Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information: Structural and thermodynamic investigations of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ between 280 K and their decomposition temperatures

Konrad Burkmann, Franziska Habermann, Erik Schumann, Jakob Kraus, Bianca Störr, Horst Schmidt, Erica Brendler, Jürgen Seidel, Klaus Bohmhammel, Jens Kortus, and Florian Mertens

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1. ^{1}H, ^{11}B and ^{91}Zr NMR spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$

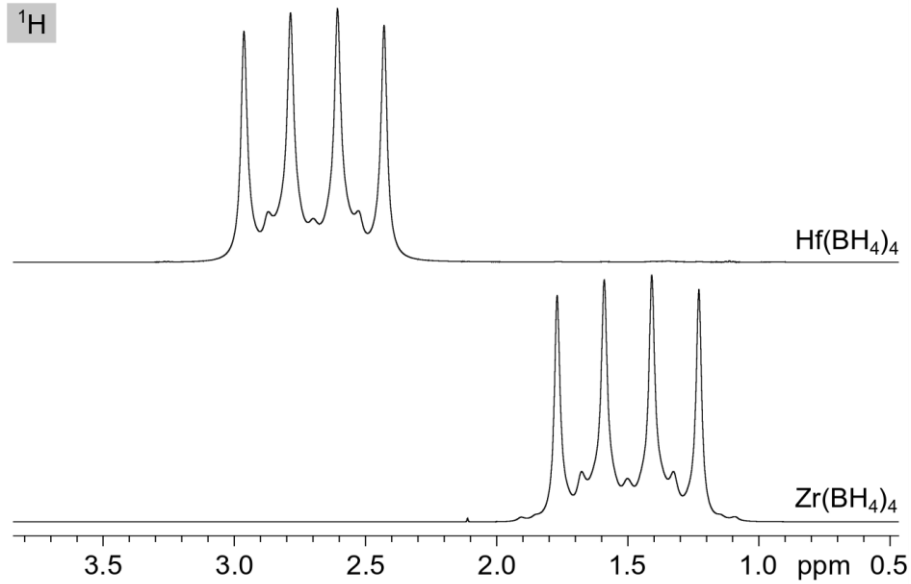

Fig. S1: ***top:*** *^{1}H spectrum of $Hf(BH_4)_4$; 28.63 mg in 0.5 mL C_6D_6; δ = 2.70 ppm; $^{1}J_{1H\text{-}11B}$ = 89.3 Hz (M = 4); $^{1}J_{1H\text{-}10B}$= 28.5 Hz (M = 7);* ***bottom:*** *^{1}H spectrum of $Zr(BH_4)_4$; 27.68 mg in 0.5 mL C_6D_6; δ = 1.50 ppm; $^{1}J_{1H\text{-}11B}$ = 90.4 Hz (M = 4); $^{1}J_{1H\text{-}10B}$ = 29.1 Hz (M = 7); signals are given relative to $SiMe_4$.*

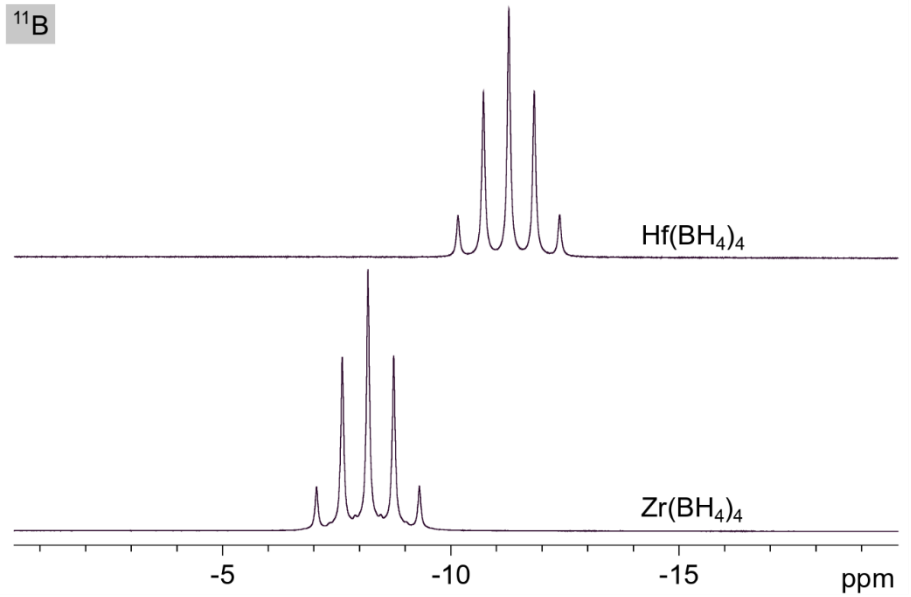

Fig. S2: ***top:*** *^{11}B spectrum of $Hf(BH_4)_4$; 28.63 mg in C_6D_6; δ = -11.27 ppm; $^{1}J_{11B\text{-}1H}$ = 89.3 Hz (M = 5);* ***bottom:*** *^{11}B spectrum of $Zr(BH_4)_4$; 27.68 mg in C_6D_6; δ = -8.19 ppm; $^{1}J_{11B\text{-}1H}$ = 90.4 Hz (M = 5); signals are given relative to 15 Vol-% Bortrifluoridetherat $BF_3{\cdot}Et_2O$ in $CDCl_3$.*

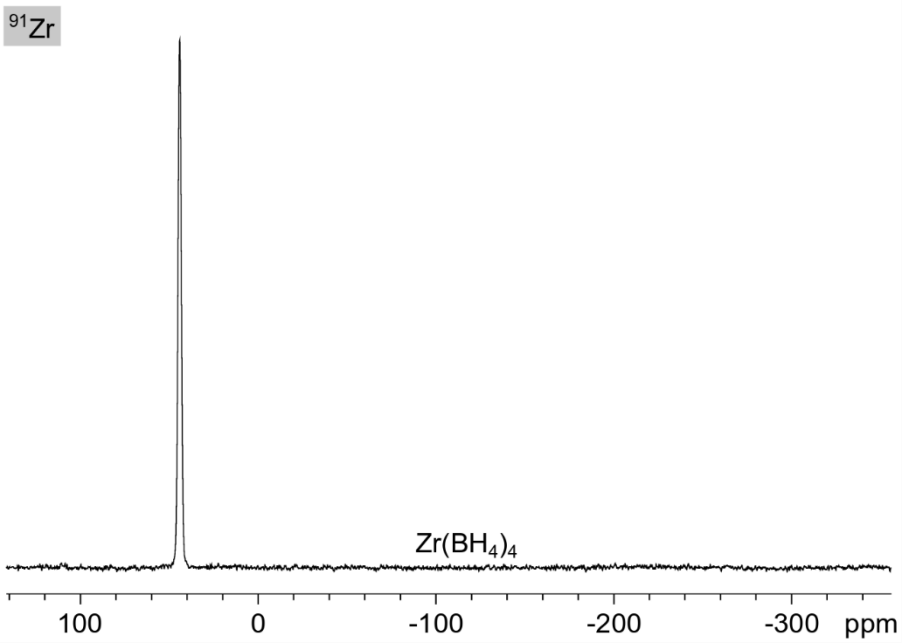

Fig. S3: ^{91}Zr spectrum $Zr(BH_4)_4$; saturated in C_6D_6:C_6H_6 (1:4); δ = 44.1 ppm; relative to Cp_2ZrBr_2 (0.2 M) in THF-d_8:THF (1:4) = 0 ppm.

2. Crystal structures of $Hf(BH_4)_4$ and $Zr(BH_4)_4$

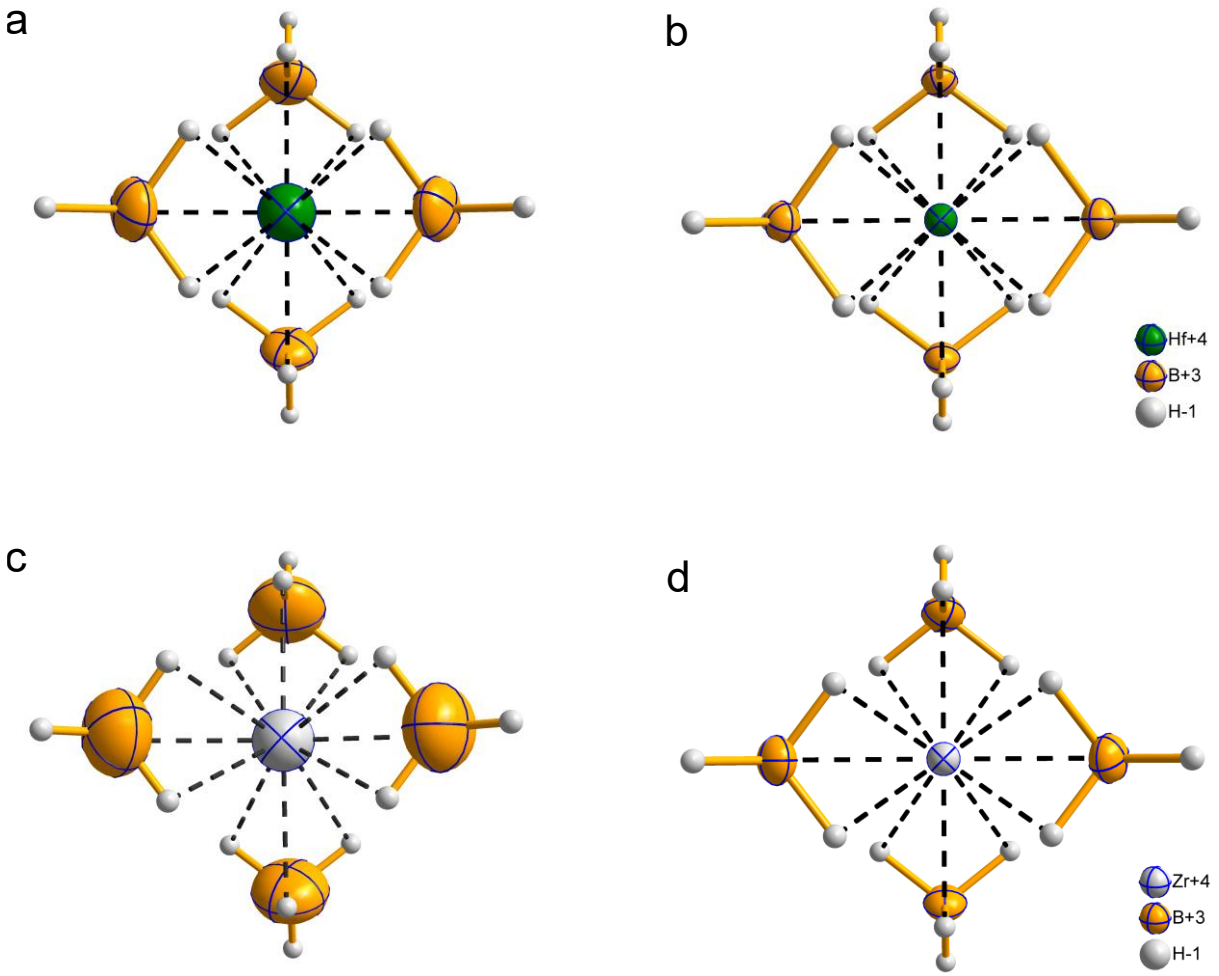

Fig. S4: Crystal structures of $Hf(BH_4)_4$ (top) and $Zr(BH_4)_4$ (bottom) measured in this study (a (288 K), c (273 K)) in comparison with already published ones (b (110 K) [1], d (100 K) [2]). The dotted lines show the M-H contacts.

3. SEM images of the decomposition products of the DSC measurements

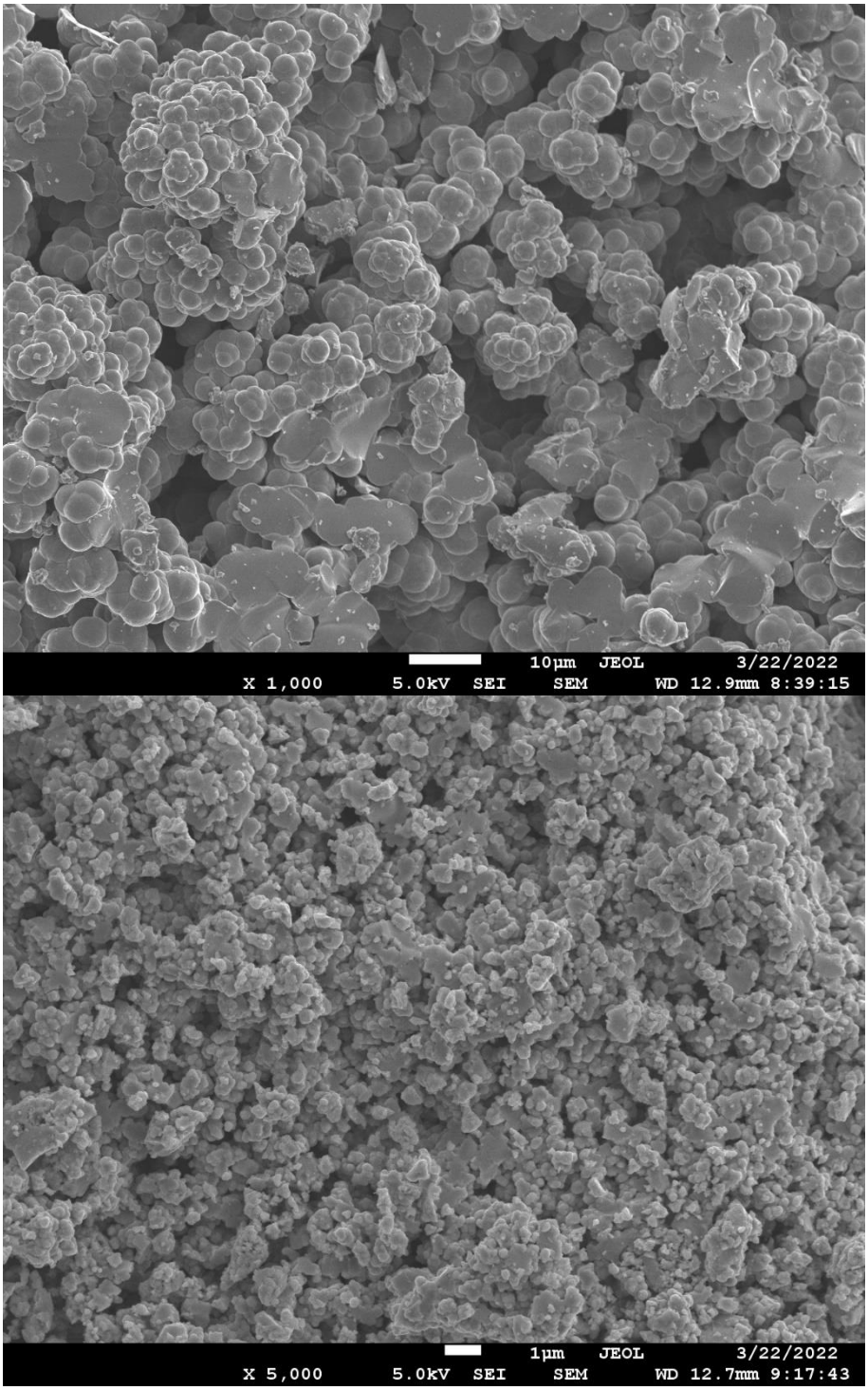

Fig. S5: SEM images of the Zr (top) and Hf (bottom) containing decomposition products after the DSC measurements. The scale is given in the images.

4. SEM images of the decomposition products after the TG-DSC measurements

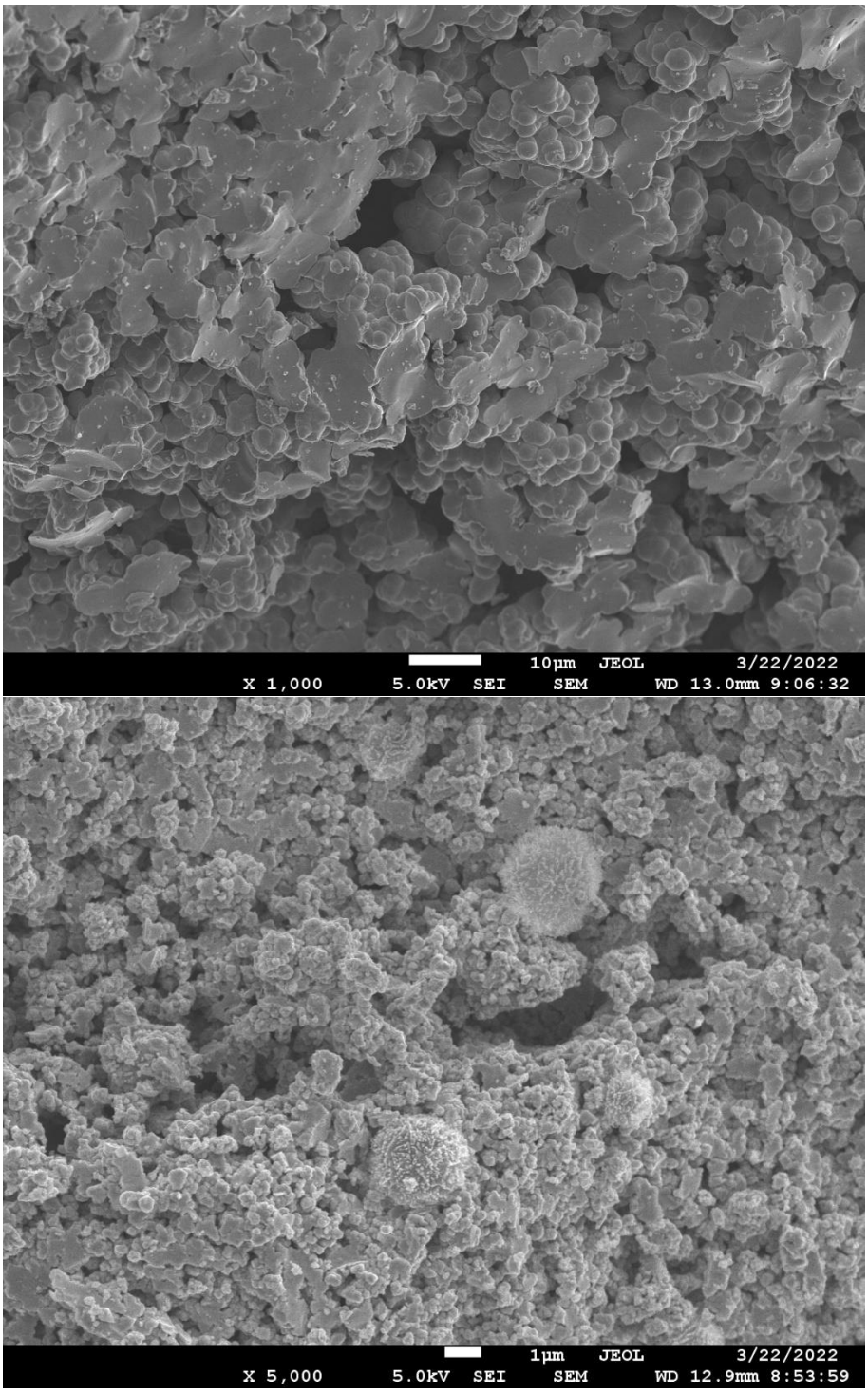

Fig. S6: SEM images of the Zr (top) and Hf (bottom) containing decomposition products after the TG-DSC measurements. The scale is given in the images.

5. C_P measurement of $Hf(BH_4)_4$

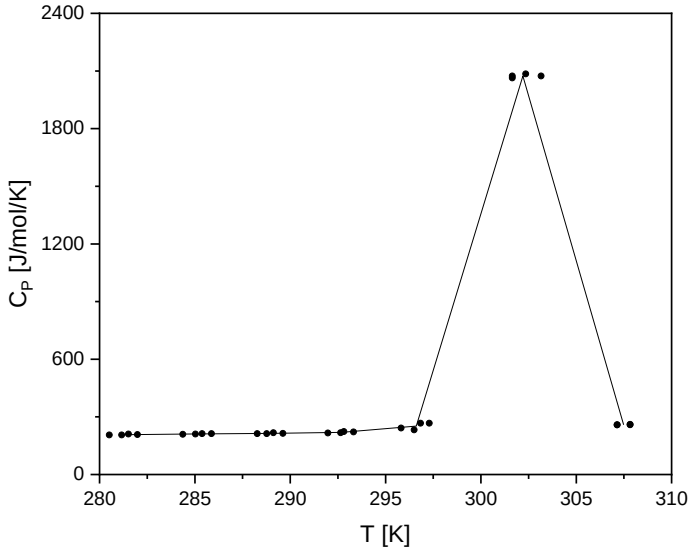

Fig. S7: Graph of the measured C_P values of $Hf(BH_4)_4$ from 280 K to 310 K (black dots; black line is drawn to guide the readers eyes).

6. Experimental heat capacity values of $Zr(BH_4)_4$ and $Hf(BH_4)_4$

Tab. S1: Mean values of the molar heat capacities of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ measured at the given temperatures between 281 K and 308 K.

phase	$Zr(BH_4)_4$		$Hf(BH_4)_4$	
	T [K]	C_P [J mol^{-1} K^{-1}]	T [K]	C_P [J mol^{-1} K^{-1}]
solid	281.79	205.85	281.30	207.50
	285.60	214.70	285.16	211.37
	289.38	224.02	288.94	214.08
			292.69	219.70
phase transition	293.42	293.77		
	297.22	577.64	296.61	251.90
	301.64	3319.00	302.20	2074.25
liquid	304.14	250.66		
	307.87	252.91	307.49	259.10

7. Comparison between the optimised values for $Hf(BH_4)_4$ from this work and the ones from the literature

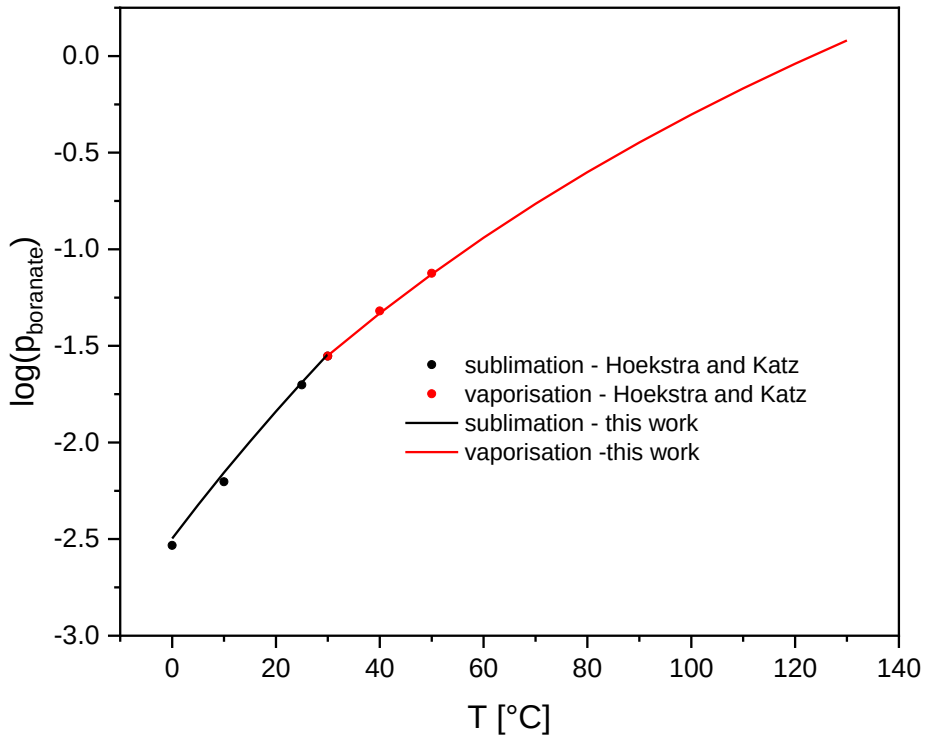

Fig. S8: Comparison between the measured vapour pressure values of Hoekstra and Katz [3] (dots) and our calculated ones (lines) for $Hf(BH_4)_4$ (sublimation: black; vaporisation: red).

8. Thermodynamic equlibrium calculations regarding the decomposition behaviour of $Zr(BH_4)_4$ and $Hf(BH_4)_4$

The Gibbs enthalpies of decomposition $\Delta_{dec}G$ in the presented graphs were calculated using our determined values from Table 6 in the main part of the manuscript for $Zr(BH_4)_4$ and $Hf(BH_4)_4$. The data for the other compounds involved were taken from the HSC [4] or the FactSage database [5] and are displayed in Tab. S2. The heat capacities were calculated using a Maier-Kelley type polynomial function [6]:

$$C_P(T) = A + B \cdot T \cdot 10^{-3} + C \cdot T^{-2} \cdot 10^{5} + D \cdot T^{2} \cdot 10^{-6}$$

Tab. S2: Summary of all used litereature thermodynamic data.

	T range [K]	$\Delta_F H$(298.15 K) [kJ/mol]	S(298.15 K) [J mol^{-1} K^{-1}]	C_P [J mol^{-1} K^{-1}]				source
				A	B	C	D	
H_2 (g)	298.15-5000	0.000	130.679	25.855	4.837	1.584	-0.372	[4]
B (s)	298.15-1500	0.000	5.900	16.033	12.895	-7.570	-3.234	[4]
B_2H_6 (g)	298.15-900	41.003	232.086	2.235	213.291	-1.075	-79.525	[4]
ZrH_2 (s)	298.15-960	-169.452	35.020	37.522	33.916	-16.359	0.000	[4]
HfH_2 (s)	298.15-2506	-125.520	38.425	64.280	8.8292	0.452	0.003	[5]
ZrB_2 (s)	100-600	-322.586	35.941	-3.916	233.340	-0.545	-196.082	[4]
ZrB_2 (s)	600-3323			65.836	7.284	-15.990	0.579	[4]
HfB_2 (s)	298.15-3000	-328.862	42.677	73.346	7.824	-23.012	0.000	[4]

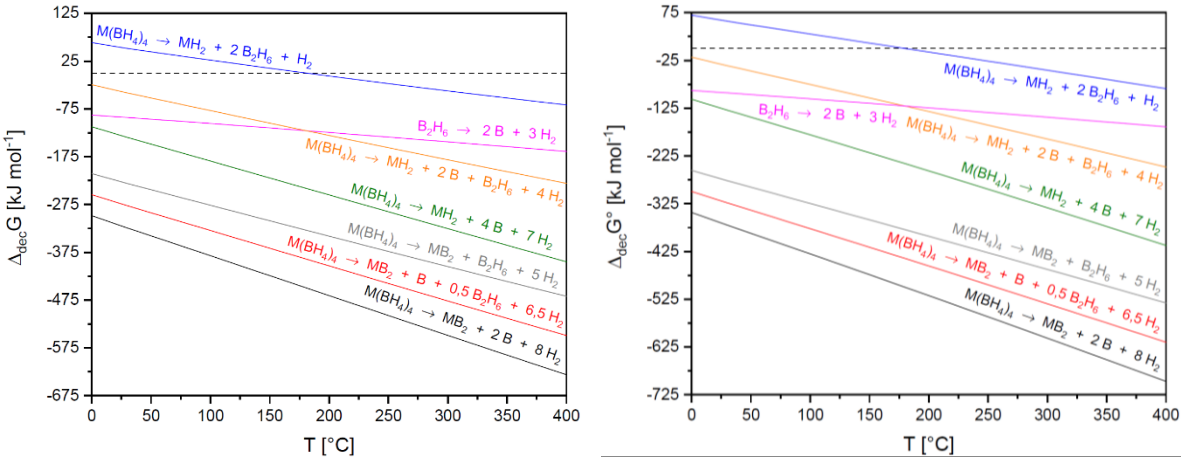

Fig. S9: Comparison between the different possible decomposition reactions of $Zr(BH_4)_4$ (left) and $Hf(BH_4)_4$ (right) calculated with our determined data for both boranates and the literature data [4,5] for the other compounds.

Fig. S9 displays the results of several theoretically possible decomposition reactions. As can be seen, the thermodynamically most favorable decompostion is the one that generates the metal diborides, two equivalents of boron and eight equivalents of hydrogen without any release of diborane. The formation of metal dihydrides as intermediates may appear because of the fact that direct decomposition into the metal diborides is kinetically hindered at these low decomposition temperatures.

9. Literature

[1] R. W. Broach, I. S. Chuang, T. J. Marks and J. M. Williams, *Inorg. Chem.*, 1983, **22**, 1081–1084.

[2] L. H. Rude, M. Corno, P. Ugliengo, M. Baricco, Y.-S. Lee, Y. W. Cho, F. Besenbacher, J. Overgaard and T. R. Jensen, *J. Phys. Chem. C*, 2012, **116**, 20239–20245.

[3] H. R. Hoekstra, J. J. Katz, *J. Am. Chem. Soc.*, 1949, **71**, 2488–2492.

[4] A. Roine, *HSC Chemistry*, 2002, https://www.hsc-chemistry.com/.

[5] C.W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, A. E. Gheribi, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer and M. A. van Ende, *Calphad*, 2016, **54**, 35–53.

[6] C. G. Maier, K. K. Kelley, J. Am. Chem. Soc., 1932, **54**, 3243–3246.