Reaction of Borane in Tetrahydrofuran with 1,1,3,3-Tetramethyldisilazane and Cyclic Disilazanes – Competition Between N-Si and N-H Bond Cleavage

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Borane-THF Adduct, Disilazanes, Aminoboranes, Borazines

Borane in tetrahydrofuran (THF-BH3/THF; 1) reacts with 1,1,3,3-tetramethyldisilazane (2a) and the cyclic disilazanes HSiMe2(CH2)2SiMe2[n = 2 (2b), 3 (2e), 4 (2d)] first by formation of amine-borane adducts (3a-d), and then to give μ-aminodiboranes (6a-d) or cleavage of N-Si bonds (5a-d), depending on the reaction conditions, in agreement with the results obtained for the reaction of 1 with hexamethyldisilazane. Further transformations proceed via the N,N-disilylaminoboranes 6a-d. In the case of the reaction between 1 and 2b, it proved possible to convert 4b and/or 5b quantitatively into the mixed diamino borane 7b which served for the synthesis of N,N,N”-tris[(2-dimethylsilyl)ethyl]dimethylsilyl]borazine (8b). The N-H functions in 5b, 7b and 8b react with CO2CO3 to afford the respective Si-Co(CO)3 derivatives 11b-13b. All compounds were characterized by their 1H, 11B, 13C, 14/15N and 29Si NMR spectra.

Introduction

The reactions of ammonia and various primary and secondary amines with boranes containing one or more B-H functions yield aminoboranes by H2 elimination [1]. In the case of N-silylamines, the question of N-H elimination [11]. In the case of N-silylamines, the question of N-H elimination [11]. In the case of N-silylamines, the question of N-H elimination [11]. In the case of N-silylamines, the question of N-H elimination [11]. In the case of N-silylamines, the question of N-H elimination [11].

Results and Discussion

Syntheses

All four disilazanes 2a-2d react with 1 by formation of the amine-borane adducts 3a-3d, corresponding to (Me3Si)2NH-BH3, as shown in the Schemes 1 and 2. The conversion of the adduct 3a into the μ-aminodiboranes (6) 4a and 5a (Scheme 1b and 1c) proceeds under the same conditions and with the same product distribution as for (Me3Si)2NH-BH3 [5]. However, the attempted transformation of the μ-aminodiboranes (6) 4a and 5a to N,N,N”-tris(dimethylsilyl)borazine led mainly to decomposition (Scheme 1); the aminoborane 6a was identified in the complex reaction mixture as a transient intermediate by its 11B and 15N NMR data (Table 1). Obviously the steric demand mentioned borazine [4]. By repeating the latter reaction, we have recently shown that μ-aminodiboranes (6) are important intermediates, and that the reaction can be controlled to give the N-silylated borazine in high yield [5]. In this work we report on the reaction of borane in THF (1) with 1,1,3,3-tetramethyldisilazane 2a and five-, six- and seven-membered cyclic disilazanes 2b-2d. It was intended to find out whether there is a close analogy to the reactivity of hexamethyldisilazane [5] or to establish potentially different reaction pathways.

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Scheme 1.

Table I. $^{11}$B, $^{13}$C, $^{14}$N and $^{29}$Si NMR data[a] of compounds 2a - 6a.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\delta^{29}$Si</th>
<th>$\delta^{14}$N</th>
<th>$\delta^{11}$B</th>
<th>$\delta^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>-11.5</td>
<td>-364.7</td>
<td>-180</td>
<td>0.6</td>
</tr>
<tr>
<td>3a</td>
<td>2.7</td>
<td>-375.9</td>
<td>-19.7 [q]</td>
<td>-2.6/-3.1</td>
</tr>
<tr>
<td>4a</td>
<td>11.9 [b]</td>
<td>-398.8</td>
<td>-23.8 [td]</td>
<td>-2.0</td>
</tr>
<tr>
<td>5a</td>
<td>11.3</td>
<td>-393.3</td>
<td>-26.8 [td]</td>
<td>-3.5</td>
</tr>
<tr>
<td>6a</td>
<td>n.o. [d]</td>
<td>-258.2</td>
<td>47.6 [t]</td>
<td>n.o. [d]</td>
</tr>
</tbody>
</table>

[a] C$_6$D$_6$, 25°C; $h_1/2$ and coupling constants in Hz; [b] calculated from $J^{29}$Si, $^{14}$N by multiplication with $^{14}$N/$^{15}$N = 0.713; [c] $J^{14}$N,$^{14}$N = 48 + 5 Hz; [d] in mixture with various decomposition products.

of the Me$_2$SiH group is insufficient for the kinetic stabilization of other intermediates such as 7b (see Scheme 3) which is an important precursor of the borazine 8b.

Scheme 2 shows that $\mu$-aminodiboranes(6) such as 4b - d and 5b - d are stable intermediates when starting from the borane adducts of the cyclic disilazanes. However, the product distribution is rather different from that found for 4a and 5a. Compounds 5b and 4c, d can be isolated in pure state by distillation, whereas 4b/5b, 5c/4c and 5d/4d are always obtained as mixtures (see Scheme 2) which cannot be separated by distillation.

The five-membered rings in 2b, 3b and 4b seem to open much more readily than the larger rings in 2c,d, 3c,d and 4c,d. Thus all reactions which require ring opening (Scheme 3) proceed rather fast.
under mild reaction conditions for the compounds containing the five-membered ring. This is shown by monitoring the changes in the reaction solution in the $^{29}$Si NMR spectra, starting from 3b (Fig. 1). Within a few minutes a large variety of compounds is formed. Most species except of one [$δ^{29}$Si $+20.5$ ($δ^{11}$B $-21.4$)] were identified unambiguously by their complete NMR data sets (Table II) as indicated. The aminoboranes 6a - d are always present as intermediates. Interestingly, the mixed diaminoborane 7b is most readily formed (Scheme 3c, d) and left in high purity if all more volatile material is removed from the reaction mixture. The analogous compound 7c (Scheme 4c, d) is also obtained, although more severe reaction conditions are required. In contrast, the transformation of 6d into 7d under comparable conditions is less straightforward (Scheme 5). Compound 7d may be present in the resulting complex mixture.

In the $^{29}$Si NMR spectrum shown in Fig. 1, it was not possible to confirm the presence of the borazine 8b in the reaction solution. In order to obtain pure samples of 8b it is necessary first to isolate pure 7b which then reacts with 5b in a 1:1 molar ratio (Scheme 3e) to give 8b (see Fig. 2 for the $^{29}$Si NMR spectrum of the reaction solution prior to removal of all volatile material).

Attempts at the conversion of 7c into the analogous borazine 8c led only to decomposition (Scheme 4e). Since the formation of 7b proceeds...
Table II. $^{11}$B, $^{13}$C, $^{14}$N and $^{29}$Si NMR data$^a$ of compounds 2b - 8b and 10b - 13b.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\delta^{29}$Si ($^1J^{(29Si,^{14}N)}$)</th>
<th>$\delta^{14}$N ($\beta/\gamma$)</th>
<th>$\delta^{11}$B ($^1J^{(11B,^{1}H)}$)</th>
<th>-N(Me$_2$Si-CH$_2$)$_2$</th>
<th>NMe$_2$Si-CH$_2$-CH$_2$-SiMe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>12.8 [9.8] $^b$</td>
<td>-354.0 (140)</td>
<td>-2.2 $^c$</td>
<td>1.9</td>
<td>9.1</td>
</tr>
<tr>
<td>3b</td>
<td>29.8</td>
<td>-370.5 (215)</td>
<td>-20.8 (q)</td>
<td>[90]</td>
<td>-2.2 $^d$</td>
</tr>
<tr>
<td>4b</td>
<td>32.3</td>
<td>-386.0 $^c$</td>
<td>-24.2 (td)</td>
<td>[127] ($\beta$-$H$)</td>
<td>-0.5</td>
</tr>
<tr>
<td>5b</td>
<td>24.0 (N-Si)</td>
<td>-391.6 (125)</td>
<td>-25.8 (td)</td>
<td>[125] ($\beta$-$H$)</td>
<td>-3.7</td>
</tr>
<tr>
<td>6b</td>
<td>19.5 (t) [6.4]</td>
<td>-248.0 (18)</td>
<td>46.6 (t)</td>
<td>[112]</td>
<td>-0.2</td>
</tr>
<tr>
<td>7b</td>
<td>15.5 (NSi$_2$) [7.6] [b]</td>
<td>-302.5 [d]</td>
<td>32.3</td>
<td>1.1</td>
<td>9.3</td>
</tr>
<tr>
<td>8b</td>
<td>13.1 (t) [8.1] (NSi)</td>
<td>-254.8 (11)</td>
<td>31.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9b</td>
<td>13.5 (NSi$_2$)</td>
<td>-305.0 [d]</td>
<td>38.7</td>
<td>1.9</td>
<td>9.7</td>
</tr>
<tr>
<td>10b$^e$</td>
<td>13.5 (NSi$_2$)</td>
<td>-305.0 [d]</td>
<td>38.7</td>
<td>1.9</td>
<td>9.7</td>
</tr>
<tr>
<td>11b$^f$</td>
<td>22.9 (N-Si)</td>
<td>-392.0 (210)</td>
<td>-24.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12b$^f$</td>
<td>15.7 (NSi$_2$)</td>
<td>-300.1 [d]</td>
<td>32.5</td>
<td>1.1</td>
<td>9.2</td>
</tr>
<tr>
<td>13b$^f$</td>
<td>13.2 (t) [7.5] (N-Si)</td>
<td>-254.5 (15)</td>
<td>33.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] C$_6$D$_6$, 25°C; $\beta/\gamma$ and coupling constants in Hz; $^b$ calculated from $^1J^{(29Si,^{15}N)}$ by multiplication with $^1J^{(14N,^{15}N)} = 0.713$; $^c$ only in mixture with 5b, $\beta/\gamma$ was not measured; $^d$ overlapping signals, $\beta/\gamma$ was not measured. $^e$ $^1J^{(13C(Bu)}} = 21.1$ [br] (C-1'); 29.9 (C-2'); 26.9 (C-3'); 14.3 (C-4'); $^f$ $^1J^{(13C(CO)}} = 200.0$.

Fig. 2. $^{29}$Si NMR spectrum (refocused INEPT based on $^2J^{(29Si,^{1}H)}$ with $^1H$ decoupling) of the reaction solution (5b + 7b) prior to removal of volatile material. The $^{29}$Si-$^{14}$N spin spin coupling is clearly resolved. The inverted signals at low frequency belong to SiMe$_2$H groups with $^1J^{(29Si,^{1}H)} = 185$ Hz.

already at 25°C (Scheme 3c, g), the presence of THF as a solvent does not pose a problem. However, in the case of 6c, d (Scheme 4, 5) heating is required to induce further transformations. If THF is still present, the compounds 9c,d are formed readily [see also ref. [4] for (Me$_3$Si)$_2$NB(H)OBu] as a result of ether cleavage [eq. (1)]. Partial formation (≈ 20%) of 9d is already observed at room temperature when the adduct 3d reacts with 1 to give 4d.

In the reactions studied, N-H cleavage is preferred at lower temperatures, whereas cleavage of the N-Si bond is enforced at elevated temperatures. The product distribution is also a function of the ring size of the disilazane. The five-membered ring is opened most readily, and the seven-membered ring also opens somewhat more readily than the six-membered ring. Further reactions seem to be much slower however, and unknown side-reactions dominate the product distribution.
Reaction of aminoborane 7b with n-butyllithium

The reaction of 7b with n-butyllithium proceeds smoothly by elimination of LiH to give the aminoborane 10b [eq. (2)]. Under the reaction conditions, N-lithiation does not take place. Instead a borate must be considered as an intermediate which is less stable than the aminoborane 10b where BN(pp) interactions contribute to its stability.

\[
\text{C_3N_3^+Cl_2} + \text{Li} \rightarrow \text{C_3N_3^+Li} + \text{Cl}_2
\]

It is known that borazines with B-H functions can be converted into B-organo substituted borazines by treatment with Grignard reagents, or, less efficiently, by reaction with organolithium compounds [6].

Reaction of \( \mu \)-aminodiborane(6) 5b, aminoborane 7b and borazine 8b with octacarbonyldicobalt \([\text{Co}_2(\text{CO})_8] \)

In order to test the potential application of the new silanes with Si-H functions in hydrosilylation reactions [7], their reactivity towards \( \text{Co}_2(\text{CO})_8 \) was studied. As shown in Scheme 6, the reactions proceed smoothly to give the tetracarbonyldicobalt derivatives 11b, 12b and 13b. Only in the case of 11b, a small amount of unidentified side-products was observed, possibly a result of the reaction of 5b with HCo(CO)_4 which is present as an intermediate.

NMR spectroscopic results

\( ^{11} \text{B}, ^{13} \text{C}, ^{14,15} \text{N} \) and \( ^{29} \text{Si} \) NMR data of the disilazanes 1a-d and the products obtained from their reactions with borane in THF are given in Tables I - IV. All \( ^{1} \text{H} \) NMR data are listed in the experimental part. The mutual assignments of many \( ^{11} \text{B}, ^{14} \text{N} \) and \( ^{1} \text{H} \) resonances were made by selective \( ^{1} \text{H}[^{11} \text{B}] \) and \( ^{1} \text{H}[^{14} \text{N}] \) heteronuclear double resonance experiments. All \( ^{11} \text{B} \) values are in the range expected for the particular structural fragments [8]. The same is true for the \( ^{14} \text{N} \) data [9]. \( ^{29} \text{Si} \) NMR spectra were recorded using the refocused INEPT pulse sequence with \( ^{1} \text{H} \) decoupling [10]. Although some of the \( ^{29} \text{Si} \) NMR signals were broad owing to partially relaxed scalar \( ^{29} \text{Si} - ^{14} \text{N} \) spin spin coupling, monitoring of the reactions was conveniently achieved by \( ^{29} \text{Si} \) NMR (Figs. 1 and 2), together with \( ^{11} \text{B} \) and \( ^{14} \text{N} \) NMR spectroscopy. The \( ^{29} \text{Si} \) nuclei become typically deshielded if they are attached to an ammonium type nitrogen atom [5], and shielding is observed for \( ^{29} \text{Si} \) nuclei linked to a tricoordinate nitrogen atom as in N-silylamines [11] or N-silylaminoboranes [2, 5].

In some cases, e.g. 6b and 8b, the coupling constants \( ^{1} J(^{29} \text{Si}, ^{14} \text{N}) \) can be measured directly from the \( ^{29} \text{Si} \) NMR spectrum (Fig. 2), since the \( ^{14} \text{N} \) quadrupolar relaxation rate is rather slow. It seems that this happens frequently if one or two alkylsilyl and a boryl group are attached to the nitrogen atom [12, 13], indicating that the electric field gradient at the \( ^{14} \text{N} \) nuclei in such surroundings is close to zero. Similar to the situation in \( \text{N}, \text{N}', \text{N}'' - \text{tris}(\text{trimethylsilyl}) \)borazine [12], the \( ^{14} \text{N} \) NMR spectra of the borazines 8b (h_1/2 = 11 Hz) and even 13b (h_1/2 = 15 Hz) show extremely sharp lines, in spite of these large molecules having predictably slow tumbling rates in solution. The magnitude of the coupling constants \( ^{1} J(^{29} \text{Si}, ^{14,15} \text{N}) \) is found in the expected range [2, 5, 12 - 14].

Experimental

All preparative work and handling of samples was carried out under \( \text{N}_2 \) atmosphere, using dry glassware and
Table III. $^{11}$B, $^{13}$C, $^{14}$N and $^{29}$Si NMR data$^{[a]}$ of compounds 2c - 7c and of 9c.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\delta^{29}$Si $[^{11}J^{(29)}$Si, $^{14}$N]</th>
<th>$\delta^{14}$N (h$_{1/2}$)</th>
<th>$\delta^{11}$B $[^{11}J^{(11)}$B, $^{1}H]$</th>
<th>$\delta^{13}$C $\text{-N(Me}<em>{2}\text{Si-CH}</em>{2}-\text{CH}_{2}\text{-}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2c</td>
<td>2.9 [8.3] [b]</td>
<td>-357.3 (190)</td>
<td>-20.6 (q)</td>
<td>2.3</td>
</tr>
<tr>
<td>3c</td>
<td>19.6</td>
<td>-366.0 (220)</td>
<td>-24.7 (td)</td>
<td>-1.9/-3.6</td>
</tr>
<tr>
<td>4c</td>
<td>23.8</td>
<td>-391.9 (55)</td>
<td>-16.9</td>
<td>17.3</td>
</tr>
<tr>
<td>5c[f]</td>
<td>22.6 (N-Si)</td>
<td>-391 [c]</td>
<td>-25.8 (td)</td>
<td>n.o.</td>
</tr>
<tr>
<td>6c</td>
<td>9.2 (t) [6.0]</td>
<td>-251.4 (13)</td>
<td>47.5 (t)</td>
<td>1.9/-3.6</td>
</tr>
<tr>
<td>7c[f]</td>
<td>3.9 (NSi)</td>
<td>-306.4 [d]</td>
<td>33.3</td>
<td>17.3</td>
</tr>
<tr>
<td>9c[g]</td>
<td>5.2</td>
<td>-302.7 (240)</td>
<td>35.5 [83]</td>
<td>1.9</td>
</tr>
</tbody>
</table>

[a] C$_6$D$_6$, 25°C; $h_{1/2}$ and coupling constants in Hz; [b] calculated from $^{11}J^{(29)}$Si,$^{15}$N by multiplication with $^{14}$N/$^{15}$N $= 0.713$; [c] only in mixture with 4c, $h_{1/2}$ was not measured; [d] overlapping signals, $h_{1/2}$ was not measured; [e] $^{13}$C(CHNMe) $= -3.4$, (HNSiMe) $= 18.2$, (HNSiCH$_2$) $= 27.0$, (CH$_2$SiH) $= 25.8$, (CH$_2$SiH) $= 14.1$, (HSiMe) $= -4.3$; [f] in mixture with various decomposition products; [g] $^{13}$C(OBu) $= 68.6$ (C-1); 34.6 (C-2); 19.3 (C-3); 14.0 (C-4).

Table IV. $^{11}$B, $^{13}$C, $^{14}$N and $^{29}$Si NMR data$^{[a]}$ of compounds 2d - 6d and of 9d.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\delta^{29}$Si $[^{11}J^{(29)}$Si, $^{14}$N]</th>
<th>$\delta^{14}$N (h$_{1/2}$)</th>
<th>$\delta^{11}$B $[^{11}J^{(11)}$B, $^{1}H]$</th>
<th>$\delta^{13}$C $\text{-N(Me}<em>{2}\text{Si-CH}</em>{2}-\text{CH}_{2}-\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2d</td>
<td>4.6 [8.3] [b]</td>
<td>-356.4 (160)</td>
<td>-19.6 (q)</td>
<td>1.6</td>
</tr>
<tr>
<td>3d</td>
<td>20.0</td>
<td>-374.0 (150)</td>
<td>-24.0 (td)</td>
<td>1.3/-2.6</td>
</tr>
<tr>
<td>4d</td>
<td>24.0</td>
<td>-363.0 (60)</td>
<td>-25.5 [c]</td>
<td>17.7</td>
</tr>
<tr>
<td>5d[f]</td>
<td>22.4 (N-Si)</td>
<td>-393 [c]</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>6d</td>
<td>12.8 (t) [6.2]</td>
<td>-247.5 (18)</td>
<td>47.3 (t)</td>
<td>1.8</td>
</tr>
<tr>
<td>9d[g]</td>
<td>8.2</td>
<td>-300.6 (290)</td>
<td>32.9</td>
<td>15.4</td>
</tr>
</tbody>
</table>

[a] C$_6$D$_6$, 25°C; $h_{1/2}$ and coupling constants in Hz; [b] calculated from $^{11}J^{(29)}$Si,$^{15}$N by multiplication with $^{14}$N/$^{15}$N $= 0.713$; [c] only in mixture with 4c, $h_{1/2}$ was not measured; [d] overlapping signals, $h_{1/2}$ was not measured; [e] $^{13}$C(CHNMe) $= -3.4$, (HNSiMe) $= 18.2$, (HNSiCH$_2$) $= 27.0$, (CH$_2$SiH) $= 25.8$, (CH$_2$SiH) $= 14.1$, (HSiMe) $= -4.3$; [f] in mixture with various decomposition products; [g] $^{13}$C(OBu) $= 68.6$ (C-1); 34.6 (C-2); 19.3 (C-3); 14.0 (C-4).

Dry solvents. Borane in THF [15] and the cyclic disilazane BH$_3$ adducts 3a - d were prepared as described. 2d, in analogy to literature procedures [16a]. 3a, 3b, n-BuLi in hexane (1.6 M) and Co$_2$(CO)$_8$ were commercial products and used without further purification. El-MS spectra (70 eV): VARIAN-MAT CH 7 with direct inlet. IR spectra: Perkin-Elmer 983 G (hexane solution). NMR spectra: Jeol EX270 ($^1$H, $^{13}$C) and Bruker ARX 250 ($^1$H, $^{15}$B, $^{13}$C, $^{14}$N, $^{15}$N, $^{29}$Si, $^{119}$Sn); chemical shifts are given with respect to Me$_4$Si ($^1$H(CHC$_1$/CDCl$_3$) 7.24, (CD$_2$)$_6$ 7.15; $^{13}$C(CDCl$_3$) 77.0, (CD$_2$)$_6$ 128.0; $^{29}$Si: $\Xi^{(29)}$Si $= 19.867184$ MHz), Et$_2$O-BF$_3$ [$^{11}$B: $\Xi^{(11)}$B $= 32.083971$ MHz] and neat MeNO$_2$ [$^{13}$N: $\Xi^{(13)}$N $= 7.223656$ MHz; $^{15}$N: $\Xi^{(15)}$N $= 10.136767$ MHz].

1. Disilazane BH$_3$ adducts 3a - d

To a stirred solution of 30 mmol of 1 at r.t. 30 mmol of the respective disilazane (2a - d) without any solvent were added. Immediate removal of THF in vacuo left the adducts 3a - d in quantitative yield as white solids. 3a decomposes within 1h into 2a, and 4a, 3b decompose within several minutes. 3a (decomposition at 25°C): $^1$H $[^{11}J$H, $^{13}$B]$= 4.33$ (m) (SiH); 2.58 [br] (NH); 1.55 [br] (BH$_3$); 0.27 (d), 0.25 (d) [3.2] (CH$_2$). 3b (decomposition at 25°C) $^1$H $[^{11}J$H, $^{13}$B]$= 3.39$ [br] (NH); 1.68 [br] (BH$_3$); 0.82 (m) (CH$_2$); 0.30 (s) / 0.25 (s) (CH$_3$). 3c [in m. 55°C (decomposition)]; $^1$H $[^{11}J$H, $^{13}$B]$= 1.58$ [br] (BH$_3$); 1.96 - 1.80 (m) ...
30 mmol of 1 were added to 30 mmol of the respective adduct 3a–d. The reaction mixture was stirred for 12h. The product distribution depends on the reaction temperature (see Schemes 1, 2). Then the solvent was removed at a pressure of 50 Torr. Compounds 4a, 5b, 4c and 4d were purified by distillation. 4a (b. p. 60°C/50 Torr): \( \text{H}^{11}\text{B} \) NMR (CD\(_2\)Cl\(_2\), 25°C): \( \delta \text{H} [\text{J}(\text{H}, \text{H})] = \text{4.25 (s)} \) (BH); 3.72 (t) (\( \text{OCH}_2\text{CCH}_2\text{SiH}_3 \)).

Isolation from the reaction mixture was not possible. 1 H \( \{^{11}\text{B}\} \) NMR (CD\(_2\)Cl\(_2\), 25°C): \( \delta \text{H} [\text{J}(\text{H}, \text{H})] = 3.85 (m) \) (SiH); 1.35 (m) (BH). 5c (only in mixture with 4c): \( \text{H}^{11}\text{B} \) NMR (CD\(_2\)Cl\(_2\), 25°C): \( \delta \text{H} [\text{J}(\text{H}, \text{H})] = 1.98 \) (m–H); 1.35 (d) [3.6] (BH); 0.80 (m) (H-3/H-5); 0.22 (s) (CH\(_3\)); -0.64 (quat) (\( \mu \)-H).

6. N,N',N'-Tris-[(2'-dimethylsilylethyl)dimethylsilyl]amino-(2,2,5,5-tetramethyl-1,2,5-azadisilacyclopent-1-yl)borazine 8b

A mixture of 3.3 g (10 mmol) of 7b and 2.0 g (10 mmol) of 5b without any solvent was stirred at 90°C for 2 d. After removing all volatile material in vacuo at 100°C 4.6 g (90%) of pure 8b was obtained as a colourless oil.

7. Butoxy-(2,2,6,6-tetramethyl-1,2,6-azadisilacyclohex-1-yl)borane 9c and butoxy-(2,2,7,7-tetramethyl-1,2,7-azadisilacyclohept-1-yl)borane 9d

A mixture of 1.73 g (10 mmol) of 2c and 2.0 g (10 mmol) of 4c without any solvent was stirred at 80°C for 3 h. After removing all volatile material in vacuo 3.6 g (100%) of pure 7c were left as a colourless oil (b. p. 123°C/10 Torr). Further purification was not necessary. 1 H \( \{^{11}\text{B}\} \) NMR (CD\(_2\)Cl\(_2\), 25°C): \( \delta \text{H} [\text{J}(\text{H}, \text{H})] = 5.50 (s) \) (BH).
1.55 (m) (SiCH₂CH₃); 1.45 (m) (OCH₂CH₃); 1.30 (m) (CH₂CH₃); 0.85 (t) [7.4] (CH₂); 0.78 (m) (SiCH₃); 0.13 (s) (SiCH₃).

8. Butyly-(2’-dimethylsilylethyl)dimethylsilylamino-(2,2,5,5-tetramethyl-1,2,5-azadisilacyclopent-1-yl)-borane 10b

0.63 ml (1 mmol) of n-BuLi (1.6 M in hexane) were added to a stirred solution of 0.33 g (1 mmol) of 7b in 5 ml of hexane at -78°C. While warming up to room temperature the mixture was stirred for 12h. Removing of the solvent in vacuo gave 3.9 g of 10b (100%, including dissolved LiH) as a colourless oil. 1H {11B} NMR (CöD₆, 25°C): $^{11}H$ [7 (H, H)] = 4.07 (m) (SiH); 2.57 [br] (s) (NH); 1.44 (m) (H -1'/H -2'); 0.97 (m) (H-3'/H-4'); 0.73 (s) (SiCH₃); 0.56 (m) (N(H)SiCH₂); 0.22 (s) (SiCH₃); 0.14 (s) (N(H)SiCH₃); 0.05 (d) [3.4] (HSiC₂).

9. (Tetracarbonylcobalt)dimethylsilyl derivatives 11c-13c

0.26 g (1.4 mmol) of 5b or 0.46 g (1.4 mmol) of 7b or 0.24 g (0.47 mmol) of 8b, respectively, in 3 ml of pentane were added slowly to a solution of 0.25 g (0.7 mmol) of Co(CO)₅ in 10 ml of pentane at 0°C. The reaction mixture was stirred at r.t. for 1h. Removing of the solvent left the desired products as violet oils, 11b: $^{11}H$ [7 (H, H)] = 2.62 [br] (NH); 1.50 (m) / 1.40 (m) (HSH); 0.69 (m) (CoSiCH₃); 0.21 (m) (N(H)SiCH₃); 0.10 (m) (N(H)SiCH₃); 0.05 (d) [3.4] (HSH). IR [cm⁻¹]: 3250 (ν-NH); 3153/ 2955/ 2917 (1/-CH); 2327 (1/-BH); 2098/ 1989/ 1895/ 1861 (i/-C=O).

12b: $^{11}H$ [7 (H, H)] = 4.49 (d) [11.3] (BH); 2.66 [br] (NH); 1.03 (m) (CoSiCH₃); 0.72 (m) (SiCH₃/5-ring); 0.57 (s) (CoSiCH₃); 0.21 (s) (N(H)SiCH₃); 0.16 (s) (SiCH₃/5-ring); 0.11 (s) (N(H)SiCH₃). IR [cm⁻¹]: 3250 (ν-NH); 3153/ 2955/ 2917 (1/-CH); 2327 (1/-BH); 2098/ 1989/ 1895/ 1861 (1/-C=O).

13b: $^{11}H$ = 4.95 (s) (BH); 1.05 (m) (CoSiCH₂); 0.72 (m) (NHSiCH₂); 0.52 (s) (CoSiCH₃); 0.31 (s) (N(H)SiCH₃).

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