Electronic Supplementary Information:

The two new derivatives of scandium borohydride, MSc(BH₄)₄, M = Rb, Cs, prepared via a one-pot solvent-mediated method

A. Starobrat,¹ᵃᵇ* T. Jarońᵇ* and W. Grochalaᵇ

¹ College of Inter-Faculty Individual Studies in Mathematics and Natural Sciences (MISMaP), University of Warsaw, Banacha 2c, 02-097 Warsaw, Poland
ᵇ Centre of New Technologies, University of Warsaw, Banacha 2c, 02-097 Warsaw, Poland

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Figure S1. Rietveld refinement of PXRD (Cu Kα) data collected for CsSc(BH₄)₄ at room temperature, wRp = 1.17%, R(obs)= 4.72%.

Figure S2. Rietveld refinement of PXRD (Cu Kα) data collected for RbSc(BH₄)₄ at room temperature, wRp = 1.23%, R(obs)= 2.29%.
Figure S3. FTIR spectra of CsSc(BH₄)₄ obtained via mechanochemical (top) and solvent-mediated (middle) synthesis as well as of by-products of solvent-mediated synthesis (down, site B), * - background compensation error.

Figure S4. FTIR spectra of RbSc(BH₄)₄ obtained via mechanochemical (top) and solvent-mediated (middle) synthesis as well as of by-products of solvent-mediated synthesis (down, site B), * - background compensation errors.
Figure S5. Sc-Rb zigzag lines along the c-axis in RbSc(BH$_4$)$_4$. Rb atoms in blue, Sc in red, Sc-Rb distance $4.487(5)$ Å.

Figure S6. Mass spectrum of gaseous decomposition products of RbSc(BH$_4$)$_4$ obtained mechanochemically (inset: spectrum with logarithmic Ion current scale). Heating rate $5$ °C/min, $t = 0$ corresponds to temperature $15$ °C.
Figure S7. Mass spectrum of gaseous decomposition products of RbSc(BH₄)₄ obtained via DMS-mediated synthesis (inset: spectrum with logarithmic Ion current scale). Heating rate 5 °C/min, t = 0 corresponds to temperature 20 °C.

Figure S8. Mass spectrum of gaseous decomposition products of CsSc(BH₄)₄ obtained mechanochemically (inset: spectrum with logarithmic Ion current scale). Heating rate 5 °C/min, t = 0 corresponds to temperature 15 °C.
Figure S9. Mass spectrum of gaseous decomposition products of CsSc(BH₄)₄ obtained via DMS-mediated synthesis (inset: spectrum with logarithmic ion current scale). Heating rate 5 °C/min, t = 0 corresponds to temperature 20 °C.

Figure S10. Crystal structure of M₃ScCl₆, M=Rb, Cs - the elpasolite-type structure. M atoms in orange, Sc - purple, Cl - green.
Figure S11. PXRD patterns of CsSc(BH$_4$)$_4$ samples obtained via the solvent-mediated (a) and the mechanochemical (c) synthesis and by-products of solvent-mediated synthesis (b), * - LiCl , ^ - CsBH$_4$, unmarked - CsSc(BH$_4$)$_4$ or Cs$_3$ScCl$_6$, respectively.

Figure S12. Rietveld refinement of PXRD (Cu K$_\alpha$) data collected for Cs$_3$ScCl$_6$ sample at room temperature, wRp = 1.20%, R(\text{obs})_{\text{CsBH}_4} = 3.66\%, R(\text{obs})_{\text{Cs}_3\text{ScCl}_6} = 3.20\%.
Figure S13. Rietveld refinement of PXRD (Cu \(K_a\)) data collected for \(\text{Rb}_3\text{ScCl}_6\) sample at room temperature, wRp = 1.48%, \(R(\text{obs})_{\text{RbBH}_4} = 2.57\%\), \(R(\text{obs})_{\text{Rb}_3\text{ScCl}_6} = 5.24\%\).

Figure S14. PXRD patterns of Rb-Y samples prepared via solvent-mediated method, site A - \(\text{Y(BH}_4)_3\)-DMS (top), and site B - \(\text{RbBH}_4\) (marked with *), and hRb\(_3\)YCl\(_6\) (bottom).
Figure S15. FTIR spectra of Rb-Y samples prepared via solvent-mediated method, site A - $\text{Y}$(BH$_4$)$_3$:DMS (top), and site B - RbBH$_4$ and ht-Rb$_3$YCl$_6$ (bottom), * - background compensation errors.
The structures of MSc(BH₄)₄ optimized computationally

**RbSc(BH₄)₄**

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**CsSc(BH₄)₄**

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Table S1. Comparison of the selected parameters for the experimental and computed structures.

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Figure S16. An overlay of the experimental (darker colors) and computationally optimized (brighter colors) structures of RbSc(BH$_4$)$_4$. Top – the sublattice of heavy atoms; bottom – the geometry of the [Sc(BH$_4$)$_4$] complex anion.
Figure S17. An overlay of the experimental (darker colors) and computationally optimized (brighter colors) structures of CsSc(BH₄)₄. Top – the sublattice of heavy atoms; bottom – the geometry of the [Sc(BH₄)₄] complex anion.