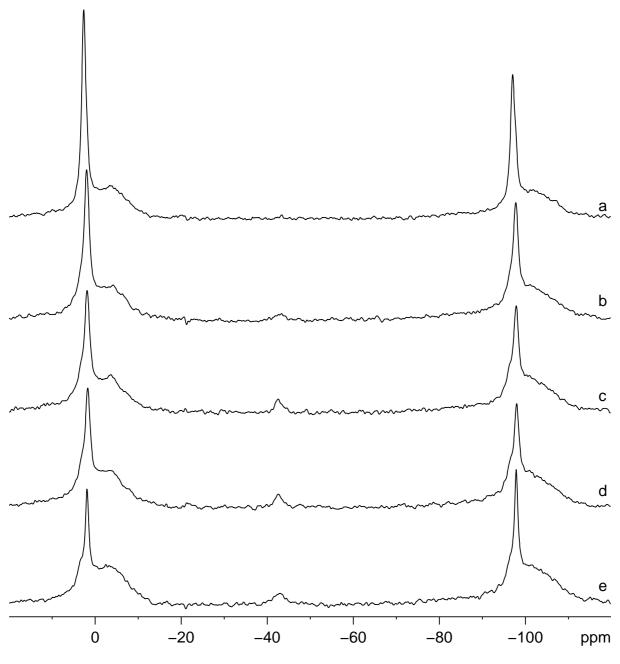
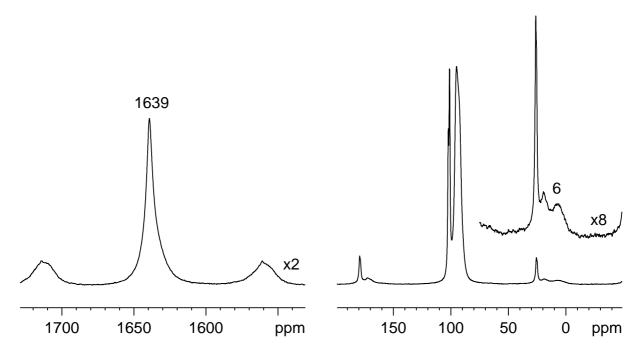
## **Supporting Information**

Formation of  $Al_2H_7^-$  anions – Indirect evidence of volatile  $AlH_3$  on sodium alanate using solid-state NMR spectroscopy

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**Fig. S1**  $^{27}$ Al MAS NMR spectra of a 10:1 mixture of NaAlH<sub>4</sub> and 18C6 after ball-milling recorded (a) at 311 K, (b) after 10 min at 338 K, (c) after 100 min at 338 K, (d) after additional 10 min at 343 K, and (e) after overnight cooling to 311 K. These are the same spectra as in Fig. 1, but showing the region with the growing line of Na<sub>3</sub>AlH<sub>6</sub> at -42.5 ppm.



**Fig. S2** <sup>27</sup>Al MAS NMR spectra of a 10:1:1 mixture of NaAlH<sub>4</sub>, 18C6 and polymeric AlH<sub>3</sub> after ball-milling at T = 77 K recorded at 304 K and  $v_{MAS} = 10$  kHz. This is the same spectrum as in Fig. 4a, but showing the regions with the lines of metallic aluminium (at about 1639 ppm, left) and the polymeric AlH<sub>3</sub> (at about 6 ppm, inset on the right).