Electronic Supplementary Information (ESI)

Novel solvates $M(BH_4)_3S(CH_3)_2$ and properties of halide-free $M(BH_4)_3$ ($M = Y$ or Gd)

by

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Experimental

Structural solution of $Y(BH_4)_3S(CH_3)_2$

**Figure S1** Rietveld refinement of SR-PXD data collected for $Y(BH_4)_3S(CH_3)_2$ (s8_Wsolv) at room temperature, $\lambda = 0.69736$ Å. Tick marks, $Y(BH_4)_3S(CH_3)_2$.

**Figure S2** Rietveld refinement of PXD data collected of Gd($BH_4)_3S(CH_3)_2$ (s9_Wsolv) at room temperature, ($\lambda = 1.540593$ Å). Tick marks, Gd($BH_4)_3S(CH_3)_2$. 

$M(BH_4)_3S(CH_3)_2$ ($M = Y$ or Gd) 

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Results and Discussion

Synthesis of $M(BH_4)_3S(CH_3)_2$ ($M = Y$ or Gd)

**Figure S3** FTIR spectra from the top of $\alpha$-Y($BH_4)_3$, Y($BH_4)_3S(CH_3)_2$, Gd($BH_4)_3$, Gd($BH_4)_3S(CH_3)_2$. Spectra of $\alpha$-Y($BH_4)_3$ and Gd($BH_4)_3$ have been obtained after removal of the solvent at $T = 140 \, ^\circ C$ in vacuum for 3 h.
**Figure S4** FTIR spectra from the top of α-Y(BH₄)₃ (s14_BMdesolv) and Gd(BH₄)₃ (s15_BMdesolv). Spectra of α-Y(BH₄)₃ and Gd(BH₄)₃ have been obtained after removal of the solvent at $T = 140 \, ^\circ\text{C}$ in vacuum for 3 h.

**Thermal analysis and mass spectrometry of Y(BH₄)₃S(CH₃)₂**

**Figure S5** Mass spectrometry data of Y(BH₄)₃S(CH₃)₂ (s8_Wsolv) in the temperature range 200 to 350 °C, $\Delta T/\Delta t = 5 \, ^\circ\text{C}/\text{min}$. 
Thermal analysis and mass spectrometry of Gd(BH$_4$)$_3$S(CH$_3$)$_2$ (M = Y or Gd)

TGA-DSC-MS data for Gd(BH$_4$)$_3$S(CH$_3$)$_2$ (s9_Wsolv) are shown in Figure S6. S(CH$_3$)$_2$ is released during heating in the temperature range 90 to 145 °C, where a 17 wt% mass loss occurs. This mass loss is smaller than the theoretically expected $\rho_m = 23$ wt%, corresponding to the loss of a single S(CH$_3$)$_2$ molecule. An endothermic peak in the DSC data at $T = 135$ °C correlates with release of S(CH$_3$)$_2$. MS shows minor hydrogen desorption from Gd(BH$_4$)$_3$, occurring between 145 and 220 °C in connection with a mass loss of 1.3 wt%. Gd(BH$_4$)$_3$ decomposes further from 220 to 320 °C observed as a mass loss of 5 wt% and by DSC as an endothermic peak at $T = 260$ °C, in agreement with previous studies of solvent-extracted Gd(BH$_4$)$_3$. The MS data show that a minor amount of B$_2$H$_6$ is released in the temperature range 255 to 295 °C. From 320 to 500 °C a mass loss of $\rho_m = 1$ wt% is observed prior to the formation of the decomposition products, GdH$_2$ and GdB$_4$.$^{1-3}$ In total, a mass loss of 7.3 wt% is recorded from 220 to 500 °C, which is slightly more than the theoretical hydrogen content in Gd(BH$_4$)$_3$ $\rho_m = 5.99$ wt% possibly due to additional release of B$_2$H$_6$.

Figure S6  Thermal analysis combined with mass spectrometry data of Gd(BH$_4$)$_3$S(CH$_3$)$_2$ (s9_Wsolv) in the temperature range 50 to 500 °C, $\Delta T/\Delta t = 5$ °C/min. Top: MS signals, Middle: TGA signal, Bottom: DSC signal.
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Figure S7  
Mass spectrometry data of Gd(BH$_4$)$_3$S(CH$_3$)$_2$ (s9_Wsolv) in the temperature range 200 to 350 °C, $\Delta T/\Delta t = 5$ °C/min.

In situ SR-PXD investigation of Gd(BH$_4$)$_3$S(CH$_3$)$_2$  
The in situ SR-PXD data for Gd(BH$_4$)$_3$S(CH$_3$)$_2$ (s9_Wsolv) heated under dynamic vacuum are shown in Figure S8. The low crystallinity of the sample and the strong X-ray absorption of Gd gives rise to the low diffracted intensity in the in situ SR-PXD data for Gd(BH$_4$)$_3$S(CH$_3$)$_2$. At RT only Bragg peaks from Gd(BH$_4$)$_3$S(CH$_3$)$_2$ are observed and the diffracted intensities are constant at between RT and 135 °C. The solvate phase decomposes to Gd(BH$_4$)$_3$ at $T = 135$ °C in accordance with the TGA-DSC-MS data. Gd(BH$_4$)$_3$ remains crystalline in the sample to $T = 230$ °C, where the diffraction peaks disappear. This may be a result of amorphisation as suggested by a halo at ~ 3 Å and an increase in the background in the in situ SR-PXD data. Gd(BH$_4$)$_3$ decomposes at $T = 260$ °C as confirmed by the TGA-DSC-MS data and no crystalline products are observed in the temperature range 260 to 300 °C.
In situ SR-PXD data for Gd(BH$_4)_3$S(CH$_3)_2$ (s9_Wsolv) from RT to 300 °C, $\Delta T/\Delta t = 5$ °C/min, vacuum, $\lambda = 1.0089$ Å. Symbols: Grey triangle Gd(BH$_4)_3$S(CH$_3)_2$, white triangle Gd(BH$_4)_3$.

Properties of Y(BH$_4)_3$:

In situ SR-PXD data for Y(BH$_4)_3$ (s12_Wdesolv) from RT to 250 °C, $\Delta T/\Delta t = 3$ °C/min, vacuum, $\lambda = 1.020345$ Å. Symbol: white circle $\alpha$-Y(BH$_4)_3$. 
Figure S10 TPD-MS quenching experiments of Y(BH₄)₃ (s12_Wdesolv). The samples are heated from RT to 250 °C, ΔT/Δt = 2 °C/min, after which one sample is left to cool naturally, while the other sample was cooled by immersion in liquid nitrogen.

Figure S11 PXD patterns of samples after quenching experiment, λ = 1.540593 Å. Symbol: white circle α-Y(BH₄)₃, circle cross Sample holder.
Figure S12 Sievert’s measurement for Y(BH₄)₃ (s₁₂_Wdesolv) from RT to 300 °C, ΔT/Δt = 2 °C/min, \( p(\text{H₂}) = 1 \) bar. The sample was afterwards used for the high-pressure absorption experiment.

Figure S13 PXD data of Y(BH₄)₃ at RT, after desorption from RT to 300 °C, ΔT/Δt = 2 °C/min, absorption at 300 °C and \( p(\text{H₂}) = 1550 \) bar and second desorption from RT to 500 °C, ΔT/Δt = 2 °C/min, \( \lambda = 1.540593 \) Å. Symbols: white circle \( \alpha-\text{Y(BH₄)}₃ \), grey diamond \( \text{YH₃} \), black diamond \( \text{YH₂} \), white square \( \text{Y₂O₃} \), cross \( \text{YB₄} \), circle cross Sample holder.
**M(BH₄)₃S(CH₃)₂ (M = Y or Gd)**

**Figure S14** TPD-MS experiment from RT to 500 °C of the sample used in the high-pressure absorption experiment, \( \Delta T/\Delta t = 2 \) °C/min.

**Decomposition for solvent-free Gd(BH₄)₃**

In situ SR-PXD studies and Sievert’s measurements have previously shown, that Gd(BH₄)₃ decomposes into GdH₂ and GdB₄ and shows limited hydrogen reversibility.¹³ Herein, thermal analysis of Gd(BH₄)₃ (s13_Wdesolv) reveals decomposition at 255 °C, observed by DSC, resulting in the release of hydrogen and diborane as a mass loss of 16 wt% (150 to 350 °C), larger than the theoretical hydrogen content \( \rho_m(Gd(BH₄)₃) = 5.99 \) wt% H₂, see Figure S15. Dimethyl sulfide is not released from this sample of Gd(BH₄)₃ as no mass loss is observed at 135 °C, which was observed for Gd(BH₄)₃S(CH₃)₂, see Figure S8. A significantly smaller release of diborane was observed in the TGA/MS experiment for Gd(BH₄)₃S(CH₃)₂. The temperature programmed photographic analysis of Gd(BH₄)₅ revealed that the sample does not melt, but remains a solid during heating from RT to 300 °C, see Figure S16. A colour change is observed for the powder from white to yellow to black, indicating decomposition in the temperature range 250 to 270 °C, comparable to thermal analysis.
**Figure S15** Thermal analysis combined with mass spectrometry data from Gd(BH$_4$)$_3$ in the temperature range 50 to 500 °C, ΔT/Δt = 5 °C/min. Top: TGA signal, Bottom: DSC signal.

**Figure S16** Temperature programmed photographic analysis of Gd(BH$_4$)$_3$, ΔT/Δt = 4 °C/min, p(Ar) = 1 bar.

**Composite samples of Gd(BH$_4$)$_3$**

Composite samples of Gd(BH$_4$)$_3$ with LiBH$_4$ (18) and LiCl (s19) were also studied. Three DSC signals are observed for Gd(BH$_4$)$_3$−LiBH$_4$ 1:1 (s18). The first endothermic event at 110 °C is assigned to the polymorphic transformation of LiBH$_4$. The two endothermic events at 210 and 233 °C are related to the decomposition of the sample, which happens at a lower temperature compared to Gd(BH$_4$)$_3$, see Figure S17. LiBH$_4$ appears to alter the decomposition pathway of Gd(BH$_4$)$_3$ through an unknown reaction and thereby lowers the decomposition temperature of Gd(BH$_4$)$_3$.

However, diborane still remains a problem as the mass loss of Gd(BH$_4$)$_3$−LiBH$_4$ 1:1 (12.5 wt%, 170 to 500 °C) exceeds the theoretical hydrogen content of the sample (7.2 wt% H$_2$). Temperature programmed photographic analysis shows no sign of melting in the composite sample during
heating in contrast to those containing Y(BH$_4$)$_3$, see Figure S18. A color change similar to the color change observed for Gd(BH$_4$)$_3$ is noted.

**Figure S17** Thermal analysis combined with mass spectrometry data from Gd(BH$_4$)$_3$−LiBH$_4$ 1:1 (s18) in the temperature range 50 to 500 °C, $\Delta T/\Delta t = 5$ °C/min. Top: TGA signal, Bottom: DSC signal.

**Figure S18** Temperature programmed photographic analysis of Gd(BH$_4$)$_3$−LiBH$_4$ 1:1 (s18), $\Delta T/\Delta t = 4$ °C/min, $p$(Ar) = 1 bar.

Gd(BH$_4$)$_3$−LiCl 1:1 (s19) is interesting as this mixture may produce LiGd(BH$_4$)$_3$Cl during heating as observed for a mixture of GdCl$_3$−LiBH$_4$ 1:3.$^1$ This may a present a new way of synthesizing LiGd(BH$_4$)$_3$Cl with out excess halide salt. Gd(BH$_4$)$_3$−LiCl 1:1 was studied using *in situ* SR-PXD, see Figure S19. Gd(BH$_4$)$_3$ and LiCl is observed at RT in the *in situ* SR-PXD experiment. At 163 °C Bragg peaks belonging to Gd(BH$_4$)$_3$ disappear completely, whilst the intensity of peaks belonging to LiCl decrease significantly, and weak peaks corresponding to LiGd(BH$_4$)$_3$Cl appear. However, the peaks corresponding to LiGd(BH$_4$)$_3$Cl do not increase in intensity during heating and disappear again at 200 °C, which indicates the production of only a minor amount of LiGd(BH$_4$)$_3$Cl.
Immediately after the disappearance of LiGd(BH$_4$)$_3$Cl, diffraction peaks belonging to GdH$_2$ appear. These increase in intensity at 260 °C corresponding to the formation of additional GdH$_2$ is in agreement with the major gas release occurring at 260 °C from borohydride decomposition. At 260 °C, the intensity of LiCl diffraction peaks increase, also pointing towards the decomposition of LiGd(BH$_4$)$_3$Cl. Thermal analysis reveals several endothermic events between 218 to 240 °C, probably related to the formation of LiGd(BH$_4$)$_3$Cl and decomposition of Gd(BH$_4$)$_3$/LiGd(BH$_4$)$_3$Cl, see Figure S20. Diborane is released because the mass loss of Gd(BH$_4$)$_3$–LiCl 1:1 (8 wt%, 170 to 500 °C) exceeds the theoretical hydrogen content of the sample (4.9 wt% H$_2$). Temperature programmed photographic analysis shows no sign of melting of the Gd(BH$_4$)$_3$–LiCl 1:1 composite sample, see Figure S21. A color change is observed from the initially white powder to black powder during decomposition in the temperature range 200 to 270 °C.

**Figure S19** In situ SR-PXD data for Gd(BH$_4$)$_3$–LiCl 1:1 (s19) from RT to 300 °C, $\Delta T/\Delta t = 10$ °C/min, $p$(Ar) = 1 bar, $\lambda = 1.020345$ Å. Symbol: white triangle Gd(BH$_4$)$_3$, black square LiCl, LiGd(BH$_4$)$_3$Cl, white diamond GdH$_2$. 
Figure S20 Thermal analysis combined with mass spectrometry data from Gd(BH₄)₃−LiCl 1:1 (s19) in the temperature range 50 to 500 °C (ΔT/Δt = 5 °C/min). Top: TGA signal, Bottom: DSC signal.

Figure S21 Temperature programmed photographic analysis of Gd(BH₄)₃−LiCl 1:1 (s19), ΔT/Δt = 4 °C/min, p(Ar) = 1 bar.

References