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Review

Recent developments in the chemistry of 1,3,2-diazaborolines-(2,3-dihydro-1*H*-1,3,2-diazaboroles)

Lothar Weber*

Fakultät für Chemie der Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany

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Contents

Abstract

1,3,2-Diazaborolines (2,3-dihydro-1*H*-1,3,2-diazaboroles) are compounds at the interface between inorganic, organometallic and organic chemistry. The planar rings with 6π-electrons may be regarded as heteroarenes, as evident by NMR and photoelectron spectra and confirmed by quantum chemical studies. High-yield syntheses of functionalized 1,3,2-diazaborolines have been elaborated, providing a prolific area of chemistry. Conjugation of the vacant $2p_z$-orbital on the boron center with the π* orbital of attached organic π-systems proved to be responsible for unique absorption and emission characteristics of 1,3,2-diazaborolinyl functionalized biphenyls, thiophenes and dithiophenes. Most of the functionalized diazaborolines show clean irreversible oxidation waves in their cyclovoltammograms.

Keywords: Diazaborolines; Heteroarenes; Luminescence; Structures

* Tel.: +49 521 1066169; fax: +49 521 1066146.
E-mail address: lothar.weber@uni-bielefeld.de.

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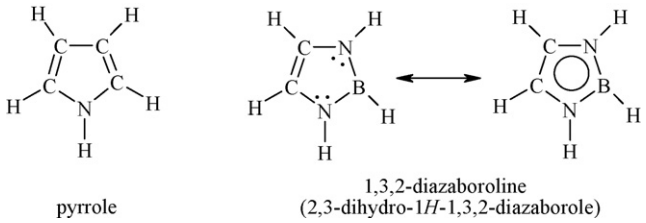


Scheme 1. Isoelectronic systems; pyrrole and 1,3,2-diazaboroline.

1. Introduction

Heterocycles containing boron and nitrogen atoms play an important and fascinating role in main group chemistry. The concept of isoelectronic and isosteric compounds was successfully applied to carbon–carbon and boron–nitrogen containing molecules [1]. Thus, the replacement of a C=C unit in pyrrole affords 2,3-dihydro-1*H*-1,3,2-diazaboroles, which were formerly addressed as 1,3,2-diazaborolines. As in a first review article on these compounds published in 2001 for the sake of clarity and readability the latter nomenclature is also preferred in this account (Scheme 1) [2].

Since the first report on a representative of this class by Merriam and Niedenzu, who catalytically dehydrogenated the corresponding fully saturated diazaborolidine (Scheme 2) [3] and an alternative protocol elaborated by Weber and Schmid who utilized the sodium amalgam reduction of diazaborolium salts (Scheme 2) the chemistry of 1,3,2-diazaborolines developed continuously [4].

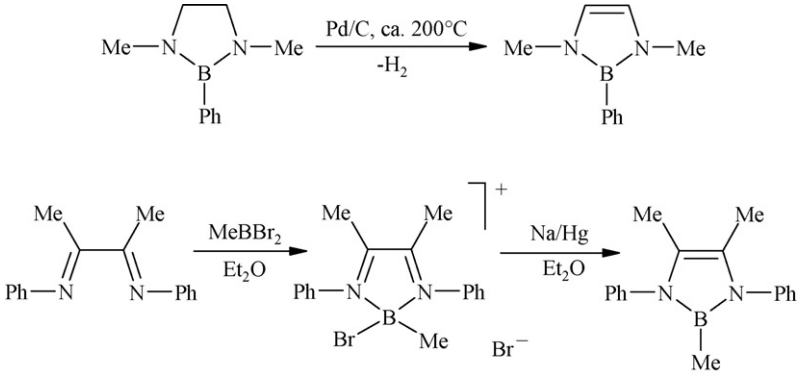
A series of 1,3,2-diazaborolines with alkyl- and aryl-substituents at the heteroatoms were synthesized, and their molecular and electronic structures were carefully studied [5–7]. Up to the middle of the 1990s comparatively little work on the chemistry of such rings was accomplished. Reports on π-complexation to the $[Cr(CO)_3]$ fragment [7–9] as well as N–Si cleavage by alkali amides and alkoxides [7,10] provided some insight into the synthetic potential of these interesting molecules. This situation changed considerably when high-yield syntheses of 1,3,2-diazaborolines with halide substituents at the boron atom were devised [11,12]. This target was reached either by a protocol according to Scheme 2 via the pregenerated 1,3,2-diazaborolium salts or by reacting a 1,4-diazabutadiene with lithium metal prior to the cyclocondensation with boron trihalides (Scheme 3).

Halide replacement by hydride, carbon-, nitrogen-, and tin-nucleophiles now became feasible [12–14]. Whereas the previous review provided an overview of 1,3,2-diazaborolines with particular emphasis placed on synthetic and structural aspects, this report highlights the remarkable richness of their chemistry with respect to the physico-chemical properties and their potential use as organic materials in optoelectronical devices. This account covers the literature of the years 2001–2006.

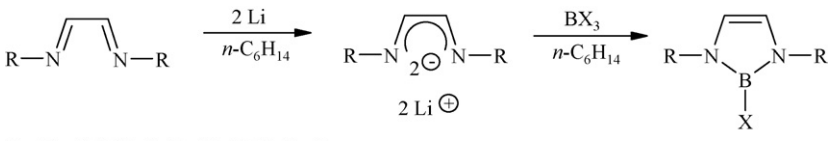
2. Synthesis of 1,3,2-diazaborolines

To date there are mainly three different methods for the construction of the ring skeleton of the title compounds: (a) the catalytic dehydrogenation of diazaborolidines; (b) the alkali-metal reduction of 2-halo-1,3,2-diazaborolium salts; and (c) the cyclocondensation of boron halides with dilithiated 1,4-diazabutadienes (Schemes 2 and 3). For several good reasons it is appropriate to also include benzo-1,3,2-diazaborolines in this review. They are readily available by the base-assisted cyclocondensation of 1,2-phenylenediamines with organoboron dihalides and/or boron trihalides (Scheme 4).

Of course halide replacement reactions by suitable nucleophiles in the sense of peripheral reactions remain an important approach to a broad variety of functionalized 1,3,2-diazaborolines (Scheme 5).

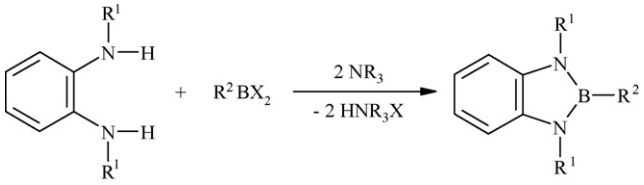


Scheme 2. Synthetic approaches to the first 1,3,2-diazaborolines.

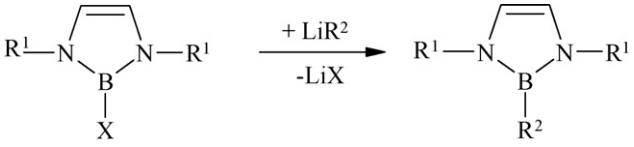


R= *t*Bu, 2,6-$Me_2C_6H_3$; X= F, Cl, Br, I

Scheme 3. Synthesis of 1,3,2-diazaboroles via dilithiated 1,4-diazabutadiene.



Scheme 4. Synthesis of benzo-1,3,2-diazaborolines.



Scheme 5. Halide replacement at 2-halo-1,3,2-diazaborolines.

In almost all papers published between the years 2001–2006 the protocol according to the first equation of Scheme 2 was of no relevance.

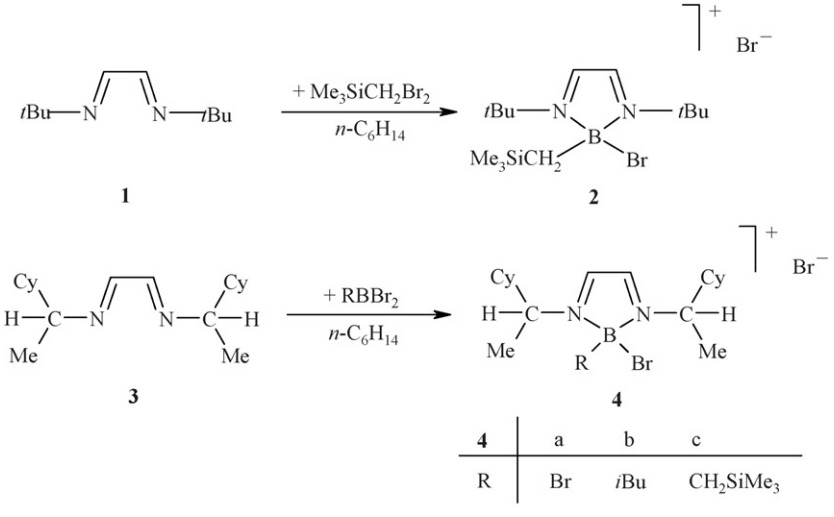
2.1. Reduction of 1,3,2-diazaborolium salts

The yellow to orange red-colored borolium salts **2**, **4a–c**, **6** and **8a**, **b** were formed by the slow combination of equimolar amounts of the corresponding 1,4-diazabutadienes **1**, **3**, **5** or **7** and organoboron dibromides or boron tribromide in hexane at 0–20 °C (yield 43–97%). The employment of large quantities of solvent was required to avoid polymerization (Scheme 6) [15,16].

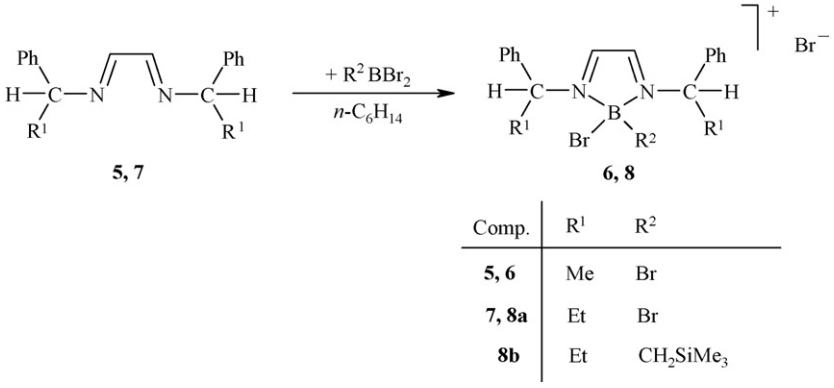
The reduction of **2**, (*S*,*S*)-**4a–c** and **8b** with sodium amalgam in hexane afforded colorless crystals of **9** (49%), **10a** (60%) and **10c** (48%). In contrast to this, the analogous reduction of **6** and **8a** gave **11** and **12a** as thermolabile oils in 32 and 44% yield. Here it was recommended to freshly reduce the saline precursors and subsequently employ these 1,3,2-diazaborolines in further reactions. Reduction of **8b** led to the formation of **12b** which was obtained as colorless crystals by crystallization from isopropanol (48%) (Scheme 7).

Compounds (*S*,*S*)-**10a–c** and (*S*,*S*)-**11** were the first chiral 1,3,2-diazaborolines, provided that enantiomerically pure (*S*)-(−)-1-phenylethylamine and (*S*)-(−)-1-cyclohexylamine were used in the formation of the diazabutadienes **5** and **3**.

The synthetic principle under discussion was extended to the preparation of multiply diazaboroline-functionalized π-systems such as benzene, biphenyl and thiophene. Here it was of interest to study the electronic communication between the heteroarene building blocks via the organic spacer. With this in mind hexane solutions of the dibromoboryl precursors **13a–e** were combined

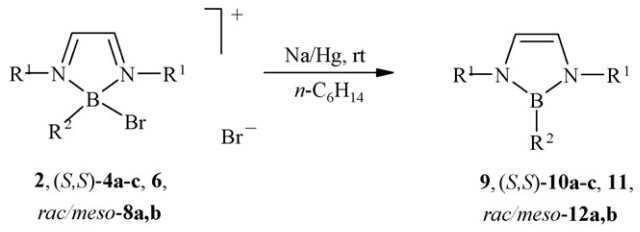


4	a	b	c
R	Br	*t*Bu	CH_2SiMe_3



Comp.	R^1	R^2
5, 6	Me	Br
7, 8a	Et	Br
8b	Et	CH_2SiMe_3

Scheme 6. Synthesis of 1,3,2-diazaborolium salts.



Comp.	R^1	R^2
2, **9**	*t*Bu	Me_3SiCH_2
(*S*,*S*)-**4a**, **-10a**	Cy(Me)CH	Br
(*S*,*S*)-**4b**, **-10b**	Cy(Me)CH	*i*Bu
(*S*,*S*)-**4c**, **-10c**	Cy(Me)CH	Me_3SiCH_2
6, **11**	Ph(Me)CH	Br
rac/*meso*-**8a**, **-12a**	Ph(Et)CH	Br
rac/*meso*-**8b**, **-12b**	Ph(Et)CH	Me_3SiCH_2

Scheme 7. Preparation of **9**, **10a–c**, **11** and **12a**, **b** by sodium amalgam reduction.

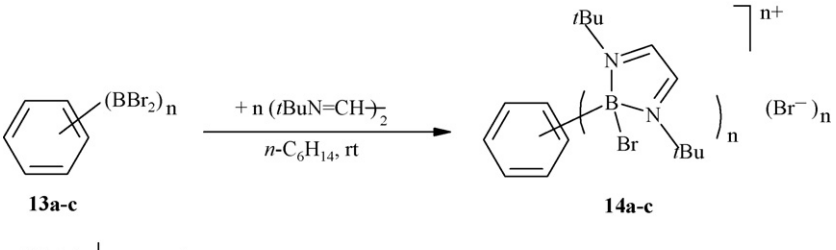
with two (**13a**, **b**, **d**, **e**) or three molar equivalents (**13c**) of 1,4-diazabutadiene **1** to yield orange yellow precipitates of the borolium salts **14a–e** (Scheme 8)

Their reduction with an excess of sodium amalgam in hexane solution led the formation of **15a–e**, as colorless crystals (69–84%) yield (Scheme 9) [17,18].

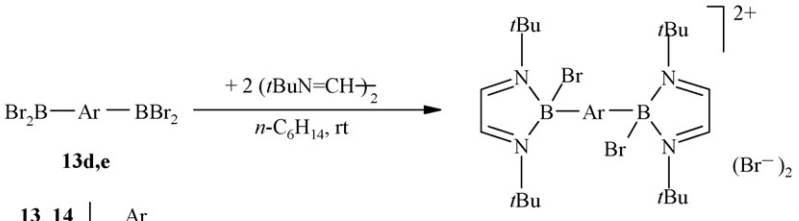
Boryl- and borate-functionalized metallocenes are of great current interest. Two recent reviews have described their applications in homogeneous catalysis, anion sensing and organometallic polymer chemistry [19a,b]. Another point of interest is related to the influence of the boryl substituent on the electronic and structural properties of the metallocene moiety. At this point it was of particular interest to combine 1,3,2-diazaborolines with metallocene fragments. It is conceivable that the 6π-electron-containing heterocycle communicates electronically with the metallocene by (pp)π-interactions and/or σ-bonding, thus altering the electronic properties of the organometallic moiety. The synthesis of ferrocenyl- and cymantrenyl-functionalized 1,3,2-diazaborolines was based on the reaction of organodibromoboranes with 1,4-diazabutadienes to afford borolium salts and the reduction of the latter species with sodium amalgam. The required precursors (dibromoboryl) ferrocene **16**, 1,1′-bis-(dibromoboryl)-ferrocene **19** and 1-dibromoboryl-3-methylcymantrene **22** are readily available from ferrocene and methylcymantrene by Friedel–Crafts-type reactions with BBr_3 [20].

Reaction of **16** with diazabutadiene **1** in *n*-hexane gave an olive-green precipitate of borolium salt **17**. The obtained slurry was reduced in situ with an excess of sodium amalgam for 2 d. Product **18** was isolated as red crystals in 74% from the resulting dark-red *n*-hexane phase. Similarly, the treatment of **19** with 2 equiv. of the diazabutadiene gave the olive-green salt **20**, which was subsequently reduced to the cherry red crystalline compound **21** (81% yield). Yellow, crystalline methylcymantrenyl-1,3,2-diazaborolene **24** was synthesized in 63% yield by the reaction of complex **22** with the diazabutadiene and the usual reduction of the dark yellow borolium salt **23** with sodium amalgam (Scheme 10) [21].

The here devised strategy to obtain diazaborolines is far less straightforward when the *tert*-butyl-groups at the nitrogen atoms

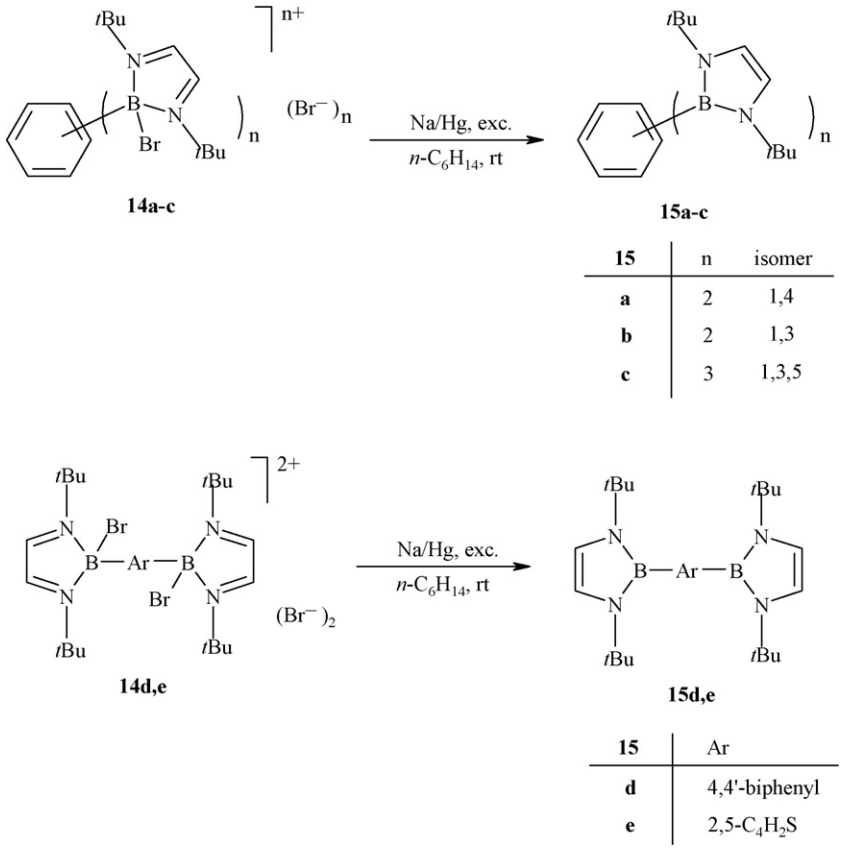


13, **14**	n	isomer
a	2	1,4
b	2	1,3
c	3	1,3,5



13, **14**	Ar
d	4,4'-biphenyl
e	2,5-C_4H_2S

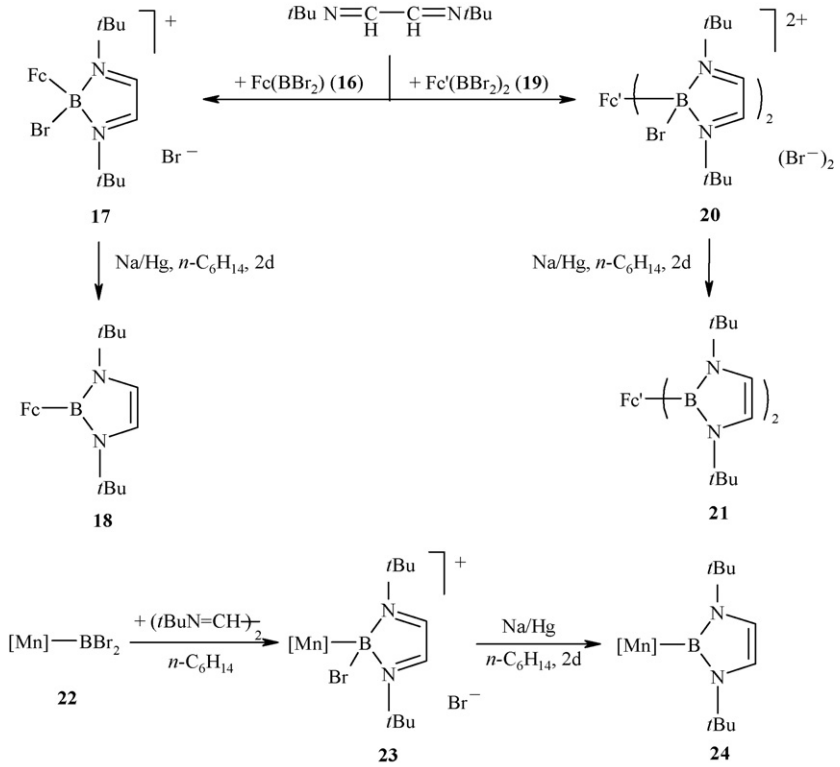
Scheme 8. Preparation of bis and tris(1,3,2-diazaborolium) salts **14a–e**.



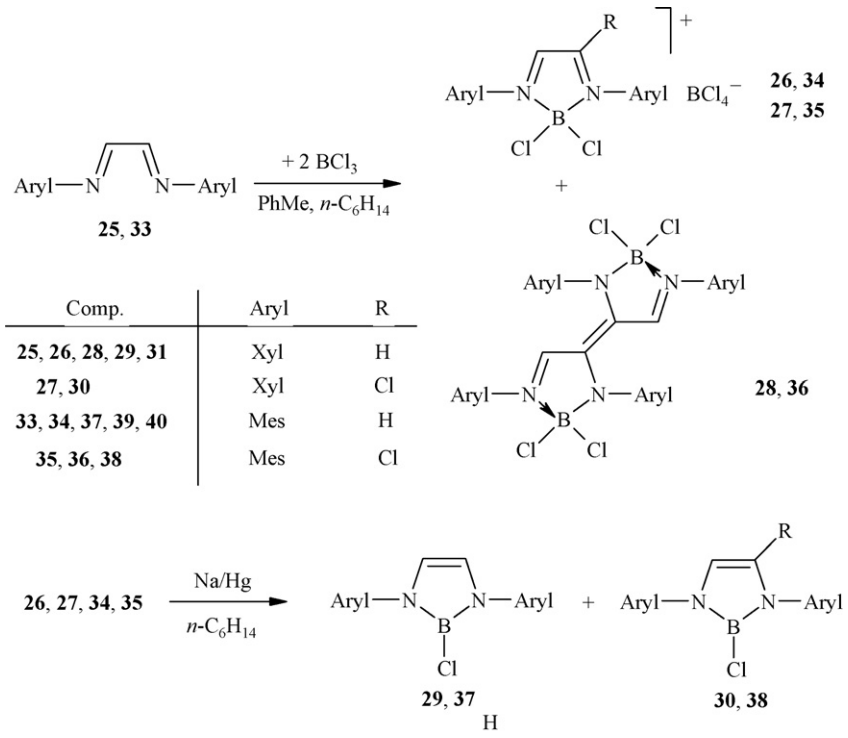
15	n	isomer
a	2	1,4
b	2	1,3
c	3	1,3,5

15	Ar
d	4,4'-biphenyl
e	2,5-C_4H_2S

Scheme 9. Synthesis of the multiply 1,3,2-diazaboroline-functionalized arenes **15a**–**d** and thiophene **15e**.



Scheme 10. Preparation of the diazaboroles **18** [Fc = $(C_5H_5)Fe(C_5H_4)$], **21** [Fc′ = $Fe(C_5H_4)_2$] and **24** [[Mn] = $(MeC_5H_4)(CO)_3Mn$].



Scheme 11. Reaction of diazabutadienes **25** and **33** with BCl_3 and subsequent reduction of salts **26**, **27**, **34** and **35**.

of the diazabutadiene are replaced by aryl rings. In only one case combination of diazabutadiene **25** with 2 equiv. of boron trichloride in a mixture of toluene and hexane in the temperature range from −50 to 20 °C led to the precipitation of the burgundy-red borolium salt **26** in ca. 70% yield. Usually an inseparable mixture of borolium salts **26** and **27** was obtained as a black precipitate. Storage of the mother liquor for 14 h at 4 °C effected crystallization of the dark-red compound **28** in 18% yield. The usual reduction of the mixture of **26** and **27** with sodium amalgam afforded an inseparable mixture of 1,3,2-diazaborolines **29** and **30** in a 10:1 ratio. Clearly this protocol is not particularly useful for the intended generation of pure **29** (Scheme 11).

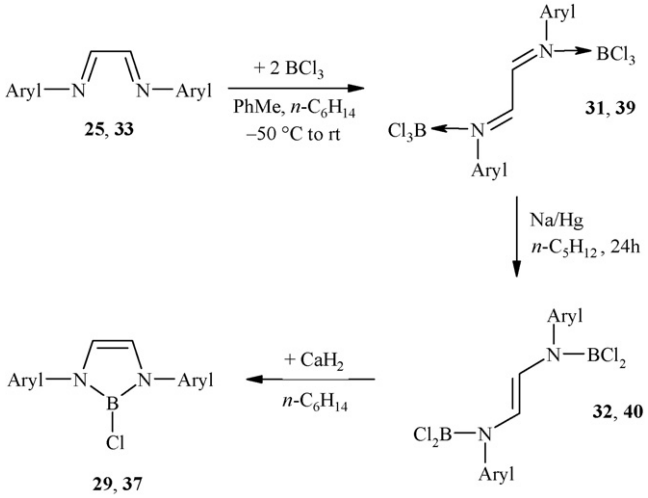
This problem was circumvented by the slow combination of a toluene solution of **25** with the pentane solution of 2 equiv. of BCl_3 at −78 °C. Adduct **31** precipitated as a red-brown solid, the reduction of which with sodium amalgam furnished the colorless crystalline *E*-*N*,*N*-bis-amino ethene **32** in 70% yield. Cyclization of the latter species to give pure **30** was accomplished by treatment with solid CaH_2 in hexane (Scheme 12) [22].

Analogously, the reaction of diazabutadiene **33** with 2 equiv. of BCl_3 at −50 °C led to a 1:1 mixture of borolium salts **34** and **35** as a black solid. From the concentrated mother liquor bicyclic compound **36** was isolated as dark green crystals in 14% yield. Sodium amalgam reduction of salts **34** and **35** afforded an inseparable mixture of diazaborolines **37** and **38** (Scheme 12) [22].

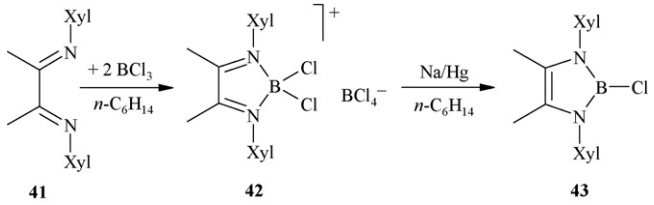
Again, the purposive synthesis of pure **37** required a detour. Violet adduct **39** resulted from the treatment of **33** with 2 equiv. of BCl_3 a −78 °C (70% yield). Sodium amalgam reduction of **39** afforded **40**, which cleanly cyclized to give **37** when brought in contact with CaH_2 (54% yield).

Undesired side reactions were completely suppressed when diazabutadiene **41** was subjected to the reaction with 2 equiv. of BCl_3 in hexane. The green borolium salt **42** (63% yield) was reduced with sodium amalgam to quantitatively yield the thermolabile diazaboroline **43** (Scheme 13) [22].

The situation completely changes with increasing steric bulk at the aryl-substituents. Thus reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diazabutadiene **44** with BCl_3 in hexane did not yield the expected borolium salt **45**. Instead orange *N*,*N*′-bis(2,6-diisopropylphenyl)-2,4,5-trichloro-1,3,2-diazaborolidine **46** was formed as the formal result of a double chloroboration (Scheme 14) [23].



Scheme 12. Alternative route to 1,3,2-diazaborolines **29** and **37**.



Scheme 13. Synthesis of diazaboroline **43**.

The synthetic principle for 1,3,2-diazaborolines from 1,4-diazabutadienes and boron halides via 1,3,2-diazaborolium intermediates was extended to the generation of 1,2-dihydro[1,3,2]-diazaborolo[1,5-*a*]pyridines which can be considered as fused 1,3,2-diazaborolines. Thus, reaction of equimolar amounts of pyridine carbaldimine **47** and boron tribromide in hexane at room temperature afforded the borolium salt **48** as an orange precipitate in 85% yield. Reduction of a slurry of **48** in hexane with an excess of sodium amalgam to compound **49** was achieved in 79%. The product was isolated as air- and moisture sensitive yellow oil (Scheme 15) [24].

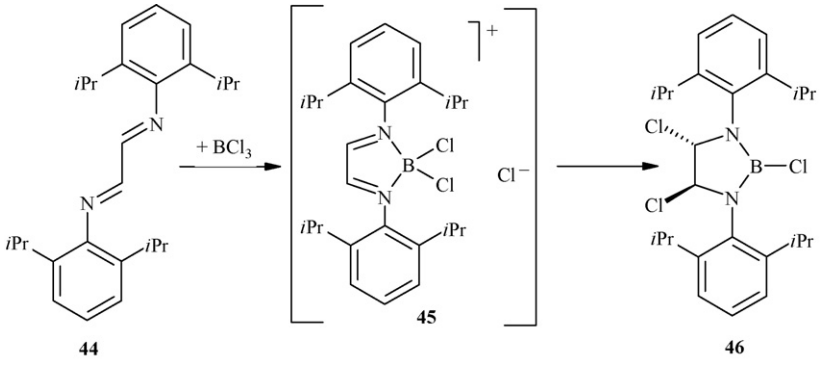
In contrast to the formation of **48**, the reaction of the pyridine carbaldimines **47** and **50** with 2 equiv. of an ethereal $BF_3{\cdot}OEt_2$ solution led to the precipitation of the yellow adducts **51** or **52** (78–81% yield). Stirring slurries of **51** or **52** in hexane in the presence of an excess of sodium amalgam during 48 h cleanly afforded bicyclic **53** as a yellow oil (67% yield) or **54** as a yellow wax (63% yield) (Scheme 16) [24].

Thermolabile 2-ferrocenyl[1,3,2]-diazaborolo[1,5-*a*]pyridine **56** was accessible as an orange solid by the treatment of ferrocenyl dibromoborane **16** with pyridine carbaldimine **47** and the subsequent reduction of borolium salt **55** with sodium amalgam (Scheme 17) [21].

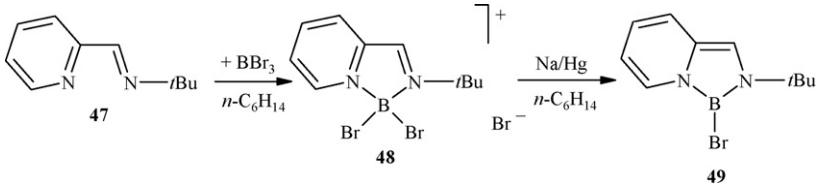
2.2. Synthesis of 1,3,2-benzodiazaborolines from *o*-phenylene diamines

For optophysical purposes 1,3,2-benzodiazaborolines proved to be valuable building blocks in organic light emitting materials. Therefore this class of compounds also deserves consideration in this account. The first report on 1,3,2-benzodiazaborolines dates back to the middle of the last century. They are mainly derived from *o*-phenylene diamine **57**, which was cyclocondensed with $PhBCl_2$ [25], BMe_3 [26], $B(NMe_2)_3$ [27], $MeBBr_2$ in the presence of sodium hydride [28] and phenyl boronic acid [29]. The parent compound **62** was synthesized from *o*-phenylene diammonium chloride **61** and $NaBH_4$ in THF at room temperature (Scheme 18) [30].

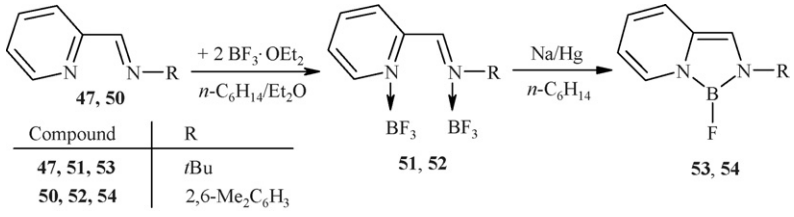
N,*N*′-Diorganyl-*o*-phenylene diamines were also used for the production of 1,3,2-benzodiazaborolines. *N*,*N*′-Diethyl-*o*-



Scheme 14. Synthesis of 1,3,2-diazaborolidine **46**.

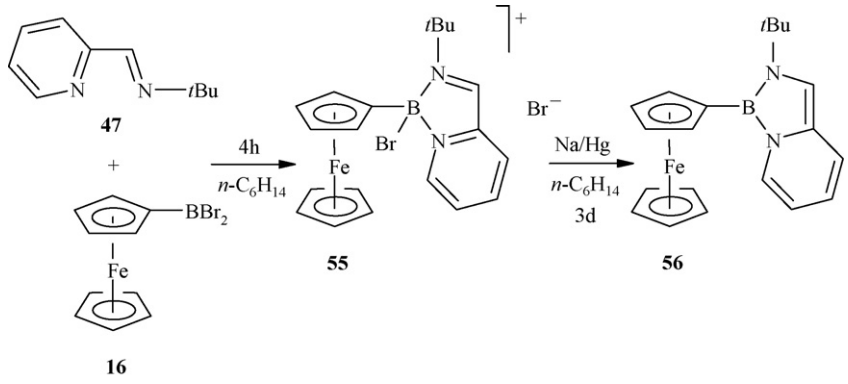


Scheme 15. Synthesis of 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridine **49**.



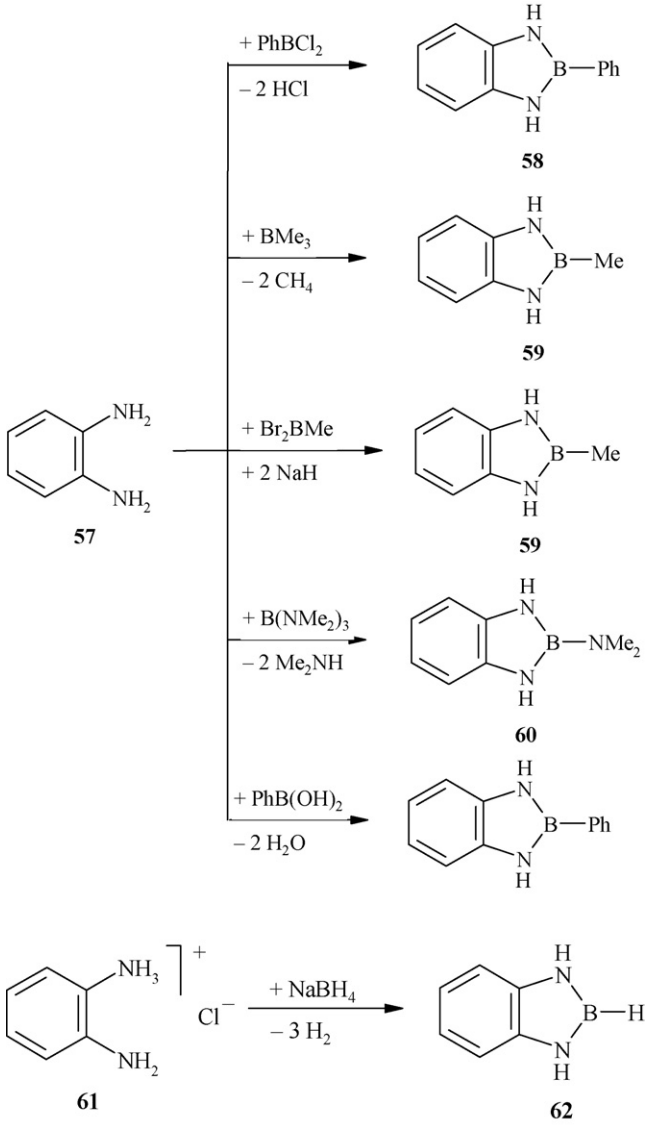
Compound	R
47, 51, 53	*t*Bu
50, 52, 54	2,6-$Me_2C_6H_3$

Scheme 16. Synthesis of **53** and **54**.



Scheme 17. Synthesis of **55**.

phenylene diamine **63** and BBr_3 underwent reaction in toluene in the presence of calcium hydride to give 2-bromo-1,3,2-benzodiazaborole **64** as colorless oil in 77% yield (Scheme 19) [31].



Scheme 18. Synthesis of 1,3,2-benzodiazaborolines from *o*-phenylene diamine.

Orange crystalline benzodiazaboroline, which is functionalized at boron by an osmium complex fragment resulted from the condensation of the dichloroboryl osmium complex **66** with 2 equiv. of *N*,*N*′-dimethyl-*o*-phenylene diamine in benzene (Scheme 19) [32]. Compounds **71**–**73** where two 1,3,2-benzodiazaboroline units are linked by a phenylene spacer are available by the cyclocondensation of the 2,5-bis(hexyloxy)-1,4-phenylene diboronic acid **68** with 2 equiv. of *o*-phenylene diamines **57**, **69** and **70** in boiling toluene, toluene–NEt_3 or toluene–DMF. Yields range from 65.8 to 78.1%. Similarly, the 1,3,2-naphthodiazaboroline **75** was prepared from **68** and 2,3-diaminonaphthalene **74** in refluxing toluene (71.3% yield) (Scheme 20) [33].

Compound **76** featuring a 4,4′-biphenyl spacer between two benzo-1,3,2-diazaboroline rings was synthesized by the cyclocondensation of 4,4′-bis(dibromoboryl)biphenyl **13d** with *N*,*N*′-diethylphenylenediamine in the presence of an excess of triethylamine in toluene at 60–80 °C. The product was isolated as colorless crystals in 58% yield (Scheme 21) [18].

Combination of 2 equiv. of **63** with the mixture of **13e** and 4 equiv. of NEt_3 in hexane and boiling the mixture for 3 h afforded product **77** as light-brown crystals (55% yield) (Scheme 21) [18].

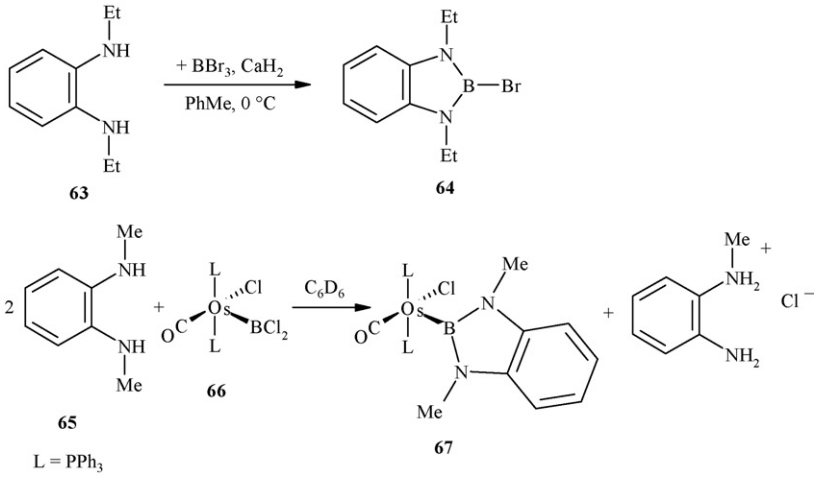
2.3. Synthesis by substitution reactions at the boron atom

In the preceding section synthetic pathways for the construction of the ring skeleton of a wide variety of 1,3,2-diazaborolines from different precursors are discussed. The replacement of good leaving groups such as halides or pseudohalides at the boron atom by nucleophiles opens the door to a plethora of novel diazaboroline derivatives.

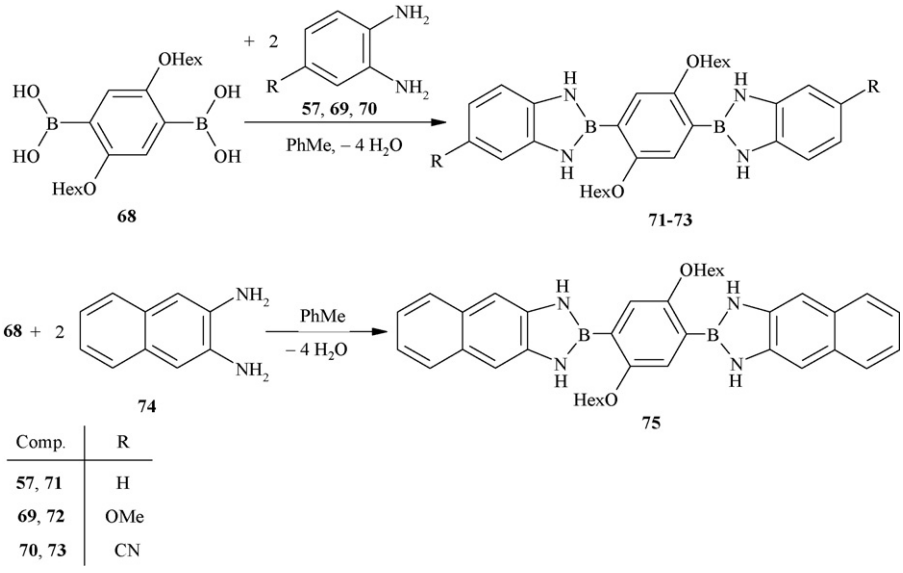
This section is organized by the nature of the nucleophile and the group of the contact atom in the periodic table.

2.3.1. Hydride

Reduction of (*S*)-**78** with lithium aluminium hydride in a THF/hexane mixture afforded the 2-hydro-1,3,2-diazaborole (*S*)-**79** as a yellow oil [15]. The yellow oily borohydride **80** was accessible in 79% yield by treatment of **49** and equimolar amounts of lithium aluminium hydride in the same solvent system (Scheme 22).

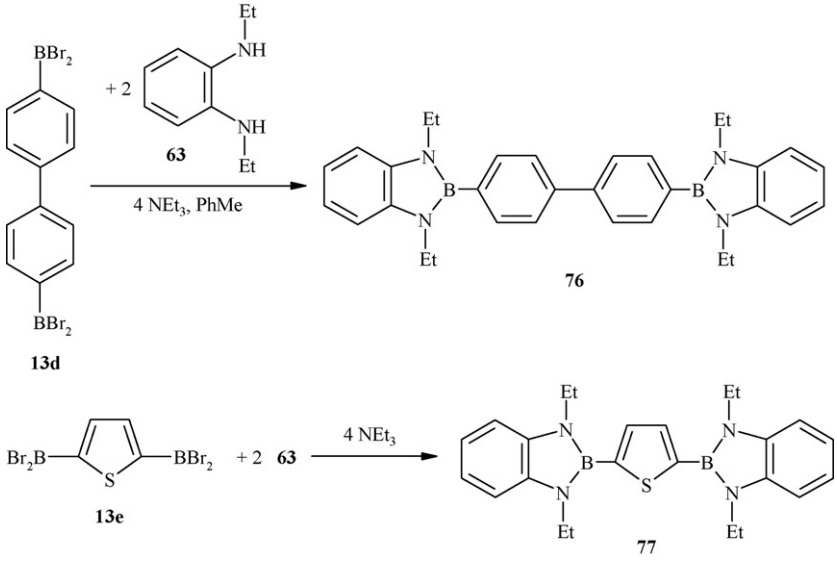


Scheme 19. Syntheses of **64** and **67**.

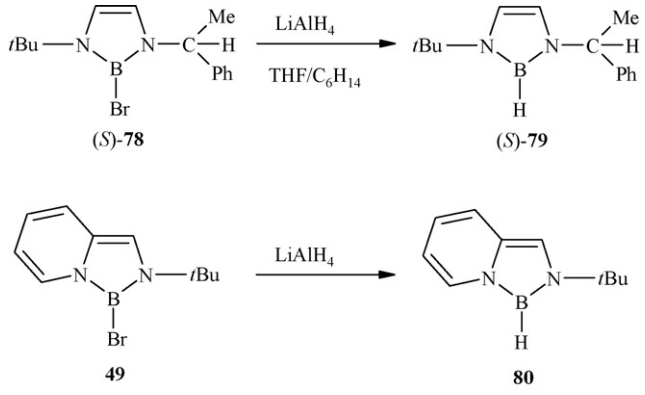


Comp.	R
57, **71**	H
69, **72**	OMe
70, **73**	CN

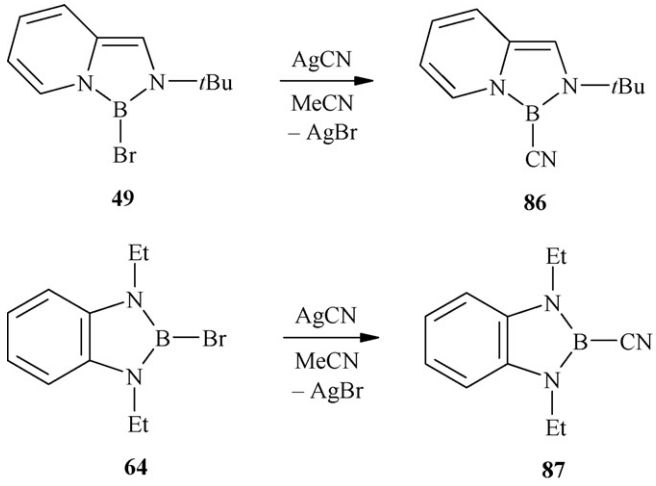
Scheme 20. Syntheses of 1,4-phenylene-bis(diazaborolines) **71**–**73** and **75**.



Scheme 21. Synthesis of **76** and **77**.



Scheme 22. $LiAlH_4$-reduction of compounds (*S*)-**78** and **49**.



Scheme 25. Preparation of bicyclic 2-cyano-1,3,2-diazaborolines.

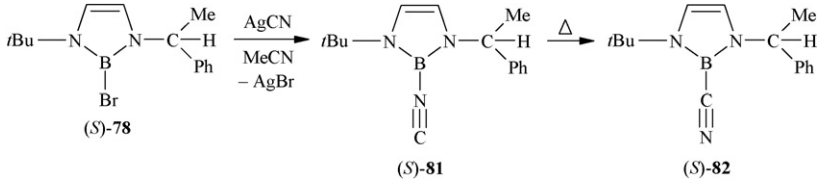
2.3.2. Group 14 nucleophiles

2.3.2.1. Carbon-based nucleophiles. The replacement of a halide substituent at the boron atom of 1,3,2-diazaborolines by the cyanide unit markedly enhances the thermostability of the ring systems. Hereby silver cyanide proved to be the reagent of choice. In most cases the resulting 2-cyano-1,3,2-diazaborolines display a similar chemical behavior as their halide counterparts. Reaction of chiral (*S*)-**78** with silver cyanide in acetonitrile for 1 h furnished a liquid mixture of 2-isocyano-1,3,2-diazaborole **81** and 2-cyano-1,3,2-diazaborole **82**, as evidenced by ^1H, ^{13}C NMR and IR-spectra of a freshly prepared sample. Vacuum distillation at 200 °C completely effected the rearrangement **81** → **82** and the pure cyano derivative was isolated as a colorless oil in 57% yield (Scheme 23) [15].

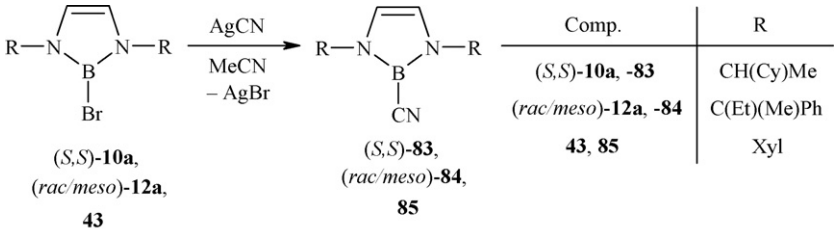
The highly functionalized crystalline 2-cyanoborolines (*S*,*S*)-**83** and the oily (*rac*/*meso*)-**84** were synthesized from 2-bromoboroles (*S*,*S*)-**10a** and (*rac*/*meso*)-**12a** and AgCN in 70 or 50% yield, respectively (Scheme 26) [16]. Thermolabile 2-chloro-1,3,2-diazaboroline **43** was in situ converted into stable **85** by treatment with AgCN during 20 h at room temperature (yield 41%) (Scheme 24) [22].

Bicyclic 2-bromo-diazaborolines were also susceptible to Br/CN-replacement. Thus cyano derivative **86** resulted from the metathesis reaction between **49** and silver cyanide in acetonitrile at room temperature in the absence of daylight. The compound was isolated by vacuum distillation as light yellow crystals in 73% yield [24]. Colorless oily **87** was synthesized analogously in 94% yield (Scheme 25) [31].

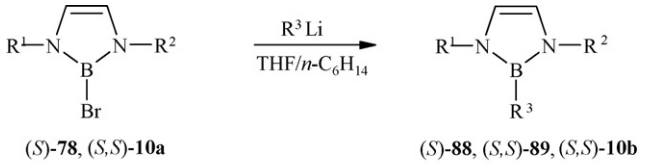
As previously discussed 2-alkyl-1,3,2-diazaborolines can be synthesized in high yield by reacting 1,4-diazabutadienes with alkyl-dibromoboranes and the subsequent reduction of the obtained borolium salts. An alternative approach to such species is based upon the nucleophilic substitution of good leaving groups at the boron atom of 1,3,2-diazaborolines by organolithium compounds. Here 2-bromo- as well as 2-cyano-1,3,2-diazaborolines proved to be equally useful. The reaction of 2-bromo-1,3,2-diazaboroline (*S*)-**78** with methyllithium in a mixture of hexane and tetrahydrofuran cleanly afforded (*S*)-**88** as a colorless oil after distillation (51%). Similarly the preparation of the 2-butyl-1,3,2-diazaboroline (*S*,*S*)-**89** was accomplished by treatment of (*S*,*S*)-**10a** with an excess of *n*-butyllithium in a hexane/THF mixture. Pure colorless oily **89** was obtained by distillation (47% yield). Compound (*S*,*S*)-**10a** was con-



Scheme 23. Synthesis of 2-cyano derivative (*S*)-**82**.



Scheme 24. Synthesis of (*S*,*S*)-**83**, (*rac*/*meso*)-**84** and **85**.



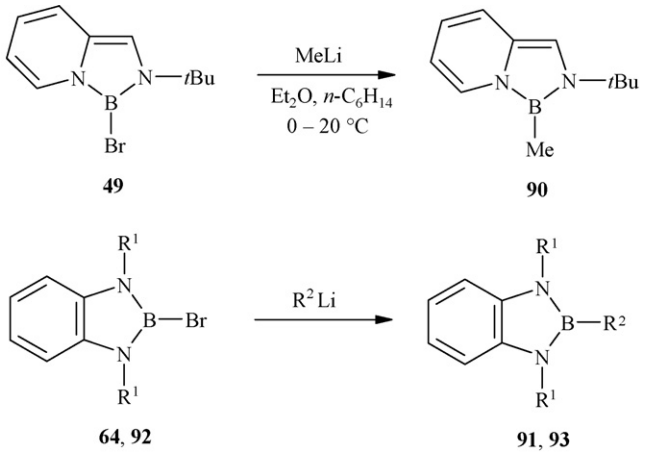
Comp.	R^1	R^2	R^3
(*S*)-**78**, **-88**	*t*Bu	CH(Me)Ph	Me
(*S,S*)-**10a**, **-89**	CH(Me)Cy	CH(Me)Cy	*n*Bu
(*S,S*)-**10b**	CH(Me)Cy	CH(Me)Cy	*i*Bu

Scheme 26. Synthesis of (*S*)-**88**, (*S,S*)-**89** and (*S,S*)-**10b**.

verted to the oily *iso*-butyl derivative (*S,S*)-**10b** by reaction with *iso*-butyllithium in a diethylether/THF mixture (61% yield) (Scheme 26) [15,16].

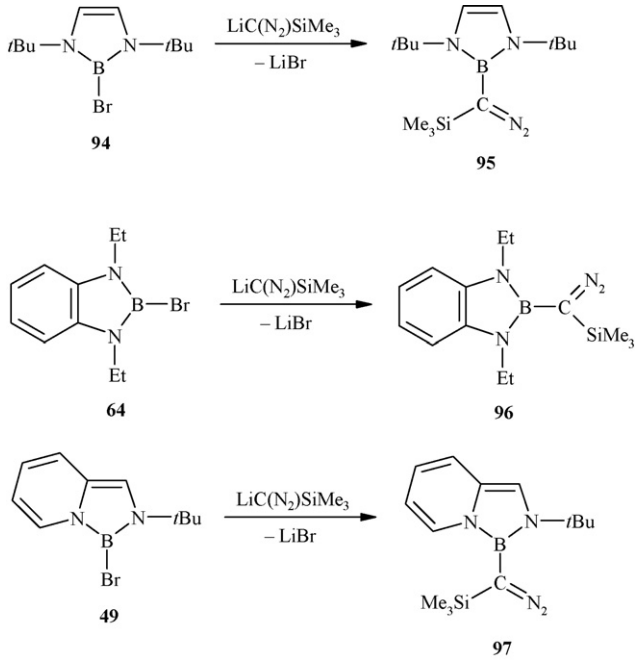
This protocol for the preparation of 2-alkyl-diazaborolines was also applied for fused systems. 2-Bromo-1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridine **49** and methyllithium underwent reaction in hexane–diethylether solution between 0 and 20 °C to generate the methylated heterocycle **90** as a yellow oil (Scheme 27) [24]. The methylation of **64** to give product **91** as a light red oil in 81% yield was realized by reaction with methyllithium in pentane–diethylether solution. Colorless prisms of compound **93** were obtained in 90% yield from the treatment of 2-bromo-1,3-di(isopropyl)benzo-1,3,2-diazaboroline **92** with *tert*-butyllithium in hexane at 0 °C [34] (Scheme 27).

Acyclic *C*-borylated diazomethanes are rare compounds. With the exception of $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{BC(N)}_2\mathrm{H}$ [35] they are thermolabile. The paucity of this class of compounds is presumably due to the ability of Lewis acids to initiate the decomposition of the diazoalkanes. The incorporation of the boron center into a diazaboroline ring greatly



Comp.	R^1	R^2
64, **91**	Et	Me
92, **93**	*i*Pr	*t*Bu

Scheme 27. Preparation of the bicyclic diazaborolines **90**, **91** and **93**.



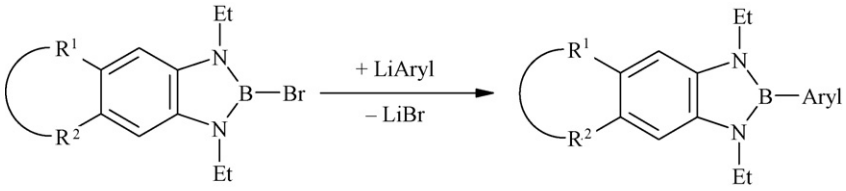
Scheme 28. Synthesis of 1,3,2-diazaborolinyl functionalized diazamethanes.

adds to the stability of *C*-boryldiazoalkanes. Reaction of lithio(trimethylsilyl)diazomethane and 1 equiv. of 1,3,2-diazaborolines **94**, **64** and **49** in hexane or hexane/toluene solutions in the temperature range −78 to 20 °C afforded the 1,3,2-diazaborolinyl(trimethylsilyl)diazomethanes **95**–**97** [36] in yields of 76–81%. Whereas compounds **95** and **96** are thermally robust enough to be purified by vacuum distillation, diazoalkane **97** decomposed under these conditions [36] (Scheme 28).

In a comparable way aryl- and heteroaryl substituted diazaborolines could be synthesized. Thienyl- and dithienyl rings were introduced as substituents at boron by the reaction of **64** with 2-thienyllithium and 2,2′-dithienyllithium in mixtures of diethyl ether and hexane to give benzodiazaboroles **98** and **99** in 62 or 57% yield, respectively [18]. Similarly, reaction of equimolar amounts of 2-bromo-1,3,2-naphthodiazaboroline **100** and thienyllithium in hexane at ambient temperature afforded compound **101** as colorless needles in 57% yield (Scheme 29).

In contrast to this, the reaction of **100** with 2-dithienyl lithium under comparable conditions gave only a few crystals of pure **102** after crystallizing the crude product from acetonitrile (Scheme 29) [18].

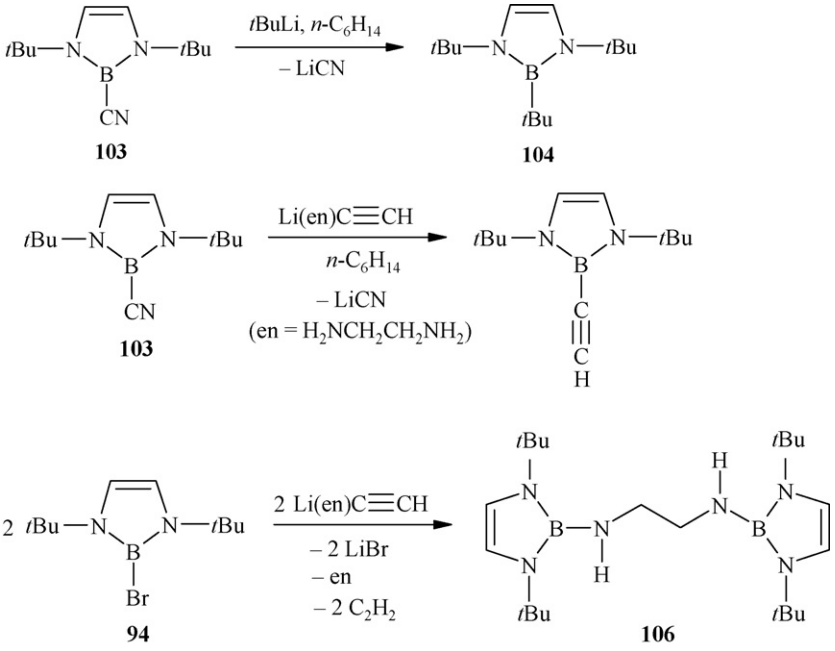
The cyano group at the boron atom may also be replaced by carbon nucleophiles. Previously, we found that *tert*-butyllithium and 2-cyano-1,3,2-diazaboroline **103** underwent reaction to give the 2-*tert*-butyl-1,3,2-diazaborole **104** in 88%, whereas the corresponding reaction with the bromo derivative **94** failed [13]. Moreover, cyano derivative **103** was converted in high yields into the 2-ethynyl-1,3,2-diazaboroline **105** by treatment with the ethylenediamine adduct of lithium acetylide. Thereby, the employment of the 2-cyano-1,3,2-diazaboroline was crucial since the bromo derivative **94** and the organolithium component gave rise to the formation of aminolysis product **106** instead of **105** (Scheme 30) [14].



64, **100** **98**, **99**, **101**, **102**

Comp.	R^1 R^2	Aryl
64, **98**	H, H	2-thienyl
99	H, H	2-dithienyl
100, **101**	–CH=CH–CH=CH–	2-thienyl
102	–CH=CH–CH=CH–	2-dithienyl

Scheme 29. Synthesis of 2-thienyl- and 2-dithienyl-functionalized diazaborolines.



103 **104**

103

94 **106**

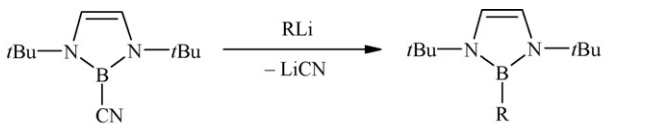
Scheme 30. Different reactivities of **94** and **103** towards *t*BuLi and Li(en)C≡CH.

These observation necessitated the study of the reactivity of 2-cyano-1,3,2-diazaborolines towards organolithiums in more detail [37].

Treatment of **103** with equimolar amounts of cyclopropyllithium, *i*-butyllithium and phenyllithium gave mirocrystalline **107** (91%), oily **108** (81%) and needles of **109** (89%) (Scheme 33) [37]. With isopropyllithium as a reagent things were somewhat different. Here the reaction with **103** in a 1:1 stoichiometry in hexane at −30 °C also gave rise to the 2-isopropyl derivative **110** as a light yellow oil in 61% yield (Scheme 31).

Treatment of cyano derivative **103** with isopropyllithium in a molar ratio 2:1 in hexane at −30 °C for 12 h, however, afforded the *C*,*N*-diborylated imine **111** as the main product. The compound was isolated as a red microcrystalline solid by distillation (60%). The isopropyl derivative **110** was formed as a minor product in only 10% yield (Scheme 32).

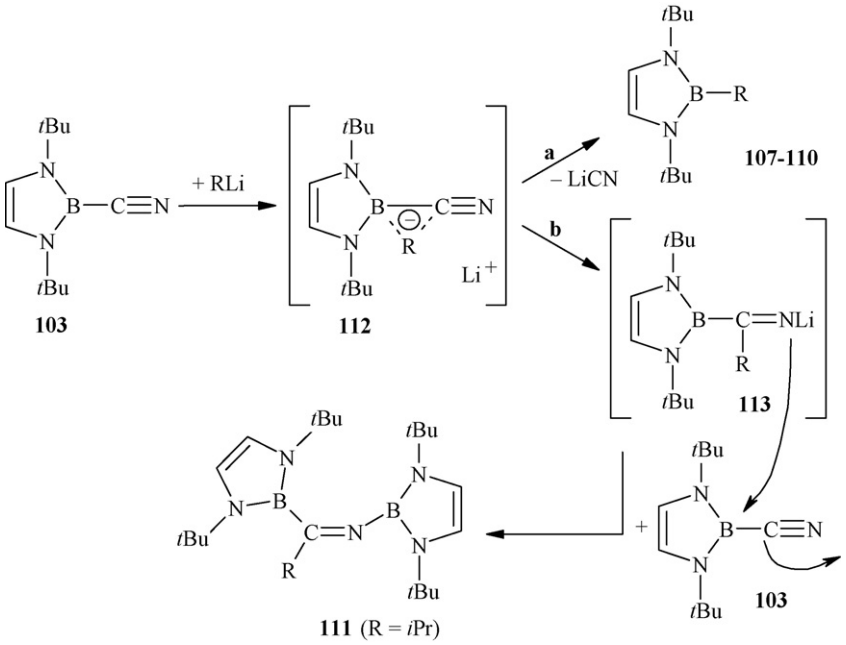
For the success of the formation of **111** obviously a 2:1 ratio of **103** and isopropyllithium and a reaction time of at least 12 h



103

107: R = *c*Pr; **108**: *i*Bu
109: Ph; **110**: *i*Pr

Scheme 31. Synthesis of **107**–**110** from **103** and organolithium reagents.



Scheme 32. Formation of **111**.

was crucial. In all other cases the increase of the amount of **103** employed was of no effect. Only, **107–110**, in addition to unreacted **103** were observed in the reaction mixtures. It is conceivable that the formation of **111** was initiated by the nucleophilic attack of the organolithium compound at the LUMO of **103** which is the π*BCN orbital to give a situation as depicted in **112**. Extrusion of LiCN on path **a** gave the substitution products **107–110**. The addition of the isopropyllithium to the CN function of **103** would lead to lithium imide **113**, the attack of which at the BC bond of a second molecule of **103** would furnish **111**. From a formal point of view **111** is the product of a diboration process at isopropyl cyanide [37].

2.3.2.2. Silicon-, germanium-, tin- and lead-based nucleophiles. When equimolar amounts of 2-bromobenzodiazaboroline **92** were added at −78 °C in THF or Et_2O to freshly prepared triphenylsilyl-, triphenylgermyl-, triphenylstannyl-, or triphenylplumbyl-lithium the 2-silyl-, 2-germyl-, 2-stannyl- and 2-plumbyl-1,3,2-benzodiazaborolines were generated as colorless solids in 40–86% yield [34] (Scheme 33).

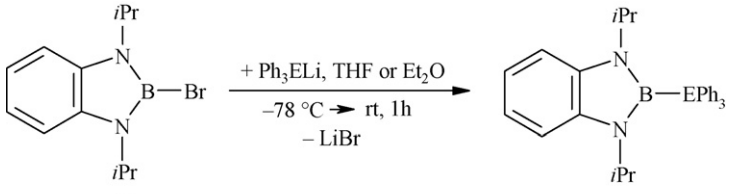
Colorless prisms of 2-trimethylstannyl-benzodiazaborole **118** were synthesized in 85% by treatment of freshly prepared trimethylstannyllithium with **92** in a THF/diethyl ether mixture in the range 0 °C to room temperature [34] (Scheme 34). Hexane solutions of the chiral diazaborolines (*S*,*S*)-**10a** or (*S*,*S*)-**11** were reacted with a slight excess of $LiSnMe_3$ in THF at 20 °C, whereupon the stannylated heterocycles (*S*,*S*)-**119** (58% yield) were formed as a colorless oil and (*S*,*S*)-**120** (67% yield) as a colorless crystalline compound [15] (Scheme 34).

2.3.3. Nitrogen-based nucleophiles

To increase the steric demand of chiral 1,3,2-diazaborolines bulky amino substitutents were introduced at the boron atom of the ring. Bromide replacement from (*S*)-**78** with an excess of *tert*-butylamine in hexane gave (*S*)-**121** as a yellow oil after vacuum distillation (74% yield) [15] (Scheme 35).

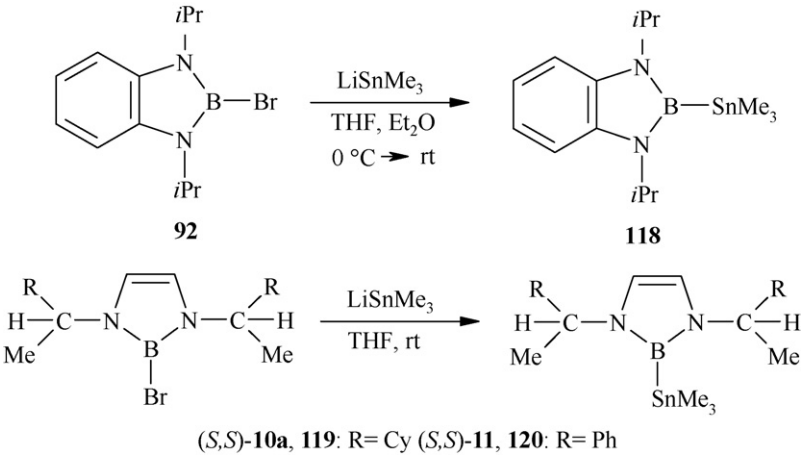
Liquid (*S*,*S*)-**122** resulted from the treatment of (*S*)-**78** with an equimolar amount of (*S*)-1-phenylethylamine in the presence of triethylamine (48% yield) [15].

The stable amino-functionalized 1,3,2-diazaboroline (*S*,*S*)-**123** resulted as a colorless liquid from the reaction of **10a**

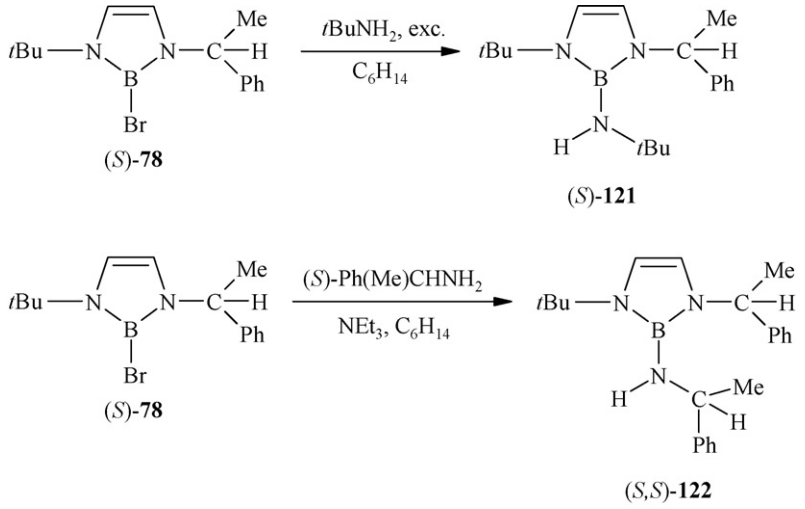


114:E = Si (62%); **115**: Ge (84%) **116**: Sn (86%); **117**: PB (40%)

Scheme 33. Preparation of **114–117**.

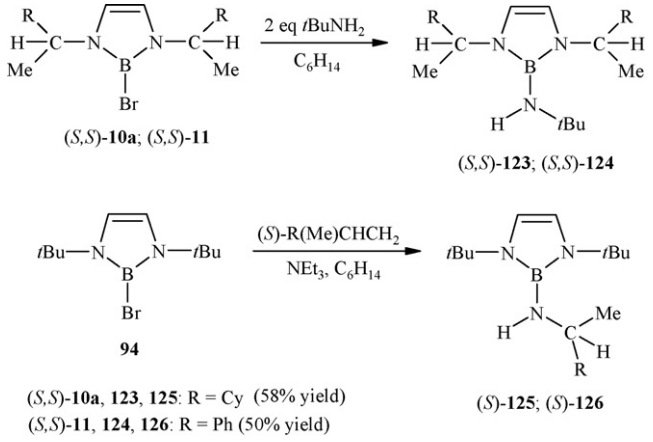


Scheme 34. Synthesis of 2-trimethylstannyl-1,3,2-diazaborolines **118–120**.



Scheme 35. Synthesis of 2-amino substituted 1,3,2-diazaboroles (*S*)-**121** and (*S*,*S*)-**122**.

with a twofold amount of *tert*-butylamine in hexane at 20 °C (58% yield). Similarly, the yellow liquid diazaboroline (*S*,*S*)-**124** was synthesized from (*S*,*S*)-**11** and *tert*-butylamine (50% yield) (Scheme 36) [15].



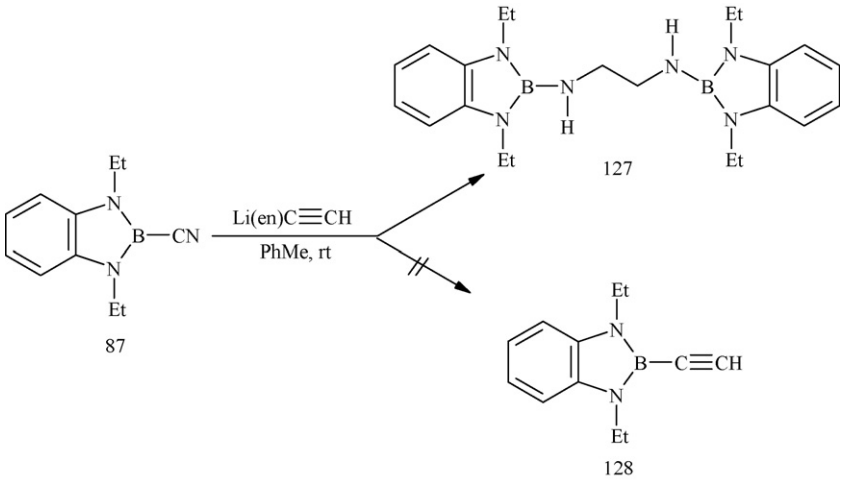
Scheme 36. Synthesis of chiral 1,3,2-diazaborolines **123–126**.

Oily colorless heterocycles (*S*)-**125** and (*S*)-**126** were formed by aminolysis of achiral **94** with chiral (*S*)-Cy(Me)CHNH$_2$ and (*S*)-Ph(Me)CHNH$_2$ in the presence of NEt$_3$ (72–74% yield) (Scheme 36) [15].

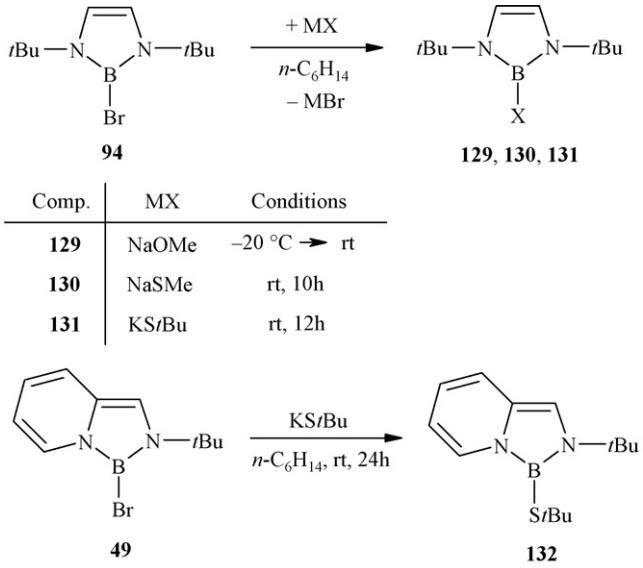
The combination of cyano derivative **87** and the ethylenediamine complex of lithium acetylide in toluene at 20 °C gave rise to the formation of the crystalline colorless aminolysis product **127** instead of the expected 2-ethynyl-1,3,2-diazaboroline **128** (Scheme 37) [31].

2.3.4. Oxygen- and sulfur-based nucleophiles

Stirring a hexane solution of diazaborole **94** with sodium methanolate between −20 °C and room temperature led to the generation of the colorless oily 2-methoxy-1,3,2-diazaboroline **129** in 66% yield (Scheme 38) [38]. The diazaborolinyl sulfanes **130** and **131** were accessible by the reaction of **94** with a slight excess of sodium methylthiolate or potassium *tert*-butylthiolate, respectively, in hexane. Compounds **130** and **131** are formed in 90 and 82% yield, respectively, as colorless solids. Similarly, yellow oily **132** was isolated in 63% yield from the reaction of



Scheme 37. Reaction of **87** with Li(en)C≡CH.

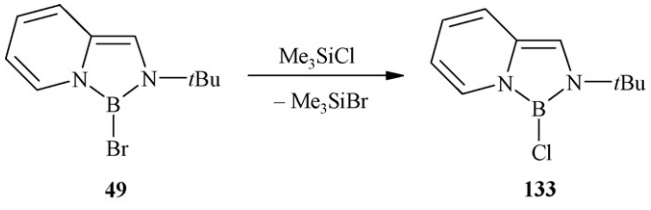


Scheme 38. Synthesis of the chalcogenolatodiazaborolines **129–132**.

49 with solid potassium *tert*-butylthiolate in hexane (Scheme 38) [38].

2.3.5. Halides

Treatment of **49** with a slight excess of chlorotrimethylsilane at 20 °C in hexane solution effected a clean Br/Cl exchange and chloro derivative **133** was isolated by vacuum distillation as a yellow oil in 95% yield (Scheme 39) [24].



Scheme 39. Synthesis of **133** by Br/Cl exchange with Me_3SiCl.

2.4. Insertion reactions

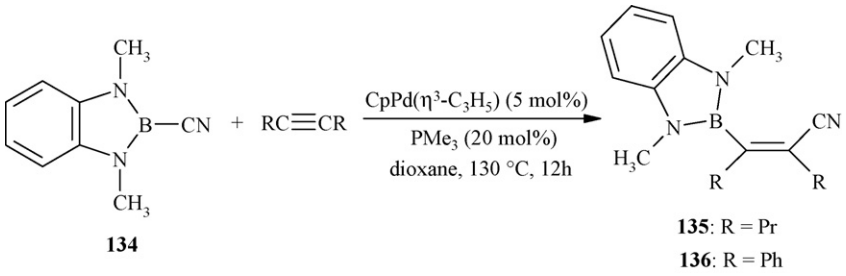
The variation of substituents at the boron atom of 1,3,2-diazaborolines is not restricted to nucleophilic substitution processes as discussed before. In a number of cases unsaturated organic molecules or low-valent and coordinatively unsaturated transition metal complexes may be inserted in the B–X bond of halo-, cyano- or trimethylstannyl-functionalized 1,3,2-diazaborolines giving rise to novel derivatives, which are not accessible by the standard routes. The regio- and stereoselective synthesis of α,β-unsaturated β-borolinyl nitriles **135** and **136** was devised by the palladium-catalyzed cyanoboration of 4-octyne and tolane with cyanoborolidine **134** in boiling dioxane in the presence of 5 mol% of $CpPd(\eta^3\text{-}C_3H_5)$ and 20 mol% of PMe_3. The yield determined by gas chromatography was nearly quantitative and underlines the efficiency of this transformation (Scheme 40) [39].

When the same type of reaction was applied to 3-phenylpropyne(2) a 83:17 mixture of the regioisomers **137** and **138** in a total yield of 96% was formed (Scheme 41) [39].

Generally, the major product was assigned as the isomer in which the cyano group is attached to the carbon atom α to the aryl group. Improved regioselectivites were observed for alkynes with bulky aryl groups and for boron heterocycles with bulky substituents at the ring nitrogen atoms. The treatment of 2-bromo-1,3,2-benzodiazaboroline **92** with a solution of $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ in toluene for 24 h gave rise to the generation of *trans*-bromo-(1,3-diisopropyl)-1,3,2-diazaborolin-2-yl-bis(triphenylphosphan)platinum(II) **139** as a brown solid in 76% yield (Scheme 42) [34].

From a formal point of view the coordinatively unsaturated complex fragment $[Pt(PPh_3)_2]$ was inserted into the B–Br-bond of the precursor. Colorless crystalline complex **140** was isolated from the reaction of the zerovalent platinum complex with 2-trimethylstannyl-1,3,2-diazaboroline **118** in toluene at ambient temperature for 3 d (Scheme 43) [34].

In contrast to this, the related 1,3,2-diazaborolines **114–117** did not react with the platinum complex [34].

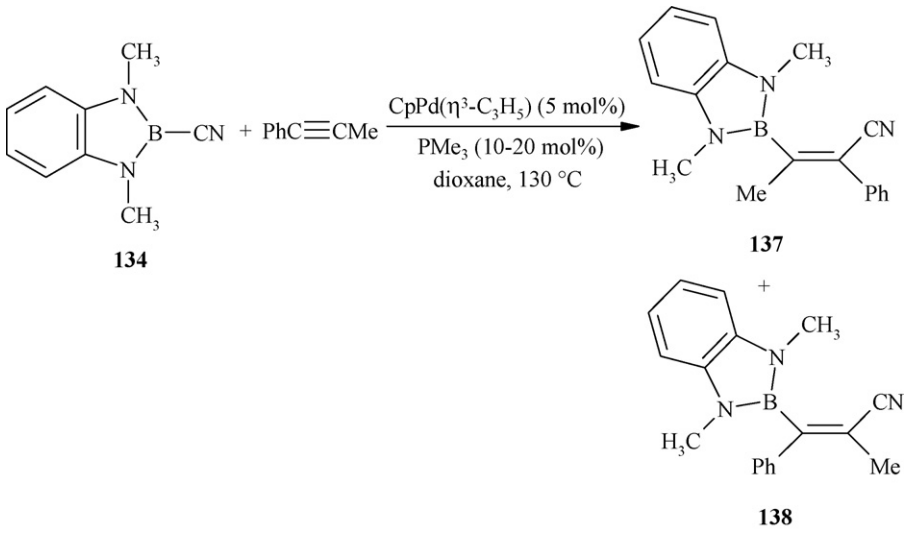


134

135: R = Pr

136: R = Ph

Scheme 40. Pd-catalyzed cyanoboration of 4-octyne and tolane.

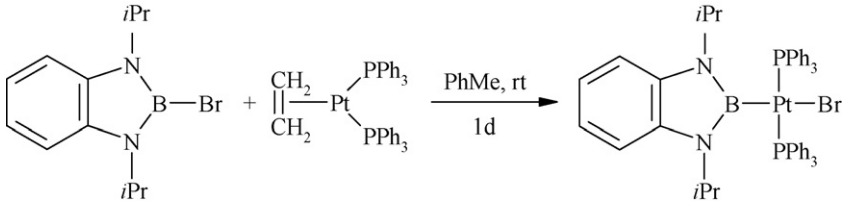


134

137

138

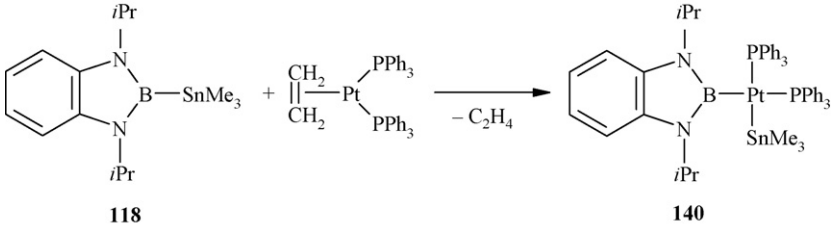
Scheme 41. Cyanoboration of 3-phenyl-propyne(2).



92

139

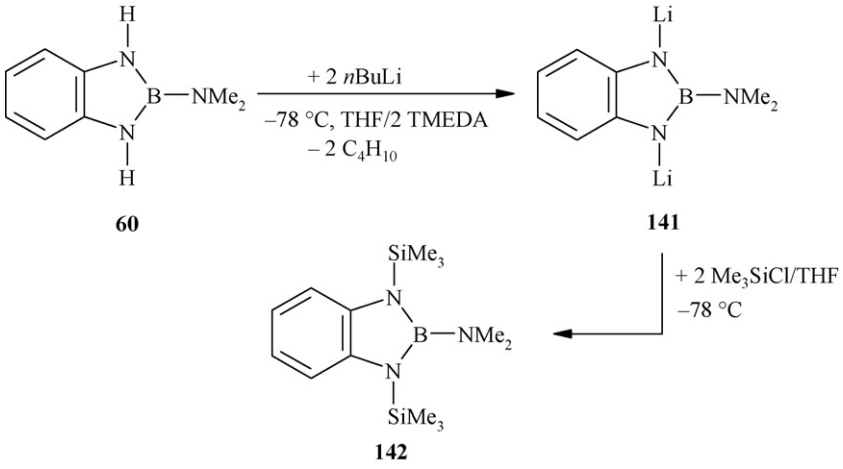
Scheme 42. Preparation of complex **139**.



118

140

Scheme 43. Preparation of **140**.



60 **141** **142**

Scheme 44. Two-fold silylation of **60**.

2.5. Miscellaneous

Chemical transformations at the nitrogen atoms in 1,3,2-diazaborolines are also conceivable. Double metallation of **60** by 2 equiv. of *n*-butyllithium at −78 °C occurred readily. At −60 °C compound **141** separated as a white solid from the mixture. Treatment of the precipitate with trimethylchlorosilane in THF in the range −78 to 20 °C resulted in the formation of **142** (Scheme 44) [40].

3. Physico-chemical and structural aspects of 1,3,2-diazaborolines

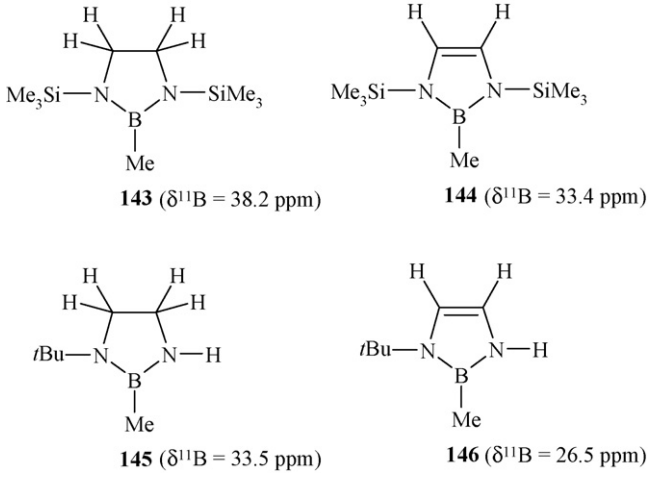
3.1. Spectroscopic data

3.1.1. NMR-studies

Inspection of the ^{11}B NMR-spectra of monocyclic 1,3,2-diazaborolines (Table 1) showed that the boron atoms in these heteroarenes are generally better shielded than those in the corresponding saturated 1,3,2-diazaborolidines. The high-field shifts $\Delta\delta$ [$\Delta\delta = \delta^{11}$B(borolidine)–$\delta^{11}$B(boroline)] range from 4.8 ppm in going from **143** to **144** [2,6] to 7.0 ppm in going from **145** to **146** [2,7] (Scheme 45).

The chemical shifts of 1,3,2-diazaborolines with alkyl or aryl-substituents at boron as well as alkyl groups at both nitrogen atoms range from $\delta = 25.3$ ppm (**18**, **21**) to $\delta = 28.4$ ppm in **12b** (av. 26.4 ppm, $\sigma = 0.79$). The ^{11}B NMR resonance of the *tert*-butyl derivative **104** ($\delta = 30.1$ ppm) appeared slightly deshielded. Significant high-field shifts were observed when the organic substituent at the boron atom were replaced by amino groups. Here the resonances were measured in the narrow range between $\delta = 21.6$ ppm in (*S*,*S*)-**122** to $\delta = 22.5$ ppm in (*S*,*S*)-**124**. Comparable chemical shifts were encountered in the 2-methoxy derivative **129** ($\delta = 22.1$ ppm) and the 2-alkylthiolato-1,3,2-diazaborolines **130** ($\delta = 23.3$ ppm) and **131** ($\delta = 21.9$ ppm). In the series *t*BuN–CH=CHN(*t*Bu)–BX the chemical shifts of the ^{11}B nuclei decrease in the series X = F ($\delta = 20.3$ ppm, **147**) ≈ Cl ($\delta = 20.2$ ppm, **148**) > Br ($\delta = 16.2$ ppm, **94**) > I ($\delta = 6.5$ ppm, **149**). The ^{11}B NMR resonances of chloro derivatives **29** ($\delta = 21.1$ ppm) and **37** ($\delta = 21.9$ ppm) and the bromo derivatives (*S*,*S*)-**10a** ($\delta = 18.2$ ppm) and **11** ($\delta = 19.0$ ppm) are similar. The corresponding signals in the 2-cyano-1,3,2-diazaborolines **103**, (*S*)-**82** and (*S*,*S*)-**83** range from $\delta = 11.6$ to 16.4 ppm. In *t*BuNCH=CH–N(*t*Bu)B–CN (**103**) ($\delta = 12.0$ ppm) the ^{11}B NMR signal is between those of the bromo- and iodo derivatives. Interestingly, the acetylide substituent in *t*BuN–CH=CH–N(*t*Bu)B–C≡CH (**150**) exerts a similar effect on the chemical shift of a diazaboroline ($\delta = 15.7$ ppm) like the bromo substituent in **94**. The ^{11}B shifts in the 2-hydrido-derivatives appear in the narrow range between $\delta = 18.9$ ppm in *t*BuN–CH=CH–N(*t*Bu)BH (**151**) and $\delta = 21.9$ ppm in XylN–CH=CH–N(Xyl)BH (**152**), and are thus close to the data in the 2-chloro-1,3,2-diazaborolines. For the coupling constants values between $^1J_{BH} = 146$–158 Hz were measured. The ^{11}B NMR resonances in the 2-trimethylstannyl derivative vary from $\delta = 25.8$ ppm ($^1J_{SnB} = 1031$ Hz) in *t*BuN–CH=CH–N(*t*Bu)BSnMe$_3$ (**153**) to $\delta = 30.8$ ppm ($^1J_{SnB} = 986$ Hz) in (*S*,*S*)-**119**.

The ^{11}B{^{1}H} NMR-spectra of the benzo-1,3,2-diazaborolines (Table 2) exhibit a similar trend than those

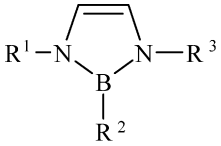


143 (δ^{11}B = 38.2 ppm) **144** (δ^{11}B = 33.4 ppm)

145 (δ^{11}B = 33.5 ppm) **146** (δ^{11}B = 26.5 ppm)

Scheme 45. ^{11}B NMR shifts of compounds **143**–**146**.

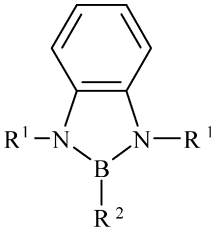
Table 1
^{11}B NMR and relevant ^{1}H and ^{13}C NMR data of selected monocyclic 1,3,2-diazaborolines



Compound	R^1	R^2	R^3	δ^{11}B	δ^{1}H (*CH*)	^{13}C (*CH*)	Reference
9	*t*Bu	CH_2SiMe_3	*t*Bu	26.4	6.31	113.1	[16]
(*S*,*S*)-**10a**	Me(Cy)HC	Br	Me(Cy)HC	18.2	6.17	113.5	[15]
(*S*,*S*)-**10b**	Me(Cy)HC	*i*Bu	Me(Cy)HC	26.7	6.21	112.3	[16]
(*S*,*S*)-**10c**	Me(Cy)HC	CH_2SiMe_3	Me(Cy)HC	26.9	6.19	112.4	[16]
11	Me(Ph)HC	Br	Me(Ph)HC	19.0	6.13	114.6	[15]
(*rac*/*meso*)-**12a**	Me(Et)(Ph)C	Br	Me(Et)(Ph)C	19.0	6.25	115.2	[16]
(*rac*/*meso*)-**12b**	Me(Et)(Ph)C	CH_2SiMe_3	Me(Et)(Ph)C	28.4	6.22	114.5	[16]
15a	*t*Bu	1,4-C_6H_4	*t*Bu	25.9	6.45	113.0	[17]
15b	*t*Bu	1,3-C_6H_4	*t*Bu	25.8	6.47	112.7	[17]
15c	*t*Bu	1,3,5-C_6H_3	*t*Bu	25.8	6.49	112.8	[17]
15d	*t*Bu	4,4′-C_6H_4-C_6H_4	*t*Bu	25.9	6.48	112.9	[17]
15e	*t*Bu	2,5-C_4H_2S	*t*Bu	23.5	6.48	112.9	[18]
18	*t*Bu	Fc	*t*Bu	25.3	6.42	112.7	[21]
21	*t*Bu	Fc′	*t*Bu	25.3	6.39	112.9	[21]
24	*t*Bu	3-Me-$C_5H_3Mn(CO)_3$	*t*Bu	23.2	6.34	113.7	[21]
29	Xyl	Cl	Xyl	21.1	5.85	117.7	[22]
37	Mes	Cl	Mes	21.9	5.92	117.8	[22]
(*S*)-**79**	*t*Bu	H	Me(Ph)HC	19.4, J_{BH} = 146 Hz	6.15d/6.40d, J = 2.0 Hz	114.4/116.2	[15]
(*S*)-**82**	*t*Bu	CN	Me(Ph)HC	11.6	6.25d/6.40d, J = 2.3 Hz	114.8/116.1	[15]
(*S*,*S*)-**83**	Me(Cy)HC	CN	Me(Cy)HC	16.4	5.98	115.7	[16]
(*rac*/*meso*)-**84**	Me(Et)(Ph)C	CN	Me(Et)(Ph)C	13.5	5.83/5.84	116.95/117.05	[16]
(*S*)-**88**	*t*Bu	Me	Me(Ph)HC	26.2	6.32d/6.48d, J = 2.5 Hz	111.1/113.5	[15]
(*S*,*S*)-**89**	Me(Cy)HC	*n*Bu	Me(Cy)HC	26.4	6.19	112.4	[15]
94	*t*Bu	Br	*t*Bu	16.2	6.27	113.6	[11]
95	*t*Bu	$C(N_2)SiMe_3$	*t*Bu	21.0	6.32	113.9	[36]
103	*t*Bu	CN	*t*Bu	12.0	6.14	114.6	[12]
104	*t*Bu	*t*Bu	*t*Bu	30.1	6.32	113.6	[13]
105	*t*Bu	C≡CH	*t*Bu	15.7	6.25	112.8	[13]
107	*t*Bu	*c*Pr	*t*Bu	27.3	6.23	112.3	[37]
108	*t*Bu	*i*Bu	*t*Bu	26.7	6.32	113.2	[37]
109	*t*Bu	Ph	*t*Bu	26.4	6.36	112.9	[37]
110	*t*Bu	*i*Pr	*t*Bu	27.4	6.31		[37]
111	*t*Bu	*i*PrC═N	*t*Bu	21.8/24.0	6.31/6.36	112.5/113.7	[37]
(*S*,*S*)-**119**	Me(Cy)HC	$SnMe_3$	Me(Cy)HC	30.8, J_{SnB} = 986 Hz	6.37	115.4	[15]
(*S*,*S*)-**120**	Me(Ph)HC	$SnMe_3$	Me(Ph)HC	28.2, J_{SnB} = 994 Hz	6.38	116.4	[15]
(*S*)-**121**	*t*Bu	NH*t*Bu	Me(Ph)HC	22.3	5.93d/6.25d, J = 2.8 Hz	109.6/113.0	[15]
(*S*,*S*)-**122**	*t*Bu	NHCH(Ph)Me	Me(Ph)HC	21.6	5.86d/6.13d, J = 2.6 Hz	109.2/111.9	[15]
(*S*,*S*)-**123**	Me(Cy)HC	NH*t*Bu	Me(Cy)HC	22.1	5.95	110.6	[15]
(*S*,*S*)-**124**	Me(Ph)HC	NH*t*Bu	Me(Ph)HC	22.5	6.12	111.9	[15]
(*S*)-**125**	*t*Bu	NHCH(Cy)Me	*t*Bu	22.0	6.06	110.0	[15]
(*S*)-**126**	*t*Bu	NHCH(Ph)Me	*t*Bu	22.3	6.19	111.3	[15]
129	*t*Bu	OMe	*t*Bu	22.1	6.12	111.5	[38]
130	*t*Bu	SMe	*t*Bu	23.3	6.35	113.4	[38]
131	*t*Bu	S*t*Bu	*t*Bu	21.9	6.43	114.8	[38]
180	2,6-*i*Pr$_2$C$_6$H$_3$	Li(DME)	2,6-*i*Pr$_2$C$_6$H$_3$	45.4	6.22	119.3	[58]

of its monocyclic congeners. With an identical substitution pattern the shielding of the ^{11}B nuclei increase in the series δ = 29.7 (X = Me, **91**) > 28.6 (4,4′-biphenyl, **76**) > 26.6 (2,5-C_4H_2S, **77**) = 26.6 (2-thienyl, **98**) > 26.2 (5,2,2′-dithienyl, **99**) > 23.1 (HN(CH_2CH_2)NH, **127**) > 22.8 (Br, **64**) > 15.7 (CN, **87**). Generally, the annulation of a benzogroup to the 1,3,2-diazaboroline unit led to a deshielding of the ^{11}B signals in comparison to the related monocyclic species. In the series with isopropyl substituents in the 1,3-positions the ^{11}B NMR data show a deshielding of the ^{11}B nucleus as the atomic weight of the group 14 element increases. Similar influences of the substituent on the shielding of the boron center in 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridines were registered (Table 3). ^{11}B NMR resonances decrease in the order δ = 23.9 (X = Me, **90**) > 19.9 (S*t*Bu, **132**) > 19.4 [$C(N_2)SiMe_3$, **97**] > 18.0 (F, H, **53** and **80**) > 17.9 (Cl, **133**) > 14.8 (Br, **49**) > 8.9 (CN, **86**).

Table 2
^{11}B NMR and ^{13}C NMR data of selected benzo-1,3,2-diazaborolines



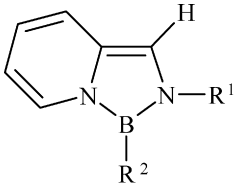
Compound	R^1	R^2	δ^{11}B	δ^{13}C(N–C=C–N)	Reference
64	Et	Br	22.8	136.7	[31]
76	Et	4,4′-C_6H_4–C_6H_4	28.6	141.4	[18]
77	Et	2,5-C_4H_2S	26.6	137.6	[18]
87	Et	CN	15.7	136.2	[31]
91	Et	Me	29.7	137.7	[31]
93	*i*Pr	*t*Bu	29.5	136.6	[34]
96	Et	$C(N_2)SiMe_3$	26.4	137.8	[36]
98	Et	2-C_4H_3S	26.6	133.7	[18]
99	Et	5-2,2′-dithienyl	26.2	n.o.	[18]
114	*i*Pr	$SiPh_3$	29.9	–	[34]
115	*i*Pr	$GePh_3$	30.5	–	[34]
116	*i*Pr	$SnPh_3$	32.4	–	[34]
117	*i*Pr	$PbPh_3$	39.6	–	[34]
118	*i*Pr	$SnMe_3$	32.8	–	[34]
127	Et	$HN(CH_2)_2NH$	23.1	138.1	[31]
139	*i*Pr	$Pt(PPh_3)_2Br$	27.9	138.1	[34]
140	*i*Pr	$Pt(PPh_3)_2(SnMe_3)$	44.7	–	[34]
142	$SiMe_3$	NMe_2	32.0	142.0	[40]

The hydrogen atoms at the ring carbon atoms in the symmetrically substituted diazaborolines with alkyl groups at the ring nitrogen atoms range from $\delta = 5.95$ ppm in (*S*,*S*)-**123** to 6.49 ppm in **15c**. The $^{13}C\{^1H\}$ NMR signals of the 1,3,2-diazaborolines with *N*-alkyl-substituents vary from $\delta = 110.0$ ppm in (*S*)-**125** to $\delta = 116.4$ ppm in (*S*,*S*)-**120**. In the *N*-arylated compounds **29** and **37** the corresponding resonances were observed at $\delta = 117.7$ and 117.8 ppm. These NMR spectroscopic results are considered as evidence for the heteroaromaticity of diazaborolines.

3.1.2. UV–vis and fluorescence spectra

Three-coordinate luminescent organoboron compounds are an important class of molecules because of their potential applications in advanced materials. Conjugation of the vacant $2p_z$-orbital on the boron center with the π^* orbital of the attached

Table 3
^{11}B NMR data of selected 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridines



Compound	R^1	R^2	δ^{11}B	$\delta^{13}CHNR^1$	$\delta^{13}CNR^1$	Reference
49	*t*Bu	Br	14.8	6.31	104.5	[24]
53	*t*Bu	F	18.0	6.14	99.7	[24]
54	Xyl	F	17.9	5.96	103.1	[24]
56	*t*Bu	Fc	23.9	6.47	105.1	[21]
80	*t*Bu	H	18.0d, $J_{BH} = 155$ Hz	6.34	104.5	[24]
86	*t*Bu	CN	8.9	6.12	106.1	[21]
90	*t*Bu	CH_3	23.9	6.45	103.5	[21]
97	*t*Bu	$C(N_2)SiMe_3$	19.4	6.36	–	[36]
132	*t*Bu	S*t*Bu	19.9	6.67	106.1	[21]
133	*t*Bu	Cl	17.9	6.46	103.7	[21]

Table 4
Photophysical data of **15c**, **13d**, **15d**

Compound	Solvent	Absorption, λ_{max} (nm)	Emission, λ_{max} (nm)[a]	Stokes shift, λ (nm)
15c	Hexane and THF	287	381	94
13d	Hexane	282	338	56
13d	THF	282	372	92
15d	Hexane	276	326	50
15d	THF	274	393	119

[a] $[c] = 1 \times 10^{-5}$ to 1×10^{-6} M L^{-1}.

Table 5
Photophysical data of the thienylborolines **98**, **99**, **101** and the bis(diazaborolines) **76** and **77** in THF

Compound	Absorption, λ_{max} (nm)	Emission, λ_{max} (nm)	$\phi_{abs.}$ (%)	Stokes shift (nm)
98	296	382	–	86
99	326	433	29	107
101	341	371	18	30
76	304	427	52	123
77	316	404	59	88

organic π-system proved to be responsible for some outstanding properties such as unique absorption and emission characteristics, a low reduction potential susceptible to doping as well as high electron-transporting abilities [41]. In the past, heavily substituted triarylboranes have been investigated for this purpose [42,43].

Solutions of benzo- and naphtho-1,3,2-diazaboroles **71**–**73** and **75** showed absorption peaks around 350 nm in their UV spectra. Compounds **71** and **73** exhibited violet emission (**71**: λ_{em}/nm = 370, 389, 405; **73**: 378, 389) using 340 nm as an excitation wavelength. Interestingly the emission maximum of **72** was observed around 438 nm which corresponds to the blue region. The absorptions (λ_{max} = 357 nm) and emissions of **75** (λ_{em}/nm = 376, 395, 417) compare well with those of **71**. Quantum yields ϕ range from 0.78 ± 0.03 to 0.99 ± 0.01 (relative to *p*-terphenyl in cyclohexane with ϕ = 0.92 at 303 nm as the excitation wavelength) [33].

The bis(borolinyl) systems **15a** and **15b** with a phenyl ring between each heterocyclic unit do not show luminescence. The UV–vis maxima of these compounds range from 245 to 252 nm, whereas the UV–vis absorption of **15c**, is shifted bathochromically to 287 nm. **15c** exhibits a moderate blue luminescence at 381 nm (Table 4).

The position of the absorption band is independent of the solvent. The optical behavior of the biphenyl derivatives **13d** and **15d** is much more pronounced. They display absorption peaks around 280 nm and a blue luminescence. When the solvent is changed from hexane to THF the emission band is shifted to a longer wavelength, whereby this tendency is most evident for **15d** ($\Delta\lambda$ = 67 nm). The Stokes shifts range from 56 nm (**13d**) to 119 nm (**15d**) in THF. Generally this shift is less pronounced in hexane. Such a solvatochromism was rationalized by the stabilization of a polar excited state by the polar solvent [17].

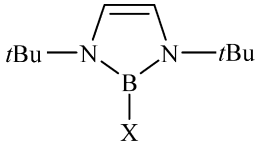
Compounds **76**, **77**, **98**, **99** and **101** exhibit blue luminescence under ultraviolet radiation (Table 5). The absorption maxima range from 296 nm (**98**) to 341 nm (**101**), and the emission maxima from 371 nm (**101**) to 433 nm (**99**). As expected, the molecule with the smallest π-conjugated system **98** exhibits maximum absorption at the shortest wavelength compared to the other systems. Enlargement of the π-system at the backbone of the benzodiazaboroline leads only to a bathchromic shift of the maximum absorption but not to that of emission. This fact leads to the extremely small Stokes shift of compound **101** (30 nm) in comparison to **98** (86 nm). Extending the π-system by using dithiophene instead of thiophene as a substituent at the boron atom effects a bathchromic shift of the maximum absorption from 296 to 326 nm as well as that of the emission from 382 to 433 nm. The optical behavior of the bis(diazaborolines) **77** and **76** is even more pronounced. They show absorption maxima at 316 and 304 nm and emission maxima at 404 and 427 nm. Both of them have quantum yields higher than the standard coumarin 120 (ϕ = 0.50).

Meanwhile it is a matter of common knowledge that the vacant p_z-orbital of boron makes conjugation with organic π-systems possible. Recent investigations have shown that three-coordinate boron can serve as a fluoride-sensor simply by the fact that the fluoride ion occupies the vacant p_z-orbital. If the systems under discussion possess a fully conjugated π-system which includes the p_z-orbital of the boron, fluoridation should lead to a change in absorption and emission properties. In keeping with this, compounds **98** and **99** give a clear fluorescence in THF under UV radiation. After addition of nBu$_4$NF the emission bands of both compounds decrease drastically (Scheme 47). The $^{11}B\{^1H\}$ NMR signal of the fluoride-adduct of **98** appears at δ = 3.4 ppm and its $^{19}F\{^1H\}$ NMR resonance at δ = −132.1 ppm. The corresponding data for the F^--adduct of **99** are $\delta^{11}B$ = 3.3 ppm and $\delta^{19}F$ = 132.2 ppm. For the equilibrium constant of adduct formation between **98** and tetrabutylammonium fluoride in $CDCl_3$ at 20 °C a value of 5.2×10^{-4} mol L^{-1} was determined by ^{19}F NMR spectroscopy. Removal of fluoride by the addition of $BF_3{\cdot}OEt_2$ leads to an increased intensity of the emission bands nearly to its original values [18].

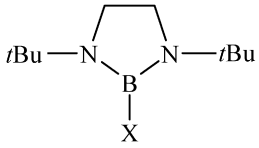
3.1.3. He(I) photoelectron spectra

He(I) photoelectron spectra were recorded for selected diazaborolines tBuN–CH=CH–N(tBu)BX [X = Me (**154**), H (**151**), SMe (**130**), Br (**94**), CN (**103**)] and diazaborolidines tBuNCH$_2$CH$_2$N(tBu)BX [X = Me (**155**), H (**156**), SMe (**157**), Br (**158**)] in order to determine their electronic properties and estimate the effect of substitution of the boron atom on the energetic position of the different molecular orbitals (MOs) (Table 6) [44]. The PE spectrum of **151** presents two first bands at 7.4 and 8.8 eV and a broad peak with a shoulder at 11.1 eV. The PE spectrum of its saturated analogue **156** displays two first bands at 7.4 and 9.4 eV and the corresponding shoulders at 10.6 and 11.5 eV. For **94** four first bands at 7.4, 9.0, 9.8 and 10.4 eV are clearly distinguished, whereas the PE spectrum of **158** presents three first ionizations at 7.7, 9.2 and 9.8 eV. For the diazaborolines of this study, the first ionization potential corresponds mainly to the bonding combination of the nitrogen lone pairs ($n^+_N\pi$) delocalized in the p-boron vacant orbital (π^*_{NBN}) in antibonding

Table 6
First ionization potentials of selected 1,3,2-diazaborolines and 1,3,2-diazaborolidines in eV



94, **103**, **130**, **151**, **154**



155 – 158

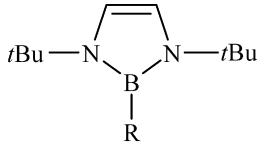
	Compounds								
	154	**130**	**151**	**94**	**103**	**155**	**156**	**157**	**158**
X	Me	SMe	H	Br	CN	Me	SMe	H	Br
1.IP	7.1	7.3	7.4	7.4	7.7	7.3	7.4	7.4	7.7

interaction with the $\pi_{C=C}$ orbital. The nature of the second ionization potential (third for **130**) with the $\pi_{C=N}{}^{-}$ orbital which is due to the antibonding nitrogen lone pairs combination in interaction with the $\pi^{*}_{C=C}$ orbital. For **130** the second IP corresponds to the ionization of the σ sulfur lone pair. The lowest value of IP is obtained for the methyl-substituted diazaboroline **154** (7.1 eV); the highest ones are observed for the cyano derivative **103** (7.7 eV) and the 2-bromoborolidine **158** (7.7 eV). For **156** the first ionization potential at 7.4 eV corresponds to the nitrogen anti-bonding combination of lone pair ($n^{-}{}_{N}\pi$) and the band at 9.4 eV to the nitrogen bonding combination of lone pair ($n^{+}{}_{N}\pi$). The first ionization potential of **158** at 7.7 eV is assigned to the removal of an electron from the $n^{-}{}_{N}\pi$ orbital in interaction with the bromine π lone pair ($n^{+}{}_{N}\pi$–$n_{Br}\pi$).

3.2. Electrochemistry

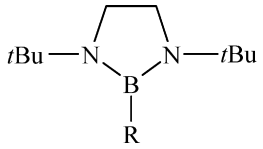
Inspection of the cyclovoltammograms of selected 1,3,2-diazaborolines **94**, **103**, **129**, **130**, **153**, **154**, **159** and **160** show a significant irreversible oxidation signal (Table 7), whereas in all cases no reductive waves were observed up to −3.0 V. The oxidation potentials vary strongly with the substituents at the boron atom. These trends can be rationalized by the donor/acceptor qualities of the respective substituent. Thus, the amino group as well as the methoxy group function essentially as π-donors toward the boron–nitrogen heterocycle, whereas bromide and cyanide have to be considered as acceptors. In keeping

Table 7
Oxidation potentials of 1,3,2-diazaborolines **94**, **103**, **129**, **130**, **153**, **154**, **159**, **160** in CH_2Cl_2 vs. Fc/Fc^{+}



	Compounds								
	159	**129**	**154**	**160**	**151**	**130**	**153**	**94**	**103**
R	NH_2	OMe	Me	NMe_2	H	SMe	$SnMe_3$	Br	CN
E_{ox} (mV)	−288	−58	124	158	310	354	396	576	752

Table 8
Oxidation potentials of 1,3,2-diazaborolidines **155–158** and **161–165** in CH_2Cl_2 vs. Fc/Fc^{+}



	Compounds								
	161	**162**	**155**	**163**	**157**	**156**	**164**	**158**	**165**
R	NH_2	OMe	Me	NMe_2	H	SMe	$SnMe_3$	Br	CN
E_{ox} (mV)	280	516	592	418	662	790	754	993	1164

with this, the observed potentials are anodically shifted in the order **159** (−288 mV) < **129** (−58 mV) < **154** (124 mV) < **160** (158 mV) < **151** (310 mV) < **130** (354 mV) < **153** (396 mV) < **94** (576 mV) < **103** (752 mV). For comparison the electrochemical oxidation of the saturated diazaborolidines **155–158** and **161–165** with an identical substitution pattern were investigated (Table 8).

A situation analogous to that with the unsaturated diazaborolines was encountered. The oxidation process is irreversible and the potentials vary in the same way with the substituents at the boron center. The compounds are less easily oxidized within the series **161** (280 mV) < **163** (418 mV) < **162** (516 mV) < **155** (592 mV) < **157** (662 mV) < **164** (754 mV) < **156** (790 mV) < **158** (993 mV) < **165** (1164 mV). It is obvious that the potentials of the 1,3,2-diazaborolidines are anodically shifted by 260–566 mV. This observation was rationalized by the fact that the nature of the HOMO is different in both classes of heterocycles [44].

The cyclovoltammograms of **71–73** and **75** were measured in DMF at 298 K versus a Fc/Fc^{+}-standard. No significant reduction waves were observed and the order of the oxidation potentials was **72** (180 mV) < **71** (460 mV) < **73** (756 mV), which could be related to the substituents at the fused aromatic unit. The oxidation potential of compound **75** (500 mV) was close to that of **71** [33].

In order to test a conceivable electronic communication between the diazaboroline units via the π-electron system in **15a–15d** cyclic voltammograms were recorded. Only one oxidative wave was observed for **15a** (180 mV), **15b** (168 mV) and **15c** (198 mV) which excludes any significant electronic communication via the π-system. In contrast to this, two irreversible waves were observed for **15d** (245 and 1066 mV). The strong luminescence and the electrochemical behavior of this species was taken as evidence for interaction and π-conjugation between the heterocycles [17].

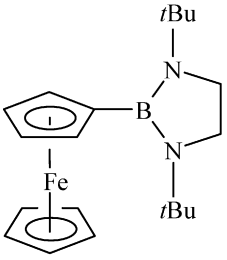
The mono- and dithienyl-substituted 1,3,2-diazaborolines **98**, **99** as well as the thienyl- and the biphenyl-bridged bis(diazaborolines) **76** and **77** were also oxidized by cyclovoltammetry to find out how the oxidation potentials are influenced by the substitution pattern at the boron atom, and whether or not these species give rise to reversible cyclic voltammograms. All cyclovoltammograms show a clean irreversible oxidative wave with increasing potentials in the

Table 9
Voltammetric data of ferrocenyl- and methylcymantrenyl-functionalized diazaborolines and diazaborolidines vs. Fc/Fc^+ standard

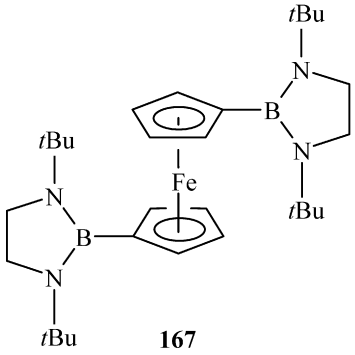
Compounds	E^0 (mV)
18	−180
21	−340
24	210
166	−110
167	−200
168	490

series **98** (435 mV) < **99** (510 mV) < **77** (589 mV) < **76** (867 mV) [18].

For similar reasons the ferrocenyl- and methylcymantrenyl-functionalized diazaborolines **18**, **21** and **24** and their saturated congeners **166–168** were also investigated by cyclic voltammetry, whereby on higher scan rates quasi-reversible Fe^{2+}/Fe^{3+} oxidations were observed (Table 9):



166

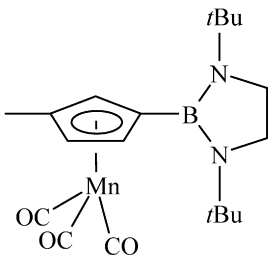


167

From these data it is obvious that the diazaboroline and the diazaborolidine groups transfer electron density onto the redox-active center of the ferrocene unit. The diborolinylated ferrocene **21** is more easily oxidized ($E^{0I} = -340$ mV) than the monoborolinidylated analogue **18** ($E^{0I} = -180$ mV), and the same trend is observed with compounds **166** ($E^{0I} = -110$ mV) and **167** ($E^{0I} = -200$ mV), where one or two diazaborolidinyl substituents are present. Moreover, it is evident that the oxidation of the ferrocanyl-diazaborolines **18** and **21** is easier than that of the saturated congeres **166** and **167**. In contrast to the ferrocene derivatives, the methylcymantrenyl systems **24** ($E^{0I} = 210$ mV) and **168** ($E^{0I} = 490$ mV) suffer thereby from an irreversible oxidation process with the formation of free methylcymantrene ($E^{0I} = 840$ mV) [21].

3.3. Molecular structures

In the previous review on this topic [2] the molecular structures of a number of typical 1,3,2-diazaborolines were discussed in detail. Thus in this account, only a brief summary of bonding parameters within a 1,3,2-diazaboroline ring is presented. Beyond this, more attention is spent to the conformational situation in some highly functionalized diazaborolines, particularly with respect of communication between different π-systems. Structural features of the novel 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridines are also considered. The most characteristic structural feature of almost all monocyclic 1,3,2-diazaborolines, as determined by single-crystal X-ray diffraction analysis, is the planarity of the heterocyclic core (Fig. 1). The BN bond lengths vary from 1.41 to 1.45 Å and show no significant differences to the BN bonds in the fully saturated borolidines [17]. In the planar aminoborane $(CF_3)_2B{=}N(i\text{Pr})_2$ the BN distance was determined to 1.37(1) Å [45] which compares well with the BN bond length of 1.38 Å calculated for H_2NBH_2 with an efficient p(π)–p(π) interaction [46]. The C–C distances in diazaborolines range from 1.32 to 1.36 Å, including the value for the localized CC double bond in ethene. The endocyclic CN bond lengths range from 1.39 to 1.41 Å, and are thus elongated compared with the calculated value for a localized CN double bond in Schiff bases (1.27 Å) [47]. For the exocyclic $N(sp^2)$–$C(sp^3)$ single bonds lengths of ca. 1.48 Å (av.) are measured. Average endocyclic angles N–B–N, B–N–C and N–C–C are 105.5°, 107.2° and 110.1°.



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In compound **95** the planes defined by the heterocycle and the atoms B(2)–C(11), Si(1) and N(3) are oriented perpendicularly ($\phi = 89.4°$). This observation and the single bond B(1)–C(11) [1.575(2) Å] exclude π-interactions between these units in the molecule. A similar situation was encountered in structure **18** where the plane of the diazaboroline ring and the attached C_5H_4 ring [B(1)–C(1) = 1.588(2) Å] enclose a dihedral angle of 73.1°. Compound **15** exhibits the conformation of a paddle wheel where the diazaborolinyl-substituents B(1) to N(2), B(2) to N(4) and B(3) to N(6) enclose interplanar angles of 89.9°, 104.1° and 87.1° with respect to the central arene unit. This fact again excludes any electronic communication between the heterocyclic units via the central arene spacer, and confirms to some extend the electrochemical data.

Compound **86** features a planar molecule which may be regarded as a 1,3,2-diazaboroline connected to a 1,3-butadiene unit via the two adjacent atoms N(1) and C(5). In contrast to a series of monocyclic 1,3,2-diazaborolines the bonding parameters within the boroline part of **86** differ significantly. The B–N distances [1.420(2) and 1.429(2) Å] indicate multiple bond character. The bond length C(4)–C(5) in **86** [1.362(2) Å] appears at the upper end of the range encountered for such bonds in diazaborolines. The endocyclic bonds N(3)–C(4) [1.395(2) Å] and N(1)–C(5) [1.416(2) Å] differ significantly in length and fall in the range measured for the CN multiple bonds in the monocyclic analogues. The calculated value for a C_{sp^2}–N_{sp^2} single bond is

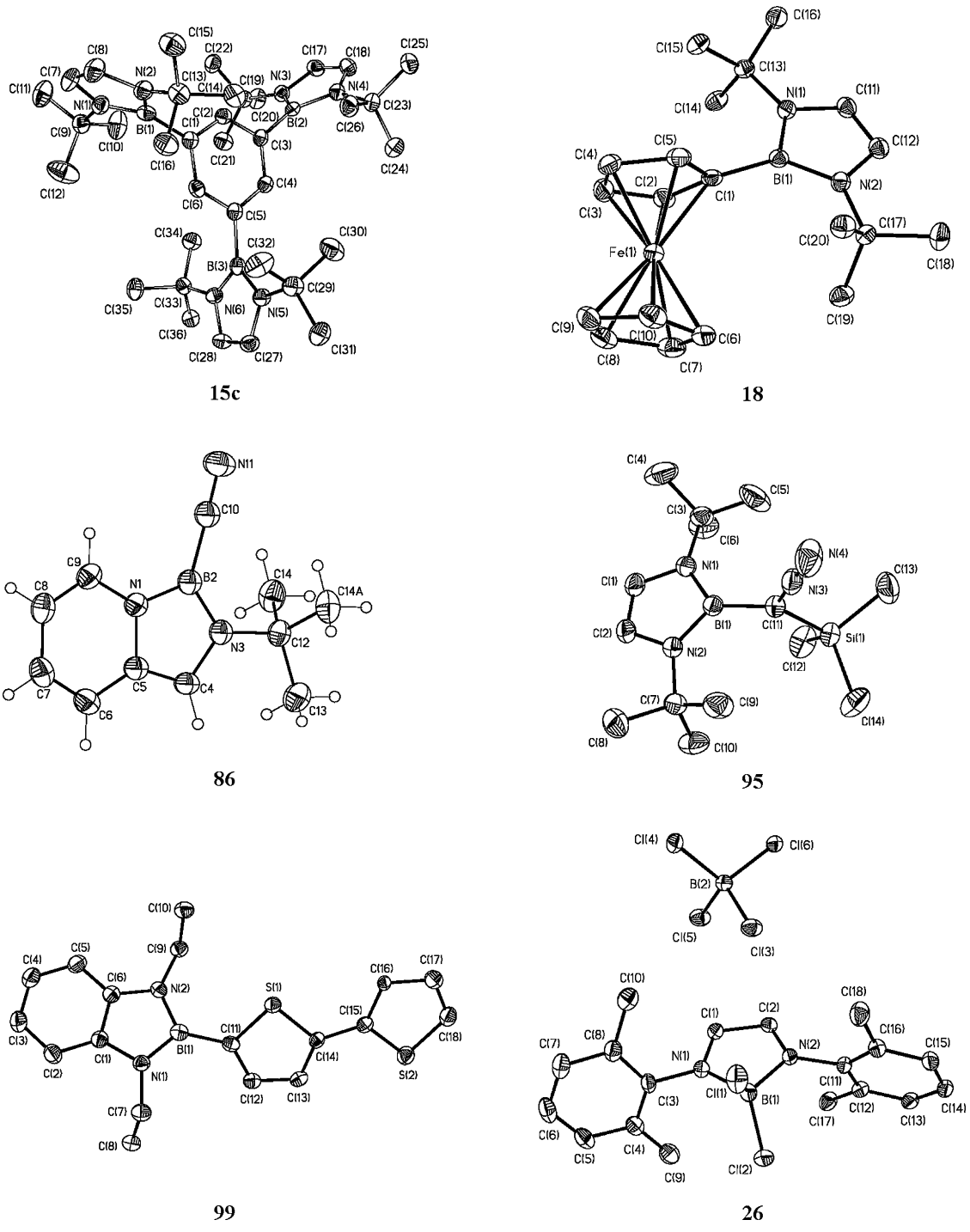


Fig. 1. Molecular structures of the 1,3,2-diazaborolines **15c**, **18**, **86**, **95**, **99** and the borolium salt **26**.

1.45 Å [47]. The carbon–carbon distances in the six-membered ring of **86** alternate. Double bonds are C(8)–C(9) [1.339(2) Å] and C(6)–C(7) [1.353(2) Å] whereas the longer bonds C(5)–C(6) [1.424(2) Å] and C(7)–C(8) [1.425(3) Å] may be considered as single bonds. The boron atom is linked to the cyano group via a B–C_{sp} single bond of 1.538(3) Å.

The molecule **99** features a planar 1,3,2-benzodiazaboroline unit which is linked to the α-carbon atom of the dithienyl fragment by a BC-single bond of 1.547(5) Å. Both rings of the dithienyl groups are present in an anti-conformation enclosing interplanar angles of 137.5° and 133.7° with the plane of the BN-heterocycle. The BN bond lengths [1.431(5); 1.440(4) Å] are at the upper end of such values in monocyclic 1,3,2-diazaborolines. Bond C(1)–C(6) [1.413(5) Å] is markedly longer than the one in the monocyclic congenors. The remaining C–C bonds average to 1.394 Å. The endocyclic bonds N(1)–C(1) [1.397(7) Å] and N(2)–C(6) [1.392(4) Å] are as expected and significantly shorter than the exocyclic CN contacts [1.464(4) and 1.465(4) Å].

The X-ray structure of a borolium salt (**26**) should also be included in this account. The analysis shows a planar diazaborolium cation in addition to a tetrachloroborate anion with no contact between the two ions. The bond lengths B(1)–Cl(1) [1.813(2) Å] and B(1)–Cl(2) [1.791(2)] are slightly shorter than the B–Cl contacts in the BCl_4^- ion, which range from 1.830(2) to 1.872(2) Å. The boron nitrogen bonds [B(1)–N(1) 1.615(2) Å, B(1)–N(2) 1.594(2) Å] slightly exceed the average B–N single bond length of 1.59 found in amine-boranes [48]. The endocyclic C–N bond lengths [C(1)–N(1) 1.276(2) Å, C(2)–N(2) 1.279(2) Å] are characteristic for double bonds. The carbon–carbon bond length in the cation [1.477(2) Å] indicates a bond order of unity. In comparison to monocyclic diazaborolines the angle at the boron atom was compressed to 95.8(1)°, whereas the endocyclic angles B(1)–N(1)–C(1) [110.7(1)°], B(1)–N(1)–C(2) [111.5(1)°] are slightly more obtuse than in diazaborolines. In contrast to this the endocyclic angles at C(1) [110.7(1)°] and C(2) [110.6(1)°] compare well with those in the neutral heteroarenes.

4. Theoretical calculations

In a recent paper [41] density functional calculations on selected 1,3,2-diazaborolines (**94**, **103**, **130**, **151**, **154**) at the B3LYP/6-311 (d,p) level of theory have been reported. The nature and the order of the two highest occupied molecular orbitals are consistent with the CNCD/S calculations of 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaborole [2,49]. The HOMO of these molecules corresponds mainly to the bonding combination of the nitrogen lone pairs ($n^+{}_N\pi$) delocalized in the p-boron vacant orbital (π^*_{NBN}) in antibonding interaction with the $\pi_{C=C}$ orbital. The following orbital energies are calculated: **154** (7.10 eV) < **94** (7.40 eV) ≈ **130** (7.40 eV) ≈ **151** (7.40 eV) < **103** (7.75 eV). They correlate well with the first ionization potentials experimentally determined by photoelectron spectroscopy. The respective value for 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaborole is 7.44 eV [48]. The nature of the second ionization potential (third one for **130**) fits with the $\pi_{C=N}{}^-$ orbital which is due to the antibonding nitrogen lone pairs combination in interaction with the $\pi^*_{C=C}$ orbital (for **130** the HOMO-1 is the σ sulfur lone pair). Energies for the HOMO-1 are: **154** (8.80 eV) < **151** (9.02 eV) < **94** (9.13 eV) < **103** (9.35 eV). The energy of the $\pi^-{}_{C=N}$ orbital of **130** is 8.94 eV. The energy of the $n_S\sigma$ orbital is 7.74 eV. In 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaborole for the energy of the HOMO-1 a value of 9.04 eV was calculated [48].

5. Chemical properties

In this section the reactivity of 1,3,2-diazaborolines towards oxidizing and reducing agents are considered. Moreover, the reaction of various diazaborolines with diphenylketene with the aim of synthesizing chiral oxazaborolidines is reported. Ligand substitution at the boron atom leading to other diazaboroline derivatives were included in the section on the synthesis of diazaborolines, and are not discussed here (vide supra).

5.1. Oxidations

As pointed out earlier the electrochemical oxidation of *N*,*N*′-di-*tert*-butyldiazaborolines **94**, **103**, **129**, **130**, **153**, **154**, **159** and **160** by cyclic voltammetry displayed clean, but irreversible waves, whereby the oxidation potentials $E_{ox,1/2}$ vary strongly in dependence of the substitution pattern at the boron center [41]. With respect to this, there was interest in the nature of the oxidation products. Therefore oxidation of these heterocycles was performed on a preparative scale using nitrosonium salts as oxidants.

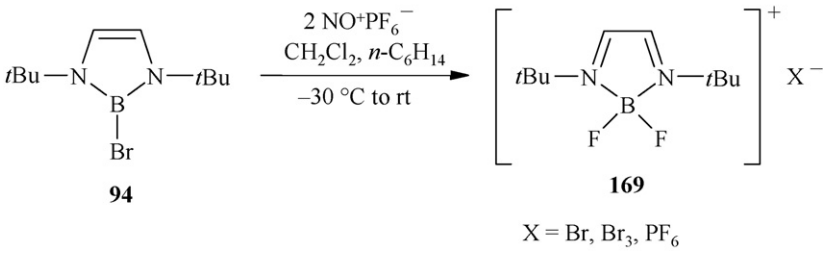
The reaction of 1 equiv. of 2-bromo-1,3,2-diazaboroline **94** with 2 equiv. of $NO^+PF_6^-$ in CH_2Cl_2/hexane led to the quantitative formation of the difluoroborolium salts **169** as yellow crystals (Scheme 46) [50].

The counterion was not uniform. Obviously the bromo ligand of **94** was replaced by fluoride, which was released from a PF_6^- ion before, and serves now as a counterion in the salt in addition to the PF_6^- ion and the tribromide ion. The Br_3^- anion could be formed from Br^- by partial oxidation with excessive $NO^+PF_6^-$.

Surprisingly, the reaction of the 1,3,2-diazaborolidine **158** with $NOPF_6$ under the same conditions also led to the formation of product **169** (Scheme 47). The employment of 4 equiv. of $NOPF_6$ did not lead to an improved yield. Instead 2 equiv. of the nitrosonium salt were recovered after the reaction [49].

When the 1,3,2-diazaboroline was substituted by poor leaving groups such as hydride, ethynyl or cyano units only one fluoride atom was added to the boron atom and borolium salts with two different ligands were formed. Thus, the treatment of **151**, **103** or **105** with 2 equiv. of $NO^+PF_6^-$ afforded the intensely yellow (**170**) or red borolium salts (**171**, **172**) in moderate to high yields (Scheme 48).

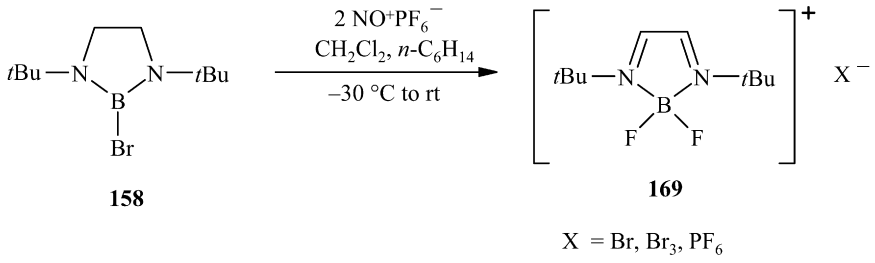
Here, the hexafluorophosphate was observed as the sole counterion. The treatment of diazaborolines containing electron-donating substituents on the boron atom like dimethylamino- or methoxy-functionalized derivatives **160** and **129** with



94 **169**

X = Br, Br_3, PF_6

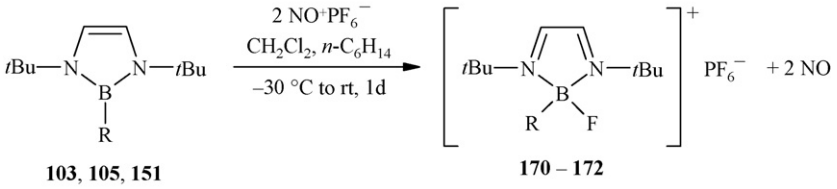
Scheme 46. Oxidation of bromoborole **94** with $NO^+PF_6^-$.



158 **169**

X = Br, Br_3, PF_6

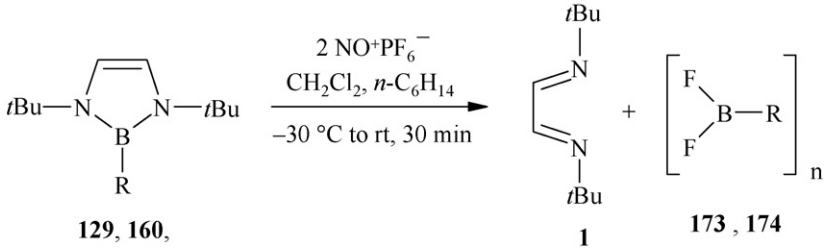
Scheme 47. Oxidation of the bromoborolidine **158** with $NO^+PF_6^-$.



103, **105**, **151** **170 – 172**

Compound	R	yield (%)
103, **171**	CN	77
105, **172**	C_2H	69
151, **170**	H	67

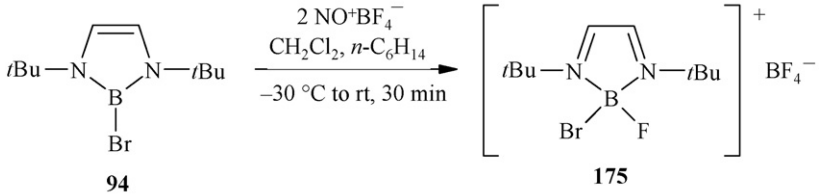
Scheme 48. Formation of salts **170–172**.



129, **160**, **1** **173** , **174**

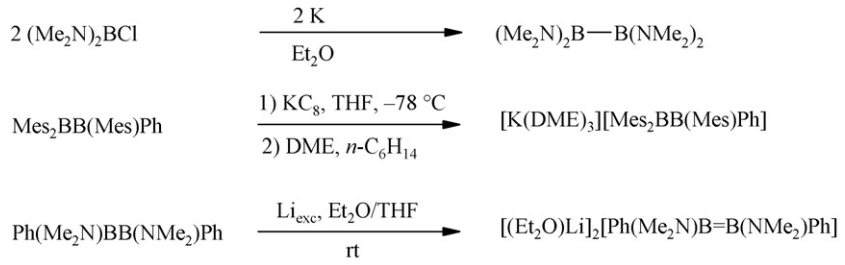
Compound	R	n
129, **174**	OMe	2,3
160, **173**	NMe_2	2

Scheme 49. Oxidation of diazaborolines **129** and **160** with $NO^+PF_6^-$.



94 **175**

Scheme 50. Synthesis of **175**.



Scheme 51.

$NOPF_6$ did not afford borolium salts. Instead ring opening occurred with the formation of *N*,*N*′-di-*tert*-butyldiazabutadiene **1**, $(Me_2NBF_2)_2$ (**173**) and $(MeOBF_2)_n$ (**174**) (Scheme 49) [49].

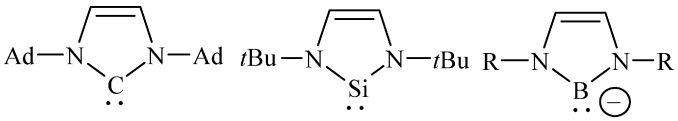
The reaction of **94** with $NO^+BF_4^-$ gave the mixed borolium salt **175** (Scheme 50).

The established protocol for the synthesis of 2-halo-1,3,2-diazaboroles involves the reduction of the corresponding diazaborolium salts with a strong reducing agent. This preparative result is supported by reductive cyclovoltammetric experiments. All borolium salts **169**–**172** show a clean, reversible curve in the range of 0 to −2 V, performed in dichloromethane or acetonitrile as a solvent. The reductive potentials $E_{1/2}$ vary from −731 mV (**170**) to −742 mV (**171**) versus the ferrocene/ferrocenium standard. No electrochemical oxidation was observed in the range of 0–3.2 V.

5.2. Reductions

The preparation of diboranes (4) by alkali-metal reduction of halogenoboranes XBR_2 (X = Cl, Br; R = Me_2N, Aryl) is meanwhile state of the art [51]. Their further reduction to dinuclear mono- and dianions was recently reported [52,53] (Scheme 51).

The complete cleavage of the dinuclear dianions to ionic species such as $M^+(BR_2)^-$, however, has never been observed. Steric bulk at the substituents at the boron centers, however, should provide a situation, where such a dissociation process becomes conceivable. Particularly, with regard to the first isolable *N*-heterocyclic carbenes **A** [54] and silylenes **B** [55] the quest for the isoelectronic *N*-heterocyclic boranides **C** was obvious [38]:



A **B** **C**

Compound **94** seemed to be a promising precursor for this target. Reduction of this 2-bromo-diazaboroline with sodium–potassium alloy in hexane was very sluggish and afforded 2-hydro-1,3,2-diazaboroline **151** as the only tractable product (Scheme 54). The same reduction of **94** with a potassium mirror in DME at ambient temperature after 36 h afforded a 2:1:1 mixture of the 2-methoxy-1,3,2-diazaborole **129**, compound **151** and the diborolinyloxane **176**. The reduction of **94** with a potassium–sodium alloy in TMEDA took 3 d to go to completion and furnished **151** as a major product in 79% isolated yield. Derivative **160** could be identified as one of the minor products in addition to traces of **177** (Scheme 52).

When a stoichiometric amount of [15]crown-5 was added to the slurry of the sodium–potassium alloy in toluene the color of the solution became deep blue and after 30 min most of the metal went into solution. Then **94** was added. After less than 2 h a 1:1 mixture of **151** and of the 2-benzyl-1,3,2-diazaboroline **172** was obtained. The same reaction in perdeuteriotoluene afforded a 1:1 mixture of **151**-d_1 and **172**-d_7. The analogous reaction in C_6D_6, however, led to the exclusive production of the 2-protio-derivative **151** (Scheme 53) [38].

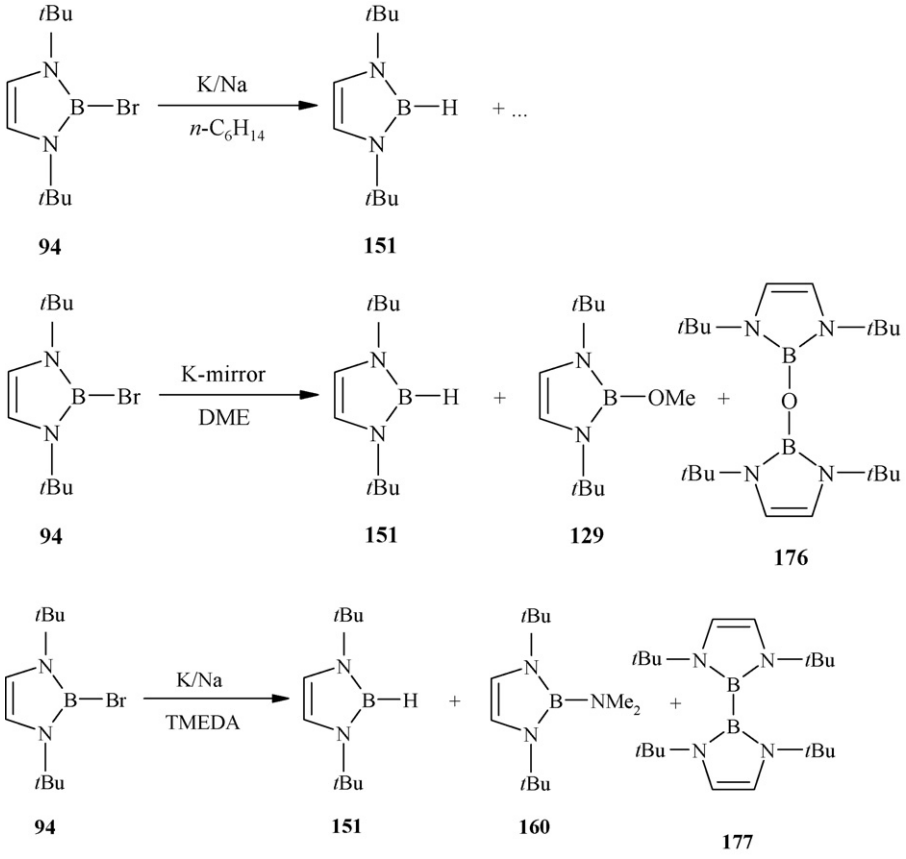
To rationalize these results the alkali-metal 1,3,2-diazaborolinide **173** was invoked as a reactive intermediate (Scheme 54).

The anion of **173** as a very strong Brønsted base abstracts a deuterium ion from the solvent to give **151**-d_1 and potassium phenylmethanide. Starting material **94** was then converted by the latter to give the 2-benzyl-1,3,2-diazaboroline **172**-d_7. In view of the straightforward desulfurization of imidaza-2-thione to imidazol-2-ylidene by potassium [56] desulfurization of **130** and **131** was also envisaged as a possible route to salts with 1,3,2-diazaborolinide anion.

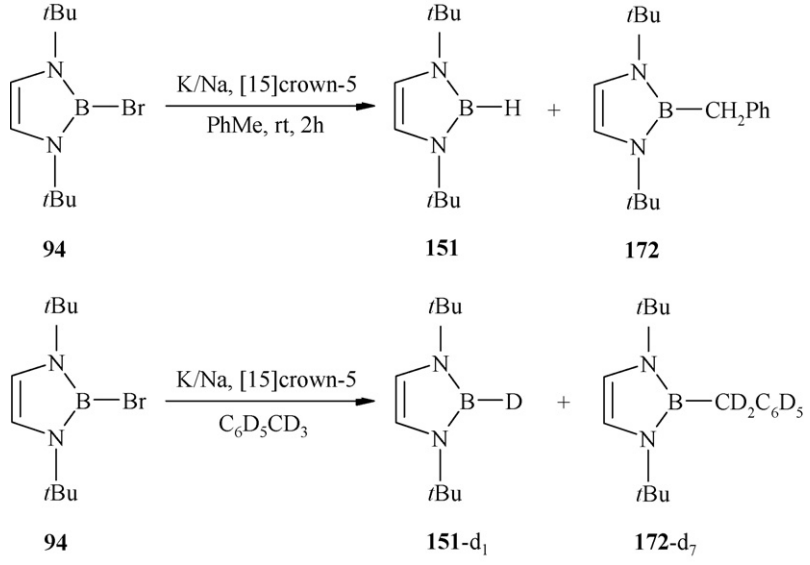
2-Methylato-1,3,2-diazaboroline **130** was allowed to react for 14 d with sodium–potassium alloy (9:91) to afford 2-methyl-1,3,2-diazaboroline **154** in 44% yield in addition to 1,4-diazabutadiene **1** (40%) (Scheme 55).

The reduction of compound **131** with sodium–potassium alloy (9:91) was performed in an ultrasound bath. Diborane-(4) **177** was isolated as a yellow oil in 38% yield from the obtained slurry after 10 h. In the $^{11}B\{^1H\}$ NMR spectrum of **177** a broad singlet at $\delta = 25.2$ ppm, $w^{1/2} = 120$ Hz was observed. In line with the fact that fused polyarenes like naphthalene or phenanthrene are more readily reduced than the monocyclic benzene [57], the reduction of 2-bromo-1,2-dihydro-1,3,2-diazaborolo[1,5-*a*]pyridine **49** by potassium–sodium alloy in hexane proceeded smoothly to furnish compound **178** as a yellow crystalline solid in 64% yield. Traces of the 2-hydro derivative **80** were detected by ^{11}B NMR spectroscopy [38] (Scheme 56).

In contrast to this, the employment of tetramethylethylenediamine as solvent or the addition of a crown ether to the reaction mixture in toluene or tetrahydropyrane invariantly led to complete deterioration of the boron heterocycle.



Scheme 52. Alkali-metal reduction of **94**.



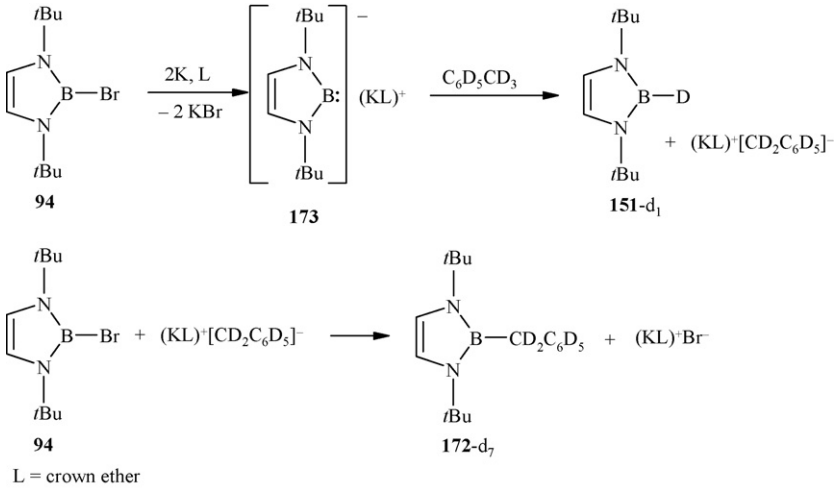
Scheme 53. Reduction of **94** with K/Na alloy in the presence of a crown ether.

A pentane slurry of sodium potassium alloy was reacted for 14 h at 20 °C with benzodiazaboroline **64**. Bis(1,3-diethyl-1,3,2-diazaborolinyl) **178** was isolated as colorless needles in 87% yield (Scheme 57).

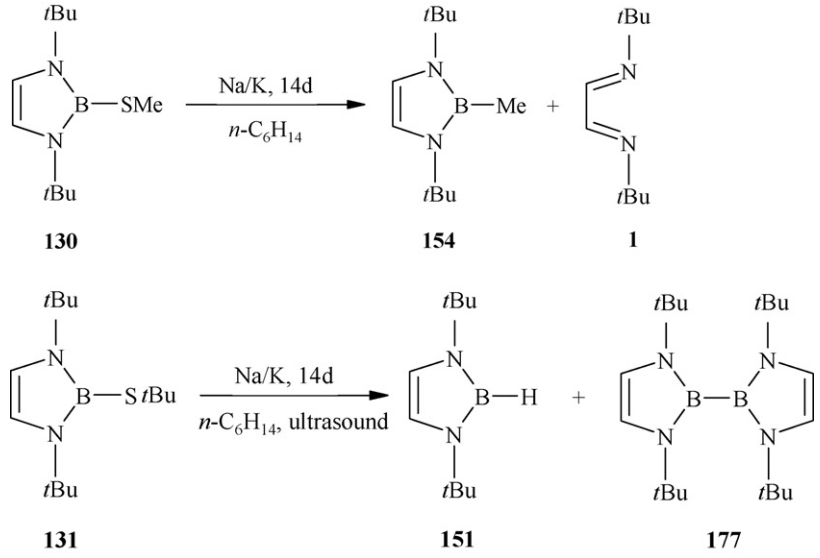
All attempts to further reduce **178** to an anion failed [31].

A compound **180** featuring the long sought boranide anion was recently synthesized by the reductive cleavage of the boron–bromine bond in diazaborole **179** by lithium naphthalenide in THF or DME at −45 °C (Scheme 58).

According to an X-ray structure analysis the lithium atoms of two molecules are bridged by two molecules of DME via their



Scheme 54. Suggested mechanism of the reduction of **94** with K/Na alloy in perdeuteriotoluene.

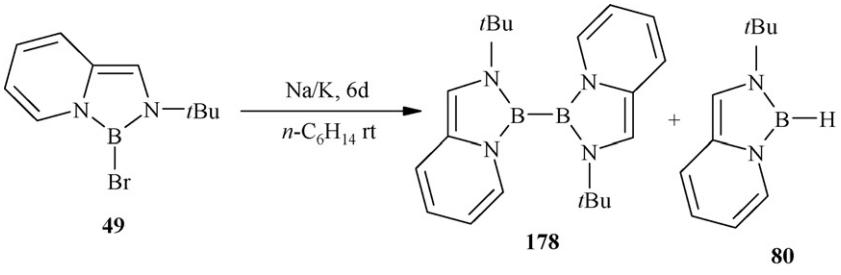


Scheme 55. Reduction of **130** and **131** with Na/K alloy.

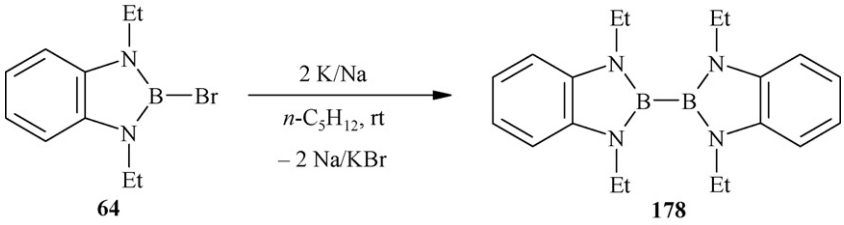
oxygen atoms. The lithium boranide reacted with electrophiles such as methyl trifluoromethylsulfonate, 1-chlorobutane and benzaldehyde to 1,3-diazaboroles **181**–**183**. Protonation by water afforded derivative **184** (Scheme 58) [58].

5.3. Reaction of 1,3,2-diazaborolines with diphenylketene

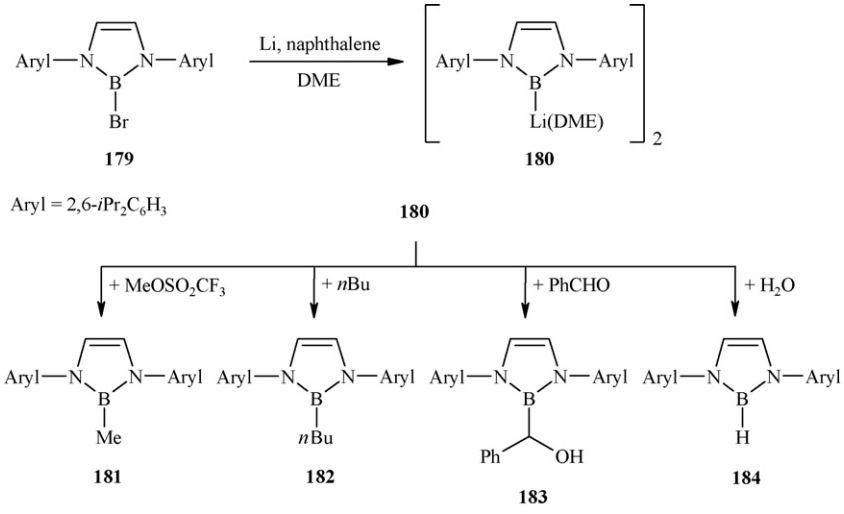
Oxazaborolidines are mild Lewis acids of current interest which efficiently catalyze a great number of organic



Scheme 56. Reduction of **49** with Na/K alloy.



Scheme 57. Reduction of **64** with sodium–potassium alloy.

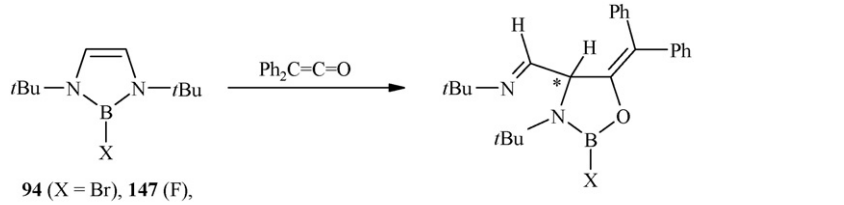


Scheme 58.

transformations [59–67]. A few years ago the reaction of 1,3,2-diazaborolines and diphenylketene was investigated. This process regioselectively led to 1,3,2-oxazaborolidines (Scheme 59) [68].

Thereby a stereogenic center at ring carbon atom C(4) was created. It was obvious to elaborate for conditions of a stereoselective synthesis of such compounds. Here chiral, heavily substituted 1,3,2-diazaborolines were the starting materials of choice. The reaction of enantiomerically pure 1,3-bis(*S*,*S*)-(1-cyclohexylethyl)-1,3,2-diazaborolines **10b**, **10c**, **89**, **123** with diphenylketene in hexane at −70 °C led to the diastereoselective formation of the (*S*,*S*,*R*/*S*)-3-(1-cyclohexyl)-4-(*E*)-(1-cyclohexylethyl)iminomethyl-1,3,2-oxazaborolidines **192–195** in good chemical yields (70–98%) (Scheme 60) [69].The diastereoselectivity increased with the steric bulk of the substituents at the boron center from de = 55% for **192** with a 2-*n*-butyl group to de ≥ 95% for **195** with a *tert*-butylamino group at the B atom.

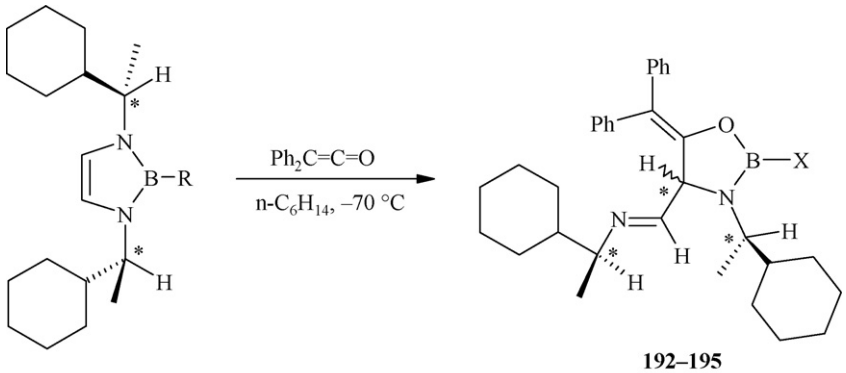
Providing the chiral information via the substituent at boron was less efficient. Reaction of (*S*)-**126** with diphenylketene under identical conditions furnished a quantitative yield of 1,3,2-oxazaborolidine **196** with a de of only 52% (Scheme 61) [69].



94 (X = Br), **147** (F),
153 ($SnMe_3$), **159** (NH_2),
160 (NMe_2), **185** (CH=C($SnMe_3$)(C_6H_4-4-Cl),

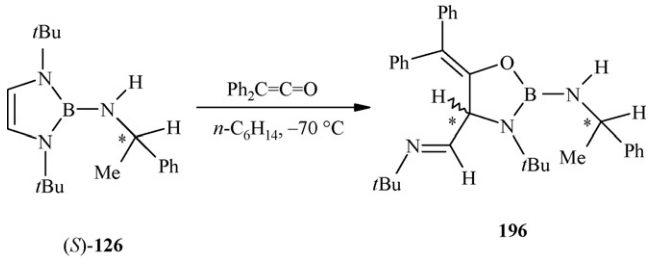
186 (X = Br), **187** (F),
188 ($SnMe_3$), **189** (NH_2),
190 (NMe_2), **191** (CH=C($SnMe_3$)(C_6H_4-4-Cl),

Scheme 59. Conversion of 1,3,2-diazaboroline into 1,3,2-oxazaborolidines.



R	nBu	iBu	CH_2SiMe_3	NHtBu
	89	**10b**	**10c**	**123**
	192	**193**	**194**	**195**
yield (%)	82	85	70	98
de	55	74	80	⩾95

Scheme 60. Synthesis of 1,3,2-oxazaborolidines **192–195**.



Scheme 61. Synthesis of **196**.

6. Conclusions and perspectives

It is obvious that the chemistry of 1,3,2-diazaborolines has developed rapidly in the recent years. In the beginning, the interest was mainly focussed on the synthesis and structure elucidation of a novel class of 6π-electron-containing heterocycles. More and more it has shifted towards the reactivity of these compounds. Here particularly substitution and insertion reactions at the BX unit to afford novel highly functionalized diazaborolines were studied. Their subsequent transformation into 1,3,2-oxazaborolidines by treatment with ketenes was extended to the asymmetric synthesis of chiral 1,3,2-oxazaborolidenes. Along with purely preparative considerations, physico-chemical investigations have gained increasing attention. Here electrochemical, photoelectron spectroscopic and optophysical investigations point to a promising future with respect to application of diazaborolines. Intense luminescence with different colorations recommend the use of such heterocycles fused to organic π-systems for application in optoelectronic devices. High yields, high thermostability and a comparatively low price for their production renders them interesting also from an economical point of view. Pyrolysis experiments with the aim of generating reactive boranediyls "BX" opens up another area of materials chemistry.

References

[1] E. Wiberg, Naturwissenschaften 35 (1948) 182, 212.
[2] L. Weber, Coord. Chem. Rev. 215 (2001) 39.
[3] J.S. Merriam, K. Niedenzu, J. Organomet. Chem. 51 (1973) 21.
[4] L. Weber, G. Schmid, Angew. Chem. 86 (1974) 519;
L. Weber, G. Schmid, Angew. Chem. Int. Ed. Engl. 13 (1974) 467.
[5] K. Niedenzu, J.S. Merriam, Z. Anorg. Allg. Chem. 406 (1974) 251.
[6] G. Schmid, J. Schulze, Chem. Ber. 110 (1977) 2744.
[7] (a) G. Schmid, M. Polk, R. Boese, Inorg. Chem. 29 (1990) 4421;
(b) M. Polk, Ph.D. Thesis, University of Essen, 1988.
[8] G. Schmid, J. Schulze, Angew. Chem. 89 (1977) 258;
G. Schmid, J. Schulze, Angew. Chem. Int. Ed. Engl. 16 (1977) 246.
[9] G. Schmid, J. Schulze, Chem. Ber. 114 (1981) 495.
[10] (a) G. Schmid, J. Lehr, M. Polk, R. Boese, Angew. Chem. 103 (1991) 1029;
G. Schmid, J. Lehr, M. Polk, R. Boese, Angew. Chem. Int. Ed. Engl. 30 (1991) 1015;
(b) J. Lehr, Ph.D. Thesis, University of Essen, 1991.
[11] L. Weber, E. Dobbert, H.-G. Stammler, B. Neumann, R. Boese, D. Bläser, Chem. Ber. Recueil 130 (1997) 705.
[12] L. Weber, E. Dobbert, R. Boese, M.T. Kirchner, D. Bläser, Eur. J. Inorg. Chem. (1998) 1145.
[13] L. Weber, E. Dobbert, H.-G. Stammler, B. Neumann, R. Boese, D. Bläser, Eur. J. Inorg. Chem. (1999) 491.
[14] L. Weber, E. Dobbert, A. Rausch, H.-G. Stammler, B. Neumann, Z. Naturforsch. 54b (1999) 363.
[15] L. Weber, A. Rausch, H.B. Wartig, H.-G. Stammler, B. Neumann, Eur. J. Inorg. Chem. (2002) 2438.
[16] L. Weber, A. Rausch, H.-G. Stammler, B. Neumann, Z. Anorg. Allg. Chem. 630 (2004) 2657.
[17] L. Weber, I. Domke, C. Schmidt, T. Braun, H.-G. Stammler, B. Neumann, Dalton Trans. (2006) 2127.
[18] L. Weber, V. Werner, I. Domke, H.-G. Stammler, B. Neumann, Dalton Trans. (2006) 3777.

[19] (a) S. Aldridge, C. Bresner, Coord. Chem. Rev. 244 (2003) 71;
(b) K. Ma, M. Scheibitz, S. Scholz, M. Wagner, J. Organomet. Chem. 652 (2002) 11.
[20] (a) N. Ruf, T. Renk, W. Siebert, Z. Naturforsch. Teil B 31 (1976) 1028;
(b) T. Renk, N. Ruf, W. Siebert, J. Organomet. Chem. 120 (1976) 1.
[21] L. Weber, I. Domke, H.-G. Stammler, B. Neumann, Eur. J. Inorg. Chem. (2005) 4715.
[22] L. Weber, J. Förster, H.-G. Stammler, B. Neumann, Eur. J. Inorg. Chem. (2006) 5048.
[23] F.S. Mair, R. Manning, R.G. Pritchard, J.E. Warren, Chem. Commun. (2001) 1136.
[24] L. Weber, M. Schnieder, R. Boese, D. Bläser, J. Chem. Soc., Dalton Trans. (2001) 378.
[25] (a) L.J. Schupp, C.A. Brown, Abstract of Papers, 128th National Meeting of the American Chemical Society, Minneapolis, MN, 1955, p. 48-R;
(b) M.D.S. Dewar, V.P. Kubba, R. Pettit, J. Chem. Soc. (1958) 3076.
[26] D. Ulmschneider, J. Goubeau, Chem. Ber. 90 (1957) 2733.
[27] H. Beyer, K. Niedenzu, J.W. Dawson, J. Org. Chem. 27 (1962) 4701.
[28] J. Schulze, Ph.D. Thesis, University of Essen, 1980.
[29] G. Kaupp, M.R. Naimi-Jamal, U. Stepanenko, Chem. Eur. J. 9 (2003) 4156.
[30] J. Goubeau, H. Schneider, Liebigs Ann. Chem. 675 (1964) 1.
[31] L. Weber, H.B. Wartig, H.-G. Stammler, B. Neumann, Z. Anorg. Allg. Chem. 627 (2001) 2663.
[32] G.R. Clark, G.J. Irvine, W.R. Roper, L.J. Wright, J. Organomet. Chem. 680 (2003) 81.
[33] S. Maruyama, Y. Kawanishi, J. Mater. Chem. 12 (2002) 2245.
[34] T. Habereder, H. Nöth, Appl. Organometal. Chem. 17 (2003) 525.
[35] (a) M.-P. Arthur, A. Baceiredo, G. Bertrand, J. Am. Chem. Soc. 113 (1991) 5856;
(b) M.-P. Arthur, H.P. Goodwin, A. Baceiredo, K.B. Dillon, G. Bertand, Organometallics 10 (1991) 3205.
[36] L. Weber, H.B. Wartig, H.-G. Stammler, B. Neumann, Organometallics 20 (2001) 5248.
[37] L. Weber, I. Domke, A. Rausch, A. Chrostowska, A. Dargelos, Dalton Trans. (2004) 2188.
[38] L. Weber, M. Schnieder, P. Lönnecke, J. Chem. Soc., Dalton Trans. (2001) 3459.
[39] M. Suginome, A. Yamamoto, M. Murakami, Angew. Chem. 117 (2005) 2432;
M. Suginome, A. Yamamoto, M. Murakami, Angew. Chem. Int. Ed. Engl. 44 (2005) 2380.
[40] U. Braun, T. Habereder, H. Nöth, H. Piotrowski, H. Warchhold, Eur. J. Iorg. Chem. (2002) 1132.
[41] (a) C.D. Entwistle, T.B. Marder, Angew. Chem. 114 (2002) 3051;
C.D. Entwistle, T.B. Marder, Angew. Chem. Int. Ed. Engl. 41 (2002) 2927;
(b) C.D. Entwistle, T.B. Marder, Chem. Mater. 16 (2004) 4574.
[42] H. Doi, M. Kinoshita, K. Okumoto, Y. Shirota, Chem. Mater. 15 (2003) 1080.
[43] M. Charlot, L. Porrès, C.D. Entwistle, A. Beeby, T.B. Marder, M. Blauchard-Desce, Phys. Chem. Phys. 7 (2005) 600.
[44] L. Weber, I. Domke, W. Greschner, K. Miqueu, A. Chrostowska, P. Baylère, Organometallics 24 (2005) 5455.
[45] D.J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke, W. Weuter, J. Organomet. Chem. 378 (1989) 125.
[46] (a) Review: A. Haaland, Angew. Chem. 101 (1989) 1017;
(b) A. Haaland, Angew. Chem. Int. Ed. Engl. 28 (1989) 992.
[47] A.N. Chernega, A.V. Ruban, V.D. Romanenko, L.N. Markovskii, A.A. Korkin, M.Y. Antipin, Y.T. Struchkov, Heteroatom. Chem. 2 (1991) 229.
[48] P. Paetzold, Adv. Inorg. Chem. 31 (1987) 123.
[49] J. Kroner, H. Nöth, K. Niedenzu, J. Organomet. Chem. 41 (1974) 165.
[50] L. Weber, I. Domke, J. Kahlert, H.G. Stammler, Eur. J. Inorg. Chem. (2006) 3419.
[51] D. Loderer, H. Nöth, H. Pommerening, W. Rattay, H. Schick, Chem. Ber. 127 (1994) 1603, and references cited therein.
[52] (a) W.J. Grigsby, P.P. Power, Chem. Eur. J. 3 (1997) 368;
(b) A. Moezzi, R.A. Bartlett, P.P. Power, Angew. Chem. 104 (1992) 1075; A. Moezzi, R.A. Bartlett, P.P. Power, Angew. Chem. Int. Ed. Engl. 31 (1992) 1082;
(c) A. Moezzi, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 114 (1992) 2715.
[53] H. Nöth, J. Knizek, W. Ponikwar, Eur. J. Inorg. Chem. (1999) 1931.
[54] (a) A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361;
(b) A.J. Arduengo III, H.V.R. Dias, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530;
(c) Review: W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256; W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162.
[55] (a) M. Denk, R. Lennon, R. Hayashi, R. West, A.V. Belyakov, H.R. Verne, M. Wagner, N. Metzler, J. Am. Chem. Soc. 116 (1994) 2691;
(b) Review: B. Gehrhus, M.F. Lappert, J. Organomet. Chem. 617–618 (2001) 609.
[56] N. Kuhn, T. Kratz, Synthesis (1993) 561.
[57] (a) C. Näther, H. Bock, Z. Havlas, T. Hauck, Organometallics 17 (1998) 4707;
(b) H. Bock, Z. Havlas, D. Heß, C. Näther, Angew. Chem. 110 (1998) 518; H. Bock, Z. Havlas, D. Heß, C. Näther, Angew. Chem. Int. Ed. Engl. 37 (1998) 502.
[58] Y. Segawa, M. Yamashita, K. Nozaki, Science 314 (2006) 113.
[59] E.J. Corey, T. Shibata, T.W. Lee, J. Am. Chem. Soc. 124 (2002) 3808.
[60] D.H. Ryu, T.W. Lee, E.J. Corey, J. Am. Chem. Soc. 124 (2002) 9992.
[61] (a) E.J. Corey, Angew. Chem. 114 (2002) 1724;
(b) E.J. Corey, Angew. Chem. Int. Ed. Engl. 41 (2002) 1650.
[62] D.H. Ryu, E.J. Corey, J. Am. Chem. Soc. 125 (2003) 6388.
[63] E.J. Corey, C.L. Cywin, T.O. Roper, Tetrahedron Lett. 33 (1992) 6907.
[64] K. Ishikara, S. Kondo, H. Yamamoto, Synlett (1999) 1283.
[65] (a) S. Kiyooka, Y. Kaneko, M. Konaura, H. Matsuo, M. Nakano, J. Org. Chem. 56 (1991) 2276;
(b) S. Kiyooka, Y. Kaneko, K. Kume, Tetrahedron Lett. 33 (1992) 4927.
[66] (a) E.R. Parmee, O. Tempkin, S. Masamune, A. Abiko, J. Am. Chem. Soc. 113 (1991) 9365;
(b) E.R. Parmee, Y. Hong, O. Tempkin, S. Masamune, Tetrahedron Lett. 33 (1992) 1729.
[67] K. Futatsugi, H. Yamamoto, Angew. Chem. 117 (2005) 1508;
K. Futatsugi, H. Yamamoto, Angew. Chem. Int. Ed. Engl. 44 (2005) 1484.
[68] L. Weber, M. Schnieder, T.C. Maciel, H.B. Wartig, M. Schimmel, R. Boese, D. Bläser, Organometallics 19 (2000) 5791.
[69] L. Weber, A. Rausch, H.-G. Stammler, B. Neumann, Z. Anorg. Allg. Chem. 631 (2005) 1633.