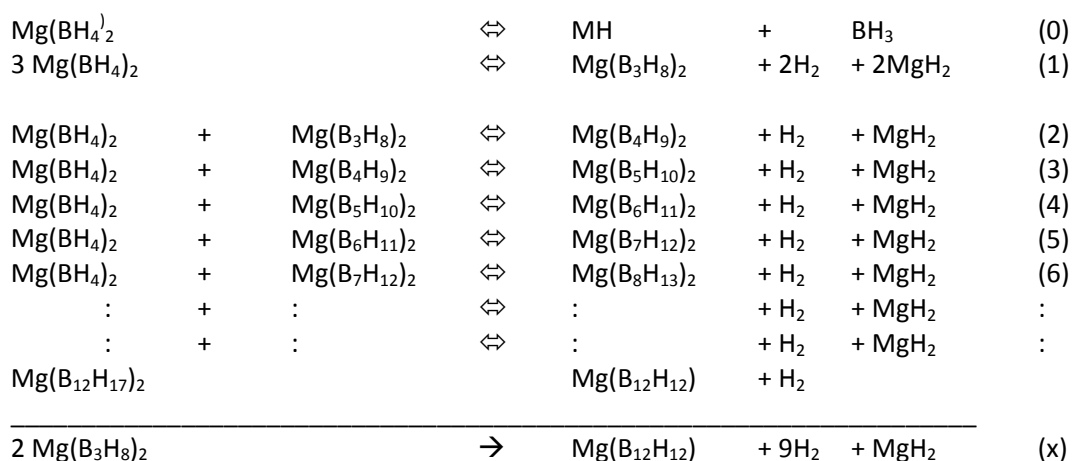


Formation of tri- and dodeca-borane in the solid state decomposition of $Mg(BH_4)_2$.

Figure S1. Potential reaction mechanism for decomposition of solid metal borohydrides.



Instrumentation and methods:

^{11}B NMR spectroscopic experiments were performed on a Varian spectrometer (500 MHz for 1H). In all cases, the spectra were recorded both with and without decoupling. The ^{11}B chemical shifts were referenced to $BF_3 \cdot OEt_2$ ($\delta=0$ ppm) at 20°C. Thermogravimetric Analysis (TGA) and Mass Spectrometry (MS): TGA/MS experiments were performed by heating the samples under flowing argon on an STA 449 Jupiter Netzsch instrument equipped with an Aelos QMS 403C MS. The MS instrument employs a standard electron impact ionization detector. The samples were loaded in alumina crucibles in the drybox, transferred under inert atmosphere and loaded in the TGA/MS instrument. PCT: Hydrogen release kinetics and quantification of hydrogen evolved during isothermal decomposition of materials were obtained with the Hy-Energy PCTPro-2000 pressure composition isothermal instrument.

Product yields. ^{11}B NMR spectroscopy was used to quantify the yields of $B_{12}H_{12}$, $B_{10}H_{10}$ and B_3H_8 formed in the thermal decomposition of magnesium borohydride. Normalized (to number of B atoms in compound) integration intensities were used to calculate yields of the magnesium borohydride decomposition products. Hydrolysis of unstable polyborane species forms boric acid whereas the dodecaborane, dodecaborane and triborane are highly soluble and stable in aqueous media. Minor amounts of other metastable polyborane species we assume to be B_4 - B_9 and B_{11} present as minor species present between 0.8-6 mol% cumulative. In the hydrolysis experiments we assume recovery of all boron species, however, if insoluble borides are formed, e.g., MgB_2 , then we obtain an upper limit to the $B_{12}H_{12}$ yields. Under these conditions the $B_{12}H_{12}$ yield would be less than calculated based on normalized ^{11}B NMR intensities of the soluble boron species. This further supports the hypothesis that $B_{12}H_{12}$ is not a major product and that the other polyborane species must be considered in the chemistry of hydrogen desorption and resorption.

