Supplementary Information

Dry Mechanochemical Synthesis of Alane from LiH and AlCl₃

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Table S1: Integrated relative peak intensities obtained from the ²⁷Al DPMAS spectra collected for Stages 1-3. Note that Al^{IV} corresponds to the signal centered at ~95 ppm (comprising LiAlCl₄ and LiAlH₄), while Al^{VI} corresponds to that at ~13 ppm (attributed to AlH₃ and/or AlCl_{3-x}H_x-type species).

Sample	Al ^{ıv} (%)	AI ^{VI} (%)	AICI₃ (%)	Li ₃ AlH ₆ (%)
9:1, 16 min	83.6	5.4	9.4	1.6
9:1, 24 min	73.2	na	3.1	23.7
9:1, 48 min	9.5	na	na	90.5
4:1, 8 min	66.3	8.4	8.2	17.1
4:1, 48 min	97.3	na	na	2.7
3:1, 10 min	45.2	54.8	na	na
3:1, 48 min	na	100.0	na	na



Fig S1: ²⁷Al DPMAS spectra of the 4:1 LiH:AlCl₃ reaction after 8 min of milling when properly isolated within the MAS rotor (black) and after inadvertent exposure to air (red). Also shown is a reference spectrum corresponding to α -alumina (Al₂O₃; gray), which was collected to confirm the identity of the contamination peak indicated by the arrow. To ensure adequate protection of the samples during analysis, additional silicon O-rings were installed on "gas-tight" caps and spacers (as purchased from Agilent Technologies, Inc.). When this approach was combined with careful packing protocols (executed within an argon-filled glove box), alumina could not be detected, even after the packed rotor was allowed to sit in ambient air for more than 8 hours.



Fig S2: Powder X-ray diffraction patterns of the 9LiH:1AlCl₃ mixture ball-milled under various applied pressures (48 min, 300 rpm, b:p=140:1). Samples milled below 300 bar show the formation of metallic Al (*).



Fig. S3: ²⁷Al DPMAS reference spectra of LiAlH₄, LiAlCl₄, and AlCl₃. The LiAlH₄ and AlCl₃ materials correspond to the as-purchased reagents, while the LiAlCl₄ material was prepared by ball-milling a 1LiCl:1AlCl₃ mixture in a SPEX mill under an argon atmosphere for 30–40 min. Note that the signal at -2 ppm seen in the LiAlCl₄ spectrum results from unreacted AlCl₃ precursor.



Fig. S4: ²⁷Al 5QMAS spectra of pristine (A) LiAlH₄ and (B) LiAlCl₄ obtained at 14.1 T.



Fig. S5: Powder X-ray diffraction patterns of products obtained after complete desorption (see Fig. 5 in the main text) of as-synthesized samples with (a) 9:1, (b) 4:1 and (c) 3:1 molar ratio of LiH and AlCl₃. (*, metallic Al; #, LiH, Bragg peaks of LiCl are unmarked). All samples analysed using TPD were obtained after 48 min of ball-milling.



Fig. S6: Powder X-ray diffraction patterns showing the comparison of progress of reaction in 3:1(bottom) and 9:1(top) LiH:AlCl₃ ratios during the initial 20 min of milling. All samples were milled under 350 bar H₂ at 300 rpm and b:p=140:1.



Fig. S7: SSNMR (²⁷Al DPMAS and ²⁷Al{¹H} CPMAS) spectra obtained for a sample having the starting ratio of 3:1 LiH:AlCl₃ after ball-milling for 20 h under 350 bar H₂ at 150 rpm with a b:p of ~140.