Y(BH₄)₃ – an old-new ternary hydrogen store aka learning from a multitude of failures.

Solid–State Synthesis from YCl₃ + 3 LiBH₄.
206 mg (9.45 milimol, 5% excess) of LiBH₄ was added to 586 mg (3 milimol) of YCl₃ 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 & ¹¹B spectra of the product solution in deuterated THF were performed.

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

<table>
<thead>
<tr>
<th>element</th>
<th>1st measurement</th>
<th>2nd measurement</th>
<th>arithmetic mean</th>
<th>calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>4.76</td>
<td>4.73</td>
<td>4.74</td>
<td>4.81</td>
</tr>
<tr>
<td>Cl</td>
<td>35.45</td>
<td>35.72</td>
<td>35.58</td>
<td>40.30</td>
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</table>

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) YCl₃ with LiBH₄; (absorbance) [arb. units] vs. wavenumber [cm⁻¹].
Table 2. The summary of the measured FTIR bands of the milled (a) and manually homogenized (b) YCl₃ with LiBH₄ (wavenumber [cm⁻¹]).

<table>
<thead>
<tr>
<th></th>
<th>a)</th>
<th>b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2555 (medium–strong)</td>
<td>2383, 2292, 2224 (very strong, broad)</td>
</tr>
<tr>
<td></td>
<td>2304, 2275 (very strong, broad)</td>
<td>1310, 1287 (weak)</td>
</tr>
<tr>
<td></td>
<td>1352 (weak)</td>
<td>1241 (medium)</td>
</tr>
<tr>
<td></td>
<td>1212 (very strong)</td>
<td>1173, 1158 (weak)</td>
</tr>
<tr>
<td></td>
<td>1128 (strong)</td>
<td>1125 (strong)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1093 (strong)</td>
</tr>
</tbody>
</table>

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).

![Raman spectra](image)

**Fig. 3.** Raman spectra of the milled (two upper) and rubbed (bottom) YCl₃ with 20% excess of LiBH₄ (green laser line, 514.5 nm).

NMR Spectra.

Both, ¹¹B and ¹H NMR spectra of the product of reaction (1) as well as LiBH₄ were recorded in deuterated THF solution (Figures 4 and 5). In ¹¹B spectra (¹¹B I = 3/2), a quintet is observed in a 1:4:6:4:1 ratio as a result of coupling with four protons in BH₄⁻ group. Magnetic resonance signal occurs around -33.666 ppm (relatively to BF₃·Et₂O), which is in lower field in comparison with LiBH₄, -41.720 ppm. The ¹H – ¹¹B spin–spin coupling constant for the reaction (1) product (~82.0 Hz) is slightly higher than for LiBH₄ (~81.2 Hz).
Similar $^1$H – $^{11}$B spin–spin coupling constant was measured in YCl(BH$_4$)$_2$ · n THF dissolved in C$_6$D$_6$, $j = 84$ Hz, $\delta = -23.2$, and in Y(BH$_4$)$_3$ · 2 THF dissolved in deuterated toluene, $j = 84$ Hz, $\delta = -24.4$ ppm, $j = 85$ 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 – BF$_3$·Et$_2$O.

$^1$H NMR spectra (Fig. 5.) appears somewhat more complicated than the $^{11}$B spectra described above. This is mainly triggered by the coupling between $^1$H 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 septet, respectively. This cannot be


observed in case of Y(BH₄)₃ due to significant signal broadening (only 3 peaks from ¹⁰B splitting are visible) although both multiplets are centred on practically the same magnetic field (Y(BH₄)₃ -0.168 ppm quartet, -0.173 ppm septet, visible as triplet, LiBH₄ -0.516 ppm vs. -0.514 ppm respectively). The multiplets can be recognised very well in LiBH₄ ¹H NMR spectrum. Spin–spin coupling constant ¹H – ¹⁰B is 3 times lower than ¹H – ¹¹B, LiBH₄ j = 27.2 Hz, Y(BH₄)₃ j = 26.7 Hz. Heavier isotope, ¹¹B is 4 times more abundant (¹¹B 80.22 % vs. ¹⁰B 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 LiBH₄, -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 LiBH₄). 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 LiBH₄.

Fig. 5. Comparison of ¹H NMR spectra of LiBH₄ (upper) and LiBH₄ milled with YCl₃ 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.

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

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).

<table>
<thead>
<tr>
<th>element</th>
<th>1st measurement</th>
<th>2nd measurement</th>
<th>arithmetic mean</th>
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<tr>
<td>H</td>
<td>0.88</td>
<td>0.91</td>
<td>0.90</td>
</tr>
<tr>
<td>Cl</td>
<td>31.80</td>
<td>31.61</td>
<td>31.70</td>
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</table>

Failed attempts of synthesis.

1.

Metathetical reaction in solid state:

\[ YX_3 + 3 \text{MBH}_4 \rightarrow Y(\text{BH}_4)_3 + 3 \text{MCl}, \quad \text{where} \quad X = \text{F, Cl}; \quad M = \text{Li, Na}. \]

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 LiBH$_4$ and YF$_3$ milled for 1h.

Closer examination of the patterns shown in Fig. A1 allows to assign the diffraction peaks to NaBH$_4$, and not to NaCl (few important NaCl reflexes are missing, the peak intensities resemble those of NaBH$_4$ 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 YCl$_3$ and LiBH$_4$. Therefore, those mixtures (containing YF$_3$ and/or NaBH$_4$) were no longer investigated.

2. Metathetical reaction in THF solution.

There are several examples of synthesis of Y(BH$_4$)$_3$·n THF or similar compounds in THF solutions in literature.$^{3,4,5,6}$

However, in the synthesis performed by the Russian group$^{7}$, it is not necessary to use very toxic and dangerous compounds (like B$_2$H$_6$ or Al(BH$_4$)$_3$). According to this publication,

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4 E. R. Bernstein, K. M. Chen, *Chem. Phys.* **10** (1975) 215; Y(OCH$_3$)$_3$ + 2B$_2$H$_6$ $\xrightarrow{\text{THF}}$ Y(BH$_4$)$_3$·3THF + B(OCH$_3$)$_3$; Y(OCH$_3$)$_3$ + 3Al(BH$_4$)$_3$ $\xrightarrow{\text{THF}}$ Y(BH$_4$)$_3$·3THF + 3Al(BH$_4$)$_2$OCH$_3$.  
5 A. Brukl, K. Rossmannith, *Monatsh. Chem.* **90** (1959) 481; YCl$_3$ + 2LiBH$_4$ $\xrightarrow{\text{THF}}$ YCl(BH$_4$)$_2$·n THF + 2LiCl.  
yttrium borohydride is obtained in reaction: $\text{YCl}_3 + 3 \text{LiBH}_4 \xrightarrow{\text{THF}} \text{Y(BH}_4)_3 \cdot 2\text{THF} + 3\text{LiCl}$. The crystals of $\text{Y(BH}_4)_3 \cdot 2\text{THF}$ are grown in vacuum sublimation on heating to ~90°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 $\text{Y(OC}_3\text{H}_9)_3$ was used to reaction with LiBH\(_4\) (non–sublimating products, solvent impossible to remove).

3.

Metathetical reaction in solid state between $\text{YCl}_3$ 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.

4.

Metathetical reaction between $\text{YCl}_3$ or $\text{YF}_3$ and $(\text{C}_4\text{H}_9)_4\text{N}^+\text{BH}_4^-$ in either $\text{CH}_2\text{Cl}_2$ or n–$\text{C}_6\text{H}_{14}$ solution. XRD and FTIR measurements were performed, Fig. A.5.

Fig. A.4. FTIR spectra of (a) TBAB, (b) TBAB + YCl\(_3\) milled for 15 minutes (absorbance vs. wavenumber).

Fig. A.5. FTIR spectra of (a) YCl\(_3\) + TBAB + n-C\(_6\)H\(_{14}\) (precipitation) stirred overnight, (b)YCl\(_3\) + TBAT + CH\(_2\)Cl\(_2\), (c) TBAB (reference).
5. Metathetical reaction $YH_3^8 + (CH_3)_3NBH_3$ or $(C_2H_5)_3NBH_3$ dissolved in CH$_2$Cl$_2$ under ambient conditions (overnight stirring). $(C_2H_5)_3NBH_3$ (liquid in room temperature) was tested without a solvent also ($(CH_3)_3NBH_3$ underwent sublimation during heating to 60°C). The FTIR spectrum of reaction of $YH_3$ and $(CH_3)_3NBH_3$ compared with $(CH_3)_3NBH_3$ is presented on the Fig. A6.

![Fig. A.6. FTIR spectra of (a) $YH_3 + (CH_3)_3NBH_3 + CH_2Cl_2$ stirred overnight, (b) $(CH_3)_3NBH_3$ (reference).](image)

6. Reagents as described in the point 5 ($YH_2$, $(CH_3)_3NBH_3$ or $(C_2H_5)_3NBH_3$), without a solvent. Reactions were performed in small Teflon reactor, placed in high–pressure reactor made of Monel alloy, heated in the stabilised furnace (~100°C for 16 h). Measured FTIR spectrum is presented in the Fig. A.7.

![Fig. A.7. FTIR spectra of (a) $YH_2 + (CH_3)_3NBH_3 + CH_2Cl_2$ stirred overnight, (b) $(CH_3)_3NBH_3$ (reference).](image)

\[ ^8 \text{Hydride } YH_{2.5-3} \text{ was kindly synthesized by Radostina Genova MSc.} \]
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).