Contribution to the Chemistry of Boron, 245[+]
A Boron–Boron Double Bond in the Dianions of Tetra(amino)diborates

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Dedicated to Prof. Dr. Wolfgang Steglich on the occasion of his 65th birthday

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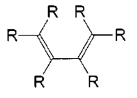
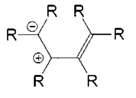
A series of mixed tetraaminodiborane(4) compounds bearing pyrrolyl, indolyl, and carbazolyl substituents besides dimethylamino groups has been prepared and subjected to reduction with elemental Li in the presence of diethyl ether. Tetraaminodiborates(2–) are formed, which feature a boron–boron double bond. The diborate anion acts as a double bidentate ligand coordinating pairwise through two of its nitrogen atoms to an Li center, which is tricoordinated by one O and the two N atoms. The new diborates are isoelectronic with tetraaminoethylenes and are expected to be electron-transfer reagents.

Introduction

One of the foremost principles in inorganic and metalorganic chemistry is that of isoelectronic or isolobal systems.[2] One of the systems where this concept first came to prominence was that of boron−nitrogen compounds since the BN atom pair is isoelectronic and isolobal with a pair of carbon atoms. The consequences of isoelectronic systems have been delineated in two classical papers by Wiberg,[3] in which physical properties and structural relationships for pairs of isoelectronic compounds were correlated. As the amount of structural information and our knowledge of the reactivity of boron−nitrogen compounds progressed, it became apparent that fundamental differences exist due to the more polar electron distribution in BN systems compared to that in CC systems. For instance, although the bis(amino)diboranes $R_2N(R)B-B(R)NR_2$[4] are isoelectronic with the 1,3-butadienes $R_2C=(R)C-C(R)=CR_2$, the bonding in the latter is best described by the canonical formulae **A** to **D**, while formulae **E** and **F** describe the bonding situation in the diborane(4) derivative.



A



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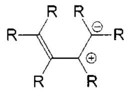

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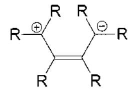

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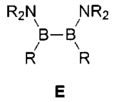
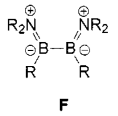


E



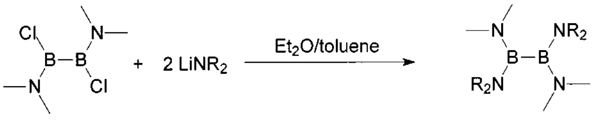
F

Typical for the diborane(4) derivative is the absence of a double-bond contribution to the boron−boron core, and this is reflected not only in the bond lengths (1.74 Å), but also in the fact that the two $(R_2N)RB$ units adopt interplanar angles between 60 and 90°, depending on the nature of the substituents.[4,5,6]

The majority of tetraaminodiboranes(4), $(R_2N)_4B_2$, are obtained by dehalogenation of bis(amino)boron halides $(R_2N)_2BHal$.[7][8] Yields of the resulting diborane species range from >70% to <1% in very unfavorable cases depending on conditions as well as on experimental skills. Dehalogenation by sodium metal is often the method of choice compared to the use of Na/K alloy, even though longer reaction times are required. One of the possible reasons for the low yields may be a further reaction of the $B_2(NR_2)_4$ formed with excess metal. We report here on this perspective.

Tetraaminodiboranes(4)

For the present study, a number of new tetraaminodiboranes(4) **2a**−**2c** were prepared by allowing bis(dimethylamino)diboron(4) dichloride **1**[9] to react with lithio amides as shown in Equation 1.



(1)

1

2a: NR_2 = pyrrolyl
2b: NR_2 = indolyl
2c: NR_2 = carbazolyl

The results of X-ray crystal structure determinations of **2a** and **2b** are depicted in Figures 1 and 2 (see also Table 1). The BN bonds to the dimethylamino groups measure 1.390(3) and 1.396(2) Å, respectively. They form interplanar angles with the $B_2(N_A)_2$ plane (the subscript A indicates the amino N atoms) of just 4° and 9° and thus can be considered as being almost coplanar. This allows the formation of strong BN_A π-bonds with a bond order close to 2, as

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reflected in the short BN_A bond lengths. In contrast, the BN_H bonds (the subscript H indicates the heterocyclic N atoms) to the indolyl and pyrrolyl ligands are much longer, with an average length of 1.48 Å. The torsion angles between the indolyl and pyrrolyl rings and the BN_AN_H units are 32° and 35°, respectively, which would still allow for a non-negligible BN_H π-interaction. On the other hand, both heterocyclic groups are electronegative substituents, which tend to avoid π-bonding through their N_H atoms. Considering its NMR data, the same holds for compound **2c**.

The dihedral angles N3−B2−B1−N4 and N2−B2−B1−N1 are 75° and 72° in **2a** and 59° and 55° in **2b**. Thus, the twisting about the B−B bond is larger in **2a** than in **2b**, which is remarkable considering the greater steric requirement of the indolyl group. Finally, the boron−boron bond lengths amount to 1.716(2) Å in **2a** and 1.723(4) Å in **2b**, which are appropriate values for B−B single bonds.[10] Therefore, the structural parameters are consistent with a significant contribution from formulae **E** and **F** to the ground states of these molecules.

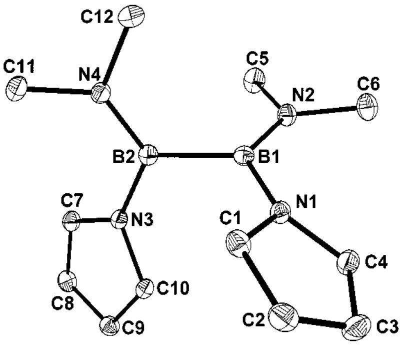


Figure 1. Molecular structure of the diborane(4) **2a** in the crystal; thermal ellipsoids are shown at a 25% probability level

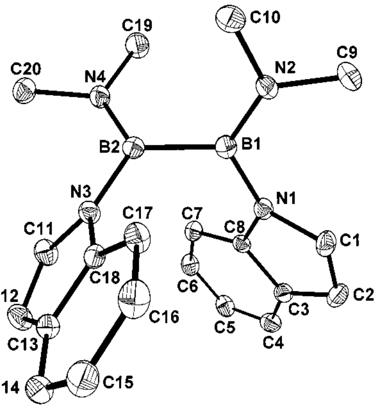


Figure 2. Molecular structure of the diborane(4) **2b** in the crystal; thermal ellipsoids are shown at a 25% probability level

Reduction to Tetraaminodiborates(2−)

Treating solutions of the $B_2(NR_2)_4$ compounds **2a**−**2c** with elemental Li (in finely dispersed form) in toluene leads to a very slow reaction of the metal. The reaction is accompanied by a slight color change of the solution and eventually the ^{11}B-NMR signal disappears, indicating that an insoluble boron-containing precipitate is formed. By carrying out these reactions of **2a** and **2c** in diethyl ether/toluene, yellow and red solutions are formed, respectively. However, for the reduction of **2b**, neat diethyl ether is required as the solvent; in this case the solution turns orange. These reactions proceed according to Equation 2.

From the red solutions of the reduced $B_2(NR_2)_4$ compounds **2a**−**2c**, yellow crystals of **3a**, orange crystals of **3b**, and red crystals of **3c** were isolated. All were found to be extremely air- and moisture-sensitive.[19] Preliminary studies of their chemical behaviour have demonstrated that they can be considered as strong reducing agents. This will be reported in a separate paper.

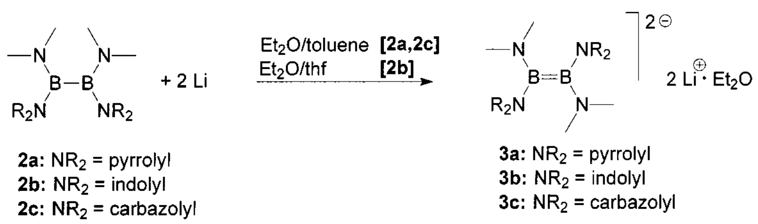
NMR Spectra

The shielding at the boron atoms of the tetraaminodiboranes(4) ($\delta^{11}B$ = 37.0 for **2a**; 36.7 for **2b**; 37.9 for **2c**) corresponds to that found for $B_2(NMe_2)_4$ ($\delta^{11}B$ = 36.6) or $B_2(NMe_2)_2Cl_2$ ($\delta^{11}B$ = 37.5). Two signals for the NMe_2 groups, both in the ^{1}H- and the ^{13}C-NMR spectra, are indicative of hindered rotation about the B−NMe_2 bond. Considering the ^{1}H-NMR data, the shift differences between these two signals are 0.12 ppm for **2a**, 0.18 ppm for **2b**, and 0.04 ppm for **2c**. The small difference found for **2c** may indicate a greater twisting of the NMe_2 groups in relation to the N_2BB planes, while for **2a** and **2b** the twisting does not exceed 10°.

On anion formation, the boron centers become more shielded by 4.0−9.6 ppm. While the NMR signals for the NMe_2 groups are slightly upfield shifted in **3a** and **3b**, a deshielding of 0.1 ppm is observed for **3c**. These observations are in accord with the trend in the ^{11}B shieldings shown by compounds $Ph(Me_2N)B{-}B(NMe_2)Ph$[14] and $[Ph(Me_2N)B{=}B(NMe_2)Ph](LiOEt_2)_2$,[14] where $\delta^{11}B$ changes from 49.3 to 33. Since in the anions **3** the amino groups are almost perpendicularly oriented in relation to the B_2N_4 plane, all effects of B−N π-bonding can be neglected and the increased shielding, as well as the decrease in the line width, indicates higher electron density at the boron atoms. This is of course due to the strong B−B π-bonding, which also has the effect that the two BN_2 planes tend to become mutually planar, in contrast to the 57−70° torsion angle found in the neutral compounds. Moreover, the much simpler ^{1}H- and ^{13}C-NMR spectra of the ”anions” **3a**−**3c** compared to those of **2a**−**2c** suggest a higher symmetry for the anions (see X-ray structure analysis).

X-ray Structure Analysis

The molecular structures of the dilithium tetraaminodiborates are depicted in Figures 3−5. The structural parameters of the compounds **2a**, **2b**, **3a**−**3c** are summarized in Table 1.



(2)

Table 1. Selected bonding parameters; bond lengths in Å, bond angles, and angles between planes in degrees

	2a	**2b**	**3a**[a]	**3b**[b]		**3c**[c]	
B1−B2	1.718(2)	1.723(4)	1.59(1)	1.584(4)	1.578(3)	1.566(9)	1.571(8)
B1−N1	1.487(6)	1.477(3)	1.562(5)	1.564(2)	1.560(2)	1.573(5)	1.564(5)
B1−N2	1.394(2)	1.387(3)	1.537(7)	1.534(3)	1.527(3)	1.540(6)	1.544(5)
B2−N3	1.489(2)	1.480(3)	−	−	1.568(2)	−	−
B2−N4	1.392(3)	1.389(3)	−	−	1.531(3)	−	−
N1−B1−N2	120.7(2)	119.3(2)	114.5(3)	114.0(2)	114.6(2)	112.6(3)	−
N1−B1−B2	116.9(1)	117.4(2)	120.8(6)	121.3(2)	120.9(2)	122.8(5)	−
N2−B1−B2	122.3(2)	123.3(2)	124.7(5)	124.3(2)	123.9(2)	124.1(5)	−
N3−B2−N4	121.1(1)	118.3(2)	−	−	113.8(2)	−	112.9(3)
N3−B2−B1	116.3(2)	118.4(2)	−	−	121.2(2)	−	122.3(4)
N4−B2−B1	122.6(2)	123.2(2)	−	−	124.5(2)	−	124.4(4)
$C_2N1-N1-B1-N2$	32	35	67	68	68	77	−
$C_2N2-N2-B1-N1$	7	10	64	62	57	62	−
$C_2N3-N3-B2-N1$	35	66	−	−	72	−	78
$C_2N4-N4-B2-N3$	3	7	−	−	64	−	63
N_2B1/N_2B2	73	57	0	0	3	0	0

[a] The molecule is centrosymmetric, therefore B2 corresponds with the symmetry-equivalent atom B1A. − [b] Of the two independent molecules of **3b** in the asymmetric unit, one is centrosymmetric (related data given as B1N1N2), while the other is non-centrosymmetric. The core of the molecule has been labelled B2N3N4 and B4N5N6. In the columns, B1 refers to B3, B2 to B4, etc. − [c] There are two independent centrosymmetric molecules in the asymmetric unit. The first molecule is labelled B1N1N2/B1AN1AN2A, the second B2N3N4/B2BN3BN4BA.

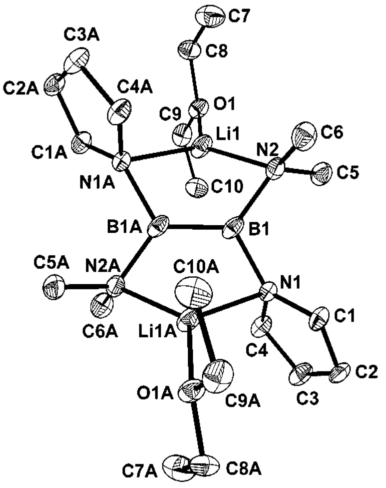


Figure 3. Molecular structure of the diborate **3a** in the crystal; thermal ellipsoids are shown at a 25% probability level

There are two independent molecules in the asymmetric unit for compounds **3b** and **3c**. One of the two molecules of **3b** lies on a crystallographic inversion center, and this also holds true for compound **3a**.

In contrast to the neutral diborane(4) compounds **2**, a planar B_2N_4 moiety is present in the anions of **3**. More importantly, the B−B bond lengths are 0.12 Å shorter than those in the corresponding tetraaminodiboranes. This, as well as the planarity of the B_2N_4 skeleton, gives an excellent indication for the presence of B=B double bonds.

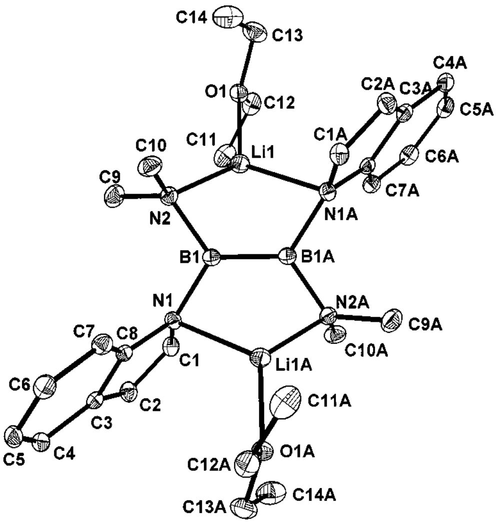


Figure 4. Molecular structure of the diborate **3b** in the crystal; thermal ellipsoids are shown at a 25% probability level

Another structural feature to be noted is that the Me_2N groups are perpendicularly arranged in relation to the B_2N_4 planes, their N atoms being pyramidal, with an average BN_A distance of 1.54 Å. BN_A π-bonding is therefore absent. Moreover, the BN_H bond lengths to the *N*-heterocycles are longer: 1.564(6) Å in **3a**, on average 1.56 Å in **3b**, and 1.562(6) Å and 1.572(6) Å in **3c**, respectively. The rings themselves are twisted in relation to the B_2N_4 plane by 64°,

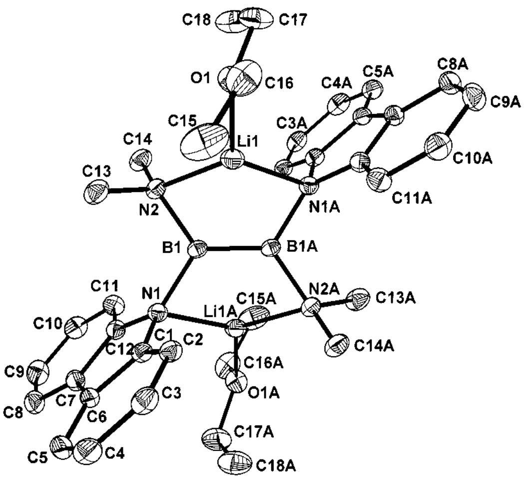


Figure 5. Molecular structure of the diborate **3c** in the crystal; thermal ellipsoids are shown at a 25% probability level

67°, and 74°; BN_H π-bonding can, therefore, also be excluded.[11]

However, the orientation of the amino groups is essential for the coordination of the lithium cations, which are surrounded in a trigonal-pyramidal geometry by two nitrogen atoms and an oxygen atom of an ether molecule. Thus, the tetraaminodiborate(4) unit acts as a bis-bidentate ligand. We assume that this feature of the molecular structure of the diborate can be considered as one reason for the ease of reduction of the tetraaminodiborane to the diborate. The LiN atom distances lie in the range 1.98 Å to 2.25 Å, and compare well with those found in many other LiN compounds.[12][13] Rather wide N−Li−N bond angles are responsible for the comparatively short Li−B distances (2.3−2.2 Å). An even more important reason for the ease of reduction of the tetraaminodiboranes to diborates seems to be that the starting material must bear an aromatic substituent. Considering literature data and our own investigations, there would seem to be no known reductions of diboranes(4) where there is not at least one aromatic ring system connected to the B_2 moiety.[14][15] This leads to the supposition that, in the mechanism of these reactions, the aromatic substituent may act as the primary electron acceptor.

MO Calculations

In order to support the experimental results and to obtain information on the bonding situation and the possibilities of delocalization of the B−B π-bond, geometry optimized MO calculations,[16] including an NBO analysis,[17] were performed on the model compound $(H_2OLi)_2(Me_2N)_2B_2(NC_4H_4)_2$ **4**. Figure 6 shows the geometry of the calculated compound. Some results are summarized in Table 2.

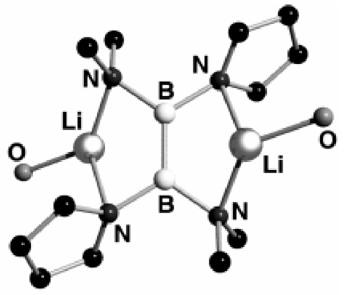


Figure 6. Calculated structure of **4**, Becke 3LYP/6-31G* optimized, NIMAG 0; H atoms have been omitted for clarity

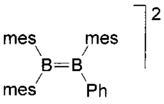
Table 2. Geometrical data for model compound **4** based on Becke 3LYP/6-31G* calculations compared with experimental data for compounds **3a**−**3c**

	Theor. $d_{(E-E)}$ [pm]	Exp. $d_{(E-E)}$ [pm]	Theor. ϕ [°]	Exp. ϕ [°]
B=B	160	157−159	0	0
$B-N_{arom}$	157	156−157	58	64−74
$B-NMe_2$	154	154	69	62−67

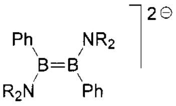
The NBO analysis shows that the B−B σ-bonding orbital and a B−B π orbital are strongly occupied, with each boron $2p_z$ orbital holding 0.9404 e. These orbitals are perpendicular to the B_2N_4 plane and therefore represent a typically localized π-bond. The "second-order pertubation analysis" shows that there is no significant donor−acceptor interaction of the B−B π-bond with orbitals of other atoms. Delocalization of the π-electron density through the BN bonds can therefore be excluded.

Discussion

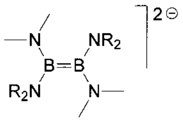
The first two-electron reduction of a diboron(4) compound was discovered by Power et al. in 1992 using tris(mesityl)phenyldiborane(4) as the diborane(4) source.[15] Shortly afterwards, the reduction of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) by lithium in the presence of diethyl ether gave access to the dianion $[Ph(Me_2N)B{=}B(NMe_2)Ph]^{2-}$.[14] Dianions of the type $[R_2N(Me_2N)B{=}B(NMe_2)NR_2]^{2-}$ (R_2N = pyrrolyl, indolyl, carbazolyl) now complete a series of tetraaminodiborates(4). Proceeding along this series from the dianion **4a** through **4b** to **4c**, one notes that the differences in the chemical shifts $\delta^{11}B$ become increasingly smaller.



4a



4b



4c

For the tetraaryldiborate(4) dianion $\Delta\delta^{11}B$ is 74.3 ppm, for the bis(dimethylamino)bis(phenyl)diborate(4) $\Delta\delta^{11}B$ is 16.3 ppm, while for the tetraaminodiborates(4) described here $\Delta\delta^{11}B$ is only 9.0−9.6 ppm. This is due to the increasing B−N π-bonding effects on the shielding of the B atoms in the neutral diboranes, as demonstrated by the short Me_2N bonds in compounds **2a** and **2b**, which are coplanar with the N_2BB plane. Therefore, the gain in electron density at the boron atoms in the dianions is largest in compound **4a**, because there is little if any B−C π-bonding in the starting material [it should be noted that the boron atoms in $t\mathrm{Bu}_3(\mathrm{Me}_3\mathrm{Si})\mathrm{B}_2$ are even more strongly deshielded; $\delta^{11}\mathrm{B} = 120$], and is obviously smallest in $(\mathrm{R}_2\mathrm{N})(\mathrm{Me}_2\mathrm{N})\mathrm{B}-\mathrm{B}(\mathrm{NMe}_2)(\mathrm{NR}_2)$, which bears four amino groups.

On the other hand, the decrease in the B−B bond lengths on reduction is largest for the tetraaminodiboron moiety (ca. 0.12 Å), while for **4a** Δd(B−B) is 0.08 Å and for **4b** it is 0.07 Å. This cannot be exclusively attributed to the fact that the B−B bond lengths are shorter in $\mathrm{mes}_2\mathrm{B}-\mathrm{BmesPh}$ [1.71(1) Å][15] and $\mathrm{Ph}(\mathrm{Me}_2\mathrm{N})\mathrm{B}-\mathrm{B}(\mathrm{NMe}_2)\mathrm{Ph}$ [1.714(4) Å][14] as compared to those in the new tetraaminodiboranes [1.718(2) Å, 1.723(4) Å]. One reason for the greater contraction of the B−B bond lengths in compounds **3** may lie in the fact that the dianion acts as a chelating ligand forming two five-membered heterocycles with the Li atoms. The lone pairs of the Li-coordinating N atoms are all orientated towards the Li atoms, which precludes delocalization of the boron π-electrons.

While there is normally an atom distance difference of 0.2 Å if a single-bonded system becomes doubly bonded (e.g. the C−C bonds in ethane and ethene, respectively), the B−B bond length difference is smaller. This is to be expected because in the diborate dianions the boron atoms do not change their coordination number and remain sp^2 hybridized. In addition, the two-electron reduction imparts to the boron atom a charge of −0.94 e, which should result in a repulsion between the two boron atoms and hence a counteractive effect on the B=B double bond length. However, the planarity of the B_2N_4 units in the new diborates(4), in addition to all the other discussed geometrical and electronic features and the results of the MO calculations, provide strong evidence for the presence of a truly localized B=B double bond.

Based on the present result, one might envisage that even the simplest tetraaminodiborane(4), $\mathrm{B}_2(\mathrm{NMe}_2)_4$, might be reducible by lithium. However, experiments carried out in analogy to those described here did not produce a $\mathrm{B}_2(\mathrm{NMe}_2)_4{}^{2-}$ anion. Therefore, we suggest that an ”aromatic” moiety must be present to allow the electron transfer from lithium (metal) to boron [of the diborane(4)].

Experimental Section

General: All experimental manipulations were conducted under anhydrous conditions employing Schlenk techniques using argon as a protecting blanket. Solvents were dried by conventional methods. Boron-containing starting materials were prepared by literature methods.[7][8] − NMR: Jeol 270 and 400 spectrometers [standards: TMS (^{1}H, ^{13}C), external $\mathrm{BF}_3{\cdot}\mathrm{OEt}_2$ (^{11}B)]. − X-ray structure determination: Siemens P4 with CCD area detector, Mo-K_α radiation, graphite monochromator, LT device.

Bis(dimethylamino)bis(pyrrolyl)diborane(4) (2a): To a vigorously stirred suspension of pyrrolyllithium (2.35 g, 29 mmol) in toluene (40 mL) at −78 °C was added a solution of dichlorobis(dimethylamino)diborane(4) (2.35 g, 13 mmol) in toluene (15 mL). The suspension was allowed to warm to ambient temperature and stirring was continued for a further 23 h. Then, THF (0.25 mL) was added and, after stirring for an additional 1 h, the insoluble material was removed by centrifugation (15 min at 15000 rpm). The solid was washed with toluene (10 mL). All volatiles were then removed from the solution in vacuo. A greenish colored oil remained, which solidified within a few minutes. Pure **2a** was obtained by sublimation (90 °C/$9{\cdot}10^{-3}$ Torr) in large colorless prisms.[18] Yield: 2.54 g of **2a** (81%), m.p. 48−51 °C. − ^{11}B NMR (64 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 37.0$ [$h_{1/2} = 320$ Hz, $\mathrm{B}_2(\mathrm{NMe}_2)_2(\mathrm{pyrrolyl})_2$]. − ^{1}H NMR (270 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 6.93$ (dd, 4 H, $\mathrm{H}^{1,4}$), 6.49 (dd, 4 H, $\mathrm{H}^{2,3}$), 2.56 [s, 6 H, $\mathrm{N}(\mathrm{CH}_3)_2$], 2.44 [s, 6 H, $\mathrm{N}(\mathrm{CH}_3)_2$]. − ^{13}C NMR (68 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 124.6$ (pyrrolyl $\mathrm{C}^{1,4}$), 111.6 (pyrrolyl $\mathrm{C}^{2,3}$), 42.6 [$\mathrm{N}(\mathrm{CH}_3)_2$], 39.3 [$\mathrm{N}(\mathrm{CH}_3)_2$]. − $\mathrm{C}_{12}\mathrm{H}_{20}\mathrm{B}_2\mathrm{N}_4$ (241.94): calcd. C 59.57, H 8.33, N 23.16; found C 59.12, H 8.35, N 22.29.

Bis(dimethylamino)bis(indolyl)diborane(4) (2b): Prepared in analogy to **2a** from indolyllithium (7.39 g, 60.0 mmol) in toluene (60 mL) and $\mathrm{B}_2(\mathrm{NMe}_2)_2\mathrm{Cl}_2$ (5.42 g, 30.0 mmol) in toluene (25 mL) with stirring for 18 h. Addition of THF (1 mL), reducing the volume of the solution by ca. 50% and storage for 4 days at −20 °C gave crystalline **2b**.[18] Yield: 8.80 g of **2b** (89%), m.p. 63−67 °C. − ^{11}B NMR (64 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 36.7$ [$h_{1/2} = 400$ Hz, $\mathrm{B}_2(\mathrm{NMe}_2)_2(\mathrm{indolyl})_2$]. − ^{1}H NMR (400 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 7.72$ (dd, 2 H, H^4), 7.49 (dd, 2 H, H^7), 7.19 (dd, 2 H, H^6), 7.12 (dd, 2 H, H^5), 7.03 (d, 2 H, $^3J_{\mathrm{HH}} = 2.7$ Hz, H^1), 6.67 (d, 2 H, $^3J_{\mathrm{HH}} = 2.7$ Hz, H^2), 2.45 [s, 6 H, $\mathrm{N}(\mathrm{CH}_3)_2$], 2.27 [s, 6 H, $\mathrm{N}(\mathrm{CH}_3)_2$]. − ^{13}C NMR (100 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 139.8$ (indolyl C^8), 131.4 (indolyl C^3), 129.5 (indolyl C^1), 122.2 (indolyl C^5), 120.9 (indolyl C^4), 120.7 (indolyl C^6), 113.1 (indolyl C^7), 106.0 (indolyl C^2), 41.2 [$\mathrm{N}(\mathrm{CH}_3)_2$], 39.9 [$\mathrm{N}(\mathrm{CH}_3)_2$]. − $\mathrm{C}_{20}\mathrm{H}_{24}\mathrm{B}_2\mathrm{N}_4$ (342.05): calcd. C 70.23, H 7.09, N 16.38; found C 69.84, H 7.06, N 16.26.

Bis(carbazolyl)bis(dimethylamino)diborane(4) (2c): Prepared in analogy to **2a** from carbazolyllithium (1.60 g, 9.2 mmol) in toluene (40 mL) and $\mathrm{B}_2(\mathrm{NMe}_2)_2\mathrm{Cl}_2$ (0.83 g, 4.6 mmol) in toluene (20 mL) with stirring for 18 h. THF (0.3 mL) was added, all volatiles were removed from the solution, and then the residue (2.92 g) was dissolved in hot toluene (60 mL). Removal of some insoluble material and cooling to −20 °C afforded small crystals. Yield: 1.95 g of **2c** (95%), m.p. 113−117 °C. − ^{11}B NMR (64 MHz, toluene): $\delta = 37.9$ [$h_{1/2} = 780$ Hz, $\mathrm{B}_2(\mathrm{NMe}_2)_2(\mathrm{Cbz})_2$]. − ^{1}H NMR (400 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 8.01$ (d, 4 H, $^3J_{\mathrm{HH}} = 7.8$ Hz, $\mathrm{H}^{6,9}$), 7.35 (d, 4 H, $^3J_{\mathrm{HH}} = 8.3$ Hz, $\mathrm{H}^{3,12}$), 7.29 (ps. t, 4 H, $^3J_{\mathrm{HH}} = 7.6$ Hz, $\mathrm{H}^{4,11}$), 7.17 (ps. t, 4 H, $^3J_{\mathrm{HH}} = 7.3$ Hz, $\mathrm{H}^{5,10}$), 2.70 [s, 6 H, $\mathrm{N}(\mathrm{CH}_3)_2$], 2.66 [s, 6 H, $\mathrm{N}(\mathrm{CH}_3)_2$]. − ^{13}C NMR (100 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 142.2$ (Cbz $\mathrm{C}^{7,8}$), 125.6 (Cbz $\mathrm{C}^{2,13}$), 125.5 (Cbz $\mathrm{C}^{4,11}$), 119.9 (Cbz $\mathrm{C}^{6,9}$), 112.6 (Cbz $\mathrm{C}^{3,12}$), 41.3 [$\mathrm{N}(\mathrm{CH}_3)_2$], 41.2 [$\mathrm{N}(\mathrm{CH}_3)_2$]. − $\mathrm{C}_{28}\mathrm{H}_{28}\mathrm{B}_2\mathrm{N}_4$ (442.18): calcd. C 76.06, H 6.38, N 12.67; found C 75.74, H 6.82, N 12.60.

Dilithium Bis(dimethylamino)bis(pyrrolyl)diborate(4) (3a): A suspension of Li powder (40 mg, 13 mmol) in diethyl ether (20 mL) was cooled to −78 °C. A solution of **2a** (1.54 g, 6.4 mmol) in toluene (20 mL) was then added under stirring and the suspension was allowed to warm to ambient temperature. After 18 h, the solution was yellow-green in color. The excess Li was then removed and the solution was concentrated in vacuo to a volume of ca. 30 mL. Cooling to −20 °C for ca. 12 h led to the deposition of light-yellow crystals.[18] Yield: 1.89 g of **3a** · 2 EtO_2 (73%). **3a** was found to decompose rapidly at 73 °C, and within 10 d at ambient temperature. − ^{11}B NMR (64 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 27.4$ [$h_{1/2} = 140$ Hz, $\mathrm{Li}_2\mathrm{B}_2(\mathrm{NMe}_2)_2(\mathrm{pyrrolyl})_2$]. − ^{1}H NMR (270 MHz, $\mathrm{C}_6\mathrm{D}_6$): $\delta = 7.13$ (m, 4 H, $\mathrm{H}^{2,3}$), 7.02 (dd, 4 H, $\mathrm{H}^{1,4}$), 3.26 [q, 8 H, ^3J(H,H) = 3.8 Hz, $(\mathrm{OC}H_2\mathrm{CH}_3)_2$], 2.10 [s, 12 H, $\mathrm{N}(\mathrm{CH}_3)_2$], 1.10 [t, 12 H, ^3J(H,H) =

3.8 Hz, $(OCH_2CH_3)_2$]. – ^{13}C NMR (68 MHz, C_6D_6): δ = 124.2 (pyrrolyl $C^{1,4}$), 111.7 (pyrrolyl $C^{2,3}$), 65.9 [$(OCH_2CH_3)_2$], 39.5 [$N(CH_3)_2$], 15.5 [$(OCH_2CH_3)_2$].

Dilithium Bis(dimethylamino)bis(indolyl)diborate(4) (3b): Prepared in analogy to **3a** from Li (50 mg, 7.2 mmol) in diethyl ether (15 mL) and **2b** (1.37 g, 4.0 mmol) in diethyl ether (25 mL). Following the addition of **2b** to the Li suspension, an orange-coloured solid separated at −10°C. It was isolated and redissolved in THF (15 mL), then the excess Li was removed by filtration. On leaving the solution to stand overnight at 4°C, orange crystals separated.[18] Yield: 1.73 g (86%). **3b** was found to decompose within 1 d at ambient temperature and within 3 d at 4°C. – ^{11}B NMR (64 MHz, C_6D_6): δ = 27.9 [$h_{1/2}$ = 130 Hz, $Li_2B_2(NMe_2)_2$(indolyl)$_2$]. – ^{1}H NMR (400 MHz, [D_8]toluene): δ = 8.28 (br. d, 2 H, H^1), 8.02 (br. d, 2 H, H^2), 7.76 (m, 2 H, H^4), 7.44 (m, 2 H, H^7), 7.20 (m, 4 H, $H^{5,6}$), 3.25 [q, 8 H, ^3J(H,H) = 3.8 Hz, $(OCH_2CH_3)_2$], 2.21 [s, 12 H, $N(CH_3)_2$], 1.10 [t, 12 H, ^3J(H,H) = 3.8 Hz, $(OCH_2CH_3)_2$]. – ^{13}C NMR (100 MHz, [D_8]toluene): δ = 140.7 (indolyl C^8), 137.8 (indolyl C^1), 134.8 (indolyl C^3), 122.4 (indolyl C^5), 121.2 (indolyl C^4), 120.1 (indolyl C^6), 113.8 (indolyl C^7), 110.4 (indolyl C^2), 65.9 [$(OCH_2CH_3)_2$], 41.5 [$N(CH_3)_2$], 15.2 [$(OCH_2CH_3)_2$].

Dilithium Bis(dimethylamino)bis(carbazolyl)diborate(4) (3c): To a stirred suspension of Li powder (50 mg, 7.2 mmol) in diethyl ether (20 mL) at 0°C was added a warm solution of **2c** (640 mg, 1.5 mmol) in toluene (25 mL). The solution rapidly turned reddish brown. After stirring for 3 days, the excess Li was removed by filtration and washed with diethyl ether (20 mL). The combined filtrate and washings were then kept at 4°C until some red-brown crystals separated.[18] – ^{11}B NMR (64 MHz, toluene/Et_2O): δ = 28.9 ($h_{1/2}$ = 200 Hz). – ^{1}H NMR (270 MHz, C_6D_6): δ = 7.73 (m, 8 H, H_{arom}), 7.21 (m, 8 H, H_{arom}), 3.14 [q, ^3J(H,H) = 7.0 Hz, $(OCH_2CH_3)_2$], 2.96 [s, 12 H, $N(CH_3)_2$], 1.02 [t, ^3J(H,H) = 7.0 Hz, $(OCH_2CH_3)_2$]. – ^{13}C NMR (68 MHz, C_6D_6): δ = 144.3 (Cbz $C^{7,8}$), 129.1 (Cbz $C^{2,13}$), 126.1 (Cbz $C^{4,11}$), 120.1 (Cbz $C^{6,9}$), 119.5 (Cbz $C^{5,10}$), 116.2 (Cbz $C^{3,12}$), 67.2 [$(OCH_2CH_3)_2$], 43.2 [$N(CH_3)_2$], 15.8 [$(OCH_2CH_3)_2$].

X-ray Structure Determinations: Crystals were covered with perfluoropolyether oil at −40°C and suitable specimens were selected and mounted on a glass fibre. Cell dimensions were determined from the reflections on 15 frames each at four different χ and ψ settings by changing ψ by 0.3° per frame at 193 K. Data collection was performed in the hemisphere mode of the SMART program at 193 K by collecting a total of 1300 frames. Data reduction was performed using the program SAINT; no absorption correction was applied. The structures were solved by direct methods (SHELXTL-97). Non-hydrogen atoms were refined anisotropically (SHELX-97) and hydrogens were placed in calculated positions by applying a riding model. Crystallographic data and selected data relating to the data collection and refinement are summarized in Table 3.

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Table 3. Crystallographic data and data referring to data collection and refinement of compounds **2a**, **2b**, **2c**, **3a**, **3b**, and **3c**

Compound	**2a**	**2b**	**3a**	**3b**	**3c**
Chem. formula	$C_{12}H_{20}B_2N_4$	$C_{20}H_{24}B_2N_4$	$C_{20}H_{40}B_2Li_2N_4O_2$	$C_{28}H_{44}B_2Li_2N_4O_2$	$C_{36}H_{48}B_2Li_2N_4O_2$
Form. wght.	241.94	342.05	404.06	504.17	604.28
Cryst. size [mm]	0.2×0.3×0.3	0.2×0.3×0.3	0.15×0.15×0.2	0.15×0.2×0.4	0.15×0.2×0.3
Cryst. system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*c*
a [Å]	7.6127(4)	9.220(4)	9.1015(5)	7833(3)	17.6037(5)
b [Å]	15.6592(8)	14.901(5)	8.7833(5)	14.531(4)	13.81160(10)
c [Å]	12.0229(6)	14.428(7)	16.1059(8)	39.826(13)	16.2832(4)
α [°]	90	90	90	90	90
β [°]	94.957(1)	105.497(7)	92.569(1)	90.94(1)	115.034(1)
γ [°]	90	90	90	90	90
V [Å^3]	1427.87(13)	1910.2(14)	1286.23(12)	4533(2)	3587.10(14)
Z	4	4	2	6	4
ρ(calcd.), [Mg/m^3]	1.125	1.189	1.043	1.108	1.119
μ [mm^{-1}]	0.068	0.070	0.065	0.068	0067
F(000)	520	728	440	1632	1296
Index range	$-8 \le h \le 6$, $-18 \le k \le 18$, $-14 \le l \le 14$	$-10 \le h \le 10$, $-14 \le k \le 17$ $-16 \le l \le 16$	$-10 \le h \le 10$ $-9 \le k \le 9$ $-17 \le l \le 12$	$-9 \le h \le 9$ $-16 \le k \le 15$ $-46 \le l \le 46$	$-20 \le h \le 15$ $-16 \le k \le 5$ $-17 \le l \le 17$
2θ [°]	49.42	4820	46.50	49.42	49.42
Temp. [K]	183(2)	193(2)	163(2)	173(2)	183(2)
Refl. collected	7015	8857	5400	22085	6864
Refl. unique	2103	2782	1583	7383	4944
Refl. observed (4σ)	1861	2505	1335	5326	3311
R (int.)	0.0319	0.0350	0.0590	0.0305	0.0466
No. variabies	167	240	141	526	423
Weighting scheme[a] *x*/*y*	0.0390/0.6830	0.0343/1.1067	0.0723/2.4569	0.0448/1.2757	0.0205/5.2607
GOOF	1.101	1.256	1.189	1.032	1.174
Final *R* (4σ)	0.0408	0.0565	0.0713	0.0465	0.0796
Final *wR*2	0.0968	0.1202	0.1693	0.0994	0.1380
Larg. res. peak [e/Å^3]	0.282	0.269	0.298	0.226	0.329

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-118113/118114/118115/118116/118117. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

[19] The stabilities of the tetraaminodiborates(4) **3** decrease rapidly if a stronger donor than diethyl ether is used for coordination of the lithium atoms. Thus, the preparation of the THF-coordinated dilithium tetraaminodiborate(4) **3a** by reduction of the corresponding tetraaminodiborane(4) **2a** in THF or via ligand exchange leads to the desired THF-coordinated dianionic species, which decomposes rapidly above −30°C. In the presence of crown ether ligands, however, the decomposition temperature decreases to less than −78°C. On the other hand, the lithium atoms are not necessary for the stability of all the diborate species: substitution of the NMe_2 groups in the diborane(4) **2a** with mesityl groups leads to the compound mes(pyrrolyl)BB(pyrrolyl)mes **2d**. By reduction of **2d** with lithium in diethyl ether or THF, dilithium tetraaminodiborates(4) can be obtained, which are stable at room temperature. These and other results will be reported shortly.

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