Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2016

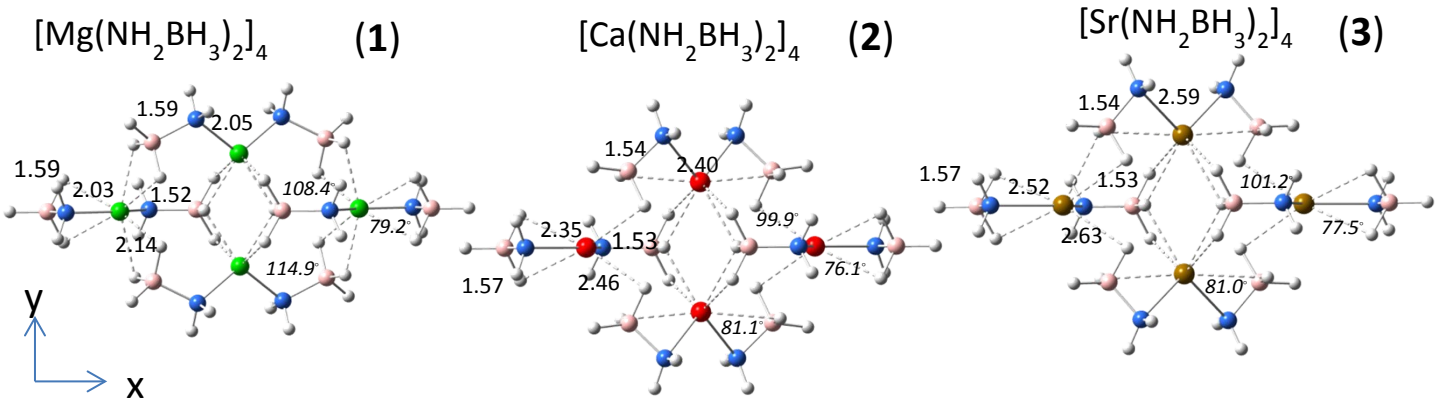

Figure S1 Optimized structures of considered clusters. Values of M–N–B angles and selective bond lengths (Å) are shown. Green/red/brown colors refer to Mg/Ca/Sr atoms, blue to N, orange to B and white to H atoms. Metal atoms form a rhombus with lengths 4.24 (Mg), 4.13 (Ca) and 4.40 (Sr) Å. Short diagonals of the rhombus are 3.58(Mg), 3.98(Ca), 4.29(Sr). Angles of the rhombus are 50.0º (Mg) 57.6º (Ca) and 58.3º (Sr). M–H(BH_3) bond network is shown by dashed lines. M–H(BH_3) bonds are 2.02 <Mg–H <2.25 Å; 2.30 <Mg–H <2.45 Å; 2.47 <Mg–H <2.60 Å.

Table S1. Bond lengths (Å) in M_3H moiety formed in $[M(NH_2BH_3)_2]_4$ after cleavage of the H–B bond.

	M=Mg	M=Ca	M=Sr
H_1–M_1	1.983	2.277	2.448
H_1–M_2	1.887	2.242	2.409
H_1–M_3	2.195	2.317	2.510
M_1–M_2	3.193	3.805	4.104
M_2–M_3	3.547	3.703	4.023
M_1–M_3	3.636	3.726	4.026

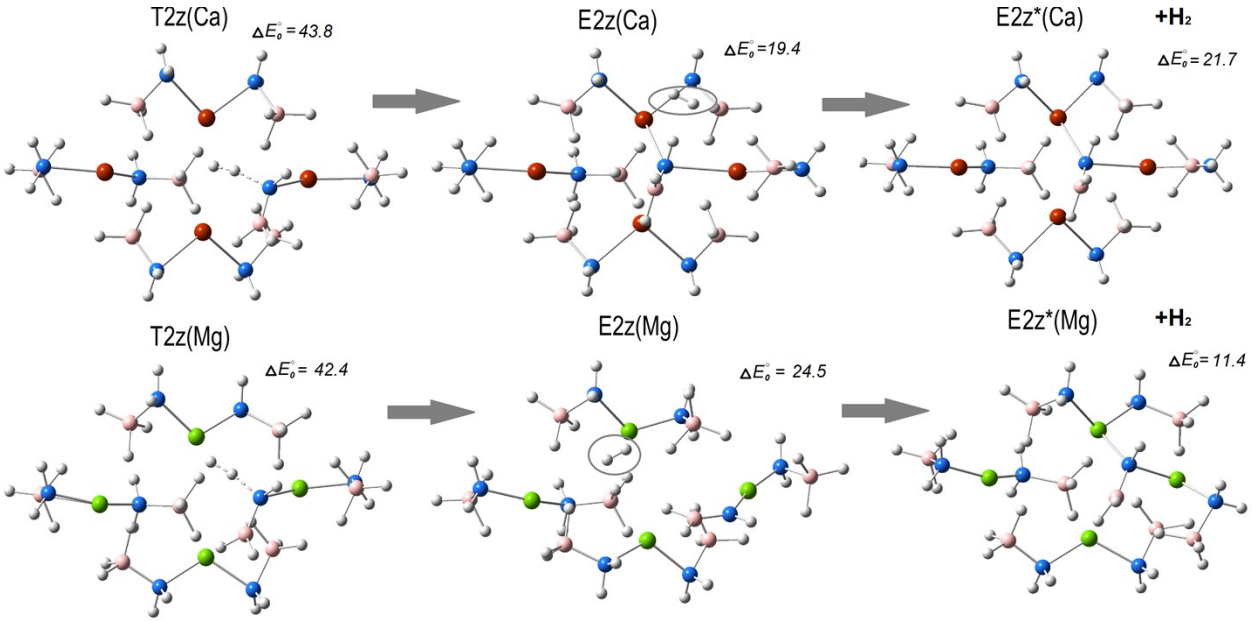

Figure S2 Optimized transition states, T2z(M), local minima, E2z(M) and dehydrogenation product E2z*(M) of M=Mg and Ca. Reaction direction from transition states are shown by dashed lines. Formed H_2 is marked by ovals in E2z(M). Energies are given in kcal·mol^{-1}.

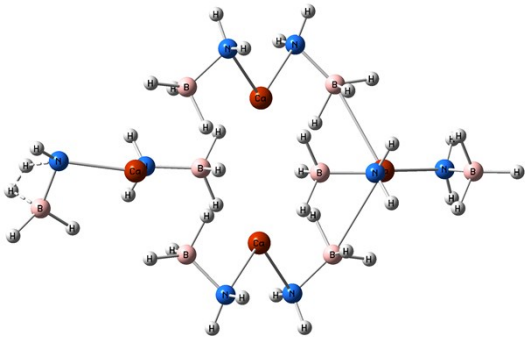

Figure S3 Optimized transition states, Tx(M), leading to direct H_2 release in $[Ca(NH_2BH_3)_2]_4$

.

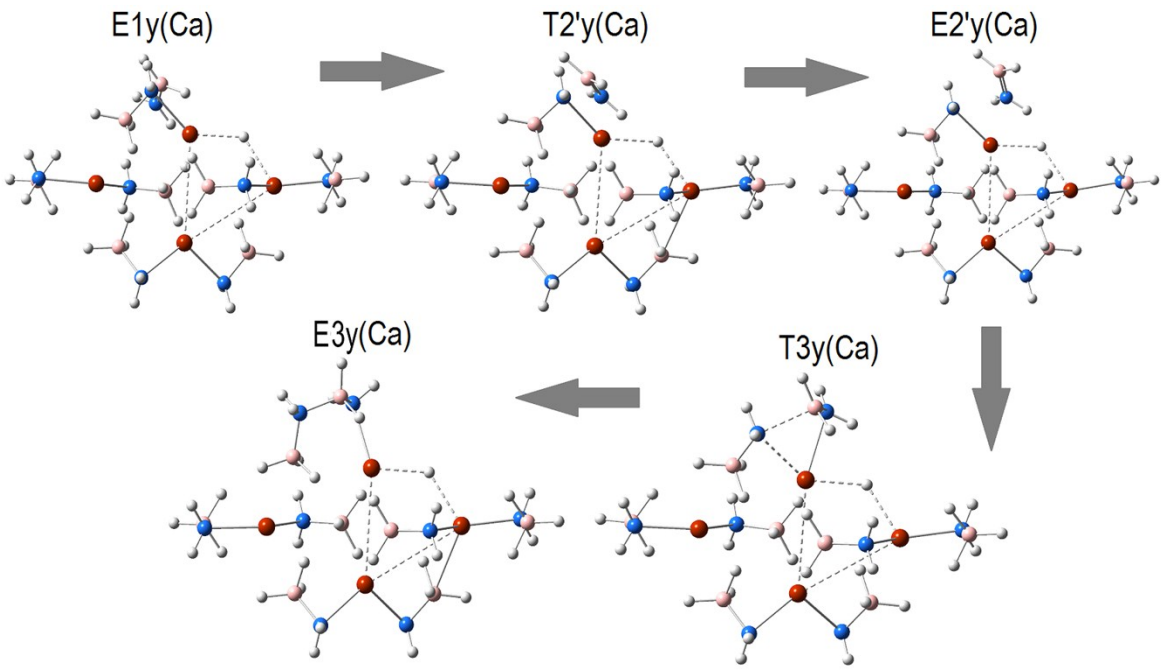

Figure S4 Y- pathway leading to direct H_2 release in $[Ca(NH_2BH_3)_2]_4$. Dashed lines show Ca_3H kite-shaped moiety.

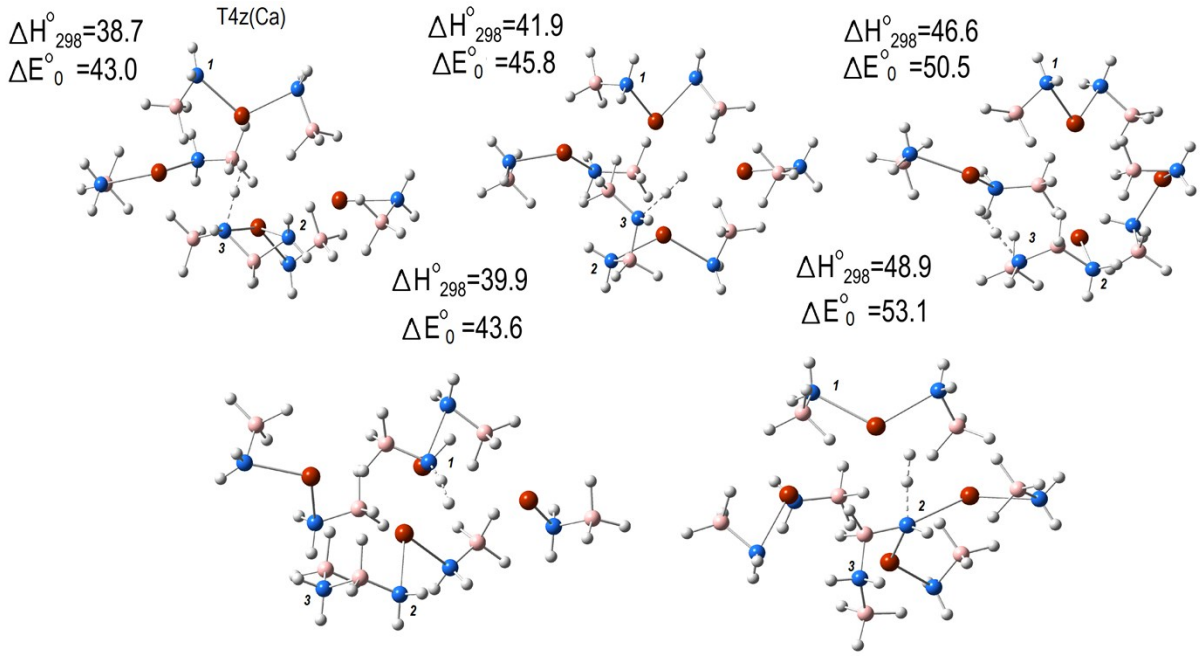

Figure S5 Optimized transition states leading to H_2 release from $[Ca(NH_2BH_3)_2]_4$ with oligomerized units. Reaction direction from the transition states are shown by dashed lines. Energies are given in kcal·mol^{-1}.

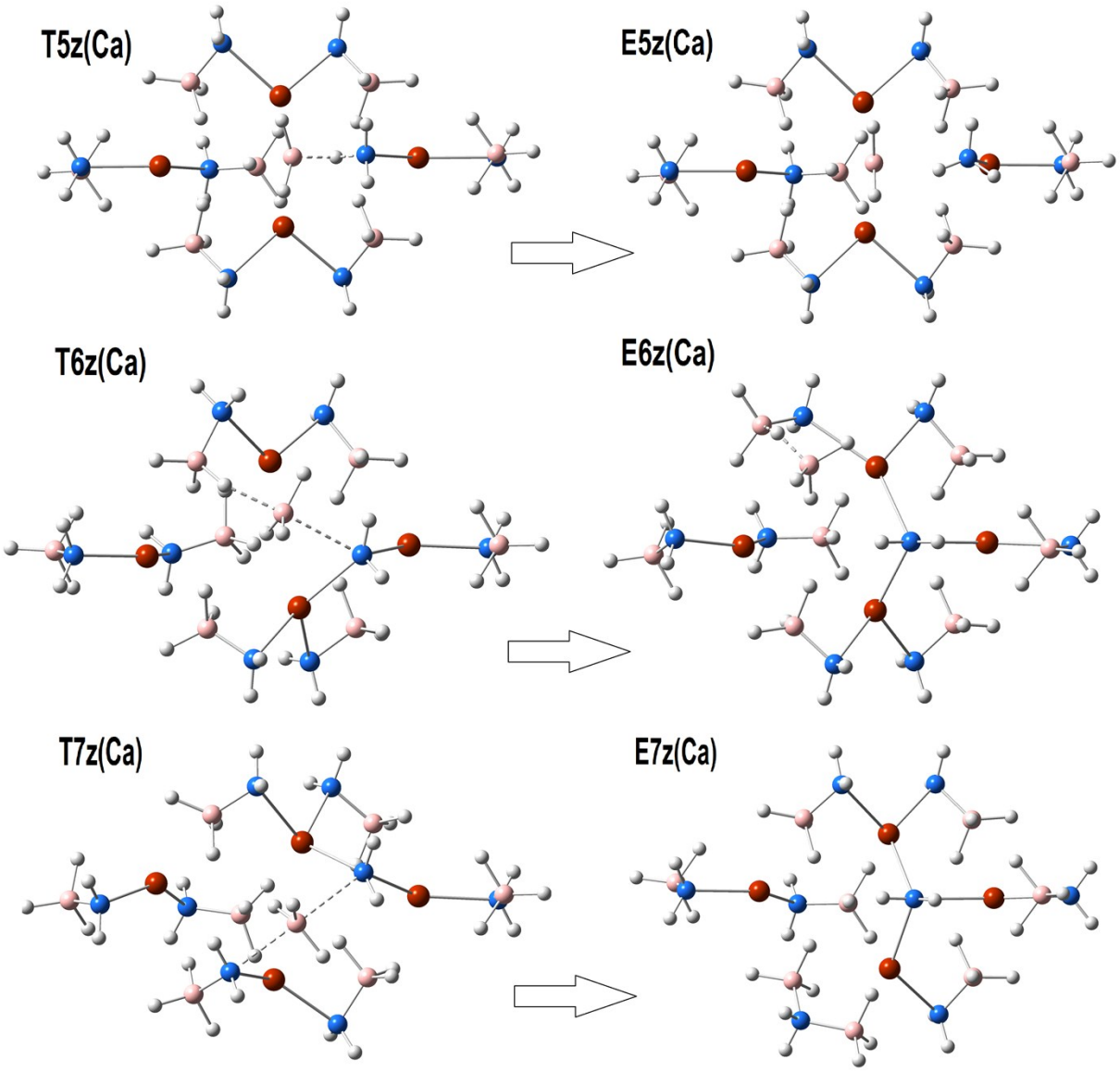

Figure S6 Optimized transition states leading to B−N bond cleavage in $[Ca(NH_2BH_3)_2]_4$ thetramer and related products. Reaction direction from the transition states are shown by dashed lines. Energies (ΔE^o_0 in kcal·mol^{-1}) of the states are following: T5z(Ca): 81.1; E5z(Ca): 68.3; T6z(Ca): 50.8; E6z(Ca): 27.7; T7z(Ca): 50.3; E7z(Ca): 6.7.