Salts of highly fluorinated weakly coordinating anions as versatile precursors towards hydrogen storage materials

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We report the most recent results related to application of a metathetic pathway towards mixed-metal borohydrides. The synthetic protocol utilizes highly-fluorinated weakly coordinating anion salts as precursors. We discuss the technicalities related to use of fluorine-rich anions as well as the improvements which are still needed to deliver the high-purity materials with potential applications for hydrogen storage. The applicability of the method is expanded beyond the previously described complex borohydrides of alkali metal Zn or Y, towards the systems containing and Mg^{II}, Sc^{III}, Mn^{II}, or Eu^{III}. We have prepared for the first time $[Ph_4P]_2[Mn(BH_4)_4]$ and $[Me_4N]_2[Mg(BH_4)_4]$, solved their crystal structures from powder x-ray diffraction, and used selected organic metal borohydride derivatives as precursors towards mixed-metal borohydrides ($K_2Mn(BH_4)_4$, $Rb_2Mg(BH_4)_4$, etc.). We have also prepared $[Ph_4P][Eu(BH_4)_4]$, which is the first derivative of Eu^{III} in the homoleptic environment of borohydride anions.

Introduction

Weakly binding anions constitute one interesting field of modern chemistry which strongly relies on fluorine-rich species. Their diversity allows for precise control of their lattice energy, coordination ability, and other properties of a salt related to constitution and size of anion. This is exemplified by application of Li^+ salts containing anions of low coordination ability[1] like $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$ or $[N(SO_2CF_3)_2]^-$ as electrolytes in lithium-based rechargeable batteries.[2] Such salts, in contrast to the simple lithium halides, guarantee satisfactory solubility in moderately polar electrochemically-inert organic solvents used in the energy storage devices, *i.e.* esters or ethers. Also, the excellent stability of these anions against oxidative decomposition or hydrolysis is the key advantage here.

Deliberate enhancement of the inductive and resonance effects via multiple H⟶F substitutions, interconnected with size increase of the anion, may lead to the anionic species of significantly lower coordination ability than those mentioned above. Such 'weakly coordinating anions' (WCA),[3,4,5] with a single negative charge dissipated over several atoms and well-shielded by fluorine-rich fragments, provide for very small lattice energies, even when they form crystals with small cations such as Li^+. This leads to solubility enhancement of the salts M[*An*], where M = Li–Cs, and [*An*] = $[Al\{OC(CF_3)_3\}_4]$ or $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, even in moderately polar solvents of low coordination ability, like dichloromethane, simultaneously eliminating the need for traditional M^+-complexing agents such as crown- or oligo-ethers. Notably, the corresponding alkali metal salts containing smaller anions ($[BF_4]^-$, $[CF_3SO_3]^-$ or $[N(SO_2CF_3)_2]^-$) are virtually insoluble in dichloromethane.

Solubility in moderately polar dichloromethane renders WCA salts an excellent source of 'naked' metal cations. This feature has been recently utilized in our group for introducing of the metathetic method for synthesis of mixed-cation borohydrides.[6,7] In this method the product is precipitated using the above-mentioned WCA salt added to the solution of anionic borohydride precursor with a large counterion, such as $[nBu_4N]^+$ or $[Ph_4P]^+$. The complete synthetic path from the commercially available halides to the mixed-metal borohydrides has been schematically presented in Fig. 1.

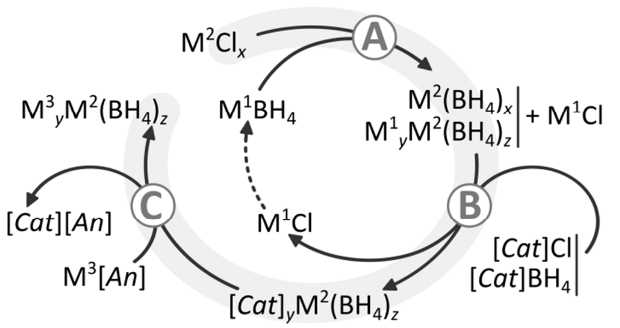

Figure 1. Synthesis of mixed-metal borohydrides, $M^3_y[M^2(BH_4)_z]$, $z = x + y$. Steps **A** and **B** – synthesis and purification of borohydride precursor, step **C** – solvent-mediated metathesis. For $Li[Sc(BH_4)_4]$ prepared this way: M^1 = Li, M^2 = Sc, M^3 = Li, [*Cat*] = $[nBu_4N]$, $[Ph_4P]$, [*An*] = $[Al\{OC(CF_3)_3\}_4]$. Reproduced with permission from Ref.6.

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Hydrogen-rich borohydrides containing light elements constitute one important family of compounds which may potentially be utilized as chemical stores of hydrogen.[8] The lack of efficient, cheap and reversible ways to chemically store hydrogen is currently a real bottleneck limiting the application of hydrogen as an energy carrier.[9,10] Therefore, search for novel systems revealing desirable properties of hydrogen storage attracts significant attention and triggers development of convenient synthetic methods aiming at metal borohydrides, as exemplified by over 1,100 papers on this topic published during the last decade. Due to the presence of light weight borohydride groups, the metal borohydrides are characterized by large gravimetric and volumetric hydrogen content; *e.g.* $LiBH_4$ contains 18.4 wt. % H and 121 kg H/m^3, while its energy density of 43 MJ/dm^3 (for oxidation reaction with O_2) exceeds that of gasoline (35 MJ/dm^3). However, there are two important drawbacks of the known single-metal borohydrides: those of Group 1 and Group 2 metals exhibit too large temperature of thermal decomposition, while those of most transition metals decompose at low temperatures, but they eliminate significant amounts of B_2H_6 impurity in hydrogen gas,[11] and the decomposed material cannot be recharged with hydrogen.[12] Numerous attempts were done to overcome these problems, such as application of catalysts to facilitate thermal decomposition of thermodynamically stable borohydrides,[13] preparation of the previously unknown pure single-metal borohydrides,[14,15] as well as syntheses of mixed-metal borohydrides[16] (in particular alkali and transition metal ones[17,18]). The latter approach results in large matrix of complex borohydrides which should be screened to fully beneficiate from property tuning offered by two types of metal present in their crystal structures. As a consequence, in addition to the well-developed mechanochemical approach, two complementary, solvent-mediated synthetic procedures have been recently introduced: one of them, based on use of SMe_2 as a solvent, leads to the novel single-cation borohydrides,[19,20] while the other, discussed here, allows for the synthesis of mixed-metal borohydrides free from the "dead mass" (typically LiCl; Fig. 2).

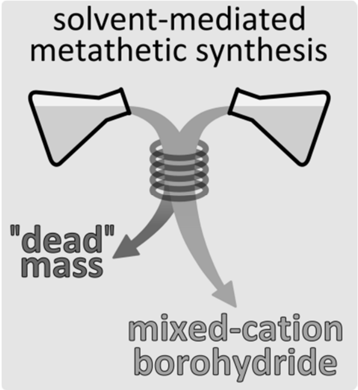

Figure 2. Schematic illustration of the combined key stages B and C (cf. Fig.1) of the synthetic protocol which enable separation of the "dead mass" (LiCl and the like) from the target product (complex borohydride). Reproduced with permission from Ref.6.

In this contribution we review the most recent results on synthesis of mixed-metal borohydrides using the metathetic protocol which utilizes highly-fluorinated WCA salts as precursors. Based on the previously described[6,7] successful preparation of the salts of M^2= Zn and Y, here we have attempted to expand the applicability of the new method towards selected systems of M^2= Sc, Mn and Mg. We focus on the advantages and disadvantages of the method, product purity, as well as general applicability of the new approach.

Methods

Most of the experimental methods used for synthesis and characterization of the products have been described in the recent papers by Jaroń *et al.*[6,7] Here we outline their most important features and also add a few improvements. All manipulations have been performed in argon atmosphere using the Schlenk–type glassware and MBraun gloveboxes (<1 ppm O_2, <1 ppm H_2O), the latter also for storage of the reagents and products.

$M[Al\{OC(CF_3)_3\}_4]$, M = Li, Na, K precursors

The suspension of $MAlH_4$ ($LiAlH_4$ – as obtained from Alfa-Aesar, $NaAlH_4$ – Sigma-Aldrich, purified by dissolution in THF, filtration and evaporation of the solvent, $KAlH_4$ – prepared from KH and $LiAlH_4$ in diglyme/THF[6]) in hexane was cooled to 0 °C and $(CF_3)_3COH$ (Fluorochem) was slowly added with excess (*ca.* 150%). The reaction mixture was refluxed for several h, cooled, another portion of $(CF_3)_3COH$ was then added (*ca.* 50%), and the mixture was refluxed again for several h. The solvent has been evaporated and the white solid product has been extracted in Soxhlet extractor using perfluorohexane (mixture of isomers, Fluorochem) for M=Li, or dichloromethane (anhydrous, Sigma-Aldrich) for M=Na and K, which yield pure products as evaluated by FTIR and PXD analyses. Typical yield: >90%.

$M[Al\{OC(CF_3)_3\}_4]$, M = Rb, Cs precursors

$Li[Al\{OC(CF_3)_3\}_4]$ and excess of MCl (200%) were mixed and milled for 30 min in 5 min cycles at 1400 rpm using stainless steel milling disc bowl and laboratory vibrating mill (Testchem; the same mill has been used in other procedures described below). The product was then extracted using dichloromethane. Typical yield: >80%.

$[Ph_4P][Eu(BH_4)_4]$ precursor

$EuCl_3$, $LiBH_4$ (Sigma-Aldrich) and $[Ph_4P]BH_4$[21] were milled in 1:3:1 molar ratio for 30 min in 5 min cycles using milling bowl with liquid N_2 cooling to maintain the temperature close to 0 °C. The product was then extracted using cold dichloromethane, desolvated, and stored at –35 °C under Ar. Typical yield: >70%.

$[Ph_4P]_2[Mn(BH_4)_4]$ precursor

$Mn(BH_4)_2{\cdot}3THF$ has been prepared from $MnCl_2$ and $NaBH_4$ in THF solution, according to the procedure of Makhaev, *et al.*[43] $[Ph_4P]_2[Mn(BH_4)_4]$ has been prepared in reaction of $Mn(BH_4)_2{\cdot}3THF$ with two equivalents of $[Ph_4P]BH_4$ in dichloromethane (30–60 min stirring, *ca.* 10 ml of solvent per 1 mmol of $Mn(BH_4)_2 \cdot 3THF$ was used) followed by evaporation of solvent and washing with benzene. Typical yield: >60%. Similar procedure with different ratio of reactants ($Mn(BH_4)_3$x3THF:$[Ph_4P]BH_4$ = 1:0.82) was described by Makhaev, *et al.,* as resulting in a different product, $[Ph_4P][Mn(BH_4)_3]$, but this has not been supported by structural analysis.[21]

$[Me_4N]_2[Mg(BH_4)_4]$ precursor

$MgCl_2$, $LiBH_4$ and $[Me_4N]BH_4$ (Sigma-Aldrich) were milled in 1:2:1 molar ratio for 30 min in 5 min cycles with liquid N_2 cooling to maintain the room temperature of the milling bowl. The product has not been purified due to the poor solubility.

Typical procedure of wet synthesis of mixed-metal borohydrides as exemplified by $Li[Sc(BH_4)_4]$

To the suspension of $Li[Al\{OC(CF_3)_3\}_4]$ in dichloromethane a solution of $[nBu_4N][Sc(BH_4)_4]$ (with *ca.* 5% excess) in the same solvent was added and the mixture was stirred for *ca.* 1 h. Typically *ca.* 50 ml of dichloromethane per 1 mmol of $Li[Al\{OC(CF_3)_3\}_4]$ and 10 ml of dichloromethane per 1 mmol of $[nBu_4N][Sc(BH_4)_4]$ were used. The suspension was then allowed to settle and the precipitate was filtered off, rinsed several times with the fresh portions of dichloromethane and dried under vacuum. Typical yield for the product of metathesis: >95%. For synthesis of the thermally less stable compounds (*e.g.* those containing Eu^{III}) the solvent has been precooled to –35 °C before the reaction and the entire procedure has been significantly shortened (to 10 min). For testing purposes similar procedure has also been carried out with use of other solvents: 1,2-difluorobenzene, toluene, acetonitrile, and perfluorohexane. In the latter case, due to immiscibility of perfluorohexane with dichloromethane, reaction was performed via vigorous shaking of the mixture for 1.5 h.

Analytical methods and data processing

FTIR spectra were measured on Vertex 80v spectrometer (Bruker) using 200 mg of KBr as a pellet material (diameter of 12 mm). Powder X-ray diffraction (PXD) patterns of the samples sealed inside quartz capillaries (diameter of 0.3–1 mm) were measured using either Bruker D8 Discover diffractometer (parallel beam; the $CuK_{\alpha1}$ and $CuK_{\alpha2}$ radiation), or Panalytical X'Pert Pro diffractometer (parallel beam; the $CoK_{\alpha1}$ and $CoK_{\alpha2}$ radiation). The Rietveld refinement including quantitative phase analysis has been performed in Jana 2006.[22] Thermal decomposition was investigated with a combined thermogravimeter (TGA) and differential scanning calorimeter (DSC) from Netzsch – STA 409 PG, at a constant Ar (99.9999 %) flow of 80 ml/min, and at 5 $^{\circ}C\ min^{-1}$ heating rate. The evolved gases were analyzed with a quadruple mass spectrometer (MS) QMS 403 C (Pfeiffer Vacuum), connected to the TGA/DSC device by quartz capillary preheated to 200 °C to avoid condensation of low-boiling volatiles.

Results and discussion

General description of the synthetic procedure

The mixed-metal borohydrides have been prepared via solvent-mediated metathesis reactions, *e.g.*:

$$Li[An] + [Cat][Sc(BH_4)_4] \rightarrow Li[Sc(BH_4)_4]\downarrow + [Cat][An] \qquad (1),$$

where $[An] = [Al\{OC(CF_3)_3\}_4]$, and $[Cat] = [nBu_4N]$ or $[Ph_4P]$. In this process the relatively small inorganic ions form borohydride product which precipitates, while $[Cat][An]$ by-product composed of bulky organic ions remains in the dichloromethane solution. This key process corresponds to the step **C** in Fig. 1, while preparation of one of the necessary precursors, $[Cat][Sc(BH_4)_4]$, constitutes steps **A** and **B**. Despite apparent simplicity of this approach, it turns out that the products not always correspond to the desired stoichiometries. Moreover, in some cases substantial occlusion of the by-product and/or solvent takes place. Below we discuss a few critical factors influencing the chemical identity and purity of obtained products, such as selection of solvent and solid precursors. We then turn to the brief characteristics of precursors and prepared compounds and we discuss general applicability of the wet method.

The solubility issue and selection of weakly coordinating solvents

Typical ethereal and amine solvents (often applied for synthesis of borohydrides of alkali and alkali earth metals) are usually not suitable for preparation of the transition metal and lanthanide borohydrides. The borohydrides of the latter two blocks are less thermally stable, which – being rather an advantage in terms of hydrogen storage – makes complete desolvation impossible or very difficult; in fact some lightweight borohydrides of this kind have been reported only in an ether-solvated form, *e.g.* $Sc(BH_4)_3 \cdot 2THF$.[23] Solvent removal is somewhat easier when volatile dimethyl sulfide is used, however heating up to 140 °C may occasionally be necessary for preparation of homoleptic borohydrides; this is unacceptable for the borohydrides which thermally decompose in the desired temperature range of 80–120 °C.[19,20] Taking into account rather simple, volatile organic liquids of low solvating ability (*i.e.* those lacking lone pairs on O, N and S atoms) two solvents seem attractive: dichloromethane, $T_{boiling} = 39.8\ ^{\circ}C$, $\varepsilon(25\ ^{\circ}C) = 8.93$, and 1,2-dichloroethane, $T_{boiling} = 83\ ^{\circ}C$, $\varepsilon(25\ ^{\circ}C) = 10.07$.[24] The dielectric constant of the latter is *ca.* 10% larger than that of the former; however, the dissociation ability and solubility of the tested WCA salts in dichloromethane is sufficient to perform the step **C** of the synthetic procedure. Dichloromethane is also significantly cheaper and less toxic as well as more volatile of the two which facilitates drying of the product.

While the low coordination ability of dichloromethane permits its easy removal after reaction, this solvent shows only moderate polarity in comparison to the solvents in which ion-ion reactions are usually performed (*e.g.* anhydrous HF $\varepsilon(0\ ^{\circ}C) = 83.6$, H_2O $\varepsilon(25\ ^{\circ}C) = 78.3$, CH_3CN $\varepsilon(25\ ^{\circ}C) = 36.7$). Therefore, due to their imperceptible solubility in dichloromethane, the salts like halides, borohydrides, triflates, alkoxides, tetraphenylborates and other non-fluorinated derivatives, cannot be utilized as $M^3[An]$ precursors.[7] On the other hand, when acetonitrile has been tested as a solvent (either pure or as an addition of *ca.* 2.5 vol% to dichloromethane) for synthesis of $K[Y(BH_4)_4]$ using $K[Al\{OC(CF_3)_3\}_4]$, only KBH_4 precipitated instead of the expected $K[Y(BH_4)_4]$ (Fig. 3a). The remaining solution clearly contained the soluble yttrium complexes with coordinated acetonitrile molecules. Contrastingly, when aromatic solvents, like toluene or 1,2-difluorobenzene (ε(27 ^{o}C) = 13.38) have been used, no precipitation was observed at all, which may be explained by formation of soluble potassium complexes with aromatic ligands.[7] Only the procedure utilizing pure dichloromethane as a solvent and $K[Al\{OC(CF_3)_3\}_4]$ + $[nBu_4N][Y(BH_4)_4]$ precursors has delivered the target compound in a high purity (Fig. 3b). This example clearly illustrates the need for a very weakly coordinating solvent, dichloromethane, for the metathetic reaction. Moreover, while targeting analogous $Li[Sc(BH_4)_4]$, shaking of $Li[Al\{OC(CF_3)_3\}_4]$ solution in an inert perfluorohexane (1 milimol in 25 ml) with $[nBu_4N][Sc(BH_4)_4]$ dissolved in dichloromethane (1.05 milimol in 10 ml) resulted in precipitation of the mixture of $LiBH_4$ and $Li[Sc(BH_4)_4]$ in a molar ratio of *ca.* 1.9:1 rather than the expected pure $Li[Sc(BH_4)_4]$. This result suggests that almost ⅔ of the Sc precursor remained in the organic layer.

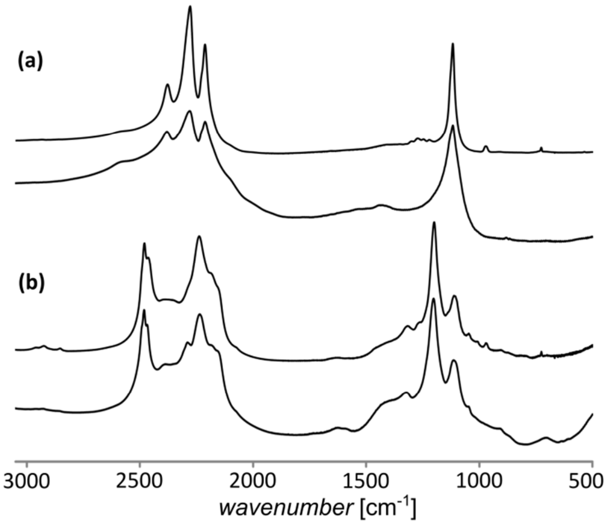

Figure 3. The FTIR spectra of the product of reaction between $K[Al\{OC(CF_3)_3\}_4]$ and $[nBu_4N][Y(BH_4)_4]$: (a) in dichloromethane with *ca.* 2.5 vol% of CH_3CN (upper curve) as compared to the spectrum of KBH_4 (lower curve), (b) in pure dichloromethane (upper curve), as compared to the spectrum of $K[Y(BH_4)_4]$ prepared mechanochemically.[35]

The sources of metal cations: WCA salts, $M^3[An]$

As already mentioned, among the alkali metal salts only those containing the most weakly coordinating anions are soluble enough in dichloromethane to enable the metathetic reaction (step **C**). Two groups of such compounds have been thoroughly tested: $M[Al\{OC(CF_3)_3\}_4]$, for M = Li–Cs and $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$. The preliminary evaluation of $K[Al(OCH(CF_3)_2]$ resulted in huge amount of the synthesis by-product, which could not be washed away with the solvent.[7]

$Li[Al\{OC(CF_3)_3\}_4]$ and $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ are available commercially from IoLiTec GmbH, and other providers worldwide. While the first compound is ready to use, the second should be dried at *ca.* 100 ^{o}C under vacuum, as it is usually sold as a mixture of hydrated and anhydrous forms. Although the synthesis of $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ has recently been improved,[25,26] it is still more laborious than the preparation of aluminate WCAs, therefore we have chosen the latter ones. The vital step in the synthesis of $M[Al\{OC(CF_3)_3\}_4]$ comprises of solvent extraction, which results in a homogenous, single phase product free from unreacted Al–H species, as evaluated by PXD and FTIR, respectively.[27]

While all the alkali metal aluminates are now available, the problem remains with the lack of good chemical pathways towards WCA salts of the 'naked' cations of higher charge (+2, +3, etc.); thus, borohydride targets are currently restricted to those containing alkali metals and hypothetical salts such as $Ba[Mn(BH_4)_4]$ or $Sr[Mg(BH_4)_4]$ are left out.

The sources of complex borohydride anions: $[Cat]_yM^2(BH_4)_z$ salts

Numerous homoleptic metal borohydride complexes containing organic cations have been reported since 1960s,[28,29] however most of them have not been fully characterized and only few crystal structures have been reported. This hampers evaluation of the true identity and purity of the compounds obtained. Currently, the following borohydrides of this kind have been structurally characterized: $[Ph_4P]_2[Mg(BH_4)_4]$,[30] $[Me_4N]_2[Mg(BH_4)_4]$ (this work), $[Cat][Al(BH_4)_4]$ for $[Cat]$ = $[Et_4N]$,[31] $[Ph_3MeP]$, $[Ph_3P{=}N{=}PPh_3]$,[32] $[Cat][Sc(BH_4)_4]$, $[Cat]$ = $[Me_4N]$, $[nBu_4N]$, $[Ph_4P]$,[33] $[Ph_4P]_2[Mn(BH_4)_4]$ (this work), $[Ph_4P][Zn(BH_4)_3]$,[34] $[Ph_4P][Zn_2(BH_4)_5]$,[6] $[Cat][Y(BH_4)_4]$ for $[Cat]$ = $[Me_4N]$,[35] $[nBu_4N]$,[36] $[Ph_4P][Eu(BH_4)_4]$ (this work), $[Ph_4P][Tm(BH_4)_4]$,[37] which correspond to the nine complex borohydride anions that can be tested via Eq.(1). Such compounds containing $[nBu_4N]$ and $[Ph_4P]$ cations show excellent solubility in dichloromethane and, especially those with $[Ph_4P]$ cations in the structure, are more thermally stable than the corresponding single metal borohydrides.[38] These features largely facilitate preparation and purification of the organic borohydride precursors and their further use for synthesis of the target borohydrides.

Some of these precursors can be conveniently prepared using one-pot mechanochemical process, where the three commercially available reagents are milled: M^1BH_4, usually M^1 = Li, $[Cat]BH_4$, and M^2Cl_x, which corresponds to the combined steps **A** and **B** (Fig. 1); if necessary, $[Cat]BH_4$ can be replaced by more accessible $[Cat]Cl$. Such convenient process works very well for the compounds of rare-earth metals, as tested before for Sc[33] and Y.[7] Similar mechanochemical procedure with combined steps **A** and **B** works for synthesis of $[Ph_4P][Zn(BH_4)_3]$,[6] while to obtain pure $[Ph_4P][Zn_2(BH_4)_5]$ complex a two-step milling is necessary.[6] The other zinc-containing precursor, $[nBu_4N][Zn(BH_4)_3]$ was achieved in a modified synthetic protocol applied by Saidov et al. [6,34]

We have tested the applicability of the above-mentioned protocol to preparation of the derivative of Eu^{III}. This is a particularly demanding target as the Eu^{III}/Eu^{II} redox pair falls at the standard redox potential as positive as –0.35 V *vs.* NHE and, consequently, the borohydride, alanate and hydride derivatives of Eu^{III} are very unstable thermally due to an internal redox process.[8] Indeed, quasi-binary $Eu(BH_4)_3$ still awaits preparation.[39] We have overcome those difficulties by lowering the temperature during the synthesis to below 0 ^{o}C (using of the ice-cold dichloromethane for extraction, and carrying out solvent removal at *ca.* 0 ^{o}C), and storing of the product at –35 ^{o}C under Ar. In this way, $[Ph_4P][Eu(BH_4)_4]$ has successfully been obtained. This salt crystallizes in the $I4_1/a$ space group, which is adopted by several analogous compounds such as $[Ph_4P][Tm(BH_4)_4]$[37] and $[Ph_4P][Sc(BH_4)_4]$.[33] $[Ph_4P][Eu(BH_4)_4]$ turns out to be the first compound which contains rather oxidizing Eu^{III} in the homoleptic environment of the borohydride anions, while forming a complex $[Eu(BH_4)_4]^{-}$ anion (Fig. 4).

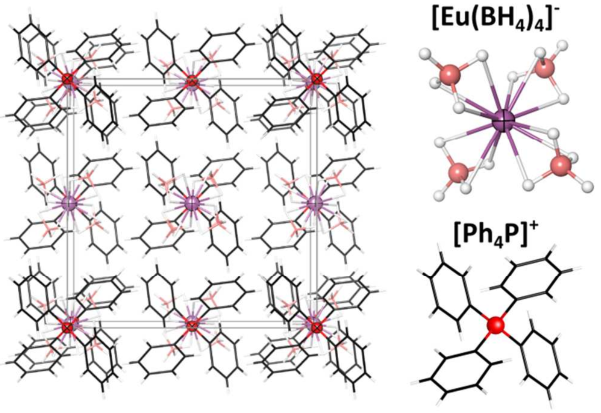

Figure 4. Unit cell of $[Ph_4P][Eu(BH_4)_4]$, presented here along the *c* axis, is composed of $[Eu(BH_4)_4]^{-}$ and $[Ph_4P]^{+}$ moieties which are drawn at the right side. Color code: black for C, white for H, pink for B, red for P, violet for Eu.

Synthesis of the organic precursors of mixed-metal borohydrides containing Mg and Mn[40] also proved quite demanding. Initially, we have successfully targeted $[Me_4N]_2[Mg(BH_4)_4]$ via a mechanochemical reaction. The crystal structure of this compound adopting $P2_1/c$ space group[41] is composed of $[Me_4N]^{+}$ cations and $[Mg(BH_4)_4]^{2-}$ dianions (Fig.5), known also from $K_2[Mg(BH_4)_4]$.[40] However, it turns out that this derivative is insoluble in organic solvents used customarily for extraction. Clearly, use of $[Me_4N]^{+}$ salts for wet metathesis is discouraged.

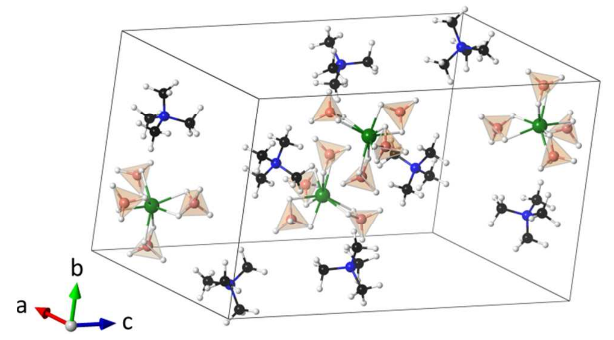

Figure 5. Unit cell of $[Me_4N]_2[Mg(BH_4)_4$. Color code: black for C, white for H, pink for B, blue for N, green for Mg.

Therefore, in the next step we have targeted analogous salts containing more hydrophobic $[nBu_4N]^{+}$ cations. We have followed the procedures proposed by Makhaev *et al.*,[30,42] by firstly preparing the solvated single-metal borohydrides:

$$MgCl_2 + 2NaBH_4 \xrightarrow{DME} Mg(BH_4)_2 \cdot 1.5DME + 2NaCl \quad (2)$$
$$MnCl_2 + 2NaBH_4 \xrightarrow{THF} Mn(BH_4)_2 \cdot 3THF + 2NaCl \quad (3),^{43}$$

where DME stands for 1,2-dimethoxyethane, and subsequently treating them with solution of $[nBu_4N]BH_4$ in dichloromethane:

$$Mg(BH_4)_2 \cdot 1.5DME + 2[n\mathrm{Bu}_4\mathrm{N}]\mathrm{BH}_4 \xrightarrow[-DME]{} [n\mathrm{Bu}_4\mathrm{N}]_2[Mg(BH_4)_4] \quad (4).$$

Unfortunately, the attempts of synthesis of a well-defined borohydride containing $[nBu_4N]$ cation (*i.e.* $[nBu_4N]_2M^2(BH_4)_4$) led in both cases to the mixture of products, which could not be separated and identified. Neither we have obtained single crystals suitable for structural analysis. We were able to prepare well-defined organic borohydrides of Mg and Mn only when $[Ph_4P]^{+}$ has been used as a counterion:

$$Mg(BH_4)_2 \cdot 1.5DME + 2[Ph_4\mathrm{P}]\mathrm{BH}_4 \xrightarrow[-DME]{} [Ph_4\mathrm{P}]_2[Mg(BH_4)_4] \quad (5)$$

$$Mn(BH_4)_2 \cdot 3THF + 2[Ph_4\mathrm{P}]BH_4 \xrightarrow[-THF]{} [Ph_4\mathrm{P}]_2[Mn(BH_4)_4] \quad (6).$$

While $[Ph_4P]_2[Mg(BH_4)_4]$ has previously been described, its Mn analogue has not. $[Ph_4P]_2[Mn(BH_4)_4]$ crystallizes in the C-centered monoclinic cell with four formula units; distinct $[Mn(BH_4)_4]^{2-}$ dianions are present in its crystal structure, Fig.6. Its excellent solubility in dichloromethane renders it a good precursor of the wet metathesis.

Summarizing this section we conclude that $[Ph_4P]^{+}$ cations prove superior to $[nBu_4N]^{+}$ ones as counterions with complex borohydride anions. The salts formed by the former have much better crystallinity which strongly facilitate their identification and purification, which is obviously a prerequisite for applying these salts in the metathetic reaction. It is expected that many more organic borohydrides such as $[Ph_4P][M^{III}(BH_4)_4]$, $[Ph_4P]_2[M^{II}(BH_4)_4]$ and $[Ph_4P][M^{I}(BH_4)_2]$ could be prepared in the way similar to those described here.

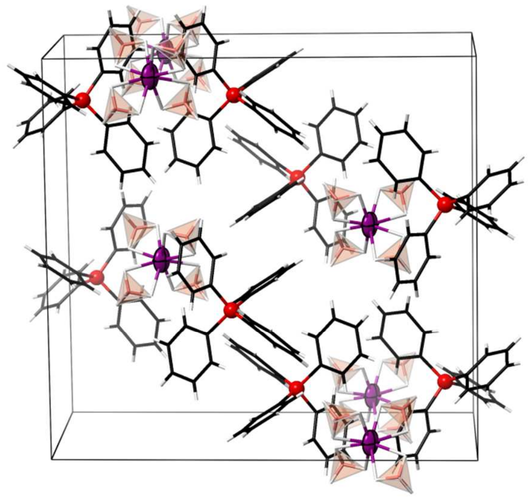

Figure 6. Unit cell of $[Ph_4P]_2[Mn(BH_4)_4$ presented approximately along *a* axis. Color code: black for C, white for H, pink for B, red for P, violet for Mn.

Technicalities of the novel synthetic protocol and purity of the targeted product

Having discussed the limitations related to the choice of both types of precursors, we now turn to the outcome of metathetic reactions between them. The results of the wet

Target compound	H amount [wt%]	Precursors	Purity of the product & other comments
$Li[Sc(BH_4)_4]$*	14.5	$Li[Al\{OC(CF_3)_3\}_4]$; $[nBu_4N][Sc(BH_4)_4]$	Variable amount of impurities; 12% LiCl in one of the samples
		$Li[Al\{OC(CF_3)_3\}_4]$ in PFH; $[nBu_4N][Sc(BH_4)_4]$ in DCM	73% $Li[Sc(BH_4)_4]$: 27% $LiBH_4$
$Li[Y(BH_4)_4]$	10.4	$Li[Al\{OC(CF_3)_3\}_4]$; $[nBu_4N][Y(BH_4)_4]$	76% $Li[Y(BH_4)_4]$: 24% $Y(BH_4)_3$; other signals in PXD moderate
$Na[Y(BH_4)_4]$	9.4	$Na[Al\{OC(CF_3)_3\}_4]$; $[nBu_4N][Y(BH_4)_4]$	Stable composition: 79% $Na[Y(BH_4)_4]$: 12% $Y(BH_4)_3$: 9% $NaBH_4$
		$Na[B\{3,5-(CF_3)_2C_6H_3\}_4]$; $[nBu_4N][Y(BH_4)_4]$	48 h after synthesis: 17% $Na[Y(BH_4)_4]$: 58% $Y(BH_4)_3$: 26% $NaBH_4$
$K[Y(BH_4)_4]$	8.6	$K[Al\{OC(CF_3)_3\}_4]$; $[nBu_4N][Y(BH_4)_4]$	**Nearly pure product**, very low foreign signals in FTIR
$Rb[Y(BH_4)_4]$	6.9	$Rb[Al\{OC(CF_3)_3\}_4]$; $[nBu_4N][Y(BH_4)_4]$	Several moderate peaks from unidentified impurities in PXD
$Cs[Y(BH_4)_4]$	5.7	$Cs[Al\{OC(CF_3)_3\}_4]$; $[nBu_4N][Y(BH_4)_4]$	**Pure product (~99%)**; two peaks from impurities barely detectable in PXD
$K[Eu(BH_4)_4]$*	6.4	$K[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P][Eu(BH_4)_4]$	Unidentified product of decomposition
$Li_2[Mg(BH_4)_4]$*	16.5	$Li[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P]_2[Mg(BH_4)_4]$	Signals from unidentified phase, $LiBH_4$ and $Li[Al\{OC(CF_3)_3\}_4]$
$K_2[Mg(BH_4)_4]$*	10.0	$K[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P]_2[Mg(BH_4)_4]$	KBH_4 detected only in two separate attempts
$Rb_2[Mg(BH_4)_4]$*	6.3	$Rb[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P]_2[Mg(BH_4)_4]$	**Very pure product (~99.8%)**
$Cs_2[Mg(BH_4)_4]$*	4.6	$Cs[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P]_2[Mg(BH_4)_4]$	Complex system / purity unknown
$K_2[Mn(BH_4)_4]$*	8.4	$K[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P]_2[Mn(BH_4)_4]$	70% $K_2[Mn(BH_4)_4]$: 30% KBH_4; unidentified products present
$Li[Zn_2(BH_4)_5]$	9.5	$Li[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P][Zn_2(BH_4)_5]$	**Very pure product (~99.8%)**; traces of LiCl (0.2%)
$Li[Zn(BH_4)_3]$	10.4	$Li[Al\{OC(CF_3)_3\}_4]$; $[Ph_4P][Zn(BH_4)_3]$	87.0% $Li[Zn_2(BH_4)_5]$: 6.6% $LiBH_4$: 6.5% LiCl
$Na[Zn(BH_4)_3]$	9.1	$Na[B\{3,5-(CF_3)_2C_6H_3\}_4]$; $[Ph_4P][Zn(BH_4)_3]$	64.4% $Na[Zn(BH_4)_3]$: 32.3% $NaBH_4$: 3.3% NaCl
		$Na[B\{3,5-(CF_3)_2C_6H_3\}_4]$; $[nBu_4N][Zn(BH_4)_3]$	92.4% $Na[Zn(BH_4)_3]$: 7.6% $NaBH_4$
$K[Zn(BH_4)_3]$	8.1	$K[Al\{OC(CF_3)_3\}_4]$; $[nBu_4N][Zn(BH_4)_3]$	93.6% $K[Zn(BH_4)_3]$: 6.4% KBH_4

Table 1. The selected mixed-metal borohydrides prepared via solvent-mediated metathesis reactions using F-rich WCA precursors.

The target compounds which have been successfully prepared are displayed in bold fonts. * marks compounds or methods of their synthesis firstly reported in this work, otherwise *cf.* Refs. 6,7. Dichloromethane (DCM) has been used as a solvent for almost all cases; PFH – perfluorohexane. Composition of some of the product mixtures has been given in wt. % (from PXD quantitative analysis).

reactions leading to mixed-metal borohydrides have been summarized in Table 1.

At the first sight one might conclude that the metathetic method has a rather broad applicability: 12 out of 16 target compounds (*i.e.* 75%) have successfully been prepared using the same general synthetic route. Among the failures, two target compounds are not stable enough at room temperature to enable their comprehensive characterization: $Li[Zn(BH_4)_3]$ instantly regroups to the mixture of more stable $Li[Zn_2(BH_4)_5]$ and $LiBH_4$, while $K[Eu(BH_4)_4]$ decomposes to unidentified derivatives of Eu^{II}. In the two remaining cases, crystalline product either does not form ($K_2[Mg(BH_4)_4]$) or a mixture is obtained and the stoichiometry of the main phase remains unclear ($Li_2[Mg(BH_4)_4]$).

Still, the metathetic approach has one considerable advantage over the dry (mechanochemical) synthesis: since instead of neutral quasi-binary precursors (for example $LiBH_4$ and $Y(BH_4)_4$) it uses ions for synthesis (for example Li^+ and $[Y(BH_4)_4]^-$), the reaction is favored thermodynamically. Thus, even some elusive thermodynamically unstable borohydrides such as $Li[Y(BH_4)_4]$ or $Na[Y(BH_4)_4]$, which never have been prepared via a mechanochemical or a thermal route, may in some instances be prepared using the wet method.[7,44]

The high purity of the product obtained is an essential feature for every procedure of synthesis; in the case of potential hydrogen storage materials the impurities may strongly affect the quality of released hydrogen gas and the efficiency of its storage. Among the samples presented in Table 1 only three (*i.e.* $Li[Zn_2(BH_4)_5]$, $Cs[Y(BH_4)_4]$, and $Rb_2[Mg(BH_4)_4]$) show fine purity (>99%) as evaluated by PXD, and they could be used for testing of hydrogen storage properties as obtained; all other products would require additional purification, which is rather not straightforward. It is worth to mention that the purity of gases evolved during the thermal decomposition of chosen mixed-cation borohydrides has been checked by the temperature-resolved mass spectrometry, revealing very low (*i.e.* less than two orders of magnitude) contamination by the precursors or by-products of their synthesis.

The metathetical route has been originally developed to eliminate the problem of 'dead-mass' such as LiCl and NaCl – which is one of serious drawbacks of the classical mechanochemical synthesis of borohydrides. These by-products may constitute >50 wt.% of the post-milling mixture and they cannot be easily removed by chemical or physical means. However, one may easily notice that these contaminations appear also in some of our samples (*e.g.*, from 3.3 wt.% NaCl in $Na[Zn(BH_4)_3]$, up to 12 wt.% LiCl in one of the batches of $Li[Sc(BH_4)_4]$). There are two possible sources of this contamination. First, the filter with the glass frit may not be dense enough to completely eliminate the by-product of synthesis of the organic borohydride precursor during extraction. This is indeed the case for Sc compounds, which require use of a very fine filter to deliver high purity product. In principle, this source of contamination may be completely eliminated. The second source is slightly more problematic: the exchange of Cl^- anions by BH_4^- groups during the synthesis of the organic borohydride precursor may not be 100% complete, which then leads in the next step of wet synthesis to the competitive reaction of synthesis of simple halides together with the mixed metal borohydrides (since chlorides have larger lattice enthalpy than borohydrides). Such problem occurred for zinc compounds for M^3 = Li, Na, which could be illustrated by the following equation (obviously, not all the possible products have been noted):

$$[Ph_4P][Zn(BH_4,Cl)_3] + M^3[An] \rightarrow aM^3[Zn(BH_4)_3]\downarrow + bM^3Cl\downarrow + ... + [Cat][An] \qquad (7)$$

However, the elongation of the reaction time (like for mechanochemical synthesis of $[Ph_4P][Zn(BH_4)_3]$ or $[nBu_4N][Sc(BH_4)_4]$ according to the steps **A** and **B**, Fig.1) from 30 min, usual to our setup, to 60–75 min and/or using an excess of inorganic borohydride reagent leads to substantial purity improvement. Indeed, when the variables of synthesis are carefully optimized, a very pure sample may be prepared, as exemplified by $Li[Zn_2(BH_4)_5]$.[6]

It should also be mentioned that the excess of unreacted $[Cat]BH_4$ should be eliminated before the metathetic step, or otherwise it may lead to significant contamination of the final product by alkali metal borohydride:

$$M^3[An] + [Cat]BH_4 \rightarrow M^3BH_4\downarrow + [Cat][An] \qquad (8).$$

This side reaction, which has been observed especially for the samples of complex zinc borohydrides, illustrates the sensitivity of the novel synthetic approach to the impurities found in the precursors.

Scalability, by-products, and cost effectiveness of the novel synthetic protocol

The economic aspects of any synthetic procedure should be taken into account.[45] The cost-effectiveness of a chemical processes is strictly related to its efficiency and minimization of the waste (thus, to the impact on environment). The yield of the multi-step procedure discussed here depends obviously on the yield of its sub-processes. The main step **C**, which leads straight to the final product, may proceed nearly quantitatively. Indeed, the yield exceeding 98% was often observed. The other reactions are not as effective; for example, the organic borohydride precursors can be synthesized with a yield of *ca.* 80−90% (*i.e.* combined steps **A** and **B**) in pure, ready-to-extract form.

As follows from Figure 1, alkali chloride and the salt of two bulky ions, [*Cat*][*An*], are produced as the only by-products. M^1Cl can easily be turned back into M^1BH_4 using the long-known technologies which are actually used nowadays on large scale. While the waste-free technologies are obviously most advantageous (economically and for the environment) the cost of the [*Cat*] moiety is rather low, which would justify the disposal of its salts.However, the derivatives of the fluorine-rich WCAs, [*An*], are simply too expensive to dispose them – indeed, their high price contributes most to the cost of the novel procedure. Although reuse of WCAs is a non-trivial task (since, according to the HSAB principle, the big soft anions prefer the big soft cations), closing the reaction loop by turning [*Cat*][*An*] back into reusable [*Cat*]Cl and $M^3[An]$ would result in a cheaper and virtually waste-free technology.

Conclusions

The recently introduced method for preparation of mixed-metal borohydrides has been critically discussed here with main focus on technical details, which significantly extends the previous reports. Application of the salts containing fluorine-rich weakly coordinating anions is a key feature here as it allows for utilization of weakly interacting, easy-removable solvents, being the major strength of the new method.

While apparently simple, this synthetic path is not straightforward as at least two separate steps are needed to reach the final product from commercially available precursors. Moreover, the process often requires testing as the reaction products not always correspond to the desired stoichiometry. While the method usually works well (after adjusting the reaction conditions to the particular system), high purity precursors should be used to assure the desired purity of the final product. Nevertheless, the method holds considerable potential for preparation of mixed-cation borohydrides, as exemplified by the first preparations of the dead-mass free $Li[Zn_2(BH_4)_5]$[6] or $Cs[Y(BH_4)_4]$, and the synthesis of $Li[Y(BH_4)_4]$ and $Na[Y(BH_4)_4]$,[7] which are not available via other routes.

To dramatically increase the cost effectiveness of the method the real challenge of reuse of WCAs must be met; closing of the reaction loop by turning [*Cat*][*An*] back into reusable [*Cat*]Cl and $M^3[An]$ would result in significantly cheaper and virtually waste-free technology.

The metathetic method of synthesis utilizing WCA salts as sources of 'naked' metal anions may be generalized, going from BH_4^- to many other inorganic salts; the extensions to $S_2O_8^{2-}$ and H-rich $BH_3NH_2BH_2NH_2BH_3^-$ anions will be described soon.

Acknowledgements

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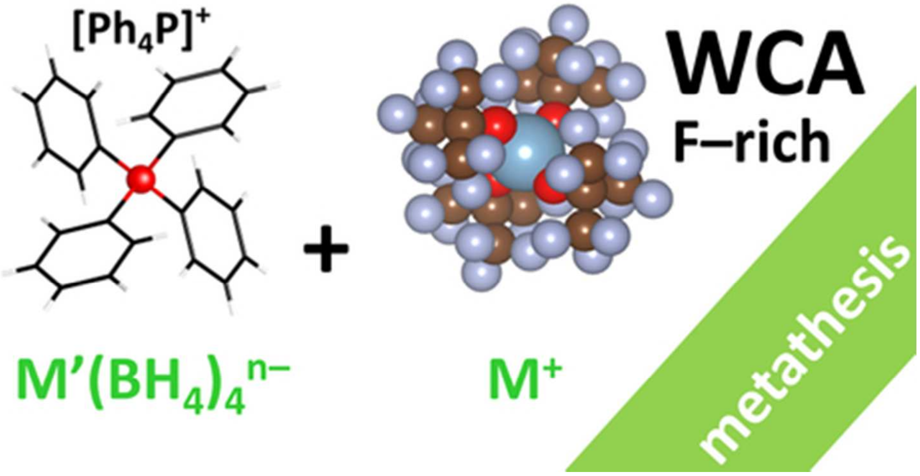

Metathetic reactions using salts of highly-fluorinated weacly coordinating anions permit synthesis of high-purity hydrogen storage materials.
39x19mm (300 x 300 DPI)