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From Metal Hydrides to Metal Borohydrides

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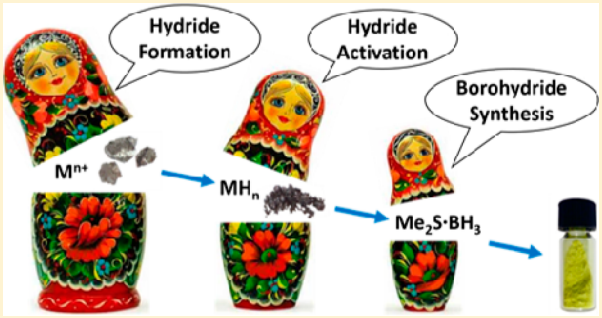
Supporting Information

ABSTRACT: Commencing from metal hydrides, versatile synthesis, purification, and desolvation approaches are presented for a wide range of metal borohydrides and their solvates. An optimized and generalized synthesis method is provided for 11 different metal borohydrides, $M(BH_4)_n$, (M = Li, Na, Mg, Ca, Sr, Ba, Y, Nd, Sm, Gd, Yb), providing controlled access to more than 15 different polymorphs and in excess of 20 metal borohydride solvate complexes. Commercially unavailable metal hydrides (MH_n, M = Sr, Ba, Y, Nd, Sm, Gd, Yb) are synthesized utilizing high pressure hydrogenation. For synthesis of metal borohydrides, all hydrides are mechanochemically activated prior to reaction with dimethylsulfide borane. A purification process is devised, alongside a complementary desolvation process for solvate complexes, yielding high purity products. An array of polymorphically pure metal borohydrides are synthesized in this manner, supporting the general applicability of this method. Additionally, new metal borohydrides, α-, α'- β-, γ-$Yb(BH_4)_2$, α-$Nd(BH_4)_3$ and new solvates $Sr(BH_4)_2{\cdot}1THF$, $Sm(BH_4)_2{\cdot}1THF$, $Yb(BH_4)_2{\cdot}xTHF$, $x = 1$ or 2, $Nd(BH_4)_3{\cdot}1Me_2S$, $Nd(BH_4)_3{\cdot}1.5THF$, $Sm(BH_4)_3{\cdot}1.5THF$ and $Yb(BH_4)_3{\cdot}xMe_2S$ ("x" = unspecified), are presented here. Synthesis conditions are optimized individually for each metal, providing insight into reactivity and mechanistic concerns. The reaction follows a nucleophilic addition/hydride-transfer mechanism. Therefore, the reaction is most efficient for ionic and polar-covalent metal hydrides. The presented synthetic approaches are widely applicable, as demonstrated by permitting facile access to a large number of materials and by performing a scale-up synthesis of $LiBH_4$.



1. INTRODUCTION

The analysis of reaction mechanisms for material synthesis is of key importance in creating high quality chemicals, possessing high polymorphic purity, for the investigation of material properties relying on specific structures. This knowledge is crucial in order to develop synthetic protocols for novel materials or precursors for further chemical processing. Metal borohydrides are recognized as a highly versatile class of materials with regard to structure, composition, and chemical and physical properties, and has expanded tremendously during the past few years.[1] Borohydrides originally served as reducing agents in organic synthesis.[2,3] Later they were also considered for solid state hydrogen storage and ion conductors for new types of solid state batteries.[4−8] More exotic applications such as explosives,[9] magnetic materials,[10] gas adsorption materials with permanent nanoporosity,[11,12] use as polymerization initiators,[13−23] and use as precursors for preparation of higher boranes were realized,[24] and some materials were even shown to be luminescent.[25] Metal borohydrides possess a richly faceted history. By 1940, the reactions of diborane with metal alkyls afforded $Al(BH_4)_3$, $Be(BH_4)_2$, and $LiBH_4$.[26−28] Further early work on borohydrides involved the reaction of diborane gas with alkali metal hydrides or alkoxides.[29−35] On the basis of this pioneering research, several other borohydrides and derivatives were synthesized and made readily available. For instance, synthesis of the selective reducing agent $NaBH(OCH_3)_3$ was devised, $LiBH_4$ and KBH_4 were synthesized, and, most importantly, a highly effective process for the synthesis of $NaBH_4$ in large quantities was established.[36−38] Among the most common synthetic approaches is the *metathesis*, conducted by solvent methods or mechanochemically, of a precursor borohydride (e.g., $NaBH_4$ or $LiBH_4$) and an appropriate metal halide salt, MX_n. This yields the respective metal borohydride, $M(BH_4)_n$, and an essentially undesired sodium or lithium halide byproduct (reaction 1).[12,39−49]

$$n[Na/Li]BH_4 + MX_n \rightarrow n[Na/Li]X + M(BH_4)_n \qquad (1)$$

Multiple studies of these metal borohydride−metal halide mixtures have been undertaken to establish the properties of the borohydride component.[1] However, the halide salt is not

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Table 1. Overview of Synthesized Metal Borohydrides and Solvent Complexes

entry	metal hydride	solv.	*n*MH (mmol)	*n*DMSB (mmol)[a]	reaction time (h)	reaction *T*/°C	product
1a	LiH	Tol.	25.0	37.5	24	RT	*o*-$LiBH_4$
1b[b]	LiH	Tol.	625.0	750.0	72	RT	*o*-$LiBH_4$
1c	LiH	THF	13.0	16.0	24	RT	$LiBH_4 \cdot x$THF[c]
1d	LiH	Et_2O	13.0	16.0	24	RT	$LiBH_4 \cdot 1Et_2O$[d]
2a	NaH	Tol.	25.0	37.5	36	40	$NaBH_4$
2b	NaH	Tol.	10.0	12.5	24	60	$NaBH_4$
3a	MgH_2	Tol.	10.0	25.0	36	40	$Mg(BH_4)_2 \cdot {}^1/_2Me_2S$
3b	MgH_2	THF	10.0	25.0	24	40	$Mg(BH_4)_2 \cdot x$THF
4a	CaH_2	Tol.	10.0	25.0	24	40	α-$Ca(BH_4)_2$
4b	CaH_2	Tol.	25.0	55.0	144	RT	α-$Ca(BH_4)_2$
4c	CaH_2	THF	5.0	15.0	24	40	$Ca(BH_4)_2 \cdot 2$THF
5a	SrH_2	Tol.	10.0	25.0	24	40	$Sr(BH_4)_2$
5b	SrH_2[e]	Tol.	10.0	30.0	36	40	$Sr(BH_4)_2$
5c	SrH_2	THF	5.0	15.0	24	40	$Sr(BH_4)_2 \cdot 2$THF
6a	BaH_2	Tol.	10.0	25.0	36	40	*o1*-$Ba(BH_4)_2$
6b	BaH_2	THF	5.0	15.0	24	40	$Ba(BH_4)_2 \cdot 2$THF
7a	YH_3	Tol.	10.0	45.0	24	40	$Y(BH_4)_3 \cdot 1Me_2S$
7b	YH_3[e]	Tol.	10.0	45.0	120	40	$Y(BH_4)_3 \cdot 1Me_2S$
7c	YH_3	THF	5.0	20.0	24	40	$Y(BH_4)_3 \cdot 3$THF
8a	NdH_3	Tol.	10.0	45.0[f]	48[f]	40	$Nd(BH_4)_3 \cdot 1Me_2S$
8b	NdH_3	THF	5.0	20.0	24	40	$Nd(BH_4)_3 \cdot 1.5$THF
9a	SmH_3	Tol.	3.75	17.0	36	RT/40	$Sm(BH_4)_2$
9b	SmH_3	THF	1.0	4.50	24	RT	$Sm(BH_4)_3 \cdot 1.5$THF[g]
9c	SmH_3	THF	1.0	4.50	24	40	$Sm(BH_4)_2 \cdot 1$THF
10a	GdH_3	Tol	10.0	45.0	24	40	$Gd(BH_4)_3 \cdot 1Me_2S$
10b	GdH_3	THF	5.0	20.0	24	40	$Gd(BH_4)_3 \cdot 3$THF
11a	YbH_3	Tol.	10.0	45.0[f]	48[f]	40	α-$Yb(BH_4)_2$
11b	YbH_3	Tol.	1.0	4.5[f]	72[f]	RT	$Yb(BH_4)_3 \cdot xMe_2S$[h]
11c	YbH_3	THF	2.5	10.0	24	40	$Yb(BH_4)_2 \cdot 2$THF

[a]5 M for reactions in toluene, 1 M for reactions in THF or Et_2O; [b]Large scale reaction at RT; [c]Mixture of *o*-$LiBH_4$/$LiBH_4 \cdot x$THF after collection, "*x*" undetermined (see SI_Li). [d]*o*-$LiBH_4$ collected after drying in vacuo. [e]Hand ground hydride. [f]4 M DMSB, reaction time extended. [g]1.5THF based on thermal analysis and comparison to $Nd(BH_4)_3 \cdot 1.5$THF (see SI_Sm). [h]"*x*" undetermined, see SI_Yb.

always an inert byproduct and can react with the metal borohydride, forming solid solutions or ordered metal borohydride halides.[5,6,50,51] In recent years, increased focus on the development of new synthesis strategies has resulted in access to many borohydrides without a halide salt impurity, allowing for more accurate determination of material properties. Solvent extraction of the desired metal borohydride produced by a metathesis reaction is considered as one alternative approach to its direct synthesis.[12,47] Yet, the formation of soluble byproducts, such as bimetallic borohydrides and/or excess or unreacted $LiBH_4$, can render this approach inadequate.[39] Other more elaborate methods have arisen, such as the continuous grinding of LiH while admitting B_2H_6 gas, serving the purpose of breaking the metal borohydride "passivation layer" that forms on the outside of the LiH particles.[52] Staying in the context of synthesis from metal hydrides, the synthesis of both calcium and magnesium borohydrides from their hydrides and triethylamine borane ($TEA \cdot BH_3$) should also be mentioned.[53] Very recently, that same method was successfully appointed to the synthesis of europium and barium borohydrides and ^{10}B-enriched $NaBH_4$.[54,55] An elegant synthesis of $Mg(BH_4)_2$, utilizing an insertion reaction, was demonstrated in 2009 by reacting dibutylmagnesium, $Mg(nBu)_2$, with dimethylsulfide borane ($Me_2S \cdot BH_3$/DMSB) yielding $Mg(BH_4)_2 \cdot {}^1/_2Me_2S$ as a precipitate.[11,56] This method eliminates the halide impurity that arises from metathesis reactions, allowing for simple isolation of the $Mg(BH_4)_2 \cdot {}^1/_2Me_2S$ solvate complex. Unfortunately, access to appropriate alkylmetal reagents is limited to, e.g., $Mg(nBu)_2$ or *n*BuLi, thus preventing this method from evolving into a general synthesis method for other metal borohydrides. In the present work, a new general approach for the synthesis of metal borohydrides is developed and optimized individually for each metal by selecting an appropriate solvent, adjusting the borane complex concentration, reaction temperature, reaction time, metal hydride particle size, etc. Hereby, we attempt to minimize the confusion arising from the large array of more or less successful synthetic approaches reported in the literature. Especially, exploiting the differences in coordination strength of sulfur/nitrogen/oxygen based donors (i.e., $Me_2S \cdot BH_3$/$Et_3N \cdot BH_3$/$THF \cdot BH_3$) to the metal of the borohydride is advantageous in order to synthesize pure, selected polymorphs of solvent free metal borohydrides. For instance, removal of Et_3N from $Mg(BH_4)_2$ synthesized from MgH_2 and $Et_3N \cdot BH_3$ is tedious and difficult to fulfill completely, while removal of THF from many more borohydrides has proven otherwise problematic. Experimental details and procedures are rationally compiled (elemental order) in the Supporting Information as "SI_M" (M = Li, Na, Mg, Ca, Sr, Ba, Y, Nd, Sm, Gd, Yb), where X-ray diffraction patterns, thermal analysis data, structural information, tables, illustrations, and relevant references are grouped as easily available, separate (metals based) sections for each individual metal borohydride

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Table 2. Solubilities of Metal Borohydrides and Corresponding Formation of Solvent Complexes

borohydride (M^{n+})	solvent	solubility (mmol/L)[a]	solvent complex	reference
Li^+	Et_2O	highly soluble	$LiBH_4{\cdot}1Et_2O$	70−74
Li^+	THF	highly soluble	$LiBH_4{\cdot}1THF/xTHF$	70, 73, this work
Li^+	monoglyme	4700.0	$LiBH_4{\cdot}$monoglyme	73
Li^+	diglyme	4250.0	$LiBH_4{\cdot}$diglyme	77
Li^+	isopropylamine	1270.0	$LiBH_4{\cdot}iPrNH_2$	73
Na^+	isopropylamine	1100.0	$NaBH_4{\cdot}iPrNH_2$	73
Na^+	RNH_2[b]	soluble	$NaBH_4{\cdot}R\text{-}NH_2$	37
Na^+	diglyme[c]	soluble	$NaBH_4{\cdot}$diglyme	80
Na^+	triglyme	highly soluble	$NaBH_4{\cdot}$triglyme	81
Na^+	DMF	highly soluble	$NaBH_4{\cdot}$DMF	81
Mg^{2+}	Me_2S	60.0	$Mg(BH_4)_2{\cdot}{}^1/_2Me_2S$	this work
Mg^{2+}	Et_2O[d]	soluble	$Mg(BH_4)_2{\cdot}2Et_2O$	82, 83
Mg^{2+}	THF[e]	soluble	$Mg(BH_4)_2{\cdot}3THF/xTHF$	84/this work
Ca^{2+}	THF	1690.0/1710.0	$Ca(BH_4)_2{\cdot}2THF$	77, 75
Ca^{2+}	diglyme	450.0	$Ca(BH_4)_2{\cdot}$diglyme	77, 75
Sr^{2+}	THF	40.0	$Sr(BH_4)_2{\cdot}2THF$	this work/31
Sr^{2+}	Et_2O	insol.	$Sr(BH_4)_2{\cdot}2THF$	31
Ba^{2+}	THF	insol.[f]/<25.0	$Ba(BH_4)_2{\cdot}2THF$	76/this work
Y^{3+}	THF	40.0	$Y(BH_4)_3{\cdot}3THF$	this work
Y^{3+}	Me_2S	50.0	$Y(BH_4)_3{\cdot}1Me_2S$	this work/47
Nd^{3+}	Me_2S	60.0	$Nd(BH_4)_3{\cdot}1Me_2S$	this work
Nd^{3+}	THF	35.0	$Nd(BH_4)_3{\cdot}1.5THF$	this work
Sm^{2+}	THF	40.0[g]	$Sm(BH_4)_2{\cdot}1THF$[g]	20/this work
Sm^{3+}	THF	<25.0	$Sm(BH_4)_3{\cdot}1.5THF$	this work
Gd^{3+}	Me_2S	<20.0	$Gd(BH_4)_3{\cdot}1Me_2S$	this work/47
Gd^{3+}	THF	40.0	$Gd(BH_4)_3{\cdot}3THF$	this work
Yb^{2+}	THF	25.0	$Yb(BH_4)_2{\cdot}2THF$	this work
Yb^{3+}	THF	60	$Yb(BH_4)_3{\cdot}3THF$	this work
Yb^{3+}	Me_2S		$Yb(BH_4)_3{\cdot}xMe_2S$	this work

[a]Approximate solubility (mmol/L) estimated at RT unless otherwise stated; see references. [b]Soluble in primary amines. [c]Soluble in diglyme. [d]$Mg(BH_4)_2$ reported as a solution in Et_2O. [e]$Mg(BH_4)_2$ reported to be readily soluble in THF. [f]$Ba(BH_4)_2$ reported to be insoluble in THF. [g]$Sm(BH_4)_2$ reported to be moderately soluble in THF, resulting in $Sm(BH_4)_2{\cdot}2THF$ (note that we collected $Sm(BH_4)_2{\cdot}1THF$).

synthesized. Increased access to metal borohydrides leaves promise for future investigations of many potentially interesting properties of this multifaceted class of materials, without influence from inherent byproducts or impurities.

2. EXPERIMENTAL SECTION

2.1. A Note on Safety. All reagents and starting materials are highly air and moisture sensitive, and care should be exercised when handling these materials outside the protective atmosphere of a glovebox. Working inert, using protective gases and dry glassware is mandatory. Any excess reagents or waste (dimethylsulfide borane, metal hydrides, metal borohydrides) were disposed of under controlled circumstances and contained in the fume hood until rendered fully inactive. Hydrolysis using alcoholic solutions (isopropanol) or water was done in fume hoods for small quantities.

2.2. Materials and Their Handling. All manipulation of any material or chemical throughout this study was conducted under inert atmosphere due to the air and moisture sensitivity of metal hydrides, borane complexes, and metal borohydrides. All powders were handled in an argon filled glovebox (MBRAUN/LabMaster) maintaining O_2 and H_2O levels at 0.1 ppm. All liquid chemicals were handled in fume hoods using standard inert syringe techniques, Schlenk equipment, and custom-made flasks with integrated filter discs (Figure S1, Supporting Information). Commercially available metals were purchased and used without further purification: strontium (pieces, Sigma-Aldrich, 99%), barium (pieces, Sigma-Aldrich, 99%), yttrium (chips, Sigma-Aldrich, 99.9%), samarium (chips, Sigma-Aldrich, 99.9%), neodymium (powder, Sigma-Aldrich, 99%, −40 mesh), gadolinium (ingot, 99.9%, cut to <8 mm), and ytterbium (chips, Sigma-Aldrich, 99.9%). The synthesized metal hydrides were collected as brittle pieces or powders and characterized using powder X-ray diffraction (PXRD). Commercially available metal hydrides, NaH (dry, 95%, Sigma-Aldrich), LiH (95%, Sigma-Aldrich), MgH_2 (hydrogen storage grade, Sigma-Aldrich), and CaH_2 (95%, Sigma-Aldrich), were used as supplied. Borane reagents and anhydrous solvents were purchased from Sigma-Aldrich; toluene ($C_6H_5CH_3$, anh., 99.8%), tetrahydrofuran (C_4H_8O, anh., > 99.9%), dimethylsulfide ($S(CH_3)_2$, anh., ≥ 99.0%), diethyl ether ($O(C_2H_5)_2$, anh., ≥ 99.7%), borane dimethylsulfide complex (DMSB; $BH_3{\cdot}S(CH_3)_2$, 10.0−10.2 M in dimethylsulfide), borane tetrahydrofuran complex solution (THFB; $BH_3{\cdot}OC_4H_8$, 1.0 M in tetrahydrofuran).

2.3. Hydrogenation of Metals. Formation of commercially unavailable metal hydrides (SrH_2, BaH_2, SmH_3, YH_3, NdH_3, GdH_3, YbH_3) was performed on a custom built Sieverts apparatus by exposing the corresponding metal to $p(H_2) \approx 135-145$ bar at RT, followed by heating at 5 °C/min to 200−450 °C and cooling under hydrogen atmosphere.[57] The decrease in hydrogen pressure during absorption allows for calculation of the gravimetric hydrogen uptake based on a known system volume. Neodymium(II) hydride, NdH_2, was also prepared from powdered Nd-metal hydrogenated at RT by stepwise addition of hydrogen up to a pressure of $p(H_2) = 60$ bar. The metal hydrides were mechanochemically "activated" in a Fritsch Pulverisette 6 planetary ball mill under inert conditions to maximize powder surface area. A material volume ∼1.5 cm^3 of metal hydride was loaded into an 80 mL tungsten carbide (WC) vial with 7 tungsten carbide balls (5.5 g each), resulting in a powder volume/ball mass ratio of 1:25. Milling speed of 350 rpm and milling time of 9 × 10 min with 2 min breaks were used for a total milling time of 90 min. For further details, see Supporting Information.

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2.4. Metal Borohydride Synthesis. *General Synthesis Method.* A mechanochemically activated metal hydride was suspended in an anhydrous solvent such as toluene (tol.), tetrahydrofuran (THF), or diethyl ether (Et_2O), and a 50% stoichiometric excess of dimethylsulfide borane complex (DMSB) was added at RT to reach a concentration between 1 and 5 M. The reaction mixture was heated to 40 °C and stirred for 24−48 h. After the reaction was complete, toluene based reaction mixtures were filtered and washed with toluene, and the solid metal borohydrides were collected and dried in vacuo at RT. For THF/Et_2O based reactions, extra solvent was added before filtration to increase the dissolved amount of metal borohydride and increase the yield. The dissolved products were extracted as a solution in THF or Et_2O, concentrated in vacuo, and collected as their respective metal borohydride solvate complexes. Yields are reported as essentially quantitative, since the reactions proceed with full consumption of the metal hydride. See Table 1 for details of specific entries and Supporting Information for further details.

Up-Scaling. Increasing the reaction scale was successfully attempted, evidenced by synthesis of $LiBH_4$ (132.5 g). LiH (6.25 mol, 50.0 g, 95% purity, mechanochemically activated) and DMSB (5 M, 7.5 mol, 1.2 equiv) were transferred to a 3 L three neck flask equipped with a magnetic stirrer and a thermometer. Using double-needle transfer techniques, 800 mL toluene (anh.) was added to form a LiH suspension, to which 750 mL DMSB (10 M) was added from an addition funnel until a concentration of 5 M was reached. To control the exothermic reaction, DMSB was added in 50 mL aliquots, and the temperature of the suspension was kept below 10 °C using an ice bath. After addition of DMSB, the reaction was allowed to heat up to RT, and stirring was maintained for 3 days, while taking out a daily sample to monitor reaction progress. Upon reaction completeness, stirring was discontinued to allow sedimentation of the products, and then toluene and excess reagent were removed using a double tipped needle. The products were dried for 16 h in vacuo at 50 °C, yielding 132.5 g of $LiBH_4$ (6.06 mol, 97% yield). See Supporting Information for details.

2.5. Extraction of Borohydrides. Purification of metal borohydrides (removal of unreacted starting reagents, impurities, or byproducts) can be achieved by extracting the metal borohydride with Et_2O, THF, or Me_2S. We found that the metal borohydrides studied were soluble at RT, depending on the individual solvents utilized. The extraction solvent was added at RT and stirred for several hours, and then stirring was discontinued and any undissolved material was allowed to sediment. The solution is separated from the solid residue by decantation or filtration, then concentrated in vacuo using a rotary evaporator, and the corresponding solid metal borohydride or metal borohydride solvate complex was collected. Extra solvent can be added and the process repeated, to ensure dissolving all metal borohydride products formed in the reaction. Alternatively a Soxhlet extractor can be employed to allow for continuous extraction and to minimize solvent waste. Table 2 contains approximate RT solubilities for the individual metal borohydrides synthesized.

2.6. Desolvation of Metal Borohydride Solvates. The temperatures for desolvation (removal of coordinated solvent) were initially determined using thermogravimetric analysis (TGA). Subsequently, heating a 300−500 mg metal borohydride solvate sample in a Schlenk tube (inner $\phi \approx 10$ mm) at the appropriate temperature in an argon atmosphere for 3−5 h, followed by subsequent extraction (in vacuo) of the formed solvent vapor, effectively removes the coordinated solvent. Detailed conditions are found in Table 3, and TGA curves are found in the relevant sections of the Supporting Information.

2.7. X-ray Diffraction. *In House Powder X-ray Diffraction.* Analysis was performed using a Rigaku Smart Lab X-ray diffractometer with a parallel beam multilayer mirror (Cu $K\alpha_1$ radiation, λ = 1.5406 Å). Data were typically collected at RT between 5° and 80° 2θ at 5°/min. All samples were mounted in 0.3−0.5 mm boron silica glass capillaries in a glovebox and sealed.

Synchrotron Radiation Powder X-ray Diffraction (SR-PXRD). Powder X-ray diffraction experiments were undertaken at the Swiss Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facilities (ESRF) in Grenoble, France. Experiments were also carried out at PETRAIII in the Deutsches Elektronen Synchrotron (DESY) in Hamburg, Germany. At ESRF, samples were mounted in glass capillaries (o.d. 0.4 mm) and sealed with glue inside an argon-filled glovebox. Two-dimensional (2D) powder data were recorded using a PILATUS2M detector at a selected wavelength of λ = 0.6945 Å. For all measurements, the capillaries were rotated 90° during 10 s X-ray exposures. For experiments at DESY, samples were mounted in glass capillaries (o.d. 0.5 mm) and sealed with glue inside an argon-filled glovebox. The 2D powder data were recorded using a PerkinElmer XRD1621CN3-EHS 410 mm detector at a selected wavelength of λ = 0.20775 Å. Single PXRD patterns were collected at three different sample to detector distances 1475, 1675, and 1875 mm.

X-ray Data Analysis. Known structure types were identified[1] and refined using the Rietveld method implemented in Fullprof.[58] Unit cells were indexed in the software program FOX (Free objects for crystallography).[59] The PXRD patterns of the new compounds are analogous to known compounds, and hence structural refinements were performed in the same space groups, using equivalent atomic coordinates. Overall scale factor, unit cell parameters, zero-point, peak shape, Gaussian profile parameters (U, V, W), and isotropic displacement (B) were refined.

2.8. Thermal Analysis. Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) were performed for all solvate complexes using a PerkinElmer STA 6000 instrument. The measurements were typically performed with a heating rate of 5 °C/

Table 3. Desolvation Protocols and Resulting Polymorphs for Metal Borohydride Solvent Complexes

metal borohydride solvent complex	desolvation temperature (°C)[a]	resulting material	reference
$LiBH_4 \cdot {}^1/_2Et_2O$[b]	RT - 60	*o*-$LiBH_4$	71, 88, this work
$LiBH_4 \cdot x$THF	200	*o*-$LiBH_4$	89, this work
$Mg(BH_4)_2 \cdot {}^1/_2Me_2S$	75−90	γ-$Mg(BH_4)_2$	11
$Mg(BH_4)_2 \cdot {}^1/_2Me_2S$	140 Ar → 140/vac.[c]	α-$Mg(BH_4)_2$	this work
$Mg(BH_4)_2 \cdot 2Et_2O$	160−180	α-$Mg(BH_4)_2$	90
$Mg(BH_4)_2 \cdot 2Et_2O$	200	β-$Mg(BH_4)_2$	90
$Mg(BH_4)_2 \cdot 3$THF/xTHF	200−250	amorphous[d]	82, this work
$Ca(BH_4)_2 \cdot 2$THF	80	$Ca(BH_4)_2 \cdot 1$THF	this work
$Ca(BH_4)_2 \cdot 2$THF	180	β-$Ca(BH_4)_2$	87
$Ca(BH_4)_2 \cdot 2$THF	160 → ice bath	α-$Ca(BH_4)_2$[e]	this work
$Sr(BH_4)_2 \cdot 2$THF	90	$Sr(BH_4)_2 \cdot 1$THF	this work
$Sr(BH_4)_2 \cdot 2$THF	170	$Sr(BH_4)_2$	this work
$Ba(BH_4)_2 \cdot 2$THF	150	*o1*-$Ba(BH_4)_2$	this work
$Y(BH_4)_3 \cdot 1Me_2S$	140	α-$Y(BH_4)_3$	47
$Y(BH_4)_3 \cdot 3$THF	175	amorphous[d]	this work
$Nd(BH_4)_3 \cdot 1Me_2S$	175	α-$Nd(BH_4)_3$	this work
$Nd(BH_4)_3 \cdot 1.5$THF	200	α-$Nd(BH_4)_3$	this work
$Sm(BH_4)_3 \cdot 1.5$THF	60−170	$Sm(BH_4)_2$[f]	48, this work
$Gd(BH_4)_3 \cdot 1Me_2S$	140	$Gd(BH_4)_3$	47
$Gd(BH_4)_3 \cdot 3$THF	200	amorphous[d]	this work
$Yb(BH_4)_2 \cdot 2$THF	90	$Yb(BH_4)_2 \cdot 1$THF	this work
$Yb(BH_4)_2 \cdot 2$THF	180	α-$Yb(BH_4)_2$	this work
$Yb(BH_4)_3 \cdot 3$THF	180	α-$Yb(BH_4)_2$[f]	this work
$Yb(BH_4)_3 \cdot xMe_2S$	140	γ-$Yb(BH_4)_2$[f]	this work

[a]Unless otherwise stated all entries are desolvated in vacuo. [b]Formation of "hemietherate" reported at RT. [c]Note that two distinct treatment steps are performed. [d]No diffraction observed. [e]Contains minor quantities of β-$Ca(BH_4)_2$. [f]Reduction takes place (see SI_Sm and SI_Yb).

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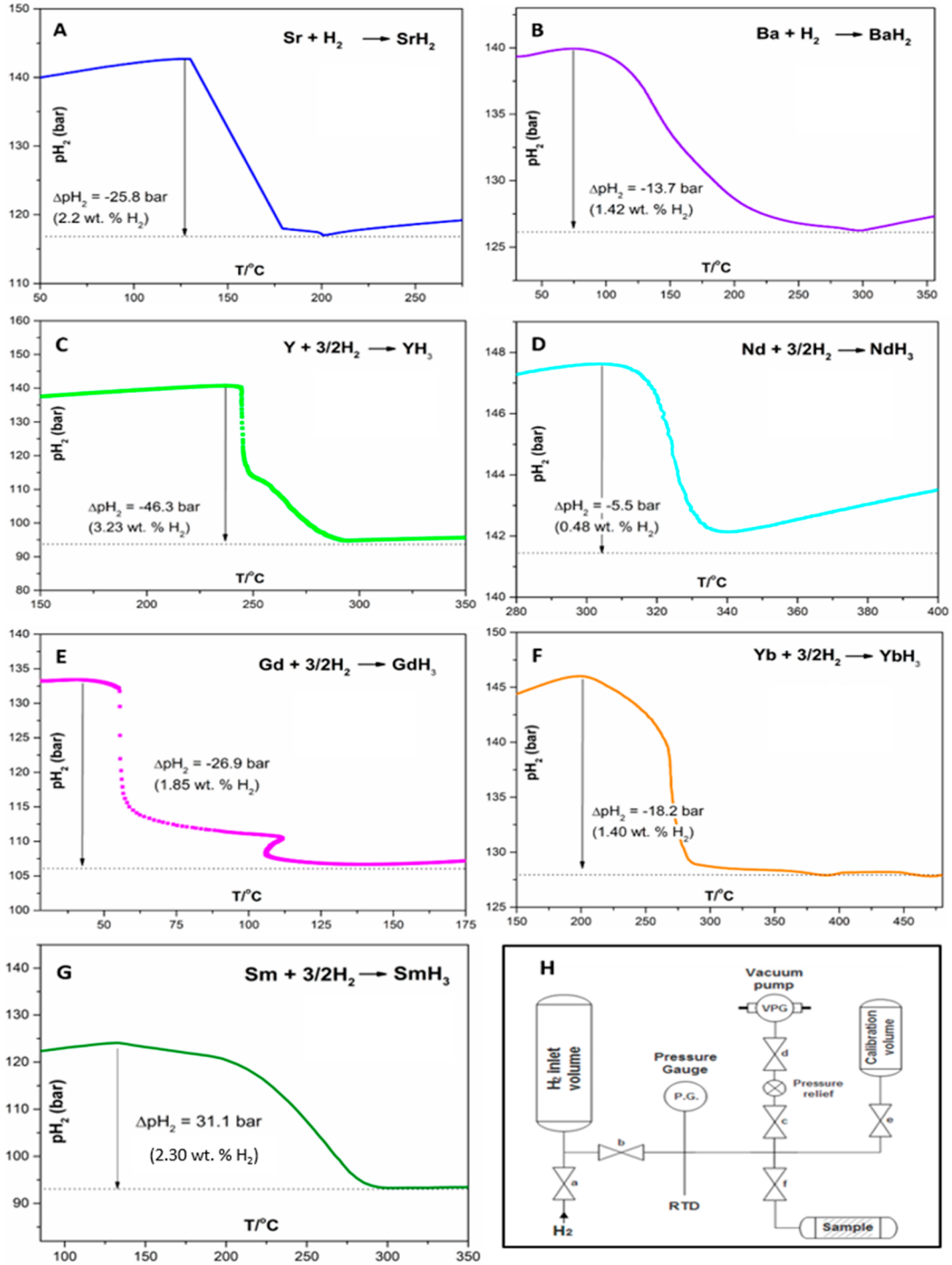

Figure 1. Hydrogenation curves measured by the Sieverts technique as a function of temperature for (A) Sr, (B) Ba, (C) Y, (D) Nd, (E) Gd, (F) Yb, and (G) Sm (heating rate 5 °C/min). Increasing pressure is caused by thermal hydrogen expansion during heating. The hydrogen uptake is displayed as wt % in brackets. (H) Schematic representation of the experimental setup.

min in a continuous flow of Ar (40 mL/min), using Al_2O_3 crucibles fitted with a lid to prevent exposure to air. Gases produced from sample decomposition during heating were vented through a small hole in the lid to avoid pressure build-up. Where relevant, the released gas was analyzed with a Hiden Analytical HPR-20 quadrupole mass spectrometer.

2.9. Transmission Electron Microscopy (TEM). TEM images for mechanochemically activated YH_3 were collected on a Talos F220A electron microscope (FEI systems) at 200 kV (Figure S2, Supporting Information). The sample was prepared by ultrasonication (10 min) of YH_3 suspended in toluene (anh.). Inside an argon filled glovebox a single drop was placed on the holey-carbon coated copper grid, left to dry, and mounted on the sample holder. The sample holder was transferred from the glovebox to the electron microscope under a blanket of argon.

2.10. Infrared Spectroscopy (FTIR). FTIR spectra were collected by a Nicolet 380 Avatar spectrometer, using attenuated total reflectance-Fourier transformed infrared spectroscopy (ATR-FTIR). The sample was placed directly on the diamond crystal and compressed with a tight screw. The collected wavenumber was 4000–400 cm^{-1} with 32 scans.

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2.11. Liquid State ^{1}H NMR Spectroscopy. Samples for ^{1}H NMR were prepared by dissolving the sample in $CDCl_3$ (0.5 mL) in an NMR tube. The measurements were performed using a Bruker AVANCE III HD spectrometer at 400 MHz. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 ppm).

3. RESULTS AND DISCUSSION

3.1. Metal Hydride Formation. Formation of metal hydrides can be observed as a decrease in hydrogen pressure in the sample cell of the precursor metal as a function of temperature; see Figure 1. The results reveal that a complete hydrogenation of the metals may occur within seconds once a critical temperature is reached. The rate of hydrogenation of gadolinium (3.75 g) is rapid and exothermic, and caused the steel sample cell (166 g) to heat up significantly, in this case well above the furnace set point (Figure 1E). A stepwise hydrogen absorption was also observed, e.g., for yttrium, where an interstitial (metallic) YH_2 forms prior to YH_3 (ρ_m = 3.29 wt % H_2, Figure 1C). Neodymium also absorbs hydrogen in two steps, and NdH_2 forms already at RT upon hydrogen exposure.[60] Thus, only 0.42 wt % H_2 was absorbed at $T \approx$ 320 °C, forming NdH_3 (calculated, 0.69 wt % H_2, Figure 1D). Samarium is fully hydrogenated to SmH_3 in two steps, from 130 °C and ending at 280 °C (Figure 1G). The compositions of the metal hydrides were confirmed by calculating the hydrogen uptake from $\Delta p(H_2)$ (Table S1, Supporting Information) and by PXRD analysis (Figure S3, Supporting Information).[61−66]

3.2. Reactivity of Metal Hydrides. Finely ground metal hydrides react much faster than coarse particles due to the larger surface area. TEM images of mechanochemically activated YH_3 reveal agglomerates, <200 nm, consisting of smaller particles, ∼20 nm (Figure S2, Supporting Information). In this work, it is shown that hand ground metal hydrides react less satisfactorily, or at least more slowly, than their mechanochemically activated counterparts. We suggest that the solvent mediated reaction between a solid metal hydride surface and a borane donor complex, e.g., dimethylsulfide borane, can be described as a nucleophilic addition mechanism (Figure 2).

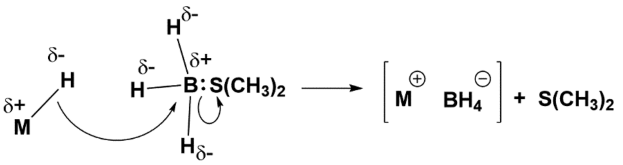

Figure 2. Proposed reaction mechanism for the hydrogen transfer from a metal hydride surface to the $Me_2S{\cdot}BH_3$ complex. The product is $M(BH_4)_n$.

A similar reaction between NaH and a different borane donor complex ($Et_3N{\cdot}BD_3$) yielding $NaBD_3H$ indicates that same mechanistic pathway to be valid.[67] This reaction mechanism is only possible for ionic or polar covalent M−H bonds, via a nucleophilic attack on the electron deficient boron of the borane complex. This is supported by the fact that the essentially metallic NdH_2 did not react with DMSB, but the ionic NdH_3 readily formed a neodymium(III) borohydride solvate, $Nd(BH_4)_3{\cdot}1Me_2S$. Synthesis of $Sm(BH_4)_2$ from SmH_2 and $THF{\cdot}BH_3$ has in fact been reported, but the yields were very low.[68] This is likely due to the presence of minute quantities of samarium(III) hydride in the samarium(II) hydride formed during hydrogenation, which has reacted. Extraction with THF provided the desired products, in low yields. Furthermore, the presence of tributoxyborane with the $Sm(BH_4)_2$ from decomposing $THF{\cdot}BH_3$ is unaccounted for in that study (see section 3.3, below). The metal borohydride initially forms a surface layer on the metal hydride particles, but will also have some, or significant, solubility in the solvent. Thus, the reaction solvent mediates the reaction and also has a tendency to dissolve and remove the reaction products from the surface. This leads to solvent mediated dissolution, transport, and recrystallization of $M(BH_4)_n$ (s) (Figure 3).

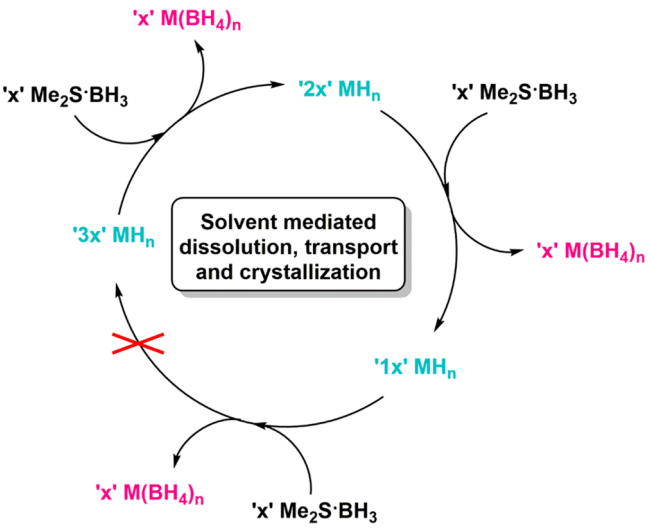

Figure 3. Formation, dissolution, and continuous transport of $M(BH_4)_n$ driving the reaction of the borane source with the remaining available metal hydride ("3x" − "1x" MH_n). The red "x" marks the full consumption of the metal hydride.

We demonstrate this solvent mediated BH_3 addition reaction for a wide range of (partly) ionic hydrides: LiH, NaH, MgH_2, CaH_2, SrH_2, BaH_2, YH_3, NdH_3, SmH_3, GdH_3, and YbH_3. The reaction described may also be considered as a Lewis base type addition of an electron pair donating H^- ion to a Lewis acid, BH_3, to form BH_4^-. The solid−gas reactions between metal hydrides and diborane, mentioned in the introduction, can be considered as the solvent free analogue to the methodology presented in this work; the mechanochemical treatment continuously removes the surface layer of the formed borohydride from the metal hydride particles, which would otherwise retard the process.[52]

3.3. Synthesis Conditions. An overview of all syntheses performed in this work is found in Table 1. Individually optimized synthesis conditions for each product entry is described in detail in the Supporting Information. The overall process is outlined in Figure 4 and can be summarized as two integrated cycles: *synthesis* and *purification*. Route "A" yields metal borohydride solvent complexes, coordinated, e.g., with Me_2S, THF, or Et_2O, while route "B" constitutes the process forming solvent free, solid metal borohydrides $M(BH_4)_n$.

Optimization of Synthesis Conditions. Reactions of LiH and SrH_2 with DMSB were employed as model reactions to converge on a general method. The progress of reaction is assessed, based on XRD data estimating the amount of metal hydrides present after a given reaction time. Initially, formation of $LiBH_4$ was obtained in 6−7 days at RT with mechanochemi-

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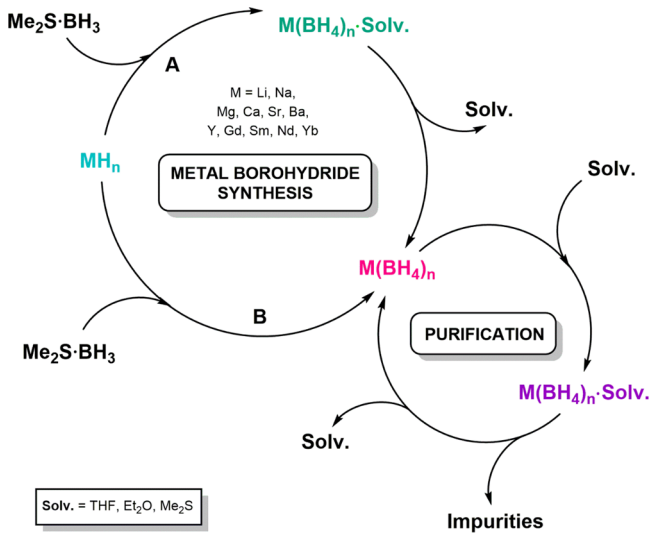

Figure 4. Simplified schematic overview of the synthesis method. (A) Mechanochemically activated metal hydrides MH_n react with DMSB providing the corresponding metal borohydrides as solvates ($M(BH_4)_n$·Solv.) or as solvent free metal borohydrides, $M(BH_4)_n$ (B).

cally activated LiH and 2 M DMSB, but the reaction was complete in 24 h using 5 M DMSB (Table 1, **1a**). For SrH_2, the reaction with 2 M DMSB proceeds slowly at RT, not complete after 6 days, but faster at 40 °C, completing within 24 h with 5 M DMSB (Table 1, **5a**). Increased DMSB concentrations, >5 M, cause higher viscosity and mixing problems, exacerbated by the fact that metal borohydrides have lower densities than their respective metal hydrides, leaving thick slurries and difficulties in homogenizing the mixtures to retard the reaction progress. Accordingly, it was concluded that mechanically activated metal hydrides in 5 M DMSB at 40 °C was optimal for a general synthesis method (Figure S5, Supporting Information).

Up-Scale Synthesis. The scale of synthesis was successfully increased from "lab scale" (5−10 mmol) to 6.25 mol (× 250), forming high purity $LiBH_4$ (132.5 g, 97.5% yield) (see Supporting Information for details). These results demonstrate that the method is practical, scalable, and can be utilized for the production of larger quantities of metal borohydride in a single batch.

Dimethylsulfide Borane (DMSB) vs Tetrahydrofuran Borane (THFB). Potentially, exchanging DMSB for THFB could serve as a practical alternative. First, the strongly unpleasant odor of dimethylsulfide would be avoided.[69] Second, a THF based reagent would promote the formation of metal borohydrides soluble in THF and essentially combine synthesis with purification. Third, the borane concentration is lower (only 1 M available), leaving a safer procedure. Ultimately, implementing THFB for DMSB failed, due to the competing formation of tributoxyborane from the decomposition of THFB (Figures S6 and S7, Supporting Information).

Other Reaction Solvents. On the basis of the above findings, and combining knowledge of metal borohydride solubilities and employing THF (or Et_2O) as solvent with DMSB, a highly efficient synthesis methodology for certain metal borohydrides was devised. For instance, $LiBH_4$ is highly soluble in THF (and Et_2O) at RT,[70−74] while $Ca(BH_4)_2$, $Sr(BH_4)_2$, and $Sm(BH_4)_2$ are reasonably soluble in THF (see Table 2 and references therein).[75−77] Thus, $LiBH_4$·xTHF, $LiBH_4$·1Et_2O, $Ca(BH_4)_2$·2THF, $Sr(BH_4)_2$·2THF, and $Sm(BH_4)_2$·1THF (Table 1 entries **1c**/**1d**/**4c**/**5c**/**9c**) are obtained after concentration of the respective THF or Et_2O solutions. Reactions performed in THF and the synthesis of $LiBH_4$ in Et_2O were all complete in less than 24 h. $NaBH_4$, however, is not appreciably soluble in Et_2O or THF, but synthesis at slightly elevated temperatures in toluene was complete after 24 h (Table 1, **2b**). Further details and more examples can be found in Table 1 and the Supporting Information. Post-synthetic purification can be performed by extraction with various solvents (see Table 2).

Reductive Synthesis; Samarium and Ytterbium Borohydrides. Reacting samarium(III) hydride, SmH_3, with DMSB in toluene at RT or 40 °C, directly yields $Sm(BH_4)_2$ (Table 1, **9a**); i.e., a reduction has occurred in the course of reaction. However, performing the reaction in THF (**9b**) reveals a new samarium(III) borohydride THF solvate, $Sm(BH_4)_3$·1.5THF. Thus, THF may stabilize the higher oxidation state, samarium(III), which is reduced to $Sm(BH_4)_2$ upon desolvation (reaction 2). The reduction is observed as a release of diborane (see SI_Sm).

$$M(BH_4)_3{\cdot}x\mathrm{THF} \rightarrow M(BH_4)_2 + x\mathrm{THF} + 1/2\,B_2H_6 + 1/2\,H_2 \quad (M = \mathrm{Sm, Yb}/x = 1.5 \text{ or } 3) \tag{2}$$

Similarly, reacting YbH_3 with DMSB in toluene at 40 °C results in reductive formation of α-$Yb(BH_4)_2$ (**11a**), whereas an ytterbium(III) borohydride solvent complex $Yb(BH_4)_3$·$x$$Me_2S$ is formed ("x" is undetermined) at RT (**11b**). Thermal analysis and mass spectroscopy reveal diborane release at 50−140 °C, indicating that ytterbium(III) is reduced to γ-$Yb(BH_4)_2$ (reaction 2), which is isostructural to γ-$Ca(BH_4)_2$ (see SI_Yb).[78] To sum up, the difficulties in obtaining Yb(III) and Sm(III) borohydrides were partially overcome by formation of solvate complexes. However, desolvation leads to metal reduction, release of diborane, and formation of divalent $M(BH_4)_2$. This procedure is similar to synthesis of Fe(II) and Co(II) borohydride solutions in Me_2S at $T \approx -50$ °C with stabilization of the M^{2+} by ammonia, forming $[Fe(NH_3)_6](BH_4)_2$ and $[Co(NH_3)_6](BH_4)_2$.[79]

3.4. Purification. Mechanical activation of metal hydrides may introduce contamination to the reaction product, from either starting materials, balls, or vial. Insufficient activation or utilization of partially hydrogenated metal samples will result in metal hydrides or metals in the reaction product. Therefore, we devised an efficient protocol for borohydride extraction and purification of reaction products by solvent extraction with, e.g., THF, Me_2S, or Et_2O (Figure 5). Continuous extraction, utilizing a Soxhlet extraction apparatus (operated under inert atmosphere), can be employed, being especially advantageous for compounds with limited solubilities. Only the metal borohydride component is soluble in THF, Me_2S, or Et_2O and metals, metal hydrides, and oxides are insoluble. Established and experimentally estimated RT solubilities of the metal borohydrides studied are listed in Table 2. Filtration of the resulting solution and concentration in vacuo yields the purified metal borohydride solvate complex. Photographs of colorful solutions of metal borohydrides are found in the Supporting Information (Figure S6).

3.5. Desolvation and Polymorphic Control. Solvents coordinated to the metal cation can normally be removed by simultaneously employing dynamic vacuum and heating. The

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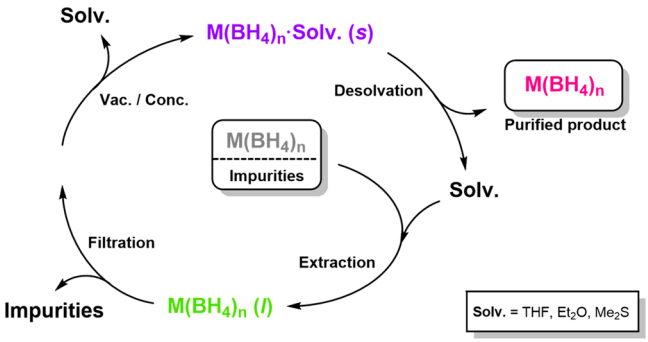

Figure 5. Schematic overview of the purification process. Starting from the "impure product" (center); "Extraction" provides a borohydride solution, $M(BH_4)_n$, leaving solid impurities undissolved; "Filtration" separates solid impurities from the metal borohydride solution. Concentration in vacuo "Vac./Conc." yields a solid metal borohydride solvate complex, $M(BH_4)_n$·Solv. (s), and "Desolvation" results in the isolation of the purified metal borohydride $M(BH_4)_n$.

specific conditions applied for desolvation are crucial to avoid decomposition of the metal borohydride and to obtain a specific polymorph hereof. For instance, removal of THF from $Mn(BH_4)_2$·3THF will result in the decomposition of $Mn(BH_4)_2$, caused by the high temperatures needed to release the ligand.[85] In certain cases, a solvated metal borohydride can also be required before attaining a desired polymorph. For instance, nanoporous γ-Mg/$Mn(BH_4)_2$ are obtainable solely by gently desolvating Mg/$Mn(BH_4)_2$·$^1/_2Me_2S$.[11,12] An efficient and controllable approach for desolvation is developed in this work. Initially, the sample is heated to a fixed temperature under ambient pressure, followed by vacuum extraction of the generated solvent vapor. Thermal analysis, TGA (see Supporting Information) is helpful to formulate the conditions for desolvation, and specific approved conditions to obtain certain polymorphs is compiled in Table 3.

Magnesium Borohydride. Preparation of nanoporous γ-$Mg(BH_4)_2$[11,12] is conducted in one step (simultaneous vacuum and heating) by desolvating $Mg(BH_4)_2$·$^1/_2Me_2S$, which demands strict control of temperature, i.e., $T < 90$ °C (Table 3 and SI_Mg, Supporting Information). Obtaining α-$Mg(BH_4)_2$ requires a two-step procedure of heating $Mg(BH_4)_2$·$^1/_2Me_2S$ to 140 °C for 3−5 h, followed by evacuation of the resulting Me_2S vapor. Desolvation of $Mg(BH_4)_2$·2Et_2O or $Mg(BH_4)_2$·3THF irreversibly results in the formation of a high temperature polymorph, β-$Mg(BH_4)_2$, at $T \approx 200$ °C.[82−84] In our work, amorphous materials were obtained when heating $Mg(BH_4)_2$·xTHF at $T > 200$ °C (Table 3 and SI_Mg).

Calcium Borohydride. Following the synthetic protocol described in this work, completely pure α-$Ca(BH_4)_2$ is formed directly at RT (Table 1, **4a**, **4b**, and Figure Ca_VI, Supporting Information). Nearly pure α-$Ca(BH_4)_2$ (with residual β-$Ca(BH_4)_2$) can be obtained by heating $Ca(BH_4)_2$·2THF to $T = 200$ °C, while removing the solvent vapors by evacuation and abruptly cooling (quenching) the sample to $T \approx 0$ °C (Figure Ca_8, Supporting Information).[86,87] β-$Ca(BH_4)_2$ is readily obtained from $Ca(BH_4)_2$·2THF at $T > 180$ °C, with minor quantities of α-$Ca(BH_4)_2$ forming.

Ytterbium Borohydride. Four halide free polymorphs of divalent $Yb(BH_4)_2$ were discovered in this work and denoted in parallel to their isostructural calcium analogues, α-$Yb(BH_4)_2$, α'-$Yb(BH_4)_2$, β-$Yb(BH_4)_2$, and γ-$Yb(BH_4)_2$. At elevated temperatures, $T \approx 230$ °C, α-$Yb(BH_4)_2$ transforms to β-$Yb(BH_4)_2$, with α'-$Yb(BH_4)_2$ and γ-$Yb(BH_4)_2$ as intermediate compounds, observed by *in situ* SR-PXD (SI_Yb). Desolvation of $Yb(BH_4)_3$·$x$$Me_2S$ at $T = 140$ °C yields γ-$Yb(BH_4)_2$ (i.e., a reduction takes place), whereas desolvation of $Yb(BH_4)_2$·2THF at $T = 180$ °C provides α-$Yb(BH_4)_2$ (Table 3). Structural details are described in section 3.6. The purification and transformation protocols presented here form the basis for transforming a large number of metal borohydride solvates, into previously unknown metal borohydride solvent complexes and further into other polymorphs of solvent free metal borohydrides.

3.6. Structural Characterization of Synthesized New Metal Borohydrides. A large number of new metal borohydrides and solvates were synthesized and structurally characterized in this study (see Supporting Information). The majority of these new materials adopt known structure-types similar to other metal borohydride solvates.

Metal Borohydride Tetrahydrofuran Complexes. $LiBH_4$·xTHF. An unknown lithium borohydride THF complex was obtained. No structural refinements were performed due to limited diffraction data. $LiBH_4$·3THF is reported to form at low temperatures, transforming into $LiBH_4$·1THF at ambient temperature.[89,91] Etherates of $LiBH_4$ have been structurally investigated elsewhere.[71,88]

$Mg(BH_4)_2$·xTHF. A magnesium borohydride THF complex was prepared (Table 1, **3b**), but detailed structural analysis was unsuccessful due to limited quality of the PXRD data. However, the recorded pattern is clearly different from the reported pattern of $Mg(BH_4)_2$·3THF.[92] Thermal analysis suggests less than 3THF in the formula unit (SI_Mg). Accordingly, we denoted it $Mg(BH_4)_2$·xTHF (Tables 1 and 3).

$M(BH_4)_2$·nTHF (M = Ca, Sr, Ba, Sm, Yb, n = 1, 2). $Ca(BH_4)_2$·2THF and $Yb(BH_4)_2$·2THF, were found to be isostructural to $M(BH_4)_2$·2THF, M = Sr, Ba, and Sm.[20,76] The structure is described as an infinite chain of "−M−$(BH_4)_2$−M−" along the *a*-axis as shown below (Figure 6). Different chains are connected by weak interactions between neighboring apolar THF moieties.

Upon heating, THF is lost from $M(BH_4)_2$·2THF (M = Ca, Sr, Yb) in two distinct steps, showing that two different, isolatable solvates exist, $M(BH_4)_2$·2THF and $M(BH_4)_2$·1THF. Thus, tetrahydrofuran complexes, $Sm(BH_4)_2$·1THF and $Yb(BH_4)_2$·1THF, were also discovered. $Sm(BH_4)_2$·1THF was collected directly after synthesis. $Sr(BH_4)_2$·1THF, $Sm(BH_4)_2$·1THF, and $Yb(BH_4)_2$·1THF are isostructural to $Ca(BH_4)_2$·1THF, described in the literature as a double-stranded, one-dimensional polymeric structure (Figure 7).[93] Note that we did not succeed in preparing $Sm(BH_4)_2$·2THF, nor $Ba(BH_4)_2$·1THF (see Table S2).

$M(BH_4)_3$·nTHF (M = Nd, Sm, Gd, Yb, Y, n = 1.5, 3). For a number of trivalent metal borohydrides, contrasting observations to earlier reported findings were experienced. Thermogravimetric data for all metal borohydride solvates investigated in this work are in accord with the expected structure and composition, except for the series of $M(BH_4)_3$·3THF, M = Y, Nd, Sm, Gd, and Yb (see also the individual sections in the Supporting Information).

$Nd(BH_4)_3$·1.5THF. Extraction of $Nd(BH_4)_3$ with THF (Table 2) results in a new monoclinic, $P2_1$, neodymium borohydride THF-complex with an apparent stoichiometry $Nd(BH_4)_3$·1.5THF (Le-Bail fit). This contrasts the reported composition $Nd(BH_4)_3$·3THF obtained from $NaBH_4$ and $NdCl_3$ in THF.[94]

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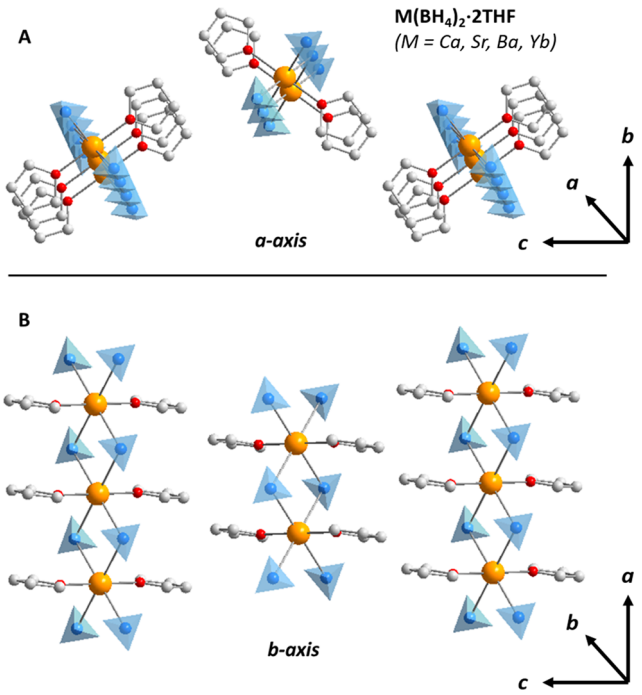

Figure 6. Representative views of crystal structure models of $M(BH_4)_2{\cdot}2THF$ (M = Ca, Sr, Ba, Yb) along the *a*-axis (A) and *b*-axis (B). Orange spheres − metal cation (M), red − oxygen, light gray − carbon, light blue − boron. Transparent tetrahedra − BH_4 groups. Hydrogens are omitted for clarity.

This observation may be explained by loss of 1.5 THF during sample collection using our methodology. Thermogravimetric data reveals three distinct, similar mass losses for the new $Nd(BH_4)_3{\cdot}1.5THF$ complex (total observed and calculated mass loss are 38.4 and 36.4 wt %, respectively). Furthermore, we recover α-$Nd(BH_4)_3$ (see below) after desolvation, clearly emphasizing that all THF is removed (SI_Nd).

$Sm(BH_4)_3{\cdot}1.5THF$. Trivalent samarium borohydride complexed with THF was synthesized (Table 1, **9b**). Collection of an off-white solid with a diffraction pattern clearly different from the reported $Sm(BH_4)_3{\cdot}3THF$[23] and a mass loss corresponding to 1.5 THF may suggest a composition of $Sm(BH_4)_3{\cdot}1.5THF$. Interestingly, the X-ray diffraction patterns of $Nd(BH_4)_3{\cdot}1.5THF$ and the trivalent samarium borohydride THF complex indicate similarities in structure and composition (see Figure Sm_VI in the Supporting Information). Thermal analysis with mass spectroscopy reveals a liberation of diborane while desolvating, but before decomposition, indicative of a reduction of a Sm(III) borohydride to a Sm(II) borohydride material. The collected (after desolvation/reduction) dark/purple material is identified as $Sm(BH_4)_2$ by XRD (Figure Sm_VIII).

$M(BH_4)_3{\cdot}3THF$ (M = Y, Gd, Yb). $Yb(BH_4)_3{\cdot}3THF$ was collected after extraction of $Yb(BH_4)_3{\cdot}xMe_2S$ (Table 1, **11b**) with THF and was found to adhere to the structure of $Y(BH_4)_3{\cdot}3THF$ and $Gd(BH_4)_3{\cdot}3THF$.[95,96] Thermal analysis fits well with the stoichiometry of 3THF, and the material releases diborane, being reduced to $Yb(BH_4)_2$ (see SI_Yb). As mentioned, $Y(BH_4)_3{\cdot}3THF$ and $Gd(BH_4)_3{\cdot}3THF$ are both structurally similar to $Yb(BH_4)_3{\cdot}3THF$, yet thermal analysis indicates release of only part of their complexed THF. We speculate that higher boranes may form, strongly complexing the remaining THF, i.e., $M(III)B_xH_y{\cdot}3{-}z THF$. We note that the THF complexes that undergo this incomplete desolvation appear to be those not reduced by BH_4^-, e.g., Mg^{2+}, Y^{3+}, and Gd^{3+}.

Metal Borohydride Dimethylsulfide Complexes. $Yb(BH_4)_3{\cdot}xMe_2S$. A new ytterbium borohydride Me_2S complex was discovered and collected as a light green solid (Table 1, **11b**). The structure appears to be composed of a large unit cell based on preliminary analysis of diffraction data (see SI_Yb).

$Nd(BH_4)_3{\cdot}1Me_2S$. A new monoclinic ($P2_1c$) neodymium(III) borohydride solvate, $Nd(BH_4)_3{\cdot}1Me_2S$ (Table 1, **8a**) is synthesized from a purple dimethylsulfide solution and crystallizes as a pale purple solid. It is isostructural to the well-known $M(BH_4)_3{\cdot}1Me_2S$ (M = Y, Gd),[47] and this structural resemblance allowed us to perform full structural characterization (Figure 8).

New Solvent Free Metal Borohydrides. $Nd(BH_4)_3$. Desolvation of $Nd(BH_4)_3{\cdot}1Me_2S$ yields α-$Nd(BH_4)_3$, which in analogy to the solvate complex described above is isostructural to $M(BH_4)_3$ (M = Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb).[47,97−99] The material is collected as a cubic (Pa-3), pale purple substance (see Supporting Information).

$Yb(BH_4)_2$. The four new ytterbium borohydrides crystallize in the same space groups as α-$Ca(BH_4)_2$ ($F2dd$), α'-$Ca(BH_4)_2$

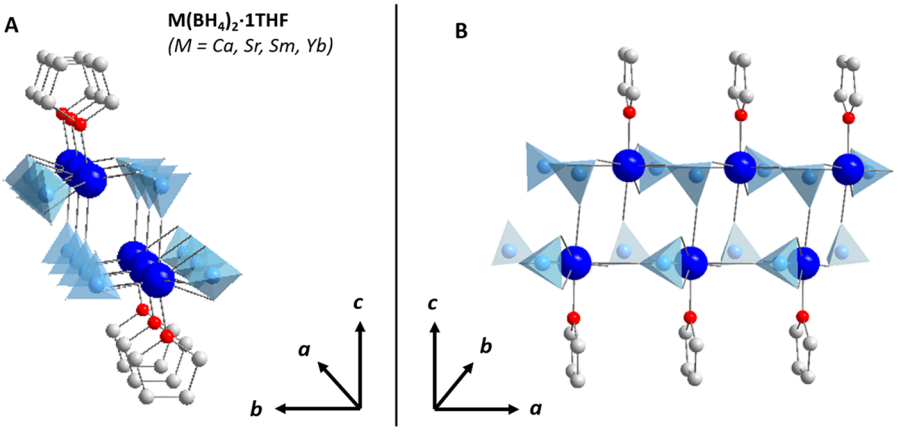

Figure 7. Representative views of crystal structure models of $M(BH_4)_2{\cdot}1THF$ (M = Ca, Sr, Sm, Yb) along the *a*-axis (A) and *b*-axis (B). Dark blue spheres − metal cation (M), red − oxygen, light gray − carbon, light blue − boron. Transparent tetrahedra − BH_4 groups. Hydrogens are omitted for clarity.

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Inorg. Chem. XXXX, XXX, XXX−XXX

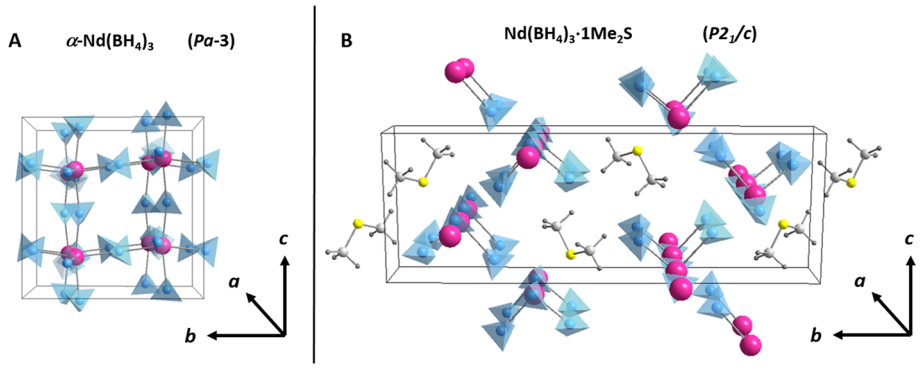

Figure 8. Representative views of crystal structure models of α-$Nd(BH_4)_3$ viewed along the *a*-axis (A), and $Nd(BH_4)_3{\cdot}1Me_2S$ also viewed along the *a*-axis (B). Color code; purple spheres − neodymium, yellow − sulfur, light gray − carbon, light blue − boron. Transparent tetrahedra − BH_4 groups, gray − hydrogen. Hydrogens in BH_4 units are omitted for clarity.

($I\bar{4}2d$), β-$Ca(BH_4)_2$ ($P\bar{4}$), and γ-$Ca(BH_4)_2$ (*Pbca*), respectively (Figure 9),[100,101] completing the full structural analogy

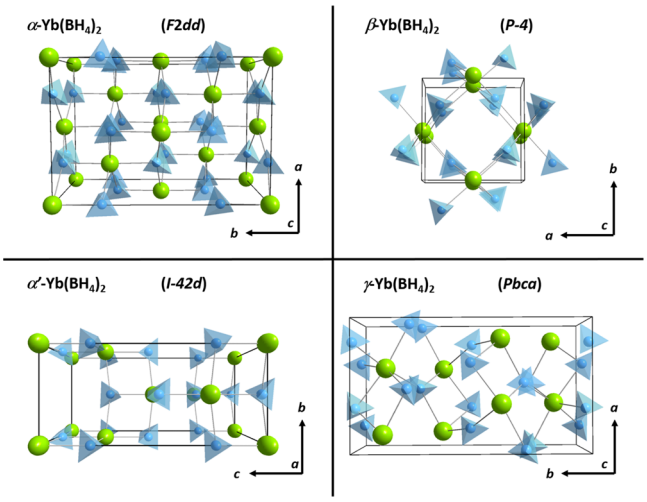

Figure 9. Crystal structure of α-$Yb(BH_4)_2$ viewed along the *c*-axis, β-$Yb(BH_4)_2$ along the *c*-axis, α'-$Yb(BH_4)_2$ along the *a*-axis, and γ-$Yb(BH_4)_2$ along the *c*-axis. Color code; green spheres − ytterbium, blue transparent tetrahedra − BH_4 complexes. Hydrogens in BH_4 units are omitted for clarity.

between calcium and ytterbium borohydride (see SI_Ca and SI_Yb, Supporting Information). Previously reported Cl-substituted *tet*- and *ortho*-$Yb(BH_4)_{2-x}Cl_x$ are isomorphous to β-$Ca(BH_4)_2$ and γ-$Ca(BH_4)_2$.[102]

4. CONCLUSIONS

A new general approach with an integrated purification step, for the synthesis of a wide variety of metal borohydrides and their solvates, from metal hydrides and a borane donating complex is demonstrated. The approach is well documented and tested, and the results are rationally compiled as a collection of individual synthesis "recipes" for Li, Na, Ca, Mg, Sr, Ba, Y, Nd, Gd, Sm, and Yb borohydrides and their solvates. Commercially unavailable metal hydrides are synthesized directly from the elements and mechanochemically activated in order to maximize their reactivity. Only ionic and polar covalent metal hydrides were found to possess reasonable reaction kinetics and form metal borohydrides. This finding correlates well to a nucleophilic addition reaction mechanism. A general purification routine is devised, utilizing a combination of coordinating solvents. As a result, five new solvent free metal borohydrides, α-$Nd(BH_4)_3$, α-$Yb(BH_4)_2$, β-$Yb(BH_4)_2$, γ-$Yb(BH_4)_2$, α'-$Yb(BH_4)_2$, and six new metal borohydride solvate complexes, $M(BH_4)_2{\cdot}2THF$ (M = Ca, Yb); $M(BH_4)_2{\cdot}1THF$ (M = Sr, Sm, Yb) and $Nd(BH_4)_3{\cdot}1Me_2S$, were discovered and characterized structurally, physically, and chemically. Additionally, three new and unknown THF and Me_2S solvate complexes, $Nd(BH_4)_3{\cdot}1.5THF$, $Sm(BH_4)_3{\cdot}1.5THF$, and $Yb(BH_4)_3{\cdot}xMe_2S$, were discovered. This totals 14 new borohydride materials synthesized, alongside the already known materials also synthesized by this method. This approach provides metal borohydrides in near quantitative yields with high purity and exhibits a high degree of polymorphic control. Postreaction transformations to obtain specific polymorphs are also described. We anticipate that this general synthesis approach can be readily extended to synthesis of other metal borohydrides for which ionic or polar covalent metal hydrides exist. This constitutes a direct pathway to high purity metal borohydrides, without the formation of halides and other impurities, thus allowing for proper investigation of physical properties, e.g., magnetism, photoluminescence, ionic conductivity, gas adsorption, hydrogen storage, and more. The metal borohydride products may also prove valuable as selective organic reduction agents, or serve as starting materials for synthesis of higher boranes. The results presented here and details about the reaction mechanism may be inspirational for further development of supplementary strategies to provide novel functional materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01398.

^{1}H NMR spectra, thermal analysis data, mass spectroscopy data, photographs and FTIR spectra (PDF)

Accession Codes

CCDC 1845345−1845355 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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