

## *Electronic Supplementary Information*

### **Substantial Emission of NH<sub>3</sub> During Thermal Decomposition of Sodium Amidoborane, NaNH<sub>2</sub>BH<sub>3</sub>**

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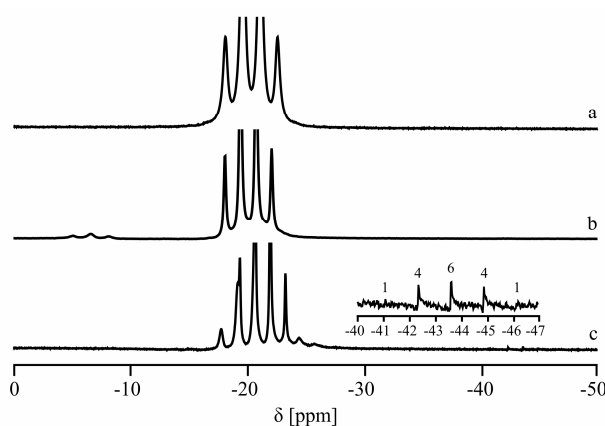
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#### 1. Remarks on solubility of various phases in THF.

Unfortunately, samples of SAB heated to 110°C and 250°C as well as Na<sub>2</sub>NH are sparingly soluble in d<sub>8</sub>-THF and their spectra will not be discussed here in detail (the <sup>11</sup>B NMR spectra contain only a small very broad signal at *ca.* -3.3 ppm while <sup>1</sup>H NMR spectra are dominated by signals from impurities). Other solvents were also tested (CD<sub>3</sub>CH, D<sub>2</sub>O) but they turned to chemically react with the samples. It should therefore be realized that intensity of various peaks appearing in the NMR spectra is not directly related to relative abundance of various phases in our samples, but rather to their solubilities in THF.

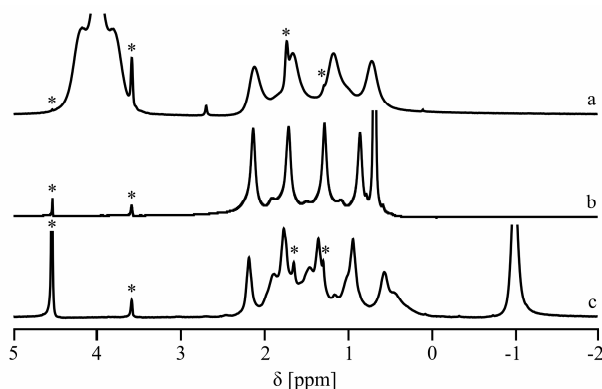
The recorded <sup>11</sup>B NMR and <sup>1</sup>H NMR spectra of various etherates are shown in Figures S1 and S2, respectively. The corresponding numerical data (chemical shift δ, <sup>1</sup>J(E,<sup>1</sup>H) magnetic coupling constant for the adjacent H and E nuclei, E=B, N) are shown in Table S1.

#### 2. The <sup>11</sup>B NMR spectra.



**Fig. S1** <sup>11</sup>B NMR spectra collected for: a) AB; b) as-synthesized SAB (25°C); c) SAB heated to 55°C. All spectra have been cut at the largest peaks to better expose the lower-intensity regions.

**3. The  $^1\text{H}$  NMR spectra.**



**Fig. S2**  $^1\text{H}$  NMR spectra collected for: a) AB; b) as-synthesized SAB SAB (25°C); c) SAB heated to 55°C. Signals coming from traces of NaH and its impurities and from non-deuterated solvent (\*) can be seen. Two spectra have been cut at the largest peak to expose the less-intense range.

**4. Chemical shifts and magnetic coupling constants.**

**Table S1.** Chemical shifts  $\delta$  [ppm] and magnetic coupling constants  $J$  [Hz] for signals appearing in the  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of AB, as-synthesized SAB (25°C) and for sample of SAB heated to 55°C and then cooled down to room temperature. Abbreviations: sin = singlet, tri = triplet, qua = quartet, qui = quintet, NA = not applicable. AB98 = 98% AB from Aviator, AB 90 = 90% AB from Aldrich. E stands for N or B.

<b>AB 98</b>		$^1\text{H}$ NMR		$^{11}\text{B}$ NMR	
<b>25°C</b>		$\delta$ [ppm]	$^1J(\text{H,E})$ [Hz]	$\delta$ [ppm]	$^1J(\text{B,H})$ [Hz]
BH <sub>3</sub>	qua	1.413	94	qua	-20.383
BH <sub>4</sub>	qua	–	–	qui	–
NH <sub>3</sub>	sin	3.988	37	NA	NA
<b>AB 90</b>		$^1\text{H}$ NMR		$^{11}\text{B}$ NMR	
<b>25°C</b>		$\delta$ [ppm]	$^1J(\text{H,E})$ [Hz]	$\delta$ [ppm]	$^1J(\text{B,H})$ [Hz]
BH <sub>3</sub>	qua	1.414	93	qua	-20.383
BH <sub>4</sub>	qua	-0.204	82	qui	-36.028
NH <sub>3</sub>	tri	3.990	37	NA	NA
<b>NaH</b>		$^1\text{H}$ NMR		$^{11}\text{B}$ NMR	
<b>25°C</b>		$\delta$ [ppm]	$^1J(\text{H,E})$ [Hz]	$\delta$ [ppm]	$^1J(\text{H,B})$ [Hz]
NaH	sin	1.729	NA	NA	NA
<b>SAB</b>		$^1\text{H}$ NMR		$^{11}\text{B}$ NMR	
<b>25°C</b>		$\delta$ [ppm]	$^1J(\text{H,E})$ [Hz]	$\delta$ [ppm]	$^1J(\text{B,H})$ [Hz]
BH <sub>2</sub>	qua	–	–	tri	-6.687
BH <sub>3</sub>	qua	1.484	85	qua	-20.094
BH <sub>4</sub>	qua	–	–	qui	–
NH <sub>2</sub>	sin	0.673	20	NA	NA
<b>SAB</b>		$^1\text{H}$ NMR		$^{11}\text{B}$ NMR	
<b>55°C</b>		$\delta$ [ppm]	$^1J(\text{H,E})$ [Hz]	$\delta$ [ppm]	$^1J(\text{B,H})$ [Hz]
BH <sub>2</sub>	qua	1.244	85	tri	-24.483
BH <sub>2</sub>	–	–	–	tri	-19.230
BH <sub>3</sub>	qua	1.553	83	qua	-21.343
BH <sub>4</sub>	qua	-0.545	81	qui	-43.643
NH <sub>2</sub>	sin	0.443	–	NA	NA
NH <sub>3</sub>	sin	-1.007	–	NA	NA

### 5. Analysis of the spectra.

Most of signals appearing in the  $^{11}\text{B}$  spectra are split into multiplets, quintet for [BH<sub>4</sub>], quartet for [BH<sub>3</sub>] and triplet for [BH<sub>2</sub>] functional groups (Table S1). The  $^{11}\text{B}$  NMR spectrum of AB (Figure 8) contains only a quartet at -20.38 ppm (BH<sub>3</sub>); the smaller-purity AB (90%) yields also small quintet at -36.03 ppm (trace BH<sub>4</sub><sup>-</sup> species). The small [BH<sub>4</sub>] signal cannot come from the diammoniate of diborane, DADB = [(BH<sub>2</sub>)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>(BH<sub>4</sub><sup>-</sup>), since it is not accompanied by the corresponding triplet from the [BH<sub>2</sub>] group.

The spectrum of freshly prepared SAB consists of a strong quartet at -20.09 ppm (BH<sub>3</sub>) and a weaker triplet at -6.69 ppm (BH<sub>2</sub>). Main signal from the BH<sub>3</sub> group downshifts only slightly upon H→Na substitution; similar effect has been observed in the MAS  $^{11}\text{B}$  NMR spectra for solid AB and SAB.<sup>1</sup> Again, the small [BH<sub>2</sub>] signal cannot come from the hypothetical sodium analogue of DADB = [(BH<sub>2</sub>)(NH<sub>2</sub>Na)<sub>2</sub>]<sup>+</sup>(BH<sub>4</sub><sup>-</sup>), since it is not accompanied by the corresponding quintet from the [BH<sub>4</sub>] group; an unidentified BH<sub>2</sub> group-containing THF-soluble minority phase must be responsible for the appearance of this signal.

$^{11}\text{B}$  NMR spectrum of SAB heated to 55°C and cooled down to room temperature is different to the one collected for the as-prepared sample (Figure S1) It contains a strong quartet at -21.34 ppm) from BH<sub>3</sub> group, two weak triplets at -19.23 ppm and -24.48 ppm (BH<sub>2</sub>) and a very weak quintet at -43.64 ppm (BH<sub>4</sub>) (Table S1). Presence of new signals from BH<sub>2</sub> and BH<sub>4</sub> groups as compared to freshly-prepared SAB indicates occurrence at

55°C of some endothermic intermolecular rearrangement reaction associated with no mass loss, which precedes thermal decomposition of SAB (see section 1 of the main paper). We notice that the appearance of similar signals from [BH<sub>2</sub>] groups (downshifted with respect to signals from [BH<sub>3</sub>] group) and [BH<sub>4</sub>] groups (upshifted) was also observed in the MAS <sup>11</sup>B NMR study of thermal decomposition of AB. Their appearance in the spectra of SAB may indicate similarity of principal mechanisms of thermal decomposition for AB and SAB.

The <sup>1</sup>H NMR spectra (Figure S2) of SAB are more complicated than the <sup>11</sup>B spectra, largely due to coupling between protons and two different isotopes of B. Coupling with <sup>11</sup>B (I=3/2, 80%) yields quartets, while coupling with <sup>10</sup>B (I=3, 20%) yields septets (usually the coupling constants differ a lot), and the two multiplets mutually overlap. In the analysis below we will not discuss the septets. In addition, signals from protons attached to N are often absent probably due to their much faster relaxation times or very fast exchange dynamics.

The <sup>1</sup>H NMR spectrum of as-prepared SAB consists of a quartet centered at 1.484 ppm from the [BH<sub>3</sub>] group (<sup>1</sup>J(H,B) of 85 Hz) and a singlet at 0.673 ppm from the [NH<sub>2</sub>] group; trace splitting of the latter with the <sup>1</sup>J(H,N) of 20 Hz is captured in our experiments. The spectrum gets more complicated as SAB is heated to 55°C and cooled down to room temperature. The main [BH<sub>3</sub>] signal is substantially upshifted (by nearly 0.07 ppm), which suggests that the [BH<sub>3</sub>] group is now found in a new chemical environment. In addition, new signals from [BH<sub>2</sub>] group appear at 1.244 ppm (corresponding to the signal in the <sup>11</sup>B NMR at -24.483 ppm); a very small quartet from the trace BH<sub>4</sub><sup>-</sup> anions is also found at -0.545 ppm (corresponding to the signal in the <sup>11</sup>B NMR at -43.64 ppm).

The large signal from the [NH<sub>2</sub>] group originally at 0.673 ppm disappears (a small singlet is found at a comparable chemical shift of 0.443 ppm) but a new very intense and substantially downshifted signal appears at -1.007 ppm. The dramatic change of the chemical shift of [NH<sub>x</sub>] protons indicate that this functional group is found in a completely new chemical environment. Since the [NH<sub>x</sub>] protons are now more shielded than for pristine SAB, we anticipate that they might be embedded in an imide [NH] group which is much more basic than the amide [NH<sub>2</sub>] one. The chemical species which contains this moiety must be much more soluble in THF than parent SAB since the former one predominates the <sup>1</sup>H NMR spectra; recollect, SAB is a major crystalline phase as evidenced by XRDPs (section 3 of main paper). Unfortunately, direct comparison with source of imide anions (Na<sub>2</sub>NH) is prohibited by scarce solubility of the latter in THF.

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<sup>i</sup> A. C. Stowe, W. J. Shaw, J. C. Linehan, B. Schmid, and T. Autrey, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1831.