Supporting Information

Table S1: Atomic coordinates of $KSc(BH_4)_4$, s.g. *Pnma*, a = 11.856(5), b = 7.800(3), c = 10.126(6) Å, V = 936.4(8) $Å^3$ at *RT*.

Atom	**site**	***x***	***y***	***z***	B_{iso} [$Å^2$]
K	4*c*	0.1947(16)	1/4	0.6527(17)	3.65(88)
Sc	4*c*	0.0640(16)	1/4	0.2152(15)	= B_{iso} (K)
B1	4*c*	0.1647(32)	1/4	0.0150(23)	= B_{iso} (K)
H11	4*c*	0.2342(48)	1/4	0.0939(74)	= B_{iso} (K)
H12	4*c*	0.2050(75)	1/4	-0.0881(39)	= B_{iso} (K)
H13	8*d*	0.1097(33)	0.37018(21)	0.0271(41)	= B_{iso} (K)
B2	4*c*	0.3819(21)	1/4	0.3840(45)	= B_{iso} (K)
H21	4*c*	0.3790(37)	1/4	0.2706(45)	= B_{iso} (K)
H22	4*c*	0.2917(28)	1/4	0.4251(69)	= B_{iso} (K)
H23	8*d*	0.4286(26)	0.37018(21)	0.4201(43)	= B_{iso} (K)
B3	8*d*	0.0901(15)	0.0137(21)	0.3431(18)	= B_{iso} (K)
H31	8*d*	0.080(13)	-0.1071(38)	0.4069(53)	= B_{iso} (K)
H32	8*d*	0.058(12)	-0.0137(51)	0.2383(28)	= B_{iso} (K)
H33	8*d*	0.183(10)	0.052(18)	0.339(10)	= B_{iso} (K)
H34	8*d*	0.0386(90)	0.124(22)	0.3886(94)	= B_{iso} (K)

Table S2: Selected bond distances and angles on the $[Sc(BH_4)_4]^-$ anion as refined from the synchrotron PXD [this work] and compared to the DFT calculations on the isolated $[Sc(BH_4)_4]^-$ anion [24].

	DFT [24]	X-ray [this work]
d(B-H1) [Å]	1.21	1.148(2)
d(B-H2) [Å]	1.24	1.148(2)
d(B-H3) [Å]	1.24	1.148(2)
d(B-H4) [Å]	1.24	1.148(2)
(Sc-H-B)min [º]	75	75(3)
(Sc-H-B)max [º]	83	86(7)
d(Sc-B)min [Å]	2.33	2.27(2)
d(Sc-B)max [Å]	2.33	2.38(3)
(B-Sc-B)min [º]	105	96(1)
(B-Sc-B)max [º]	113	114.9(4)

The angles (Sc-H-B) are calculated only on the three hydrogen atoms pointing towards scandium.

Table S3: Atomic coordinates of K_3ScCl_6, s.g. $P2_1/a$ (14), a = 12.729(3), b = 7.367(2), c = 12.825(3) Å, β = 109.22(2) °, V = 1135.6(4) Å^3 at *RT*.

Atom	**site**	***x***	***y***	***z***	B_{iso} [Å^2]
K1	4*e*	0.1252(13)	0.0100(24)	0.39531(98)	2.71(26)
K2	4*e*	0.3774(13)	0.0852(18)	0.16430(97)	$=B_{iso}$ (K1)
K3	4*e*	0.2279(19)	0.5550(19)	0.19276(87)	$=B_{iso}$ (K1)
Sc1	2*a*	0	0	0	1.29(17)
Sc2	2*b*	1/2	0	1/2	$=B_{iso}$ (Sc1)
Cl1	4*e*	0.1209(17)	0.1762(28)	0.1543(17)	2.80(17)
Cl2	4*e*	0.3938(13)	0.2774(15)	0.4006(15)	$=B_{iso}$ (Cl1)
Cl3	4*e*	0.3496(18)	0.8186(23)	0.3723(12)	$=B_{iso}$ (Cl1)
Cl4	4*e*	0.1658(16)	0.8444(19)	-0.0160(20)	$=B_{iso}$ (Cl1)
Cl5	4*e*	1.0184(14)	0.7843(27)	0.1597(13)	$=B_{iso}$ (Cl1)
Cl6	4*e*	0.1018(15)	0.5509(36)	0.3695(16)	$=B_{iso}$ (Cl1)

Table S4 IR frequencies (in cm^{-1}) as calculated by the DFT calculation of the isolated complex anion $[Sc(BH_4)_4]^-$ [24], and as observed on related compounds [24,25,43,44] (w=weak, br = broad, vs =very strong, sh = shoulder). The symmetry assignment in T_d symmetry is given for the bands of the Hf compound [44].

$[Sc(BH_4)_4]^-$	Li $Sc(BH_4)_4$	Na $Sc(BH_4)_4$	K $Sc(BH_4)_4$	$Zr(BH_4)_4$	$Hf(BH_4)_4$	Assignment
2492 2488 2485	2468	2486 2461	2506sh 2485	2576	2572 (A_1) 2570s (T_2)	outer B-H stretching
2287 2286 2269 2266 2253 2250 2246 2243	2259 2240 2199 2121w	2240 2160	2288 2223br	2180 2123	2197s (T_2) 2193 (A_1) 2123s (T_2)	inner B-H stretching
1242 1232 1226 1212 1203 1189	1325 1194vs	ca1340 1189vs	1337w 1188vs	1284 1221vs 1180	1287 (A_1) 1218s (T_2)	B-H deformations
1112 1103 1099 1075 1070 1059 1034 1033	1113 1071w	1105	1121 1109sh 1091sh	1057	1088 (E)	B-H deformations
506 500 481 470 459 439	423			504 489	552 (A_1) 480s (T_2)	Metal-B stretching
327 286 277 272 264						
221 210 205 202 179				198		

Table S5 Peak temperatures and enthalpies for the endothermic events during decomposition observed by DSC for ball milled samples of KBH_4-$ScCl_3$ (2:1), (3:1) and (4:1).

Sample	T (K)	ΔH (J/g)
KBH_4-$ScCl_3$ (2:1)	414	-5.3
	422	-12.2
	490	-27.8
	527	-25.7
KBH_4-$ScCl_3$ (3:1)	410	-5.8
	490	-12.1
	526	-113.8
KBH_4-$ScCl_3$ (4:1)	412	-4.8
	421	-2.2
	488	-28.9
	526	-84.7

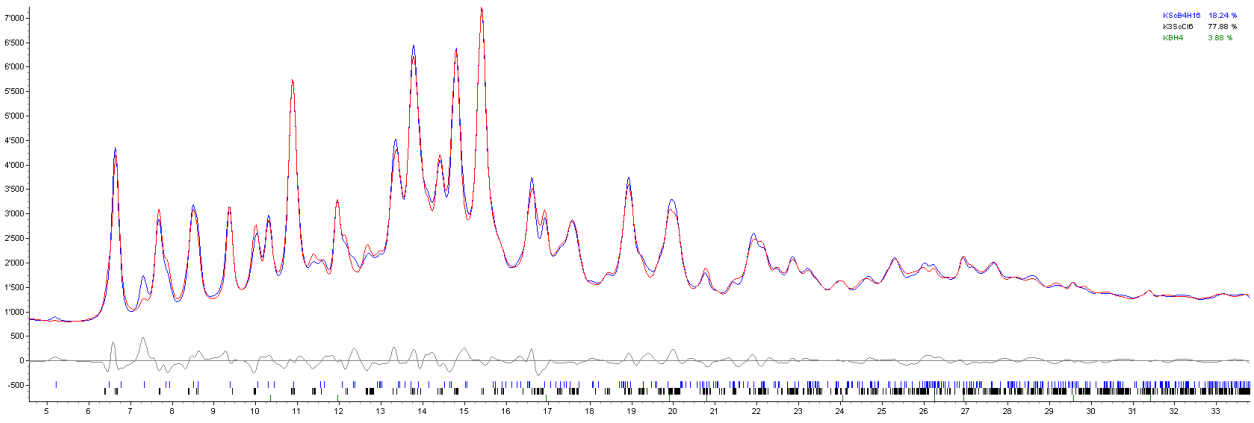

Figure S1. Rietveld plot (Intensity *vs*. 2θ) for $KSc(BH_4)_4$ + K_3ScCl_6 sample based on the image-plate powder diffraction data measured at *RT*, using 0.700128 Å wavelength.

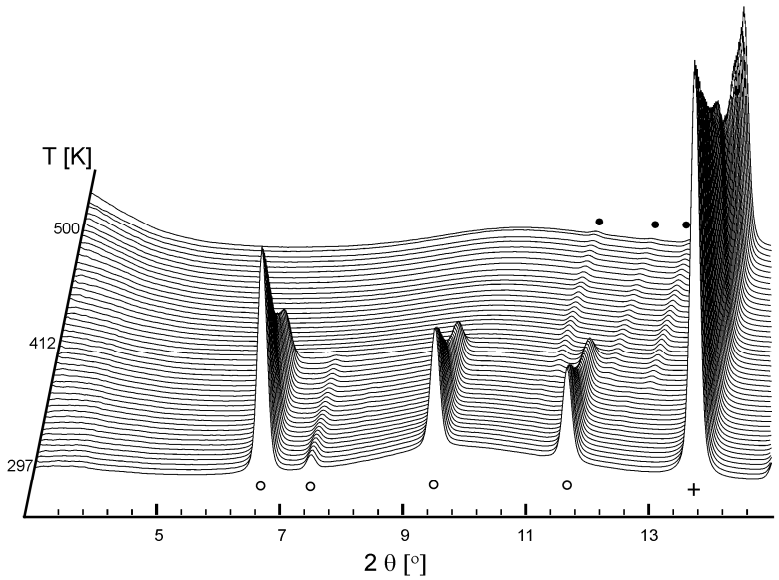

Figure S2. Series of SR-PXD patterns, using 0.711443 Å wavelength, as a function of temperature showing $LiSc(BH_4)_4$ (o) and LiCl (+). Between 390 and 412 K $LiSc(BH_4)_4$ decomposes to HT-$LiBH_4$ (•) and amorphous decomposition product [50].

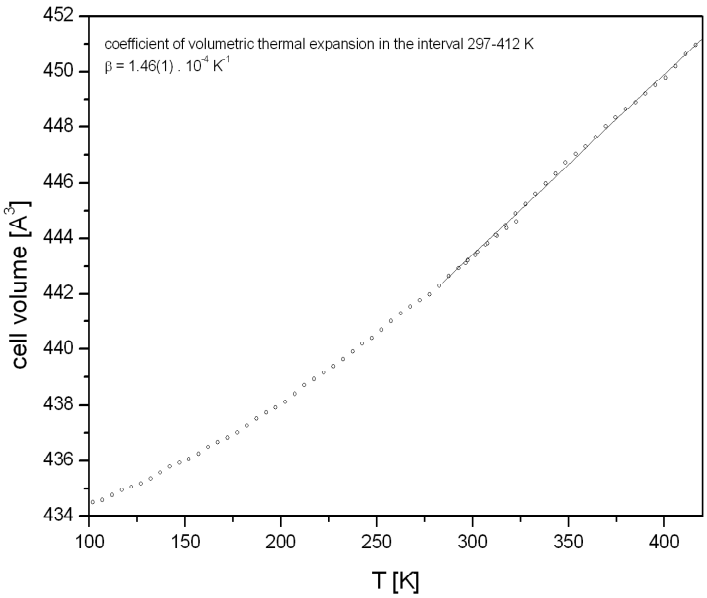

Figure S3. Cell volume of $LiSc(BH_4)_4$ as a function of temperature [50].

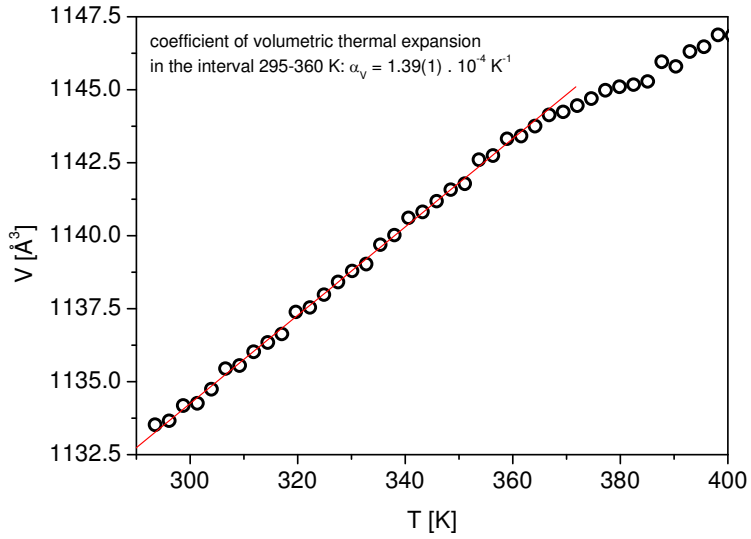

Figure S4 Cell volume of K_3ScCl_6 as a function of temperature.

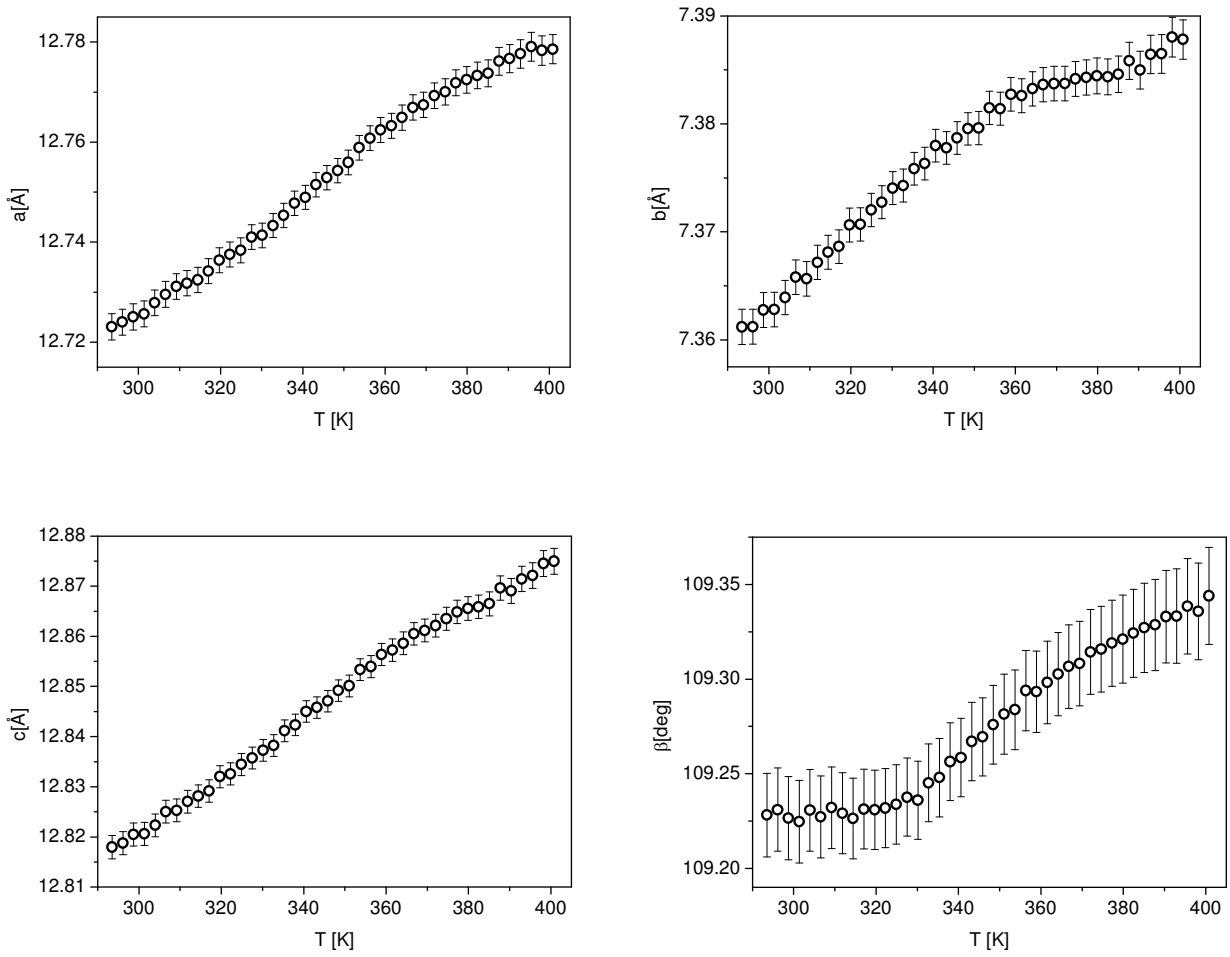

Figure S5 Lattice parameters of K_3ScCl_6 as a function of temperature.