THF)₄ × 0.5C₁₀H₈ is 2.265(4) Å, which is 0.655 Å shorter than that in its precursor 18 (2.920(6) Å) (Fig. 6),⁸⁴ and lies between those of 18 (no B-B bond) and [HBf-HBf][K · Et₂O]K (1.83(2) Å) or [HBf-HBf][Na · (THF)₃]₂ (1.822(4) Å, B-B two electron σ -bond. It is important to note that [HBf-HBf]Na₂ can be prepared in quantitative yields and represents an extremely rare example of diborane(6) dianions).^{155–158} In [18]Li·(THF)₄ × 0.5C₁₀H₈, only a moderate pyramidalization of the two boron centers was observed ($\sum_{C-B-C} = 351.6^{\circ}$ and 353.0°). The EPR spectrum of [18]Li in THF exhibits a seven-line signal. The spectrum was successfully simulated, assuming the two boron nuclei to be magnetically equivalent $(a(^{11}B) = 4.8 \pm 0.1 \text{ G and})$ $a(^{10}B) = 1.6 \pm 0.1$ G), and the small $a(^{11}B)$ value strongly supports the contribution of the unpaired electron to a 2p_z- $\sigma(B \cdot B)$ bond. The computed SOMO and the localization of the spin-density mainly between the two boron centers further

confirm the existence of a B·B one electron σ -bond. [18] Li·(THF)₄ × 0.5C₁₀H₈ is the first crystallographic characterized compound to have a B·B one electron σ -bond.

One year later, a radical anion containing two 9-borafluorenes linked by a substituted methylene group, **[19]**Li, was synthesized by a comproportionation reaction between neutral **19** and its dianion, **[19]**Li₂.¹⁵⁸ The radical anion [Li(THF)₄][**19**]·(THF)₄ × THF was characterized by single-crystal X-ray diffraction and exhibits a B···B distance of 2.166(4) Å. *Via* simulation of the EPR spectrum, comparable hyperfine coupling values of [**19**]⁻⁻ ($a(^{11}B) = 5.1 \pm 0.1$ G and $a(^{10}B) = 1.7 \pm 0.2$ G) to that of [**18**]⁻⁻ were obtained. Based on the small $a(^{11}B)$ value, as well as the low degree of pyramidalization of the boron atom in [Li(THF)₄][**19**]·(THF)₄ × THF, the authors concluded that there is a strong contribution from p_z orbital on each boron to the SOMO. This is similar to the situation in [**18**]⁻⁻, but the hyperfine coupling to protons in [**19**]⁻⁻ suggests that the spin density is delocalized over the π -systems.

The tetrakis-CF₃-functionalized ^FMesBf, 1b synthesized by Marder and co-workers exhibits a first half-reduction potential at -1.13 V, and thus can be reduced by Cp₂Co ($E^{0\prime}$ (Cp₂Co) = -1.3V).154 [1b][Cp2Co] was obtained as a dark purple solid with a complex EPR signal centered at $g_{iso} = 2.004$ in THF, consisting of hyperfine splitting to boron ($a(^{11}B) = 3.3$ G), the fluorine atoms $(a(^{19}\text{F}) = 11.3 \text{ and } 6.0 \text{ G})$ from the CF₃ groups at the 9-borafluorene core, and the hydrogen atoms $(a(^{1}H) = 6.1 \text{ and } 2.9 \text{ G})$ at the 9borafluorene core. The relatively large proton and fluorine hyperfine couplings, in contrast to the relatively small boron hyperfine coupling, indicates that the spin density is delocalized significantly over the biphenyl core of the 9-borafluorene. Compared to the crystal structure of neutral 1b, changes in bond lengths of [1b] [Cp₂Co] were mainly observed on the 9-borafluorene core, indicating delocalization of the unpaired electron on the 9-borafluorene core, with no contribution from the exo-aryl ^FMes group.⁶⁸

The discovery and study of 9-borafluorenyl dianions were reported earlier than that of the radical anions of 9-borafluorenes. In 1996, during an investigation of the reduction of sterically encumbered arylboron dihalides, the Power group isolated a bislithium-9-borafluorenyl complex [20]Li₂·(Et₂O)₂ (Scheme 22),¹⁵⁵ obtained directly by treatment of 2,6-Mes₂C₆H₃BX₂ (X = Br or Cl) with an excess of lithium in Et₂O. [20]Li₂·(Et₂O)₂ is a red solid with a ¹¹B NMR (C₆D₆) chemical shift of 14.3 ppm (s, $W_{1/2} \approx 380$



Fig. 6 Molecular structure of [18]^{•–}. Hydrogen atoms, THF, C₁₀H₈ and the lithium cation are omitted for clarity. The dashed red line indicates the one-electron σ -bond. Selected bond lengths (Å) and angles (°): B1–B2 2.265(4), B1–C1 1.579(3), B1–C11 1.582(3), B1–C21 1.583(3), B2–C41 1.582(3), B2–C51 1.578(3), B2–C31 1.576(3), sum of \angle C–B1–C 351.6, sum of \angle C–B2–C 353.0.



Hz). [20]Li₂·(Et₂O)₂ was the first structurally characterized 9-borafluorenyl dianion, the core of which is still planar. The lithium ions are solvated by diethyl ether and adopt an η^5 -coordination to the 5membered borole ring. Reduction of 2,6-Mes₂C₆H₃BBr₂ with lithium in benzene over 5 days and extraction with ether/hexane gave a dimer that has a structure analogous to that of [20]Li₂-·(Et₂O)₂. [2a]Li₂ (ref. 75) and [PhBf]Li₂ (ref. 65) were isolated by treatment of the corresponding 9-borafluorenes with lithium in diethyl ether or THF. [2a]Li2 is a deep red, almost black solid with a ¹¹B NMR (C₆D₆) chemical shift of 13.6 ppm (s, $W_{1/2} \approx 430$ Hz). The two lithium ions in [2a]Li₂·(Et₂O)₂ are also solvated by diethyl ether and are situated almost symmetrically above and below of the 5-membered borole core. The ¹¹B NMR (d_8 -THF) chemical shift of [PhBf]Li₂ shows a sharp peak at 6.3 ppm. By treatment of diborole 4 with potassium naphthalenide (2 eq.) in THF, $[4]K_2$ was isolated as a red solid with a ¹¹B NMR (C₆D₆) chemical shift of 32.1 ppm. Its Xray crystal structure indicates that the two potassium atoms are situated above and below the center of the dibenzo-fused-diborole core in a centrosymmetric arrangement.⁸⁰ Similarly to diborole 4, compound 19 possesses two 9-borafluorene moieties and thus can easily accept two electrons.¹⁵⁸ The dianion [19]Li₂ was obtained as a red solid with a ¹¹B NMR (d_8 -THF) chemical shift of -6.7 ppm ($h_{1/}$ $_{2} = 270$ Hz). The distance between the two boron atoms in [19] $[Li(Et_2O)_2]$ $[Li(Et_2O)]$ is 1.906(3) Å, which is shorter than that in its radical anion ([Li(THF)₄][19] \cdot (THF)₄ × THF, 2.166(4) Å) and neutral form (19, 2.534(2) Å). The \angle B–C–B angles decrease from 105.5(2)° $([19][Li(Et_2O)_2][Li(Et_2O)])$ to 86.9(2)° (radical anion $[Li(THF)_4]$ $[19] \cdot (\text{THF})_4 \times \text{THF}$, and to 73.2(1)° (neutral form 19). The spectroscopic and structural parameters clearly suggest the presence of a covalent two center-two electron (2c-2e⁻) B-B bond in [19]Li₂, which was further supported by theoretical studies.

The Wagner group also investigated the redox chemistry of 9-H-9-borafluorene, **21** (Scheme 22).^{159,160} Upon reduction, adducts arising from extensive structural rearrangement were



Scheme 23 Pyridine or acridine coordinated borafluorenium cations.



Scheme 24 Carbene-stabilized borafluorenium cations.

formed and the corresponding mechanism was studied. Besides rearrangement adducts, recently, the dianion $[21]^{2-}$ was isolated upon reduction of monomeric $21 \cdot \text{THF}.^{157}$ Treatment of **21** with lithium, sodium or potassium in THF led to the isolation of the respective dianions. $[21]\text{Li}_2 \cdot (\text{THF})_3$ and [21] $[\text{Na} \cdot (\text{THF})_3][\text{Na} \cdot \text{THF}]$ were obtained as greenish-brown solids and $[21]\text{K}_2 \cdot (\text{THF})$ is a brown solid. The ¹¹B NMR (d_8 -THF) chemical shifts are 3.7 ppm (s, $W_{1/2} \approx 290$ Hz, $[21]\text{Li}_2$), 3.9 ppm (s, $W_{1/2} \approx 290$ Hz, $[21]\text{Na}_2$) and 8.0 ppm (s, $W_{1/2} \approx 360$ Hz, 21K_2). From a comparison of the bond lengths of the computed structure of neutral **21** and of the reduced form $[21][\text{Na} \cdot (\text{THF})_3]$ [Na·THF], the authors draw the conclusion that the two added electrons are delocalized over the 9-borafluorene core, rather than being localized at the p_z -orbital of boron. $[21]^{2-}$ is the first example of a hydride ligand-stabilized 9-borafluorene anion. Due to the easy abstraction of the hydride, $[21]^{2-}$ is a surrogate of a nucleophilic 9-borafluorene anion. The reaction of $[21]^{2-}$ with MeI and Et₃SiCl further proves that $[21]^{2-}$ can be applied as a 9-borafluorene anion. Similarly, reaction of B–B dianions with MeI led to the formation of 9-methyl-borafluorenes.^{161,162} At the same time, radical reactivity of $[21]^{2-}$ was found, *e.g.*, by the reaction of $[21]^{2-}$ with Me₃SnCl or (bromomethyl)cyclopropane.

Three-coordinate borafluorenium cations

Instead of adding electrons to **Bf**s in a reduction process, another interesting topic is extracting an anion from 3-coordinate **Bf** to generate a 3-coordinate borafluorenium cation. In 1985, Nöth and co-workers applied GaCl₃ and AlCl₃ as a Cl⁻ acceptor for the pyridine adduct of **ClBf** and the acridine adduct of **ClBf** (Scheme 23).¹⁶³



Scheme 25 Structures of compounds with Arabic numbers.

Both **[PyBf]**[GaCl₄] and **[AcrBf]**[GaCl₄] are red solids. Due to the insolubility of **[PyBf]**[GaCl₄] in most solvents, the only direct proof of the formation of **[PyBf]**[GaCl₄] is its IR spectrum which exhibits a strong band at 373 cm⁻¹. This band is in the typical range for ν_{abs} (GaCl₄).¹⁶⁴ The structure of **[AcrBf]**[GaCl₄] was confirmed by single crystal X-ray diffraction, but without further characterization or study.

Interested in the properties of borafluorenium cations, recently, Gilliard Jr and co-workers extracted a bromide ion from carbene-stabilized **BrBf**s with AgSbF₆ and synthesized **[IPrBf]**[SbF₆] and [^{Et2}CAACBf][SbF₆] (Scheme 24).¹⁶⁵ The ¹¹B NMR spectra of [**IPrBf**][SbF₆] and [^{Et2}CAACBf][SbF₆] show signals at 63.6 and 65.5 ppm, respectively, confirming that these two borafluorenium cations are 3-coordinate. Inspired by the decolorization upon addition of THF, they designed [**IPr^{MeO}Bf**] [SbF₆] to tune the color.

The single-crystal X-ray diffraction analyses indicate that the two C-B bond lengths in the borole ring are the same for $[IPrBf][SbF_6]$ (C1-B1 1.615(11) and C2-B1 1.57(2) Å, Fig. 7) and [Et2CAACBf [SbF₆] (C1-B1 1.553(10) and C2-B1 1.567(10) Å). However, in [IPr^{MeO}Bf] [SbF₆], the C1–B1 bond (1.509(7) Å) is much shorter than the C2–B1 bond (1.602(7) Å). The authors suggested that this is caused by the conjugation of the lone pair on oxygen with the cationic boron center. Interestingly, compared to [IPrBf [SbF₆] and [^{Et2}CAACBf] [SbF₆] which exhibit a very weak absorbance in the 400–600 nm range in CH₂Cl₂, a strong absorbance at 430-600 nm in CH₂Cl₂ was found for [IPr^{MeO}Bf][SbF₆]. Another interesting finding is that [IPr- $^{MeO}Bf[SbF_6]$ shows thermochromic behavior; the red color of [IPr-MeOBf[[SbF₆] faded to colorless in non-coordinating solvents upon cooling. The authors suggested that this phenomenon is caused by an intermolecular O···B interaction of [IPr^{MeO}Bf[[SbF₆] which is favored at low temperature. Attempts to grow colorless crystals of [IPr^{MeO}Bf][SbF₆] which feature an O…B interaction at low temperature were unsuccessful. Furthermore, to support their hypothesis, THF was added to simulate the intermolecular coordination. After addition of 50 equivalents of THF to a red CH₂Cl₂ solution of [IPr-MeOBf[[SbF₆], the solution became colorless. When this solution was heated to 40 °C, the red color was recovered. After cooling, this solution became colorless again. These phenomena further support the hypothesis of an intermolecular O···B interaction at low temperature.



Fig. 7 Molecular structures of **[IPrBf]**[SbF₆] (left), [^{Et2}CAACBf][SbF₆] (middle) and **[IPr^{MeO}Bf**][SbF₆] (right). H atoms, isopropyl groups and [SbF₆][−] are omitted for clarity. Selected bond lengths (Å) and angles (°) **[IPrBf**][SbF₆]: B1–C1 1.57(2), B1–C2 1.528(3), B1–C3 1.618(2), ∠C1–B1–C2 111.9(10). [^{Et2}CAACBf][SbF₆]: B1–C1 1.553(10), B1–C2 1.567(10), B1–C3 1.581(10), ∠C1–B1–C2 104.7(6). **[IPr^{MeO}Bf**][SbF₆]: B1–C1 1.509(7), B1–C2 1.602(7), B1–C3 1.586(6), C_{sp²}–O 1.354(8), ∠C1–B1–C2 106.4(4).

Conclusions and outlook

This review begins with the fundamental synthetic strategies for preparing (hetero)arene-fused boroles and the stability of different 9-substituent-9-borafluorenes, and then discusses functionalized (hetero)arene-fused boroles which can be applied as Lewis acids, activators of H_2 , fluorescent materials, electron accepting units, *etc.* For functionalized (hetero)arenefused boroles, the chemistry of reported 9-borafluorenes is classified, and a guide for the design of novel (hetero)arenefused boroles to achieve different properties is provided.

Compared to the corresponding triarylboranes, (hetero) arene-fused boroles exhibit an enhanced electron accepting ability, which is attributed to the antiaromaticity and strain of the 5-membered borole ring. Triarylboranes have found wide application, *e.g.*, as acceptors in TADF materials. The *exo*-aryl group of 9-aryl-9-borafluorene adopts a twisted arrangement with respect to the 9-borafluorene core and thus, by functionalization, may also generate good candidates for TADF materials. Surprisingly, thus far, only one such example was reported outside of patents. More studies on the functionalization of the *exo*-aryl moiety will be of particular interest.

Compared to non-fused "free" boroles, arene-fused boroles exhibit higher stability and potential for functionalization. Depending on the fused aryl groups, enhanced electron accepting ability and enhanced antiaromaticity, even greater than that of non-fused "free" boroles, unique coordination modes, and dual fluorescence can be realized. Heteroarenefused boroles are interesting compounds which require further study, (*e.g.*, other electron-rich or -poor heteroarenefused boroles), as they have many potential applications.

Conflicts of interest

There are no conflicts to declare.

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