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Review

9-Borafluorenes: Synthesis, Properties, and Reactivity

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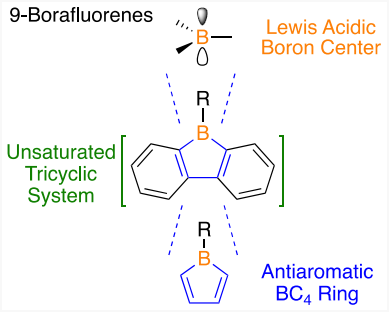
ABSTRACT: This review covers all aspects of 9-borafluorene chemistry, from the first attempted synthesis in 1960 to the present. This class of molecules consists of a tricyclic system featuring a central antiaromatic BC_4 ring with two fused arene groups. The synthetic routes to all 9-borafluorenes and their adducts are presented. The Lewis acidity and photophysical properties outlined demonstrate potential utility as sensors and in electronic materials. The reactivity of borafluorenes reveals their prospects as reagents for the synthesis of other boron-containing molecules. The appealing traits of 9-borafluorenes have stimulated investigations into analogues that bear different aromatic groups fused to the central BC_4 ring. Finally, we offer our views on the challenges and future of borafluorene chemistry.



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1. INTRODUCTION

9-Borafluorenes consist of a tricyclic system featuring a BC_4 ring with two fused arene groups. These molecules can be viewed as polycyclic variants of boroles with extended conjugation as boroles and 9-borafluorenes both contain an antiaromatic unsaturated four π-electron BC_4 ring. Alternatively, 9-borafluorenes can be described as boron congeners of fluorene in which the tetrahedral carbon center linking the biphenyl unit is replaced by a trigonal planar boron center with a vacant p-orbital. The extended conjugation and antiaromatic state of 9-borafluorenes engender unique optoelectronic properties and diverse reactivity.

Polycyclic aromatic hydrocarbons (PAHs) are widely used in electronic materials due to their low HOMO−LUMO energy gaps and conducting properties.[1−7] Doping PAHs with boron, such as in 9-borafluorenes, introduces a vacant orbital that can alter these properties, in many cases enhancing them for potential utility in devices. Boron doped PAHs have been recognized to have appealing properties for components in electronic materials, including organic light emitting diodes (OLEDs),[8−17] organic photovoltaic cells (OPVs),[8,10−18] organic field-effect transistors (OFETs),[9,11,12,14,15,17,18] medical imaging agents,[11,14,18] and sensors.[8−11,13,14,16,18,19]

This review covers the entire history of 9-borafluorene chemistry beginning with the initial synthetic attempts by Davidson and French in 1960[20] to the present day. Despite the seminal synthesis of 9-borafluorene derivatives by Köster and Benedikt in 1963,[21] only sporadic research on borafluorenes was published in the remainder of the 20th century. In general, boron heterocycle research has become a rapidly growing field since the turn of the century,[10−12,15,17,22−43] and borafluorene research is no exception. At the beginning of the 21st century, conjugated boracycles were recognized for their potential as components in electronic materials and devices with recent research focused on enhancing photophysical properties of these species and developing their utility as reagents.[8−16,18,19,30,35,37,44−48]

The scope of the review is comprehensive and includes all aspects of borafluorene chemistry. The synthesis of all known borafluorenes and their Lewis acid−base adducts are presented. The methods employed to construct the central borafluorene core, modification of the substituent at boron, and functionalization of the biphenyl backbone are all disclosed. The properties of borafluorenes are discussed with an emphasis on the Lewis acidity, absorbance, and fluorescence that can be taken advantage of in sensory applications and in electronic devices. The Lewis acidic boron center and antiaromatic ring give diverse synthetic opportunities to construct more sophisticated boron-containing molecules. The reactivity spans deborylative ring opening, intra- and intermolecular ring expansion reactions, thermal rearrangements, reduction, and metal complexation. There have been several reports of molecules that share the same borole core but have different aromatic groups fused to the BC_4 ring: a brief summary of these compounds is also included. Finally, an outlook on the field is presented.

Despite being known since 1963, a compilation focused on 9-borafluorenes is absent in the literature.[49] In contrast, their nonannulated analogues, boroles, have been the subject of multiple reviews.[38,50−54] Boron heterocycles and boron-doped polycyclic aromatic hydrocarbons have been covered extensively in the secondary literature.[8−19,22−44,47,55−71] The aim of this document is to present a comprehensive review on 9-borafluorene species to serve as a resource for research and teaching.

2. SYNTHESIS

Constructing the central borole ring is a crucial step in the synthesis of 9-borafluorenes, which can be accomplished through intramolecular ring closure reactions and transmetalation reactions. Functionalization of 9-halo-9-borafluorenes at boron is an efficient method to diversify 9-borafluorene derivatives, which is appealing as the substituent on boron can alter the optical/electronic properties and stability. The synthetic strategies are addressed thoroughly in this section. Because 9-borafluorenes feature a tricoordinate boron center that is susceptible to bind Lewis bases to form tetracoordinate species, many 9-borafluorene Lewis acid−base adducts have been synthesized and are included in this section.

2.1. Intramolecular Ring Closure Reactions

2.1.1. Thermolysis of 2-Biphenylylboranes. Attempts toward the synthesis of 9-borafluorenes by a ring closure strategy date to 1960, in which 2-(dichloroboryl)biphenyl (**1**) was used as a precursor to attempt to prepare 9-borafluorenes (**2** and **3**) by Davidson and French (Figure 1a).[20] Their attempts were

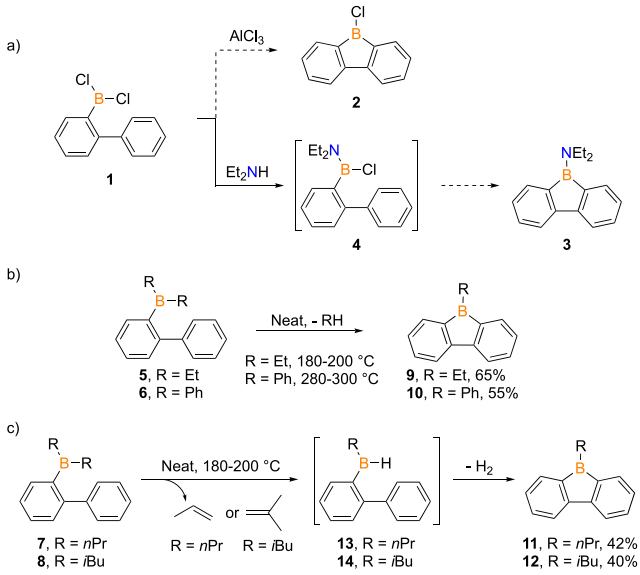

Figure 1. (a) Original attempts to synthesize 9-borafluorenes. (b) Pioneering thermochemical synthesis of 9-borafluorenes. (c) Reaction mechanism for the synthesis of *n*Pr and *i*Bu substituted 9-borafluorenes.

unsuccessful in generating 9-chloro-9-borafluorene (**2**) because the $AlCl_3$, used as the arylation catalyst, reacted uncontrollably. Preparation of 9-diethylamino-9-borafluorene (**3**) from this method also failed as 2-(1-chloro-1-diethylaminoboryl)biphenyl (**4**) could not be isolated and the in situ reaction resulted in a complex mixture of compounds.[20]

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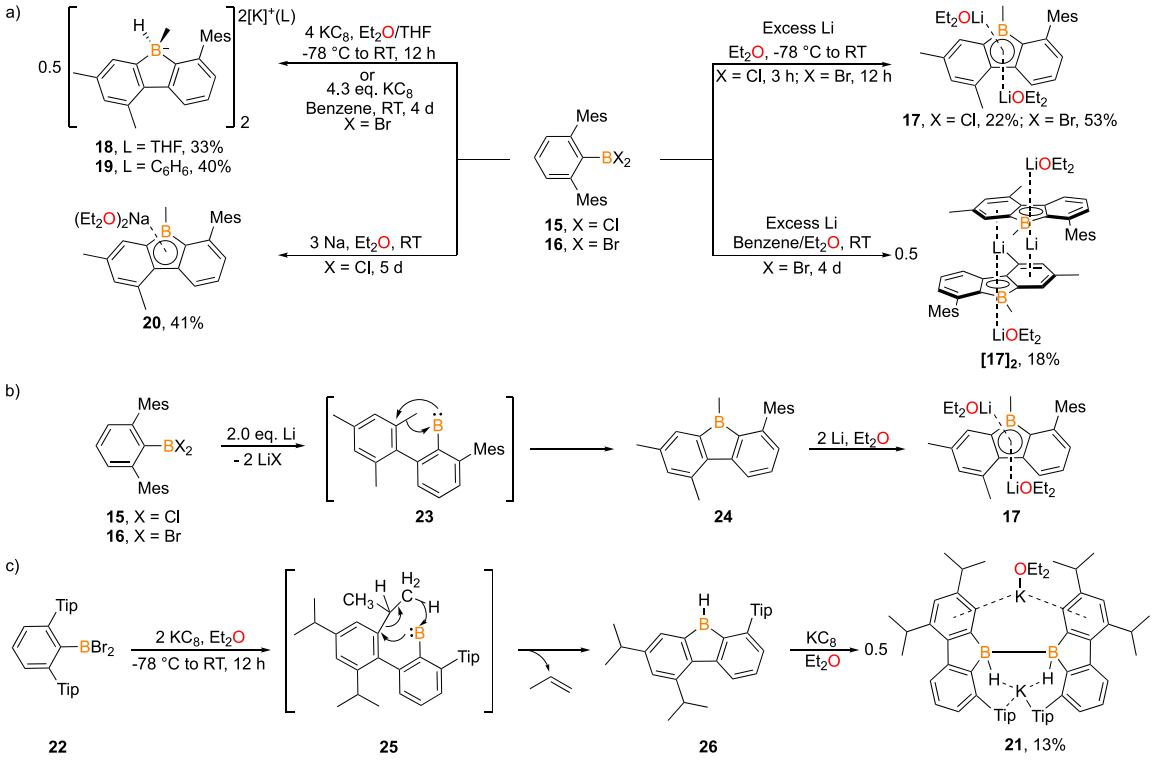

Figure 2. (a) Reduction of $ArBX_2$ reagents (Ar = 2,6-$Mes_2C_6H_3$), Mes = 2,4,6-trimethylphenyl. (b) Mechanism to generate **17**. (c) Reduction of Tip-terphenylBBr_2 with KC_8 (Tip = 2,4,6-triisopropylphenyl).

The pioneering report by Köster and Benedikt in 1963 disclosed the thermolysis of 2-biphenylyldialkylboranes, and 2-biphenylyldiphenylborane (**5**−**8**) induced the ring closure to access 9-borafluorenes (**9**−**12**) in moderate yields (40−65%) with a hydrocarbon byproduct (Figure 1b).[21] It is notable that the substituent on boron impacts the reaction. For 9-propyl-9-borafluorene (**11**) or 9-isobutyl-9-borafluorene (**12**), a dehydroboration (propylene or isobutene release) first generates a secondary borane intermediate (**13** and **14**, respectively) that subsequently rearranges to the target 9-alkyl-9-borafluorene (**11** and **12**), concomitant with H_2 elimination (Figure 1c). In these reactions, the target compounds were obtained in lower yields (40−42%) than those that did not proceed through secondary borane intermediates (55−65%).[21] Although a milestone in borafluorene synthesis, this synthetic route is limited by the high temperatures required.

2.1.2. Alkali Metal Reduction of Arylboron Dihalides. In 1996, Grigsby and Power reported the isolation of a series of anionic and dianionic 9-borafluorene species (**17**−**21**) from the alkali metal reductions of sterically hindered arylboron dihalides.[72] Although the motivation for conducting the reactions was targeting diborenes (RB=BR), the reduction of $ArBX_2$ species (Ar = 2,6-$Mes_2C_6H_3$; X = Cl, **15**; X = Br, **16**) with excess lithium generated the dianionic 9-methyl-9-borafluorene species isolated as a monomer (**17**) in diethyl ether or a dimer ($[\mathbf{17}]_2$) in benzene (Figure 2a). The generation of dianionic **17** is believed to occur by reduction of **15** or **16** to borylene **23** that is unstable and rearranges to 9-methyl-9-borafluorene **24**, which is reduced to dianion **17** (Figure 2b). Reductions of terphenylboron dihalides with excess KC_8 gave anionic 9-borafluorenes **18** and **19** with B−H bonds. The reduction with sodium generates a monoanionic 9-borafluorene species with sodium bound to the central BC_4 ring (**20**, Figure 2a). Reduction of a bulkier triisopropyl-terphenylboron dibromide (**22**) with excess KC_8 in diethyl ether affords a diborate with a B−B bond and hydrides on each boron in 13% yield (**21**, Figure 2c). The presumed mechanism involves a rearrangement of borylene intermediate **25** to 9-H-9-borafluorene derivative **26** accompanied by the elimination of propylene. The resulting species (**26**) undergoes a one-electron reduction to form a radical that dimerizes to diborate **21**.

2.1.3. Reaction of Terphenyllithium Reagents with $H_2ClB{\cdot}SMe_2$. Ring closure reactions can also be mediated by tetracoordinate boron hydride reagents, exemplified in the synthesis of unsymmetrical 9-borafluorene **27** by the reaction of 2,6-bis(4-*tert*-butylphenyl)phenyllithium with $H_2ClB{\cdot}SMe_2$ (Figure 3a). The yield is solvent dependent (70−75% in hexanes, 50−53% in diethyl ether, no product observed in THF), with coordinating solvents suppressing the formation of **27**.[73] The effect of substitution on the 2,6-aryl groups on the reactivity was evaluated by altering the terphenyllithium reagent with 3,5-dimethylphenyl-, 2-methylphenyl- and 2,6-dimesitylphenyllithium compounds in place of the 4-*tert*-butylphenyl substituents (Figure 3b). Interestingly, only the reaction of 2,6-$(3,5\text{-}Me_2C_6H_3)_2C_6H_3Li$ with $H_2ClB{\cdot}SMe_2$ resulted in the formation of an unsymmetrical 9-borafluorene akin to **28**, albeit in low yield (21%). The other two reactions furnished dimeric arylborane species $[(ArBH_2)_2$; **29** and **30**$]$, which have a tendency to suffer from ligand scrambling to form Ar_2BH and BH_3.[74,75] The reactivity is governed by the availability of hydrogens on the aryl substituent in the *o*,*o*′-positions. For instance, if one of the two hydrogens at the *ortho*-positions of the aryl substituent is replaced by methyl group, the dimeric borane (e.g., **29**) is isolated. However, if the *ortho*-positions of the aryl group are all unsubstituted, the dimeric borane is not obtained as intramolecular C−H activation takes place at room temperature

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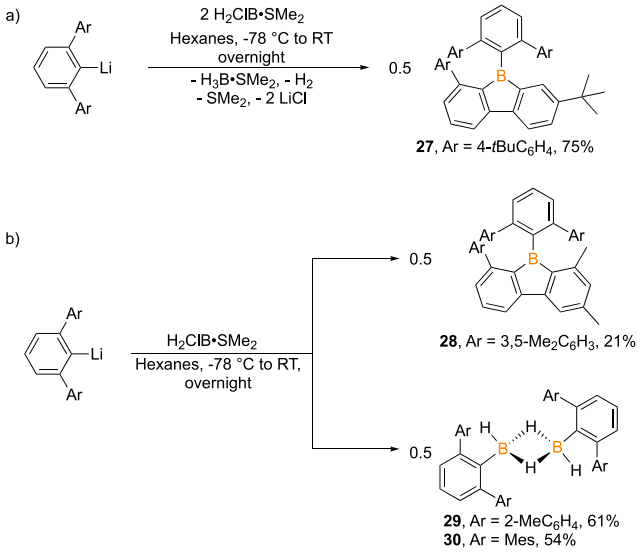

Figure 3. Reactions of substituted terphenyllithium reagents with $H_2ClB{\cdot}SMe_2$ to access borafluorenes.

to generate the terphenyl-substituted 9-borafluorene (e.g., **28**).[76]

2.1.4. Ring Closure Reactions from Boronic Esters. Boronic esters can be used as precursors to 9-borafluorene derivatives through ring closure reactions. In 2019, Urban, Durka, and coworkers reported the synthesis of 9-borafluorenes by the reaction of 2-bromo-2′-(dimethoxyboryl)biphenyl (**31**) or 2-bromo-2′-(dimethoxyboryl)octafluorobiphenyl (**32**) with *t*BuLi in THF at −105 °C (**35** and **36**, Figure 4). Four-coordinate dimethoxyborate species **33** and **34** were proposed intermediates, which were quenched with HCl to afford the 9-methoxy-9-borafluorenes.[77] Although yields were not reported, the crude products readily react with 8-hydroxyquinoline to generate the corresponding adducts (**153** and **154**) in good yields (70 and 75%, see Section 2.4.2, Table 9, entries 10 and 11). Similarly, 2-biphenylboronic acid 2,2-dimethyl-1,3-propanediol ester **37** can react with mesitylmagnesium bromide to introduce a Mes group on boron, the resulting intermediate **38** undergoes lithiation with *t*BuLi followed by the intramolecular ring closure reaction to produce 9-mesityl-9-borafluorene **39** in a yield of 37% (Figure 4b).[78]

2.2. Transmetalation

2,2′-Dilithiobiphenyl compounds are good precursors for assembling the 9-borafluorene scaffold via addition of a boron electrophile bearing two leaving groups.[79−85] The dilithio compounds can be generated by lithium−halogen exchange from 2,2′-dihalobiphenyl compounds such as 2,2′-diiodobiphenyl or 2,2′-dibromobiphenyl.[86] Derivatives of 2,2′-dilithiobiphenyl are important reagents in many synthetic routes toward 9-borafluorenes as they can serve as direct precursors to 9-borafluorenes or to other metallacycles,[75,87−93] which can act as mild reagents for borafluorene synthesis.

2.2.1. Metathesis of 2,2′-Dilithiobiphenyl Reagents with Boron Electrophiles. The reaction of a dilithiobiphenyl reagent with a boron electrophile was employed by Chung in 2002 to prepare 9-chloro-9-borafluorene (**2**) in 70% yield by the reaction of dilithiobiphenyl with boron trichloride (Table 1, entry 1). The dilithiobiphenyl intermediate was generated by lithium-halogen exchange of 2,2′-dibromobiphenyl with *n*BuLi.[94,95] Bettinger and coworkers later adapted the reaction conditions by altering the solvent from diethyl ether to hexanes for the lithiation and extending the reaction time to 3 days to produce **2** in 90% yield,[96] although a later manuscript indicated a yield of only 49% (Table 1, entries 2 and 3).[97]

The 2,2′-dilithiobiphenyl mediated approach to 9-halo-9-borafluorenes is practical for the synthesis of 9-aryl-9-borafluorenes by replacing the BX_3 reagent (X = Cl or Br) with $TipB(OMe)_2$[81,98] or 4-cyanophenylboronic acid pinacol ester.[99] Yamaguchi and coworkers used 2,2′-dibromobiphenyl, *n*BuLi, and $TipB(OMe)_2$ as a reagent combination to prepare 9-Tip-9-borafluorene (**40**) in one pot (Table 1, entry 4).[100] The reaction tolerated substitution on the biphenyl reagent to furnish 9-borafluorene derivatives with functional groups on the carbon backbone; however, the installation of substituents on the biphenyl backbone reduced the yield drastically with a range of 6−29% (**41**−**44**, Table 1, entries 5−8).[81,98,99,101]

2.2.2. 9-Mercurafluorene and Magnesium Heterole Transmetalation Reactions. 2,2′-Dilithiobiphenyl intermediates enable access to 9-borafluorene derivatives; however, poor selectivity and yields were encountered with biphenyl substrates featuring halogen or methoxy substituents at the 4/4′ and 5/5′-positions on the biphenyl framework.[81,98,101] Main group heterofluorenes in which a heteroatom occupies the 9-position can undergo transmetalation reactions with boron reagents to furnish 9-borafluorenes, and this method can often tolerate

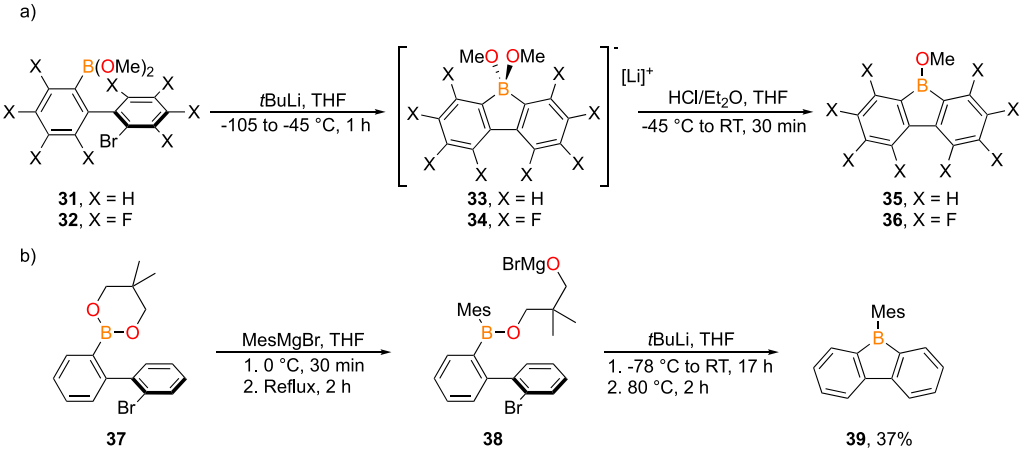

Figure 4. Synthesis of **35**, **36**, and **39** via ring closure reactions of boronic esters.

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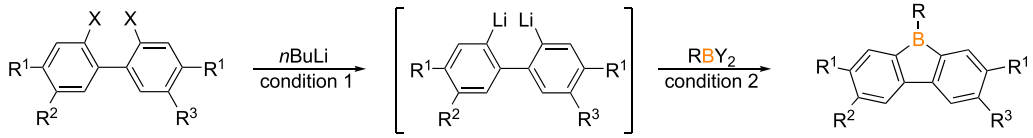
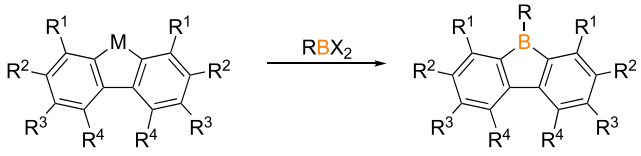
Table 1. 9-Borafluorene Syntheses from 2,2′-Dilithiobiphenyl Reagents



entry	X	R^1	R^2	R^3	R	Y	conditions	yield (%)	product
1	Br	H	H	H	Cl	Cl	1. Et_2O, ∼−10 to −5 °C, 6 h 2. hexanes, −10 °C, 7 h	70	**2**[94,95]
2	Br	H	H	H	Cl	Cl	1. hexanes, RT, 3 d 2. hexanes, 0 °C, overnight	90	**2**[96]
3	Br	H	H	H	Cl	Cl	1. hexanes, RT, 3 d 2. hexanes, 0 °C, overnight	49	**2**[97]
4	Br	H	H	H	Tip	MeO	1. hexanes, −78 °C, 1 h 2. THF, RT, 19 h then reflux, 2 h	63	**40**[100]
5	I	Br	H	H	Tip	MeO	1. Et_2O, −100 °C, 1 h 2. Et_2O, RT, 12 h	20	**41**[98]
6	Br	H	MeO	H	Br	Br	1. hexanes, RT, 3 d 2. hexanes, RT, 12 h	29	**42**[101]
7	Br	H	MeO	MeO	Tip	MeO	1. THF, −78 °C, 30 min 2. THF, RT, overnight	19	**43**[81]
8[a]	I	Br	H	H	*p*-C_6H_4CN	Y_2[a]	1. THF, −100 °C, 30 min 2. THF, RT, overnight	6	**44**[99]

[a]For entry 8, RBY_2 = 4-cyanophenylboronic acid pinacol ester where Y_2 = pinacolato.

Table 2. Metallacycle Mediated 9-Borafluorene Synthesis



entry	M	R^1	R^2	R^3	R^4	R	X	conditions	yield (%)[a]	compound
1	Hg	H	H	H	H	Cl	Cl	hexanes, −78 °C to RT, overnight	75	**2**[102]
2	Hg	H	H	H	H	Br	Br	hexanes, −78 °C to RT, overnight	75	**45**[102]
3	Hg	H	H	H	H	I	I	hexanes, −78 °C to RT, overnight	77	**46**[102]
4	Mg	H	H	H	H	Tip	MeO	THF	45	**40**[88]
5	Mg	H	Br	MeO	H	Tip	MeO	THF	38	**47**[88]
6	$SiMe_2$	H	H	H	H	Br	Br	neat, RT, 2 d	80	**45**[89]
7	$SiMe_2$	H	H	H	H	Br	Br	neat, 50 °C, 2 d	92	**45**[90]
8	$SiMe_2$	H	*t*Bu	H	H	Br	Br	neat, 70 °C, 6 d	96	**48**[75]
9	$SnMe_2$	F	F	F	F	Br	Br	benzene, −78 °C to RT, 4 h	77	**49**[91]
10	$SnMe_2$	F	F	F	F	C_6F_5	Cl	benzene, 70 °C, 7 d	44	**50**[91]
11	$SnMe_2$	H	H	H	H	C_6H_5	Cl	toluene, −78 °C to RT, overnight	99	**10**[92]
12	$Sn(nBu)_2$	H	I	H	H	Cl	Cl	toluene, −78 °C to RT, 1 h	NR	**51**[90]
13	$Sn(nBu)_2$	H	I	H	H	Br	Br	toluene, −78 °C to RT, 1 h	NR	**52**[93]

[a]NR: Not reported.

substitution. In 1985, Narula and Nöth reported the synthesis of 9-halo-9-borafluorenes by the reactions of 9-mercurafluorene[87] with boron trihalides.[102] The transmetalation proved to be an efficient method for the preparation of 9-borafluorenes in good yields among the chloro-, bromo-, and iodo-substituted compounds (**2**, **45**, **46**, Table 2, entries 1−3). However, reaction of 9-mercurafluorene with boron trifluoride did not produce the desired 9-fluoro-9-borafluorene.[102] Dibenzo fused magnesium heteroles can also be used as precursors to 9-borafluorenes exemplified in the synthesis of the 9-aryl-9-borafluorenes **40** and **47** by the Yamaguchi group (Table 2, entries 4 and 5).[88] 2,2′-Diiodobiphenyl compounds were first converted to magnesium heteroles by directly reacting with magnesium metal or by the transmetalation of $MgBr_2$ with in situ generated dilithiobiphenyl. The resulting magnesium heteroles react with $TipB(OMe)_2$ to give 9-borafluorenes **40** and **47** in 45% and 38% yields, respectively.[88]

2.2.3. 9-Silafluorene Mediated Transmetalation. 9-Bromo-9-borafluorene (**45**) can also be accessed via the transmetalation of 9,9-dimethyl-9-silafluorene with boron tribromide (80% yield, Table 2, entry 6).[89] Yamaguchi and coworkers improved the yield to 92% by increasing the reaction temperature from room temperature to 50 °C (Table 2, entry 7).[90] A similar method proved to be effective for the synthesis of 2,7-di-*t*-butyl-9-bromo-9-borafluorene **48** (96% yield), which

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was prepared by treating 2,7-di-*t*-butyl-9,9-dimethyl-9-silafluorene with BBr_3 at 70 °C for 6 days (Table 2, entry 8).[75]

2.2.4. 9-Stannafluorene Mediated Transmetalation Reactions. The reactions of 9-stannafluorenes with BBr_3,[91] $C_6F_5BCl_2$,[91] and $C_6H_5BCl_2$[92] generate the corresponding 9-borafluorenes (**10**, **49**−**52**, Table 2, entries 9−13). The method was effective for variants that have halides on the biphenyl unit. Although no yields were reported, the stannafluorene **53** reacts with BCl_3 to generate the 9-chloro-species which can react with Mes*Li (Mes* = 2,4,6-tri*tert*-butylphenyl) to produce 2,7-diiodo-9-Mes*-9-borafluorene (**54**,Figure 5a) in 62% yield.[90,93] The 2:1 stoichiometric reaction of perfluorinated stannafluorene **55** with 1,2-$(BBr_2)_2C_6F_4$ furnished bis-9-borafluorene **56** in 81% yield (Figure 5b).[103]

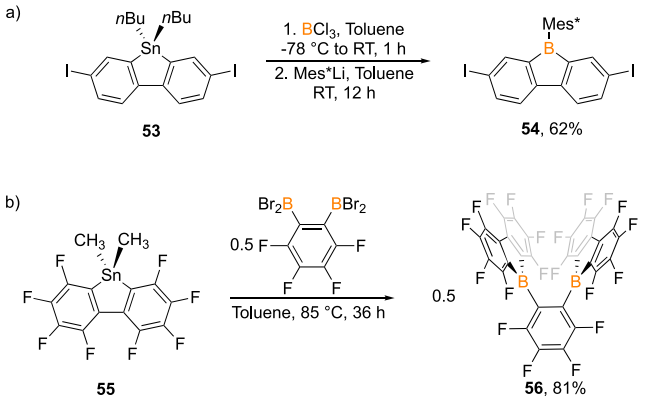


Figure 5. (a) Synthesis of 2,7-diiodo-9-Mes*-9-borafluorene **54**. (b) Preparation of perfluorinated bis-9-borafluorene **56** via transmetalation of a stannafluorene.

2.3. Late Stage Functionalization on 9-Borafluorene Frameworks

2.3.1. Functionalization of 9-Halo-9-borafluorenes. The properties of organoboron compounds can be tuned by varying the substituent on the boron center[104] and borafluorenes are no exception. 9-Halo-9-borafluorenes are effective precursors to diversify 9-borafluorenes via modification of the substituent on boron. The types of reactions can be classified based on the byproduct: (1) substitution reactions with E−H substrates (e.g., HNR_2) to eliminate HCl/HBr; (2) reactions with trialkylsilyl substituted substrates to eliminate trialkylsilyl halides; and (3) reactions with organic nucleophiles with inorganic salts as the byproduct.

2.3.1.1. Hydrogen Halide Elimination. Reactions of 9-halo-9-borafluorenes with primary/secondary amines or alcohols can furnish 9-borafluorenes containing exocyclic B−N/B-O bonds with the hydrohalide byproduct sequestered by a base (Table 3). For example, reactions of 9-chloro-9-borafluorene (**2**) with two equivalents of diethylamine, diisopropylamine in the presence of triethylamine, or isopropanol, generate 9-diethylamino-9-borafluorene (**3**, Table 3, entry 1),[102] 9-diisopropylamino-9-borafluorene (**57**, Table 3, entry 2),[81] and 9-isopropoxy-9-borafluorene (**58**, Table 3, entry 3),[105] respectively, in good yields (75−84%). Similarly, 9-methoxy-9-borafluorene (**35**) can be accessed in 53% yield from the reaction of 9-bromo-9-borafluorene (**45**) with methanol in the presence of 2,6-lutidine as a base (Table 3, entry 4).[102]

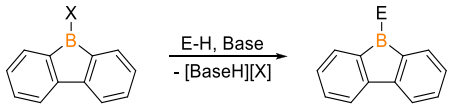
2.3.1.2. Trialkylsilyl Halide Elimination. Trialkylsilyl reagents can react with main group halides to eliminate trialkylsilyl halides and form a bond to the main group element with the trialkylsilyl halide byproduct removed by vacuum. The reactions of 9-chloro-9-borafluorene (**2**) with trimethylsilyl triflate and bis(trimethylsilyl)amine give rise to 9-triflato-9-borafluorene (**59**)[106] and 9-trimethylsilylamino-9-borafluorene (**60**)[107] in 74% and quantitative yield, respectively, concomitant with the formation of trimethylsilyl chloride (TMSCl, Table 4, entries 1 and 2). In 2010, Bettinger and coworkers reported the reaction of 9-chloro-9-borafluorene (**2**) with trimethylsilyl azide ($TMSN_3$) to afford 9-azido-9-borafluorene (**61**, Table 4, entry 3). Although **61** exists in an equilibrium between the monomer and cyclic trimer $[\mathbf{61}]_3$ in CH_2Cl_2 (Figure 6a), it readily reacts with pyridine and 4-*t*Bu-pyridine to form the corresponding adducts **137** and **138** in good yields (See section 2.4.1, Table 8, entries 5 and 6).[96] The TMSCl elimination strategy was also applied to prepare bis-9-borafluorenes **62** and **63** via the 2:1 stoichiometric reaction of 9-chloro-9-borafluorene (**2**) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine derivatives in good yields (Figure 6b).[108]

9-H-9-Borafluorene (**64**) and 2,7-di-*tert*-butyl-9-H-9-borafluorene (**65**) can be generated in situ by reaction of 9-bromo-9-borafluorenes (**45** and **52**) with two equivalents of Et_3SiH (Table 4, entries 4 and 5).[75,109,110] Compounds **64** and **65** are not isolable as monomers, existing as dimers. Despite the tendency of **64** and **65** to undergo dimerization, the corresponding dimethyl sulfide and/or pyridine adducts are isolable as monomers (**133**−**136**, see Section 2.4.1, Table 8, entries 1−4).[75,109,110]

2.3.1.3. Salt Elimination Reactions. Reaction of 9-halo-9-borafluorenes with organometallic reagents, e.g. aryllithium compounds, is a powerful strategy to access 9-borafluorenes via the elimination of inorganic salts. The formation of metal halide byproducts provides a driving force for the reaction and can be easily removed due to their poor solubility in nonpolar solvents. It has been demonstrated that treating 9-halo-9-borafluorenes (**2** or **45**) with lithium (di-*tert*-butylboryl)methylamide,[111] 2,4,6-tri*tert*-butylphenyl lithium (Mes*Li),[90] Li[P(*t*Bu)$_2$],[112] potassium bis(trimethylsilyl)amide (K[N(SiMe$_3$)$_2$]),[107,113] 2,4,6-tris(trifluoromethyl)phenyl lithium (Mes^FLi),[81,114] LiF,[115] *t*BuONa,[81] *t*BuOK,[105] bis(methylthio)lead [Pb(SCH$_3$)$_2$],[102] chloromercuriferrocene (FcHgCl)[116] and bis(cyclopentadienyl)zirconium(IV) dimethyl (Cp_2ZrMe_2)[91] can generate the corresponding 9-borafluorenes (**66**−**75**) in moderate to good yields (Table 5, entries 1−12).

The reactions of borafluorenes with organic nucleophiles can also generate bisborane species. The 2:1 stoichiometric reaction of 9-bromo-9-borafluorene (**45**) with 2,2′-dilithiobiphenyl

Table 3. Synthesis of 9-Borafluorenes via Functionalization of 9-Halo-9-borafluorenes with Alcohols and Amines



entry	X	E	base	conditions	yield (%)	compound
1	Cl	Et_2N	Et_2NH	hexanes, −78 °C to reflux, 2 h	75	**3**[102]
2	Cl	iPr_2N	Et_3N	Et_3N, toluene, −78 °C to RT, 18 h	84	**57**[81]
3	Cl	*i*PrO	none	hexanes, 0 °C, 1 h	77	**58**[105]
4	Br	MeO	2,6-lutidine	hexanes, −78 °C	53	**35**[102]

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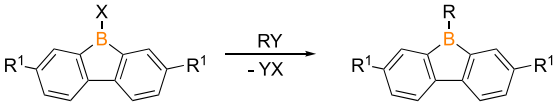
Table 4. Synthesis of 9-Borafluorenes via Functionalization of 9-Halo-9-borafluorenes with Trialkylsilyl Reagents[a]



entry	X	R^1	R	Y	conditions	yield (%)	compound
1	Cl	H	OTf	TMS	DCE, 25 °C, 12 h	74	**59**[106]
2	Cl	H	TMSNH	TMS	hexanes, RT, 1 h	quantitative	**60**[107]
3	Cl	H	N_3	TMS	CH_2Cl_2, −78 °C to RT, overnight	NR	**61**[96]
4	Br	H	H	TES	benzene, RT, 10 min	NR	**64**[109,110]
5	Br	*t*Bu	H	TES	benzene, RT, 5 h	NR	**65**[75]

[a]NR: Not reported; TES = triethylsilyl.

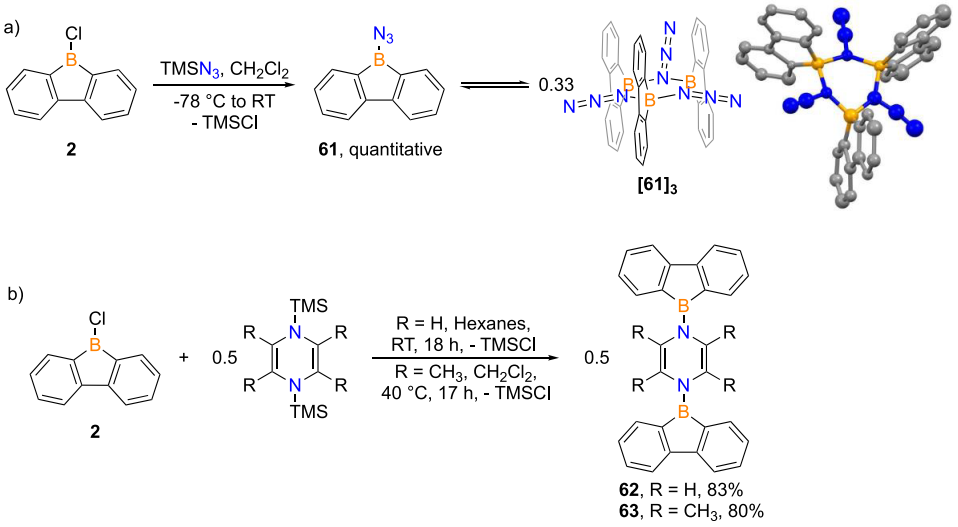
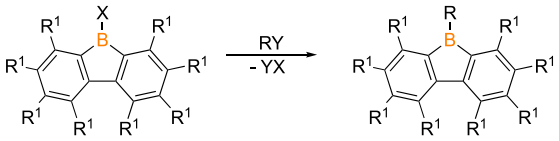


Figure 6. (a) Synthesis of 9-azido-9-borafluorene (**61**) with ball and stick representation of solid-state structure and (b) synthesis of bis-9-borafluorenes **62** and **63**.

Table 5. Synthesis of 9-Borafluorenes via Functionalization of 9-Halo-9-borafluorenes with Nucleophiles[a]



entry	X	R^1	R	Y	conditions	yield (%)	compound
1	Cl	H	$(t\text{Bu})_2\text{BNCH}_3$	Li	pentane, −69 °C to RT, 2 d	69	**66**[111]
2	Br	H	Mes*	Li	toluene, RT, 22 h	64	**67**[90]
3	Br	H	$(t\text{Bu})_2\text{P}$	Li	toluene, −30 °C to RT, overnight	NR	**68**[112]
4	Cl	H	Mes^F	Li	toluene, RT, overnight	19[b]	**69**[81]
5	Cl	H	F	Li	Et_2O, RT, 3 h	73	**70**[115]
6	Cl	H	$(\text{TMS})_2\text{N}$	K	benzene, RT, 1 min	69	**71**[107]
7	Br	H	$(\text{TMS})_2\text{N}$	K	benzene, RT, overnight	76	**71**[113]
8	Br	H	*t*BuO	Na	hexanes	quantitative	**72**[81]
9	Cl	H	*t*BuO	K	THF, 0 °C, 1 h	82	**72**[105]
10	Br	H	CH_3S	0.5Pb	hexanes, reflux, 1 h	92	**73**[102]
11	Br	H	Fc	HgCl	hexanes, −78 °C to RT, overnight	75	**74**[116]
12	Br	F	Me	$0.5Cp_2Zr$	hexanes, RT, overnight	46	**75**[91]

[a]NR: not reported; $(\text{TMS})_2N$ = bis(trimethylsilyl)amide; Mes^F = 2,4,6-tris(trifluoromethyl)phenyl. [b]The low yield for this reaction may be a consequence in generating the aryllithium intermediate in situ.

generates a biphenyl bridged bis-9-borafluorene (**76**) in 96% yield (Figure 7a).[117] Gabbaï and coworkers used a dimesityl-1,8-naphthalenediylborate anion (**77**) as a nucleophile in a reaction with 9-chloro-9-borafluorene (**2**) to access a 9-borafluorene with a naphthyl group on boron and a pendent dimesitylboryl substituent on the *peri*-position (39% yield, Figure 7b).[118]

2.3.2. Functionalization on the Carbon Backbone.

Halides on the dibenzo framework of 9-borafluorenes enable

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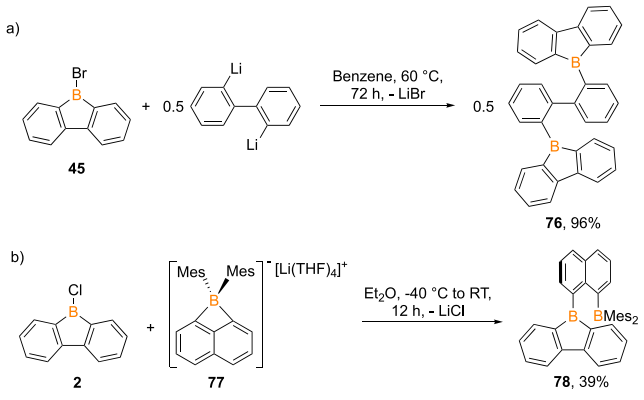

Figure 7. Reactions of 9-halo-9-borafluorenes with anionic nucleophiles to generate bisboranes **76** and **78**.

access to diverse 9-borafluorene derivatives via C−C cross-coupling reactions (**79**−**83**, Figure 8a and 8b). This strategy was

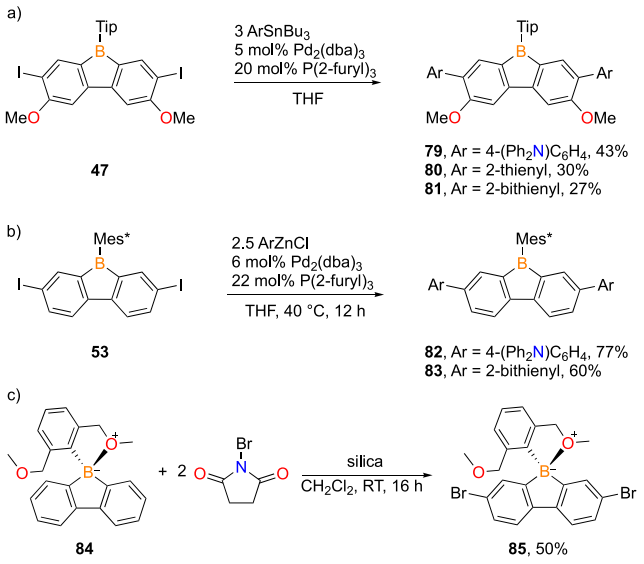

Figure 8. Cross-coupling reactions of 2,7-diiodo-9-borafluorenes with (a) organostannanes (reaction time not reported, dba = dibenzylideneacetone), (b) organozinc compounds to access 9-borafluorenes **79**−**83**, and (c) bromination of ether adduct **84**.

employed by the Yamaguchi group in the synthesis of 9-borafluorenes with π-conjugated substituents. Specifically, (4-diphenylamino)phenyl, 2-thienyl, and 2-bithienyl groups were introduced at the 2,7-positions via palladium-catalyzed coupling reactions of 2,7-diiodo-9-borafluorenes (**47** and **54**) with organostannanes (Figure 8a) or organozinc compounds (Figure 8b).[88,90] Bromination of ether adduct **84** with *N*-bromosuccinimide (NBS) furnishes the 2,7-dibromo substituted 9-borafluorene **85** in 50% yield (Figure 8c).[119]

2.3.3. Functionalization of Other Boron Containing Heterocycles. Mixing an *N*-heterocyclic olefin adduct $IPrCH_2$ [$(HCNDipp)_2C = CH_2$] of 9-bromo-9-borafluorene (**86**) with $K[N(SiMe_3)_2]$ in toluene generates the 9-bis(trimethylsilyl)-amino-9-borafluorene (**71**) as well as the free Lewis base, as confirmed by in situ NMR spectroscopy (Figure 9).[113] As noted in Table 5, **71** can be accessed, more directly, without the $IPrCH_2$ base (Table 5, entries 6 and 7).

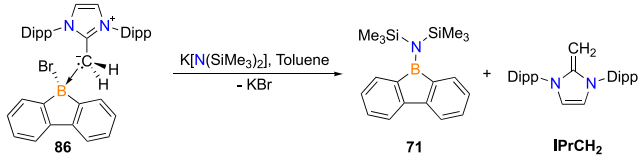

Figure 9. In situ formation of 9-bis(trimethylsilyl)amino-9-borafluorene (**71**) from the $IPrCH_2$ 9-bromo-9-borafluorene adduct (**86**); no yield was reported. Dipp = 2,6-diisopropylphenyl.

Wagner and coworkers investigated nucleophilic substitution reactions on the unsaturated diborate platform **87** that furnished 9-borafluorenes (Figure 10a). The reaction of **87** with CH_3Cl produces the diborane product **88** containing two four-coordinate boron centers bridged by a hydride and a methylene group. Replacing CH_3Cl with three equivalents of CH_3I affords 9-methyl-9-borafluorene **89** quantitatively based on NMR spectroscopy. The same quantitative conversion of **87** to **89** can be achieved with two equivalents of methyl triflate. The proposed mechanism suggests that the carbene-like intermediate **87Int** generated from the reaction of **87** with CH_3X (X = Cl, I, or OTf) can either undergo intramolecular C(sp^3)−H activation to form the methylene-*C* and H-bridged diborane (**88**, X = Cl) or nucleophilic substitution with another equivalent of CH_3X to produce 9-methyl-9-borafluorene (**89**, X = I or OTf). The reaction pathway is governed by the stoichiometry of CH_3X and the bond strength of the halide/pseudo halide, X (Figure 10b). The competition between C(sp^3)−H activation and nucleophilic substitution was also studied using α,ω-dihaloalkanes as the substrate. Reactions of diborate **87** with dihaloalkanes [$X(CH_2)_nX$, $n \leq 4$] produces the alkyl linked bis-9-borafluorenes **90**−**92**, with dibromoalkanes giving products in higher yields than dichloroalkanes. However, methylene-*C* and H-bridged diboranes **93**−**97** are generated as the major products when dihaloalkane reagents containing longer chains are reacted, especially 1,5-dihalopentane and 1,6-dihalohexane reagents (Figure 10a).[120]

The tetraaryl μ-hydridodiborane anion with lithium and potassium countercations (**98** and **99**, respectively) can also be employed to access 9-borafluorenes (Figure 10c).[121] The reaction of **98** with excess CH_3I or **99** with excess $(CH_3)_3SiCl$ in THF produces half an equivalent of 9-Me-9-borafluorene (**89**) or 9-TMS-9-borafluorene (**100**) as well as half an equivalent of the THF adduct of 9-H-9-borafluorene **130**. The 1:1 stochiometric reaction of **98** and allyl bromide generates the known bis-9-borafluorene **91** in quantitative yield in which the product is rationalized by a mechanism similar to that in the formation of **88**, but in this case the species undergoes in situ hydroboration in the presence of the byproduct of 9-H-9-borafluorene **65**. Replacing allyl bromide with excess allyl iodide furnishes 9-allyl-9-borafluorene **101** as the major product (82%). The reaction of **99** with excess 2,3-dimethylbutadiene furnishes to the bis-9-borafluorene **102** as well as the [4 + 1] cycloaddition product **103** in a stoichiometric ratio of 1:2.[121]

2.4. Synthesis of 9-Borafluorene Adducts

2.4.1. Reactions of 9-Borafluorenes with Intermolecular Lewis Bases. 9-Borafluorenes readily form Lewis acid/base adducts to satisfy the octet on boron. For the stable 9-borafluorenes, the simple reaction of the Lewis base with a 9-borafluorene at low temperature, or room temperature, generates the corresponding adducts. This has been successful with pyridines (**104**−**110**, Table 6, entries 1−7),[122] carbenes

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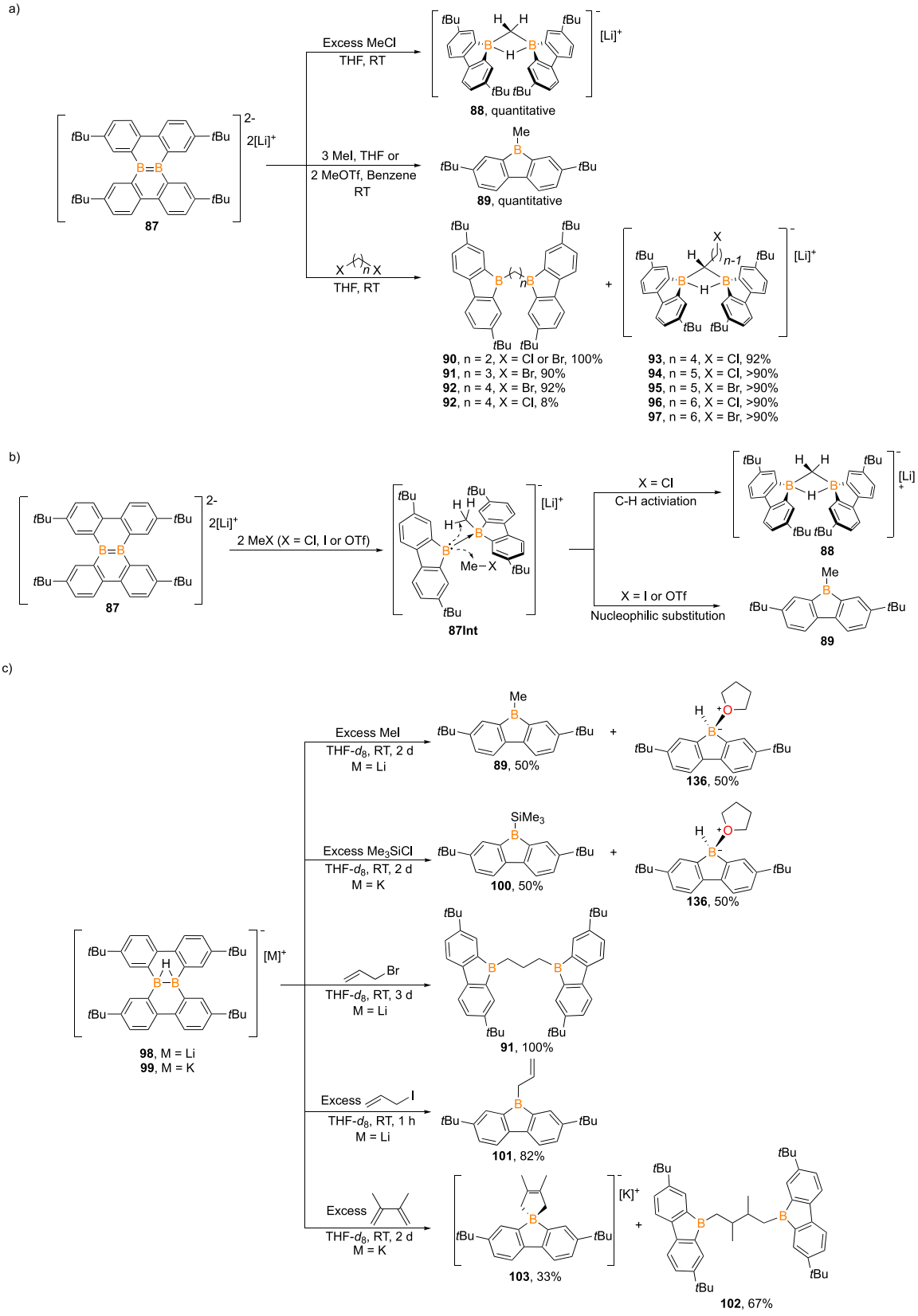

Figure 10. (a) Synthesis of 9-borafluorenes from the reactions of diborate **87** with CH_3Cl, CH_3I, CH_3OTf, and dihaloalkanes. (b) Proposed mechanism of the reaction of diborate **87** with CH_3Cl and CH_3OTf. (c) Synthesis of 9-borafluorenes from anionic species **98** and **99**.

[**86**, **111**−**113**, Table 6, entries 8−12, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, CAAC = *N*-(2,6-diisopropylphenyl)-4,4-diethyl-2,2-dimethyl-pyrrolidin-5-ylidene],[101,113] phosphines (**114**−**116**, Table 6, entries 13−15 and **122** and **123**, Table 7, entries 1 and 2),[113,123] PhN=CHPh (**117**, Table 6, entry 16),[124] *t*BuCN (**118**, Table 6, entry 17),[124]

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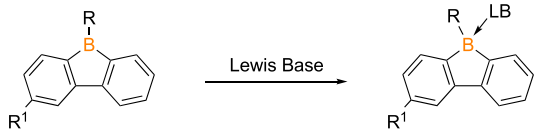
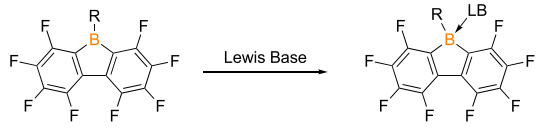
Table 6. Synthesis of 9-Borafluorene Adducts Using Intermolecular Lewis Bases[a]



entry	R	R^1	Lewis base	conditions	yield (%)	compound
1	OTf	H	pyridine	hexanes, −78 °C to RT, immediately	68	**104**[122]
2	OTf	H	2,4-lutidine	hexanes, −78 °C to RT, immediately	40	**105**[122]
3	OTf	H	2,6-lutidine	hexanes, −78 °C to RT, immediately	73	**106**[122]
4	Cl	H	pyridine	hexanes, −78 °C to RT, immediately	71	**107**[122]
5	Cl	H	2,4-lutidine	hexanes, −78 °C to RT, immediately	77	**108**[122]
6	Cl	H	2,6-lutidine	hexanes, −78 °C to RT, immediately	80	**109**[122]
7	Cl	H	acridine	hexanes/CH_2Cl_2, −78 °C, immediately	78	**120**[122]
8	Br	H	IPr	toluene, RT, 12 h	93	**122**[113]
9	Br	H	$IPrCH_2$	toluene, RT, 12 h	93	**86**[113]
10	Br	H	IPr	toluene, RT, 12 h	76	**111**[101]
11	Br	H	CAAC	hexanes, RT, 1.5 h	82	**112**[101]
12	Br	MeO	IPr	toluene, RT, 12 h	69	**113**[101]
13	Br	H	PPh_3	toluene, RT, 12 h	92	**114**[113]
14	Br	H	PCy_3	toluene, RT, 2 h	87	**115**[113]
15	Ph	H	$PhPH_2$	CH_2Cl_2, RT, 5 min	58	**116**[126]
16	Ph	H	PhN = CHPh	CH_2Cl_2, RT, 5 min	94	**117**[124]
17	Ph	H	*t*BuCN	CH_2Cl_2, RT, 5 min	90	**118**[124]
18	Ph	H	THF	THF/hexane, −35 °C, overnight	87	**119**[125]
19	Ph	H	MeCN	CH_2Cl_2, RT, 5 min	85	**120**[124]
20	Ph	H	$PhNH_2$	$CDCl_3$, RT, immediately	NR	**121**[126]

[a]NR: Not reported; LB = Lewis base; PCy_3 = tricyclohexylphosphine; PPh_3 = triphenylphosphine.

Table 7. Synthesis of Perfluorinated-9-borafluorene Adducts Using Intermolecular Lewis Bases[a]



entry	R	Lewis base	conditions	yield	compound
1	Me	PMe_3	CH_2Cl_2, −78 °C to RT, 0.5 h	92	**122**[123]
2	C_6F_5	PMe_3	CH_2Cl_2, −78 °C to RT, 0.5 h	99	**123**[123]
3	Me	THF	CH_2Cl_2, −78 °C to RT, 0.5 h	99	**124**[123]
4	C_6F_5	THF	CH_2Cl_2, −78 °C to RT, 0.5 h	100	**125**[123]
5	Me	MeCN	CH_2Cl_2, −78 °C to RT, 0.5 h	97	**126**[123]
6	C_6F_5	MeCN	CH_2Cl_2, −78 °C to RT, 0.5 h	99	**127**[123]

[a]LB = Lewis base; PMe_3 = trimethylphosphine.

THF (**119**, Table 6, entry 18 and **124** and **125**, Table 7, entries 3 and 4),[123,125] MeCN (**120**, Table 6, entry 19 and **126** and **127**, Table 7, entries 5 and 6),[123,124] and $PhNH_2$ (**121**, Table 6, entry 20).[124] With acetonitrile, the adduct **120** forms but is labile as confirmed by variable temperature ^{11}B NMR spectroscopy.[124] Reactions of bis-9-borafluorenes (**56** and **76**) with excess Lewis bases afford bis-9-borafluorene adducts (**128** and **129**, **132**) with two tetracoordinate boron centers (Figure 11a).[103,117] Bis-9-borafluorene adducts **130** and **131** with a single tetracoordinate boron center can also be obtained via the 1:1 stoichiometric reactions of bis-9-borafluorene (**56**) with MeCN and THF in CH_2Cl_2.[103]

The 9-H-9-borafluorenes **64** and **65** dimerize but can be trapped as their Lewis base adducts with pyridine, DMS, and THF in quantitative yields (**133**−**136**, Table 8, entries 1−4).[75,109,110] Pyridine adduct **133** was first prepared in 1973 via pyrolysis of the pyridine adduct of 2-biphenylborane by van Veen and Bickelhaupt (Figure 11b).[127] Similarly, reactions of 9-azido-9-borafluorene (**61**) and unsymmetrical 9-borafluorenes **27** and **28** with pyridine or 4-*tert*-butylpyridine form the corresponding adducts (**137**−**140**) and the structures were confirmed by single crystal X-ray crystallography (Table 8, entries 5−8).[73,76,96,117]

Adducts can be functionalized if a labile substituent is on boron. Adducts **86** and **111** with a bromine on boron react with excess $LiAlH_4$ to generate NHC coordinated 9-H-9-borafluorene species **141** and **142** in 86 and 27% yield, respectively (Figure 11c). Treatment of adduct **111** with one equivalent of AgOTf generates a new 9-borafluorene adduct (**143**) via anion exchange.[113]

2.4.2. Synthesis of Intramolecular 9-Borafluorene Adducts. Substitution reactions of 9-halo-9-borafluorenes (**2**, **45**, **49**, and **52**) or 9-methoxy-9-borafluorenes (**35** and **36**) with substrates that bear a pendent Lewis base (N, O, P, or NHC) generate the corresponding 9-borafluorenes with a tetracoordinate boron center resulting from the intramolecular interaction of boron with the Lewis base (Table 9). This is effective for secondary amines and phenols that bear a pendent Lewis base in reactions with 9-halo- or 9-MeO-9-borafluorenes to afford the tetracoordinate 9-borafluorenes **144**−**159** (Table 9, entries 1−17) and the byproduct, is typically removed by sequestration with bases such as Et_3N, iPr_2NEt, and 1,8-bis(dimethylamino)-naphthalene (proton sponge).[77,93,129−131] The 2:1 stoichiometric reaction of 9-methoxy-9-borafluorene (**35**) with a diol generates a naphthalene bridged four-coordinate bis-9-borafluorene (**160**, Table 9, entry 18).[77]

For adducts with a carbon−boron bond and a chelated base, aryllithium reagents are generated in situ from the halogenated aromatics and *n*BuLi and react with 9-halo-9-borafluorenes (**2** and **45**) to give rise to 9-borafluorenes **84** and **161**−**167** (Table 9, entry 19−26).[119,133−136] Shimizu and Kawachi synthesized a series of tetracoordinate 9-borafluorenes (**173**−**175**) starting from the lithium halogen exchange of *o*-(dimethylsilyl)-bromobenzene (**168**) with *t*BuLi (Figure 12).[105] The resulting *o*-silyl(lithio)benzene reacts with 9-isopropoxy-9-borafluorene (**58**) or 9-*tert*-butoxy-9-borafluorene (**72**) to form the borate intermediate (**169** or **170**), which undergoes hydride-alkoxy exchange to form the hydroborate (**171** or **172**). Quenching the intermediate with TMSCl furnishes the intramolecular 9-borafluorene adduct (**173** or **174**) in good yield (Figure 12a). 9-Borafluorene **173** can undergo silyl ether exchange with MeOH and EtOH to generate **175** and **176** in 66 and 77% yield, respectively (Figure 12b).

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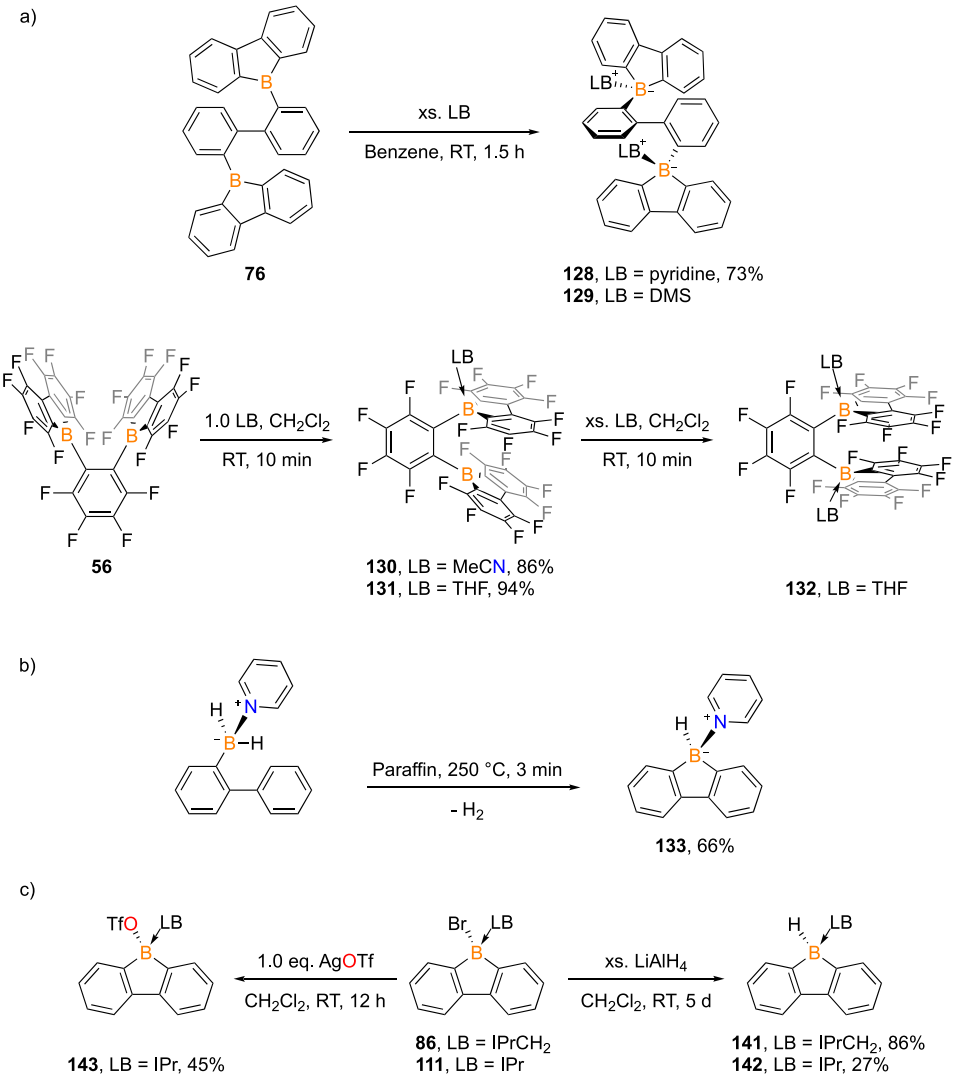
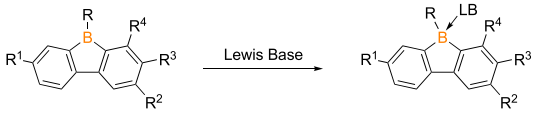


Figure 11. (a) Synthesis of bis-9-borafluorene adducts **128**−**132** (DMS = dimethyl sulfide). (b) Synthesis of 9-H-9-borafluorene pyridine adduct **133** via pyrolysis of the 2-biphenylylborane pyridine adduct. (c) Functionalization of 9-Br-9-borafluorene adducts with AgOTf and excess $LiAlH_4$. Yields for **129** and **132** were not reported.

Table 8. Synthesis of 9-Borafluorene Adducts Using Intermolecular Lewis Bases for Structural Characterization[a]



entry	R	R^1	R^2	R^3	R^4	Lewis base	conditions	yield (%)	adduct
1	H	H	H	H	H	pyridine	benzene, RT, immediately	quantitative	**133**[110]
2	H	H	H	H	H	DMS	benzene, RT, immediately	95	**134**[109]
3	H	*t*Bu	H	*t*Bu	H	pyridine	benzene, RT, 17 h	93	**135**[75]
4	H	*t*Bu	H	*t*Bu	H	THF	THF, RT, 1 h	quantitative	**136**[128]
5	N_3	H	H	H	H	pyridine	CH_2Cl_2, RT	91	**137**[96]
6	N_3	H	H	H	H	4-*t*Bu-pyridine	CH_2Cl_2, RT	88	**138**[96]
7	(2,6-Ar^1_2) C_6H_3	Ar^1	H	*t*Bu	H	pyridine	hexanes, RT, immediately	NR[a]	**139**[73]
8	(2,6-Ar^2_2)C_6H_3	Ar^2	Me	H	Me	pyridine	hexanes, RT, immediately	NR[a]	**140**[76]

[a]NR: Not reported; Ar^1 = 4-*t*BuC_6H_4; Ar^2 = 3,5-$Me_2C_6H_3$; LB = Lewis base. Note: for entries **5** and **6**, the reaction times were not reported.

2.5. Summary of Synthetic Strategies

In this section, synthetic strategies to access all known 9-borafluorenes were presented, spanning ring closure reactions, transmetalation reactions, and the functionalization of 9-borafluorenes. The former two methods construct the central borole ring for 9-borafluorenes, and latter serves as a method to functionalize of 9-borafluorenes at boron or the carbonaceous backbone. Although significant progress has been made, challenges remain in accessing 9-borafluorenes with substitution

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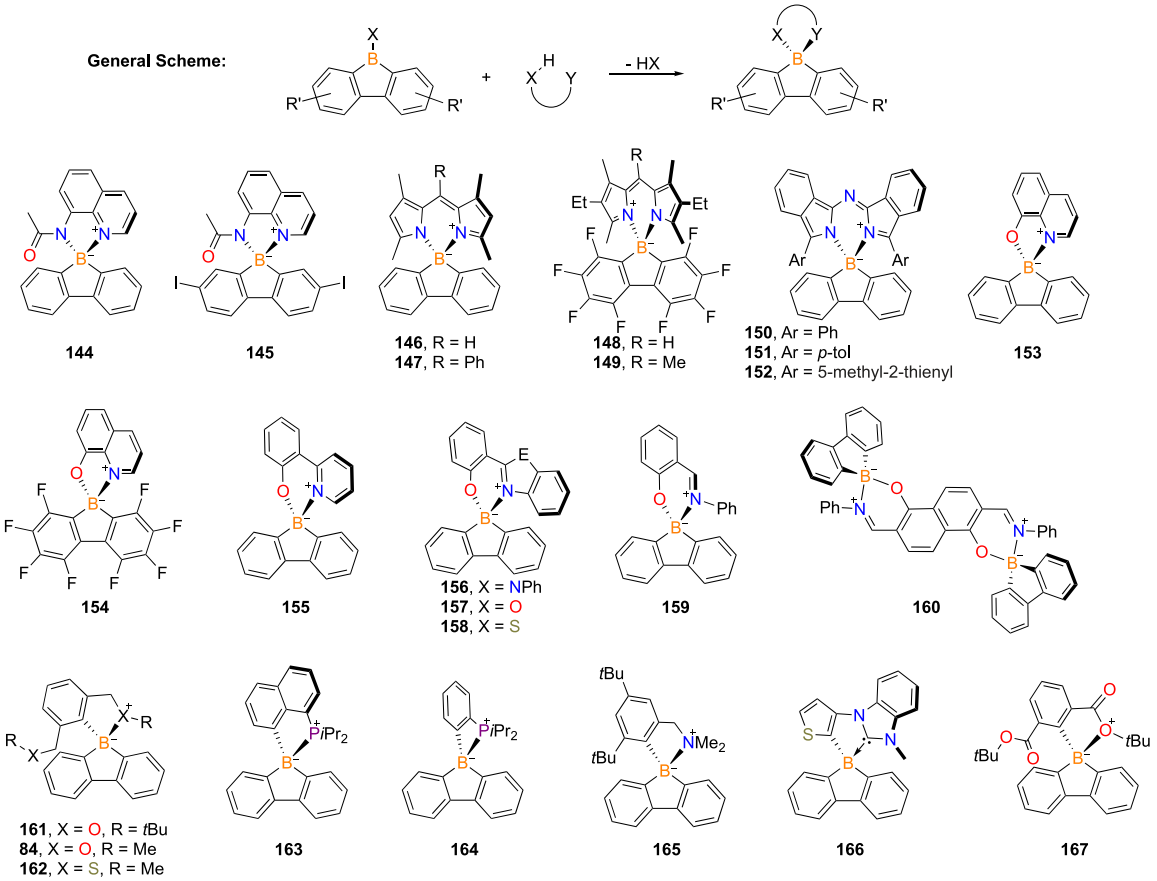
Table 9. Synthesis of Intramolecular 9-Borafluorene Adducts[a]



entry	SM	X	Y	conditions	yield	product
1	**45**	N	N	toluene, Et_3N, 80 °C, 12 h	45	**144**[93]
2	**52**	N	N	toluene, Et_3N, 80 °C, 12 h	24	**145**[93]
3	**45**	N	N	CH_2Cl_2, proton sponge, 0 °C to RT, overnight	43	**146**[129]
4	**45**	N	N	CH_2Cl_2, proton sponge, 0 °C to RT, overnight	48	**147**[129]
5	**49**	N	N	CH_2Cl_2, Et_3N, RT, 0.5 h	62	**148**[130]
6	**49**	N	N	CH_2Cl_2, Et_3N, RT, 0.5 h	16	**149**[130]
7	**2**	N	N	CH_2Cl_2, *i*Pr_2NEt, RT, 8 h	71	**150**[131]
8	**2**	N	N	CH_2Cl_2, *i*Pr_2NEt, RT, 8 h	81	**151**[131]
9	**2**	N	N	CH_2Cl_2, *i*Pr_2NEt, RT, 8 h	61	**152**[131]
10	**35**	O	N	CH_2Cl_2, RT, 2 h	70	**153**[77]
11	**36**	O	N	CH_2Cl_2, RT, 2 h	75	**154**[77]
12	**35**	O	N	CH_2Cl_2, RT, overnight	62	**155**[77]
13	**36**	O	N	CH_2Cl_2, RT, overnight	75	**156**[77]
14	**45**	O	N	THF, reflux, 12 h	78	**156**[132]
15	**35**	O	N	CH_2Cl_2, RT, overnight	67	**157**[77]
16	**35**	O	N	CH_2Cl_2, RT, overnight	78	**158**[77]
17	**35**	O	N	CH_2Cl_2, RT, overnight	60	**159**[77]
18	**35**	O	N	DCE, 50 °C, 3 d	47	**160**[77]
19	**2**	C	O	1. *n*BuLi, THF, −78 °C, 50 min 2. toluene, −78 °C to RT, 16 h	49	**84**[119]
20	**2**	C	O	1. *n*BuLi, toluene, −78 °C to RT, 3 h 2. toluene, −78 °C to RT, 17 h	46	**161**[119]
21	**2**	C	S	1. *n*BuLi, toluene, −78 °C to RT, 5 h 2. toluene, −78 °C to RT, 17 h	35	**162**[119]
22	**2**	C	P	1. *n*BuLi, Et_2O, −50 °C, 0.5 h 2. toluene, −78 °C to RT, overnight	52	**163**[133]
23	**45**	C	P	1. *n*BuLi, toluene, −40 °C 2. toluene, −60 °C	16	**164**[134]
24	**45**	C	N	1. *n*BuLi, Et_2O, −78 °C to RT, 2 h 2. toluene, −78 °C to RT, 40 h	47	**165**[135]

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Table 9. continued

entry	SM	X	Y	conditions	yield	product
25	**45**	C	C	1. 2.0 *n*BuLi, Et_2O, −78 to 0 °C, 1 h 2. toluene, −78 °C to RT, 15 h	61	**166**[136]
26	**45**	C	O	1. *n*BuLi, Et_2O, −78 °C, 1 h 2. THF, −78 °C to RT, 15 h	44	**167**[114]

[a]Note: The low to moderate yields for entries 19−26 are postulated to occur from incomplete lithium halogen exchange in the one-pot reaction protocol.

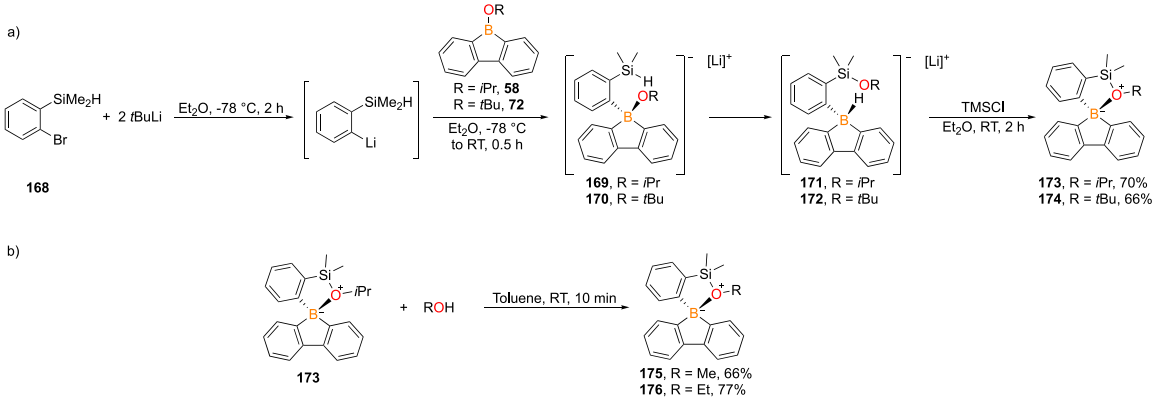

Figure 12. (a) Synthesis of silyl ether chelated 9-borafluorenes **173** and **174**. (b) Synthesis of 9-borafluorenes **175** and **176** via transesterification of **173**.

on the biphenyl frameworks. Preparing 9-borafluorene adducts is straightforward using free Lewis bases which donate into the empty p orbital of the tricoordinate boron center to satisfy its octet. Tetracoordinate 9-borafluorenes can also be obtained via substitution of 9-halo-9-borafluorenes or 9-methoxy-9-borafluorenes with substrates that bear a pendent Lewis base which undergo self-assembly to four-coordinate 9-borafluorenes driven by the chelate effect. The structures and ^{11}B NMR shifts of known 9-borafluorenes and 9-borafluorene Lewis adducts are summarized in Figure 13 and Figure 14, respectively.

3. PROPERTIES

9-Borafluorenes can be described as a biphenyl unit linked by a tricoordinate boron center or as an antiaromatic BC_4 ring with two fused arene rings. Lewis bases can coordinate to the boron center with a wide range of Lewis acidities for 9-borafluorenes, dependent on the substitution at boron. As a result of the vacant p orbital extending π-conjugation through the tricyclic system, this class of compounds has interesting photophysical properties, much like polycyclic aromatic hydrocarbons (PAHs). Adduct formation results in a disruption of conjugation as well as altered fluorescence, which can be taken advantage of in molecular sensing.[16] This section discusses the properties of 9-borafluorenes, some of which offer potential utility in materials and devices.

3.1. Lewis Acidity

Multiple methods of quantifying Lewis acidity by computational or experimental means have been developed.[137−149] The Lewis acidity of 9-borafluorenes has been evaluated using the Gutmann−Beckett method, an experimental method using solution ^{31}P NMR spectroscopy to measure the change in ^{31}P shift upon binding to triethylphosphine oxide (Et_3PO).[138,150] An acceptor number (AN) is determined using the equation $AN = 2.21 \times (\delta_{sample} - \delta_{phosphine\ oxide})$ and is positively correlated to the Lewis acidity. Although many 9-borafluorenes exist, only 9 of them have been assessed by the Gutmann−Beckett method (Table 10). Although a small sample size, some observations are apparent. The strongest Lewis acid measured is 9-Br-9-borafluorene (**45**) with an acceptor number of 93.5. 9-Cl-9-borafluorene and 9-OTf-9-borafluorene were close in values (AN range = 78.7−91.5) and collectively, the Lewis acidity in this class can be rationalized by the electron withdrawing effect of the halide/pseudo halide.[81,106] It is apparent that π donation, exemplified in B-diisopropylamino and B-*tert*-butoxy substituted species, greatly diminishes the Lewis acidity (AN = 13.5 and 28.8, respectively).[81] A phenyl substituent still gave high Lewis acidity (AN = 73.4) but bulky aryl groups reduced the Lewis acidity (Tip or Mes^F substitution, AN range = 10.6−14.1).[81,151,152]

3.2. Photophysical Properties

Rivard and coworkers studied the fluorescence of a series of 9-H-9-borafluorene and 9-Br-9-borafluorene adducts.[113] For the bromo species, the IPr, PPh_3, PCy_3 and $IPrCH_2$ adducts as well as the bis-DMAP cation (DMAP = 4-dimethylaminopyridine), have blue fluorescence with quantum yields ranging from 19 to 63% (Figure 15a). The $IPrCH_2$ 9-H-9-borafluorene adduct (**141**) was noted to contain an inseparable impurity that may contribute to the fluorescence, but had a quantum yield of 19%. Emission bands for all monoadducts were identical at 435 nm, indicating that the Lewis base is not influential and that the emission arises from the borafluorene scaffold, as corroborated by time-dependent density functional theory (TD-DFT) calculations. The bis-DMAP cation $[(DMAP)_2BC_{12}H_8]^+$ (**177**) has an emission at 355 nm with a quantum yield of 51%. In the related carbene stabilized neutral borafluorene radicals **178** and **179** reported by Gilliard, the carbene affected the absorbance with the CAAC supported species displaying a maximum absorbance (λ_{max}) at 550 nm and the NHC coordinated variant red-shifted at 610 nm (Figure 15b).[153]

Urban, Durka, and coworkers explored the photophysical properties of aryloxy substituted 9-borafluorenes with pendent

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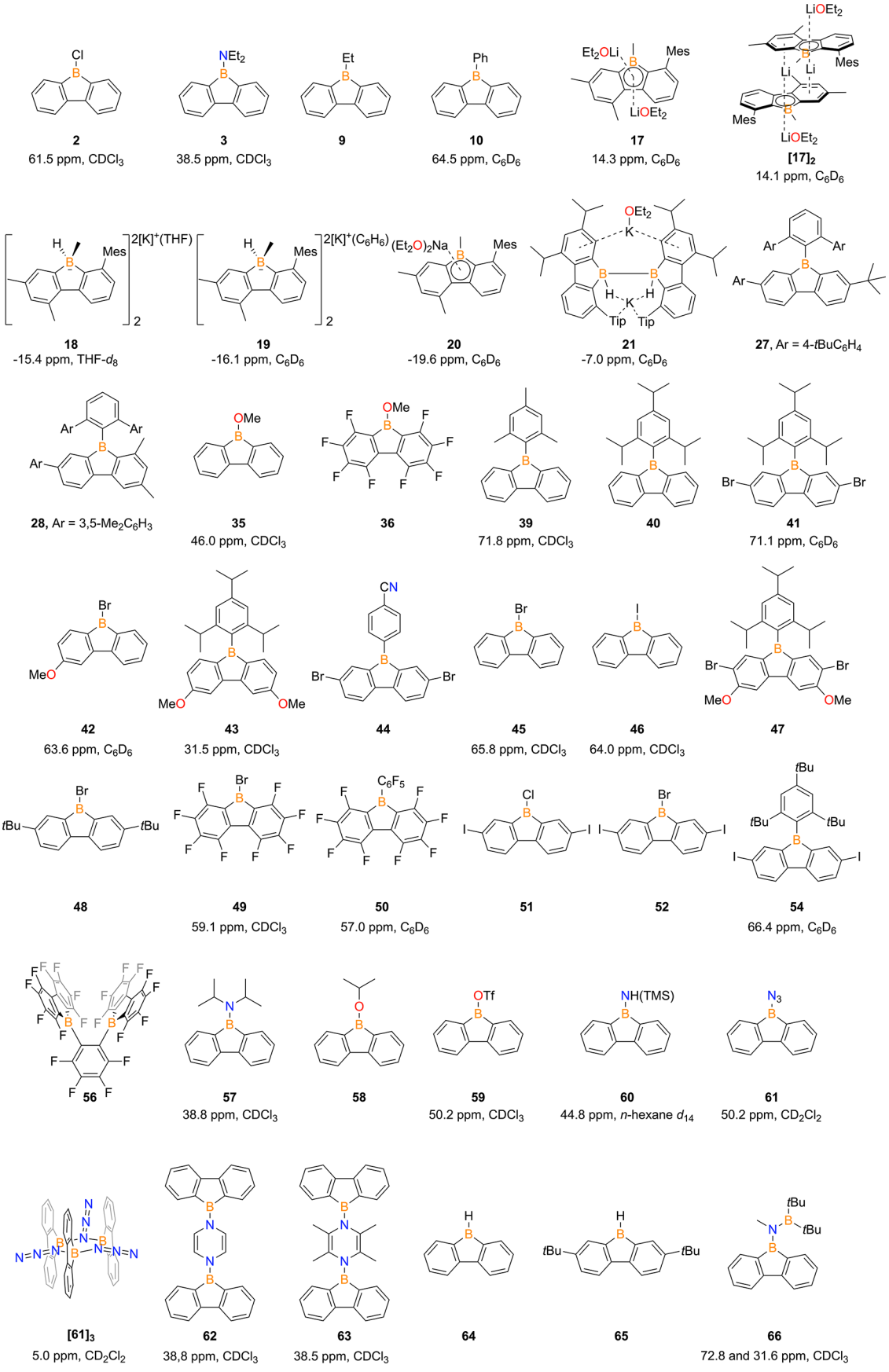

Figure 13. continued

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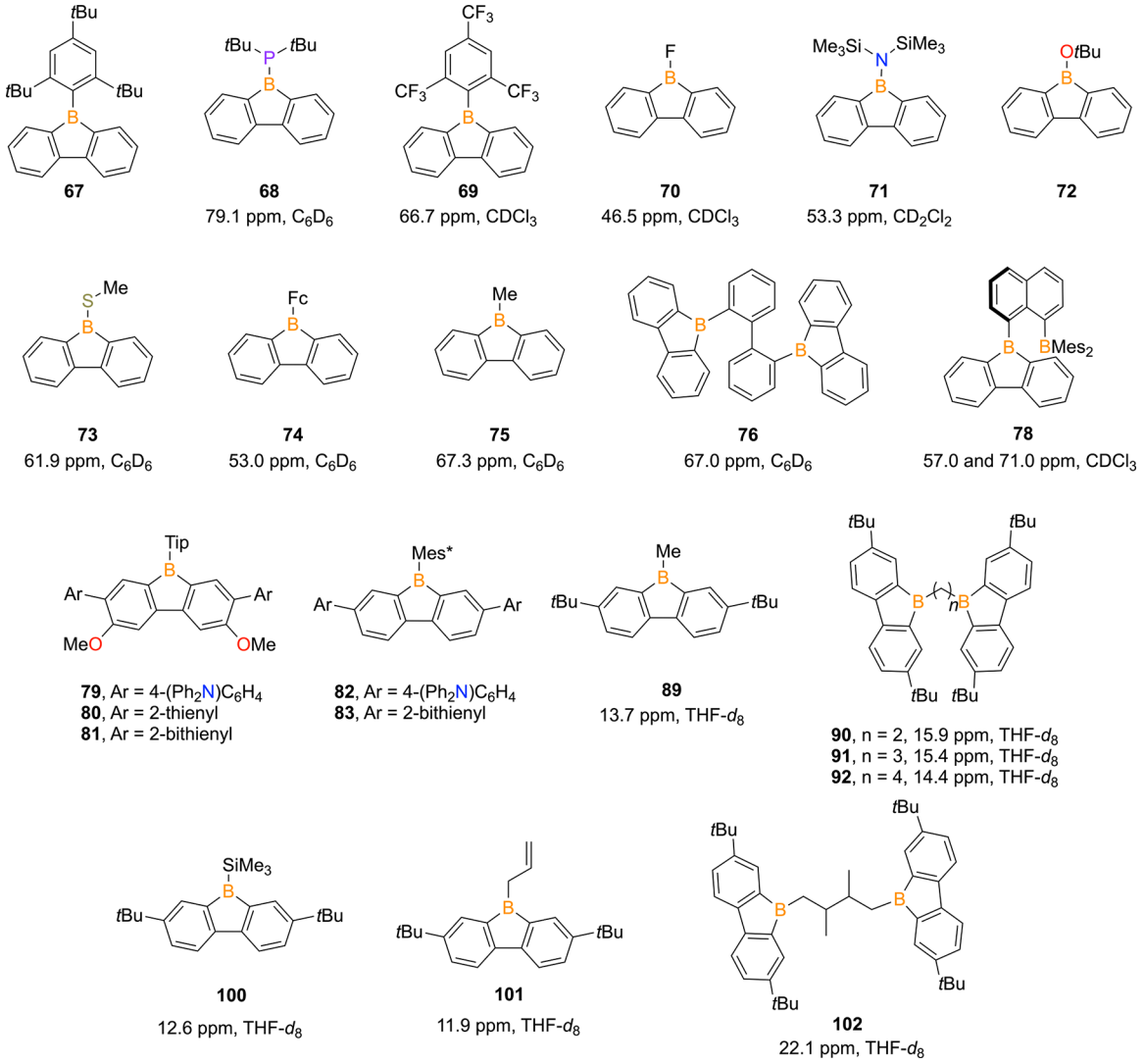

Figure 13. Structures of known 9-borafluorenes and their ^{11}B NMR shifts (if reported). Note: compounds **64** and **65** cannot be isolated as monomers, existing as dimers **291** and **294** in the absence of Lewis bases.

nitrogen adducts that formed $OBNC_2$ and $OBNC_3$ rings (**153**–**160**, Figure 16).[77] The conjugated borafluorene and ligand are orthogonal and are linked by a boron spirocenter that precludes π-stacking. In comparison to nonchelated variants, the borafluorene species exhibited improved emission, charge mobility, and thermal stability (i.e., **160** decomposed over ca. 450 °C, and the overall melting and decomposition temperatures of the chelated species are 50–100 °C higher). Bis(borafluorene) **160** had the highest quantum yield at 65%.

In 2009, Piers, Thompson, and coworkers synthesized two BODIPY/borafluorene hybrids (**148** and **149**, Figure 17) that feature tetracoordinate spiroboron centers shared between BODIPY and perfluorinated borafluorene scaffolds.[130] Photophysical and electrochemical analyses revealed that their optical band gaps are not significantly different from those of other BODIPY compounds but the rigidity of the bidentate ligands led to high quantum yields (**148** = 67% and **149** = 92%, respectively). Ortmann, Leo, and coworkers prepared aza-BODIPY fused 9-borafluorenes **150**–**152** and studied their ability as near IR absorbers in vacuum deposited organic solar cells (OSCs).[131] The high thermal stability (mass loss not observed by thermogravimetric analysis until 350 °C) enables high sublimation yields of **150**–**152** for this process. All three have notably strong near IR absorbances in solution and as thin films with maxima ranging between 670 and 715 nm and 700–750 nm, respectively. Bulk heterojunction solar cells were made featuring **150**–**152** as the donor and C_{60} as the acceptor. Remarkable power conversion efficiencies were achieved that reached 4.5% for **150** with high (62%) external quantum efficiency at 690 nm making these borafluorene species competitive to other evaluated donor molecules.[131]

Rupar and coworkers studied intramolecularly coordinated species in which an aryl group had a pendent ether or thioether substituent from the *ortho*-position (**84**, **161**, **162**, and **180**, Figure 18).[119] The species with unsubstituted carbon backbones (**84**, **161**, and **162**) absorb in the UV region (λ_{max} = 284, 286, and 284 nm, respectively), and the corresponding emissions are 539, 530, and 536 nm, respectively. This represents very large Stokes shifts of 16 600, 16 100, and 16 500 cm^{-1}, respectively. The lifetimes of the emissions of **84**, **161**, and **162** were notably long, exceeding 100 ns. In examining lifetimes of other 9-borafluorenes, the 9-Mes*-9-borafluorene **67** has a long lifetime of 150 ns. It was concluded from supporting calculations that the large observed Stokes shifts are due to the dissociation of the

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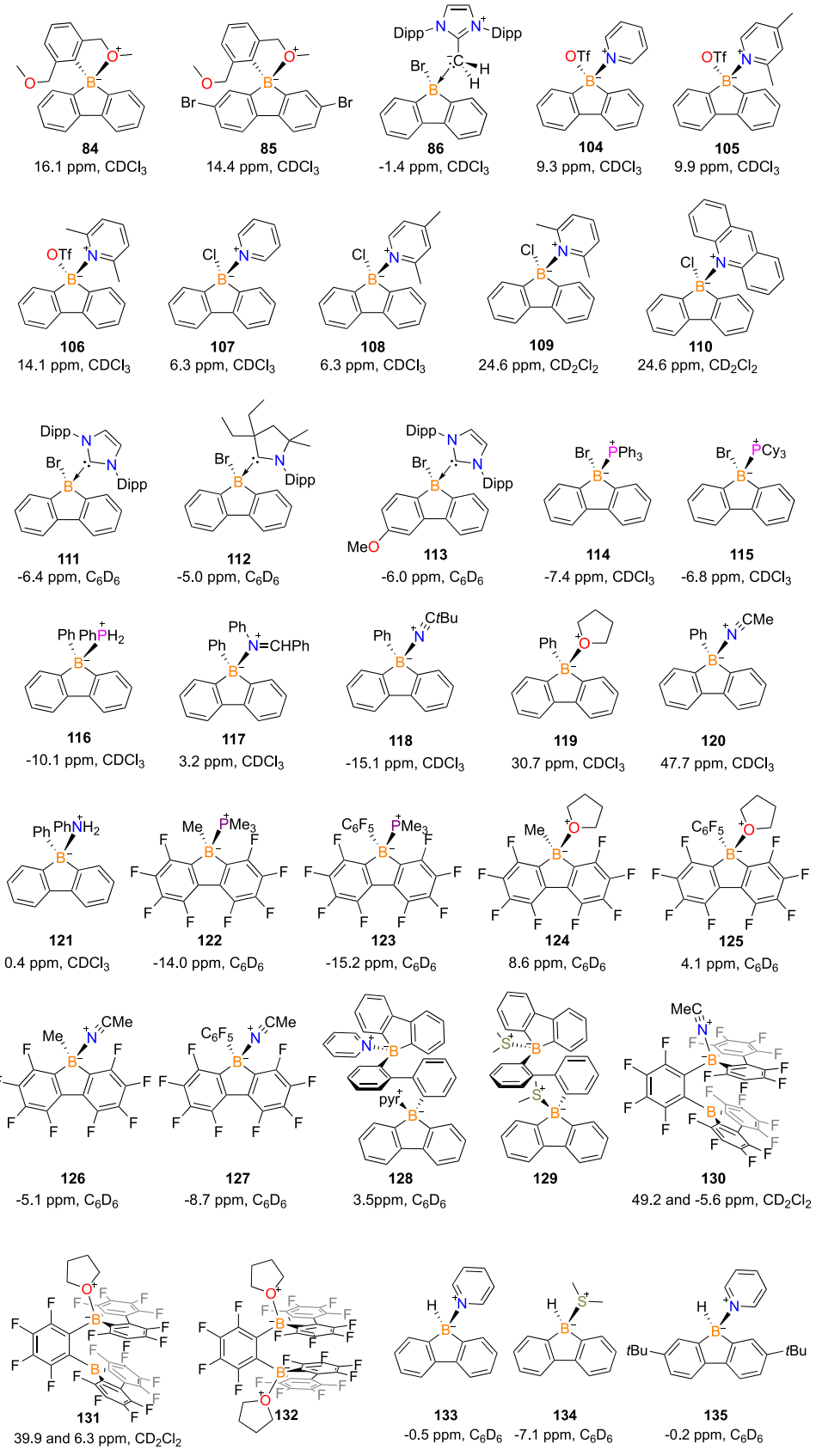

Figure 14. continued

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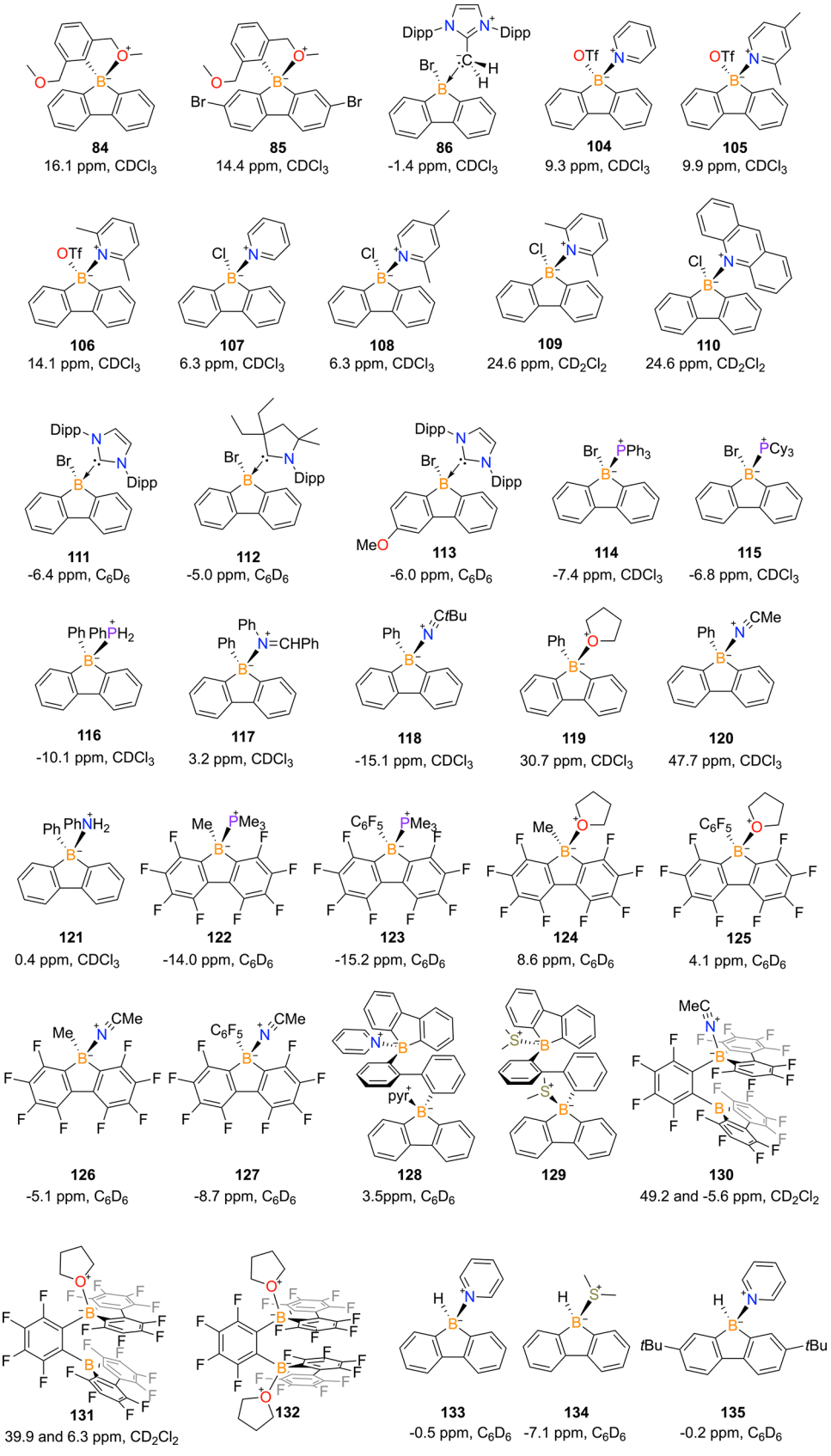

Figure 14. Structures of known 9-borafluorene adducts and their ^{11}B NMR shifts (if reported).

boron−oxygen bond during photoexcitation, forming a tricoordinate boron species. This phenomenon is akin to that observed in amine appended species **197**−**199** (vide supra, Figure 23) but with larger Stokes shifts, which are likely due to the weaker B−O/B−S Lewis acid−base interactions. Bithiophene substituted variant **180** absorbs in the visible region (λ_{max}

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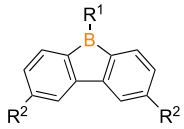
Table 10. Gutmann–Beckett Studies on 9-Borafluorenes (Solvent Specified As It Can Influence the Value)



compound	R^1	R^2	solvent	^{31}P δ (ppm)	$\Delta^{31}P$ δ (ppm)	AN
45[106]	Br	H	$CDCl_3$	55.2	28.0	93.5
2[81]	Cl	H	C_6D_6	76.6	35.6	78.7
2[106]	Cl	H	$CDCl_3$	55.2	26.3	89.7
69[81]	Mes^F	H	C_6D_6	47.4	6.4	14.1
10[151]	Ph	H	C_6D_6	41.0	33.1	73.4
40[81]	Tip	H	C_6D_6	45.8	4.8	10.6
43[81]	Tip	OMe	C_6D_6	45.9	4.9	10.8
57[81]	iPr_2N	H	C_6D_6	47.1	6.1	13.5
72[81]	tBuO	H	C_6D_6	54.0	13.0	28.8
59[106]	OTf	H	$CDCl_3$	55.2	27.1	91.5

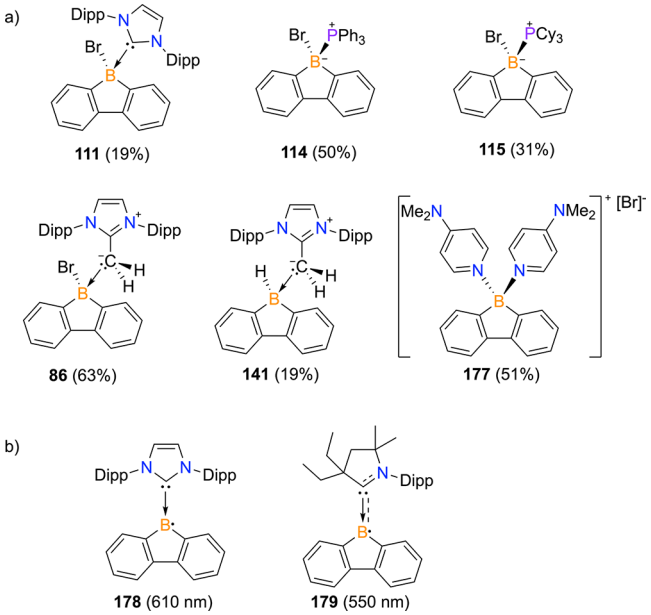


Figure 15. (a) Borafluorene adducts **86**, **111**, **114**, **115**, **141**, and base-stabilized borafluorenium cation **177**; quantum yields are in parentheses. (b) Carbene stabilized borafluorene radicals **178** and **179**; λ_{max} are listed in parentheses.[154]

= 408 nm) due to increased conjugation resulting from the bithiophene moieties on the 2- and 7-positions of the biphenyl backbone and has dual emission at 446 and 639 nm with smaller reported Stokes shifts than **84**, **161**, and **162** (Figure 18). The rare dual emission was investigated by TD-DFT studies and rationalized by two stable excited state structures, the high energy emission (446 nm) from an excited state with a B–O bond interaction and the lower energy emission (639 nm) from an excited state with the B–O bond cleaved.[119]

Marder and coworkers studied the photophysical properties of 9-aryl-9-borafluorenes featuring four $-CF_3$ groups on the biphenylene unit and at the *ortho*-positions of the phenyl substituent on boron with a –H, $-CF_3$, or $-NMe_2$ group on the *para*-position (**181–183**, respectively, Figure 19).[155] All three had broad lowest energy absorption maxima in the UV/vis spectra with absorbances at 400, 386, and 396 nm for **181–183**,

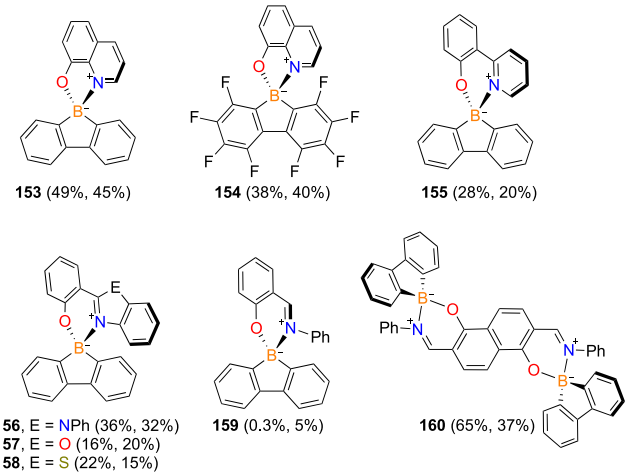


Figure 16. Intramolecular borafluorene adducts **153–160**. Quantum yields are in parentheses with solution values first and powder values second.

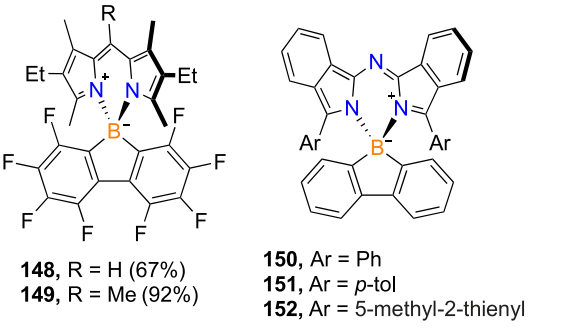


Figure 17. Borafluorene substituted BODIPY compounds (**148** and **149** with quantum yields in brackets) and borafluorene-substituted aza-BODIPY derivatives (**150–152**).

respectively. The corresponding excitations in the fluorescence spectra resulted in emissions for **181** and **182** at 521 and 510 nm, respectively, while the amino-variant **183** is red-shifted considerably at 627 nm. All three fluorinated species had extremely long fluorescence emission lifetimes in hexanes (exceeding 200 ns), with the highest lifetime of 1.6 μs for **183** attributed to TADF (thermally activated delayed fluorescence). The quantum yields for **181** and **182** are modest at 37% and 30%, respectively, while **183** had a very low quantum yield of 3%.

Rupar and coworkers analyzed the properties of 9-borafluorenes **2**, **40**, **43**, **57**, **69**, and **72** based on the substituent at boron (Figure 19).[81] The π-donor substituents tBuO (**72**) and iPr_2N (**57**) increase the energy of their respective lowest unoccupied molecular orbital (LUMO) levels resulting in a blue-shift in the absorbance (364 and 354 nm, respectively). The electron withdrawing Mes^F group (**69**) lowers the LUMO level causing a red-shift in the absorbance (414 nm). The quantum yields in the emission spectra were low, between 2 and 10%.

Chujo and coworkers evaluated the optical and morphological properties of 9-borafluorene copolymers **184–186** (Figure 20).[156] High emission quantum yields were detected with **185** being the highest at 80%, with **184** and **186** having quantum yields of 52% and 29%. X-ray diffraction analysis of the film states of **184–186** revealed peaks at ~2° = 20° corresponding to the alignment of the polymer backbone.

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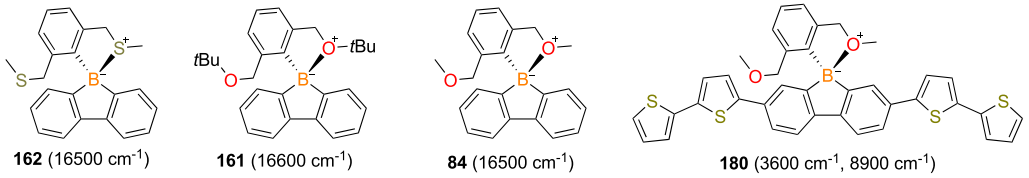

Figure 18. Borafluorenes **84**, **161**, **162**, and **180** with thioether and ether appended substituents. Stokes shifts are in parentheses.

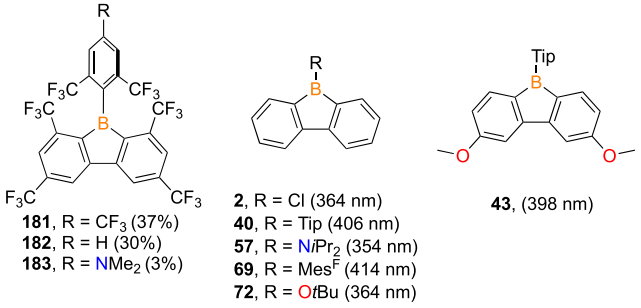

Figure 19. Trifluoromethylated borafluorenes **181**−**183** (quantum yield in parentheses) studied by Marder and nonfluorinated borafluorenes **2**, **40**, **43**, **57**, **69**, and **72** (absorbance in parentheses) studied by Rupar.

3.3. Sensors

The coordination of Lewis bases to the sp^2 boron center changes the hybridization to sp^3 and alters the photophysical properties.[16] This can serve as a way to sense anions and small nucleophilic molecules. A particularly notable anion that can bind to Lewis acids is fluoride, an additive to drinking water for which accurate concentration determination is important.[19,157−159] In 2002, Yamaguchi and coworkers examined the fluoride ion sensing ability of 9-aryl-9-borafluorene **187** (Figure 21).[88] It was shown that **187**, in THF, exhibits green fluorescence at ca. 17 800 cm^{-1} with a Stokes shift of ca. 3010 cm^{-1}. The borafluorene featured a bulky 2,4,6-triisopropylphenyl (Tip) group on boron, which aided binding specificity toward the small fluoride anion. Upon binding fluoride, the intensity increased drastically leading to a "turn-on" of the fluorescence which also corresponded to a blueshift in the emission (ca. 23 900 cm^{-1}). TD-DFT studies by Gwaltney and coworkers revealed that the changes in hybridization at boron from sp^2 to sp^3 upon fluoride coordination is responsible for the drastic change in fluorescence.[160] In this computational study, the binding of CN^- and CH_3^- anions were also studied. Although fluorescence is the most practical method for analyzing anion detection, the absorbance also changed with a significant red-shift in the absorption maximum upon coordination of fluoride to boron.

In 2009, Su and coworkers conducted a quantum mechanical study on the effects on the nonlinear optical (NLO) properties of 9-borafluorenes with arene substitution on the backbone

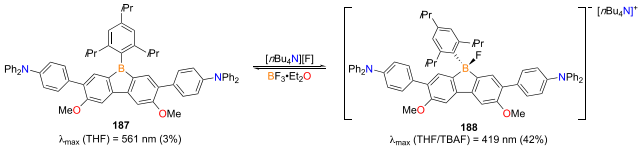

Figure 21. Fluoride sensing with borafluorene **187** (λ_{max} listed, quantum yields in parentheses).

upon fluoride coordination or a one electron reduction (Figure 22).[161] Both fluoride coordination and reduction result in a

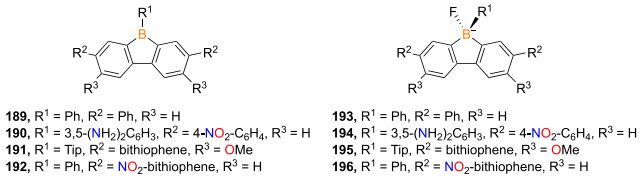

Figure 22. Borafluorenes **189**−**192** examined for use as nonlinear optical switches and their fluoride adducts **193**−**196**.

change in the charge transfer that leads to a switching of a large NLO response. The static first hyperpolarizablities (β) increased 2−12-fold upon fluoride complexation and 15−47-fold upon one electron reduction with **191** having the greatest changes in values, while **192** had the largest β values overall. Accordingly, the authors suggest that 9-borafluorenes could serve as molecular NLO switches or sensors.

In 2017, Chujo and coworkers reported a series of 9-borafluorene adducts featuring intramolecularly coordinated amino groups (**197**−**199**, Figure 23) that are capable of discriminating chain lengths of alkanes (5−16 carbon atoms) in mineral oils, gasoline, and solvents.[162] Theoretical calculations reveal that the formal negative charge at boron is enhanced upon excitation, inducing B−N bond cleavage to the three-coordinate species thereby altering the luminescence. Species with electron donating groups on the periphery were better sensors as they facilitated B−N bond cleavage. In *n*-alkane sensing, from measuring the intensity ratios of the two BICT emission bands, it was concluded that increasing the number of carbons in the hydrocarbon (C_nH_{2n+2}, n = 5−16) resulted in a decreased relative intensity of the 535 nm emission band in **199**. Solvatochromism, displayed by minor change in emission

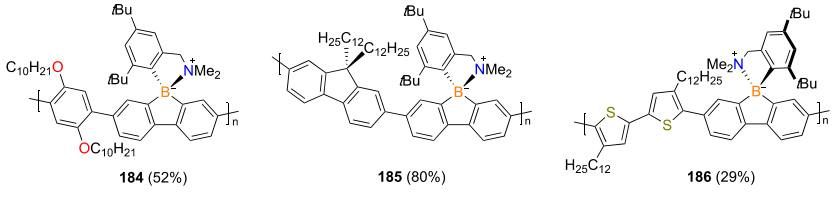

Figure 20. Borafluorene copolymers **184**−**186** with high crystallinity and quantum yields (in parentheses).

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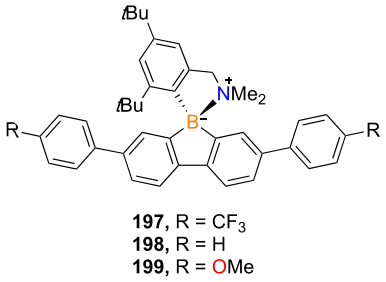

Figure 23. Intramolecular 9-borafluorene adducts **197**−**199** evaluated for alkane sensing.

bands, was attributed to polarity and microenvironmental viscosity changes that fit the Förster−Hoffman equation.[163]

Bonifácio and coworkers accessed a 9-borafluorene random copolymer with fluorene units by Yamamoto-type C−C coupling of the reagents in a 1:9 ratio (**201**, Figure 24).[99,164,165] Dilute THF solutions and drop-cast films on glass slides of the copolymer were analyzed for anion binding with I^-, Br^-, Cl^-, F^-, BF_4^-, CN^-, HSO_4^-, $H_2PO_4^-$, and NO_3^-. Analysis by fluorescence spectroscopy indicated that the coordination of anions to the boron center quenches the photoluminescence. The polymer exhibited high sensitivity toward fluoride, moderate sensitivity for cyanide and iodide anions, and low affinity for $H_2PO_4^-$ ions. Br^-, Cl^-, BF_4^-, HSO_4^-, and NO_3^- did not exhibit any detectable interaction with copolymer **201**.

In 2015, Rupar and coworkers reported the synthesis of a 9-borafluorene homopolymer and vinylene copolymer (**202** and **203**, Figure 25).[98] Solid samples of **202** and **203** act as colorimetric sensors for ammonia vapor with a visible change in the fluorescence from yellow to blue upon ammonia coordination. The color change is reversible upon removal of the ammonia atmosphere as confirmed by fluorescence spectroscopy. Titration of dilute THF solutions of both **202** and **203** indicate fluoride binding by fluorescence spectroscopy, akin to the monomeric species (Figure 21).

Chujo and coworkers examined aminoquinoline-9-borafluorene containing polymers **204** and **205** revealing that the species with a fluorinated linker (**205**, Figure 26) had a significantly higher quantum yield than the nonfluorinated linker **204** (53% c.f. 2%).[93] Calculations revealed that this phenomenon is a consequence of the electron withdrawing per-fluoroalkyl chains lowering the energy of the LUMO. The authors indicate that this effect can be taken advantage of in solar cells, photocatalysis, and sensing materials.

Gilliard and coworkers demonstrated thermochromism in the carbene-stabilized borafluorenium cation **206** (Figure 26).[101] Borafluorenium cation **206** is red when dissolved in weakly coordinating solvents (dichloromethane, toluene, or benzene) at room temperature. Upon cooling, the solutions became

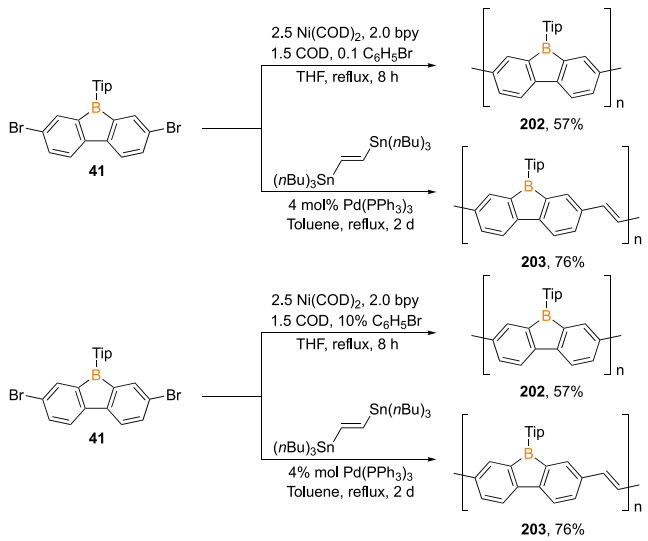

Figure 25. Synthesis of polymeric 9-borafluorenes **202** and **203**.

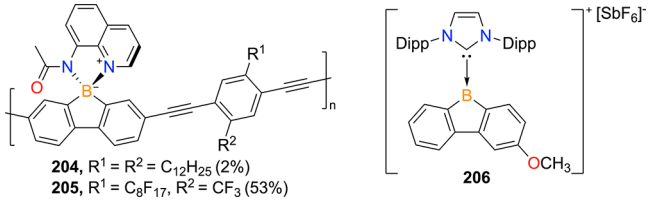

Figure 26. Structures of conjugated borafluorene-based polymers **204** and **205** and thermochromic carbene-stabilized 9-borafluorenium cation **206**.

colorless, which was also reflected in the absorbance spectrum, and reversibility was observed upon warming to room temperature. The thermochromism is attributed to coordination of the oxygen atom of the methoxy group to the boron center of another molecule of **206**. In two other carbene-stabilized borafluorenium cations studied (**178** and **179**) that lacked the methoxy group, thermochromic behavior was not observed, with calculations corroborating the importance of the methoxy group. Addition of THF to **206** also resulted in the same color change, further supporting the O−B donation to form a four-coordinate colorless adduct.

4. REACTIVITY

The Lewis acidic boron center, ring strain, and antiaromatic four π-electron core render the central BC_4 ring of 9-borafluorenes reactive with diverse synthetic opportunities. The endocyclic B−C bond is labile and can engage in intra- and intermolecular ring insertions to access larger boracycles in addition to undergoing ring opening reactions. In the following subsections, these

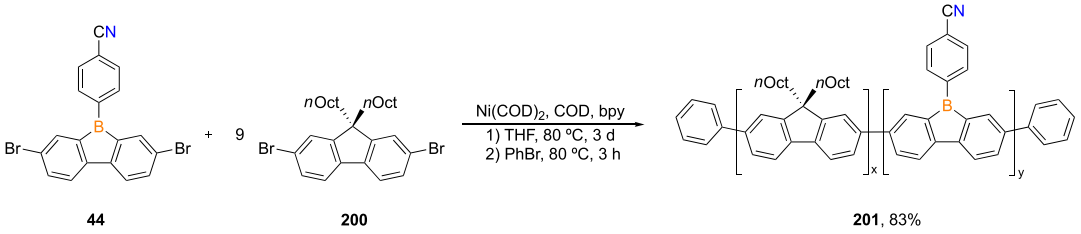

Figure 24. Claimed synthesis of copolymer **201** effective in anion sensing (COD = 1,5-cyclooctadiene, bpy = 2,2′-bipyridine).[165]

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different modes of reactivity are addressed with a focus on the stability of 9-borafluorenes and their utility as reagents.

4.1. Stability and Ring Opening Reactions

The impact of the substituent at boron on the stability of 9-borafluorenes toward air and moisture was studied via ^{1}H NMR spectroscopy by Rupar and coworkers using substituents with varied electronic and steric properties (summarized in Figure 27).[81] Despite the opportunity for N−B π-donation, the

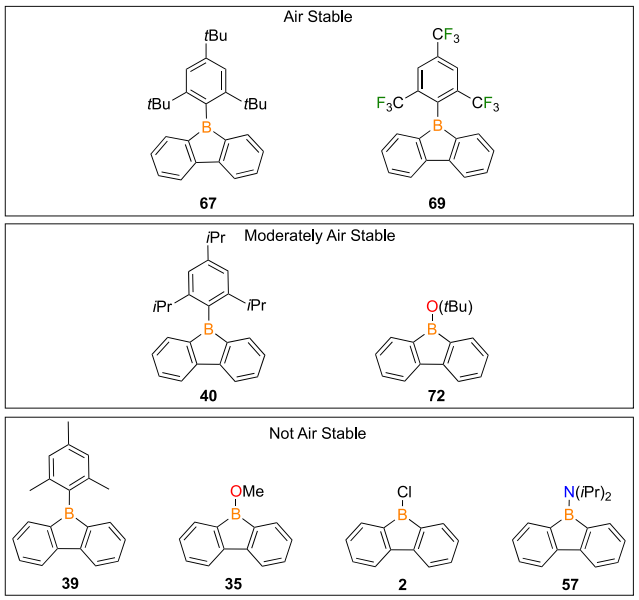

Figure 27. Borafluorenes that have been investigated for stability in the open atmosphere.

diisopropylamino substituent of 9-diisopropylamino-9-borafluorene (**57**) did not provide additional stability by steric or electronic effects in comparison to the chloride substituent in 9-chloro-9-borafluorene (**2**). However, 9-*t*-butoxy-9-borafluorene (**72**) is moderately stable to air and moisture. To discern whether the increased stability is due to steric hindrance from the *t*-butyl group or the electronic effect associated with the oxygen atom, the methoxy-substituted analogue (**35**) was evaluated and found to have stability comparable to that observed for **2** and **57**, indicating that the stability of **35** is a consequence of steric effects. Bulky aryl-substituted 9-borafluorene derivatives featuring mesityl (**39**) and fluoromesityl (**69**) substituents were also examined and compared to 9-Tip-9-borafluorene (**40**). It was confirmed that **40** could be purified by silica gel chromatography by Yamaguchi and Rupar, although Rupar documented that $CDCl_3$ solutions of **40** decomposed slightly upon exposure to air.[81,88] Similar stability was observed for the fluoromesityl-substituted species **69**.[81] In contrast, **39** rapidly decomposes upon exposure to air and does not survive column chromatography. Comparing the two mesityl-containing species, it is evident that the trifluoromethyl groups play an important role in the stabilization. Stabilization resulting from bulky aryl substituents was also observed for the 2,4,6-tri-*t*-butylphenyl derivative **67**, which was reported by Yamaguchi and coworkers to survive silica gel chromatography in the open air.[90] A 9-borafluorene featuring a *p*-cyanophenyl substituent at boron (**44**) was reported by Bonifácio and coworkers.[99] The compound was claimed to be purified by diethyl ether/water extraction and silica gel chromatography, suggesting partial stability toward water; however, the compound was isolated with only 6% yield, and the characterization data are insufficient to conclusively prove its existence.[166] In summary, these studies demonstrate that sterically bulky aryl and alkoxyl groups stabilize 9-borafluorenes.

The decomposition studies provided insight into the stability of 9-borafluorenes but did not identify their decomposition products. Our group investigated the reaction of water with 9-phenyl-9-borafluorene (**10**) to determine the nature of the hydrolysis products.[126] The 1:2 stoichiometric reaction of water with **10** furnished an oxo-bridged product (**207**) in which each of the O−H bonds reacted with an equivalent of **10**, resulting in protodeborylative ring opening (Figure 28a). In the 1:1

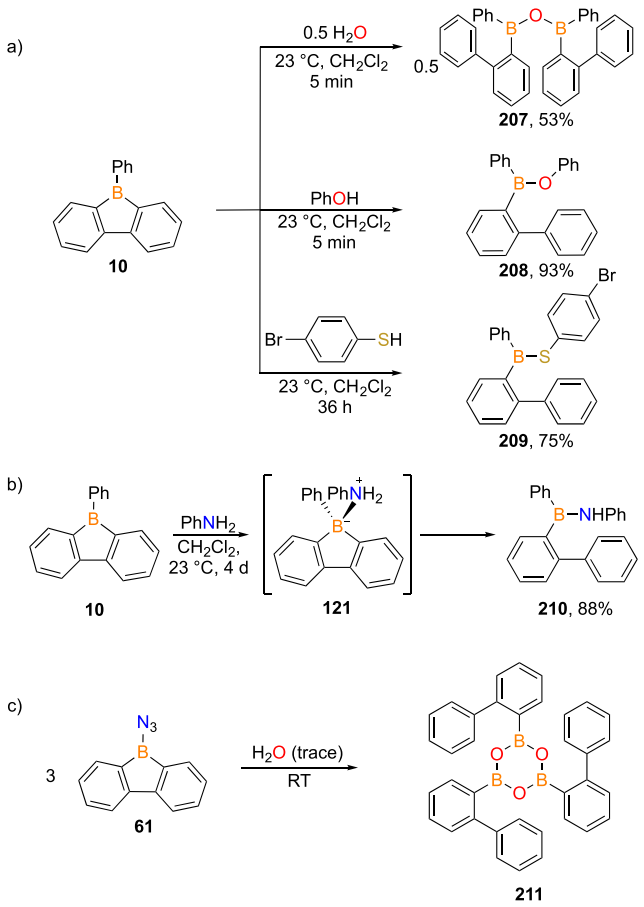

Figure 28. (a) Reaction of **10** with O−H reagents and *p*-bromothiophenol. (b) Reactivity of **10** with aniline. (c) Decomposition of **61** in the open atmosphere (yield not reported). (c) Adapted with permission from ref 126, Laperriere, L. E.; Yruegas, S.; Martin, C. D. Investigating the reactivity of 9-phenyl-9-borafluorene with N−H, O−H, P−H, and S−H bonds. *Tetrahedron* **2019**, 75 (8), 937. Copyright 2019 Elsevier Ltd.

reaction, only starting material and **207** were observed with no evidence of a monoprotodeborylated product with an unreacted O−H. Examining the susceptibility of the ring opening reactions with other E−H bonds using phenol, *p*-bromothiophenol, and aniline as substrates all generated the singly protodeborylated products (**208**, **209**, and **210**, respectively).[126] In contrast, the reaction of **10** with phenylphosphine generated an adduct (**116**, Table 6, entry 14), and 1-naphthyl mercaptan was found to be unreactive with **10**. The reaction with aniline was sluggish and enabled monitoring by in

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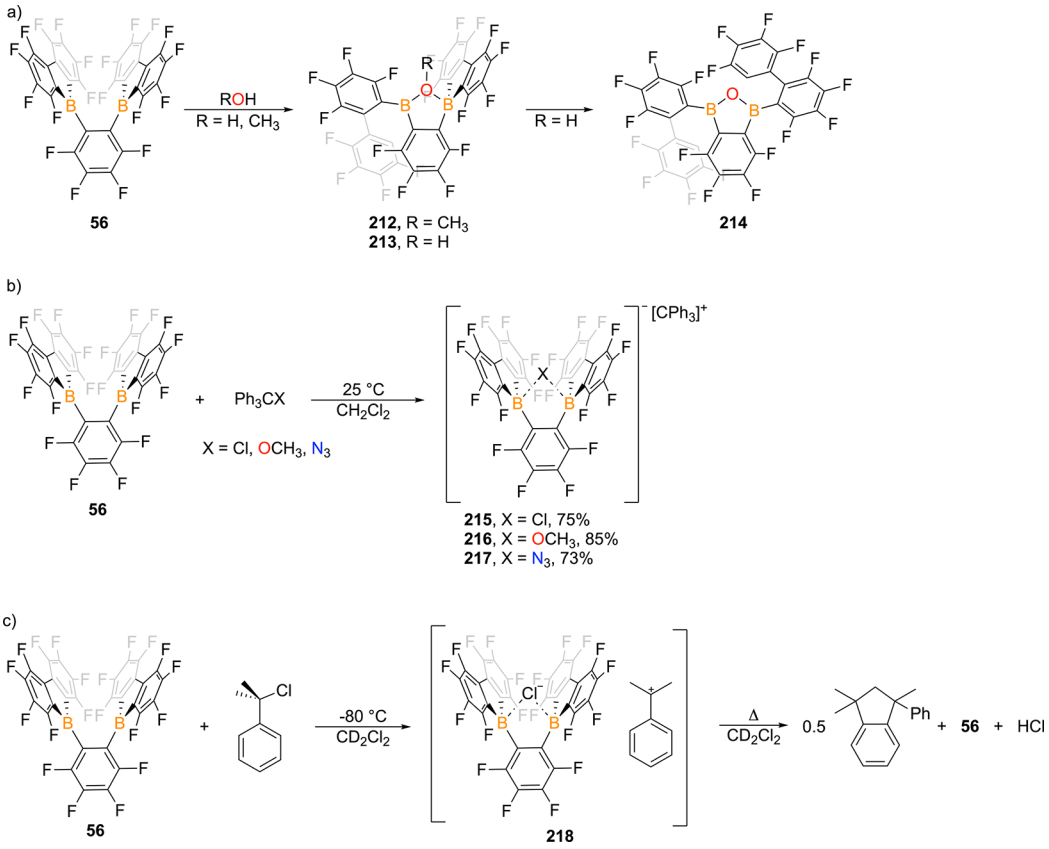

Figure 29. (a)Ring opening reactions of **56** with methanol and water. (b) Reactions of trityl species with **56** to produce chelated anions. (c) Reaction with cumyl chloride to produce an indane.

situ ^{11}B NMR spectroscopy, revealing that a tetracoordinate intermediate (δ = 0.4 ppm) is generated that ultimately converts to the ring opened product (Figure 28b). The proposed mechanism involves the formation of adduct intermediate **121** followed by endocyclic B−C bond cleavage to produce the protodeborylated product **210**. Addition of a second equivalent of **10** did not result in any reaction with the second N−H bond, even with heating at 100 °C in toluene. Protodeborylative ring opening was also observed by Bettinger and coworkers upon reaction of 9-azido-9-borafluorene (**61**) with water (even trace quantities) to produce boroxine **211** (Figure 28c).[96]

The perfluorinated diborole **56** (Section 2.4.1)[103] was demonstrated by Collins, Piers, and coworkers to undergo ring opening upon treatment with methanol or water (Figure 29a).[167] For methanol, a monodeborylated product **212** was obtained, while for water, both the mono- and the dideborylated product (**213** and **214**, respectively) were obtained. In studying the abstraction of substituents from hydrocarbons for olefin polymerization, bis(borafluorene) **56** was effective in generating trityl cations with the chelated counteranions **215**−**217** with methoxide, azide, and chloride (Figure 29b).[168] The attempted halide abstraction with cumyl chloride resulted in a rearrangement to the indane (Figure 29c).

4.2. Endocyclic B−C Bond Insertion Reactions for Heterocycle Synthesis

The biphenyl backbone fused to the central BC_4 ring in 9-borafluorenes results in a boron-containing tricyclic system; such fused polycyclic boracycles are garnering attention for potential utility in electronic materials.[12,15,17,18] The facile B−C bond cleavage observed in the ring opening reactions can also be exploited to insert molecular fragments or small molecules into the BC_4 ring to generate larger boracyclic systems. This has been demonstrated both intra- and intermolecularly to generate six- and seven-membered ring systems with extended conjugation.

4.2.1. Intramolecular Insertion Reactions. The thermolysis (98 °C) of 9-azido-9-borafluorene **61** was found by Bettinger and coworkers to generate a tetrameric system with a central B_4N_4 ring and N_2 as the byproduct (**219**, Figure 30).[97]

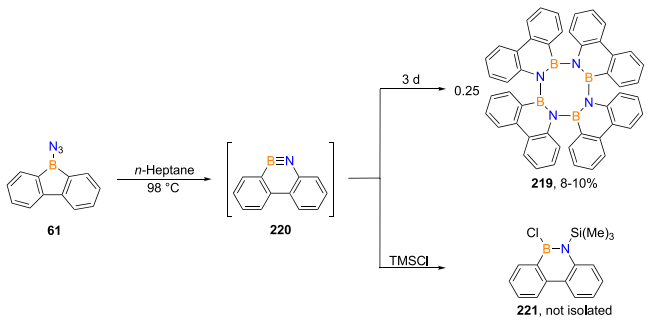

Figure 30. Thermolysis of **61** to generate tetramer **219** and trapping of azaboraphenanthryne intermediate **220** with TMSCl.

The resulting compound **219** was isolated in low yields (8−10%) due to the formation of multiple products that could not be definitively characterized. A trapping experiment in the presence of trimethylsilyl chloride resulted in the formation of the Si−Cl addition product **221** supporting the generation of 9,10-B,N-phenanthryne **220** in the reaction. In depth computational investigations revealed that N_2 is eliminated in a concerted

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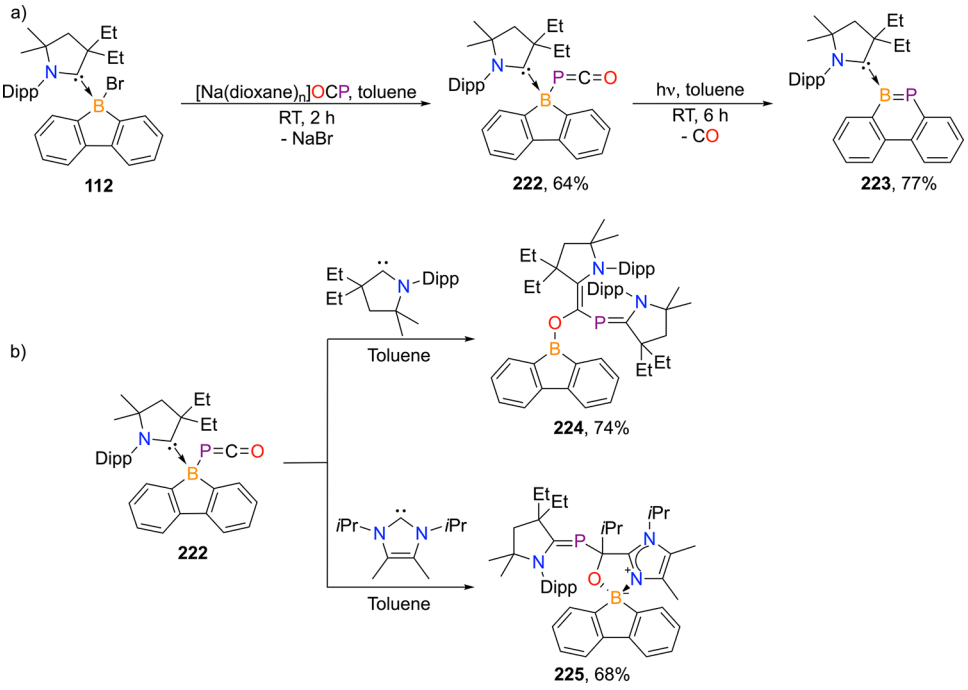

Figure 31. (a) Synthesis of carbene stabilized BP-phenanthryne **223** and (b) reactivity of boraphosphaketene **222** with carbene reagents.

manner to generate intermediate **220**. Intermediate **220** undergoes a series of rearrangements and oligomerizations to ultimately furnish tetrameric **219** in an extremely exothermic process (−1319 kJ/mol).[97,169]

A B,P-containing analogue of **220** stabilized by a carbene ligand at boron was recently reported by Gilliard and coworkers (**223**, Figure 31a).[170] This species was synthesized via reaction of a cyclic(alkyl)(amino) carbene (CAAC) adduct of 9-bromo-9-borafluorene (**112**) with sodium phosphaethynolate (NaOCP) to produce a boraphosphaketene (**222**), which was photolyzed to form the CAAC-stabilized BP-phenanthryne **223** with elimination of carbon monoxide. The boraphosphaketene intermediate also reacts with an additional equivalent of carbene, either CAAC or NHC, to produce compounds **224** or **225**, respectively, resulting from activation of the phosphaketene moiety (Figure 31b).

The Bettinger group investigated the reaction of **2** with amines and amides as a potential method to generate amino-substituted 9-borafluorenes. Surprisingly, in the reaction with *N*,*O*-bis(trimethylsilyl)hydroxylamine, the aminoborafluorene (**226**) was not isolated; instead, 9,10-azaboraphenanthrene **227** was obtained in which the OTMS group is bound to boron (Figure 32).[171] Monitoring the reaction by variable-temperature (−10 to 26 °C) ^{11}B NMR spectroscopy revealed a number of species, one of which was assigned as the aminoborafluorene intermediate **226** resulting from the anticipated substitution at the boron and the assignment based upon agreement with

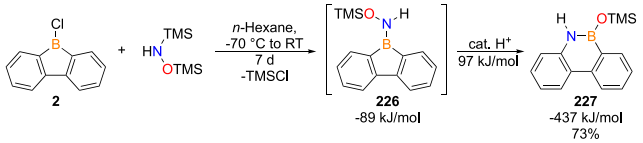

Figure 32. Synthesis of 9,10-azaboraphenanthrene **227** via aminoborole rearrangement from the reaction of **2** and *N*,*O*-bis(trimethylsilyl)hydroxylamine.

chemical shift calculations. The most rational reaction pathway was calculated to be aminoborafluorene formation through the elimination of trimethylsilyl chloride and rearrangement promoted by catalytic acid from the reaction mixture. The conversion of **2** to **227** proceeds with exothermicities of 348 kJ/mol for the rearrangement step and 437 kJ/mol for the overall reaction.

In 2018 Wagner, Wang, and coworkers investigated the photolysis of tetraarylborates with two aryl groups linked forming a 9-borafluorene backbone (Figure 33).[172] When

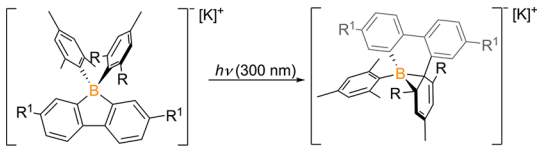

Figure 33. Photolysis of **228**−**231** leading to borirane containing derivatives **232**−**235**. Yields are not reported, but in situ multinuclear NMR spectra indicate high conversion.

compounds **228**−**231**, containing one or two mesityl groups on boron, were exposed to UV light, an isomerization occurred, inserting the *ipso* carbon of either a mesityl or *p*-tolyl group into the BC_4 ring and forming a B−C bond with the *ortho* carbon. The products feature fused BC_2 and BC_5 rings from the dearomatization of the aryl substituent. Potassium counter cations enabled the isolation of the photoisomerization products while lithium counterions allowed the photoisomerization but did not result in thermally stable products. If the borate contained two tolyl groups, complex mixtures were obtained, rationalized by lower charge-transition character in comparison to the mesityl-containing species making the formation of the BC_2/C_6 ring system less favorable.

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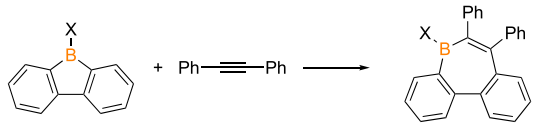
4.2.2. Intermolecular Insertion Reactions. The intramolecular insertions described provide access to interesting species but are limited in scope based on accessible precursors. Intermolecular insertion reactions, however, allow for a comparatively larger substrate scope and are a versatile method for the synthesis of larger boracycles. In a 2016 study by Fukushima and coworkers, 9-chloro-9-borafluorene (**2**) was reacted with a series of alkynes to generate seven-membered rings (Table 11).[173] The reactions furnished the 1:1

Table 11. Reactions of Diphenylacetylene with 9-Borafluorenes in 1,2-Dichloroethane[a]



X	conditions	yield (%)	compound
Cl	25 °C, 6 h	23	**236**[106]
Br	25 °C, 6 h	99	**237**[106]
OTf	25 °C, 6 h	89	**238**[106]
Cl	25 °C, 4 d[b]	quantitative	**236**[173]
Cl	80 °C, 12 h	quantitative (87)	**236**[106,173]
Br	80 °C, 12 h	quantitative (76)	**237**[106]
OTf	80 °C, 12 h	quantitative (73)	**238**[106]

[a]Yields were determined by quantitative ^{1}H NMR analysis; isolated yields, if available, are in parentheses. [b]Experiment in CH_2Cl_2.

stoichiometric BC_6 borepin systems **236**–**238** with the exception of one alkyne, bis(trimethylsilyl)acetylene, which reacted in a 2:1 stoichiometry to produce a seven-membered ring with an exocyclic allene resulting from TMS migration (Figure 34). The scope of alkynes was broad and included

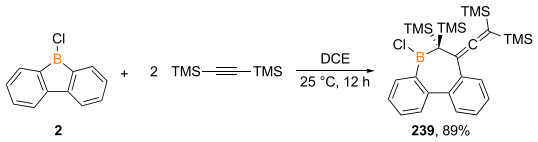


Figure 34. Reaction of **2** with two equivalents of bis(trimethylsilyl)-acetylene, DCE = 1,2-dichloroethane.

substrates containing aryl (including 2-thienyl), alkyl, and proton substituents on the alkyne (Table 12). The resulting dibenzoborepin species could be oxidized in a one-pot process to produce substituted phenanthrenes. This synthetic method was later extended to reactions of 9-borafluorenes with poly(phenylene ethynylene) (PPE) derivatives followed by oxidation to produce "zigzag" 9,10-diarylphenanthrene polymers (Figure 35).[174] The thermodynamics and kinetics for the alkyne insertion were also investigated with the Cl-, Br-, and OTf-substituted 9-borafluorenes.[106] For all diarylalkyne substrates tested, 9-Cl-9-borafluorene has the slowest reaction rate while 9-Br-9-borafluorene has the fastest reaction rate. This is consistent with the relative Lewis acidities of the three 9-borafluorenes (Cl < OTf < Br, Table 10); thus, 9-Br-9-borafluorene was demonstrated to be the most effective reagent for the synthesis of dibenzoborepins.

Mechanistic calculations on the reactions of diphenylacetylene with 9-chloro-9-borafluorene and 9-bromo-9-borafluorene revealed that a π-bond first coordinates to boron (**246/247Int**, Figure 36).[106] The endocyclic B–C bond is cleaved and the new B–C and C–C bonds are formed in a concerted transition state (**246/247TS**). The barriers are 72.0 kJ/mol (X = Cl) and 49.8 kJ/mol (X = Br), and the overall reactions are exergonic by 113 and 120 kJ/mol, respectively. The reduced barrier for the bromo species corroborates the experimental data. In a separate computational study, Braunschweig and Lin obtained similar results for the insertion of diphenylacetylene into 9-chloro-9-borafluorene proceeding directly to the transition state with a barrier of 92.9 kJ/mol and an overall exergonic reaction by 90.0 kJ/mol.[175] For the alternate product with bis(trimethylsilyl)-acetylene, the proposed pathway is much more complex.

Our group and the He group investigated the reactions of organic azides with 9-borafluorenes.[151,176] The reactions of 9-phenyl- and 9-chloro-9-borafluorene with 1-azidoadamantane resulted in the formation of 9,10-azaboraphenanthrenes by N_2 expulsion and insertion of the α-nitrogen of the azide (Table 13).[151] Similar 9,10-azaboraphenanthrene products are obtained from the reaction of 9-phenyl-9-borafluorene and 2,7-dibromo-9-phenyl-9-borafluorene with mesityl azide.[176] Phenyl azide reacted with 9-chloro-9-borafluorene in the same manner, but the reaction with 9-phenyl-9-borafluorene resulted in the insertion of the γ-nitrogen atom to generate a diazene-substituted 9,10-azaboraphenanthrene (**268**, Figure 37).[151] These were the first intermolecular heteroatom insertions into 9-borafluorenes reported.

Wagner and coworkers exposed benzene solutions of neutral B-Mes (**39**) or anionic B-Mes_2 (**274**) substituted 9-borafluorenes to dry air as an oxygen source to furnish 9,10-oxaboraphenanthrene **275** (Figure 38).[177] Although not quantified, over a week, the reaction of the anion generated oxaboraphenanthrene **275** much more slowly and contained compound **39** in the reaction mixture. Based on these results, it was inferred that the reaction proceeds via the neutral compound and accordingly, the reaction with the tetracoordinate borafluorene anion was much slower.

The N_2 elimination route demonstrated for azide insertion was also effective for diazoalkanes. The reaction of 9-phenyl-9-borafluorene with trimethylsilyldiazomethane resulted in the insertion of a carbene unit into the endocyclic B–C bond to furnish the BC_5 heterocycle **276** (Figure 39).[178] Interestingly, a second equivalent of trimethylsilyldiazomethane reacted to insert a carbene unit into the other B–C bond to access a seven membered BC_6 ring in which the TMS groups were *syn* with respect to each other. No evidence for further insertion reactivity was noted. This is the only example of insertion occurring into both endocyclic B–C bonds of a 9-borafluorene.

The insertion of unsaturated 1,2-dipolar molecules into the endocyclic B–C bond of 9-phenyl-9-borafluorene (**10**) has been investigated extensively. The reaction between 1-adamantylphosphaalkyne and 9-phenyl-9-borafluorene (**10**) formed the corresponding 1,3-phosphaborepin product (**278**, Figure 40).[179] Computational studies provided mechanistic insight suggesting that the reaction proceeds via a single transition state with a bond metathesis of a π-bond of the phosphaalkyne and one of the endocyclic B–C bonds. This single step is thermodynamically favored by 17 kJ/mol with a barrier of 88 kJ/mol.

Our group studied the reactivity of **10** with a series of 1,2-dipolar unsaturated organic molecules containing oxygen and nitrogen (Figure 41).[124] The reactions with C=O containing substrates benzaldehyde, benzophenone, and diphenylketene all resulted in BOC_5 ring containing products via insertion of the C=O moiety into the BC_4 ring (**279**–**281**) in good yields. The

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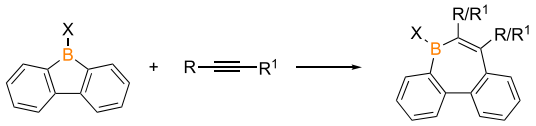
Table 12. Reactions of Substituted Alkynes with 9-Borafluorenes[a]



X	R	R^1	conditions	yield (%)	compound
Cl	*p*-tolyl	*p*-tolyl	25 °C, 4 h	36	**248**[106]
Br	*p*-tolyl	*p*-tolyl	25 °C, 4 h	99	**249**[106]
OTf	*p*-tolyl	*p*-tolyl	25 °C, 4 h	91	**250**[106]
Cl	*p*-tolyl	*p*-tolyl	80 °C, 12 h	99	**248**[173]
Cl	*p*-MeO-C_6H_4	*p*-MeO-C_6H_4	25 °C, 1 h	46	**251**[106]
Br	*p*-MeO-C_6H_4	*p*-MeO-C_6H_4	25 °C, 1 h	99	**252**[106]
Otf	*p*-MeO-C_6H_4	*p*-MeO-C_6H_4	25 °C, 1 h	97	**253**[106]
Cl	*p*-MeO-C_6H_4	*p*-MeO-C_6H_4	80 °C, 12 h	99	**251**[173]
Cl	*p*−Br-C_6H_4	*p*-Br-C_6H_4	25 °C, 24 h	12	**254**[106]
Br	*p*-Br-C_6H_4	*p*-Br-C_6H_4	25 °C, 24 h	92	**255**[106]
Otf	*p*-Br-C_6H_4	*p*-Br-C_6H_4	25 °C, 24 h	66	**256**[106]
Cl	*p*-Br-C_6H_4	*p*-Br-C_6H_4	80 °C, 12 h	96	**254**[173]
Cl	*p*-CF_3-C_6H_4	*p*-CF_3-C_6H_4	25 °C, 68 h	25	**257**[106]
Br	*p*-CF_3-C_6H_4	*p*-CF_3-C_6H_4	25 °C, 68 h	98	**258**[106]
Otf	*p*-CF_3-C_6H_4	*p*-CF_3-C_6H_4	25 °C, 68 h	n.d. (mixture)	**259**[106]
Cl	*p*-CF_3-C_6H_4	*p*-CF_3-C_6H_4	80 °C, 12 h	83	**257**[173]
Cl	*p*-CO_2Me-C_6H_4	*p*-CO_2Me-C_6H_4	80 °C, 16 h	57	**260**[106]
Br	*p*-CO_2Me-C_6H_4	*p*-CO_2Me-C_6H_4	80 °C, 16 h	91	**261**[106]
Otf	*p*-CO_2Me-C_6H_4	*p*-CO_2Me-C_6H_4	80 °C, 16 h	n.d. (mixture)	**262**[106]
Cl	*p*-CO_2Me-C_6H_4	*p*-CO_2Me-C_6H_4	80 °C, 12 h	92	**260**[173]
Cl	*p*-I-C_6H_4	*p*-I-C_6H_4	80 °C, 12 h	83	**263**[173]
Cl	2-thienyl	2-thienyl	80 °C, 12 h	99	**264**[173]
Cl	Ph	Et	80 °C, 12 h	84	**265**[173]
Cl	Et	Et	80 °C, 12 h	94	**266**[173]
Cl	Ph	H	80 °C, 12 h	43	**267**[173]

[a]Yields were determined by quantitative ^{1}H NMR analysis, and all reactions are in 1,2-dichloroethane. Regiochemistry of the borepin products from the nonsymmetric alkynes was not specified. Note: n.d. = not determined.

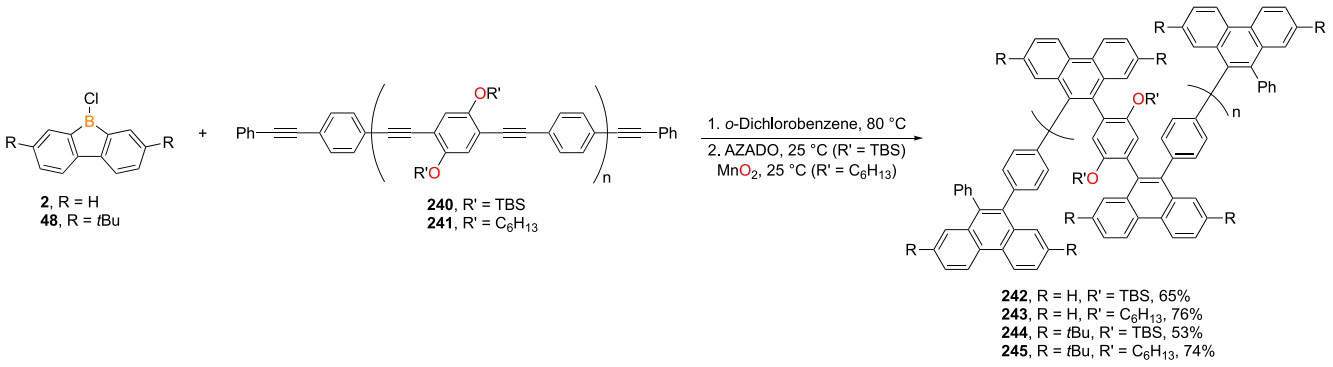


Figure 35. Synthesis of 9,10-diarylphenanthrene polymers from 9-chloro-9-borafluorenes. AZADO = 2-azaadamantane-N-oxyl, TBS = *tert*-butyldimethylsilyl.

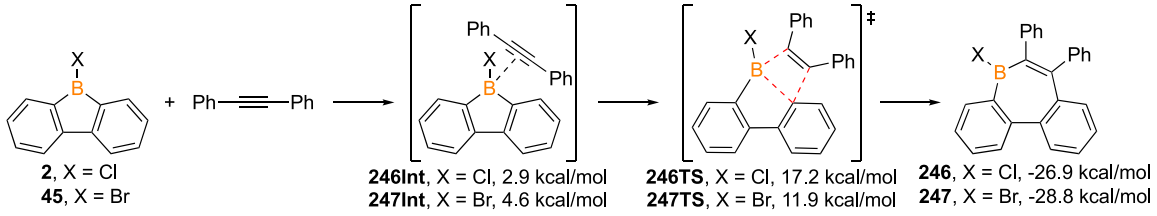


Figure 36. Computed mechanism by Fukushima and coworkers for the insertion of diphenylacetylene into 9-Cl- and 9-Br-9-borafluorene.

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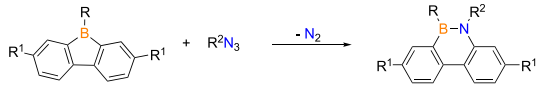
Table 13. Reactions of Azides with 9-Borafluorenes to Furnish 9,10-Azaboraphenanthrenes



R	R^1	R^2[a]	conditions	yield (%)	compound
Ph	H	Ad	toluene, 110 °C, 5 d	64	**269**[151]
Cl	H	Ad	toluene, 110 °C, 2 d	54	**270**[151]
Cl	H	Ph	*n*-pentane, −35 to 28 °C, 3 h	74	**271**[151]
Ph	H	Mes	toluene, RT, 12 h	50	**272**[176]
Ph	Br	Mes	toluene, 40 °C, 12 h	71	**273**[176]

[a]Ad = 1-adamantyl.

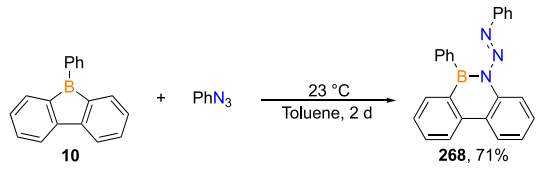


Figure 37. Reaction of 9-phenyl-9-borafluorene with phenyl azide.

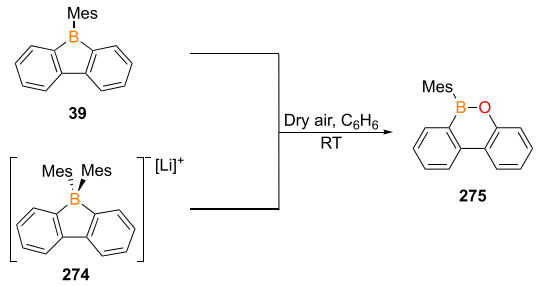


Figure 38. Synthesis of 9,10-oxaboraphenanthrene **275** by oxidation of 9-borafluorenes.

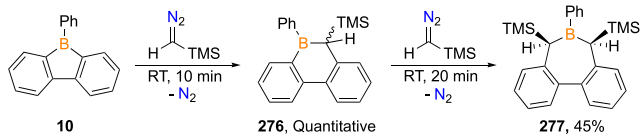


Figure 39. Carbene insertion into the endocyclic B−C bonds of 9-phenyl-9-borafluorene. Adapted with permission from ref 178. Bartholome, T. A.; Bluer, K. R.; Martin, C. D. Successive carbene insertion into 9-phenyl-9-borafluorene. *Dalton Trans.* **2019**, 48 (19), 6319. Copyright 2019 The Royal Society of Chemistry.

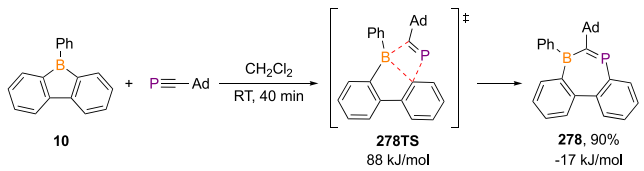


Figure 40. Mechanism for the reaction between 9-phenyl-9-borafluorene (**10**) and 1-adamantylphosphaalkyne. Adapted with permission from ref 124. Yruegas, S.; Barnard, J. H.; Al-Furaiji, K.; Dutton, J. L.; Wilson, D. J. D.; Martin, C. D. Boraphosphaalkene Synthesis via Phosphaalkyne Insertion into 9-Borafluorene. *Organometallics* **2018**, 37 (10), 1515. Copyright 2018 American Chemical Society.

reaction of **10** with isocyanates gave two different outcomes depending on the substituent at the isocyanate nitrogen. The reaction with 1-adamantyl isocyanate gave a BNC_5 heterocycle (**282**) with an amide moiety by C−N insertion while the reaction with *p*-methoxyphenyl isocyanate resulted in the insertion of the C−O moiety to produce a BOC_5 heterocycle with an exocyclic imine functionality (**283**). This difference in reactivity was rationalized by the polarization of the isocyanates. For 1-adamantyl isocyanate, the nitrogen atom is more electron rich than the oxygen atom while for *p*-methoxyphenyl isocyanate, the oxygen is more electron rich than the nitrogen. Compound **283** dimerizes in the solid state as confirmed by X-ray crystallography, but solution ^{11}B NMR spectroscopy indicates a monomer based on a resonance in the tricoordinate region (47.4 ppm). The reactions of 9-borafluorenes with carbodiimides were demonstrated by Kashida, Shoji, and Fukushima to furnish BNC_5 heterocyclic products **284**−**286** with exocyclic imines similar to **283** via C−N insertion into the endocyclic B−C bond.[180]

In contrast with 9-phenyl-9-borafluorene, a di-*t*-butylphosphino-substituted 9-borafluorene reported by Wagner and coworkers was found to undergo carbonyl insertion into the B═P bond upon reaction with benzophenone (**289**, Figure 42).[112] The same species is capable of inserting a nitrile group into the B═P bond upon reaction with acetonitrile to form dimeric imine-substituted borafluorene **288** whereas 9-phenyl-9-borafluorene forms an adduct (**120**, Table 6, entry 19).[112,124] The B═P bond of **68** can also undergo hydrogenation (**287**) and act as a dienophile in a Diels−Alder reaction with 2,3-dimethylbutadiene (**290**).[112]

4.3. Ring Opening Oligomerizations

9-Borafluorenes can be reagents to access boron-containing π-conjugated oligomeric species. It has been widely reported that 9-H-9-borafluorene (**64**) undergoes dimerization to fill the empty p orbital at the tricoordinate boron center (Section 2.3.1.2). This feature can give rise to other types of reactivity including oligomerization, as reported by Wagner and coworkers in their extensive studies on the synthesis and characterization of **64**.[110] Monomeric **64** was generated in situ from 9-bromo-9-borafluorene (**45**) by Br/H exchange with triethylsilane. Storing a hexane solution of 9-H-9-borafluorene dimer **291** at 5 °C for 7 days generated a precipitate; the ring opened dimeric adduct **292** was isolated after addition of pyridine to a benzene solution of this precipitate (Figure 43a). In the absence of a trapping agent, a mixture of B(H)-bridged biphenylenes was obtained as a result of ring opening oligomerization, including a species formed from five equivalents of **64** (**293**, Figure 43b), as confirmed by a single crystal X-ray diffraction study. The reaction mechanism was proposed via DFT studies to include B−H/B−H, B−C/B−C, and B−H/B−C addition steps. However, the exact relationship between 9-borafluorene structure and reactivity toward ring opening oligomerizations was not entirely clear. In this context, a 2014 computational study by Zhu and Qu investigated the 2,7-di-*tert*-butyl substituted 9-H-9-borafluorene analogue (**65**).[181] It was concluded that the oligomerization reactions could be controlled via reaction temperatures and the addition of bulky substituents. The addition of *t*-butyl substituents at the 2- and 7-positions provides increased stability to the dimeric species **294**.

The 9-H-9-borafluorene dimer was predicted by NMR studies and DFT calculations to adopt a structure in which the two boron centers are bridged by a hydride and a phenyl ring (**291**,

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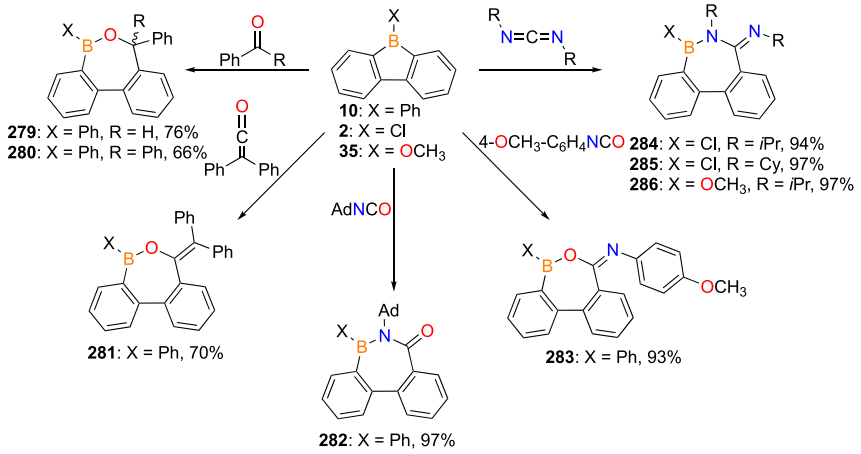

Figure 41. 1,2-Dipolar insertion reactions into 9-borafluorenes. Reaction conditions for the synthesis of **279**: toluene, 100 °C, 48 h; **280**: toluene, 100 °C, 10 d; **281**: toluene, 100 °C, 7 d; **282** and **283**: CH_2Cl_2, RT, 5 min; **284**−**286**: 1,2-DCE, 80 °C, 24 h. Cy = cyclohexyl.

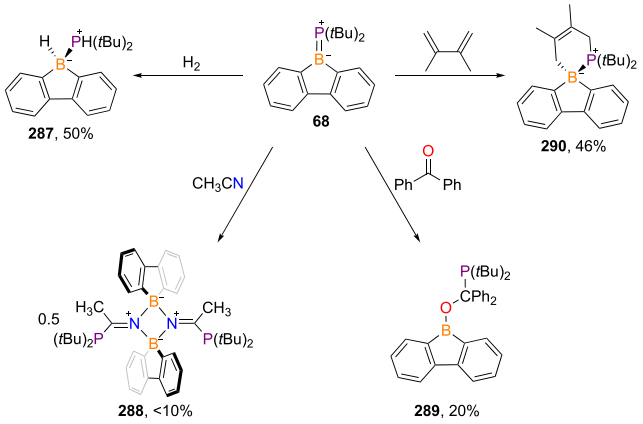

Figure 42. P═B bond reactivity of 9-di-*t*-butylphosphino-9-borafluorene. All reactions conducted in toluene at room temperature. Reaction time for the synthesis of **287**: 2 h; **289** and **290**: overnight.

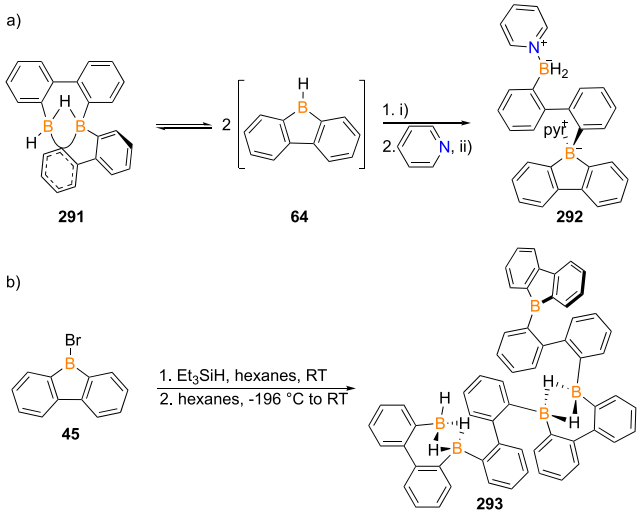

Figure 43. (a) Reaction of 9-H-9-borafluorene dimer with excess pyridine; (i) hexanes, RT to 5 °C, 7 d; (ii) redissolve precipitate in benzene, then excess pyridine, RT, 30 min (pyr = pyridine). (b) Ring opening oligomerization of in situ generated 9-H-9-borafluorene.

Figure 43). However, this dimer could not be isolated due to its instability.[110] The structural assignment was confirmed via the X-ray crystal structure of the analogous 2,7-di-*t*-butyl-9-H-9-borafluorene dimer (**294**).[75] X-ray crystallography indicated that the structure of **294** contains B−H−B and B−C−B three-center two-electron bonds. Dimer **294** thermally isomerizes at 140 °C in hexanes to produce **295** with two bridging hydrides between the boron centers (Figure 44). Compound **295** is more stable than **294** toward hydrolysis and coordination with pyridine.

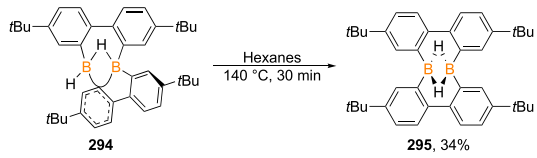

Figure 44. Thermally induced isomerization of **294**.

In addition to the ring opening oligomerization observed at room temperature in hexanes, 9-H-9-borafluorene produces a mixture of compounds containing two boron centers upon thermolysis at 120 °C in toluene (Figure 45).[117] The ring

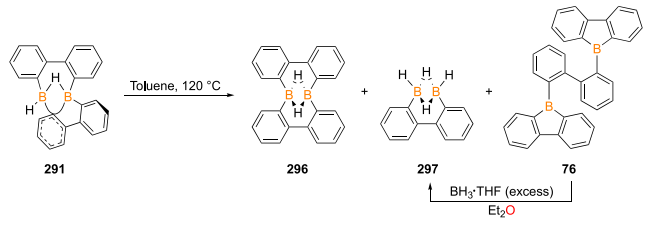

Figure 45. Thermolysis of 9-H-9-borafluorene dimer **291** in toluene.

opened dimer **296**, the biphenyl-bridged diborane(6) derivative **297**, and 2,2′-bis(9-borafluorenyl)biphenyl (**76**) were observed as products. 2,2′-Bis(9-borafluorenyl)biphenyl (**76**) was characterized by X-ray crystallography as the free borafluorene and as a pyridine adduct (**128**, Figure 14). Compound **76** can also be converted to **297** upon reaction with excess BH_3·THF.

The central borole ring of 9-borafluorenes can undergo ring opening upon reaction with borohydrides, including $NaBH_4$ and $NaBHEt_3$ as demonstrated by Hong and Chung (Figure 46).[182] The reaction of 9-chloro-9-borafluorene with sodium borohydride results in the formation of the biphenyl-bridged diborane

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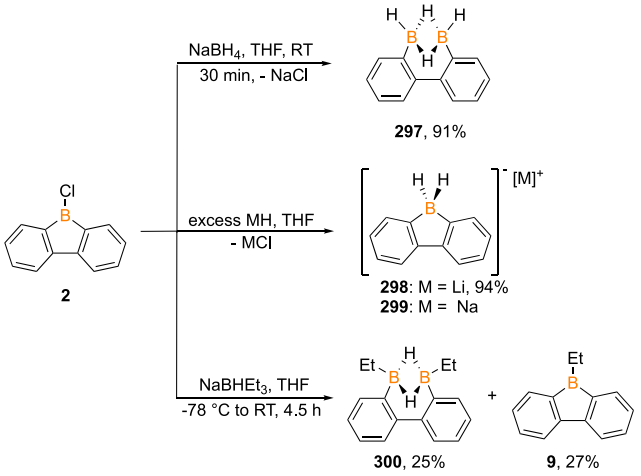

Figure 46. Reactions of 9-chloro-9-borafluorene with hydride reagents.

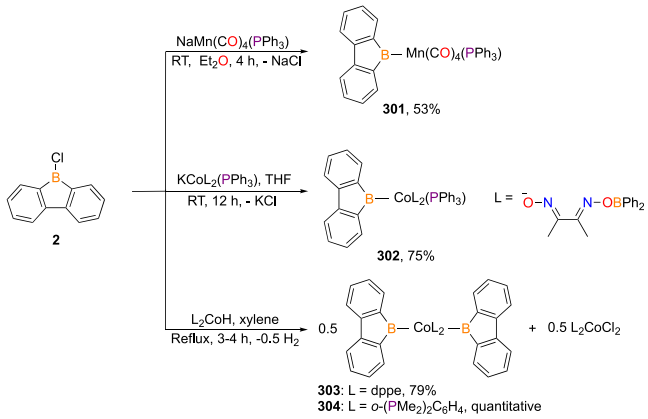

Figure 47. Synthesis of 9-borafluorenyl Mn(I), Co(II), and Co(III) complexes from 9-chloro-9-borafluorene (dppe = 1,2-bis-(diphenylphosphino)ethane).

297 with the elimination of sodium chloride. The reaction with $NaBH_4$ was determined to proceed via formation of 9-H-9-borafluorene followed by cleavage of the endocyclic B−C bond with in situ generated BH_3. The reaction of 9-chloro-9-borafluorene with sodium hydride generated 9-H-9-borafluorene (**64**), observed by ^{11}B NMR spectroscopy, followed by the formation of hydride adduct **298** in the presence of excess NaH or 9-ethyl-9-borafluorene in the presence of ethylene. Hydride adduct **299** had been previously prepared as a lithium salt (**298**) by Knizek and Nöth via reaction of 9-chloro-9-borafluorene with lithium hydride.[183] While the reaction of 9-chloro-9-borafluorene with $NaBH_4$ results solely in the formation of **297**, the analogous reaction with $NaBHEt_3$ produces a mixture of a diborane(6) derivative (**300**) and 9-ethyl-9-borafluorene (**9**), presumably from H/Et exchange with triethylborane formed during the reaction.[182] Notably, both the hydride- and ethyl-substituted diborane species (**297** and **300**) had previously been synthesized from biphenyl-substituted boranes by Köster and Willemsen in 1974.[184] In this study, **300** was found to exist in equilibrium with 9-ethyl-9-borafluorene and the dimer $(EtBH_2)_2$.

4.4. Reduction and Metal Complexes

4.4.1. 9-Borafluorene Metal Complexes. Early examples of 9-borafluorene metal complexes included boron-bound Mn(I), Co(II), and Co(III) complexes synthesized by Nöth and coworkers in the late 1960s.[185−187] In these complexes, the 9-borafluorenyl ligands coordinated to the metal center as fused diarylboryl anions. The complexes are prepared from 9-chloro-9-borafluorene in moderate to high yields by two methods (Figure 47). For the Mn(I) and Co(III) complexes (**301** and **302**), 9-chloro-9-borafluorene was reacted with alkali metal salts of anionic Mn(-I) and Co(I) complexes, resulting in two-electron oxidation of the metal centers accompanied by elimination of alkali metal chlorides.[185,187] In contrast, the Co(II) complexes (**303** and **304**) were prepared by one-electron oxidation of a Co(I) hydrido complex accompanied by the elimination of hydrogen gas and formation of a ligated dichloro Co(II) complex.[186] Compounds **301**−**304**, however, were not characterized by X-ray crystallography, and **304** exhibited a ^{11}B NMR shift significantly upfield (−15 ppm) from later crystallographically characterized examples of metal-bound alkyl- and aryl-substituted boryl anions (76−121 ppm).[188−191]

In 2003, Piers and coworkers demonstrated that 9-borafluorenes can form η^1 complexes with AlCp* (Cp* = pentamethylcyclopentadienyl) upon reaction with $[AlCp^*]_4$

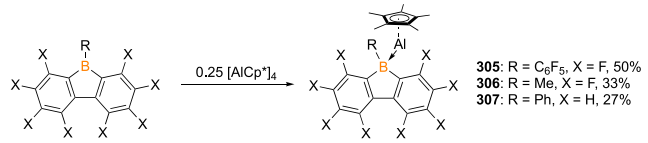

Figure 48. Reactivity of $[AlCp^*]_4$ with 9-borafluorenes.

(Figure 48).[92] The η^1 coordination instead of η^5 was attributed to the flanking aryl groups retaining aromaticity; the preference for η^1 coordination was also supported by DFT calculations revealing that the LUMO of 9-H-9-borafluorene is largely localized at boron. The aluminum center retained the +1 oxidation state rather than undergoing oxidation to aluminum-(III), and the resulting compounds (**305**−**307**) are viewed as coordination complexes with the aluminum(I) center donating into the vacant p orbital at boron. In an attempt to prepare the corresponding η^5-aluminum(III) complex, the dilithio salt of the 9-phenyl-9-borafluorene dianion was reacted with $[Cp^*AlCl_2]_2$ and $Cp^*AlCl_2(THF)$ but produced a mixture of products with no evidence of formation of the targeted η^5 aluminum(III) complex.

Miqueu, Bourissou, and coworkers prepared an ambiphilic ligand featuring a diisopropylphosphino group linked to a 9-borafluorene via an *ortho*-phenylene unit (**164**).[192] The reaction of ligand **164** with $(Me_2S)AuCl$ resulted in coordination of the phosphine moiety to gold and a Z-type interaction between the electron rich gold center and boron akin to that observed in the AlCp* complexes (**308**, Figure 49). Harman and coworkers examined the reaction of the same ligand with $Ni(PPh_3)_4$ to produce an η^5-borafluorene complex (**309**).[134] On the basis of a long Ni−B bond [2.135(2) Å] and DFT calculations, the interaction of the BC_4 unit to the metal was classified as L_2Z with a Ni(0) center.

Another route to borafluorene-containing metal complexes involves the functionalization of 9-ferrocenyl-9-borafluorene (**74**). This compound, first reported by Wagner in 2008, was found to form the Fe(II)/Fe(III) mixed-valent complex **310** upon treatment with 1,1′-dilithioferrocene followed by exposure

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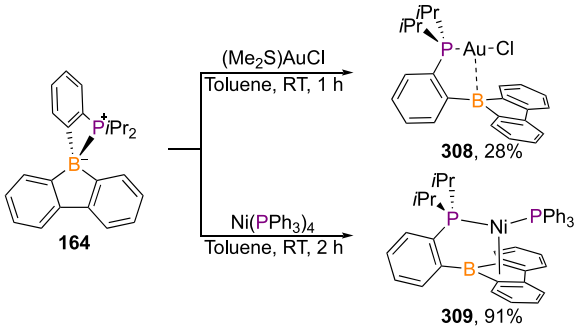

Figure 49. Reactivity of ambiphilic 9-borafluorene **164** with Au(I) and Ni(0) sources.

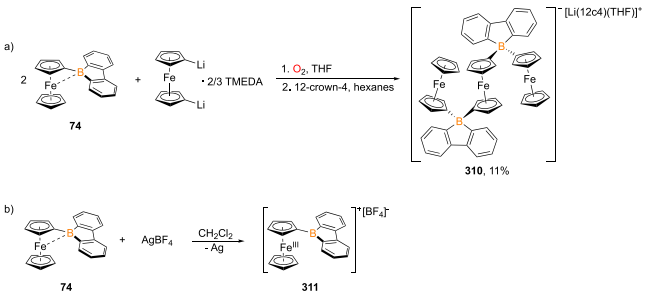

Figure 50. (a)Reaction of 9-ferrocenyl-9-borafluorene **74** with 1,1′-dilithioferrocene. (b) Oxidation of 9-ferrocenyl-9-borafluorene **74** with $AgBF_4$. 12-crown-4 = 1,4,7,10-tetraoxacyclododecane.

to air (Figure 50a).[116] Characterization by X-ray crystallography and cyclic voltammetry indicated that the two terminal ferrocenyl groups contain Fe(II) centers while the third iron center in the bridging ferrocene unit is Fe(III). The geometry of compound **74** was also shown to undergo significant change upon oxidation of the iron center. For neutral **74**, X-ray diffraction studies reveal that the dip angle of the Cp ligand bearing the borafluorene is 25.5° and 17.1° for the two independent molecules in the asymmetric unit, attributed to a strong Fe−B interaction. Oxidation to Fe(III) with $AgBF_4$ to **311** caused a decrease in the dip angle dramatically to 6.3° as the σ-donation was effectively eliminated due to the decreased electron density at the iron center (Figure 50b).

In 2005, Piers and coworkers demonstrated that perfluorinated 9-phenyl-9-borafluorene (**50**) can abstract alkyl groups from scandium(III)-alkyl complexes containing diketiminate ligands (e.g., **312**). With one equivalent of **50**, the *endo*/*exo* isomers **313** were obtained with a bridging methyl ligand between boron and scandium centers while with a second equivalent, the second alkyl group is also abstracted (**314**, Figure 51).[193] The interconversion of these species was studied in detail.

4.4.2. Reduction of 9-Borafluorenes. 9-Borafluorenes possess four π-electrons in the central ring and are capable of forming aromatic dianions upon reduction. Despite the interesting potential applications of dianionic 9-borafluorene derivatives, this chemistry has not been explored in depth, and only a few examples are documented in the literature. In 1996, Grigsby and Power reported the syntheses of a series of 9-borafluorene derivatives as resulting from alkali metal reduction of arylboron dihalides (Figure 2).[72] In the cases herein described, the dilithium-9-borafluorenyl complex (**17**) was obtained along with other similar complexes. It was demonstrated that in the presence of an excess of lithium in diethyl ether, the in situ generated 9-borafluorene derivative (**24**) was reduced to generate the aforementioned complex **17**. With these early examples, it was confirmed that 9-borafluorenes, like monocyclic boroles, are readily reduced to their dianionic species. Accordingly, Wehmschulte and coworkers reported the formation of the dianionic form of compound **27** via reduction with lithium metal (Figure 52a).[73] An analogous reduction of 9-phenyl-9-borafluorene to its dianion (**316**) was also reported in 2003 by Piers, Woo, and coworkers (Figure 52b).[92] X-ray diffraction studies on **315** revealed that the lithium atoms are positioned nearly symmetrically on each side of the planar 9-borafluorene dianion in an η^5 coordination mode with the central BC_4 ring.[73] The B−C bond lengths within the borole core are contracted relative to typical B−C single bonds, attributed to the aromaticity of the BC_4 ring resulting in B−C multiple bonding.

Wagner and coworkers investigated the lithium reduction of the 9-H-9-borafluorene derivative **294** (Figure 53).[194] The

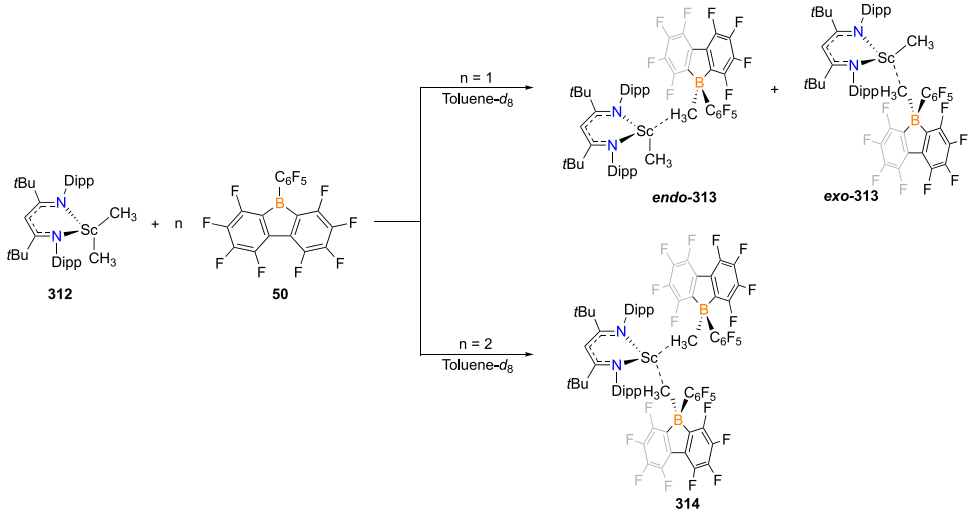

Figure 51. Alkyl abstraction of organoscandium complexes featuring perfluorinated 9-phenyl-9-borafluorene exemplified with methylated scandium complex **314**. Similar chemistry has been demonstrated for $-CH_2Si(CH_3)_3$ and $-CH_2C(CH_3)_3$ substituted scandium species.

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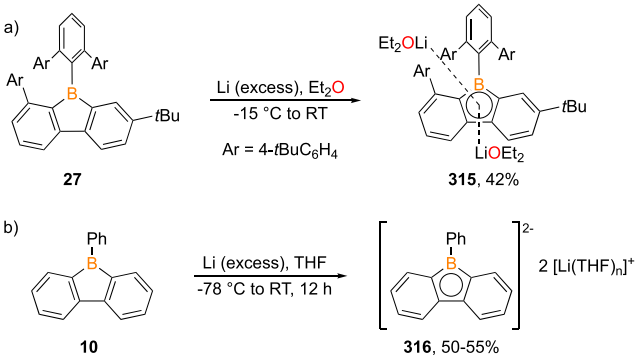

Figure 52. Reduction reactions of (a) **27** and (b) 9-phenyl-9-borafluorene **10** with lithium metal.

reaction of compound **294** with lithium metal yielded an array of structurally diverse compounds (**87**, **317**−**319**). Particularly notable among these products are the diborate **87** and compound **319**, which exhibits structural features resembling both conventional organoboranes and boron-hydride clusters. When the reaction was carried out in THF instead of toluene, **87** was obtained as the major product and could be isolated in 43% yield.

Through elaborate mechanistic studies, the pathways for the formation of the four products observed from the reduction of **294** with excess lithium were determined.[195] The THF adduct of 2,7-di-*t*-butyl-9-H-9-borafluorene (**136**) was demonstrated by Wagner and coworkers to undergo two-electron reduction with lithium, sodium, or potassium to produce the corresponding dianionic species **320**−**322** (Figure 54a).[196] The sodium salt **321** reacts with **136** to form a dimeric dianion (**323**), which could be further reduced with excess sodium to regenerate **321** (Figure 54b). The dimeric dianion was also shown to undergo hydride transfer with **136** to produce the monoanionic species **324** and **325** (Figure 54c). This sequence accounts for the formation of **317** in the lithium reduction of **294**. In contrast, **318**, the triethylsilyl-substituted variant of **317**, was determined to be formed by reaction of dianionic **320** with Et_3SiBr based on an analogous reaction with Et_3SiCl.[196] The lithium and potassium analogues of **324**, **98** and **99**, were demonstrated to react with an additional equivalent of **136** to produce **326** and **327**, which subsequently rearrange slowly at room temperature (or within hours at 55 °C) to produce **319** and **328** (Figure 54d), thus accounting for the formation of **319** upon reduction of **294**.[121] Finally, the formation of dianionic **87** was determined to result from reduction of monoanionic **98** with excess lithium.[195,197]

While the reduction of borafluorenes has been extensively studied with alkali metals, Piers and coworkers demonstrated that perfluorinated 9-phenyl-9-borafluorene (**50**) is capable of undergoing reduction with decamethylcobaltocene in dichloromethane to produce the tetracoordinate chloroborate anion **329** with a decamethylcobaltocenium countercation (Figure 55).[123] The reaction was proposed to proceed via formation of a radical anion, that abstracts a chlorine atom from dichloromethane. Attempts to reduce **50** to the aromatic dianion with decamethylcobaltocene were unsuccessful.

Holthausen, Wagner, and coworkers demonstrated that 2,2′-bis(9-borafluorenyl)biphenyl can undergo a one-electron reduction to radical anion **330** upon treatment with lithium naphthalenide (Figure 56).[198] Anion **330** contains an unconventional two-center one-electron σ bond between the two boron centers as evidenced by X-ray crystallography, EPR spectroscopy, and computational studies. A similar radical anion was synthesized via two-electron reduction of geminal bis(9-borafluorenyl)alkane **331** with lithium metal (Figure 57a) followed by comproportionation of **331** with the resulting dianion **332** (Figure 57b).[199] Compound **331** could be reduced with lithium triethylborohydride to produce the hydrido-bridged anion **333**, which is also accessible via protonation of **332** with triflic acid (Figure 57a). Conversion of **333** to **332** is possible via deprotonation with tris(trimethylsilyl)-methyllithium, albeit in a low yield.[197]

In addition to the anionic species that have been synthesized by reduction of 9-borafluorenes, isolable examples of neutral borafluorene radicals were recently reported by Gilliard and coworkers.[153] These species were synthesized via reduction of NHC and CAAC adducts of 9-bromo-9-borafluorene with KC_8 and exhibit remarkable stability both in solution and in the solid state (Figure 58). Spin density calculations reveal delocalization of the unpaired electron extends significantly to the carbene ligand in the CAAC-stabilized species whereas in the NHC-stabilized species, the unpaired electron resides primarily on the 9-borafluorene scaffold due to the superior π-accepting ability of the CAAC.[200−203]

4.5. Exocyclic Reactivity at Boron

In 1985, Narula and Nöth reported the syntheses of pyridine- and acridine-stabilized 9-borafluorenium cations (**335** and **336**, Figure 59).[122] The pyridine adduct of 9-chloro-9-borafluorene undergoes chloride abstraction upon reaction with gallium trichloride to produce a pyridine-stabilized 9-borafluorenium

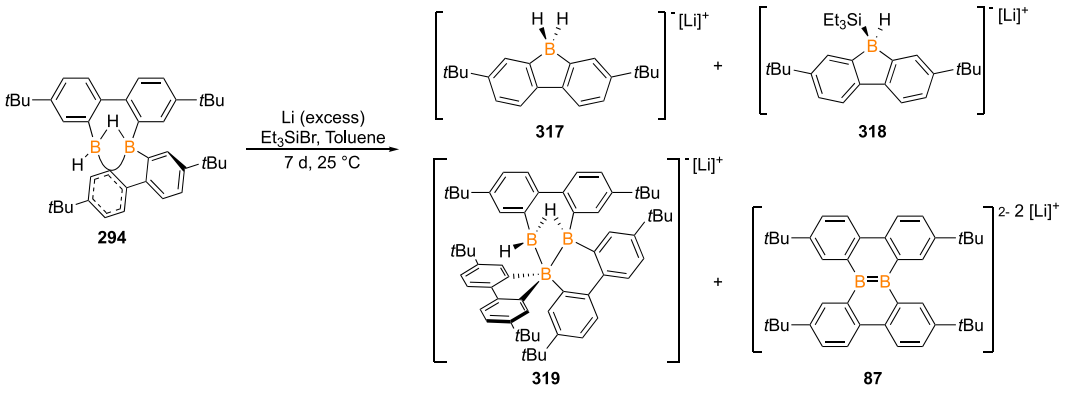

Figure 53. Reduction of **294** with lithium metal.

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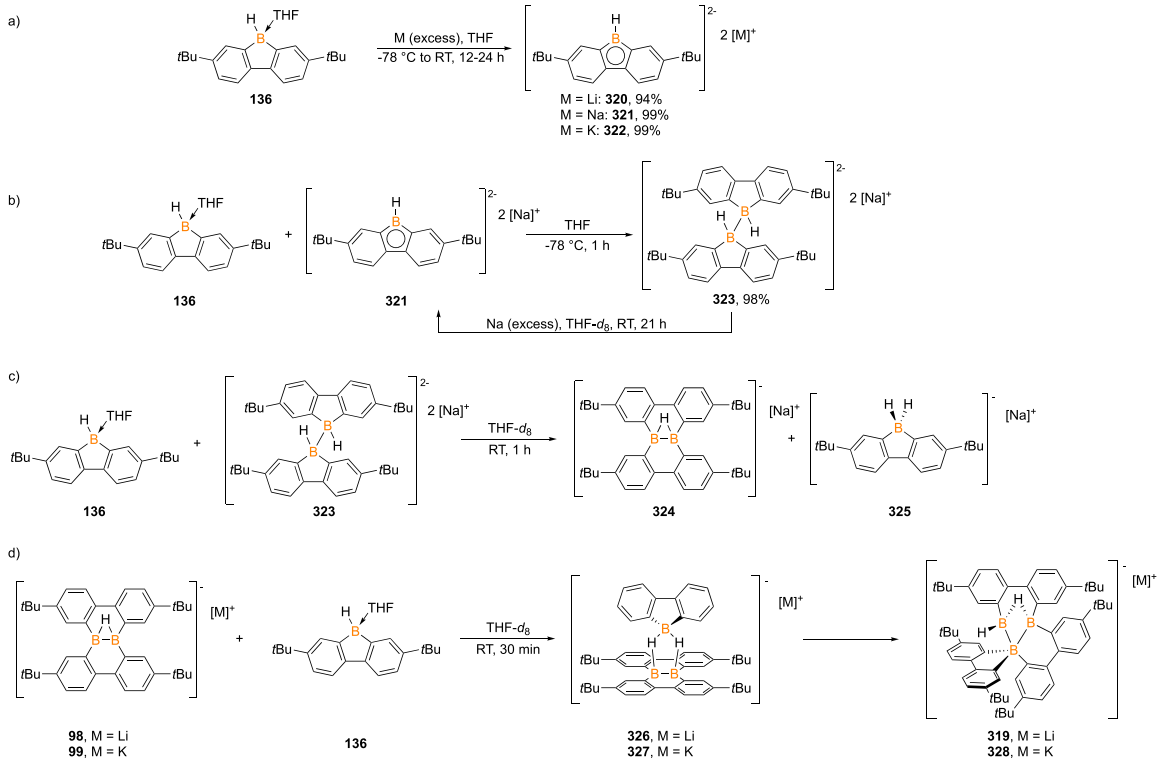

Figure 54. (a) Reduction of **136** to dianion **320**−**322**. (b) Subsequent reactivity of reduced species. (c) Reaction of **323** with the THF adduct **136**. (d) Reaction of **98**/**99** with **136** and subsequent rearrangement.

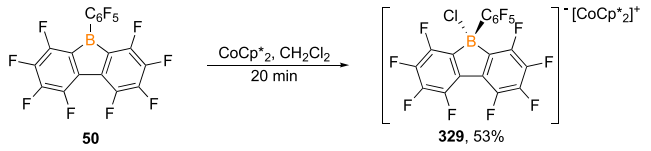

Figure 55. Reduction of perfluorinated 9-phenyl-9-borafluorene with decamethylcobaltocene in dichloromethane.

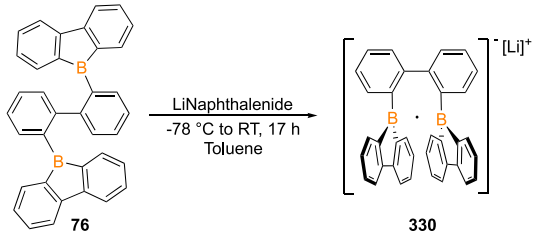

Figure 56. Reduction of 2,2′-bis(9-borafluorenyl)biphenyl with lithium naphthalenide.

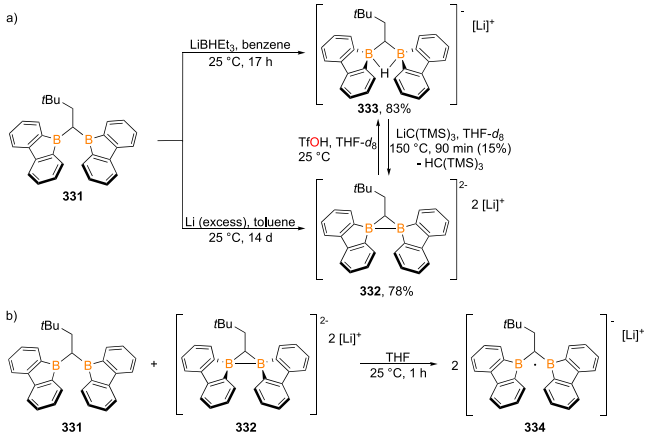

Figure 57. Reduction chemistry of geminal bis(9-borafluorenyl)alkane **331**. The synthesis of **332** from **331** could also be carried out over 7 d in toluene with only a slight decrease in yield or in THF with complete consumption (but lower selectivity) within hours.

cation with a tetrachlorogallate counteranion (**335**, Figure 59a). Similarly, the reaction of the acridine adduct of 9-chloro-9-borafluorene with aluminum trichloride produced the acridine-stabilized 9-borafluorenium cation with a tetrachloroaluminate counteranion. This product was stated to be the major product and characterized by X-ray crystallography. However, 9-chloro-9-borafluorene and acridine-$AlCl_3$ were also observed as minor products. The observation of 9-borafluorenium Lewis base adducts contradicts a 1966 computational study by Armstrong and Perkins, which predicted a stable 9-borafluorenium cation with a dicoordinate boron center.[204] More recently, Wilson, Gilliard, and coworkers reported the synthesis of a set of carbene-stabilized 9-borafluorenium cations from 9-bromo-9-borafluorenes (Figure 59b).[101] The Lewis acid−base adducts of 9-bromo-9-borafluorene and its 3-methoxy substituted variant with NHC and CAAC ligands underwent bromide abstraction with silver hexafluoroantimonate to produce carbene-stabilized 9-borafluorenium hexafluoroantimonate salts **206**, **335**, **337**, and **338** in high yields.

In 2004, Hong and Chung demonstrated that the reaction of 9-chloro-9-borafluorene with sodium hydride in the presence of ethylene produces 9-ethyl-9-borafluorene (**9**, Figure 60a), presumably proceeding through 9-H-9-borafluorene as an intermediate.[182] Holthausen, Wagner, and coworkers later demonstrated that 9-H-9-borafluorene and its dimethyl sulfide adduct can act as hydroboration reagents for *t*-butylacetylene to

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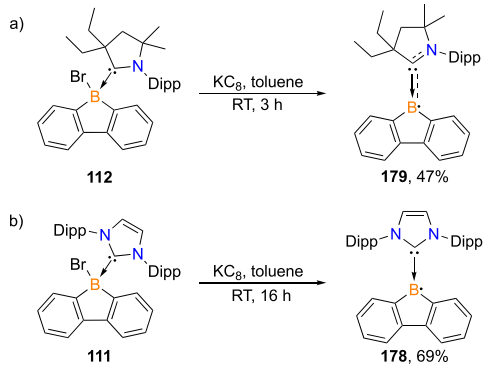

Figure 58. Synthesis of neutral 9-borafluorene radicals via reduction of 9-Br-9-borafluorene-carbene adducts.

produce the single and double hydroboration products **339** and **331**, depending on stoichiometry (Figure 60b).[109,110] The dimethyl sulfide adduct is a convenient reagent as it is not susceptible to ring opening oligomerization.[109] Renaud and coworkers expanded upon the hydroboration reactivity of 9-H-9-borafluorene, demonstrating that the hydroboration products resulting from reactions of 9-H-9-borafluorene can be further functionalized by deborylation with radical sources.[205] In this study, a series of 9-H-9-borafluorene/olefin hydroboration products were generated as intermediates which subsequently underwent radical sulfurization, oxidation, chlorination, or allylation, resulting in the net conversion of olefins to sulfides, alcohols, alkyl chlorides, or allyl-substituted alkanes, respectively (selected examples shown in Figure 60c and d). The 2,7-di-*t*-butyl substituted variant of 9-H-9-borafluorene was recently demonstrated by Pammer and coworkers to act as a hydroboration reagent.[206] In this study, hydroboration of a 2-(*o*-styryl)pyridine derivative resulted in the formation of the intramolecular pyridine-borafluorene adduct **345** (Figure 60e).

Modification of the boron-bound substituent in 9-borafluorenes has been employed as a method for synthesizing heterocycles containing tetracoordinate boron atoms. Several of such compounds were synthesized from 9-bromo-9-borafluorene in 2009 by Yamaguchi and coworkers.[207] The Lewis adducts of 9-Br-9-borafluorene with di(2-pyridyl)-acetylene and di(2-thiazolyl)acetylene were shown to undergo alkyne hydration and subsequent ring closing upon treatment with water to form compounds **348** and **352** featuring BNC_3O heterocyclic rings and compounds **349** and **353** featuring BNC_3 rings in addition to the BNC_3O rings (Figure 61). In 2012, Son and Hoefelmeyer reported the synthesis of an eight-membered $(BC_2N)_2$ ring species (**355**), from 9-methoxy-9-borafluorene.[208] Treatment of 2-picoline with *n*BuLi followed by reaction with 9-methoxy-9-borafluorene produced the 9-(2-picolyl)-9-borafluorene lithium methoxide adduct **354**, that is converted to the 9-(2-picolyl)-9-borafluorene dimer **355** upon methoxide abstraction with boron trifluoride (Figure 62). More recently, Shimizu and Kawachi reported ring closing reactions of 9-aryl-9-borafluorenes bearing alkoxysilyl substituents at the *ortho*-positions of the boron-bound phenyl rings (Figure 63).[105] The alkoxylsilyl groups were shown to undergo C−O bond cleavage upon reaction with potassium fluoride or DABCO to produce the anionic intramolecular 9-borafluorene Lewis base adduct **356**, which features a five-membered BC_2SiO ring. The isopropoxy-containing borafluorene **173** can undergo exchange of the silicon-bound alkoxy group upon treatment with methanol or ethanol, as shown in Figure 12b (Section 2.4.2).

5. COMPOUNDS RELATED TO 9-BORAFLUORENES

9-Borafluorenes are variants of boroles in which the common unsaturated BC_4 ring has two fused benzene rings. The following subsections present a discussion of compounds related to these two families in which at least one aromatic group is fused to the central antiaromatic BC_4 ring. These compounds differ from borafluorenes as they do not exclusively have the $C_6/BC_4/C_6$ fused tricyclic ring system.

5.1. 1-Boraindenes

1-Boraindenes differ from 9-borafluorenes in having only one fused arene group. The first 1-boraindene **358** was generated in 1987 by flash vacuum pyrolysis of dichloro(2-ethylphenyl)-borane (**357**) at 900 °C (Figure 64).[209] Flash pyrolysis at 700 °C furnished 1-chloro-1-boraindane (**359**) by HCl elimination. Compound **359** could then be dehydrogenated at 900 °C to generate 1-chloro-1-boraindene (**358**), indicating a sequential

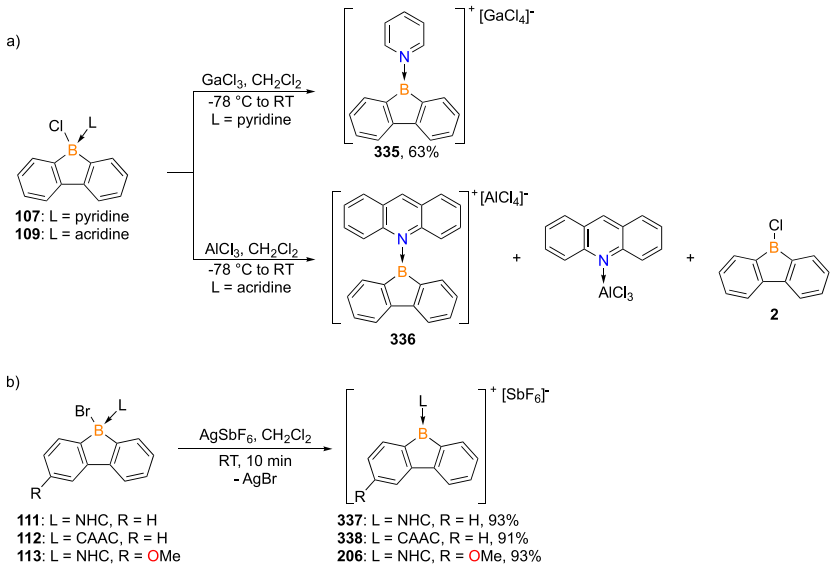

Figure 59. Synthesis of Lewis base-stabilized 9-borafluorenium cations from 9-halo-9-borafluorene adducts.

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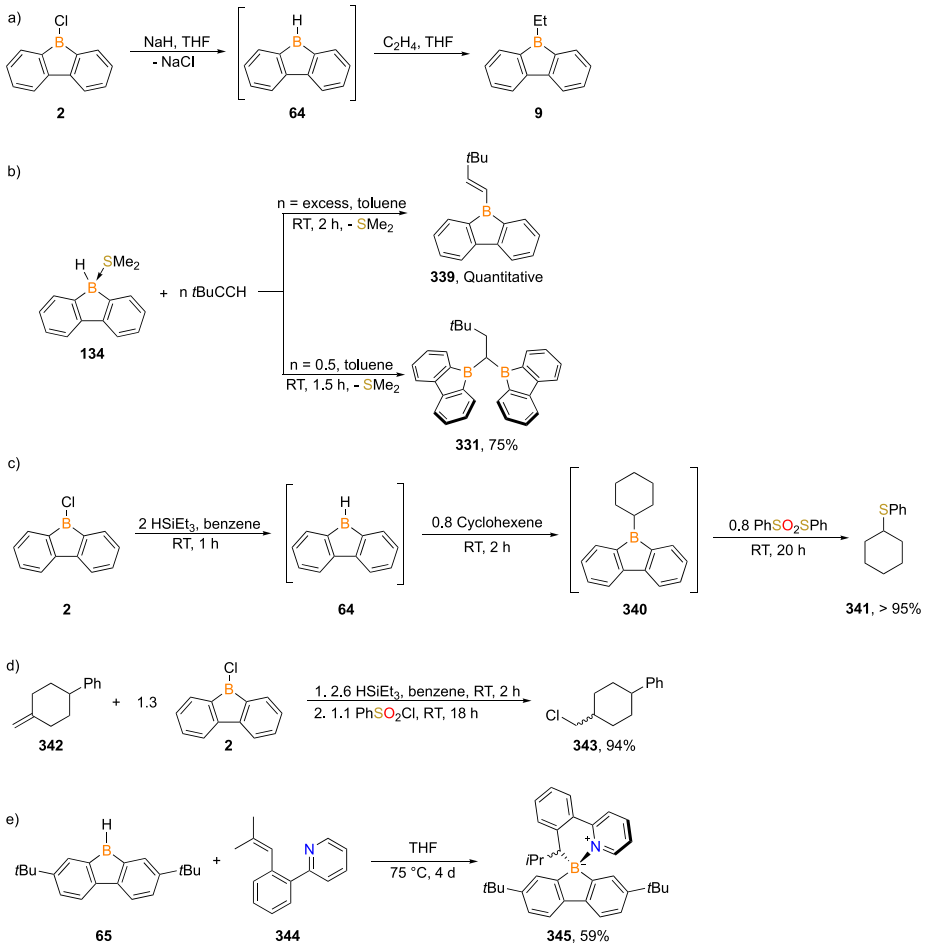

Figure 60. Selected examples of hydroboration reactions involving 9-H-9-borafluorene and its derivatives.

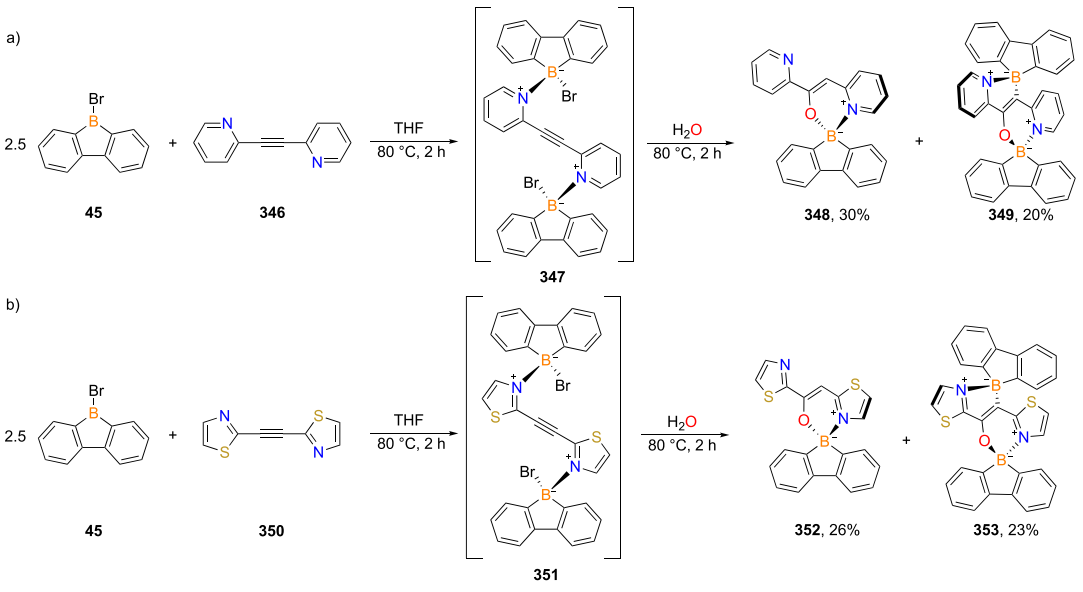

Figure 61. Reactions of 9-bromo-9-borafluorene adducts with water to form heterocycles containing tetracoordinate boron atoms.

process. 1-Boraindene **358** is unstable as a monomer; however, the authors were able to isolate a dimerized product, a fused tetracyclic $C_6/BC_4/BC_6/C_6$ system (**360**), resulting from the insertion of the alkene moiety into the B−C_{alkene} bond of a second molecule of **358**. Trapping reactions provided further evidence for the generation of 1-boraindene **358**. Generating 1-boraindene **358** in the presence of *Z*-2-butene or cyclopentadiene did not furnish insertion products, but generation of **358** in the presence of 2-butyne resulted in the formation of benzoborepin **361** from insertion of the alkyne into the B−C_{alkene} bond. The reaction of **358** with DCl furnished the ring opened product **362** with the chloride bound to boron and the

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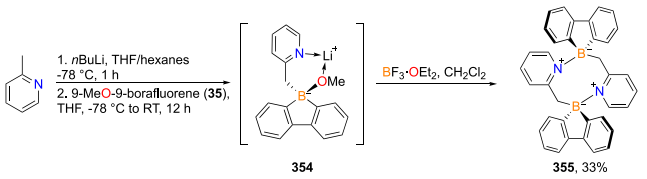

Figure 62. Synthesis of 9-(2-picolyl)-9-borafluorene dimer **355**.

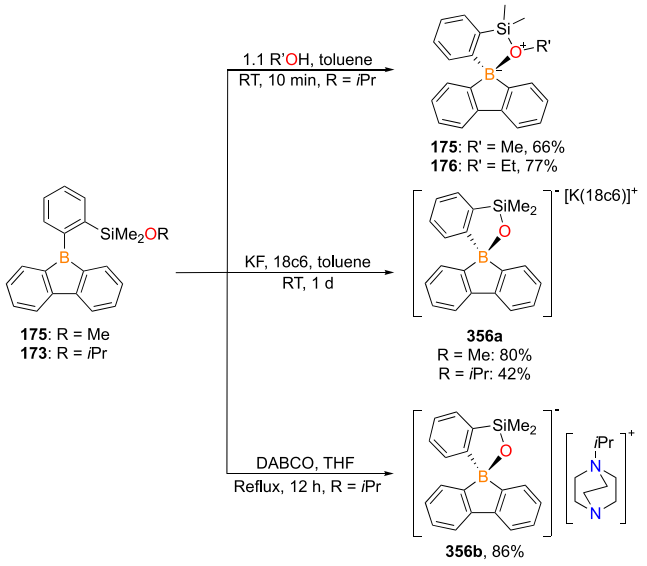

Figure 63. Reactions of 9-aryl-9-borafluorenes bearing alkoxysilyl substituents at the *ortho*-position of a boron-bound phenyl ring. DABCO = 1,4-diazabicyclo[2.2.2]octane.

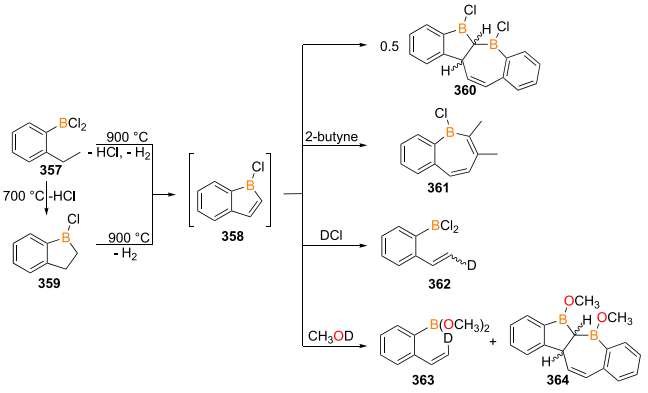

Figure 64. Flash vacuum pyrolysis generation of 1-chloro-1-boraindene **358** and subsequent reactivity.

deuterium to the alkene carbon with a 1:1 mixture of the *E* and *Z* isomers. Reaction of **358** with CH_3OD furnished the ring opened alkene **363** (73%) as the major product as the *Z*-stereoisomer. The methoxy-substituted variant of dimer **360** was produced as the minor product (**364**), which was confirmed independently by reacting **360** with methanol, but the stereochemistry and regiochemistry of the deuterium addition was not specified.

It was not until 27 years later that a 1-boraindene was isolated in the condensed phase by Piers and coworkers (**365**, Figure 65a).[210,211] The synthesis of bromo-boraindene **365** was accomplished via transmetalation of a 1-stannaindene precursor (**366**) with boron tribromide. To access the pentafluorophenyl-substituted species (**367**), reaction with half an equivalent of $Zn(C_6F_5)_2$ introduced a $-C_6F_5$ group at boron. Nucleus independent chemical shift (NICS) calculations at the centroid of the BC_4 ring in **367** confirmed antiaromaticity ([NICS(0)] = 14.3 ppm). A Gutmann–Beckett study indicated that the Lewis acidity of **367** exceeds that of the powerful Lewis acid $B(C_6F_5)_3$ (AN for **367** = 66.5, c.f. for $B(C_6F_5)_3$ = 58.8; in CD_2Cl_2). The strong Lewis acidity enabled access to a unique borane-H-$SiEt_3$ complex **368** at low temperatures. This complex features an interaction of the hydride with boron in the solid state without rupturing the Si–H bond (Figure 65b).[212] The binding of $HSiEt_3$ is reversible at higher temperatures. Addition of bis(triphenylphosphine)iminium chloride, [PPN][Cl], to the silane complex cleaves the Si–H bond to give the hydridoborate (**369**). Adding [PPN][Cl] to the 1-boraindene provided the corresponding chloroborate (**370**) but attempts to generate hydride **369** via reaction of **370** with $HSiEt_3$ were unsuccessful, indicating that the borane-H-$SiEt_3$ complex is required to access hydridoborate **369**. The significance of the borane-H-$SiEt_3$ complex is that this species had only been observed as an intermediate in borane-mediated hydrosilylation reactions,[213] but had not been crystallized or isolated.

H_2 did not react with **367** at room temperature, but at 125 °C, ^{19}F NMR spectroscopy indicated that the ring opened hydrogenation product **371** was generated but was not thermally stable, making hydrogenation at high temperatures impractical (Figure 66).[210] Accessing **371** under milder conditions at room temperature by reaction of **367** with HCl to access the ring opened chloroborane **372**, and subsequent reaction with $Si(CH_3)_2(H)Cl$ resulted in clean formation of boraindene **367** and H_2. This implies that the ring opened "hydrogenated" species **371** eliminates H_2 in a ring closing reverse hydrogenation process. However, hydrogenation product **371** could be trapped with cyclohexene to generate the corresponding hydroboration product **373**. Treatment of **373** with $Si(CH_3)_2(H)Cl$ resulted in elimination of cyclohexane to regenerate 1-boraindene **367**. Catalytic hydrogenation of cyclohexene could be performed, albeit with only ~4–5 turnovers using 10 or 20% catalyst loading at 140 °C in benzene-d_6 under ~5 atm of H_2. Although not practical, this is a unique method for metal-free catalytic olefin hydrogenation and could provide important insight for other systems.

5.2. Ladder Borole Compounds

Regarding structures featuring more than one fused borole ring, Piers and coworkers prepared a ladder diborole via photoisomerization of bis-benzocycloborabutylidene **374** at 254 nm (Figure 67).[214] Theoretical calculations support a pathway in which the B–C bonds of the fused aryl groups are cleaved to from a radical intermediate (**375**) and an intramolecular radical coupling occurs to furnish the ladder product **376**, a process which was calculated to be exergonic by 177 kJ/mol. The bis(benzoborole) unsaturated framework is planar, and NICS calculations indicate that the BC_4 rings are antiaromatic [NICS(0) = 14.9, NICS(1) = 6.3, and $NICS(1)_{zz}$ = 21.8] while the fused benzene rings are aromatic [NICS(0) = −3.2, NICS(1) = −6.2].[215]

Cyclic voltammetry on **376** reveals a reversible reduction at −1.51 V vs $Fc^{+/0}$ and a second irreversible reduction at −2.42 V.[216] Reaction with one equivalent of potassium graphite or decamethylcobaltocene generated the radical anion, featuring potassium and decamethylcobaltocenium counterions, respectively (**377** and **378**, Figure 68). The latter reaction enabled the isolation and crystallization of the radical anion **378** which

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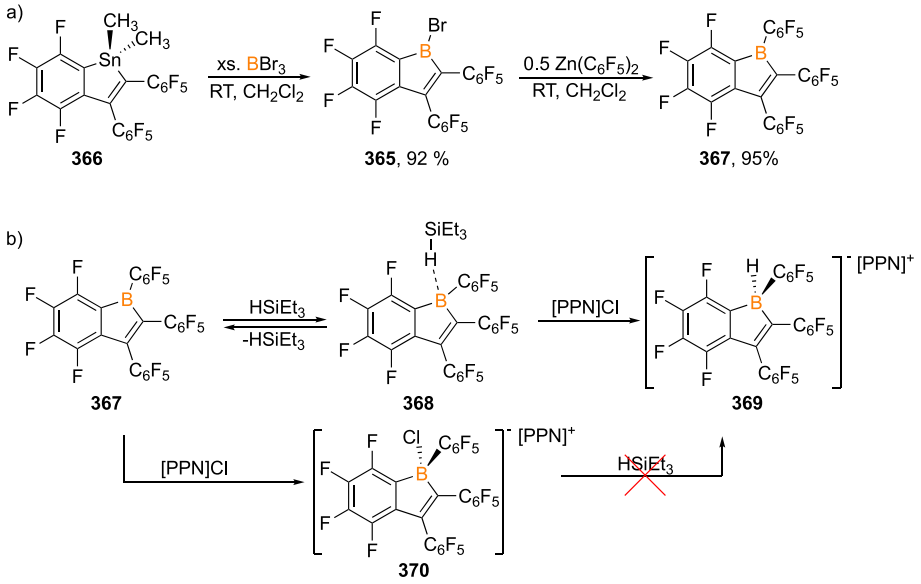

Figure 65. (a) Synthesis of stable 1-boraindenes under ambient conditions. (b) Chemistry of borane-silane complex **368** (PPN = bis(triphenylphosphine)iminium).

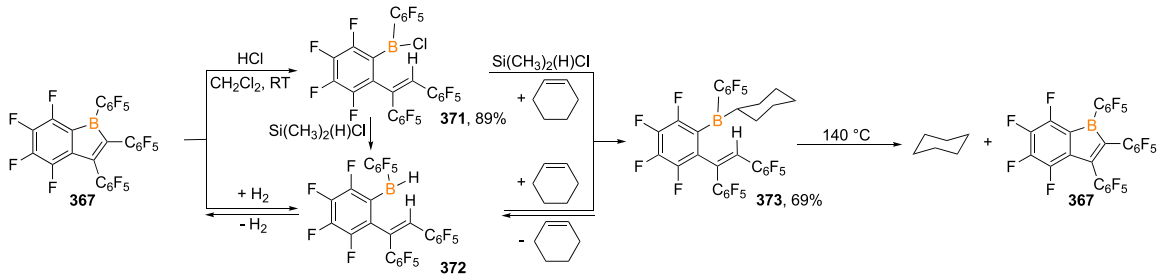

Figure 66. Hydrogenation and hydrochlorination of 1-boraindene **367** with subsequent delivery of hydrogen to cyclohexene.

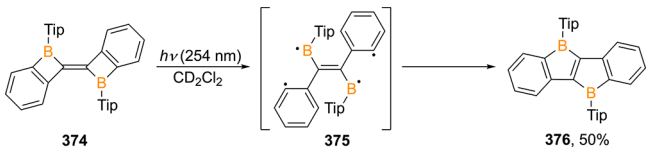

Figure 67. Photochemical isomerization to access ladder diborole **376**.

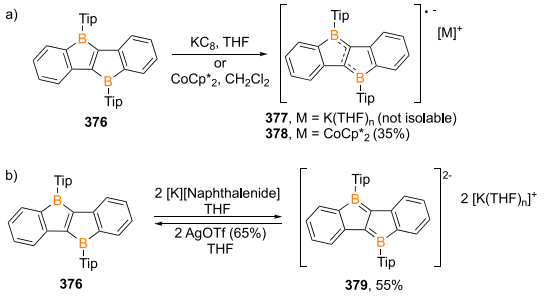

Figure 68. Redox chemistry of **376**.

retains planarity in the polycyclic system. This species is unstable but could be characterized by electron paramagnetic resonance (EPR) spectroscopy with a resonance in the range for organic π-radicals at g_{iso} = 2.00248, although hyperfine coupling was not resolved. Calculations indicate that the singly occupied molecular orbital (SOMO) is delocalized on the polycyclic framework with the largest contributions on the boron containing rings.

Reduction of **376** with two equivalents of potassium naphthalenide furnished the dianion, which has a notable upfield ^{11}B shift from the neutral starting material (**379** δ = 38.7 ppm c.f. **376** δ = 68.6 ppm). The potassium cations are positioned above and below the diboratapentalene framework in the X-ray diffraction structure. Interestingly, NICS calculations on **379** indicate that the BC_4 rings are antiaromatic [NICS(0) = 6.1, NICS(1) = 1.3], while the fused benzene rings have slight aromatic character [NICS(0) = −0.9, NICS(1) = −3.9]. Neutral **376** can be accessed by the oxidation of **379** with two equivalents of silver triflate.

The dianionic variant of **374** (**380**) isomerized to **379** using excess *tert*-butanol as a proton source (Figure 69a).[216] The reaction also proceeded using a catalytic amount (20%) of 2,6-dimethylphenol but generated the doubly protonated species **381** in which the hydrogen atoms are bound to the two carbons at the ring junction when two equivalents of 2,6-dimethylphenol were used (Figure 69b). Exclusive formation of the *syn* diastereomer was observed which was calculated to be thermodynamically more stable than the *anti* diastereomer by 73.6 kJ/mol. Dianion **379** could be regenerated upon deprotonation of **381** with potassium *tert*-butoxide.

The reaction of **379** with CO_2 resulted in the incorporation of a carbon and oxygen atom into the heterocyclic framework to give a boron−oxygen containing analogue of 1,1′-binaphthyl

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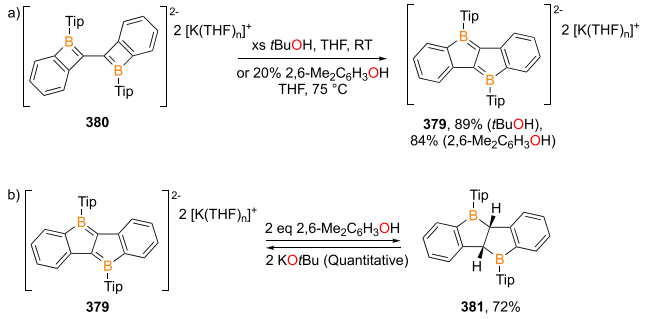

Figure 69. (a) Alcohol promoted isomerization route to **379**. (b) Reaction of **379** with 2,6-dimethylphenol.

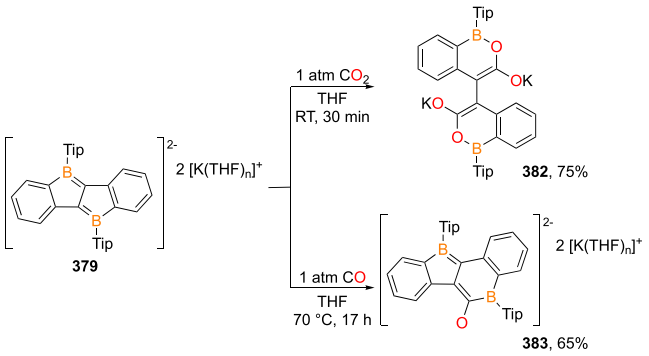

Figure 70. Ring expansion reactions of dianionic ladder diborole **379** with CO_2 and CO.

(**382**, Figure 70).[217] In the solid state, the complex exists as a trimer with units linked via the potassium ions. Reaction of **379** with an atmosphere of CO resulted in the insertion of the CO carbon into one of the B−C_{alkene} bonds to furnish compound **383** containing a BC_5 ring and an exocyclic alkoxide with two potassium countercations. In the solid state, compound **383** adopts a dimeric structure with potassium cations bridging the oxygens.

5.3. Heteroarene Fused Boroles

A thiophene fused borole featuring a bis(9,9-dimethylfluorenyl)amino donor group linked via a π-bridge (**385**) was claimed to be prepared by Kang and Ko via the lithiation of a dibromo precursor followed by reaction with $TipB(OMe)_2$ (Figure 71),[218] a route commonly exploited in borafluorene syntheses (Section 2.2.1). However, the ^{11}B NMR shift was reported at −16.2 ppm, which is in the tetracoordinate region and is not consistent with any other known borole ring systems. It is possible that an adduct of **385** was isolated or a decomposition product. Compound **385** was reported to be air stable due to the bulky triisopropylphenyl group, but this contrasts with a similar compound later prepared by Yamaguchi (**387**, Figure 72).[100]

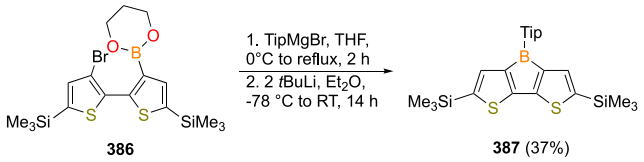

Figure 72. Synthesis of thiophene fused borole **387** by Yamaguchi.

Yamaguchi reported the synthesis, and unambiguous characterization by X-ray diffraction, of a compound that features the same thiophene fused core as **385** but with trimethylsilyl groups on the 5-positions of the fused thiophene rings (**387**, Figure 72).[100] Initial attempts to make **387** by dilithiating a dibromo precursor and reacting with $ArBX_2$ sources, like the method claimed for the synthesis of **385**, were unsuccessful. The successful synthetic route is by reaction of a bromo/boronic ester substituted bithienyl precursor (**386**) with TipMgBr to install the Tip group on boron followed by lithiation to induce ring closure to **387**. Biothiophene fused borole **387** was found to be air and moisture sensitive and featured a ^{11}B NMR resonance at 62.3 ppm, consistent with other unsaturated four π-electron BC_4 ring systems and very different from the reported resonance at −16.2 ppm for **385**.[218]

Recently, He and coworkers attempted the synthesis of thiophene fused boroles featuring phenyl substituents at boron.[125] The THF adduct of a monothiophene fused species (**389**) could be accessed by transmetalation with a stannole precursor and work up in THF (Figure 73). Attempts at transmetalation with $MesBCl_2$ were not successful as a result of lower reactivity of $MesBCl_2$ in comparison to $PhBCl_2$. Reactions with tin-substituted bithiophene precursors (**390** and **391**) generated a 10-membered B_2C_8 ring system with four fused thiophene rings (**392**, **393**, and Figure 73b). Slow addition of pyridine to a solution of **393** induced a rearrangement to a bithiophene fused borole as its pyridine adduct with a bithiophene substituent at boron (**394**, Figure 73c). Collectively, the reports by Yamaguchi and He indicate that specific routes and substitution are required to access such bithiophene fused systems.[100,125] Attempts to prepare diselenophene-containing variants via the corresponding tin reagents resulted in complex mixtures.[125]

Benzothiophene fused boroles **396** and **398** (Figure 74) could be accessed via domino-type intramolecular double cyclizations of dimeric precursors **395** and **397** by lithiation with *t*BuLi and subsequent addition of elemental sulfur.[100] Both were air and

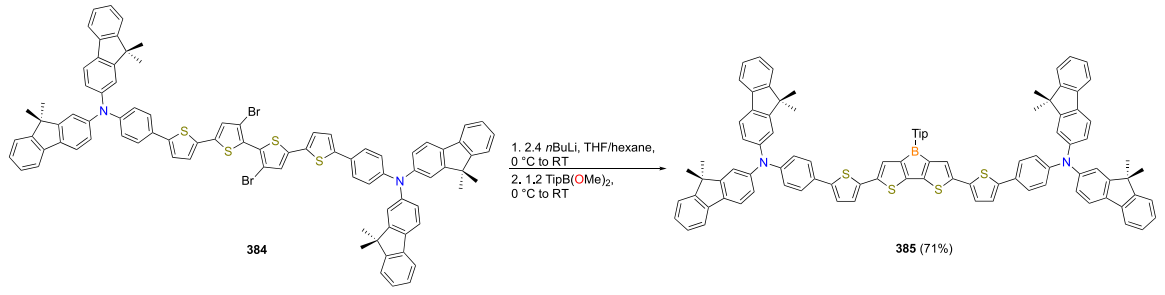

Figure 71. Claimed synthesis of thiophene fused borole **385**.

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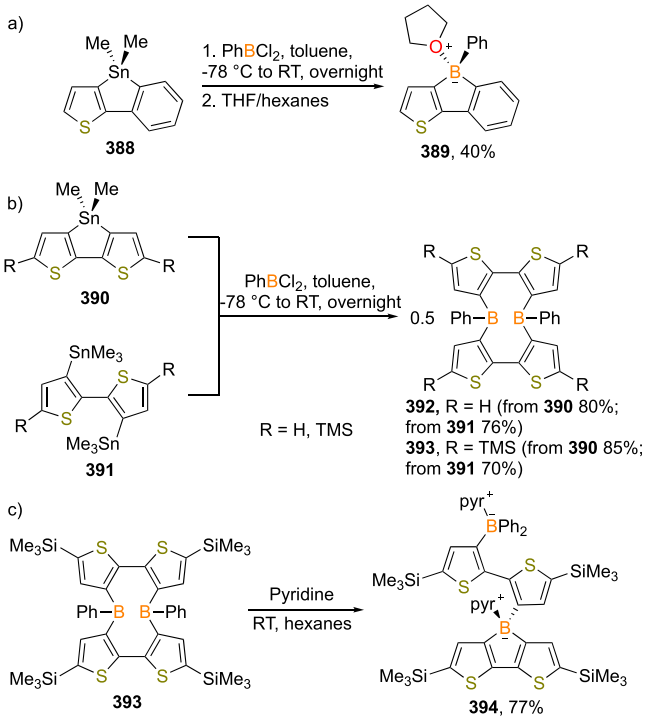

Figure 73. (a) Synthesis of **389**. (b) Attempted preparation of bithiophene fused boroles. (c) Reaction of **393** with pyridine.

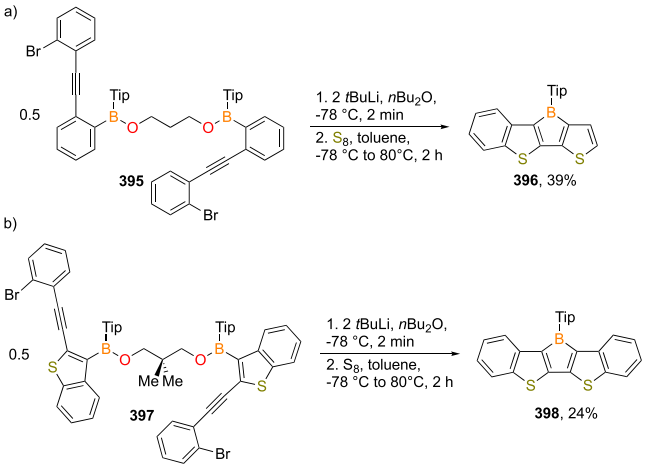

Figure 74. Synthesis of benzothiophene fused boroles (a) **396** and (b) **398**.

moisture sensitive, in contrast to the B-Tip substituted 9-borafluorene (**40**), which can be purified by column chromatography on silica gel in the open atmosphere.[81,88]

Boroles featuring one fused benzoheteroarene, one fused benzene, and mesityl groups on boron were prepared with *N*-methylpyrrole, furan, and thiophene as heteroarenes via a route analogous with that used to access **387** (**402**−**404**, Figure 75).[78] A boronic ester and bromo-substituted precursor was reacted with MesMgBr to introduce the mesityl group. Subsequent treatment with *t*BuLi enabled the ring closure to the boracyclic core. The reactions proceeded cleanly, and the low isolated yields (19−56%) are attributed to the high solubilities of the products hampering crystallizations.

NICS calculations indicate that the BC_4 rings are substantially antiaromatic based on NICS(1)$_{zz}$ values with the following

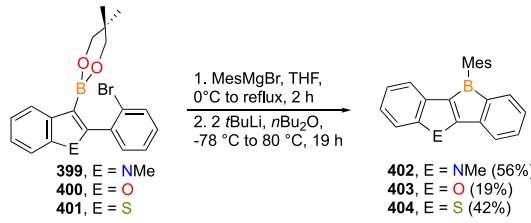

Figure 75. Synthesis of heteroarene/benzo fused boroles **402**−**404**.

Table 14. Properties of Heteroarene Fused Boroles in CH_2Cl_2[78,100,219,220]

		UV/vis		electrochemistry	
compound	NICS(1)$_{zz}$ (ppm)	λ_{max} (nm)	log ε	$E_{1/2}$ (V)	E_{pc} (V)
40	24.5	420	2.33	−2.11	−3.05
387	40.3	552	3.05	−1.98	−2.79
396	30.2	467	2.93	−1.96	−2.89
398	45.3	600	3.04	−1.72	−2.61
402	31.7	479	3.09	−2.25	−3.04
403	27.6	468	3.06	−1.97	−2.85
404	30.4	474	3.05	−1.89	−2.78
408	21.2	375	2.95	−1.94[b]	−2.90[b]
409	16.4	400	NR[a]	−1.23	−2.17/−2.31
411	−1.9	399	4.07	−2.95[c]	−3.12

[a]Note: NR = not reported. [b]CVs measured in THF. [c]Not reversible.

order: **398**> **387** > **402** > **404** > **396** > **403** (Table 14).[78,100] In fact, all values exceed those for both the B-Tip substituted 9-borafluorene [**40**, NICS(1)$_{zz}$ = 24.5 ppm] and most exceed that of the B-Tip substituted borole with hydrogens on the carbon atoms [NICS(1)$_{zz}$ = 29.4 ppm] which is surprising given that increasing conjugation generally diminishes the antiaromaticity in borafluorenes versus boroles.[100] The NICS values for **387**, **396**, and **398** are correlated to the experimental chemical shifts of the methine protons on the *ortho*-isopropyl groups that are positioned over the borole ring. In compounds **402**−**404**, a correlation between the computed LUMO energy and the NICS(1)$_{zz}$ values is observed.[78] The λ_{max} values for all compounds were correlated using TD-DFT calculations with energies that corresponded to HOMO−LUMO transitions which are all red-shifted from **40** and feature larger extinction coefficients. Despite **40** being fluorescent (522 nm, quantum yield = 48%),[100] none of the heteroarene fused species were emissive.[78] The cyclic voltammograms of the heteroarene fused boroles each had a first reversible reduction (range −2.25 to −1.72 V) and a second irreversible reduction (range −3.04 to −2.61 V) which were similar to **40** (−2.11 and −3.05 V).[78,100] A Gutmann−Beckett study revealed a $\Delta\delta$ of 3.6 and 4.2 ppm for **403** and **404**, respectively, while **402** had a negligible shift, indicating weak Lewis acidity resulting from the electron-donating ability of the nitrogen in the pyrrole.[78]

Finze, Marder, and coworkers synthesized two phenylpyridyl fused boroles with the nitrogen in different positions (**407** and **408**, Figure 76) by dilithiation of the corresponding dibromo precursors (**405** and **406**) and in situ reaction with TipB(OMe)$_2$. Compound **407** exists as a tetramer in the solid-state and in a benzene-d_6 solution assembled through coordination of the pyridine nitrogen to the boron in another unit. The structure of **408** is a dimer in the solid-state but a monomer in $CDCl_3$ solution.[219] A stepwise route to **407** was also investigated, using B(OMe)$_3$ as the boron source but in this case the pyridine ring

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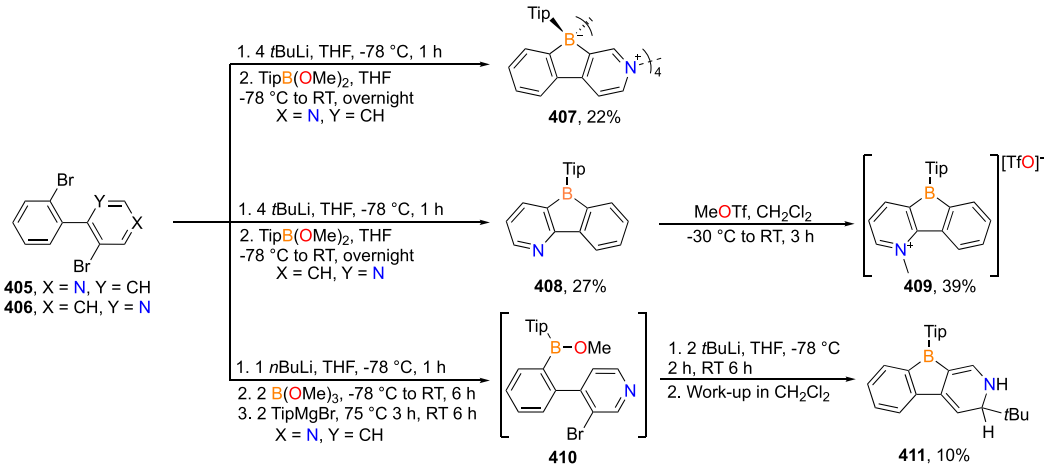

Figure 76. Synthesis of phenylpyridyl fused borole variants.

was dearomatized into a dihydropyridine with a *t*Bu group adjacent to nitrogen and a hydrogen the nitrogen (**411**). The nitrogen of **408** could be alkylated with methyl triflate to generate cationic **409** which has different electronic properties than its neutral precursor.[220] For example, THF reversibly coordinates to **409**, suggesting that the boron center is extremely electron deficient as this does not occur with neutral 9-Tip-9-borafluorenes (**40**, **41**, **43**, and **47**).[88]

Fluorescence studies indicate that **407** has a short emission lifetime in both THF and hexane due to the tetrameric nature. Dual fluorescence was observed for **408** in a variety of solvents (hexane, CH_2Cl_2, THF, and MeCN) attributed to the equilibrium between monomeric **408** and the dimer that was corroborated by variable temperature NMR spectroscopy and photophysical studies.[219] An intense emission band at 520 nm was observed for **408** with a higher quantum yield (~0.27 in THF, ~0.21 in MeCN).[81,100] The UV/vis spectrum of methylated cation **409** featured the lowest energy absorption maximum at ~400 nm in CH_2Cl_2, red-shifted by ~25 nm in comparison neutral **408** due to the enhanced electron accepting ability in the molecule.[220] NICS(1)$_{zz}$ values for compounds **408**, **409**, and **411** were computed to be 21.2 ppm, 16.4 ppm and −1.9 ppm, respectively. Based on this, **411** is neither aromatic nor antiaromatic.[220]

5.4. Other Related Species

An anionic biphenylene fused variant of borafluorene (**413**) was prepared by the reaction of Mes_2BF with in situ generated dilithio(bis)diphenylene from lithiation of dibromo(bis)-

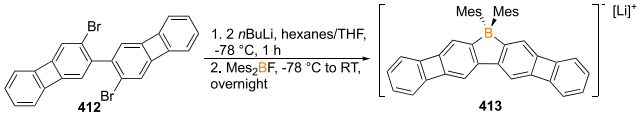

Figure 77. Synthesis of biphenylene fused anionic analogue of 9-borafluorenes (yield was not reported).

diphenylene (**412**) with *n*BuLi (Figure 77).[177] Although the authors claim to prepare a neutral variant with only one mesityl group on boron, no characterization was provided. These species were prepared to confirm their viability as intermediates in an unusual aryl-coupling reaction.

Benzene has 2D aromaticity from the cyclic conjugated π-system that results in enhanced stability. Carboranes are icosahedral $B_{10}C_2$ clusters that exhibit 3D aromaticity and are often compared to their two-dimensional aryl counterparts.[221−224] The preparation of fused bis(*ortho*-carborane) variants of 9-borafluorene could be accomplished by the double deprotonation of 1,1′-bis(*ortho*-carboranes) with potassium bis(trimethylsilyl)amide (KHMDS) followed by treatment with

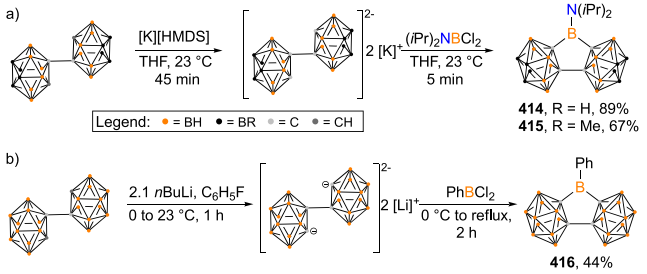

Figure 78. Synthesis of bis(*ortho*-carborane) containing analogues of 9-borafluorenes. (a) Adapted with permission from ref 225. Yruegas, S.; Axtell, J. C.; Kirlikovali, K. O.; Spokoyny, A. M.; Martin, C. D. Synthesis of 9-borafluorene analogues featuring a three-dimensional 1,1′-bis(*o*-carborane) backbone. *Chem. Commun.* **2019**, 55 (20), 2892. Copyright 2019 The Royal Society of Chemistry.

iPr_2NBCl_2 (Figure 78a).[225] The parent 1,1′-bis(*ortho*-carborane) fused species and its octamethylated variant (**414** and **415**, respectively) were accessed in good yields and the compounds compared to the analogous 9-diisopropylamino-9-borafluorene (**57**). Given the rigidity of the cage and hypervalent carbon atoms, the C−C bonds in the BC_4 central ring of **414** and **415** are markedly longer than those in the analogous 9-diisopropylamino-9-borafluorene (**57**), but **414** and **415** have shortened B−N bond lengths. Cyclic voltammetry studies revealed irreversible reductions at −2.09 V vs $Fc^{+/0}$ for the parent species (**414**) and −1.89 V for the octamethylated species (**415**) which are easier to reduce than 9-diisopropylamino-9-borafluorene (−2.95 V vs $Fc^{+/0}$). The absorption maxima at 232 nm (**414**) and 233 nm (**415**) are blueshifted from the analogous borafluorene (248 nm). Welch, Benton, and coworkers accessed a variant of **414** that features a phenyl group on boron by using *n*BuLi as a base and $PhBCl_2$ as the boron source (**416**, Figure 78b).[226] Gutmann−Beckett studies indicate that the Lewis acidity is enhanced by the carborane scaffold with acceptor numbers of 15.3 (**414**) and 20.3 (**415**), which exceed

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that of 9-diisopropylamino-9-borafluorene (AN = 13.5).[225] The acceptor number is much higher for phenyl substituted **416** with a value of 86.4 that is attributed to the lack of N−B π-donation.[226]

6. CONCLUSION

Over half a century has elapsed since 9-borafluorene research began. Since its inception, the field has advanced significantly with the majority of progress in their chemistry disseminated in the past two decades. Many synthetic methods have been developed to access a wide range of 9-borafluorenes and their Lewis adducts, including ring closures, transmetalation, and late stage functionalization to diversify 9-borafluorenes. The Lewis acidity at boron and the antiaromatic state of the central BC_4 ring result in unusual reactivity that can be taken advantage of for the synthesis of other boron compounds via ring opening, ring expansion, oligomerization, reduction, and metal complexation. The fused tricyclic network engenders unique photophysical properties, leading to promising preliminary studies as components in solar cells, molecular and ion sensors, NLO switches, and catalyst initiators.

Despite the numerous advances in 9-borafluorene chemistry in recent decades, many hurdles still exist for the implementation of 9-borafluorenes in applications, and there are notable synthetic challenges. 9-Borafluorenes can be prepared in as little as two steps from commercially available reagents; however, many species require longer routes, and several effective methods involve hazardous organotin and organomercury intermediates. Although alternate synthetic routes have been developed, many of which are scalable and high-yielding, further development could facilitate implementation of these species in electronic materials. The high Lewis acidity in many 9-borafluorenes prevents manipulations in coordinating solvents, but this can be circumvented by installing sterically bulky substituents at boron. Although the electronic and photophysical properties of 9-borafluorenes have been investigated, incorporation of 9-borafluorenes into devices such as sensors and solar cell components has not yet occurred. A major obstacle in this area is their sensitivity toward air; this can also potentially be mitigated by increasing steric protection at boron.

The recent growth of boron heterocycle and 9-borafluorene research signifies a great trajectory for the field. The advances in 9-borafluorene research have stimulated investigations into related species that contain aromatic groups fused to boroles. To date, benzene, borole, thiophene, furan, pyrrole, and carborane fused variants have been accessed, but there is a vast synthetic space that has yet to be explored in the realm of borole-containing PAH analogues. It is known that increasing conjugation and installing certain functional groups or heterocycles can enhance electronic properties; hence, the studies outlined on 9-borafluorenes can be parlayed to optimize systems. As a whole, the future of 9-borafluorene chemistry is bright, and the prospect of their development into widely used reagents and usage in devices is realistic.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemrev.0c01068.

Electrochemical and photophysical data (PDF)

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Notes

The authors declare no competing financial interest.

Biographies

Xiaojun Su received his B.S. degree in Statistics from China University of Geosciences in 2011. He then obtained his M.S. degree in Chemistry from the Beijing Institute of Technology under the supervision of Zhiming Zhou in 2013. He completed his Ph.D. degree from Tsinghua University under the supervision of Jinpei Cheng and Mingtian Zhang in 2016. Following a 2.5 year postdoctoral position at the University of Mississippi with Jonah Jurss, he joined the group of Caleb Martin at Baylor University as a postdoctoral researcher in 2019. His current research is focused on the development of efficient synthetic routes to boron-containing heterocycles.

Tyler A. Bartholome is from Lake Jackson, Texas, and obtained his B.S. degree in chemical engineering from Texas A&M University in 2018. In the same year, he joined the research group of Caleb Martin at Baylor University as a Ph.D. student in inorganic chemistry. His research is focused primarily on the chemistry of fused polycyclic boron heterocycles, including 9-borafluorenes and 9-borataphenanthrenes.

John R. Tidwell received his B.S. degree in Chemistry from Cameron University in 2018 after growing up in Duncan, Oklahoma. During his B.S. he worked on X-ray crystallography under the supervision of Clinton Bryan. Following his B.S., he enrolled in the Ph.D. program at Baylor University, where he is currently working on exploring the coordination chemistry and reactivity of main group elements under the tutelage of Caleb Martin.

Alba Pujol graduated with a B.S. degree from Universitat Rovira i Virgili (Spain) in 2013, working under the supervision of Elena Fernandez on the study of catalytic addition of diborated reagents into β-lactone substrates. She then moved to Durham (UK) where she received her

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Ph.D. in 2017, working under the supervision of Andy Whiting at Durham University on the development of novel catalytic asymmetric diborylation methodologies. In 2017, Alba joined Caleb Martin's group as a postdoctoral research associate at Baylor University working on the synthesis and reactivity of borole compounds. Alba is currently working as a research chemist on the development of novel drugs for targeted photoeradication of cancerous and precancerous cells at LightOx Ltd (UK).

Sam Yruegas was born and raised in Laredo, Texas. She obtained a B.S. in Chemistry at Texas A&M University in 2014 where she worked on carborane clusters with Oleg Ozerov. Upon completion of her undergraduate studies, she completed a Ph.D. in 2019 at Baylor University conducting research with Caleb Martin on boron heterocycle chemistry. She is currently a postdoctoral researcher at Princeton University studying nickel catalysis under the supervision of Paul Chirik.

Jesse J. Martinez was born in 1998 in Freeport, Texas. He obtained a B.S. in Chemistry at Baylor University in 2019. From 2016−2019, he worked on boron heterocycle chemistry with Caleb Martin. He spent the summer of 2019 in the NSF REU program at Texas A&M University in Michael Nippe's laboratory studying the binding of boron ligands to lanthanides. He is now in the Ph.D. program at the University of Wisconsin−Madison studying inorganic chemistry under the supervision of Shannon Stahl.

Caleb Martin grew up in Waweig, New Brunswick, Canada. He began his studies in chemistry at Mount Allison University, where he obtained his B.Sc. in 2007 working with Glen Briand and Steve Westcott on indium and palladium chemistry, respectively. He completed his Ph.D. on group 16 cations at Western University in 2012 with Paul Ragogna. Upon completion of postdoctoral studies on carbene chemistry at UC Riverside and UCSD with Guy Bertrand, he began his independent career at Baylor University in Waco, TX in the Department of Chemistry and Biochemistry in 2013. His research group's interests are focused on the synthesis, reactivity, and properties of unusual boron species.

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ABBREVIATIONS

Ad, adamantyl
AN, acceptor number
AZADO, 2-azaadamantane-*N*-oxyl
bpy, 2,2′-bipyridine
CAAC, *N*-(2,6-diisopropylphenyl)-4,4-diethyl-2,2-dimethylpyrrolidin-5-ylidene
COD, 1,5-cyclooctadiene
Cp, cyclopentadienyl
Cp*, pentamethylcyclopentadienyl
12-Crown-4 or 12C4, 1,4,7,10-tetraoxacyclododecane
Cy, cyclohexyl
DABCO, 1,4-diazabicyclo[2.2.2]octane
dba, dibenzylideneacetone
DCE, 1,2-dichloroethane
DFT, density functional theory
Dipp, 2,6-diisopropylphenyl
DMAP, 4-dimethylaminopyridine
DMS, dimethyl sulfide
dppe, 1,2-bis(diphenylphosphino)ethane
EPR, electron paramagnetic resonance
Et, ethyl
Et_3PO, triethylphosphine oxide
Fc, ferrocene
HOMO, highest occupied molecular orbital
*i*Pr, isopropyl
IPr, [(HCNDipp)$_2$C:],1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene
$IPrCH_2$, [(HCNDipp)$_2$C═CH_2]
KHMDS, potassium bis(trimethylsilyl)amide
LUMO, lowest unoccupied molecular orbital
Me, methyl
Mes, 2,4,6-trimethylphenyl
Mes^F, 2,4,6-tris(trifluoromethyl)phenyl
Mes*, 2,4,6-tri*tert*-butylphenyl
NaOCP, sodium phosphaethynolate
NBS, *N*-bromosuccinimide
NHC, *N*-heterocyclic carbene
NICS, nucleus independent chemical shift
NLO, nonlinear optical
NMR, nuclear magnetic resonance
OLED, organic light-emitting diode
OSCs, organic solar cells
OTf, trifluoromethanesulfonate
Ph, phenyl
PPE, poly(phenylene ethynylene)
PPN, bis(triphenylphosphine)iminium
proton sponge, 1,8-bis(dimethylamino)naphthalene
pyr, pyridine
SOMO, singly occupied molecular orbital
[*n*Bu$_4$N][F], tetra-*n*-butylammonium fluoride
TBS, *tert*-butyldimethylsilyl
*t*Bu, *tert*-butyl
TDDFT, time-dependent density functional theory
TES, triethylsilyl
THF, tetrahydrofuran
Tip, 2,4,6-triisopropylphenyl
TICT, twisted intramolecular charge transfer
TMS, trimethylsilyl
TMSCl, trimethylsilyl chloride
$TMSN_3$, trimethylsilyl azide
$(TMS)_2N$, bis(trimethylsilyl)amide
β, hyperpolarizability
λ_{max}, maximum absorbance

REFERENCES

(1) Anthony, J. E. Functionalized Acenes and Heteroacenes for Organic Electronics. *Chem. Rev.* **2006**, *106*, 5028−5048.
(2) Zhang, L.; Cao, Y.; Colella, N. S.; Liang, Y.; Brédas, J.-L.; Houk, K. N.; Briseno, A. L. Unconventional, Chemically Stable, and Soluble Two-Dimensional Angular Polycyclic Aromatic Hydrocarbons: From Molecular Design to Device Applications. *Acc. Chem. Res.* **2015**, *48*, 500−509.
(3) Watson, M. D.; Fechtenkötter, A.; Müllen, K. Big is Beautiful-"Aromaticity" Revisited from the Viewpoint of Macromolecular and Supramolecular Benzene Chemistry. *Chem. Rev.* **2001**, *101*, 1267−1300.
(4) Wu, J.; Pisula, W.; Müllen, K. Graphenes as Potential Material for Electronics. *Chem. Rev.* **2007**, *107*, 718−747.
(5) Sun, Z.; Ye, Q.; Chi, C.; Wu, J. Low Band Gap Polycyclic Hydrocarbons: From Closed-Shell Near Infrared Dyes and Semi-

https://dx.doi.org/10.1021/acs.chemrev.0c01068
Chem. Rev. 2021, 121, 4147−4192

conductors to Open-Shell Radicals. *Chem. Soc. Rev.* **2012**, *41*, 7857−7889.
(6) Sergeyev, S.; Pisula, W.; Geerts, Y. H. Discotic Liquid Crystals: A New Generation of Organic Semiconductors. *Chem. Soc. Rev.* **2007**, *36*, 1902−1929.
(7) Li, C.; Liu, M. Y.; Pschirer, N. G.; Baumgarten, M.; Mullen, K. Polyphenylene-Based Materials for Organic Photovoltaics. *Chem. Rev.* **2010**, *110*, 6817−6855.
(8) Entwistle, C. D.; Marder, T. B. Boron Chemistry Lights the Way: Optical Properties of Molecular and Polymeric Systems. *Angew. Chem., Int. Ed.* **2002**, *41*, 2927−2931.
(9) Entwistle, C. D.; Marder, T. B. Applications of Three-Coordinate Organoboron Compounds and Polymers in Optoelectronics. *Chem. Mater.* **2004**, *16*, 4574−4585.
(10) Jäkle, F. Lewis Acidic Organoboron Polymers. *Coord. Chem. Rev.* **2006**, *250*, 1107−1121.
(11) Jákle, F. Advances in the Synthesis of Organoborane Polymers for Optical, Electronic, and Sensory Applications. *Chem. Rev.* **2010**, *110*, 3985−4022.
(12) Escande, A.; Ingleson, M. J. Fused Polycyclic Aromatics Incorporating Boron in the Core: Fundamentals and Applications. *Chem. Commun.* **2015**, *51*, 6257−6274.
(13) Wakamiya, A.; Yamaguchi, S. Designs of Functional π-Electron Materials Based on the Characteristic Features of Boron. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1357−1377.
(14) Ji, L.; Griesbeck, S.; Marder, T. B. Recent Developments in and Perspectives on Three-Coordinate Boron Materials: A Bright Future. *Chem. Sci.* **2017**, *8*, 846−863.
(15) von Grotthuss, E.; John, A.; Kaese, T.; Wagner, M. Doping Polycyclic Aromatics with Boron for Superior Performance in Materials Science and Catalysis. *Asian J. Org. Chem.* **2018**, *7*, 37−53.
(16) Yamaguchi, S.; Wakamiya, A. Boron as a Key Component for New π-Electron Materials. *Pure Appl. Chem.* **2006**, *78*, 1413−1424.
(17) Mellerup, S. K.; Wang, S. N. Boron-Doped Molecules for Optoelectronics. *Trends Chem.* **2019**, *1*, 77−89.
(18) Agnoli, S.; Favaro, M. Doping Graphene with Boron: A Review of Synthesis Methods, Physicochemical Characterization, and Emerging Applications. *J. Mater. Chem. A* **2016**, *4*, 5002−5025.
(19) Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbaï, F. P. Fluoride Ion Complexation and Sensing Using Organoboron Compounds. *Chem. Rev.* **2010**, *110*, 3958−3984.
(20) Davidson, J. M.; French, C. M. The Synthesis and Structure of Aromatic Boron Compounds. *J. Chem. Soc.* **1960**, 191−195.
(21) Köster, R.; Benedikt, G. 9-Borafluorenes. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 323−324.
(22) Feng, L. Y.; Li, R.; Zhai, H. J. Boron-Based Inorganic Heterocyclic Clusters: Electronic Structure, Chemical Bonding, Aromaticity, and Analogy to Hydrocarbons. *Phys. Chem. Chem. Phys.* **2019**, *21*, 20523−20537.
(23) McConnell, C. R.; Liu, S.-Y. Late-Stage Functionalization of BN-Heterocycles. *Chem. Soc. Rev.* **2019**, *48*, 3436−3453.
(24) Su, Y. T.; Kinjo, R. Small Molecule Activation by Boron-Containing Heterocycles. *Chem. Soc. Rev.* **2019**, *48*, 3613−3659.
(25) Hirai, M.; Tanaka, N.; Sakai, M.; Yamaguchi, S. Structurally Constrained Boron-, Nitrogen-, Silicon-, and Phosphorus-Centered Polycyclic π-Conjugated Systems. *Chem. Rev.* **2019**, *119*, 8291−8331.
(26) Wang, B. J.; Groziak, M. P. In *Adv. Heterocycl. Chem.*; Elsevier, 2016; Vol. *118*.
(27) Mereddy, G. R.; Chakradhar, A.; Rutkoski, R. M.; Jonnalagadda, S. C. Benzoboroxoles: Synthesis and Applications in Medicinal Chemistry. *J. Organomet. Chem.* **2018**, *865*, 12−22.
(28) Jun, J. H.; Javed, S.; Ndi, C. N.; Hanson, P. R. In *Synthesis of Heterocycles by Metathesis Reactions*; Springer, 2015.
(29) Su, B.; Kinjo, R. Construction of Boron-Containing Aromatic Heterocycles. *Synthesis* **2017**, *49*, 2985−3034.
(30) Wang, X.-Y.; Wang, J.-Y.; Pei, J. BN Heterosuperbenzenes: Synthesis and Properties. *Chem. - Eur. J.* **2015**, *21*, 3528−3539.
(31) Weber, L.; Bohling, L. The Role of 2,3-Dihydro-1-H-1,3,2-Diazaboroles in Luminescent Molecules. *Coord. Chem. Rev.* **2015**, *284*, 236−275.
(32) Melen, R. L. Applications of Pentafluorophenyl Boron Reagents in the Synthesis of Heterocyclic and Aromatic Compounds. *Chem. Commun.* **2014**, *50*, 1161−1174.
(33) Abbey, E. R.; Liu, S. Y. BN Isosteres of Indole. *Org. Biomol. Chem.* **2013**, *11*, 2060−2069.
(34) Weber, L. Modern 1,3,2-Diazaborole Chemistry - A Metamorphosis from Electrophilic to Nucleophilic Boron. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5595−5609.
(35) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. Recent Advances in Azaborine Chemistry. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074−6092.
(36) Gabbaï, F. P. Incorporation of Boron in the Walls of an "All-Carbon" Cyclophane: A Novel Approach to Lewis Acidic Macrocycles. *Angew. Chem., Int. Ed.* **2012**, *51*, 6316−6318.
(37) Bosdet, M. J. D.; Piers, W. E. B-N as a C-C Substitute in Aromatic Systems. *Can. J. Chem.* **2009**, *87*, 8−29.
(38) Braunschweig, H.; Kupfer, T. Recent Developments in the Chemistry of Antiaromatic Boroles. *Chem. Commun.* **2011**, *47*, 10903−10914.
(39) Marder, T. B. Boron Goes on the Attack. *Science* **2006**, *314*, 69−70.
(40) Kirschner, S.; Uecker, I.; Bolte, M.; Lerner, H.-W.; Wagner, M. How π Extension or Structural Bending Alters the Properties of Boron-Doped Phenylene-Containing Oligoacenes. *Organometallics* **2019**, *38*, 2818−2823.
(41) Mellerup, S. K.; Wang, S. N. Isomerization and Rearrangement of Boriranes: From Chemical Rarities to Functional Materials. *Sci. China Mater.* **2018**, *61*, 1249−1256.
(42) Huang, Z. G.; Wang, S. N.; Dewhurst, R. D.; Ignat'ev, N. V.; Finze, M.; Braunschweig, H. Boron: Its Role in Energy-Related Processes and Applications. *Angew. Chem., Int. Ed.* **2020**, *59*, 8800−8816.
(43) Mellerup, S. K.; Wang, S. N. Boron-Based Stimuli Responsive Materials. *Chem. Soc. Rev.* **2019**, *48*, 3537−3549.
(44) Stepien, M.; Gonka, E.; Żyła, M.; Sprutta, N. Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds: Synthetic Routes, Properties, and Applications. *Chem. Rev.* **2017**, *117*, 3479−3716.
(45) Wang, X. Y.; Lin, H. R.; Lei, T.; Yang, D. C.; Zhuang, F. D.; Wang, J. Y.; Yuan, S. C.; Pei, J. Azaborine Compounds for Organic Field-Effect Transistors: Efficient Synthesis, Remarkable Stability, and BN Dipole Interactions. *Angew. Chem., Int. Ed.* **2013**, *52*, 3117−3120.
(46) Frath, D.; Massue, J.; Ulrich, G.; Ziessel, R. Luminescent Materials: Locking π-Conjugated and Heterocyclic Ligands with Boron(III). *Angew. Chem., Int. Ed.* **2014**, *53*, 2290−2310.
(47) Krantz, K. E.; Weisflog, S. L.; Frey, N. C.; Yang, W. L.; Dickie, D. A.; Webster, C. E.; Gilliard, R. J., Jr. Planar, Stair-Stepped, and Twisted: Modulating Structure and Photophysics in Pyrene- and Benzene-Fused N-Heterocyclic Boranes. *Chem. - Eur. J.* **2020**, *26*, 10072−10082.
(48) Cappello, D.; Therien, D. A. B.; Staroverov, V. N.; Lagugne-Labarthet, F.; Gilroy, J. B. Optoelectronic, Aggregation, and Redox Properties of Double-Rotor Boron Difluoride Hydrazone Dyes. *Chem. - Eur. J.* **2019**, *25*, 5994−6006.
(49) The following review on arene and heteroarene fused boroles was published after the submission of this manuscript: He, J.; Rauch, F.; Finze, M.; Marder, T. B. (Hetero)arene-Fused Boroles: A Broad Spectrum of Applications. *Chem. Sci.* **2021**, *12*, 128−147.
(50) Barnard, J. H.; Yruegas, S.; Huang, K. X.; Martin, C. D. Ring Expansion Reactions of Anti-Aromatic Boroles: A Promising Synthetic Avenue to Unsaturated Boracycles. *Chem. Commun.* **2016**, *52*, 9985−9991.
(51) Braunschweig, H.; Krummenacher, I.; Wahler, J. Free Boroles: The Effect of Antiaromaticity on Their Physical Properties and Chemical Reactivity. *Adv. Organomet. Chem.* **2013**, *61*, 1−53.
(52) Steffen, A.; Ward, R. M.; Jones, W. D.; Marder, T. B. Dibenzometallacyclopentadienes, Boroles and Selected Transition

https://dx.doi.org/10.1021/acs.chemrev.0c01068
Chem. Rev. 2021, 121, 4147−4192

Metal and Main Group Heterocyclopentadienes: Synthesis, Catalytic and Optical Properties. *Coord. Chem. Rev.* **2010**, *254*, 1950−1976.
(53) Sadimenko, A. P. Organometallic Compounds of Pyrrole, Indole, Carbazole, Phospholes, Siloles, and Boroles. *Adv. Heterocycl. Chem.* **2001**, *79*, 115−157.
(54) Zhang, W. D.; Zhang, B. J.; Yu, D. M.; He, G. Construction of Highly Antiaromatic Boroles. *Sci. Bull.* **2017**, *62*, 899−900.
(55) Karamanis, P.; Otero, N.; Xenides, D.; Denawi, H.; Mandado, M.; Rérat, M. From Pyridine Adduct of Borabenzene to (In)finite Graphene Architectures Functionalized with N - B Dative Bonds. Prototype Systems of Strong One and Two Photon Quantum Transitions Triggering Large Nonlinear Optical Responses. *J. Phys. Chem. C* **2020**, *124*, 21063−21074.
(56) Yuan, K.; Kahan, R.; Si, C.; Williams, A.; Kirschner, S.; Uzelac, M.; Zysman-Colman, E.; Ingleson, M. The Synthesis of Brominated-Boron-Doped PAHs by Alkyne 1,1-Bromoboration: Mechanistic and Functionalisation Studies. *Chem. Sci.* **2020**, *11*, 3258−3267.
(57) Stoycheva, J.; Tadjer, A.; Garavelli, M.; Spassova, M.; Nenov, A.; Romanova, J. Boron-Doped Polycyclic Aromatic Hydrocarbons: A Molecular Set Revealing the Interplay between Topology and Singlet Fission Propensity. *J. Phys. Chem. Lett.* **2020**, *11*, 1390−1396.
(58) Karamanis, P.; Charistos, N. D.; Sigalas, M. P.; Rerat, M. Polyaromatic Systems Combining Increasing Optical Gaps and Amplified Nonlinear Optical Properties. A Comprehensive Theoretical Study on B_3N_3 Doped Nanographenes. *J. Phys. Chem. C* **2019**, *123*, 21135−21149.
(59) Farrell, J. M.; Mützel, C.; Bialas, D.; Rudolf, M.; Menekse, K.; Krause, A.-M.; Stolte, M.; Würthner, F. Tunable Low-LUMO Boron-Doped Polycyclic Aromatic Hydrocarbons by General One-Pot C-H Borylations. *J. Am. Chem. Soc.* **2019**, *141*, 9096−9104.
(60) Kahan, R. J.; Hirunpinyopas, W.; Cid, J.; Ingleson, M. J.; Dryfe, R. A. Well-Defined Boron/Nitrogen-Doped Polycyclic Aromatic Hydrocarbons are Active Electrocatalysts for the Oxygen Reduction Reaction. *Chem. Mater.* **2019**, *31*, 1891−1898.
(61) Yang, D. T.; Nakamura, T.; He, Z. C.; Wang, X.; Wakamiya, A.; Peng, T.; Wang, S. N. Doping Polycyclic Arenes with Nitrogen-Boron-Nitrogen (NBN) Units. *Org. Lett.* **2018**, *20*, 6741−6745.
(62) Kahan, R.; Crossley, D.; Cid, J.; Radcliffe, J.; Woodward, A.; Fasano, V.; Endres, S.; Whitehead, G.; Ingleson, M. Generation of a Series of B N Fused Oligo-Naphthalenes (n= 1 to 3) from a B 1-Polycyclic Aromatic Hydrocarbon. *Chem. Commun.* **2018**, *54*, 9490−9493.
(63) Crossley, D. L.; Kahan, R.; Endres, S.; Warner, A.; Smith, R.; Cid, J.; Dunsford, J.; Jones, J.; Vitorica-Yrezabal, I.; Ingleson, M. J. A Modular Route to Boron Doped PAHs by Combining Borylative Cyclisation and Electrophilic C-H Borylation. *Chem. Sci.* **2017**, *8*, 7969−7977.
(64) Snyder, J. A.; Gruninger, P.; Bettinger, H. F.; Bragg, A. E. BN Doping and the Photochemistry of Polyaromatic Hydrocarbons: Photocyclization of Hexaphenyl Benzene and Hexaphenyl Borazine. *J. Phys. Chem. A* **2017**, *121*, 8359−8367.
(65) Snyder, J. A.; Gruninger, P.; Bettinger, H. F.; Bragg, A. E. Excited-State Deactivation Pathways and the Photocyclization of BN-Doped Polyaromatics. *J. Phys. Chem. A* **2017**, *121*, 5136−5146.
(66) Hertz, V. M.; Ando, N.; Hirai, M.; Bolte, M.; Lerner, H.-W.; Yamaguchi, S.; Wagner, M. Steric Shielding vs Structural Constraint in a Boron-Containing Polycyclic Aromatic Hydrocarbon. *Organometallics* **2017**, *36*, 2512−2519.
(67) Hertz, V. M.; Massoth, J. G.; Bolte, M.; Lerner, H. W.; Wagner, M. En Route to Stimuli-Responsive Boron-, Nitrogen-, and Sulfur-Doped Polycyclic Aromatic Hydrocarbons. *Chem. - Eur. J.* **2016**, *22*, 13181−13188.
(68) Miyamoto, F.; Nakatsuka, S.; Yamada, K.; Nakayama, K.-i.; Hatakeyama, T. Synthesis of Boron-Doped Polycyclic Aromatic Hydrocarbons by Tandem Intramolecular Electrophilic Arene Borylation. *Org. Lett.* **2015**, *17*, 6158−6161.
(69) Hertz, V. M.; Bolte, M.; Lerner, H. W.; Wagner, M. Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores. *Angew. Chem., Int. Ed.* **2015**, *54*, 8800−8804.
(70) Dou, C.; Saito, S.; Matsuo, K.; Hisaki, I.; Yamaguchi, S. A Boron-Containing PAH as a Substructure of Boron-Doped Graphene. *Angew. Chem., Int. Ed.* **2012**, *51*, 12206−12210.
(71) Staykov, A.; Li, X. Q.; Tsuji, Y.; Yoshizawa, K. Current Rectification in Nitrogen- and Boron-Doped Nanographenes and Cyclophanes. *J. Phys. Chem. C* **2012**, *116*, 18451−18459.
(72) Grigsby, W. J.; Power, P. P. Isolation and Reduction of Sterically Encumbered Arylboron Dihalides: Novel Boranediyl Insertion into C-C σ-Bonds. *J. Am. Chem. Soc.* **1996**, *118*, 7981−7988.
(73) Wehmschulte, R. J.; Khan, M. A.; Twamley, B.; Schiemenz, B. Synthesis and Characterization of a Sterically Encumbered Unsymmetrical 9-Borafluorene, Its Pyridine Adduct, and Its Dilithium Salt. *Organometallics* **2001**, *20*, 844−849.
(74) Breunig, J. M.; Lehmann, F.; Bolte, M.; Lerner, H.-W.; Wagner, M. Synthesis and Reactivity of *o*-Phosphane Oxide Substituted Aryl(hydro)borates and Aryl(hydro)boranes. *Organometallics* **2014**, *33*, 3163−3172.
(75) Hübner, A.; Diefenbach, M.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. Confirmation of an Early Postulate: B-C-B Two-Electron-Three-Center Bonding in Organo(hydro)-boranes. *Angew. Chem., Int. Ed.* **2012**, *51*, 12514−12518.
(76) Wehmschulte, R. J.; Diaz, A. A.; Khan, M. A. Unsymmetrical 9-Borafluorenes via Low-Temperature C-H Activation of *m*-Terphenylboranes. *Organometallics* **2003**, *22*, 83−92.
(77) Urban, M.; Durka, K.; Górka, P.; Wiosna-Sałyga, G.; Nawara, K.; Jankowski, P.; Luliński, S. The Effect of Locking π-Conjugation in Organoboron Moieties in the Structures of Luminescent Tetracoordinate Boron Complexes. *Dalton Trans.* **2019**, *48*, 8642−8663.
(78) Iida, A.; Sekioka, A.; Yamaguchi, S. Heteroarene-Fused Boroles: What Governs the Antiaromaticity and Lewis Acidity of the Borole Skeleton? *Chem. Sci.* **2012**, *3*, 1461−1466.
(79) Mike, C. A.; Ferede, R.; Allison, N. T. Evidence for Rhenaphenanthrene Formation and Its Conversion to Fluorenone. *Organometallics* **1988**, *7*, 1457−1459.
(80) Teunissen, H. T.; Hansen, C. B.; Bickelhaupt, F. A Simple One Pot Synthesis of 1-Chlorophospholes. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *118*, 309−312.
(81) Smith, M. F.; Cassidy, S. J.; Adams, I. A.; Vasiliu, M.; Gerlach, D. L.; Dixon, D. A.; Rupar, P. A. Substituent Effects on the Properties of Borafluorenes. *Organometallics* **2016**, *35*, 3182−3191.
(82) Decken, A.; Gabbaie, F. P.; Cowley, A. H. The Benzannelation Approach to Novel Gallium and Indium Heterocycles. *Inorg. Chem.* **1995**, *34*, 3853−3854.
(83) Cava, M. P.; Stucker, J. F. Condensed Cyclobutane Aromatic Systems. 1. The Synthesis of 1,2-Benzobiphenylene and 1,2-Binaphthylene. *J. Am. Chem. Soc.* **1955**, *77*, 6022−6026.
(84) Becker, B.; Corriu, R. J. P.; Henner, B. J. L.; Wojnowski, W.; Peters, K.; Vonschnering, H. G. Contributions to the Chemistry of Silicon Sulfur-Compounds. 42. Bis(1-Methyldibenzosilole)Sulphide - Its Synthesis, Crystal-Structure, and Reaction with Chromium Hexacarbonyl. *J. Organomet. Chem.* **1986**, *312*, 305−311.
(85) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. Regioselective Dimetallation of Aromatics - Easy Access to 2,2′-Disubstituted Biphenyl Derivatives. *J. Organomet. Chem.* **1982**, *228*, 107−118.
(86) Gilman, H.; Langham, W.; Jacoby, A. L. Metalation as a Side Reaction in the Preparation of Organolithium Compounds. *J. Am. Chem. Soc.* **1939**, *61*, 106−109.
(87) Wittig, G.; Herwig, W.; Reiss, W. Zur Synthese des Diphenylens. *Chem. Ber.* **1954**, *87*, 1511−1512.
(88) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. Dibenzoborole-Containing π-Electron Systems: Remarkable Fluorescence Change Based on the "On/Off" Control of the pπ-π* Conjugation. *J. Am. Chem. Soc.* **2002**, *124*, 8816−8817.
(89) Gross, U.; Kaufmann, D. Borylation of Arylsilanes. 3. Reaction of Silylated Biphenyls and 9H-9-Silafluorenes with Tribromoborane. *Chem. Ber.* **1987**, *120*, 991−994.

https://dx.doi.org/10.1021/acs.chemrev.0c01068
Chem. Rev. 2021, 121, 4147−4192

(90) Wakamiya, A.; Mishima, K.; Ekawa, K.; Yamaguchi, S. Kinetically Stabilized Dibenzoborole as an Electron-Accepting Building Unit. *Chem. Commun.* **2008**, 579−581.
(91) Chase, P. A.; Piers, W. E.; Patrick, B. O. New Fluorinated 9-Borafluorene Lewis Acids. *J. Am. Chem. Soc.* **2000**, *122*, 12911−12912.
(92) Romero, P. E.; Piers, W. E.; Decker, S. A.; Chau, D.; Woo, T. K.; Parvez, M. η^1 versus η^5 Bonding Modes in Cp*Al(I) Adducts of 9-Borafluorenes. *Organometallics* **2003**, *22*, 1266−1274.
(93) Tokoro, Y.; Nagai, A.; Tanaka, K.; Chujo, Y. Synthesis of π-Conjugated Polymers Containing Aminoquinoline-Borafluorene Complexes in the Main-Chain. *Macromol. Rapid Commun.* **2012**, *33*, 550−555.
(94) Chung, T.-C. US Patent 6420502, 2002.
(95) Chung, T.-C. US Patent 6515088, 2003.
(96) Biswas, S.; Oppel, I. M.; Bettinger, H. F. Synthesis and Structural Characterization of 9-Azido-9-Borafluorene: Monomer and Cyclotrimer of a Borole Azide. *Inorg. Chem.* **2010**, *49*, 4499−4506.
(97) Müller, M.; Maichle-Mössmer, C.; Bettinger, H. F. BN-Phenanthryne: Cyclotetramerization of an 1,2-Azaborine Derivative. *Angew. Chem., Int. Ed.* **2014**, *53*, 9380−9383.
(98) Adams, I. A.; Rupar, P. A. A Poly(9-Borafluorene) Homopolymer: An Electron-Deficient Polyfluorene with "Turn-On" Fluorescence Sensing of NH_3 Vapor. *Macromol. Rapid Commun.* **2015**, *36*, 1336−1340.
(99) Bonifácio, V. D. B.; Morgado, J.; Scherf, U. Polyfluorenes with On-Chain Dibenzoborole Units—Synthesis and Anion-Induced Photoluminescence Quenching. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2878−2883.
(100) Iida, A.; Yamaguchi, S. Thiophene-Fused Ladder Boroles with High Antiaromaticity. *J. Am. Chem. Soc.* **2011**, *133*, 6952−6955.
(101) Yang, W.; Krantz, K. E.; Freeman, L. A.; Dickie, D. A.; Molino, A.; Kaur, A.; Wilson, D. J. D.; Gilliard, R. J., Jr. Stable Borepinium and Borafluorenium Heterocycles: A Reversible Thermochromic "Switch" Based on Boron-Oxygen Interactions. *Chem. - Eur. J.* **2019**, *25*, 12512−12516.
(102) Narula, C. K.; Nöth, H. Contributions to the Chemistry of Boron. 156. A Convenient Route to 9-Borafluorenes. *J. Organomet. Chem.* **1985**, *281*, 131−134.
(103) Chase, P. A.; Henderson, L. D.; Piers, W. E.; Parvez, M.; Clegg, W.; Elsegood, M. R. J. Bifunctional Perfluoroaryl Boranes: Synthesis and Coordination Chemistry with Neutral Lewis Base Donors. *Organometallics* **2006**, *25*, 349−357.
(104) Fyfe, J. W. B.; Watson, A. J. B. Recent Developments in Organoboron Chemistry: Old Dogs, New Tricks. *Chem.* **2017**, *3*, 31−55.
(105) Shimizu, T.; Kawachi, A. Synthesis, Reactions, and Photophysical Properties of *o*-(Alkoxysilyl)(borafluorenyl)benzenes. *J. Organomet. Chem.* **2020**, *912*, 121179.
(106) Shoji, Y.; Shigeno, N.; Takenouchi, K.; Sugimoto, M.; Fukushima, T. Mechanistic Study of Highly Efficient Direct 1,2-Carboboration of Alkynes with 9-Borafluorenes. *Chem. - Eur. J.* **2018**, *24*, 13223−13230.
(107) Keck, C.; Maichle-Mossmer, C.; Bettinger, H. F. Photo Electron Transfer Induced Desilylation of N,N-Bis(trimethylsilyl)-aminodibenzoborole to Aminodibenzoborole. *Chem. Commun.* **2019**, *55*, 7470−7473.
(108) Noguchi, M.; Suzuki, K.; Kobayashi, J.; Yurino, T.; Tsurugi, H.; Mashima, K.; Yamashita, M. Planar and Bent BN-Embedded *p*-Quinodimethanes Synthesized by Transmetalation of Bis-(trimethylsilyl)-1,4-dihydropyrazines with Chloroborane. *Organometallics* **2018**, *37*, 1833−1836.
(109) Das, A.; Hübner, A.; Weber, M.; Bolte, M.; Lerner, H.-W.; Wagner, M. 9-H-9-Borafluorene Dimethyl Sulfide Adduct: A Product of a Unique Ring-Contraction Reaction and a Useful Hydroboration Reagent. *Chem. Commun.* **2011**, *47*, 11339−11341.
(110) Hübner, A.; Qu, Z.-W.; Englert, U.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. Main-Chain Boron-Containing Oligophenylenes via Ring-Opening Polymerization of 9-H-9-Borafluorene. *J. Am. Chem. Soc.* **2011**, *133*, 4596−4609.
(111) Mannig, D.; Nöth, H.; Prigge, H.; Rotsch, A. R.; Gopinathan, S.; Wilson, J. W. Contribution on Boron Chemistry. 75. The Influence of Steric Factors on the Conformation of Diborylamines. *J. Organomet. Chem.* **1986**, *310*, 1−20.
(112) Breunig, J. M.; Hübner, A.; Bolte, M.; Wagner, M.; Lerner, H.-W. Reactivity of Phosphaboradibenzofulvene toward Hydrogen, Acetonitrile, Benzophenone, and 2,3-Dimethylbutadiene. *Organometallics* **2013**, *32*, 6792−6799.
(113) Berger, C. J.; He, G.; Merten, C.; McDonald, R.; Ferguson, M. J.; Rivard, E. Synthesis and Luminescent Properties of Lewis Base-Appended Borafluorenes. *Inorg. Chem.* **2014**, *53*, 1475−1486.
(114) Nakatsuji, J. Y.; Yamamoto, Y. Synthesis and Structure of Boron Compounds Bearing Tridentate Ligands with 1,3-Bicarbonylbenzene Skeleton. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 767−776.
(115) Bir, G.; Schacht, W.; Kaufmann, D. Eine Allgemeine, Einfache und Schonende Synthesemethode für Fluororganylborane. *J. Organomet. Chem.* **1988**, *340*, 267−271.
(116) Kaufmann, L.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. 9-Ferrocenyl-9-borafluorene—A Redox-Switchable Main Group Lewis Acid. *Organometallics* **2008**, *27*, 6215−6221.
(117) Hübner, A.; Diehl, A. M.; Bolte, M.; Lerner, H.-W.; Wagner, M. High-Temperature Reactivity of the Strongly Electrophilic Pristine 9 H-9-Borafluorene. *Organometallics* **2013**, *32*, 6827−6833.
(118) Hoefelmeyer, J. D.; Sole, S.; Gabbaï, F. P. Reactivity of the Dimesityl-1,8-Naphthalenediylborate Anion: Isolation of the Borataalkene Isomer and Synthesis of 1,8-Diborylnaphthalenes. *Dalton Trans.* **2004**, 1254−1258.
(119) Cassidy, S. J.; Brettell-Adams, I.; McNamara, L. E.; Smith, M. F.; Bautista, M.; Cao, H. D.; Vasiliu, M.; Gerlach, D. L.; Qu, F. R.; Hammer, N. I.; Dixon, D. A.; Rupar, P. A. Boranes with Ultra-High Stokes Shift Fluorescence. *Organometallics* **2018**, *37*, 3732−3741.
(120) Kaese, T.; Trageser, T.; Budy, H.; Bolte, M.; Lerner, H. W.; Wagner, M. A Redox-Active Diborane Platform Performs C(sp^3)-H Activation and Nucleophilic Substitution Reactions. *Chem. Sci.* **2018**, *9*, 3881−3891.
(121) Trageser, T.; Bolte, M.; Lerner, H.-W.; Wagner, M. B-B Bond Nucleophilicity in a Tetraaryl μ-Hydridodiborane(4) Anion. *Angew. Chem., Int. Ed.* **2020**, *59*, 7726−7731.
(122) Narula, C. K.; Nöth, H. Contribution to the Chemistry of Boron. 150. Competition between Adduct and Cation Formation in Reactions between Diorganylborane Derivatives and Pyridine or Lutidines. *Inorg. Chem.* **1985**, *24*, 2532−2539.
(123) Chase, P. A.; Romero, P. E.; Piers, W. E.; Parvez, M.; Patrick, B. O. Fluorinated 9-Borafluorenes vs. Conventional Perfluoroaryl Boranes—Comparative Lewis Acidity. *Can. J. Chem.* **2005**, *83*, 2098−2105.
(124) Bluer, K. R.; Laperriere, L. E.; Pujol, A.; Yruegas, S.; Adiraju, V. A. K.; Martin, C. D. Coordination and Ring Expansion of 1,2-Dipolar Molecules with 9-Phenyl-9-borafluorene. *Organometallics* **2018**, *37*, 2917−2927.
(125) Zhang, W.; Yu, D.; Wang, Z.; Zhang, B.; Xu, L.; Li, G.; Yan, N.; Rivard, E.; He, G. Dibora [10] annulenes: Construction, Properties, and Their Ring-Opening Reactions. *Org. Lett.* **2019**, *21*, 109−113.
(126) Laperriere, L. E.; Yruegas, S.; Martin, C. D. Investigating the Reactivity of 9-Phenyl-9-Borafluorene with N-H, O-H, P-H, and S-H Bonds. *Tetrahedron* **2019**, *75*, 937−943.
(127) van Veen, R.; Bickelhaupt, F. Synthesis of 5-and 6-Membered Carbon-Boron Heterocycles by Pyrolysis of Pyridine-Arylboranes. *J. Organomet. Chem.* **1973**, *47*, 33−38.
(128) Kaese, T.; Hubner, A.; Bolte, M.; Lerner, H. W.; Wagner, M. Forming B-B Bonds by the Controlled Reduction of a Tetraaryldiborane(6). *J. Am. Chem. Soc.* **2016**, *138*, 6224−6233.
(129) Yuan, K.; Wang, X.; Mellerup, S. K.; Kozin, I.; Wang, S. N. Spiro-BODIPYs with a Diaryl Chelate: Impact on Aggregation and Luminescence. *J. Org. Chem.* **2017**, *82*, 13481−13487.
(130) Bonnier, C.; Piers, W. E.; Al-Sheikh Ali, A.; Thompson, A.; Parvez, M. Perfluoroaryl-Substituted Boron Dipyrrinato Complexes. *Organometallics* **2009**, *28*, 4845−4851.

https://dx.doi.org/10.1021/acs.chemrev.0c01068
Chem. Rev. 2021, 121, 4147−4192

(131) Lorenz-Rothe, M.; Schellhammer, K. S.; Jägeler-Hoheisel, T.; Meerheim, R.; Kraner, S.; Hein, M. P.; Schünemann, C.; Tietze, M. L.; Hummert, M.; Ortmann, F.; et al. From Fluorine to Fluorene—A Route to Thermally Stable aza-BODIPYs for Organic Solar Cell Application. *Adv. Electron. Mater.* **2016**, *2*, 1600152.
(132) Zhang, Z.; Zhang, H.; Jiao, C.; Ye, K.; Zhang, H.; Zhang, J.; Wang, Y. 2-(2-Hydroxyphenyl) Benzimidazole-Based Four-Coordinate Boron-Containing Materials with Highly Efficient Deep-Blue Photoluminescence and Electroluminescence. *Inorg. Chem.* **2015**, *54*, 2652−2659.
(133) Bontemps, S.; Devillard, M.; Mallet-Ladeira, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. Phosphino-Boryl-Naphthalenes: Geometrically Enforced, Yet Lewis Acid Responsive P- B Interactions. *Inorg. Chem.* **2013**, *52*, 4714−4720.
(134) Essex, L. A.; Taylor, J. W.; Harman, W. H. Nickel Complexes of Phosphine-Appended Benzannulated Boron Heterocycles. *Tetrahedron* **2019**, *75*, 2255−2260.
(135) Matsumoto, T.; Tanaka, K.; Tanaka, K.; Chujo, Y. Synthesis and Characterization of Heterofluorenes Containing Four-Coordinated Group 13 Elements: Theoretical and Experimental Analyses and Comparison of Structures, Optical Properties and Electronic States. *Dalton Trans.* **2015**, *44*, 8697−8707.
(136) Nagura, K.; Saito, S.; Fröhlich, R.; Glorius, F.; Yamaguchi, S. N-Heterocyclic Carbene Boranes as Electron-Donating and Electron-Accepting Components of π-Conjugated Systems. *Angew. Chem., Int. Ed.* **2012**, *51*, 7762−7766.
(137) Gaffen, J. R.; Bentley, J. N.; Torres, L. C.; Chu, C.; Baumgartner, T.; Caputo, C. B. A Simple and Effective Method of Determining Lewis Acidity by Using Fluorescence. *Chem.* **2019**, *5*, 1567−1583.
(138) Beckett, M. A.; Strickland, G. C.; Holland, J. R.; Sukumar Varma, K. A Convenient N.M.R. Method for the Measurement of Lewis Acidity at Boron Centres: Correlation of Reaction Rates of Lewis Acid Initiated Epoxide Polymerizations with Lewis Acidity. *Polymer* **1996**, *37* (20), 4629−4631.
(139) Mayer, U.; Gutmann, V.; Gerger, W. The Acceptor Number — A Quantitative Empirical Parameter for the Electrophilic Properties of Solvents. *Monatsh. Chem.* **1975**, *106*, 1235−1257.
(140) Childs, R. F.; Mulholland, D. L.; Nixon, A. The Lewis Acid Complexes of α,β-Unsaturated Carbonyl and Nitrile Compounds. A Nuclear Magnetic Resonance Study. *Can. J. Chem.* **1982**, *60*, 801−808.
(141) Morgan, M. M.; Marwitz, A. J. V.; Piers, W. E.; Parvez, M. Comparative Lewis Acidity in Fluoroarylboranes: $B(o\text{-}HC_6F_4)_3$, $B(p\text{-}HC_6F_4)_3$, and $B(C_6F_5)_3$. *Organometallics* **2013**, *32*, 317−322.
(142) Hilt, G.; Nödling, A. The Correlation of Lewis Acidities of Silyl Triflates with Reaction Rates of Catalyzed Diels-Alder Reactions. *Eur. J. Org. Chem.* **2011**, *2011*, 7071−7075.
(143) Müller, L. O.; Himmel, D.; Stauffer, J.; Steinfeld, G.; Slattery, J.; Santiso-Quiñones, G.; Brecht, V.; Krossing, I. Simple Access to the Non-Oxidizing Lewis Superacid PhF-$Al(OR^F)_3$ (R^F=$C(CF_3)_3$). *Angew. Chem., Int. Ed.* **2008**, *47*, 7659−7663.
(144) Böhrer, H.; Trapp, N.; Himmel, D.; Schleep, M.; Krossing, I. From Unsuccessful H_2-Activation with FLPs Containing $B(Ohfip)_3$ to a Systematic Evaluation of the Lewis Acidity of 33 Lewis Acids Based on Fluoride, Chloride, Hydride and Methyl Ion Affinities. *Dalton Trans.* **2015**, *44*, 7489−7499.
(145) Jupp, A. R.; Johnstone, T. C.; Stephan, D. W. The Global Electrophilicity Index as a Metric for Lewis Acidity. *Dalton Trans.* **2018**, *47*, 7029−7035.
(146) Greb, L. Lewis Superacids: Classifications, Candidates, and Applications. *Chem. - Eur. J.* **2018**, *24*, 17881−17896.
(147) Branchadell, V.; Oliva, A. The Lewis Acidity Scale of Boron Trihalides: An ab initio Study. *J. Mol. Struct.: THEOCHEM* **1991**, *236*, 75−84.
(148) Ayers, P. W.; Parr, R. G.; Pearson, R. G. Elucidating the Hard/Soft Acid/Base Principle: A Perspective Based on Half-Reactions. *J. Chem. Phys.* **2006**, *124*, 194107.
(149) Jupp, A. R.; Johnstone, T. C.; Stephan, D. W. Improving the Global Electrophilicity Index (GEI) as a Measure of Lewis Acidity. *Inorg. Chem.* **2018**, *57*, 14764−14771.
(150) Sivaev, I. B.; Bregadze, V. I. Lewis Acidity of Boron Compounds. *Coord. Chem. Rev.* **2014**, *270*−*271*, 75−88.
(151) Yruegas, S.; Martinez, J. J.; Martin, C. D. Intermolecular Insertion Reactions of Azides into 9-Borafluorenes to Generate 9,10-B,N-Phenanthrenes. *Chem. Commun.* **2018**, *54*, 6808−6811.
(152) B−F interactions could also play a role in the reduction of Lewis acidity.
(153) Yang, W.; Krantz, K. E.; Freeman, L. A.; Dickie, D. A.; Molino, A.; Frenking, G.; Pan, S.; Wilson, D. J. D.; Gilliard, R. J., Jr. Persistent Borafluorene Radicals. *Angew. Chem., Int. Ed.* **2020**, *59*, 3850−3854.
(154) It was noted that the 19% quantum yield for **15** should be taken with caution due to the presence of an unidentifiable and inseparable impurity in the sample.
(155) Rauch, F.; Fuchs, S.; Friedrich, A.; Sieh, D.; Krummenacher, I.; Braunschweig, H.; Finze, M.; Marder, T. B. Highly Stable, Readily Reducible, Fluorescent, Trifluoromethylated 9-Borafluorenes. *Chem. - Eur. J.* **2020**, *26*, 12794−12808.
(156) Matsumoto, T.; Ito, S.; Tanaka, K.; Chujo, Y. Synthesis, Properties and Structure of Borafluorene-Based Conjugated Polymers with Kinetically and Thermodynamically Stabilized Tetracoordinated Boron Atoms. *Polym. J.* **2018**, *50*, 197−202.
(157) Galbraith, E.; James, T. D. Boron Based Anion Receptors as Sensors. *Chem. Soc. Rev.* **2010**, *39*, 3831−3842.
(158) Kubik, S. Anion Recognition in Water. *Chem. Soc. Rev.* **2010**, *39*, 3648−3663.
(159) Jagtap, S.; Yenkie, M. K.; Labhsetwar, N.; Rayalu, S. Fluoride in Drinking Water and Defluoridation of Water. *Chem. Rev.* **2012**, *112*, 2454−2466.
(160) Thanthiriwatte, K. S.; Gwaltney, S. R. Excitation Spectra of Dibenzoborole Containing π-Electron Systems: Controlling the Electronic Spectra by Changing the pπ-π* Conjugation. *J. Phys. Chem. A* **2006**, *110*, 2434−2439.
(161) Muhammad, S.; Janjua, M. R. S. A.; Su, Z. Investigation of Dibenzoboroles Having π-Electrons: Toward a New Type of Two-Dimensional NLO Molecular Switch? *J. Phys. Chem. C* **2009**, *113*, 12551−12557.
(162) Matsumoto, T.; Takamine, H.; Tanaka, K.; Chujo, Y. Design of Bond-Cleavage-Induced Intramolecular Charge Transfer Emission with Dibenzoboroles and Their Application to Ratiometric Sensors for Discriminating Chain Lengths of Alkanes. *Mater. Chem. Front.* **2017**, *1*, 2368−2375.
(163) Förster, T.; Hoffmann, G. Die Viskositätsabhängigkeit der Fluoreszenzquantenausbeuten einiger Farbstoffsysteme. *Z. Phys. Chem.* **1971**, *75*, 63−76.
(164) Ribeiro, C.; Brogueira, P.; Lavareda, G.; Carvalho, C. N.; Amaral, A.; Santos, L.; Morgado, J.; Scherf, U.; Bonifácio, V. D. B. Ultrasensitive Microchip Sensor Based on Boron-Containing Polyfluorene Nanofilms. *Biosens. Bioelectron.* **2010**, *26*, 1662−1665.
(165) The workup for this polymer involves a biphasic extraction with 2 N HCl/chloroform, and it is well-known that aqueous acids are routinely used to cleave B−C bonds in organic synthesis. It would be surprising that this species without any steric protection would survive these harsh conditions given that borafluorenes have more sensitive B−C bonds than typical boranes. Given the aforementioned doubts in the synthesis of the monomer, it seems unlikely that these compounds contain a borafluorene in the polymer. The material the authors used for the described anion sensing may function as indicated, but based on the information on borafluorenes presented in this review, it is unlikely that this is a result of a borafluorene being present.
(166) The mass spectrometric data was not high resolution, there is not an X-ray structure, a ^{11}B NMR shift is not reported, and the supporting spectra were not included in the publication. Given that the only 9-borafluorenes with very bulky aryl groups survive chromatography and exposure to water, there are doubts that this compound was isolated.
(167) Lewis, S. P.; Chai, J.; Collins, S.; Sciarone, T. J. J.; Henderson, L. D.; Fan, C.; Parvez, M.; Piers, W. E. Isobutene Polymerization Using Chelating Diboranes: Polymerization in Aqueous Suspension and Hydrocarbon Solution. *Organometallics* **2009**, *28*, 249−263.

https://dx.doi.org/10.1021/acs.chemrev.0c01068
Chem. Rev. 2021, 121, 4147−4192

(168) Chai, J.; Lewis, S. P.; Collins, S.; Sciarone, T. J. J.; Henderson, L. D.; Chase, P. A.; Irvine, G. J.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W. Formation of Chelated Counteranions Using Lewis Acidic Diboranes: Relevance to Isobutene Polymerization. *Organometallics* **2007**, *26*, 5667−5679.
(169) Bettinger, H. F.; Müller, M. Pathways for the Cyclotetramerization of Dibenz[c, e][1,2]azaborine, a BN-Phenanthryne. *J. Phys. Org. Chem.* **2015**, *28*, 97−103.
(170) Yang, W.; Krantz, K. E.; Dickie, D. A.; Molino, A.; Wilson, D. J. D.; Gilliard, R. J., Jr. Crystalline BP-Doped Phenanthryne via Photolysis of The Elusive Boraphosphaketene. *Angew. Chem., Int. Ed.* **2020**, *59*, 3971−3975.
(171) Biswas, S.; Maichle-Mössmer, C.; Bettinger, H. F. Rearrangement from the Heteroantiaromatic Borole to the Heteroaromatic Azaborine Motif. *Chem. Commun.* **2012**, *48*, 4564−4566.
(172) Radtke, J.; Mellerup, S. K.; Bolte, M.; Lerner, H.-W.; Wang, S.; Wagner, M. Aryl Insertion vs Aryl-Aryl Coupling in C,C-Chelated Organoborates: The "Missing Link" of Tetraarylborate Photochemistry. *Org. Lett.* **2018**, *20*, 3966−3970.
(173) Shoji, Y.; Tanaka, N.; Muranaka, S.; Shigeno, N.; Sugiyama, H.; Takenouchi, K.; Hajjaj, F.; Fukushima, T. Boron-Mediated Sequential Alkyne Insertion and C-C Coupling Reactions Affording Extended π-Conjugated Molecules. *Nat. Commun.* **2016**, *7*, 12704.
(174) Shoji, Y.; Hwang, M.; Sugiyama, H.; Ishiwari, F.; Takenouchi, K.; Osuga, R.; Kondo, J. N.; Fujikawa, S.; Fukushima, T. Highly Efficient Transformation of Linear Poly(phenylene ethynylene)s into Zigzag-Shaped π-Conjugated Microporous Polymers through Boron-Mediated Alkyne Benzannulation. *Mater. Chem. Front.* **2018**, *2*, 807−814.
(175) Wang, Z.; Zhou, Y.; Zhang, J.-X.; Krummenacher, I.; Braunschweig, H.; Lin, Z. DFT Studies on the Reactions of Boroles with Alkynes. *Chem. - Eur. J.* **2018**, *24*, 9612−9621.
(176) Zhang, W.; Li, G.; Xu, L.; Zhuo, Y.; Wan, W.; Yan, N.; He, G. 9,10-Azaboraphenanthrene-Containing Small Molecules and Conjugated Polymers: Synthesis and Their Application in Chemodosimeters for the Ratiometric Detection of Fluoride Ions. *Chem. Sci.* **2018**, *9*, 4444−4450.
(177) Kirschner, S.; Bao, S.-S.; Fengel, M. K.; Bolte, M.; Lerner, H.-W.; Wagner, M. Aryl-aryl Coupling in a Polycyclic Aromatic Hydrocarbon with Embedded Tetracoordinate Boron Centre. *Org. Biomol. Chem.* **2019**, *17*, 5060−5065.
(178) Bartholome, T. A.; Bluer, K. R.; Martin, C. D. Successive Carbene Insertion into 9-Phenyl-9-Borafluorene. *Dalton Trans.* **2019**, *48*, 6319−6322.
(179) Yruegas, S.; Barnard, J. H.; Al-Furaiji, K.; Dutton, J. L.; Wilson, D. J. D.; Martin, C. D. Boraphosphaalkene Synthesis via Phosphaalkyne Insertion into 9-Borafluorene. *Organometallics* **2018**, *37*, 1515−1518.
(180) Kashida, J.; Shoji, Y.; Fukushima, T. Synthesis and Reactivity of Cyclic Borane-Amidine Conjugated Molecules Formed by Direct 1,2-Carboboration of Carbodiimides with 9-Borafluorenes. *Chem. - Asian J.* **2019**, *14*, 1879−1885.
(181) Zhu, H.; Qu, Z.-W. Toward Product Control in Ring-Opening Oligomerization of 9-H-9-Borafluorenes. *J. Comput. Chem.* **2014**, *35*, 1107−1110.
(182) Hong, H.; Chung, T. C. Doubly Hydrogen-Bridged 1,2-Diphenylenediboranes Derived from 9-Chloro-9-Borafluorene and Ligand Exchange Reactions. *J. Organomet. Chem.* **2004**, *689*, 58−64.
(183) Knizek, J.; Nöth, H. Hydridoborates and Hydridoborato Metallates: Part 26. Preparation and Structures of Dihydridoborates of Lithium and Potassium. *J. Organomet. Chem.* **2000**, *614*−*615*, 168−187.
(184) Köster, R.; Willemsen, H.-G. Borverbindungen. XXVIII. 1,2-(2,2′-Biphenylylen)diborane(6). *Justus Liebigs Ann. Chem.* **1974**, *1974*, 1843−1850.
(185) Nöth, H.; Schmid, G. Metall-Bor-Verbindungen. III. Über Triphenylphosphin-Tetracarbonylmangan-Bor-Verbindungen. *Z. Anorg. Allg. Chem.* **1966**, *345*, 69−78.
(186) Schmid, G.; Noth, H. Metall-Bor-Verbindungen, V. Die Diarylbor-Gruppe als Ligand in Phosphin-kobalt(II)-Verbindungen. *Chem. Ber.* **1967**, *100*, 2899−2907.
(187) Schmid, G.; Powell, P.; Nöth, H. Metall-Bor-Verbindungen, VI. Bis(dimethylglyoximato)-kobalt(III)-Verbindungen mit Co-B-Bindungen. *Chem. Ber.* **1968**, *101*, 1205−1214.
(188) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. Transition Metal-Boryl Compounds: Synthesis, Reactivity, and Structure. *Chem. Rev.* **1998**, *98*, 2685−2722.
(189) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. Boryliridium and Boraethyliridium Complexes *fac*-[$IrH_2(PMe_3)_3$(BRR')] and *fac*-[$IrH(PMe_3)_3(\eta^2$-CH_2BHRR')]. *J. Am. Chem. Soc.* **1990**, *112*, 9399−9400.
(190) Hartwig, J. F.; Huber, S. Transition-Metal Boryl Complexes: Structure and Reactivity of $CpFe(CO)_2$Bcat and $CpFe(CO)_2BPh_2$. *J. Am. Chem. Soc.* **1993**, *115*, 4908−4909.
(191) Wadepohl, H.; Arnold, U.; Pritzkow, H. Synthesis of Boryl Metal Complexes with Additional Agostic Stabilization by Hydroboration of Fischer Carbyne Complexes. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 974−976.
(192) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. On the Versatile and Unusual Coordination Behavior of Ambiphilic Ligands *o*-$R_2P(Ph)BR'_2$. *J. Am. Chem. Soc.* **2006**, *128*, 12056−12057.
(193) Hayes, P. G.; Piers, W. E.; Parvez, M. Synthesis, Structure, and Ion Pair Dynamics of β-Diketiminato-Supported Organoscandium Contact Ion Pairs. *Organometallics* **2005**, *24*, 1173−1183.
(194) Hübner, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. Extensive Structural Rearrangements upon Reduction of 9-H-9-Borafluorene. *Angew. Chem., Int. Ed.* **2014**, *53*, 10408−10411.
(195) Budy, H.; Gilmer, J.; Trageser, T.; Wagner, M. Anionic Organoboranes: Delicate Flowers Worth Caring for. *Eur. J. Inorg. Chem.* **2020**, *2020*, 4148−4162.
(196) Gilmer, J.; Budy, H.; Kaese, T.; Bolte, M.; Lerner, H.-W.; Wagner, M. The 9-*H*-9-Borafluorene Dianion: A Surrogate for Elusive Diarylboryl Anion Nucleophiles. *Angew. Chem., Int. Ed.* **2020**, *59*, 5621−5625.
(197) Kaese, T.; Budy, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. Deprotonation of a Seemingly Hydridic Diborane(6) To Build a B-B Bond. *Angew. Chem., Int. Ed.* **2017**, *56*, 7546−7550.
(198) Hübner, A.; Diehl, A. M.; Diefenbach, M.; Endeward, B.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. Confirmed by X-ray Crystallography: The B÷B One-Electron σ Bond. *Angew. Chem., Int. Ed.* **2014**, *53*, 4832−4835.
(199) Hübner, A.; Kaese, T.; Diefenbach, M.; Endeward, B.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. A Preorganized Ditopic Borane as Highly Efficient One- or Two-Electron Trap. *J. Am. Chem. Soc.* **2015**, *137*, 3705−3714.
(200) Back, O.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G. ^{31}P NMR Chemical Shifts of Carbene-Phosphinidene Adducts as an Indicator of the π-Accepting Properties of Carbenes. *Angew. Chem., Int. Ed.* **2013**, *52*, 2939−2943.
(201) Liske, A.; Verlinden, K.; Buhl, H.; Schaper, K.; Ganter, C. Determining the π-Acceptor Properties of N-Heterocyclic Carbenes by Measuring the ^{77}Se NMR Chemical Shifts of Their Selenium Adducts. *Organometallics* **2013**, *32*, 5269−5272.
(202) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. Carbene-Stabilized Main Group Radicals and Radical Ions. *Chem. Sci.* **2013**, *4* (8), 3020−3030.
(203) Junor, G. P.; Lorkowski, J.; Weinstein, C. M.; Jazzar, R.; Pietraszuk, C.; Bertrand, G. The Influence of C(sp^3)H-Selenium Interactions on the ^{77}Se NMR Quantification of the π-Accepting Properties of Carbenes. *Angew. Chem., Int. Ed.* **2020**, *59*, 22028−22033.
(204) Armstrong, D. R.; Perkins, P. G. The Electronic Sructure of the Diphenylboron Cation and the 9-Borafluorenes. *J. Chem. Soc. A* **1966**, 1026−1031.
(205) Gorokhovik, I.; Rieder, S.; Povie, G.; Renaud, P. Radical Chain Reactions Involving 9-Alkyl-9-Borafluorenes. *ARKIVOC* **2014**, *2014*, 274−286.
(206) Grandl, M.; Kaese, T.; Krautsieder, A.; Sun, Y.; Pammer, F. Hydroboration as an Efficient Tool for the Preparation of Electronically

https://dx.doi.org/10.1021/acs.chemrev.0c01068
Chem. Rev. 2021, 121, 4147−4192

and Structurally Diverse N-B-Heterocycles. *Chem. - Eur. J.* **2016**, *22*, 14373−14382.
(207) Zhao, Q.; Zhang, H.; Wakamiya, A.; Yamaguchi, S. Coordination-Induced Intramolecular Double Cyclization: Synthesis of Boron-Bridged Dipyridylvinylenes and Dithiazolylvinylenes. *Synthesis* **2009**, *2009*, 127−132.
(208) Son, J.-H.; Hoefelmeyer, J. D. 1,2-Nucleophilic Addition of 2-(Picolyl)organoboranes to Nitrile, Aldehyde, Ketone, and Amide. *Org. Biomol. Chem.* **2012**, *10*, 6656−6664.
(209) Schacht, W.; Kaufmann, D. The First Synthesis of a Benzoborole. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 665−666.
(210) Houghton, A. Y.; Karttunen, V. A.; Piers, W. E.; Tuononen, H. M. Hydrogen Activation with Perfluorinated Organoboranes: 1,2,3-Tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene. *Chem. Commun.* **2014**, *50*, 1295−1298.
(211) Houghton, A. Y.. On the Syntheses and Reactions of Boroles and Boraindenes. Doctoral thesis, University of Calgary, Calgary, Alberta, 2014, DOI: 10.11575/PRISM/27197.
(212) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. M. Direct Observation of a Borane-Silane Complex Involved in Frustrated Lewis-Pair-Mediated Hydrosilylations. *Nat. Chem.* **2014**, *6*, 983−988.
(213) Jiang, Y.; Schirmer, B.; Blacque, O.; Fox, T.; Grimme, S.; Berke, H. The "Catalytic Nitrosyl Effect": NO Bending Boosting the Efficiency of Rhenium Based Alkene Hydrogenations. *J. Am. Chem. Soc.* **2013**, *135*, 4088−4102.
(214) Araneda, J. F.; Neue, B.; Piers, W. E.; Parvez, M. Photochemical Synthesis of a Ladder Diborole: A New Boron-Containing Conjugate Material. *Angew. Chem., Int. Ed.* **2012**, *51*, 8546−8550.
(215) Only select data points for NICS values were reported in the manuscripts and are discussed in the interpretations of aromaticity/antiaromaticity. A more meaningful analysis can be drawn from NICS plots versus distance. The degree of aromaticity and antiaromaticity in many instances may change upon undertaking computations of NICS plots for these species.
(216) Araneda, J. F.; Piers, W. E.; Sgro, M. J.; Parvez, M. Bronsted Acid-Catalyzed Skeletal Rearrangements in Polycyclic Conjugated Boracycles: A Thermal Route to a Ladder Diborole. *Chem. Sci.* **2014**, *5*, 3189−3196.
(217) Araneda, J. F.; Piers, W. E.; Sgro, M. J.; Parvez, M. Ring Expansion Reactions of Electron-Rich Boron-Containing Heterocycles. *Organometallics* **2015**, *34*, 3408−3413.
(218) Kim, S.; Song, K.-h.; Kang, S. O.; Ko, J. The Role of Borole in a Fully Conjugated Electron-Rich System. *Chem. Commun.* **2004**, 68−69.
(219) He, J.; Rauch, F.; Friedrich, A.; Krebs, J.; Krummenacher, I.; Bertermann, R.; Nitsch, J.; Braunschweig, H.; Finze, M.; Marder, T. B. Phenylpyridyl-Fused Boroles: A Unique Coordination Mode and Weak B-N Coordination-Induced Dual Fluorescence. *Angew. Chem., Int. Ed.* **2021**, DOI: 10.1002/anie.202013692.
(220) He, J.; Rauch, F.; Krummenacher, I.; Braunschweig, H.; Finze, M.; Marder, T. B. Two Derivatives of Phenylpyridyl-Fused Boroles with Contrasting Electronic Properties: Decreasing and Enhancing the Electron Accepting Ability. *Dalton Trans.* **2021**, *50*, 355−361.
(221) Spokoyny, A. M. New Ligand Platforms Featuring Boron-Rich Clusters as Organomimetic Substituents. *Pure Appl. Chem.* **2013**, *85*, 903−919.
(222) Kirlikovali, K. O.; Axtell, J. C.; Gonzalez, A.; Phung, A. C.; Khan, S. I.; Spokoyny, A. M. Luminescent Metal Complexes Featuring Photophysically Innocent Boron Cluster Ligands. *Chem. Sci.* **2016**, *7*, 5132−5138.
(223) Axtell, J. C.; Kirlikovali, K. O.; Dziedzic, R. M.; Gembicky, M.; Rheingold, A. L.; Spokoyny, A. M. Magnesium Reagents Featuring a 1,1'-Bis(*o*-carborane) Ligand Platform. *Eur. J. Inorg. Chem.* **2017**, *2017*, 4411−4416.
(224) Kirlikovali, K. O.; Axtell, J. C.; Anderson, K.; Djurovich, P. I.; Rheingold, A. L.; Spokoyny, A. M. Fine-Tuning Electronic Properties of Luminescent Pt(II) Complexes via Vertex-Differentiated Coordination of Sterically Invariant Carborane-Based Ligands. *Organometallics* **2018**, *37*, 3122−3131.
(225) Yruegas, S.; Axtell, J. C.; Kirlikovali, K. O.; Spokoyny, A. M.; Martin, C. D. Synthesis of 9-Borafluorene Analogues Featuring a Three-Dimensional 1,1'-Bis(*o*-carborane) Backbone. *Chem. Commun.* **2019**, *55*, 2892−2895.
(226) Benton, A.; Watson, J. D.; Mansell, S. M.; Rosair, G. M.; Welch, A. J. The Lewis Acidity of Borylcarboranes. *J. Organomet. Chem.* **2020**, *907*, 121057.

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