

Electronic Supplementary Information for paper by T. Jaroń & W. Grochala

$\text{Y}(\text{BH}_4)_3$ – an old-new ternary hydrogen store *aka* learning from a multitude of failures.

Solid–State Synthesis from $\text{YCl}_3 + 3 \text{LiBH}_4$.

206 mg (9.45 milimol, 5% excess) of LiBH_4 was added to 586 mg (3 milimol) of YCl_3 and the mixture was milled for 50 minutes (periodically: 3 – 5 minutes of milling, 3 – 5 minutes pause to cool down the milling vessel; the temperature of external vessel walls did not exceed 50 °C). Obtained white powder was afterwards examined with powder elemental analysis, XRD, FTIR, Raman, also the decomposition process was investigated *via* TGA & DSC measurements. Moreover, NMR ^1H & ^{11}B spectra of the product solution in deuterated THF were performed.

Elemental Analysis.

Tab. 1. Elemental analysis results [w/w %] (milling time: 50 minutes).

element	1 st measurement	2 nd measurement	arithmetic mean	calculated
H	4.76	4.73	4.74	4.81
Cl	35.45	35.72	35.58	40.30

The amount of hydrogen in the reaction products corresponds with the calculated value. However, the amount of chlorine is significantly lower than it was expected. The difference might be caused by the reaction of this highly-hygroscopic compound with atmospheric water during the sample preparation and weighing, etc. and the not-completely decomposition of investigated compounds during the analytical procedure.

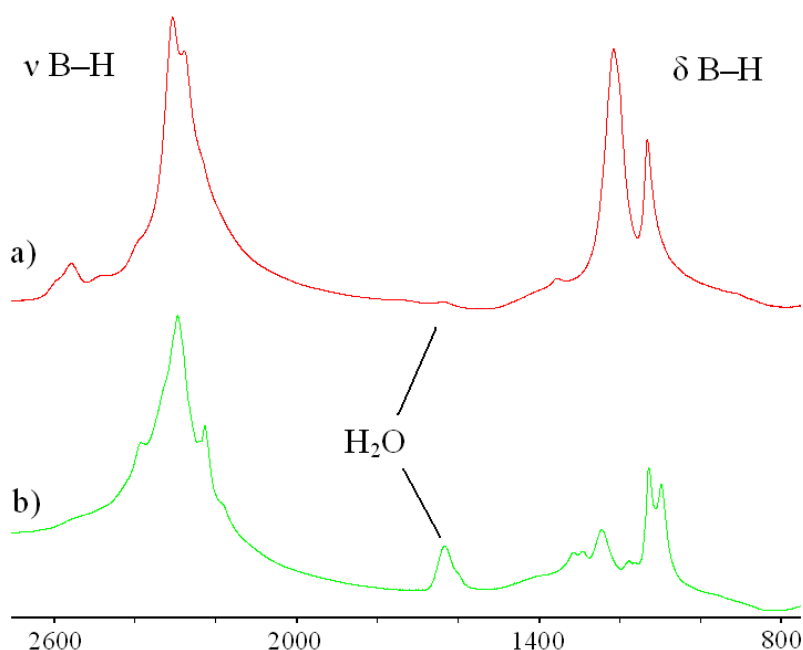


Fig. 2. FTIR spectra of the milled (a) and manually homogenized (b) YCl_3 with LiBH_4 ; (absorbance) [arb. units] vs. wavenumber [cm^{-1}]).

Table 2. The summary of the measured FTIR bands of the milled (a) and manually homogenized (b) YCl_3 with $LiBH_4$ (wavenumber [cm^{-1}]).

a)	2555 (medium–strong) 2304, 2275 (very strong, broad) 1352 (weak) 1212 (very strong) 1128 (strong)	b)	2383, 2292, 2224 (very strong, broad) 1310, 1287 (weak) 1241 (medium) 1173, 1158 (weak) 1125 (strong) 1093 (strong)
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Raman Spectra.

The main features of the observed Raman spectra (Fig. 3.) are similar to the previously described FTIR spectra. Both, stretching and deformation bands, increase their frequencies after milling (11 and 36 cm^{-1} respectively).

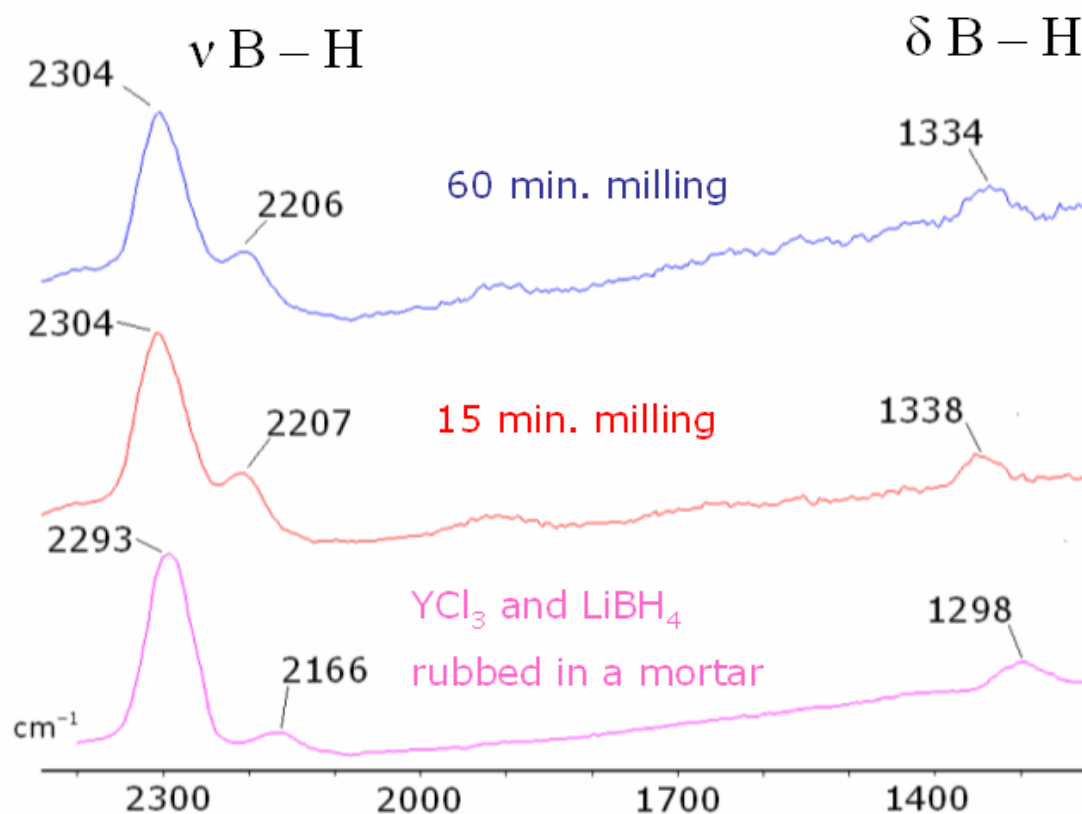


Fig. 3. Raman spectra of the milled (two upper) and rubbed (bottom) YCl_3 with 20% excess of $LiBH_4$ (green laser line, 514,5 nm).

NMR Spectra.

Both, ^{11}B and 1H NMR spectra of the product of reaction (1) as well as $LiBH_4$ were recorded in deuterated THF solution (Figures 4 and 5). In ^{11}B spectra (^{11}B I = 3/2), a quintet is observed in a 1:4:6:4:1 ratio as a result of coupling with four protons in BH_4^- group. Magnetic resonance signal occurs around -33.666 ppm (relatively to $BF_3 \cdot Et_2O$), which is in lower field in comparison with $LiBH_4$, -41.720 ppm. The $^1H - ^{11}B$ spin-spin coupling constant for the reaction (1) product (~82.0 Hz) is slightly higher than for $LiBH_4$ (~81.2 Hz).

Similar $^1\text{H} - ^{11}\text{B}$ spin-spin coupling constant was measured in $\text{YCl}(\text{BH}_4)_2 \cdot n \text{ THF}$ dissolved in C_6D_6 ¹, $j = 84 \text{ Hz}$, $\delta = -23.2$, and in $\text{Y}(\text{BH}_4)_3 \cdot 2 \text{ THF}$ dissolved in deuterated toluene², $j = 84 \text{ Hz}$, $\delta = -24.4 \text{ ppm}$, $j = 85 \text{ Hz}$.

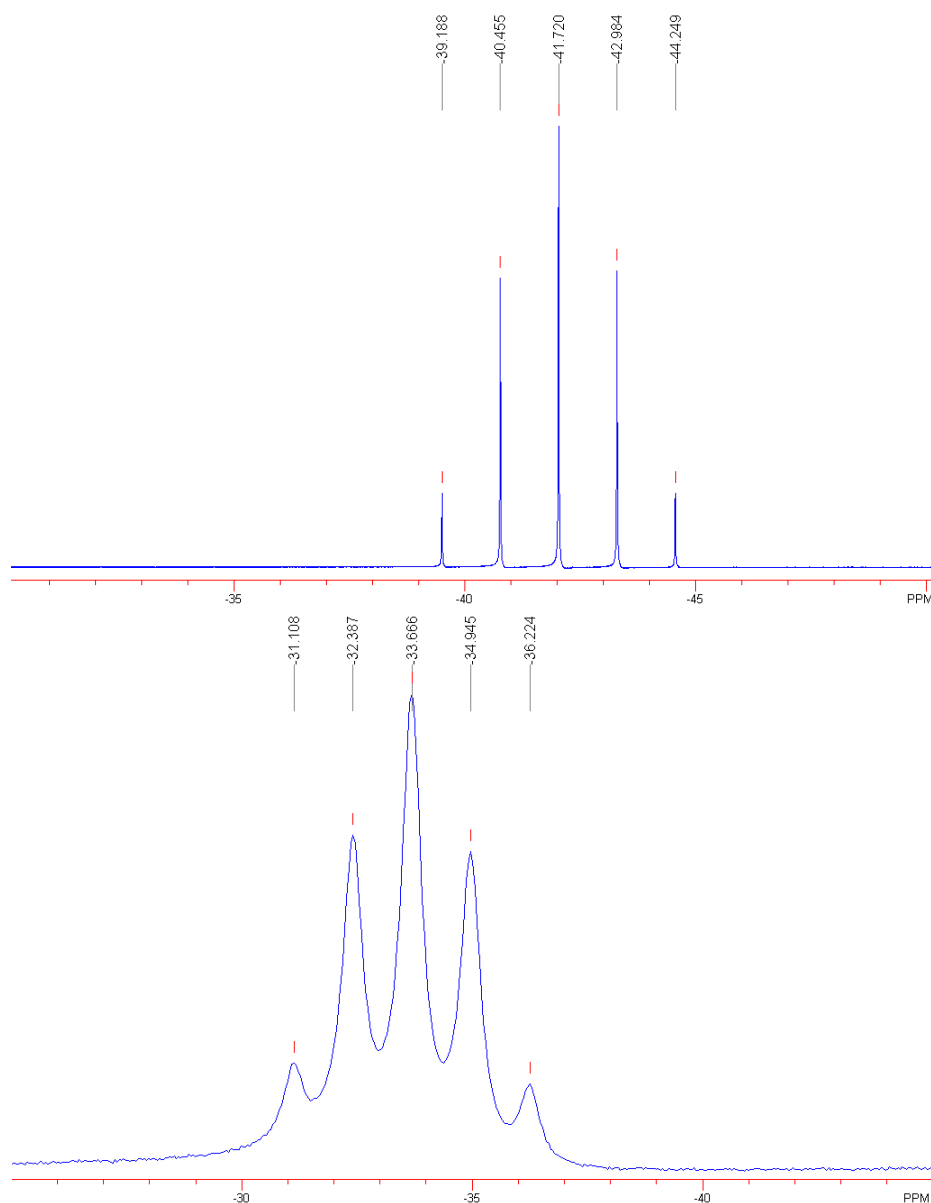


Fig. 4. Comparison of ^{11}B NMR spectra of LiBH_4 (upper) and LiBH_4 milled with YCl_3 for 50 minutes (lower); external standard – $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

^1H NMR spectra (Fig. 5.) appears somewhat more complicated than the ^{11}B spectra described above. This is mainly triggered by the coupling between ^1H and ^{11}B ($I = 3/2$) or ^{10}B ($I = 3$), which lead to 1:1:1:1 quartet and 1:1:1:1:1:1:1 septet, respectively. This cannot be

¹ M. Mancini, P. Bougeard, R. C. Burns, M. Mlekuz, B. G. Sayer, J. I. A. Thompson, M. J. McGlinchey, *Inorg. Chem.* **23** (1984) 1072. Authors write yttrium hydroborate as $\text{Y}(\text{BH}_4)_3$, although in the original paper which they cite reports synthesis of the compound best described as $\text{YCl}(\text{BH}_4)_2$ solvated with THF (K. Rossmannith, *Monatsh. Chem.* **92** (1961) 768).

² G. N. Bolko, S. E. Kravchenko, K. N. Semenenko, *Russ. Chem. Bull. (translated to English)* **30** (1981) 940.

observed in case of $\text{Y}(\text{BH}_4)_3$ due to significant signal broadening (only 3 peaks from ^{10}B splitting are visible) although both multiplets are centred on practically the same magnetic field ($\text{Y}(\text{BH}_4)_3$ -0.168 ppm quartet, -0.173 ppm septet, visible as triplet, LiBH_4 -0.516 ppm vs. -0.514 ppm respectively). The multiplets can be recognised very well in LiBH_4 ^1H NMR spectrum. Spin–spin coupling constant $^1\text{H} - ^{10}\text{B}$ is 3 times lower than $^1\text{H} - ^{11}\text{B}$, LiBH_4 $j = 27.2$ Hz, $\text{Y}(\text{BH}_4)_3$ $j = 26.7$ Hz. Heavier isotope, ^{11}B is 4 times more abundant (^{11}B 80.22 % vs. ^{10}B 19.78%), and it has higher resonance sensitivity. Therefore, the quartet is considerably stronger in comparison to the septet. Again, multiplet, centred for the *reaction (1)* product in -0.168 ppm is moved to lower field in comparison with LiBH_4 , -0.516 ppm. Besides the described multiplets, coming from H – B coupling, there are a few intensive signals in the spectrum of *reaction (1)* product (and some weak in case of LiBH_4). Two of them (1.718 ppm, 3.580 ppm) come from residues of not completely deuterated THF. The remaining signals (0.867 ppm, 1.267 ppm, 4.525 ppm) come from unknown pollutions of LiBH_4 .

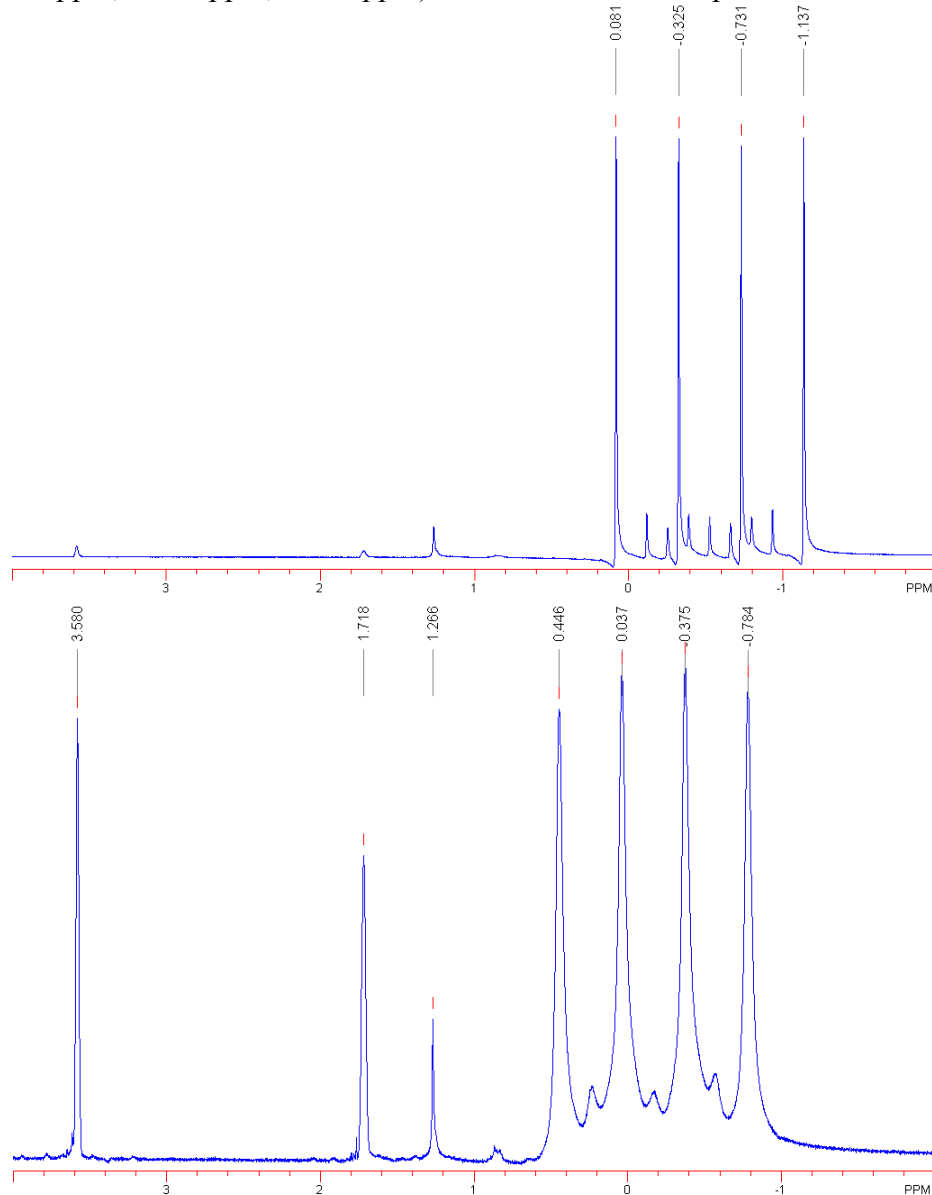


Fig. 5. Comparison of ^1H NMR spectra of LiBH_4 (upper) and LiBH_4 milled with YCl_3 for 50 minutes (lower); external standard – TMS.

Powder XRD.

Powder X-ray diffraction pattern of the mixture obtained in *reaction (1)* is presented in the *Figure 1* in comparison to LiCl. All of the LiCl peaks are well-represented in the diffraction pattern of the products; there is no sign of YCl₃, neither LiBH₄ in the sample.

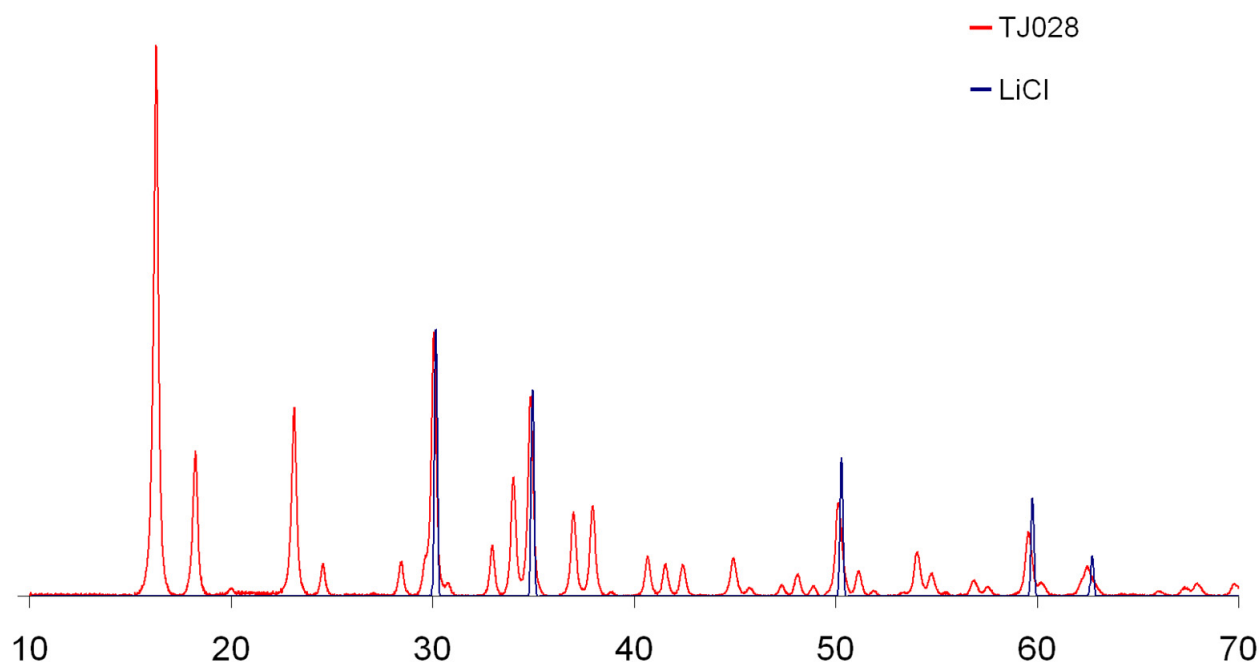


Fig. 1. X-ray powder diffraction pattern of the mixture of YCl₃ and LiBH₄ milled for 50 min (TJ028) as compared with that of pure LiCl.

Products of thermal decomposition of Y(BH₄)₃.

Elemental Analysis.

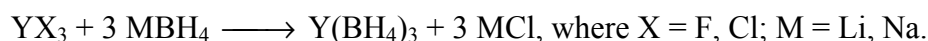
Tab. 3. Elemental analysis results [w/w %] (products of decomposition at 300 °C).

element	1 st measurement	2 nd measurement	arithmetic mean
H	0.88	0.91	0.90
Cl	31.80	31.61	31.70

Failed attempts of synthesis.

1.

Metathetical reaction in solid state:



Reactions were performed in the same way, as described above (periodically: 3 – 5 minutes of milling, 3 – 5 minutes pause). Total milling time was: YCl₃ + NaBH₄ 120 and 30 minutes (two samples); YF₃ + LiBH₄ or NaBH₄ 60 minutes (both). Due to the balance malfunction, substrates of the last two reactions (YF₃, LiBH₄ and NaBH₄) were weighted quickly in the air (although the substrates were milled in the Ar atmosphere). The products of these reactions were greyish while the products of the other reactions (with no contact of reagents with the air) were usually white powders.

To estimate the conversion level, XRD diffraction patterns (Figs A1, A2, A3) and FTIR spectra (not shown in this report version) were measured.

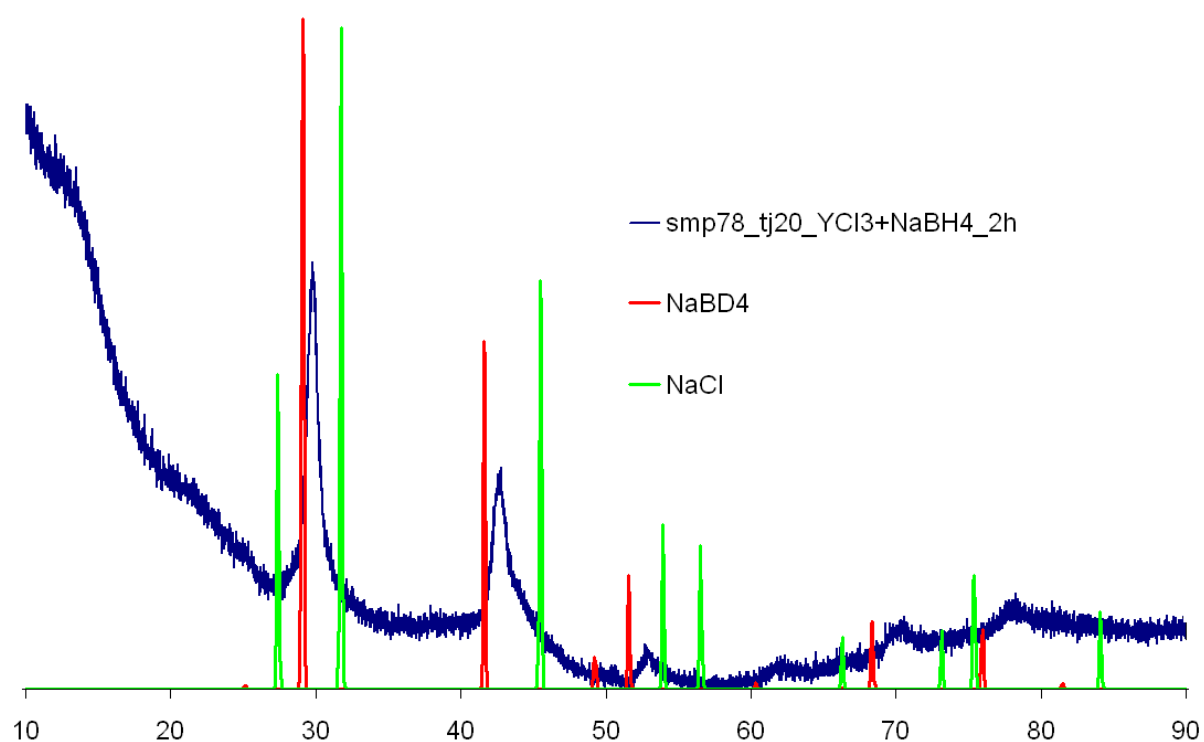


Fig. A1. Powder XRD pattern of the mixture of NaBH₄ and YCl₃ milled for 2h (identical to the pattern obtained for the mixture milled for 30 minutes).

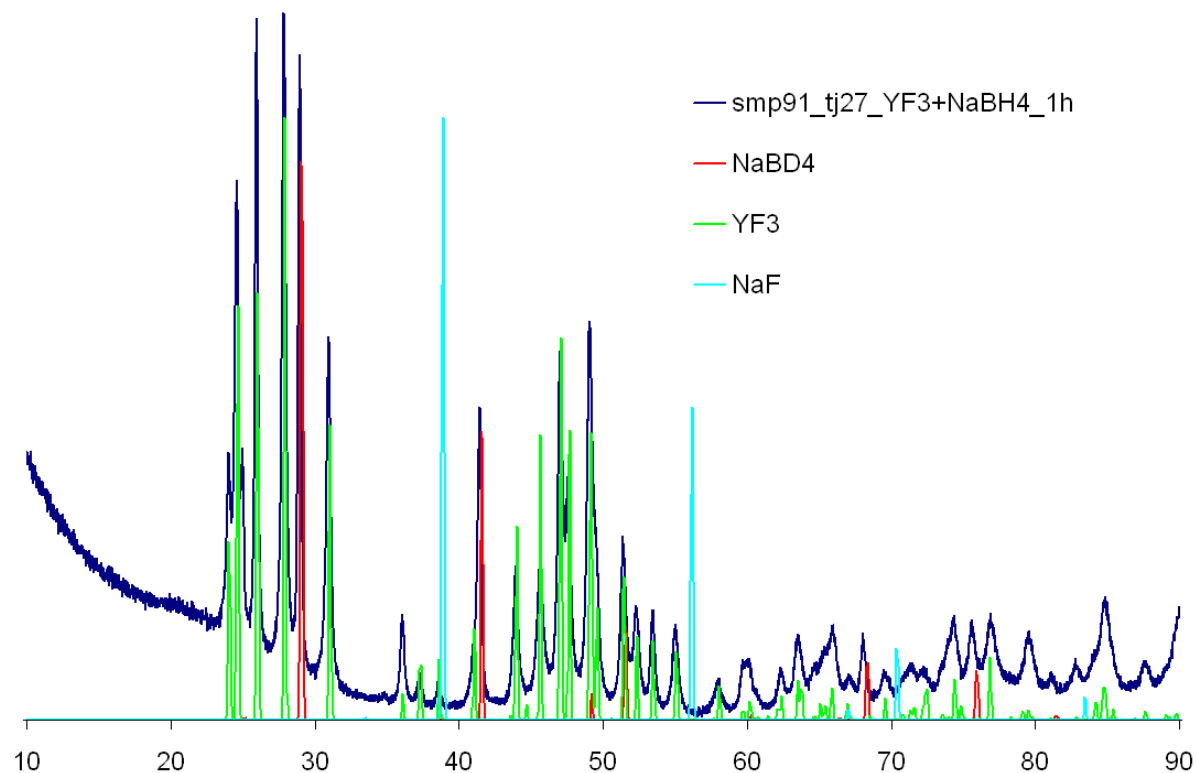


Fig. A2. Powder XRD pattern of the mixture of NaBH₄ and YF₃ milled for 1h.

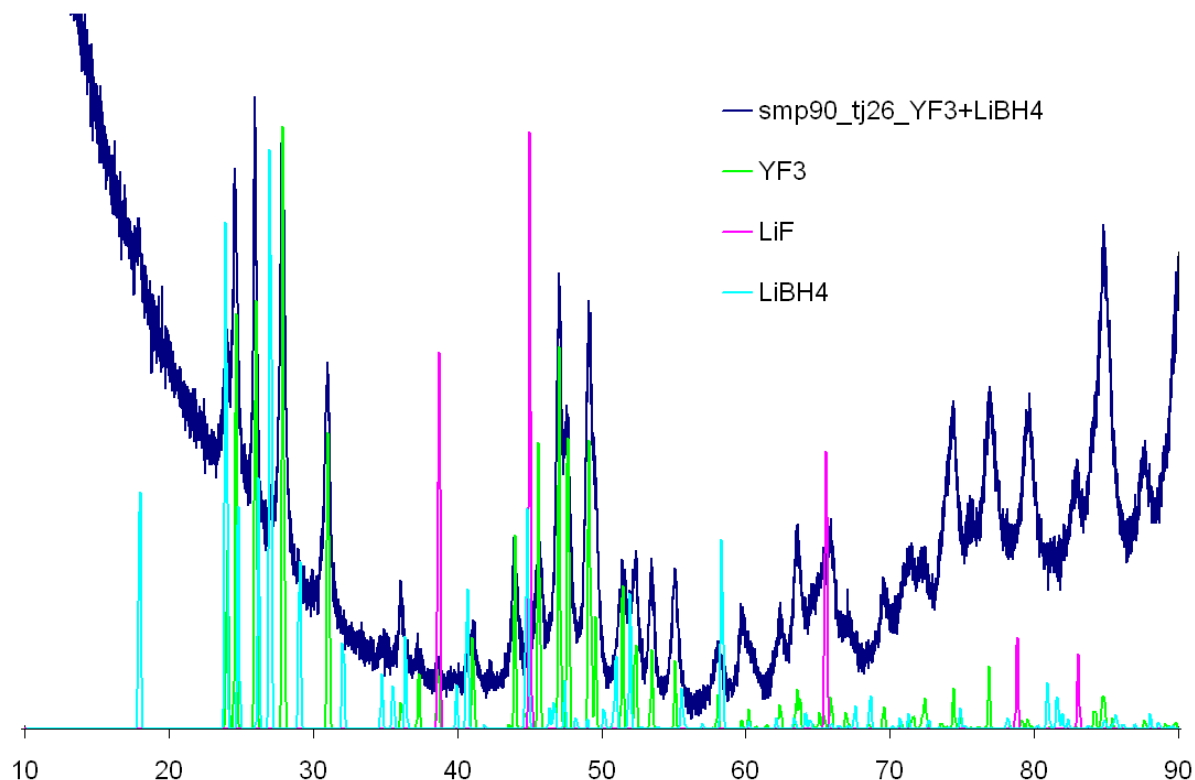


Fig. A3. Powder XRD pattern of the mixture of LiBH₄ and YF₃ milled for 1h.

Closer examination of the patterns shown in Fig.A1 allows to assign the diffraction peaks to NaBH₄, and not to NaCl (few important NaCl reflexes are missing, the peak intensities resemble those of NaBH₄ and not of NaCl).

According to the obtained XRD patterns conversion level is imperceptible (even after 2h milling there were no traces of expected alkali halide), in contrast to the mixture of YCl₃ and LiBH₄. Therefore, those mixtures (containing YF₃ and/or NaBH₄) were no longer investigated.

2.

Metathetical reaction in THF solution.

There are several examples of synthesis of Y(BH₄)₃ · n THF or similar compounds in THF solutions in literature^{3,4,5,6}.

However, in the synthesis performed by the Russian group⁷, it is not necessary to use very toxic and dangerous compounds (like B₂H₆ or Al(BH₄)₃). According to this publication,

³ E. Zange, *Chem. Berichte* **93** (1960) 652; $Y(OCH_3)_3 + 2B_2H_6 \xrightarrow{THF} Y(BH_4)_3 \cdot n THF + B(OCH_3)_3 \uparrow$.

⁴ E. R. Bernstein, K. M. Chen, *Chem. Phys.* **10** (1975) 215; $Y(OCH_3)_3 + 2B_2H_6 \xrightarrow{THF} Y(BH_4)_3 \cdot 3THF + B(OCH_3)_3 \uparrow$; $Y(OCH_3)_3 + 3Al(BH_4)_3 \xrightarrow{THF} Y(BH_4)_3 \cdot 3THF + 3Al(BH_4)_2OCH_3 \uparrow$.

⁵ A. Brukl, K. Rossmanith, *Monatsh. Chem.* **90** (1959) 481; $YCl_3 + 2LiBH_4 \xrightarrow{THF} YCl(BH_4)_2 \cdot n THF + 2LiCl$.

⁶ J. H. Morris, W. E. Smith, *J. Chem. Soc. D, Chem. Commun.* (1970) 245; $ScCl_3 + LiBH_4 \xrightarrow{THF} Sc(BH_4)_3 \cdot n THF \uparrow + 3 LiCl$.

⁷ O. V. Kravchenko, S. E. Kravchenko, V. B. Polyakova, K. N. Semenenko, *Koord. Khim.* **6** (1980) 76.

yttrium borohydride is obtained in reaction: $\text{YCl}_3 + 3 \text{LiBH}_4 \xrightarrow{\text{THF}} \text{Y}(\text{BH}_4)_3 \cdot 2 \text{THF} + 3 \text{LiCl}$. The crystals of $\text{Y}(\text{BH}_4)_3 \cdot 2 \text{THF}$ are grown in vacuum sublimation on heating to $\sim 90^\circ\text{C}$.

Using anhydrous reagents and dry THF (stored above Na) I decided to repeat this synthesis way. After overnight stirring in the inert atmosphere (Ar or N_2) and removing the solvent in vacuum (as it was possible), product did not undergo vacuum sublimation.

Similar results were obtained when $\text{Y}(\text{OC}_4\text{H}_9)_3$ was used to reaction with LiBH_4 (non-sublimating products, solvent impossible to remove).

3.

Metathetical reaction in solid state between YCl_3 and $(\text{C}_4\text{H}_9)_4\text{N}^+ \text{BH}_4^-$ (tetrabutylammonium borohydride - TBAB). Milling time 15 minutes (2.5 min. milling / 2.5 min. pause). XRD and FTIR measurements were performed, Fig. A.4. FTIR spectrum of TBAB is highly similar to the spectrum of milled substrates.

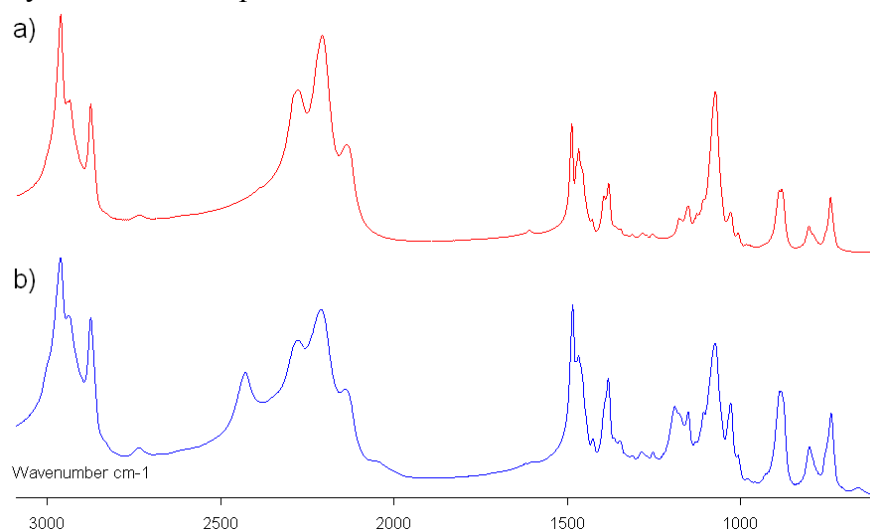


Fig. A.4. FTIR spectra of (a) TBAB, (b) TBAB + YCl_3 milled for 15 minutes (absorbance vs. wavenumber).

4.

Metathetical reaction between YCl_3 or YF_3 and $(\text{C}_4\text{H}_9)_4\text{N}^+ \text{BH}_4^-$ in either CH_2Cl_2 or $n\text{-C}_6\text{H}_{14}$ solution. XRD and FTIR measurements were performed, Fig. A.5.

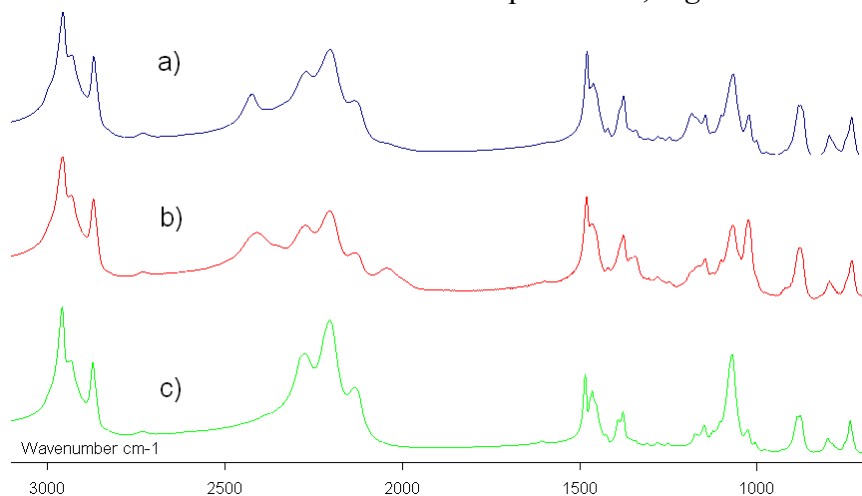


Fig. A.5. FTIR spectra of (a) $\text{YCl}_3 + \text{TBAB} + n\text{-C}_6\text{H}_{14}$ (precipitation) stirred overnight, (b) $\text{YCl}_3 + \text{TBAB} + \text{CH}_2\text{Cl}_2$, (c) TBAB (reference).

5.

Metathetical reaction $\text{YH}_3^8 + (\text{CH}_3)_3\text{NBH}_3$ or $(\text{C}_2\text{H}_5)_3\text{NBH}_3$ dissolved in CH_2Cl_2 under ambient conditions (overnight stirring). $(\text{C}_2\text{H}_5)_3\text{NBH}_3$ (liquid in room temperature) was tested without a solvent also ($(\text{CH}_3)_3\text{NBH}_3$ underwent sublimation during heating to 60°C). The FTIR spectrum of reaction of YH_3 and $(\text{CH}_3)_3\text{NBH}_3$ compared with $(\text{CH}_3)_3\text{NBH}_3$ is presented on the *Fig. A6.*

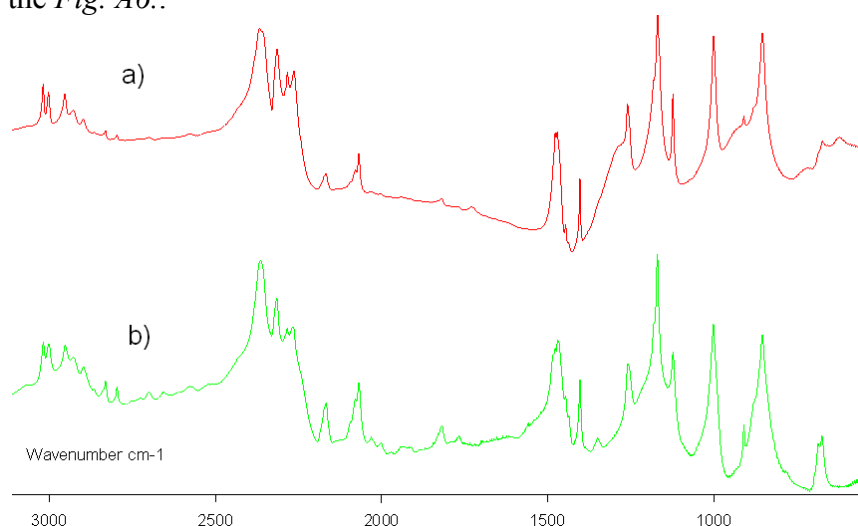
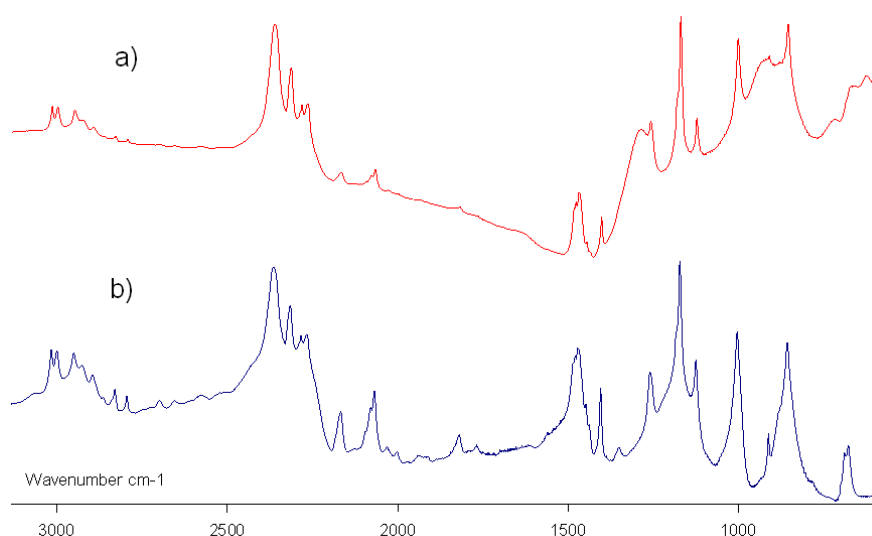


Fig. A.6. FTIR spectra of (a) $\text{YH}_3 + (\text{CH}_3)_3\text{NBH}_3 + \text{CH}_2\text{Cl}_2$ stirred overnight, (b) $(\text{CH}_3)_3\text{NBH}_3$ (reference).

6.

Reagents as described in the point 5 (YH_2 , $(\text{CH}_3)_3\text{NBH}_3$ or $(\text{C}_2\text{H}_5)_3\text{NBH}_3$), without a solvent. Reactions were performed in small Teflon reactor, placed in high-pressure reactor made of Monel alloy, heated in the stabilised furnace ($\sim 100^\circ\text{C}$ for 16 h). Measured FTIR spectrum is presented in the *Fig. A.7.*



⁸ Hydride $\text{YH}_{2,5-3}$ was kindly synthesized by Radostina Genova MSc.

Fig. A.7. FTIR spectra of (a) $\text{YH}_3 + (\text{CH}_3)_3\text{NBH}_3$ heated in closed reactor for 16 h, (b) $(\text{CH}_3)_3\text{NBH}_3$ (reference).