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FULL PAPER

Alkali metal reduction of 2-halogeno- and 2-thiolato-2,3-dihydro-1*H*-1,3,2-diazaboroles

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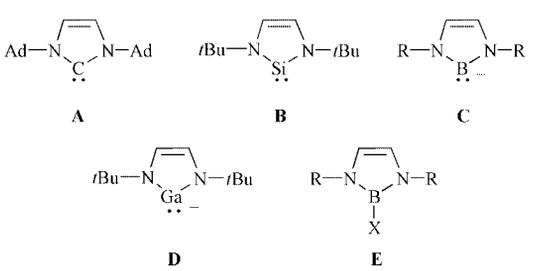
The reduction of 2-bromo-1,3,2-diazaborole *t*BuNCH=CH(*t*Bu)BBr (**4c**) with a potassium mirror in 1,2-dimethoxyethane afforded a non-separable 1 : 2 : 1 mixture of the compounds *t*BuNCH=CHN(*t*Bu)BH (**5**), *t*BuNCH=CHN(*t*Bu)BOCH$_3$ (**6**) and {*t*BuNCH=CHN(*t*Bu)B}$_2$O (**7**). Reaction of **4c** with a potassium–sodium alloy in *N*,*N*,*N*′,*N*′-tetramethylethylenediamine led to **5** as the major product. 1,3,2-Diazaboroles *t*BuNCH=CHN(*t*Bu)BNMe$_2$ (**8**) and {*t*BuNCH=CHN(*t*Bu)B}$_2$ (**9**) were spectroscopically identified as minor products. The treatment of **4c** with potassium–sodium alloy in toluene solution in the presence of [15]crown-5 yielded a 1 : 1 mixture of **5** and the benzyl derivative *t*BuNCH=CHN(*t*Bu)BCH$_2$Ph (**12**). The same reaction in toluene-d$_8$ produced the deuterated species **5**-d$_1$ and **12**-d$_7$. *t*BuNCH=CHN(*t*Bu)BCH$_3$ (**17**) and 1,4-diazabutadiene (*t*BuN=CH)$_2$ (**18**) resulted from the treatment of *t*BuNCH=CHN(*t*Bu)BSCH$_3$ (**15**) with potassium–sodium alloy in *n*-hexane. In contrast to this, compound **9** was obtained as the main product of the reduction of *t*BuNCH=CHN(*t*Bu)BS*t*Bu (**16**) under similar conditions. The reduction of the 1-bromo-2-*tert*-butyl-1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridine (**19**) smoothly produced the respective diborane(4) derivative (**20**) which was subjected to X-ray diffraction analysis.

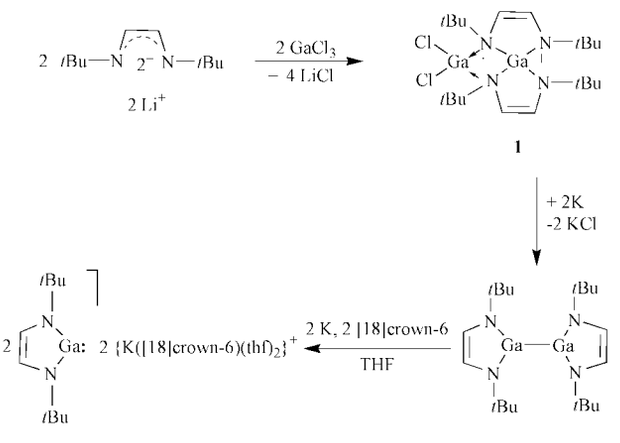
Introduction

The preparation and full characterisation of the first stable carbene **A**[1] and the first isolable silylene **B**[2] are landmarks in the chemistry of these otherwise elusive electron-sextet species.



The diagonal relationship of boron and silicon in the periodic table as well as the concept of isoelectronic compounds has motivated us to look for the yet unknown boranide anions **C**. Quantum chemical calculations have indicated that salts with the anion **C** should be accessible in a chemical laboratory.[3] Moreover, in the homologous series of the elements, B, Al, Ga, In, and Tl anions based on gallium (**D**) should be the most stable. This prediction has recently been verified by the synthesis and X-ray structural characterisation of [K{[18]crown-6}(thf)$_2$][*t*BuNCH=CHN(*t*Bu)Ga]$^-$ (**3**) in the research group of Schmidbaur (Scheme 1).[4]

Recently, we developed high-yield syntheses of 2-halogeno-2,3-dihydro-1*H*-1,3,2-diazaboroles (**E**) as the required precursors for the generation of anions such as **C**.[5,6] It is conceivable that the reduction of compound **E** to anion **C** proceeds *via* bis(1,3,2-diazaborol-2-yls) as intermediates. Acyclic diborane(4)s are accessible by alkali-metal reduction of the respective



Scheme 1

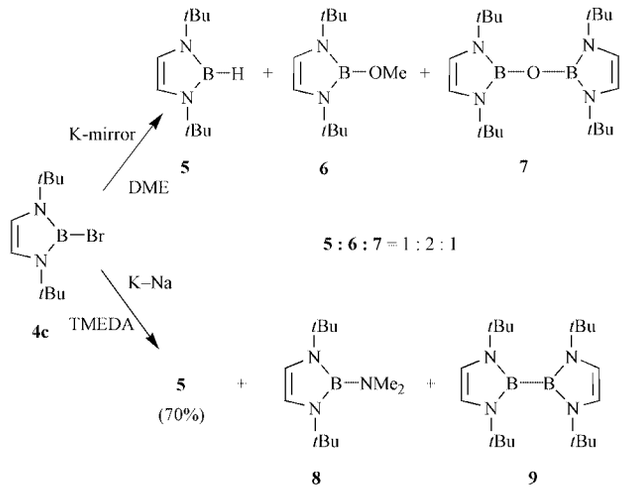
monohalogenoboranes.[7] Their further reduction to dinuclear mono- and di-anions was recently reported.[8,9] Ionic species such as $M^+(BR_2)^-$, however, have never been observed.

In this paper we give an account of the alkali-metal reduction of selected 1,3,2-diazaboroles and on the synthesis of novel diborane(4)s.

Results and discussion

Preliminary investigations have shown that reduction of the 2-halogeno-1,3,2-diazaboroles *t*BuNCH=CHN(*t*Bu)BX (**4b**: X = Cl; **4c**: Br; **4d**: I) with sodium–potassium alloy in *n*-hexane is very sluggish and affords 2-hydro-1,3,2-diazaborole *t*BuNCH=CHN(*t*Bu)BH (**5**) as the only tractable product.[10]

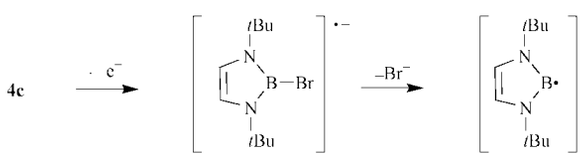
In order to improve the reducing capability of the alkali metals we repeated the reduction of **4c** in coordinating solvents such as 1,2-dimethoxyethane (DME) and tetramethylethylenediamine (TMEDA) (Scheme 2).



Scheme 2

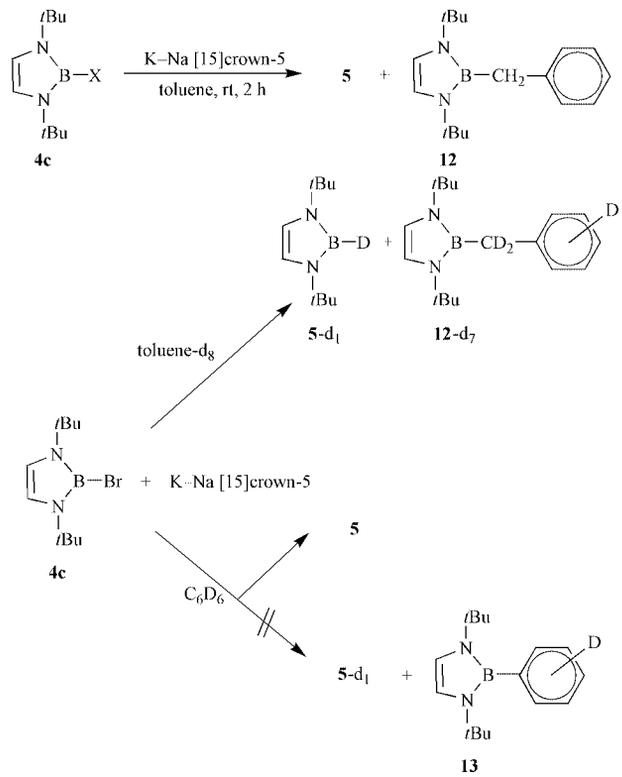
The reaction of the 2-bromo-derivative **4c** with a potassium mirror in DME at ambient temperature took 36 h (monitored by ^{11}B-NMR) and afforded a 2 : 1 : 1 mixture of the 2-methoxy-1,3,2-diazaborole **6**, compound **5**[11] and the diborolyloxane **7**.[5] Due to their similar volatilities and solubilities, compounds **6** and **7** could not be separated. In order to unambiguously identify the 2-methoxy derivative **6**, this species was synthesised independently from **4c** and sodium methoxide in *n*-hexane. The product was isolated as a colourless oil by distillation (10^{-3} Torr, 100–150 °C, 66% yield).

The reduction of diazaborole **4c** with sodium–potassium alloy in TMEDA at room temperature came to an end (by ^{11}B-NMR) after 3 d. The major product was the 2-hydro derivative **5**, which was separated in 70% yield by distillation. The remaining material was an inseparable mixture of three diazaboroles in equal amounts. Two of these minor products were spectroscopically identified as compound **8**, which was previously synthesised by reaction of **4c** with gaseous dimethylamine,[12] and bis(1,3,2-diazaborol-2-yl) **9**. As solutions of compound **4c** in dimethoxyethane or tetramethylethylenediamine are stable, the formation of **6** and **8** must involve radical **11**, which results from electron transfer processes (Scheme 3).



Scheme 3

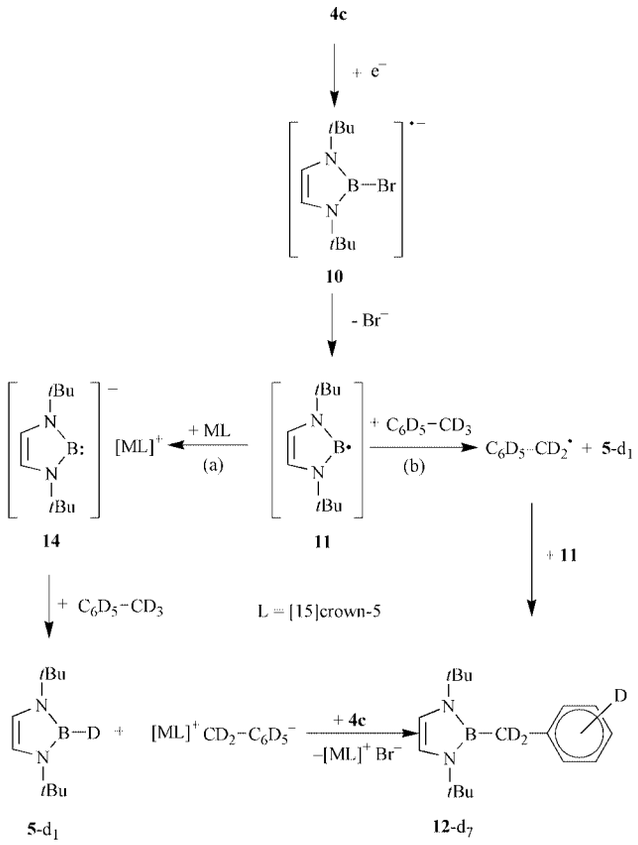
Hydrogen abstraction from the reaction medium converts radical **11** into the 2-hydro derivative **5**. In TMEDA solutions the latter process is the main reaction, whereas dimerization of **11** accounts for the formation of **9**. Obviously under the conditions employed here the generation of diborane(4) **9** is not a favourable process. We then tried to improve the reducing capability of the alkali metal by the addition of crown ether. Here, as in the case of the gallanide **3**,[4] the eventual formation of a boranide of type **C** was envisaged. A stoichiometric amount of [15]crown-5 was added to the slurry of the sodium–potassium alloy in toluene. The solution spontaneously became dark blue and, after 30 min of stirring at 20 °C, most of the metal went into solution. The reaction of this solution with 2-bromo-1,3,2-diazaborole **4c** was complete in less than 2 h and gave a 1 : 1 mixture of **5** and the 2-benzyl-1,3,2-diazaborole **12**. As it was not possible to separate the materials, compound **12** was independently prepared from **4c** and benzyllithium in a toluene–*n*-hexane mixture. Diazaborole **12** was obtained as a colourless solid in 88% yield. For a better understanding, the reaction was repeated in toluene-d_8 and in benzene-d_6. Treatment of **4c** with the blue solution in toluene-d_8 furnished a 1 : 1 mixture of the 2-deutero-1,3,2-diazaborole **5**-d_1 and the 2-benzyl-1,3,2-diazaborole **12**-d_7. An analogous reaction in benzene-d_6, however, led to the exclusive production of the 2-protio-1,3,2-diazaborole **5** (Scheme 4).



Scheme 4

There was no evidence for the formation of **5**-d_1 or 2-phenyl-1,3,2-diazaborole-d_5 (**13**). Clearly, the solvent C_6D_6 did not participate as a source of deuterium or of the phenyl substituent, as was the case in toluene as solvent. In order to rationalize these results, at least two pathways are conceivable (Scheme 5).

As already depicted in Scheme 3, precursor **4c** may be reduced to radical **11** *via* radical anion **10**. Radical **11** could be further reduced to the boranide salt **14**, which, as a strong Brønsted base, abstracts a deuteron from the solvent to give **5**-d_1 and a perdeuterated benzyl anion (path a). The latter might replace bromide from the starting material **4c** to produce **12**-d_7. Alternatively, radical **11** could remove a deuterium atom from the solvent with formation of **5**-d_1 and a perdeuterated benzyl radical. Combination of the latter with intermediate **11** would also generate product **12**-d_7. Usually, such a radical mechanism involving toluene also affords considerable amounts of dibenzyl by dimerisation of the benzyl radicals. Here however, neither dibenzyl, nor its perdeuterated form, could be detected (^{1}H-, ^{13}C-NMR, MS). The reluctance of benzene and C_6D_6 to provide hydrogen or deuterium atoms in the reduction of **4c** is in line with the increased dissociation enthalpy $C_6H_6 \longrightarrow H^{\bullet} + C_6H_5^{\bullet}$ (110 kcal mol^{-1})[13] *versus* $C_6H_5CH_3 \longrightarrow H^{\bullet} + C_6H_5CH_2^{\bullet}$ (85 kcal mol^{-1})[13] and the decreased CH acidity of benzene $C_6H_6 \longrightarrow H^+ + C_6H_5^-$ (pK_a = 43)[14] *versus* that of toluene $C_6H_5CH_3 \longrightarrow H^+ + C_6H_5CH_2^-$ (pK_a = 41).[14] In the absence of further experimental evidence, we favour path (a) over path (b).

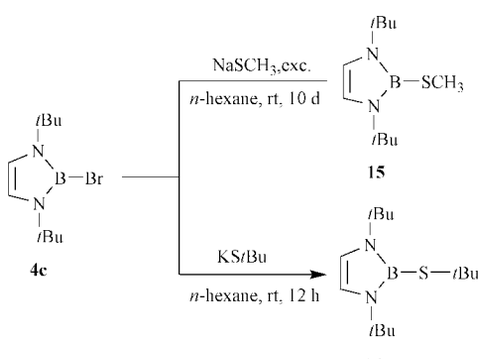


Scheme 5

Regarding the facile reduction of various halogenoboranes to diborane(4)s with sodium–potassium alloy, the behaviour of **4a–d** observed here is surprising.

In view of the straightforward desulfurization of imidazo-2-thione to imidazol-2-ylidene by potassium,[15] we also envisaged desulfurisation processes as viable routes to our goal.

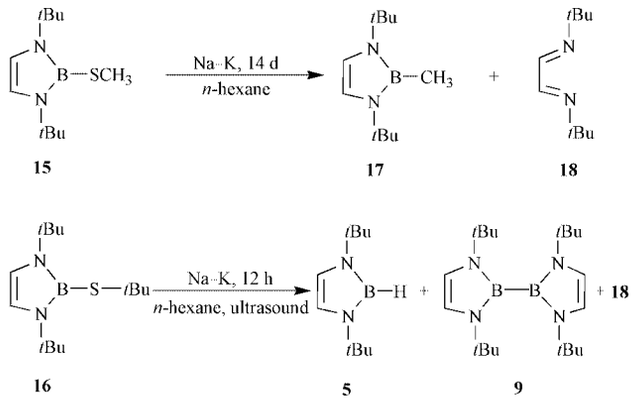
The required diazaborolyl sulfanes **15** and **16** were synthesised by the reaction of **4c** with a slight excess of sodium methylthiolate or potassium *tert*-butylthiolate, respectively, in *n*-hexane. Compounds **15** and **16** are formed in 90 and 82% yield, respectively, as colourless solids (Scheme 6).



Scheme 6

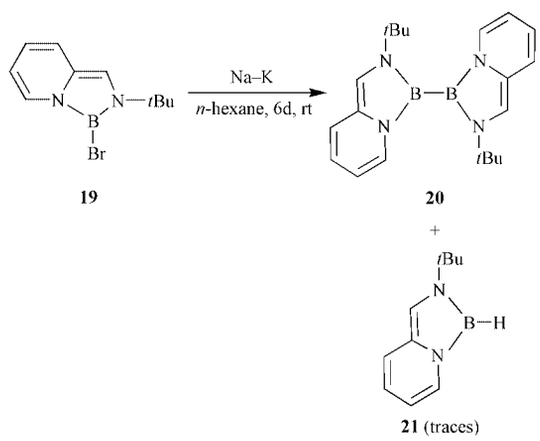
2-Methylthiolato-1,3,2-diazaborole **15** was allowed to react for 14 d with sodium–potassium alloy (9 : 91) to afford the 2-methyl-1,3,2-diazaborole **17** in 44% yield, in addition to diazabutadiene **18** (40%) (Scheme 7).

The reduction of compound **16** by potassium–sodium alloy (91 : 9) was performed in an ultrasound bath and carefully followed by ^{11}B-NMR. After 10–12 h, precursor **16** was completely consumed. The slurry obtained was centrifuged and from the supernatant solution diborane(4) **9** was isolated as an



Scheme 7

analytically pure yellow solid in 38% yield. It is well known that fused polyarenes (*e.g.* naphthalene, phenanthrene, *etc.*) are more readily reduced than monocyclic arenes (*e.g.* benzene).[16] Accordingly, the reduction of 2-bromo-1,2-dihydro[1,3,2]-diazaborolo[1,5-*a*]pyridine **19**[17] by sodium–potassium alloy in *n*-hexane proceeded smoothly to furnish compound **20** as a yellow crystalline solid in 64% yield. The only boron containing by-product was the 2-hydro derivative **21**, as evidenced by ^{11}B-NMR spectroscopy (Scheme 8).



Scheme 8

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

The ^{11}B-NMR shifts of the novel 1,3,2-diazaboroles fit well into a series of known values. Increased shielding was observed for the monocyclic 1,2-dihydro-1,3,2-diazaboroles *t*Bu-NCH=CHN(*t*Bu)BX as follows: X = CH_3 (δ 26.2) > CH_2Ph (δ 25.5), {*t*BuNCH=CHN(*t*Bu)B}$_2$ (δ 25.2) > S*t*Bu (δ 21.9) > {*t*BuNCH=CHN(*t*Bu)B}$_2$O (δ 21.1) > F (δ 20.3) ≅ Cl (δ 20.2) > H (δ 18.9) > Br (δ 16.2) > CN (δ 12).[18]

The ^{11}B-NMR signal of the 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridine derivative **20** (δ 23.3) is slightly more shielded than that of **9** (δ 25.2). A similar trend is obvious for other monocyclic 1,2-dihydro-1,3,2-diazaboroles and bicyclic 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridines.[17] Moreover, it is noteworthy that the ^{11}B-NMR absorptions of **9** and **20** are considerably shifted to higher field when compared with those of bis(dimethylamino)bis(pyrrolyl)diborane(4) (δ 37.0)[9] and bis(dimethylamino)bis(indoyl)diborane(4) (δ 36.7).[9] The high field shift in **9** and **20** is obviously caused by the incorporation of the boron atom in an aromatic ring system. The ^{11}B-NMR signal of diborane(4)s are significantly broadened due to $^{1}J(^{11}B–^{10}B)$ couplings with $w_{1/2}$ = 120 (**9**) and 180 Hz (**20**). In

Table 1 Selected bond lengths (Å) and angles (°) for compound **20**

B(1)–B(1A)	1.697(3)	B(1)–N(1)	1.452(2)
B(1)–N(2)	1.436(2)	N(1)–C(1)	1.420(2)
C(1)–C(6)	1.350(2)	N(2)–C(6)	1.399(2)
N(1)–C(5)	1.381(2)	C(1)–C(2)	1.425(2)
C(2)–C(3)	1.345(2)	C(3)–C(4)	1.437(2)
C(4)–C(5)	1.344(2)		
N(1)–B(1)–N(2)	103.0(1)	B(1)–N(2)–C(6)	109.5(1)
N(2)–C(6)–C(1)	110.3(1)	N(1)–C(1)–C(6)	107.4(1)
B(1)–N(1)–C(1)	109.7(1)	N(1)–C(5)–C(4)	121.4(1)
C(3)–C(4)–C(5)	120.2(1)	C(2)–C(3)–C(4)	119.9(1)
B(1A)–B(1)–N(1)	123.8(1)	B(1A)–B(1)–N(2)	133.2(1)
C(6)–N(2)–C(7)	118.9(1)		

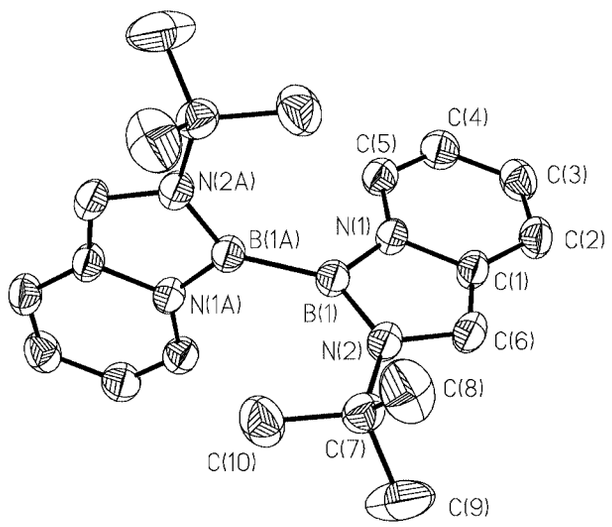


Fig. 1 ORTEP drawing of the structure of compound **20**. Thermal ellipoids are shown at the 50% probability level.

bis(dimethylamino)bis(pyrrolyl)diborane(4) and bis(dimethylamino)bis(indoyl)diborane(4), values of 320 and 400 Hz were measured.[9]

In the ^{1}H-NMR spectra of **6**, **9**, **15** and **16**, the resonances for the ring protons of the HC=CH unit were observed in the narrow range between δ 6.12 (X = OCH_3) and 6.43 (X = S*t*Bu), which is characteristic for monocyclic 1,3,2-diazaboroles of this type.[18] In the ^{13}C{^{1}H}-NMR spectra, the ^{13}C nuclei of the CH=CH unit in *t*BuNCH=CHN(*t*Bu)BX give rise to a singlet in the region between δ 109.9 (X = F) and 114.8 (X = S*t*Bu),[18] which includes compounds **6** (X = OCH_3; δ 111.5), **9** (X = *t*BuNCH=CHN(*t*Bu)B; δ 113.1), **12** (X = CH_2Ph; δ 113.2), **15** (X = SCH_3; δ 113.4) and **16** (X = S*t*Bu; δ 114.8).

X-Ray structural analysis of compound 20

For a full characterization of one of the diborane(4)s, an X-ray structural analysis of compound **20** was performed. Light yellow single crystals were grown from *n*-hexane at −30 °C. Selected bonding parameters are compiled in Table 1. The structure (Fig. 1) features a molecule which may be described as the combination of two planar 1,3,2-diazaborolo[1,5-*a*]pyridine fragments *via* a boron–boron single bond of 1.697(3) Å. This distance falls into the region of 1.674(4) and 1.723(4) Å, as determined in $Cp(CO)_2RuB(NMe_2)B(NMe_2)Br$[19] and bis(dimethylamino)bis(indoyl)diborane(4),[9] respectively. Both planes enclose a dihedral angle of 85.6°. The bonding parameters within the fused rings compare well with recently characterized 2,3-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridine **22**.[17]

The distances B(1)–N(2) [1.436(2) Å] and B(1)–N(1) [1.452(2) Å] indicate multiple bonding, with B(1)–N(1) being slightly longer than B(1)–N(2). In **22**, the corresponding bond lengths are 1.429(2) and 1.420(2) Å. In 1,3,2-diazaboroles, the BN bond lengths range from 1.395(4) to 1.450(2) Å. There is a significant difference between the endocyclic bond lengths N(1)–C(1) [1.420(2) Å] and N(2)–C(6) [1.399(2) Å]. The same effect has previously been observed in molecule **22** [1.416(2) and 1.395(2) Å]. In [*t*BuNCH=CHN(*t*Bu)BCN⟶$Cr(CO)_5$], these CN separations are 1.373(6) and 1.389(7) Å, and have been regarded as multiple bonds.[11] The calculated value for a C_{sp^2}–N_{sp^2} single bond is 1.45 Å.[20] In **20**, this is only valid for N(2)–C(6). The bridging CN bond is lengthened and compares with one of the exocyclic single bonds N_{sp^2}–C_{sp^2} measured in 2,6-$Me_2C_6H_3$NCH=CHN(2,6-$Me_2C_6H_3$)BH [1.421(3) Å].[11] In the six-membered ring of **20**, the N(1)–C(5) bond length of 1.381(2) Å also shows multiple bonding. As previously observed in **22**, the carbon–carbon distances in the six-membered ring of **20** alternate. Double bonds are C(4)–C(5) [1.344(2) Å], C(2)–C(3) [1.345(2) Å], whereas the bond order of the longer bonds C(1)–C(2) [1.425(2) Å] and C(3)–C(4) [1.437(2) Å] is close to unity.

Conclusion

In marked contrast to the facile alkali metal reduction of a variety of acyclic bis(amino)halogenoboranes to the corresponding diborane(4)s, such a process in the chemistry of 2-halogeno-2,3-dihydro-1*H*-1,3,2-diazaboroles **4b**–**d** is not favourable. Treatment of 2-bromo derivative **4c** with K–Na alloys in solvents such as DME, TMEDA, and toluene led to 1,3,2-diazaboroles with substituents at the boron atom that were abstracted from the respective reaction media. Predominantly, the formation of the 2-hydro-1,3,2-diazaborole **5** was observed. Interestingly, in toluene and toluene-d_8, equimolar amounts of **5** and the 2-benzyl derivative **12** were obtained, which can be tentatively interpreted with the intermediacy of a salt with the sought-after boranide anion {*t*BuNCH=CHN(*t*Bu)B}$^-$. The latter would be the boron analogue of Schmidbaur's gallanide anion **D**. The bi(1,3,2-diazaborol-2-yl) **9** was formed as a minor product from **4c** and K–Na alloy in TMEDA. A more effective route to this diborane(4) is based on the K–Na reduction of the 2-*tert*-butylthiolato-1,3,2-diazaborole **16** in *n*-hexane. Such difficulties were not encountered in the reduction of the 1-bromo-2-*tert*-butyl-1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridine **19**, which smoothly afforded the diborane(4) derivative **20**. These observations may be rationalized by the availabity of low-lying unoccupied orbitals and reduced aromaticity in the fused diazaborole system. Similar observations were previously made with related 2-bromo-benzo-1,3,2-diazaboroles.[21] These diboranes(4) have to be subjected to reduction processes under varying conditions to eventually accomplish the synthesis of the as yet elusive metal boranides.

Experimental

General procedures

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. The compounds *t*BuNCH=CHN(*t*Bu)BBr (**4c**)[5] and *t*Bu-N–CH=C–CH=CH–CH=CH–N–B–Br (**19**)[17] were prepared according to literature methods. MeSH, *t*BuSH, NaSMe, C_7D_8 and [15]crown-5 were purchased commercially. NMR spectra were recorded on a Bruker AM Avance DRX 500 (^{1}H, ^{11}B, ^{13}C) using $SiMe_4$ and $BF_3{\cdot}OEt_2$ as external standards. The IR spectra were recorded on Bruker FT-IR Vector 22 instruments, and mass spectra on a VG Autospec sector field mass spectrometer (Micromass).

Preparations

Reaction of 4c with potassium in DME. In a flask a mirror of 0.25 g (6.4 mmol) potassium metal was prepared. A solution of 2-bromo-1,3,2-diazaborole **4c** (0.80 g, 3.1 mmol) in 50 ml of 1,2-dimethoxyethane (DME) was added and stirred for 18 h at room temperature. Solvent and volatile components were removed *in vacuo* (10^{-3} mbar) to give an oily yellow residue. Spectroscopically the 1,3,2-diazaboroles **5** (δ ^{11}B = 18.9), **6** (δ ^{11}B = 22.0), and **7** (δ ^{11}B = 21.1) were identified in a molar ratio of 1 : 2 : 1. Attempts to separate these compounds failed.

***t*BuNCH=CHN(*t*Bu)BOCH$_3$ (6).** A solution of **4c** (1.20 g, 4.7 mmol) in *n*-hexane (30 ml) was slowly added to a chilled slurry (−20 °C) of sodium methanolate in 10 ml of *n*-hexane. The mixture was warmed to ambient temperature and filtered. Solvents was removed from the filtrate to afford a yellow oil, which was purified by distillation (10^{-3} mbar, 100–150 °C). Compound **6** was isolated as a colourless oil, yield 0.65 g (66%) (found: C, 62.74; H, 10.73; N, 13.32; $C_{11}H_{23}BN_2O$ requires C, 62.88; H, 11.03; N, 13.33%). ^{1}H-NMR (C_6D_6): δ 1.34 (s, 18H, *t*Bu), 3.49 (s, 3H, OCH_3), 6.12 (s, 2H, NCH). ^{13}C{^{1}H}-NMR (C_6D_6): δ 31.4 [s, C(CH_3)$_3$], 51.7 [s, C(CH_3)$_3$], 55.3 [s, OCH_3], 111.5 [s, NCH]. ^{11}B{^{1}H}-NMR (C_6D_6): δ 22.1 (s). MS/EI (70eV): m/z = 210 (M^+, 50%).

Reaction of 4c with Na–K in TMEDA. K–Na alloy (0.50 g; 58 : 42) was suspended in TMEDA (40 ml) with the aid of an ultrasound bath to give a dark blue slurry after 30 min. A solution of **4c** (1.04 g, 4.0 mmol) in 20 ml of TMEDA was added, and the mixture was stirred for 3 d at 20 °C. The solution was decanted and freed from TMEDA at ambient temperature and 8 mbar, to give a yellow waxy residue. 2-Hydro-1,3,2-diazaborole **5** (0.50 g, 70%) was separated by distillation. The oily residue consists of an inseparable mixture of **7**, **8** and **9**, as evidenced by NMR spectroscopy and mass spectrometry.

Reaction of 4c with Na–K and [15]crown-5 in toluene. To a slurry of K–Na alloy (0.20 g, 58 : 42) in toluene (10 ml) a solution of 2.40 g (10.9 mmol) of [15]crown-5 in toluene (20 ml) was added to afford a dark blue solution. After 20 min, a solution of **4c** (1.41 g, 5.4 mmol) in toluene (30 ml) was added dropwise. Stirring at room temperature was continued for another hour. After the sedimentation of a dark blue solid had ceased, the yellow solution was decanted and evaporated to dryness. According to NMR and MS evidence, the residue (3.10 g) was a 1 : 1 mixture of 1,3,2-diazaboroles **5** and **12** which could not be separated from the crown ether.

***t*BuNCH=CHN(*t*Bu)BCH$_2$Ph (12).** A solution of benzyllithium (0.70 g, 7.1 mmol) in toluene (20 ml) was combined at 0 °C with a solution of **4c** (1.31 g, 5.1 mmol) in *n*-hexane (40 ml) and stirred for 2 h at 20 °C. Solvent and volatile compounds were removed *in vacuo* and the remaining solid was dissolved in *n*-hexane (80 ml). The solution was filtered and the filtrate was evaporated to dryness to give compound **12** as a colourless solid, yield 1.21 g (88%) (found: C, 75.57; H, 10.02; N, 9.63; $C_{17}H_{27}BN$ requires C, 75.56; H, 10.07; N, 10.37%). ^{1}H-NMR (C_6D_6): δ 1.27 (s, 18H, *t*Bu), 3.05 (s, 2H, CH_2), 6.41 (s, 2H, NCH), 7.02 (t, $^3J_{H,H}$ = 7.7 Hz, 1H, *p*-H-phenyl), 7.13–7.20 (m, 4H, *o,m*-H-phenyl). ^{13}C{^{1}H}-NMR (C_6D_6): δ 31.9 [s, C(CH_3)$_3$], 53.1 [s, C(CH_3)$_3$], 113.2 [s, NCH], 125.0 (s, *p*-C-phenyl), 128.4 (s, *m*-C-phenyl), 131.0 (s, *o*-C-phenyl), 143.2 (s, *i*-C-phenyl). ^{11}B{^{1}H}-NMR (C_6D_6): δ 25.5 (s). MS/EI (70eV): m/z = 270 [M^+, 100%].

Reaction of 4c with Na–K and [15]crown-5 in toluene-d$_8$. [15]crown-5 (0.42 g, 1.9 mmol) was added to the slurry of K–Na alloy in 3 ml of toluene-d$_8$ to give a dark blue solution. Then, a solution of **4c** (0.25 g, 0.9 mmol) in toluene-d$_8$ (5 ml) was added. After 30 min of stirring at ambient temperature, NMR and mass spectra of the reaction mixture were taken, ^{1}H-NMR (toluene-d$_8$) **5**-d$_1$: δ 1.30 (s, 18H, *t*Bu), 6.34 (s, 2H, NCH); **12**-d$_7$: δ 1.26 (s, 18H, *t*Bu), 6.35 (s, 2H, NCH). A singlet at δ 3.47 was attributed to [15]crown-5. ^{13}C{^{1}H}-NMR (toluene-d$_8$) **5**-d$_1$: δ 31.8 [s, C(CH_3)$_3$], 51.4 [s, C(CH_3)$_3$], 114.1 [s, NCH]; **12**-d$_7$: δ 31.9 [s, C(CH_3)$_3$], 53.1 [s, C(CH_3)$_3$], 113.1 [s, NCH]. A singlet at δ 71.0 was assigned to [15]crown-5. ^{11}B{^{1}H}-NMR (toluene-d$_8$): **5**-d$_1$: δ 18.4 (s); **12**-d$_7$: δ 25.5 (s). MS/EI (70eV) **5**-d$_1$: m/z = 181 (M^+, < 5%); **12**-d$_7$: m/z = 277 [M^+, 31%], 221 [$M^+ - (CH_3)_2C{=}CH_2$, 9%].

***t*BuNCH=CHN(*t*Bu)BSCH$_3$ (15).** A sample of sodium methylthiolate (0.50 g, 7.1 mmol) was combined with a solution of **4c** (1.30 g, 5.0 mmol) in *n*-hexane (50 ml) and stirred for 10 d at room temperature. The hexane phase was decanted from a colourless solid and then concentrated to the beginning of crystallization. Storing the solution at −30 °C afforded **15** (1.02 g, 90% yield) as colourless crystals (found: C, 58.13; H, 9.96; N, 12.19; $C_{11}H_{23}BN_2S$ requires C, 58.41; H, 10.25; N, 12.38%). ^{1}H-NMR (C_6D_6): δ 1.50 (s, 18H, *t*Bu), 1.98 (s, 3H, SCH_3), 6.35 (s, 2H, NCH). ^{13}C{^{1}H}-NMR (C_6D_6): δ 15.6 [s, SCH_3], 31.9 [s, C(CH_3)$_3$], 53.9 [s, C(CH_3)$_3$], 113.4 [s, NCH]. ^{11}B{^{1}H}-NMR (C_6D_6): δ 23.3 (s). MS/EI (70eV): m/z = 226 [M^+, 37%], 114 [$M^+ - 2\ (CH_3)_2C{=}CH_2$, 100%].

***t*BuNCH=CHN(*t*Bu)BS*t*Bu (16).** Potassium *tert*-butylthiolate (0.71 g, 5.5 mmol) was added at 20 °C to a solution of **4c** (1.29 g, 5.0 mmol) in *n*-hexane (60 ml) and vigorously stirred for 12 h. The solution was filtered, and the filtrate was evaporated to dryness. Compound **16** was obtained as a waxy solid, yield 1.09 g (82%) (found: C, 62.53; H, 10.91; N, 10.47; $C_{14}H_{29}BN_2S$ requires C, 62.68; H, 10.90; N, 10.44%). ^{1}H-NMR (C_6D_6): δ 1.44 [s, 9H, *t*BuS], 1.55 (s, 18H, *t*BuN), 6.43 (s, 2H, NCH). ^{13}C{^{1}H}-NMR (C_6D_6): δ 32.8 [s, NC(CH_3)$_3$], 34.8 [s, SCCH_3], 45.2 [s, SC(CH_3)$_3$], 54.5 [s, NC(CH_3)$_3$], 114.8 [s, NCH]. ^{11}B{^{1}H}-NMR (C_6D_6): δ 21.9 (s). MS/EI (70eV): m/z = 268 [M^+, 16%].

Reaction of 15 with Na–K. K–Na alloy (0.20 g; 91 : 9) was added to a solution of **15** (0.55 g, 2.4 mmol) in *n*-hexane (30 ml), and the slurry was stirred at ambient temperature for 14 d. The course of the reaction was monitored by ^{11}B NMR spectroscopy. Then, hexane (20 ml) was added to the reaction mixture and the liquid phase decanted. Solvent was removed from the clear solution *in vacuo* (10 mbar) to give 0.40 g of a yellow solid.

According to NMR spectra, this residue is a mixture of the 2-methyl-1,3,2-diazaborole **17** and 1,2-bis(*tert*-butyl-imino)-ethane **18** in a molar ratio of 4 : 1. Sublimation at 40 °C and 7 mbar afforded 0.16 g of pure **18** (40%) and 0.21 g (44%) of yellow solid **17**. The spectra of the products are identical with analytic samples.

{*t*BuNCH=CHN(*t*Bu)B}$_2$ (9). A slurry of 0.5 g of K–Na alloy (91 : 9), **16** (0.81 g, 3.0 mmol) and 50 ml of *n*-hexane was stirred for 10–12 h at 20 °C in an ultrasound bath. At the end of the reduction (monitered by ^{11}B-NMR), the solids were separated from the liquid phase by centrifugation. The decanted solution was evaporated to dryness at 10^{-3} mbar to yield 0.41 g (38%) of compound **9** (found: C, 66.61; H, 11.31; N, 15.49; $C_{20}H_{40}B_2N_4$ requires C, 67.07; H, 11.26; N, 15.64%). ^{1}H-NMR (C_6D_6): δ 1.36 (s, 36H, *t*Bu), 6.37 (s, 4H, NCH). ^{13}C{^{1}H}-NMR (C_6D_6): δ 31.7 [s, C(CH_3)$_3$], 53.1 [s, C(CH_3)$_3$], 113.1 [s, NCH]. ^{11}B{^{1}H}-NMR (C_6D_6): δ 25.2 (s, $w_{1/2}$ = 120 Hz). MS/EI (70eV): m/z = 358 [M^+, 58%].

Table 2 Crystallographic data for compound **20**

Empirical formula	$C_{20}H_{28}B_2N_4$
M_r	346.08
T/K	223
Space group	*Pbcn*
Crystal system	Orthorhombic
a/Å	18.582(5)
b/Å	6.952(2)
c/Å	15.511(5)
V/Å^3	2003.8(1)
Z	4
μ(Mo-Kα)/mm^{-1}	0.068
Reflections collected	11876
Independent reflections	2430 ([$R_{(int)}$ = 0.0391])
Reflections with $I > 2\sigma(I)$/parameters	2430/175
Final R_1, wR_2 [$I > 2\sigma(I)$] (all data)	0.0429/0.1135 0.0659/0.1295

{*t*BuN–CH=C–CH=CH–CH=CH–N–B–}$_2$ (20). A solution of compound **19** (1.62 g, 6.4 mmol) in *n*-hexane (100 ml) was combined with 0.52 g of K–Na alloy (58 : 42) and the resulting slurry was vigorously stirred at room temperature (6 h). After the sedimentation of the solids had ceased, the light yellow liquid phase was decanted and the solvent removed *in vacuo*. Traces of the 2-hydro derivative **21** were removed by distillation with a hot air gun. The resulting solid residue was dissolved in *n*-hexane (50 ml), filtered, and the filtrate was stored at −30 °C. Compound **20** separated as light yellow crystals, yield 0.71 g (64%). Due to the air and moisture sensitivity of the product, no reliable elemental analyses could be obtained from the Microanalytical Laboratory of our department. ^{1}H-NMR (C_6D_6): δ 1.29 (s, 18H, *t*Bu), 5.54 (t, $^3J_{H,H}$ = 6.7 Hz, 2H, CH), 6.08–6.14 (m, 2H, CH), 6.55 (s, 2H, *t*BuN-C*H*), 6.81 (d, $^3J_{H,H}$ = 9.5 Hz, 2H, CH), 6.99 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, CH). ^{1}H-NMR ($CDCl_3$): δ 1.39 (s, 18H, *t*Bu), 5.65 (t, $^3J_{H,H}$ = 6.3 Hz, 2H, CH), 6.15–6.18 (m, 1H, CH), 6.66 (s, 2H, *t*BuN–C*H*), 6.80 (d, $^3J_{H,H}$ = 9.4 Hz, 2H, CH), 7.10 (d, $^3J_{H,H}$ = 6.3 Hz, 2H, CH). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 32.2 [s, C(*C*H$_3$)$_3$], 53.5 [s, *C*(CH$_3$)$_3$], 105.5 [s, *t*BuN–*C*H], 105.9 [s, CH], 118.1 [s, CH], 118.2 [s, CH], 128.5 [s, NCH=*C*], 131.5 [s, CH]. ^{11}B{^{1}H}-NMR ($CDCl_3$): δ 23.3 [s, $w_{1/2}$ = 180 Hz]. MS/EI (70eV): *m*/*z* = 346 [M$^+$, 100%], 290 [M$^+$ − (CH$_3$)$_2$C=CH$_2$, 16%].

Crystal structure determination of compound 20

The data were collected with a Siemens CCD SMART100 detector system on a three-axis platform using graphite-monochromated Mo-Kα radiation. Software for structure solution/refinement: Bruker AXS SHELXTL Ver. 5.10 DOS/WIN95/NT, treatment of hydrogen atoms as riding groups in idealized positions. All other data are summarized in Table 2.

CCDC reference number 167157.

See http://www.rsc.org/suppdata/dt/b1/b106128n/ for crystallographic data in CIF or other electronic format.

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