

Contribution to the Chemistry of Boron, 245<sup>[‡]</sup>Deprotonation of *B,B'*-Di-*tert*-butyl-*B,B'*-difluorenyldiborane(4) and the Structure of the Di-*tert*-butyl-difluorenylidenediborate(2−) AnionRalf Littger,<sup>[a]</sup> Heinrich Nöth\*<sup>[a]</sup> and Max Suter<sup>[a]</sup>*Dedicated to Prof. Dr. D. Walther on the occasion of his 60th birthday***Keywords:** Boranes / Borates / Deprotonation / Anions / Alkali metals

In contrast to the deprotonation of the diorganyl(fluorenyl)-boranes *t*Bu<sub>2</sub>B(fl-H) and Me<sub>2</sub>B(fl-H), which cannot be achieved uniformly, the deprotonation of B<sub>2</sub>(*t*Bu)<sub>2</sub>(fl-H)<sub>2</sub> in THF proceeds smoothly to give the anion B<sub>2</sub>(*t*Bu)<sub>2</sub>(fl)<sub>2</sub><sup>2−</sup>. The isolated salts have been identified as [Na(thf)<sub>n</sub>]<sub>2</sub>[B<sub>2</sub>(*t*Bu)<sub>2</sub>(fl)<sub>2</sub>] and [Na(thf)(OEt<sub>2</sub>)]<sub>2</sub>[Na(OEt<sub>2</sub>)<sub>2</sub>][B<sub>2</sub>(*t*Bu)<sub>2</sub>(fl)<sub>2</sub>]. The X-ray structure of the latter compound reveals a longer B–B bond

[1.744(9) Å] than that in the parent compound B<sub>2</sub>(*t*Bu)<sub>2</sub>(fl-H)<sub>2</sub> [1.687(7) Å]. One sodium center is coordinated to the five-membered ring of one fluorenylidene substituent, while the other is coordinated to three C atoms of one of the six-membered rings. This results in a rather asymmetric structure. Each sodium center is also coordinated by two ether ligands.

## Introduction

We have recently reported on the synthesis, molecular structures,<sup>[2]</sup> and synthetic potential<sup>[3]</sup> of the alkali and alkaline earth metal salts of bis(dimethylamino)difluorenyldiborane(4),<sup>[4]</sup> (Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(fl-H)<sub>2</sub> (fl-H = fluorenyl = C<sub>13</sub>H<sub>9</sub>). A common feature of these compounds is a bent metallocene-type structure, in which the metal cations (Li, K, or Ca) are complexed by the two fluorenylidene ligands of the [(Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(fl)<sub>2</sub>]<sup>2−</sup> unit. The two fluorenylidene ligands are connected by a diborane(4)-*ansa*-bridge. The boron centers of (Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(fl-H)<sub>2</sub> are shielded electronically by N–B  $\pi$ -bonding. Thus, in the dianion [(Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(fl)<sub>2</sub>]<sup>2−</sup>, the lone pairs on the dimethylamino groups and the  $\pi$ -systems of the deprotonated fluorenyl substituents compete for the vacant p<sub>z</sub> orbitals at the boron centers. The  $\pi$ -interactions of the fluorenylidene substituents with the boron centers are, however, reduced by the complexation of the counteranions, resulting in larger angles between the planes at the boron atoms and the planes of the fluorenylidene substituents than one might observe in the free dianions. Our interest has now been drawn to how substitution of the dimethylamino groups of [(Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(fl)<sub>2</sub>]<sup>2−</sup> by non- $\pi$ -donor ligands affects the degree of  $\pi$ -interaction between the anionic fluorenyl groups and the boron centers and how this influences the ligand capacity of the [R<sub>2</sub>B<sub>2</sub>(fl)<sub>2</sub>]<sup>2−</sup> unit (R = organyl group). To answer these questions, we have synthesized di-*tert*-butyl-difluorenyldiborane(4), (*t*Bu)<sub>2</sub>B<sub>2</sub>(fl-H)<sub>2</sub>, and have studied its deprotonation by sodium. For compar-

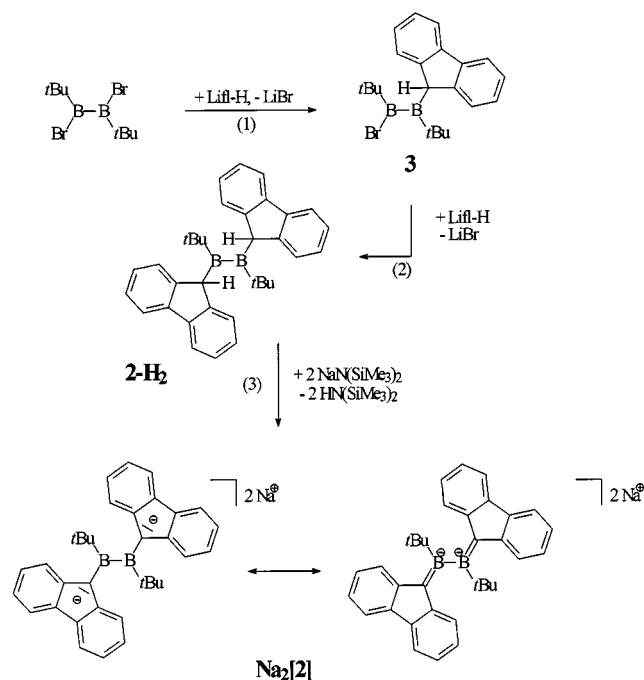
ison purposes, we have also investigated the deprotonation of some related monoboranes, specifically fluorenyldimethylborane, Me<sub>2</sub>B(fl-H), and di-*tert*-butyl-fluorenylborane, *t*Bu<sub>2</sub>B(fl-H).

## Synthesis

In order to obtain a stable difluorenyl-diorganyl-diborane(4), we decided to replace the dimethylamino groups of (Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(fl-H)<sub>2</sub> (1-H<sub>2</sub>) by *tert*-butyl groups. This group is known<sup>[5,6]</sup> to be sufficiently bulky to prevent redox disproportionation, which occurs in diborane(4) compounds that lack adequate electronic shielding. Indeed, di-*tert*-butyl-difluorenyldiborane(4) (2-H<sub>2</sub>) could be readily prepared by the stepwise substitution of the bromine atoms of dibromodi-*tert*-butyldiborane(4)<sup>[7]</sup> by the fl<sup>−</sup> anion. Unexpectedly, however, MeO substitution of (*t*Bu)<sub>2</sub>B<sub>2</sub>(OMe)<sub>2</sub>, which has been successfully employed for the preparation of the tetraalkyldiborane(4) derivatives (*t*Bu)<sub>2</sub>B<sub>2</sub>(*t*Bu)R (R = Me,<sup>[5]</sup> CH<sub>2</sub>SiMe<sub>3</sub>,<sup>[5]</sup> CH<sub>2</sub>CMe<sub>3</sub><sup>[6]</sup>) and (*t*Bu)<sub>2</sub>B<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>,<sup>[6]</sup> did not work in the present case. No reaction occurred between (*t*Bu)<sub>2</sub>B<sub>2</sub>(OMe)<sub>2</sub> and fluorenyllithium. On the other hand, (*t*Bu)<sub>2</sub>B<sub>2</sub>(fl-H)Br (3), could be obtained almost quantitatively from the reaction of (*t*Bu)<sub>2</sub>B<sub>2</sub>Br<sub>2</sub> with one equivalent of fluorenyllithium [Scheme 1, (1)]. The reaction of pure 3 with a further equivalent of fluorenyllithium also proceeded quantitatively [Scheme 1, (2)], as shown by the <sup>11</sup>B-NMR spectrum of the reaction mixture. The diborane(4) compounds 2-H<sub>2</sub> and 3 were isolated as colorless solids. At room temperature, they were found to be stable in solution as well as in the solid state.

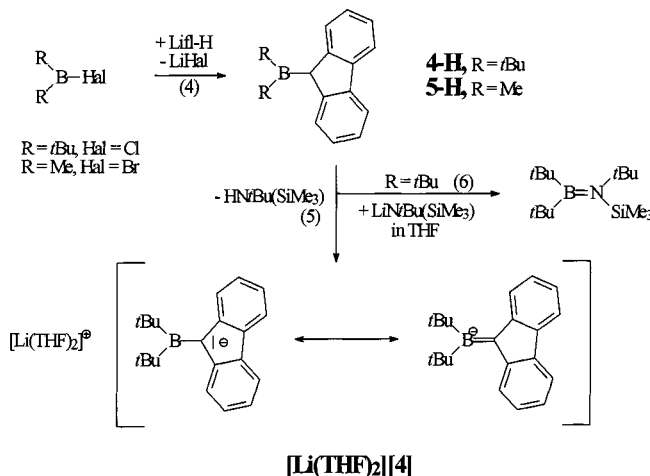
The syntheses of di-*tert*-butyl-fluorenylborane (4-H) and fluorenyl-dimethylborane (5-H) proved to be straightforward.

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Scheme 1

ward. These compounds could be obtained by treating fluorenyllithium with one equivalent of  $\text{tBu}_2\text{BCl}$  or  $\text{Me}_2\text{BBR}$ , respectively [Scheme 2, (4)], and were isolated as colorless, crystalline solids. Other diorganyl-fluorenylboranes,  $\text{R}_2\text{B(fl-H)}$  ( $\text{R} = \text{Et}, \text{Ph}$ ), have been reported previously.<sup>[8]</sup>



Scheme 2

On treatment with two equivalents of  $\text{NaN(SiMe}_3)_2$  in tetrahydrofuran solution,  $\text{2-H}_2$  is doubly deprotonated [Scheme 1, (3)]. According to the  $^{11}\text{B}$ -NMR spectrum of the reaction mixture, the dianion  $[(\text{tBu})_2\text{B}_2(\text{fl})_2]^{2-}$  ( $\text{2}^{2-}$ ) is the main product (90%). Unidentified boron species give rise to signals in the region  $\delta(^{11}\text{B}) = +5$  to  $-20$  (altogether 10%). This indicates that the steric shielding of the boron centers of  $\text{2-H}_2$  is insufficient to completely suppress the nucleophilic attack of  $\text{Li(H)f}$ . On the other hand, the double deprotonation of the sterically less shielded  $\text{1-H}_2$  is quantitative as a result of the additional electronic shielding of the

boron atoms in this compound. The disodium salt of the dianion  $[\text{2}]^{2-}$  was isolated as an orange solid as a THF solvate  $[\text{Na}(\text{thf})_x]_2[\text{2}]$  and was characterized by multinuclear NMR spectroscopy. The dimetallation of  $\text{2-H}_2$  was further confirmed by performing a single-crystal X-ray structure analysis on the related solvate  $[\text{Na}(\text{thf})(\text{OEt}_2)][\text{Na}(\text{OEt}_2)_2][\text{2}]$ .

The lithium monoborate, containing the anion  $[\text{tBu}_2\text{B(fl)}]^-$  ( $[\text{4}]^-$ ) is the main product of the reaction between  $\text{tBu}_2\text{B(fl-H)}$  ( $\text{4-H}$ ) and one equivalent of  $\text{LiNtBu(SiMe}_3)$  in tetrahydrofuran solution [Scheme 2, (5)]. The  $^{11}\text{B}$ -NMR spectrum of the reaction mixture not only shows a signal due to this anion ( $\delta = 77.9$ ), but further signals at  $\delta(^{11}\text{B}) = 87.9$  [ $\text{tBu}_2\text{B(fl-H)}$ ] and  $54.0$  [possibly  $\text{tBu}_2\text{B-NtBu(SiMe}_3)$ , 8%] and minor signals in the region  $\delta(^{11}\text{B}) = +10.0$  to  $0.0$  (tetracoordinated borates, 5%). The lithium salt  $[\text{Li}(\text{thf})_2][\text{4}]$  was recovered as a 4:1 mixture with fluorenyllithium. All attempts to separate these compounds by crystallization were unsuccessful. The formation of fluorenyllithium leads us to believe that the fluorenyl ligand of  $\text{4-H}$  is substituted by the amide  $[\text{NtBu(SiMe}_3)]^-$  in a competing reaction [Scheme 2, (6)]. This hypothesis is supported by the  $^{11}\text{B}$ -NMR signal at  $\delta(^{11}\text{B}) = 54.0$ , which is consistent with an amino-diorganylborane  $\text{tBu}_2\text{B-NtBu(SiMe}_3)$ , a compound that could be formed through such a substitution reaction [cf. the  $^{11}\text{B}$  resonance of  $\text{Me}_2\text{B-NtBu(SiMe}_3)$ :  $\delta(^{11}\text{B}) = 56.2$ ].<sup>[9]</sup> The deborylation of alkylboranes upon treatment with strong bases is well known for  $\text{Et}_2\text{B(Cp)}$ ,<sup>[10,11]</sup> a compound akin to  $\text{4-H}$ .

The lithium salt  $[\text{Li}(\text{thf})_2][\text{4}]$  has been characterized by multinuclear NMR spectroscopy. Its data are especially interesting with regard to the interpretation of the NMR data of the title dianion  $[\text{2}]^{2-}$ . These will be discussed later.

The deprotonation of  $\text{Me}_2\text{B(fl-H)}$  ( $\text{5-H}$ ) which contains a sterically and electronically poorly shielded boron center is difficult. As yet, we have been unable to extract any useful information from the NMR spectra of the reaction mixture generated when  $\text{5-H}$  is treated with alkali metal amides or sodium metal. From the reaction of  $\text{Et}_2\text{B(fl-H)}$  with  $\text{Na[BHET}_3]$ , a compound claimed<sup>[8]</sup> to be  $[\text{Na}(\text{digly-}$

me)<sub>1.5</sub>][Et<sub>2</sub>B(fl)] has been isolated. However, its NMR data are not compatible with a tricoordinated boron atom (vide infra).

## NMR Spectra

The NMR-spectroscopic data of compounds **3**, **2-H<sub>2</sub>**, **4-H**, **5-H**, Na<sub>2</sub>[**2**], and [Li(thf)<sub>2</sub>][**4**] are reported in the Experimental Section. The <sup>11</sup>B-NMR resonance of **2-H<sub>2</sub>** at δ(<sup>11</sup>B) = 102.5 is indicative of a tetraalkyldiborane(4) compound.<sup>[5,6]</sup> However, only a single, albeit broad resonance at δ(<sup>11</sup>B) = 92.9 is observed for the two different boron atoms of **3**, this chemical shift being intermediate between those of the resonances of the corresponding symmetric species **2-H<sub>2</sub>** [δ(<sup>11</sup>B) = 102.5] and (*t*Bu)<sub>2</sub>B<sub>2</sub>Br<sub>2</sub> [δ(<sup>11</sup>B) = 88.0].<sup>[7]</sup> The asymmetric structure of **3** is, however, reflected in its <sup>1</sup>H- and <sup>13</sup>C-NMR spectra, which show discrete signals due to the two different *tert*-butyl groups. The fluorenyl substituents of both **3** and **2-H<sub>2</sub>** give rise to double sets of signals. In the case of **3**, all the nuclei of the single fluorenyl group are chemically inequivalent, but the two fluorenyl substituents of **2-H<sub>2</sub>** should be equivalent. At the present time, the question as to whether the observed inequivalence is due to hindered rotation about the B–B bond and/or about the B–C<sub>fl</sub> bonds remains unclear. Most probably, the barrier associated with rotation about the B–B bond is higher than that for rotation about the B–C bond and hence diastereomers arise. Indeed, diastereomers have been found for much less sterically demanding substituted diborane(4) derivatives, such as (Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>*i*Pr<sub>2</sub> and (Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(benzyl)<sub>2</sub> (room temperature, 400 MHz).<sup>[12]</sup>

The NMR data of the monoboranes **4-H** and **5-H** are unexceptional: **4-H** shows two sets of signals due to the two *tert*-butyl groups in the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra and a single set of signals due to the fluorenyl substituent. This corresponds to a preferred conformation in which the plane of the fluorenyl substituent is oriented perpendicular to the plane at the boron center, with hindered rotation about the B–C<sub>fl</sub> bond. The two methyl groups of **5-H** are chemically equivalent and the observation of one set of signals due to the fluorenyl group indicates free rotation about the B–C<sub>fl</sub> bond. This difference between **4-H** and **5-H** (one signal in the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra due to the *B*-methyl groups for the latter) can therefore be attributed purely to steric factors.

The boron atoms in the disodium salt Na<sub>2</sub>[**2**] [δ(<sup>11</sup>B) = 74.0] are better shielded by 28 ppm than in the protonated **2-H<sub>2</sub>** [δ(<sup>11</sup>B) = 102.5]. This can be rationalized in terms of a strong π interaction between the deprotonated fluorenyl substituents and the boron centers. Even larger shielding effects have been observed in other cases, e.g. Δδ = 43.2 for the couple Mes<sub>2</sub>B–CH<sub>3</sub> [δ(<sup>11</sup>B, THF) = 83.6]/[Mes<sub>2</sub>B–CH<sub>2</sub>]<sup>–</sup> [δ(<sup>11</sup>B, THF) = 40.4] (Mes = 2,4,6-trimethylphenyl)<sup>[13]</sup> and Δδ = 38.6 for the couple Mes<sub>3</sub>B/[Mes<sub>2</sub>B–(3,5-Me<sub>2</sub>)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>]<sup>–</sup>.<sup>[14]</sup> We assume that the negative charges in Na<sub>2</sub>[**2**] are not only stabilized by the boron centers, but by the π system of the fluorenyl substitu-

ents as well. Such additional stabilization is naturally not possible for a CH<sub>2</sub><sup>–</sup> group, even less so for a PhCH<sup>–</sup> group. In this context, it seems unlikely that the anion of [Na(diglyme)<sub>1.5</sub>][Et<sub>2</sub>B(fl)]<sup>[8]</sup> has the structure of a deprotonated trialkylborane with a trigonal-planar coordinated boron atom. For the system Et<sub>2</sub>B(fl-H) [δ(<sup>11</sup>B, THF) = 50.9]/[Et<sub>2</sub>B(fl)]<sup>–</sup> [δ(<sup>11</sup>B, THF) = –25.5], a shielding difference of Δδ<sup>11</sup>B = 76.4 has been reported. However, the <sup>11</sup>B resonance for [Et<sub>2</sub>B(fl)]<sup>–</sup> would be consistent with a tetracoordinated borate anion (dimeric species?).<sup>[15]</sup>

Compared to the corresponding resonances in Na<sub>2</sub>[(–Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>(fl)<sub>2</sub>], Na<sub>2</sub>[**1**],<sup>[2]</sup> the <sup>13</sup>C nuclei of the fluorenyl substituents are seen to be deshielded in Na<sub>2</sub>[(*t*Bu)<sub>2</sub>B<sub>2</sub>(fl)<sub>2</sub>], Na<sub>2</sub>[**2**], on average by 2.4 ppm (see Table 1), thus indicating a stronger π interaction between the fluorenyl substituents and the boron centers in the latter compound.

Even more deshielded are the C atoms in fluorenylidene-(tetramethylpiperidino)borane,<sup>[17]</sup> tmp–B=fl (tmp = 2,2,6,6-tetramethylpiperidyl), a compound related to Na<sub>2</sub>[**2**] containing a true B=C<sub>fl</sub> double bond. In this case, one observes a Δδ(<sup>13</sup>C) value of 2.3 ppm (average for C2 to C13) compared to Na<sub>2</sub>[**2**].

Despite the partial B=C<sub>fl</sub> double-bond character in Na<sub>2</sub>[**2**], the fluorenyl substituents give rise to single sets of signals in the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra. This indicates that the rotation about the B–C<sub>fl</sub> bond is still a fast process on the NMR time scale. On the other hand, the signals due to C-2,13, C-4,11, and 5-,10-H are significantly broader, showing the onset of coalescence.

The <sup>11</sup>B resonance of [Li(thf)<sub>2</sub>][**4**] is shifted to higher field by just 8.4 ppm compared with that of protonated **4-H**. This is surprising as deprotonation of the fluorenyl substituents in the related **2-H<sub>2</sub>**/[**2**]<sup>2–</sup> system leads to a downfield shift in the resonance of the <sup>11</sup>B nuclei by 28 ppm. In comparison with Na<sub>2</sub>[**2**], the <sup>13</sup>C-NMR signals of the fluorenyl substituents in [Li(thf)<sub>2</sub>][**4**] are upfield shifted by an average of 2.6 ppm (see Table 2). These observations are consistent with a lesser degree of B–C<sub>fl</sub>–π interaction in the monoborane case, with more electron density residing in the fluorenyl system. This complies with a noncoplanar orientation of the plane of the fluorenyl substituent and the plane about the boron center in [**4**]<sup>–</sup> due to the presence of the two bulky *tert*-butyl substituents at the boron atom. The small difference in shielding can then readily be explained in terms of an essentially perpendicular arrangement of the fl-H and fl<sup>–</sup> group with respect to the *t*Bu<sub>2</sub>B moiety.

The <sup>1</sup>H- and <sup>13</sup>C-NMR data of [Li(thf)<sub>2</sub>][**4**] are strongly solvent-dependent. In C<sub>6</sub>D<sub>6</sub> solution, the <sup>13</sup>C nuclei of the central five-membered ring (C-1, C-2,13, C-7,8) of the fluorenyl substituent are better shielded by 4.5 ppm (average) than in THF solution (see Table 2). On the other hand, the protonated benzoid <sup>13</sup>C nuclei of the fluorenyl substituent are deshielded by 2.4 ppm (average) in C<sub>6</sub>D<sub>6</sub> solution. The same is true for the <sup>1</sup>H nuclei, which are deshielded by 0.53 ppm (average) in C<sub>6</sub>D<sub>6</sub> solution as compared to their resonances in THF solution. This behavior is not unusual for alkali metal fluorenides and can be explained in terms of a solvent dependency of the formation of contact ion

Table 1. Comparison of the  $^{13}\text{C}$ -NMR data of the fluorenyl substituents of  $\text{Li}_2[\text{fl}-(\text{CH}_2)_2-\text{fl}]$ ,  $\text{Na}_2[\mathbf{1}]$ ,  $\text{Na}_2[\mathbf{2}]$ , and  $\text{tmp}-\text{B}=\text{fl}^{[17]}$ 

| Solvent  | $\text{Li}_2[(\text{CH}_2)_2(\text{fl})_2]^{[16]}$<br>[D <sub>8</sub> ]THF | $\Delta$ | $\text{Na}_2[\mathbf{1}]^{[2]}$<br>THF | $\Delta$ | $\text{Na}_2[\mathbf{2}]$<br>THF | $\Delta$ | $\text{tmp}-\text{B}=\text{fl}^{[17]}$<br>$\text{CDCl}_3$ |
|----------|----------------------------------------------------------------------------|----------|----------------------------------------|----------|----------------------------------|----------|-----------------------------------------------------------|
| C-2,13   | 135.9                                                                      | +5.2     | 141.1                                  | +4.9     | 146.0                            | −1.9     | 144.1                                                     |
| C-7,8    | 123.4                                                                      | +2.3     | 125.7                                  | +4.5     | 130.2                            | +3.5     | 133.7                                                     |
| C-4,11   | 118.9                                                                      | +1.7     | 120.6                                  | +1.9     | 122.5                            | +2.3     | 124.8                                                     |
| C-6,9    | 118.9                                                                      | +0.8     | 119.7                                  | +1.3     | 121.0                            | −1.2     | 119.8                                                     |
| C-3,12   | 114.8                                                                      | +3.7     | 118.5                                  | −0.4     | 118.1                            | +2.9     | 121.0                                                     |
| C-5,10   | 107.2                                                                      | +3.5     | 110.7                                  | +2.1     | 112.8                            | +8.1     | 120.9                                                     |
| $\Delta$ |                                                                            | +2.9     |                                        | +2.4     |                                  | +2.3     |                                                           |

Table 2. Comparison of the  $^{13}\text{C}$ -NMR data of the fluorenyl group of  $[\text{Li}(\text{thf})_2][\mathbf{4}]$  (solvent-dependent) with those of the fluorenyl groups of  $\text{Na}_2[\mathbf{2}]$ 

| Solvent  | $[\text{Li}(\text{thf})_2][\mathbf{4}]$<br>$\text{C}_6\text{D}_6$ | $\Delta$ | $[\text{Li}(\text{thf})_2][\mathbf{4}]$<br>THF | $\Delta$ | $\text{Na}_2[\mathbf{2}]$<br>THF |
|----------|-------------------------------------------------------------------|----------|------------------------------------------------|----------|----------------------------------|
| C-2,13   | 137.4                                                             | +4.7     | 142.1                                          | +3.9     | 146.0                            |
| C-7,8    | 122.0                                                             | +4.4     | 126.4                                          | +3.8     | 130.2                            |
| C-4,11   | 121.6                                                             | −1.2     | 120.4                                          | +2.1     | 122.5                            |
| C-6,9    | 121.5                                                             | −2.3     | 119.2                                          | +1.8     | 121.0                            |
| C-3,12   | 120.3                                                             | −2.0     | 118.3                                          | −0.2     | 118.1                            |
| C-5,10   | 112.6                                                             | −3.9     | 108.7                                          | +4.1     | 112.8                            |
| C-1      | 100.7                                                             |          | 105.2                                          |          | n.b.                             |
| $\Delta$ |                                                                   |          |                                                | +2.6     |                                  |

pairs (CIPs) and solvent-separated ion pairs (SSIPs).<sup>[18]</sup> In the poorly solvating solvent  $\text{C}_6\text{D}_6$ , CIPs are formed between  $[\text{Li}(\text{thf})_2]^+$  and  $[\mathbf{4}]^-$ . The cation  $[\text{Li}(\text{thf})_2]^+$  is located above the five-membered ring of the fluorenyl substituent, polarizing the  $\pi$  electrons towards this central ring, thereby accounting for the enhanced shielding of the central  $^{13}\text{C}$  nuclei and the deshielding of the nuclei of the peripheral carbon atoms. In the strongly solvating solvent THF, an equilibrium exists between CIPs and SSIPs, as a result of which the polarizing effect of the cation  $[\text{Li}(\text{thf})_2]^+$  towards the fluorenyl substituent is somewhat diminished.

## Molecular Structures

In order to obtain further information on the degree of  $\text{C}_{\text{fl}}-\text{B}-\pi$  bonding in the dianion  $[\mathbf{2}]^{2-}$ , an X-ray structure determination of  $[\text{Na}(\text{thf})(\text{Et}_2\text{O})][\text{Na}(\text{Et}_2\text{O})_2][\mathbf{2}]$  was performed. The protonated compounds  $\mathbf{2}\text{-H}_2$  (Figure 1) and  $\mathbf{4}\text{-H}$  were also subjected to X-ray structure analyses for comparison purposes. To the best of our knowledge, the crystal structure of  $\mathbf{2}\text{-H}_2$  represents the first solid-state structure of a noncyclic tetraalkyldiborane(4). A structure useful for making comparisons is that of the cyclic diborane(4) derivative  $[-\text{B}(\text{Me})-\text{B}(\text{Me})-\text{C}(\text{SiMe}_3)_2-\text{Si}(\text{Me})_2-\text{C}(\text{SiMe}_3)_2-]$ , in which all the atoms connected to the diborane(4) unit are  $\text{C}(\text{sp}^3)$  atoms.<sup>[19]</sup> The most striking feature of  $\mathbf{2}\text{-H}_2$  is that the planes at B1 and B2 are arranged perpendicularly to one another ( $\text{C1}-\text{B1}-\text{C27}/\text{C14}-\text{B2}-\text{C31} = 89.2^\circ$ ). Normally, the planes at the boron atoms in diborane(4) derivatives form angles in the range  $60\text{--}80^\circ$ . The orthogonal orientation of the planes at the boron atoms in  $\mathbf{2}\text{-H}_2$  can be attributed to the presence of

the sterically demanding *tert*-butyl groups in this compound. Despite the bulky substitution of  $\mathbf{2}\text{-H}_2$ , the B1–B2 distance is quite short at 1.688(8) Å and, indeed, is the shortest yet found for a neutral tetraorganyldiborane(4). Comparable diborane(4) derivatives are  $\text{Mes}_2\text{B}-\text{BMesPh}$  [1.706(12) Å],<sup>[20]</sup>  $\text{Mes}_2\text{B}-\text{BMes}(\text{CH}_2\text{SiMe}_3)$  [1.71(2) Å],<sup>[20]</sup>  $\text{Mes}_2\text{B}_2[\text{CH}(\text{SiMe}_3)_2]_2$  [1.739(7) Å],<sup>[21]</sup> and the aforementioned diboracyclopentane [1.729(8), 1.709(9) Å].<sup>[19]</sup> The two fluorenyl substituents of  $\mathbf{2}\text{-H}_2$  show significantly different B–C<sub>fl</sub> bond lengths [ $\text{B1}-\text{C1} = 1.609(6)$  Å,  $\text{B2}-\text{C14} = 1.641(6)$  Å] and two different orientations with respect to the diborane(4) unit, as indicated by the dihedral angles  $\text{C31}-\text{B2}-\text{C14}-\text{H14a} = 171.6^\circ$  and  $\text{C27}-\text{B1}-\text{C1}-\text{H1a} = 9.4^\circ$ . For the trialkylborane  $\mathbf{4}\text{-H}$  (Figure 2), a B–C<sub>fl</sub> distance of 1.612(8) Å is found. The most significant feature of the molecular structure of  $\mathbf{4}\text{-H}$  is the perpendicular arrangement of the plane at the boron center and the plane of the fluorenyl substituent ( $\text{C1}-\text{C14}-\text{C18}/\text{C1 to C13} = 89.0^\circ$ ), which has already been established on the basis of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data.

We were unable to obtain single crystals of a THF solvate of  $\text{Na}_2[\mathbf{2}]$  from THF or THF/hexane mixtures. However, crystals suitable for X-ray crystallography were formed when  $[\text{Na}(\text{thf})_x][\mathbf{2}]$  (Figure 3) was crystallized from diethyl

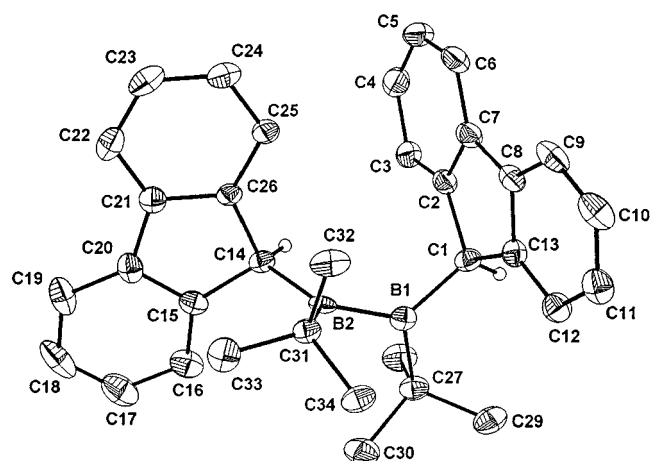


Figure 1. Molecular structure of  $(t\text{Bu})_2\text{B}_2(\text{fl-H})_2$  ( $\mathbf{2}\text{-H}_2$ ); thermal ellipsoids are drawn at a 25% probability level; hydrogen atoms, except those on atoms C-1 and C-14, have been omitted for the sake of clarity; selected bond lengths [Å]: B1–B2 1.687(7), B1–C1 1.609(6), B2–C14 1.641(6), B1–C27 1.615(6), B2–C31 1.586(6); selected angles  $^\circ$ : B2–B1–C1 124.1(3), B2–B1–C27 120.4(4), C1–B1–C27 115.1(4), B1–B2–C14 116.2(3), B1–B2–C31 121.6(3), C14–B2–C31 122.2(3), C1–B2–C27/C14–B1–C31 89.3, C1–B2–C27/C1 to C13 81.5, C14–B1–C31/C14 to C26 82.8



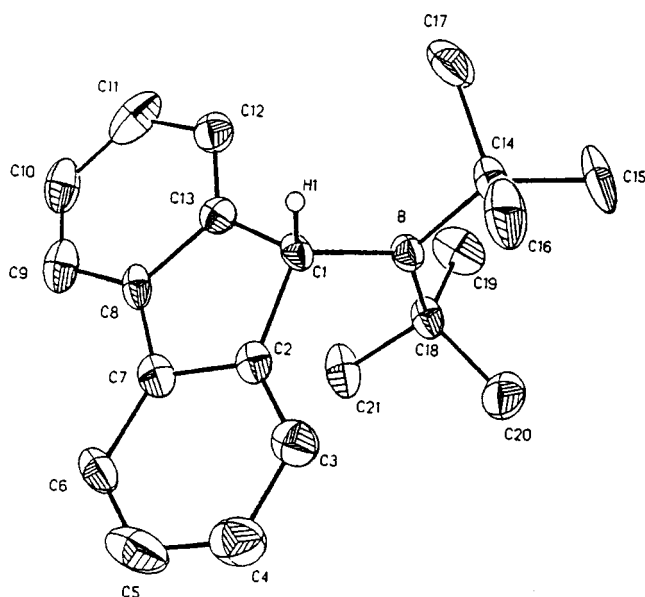


Figure 2. Molecular structure of *t*Bu<sub>2</sub>B(fl-H) (**4-H**); thermal ellipsoids are shown at a 25% probability level; hydrogen atoms, except that on atom C-1, have been omitted for the sake of clarity; selected bond lengths [Å]: B–C1 1.616(3), B–C14 1.594(3), B–C18 1.607(4); selected angles [°]: C1–B–C14 113.6(2), C1–B–C18 120.7(2), C14–B–C18 125.7(2), C1–C14–C18/C1 to C13 89.0

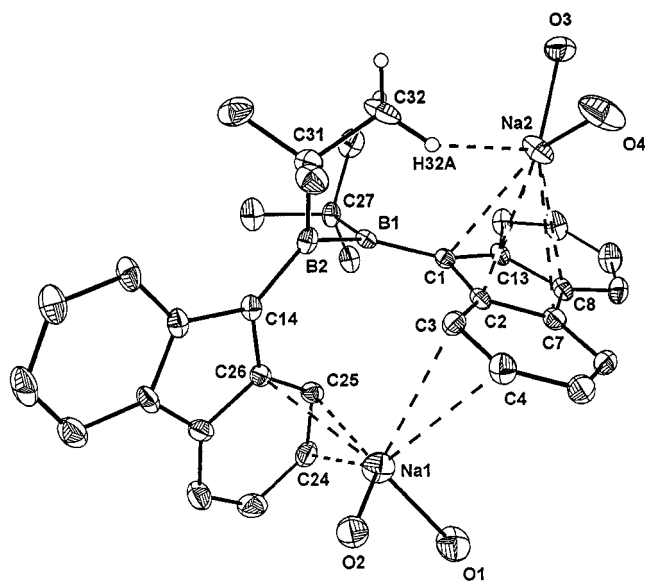


Figure 3. Molecular structure of [Na(thf)(OEt<sub>2</sub>)]Na(OEt<sub>2</sub>)<sub>2</sub>[**2**]; thermal ellipsoids are shown at a 25% probability level; carbon atoms of the ether ligands and hydrogen atoms, except those at atom C-32, have been omitted for the sake of clarity; selected bond lengths [Å]: B1–B2 1.744(9), B1–C1 1.529(8), B1–C27 1.615(9), B2–C14 1.533(9), B2–C31 1.626(9), Na1–C25 2.720(6), Na1–C3 2.818(6), Na1–C26 2.822(6), Na1–C4 2.987(7), Na1–C24 3.071(7), Na1–O1 2.301(6), Na1–O2 2.329(5), Na2–C13 2.599(6), Na2–C1 2.671(6), Na2–C8 2.898(6), Na2–C2 2.912(6), Na2–C7 3.075(7), Na2–O4 2.242(6), Na2–O3 2.250(5), Na2–H32A 2.495; selected angles [°]: B2–B1–C1 121.6(5), B2–B1–C27 115.6(5), C1–B1–C27 122.8(5), B1–B2–C14 121.0(5), B1–B2–C31 116.0(5), C14–B2–C31 122.9(5), C27–B2–C1/C31–B1–C14 82.1, C27–B2–C1/C1 to C13 13.8, C31–B1–C14/C14 to C26 12.7, O1–Na1–O2 109.4(2), O3–Na2–O4 96.4(2)

ether at  $-20\text{ }^{\circ}\text{C}$ . The structure determination confirmed the dimetallation of **2-H**<sub>2</sub> by sodium. The absence of protons at the fluorenyl carbon atoms bonded to the boron atoms

is evident from the sum of the bond angles about these atoms (C1:  $359.7^{\circ}$ ; C14:  $360.0^{\circ}$ ). The dianion [**2**]<sup>2−</sup> and the two sodium cations form a monomeric contact ion triple. The sodium cations are complexed by one (Na2) or both (Na1) fluorenyl substituents of the dianion and by two additional ether molecules.

The angles between the planes at the boron atoms and the planes of the fluorenyl substituents are  $12.7^{\circ}$  and  $13.8^{\circ}$ , respectively. In the related dimetallated derivatives of **1-H**<sub>2</sub>, the corresponding angles are  $40.2$  and  $49.4^{\circ}$ . The B–C<sub>fl</sub> distances in Na<sub>2</sub>[**2**] are  $10\text{ pm}$  shorter [ $1.529(8)$  and  $1.533(9)\text{ Å}$ ] than those in the protonated **2-H**<sub>2</sub>. These distances are also significantly shorter than those in (Me<sub>2</sub>N)<sub>2</sub>B<sub>2</sub>Ph<sub>2</sub>, a related compound with a B–C<sub>sp2</sub> bond (average B–C distance =  $1.585\text{ Å}$ ), but shorter than those in the analogous M<sub>2</sub>[**1**] compounds (M<sub>2</sub> = Li<sub>2</sub>, K<sub>2</sub>, Ca) (average B–C<sub>fl</sub> distance of  $1.547\text{ Å}$ ). Together with the almost coplanar arrangement of the planes at the boron atoms and the fluorenyl planes, this gives an additional indication of significant B–C<sub>fl</sub>– $\pi$  bonding in Na<sub>2</sub>[**2**].

The B–C<sub>fl</sub> distances in Na<sub>2</sub>[**2**] are best compared with the B–C distance of  $1.52(1)\text{ Å}$  [22] in the anion [Mes<sub>2</sub>B–(3,5-Me<sub>2</sub>)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>]<sup>−</sup>, as the boron atom has a similar acidity and the negative charge is also stabilized by an organic  $\pi$  system. In Na<sub>2</sub>[**2**], steric repulsion between the fluorenyl substituents and the *tert*-butyl groups connected to the same boron atom is to be expected, and this indeed becomes apparent on comparing the pairs of angles B1–C1–C2/B1–C1–C13 =  $122.5^{\circ}/134.7^{\circ}$  and B2–C14–C26/B2–C14–C15 =  $122.5^{\circ}/133.9^{\circ}$  (see Figure 4). The two fluorenyl substituents are forced apart by the *tert*-butyl group connected to the same boron atom. This most probably accounts for the fact that the B–C<sub>fl</sub> distances in Na<sub>2</sub>[**2**] are longer than they would be in a sterically less strained system. The two planes form an angle of  $82.1^{\circ}$ . Like the similar planes in the C<sub>2</sub>BB starting material **2-H**<sub>2</sub>, these are oriented almost perpendicularly to one another. The B–B distance in the dianion is  $1.744(9)\text{ Å}$ , which is  $5.7\text{ pm}$  longer than the B–B distance in the parent protonated compound **2-H**<sub>2</sub> [ $1.687(7)\text{ Å}$ ]. An even more elongated B–B bond [ $1.859(8)\text{ Å}$ ] occurs in the less twisted ( $43^{\circ}$ ) diborane(4) unit of the related Li<sub>2</sub>[Mes<sub>2</sub>B<sub>2</sub>{C(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]. [23]

It is interesting to compare the rather unusual coordination modes of Na2 and especially of Na1 in Na<sub>2</sub>[**2**] (Figure 4) with those observed in other fluorenyl sodium compounds.

Na2 is bonded in an asymmetric  $\eta^5$  mode to the central five-membered ring of the fluorenyl substituent C1 to C13 (see Figure 4, top). It is not located centrally above the fluorenyl substituent, but is rather shifted towards C13 and C1, resulting in shorter contacts between Na2 and these carbon atoms [Na2–C13 =  $2.599(6)\text{ Å}$ , Na2–C1 =  $2.671(6)\text{ Å}$ ]. A similar shift and similar Na–C distances have been reported for monomeric Nafl-PMDTA. [24] In both cases, the two shortest Na–C contacts are those to C1 and one of its neighbors. The coordination sphere about Na2 is completed by two ether molecules (one molecule of tetrahydrofuran

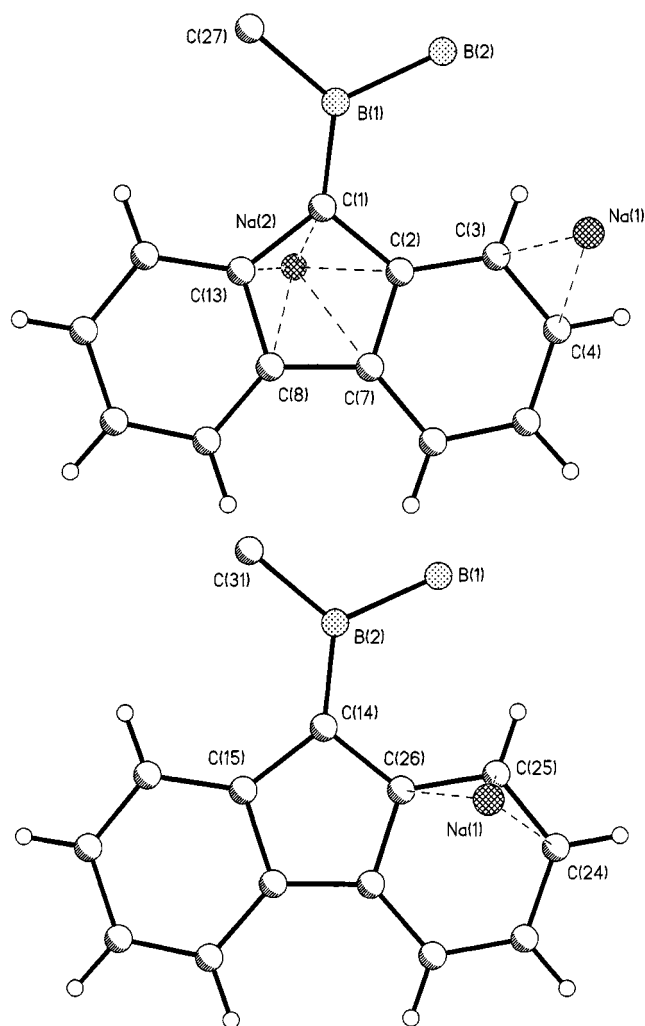


Figure 4. Plots showing the positions of the sodium cations Na1 and Na2 in  $[\text{Na}(\text{thf})(\text{OEt}_2)]_2[\text{Na}(\text{OEt}_2)_2][\mathbf{2}]$  with respect to the planes of the fluorenyl substituents C1 to C13 (top) and C14 to C26 (bottom); distances between the sodium cations and the fluorenyl planes [Å]: Na2–(C1 to C13) 2.401, Na1–(C1 to C13) 2.642, Na1–(C14 to C26) 2.673

and one molecule of diethyl ether) and there is a weak interaction ( $\text{Na2-H32a} = 2.495 \text{ Å}$ ) between Na2 and a methyl group of the *tert*-butyl substituent bonded to B2. In contrast to monomeric  $[\text{Na}(\text{thf})(\text{OEt}_2)]_2[\text{Na}(\text{OEt}_2)_2][\mathbf{2}]$ , solvates of fluorenylsodium in which the sodium cation is also coordinated to the fluorenyl anion and two donor atoms are either polymeric, such as  $[\text{Na}(\text{fl})\cdot\text{TMEDA}]_\infty$ , or oligomeric, such as  $[\text{Na}(\text{fl})\cdot\text{TMPDA}]_4$ . A monomeric solvate of fluorenylsodium is only formed with the tridentate PMDTA ligand.<sup>[24]</sup>

Na1 interacts with both fluorenyl substituents of the dianion  $[\mathbf{2}]^{2-}$ . The fluorenyl substituents do not coordinate Na1 through the carbon atoms of the central five-membered rings as has been observed for alkali metal compounds of the analogous dianion  $[\mathbf{1}]^{2-}$ . Such a di- $\eta^5$  coordination is impossible in the case of  $[\mathbf{2}]^{2-}$  because of the almost perpendicular orientation of the planes at the boron atoms and the small angles between the planes at the boron atoms and the planes of the fluorenyl substituents. Na1 is

coordinated by the benzoid carbon atoms of the fluorenyl substituents instead. It shows three contacts to the fluorenyl substituent C14 to C26 with Na–C distances of  $\text{Na1-C25} = 2.720(6) \text{ Å}$ ,  $\text{Na1-C26} = 2.822(6) \text{ Å}$ , and  $\text{Na1-C24} = 3.071(7) \text{ Å}$ , and two contacts to the fluorenyl substituent C1 to C13 with Na–C distances of  $\text{Na1-C3} = 2.818(6) \text{ Å}$  and  $\text{Na1-C4} = 2.987(7) \text{ Å}$  (see Figure 4). If Na1 is projected perpendicularly onto the fluorenyl plane defined by the carbon atoms C1 to C13, it can be seen that this cation lies outside of the area of this fluorenyl substituent (see Figure 4, bottom). This coordination is strongly reminiscent of that of one of the sodium atoms in the cyclic tetramer  $[\text{Na}(\text{fl})\cdot\text{TMPDA}]_4$ , in which the Na–C distances measure 3.025(5) and 3.032(5) Å.<sup>[24]</sup> Similar “out-of-ring coordination” has been observed in the dipotassium salt  $[\text{K}(\text{DME})_2][\mathbf{1}]$ .<sup>[2]</sup> The coordination sphere of Na1 is completed by two molecules of diethyl ether. The average Na–O distance is 2.315 Å, 7 pm longer than for Na2; the O–Na–O angle is 13° wider for Na1 ( $\text{O1-Na1-O2} = 109.4^\circ$ ) compared to that at Na2 ( $\text{O3-Na2-O4} = 96.4^\circ$ ).

## Conclusion

The present study has again shown that the quantitative deprotonation of alkylboranes is not easily achieved. Even in the case of the compounds **2-H** and **4-H**, in which the boron centers are sterically very shielded, the action of the weak nucleophilic bases  $\text{NaN}(\text{SiMe}_3)_2$  and  $\text{LiN}t\text{Bu}(\text{SiMe}_3)$  leads to products in which significant numbers of boron atoms are tetracoordinated. As expected, the dianion  $[\mathbf{2}]^{2-}$  displays a higher degree of C–B- $\pi$  bonding than the related dimethylamino derivative  $[\mathbf{1}]^{2-}$ , as has been established on the basis of the following criteria: the B–C<sub>fl</sub> bond lengths are shorter, the angles between the planes at the boron atoms and the planes of the corresponding fluorenyl substituents are smaller, and NMR studies show the  $^1\text{H}$  and the  $^{13}\text{C}$  nuclei of the fluorenyl substituents to be more deshielded. In  $[\mathbf{2}]^{2-}$ , the  $\pi$  system is not delocalized over the C<sub>fl</sub>–B–B–C<sub>fl</sub> unit as might be expected for an isoelectronic butadiene system. This is obvious as the planes at the boron atoms adopt an almost perpendicular arrangement. Therefore,  $[\mathbf{2}]^{2-}$  is best described as a system in which two borylated carbanions are connected by a B–B single bond without B–C- $\pi$  bond character. The question remains as to why butadiene-like structures are not realized for  $[\mathbf{2}]^{2-}$  and the related anion  $[\text{Mes}_2\text{B}_2\{\text{C}(\text{SiMe}_3)_2\}_2]^{2-}$ , i.e. whether this is due to steric reasons or also due to the electronic situation.

## Experimental Section

**General:** All manipulations were carried out under  $\text{N}_2$  using Schlenk techniques. Solvents were dried by standard procedures. Commercial chemicals were purified prior to use as necessary;  $(t\text{Bu})_2\text{B}_2\text{Br}_2$ ,<sup>[25]</sup>  $(t\text{Bu})_2\text{BCl}$ ,<sup>[26]</sup>  $\text{Me}_2\text{BBr}$ ,<sup>[27]</sup>  $\text{Li}(\text{fl})$ ,<sup>[28]</sup>  $\text{NaN}(\text{SiMe}_3)_2$ , and  $\text{LiN}t\text{Bu}(\text{SiMe}_3)$ <sup>[29]</sup> were prepared according to literature procedures. – NMR: Bruker AC-P 200 ( $^1\text{H}$ ), Jeol EX 400 ( $^1\text{H}$ ,  $^{13}\text{C}$ );

standards: ext.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  ( $^{11}\text{B}$ ), int. TMS or  $\text{C}_6\text{D}_6$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ). – IR: Perkin–Elmer 325. – MS: Varian CH7 (70 eV). – X-ray structure determinations: Siemens P4 or Nicolet R3m diffractometer, Mo- $K_\alpha$  radiation, graphite monochromator.

**1-Bromo-1,2-di-*tert*-butyl-2-(1-fluorenyl)diborane(4) (3):** A suspension of fluorenyllithium (0.69 g, 4.01 mmol) in toluene (20 mL) was added dropwise to a solution of  $(t\text{Bu})_2\text{B}_2\text{Br}_2$  (1.18 g, 3.99 mmol) in toluene (25 mL) at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature, stirred for 6 h, and then the insoluble material (0.32 g) was removed by centrifugation. The solution was concentrated to dryness, the residue was redissolved in hexane (12 mL), and this solution stored for 20 h at  $-20^\circ\text{C}$ . A colorless solid separated, which was filtered off, washed with cold hexane, and dried in vacuo. – Yield: 0.40 g of **3** (26%); m.p.  $92\text{--}93^\circ\text{C}$ . –  $\text{C}_{21}\text{H}_{27}\text{B}_2\text{Br}$  (381.0): calcd. C 66.21, H 7.14; found C 64.74, H 6.37. – MS (70 eV);  $m/z$  (%): 380 (100) [ $\text{M}^{+\bullet}$ ], 233 (45) [ $\text{M}^{+\bullet} - \text{B}(\text{fl-H})\text{Br}$ ], 165 (56) [fl-H]. –  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CDCl}_3$ ):  $\delta = 92.9$  ( $h_{1/2} = 940$  Hz). –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.84$ , 7.78, 7.50, 7.45 [d, 1 H,  $^3J(\text{H,H}) = 7.3$  Hz; d, 1 H,  $^3J(\text{H,H}) = 7.3$  Hz; d, 1 H,  $^3J(\text{H,H}) = 6.8$  Hz; d, 1 H,  $^3J(\text{H,H}) = 7.3$  Hz, 3-,6-,9-,12-H], 7.32 (m, 4 H, 4-,5-,10-,11-H), 4.57 (s, 1 H, 1-H), 1.29, 0.37 [2 s,  $2 \times 9$  H, 2  $\text{C}(\text{CH}_3)_3$ ]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta = 147.1$ , 143.9 (C-2,13), 142.2, 140.5 (C-7,8), 126.7, 126.6, 126.5, 126.3, 126.1, 125.8 (C-3,4,5,10,11,12), 120.4, 119.9 (C-6,9), 49.3 (C-1), 30.1, 29.3 [ $\text{C}(\text{CH}_3)_3$ ], 27.5, 26.2 [ $\text{C}(\text{CH}_3)_3$ ].

**1,2-Di-*tert*-butyl-1,2-bis(1-fluorenyl)diborane(4) (2-H<sub>2</sub>):** A suspension of fluorenyllithium (0.40 g, 2.32 mmol) in toluene (15 mL) was slowly added to a stirred solution of **3** (0.87 g, 2.28 mmol) in toluene (10 mL) at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature, stirred for 20 h, and then the insoluble material was separated by centrifugation. The solution was then concentrated to dryness in vacuo and the residue was redissolved in hexane (10 mL). Storing this solution for 3 d at  $-25^\circ\text{C}$  gave colorless, microcrystalline **2-H<sub>2</sub>**, which was filtered off, washed with cold hexane (3 mL), and dried in vacuo for several hours. – Yield: 0.44 g of **2-H<sub>2</sub>** (41%); m.p.  $138\text{--}139^\circ\text{C}$ . –  $\text{C}_{34}\text{H}_{36}\text{B}_2$  (466.3): calcd. C 87.58, H 7.78; found C 85.47, H 7.57. – MS (70 eV);  $m/z$  (%): 466 (11) [ $\text{M}^{+\bullet}$ ], 409 (5) [ $\text{M}^{+\bullet} - \text{C}(\text{CH}_3)_3$ ], 301 (91) [ $\text{M}^{+\bullet} - \text{C}_{13}\text{H}_9$ ], 233 (34) [ $\text{M}^{+\bullet}/2$ ], 176 (77) [B(fl-H)], 165 (100) [fl-H]. –  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 102.5$  ( $h_{1/2} = 2250$  Hz). –  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.76$  [d, 2 H,  $^3J(\text{H,H}) = 7.3$  Hz, 6-H], 7.68 [d, 2 H,  $^3J(\text{H,H}) = 7.3$  Hz, 9-H], 7.57 [d, 2 H,  $^3J(\text{H,H}) = 6.4$  Hz, 3-H], 7.28 (pseudo-t, 2 H, 5-H), 7.19 (pseudo-t, 2 H, 10-H), 7.14 (pseudo-t, 2 H, 4-H), 7.04 (pseudo-t, 2 H, 11-H), 6.35 (m, very broad, 12-H), 4.66 (s, 2 H, 1-H), 0.75 [s, 18 H,  $\text{C}(\text{CH}_3)_3$ ]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 147.2$ , 145.6 (C-2,13), 142.9, 142.6 (C-7,8), 127.0 (C-4), 126.4 (C-5,10,11,12), 125.6 (C-3), 120.6 (C-6), 120.3 (C-9), 50.5 (C-1), 32.5 [ $\text{C}(\text{CH}_3)_3$ ], 28.7 [ $\text{C}(\text{CH}_3)_3$ ]. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances were assigned on the basis of  $^1\text{H}$ - $^1\text{H}$ -COSY and  $^1\text{H}$ - $^{13}\text{C}$ -HETCOR NMR experiments.

**Di-*tert*-butyl-(1-fluorenyl)borane (4-H):** A suspension of fluorenyllithium (2.14 g, 12.43 mmol) in toluene (30 mL) was slowly added to a stirred solution of  $t\text{Bu}_2\text{BCl}$  (1.99 g, 12.40 mmol) in toluene (20 mL) at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature, in the course of which a brown-red color developed. After stirring for a further 20 h at room temperature, the insoluble material was separated by centrifugation and this solid was extracted with toluene (10 mL). The toluene solutions were combined and concentrated to dryness in vacuo. The residue (3.31 g) was redissolved in hexane (15 mL) and storage of this solution at  $-25^\circ\text{C}$  led to the deposition of large, colorless needles (0.50 g). Concentration of the mother liquor and further storage at  $-25^\circ\text{C}$  furnished

a second crop of crystals (1.32 g). – Yield: 1.82 g of **4-H** (51%); m.p.  $70\text{--}72^\circ\text{C}$ . –  $\text{C}_{21}\text{H}_{27}\text{B}$  (290.3): calcd. C 86.90, H 9.38; found C 83.69, H 7.77. –  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 86.3$  ( $h_{1/2} = 670$  Hz). –  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.75$  [d, 2 H,  $^3J(\text{H,H}) = 7.3$  Hz, 6-,9-H], 7.28 [pseudo-t,  $^3J(\text{H,H}) = 7.3$  Hz, 2 H, 4-,11-H or 5-,10-H], 7.23 [d, 2 H,  $^3J(\text{H,H}) = 6.8$  Hz, 3-,12-H], 7.18 [pseudo-t, 2 H,  $^3J(\text{H,H}) = 7.3$  Hz, 4-,11-H or 5-,10-H], 4.41 (s, 1 H, 1-H), 1.24, 0.53 [2 s,  $2 \times 9$  H, 2  $\text{C}(\text{CH}_3)_3$ ]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 147.9$  (C-2,13), 143.2 (C-7,8), 126.8, 126.2 (C-4,5,10,11), 124.4 (C-3,12), 120.6 (C-6,9), 48.8 (C-1), 30.3, 29.9 [ $\text{C}(\text{CH}_3)_3$ ], 28.6, 27.6 [ $\text{C}(\text{CH}_3)_3$ ].

**(1-Fluorenyl)dimethylborane (5-H):** A suspension of fluorenyllithium (3.37 g, 19.6 mmol) in toluene (20 mL) was added dropwise to a stirred solution of  $\text{Me}_2\text{BBr}$  (2.37 g, 19.6 mmol) in toluene (20 mL) at  $-78^\circ\text{C}$ . The mixture was allowed to warm to ambient temperature, stirred for a further 3 d, and then the insoluble material (1.75 g) was separated by centrifugation. This solid was extracted with toluene (7 mL) and the toluene solutions were combined. Removal of all volatile compounds in vacuo left a red oil (3.45 g), heating of which at  $110\text{--}130^\circ\text{C}/10^{-3}$  Torr resulted in the formation of very thin, colorless needles. – Yield: 2.79 g of **5-H** (69%); m.p.  $49\text{--}50^\circ\text{C}$ . –  $\text{C}_{15}\text{H}_{15}\text{B}$  (206.1): calcd. C 87.42, H 7.34; found C 86.67, H 7.87. –  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 83.8$  ( $h_{1/2} = 310$  Hz). –  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.74$  [d, 2 H,  $^3J(\text{H,H}) = 7.3$  Hz, 6-,9-H], 7.22 (m, 6 H, 3-,4-,5-,10-,11-,12-H), 4.29 (s, 1 H, 1-H), 0.53 (s, 6 H,  $\text{CH}_3$ ). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 145.4$  (C-2,13), 142.1 (C-7,8), 126.8, 126.3 (C-4,5,10,11), 124.8 (C-3,12), 120.5 (C-6,9), 53.8 (C-1), 13.0 ( $\text{CH}_3$ ).

**[Na(thf)<sub>x</sub>]<sub>2</sub>[(*rtBu*)<sub>2</sub>B<sub>2</sub>(fl)]<sub>2</sub> {[Na(thf)<sub>x</sub>]<sub>2</sub>[2]}:** A solution of NaN-(SiMe<sub>3</sub>)<sub>2</sub> (0.31 g, 1.69 mmol) in tetrahydrofuran (7 mL) was added dropwise to a stirred solution of **2-H<sub>2</sub>** (0.41 g, 0.88 mmol) in tetrahydrofuran (10 mL) at room temperature. During the addition of the base, the color of the reaction mixture turned orange. Stirring was continued for 20 h and then the deep-red mixture was concentrated to dryness in vacuo. On treating the residue with hexane (10 mL), an orange powder formed, which was collected by filtration (0.28 g), washed with hexane (3 mL), and dried in vacuo.  $^{11}\text{B}$ -,  $^1\text{H}$ -, and  $^{13}\text{C}$ -NMR spectroscopy showed the product to be a THF solvate of the disodium salt [Na(thf)<sub>x</sub>]<sub>2</sub>[2]. Crystals of the solvate [Na(thf)(OEt<sub>2</sub>)]<sub>2</sub>[Na(OEt<sub>2</sub>)<sub>2</sub>][2] suitable for X-ray crystallography were obtained by recrystallizing the orange powdery [Na(thf)<sub>x</sub>]<sub>2</sub>[2] from diethyl ether at  $-20^\circ\text{C}$ . –  $^{11}\text{B}$  NMR (64.2 MHz, THF/ $\text{C}_6\text{D}_6$ ):  $\delta = 72.0$  ( $h_{1/2} = 4100$  Hz). –  $^1\text{H}$  NMR (400 MHz, THF/ $\text{C}_6\text{D}_6$ ):  $\delta = 8.27$  [d, 4 H,  $^3J(\text{H,H}) = 8.3$  Hz, 6-,9-H], 7.88 [d, 4 H,  $^3J(\text{H,H}) = 7.3$  Hz, 3-,12-H], 6.77 [(at  $+55^\circ\text{C}$ , t), 4 H, 4-,11-H], 6.60 (pseudo-t, 4 H, broad, 5-,10-H), 1.44 [s, 18 H,  $\text{C}(\text{CH}_3)_3$ ]. –  $^{13}\text{C}$  NMR (100.6 MHz, THF/ $\text{C}_6\text{D}_6$ ):  $\delta = 146.0$  (broad, C-2,13), 130.2 (C-7,8), 122.5 (broad, C-4,11), 121.0 (C-6,9), 118.1 (C-3,12), 112.8 (C-5,10); (C-1) and [ $\text{C}(\text{CH}_3)_3$ ] could not be detected; 34.7 [ $\text{C}(\text{CH}_3)_3$ ].

**Reaction of 4-H with LiN(*rtBu*)(SiMe<sub>3</sub>):** A solution of LiN(*rtBu*)(SiMe<sub>3</sub>) (0.51 g, 3.37 mmol) in tetrahydrofuran (15 mL) was added dropwise to a solution of **4-H** (0.96 g, 3.31 mmol) in tetrahydrofuran (15 mL) at room temperature. The mixture was stirred for 1 d, in the course of which a deep-red color developed. After removing all volatile material in vacuo, a dark-red resinous residue (1.88 g) remained. Addition of hexane (20 mL) produced an orange powder (0.75 g), which was collected by filtration, washed with hexane (5 mL), and dried in vacuo.  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{11}\text{B}$ -NMR spectroscopy showed this powder to consist of a 4:1 mixture of [Li(thf)<sub>2</sub>][4] and fluorenyllithium. The powder proved to be very soluble in THF and benzene and moderately soluble in hexane. Separation of the



Table 3. Crystallographic data for the structures of **2-H<sub>2</sub>**, **4-H**, and **[Na(thf)(Et<sub>2</sub>O)][Na(Et<sub>2</sub>O)<sub>2</sub>][2]** and details relating to data collection and structure refinement

|                                 | <b>2-H<sub>2</sub></b>                                          | <b>4-H</b>                                                      | <b>[Na(thf)(Et<sub>2</sub>O)][Na(Et<sub>2</sub>O)<sub>2</sub>][2]</b>         |
|---------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------------------------------------|
| Empirical formula               | C <sub>34</sub> H <sub>36</sub> B <sub>2</sub>                  | C <sub>21</sub> H <sub>27</sub> B                               | C <sub>50</sub> H <sub>72</sub> B <sub>2</sub> Na <sub>2</sub> O <sub>4</sub> |
| Molecular mass                  | 466.28                                                          | 290.24                                                          | 804.68                                                                        |
| Crystal size [mm]               | 0.35 × 0.20 × 0.35                                              | 0.6 × 0.4 × 0.4                                                 | 0.50 × 0.45 × 0.42                                                            |
| Crystal system                  | Orthorhombic                                                    | Monoclinic                                                      | Monoclinic                                                                    |
| Space group                     | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>           | <i>P</i> 2(1)/ <i>c</i>                                         | <i>P</i> 2(1)/ <i>n</i>                                                       |
| <i>a</i> [Å]                    | 9.269(2)                                                        | 13.967(3)                                                       | 12.282(4)                                                                     |
| <i>b</i> [Å]                    | 14.470(3)                                                       | 14.502(3)                                                       | 25.00(1)                                                                      |
| <i>c</i> [Å]                    | 20.579(8)                                                       | 8.999(2)                                                        | 16.04(1)                                                                      |
| β [°]                           | 90                                                              | 90.119(4)                                                       | 103.15(4)                                                                     |
| <i>V</i> [Å <sup>3</sup> ]      | 2760.1(15)                                                      | 1822.9(7)                                                       | 4796(5)                                                                       |
| <i>Z</i>                        | 4                                                               | 4                                                               | 4                                                                             |
| ρ(calcd.) [Mg/mm <sup>3</sup> ] | 1.122                                                           | 1.058                                                           | 1.114                                                                         |
| μ [mm <sup>-1</sup> ]           | 0.062                                                           | 0.058                                                           | 0.083                                                                         |
| <i>F</i> (000)                  | 1000                                                            | 632                                                             | 1744                                                                          |
| Index range                     | −1 ≤ <i>h</i> ≤ 10<br>−1 ≤ <i>k</i> ≤ 16<br>−22 ≤ <i>l</i> ≤ 23 | −17 ≤ <i>h</i> ≤ 17<br>−18 ≤ <i>k</i> ≤ 18<br>8 ≤ <i>l</i> ≤ 12 | 0 ≤ <i>h</i> ≤ 12<br>−1 ≤ <i>k</i> ≤ 25<br>−16 ≤ <i>l</i> ≤ 16                |
| 2θ [°]                          | 4.0 to 47.0                                                     | 5.34 to 57.88                                                   | 3.08 to 43.00                                                                 |
| <i>T</i> [K]                    | 203                                                             | 193(2)                                                          | 173                                                                           |
| Refl. collected                 | 5285                                                            | 10492                                                           | 6033                                                                          |
| Refl. unique                    | 4073                                                            | 3397                                                            | 5404                                                                          |
| Refl. observed (4σ)             | 2451                                                            | 2085                                                            | 2766                                                                          |
| No. of variables                | 325                                                             | 208                                                             | 559                                                                           |
| GooF                            | 0.88                                                            | 0.987                                                           | 1.085                                                                         |
| <i>R</i>                        | 0.0551                                                          | 0.0599                                                          | 0.0729                                                                        |
| <i>wR</i> <sub>2</sub>          | 0.0663                                                          | 0.1714                                                          | 0.1580                                                                        |
| [ <i>e</i> /Å <sup>3</sup> ]    | 0.25                                                            | 0.223                                                           | 0.297                                                                         |

two components by fractional crystallization could not be achieved.

– **NMR Data for [Li(thf)<sub>2</sub>][4]:** <sup>1</sup>B NMR (64.2 MHz, THF/C<sub>6</sub>D<sub>6</sub>): δ = 77.9 (h<sub>1/2</sub> = 950 Hz). – <sup>1</sup>H NMR (400 MHz, THF/C<sub>6</sub>D<sub>6</sub>): δ = 7.76 [d, 2 H, <sup>3</sup>*J*(H,H) = 7.3 Hz, 6-,9-H], 7.19 [d, 2 H, <sup>3</sup>*J*(H,H) = 8.3 Hz, 3-,12-H], 6.71 [pseudo-t, 2 H, <sup>3</sup>*J*(H,H) = 7.1 Hz, 4-,11-H], 6.35 [pseudo-t, 2 H, <sup>3</sup>*J*(H,H) = 7.3 Hz, 5-,10-H], 1.15 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>]. – <sup>13</sup>C NMR (100.6 MHz, THF/C<sub>6</sub>D<sub>6</sub>): δ = 142.1 (C-2,13), 126.4 (C-7,8), 120.4 (C-4,11), 119.2 (C-6,9), 118.3 (C-3,12), 108.7 (C-5,10), 105.2 (C-1), 31.0 [C(CH<sub>3</sub>)<sub>3</sub>], 30.3 [C(CH<sub>3</sub>)<sub>3</sub>]. – <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 8.27 [d, 2 H, <sup>3</sup>*J*(H,H) = 7.8 Hz, 6-,9-H], 7.61 [d, 2 H, <sup>3</sup>*J*(H,H) = 8.3 Hz, 3-,12-H], 7.25 [pseudo-t, 2 H, <sup>3</sup>*J*(H,H) = 7.6 Hz, 4-,11-H], 6.99 [pseudo-t, 2 H, <sup>3</sup>*J*(H,H) = 7.3 Hz, 5-,10-H], 2.66 (m, 8 H, THF), 1.35 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.04 (m, 8 H, THF). – <sup>13</sup>C NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 137.4 (C-2,13), 122.0 (C-7,8), 121.6 (C-4,11), 121.5 (C-6,9), 120.3 (C-3,12), 112.6 (C-5,10), 100.7 (C-1), 67.6 (THF), 30.9 [C(CH<sub>3</sub>)<sub>3</sub>], 29.4 [C(CH<sub>3</sub>)<sub>3</sub>], 25.0 (THF). – **NMR Data for Fluorenyllithium:** <sup>1</sup>H NMR (400 MHz, THF/C<sub>6</sub>D<sub>6</sub>): δ = 7.85 (d, 2 H, 6-,9-H), 7.24 (d, 2 H, 3-,12-H), 6.75 (pseudo-t, 2 H, 4-,11-H), 6.37 (pseudo-t, 2 H, 5-,10-H), 5.87 (s, 1 H, 1-H). – <sup>13</sup>C NMR (100.6 MHz, THF/C<sub>6</sub>D<sub>6</sub>): δ = 138.0 (C-2,13), 123.4 (C-7,8), 119.4 (C-4,11), 118.9 (C-6,9), 116.5 (C-3,12), 108.4 (C-5,10), 81.4 (C-1).

**X-ray Structure Determination:** Single crystals were coated with perfluoroether oil and mounted on glass fibres. They were cooled to −80 °C on the goniometer head. Cell dimensions were determined by automatically centering reflections taken from rotation photographs. Data collections were performed in the ω/2θ mode with variable scan speeds and adjusted scan widths. After data reduction (Lorentz and polarization correction), direct methods were applied for structure solution. The model was initially refined after atom assignment with isotropic temperature parameters, and then the positions of the atoms were refined using an anisotropic description. Hydrogen atom positions were calculated and included in the final calculation with fixed isotropic thermal parameters as

riding on the respective C-atoms. Selected crystallographic data and data related to the structure solution and refinement are summarized in Table 3. Programs used: SHELXTL and SHELXL-93. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143688 to -143690. 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.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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