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The chemistry of 1,3,2-diazaborolines (2,3-dihydro-1*H*-1,3,2-diazaboroles)

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Contents

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Abstract

1,3,2-Diazaborolines (2,3-dihydro-1*H*-1,3,2-diazaboroles) are at the interface between inorganic, organometallic and organic chemistry. The planar rings with 6π-electrons may be regarded as heteroarenes, as evidenced by NMR and photoelectron spectra and confirmed by quantum mechanical calculations. The capability of 1,3,2-diazaborolines to act as η^5-ligands adds chemical proof to this idea. High-yield syntheses of 1,3,2-diazaborolines with functional groups at boron have recently become available, providing a rich area of chemistry ranging from substitution processes via borylstannations to their conversion into oxazaborolidines.

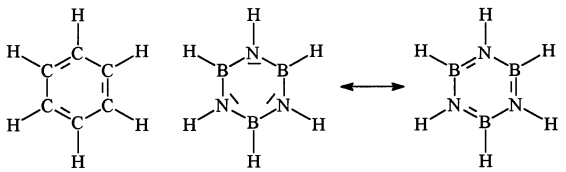
Keywords: Heterocycles; Diazaborolines; Cyclocondensation; Dehydrogenation; Displacement reactions; Borylstannation

1. Introduction

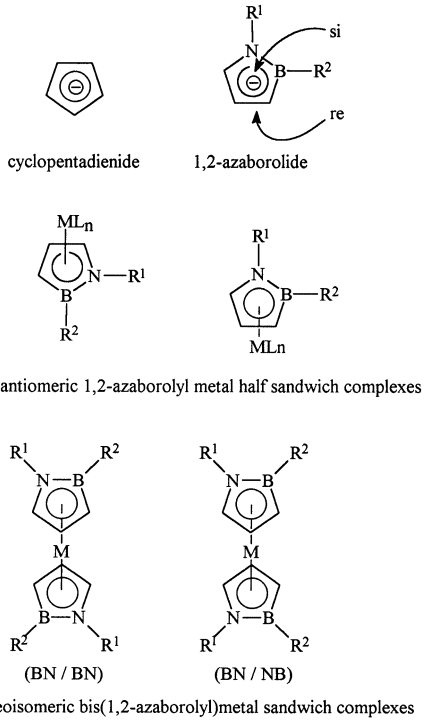
Heterocycles containing boron and nitrogen atoms play an important and fascinating role in main group chemistry. The concept of isoelectronic and isosteric compounds was successfully applied by Wiberg to carbon–carbon- and boron–nitrogen-containing molecules [1]. A typical example for this relationship has been the pair of benzene and borazene, whereby the BN multiple bonding results from a partial overlap of the occupied $2p_z$ orbital of the nitrogen and the empty $2p_z$ orbitals of the boron atoms (Scheme 1). This simple description implies that, in contrast to the non-polar carbon–carbon double bond, such a BN double bond behaves as an electric dipole.

More recently, replacement of a C=C fragment in the Hückel-aromatic cyclopentadienide anion by a BN moiety provided an entry into the rich and versatile chemistry of the isoelectronic 1,2-azaborolyl rings [2]. They function as BN-perturbed 6π-electron ligands in a series of sandwich and half-sandwich complexes. Owing to the inherent prochirality of a 1,2-azaborolyl ring with different re and si faces, its simple half-sandwich complexes exhibit chirality and usually were obtained as pairs of enantiomers. Consistently, sandwich complexes were built up as diastereoisomers (Scheme 2).

In one type of the latter compounds both ring ligands were coordinated to a metal atom via the same face (re *or* si) (BN/BN), whereas in the other type a coordination to different faces (re *and* si) (BN/NB) was realized.



Scheme 1. Isoelectronic systems: benzene and borazene.



Scheme 2. 1,2-Azaborolyl half-sandwich and sandwich complexes.

One highlight in 1,2-azaborolyl coordination chemistry contributes to the obstinate problem of the beryllocene structure. In contrast to the X-ray structure of beryllocene at low temperature, which suffered from disorder, the structure of the corresponding bis(1,2-azaborolyl)beryllium unambiguously displayed η^1- and η^5-coordination in the same molecule, providing a total of eight valence electrons to the beryllium center [3,4] (Fig. 1).

A comparable 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. For the sake of clarity and readability, in this account the latter nomenclature is given preference (Scheme 3).

The first report, by Merriam and Niedenzu, on a representative of this class of heterocycles dates back to 1973 [5]. A few months later an alternative approach to 1,3,2-diazaborolines was developed by Weber and Schmid [6]. A series of 1,3,2-diazaborolines were synthesized, and their molecular and electronic structures were carefully studied [7–9]. Comparatively little work was accomplished concerning the chemical behavior of such rings, which may be rationalized by the lack of functional groups. Reports of π-complexation to the $[Cr(CO)_3]$ fragment [9–11], as well as N–Si cleavage by alkali amides and alkoxides [9,12], provided some insight into the synthetic potential of these interesting molecules. This situation improved

considerably when high-yield syntheses of 1,3,2-diazaborolines with halide substituents at the boron atom were devised [13,14]. Halide substitution by hydride, carbon-, nitrogen- and tin-nucleophiles now became feasible [13–15]. The 2-trimethylstannyl-functionalized 1,3,2-diazaborolines turned out to be valuable reagents in the catalytic borostannation of alkynes [16].

2. Synthesis of 1,3,2-diazaborolines

To date there are mainly three different synthetic pathways to 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.

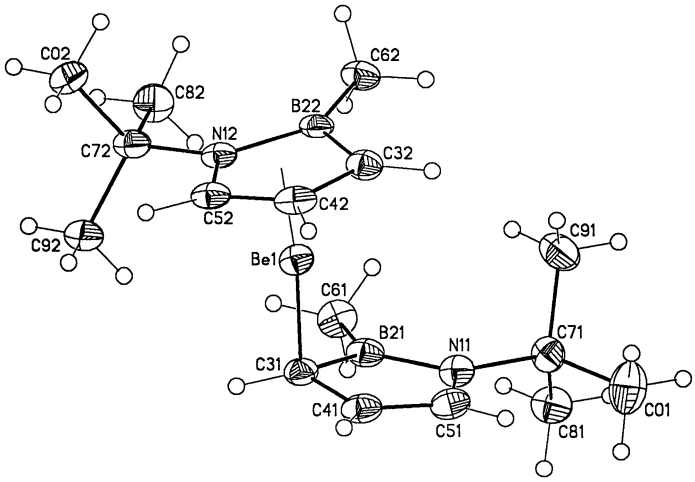
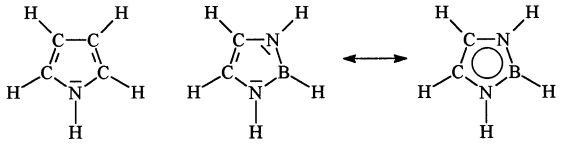


Fig. 1. Molecular structure of the BN/NB isomer of bis(1-*tert*-butyl-2-methyl-1,2-azaborolyl)beryllium at −150°C.



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

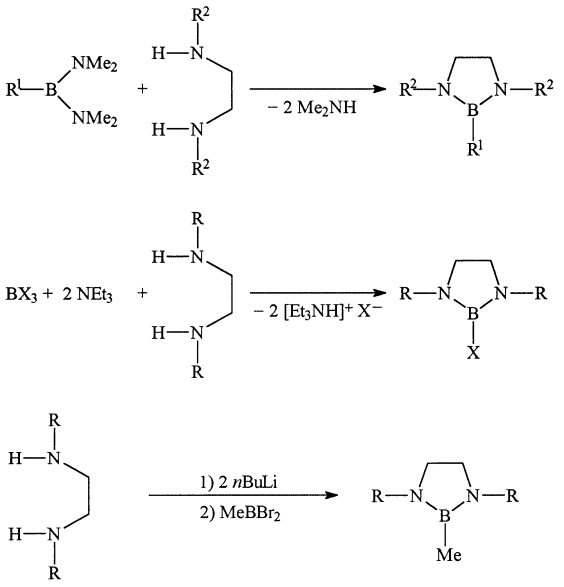
2.1. Catalytic dehydrogenations of 1,3,2-diazaborolidines

A prerequisite for the successful application of this synthetic method is the ready availability of the corresponding saturated heterocycles, the 1,3,2-diazaborolidines. To this aim, transamination and dehydrohalogenation processes have been particularly appropriate [17–24] (Scheme 4).

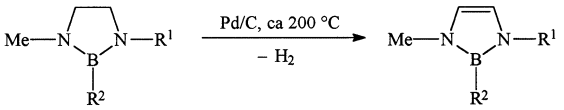
A third approach makes use of the lithiation of a secondary ethylenediamine by *n*-butyllithium prior to its cyclocondensation with dibromomethylborane [25]. Heating 1,3,2-diazaborolidines **1a**–**c** to reflux in an argon atmosphere over 10% palladium-on-charcoal catalyst for 24 h at atmospheric pressure afforded 1,3,2-diazaborolines **2a**–**c** as colorless products after distillation [7]. The reaction vessel was permanently flushed with a gentle stream of argon to remove hydrogen. In order to isolate the desired products it was crucial to bring the dehydrogenation to completion, because it was not possible to separate product and starting material by distillation (Scheme 5).

Later, the application of this method was extended to the preparation of **4b**, **4c** and **4d** with alkyl substituents at the nitrogen and boron atoms [9], and also to species where at least one nitrogen atom bears a trimethylsilyl group [11,12] (Scheme 6).

The formation of compounds **4b**–**d** took several weeks to reach completion, whereas only 1–3 days were required for the syntheses of **6a**–**e**. The purity of the starting materials is of crucial importance for the rate of the reaction and its success. Solvents and impurities cause prolonged reaction times and incomplete conversions.



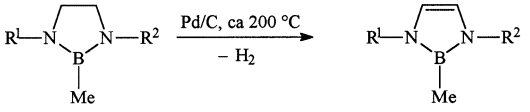
Scheme 4. Synthetic pathways to 1,3,2-diazaborolidines.



1 **2**

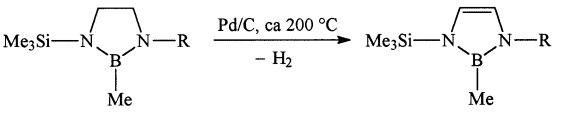
1,2	R^1	R^2	yield (%)
a	Me	Ph	100
b	H	Ph	30
c	Me	*t*Bu	52

Scheme 5. Synthesis of 1,3,2-diazaborolines **2a**–**c**.



3b-d **4b-d**

3,4	b	c	d
R^1	Et	Et	*i*Pr
R^2	Me	Et	*i*Pr



5a-e **6a-e**

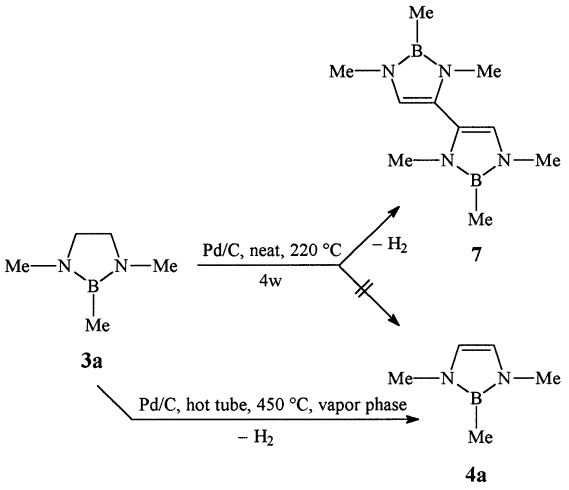
5,6	a	b	c	d	e
R	Me_3Si	Me	Et	*i*Pr	*t*Bu

Scheme 6. Synthesis of **4b**–**d** and **6a**–**e**.

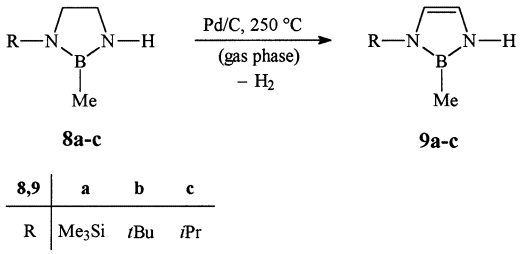
An attempt to synthesize the 1,2,3-trimethyl derivative **4a** by heating neat diazaborolidine **3a** in the presence of palladium-on-charcoal for 4 weeks was thwarted by the formation of the dinuclear compound **7** [9] (Scheme 7).

However, when the catalytic dehydrogenation was conducted in a hot tube at 450°C with vaporized **3a** the anticipated product **4a** was obtained in 87% yield. The complete conversion required exposure of the reaction mixture to the hot zone 10–15 times.

Analogous gas-phase reactions of the HN-functionalized 1,3,2-diazaborolidines **8a**–**c** at a furnace temperature of 250°C afforded the unsymmetrically substituted 1,3,2-diazaborolines **9a**–**c** (Scheme 8) [9].



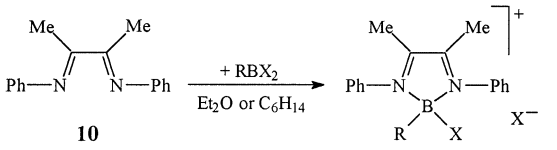
Scheme 7. Catalytic dehydrogenation of **3a**.



Scheme 8. Preparation of **9a**–**c**.

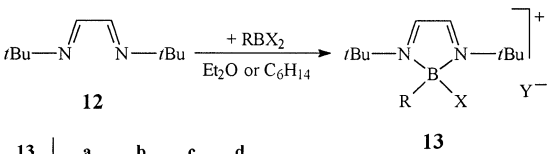
2.2. Reduction of 1,3,2-diazaborolium salts

A completely different synthetic strategy for 1,3,2-diazaborolines is based upon the reduction of 2-halide-functionalized 1,3,2-diazaborolium salts with sodium amalgam. The intensely colored borolium salts **11**, **13**, **15** and **17** were formed by the slow combination of equimolar amounts of the corresponding 1,4-diazabutadienes **10**, **12**, **14** or **16** and organoboron dihalides or boron trihalides in diethyl ether or *n*-hexane [6,8,14]. The employment of large quantities of solvent was recommended to avoid polymerization (Scheme 9). Surprisingly, the treatment of **14** with BCl_3 under these conditions gave a 5:1 mixture of the corresponding borolium chloride **15a** and borolium tetrachloroborate **15b**, which were separated by fractional crystallization. The diazaborolium tetrachloroborate **13d** was obtained by the reaction of **12** with two equivalents of BCl_3 in *n*-hexane [14]. In marked contrast to this the corresponding borolium fluorides or tetrafluoroborates were elusive. The combination of the 1,4-diazabutadienes **10** and **12** with boron trifluoride diethyl etherate furnished the 1:2 adducts **18a** and **18b** [8,14] (Scheme 10).



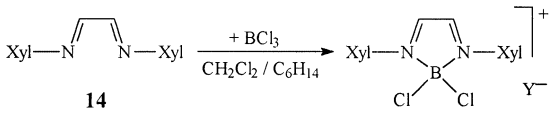
10 11

11	a	b	c	d
R	Me	Ph	Br	Cl
X	Br	Cl	Br	Cl



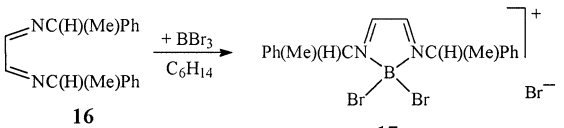
12 13

13	a	b	c	d
R	Me	Ph	Br	Cl
X	Br	Cl	Br	Cl
Y	Br	Cl	Br	BCl_4



14

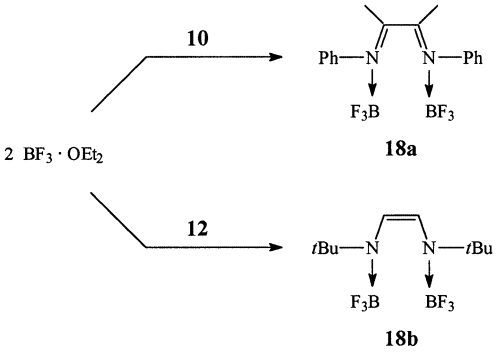
15a (Y = Cl)
15b (Y = BCl_4)



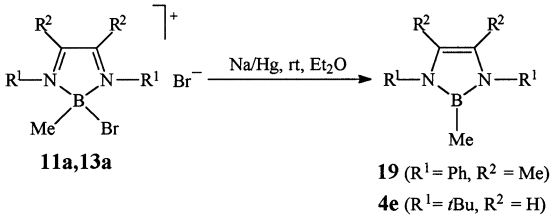
16 17

Scheme 9. Synthesis of 1,3,2-diazaborolium salts.

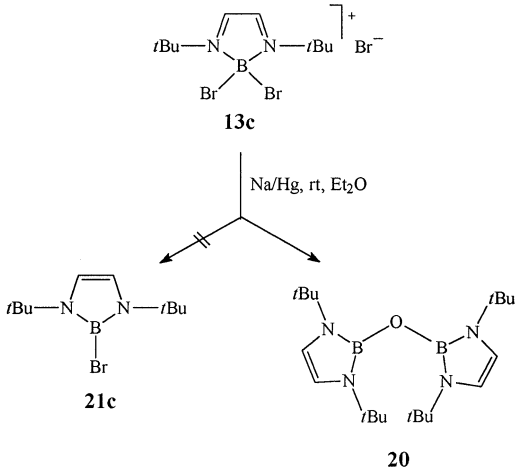
Surprisingly, only the reduction of **11a** and **13a** with sodium amalgam in diethyl ether at room temperature afforded the 1,3,2-diazaborolines **19** and **4e** cleanly (Scheme 11). In all other cases the sodium amalgam reduction in diethyl ether under comparable conditions provided only spectroscopic evidence for the generation of the anticipated products. A reassessment of the reduction of **13c** in solvents such as diethyl ether, tetrahydrofuran, dioxane or 1,2-dimethoxyethane invariably led to the formation of the diboroxane **20**, which was isolated as a crystalline solid in good yield [13] (Scheme 12). Moisture cannot be considered as a source of the oxygen atom in **20**, because all the solvents were freshly distilled from $LiAlH_4$, and Karl–Fischer determinations proved the absence of traces of water. Therefore, most likely, ether cleavage must have occurred in this reaction.



Scheme 10. Formation of **18a** and **18b**.



Scheme 11. Synthesis of **4e** and **19**.



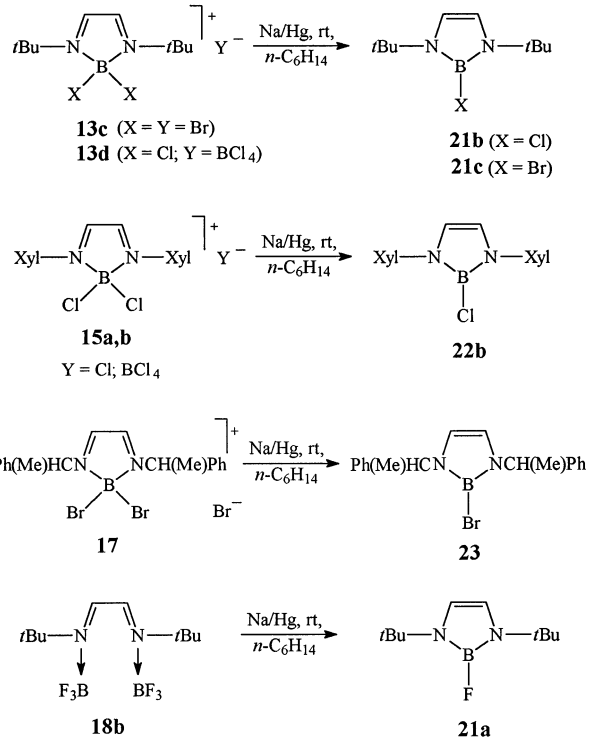
Scheme 12. Synthesis of **20**.

Accordingly, the reduction of **13c** with sodium amalgam in hexane afforded **21c** cleanly in 85% yield [13]. The same holds true for the conversion of the BF_3 adduct **18b** and the chloro-compounds **13d** and **15a**,**b** into the thermally stable 2-fluoro-1,3,2-diazaboroline **21a** and the 2-chloro-derivatives **21b** and **22b**, respectively

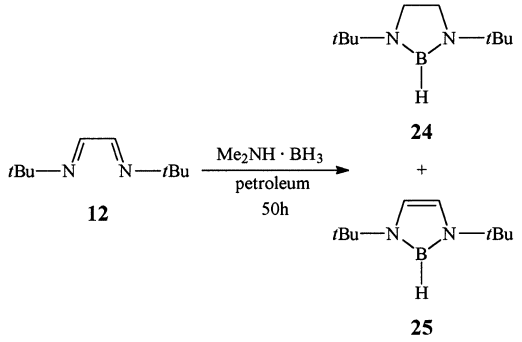
(Scheme 13). Compound **23** is the first chiral 1,3,2-diazaboroline, provided that enantiomerically pure (*S*)-(−)-1-phenylethylamine was used in the formation of 1,4-diazabutadiene **16** [26].

2.3. Cyclocondensations

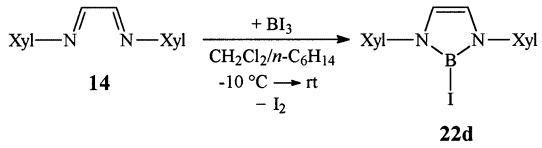
Cyclocondensations of 1,4-diazabutadienes and boron compounds with the direct production of 1,3,2-diazaborolines were realized in two cases. The reduction of **12** with dimethylamine-borane in boiling petroleum ether (40–60°C) for 50 h gave an inseparable 4:1 mixture of the 1,3,2-diazaborolidine **24** and 1,3,2-diazaboroline **25** [27] (Scheme 14). The 2-iodo-1,3,2-diazaboroline was accessible directly by a redox reaction between **14** and BI_3 in a mixture of CH_2Cl_2 and *n*-hexane at −10 to +20°C. The compound was sublimed at 380°C/0.01 Torr without significant decomposition [14] (Scheme 15). In all the remaining cases the respective 1,4-diazabutadienes had to be reduced to their dilithium salts prior to cyclocondensation with the boron trihalide. The lithium reduction, as well as the cyclocondensation process, was performed in *n*-hexane slurries over a period of 7–10 days to furnish the 1,3,2-diazaborolines **21a**–**d**, **22b**,**c** and **27b**,**c** in 54–83% yield [13,14] (Scheme



Scheme 13. Preparation of **21a**–**c**, **22b** and **23** by sodium amalgam reduction.



Scheme 14. Preparation of **24** and **25**.



Scheme 15. Preparation of **22d** by a redox reaction.

16). With the exception of **21d** and **27b,c**, which decompose rapidly at ambient temperature, the novel halide-functionalized 1,3,2-diazaborolines are thermally stable compounds.

According to our current knowledge, the synthetic route to 1,3,2-diazaborolines via the dilithiated 1,4-diazabutadiene seems to be the most effective one, provided that the organic precursor is stable enough at room temperature to overcome the reduction period without significant deterioration. If the parent 1,4-diazabutadiene is not stable enough at room temperature the catalytic dehydrogenation of the corresponding 1,3,2-diazaborolidines is recommended. Here, however, functional groups are usually not tolerated. A severe limitation of the sodium amalgam reduction of borolium salts is connected with the nature of the substituents at nitrogen. The reaction usually works well with *tert*-butyl- and aryl-groups at the N-atoms, but failed with *N*-isopropyl substituents.

3. Structure and bonding

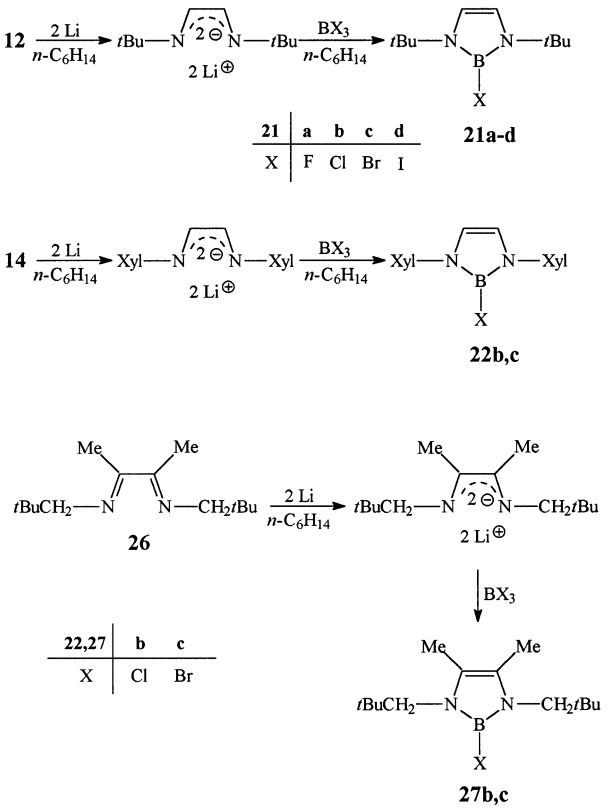
3.1. Molecular structures

The most characteristic common structural feature of a number of 1,3,2-diazaborolines, as determined by single-crystal X-ray diffraction analysis, is the planarity of the heterocyclic core (Fig. 2). The BN bond lengths in the 1,3,2-diazaborolines **4a**, **4c**, **4d** [9] and **22d** [14] vary from 1.41 to 1.43 Å and thus show no significant differences when compared with the B–N bond in the 1,3,2-

borolidines **3a** and **3c** (Fig. 3). The atomic distance B–N in H_2NBH_2 was calculated to be 1.38 Å, which points to a localized multiple bond with an efficient p(π)–p(π) interaction. If the BH_2 unit is oriented perpendicularly to the NH_2 part of the molecule then the π-interaction can be neglected, and the BN bond is elongated to 1.47 Å according to the bond order of unity [28]. The B–N bond lengths in **3a**, **3c** and in **4a**, **4c**, **4d** and **22d** thus indicate a bond order of ca. 1.5. The C–C distances in the diazaborolines range from 1.33 to 1.36 Å, including the value for the localized CC double bond in ethene (1.35 Å) (Fig. 3).

The endocyclic CN bond lengths in **4a**, **4c**, **4d** and **22d** range from 1.39 to 1.41 Å and are thus significantly shortened compared with the exocyclic C_{sp^2}–N_{sp^2} bond length in **22d** of 1.44 Å. The calculated value for a CN double bond in Schiff bases is 1.27 Å [29]. To get an impression of the cyclic delocalization of the 6π electrons in 1,3,2-diazaborolines such as **4a**, **4c**, **4d** and **22d**, it is helpful to compare the relevant C–N and C–C distances with those of the isoelectronic pyrrole as determined by an electron diffraction study [30].

Here the N–C_α bonds of 1.370 Å and the C_β–$C_{\beta'}$ bond (1.417 Å) are shorter than normal single bonds and the C_α–C_β bonds (1.382 Å) are longer than normal



Scheme 16. Synthesis of **21a**–**d**, **22b**,**c** and **27b**,**c** via dilithiated 1,4-diazabutadienes.

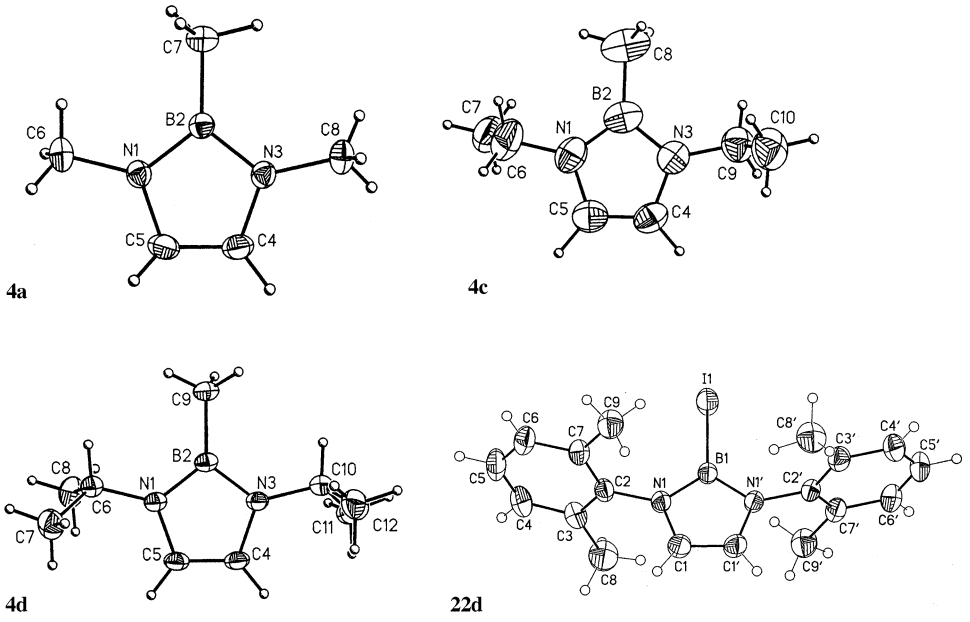


Fig. 2. Molecular structures of the 1,3,2-diazaborolines **4a**, **4c**, **4d** and **22d**.

localized double bonds. Thus the formal replacement of a C=C unit in pyrrole by a BN building block causes an elongation of the CN bond from 1.37 to 1.39–1.41 Å in the diazaborolines. If one accepts the shortening of a C–C single bond and the bond lengthening of a C=C double bond as an argument for electron delocalization, than the cyclic delocalization of the 6π electrons in pyrrole is much more pronounced than in 1,3,2-diazaborolines.

The difference electron densities of 1,3,2-trimethyl-1,3,2-diazaborolidine (**3a**), 1,3-diethyl-2-methyl-1,3,2-diazaborolidine (**3c**), and 1,2,3-trimethyl-1,3,2-diazaboroline (**4a**) show that the B–N bonds in the saturated molecules **3a** and **3c** possess a remarkable double bond character and that the maxima of the bonding electron densities are shifted to the nitrogen atoms as the more electronegative bonding partner. It is interesting to note that the difference electron density in the NBN plane of 1,3,2-diazaboroline **4a**, in contrast to that of the saturated ring **3a**, is similar in all five bonds. The shift of the maxima in the BN bonds toward the nitrogen atoms cannot be observed to the same extent as in **3a** due to the improved delocalization of the 6π-electrons (Fig. 4) [9].

3.2. Spectra

The ^{11}B-NMR spectra (Table 1) show that the boron atoms in the 1,3,2-diazaborolines **2a**–**c**, **4a**–**d**, **6a**–**e** and **9a**–**c** are better shielded than those in the corresponding saturated 1,3,2-diazaborolidines. These high-field shifts $\Delta\delta$ [$\Delta\delta =$

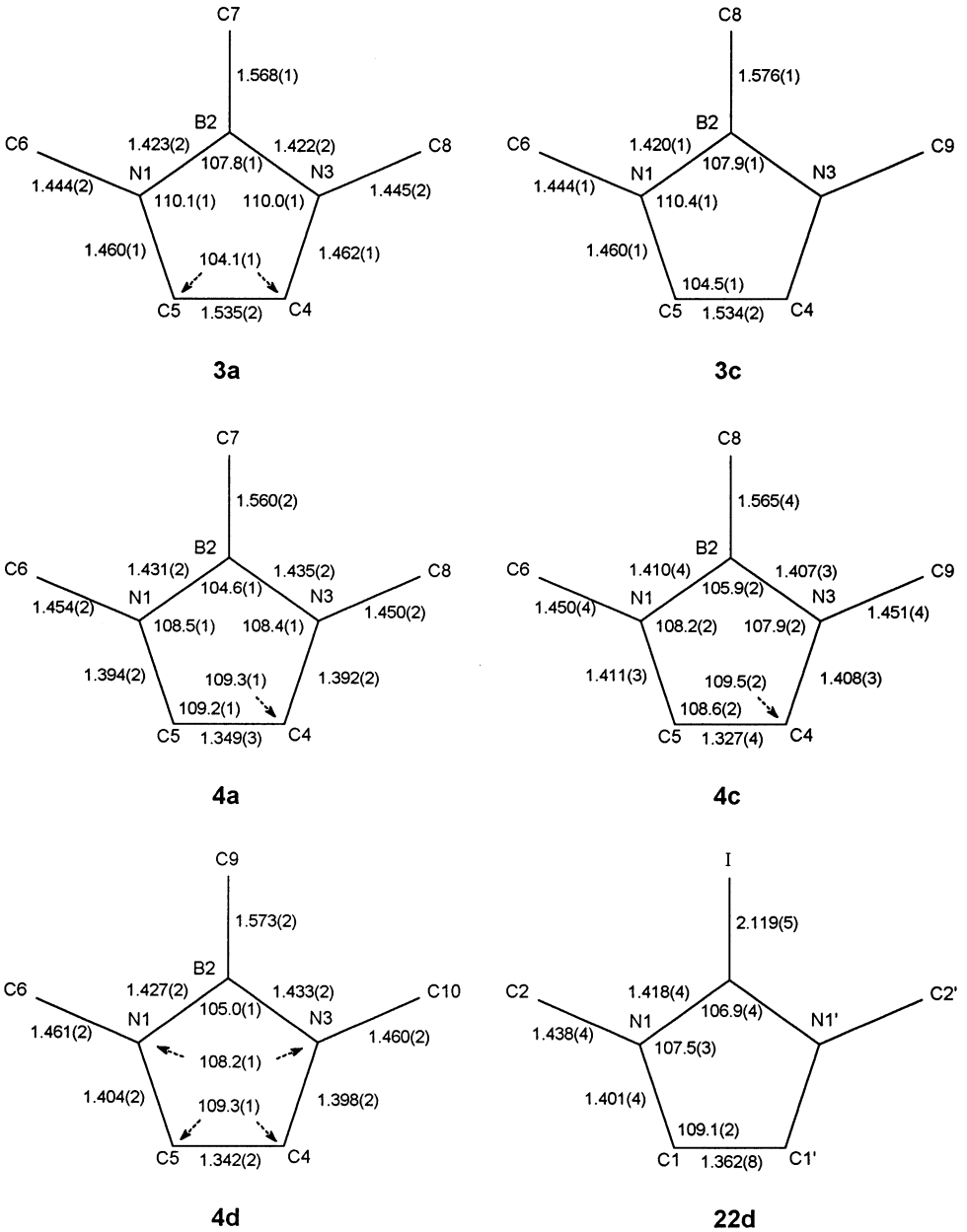


Fig. 3. Selected bond lengths and bond angles in 1,3,2-diazaborolidines **3a**, **3c** and in 1,3,2-diazaborolines **4a**, **4c**, **4d** and **22d**.

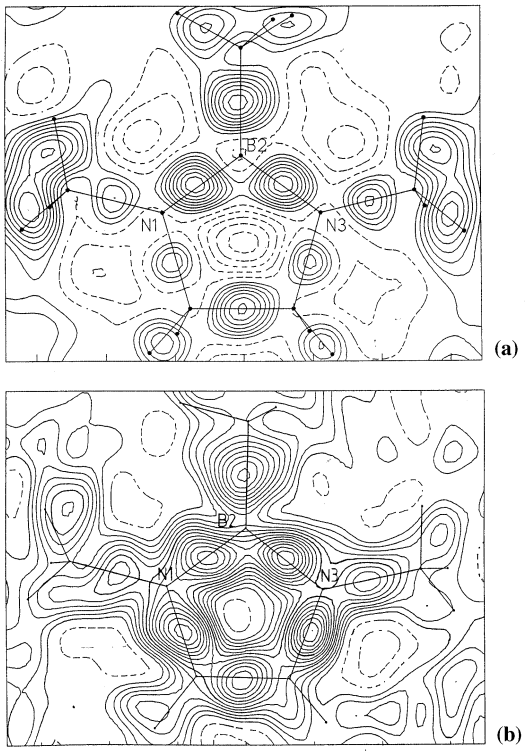
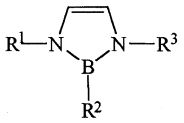


Fig. 4. (a) Difference electron density in the NBN plane of **3a**. Contour lines are in e^{-} Å^{-3}; min = −0.55; max = 0.37. Distance: positive 0.05 e^{-} Å^{-3}, negative 0.1 e^{-} Å^{-3} (dotted). Reference line: first solid line. (b) Difference electron density in the NBN plane of **4a**. Contour lines are in e^{-} Å^{-3}; min = −0.13, max = 0.33. Distance: positive 0.025 e^{-} Å^{-3}, negative 0.05 e^{-} Å^{-3} (dotted). Reference line: first solid line.

δ^{11}B(borolidine) − δ^{11}B(boroline)] range from 4.8 ppm in going from **5a** to **6a** to 7.0 ppm in going from **8b** to **9b**. The chemical shifts of 1,3,2-diazaborolines with alkyl or aryl substituents at boron, as well as alkyl or aryl groups at both nitrogen atoms, are centered around $\delta = 26 \pm 1$ ppm. The ^{11}B nuclei in diazaborolines with one or two *N*-silyl groups experience some deshielding and are registered between $\delta = 28.9$ in **6d** and 33.4 in **6a**. High-field shifts relative to **2a**–**c** and **4a**–**e** were observed when the organic substituent at boron was replaced by a halogen atom, as demonstrated in the series: **21a** ($\delta = 20.3$) ≈ **21b** (δ 20.2) > **21c** ($\delta = 16.2$) > **21d** ($\delta = 6.5$). A similar trend is obvious in the series **22b** (δ 21.1) > **22c** ($\delta = 19.2$) > **22d** ($\delta = 11.8$). The replacement of the methyl group in **4e** ($\delta = 26.2$) by a hydrogen atom in **24** is accompanied by a high-field shift to $\delta = 18.9$ ppm.

The hydrogen atoms at the ring carbon atoms in the symmetrically substituted 1,3,2-diazaborolines with alkyl or silyl groups at the ring nitrogen atoms range from $\delta = 5.90$ in the ^{1}H-NMR spectra of **2c** and **6a** to $\delta = 6.40$ in the spectrum of **21d**. In the corresponding *N*-xylyl-substituted species **22b**–**d** the ^{1}H-NMR reso-

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



Compound	R^1	R^2	R^3	δ^{11}B	δ^{1}H (C*H*)	δ^{13}C (*C*H)	Ref.
2a	Me	Ph	Me	25.6	6.14		[7]
2b	Me	Ph	H	25.8	5.98		[7]
2c	Me	*t*-Bu	Me	27.0	5.90		[7]
4a	Me	Me	Me	26.5	5.99	117.9	[9]
4b	Me	Me	Et	26.5	6.12/6.18	115/117	[9]
4c	Et	Me	Et	26.5	6.18	115.1	[9]
4d	*i*-Pr	Me	*i*-Pr	26.7	6.21	111.5	[9]
4e	*t*-Bu	Me	*t*-Bu	26.2	6.16	111.5	[11]
6a	Me_3Si	Me	Me_3Si	33.4	5.90	118.8	[11]
6b	Me_3Si	Me	Me	29.4	6.10/6.15	115.2/121.1	[12]
6c	Me_3Si	Me	Et	29.1	6.19	115.4/119.1	[12]
6d	Me_3Si	Me	*i*-Pr	28.9	6.23/6.77	115.2/115.6	[12]
6e	Me_3Si	Me	*t*-Bu	29.1	6.19/6.43	114.5/117.0	[12]
9a	Me_3Si	Me	H	30.1	6.22/6.23	114.9/116.5	[9]
9b	*t*-Bu	Me	H	26.5	6.17/6.35	110.7/114.8	[9]
9c	*i*-Pr	Me	H	26.4	6.27	111.6/113.2	[9]
21a	*t*-Bu	F	*t*-Bu	20.3	5.99	109.9	[14]
21b	*t*-Bu	Cl	*t*-Bu	20.2	6.19	112.0	[14]
21c	*t*-Bu	Br	*t*-Bu	16.2	6.27	113.6	[13]
21d	*t*-Bu	I	*t*-Bu	6.5	6.40	114.6	[14]
22b	Xyl	Cl	Xyl	21.1	5.86	117.7	[14]
22c	Xyl	Br	Xyl	19.2	5.90	118.6	[13]
22d	Xyl	I	Xyl	11.8	5.99	120.0	[14]
24	*t*-Bu	H	*t*-Bu	18.9	6.39	114.2	[11]

nances are shielded by 0.3–0.4 ppm. The ^{13}C{^{1}H}-NMR signals of the 1,3,2-diazaborolines with *N*-alkyl substituents were observed in the range of $\delta = 109.9$ in **21a** to $\delta = 117.9$ in **4a**. In the disilylated derivative **6a** this resonance appears at $\delta = 118.8$, whereas in the unsymmetrical 1,3,2-diazaboroline **6b** the CH-carbon atom next to the $NSiMe_3$ groups resonates at $\delta = 121.1$. In the *N*-arylated compounds **22b**–**d** the ^{13}C nuclei of the ring carbon atoms are deshielded by ca. 5 ppm compared with the *N*-alkylated analogues **21b**–**d**. These NMR spectroscopic results have usually been taken as further evidence for the heteroaromaticity of 1,3,2-diazaborolines [6,7,9].

He (I) photoelectron spectra were recorded for the 1,3,2-diazaborolines **2a**–**c** and for the corresponding saturated heterocycles **1a**–**c** [31]. The first two bands in the spectra of **2c** at 7.25 and 8.98 eV and in **1c** at 7.46 and 9.37 eV were assigned to ionization from π-orbitals in both ring systems. The sequence of these two bands, however, is reversed in going from **1c** to **2c**. The HOMO of the 1,3,2-diazaboro-

lidine is the π*MO of an NBN group, as is typical for diaminoboranes, whereas the second HOMO is the corresponding π-bonding MO. In **2c** the antibonding interaction of the bonding π-MO with the π-orbital of ethene ($IE_1 = 10.51$ eV) [32] results in a destabilization by ca. 2 eV, and the ionization of this orbital gives rise to the band at 7.25 eV in **2c**. The antibonding π-orbital of **1c** is stabilized by 1.5 eV as a consequence of its linear combination with the π*MO of the ethene unit, accounting for the band at 8.98 eV in the spectrum of **2c**. A broad band at 12.75 eV in **2c** reflects the ionization of the π-orbital, which results from the bonding interaction of the ethene and the NBN part of the molecule.

3.3. Theoretical calculations

According to CNCD/S calculations on 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaborolidine (**1c**) and 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaboroline (**2c**) the π-orbitals in **1c** are similar to those in acyclic diaminoboranes [31] (Fig. 5). Thus the HOMO of the

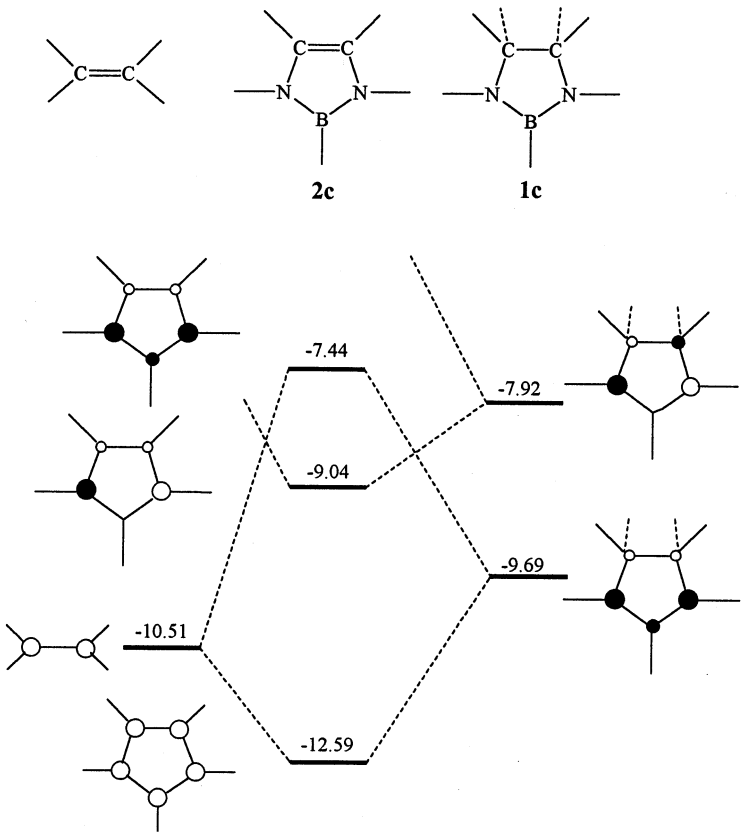


Fig. 5. Diagram of the π-interactions in 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaboroline (**2c**) and 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaborolidine (**1c**).

molecule with an orbital energy of −7.92 eV corresponds to the non-bonding π-orbital in an heteroallylic chain with a nodal plane bisecting the center of the C–C bond and the boron atom. The bonding NBN-π-orbital is found at −9.69 eV. The π-orbital sequence in the 1,3,2-diazaboroline is derived from the linear combination of these two BNB-π-orbitals of **1c** with two π-orbitals of ethene. Thus the lowest π-orbital of the five-membered ring is calculated to have an orbital energy of −12.59 eV. The antibonding combination of both π-orbitals gave rise to the HOMO with an orbital energy of −7.44 eV. The HOMO of the borolidine is stabilized to −9.04 eV by linear combination with the π*-orbital of the ethene. The π-orbital sequence and the calculated orbital energies are substantiated by He (I) photoelectron spectroscopy and, in addition to ^{11}B-NMR and UV data, these results were taken as evidence for the heteroaromaticity of the 1,3,2-diazaboroline ring system.

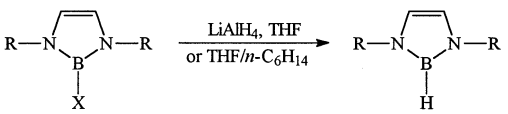
4. Reactivity of 1,3,2-diazaborolines

4.1. Substitutions at boron

The presence of a reactive boron–halogen bond comprising an electrophilic boron center renders 1,3,2-diazaborolines, such as **21a–d**, **22b–d** and **23**, valuable starting materials for a number of chemical transformations. In particular, the reaction with nucleophiles is well suited as an entry into the wide field of 1,3,2-diazaborolines with functional groups, which are not accessible by the synthetic strategies discussed in Section 2.

4.1.1. Hydride substitution

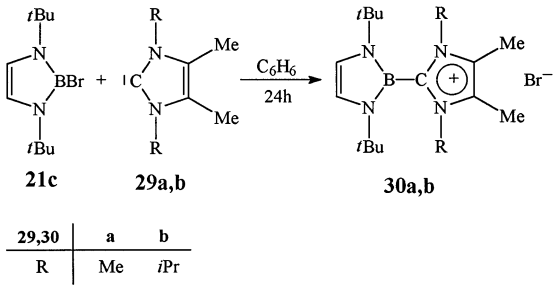
As described before in Section 2.3 (Scheme 14), the first BH-functionalized 1,3,2-diazaboroline **25** was prepared as a minor product in an inseparable mixture with its corresponding 1,3,2-diazaborolidine **24** [27]. The availability of 2-halide-functionalized 1,3,2-diazaborolines provides an alternative access to such molecules. Thus, the treatment of **22d** with equimolar amounts of $LiAlH_4$ in a hexane–THF mixture or in THF led cleanly to the 1,3,2-diazaborolines **25** and **28** (Scheme 17) [15].



21c,22d **25,28**

	R	X
21c,25	*t*Bu	Br
22d,28	Xyl	I

Scheme 17. Formation of **25** and **28**.



Scheme 18. Formation of salts **30a**,**b**.

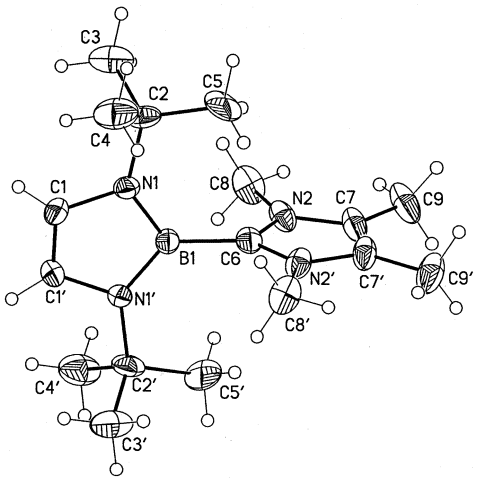


Fig. 6. Structure of the cation of **30a**; selected bond lengths (Å) and angles (°): B(1)–N(1) 1.434(6), N(1)–C(1) 1.414(7), C(1)–C(1′) 1.315(11), B(1)–C(6) 1.580(11); N(1)–B(1)–N(1′) 107.1(6).

The crude products were purified by sublimation at 50°C and 10^{-3} Torr (**25**) or 210°C and 10^{-4} Torr (**28**) to give colorless air- and moisture-sensitive solids. In the proton coupled ^{11}B-NMR spectra (C_6D_6) compounds **25** and **28** exhibit doublets at $\delta = 18.9$ ($^1J_{BH} = 149$ Hz) and 21.9 ($^1J_{BH} = 158$ Hz).

4.1.2. Group 14 element-based nucleophiles

Upon mixing a benzene solution of **21c** with equimolar amounts of the imidazol-2-ylidenes **29a**,**b** (**a**: R = Me; **b**: *i*-Pr) the colorless salts **30a**,**b** precipitated in high yields (Scheme 18). The cations of these thermally stable compounds can be regarded as 1,3,2-diazaborolinyl-functionalized imidazolium salts or as the first boryl-substituted carbocations. Compared with **21c**, the ^{11}B-NMR resonances of the salts **30a**,**b** ($CDCl_3$) appear slightly shielded [$\delta = 15.3$ (**a**); 15.0 (**b**)] [13].

The X-ray structural determination of **30a** (Fig. 6) revealed the novel 2-(1,3,2-diazaborolinyl)-1,3,4,5-tetramethylimidazolium cation and four molecules of chloroform in the asymmetric unit. There are no bonding contacts with the bromide ion, which is located above the B–C vector [Br···B(1) 5.68 Å; Br···C(6) 5.63 Å]. Both five-membered heterocycles are planar, with an interplanar angle of 92.9°. Bond lengths and bond angles in the 1,3,2-diazaborolinyl unit of the cation are in accordance with the structural parameters observed for **4a** (Section 3.1).

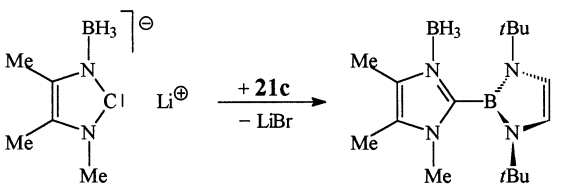
2-Bromo-1,3,2-diazaboroline (**21c**) reacted with the anion of salt **31** to give the 2-(1,3,2-diazaborolinyl)imidazole **32** (Scheme 19). In the ^{11}B-NMR spectrum of **32** two signals at $\delta = 19.1$ (C–BN_2) and -20.1 (NBH_3) are found [33].

Treatment of **21b**, **21c** and **21d** with an equimolar amount of *tert*-butyl isocyanide in *n*-hexane led to the formation of the 2-cyano-1,3,2-diazaboroline **34** instead of the anticipated nitrilium salt **33**. The formation of *tert*-butylbromide as a by-product was proven by ^{1}H-NMR spectroscopy.

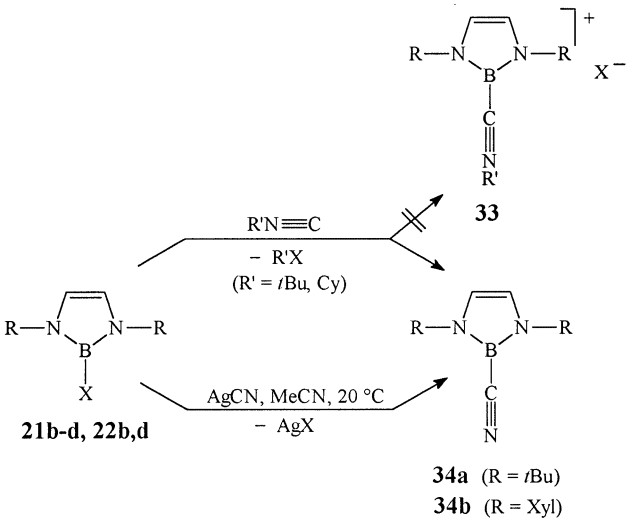
The corresponding transformation of **21c** with cyclohexyl isocyanide afforded **34a** in 38% yield after 5 days. Similarly, **22b** and **22d** were converted into **34b**. *o*-Xylyl isocyanide appeared to be inert towards the 2-halo-1,3,2-diazaborolines [15] (Scheme 20). **34a** and **34b** were also obtained in high yield by the combination of **21b** (or **21c**) and **22d** with silver cyanide in acetonitrile at room temperature.

In the ^{11}B-NMR spectra, **34a** and **34b** gave rise to singlets at $\delta = 12.0$ and 13.5, respectively. The reaction of **21c** with a stoichiometric amount of *n*-butyl lithium in hexane at room temperature afforded **35** as a colorless hygroscopic solid after distillation at 200–250°C and 10^{-3} Torr (84% yield). Similarly, the 2-cyano-1,3,2-diazaboroline (**34a**) was converted in high yield into the 2-*tert*-butyl- and the 2-ethynyl-1,3,2-diazaborolines **36** and **37**, respectively, by treatment with *t*-BuLi or the ethylenediamine adduct of lithium acetylide. In the case of **37** the employment of the cyano derivative **34a** as a starting material was crucial, since the reaction of the bromo compound **21c** with the organolithium component yielded the aminolysis product **38** (Scheme 21).

The ^{11}B{^{1}H}-NMR signal of **35** ($\delta = 26.4$) compares well with that in **4e** (B–Me instead of B–*n*-Bu; $\delta = 26.2$), whereas the ^{11}B-NMR resonance of **36** ($\delta = 30.1$) appeared slightly deshielded. In a series of bisaminoboryl acetylenes the ^{11}B-NMR absorbances were registered in the narrow range of $\delta = 23.8$–24.9 regardless of the remaining substituents at the C≡C triple bond [34]. In comparison, the ^{11}B-NMR



Scheme 19. Formation of **32**.



Scheme 20. Synthesis of **34a**,**b**.

signal of **37** ($\delta = 15.7$) is shielded markedly. This observation may be explained by the aromaticity of the diazaboroline ring.

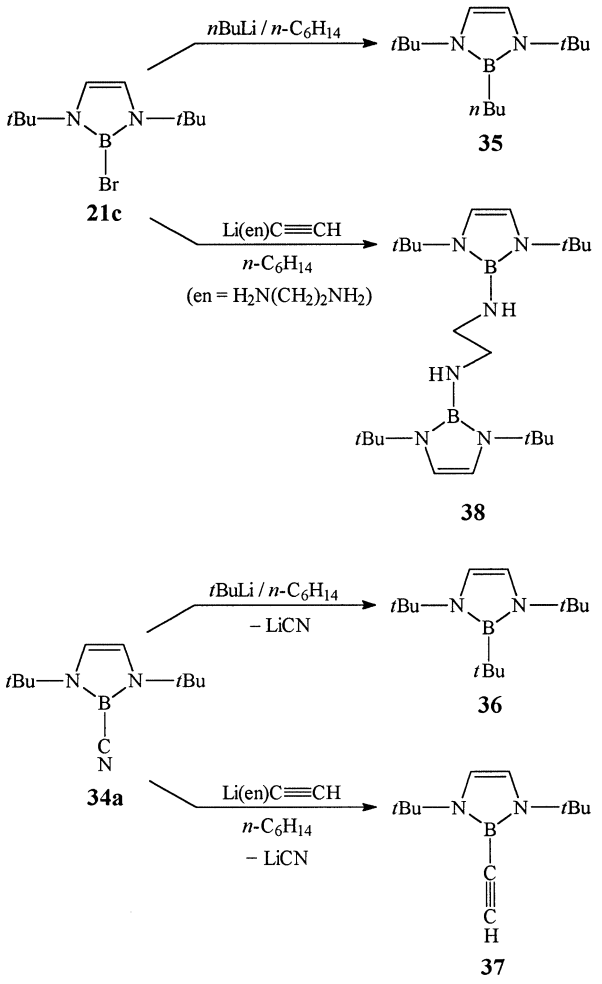
The first B-stannylated 1,3,2-diazaboroles **39a**,**b** were synthesized from **21c** and **22d** and stoichiometric amounts of trimethylstannyllithium in a THF–*n*-hexane mixture at ambient temperature. Purification of the colorless solid **39a** was achieved by distillation at 190°C and 10^{-3} Torr and subsequent crystallization of the distillate from *n*-hexane at -30°C (89%). The colorless crystalline **39b** precipitated from an *n*-hexane solution at -10°C (60%) (Scheme 22).

The $^{11}B\{^1H\}$-NMR spectrum of **39a** is characterized by a singlet at $\delta = 25.8$ with ^{119}Sn satellites ($^1J_{SnB} = 1031$ Hz). In accordance with this, a quadruplet at $\delta = 152$ ($^1J_{SnB} = 1032$ Hz) was observed in the $^{119}Sn\{^1H\}$-NMR spectrum of the compound. Similarly, the ^{11}B chemical shift of **39b** ($\delta = 28.2$) shows a ^{119}Sn–^{11}B coupling of $^1J_{SnB} = 960$ Hz. The $^{119}Sn\{^1H\}$-NMR resonance of **39b** is found as a quadruplet at $\delta = 146$ with $^1J_{SnB} = 960$ Hz. The saturated compound (Me)N–CH_2CH_2N(Me)B-($SnMe_3$) displayed an ^{11}B signal at markedly lower field ($\delta = 36.5$, $^1J_{SnB} = 930$ Hz) and a ^{119}Sn-NMR resonance at $\delta = 154$ [35].

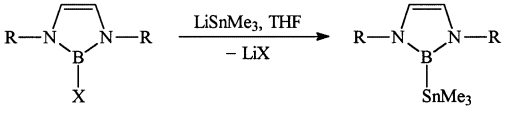
The molecular structure of **39a** (Fig. 7) features a planar 1,3,2-diazaboroline ring with a trimethylstannyl substituent at the boron atom [B(1)–Sn(1) = 2.274(5) Å]. Atomic distances and valence angles within the heterocycle are in good agreement with the equivalent data for the borolinylimidazolium cation **30a** (Fig. 6) and for **22d** (Fig. 2).

4.1.3. Group 15 element-based nucleophiles

Generally, three synthetic pathways for the transformation of 2-halo-1,3,2-diazaborolines into diazaborolines with exocyclic nitrogen-based substituents at the boron center are conceivable (Scheme 23).



Scheme 21. Formation of **35**–**38**.



	R	X
21c,39a	*t*Bu	Br
22d,39b	Xyl	I

Scheme 22. Preparation of **39a**,**b**.

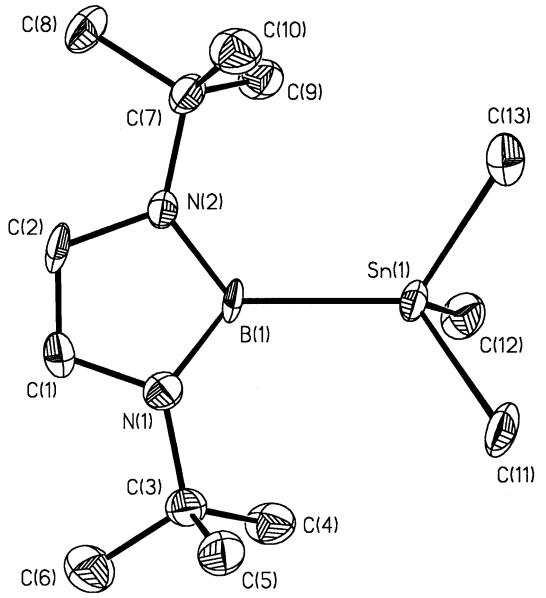
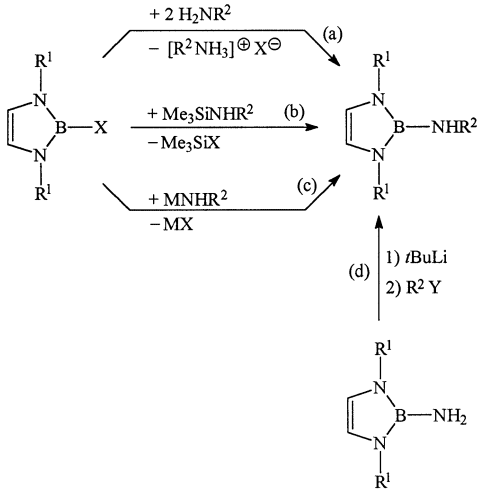


Fig. 7. Molecular structure of **39a**; selected bond lengths (Å) and angles (°): B(1)–Sn(1) 2.274(5), B(1)–N(1) 1.439(7), N(1)–C(1) 1.379(7), C(1)–C(2) 1.344(8), N(2)–C(2) 1.399(7), B(1)–N(2) 1.450(7); N(1)–B(1)–N(2) 105.0(4), N(1)–B(1)–Sn(1) 127.5(4), N(2)–B(1)–Sn(1) 127.5(4).



Scheme 23. Synthesis of 2-amino-1,3,2-diazaborolines.

Approach (a) is based upon ammonolysis of the boron–halogen bond in 2-halogeno-1,3,2-diazaborolines by ammonia and primary amines. An alternative synthesis makes use of the SiN cleavage of suitable aminosilanes by the 2-halo-

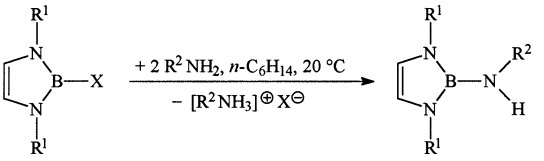
1,3,2-diazaboroline (path (b)). A metathesis-type reaction as depicted in path (c) may also be successful in selected situations.

These three methods are complemented by route (d), where the amino groups of the 2-amino-1,3,2-diazaborolines are involved in chemical transformations. According to path (a), 1,3,2-diazaboroles **21c** and **22d** react smoothly at room temperature with dry gaseous ammonia in *n*-hexane solution to afford the 2-amino-1,3,2-diazaborolines **40a** and **40b** in high yield. The colorless solids are surprisingly thermally stable. Thus, **40b** can be sublimed at 320°C at 10^{-3} Torr (Scheme 24) [36].

Usually, the primary borylamines R_2BNH_2 are thermolabile when they are not protected by sterically demanding substituents to prevent them from amine extrusion and oligomerization [37–40]. The remarkable thermostability of **40a** and **40b** is presumably due to the bulky substituents and the aromaticity of the heterocycle. Upon exposure to twice the molar amount of *tert*-butylamine or 2,6-dimethylaniline, compound **21c** was transformed smoothly into the diazaborolines **41a** and **41b**.

All attempts to react **21c** with secondary amines failed. The diborolinylamine **42** (Scheme 25) was conveniently prepared by reaction of hexamethyldisilazane with two molar equivalents of **21c** in boiling hexane (path (b)).

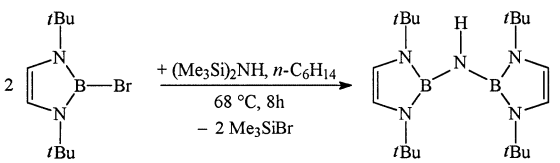
Si–N cleavage also occurred in the synthesis of the orange microcrystalline 1,3,2-diazaborolinyl ketimine **43** (83% yield; Scheme 26). This result is interesting



21c,22d **40a,b 41a,b**

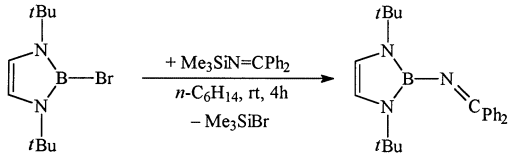
	R1	R2
40a	*t*Bu	H
40b	Xyl	H
41a	*t*Bu	*t*Bu
41b	*t*Bu	Xyl

Scheme 24. Synthesis of **40a**,**b** and **41a**,**b**.

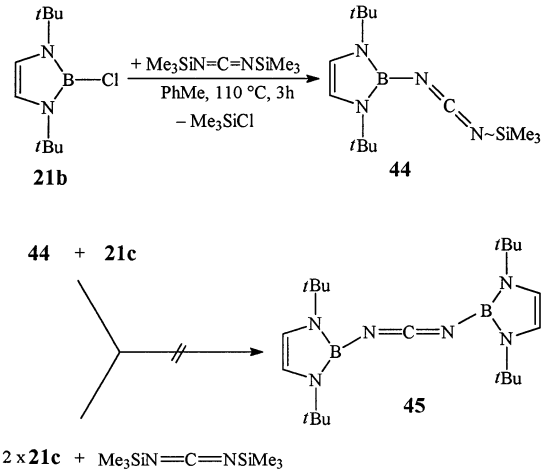


21c **42**

Scheme 25. Synthesis of **42**.



Scheme 26. Synthesis of **43**.



Scheme 27. Synthesis of **44** and attempted preparation of **45**.

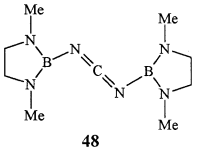
with respect to the reaction of $Ph_2C{=}NSiMe_3$ with the acyclic aminoborane $(Me_2N)_2BCl$, which did not furnish the expected ketiminoborane $Ph_2C{=}NB(NMe_2)_2$ but led to its dismutation products $(Ph_2C{=}N)_2BNMe_2$ and $B(NMe_2)_3$ instead [41].

The 2-chloro-1,3,2-diazaboroline **21b** and an excess of *N*,*N*′-bis(trimethylsilyl) carbodiimide underwent reaction in boiling toluene to yield 1,3,2-diazaborolyl carbodiimide **44**, which was isolated from the reaction mixture by vacuum distillation as a crude brown oil. Solidification and purification of **44** was effected by treating the oil with *n*-hexane. All attempts to synthesize the bis-(1,3,2-diazaborolinyl) carbodiimide **45** failed (Scheme 27). In accordance with the literature [42], the incorporation of the boron atom into a five-membered ring and the vicinity of π-donor atoms account for the thermal stability of **44**. In contrast to this, dialkylboryl- and diarylboryl-carbodiimides suffer from facile dismutation into triorganoboranes and oligomers $(RBNCN)_n$ [42].

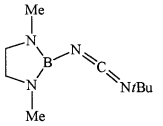
As already mentioned in Scheme 21, the reaction of **21c** with the ethylenediamine adduct of lithium acetylide gave rise to the formation of the bis-borylated diamine **38**. Here, obviously, the acetylide ion has functioned as a Brønsted base in the deprotonation of the amine prior to bromide displacement. Such a strategy would represent path (c) in Scheme 23.

In line with the synthetic approach to isocyanato boranes and isothiocyanato boranes devised by Lappert and Pyszora [42–44], diazaborolines **21b**,**c** were converted into 2-isocyanato diazaborolines **46** by treatment with silver cyanate in acetonitrile. The products were isolated as colorless thermolabile oils in 78% (from **21b**) and 83% (from **21c**) yields. The corresponding isothiocyanato diazaborolines **47a**,**b** resulted from the reaction of **21b**,**c** or **22b**–**d**, respectively, with AgSCN under similar conditions (Scheme 28).

The $^{11}B\{^{1}H\}$-NMR spectra of the 2-amino-1,3,2-diazaborolines **38**, **40a**,**b**, **41a**,**b** and **42** show singlets in the narrow region of $\delta = 21–23$. In contrast to this, carbodiimide **44** features a resonance at much higher field ($\delta^{11}B = 15.9$). In the borolidinyl analogues **48** and **49**, chemical shifts of $\delta^{11}B = 21.4$ and 22.4 were observed.



48

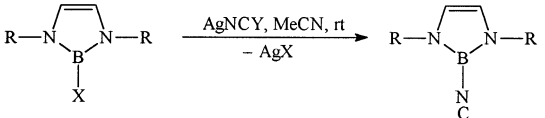


49

The deshielding of the ^{11}B-NMR signal of **44** is obviously due to the aromaticity of the diazaborolidine ring. The ^{11}B-NMR shift of **43** ($\delta = 24.0$) clearly agrees with a monomeric species featuring a three-coordinate boron atom. In $(Ph_2C{=}N)_2BNMe_2$ a singlet at lower-field ($\delta^{11}B = 29.8$) was registered [41]. The boron atoms in the isocyanato and isothiocyanato 1,3,2-diazaborolines **46** and **47a**,**b** resonate as singlets at $\delta = 14.7$ and 14.5.

4.1.4. Group 16 element-based nucleophiles

Diboroxane **20** was also synthesized by controlled hydrolysis of **21c** in a hexane–chloroform mixture (Scheme 29). This reaction parallels the formation of

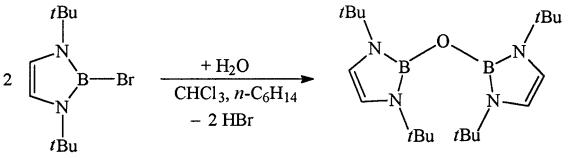


21b,c, 22b,c,d

46,47a,b

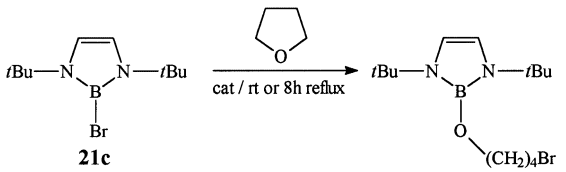
	R	Y
46	*t*Bu	O
47a	*t*Bu	S
47b	Xyl	S

Scheme 28. Preparation of **46** and **47a**,**b**.



21c 20

Scheme 29. Formation of **20** by hydrolysis of **21c**.



21c 50

Scheme 30. Cleavage of THF by **21c**.

the saturated diboroxanes $MeN(CH_2)_nN(Me)B_2O$ ($n = 2, 3$) by hydrolysis of the corresponding methylthiolates [45].

An ether cleavage with the formation of **50** occurred when either a solution of **21c** was heated in boiling tetrahydrofuran for 8 h or when an *n*-hexane solution of **21c** was treated at room temperature with an excess of THF in the presence of catalytic amounts of [(*Z*)-cyclooctene] pentacarbonyl chromium (88% yield) [46] (Scheme 30). The ^{11}B-NMR spectrum of the colorless crystalline product was characterized by a singlet at $\delta = 22.3$.

4.2. Substitutions at nitrogen

Current developments and progress in the chemistry of heavily substituted pyrrolyl anions made the quest for 1,3,2-diazaborolinyl anions relevant. Thus it was possible to remove one silyl group in **6a** either by means of $NaNH_2$ or by KO*t*-Bu. The sodium and potassium salts **51a**,**b** were isolated as pyrophoric, colorless powders [9] (Scheme 31).

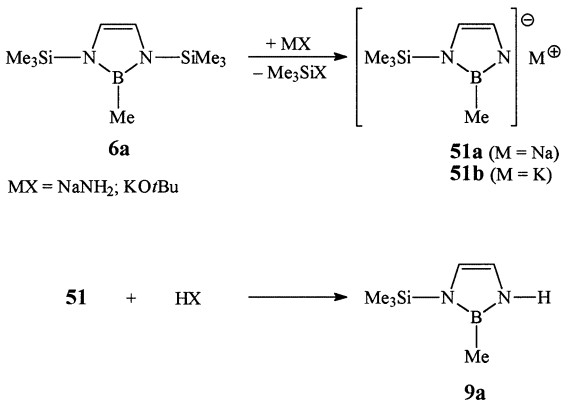
Proton-active compounds, like ethereal hydrochloric acid or methanol, were used to generate the diazaboroline **9a** in low yield. Complications of these processes due to double desilylation and polymerizations have led to the employment of the monosilylated 1,3,2-diazaboroles **6b**–**d**. Their reactions with potassium *tert*-butanolate in boiling THF for 1 h afforded the 1,3,2-diazaborolinyl potassium salts as pyrophoric colorless powders in 59–69% yields [12].

The corresponding tetrabutylammonium 1,3,2-diazaborolinyls were generated by the combination of **6b**–**e** with tetrabutylammonium fluoride in THF within 5 min (Scheme 32).

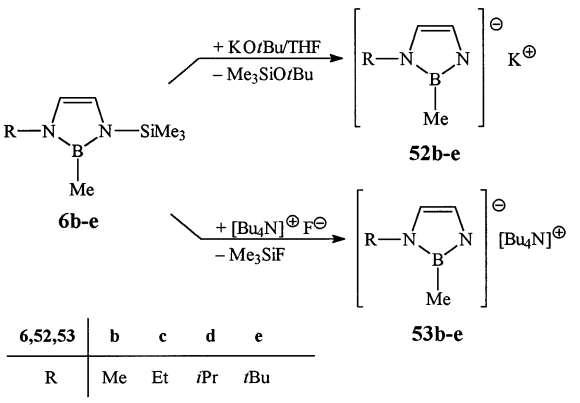
The desilylation of **6b**–**d** to afford the potassium or tetrabutylammonium 1,3,2-diazaborolinyls is accompanied by small high-field shifts ranging from $\Delta\delta^{11}B = 0$ to 2.6 (for **52b**–**e**) and $\Delta\delta^{11}B = 2.9$ to 3.5 (for **53b**–**e**) in the ^{11}B-NMR spectra [12].

4.3. Insertion reactions into the BX bond of 1,3,2-diazaborolines

Hydroboration of the carbon–carbon multiple bond constitutes a classical and well established type of reaction in both organic and organoelement chemistry [47,48]. The 1,2-diboration of alkynes by B_2Cl_4 and B_2F_4 has been equally well known for more than 40 years [49,50], but its wide application suffers from the extreme sensitivity of the diboron tetrahalides towards temperature, oxygen and moisture, thus preventing them from becoming convenient laboratory chemicals. This hurdle was overcome by the recent discovery of the clean and efficient 1,2-cis

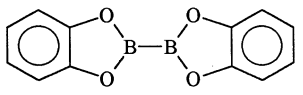


Scheme 31. Formation of salts **51a**,**b** and **9a**.

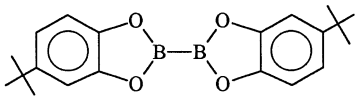


Scheme 32. Desilylation of **6b**–**e**.

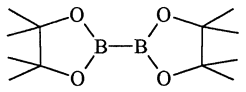
addition of diboranes (**4**) such as **A**–**C** under the catalysis of low-valent Pt– and Pd–phosphine complexes [51–54].



A



B



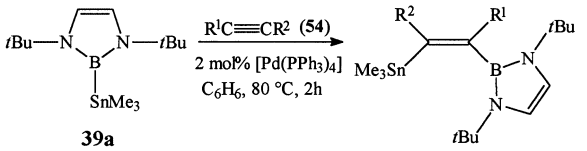
C

The catalytically active species is a result of the oxidative addition of the B–B bond to the low-valent metal center. Comparable additions of boron–silicon [55–57] or boron–tin bonds [56] have also been described in the recent literature. $(Me_2N)_2BSiMe_3$ and $MeNCH_2CH_2N(Me)BSnMe_3$ have been added smoothly to alkynes, α,ω-diynes, enynes, 1,3-dienes and allenes [58–61]. The resulting products are extremely useful as synthetic reagents because the two different heteroatom substituents with their different inherent reactivites allow more elaborate synthetic applications. As the chemo-, regio-, and stereo-selectivity of these boryl metalations are also influenced by the substitution pattern of the compound involved, it was obvious to test 2-stannyl-1,3,2-diazaboroline **39a** in the palladium-assisted boryl-stannation reaction of alkynes.

Reaction of **39a** with equimolar amounts of the alkynes **54a**–**i** in the presence of a catalytic amount (2 mol%) of $[Pd(PPh_3)_4]$ in boiling benzene led to the regio- and stereo-selective generation of the 2-alkenyl-1,3,2-diazaborolines **55a**–**i**. Products **55a**–**i** were isolated as colorless oils by vacuum distillation (Scheme 33). It is obvious that this addition reaction proceeds equally well with terminal and internal alkynes. However, the attempted borylstannation of *tert*-butylacetylene, phenyl(trimethylsilyl)acetylene, propargylic alcohol and dimethyl acetylenedicarboxylate with **39a** failed [16]. The ^{11}B-NMR resonances of **55a**–**i** range from $\delta = 21.1$ to 24.0.

4.4. Periphery reactions at substituents

Path (d) in Scheme 23 implies that novel 1,3,2-diazaborolines may also be accessible by reactions at the amino substituent at the boron center without affecting other parts of the molecule.



39a **55a-i**

54,55	R^1	R^2	Yield%
a	H	Ph	84
b	H	4-ClC_6H_4	78
c	H	4-BrC_6H_4	52
d	H	Ph	74
e	Me	Ph	84
f	Et	Ph	89
g	H	*n*Bu	77
h	Et	Et	66
i	H	*n*-C_6H_{13}	82

Scheme 33. Borylstannation of alkynes with **39a**.

Trimethylsilylamino and trimethylstannylamino groups can easily be introduced as substituents by metalation of **40a** with *tert*-butyllithium and the subsequent treatment of the lithium derivative with trimethylchlorosilane [36] or trimethylchlorostannane [62].

SiN cleavage took place in the reaction of **56a** and 2-bromo-1,3,2-diazaboroline **21c** in boiling *n*-hexane affording diborolinylamine **42** (Scheme 34). Singlets in the $^{11}B\{^1H\}$-NMR spectra at $\delta = 22.9$ and 24.3 are attributed to the boron nuclei in **56a** and **56b**, respectively.

When the lithiation product derived from **40a** was allowed to react with an excess of ethyl chloroformate in *n*-hexane at -20°C the acylation product **57** was isolated as colorless crystals in 21% yield [62] (Scheme 35). Here an ^{11}B-NMR signal at $\delta = 19.7$ was encountered.

The X-ray structure analysis of **57** shows a planar 1,3,2-diazaboroline ring with a di(carbethoxy)amino substituent orthogonally attached to the boron atom via a boron–nitrogen single bond of 1.507(2) Å (Fig. 8). The N-atom of the substituent is planar. The bonding parameters within the heterocycle compare well with other 1,3,2-diazaborolines discussed previously.

Equimolar amounts of **40a** and phenyl isocyanate in an acetonitrile–*n*-hexane mixture underwent reaction to yield the unsymmetrically substituted urea **58** in 49% yield as a colorless solid (Scheme 36). As observed in the formation of **57**, the boron atom remains ligated to the nitrogen atom [62].

4.5. Reaction with ketenes

Compound **40a** was also treated with an equimolar amount of diphenylketene in *n*-hexane in the temperature region between -40 and $+20$°C to afford a 1:1

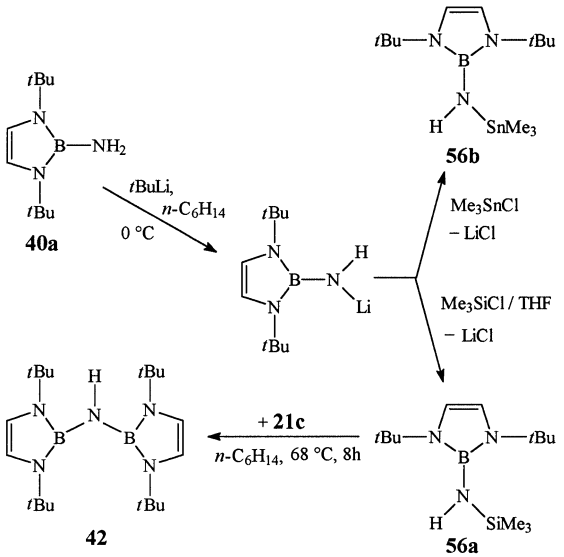
adduct as a white solid. Instead of the anticipated *N*-borylated diphenylacetamide **59**, the product was revealed as the 1,3,2-oxazaborolidine derivative **60** (Scheme 37; Fig. 9)).

In line with this, the mirror plane of the starting material perpendicular to the ring plane and bisecting the C=C bond is no longer present in the product, giving rise to two discrete resonances for the *tert*-butyl groups and the CH units.

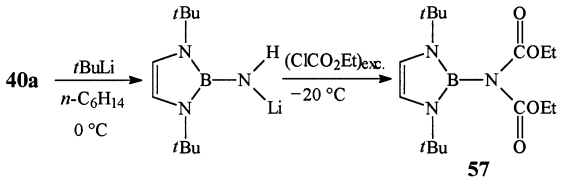
The same type of transformation was realized with diphenylketene and the diazaborolines **4e**, **21a**,**c**, **39a** or **55b**,**i** [63].

4.6. Coordination chemistry

One of the most prominent properties of arenes and heteroarenes as planar 6π-electron systems is the propensity to form half-sandwich and sandwich com-



Scheme 34. Formation of **56a**,**b** and **42** from **40a**.



Scheme 35. Preparation of **57**.

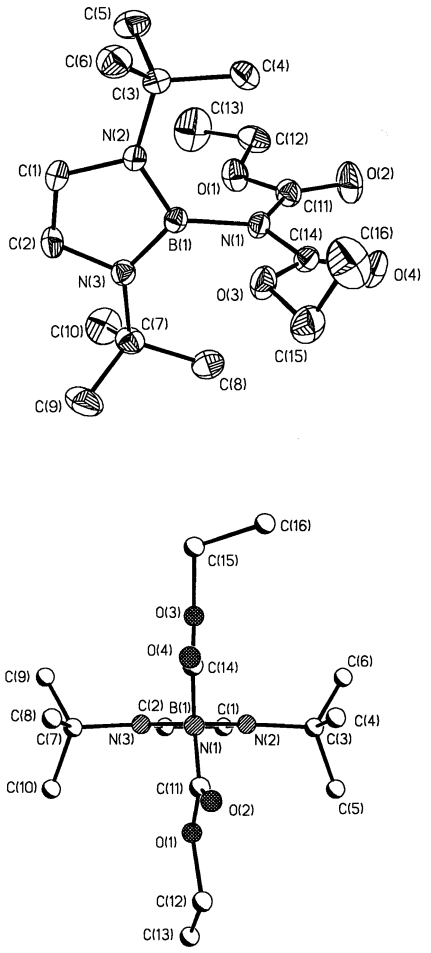
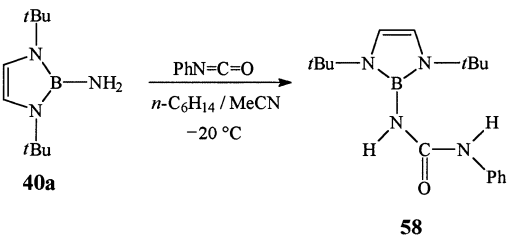
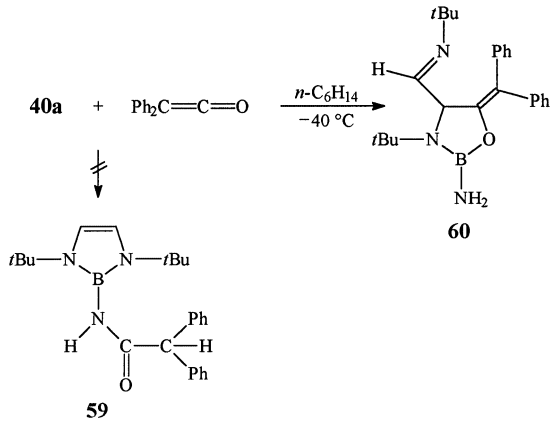


Fig. 8. Two views of the molecular structure of **57**; selected bond lengths (Å) and angles (°): B(1)–N(1) 1.507(2), B(1)–N(2) 1.430(2), B(1)–N(3) 1.428(2), N(2)–C(1) 1.408(2), N(3)–C(2) 1.406(2), C(1)–C(2) 1.336(2), N(1)–C(11) 1.392(2), N(1)–C(14) 1.392(2); N(2)–B(1)–N(3) 107.6(1), B(1)–N(1)–C(11) 119.2(1), B(1)–N(1)–C(14) 121.0(1), C(11)–N(1)–C(14) 119.7(1).



40a **58**

Scheme 36. Synthesis of urea **58**.



Scheme 37. Formation of **60**.

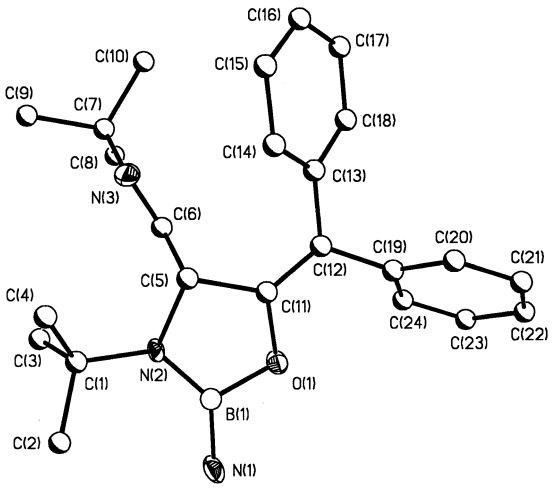
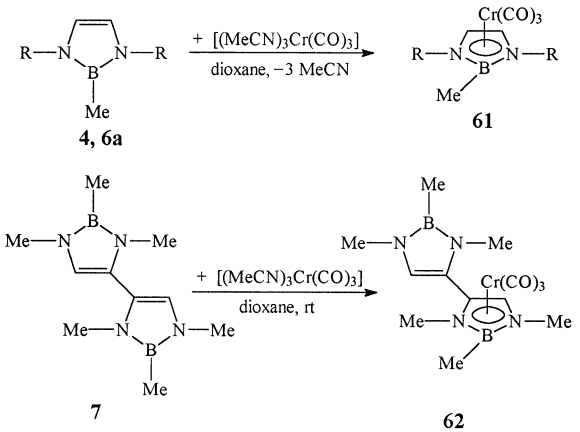


Fig. 9. Molecular structure of **60**.

plexes with appropriate transition metals. The large number of [(arene)$Cr(CO)_3$] complexes renders it relevant to test the ligating properties of the 6π-electrons containing 1,3,2-diazaborolines towards the [$Cr(CO)_3$] moiety. 1,3,2-Diazaborolines **4e** and **6a** reacted with [$(CH_3CN)_3Cr(CO)_3$] in 1,4-dioxane at 80–90°C to give the yellow π-complexes **61a** and **61b** [10,11] (Scheme 38).

Under comparable conditions a complex with **4a** (R = Me) could not be obtained. This suggests that the size and nature of the substituents of the heterocycle determine the tendency of complex formation as well as the stability of the anticipated complexes. Whereas **4d** was converted smoothly into **61c** at 60°C, the remaining 1,3,2-diazaborolines **4a**, **4b** (R = Me, Et), **4c** (R = Et) and **7** must be treated with the precursor complex at room temperature [9].



61	R	T / °C	yield (%)	δ^{11}B	$\Delta\delta^{11}$B
a	*t*Bu	85	91	17.6	7.9
b	Me_3Si	85	59	20.9	12.5
c	*i*Pr	60	54	17.4	9.3
d	Et	20	29	17.3	9.2
e	Me/Et	20	39	17.1	9.4
f	Me	20	29	17.4	9.1

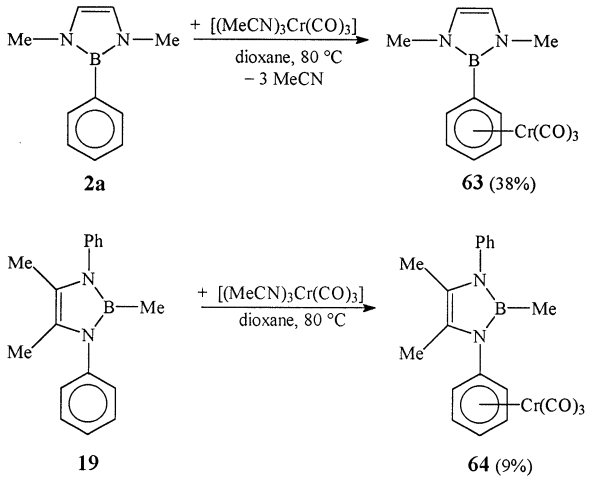
Scheme 38. Preparation of **61a**–**f** and **62** and ^{11}B-NMR data.

The reaction of $[(MeCN)_3Cr(CO)_3]$ with the phenyl-substituted 1,3,2-diazaborolines **2a** [64] and **19** [11] took a different course. Here the 12 valence electron fragment was attached to one of the phenyl rings available, which are obviously the better 6π-electron ligands when compared with the heterocycle (Scheme 39).

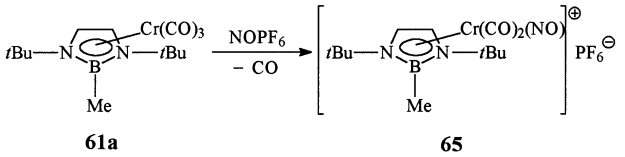
The latter observation agrees with the kinetic lability of [(η^5-1,3,2-diazaborolineCr(CO)$_3$] complexes. Mesitylene liberates the diazaboroline ligand smoothly from **61a** with formation of (η^6-mesitylene)Cr(CO)$_3$ in 87% yield. The irradiation of a THF solution of **61a** lead to the replacement of the heterocycle. The subsequent addition of one equivalent of PPh_3 gave high yields of $[Cr(CO)_4(PPh_3)_2]$. This clearly contrasts with the situation in (arene)tricarbonylchromium complexes, where the photolysis of THF solutions brought about the extrusion of one molecule of CO [65,66].

Stirring a toluene solution of **61a** in the presence of solid $NOPF_6$ gave rise to the formation of the nitrosyl complex **65** in 78% yield [11] (Scheme 40).

The combination of a BN system with a transition metal in most cases led to a considerable high-field shift of the ^{11}B-NMR resonances. This also holds true for the complexes **61a**–**f**, where ^{11}B-NMR signals are observed between $\delta = 17.1$ and 20.9 ppm, displaying coordination shifts $\Delta\delta$ of 7.9–12.5 ppm. Upon coordination,



Scheme 39. Preparation of **63** and **64**.



Scheme 40. Formation of **65**.

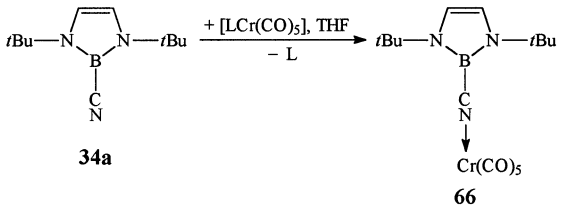
the singlet of **7** at δ 26.9 was replaced by singlets at $\delta = 16.4$ and 27.5 for the coordinated and the uncoordinated rings of **62**, respectively [64].

Carbonyl bands of low wavenumbers in the IR spectra of **61a–f** [e.g. **61a**: $\nu(CO) = 1919$ vs, 1830 sh, 1820 cm^{-1} vs (Nujol)], as well as very small coordination shifts of the ^{1}H-NMR resonances of the HC=CH unit (ca. 0.2 ppm), were rationalized by the strong σ-donor and the poor π-acceptor capacity of 1,3,2-diazaborolines in comparison with arenes [e.g. **64**: $\nu(CO) = 1955$ vs, 1900 sh, 1880 cm^{-1} vs (Nujol)].

To date, all attempts to synthesize molybdenum- and tungsten-tricarbonyl complexes analogous to **61a–h** and **62** have failed.

Principally, the 2-cyano-1,3,2-diazaboroline **34a** is a polyfunctional ligand with different donor sites. Synthesis of complex **66** featuring η^1-coordination of the ligand via the cyano group was achieved by treatment of **34a** with an equimolar amount of [{(*Z*)-cyclooctene}$Cr(CO)_5$] in THF at ambient temperature (Scheme 41). The product was isolated as yellow needles after crystallization from *n*-hexane at -10°C (83%). The ^{11}B-NMR signal of the complex appeared at $\delta = 9.4$ and is thus shielded by $\Delta\delta = 2.6$ ppm with respect to that of the free ligand.

The molecular structure determination of **66** reveals a nearly undistorted octahedron with the η^1-2-cyano-1,3,2-diazaboroline attached to one apex (Fig. 10). The



Scheme 41. Formation of **66** [L = (*Z*)-cyclooctene].

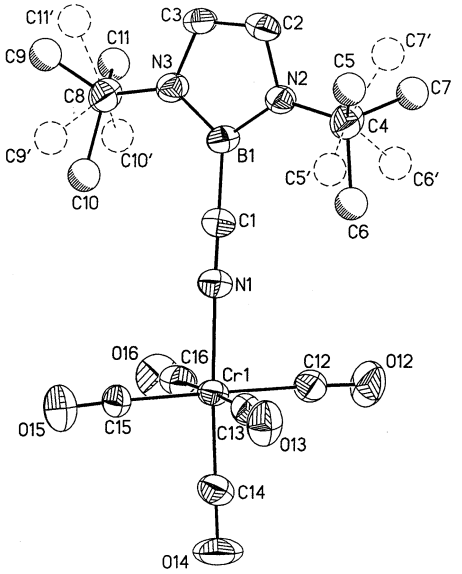


Fig. 10. Molecular structure of complex **66**; selected bond lengths (Å) and angles (°): B(1)–N(2) 1.416(7), B(1)–N(3) 1.433(7), N(2)–C(2) 1.389(7), N(3)–C(3) 1.373(6), C(2)–C(3) 1.312(8), B(1)–C(1) 1.547(8), C(1)–N(1) 1.140(6), Cr(1)–N(1) 2.051(5), Cr(1)–C(14) 1.825(7); N(2)–B(1)–N(3) 107.5(4), B(1)–C(1)–N(1) 178.2(5), C(1)–N(1)–Cr(1) 177.5(5).

atoms B(1), C(1), N(1), Cr(1), C(14) and O(14) lie in a linear arrangement, and the plane of the heterocycle is staggered with respect to the plane defined by the metal center and the four equatorial carbonyls. The bond Cr(1)–C(14) trans to the cyanide ligand [1.825(7) Å] is significantly shortened compared with the remaining Cr(1)–C(CO) bond lengths [1.899(6)–1.917(6) Å], which characterizes **34a** as a donor ligand without appreciable π back-bonding [15].

5. Conclusions and perspectives

It is obvious that the chemistry of 1,3,2-diazaborolines lies at the interface of several research areas of current interest. Nearly three decades ago, when the first

representatives of this class of heterocycles were prepared, their molecular and electronic structures were the focus of interest, mainly with respect to their coordinating behavior. In recent years the introduction of functionalities at the boron atom renders them useful as promising reagents in organic and organometallic synthesis. Convincing examples comprise substitution and insertion reactions at the BX unit to afford novel highly functionalized 1,3,2-diazaborolines and their subsequent transformation into highly substituted 1,3,2-oxazaborolidines by addition of ketenes. The latter heterocycles are useful as catalysts or as stoichiometric reagents for a series of organic processes, including borane reduction of ketones [67,68], hydroboration of alkenes [69], diethylzinc addition to ketones [70], Diels–Alder reactions [71], Mukaiyama–Aldol reactions [72], the enantioselective ring-cleavage reaction of 2-substituted 1,3-dioxolanes with subsequent addition to nucleophiles [73], and the 1,3 dipolar cycloaddition of nitrones to ketene acetals [74] or alkylvinyl ethers [75].

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