Contribution to the Chemistry of Boron, 243[◇]

# Synthesis and Structures of Dimesityldiboranes(4)[☆]

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An efficient route to *B*,*B*′-dihalo-*B*,*B*′-dimesityldiboranes(4) is reported, as well as the conversion of these and of *B*,*B*′-dimesityl-*B*,*B*′-dimethoxydiborane(4) into other *B*,*B*′-dimesityldiboranes $B_2mes_2X_2$ (X = OR, SR, $NR_2$, NHR). The substituents X influence the shielding of the $^{11}B$ nucleus in the expected manner. Hindered rotation about the B–N bond is observed for X = pyrrolyl, while in solution there is free rotation about the B–C bond. However, X-ray structural results reveal that the mesityl group is almost orthogonal to the B(B)CY plane in the solid state. The shortest B–B bond is observed in $mes_2B_2I_2$, indicating that the iodide is the strongest Lewis acid in the reported series of $mes_2B_2Y_2$ compounds. This is also reflected in short B–C bonds. Moreover, the two mes(Y)B units also approach orthogonality in these diborane(4) compounds, and thus enforce this as a typical structural feature of diborane(4) derivatives. For this reason, the planar C(N)B–B(N)C unit of *B*,*B*′-di(benzylamino)-*B*,*B*′-dimesityldiborane(4) is regarded as exceptional for aminodiboranes(4).

## Introduction

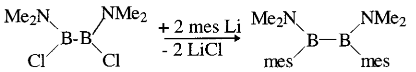
Although $B_2Cl_4$, the first diborane(4) compound, was synthesized as long ago as 1925[2], the intensive study of diborane(4) derivatives only began in the early 1960s, when an easy access to $B_2(NMe_2)_4$ was found[3][4]. Because $B_2(NMe_2)_4$ can be converted into $B_2(NMe_2)_3X$ or *sym*-$B_2(NMe_2)_2X_2$ (X = Cl, Br) by reaction with $BX_3$, a very useful synthon for the synthesis of amino-substituted diborane(4) derivatives was available on a preparative scale[4]. It was soon recognized that the stability of diborane(4) compounds $B_2X_4$ could be enhanced by increasing the electronic and steric shielding at the boron centers, so as to suppress decomposition into $BX_3$ and $(BX)_n$[5]. Thus, $B_2(NMe_2)_4$ is the most stable derivative due to N−B π-bonding in addition to the steric effect of the $Me_2N$ groups, while $B_2Me_4$ remains unknown. Nevertheless, the first stable tetraorganyldiborane(4) derivatives, such as $(tBu)_2B{-}B(tBu)Me$[6] and $(tBu)_2B{-}B(tBu)(CH_2tBu)$[7], were reported in 1980, demonstrating that only steric hindrance is required for the stabilization of diborane(4) species of this type. Although the *tert*-butyl groups are able to prevent redox disproportionation of these tetraalkyldiborane(4) derivatives, the halogenated species $tBu_2B_2X_2$ (X = Cl, Br) decompose readily[8].

While in alkyl-substituted diborane(4) derivatives the boron−carbon bonds can be described purely as σ-bonds, a B−C π-interaction can be expected in cases where aryl substituents are attached at the boron atoms, as the π-electrons of the aryl ligand can interact with the empty p-orbital of the boron atom. This has been documented in several examples[9][10]. Therefore, aryl-substituted diborane(4) derivatives might be expected to show an enhanced stability in comparison with their alkyl counterparts due to B−C π-bonding in $B_2R_4$. Indeed, some aryl-substituted diborane(4) derivatives such as $mes_2B{-}B(mes)Ph$ and $mes_2B{-}B(mes)CH_2SiMe_3$ are thermally stable, although little evidence for π-bonding or hyperconjugation was found[11].

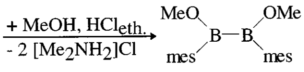
We now report on the synthesis and crystallographic characterization of a variety of mesityl-substituted diborane(4) derivatives. These studies were undertaken in order to gain further insight into the stabilities, electronic properties, and conformations of such species.

## Synthesis

As mentioned above, $B_2(NMe_2)_4$ and $B_2(NMe_2)_2X_2$ (X = Cl, Br) are key species in diborane(4) chemistry. The reaction of bis(dimethylamino)diborane(4) dichloride with mesityllithium, mesLi, for example, leads to $mes_2B_2(NMe_2)_2$[12][13] (Eq. 1a), which can be converted into $mes_2B_2(OMe)_2$ in very good yield according to Eq. 1b[11][13].



(1a)



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(1b)

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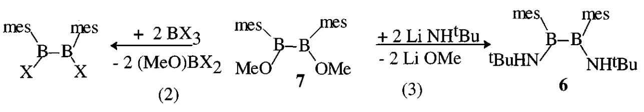
[◇] For Part 242, see ref.[1].

[+] Crystal structure determination.

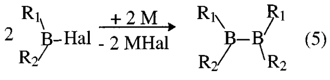
As shown in Eqs. 2 and 3, $mes_2B_2(OMe)_2$ itself can be further used as a starting material for the synthesis of various mesityl-substituted diboranes(4), e.g. the dihalides $mes_2B_2X_2$. In particular, the iodide **1c** is readily available under mild conditions and is obtained in good yield. Additionally, several diaminodimesityldiboranes(4) **2−6** were synthesized by allowing $mes_2B_2(OMe)_2$ to react with LiNH*t*Bu or $mes_2B_2Cl_2$ to react with amines or lithium amides (Eqs. 3, 4a, and 4b).



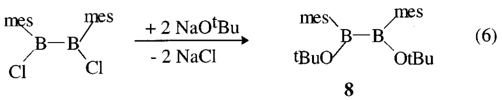
X = Cl Br I
**1a 1b 1c**

| amine | | Li NRR´ | | |
|---|---|---|---|---|
| $MeNH_2$ | **2** | Li NH$^i$Pr | **4** | bzl = benzyl |
| $bzlNH_2$ | **3** | Li pyr | **5** | pyr = pyrrolyl |

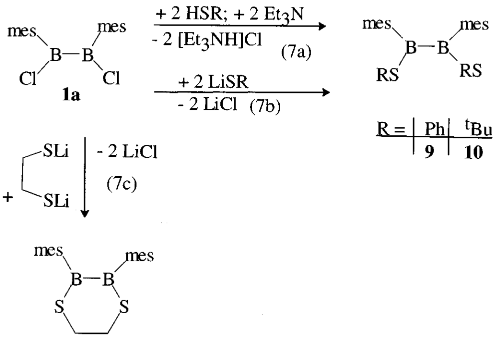
Although all these reactions provided the diaminodimesityldiboranes(4) in yields > 70%, better results were obtained when lithium amides were allowed to react with $mes_2B_2Cl_2$ rather than $mes_2B_2(OMe)_2$. This is due to the enhanced reactivity of the halogenated species. Moreover, the reactions can be carried out at lower temperatures and in less time. Furthermore, compared to the preparation of di(benzylamino)dimesityldiborane(4) (**3**) by the amine route, where a voluminous precipitate of benzylammonium chloride is formed, the by-product LiCl precipitates as a fine powder, and the reaction mixture can be stirred more readily. On the other hand, the method using amines as auxiliary bases can be advantageous when gaseous amines such as $MeNH_2$ are employed. $mes_2B_2(NHtBu)_2$ is also obtained in good yield by ligand exchange from $mes_2B_2(OMe)_2$ according to Eq. 3, but not by dehalogenation of haloboranes to diboranes(4), as shown in Eq. 5. The latter method fails when bulky substituents are attached to the boron atom.



Earlier attempts to synthesize dialkyldialkoxydiboranes(4) as well as dialkyldialkylthiodiboranes(4) were unsuccessful, and compounds of the type $R_2B_2X_2$ (X = OR, SR) were regarded as unstable as only borane(III) derivatives could be isolated[5]. Thus, only a few dialkyldiborane(4) derivatives with elements of the sixth main group are known[8]. In order to avoid redox disproportionation of these derivatives into $R_2BX$ and "BX", one *t*Bu group was attached at each boron atom in order to stabilize the diborane(4) compounds. However, most of these dialkyldiborane(4) compounds are liquids and structural characterization by X-ray diffraction has as yet been impossible[8]. In order to gain further structural insight into the conformation of dialkoxydimesityldiborane(4) derivatives and to compare them with the structure of $mes_2B_2(OMe)_2$ (**7**)[11] (see Eq. 1b), we synthesized $mes_2B_2(OtBu)_2$ (**8**) (Eq. 6), as well as several mercapto derivatives $mes_2B_2(SR)_2$. The latter were prepared from $mes_2B_2Cl_2$ with either a mixture of the respective thiol and $Et_3N$ as auxiliary base, or with lithium mercaptides, as shown in Eqs. 7a, 7b, and 7c. The best results were obtained using the latter method.



**1c** **8**



| R = | Ph | $^t$Bu |
|---|---|---|
| | **9** | **10** |

**11**

Efforts were also made to synthesize phosphanyl-substituted dimesityldiborane(4) derivatives. However, the reactions of $mes_2B_2Cl_2$ and LiPH*t*Bu in a 1:1 and in a 1:2 stoichiometry, as well as the reaction with one equivalent of $Li_2PtBu$, led only to ill-defined, multicomponent mixtures, as was evident from the many signals in the $^{11}$B-NMR spectra, which ranged from δ = 90 to −25. On the other hand, when $mes_2B_2Cl_2$ was allowed to react with lithiated 1,2-bis(isopropylphosphanyl)benzene, a planar heteroaromatic B−P−C cyclic product was formed in quantitative yield[14].

## NMR Spectra

The $^{11}$B-NMR shifts of the amino derivatives **2−6** are found in the range δ = 45−60, which is typical for diaminodiorganyldiboranes(4)[15]. The signals for $B_2mes_2(NHR)_2$ compounds (R = Me, *i*Pr, *t*Bu) are shifted to higher field compared to those of $(Me_2N)mesB{-}Bmes(NMe_2)$ [$\delta^{11}B$ $(CDCl_3)$ = 55]. The magnitude of the shift difference increases in the order NHMe < NHBz < NH*i*Pr < NH*t*Bu ($\delta^{11}B$ = 48.3, 47.9, 46.3, and 45.3, respectively) as the branching of R at the nitrogen atom increases. On the contrary, the $^{11}$B resonance shows a deshielding (δ = 60.5 for **5**) when an aromatic amine ligand is attached to the boron atoms, because the electrons of the $p_z$ orbital at the nitrogen atom contribute to the aromaticity of the pyrrole heterocycle. Consequently, the B−N bonds possess less π-bond character. Nevertheless, the $^1$H- and $^{13}$C-NMR spectra show a discrete signal for each H and C atom of the pyrrole ligand, indicating hindered rotation of this subunit at ambient temperature, and therefore N−B back bonding (vide infra).

In analogy to borane(3) derivatives, the replacement of an amino group by an alkoxy group leads to a deshielding of the $^{11}B$ nucleus due to the higher electronegativity of the substituent. The resonance signals of the two alkoxy compounds **7** and **8** are found at $\delta^{11}B \approx 60$ (±5) depending on the solvent. In the $^{13}C$-NMR spectra, the signals of the oxygen-bonded carbon atoms of the alkoxy ligands are shifted to lower field by about 5−7 ppm compared to those of the free alcohol[16]. This effect can be explained in terms of an O−B π-back donation, reducing the electron deficiency at the boron atom, leading to a deshielding of the respective C atom.

Within the dimercaptodimesityldiborane(4) series, the $^{11}B$-NMR signals span a range from $\delta = 69-81$. The thiophenolate derivative **9** shows the least shielded boron atom ($\delta^{11}B = 80.6$), while those of the cyclic dithiadiborinane **11** ($\delta^{11}B = 69.4$) are the best shielded among these compounds. Furthermore, the signal of the latter compound shows a relatively narrow half-width of ca. 210 Hz, while the signals of the acyclic derivatives exhibit half-widths of 1000−1550 Hz. In analogy to the alkoxydiboranes(4) **7** and **8**, the signals of the sulfur-bonded carbon atoms of the mercapto ligands are shifted to lower field compared with those of the free thiol[16], indicating partial π-character of the S−B bond (vide infra). The magnitude of shift difference is about 4−8 ppm, as is observed for the alkoxy analogues.

## Molecular Structures

In order to obtain information on the preferred conformations, and to gain further insight into steric and/or electronic effects of the ligands in the solid state of dimesityldiboranes(4), X-ray structure determinations of some representative derivatives were carried out.

Table 1 shows that the B−B bond lengths span a range from 1.709(5) Å in **5** to 1.735(7) Å in **8**. These can be compared with the B−B bond lengths in tetraaminodiboranes(4) **12**[17] and **13**[18] [1.693(9) Å and 1.750(8) Å, respectively]. Within the amino-substituted dimesityldiborane(4) series, compounds **6** and **3** show B−N bond lengths between 1.388(5) Å and 1.394(2) Å. These are slightly shorter than those in **12** and **13** (average of 1.415 and 1.426 Å)[17][18] and correspond, within the limits of significance, to the values determined for mes($Me_2N$)B−B($NMe_2$)mes (1.40 Å)[12]. It is interesting to note that the B−N bond lengths to the aromatic pyrrole ligands in compound **5** are significantly longer [1.434(4) and 1.438(4) Å] compared to those in the non-aromatic analogues $mes_2B_2(NMe_2)_2$[12] and $mes_2B_2(NHtBu)_2$ **6**.

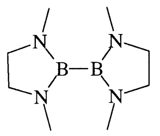
As expected, the boron atoms reside in planar environments (sum of bond angles = 360°). Nevertheless, although the $NBC_{mes}$ bond angles of the bis(dimethylamino)- as well as the dimesityldipyrrolyldiborane(4) are all 120 ± 2.5°, in compound **6** this angle is widened to 126.7° due to the steric repulsion between the mesityl and *tert*-butylamino groups. Consequently, the B−B−N bond angle in **6** is reduced to 114.9°. It is quite interesting that compounds **3** and **6** exhibit point group symmetry $C_i$ in the solid state and thus possess planar $C_2B_2N_2$ skeletons. Normally, diborane(4) derivatives show a dihedral angle between the two planes at the boron atoms in the range 60−80°. It seems that only packing effects are responsible for the conformation in the solid state, because no intermolecular interactions between the molecules other than van der Waals contacts are detectable.

A comparison of the crystal structures of $mes_2B_2(OMe)_2$ (**7**)[11] and $mes_2B_2(OtBu)_2$ (**8**) reveals no significant differences in the B−B, B−O, and B−C bond lengths. The B−B bonds are only marginally longer than in the tetraalkoxy-substituted diborane(4) **14** [1.711(6) Å][19], but are significantly longer compared to those in compounds **15a** and **15b**, where the B−B bond lengths are 1.687(3) and 1.684(3), respectively[20]. The B−O bonds of **8** [1.348(6) and 1.366(7) Å] are intermediate between single and double bond lengths (1.46 and 1.26 Å)[21], indicating partial B−O π-bonding[22][23]. In comparison, the B−O bonds in $mes_2B(OMe)$ (1.352 Å)[23] and compound **16** (average 1.367 Å)[24] are equally long, while in the triborane(5) derivative **17** a value of 1.396(5) Å is observed[25]. Due to enhanced steric repulsion between the *tert*-butyloxy group and the mesityl ligand, the $OBC_{mes}$ angles in **8** are widened to 128° compared with the corresponding bond angles in the methoxy derivative **7** [121.9(5)° and 123.2(5)°][11]. B−B−O and $B-B-C_{mes}$ bond angles are smaller (114.8−116.9°) as the sum of the bond angles around each boron atom is 360°. Most probably as a result of the aforementioned steric repulsion, the $B-O-C_{tBu}$ angles in **8** are even wider (131°) than the $B-O-C_{Me}$ angles in **7** (121° and 123.4°) and mes(OMe)B−Bmes$_2$ [125.0(9)°][11], but are very similar to that in compound **17** [130.7(4)°][25].

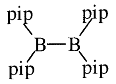
Table 1. Selected bond lengths [Å] and angles [°] for compounds **3**, **5**, **6**, **8**, and **10**

| Compound | **5** | **3** | **6** | **8** | **10** |
|---|---|---|---|---|---|
| Formula | $C_{26}H_{30}B_2N_2$ | $C_{32}H_{38}B_2N_2$ | $C_{26}H_{42}B_2N_2$ | $C_{26}H_{40}B_2O_2$ | $C_{26}H_{40}B_2S_2$ |
| $d_{BB}$ | 1.709(5) | 1.717(4) | 1.732(8) | 1.735(7) | 1.712(6) |
| $d_{B(1)X(1)}$[a] | 1.434(4) | 1.394(2) | 1.388(5) | 1.348(6) | 1.771(4) |
| $d_{B(2)X(2)}$[a] | 1.438(4) | 1.394(2) | 1.388(5) | 1.366(7) | 1.771(4) |
| $d_{B(1)C(1)}$[a] | 1.576(5) | 1.590(2) | 1.578(5) | 1.595(7) | 1.576(5) |
| $d_{B(1)C(10)}$[a] | 1.578(4) | 1.590(2) | 1.578(5) | 1.578(8) | 1.572(5) |
| angle betw. planes at B(1) and B(2) | 1.0 | 58.8 | 180 (“*trans*”) | 110.9 | 115.2 |
| angle betw. planes at B(1) and C(1) | 86.4 | | 79.5 | 83.6 | 88.5 |
| angle betw. planes at B(2) and C(10) | 86.4 | | 79.5 | 94.0 | 92.1 |

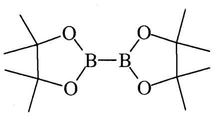
[a] X is either N, O or S.



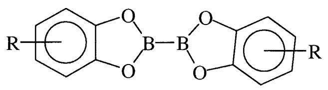
**12**



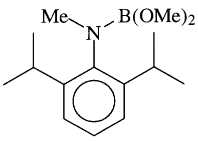
**13**



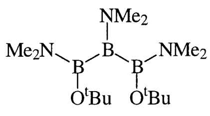
**14**



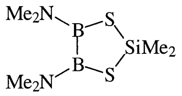
| R= | 4-$^t$Bu | 3,5-$^t$Bu |
|---|---|---|
| | **15a** | **15b** |



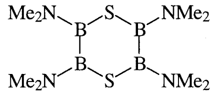
**16**



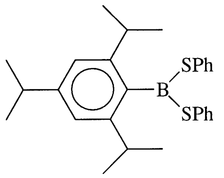
**17**



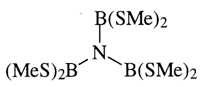
**18**



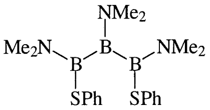
**19**



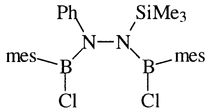
**20**



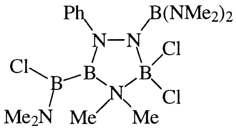
**21**



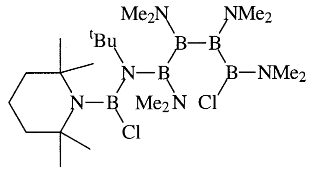
**22**



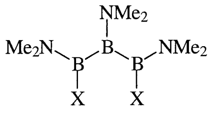
**23**



**24**



**25**



| X= | Br | I |
|---|---|---|
| | **26** | **27** |

Figure 1. ORTEP representation of the molecular structure of **3**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level

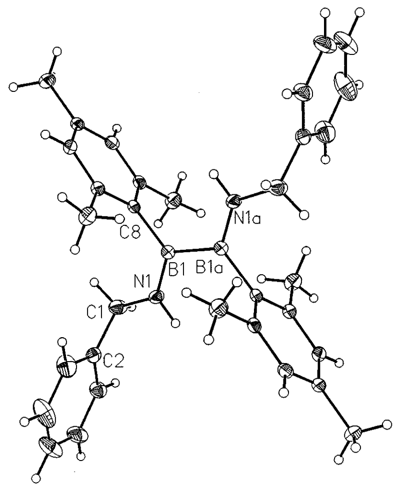
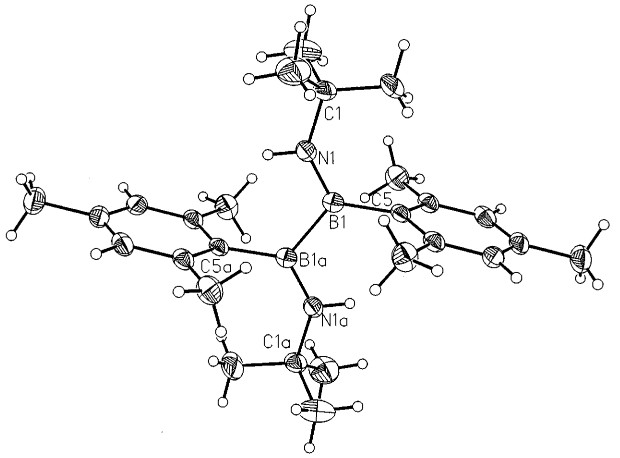


Figure 2. ORTEP representation of the molecular structure of **6**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level



The mercaptodiborane(4) mes(*t*BuS)B−B(S*t*Bu)mes (**10**) exhibits a B−B bond length of 1.712(6) Å, which is intermediate between the corresponding bond lengths of the amino-substituted B−S heterocycles **18** [1.72(1) Å] and **19** [1.66(1) and 1.69(1) Å][26]. The B−S distance in **10** was found to be 1.771(4) Å, which is intermediate between a

Figure 3. ORTEP representation of the molecular structure of **5**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level

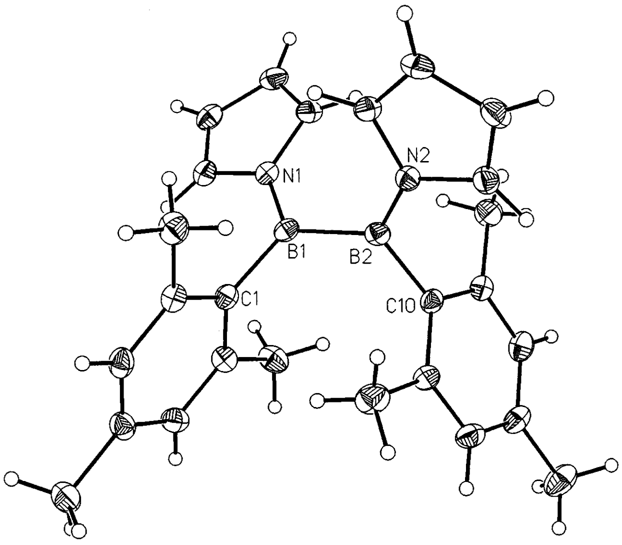
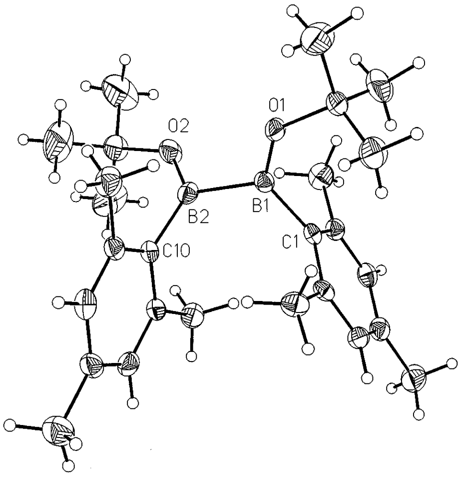


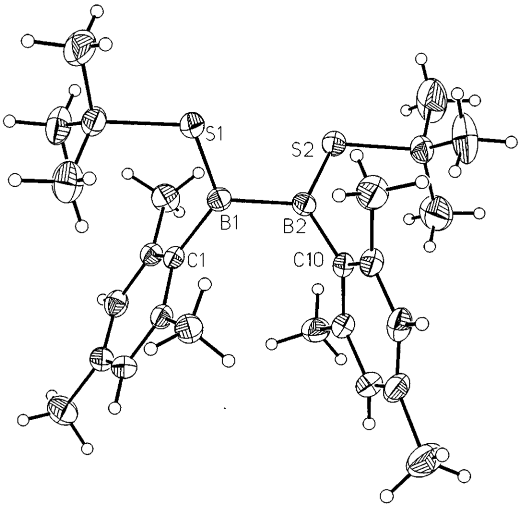
Figure 4. ORTEP representation of the molecular structure of **8**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level[a]



[a] Selected bond angles [°]: O1−B1−C1 128.1(4), O1−B1−B2 116.9(4), C1−B1−B2 114.9(4), O2−B2−C10 128.2(4), O2−B2−B1 114.8(5), C10−B2−B1 116.9(4), B1−O1−C19 130.7(3), B2−O2−C23 131.0(4).

B−S single bond (1.89 Å) and a B−S double bond (1.69 Å)[21]. Similar B−S bond lengths were observed in the trithiadiborolanes $(MeB)_2S_3$ (1.803 Å)[27a] and $(ClB)_2S_3$ (1.794 Å)[27b], as well as in the tris(methylthio)borane $B(SMe)_3$ (1.805 Å)[28], where partial S−B π-bonding is discussed. Furthermore, the B−S bond length in **10** matches very well those found in the acyclic derivatives $mes_2BSMe$ [1.787(6) Å][23] and $mes_2BSPh$ [1.790(6) Å][29], as well as in compounds **20** [1.799(6) and 1.802(6) Å][30] and **21** (average 1.80 Å)[30]. In molecules with less B−S π-bond character, such as the triborane(5) **22**, the B−S bonds are noticeably longer [1.864(2) and 1.849(2) Å][25].

Figure 5. ORTEP representation of the molecular structure of **10**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level[a]



[a] Selected bond angles [°]: C1−B1−B2 118.0(3), C1−B1−S1 127.6(3), B2−B1−S1 114.4(3), C10−B2−B1 115.5(3), C10−B2−S2 129.4(3), B1−B2−S2 115.1(3), B1−S1−C19 114.0(2), B2−S2−C23 114.1(2).

The S−B−$C_{mes}$ angles are on average 128.5° and are thus of the same order as those in the *tert*-butyloxy analogue **8**, but the B−B−S and B−B−$C_{mes}$ angles are smaller (114.4° and 118.0°, respectively). Owing to the steric repulsion between the mesityl ligand and the *tert*-butyl group, the B−S−$C_{tBu}$ angles in **10** are larger (114°) than those in $mes_2B(SMe)$ (109.8°)[23] or in the derivatives **20**−**23**, where B−S−R angles in the range 104.8−107.3° were measured[25][29][30].

The mesityl rings adopt an orientation almost perpendicular to the plane around the boron centers. This is a common feature of all the newly studied compounds.

Table 2. Selected bond lengths [Å] and interplanar angles [°] for compounds **1a**, **1b**, and **1c**

| | **1a** | **1b** | **1c** |
|---|---|---|---|
| Formula | $C_{18}H_{22}B_2Cl_2$ | $C_{18}H_{22}B_2Br_2$ | $C_{18}H_{22}B_2I_2$ |
| $d_{BB}$ | 1.680(6) | 1.673(6) | 1.664(9) |
| $d_{B(1)Hal(1)}$ | 1.770(5) | 1.928(4) | 2.165(6) |
| $d_{B(2)Hal(2)}$ | 1.774(4) | 1.932(4) | 2.158(7) |
| $d_{B(1)C(1)}$ | 1.551(5) | 1.557(5) | 1.558(8) |
| $d_{B(1)C(10)}$ | 1.558(6) | 1.560(5) | 1.548(8) |
| dihedr. angle HalB−BHal | 73.4 | 71.6 | 71.5 |
| angle betw. planes at B(1) and C(1) | 88.5 | 87.5 | 88.5 |
| angle betw. planes at B(2) and C(10) | 85.8 | 88.6 | 85.9 |

The crystal structures of the dihalogenodimesityldiborane(4) compounds reveal some interesting characteristics. Among all studied diborane(4) compounds, they exhibit the shortest B−B bonds. With an average of 1.67 Å, they are at the lower end of the range for B−B single bonds and, within the series, an interesting trend is observed (Table 2). Surprisingly, the bond lengths vary in a manner opposite to what might have been expected. As the covalent radius of the halogen atom increases on going from chlorine to iodine, the

Figure 6. ORTEP representation of the molecular structure of **1a**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level

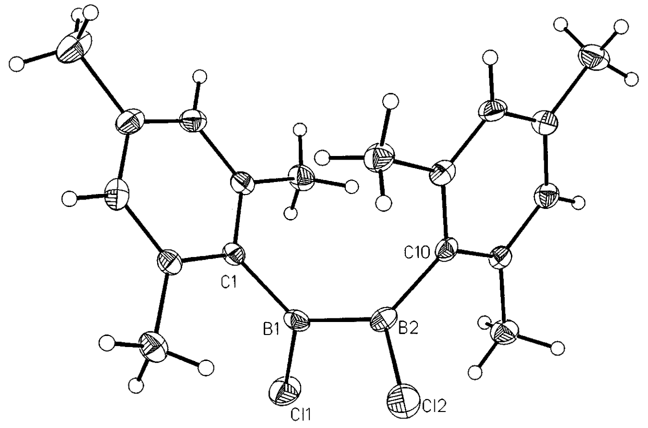


Figure 7. ORTEP representation of the molecular structure of **1b**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level

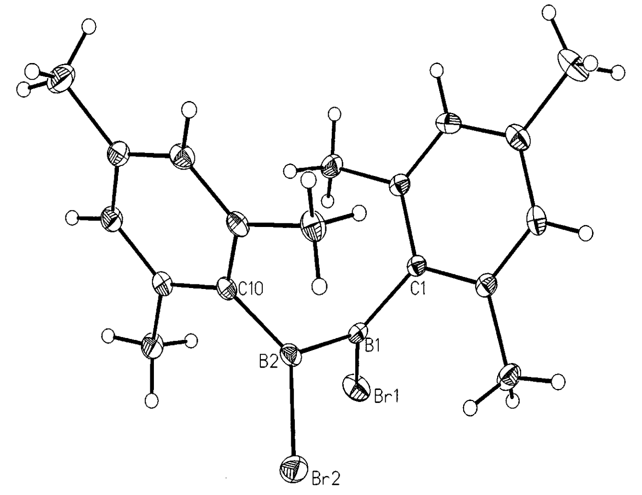
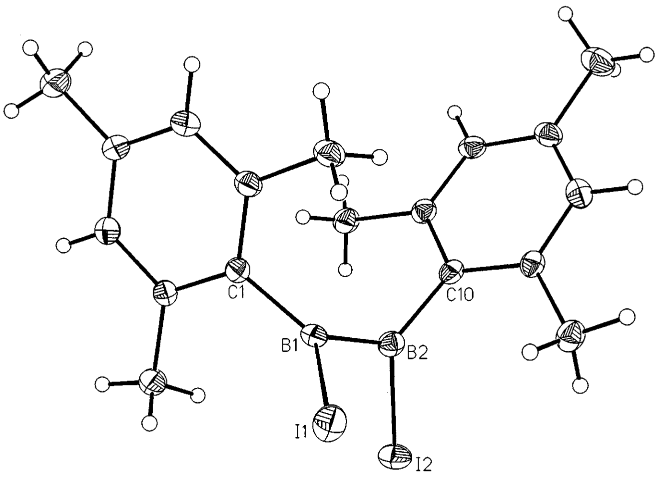


Figure 8. ORTEP representation of the molecular structure of **1c**; esd's in parentheses; thermal ellipsoids are represented at a 25% probability level



B−B distances *decrease*. This shrinkage is contrary to expectation in terms of the $-I$ effect of the halogen atoms, but fits the Lewis acidity scale of the boron halides. We regard this as further experimental evidence that π-bonding at boron halides decreases on ascending the series F > Cl > Br > I, with the consequence that in most cases the iodides are the most Lewis acidic compounds among such species. Moreover, electron diffraction experiments on the tetrahalodiboranes(4) $B_2Cl_4$[31] and $B_2Br_4$[32] show the same trend and lengths 1.70(7) Å and 1.69(2) Å], although these distances have large standard errors associated with them and do not differ significantly. At 1.68(2) Å[12], the B−B bond length in $(Me_2N)_2B_2Br_2$ fits very well into this series. The B−Cl bond lengths in **1a** (see Table 2) are significantly shorter than those observed for compounds **23**[33] [1.790(4) Å, 1.805(4) Å] and **24**[33] [1.814(5) Å]. This implies partial π-bond character. In comparison, the B−Cl bond lengths in the tetraborane(6) derivative **25**[25] are 1.809(5) Å for the terminal boron atom of the tetraborane chain and 1.870(4) Å for the di(aminoboryl) subunit. The same trend, i.e. a short B−Hal bond length, is also observed in $B_2Br_4$. The B−Br bond lengths in **1b** [1.928(4) Å, 1.932(4) Å] are obviously short, since a single bond would be expected to have a length of 1.99 Å [atomic radii of boron (0.85 Å) and bromine (1.14 Å)[21]], as observed in $(Me_2N)_2B_2Br_2$[12] [1.97(1) Å and 1.99(1) Å] and in compound **26**[25] [1.99(1) Å and 2.00(1) Å]. Even $mes_2B_2I_2$ exhibits a B−I bond length (average 2.16 Å) that is slightly smaller than the sum of the atomic radii[21] (0.85 Å and 1.33 Å, giving 2.18 Å). In this respect, it is interesting to note that the diiodotriborane(5) derivative **27** has longer B−I bonds [2.224(6) and 2.237(6) Å][25], which seems to be due to the presence of the amino groups.

However, all the halogen derivatives **1a**−**1c** show the common feature of shorter $B-C_{mes}$ bonds compared to the compounds listed in Table 1. In all cases, the mesityl rings are almost orthogonally orientated with respect to the plane at the boron atom. Furthermore, irrespective of the nature of the halogen atom, compounds **1a**−**1c** exhibit an X−B−B−X dihedral angle of 71°.

## Conclusions

A comparison of the chemistry of *B,B′*-di-*tert*-butyldiboranes(4) with that of *B,B′*-dimesityldiboranes(4) reveals the higher stability of the latter compounds. This is particularly evident for the dihalides $mes_2B_2X_2$ (X = Cl, Br, I) and $tBu_2B_2X_2$. Because there is *no* significant electronic contribution to stabilize the B−B bond by decreasing the electron deficiency at the boron atoms by X by B−C π-bonding, it is evident that the stability of $R_2B_2Y_2$ compounds with respect to dismutation into $B^I$ and $B^{III}$ species is kinetically but not thermodynamically controlled. This is also supported by the geometry of the structure of *B,B′*-dimesityldiborane(4) in the solid state, because possible π-overlap as in 1,4-butadienes is prevented by an almost orthogonal arrangement of the CB(B)Y planes and the $C_3B$ plane to the B(C)B(Y) plane. All the structural and chemical evidence collected for diborane(4) derivatives indicates that the B−B bond lengths are primarily determined by the character of the group Y. Thus, it appears that kinetically stable tetraorganyldiboranes $B_2R_4$ can be prepared with bulky groups R, as verified for $B_2(tBu)_3SiMe_3$[6] and similar compounds. The former may be used to generate $B_2H_2(tBu)SiMe_3$, an unstable molecule that may be used to determine whether hydroboration or diboration prevails in kinetic experiments.

We are grateful to the *Fonds der Chemischen Industrie* and the *Chemetall GmbH* for support of our research, and to the technical staff at the *Institute of Inorganic Chemistry* for recording NMR, IR and mass spectra, as well as for performing elemental analyses.

## Experimental Section

Schlenk techniques were used in all experiments with nitrogen gas as a blanket. Solvents were dried by standard procedures. Commercial chemicals were purified before use as necessary. Literature procedures were employed for the preparation of $B_2(NMe_2)_4$[3][4], $(Me_2N)_2B_2Cl_2$[4], $mes_2B_2(NMe_2)_2$[13], $mes_2B_2(OMe)_2$[13], and $mes_2B_2Cl_2$[13]. − NMR: Bruker AC-P 200 ($^{11}B$), Jeol GSX 270 ($^1H$, $^{13}C$); standards: int. TMS, ext. $BF_3 \cdot OEt_2$. − IR: Perkin-Elmer 325. − MS: Varian CH7 (70 eV). − X-ray analyses: Siemens P4 and Nicolet R3m diffractometer, Mo-$K_\alpha$ radiation, graphite monochromator.

*B,B′-Dibromo-B,B′-dimesityldiborane(4)* (**1b**): To a stirred suspension of $mes_2B_2(OMe)_2$ (510 mg, 1.6 mmol) in 60 ml of hexane at −30°C was added $BBr_3$ (1.00 g, 3.99 mmol, 0.38 ml). The reaction mixture was allowed to warm to 0°C and was kept at this temperature for at least 1 h. A clear, light-yellow solution resulted. The solution was stored at −20°C overnight, and then concentrated to a volume of about 20 ml. At −20°C, yellow crystals of $mes_2B_2Br_2$ (**1b**) separated (450 mg, 1.1 mmol). A second crop of **1b** was isolated by reducing the volume of the solution still further. Total yield: 0.53 g (80%); m.p. 98−101°C. **1b** can be stored under an inert atmosphere at low temperatures ($< -20$°C) for several months without decomposition. Even in solution at −20°C, **1b** is stable for weeks, while at ambient temperature it decomposes readily into $mesBBr_2$ ($\delta^{11}B = 62.8$) and other boron-containing compounds [$\delta^{11}B = 42.5$, 30 (br.), −6]. − NMR ($C_6D_6$): $\delta^1H = 2.05$ (s, 6 H, $p$-$CH_3$), 2.18 (s, 12 H, $o$-$CH_3$), 6.58 (s, 4 H, $m$-H). − $\delta^{11}B =$ 86 ($h_{1/2} \approx 1000$ Hz). − $\delta^{13}C = 21.1$ ($p$-$CH_3$), 22.3 ($o$-$CH_3$), 127.8 ($m$-C), 135.7 ($o$-C), 139.3 ($p$-C), *ipso*-C signal not obsd. − $C_{18}H_{22}B_2Br_2$ (419.80): calcd. C 51.50, H 5.28; found C 51.20, H 5.13.

*B,B′-Diiodo-B,B′-dimesityldiborane(4)* (**1c**): To a stirred solution of $mes_2B_2(OMe)_2$ (1.21 g, 3.76 mmol) in 40 ml of hexane, a solution of $BI_3$ (3.51 g, 8.94 mmol, 19% excess) in hexane (60 ml) was added at 0°C with the exclusion of light. After stirring for 2 h at this temperature, an $^{11}B$-NMR spectrum showed the signals of excess $BI_3$ ($\delta^{11}B = -7.5$), of $(MeO)BI_2$ ($\delta^{11}B = 6.5$), and of $mes_2B_2I_2$ ($\delta^{11}B = 89$). Insoluble material was then removed by filtration and the filtrate was stored at −20°C overnight. A small amount of $mes_2B_2I_2$ (**1c**) was obtained in the form of yellow crystals, suitable for X-ray diffraction. Fractional crystallization by reducing the volume of the solution in a stepwise manner to about 30 ml, provided additional **1c**. Yield: 1.32 g (2.57 mmol, 68%); m.p. ca. 89°C (decomp.). − NMR ($C_6D_6$): $\delta^1H = 2.08$ (s, 6 H, $p$-$CH_3$), 2.21 (s, 12 H, $o$-$CH_3$), 6.59 (s, 4 H, $m$-H). − $\delta^{11}B = 89$. − $\delta^{13}C = 21.1$ ($p$-$CH_3$), 23.0 ($o$-$CH_3$), 128.5 ($m$-C), 134.1 ($o$-C), 139.3 ($p$-C), *ipso*-C signal not obsd. − $C_{18}H_{22}B_2I_2$ (513.78): calcd. C 42.08, H 4.32; found C 40.20, H 4.36.

*B,B′-Dimesityl-B,B′-bis(methylamino)diborane(4)* (**2**): At −30°C, methylamine (3.0 ml, 68 mmol) was condensed into a stirred solution of $mes_2B_2Cl_2$ (1.80 g, 5.44 mmol) in 50 ml of hexane, resulting in the immediate precipitation of methylammonium chloride. The reaction mixture was allowed to warm to ambient temp. while stirring overnight. After separation of the solid (0.88 g, 119% "$[MeNH_3]Cl$"), the solvent and all volatile materials were removed in vacuo. The residue was treated with 50 ml of hexane, and insoluble material was removed by centrifugation for 10 min (1200 rpm). The clear solution was then stored at −78°C, whereupon **2** precipitated as a white solid. Yield: 1.55 g (4.84 mmol, 89%). Within 2 d, **2** crystallized in the form of colorless cubes in an NMR tube, m.p. 190°C. − NMR ($CDCl_3$): $\delta^1H = 2.17$ (s, 12 H, $o$-$CH_3$), 2.30 (s, 6 H, $p$-$CH_3$), 2.49 (d, 6 H, NMe, $^3J_{HH} = 8$ Hz), 4.7 (br., 2 H, NH), 6.81 (s, 4 H, $m$-H). − $\delta^{11}B = 48.3$. − $\delta^{13}C =$ 21.2 ($p$-$CH_3$), 21.7 ($o$-$CH_3$), 31.4 (NMe), 127.0 ($m$-C), 135.7 ($p$-C), 138.4 ($o$-C), *ipso*-C signal not obsd. − $C_{20}H_{30}B_2N_2$ (320.10): calcd. C 75.05, H 9.45, N 8.75; found C 74.66, H 9.31, N 8.22.

*B,B′-Di(benzylamino)-B,B′-dimesityldiborane(4)* (**3**): $mes_2B_2Cl_2$ (1.77 g, 5.35 mmol) was dissolved in 60 ml of pentane and the flask was placed in an ice bath. Under stirring, benzylamine (2.50 ml, 2.46 g, 22.9 mmol) was added, resulting in the immediate precipitation of benzylammonium chloride. The suspension was allowed to warm to ambient temp., and then stirring was continued for a further 4 h. The insoluble material was then removed by filtration (1.98 g), and the filtrate was concentrated to dryness in vacuo. Since the residue was found to be moderately soluble in pentane and hexane, it was treated with a few mls of pentane and the solid was recovered by filtration. After drying in vacuo, **3** was obtained as a white powder (1.20 g, 2.54 mmol, 47%), essentially pure on the basis of its NMR spectra. Recrystallization from 5 ml of diethyl ether gave colorless crystals, suitable for X-ray diffraction; m.p. 115−117°C. − NMR ($CDCl_3$): $\delta^1H = 2.26$ (s, 12 H, $o$-$CH_3$), 2.30 (s, 6 H, $p$-$CH_3$), 4.08 (d, 4 H, $CH_2$, $^3J_{HH} = 7.3$ Hz), 5.16 (t, 2 H, NH), 6.82 (s, 4 H, $m$-H), 7.14−7.27 (m, 10 H, Ph). − $\delta^{11}B = 47.9$ ($h1/2 \approx 980$ Hz). − $\delta^{13}C = 21.1$ ($p$-$CH_3$), 22.0 ($o$-$CH_3$), 49.0 ($CH_2$), 126.5 ($m$-mes), 126.8 ($p$-Ph), 127.0 ($o$-Ph), 128.2 ($m$-Ph), 135.7 ($p$-mes), 138.2 ($o$-mes), 141.2 (*ipso*-Ph), *ipso*-mes signal not obsd. − $C_{32}H_{38}B_2N_2$ (472.29): calcd. C 81.38, H 8.11, N 5.93; found C 80.98, H 8.00, N 5.84.

*B,B′-Di(isopropylamino)-B,B′-dimesityldiborane(4)* (**4**): $mes_2B_2Cl_2$ (1.37 g, 4.14 mmol) was dissolved in 30 ml of hexane and the solution was cooled to −35°C. To the stirred solution, a suspension of $iPr_2NLi$ (0.54 g, 8.27 mmol) in 20 ml of hexane was added. After allowing the mixture to warm to ambient temp. overnight, the insoluble material (LiCl) was removed by filtration. The filtrate was then concentrated in vacuo to a volume of about 20 ml. Compound **4** separated as a white solid at −50°C. Yield: 1.34 g (3.56 mmol, 86%); m.p. 185°C. − NMR ($CDCl_3$): $\delta^1H = 0.91$ (d, 12 H, $CHMe$, $^3J_{HH} = 8$ Hz), 2.18 (s, 12 H, $o$-$CH_3$), 2.31 (s, 6 H, $p$-$CH_3$), 3.12 (sept, 2 H, $CHMe$), 4.55 (d, 2 H, NH), 6.80 (s, 4 H, $m$-H). − $\delta^{11}B =$ 46.3. − $\delta^{13}C = 21.2$ ($p$-$CH_3$), 22.0 ($o$-$CH_3$), 25.5 ($CHMe$), 46.1 ($CHMe$), 126.8 ($m$-C), 135.2 ($p$-C), 138.4 ($o$-C), 141.0 (*ipso*-C, low intensity). − $C_{24}H_{38}B_2N_2$ (376.20): calcd. C 76.63, H 10.18, N 7.45; found C 76.77, H 10.50, N 7.23.

*B,B′-Dimesityl-B,B′-dipyrrolyldiborane(4)* (**5**): To a solution of $mes_2B_2(OMe)_2$ (2.04 g, 6.17 mmol) in 50 ml of toluene at 0°C, was added a suspension of pyrLi (0.90 g, 12.3 mmol) in 20 ml of hexane. The reaction mixture was stirred overnight at ambient temp. All solid material was then removed by filtration (0.58 g), the filtrate was concentrated to a volume of 15 ml in vacuo, and cooled to −20°C. Colorless crystals, suitable for X-ray diffraction were obtained after recrystallization from $n$-hexane. Yield: 5.1 g, (2.0 mmol, (82%); m.p. 148−150°C. − NMR ($CDCl_3$): $\delta^1H = 1.90$ (s, 12 H, $o$-$CH_3$), 2.30 (s, 6 H, $p$-$CH_3$), 6.41, 6.53 (each m, 4 H, $H_{2,3}$-

Table 3. Crystal data and parameters related to data collection and structure solution of the mesityl-substituted diboranes(4); all crystals were monoclinic

| Compound | **5** | **3** | **6** | **8** | **10** | **1a** | **1b** | **1c** |
|---|---|---|---|---|---|---|---|---|
| Formula | $C_{26}H_{30}B_2N_2$ | $C_{32}H_{38}B_2N_2$ | $C_{26}H_{42}B_2N_2$ | $C_{26}H_{40}B_2O_2$ | $C_{26}H_{40}B_2S_2$ | $C_{18}H_{22}B_2Cl_2$ | $C_{18}H_{22}B_2Br_2$ | $C_{18}H_{22}B_2I_2$ |
| Formula weight | 392.14 | 472.26 | 404.24 | 406.20 | 438.32 | 330.88 | 419.80 | 513.78 |
| Cryst. size [mm] | 0.3 × 0.2 × 0.2 | 0.5 × 0.4 × 0.4 | 0.35 × 0.25 × 0.2 | 0.65 × 0.6 × 0.4 | 0.6 × 0.5 × 0.4 | 0.4 × 0.2 × 0.2 | 0.25 × 0.2 × 0.2 | 0.2 × 0.2 × 0.1 |
| Space group | $P2_1/c$ | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$ [Å] | 17.931(7) | 10.8233(2) | 10.051(4) | 18.656(4) | 8.941(4) | 8.169(3) | 8.2064(2) | 8.2702(2) |
| $b$ [Å] | 8.610(3) | 10.5265(1) | 16.029(8) | 12.180(2) | 24.264(10) | 29.805(11) | 29.7746(4) | 29.8558(9) |
| $c$ [A] | 15.077(4) | 13.4730(1) | 8.722(3) | 11.936(2) | 12.589(7) | 7.592(2) | 7.6856(2) | 7.9733(2) |
| β [°] | 99.10(1) | 112.483(1) | 106.98(2) | 107.28(3) | 93.54(4) | 98.321(2) | 98.070(1) | 97.335(1) |
| $V$ [Å3] | 2298(1) | 1418.33(3) | 1344(1) | 2589.8(8) | 2725.9(22) | 1829(1) | 1859.32(7) | 1952.60(9) |
| $Z$ | 4 | 2 | 2 | 4 | 4 | 4 | 4 | 4 |
| $d_{calcd.}$ [Mg/m$^3$] | 1.133 | 1.106 | 0.999 | 1.042 | 1.068 | 1.202 | 1.500 | 1.748 |
| μ [mm$^{-1}$] | 0.064 | 0.063 | 0.056 | 0.062 | 0.206 | 0.348 | 4.353 | 3.215 |
| $F$ (000) | 840 | 508 | 444 | 888 | 952 | 696 | 840 | 984 |
| $T$ [K] | 183(3) | 193(2) | 183(3) | 298 | 298 | 193(3) | 193(2) | 193(2) |
| 2θ [°] | 4−49.4 | 4−49.4 | 4.2−57.8 | 2.28−44.00 | 3.36−44.10 | 13.62−49.42 | 2.74−59.06 | 2.72−58.62 |
| Index range | $-21 < h < 21$<br>$-10 < k < 10$<br>$-17 < l < 13$ | $-11 < h < 12$<br>$-12 < k < 12$<br>$-15 < l < 15$ | $-12 < h < 12$<br>$-20 < k < 20$<br>$-11 < l < 8$ | $-19 < h < 19$<br>$-12 < k < 0$<br>$-1 < l < 8$ | $0 < h < 9$<br>$0 < k < 25$<br>$-13 < l < 13$ | $-9 < h < 9$<br>$-35 < k < 34$<br>$-8 < l < 8$ | $-10 < h < 10$<br>$-38 < k < 38$<br>$-9 < l < 9$ | $-10 < h < 9$<br>$-39 < k < 38$<br>$-10 < l < 10$ |
| Refl. coll. | 10651 | 6617 | 7546 | 3109 | 3614 | 8504 | 10780 | 11501 |
| Refl. indep. | 3453 | 2021 | 2512 | 2569 | 3361 | 2480 | 3686 | 3853 |
| Refl. obsd. [> 4σ($F$)] | 2780 | 1758 | 1239 | | | 2147 | 2945 | 2937 |
| Absorp. corr. | none | none | none | none | none | none | Sadabs | Sadabs |
| $R$ | 7.95 | 4.6 | 8.31 | 7.24 | 5.11 | 6.79 | 4.14 | 4.69 |
| $wR2$ | 5.19 | 11.5 | 16.88 | | | 13.41 | 10.05 | 12.66 |
| GooF | 0.220 | 1.063 | 1.208 | 1.544 | 1.011 | 1.222 | 1.069 | 1.168 |
| diff. peak [e/Å$^3$] | | 0.212 | 0.196 | 0.374 | 0.244 | 0.263 | 0.781 | 1.524 |

$_{pyr}$), 6.74 (s, 4 H, *m*-H), 6.81, 7.25 (each m, 4 H, $H_{1,4\text{-}pyr}$). − $\delta^{11}B$ = 60 ($h_{1/2}$ ≈ 1500 Hz). − $\delta^{13}C$ = 21.1 (*o*-$CH_3$), 21.7 (*p*-$CH_3$), 114.8, 115.6 (pyr-C-3, -C-4), 126.9, 127.1 (pyr-C-2, -C-5), 129.6 (*m*-$C_{mes}$), 137.2 (*o*-$C_{mes}$), 137.6 (*p*-$C_{mes}$), 138.2 (*ipso*-$C_{mes}$, br. low intensity). − $C_{26}H_{30}B_2N_2$ (392.16): calcd. C 79.63, H 7.71, N 7.14; found C 79.39, H 7.68, N 7.00.

*B,B′-Di(tert-butylamino)-B,B′-dimesityldiborane(4)* (**6**): $mes_2B_2(OMe)_2$ (0.86 g, 2.7 mmol) was dissolved in 25 ml of hexane and 15 ml of diethyl ether. A suspension of *t*BuNHLi (0.42 g, 5.3 mmol) was added at 0°C, and the resulting mixture was stirred at ambient temp. for 2 d. The reaction was completed by heating the suspension for 4 h. The insoluble material (0.25 g) was removed by filtration and the filtrate was concentrated to a volume of 25−30 ml. After 5 d, colorless crystals separated. A second crop of **6** was isolated after storage of the mother liquor at −20°C for 2 weeks. Total yield: 0.75 g (1.9 mmol, 70%); m.p. 194−195°C. − NMR ($C_6D_6$): $\delta^1H$ = 0.91 (s, 18 H, $CMe_3$), 2.25 (s, 6 H, *p*-$CH_3$), 2.40 (s, 12 H, *o*-$CH_3$), 4.99 (s, 2 H, NH), 6.88 (s, 4 H, *m*-H). − $\delta^{11}B$ ($CDCl_3$) = 45.3. − $\delta^{13}C$ ($C_6D_6$) = 21.3 (*o*-$CH_3$), 22.9 (*p*-$CH_3$), 31.6 (C*Me*$_3$), 52.9 (*C*Me$_3$), 127.7 (*m*-C), 135.4 (*p*-C), 137.3 (*o*-C), *ipso*-C signal not obsd. − $C_{26}H_{42}B_2N_2$ (404.26): calcd. C 77.25, H 10.47, N 6.93; found C 77.08, H 10.40, N 6.92.

*B,B′-Di(tert-butyloxy)-B,B′-dimesityldiborane(4)* (**8**): Dichlorodimesityldiborane(4) (0.90 g, 2.7 mmol) was dissolved in 40 ml of hexane. At −35°C, a suspension of NaO*t*Bu (0.52 g, 5.4 mmol) in 30 ml hexane was added to the stirred solution. Stirring was continued overnight, while the mixture was allowed to reach ambient temp. The insoluble material (0.34 g) was removed by filtration and the filtrate was kept at −20°C, resulting in the deposition of 0.83 g of **8** (2.05 mmol, 75%) in the form of cubic crystals within 1 d; m.p. 158−162°C. − NMR ($C_6D_6$): $\delta^1H$ = 1.27 (s, 18 H, $OCMe_3$), 2.00 (s, 12 H, *o*-$CH_3$), 2.23 (s, 6 H, *p*-$CH_3$), 6.63 (s, 4 H, *m*-H). − $\delta^{11}B$ = 57.0. − $\delta^{13}C$ = 21.1 (*p*-$CH_3$), 22.1 (*o*-$CH_3$), 30.8 (OC*Me*$_3$), 77.4 (O*C*Me$_3$), 126.8 (*m*-C), 135.6 (*p*-C), 136.8 (*o*-C), *ipso*-C signal not obsd. − MS (70 eV): *m/z* (%): 406 (2) [$M^{•+}$], 349 (100) [$M^{•+}$ − *t*Bu], 333 (27) [$M^{•+}$ − O*t*Bu], 173 (90) [$M^{•+}$ − *t*Bu − $C_4H_8$ − mesH], 147 (85) [$M^{•+}$ − *t*Bu − $C_4H_8$ − OBmes]. − $C_{26}H_{40}B_2O_2$ (406.23): calcd. C 76.88, H 9.93; found C 75.06, H 9.52.

*B,B′-Dimesityl-B,B′-di(phenylthio)diborane(4)* (**9**): (a) To a stirred solution of $mes_2B_2Cl_2$ (1.20 g, 3.66 mmol) in 35 ml of hexane at −30°C, was added a mixture of thiophenol (0.81 g, 7.3 mmol) and triethylamine (0.74 g, 7.3 mmol, 1.01 ml), dissolved in 10 ml of hexane. A voluminous white precipitate of [$Et_3N·HCl$] formed immediately. To allow better stirring, the reaction mixture was quickly warmed to 0°C and 20 ml of benzene was added. After stirring overnight, the solid was removed by filtration (0.96 g, 95% [$Et_3NH$]Cl), and the filtrate was concentrated to dryness in vacuo. After adding 20 ml of hexane to the residue, insoluble material was removed by filtration. Cooling the clear filtrate to −20°C yielded 0.70 g of **9** (1.46 mmol, 40%).

(b) To a stirred solution of $mes_2B_2Cl_2$ (0.89g, 2.96 mmol) in 30 ml of hexane at −35°C was added a suspension of LiSPh (0.69 g, 5.9 mmol) in 20 ml of hexane. The reaction mixture was allowed to warm to ambient temp. and then stirred overnight. The white precipitate (0.30 g, 120% "LiCl") was removed by filtration and the filtrate was concentrated to a volume of approximately 30 ml. Storing this solution at −50°C yielded a colorless crystalline mass within 3 d, which was collected and dried in vacuo. The crystals turned slightly yellowish, but no decomposition was detectable. Yield 0.96 g (2.01 mmol, 68%); m.p. 58−62°C. − NMR ($CDCl_3$): $\delta^1H$ = 1.95 (s, 12 H, *o*-$CH_3$), 2.13 (s, 6 H, *p*-$CH_3$), 6.54 (s, 4 H, *m*-H), 7.0−7.12 (m, 10 H, Ph). − $\delta^{11}B$ = 80.6. − $\delta^{13}C$ = 21.0 (*p*-$CH_3$), 22.0 (*o*-$CH_3$), 126.9 (*m*-$C_{mes}$), 127.3 (*p*-$C_{Ph}$), 128.3 (*o*-$C_{Ph}$), 131.2 (*m*-$C_{Ph}$), 134.0 (*i*-$C_{Ph}$), 135.6 (*o*-$C_{mes}$), 136.6 (*p*-$C_{mes}$), 137.8

(*i*-$\mathrm{C_{mes}}$). − $C_{30}H_{32}B_2S_2$ (478.34): calcd. C 75.33, H 6.74, S 13.41; found C 75.04, H 6.74, S 13.45.

*B,B′-Di(tert-butylthio)-B,B′-dimesityldiborane(4)* (**10**): To a solution of $\mathrm{mes_2B_2Cl_2}$ (1.62 g, 4.89 mmol) in 70 ml of hexane at −40°C was added a suspension of LiS*t*Bu (0.94 g, 9.8 mmol) in 30 ml of hexane. The reaction mixture was stirred overnight while it warmed to ambient temp. The insoluble material (0.49 g, 118% "LiCl") was filtered off, and the light-yellow filtrate was stored at −20°C. Colorless, rectangular crystals of **10** separated. On concentrating the solution still further to less than half of its original volume, a second crop of **10** was obtained. Total yield: 1.80 g (84%); m.p. 183−185°C. − NMR ($CDCl_3$): $\delta^1$H = 1.24 (s, 18 H, $CMe_3$), 1.91 (s, 12 H, *o*-$CH_3$), 2.23 (s, 6 H, *p*-$CH_3$), 6.65 (s, 4 H, *m*-H). − $\delta^{11}$B = 77.0. − $\delta^{13}$C = 21.0 (*p*-$CH_3$), 22.3 (*o*-$CH_3$), 32.0 (C*Me*$_3$), 49.2 (*C*Me$_3$), 127.1 (*m*-C), 135.7 (*o*-C), 136.3 (*p*-C), *ipso*-C signal not obsd. − MS (70 eV); *m/z* (%): 438 (11) [$M^{\bullet+}$], 381 (26) [$M^{\bullet+}$ − *t*Bu], 324 (100) [$M^{\bullet+}$ − 2 *t*Bu], 219 (10) [mesBS*t*Bu$^+$], 162 (100) [mesBS$^{\bullet+}$]. − $C_{26}H_{40}B_2S_2$ (438.36): calcd. C 71.24, H 9.42, S 14.63; found C 71.08, H 8.92, S 13.70.

*2,3-Dimesityl-1,4,2,3-dithiadiborinane* (**11**): To a solution of $\mathrm{mes_2B_2Cl_2}$ (1.00 g, 3.02 mmol) in 40 ml of hexane at −35°C was added a suspension of dilithium ethanedithiolate (0.32 g, 3.0 mmol) in 30 ml of hexane. The reaction mixture was allowed to warm to ambient temp. and stirring was continued overnight. The white precipitate (0.28 g, 109% "LiCl") was separated, and the filtrate was concentrated to dryness in vacuo. The yellow residue was treated with 30 ml of hexane, centrifuged for 10 min (1200 rpm), and the clear solution was stored at −20°C. Within 3 d, a yellow crystalline mass had formed, which was separated and dried in vacuo. Yield: 0.43 g of **11** (1.2 mmol, 40%), m.p. 115−118 °C. − NMR ($CDCl_3$): $\delta^1$H = 2.17 (s, 6 H, *p*-$CH_3$), 2.20 (s, 12 H, *o*-$CH_3$), 2.55 (s, 4 H, $CH_2$), 6.71 (s, 4 H, *m*-H). − $\delta^{11}$B = 69.4. − $\delta^{13}$C = 21.1 (*p*-$CH_3$), 22.5 (*o*-$CH_3$), 30.5 ($CH_2$), 127.8 (*m*-C), 136.6 (*p*-C), 137.0 (*o*-C), *ipso*-C signal not obsd. − $C_{20}H_{26}B_2S_2$ (352.18): calcd. C 68.21, H 7.44, S 18.21; found C 68.33, H 7.78, S 17.26.

*X-ray Structure Determinations*: Single crystals were either sealed in glass capillaries under argon or were covered and mounted with perfluoroether oil on glass fibres. The setting angles of 15−20 well-centered reflections were used for the determination of the dimensions of the unit cells (Siemens P4) or the data on 60 frames collected with a Siemens P4 instrument equipped with a CCD detector. Data collection was performed by using a graphite monochromator and Mo-$K_\alpha$ radiation, either in the $\omega/2\theta$ scan mode with variable scan speed, or in the hemisphere mode with 10 s exposures per frame and $\Delta\omega = 0.3$. Data reduction was performed by applying Lorentz and polarization corrections or with the SAINT routine. The structures were solved by direct methods; non-hydrogen atoms were refined anisotropically and, unless stated otherwise, H atoms were refined in calculated positions using a riding model. Programs used: SHELXTL-PC plus[34] and SHELXL-93/97[35]. A summary of the data is given in Table 3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102212 (**5**), -102213 (**6**), -102214 (**3**), -102211 (**8**), -102210 (**10**), -102209 (**1a**), -102208 (**1b**), -102207 (**1c**). Copies of the data can be obtained free of charge on application to CCCD, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Prof. Dr. Dr. h. c. *Hans Bock* on the occasion of his 70th birthday.

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