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# Rearrangement of Bis(dimethylamino)bis(1-indenyl)diborane(4) into Bis(dimethylamino)bis(3-indenyl)diborane(4)[☆]

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Indenyllithium reacts with dichlorobis(dimethylamino)diborane(4) with formation of bis(dimethylamino)bis(1-indenyl)diborane(4) which rearranges on heating to the isomer bis(dimethylamino)bis(3-indenyl)diborane(4). The "mixed" bis(dimethylamino)(1-indenyl)(3-indenyl)diborane(4) is obtained from indenyllithium and chlorobis(dimethylamino)(3-indenyl)diborane(4). The main structural differences between the two isomers **3** and **4** are a slightly shorter B−B bond in **4**, as well as a stronger twist about the B−B bond (89.9° vs. 67.4°) and, as expected, a shorter B−C bond. There is, however, no significant B−C π bonding.

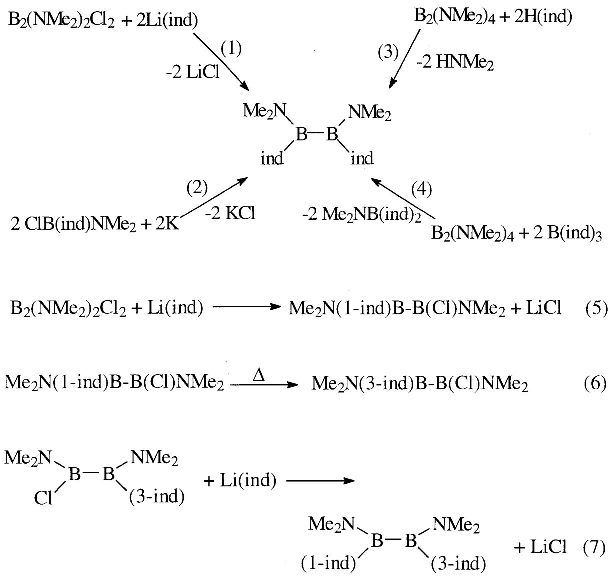
Bis(dimethylamino)diorganyldiboranes(4) $(Me_2N)RB-BR(NMe_2)$ may either be reduced to their dianions $[B_2(NMe_2)_2R_2]^{2-}$ which feature a B=B double bond[2] or may be deprotonated to a diborabutadiene dianion $[R'_2{=}B(NMe_2)-B(NMe_2){=}R']^{2-}$ ($R' = CHR'_2$) provided that the organyl group carries a sufficiently acidic hydrogen atom[3]. The first route has been verified for R = phenyl,[2] the second for R′ = fluorenyl[3][4] and benzyl[5]. The alkali-metal salts of $B_2(NMe_2)_2(CR'_2)_2{}^{2-}$ not only show a noticeable variation of structures[3][5] but have also proved to be useful reagents for the preparation of new heterocycles such as 1-stanna-3,4-diborolanes or 1-plumba-3,4-diborolanes and 1,2-diboretanes[6]. Other diorganyldiboranes(4) that might readily be deprotonated are indenyl and cyclopentadienyl derivatives. These are expected to exhibit a different reactivity compared to the fluorenyldiborane(4) compounds because they are less acidic, are sterically less demanding, and their alkali-metal salts may therefore display different structural motifs. Here we report on the synthesis and structural characterisation of bis(dimethylamino)bis(indenyl)diboranes(4)[7].

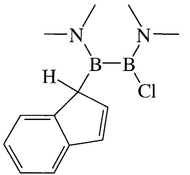
## Synthesis

There are at least four different synthetic pathways by which the synthesis of bis(dimethylamino)bis(indenyl)diboranes(4) can be achieved. These are summarized in Scheme 1.

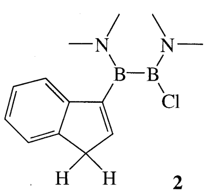
The most straightforward pathway is described by eq. 1 while the route shown in eq. 2 may suffer from deprotonation of the indenyl group; this would lead to B−C bond formation in competition to B−B bond formation.

Scheme 1





**1**



**2**

The results of eq. 3 depend on the acidity of indene and the Lewis acidity of the boron atoms in $B_2(NMe_2)_2(ind)_2$ which may prevent the liberation of $Me_2NH$ and hence the synthesis of $B_2(NMe_2)_2(ind)_2$. The substituent exchange according to eq. 4 is prevented simply by the access to tri(in-

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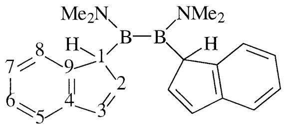
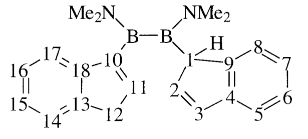
denyl)borane, an as yet unknown triorganylborane. Consequently we studied the reaction described by eq. 1.

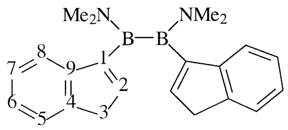
In toluene a surprising result was observed as even after 20 h at ambient temperature only monosubstitution with formation of chlorobis(dimethylamino)(indenyl)diborane(4) (**1**) occurred which was present in solution as the 1-indenyl isomer (eq. 5). On distillation **1** converted into the 3-indenyl isomer **2** (eq. 6).



**3**



**4**



**5**

However, when a small amount of THF was added to the reaction mixture as described by eq. 1 then **1** was only an intermediate on route to bis(dimethylamino)bis(1-indenyl)diborane. Under these conditions **3** was formed and isolated in acceptable yields (55%).

Heating solutions of **3** in toluene under reflux converted this compound into its bis(3-indenyl)derivative **5**. Following this rearrangement using $^1$H- and $^{13}$C-NMR spectroscopy provided evidence that the "mixed" isomer **4** is an intermediate. Actually, **4** can be readily prepared from the chloro(3-indenyl)diborane(4) **2** by allowing it to react with Li(ind) at ambient temperature as shown in eq. 7.

Experiments designed to obtain bis(cyclopentadienyl)bis(dimethylamino)diborane(4) have so far failed. The reaction of TlCp with $(Me_2N)_2B_2Cl_2$ in toluene led to a solution that contained primarily the starting diborane(4) compound in addition to unidentified products (ratio 9:1 according to $^{11}$B-NMR spectroscopy). Activation by ultrasound or replacement of TlCp by NaCp and the use of THF as a solvent lead to ether cleavage.

## NMR Spectra

NMR-spectroscopic data on compounds **2**−**5** are summarized in the Experimental Section. Assignments were made from the analysis of $^1$H-$^1$H-COSY and $^1$H-$^{13}$C-HETCOR experiments.

The $^{11}$B resonances of the indenyldiboranes(4) **3**−**5** all lie in a very narrow range, $\delta = 48 \pm 2$, irrespective of whether the indenyl group is present as the 1- or 3-isomer. However, the linewidth increases as the number of the 3-indenyl groups increases. The observed shielding corresponds to dialkylbis(dimethylamino)diboranes(4)[8]. 3-Indenyl groups should actually lead to a better shielding due to possible B−C π bonding as observed for amino(vinyl)boranes[9]. Therefore, we can assume that the 3-indenyl group is not coplanar with the $B_2NC$ plane. Two $^1$H- and $^{13}$C-NMR signals for the dimethylamino group in **5** indicate hindered rotation about the B−N bonds. In the case of compound **4** there are even four $^1$H-NMR signals of equal intensity as well as four $^{13}$C resonances, which again demonstrate hindered rotation about the B−N bonds. Surprisingly, compound **3** displays eight signals for the $Me_2N$ groups in the $^1$H-NMR spectrum and shows six $^{13}$C resonances. This fact can only be rationalized by assuming the presence of rotamers.

Compound **2** is exceptional in so far as one would expect two separated $^{11}$B-NMR signals but only one is actually observed. This can be explained by an inductive effect of the $B(Cl)NMe_2$ group which brings about stronger B−N bonding on the neighbouring $R(Me_2N)B$ group, as indicated by a deshielding of the protons of the dimethylamino groups. It is a well-known phenomenon that the $^{13}$C resonances of carbon atoms bound to a boron atom are often difficult to detect due to the quadrupole-induced broadening of its resonance[8]. Thus only the $^{13}$C resonances of the C atom of the 1-indenyl compounds could be determined but not those of the 3-indenyl groups.

The NMR data also suggest free rotation about the B−B bond. However, for the bis(1-indenyl)diborane(4) **3** hindered rotation about the B−C bonds may also be possible. Nevertheless, no firm conclusions as to the structure of the dominant conformation could be derived from NMR experiments. We therefore determined the molecular structures by X-ray crystallography although the results are, of course, restricted to the solid state.

## Molecular Structures

Two of the indenyldiboranes(4) gave single crystals from hexane solutions suitable for an X-ray diffraction study. Figures 1 and 2 depict the results whilst Table 1 contains the bonding parameters.

The molecular structures of **3** and **4** confirm the conclusions drawn from the NMR data that **3** contains 1-indenyl groups only, while **4** carries both a 1-indenyl and 3-indenyl substituent.

A significant structural feature of both compounds is the B−B bond, which seems to be slightly longer in **3** than in **4**. However, both B−B bonds are longer than found for the comparable diborane(4) derivatives 1,2-difluorenyl-1,2-dipyrrolidinodiborane(4) [1.697(4) Å][10], 1,2-bis(dimethylamino)-1,2-bis(phenylethynyl)diborane(4) [1.696(8) Å][10], 1,2-bis(dimethylamino)-1,1-diphenyldiborane(4) [1.714(4) Å] and 1,2-bis(dimethylamino)-1,2-dimesityldiborane(4) [1.72(1) Å][11]. It appears from these data that the B−B bond length increases slightly when tetracoordinated C atoms are replaced by trigonal-planar C atoms.

B−N π bonding is indicated by the B−N bond lengths in compounds **3** and **4** which range from 1.386(4)−1.403(2) Å; this fits not only with the hindered rotation about the B−N bonds but also with many other B−N bond lengths of aminoboranes(4)[11]. However, one should note that in compound **4** the longer B−N bond is associated with the boron atom that carries the 1-indenyl substituent. The shorter B−N bond is found at the boron atom with the 3-

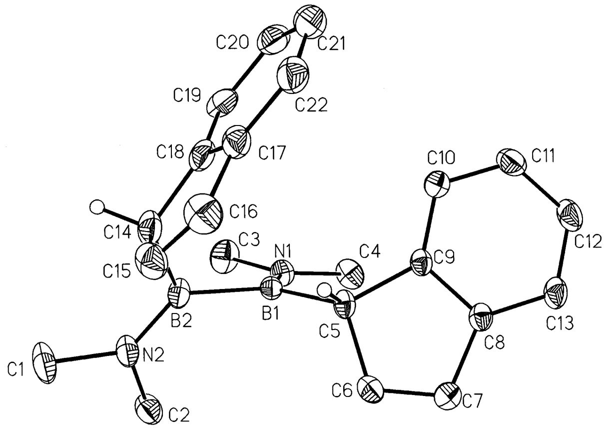
Table 1a. Selected bond lengths [Å] and bond angles [°] of compounds **3** and **4**; estimated standard deviations are given in parantheses

| Bond lengths | **3** | **4** | Bond angles | **3** | **4** |
|---|---|---|---|---|---|
| B1−B2 | 1.726(4) | 1.716(3) | N1−B1−C5 | 121.6(2) | 119.3(2) |
| B1−N1 | 1.393(4) | 1.403(2) | N1−B1−B2 | 122.1(3) | 121.8(2) |
| B2−N2 | 1.386(4) | 1.390(4) | C5−B1−B2 | 116.3(2) | 118.8(1) |
| B1−C5 | 1.631(4) | 1.621(3) | C14−B2−N2 | 118.0(3) | 120.4(2) |
| B2−C14 | 1.640(5) | 1.583(5) | N2−B2−B1 | 123.2(3) | 125.7(2) |
| C5−C6 | 1.495(5) | 1.512(2) | C14−B2−B1 | 118.6(3) | 113.9(2) |
| C6−C7 | 1.341(4) | 1.331(3) | B1−N1−C4 | 126.1(3) | 126.7(2) |
| C7−C8 | 1.459(5) | 1.470(3) | C4−N1−C3 | 111.4(3) | 111.2(2) |
| C8−C9 | 1.401(4) | 1.402(3) | B1−N1−C3 | 122.5(3) | 122.1(2) |
| C9−C5 | 1.516(4) | 1.509(3) | B2−N2−C2 | 122.9(3) | 123.1(2) |
| C14−C15 | 1.537(5) | 1.351(3) | B2−N2−C1 | 126.2(3) | 124.9(2) |
| C15−C16 | 1.307(5) | 1.505(3) | C1−N2−C2 | 110.9(3) | 111.9(2) |
| C16−C17 | 1.498(5) | 1.504(3) | B1−C5−C9 | 120.9(2) | 107.0(1) |
| C17−C18 | 1.386(5) | 1.403(3) | B1−C5−C6 | 113.1(2) | 114.4(1) |
| C14−C18 | 1.484(5) | 1.488(2) | B2−C14−C18 | 115.5(2) | 127.3(2) |
|  |  |  | B2−C14−C15 | 113.0(3) | 125.8(2) |

Table 1b. Selected torsion and interplanar angles [°] of compounds **3** and **4**

| Torsion angles | **3** | **4** | Interplanar angles | **3** | **4** |
|---|---|---|---|---|---|
| N1−B1−B2−N2 | 67.4 | 89.9 | C5−C9/C14−C18 | 104.2 | 3.4 |
| C1−N2−B2−B1 | 177.6 | −178.6 | C8−C13/C17−C22 | 105.9 | 5.6 |
| C4−N2−B1−B2 | −174.4 | 168.8 | C14−B2−N2/ C5−B−N1 | 65.3 | 92.3 |
| C5−B1−B2−C14 | 63.6 | 85.9 |  |  |  |

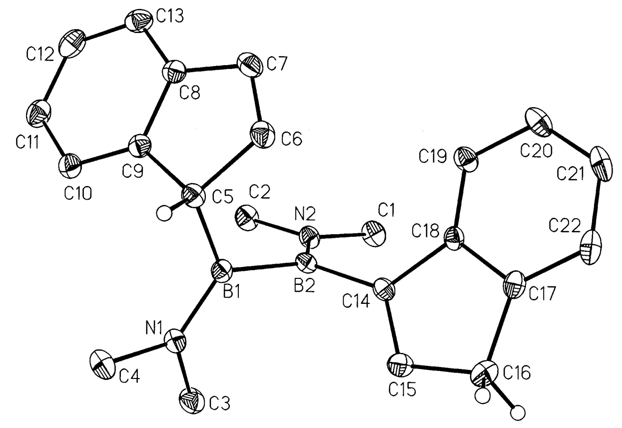
Figure 1. The molecular structure of the bis(1-indenyl)diborane(4) derivative **3** in the crystal; thermal ellipsoids are shown on a 25% probability level; hydrogen atoms (except those of the unique $CH_2$ groups) are omitted for clarity



indenyl group; this atom is expected to participate in B−C π bonding with a consequent weakening of B−N π bonding.

As expected the lengths of the B−C bonds to the 1-indenyl groups are longer than the B−C bonds of the 3-indenyl substituent reflecting the different hybridization at the carbon atoms. Moreover, the C−C bond lengths clearly show that there is no electron delocalisation in the five-membered rings, and even the benzo rings show significantly different C−C bond lengths due to the disturbance by the *o*-disubstitution.

Figure 2. The molecular structure of the "mixed" bis(1-indenyl)diborane(4) derivative **4** in the crystal; thermal ellipsoids are drawn on a 25% probability level; hydrogen atoms (except for the unique CH and $CH_2$ group) are omitted for clarity

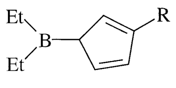


Strong B−N π bonding is indicated not only by short B−N bond lengths but also by planar geometry around the nitrogen and boron atoms. This is the case for these atoms in **3** and **4**. Moreover, the $C_2N$ plane should be coplanar with the $B_2C$ plane, e.g. the torsion angle C−N−B−B should be 0°. This is almost fulfilled for both compounds under consideration, the largest torsion angle being 11.0° (C11−N1−B1−B2 in **4**). While there is little difference between the two molecules there is a large conformational difference in the N−B−B−N torsion angle which is 67.4° for **3** but 89.9° for **4**. Another feature that determines the molecular shape of these molecules in the solid state is the orientation of the respective $C^3$ parts of the indenyl groups. For **3** the C5C6C9 plane is twisted against the N1B1B2 plane by 75.2°, and the C14C15C18 plane twisted against the N2B2B1 plane by 68.6°. In contrast, the C14C15C18 plane of the 3-indenyl group is rotated out of the N2B2B1 plane by 63.0° while the C5C6C9 plane is twisted against the N1B1B2 plane by 71.6°. As can be seen from Figure 1 the 1-indenyl groups are arranged in such a manner that the unique CH protons (on C5, C14) point in the same direction. This conformation is rather similar to that found in bis(dimethylamino)difluorenyldiborane(4)[10].

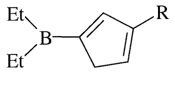
## Discussion

The study of the indenyldiboranes(4) **2−5** show conclusively that the 1-indenyl derivatives represent the kinetic products while the 3-indenyl isomers are the stable thermodynamic products. The former are obtained from indenyllithium and $B_2Cl_2(NMe_2)_2$ at ambient temperature and rearrange to the latter on heating of their toluene solutions or on distillation. Although one might expect that the driving force for the rearrangement is due to B−C π bonding, the molecular structure of **4** provides no support for this assumption because the 3-indenyl group is oriented orthogonally to the $NB_2$ plane, thus ruling out any B−C π-bonding contribution. This, however, need not be the case in solution.

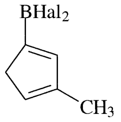
Similar behaviour has been observed for cyclopentadienylboranes. Grundke and Paetzold[12] have shown that cyclo-



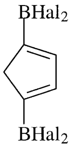
**A**



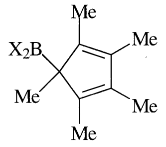
**B**



**C**



**D**



**E**

pentadienylboranes RCp$-$BEt$_2$ are present as the isomer **A**, and they found no NMR-spectroscopic evidence for isomer **B**.

Moreover, Jutzi and Seufert demonstrated that both the methyl and dihalogenoboryl group of the cyclopentadienyldihalogenoborane are only bonded to a vinylic carbon atom, e.g. like **C**, and the structure **D** follows for bis(dihalogenoborylcyclopentadiene) from NMR data[13]. When protic shifts are excluded, as is the case for (pentamethylcyclopentadienyl)boranes Cp*BX$_2$ (X = Cl, Br, I, NMe$_2$) rapid sigmatropic rearrangements are observed, except for X = NMe$_2$ which possesses a static structure **E** at ambient temperature showing both vinylic- and allylic-bound methyl groups[14]. The indenyldiboranes reported here therefore represent the first examples where both the allylic and the vinylic isomeric species could not only be detected by NMR methods but also isolated. This is due to the fact that the 1,3-sigmatropic rearrangement of the proton occurs slowly and, of course, raises the question of whether indenylboranes (ind)$_{3-x}$BX$_x$ behave similarly. We will report on these results in due course.

## Experimental Section

*General:* All experiments were performed under anhydrous conditions using Schlenk techniques under N$_2$ or Ar. All reagents were purified before use either by distillation or crystallization. – Elemental analysis using a Haereus MX instrument were done at the Institute's microanalytical laboratory. – IR: Perkin FT. – MS: Atlas CH7, 70 eV ionisation energy. – NMR: JEOL GSX 270 and JEOL EX 400, internal TMS ($^1$H, $^{13}$C), external BF$_3\cdot$OEt$_2$ ($^{11}$B). – X-ray: Siemens P4 with CCD area detector, SAINT software for data reduction; SHELX97 program package for structure solution and refinement. Numbering scheme of the NMR data refer to formulae **3**–**5**.

*1-Chloro-1,2-bis(dimethylamino)-2-(3-indenyl)diborane(4)* (**2**): By analogy to the preparation of **3**, B$_2$Cl$_2$(NMe)$_2$ (2.96 g, 16.4 mmol) in toluene (50 ml) was treated with a suspension of Li(ind) (2.0 g, 16.4 mmol) in toluene (30 ml) at $-78$ °C. The insoluble material (found 0.67 g, calcd. for LiCl: 0.69 g) was removed after 2 d. **2** could not be crystallized from hexane, but was distilled at 95–98 °C/10$^{-3}$ Torr as a colourless viscous oil. Yield: 2.53 g of **2** (63%).– C$_{13}$H$_{19}$B$_2$ClN$_2$ (260.38): calcd. C 59.97, H 7.35, N 10.76; found C 59.48, H 7.37, N 10.59. – $^{11}$B NMR (64 MHz, C$_6$D$_6$): $\delta$ = 43.6 [$h_{1/2}$ = 480 Hz, $B_2$(NMe$_2$)$_2$(1-ind)$_2$] – $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.53 [d, 1 H, $^3J$(H,H) = 7.7 Hz, indenyl: H$^{5/8}$], 7.37 [d, 1 H, $^3J$(H,H) = 7.4 Hz, indenyl: H$^{5/8}$], 7.29 [t, 1 H, $^3J$(H,H) = 7.7 Hz, indenyl: H$^{6/7}$], 7.15 [t, 1 H, $^3J$(H,H) = 7.4 Hz, indenyl: H$^{6/7}$], 6.55 [t, 1 H, $^3J$(H,H) = 2.1 Hz, indenyl: H$^2$], 3.21 [d, 2 H, $^3J$(H,H) = 1.8 Hz, indenyl: H$^3$], 2.74 [s, 3 H, N(C$H_3$)], 2.61 [s, 3 H, N(C$H_3$)], 2.54 [s, 3 H, N(C$H_3$)], 2.52 [s, 3 H, N(C$H_3$)] – $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$ = 148.5 (indenyl: C$^4$), 144.9 (indenyl: C$^9$), 137.1(indenyl: C$^2$), 126.5 (indenyl: C$^8$), 124.5 (indenyl: C$^5$), 124.1 (indenyl: C$^7$), 122.5 (indenyl: C$^6$), 44.2 [$-$N($C$H$_3$)], 41.9 [$-$N($C$H$_3$)], 41.1 [$-$N($C$H$_3$)], 40.6 (indenyl: C$^3$), 37.5 [$-$N($C$H$_3$)].

*1,2-Bis(dimethylamino)-1,2-bis(1-indenyl)diborane(4)* (**3**): B$_2$(NMe$_2$)$_2$Cl$_2$ [15] (5.06 g, 28.0 mmol) was dissolved in toluene (20 ml) and the solution cooled to $-78$ °C. A suspension of lithiumindenide (6.84 g, 56.0 mmol), which had been freshly prepared from indene and butyllithium in toluene (90 ml), was added under vigorous stirring. The suspension was allowed to attain ambient temperature within 18 h, and was then heated for 3 h at 68 °C, while stirring was continued. At this time the $^{11}$B-NMR spectrum showed only a single-resonance signal of the monosubstituted product Cl(Me$_2$N)B$-$B(NMe$_2$)ind; 0.3 ml of THF was then added to the yellow suspension and the insoluble material was removed by centrifugation after 1h. After washing with toluene (20 ml) and drying in vacuum, 2.25 g (calcd. 2.38 g for LiCl) of the almost white insoluble material were obtained. Toluene was removed from the combined solutions in vacuum leaving behind a yellowish mass of honey-like appearance. It was then dissolved in hot hexane (75 ml). Some insoluble materials were removed by filtration, and crystals separated within 7 d at $-20$ °C. Yield: 5.2 g of **3** (55%), m.p. 143–145 °C. – C$_{22}$H$_{26}$B$_2$N$_2$ (340.08): calcd. C 77.70, H 7.71, N 8.24; found C 75.94, H 7.75, N 8.14. – $^{11}$B NMR (64 MHz, C$_6$D$_6$): $\delta$ = 48.6 [$h_{1/2}$ = 520 Hz, $B_2$(NMe$_2$)$_2$(1-ind)$_2$] – $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 7.44 ( m, indenyl: H$_{\mathrm{arom}}$), 7.38 (m, indenyl: H$_{\mathrm{arom}}$), 7.23 (m, indenyl: H$_{\mathrm{arom}}$), 6.88 [dd, 2 H, $^3J$(H,H) = 5.4 Hz, $^4J$(H,H) = 2.2 Hz, indenyl: H$^3$], 6.81 [dd, 4 H, $^3J$(H,H) = 5.4 Hz, $^4J$(H,H) = 2.2 Hz, indenyl: H$^3$], 6.78 [dd, 1 H, $^3J$(H,H) = 5.4 Hz, $^4J$(H,H) = 2.2 Hz, indenyl: H$^3$], 6.62 [dd, 2 H, $^3J$(H,H) = 5.4 Hz, $^4J$(H,H) = 2.0 Hz, indenyl: H$^3$], 6.29 (dd, 4 H, $^3J$(H,H) = 5.4 Hz, $^3J$(H,H) = 1.9 Hz, indenyl: H$^2$], 6.25 [dd, 2 H, $^3J$(H,H) = 5.4 Hz, $^3J$(H,H) = 1.8 Hz, indenyl: H$^2$], 6.24 [dd, 1 H, $^3J$(H,H) = 5.4 Hz, $^3J$(H,H) = 1.9 Hz, indenyl: H$^2$], 6.13 [dd, 2 H, $^3J$(H,H) = 5.4 Hz, $^3J$(H,H) = 1.8 Hz, indenyl: H$^2$], 3.42 (br. s, indenyl: H$^1$), 3.39 (br. s, indenyl: H$^1$), 3.37 (br. s, indenyl: H$^1$), 3.36 (br. s, indenyl: H$^1$), 2.58 [s, 6 H, N(C$H_3$)$_2$], 2.50 [s, 6 H, N(C$H_3$)$_2$], 2.48 [s, 3 H, N(C$H_3$)$_2$], 2.35 [s, 12 H, N(C$H_3$)$_2$], 2.34 [s, 12 H, N(C$H_3$)$_2$], 2.27 [s, 3 H, N(C$H_3$)$_2$], 2.23 [s, 36 H, N(C$H_3$)$_2$], 2.18 [s, 6 H, N(C$H_3$)$_2$]. – $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$ = 148.9 (C$_{\mathrm{q(arom.)}}$), 148.6 (C$_{\mathrm{q(arom.)}}$), 148.3 (C$_{\mathrm{q(arom.)}}$), 148.0 (C$_{\mathrm{q(arom.)}}$), 145.9 (C$_{\mathrm{q(arom.)}}$), 145.7 (C$_{\mathrm{q(arom.)}}$), 139.8 (indenyl: C$^2$), 138.7 (indenyl: C$^2$), 138.3 (indenyl: C$^2$), 138.0 (indenyl: C$^2$), 129.6 (indenyl: C$^3$), 129.6 (indenyl: C$^3$), 129.4 (indenyl: C$^3$), 129.3 (indenyl: C$^3$), 125.3 (C$_{\mathrm{arom.}}$), 125.3 (C$_{\mathrm{arom.}}$), 124.2 (C$_{\mathrm{arom.}}$), 124.1 (C$_{\mathrm{arom.}}$), 124.0 (C$_{\mathrm{arom.}}$), 123.9 (C$_{\mathrm{arom.}}$), 123.9 (C$_{\mathrm{arom.}}$), 123.8 (C$_{\mathrm{arom.}}$), 123.8 (C$_{\mathrm{arom.}}$), 123.7 (C$_{\mathrm{arom.}}$), 121.3 (indenyl: C$^{5,8}$), 121.2 (indenyl: C$^{5,8}$), 121.2 (indenyl: C$^{5,8}$), 121.1 (indenyl: C$^{5,8}$), 49.4 (indenyl: C$^1$), 45.0 [N($C$H$_3$)$_2$], 44.8 [N($C$H$_3$)$_2$], 44.8 [N($C$H$_3$)$_2$], 39.1 [N($C$H$_3$)$_2$], 38.9 [N($C$H$_3$)$_2$], 38.8 [N($C$H$_3$)$_2$].

*1,2-Bis(dimethylamino)-1-(1-indenyl)-2-(3-indenyl)diborane(4)* (**4**): Cl(Me$_2$N)B$-$B(NMe$_2$)(3-ind) (750 mg, 2.88 mmol) was dissolved in toluene (10 ml) and the solution cooled to $-78$ °C. The vigorously stirred solution was added to a suspension of Li(ind) (350 mg), 2.87 mmol) in toluene (20 ml). The suspension was allowed to attain ambient temperature within 2 h, and stirring was continued for additional 41 h. After that time, the $^{11}$B-NMR spectrum revealed that no reaction had occurred. Addition of 0.2 ml of THF caused the formation of an almost clear solution which became turbid within a few minutes. The insoluble product was removed using a centrifuge and provided 0.13 g of an off-white material soluble in water (calcd. 0.12 g for LiCl). Toluene was evaporated from the toluene solution. The slightly yellow, partly crystalline residue was redissolved in hexane (15 ml) and the crystals that grew from the solution at −20°C were recovered after 2 weeks. − Yield: 0.91 g of **4** (93%), m.p. 136−138°C. − $C_{22}H_{26}B_2N_2$ (340.08): calcd. C 77.70, H 7.71, N 8.24; found C 76.41, H 7.69, N 8.02. − $^{11}B$ NMR (64 MHz, $C_6D_6$): δ = 48.4 [$h_{1/2}$ = 600 Hz, $B_2(NMe_2)_2$(-ind)$_2$] − $^1H$ NMR (270 MHz, $C_6D_6$): δ = 7.43 [d, 1 H, $^3J$(H,H) = 7.2 Hz, indenyl: $H^{5/8}$], 7.38 (d, 1 H, bad resolution, indenyl: $H^{5/8}$), 7.28 (m, 2 H, $H_{arom.}$), 7.16 (m, 4 H, $H_{arom.}$), 6.78 [d, 1 H, $^3J$(H,H) = 4.3 Hz, indenyl: $H^3$], 6.50 [d, 1 H, $^3J$(H,H) = 4.5 Hz, indenyl: $H^2$], 6.34 [t, 1 H, $^3J$(H,H) = 1.9 Hz, indenyl: $H^{11}$], 3.75 (s, 1 H, indenyl: $H^1$), 3.22 [d, 2 H, $^3J$(H,H) = 2.1 Hz, indenyl: $H^{12}$], 2.77 [s, 3 H, N(C$H_3$)], 2.65 [s, 3 H, N(C$H_3$)], 2.38 [s, 3 H, N(C$H_3$)], 2.37 [s, 3 H, N(C$H_3$)] − $^{13}C$ NMR (68 MHz, $C_6D_6$): δ = 150.4 (indenyl: $C^{13/18}$), 148.5 (indenyl: $C^{13/18}$), 148.3 (indenyl: $C^{4/9}$), 144.7 (indenyl: $C^{4/9}$), 139.4 (indenyl: $C^{11}$), 136.0 (indenyl: $C^{13}$), 129.4 (indenyl: $C^{11}$), 126.0 (indenyl: $C^{8/17}$), 125.3 (indenyl: $C^{8/17}$), 124.1 (indenyl: $C^{5/14}$), 123.9 (indenyl: $C^{7/16}$), 123.7 (indenyl: $C^{7/16}$), 122.9 (indenyl: $C^{6/15}$), 121.2 (indenyl: $C^{6/15}$), 49.4 (indenyl: $C^{10}$), 45.0 [−N($C$H$_3$)], 44.1 [−N($C$H$_3$)], 41.1 (indenyl: $C^{12}$), 40.3 [−N($C$H$_3$)], 39.1 [−N($C$H$_3$)].

*1,2-Bis(dimethylamino)-1,2-(3-indenyl)diborane(4)* (**5**): A solution of **3** (200 mg, 0.59 mmol) in toluene (10 ml) was heated to reflux for 48 h. All volatiles were then removed in vacuum leaving behind **5** in colourless microcrystaline form. − Yield: 200 mg of **5** (100%), m.p. 148−151°C. − $C_{22}H_{26}B_2N_2$ (340.04): calcd. C 77.70, H 7.71, N 8.24, found: C 75.91 H 7.76, N 8.12. − $^{11}B$ NMR (64 MHz, $C_6D_6$): δ = 48.3 [$h_{1/2}$ = 650 Hz, $B_2(NMe_2)_2(ind)_2$] − $^1H$ NMR (270 MHz, $C_6D_6$): δ = 7.43 [d, 2 H, $J^3$(H,H) = 7.1 Hz, indenyl: $H^{5,8}$], 7.30 (m, 4 H, indenyl: $H^{5,8}/H^{6,7}$), 7.12 [pseudo t, 2 H, $J^3$(H,H) = 7.5 Hz, indenyl: $H^{6,7}$], 6.34 [t, 2 H, $J^3$(H,H) = 1.9 Hz, indenyl: $H^2$], 3.22 [d, 4 H, $J^3$(H,H) = 1.9 Hz, indenyl: $H^3$], 2.90 [s, 6 H, N(C$H_3$)$_2$], 2.59 [s, 6 H, N(C$H_3$)$_2$] − $^{13}C$ NMR (68 MHz, $C_6D_6$): δ = 148.6 ($C^4$), 148.1 ($C^1$), 144.7 ($C^9$), 138.7 ($C^2$), 126.6 ($C^8$), 124.3 ($C^5$), 124.0 ($C^7$), 122.6 ($C^6$), 44.9 [N($C$H$_3$)$_2$], 41.2 ($C^3$), 40.5 [N($C$H$_3$)$_2$].

Table 2. Selected crystallographic data for the structures of **3** and **4** and data refering to data collectiion and structure refinement

| | **3** | **4** |
|---|---|---|
| Empirical formula | $C_{22}H_{26}B_2N_2$ | $C_{22}H_{26}B_2N_2$ |
| Formula mass | 340.07 | 340.07 |
| Crystal size [mm] | 0.15 × 0.2 × 0.3 | 0.06 × 0.3 × 0.7 |
| Crystal system | Monoclinic | Triclinic |
| Space group | *P*2(1)/*c* | *P*1bar |
| *a* [Å] | 15.8977(3) | 8.8466(1) |
| *b* [Å] | 7.5756(1) | 10.3594(2) |
| *c* [Å] | 16.8297(3) | 11.1737(3) |
| α [°] | 90 | 77.403(1) |
| β [°] | 93.323(1) | 85.428(1) |
| γ [°] | 90 | 83.222(1) |
| *V* [Å$^3$] | 2023.47(6) | 990.84(3) |
| *Z* | 4 | 2 |
| ρ(calcd.) [Mg/m$^3$] | 1.116 | 1.140 |
| μ [mm$^{-1}$] | 0.064 | 0.065 |
| *F*(000) | 728 | 364 |
| Index range | $-19 \leq h \leq 19$<br>$-9 \leq k \leq 9$<br>$-21 \leq l \leq 22$ | $-11 \leq h \leq 11$<br>$-13 \leq k \leq 12$<br>$-14 \leq l \leq 14$ |
| 2 θ [°] | 57.46 | 58.54 |
| *T* [K] | 193 | 193 |
| Refl. collected | 10800 | 5635 |
| Refl. unique | 3467 | 3048 |
| Refl. observed (4σ) | 2781 | 2640 |
| *R* (int.) | 0.0398 | 0.0249 |
| No. of variables | 339 | 263 |
| Weighting$_{x/y}$ scheme[a] | 0.0628/2.2247 | 0.0435/0.4055 |
| GOOF | 1.130 | 1.129 |
| Final *R* (4σ) | 0.0789 | 0.0474 |
| Final *wR*2 | 0.1812 | 0.1141 |
| Larg. res. peak [e/Å$^3$] | 0.509 | 0.331 |

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

*X-ray Structure Determinations:* Single crystals of compounds **3** and **4** were grown from hexane solutions at −20°C. The selected crystals were covered with perfluoroether oil, and mounted on a glass fibre, placed on the goniometer head and cooled with a gas flow of cold $N_2$. Preliminary dimensions of the unit cells were calculated from the reflection collected at four different settings of the crystal by recording 15 frames each with a CCD area detector. Data collection was performed with 10 s exposure time per frame by rotating the crystal by 0.3° in φ at two different χ settings. The data on 1350 frames were reduced by using the program SAINT[16] and the structures solved by direct methods using the XS and SHELX97 programs for structure solution and refinement. Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included as a riding model in the final cycles of refinement. Relevant data are presented in Table 3.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 101104. Copies of the data can be obtained free of charge on application to CCCD, 12 Union Park, Cambridge, UK, CB2 1EZ [Fax: int. code + 44(0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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☆ Dedicated to Prof. Dr. *H.-P. Boehm* on the occasion of his 70th birthday.

[1] H. Nöth, H. Sachdev, *Z. Naturforsch. Part B* **1997**, *52*, 1345-1348.

[2] [2a] A. Moezzi, R. A. Bartlett, P. P. Power, *Angew. Chem.* **1992**, *104*, 1075−1076; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1082. − [2b] A. Moezzi, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *144*, 2715−2717.

[3] R. Littger, N. Metzler, H. Nöth, M. Wagner, M. Thomann, *Chem. Ber.* **1994**, *127*, 1901−1908.

[4] R. Littger, H. Nöth, in preparation.

[5] R. Littger, Dissertation, University of Munich, **1995**.

[6] R. Littger, H. Nöth, M. Wagner, *Angew. Chem.* **1993**, *32*, 295−297; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 295−297.

[7] Part of the diploma thesis of W. Ponikwar, University of Munich, **1997**.

[8] H. Nöth, B. Wrackmeyer, *NMR Spectroscopy of Boron Compounds, NMR-Principles and Progress*, vol. 14 (Eds.: R. Diehl, E. Fluck, R. Kosfeld), Springer Publishers, Heidelberg, New York, **1973**.

[9] L. W. Hall, J. D. Odom, P. D. Ellis, *J. Am. Chem. Soc.* **1975**, *97*, 4527; B. Wrackmeyer, H. Nöth, *Chem. Ber.* **1976**, *109*, 1075−1088.

[10] H. Nöth, M. Wagner, *Chem. Ber.* **1991**, *124*, 1963−1972; H. Fußstetter, Dissertation, University of Munich, **1997**.

[11] A. Moezzi, M. M. Olmstead, P. P. Power, *J. Chem. Soc., Dalton Trans.* **1992**, 2429−2434.

[12] H. Grundke, P. Paetzold, *Chem. Ber.* **1971**, *104*, 1136−1146.

[13] P. Jutzi, A. Seufert, *Angew. Chem.* **1976**, *88*, 333−334; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 295−296.

[14] P. Jutzi. A, Seufert, *Chem. Ber.* **1979**, *112*, 2481−1487.

[15] H. Nöth, W. Meister, *Z. Naturforsch., Part B* **1962**, *17*, 714−718; R. Littger, N. Metzler, H. Nöth, M. Wagner, M. Thomann, *Chem. Ber.* **1994**, *127*, 1901−1908.

[16] *SHELXTL,* Vers. 5, Siemens X-Ray Analytical Instruments, **1994**.

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