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Facile High-Yield Synthesis of Pure, Crystalline $Mg(BH_4)_2$

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Magnesium borohydride, $Mg(BH_4)_2$, a long-sought candidate for efficient hydrogen storage chemisorption technology, has been obtained in a pure and crystalline form by two new synthetic routes in a hydrocarbon solvent. A first synthetic approach involves a metathetical reaction between organometallic magnesium compounds; a second route consists of an insertion reaction of BH_3 species, released from $BH_3 \cdot S(CH_3)_2$, into the Mg–C bonds of MgR_2, with complete replacement of R groups with BH_4 groups. Both methods, based on commercially available reagents, afford identical, pure, polycrystalline materials, identified by X-ray diffraction as the so-called low-temperature hexagonal form of $Mg(BH_4)_2$, stable below 180 °C, recently shown to possess a complex, unpredictable, crystal structure.

Magnesium borohydride, $Mg(BH_4)_2$, has been described in the chemical literature from many years and, like many other metallic borohydrides, has been employed as a reducing agent in synthetic organic chemistry.[1] Given that it easily forms a number of adducts with many Lewis bases (including a variety of common solvents), its purity was seldom assessed,[2] and clear evidence for the existence of a pure, crystalline and unsolvated compound of the $Mg(BH_4)_2$ formula was not available until very recently.[3,4] Indeed, the interest for this (apparently simple) compound was recently renewed because it is an ideal candidate for a chemisorptive hydrogen storage material and a potential chemical precursor to be used in the deposition process of superconducting MgB_2 thin films.[4] The fact that this species can be prepared and isolated (although, in some cases, within a mixture of salts) was nicely shown by the complete X-ray structural characterization (from synchrotron powder diffraction data) of the complex crystal structures of two (structurally related) polymorphs, which just appeared in the scientific literature,[3a,b] and by the coincidence of the products of two independent preparation routes, reported in a yet undisclosed patent application.[4]

Classical synthetic routes to $Mg(BH_4)_2$ were based on the thermal dissociation of solvated products, mainly the diethyl ether adduct, but even though a purity as high as 98% was claimed (with no clear analytical crystallographic analysis),[2] the dissociation reaction lasted almost 1 week, clearly preventing any practical industrial exploitation of such a process. If higher temperatures (up to 230 °C) are employed during the dissociation process, to increase the reaction rate, undesired decomposition products are easily formed. Alternatively, solvent dissociation under a medium-high vacuum, 10^{-3} Torr, in 12 h has been attempted.[2,5] A further preparation method is described in the old literature,[6] based on the metathesis betweeen magnesium dichloride and sodium borohydride in diethyl ether; whatever compound was then isolated, its X-ray diffraction pattern cannot be matched to that of any $Mg(BH_4)_2$ polymorph. Interestingly, the recently reported preparation[3b] of $Mg(BH_4)_2$ also employs $MgCl_2$ and $NaBH_4$ and, apparently, can give pure phases (or mixture of compounds) depending on the actual reaction conditions; moreover, by replacement of $NaBH_4$ with $LiBH_4$, $Mg(BH_4)_2$ was recovered as a ca. 30% component of a complex salt mixture.[3a] Apparently, the most efficient method reported so far is the direct synthesis from magnesium dihydride and the triethylamineborane complex, very recently proposed by Chłopek et al.[3c]

Fifty years of attempted synthesis of $Mg(BH_4)_2$ have evidenced the following main difficulties: (i) metathesis reactions generally lead to the formation of a mixture of products ($Mg(BH_4)_{2-n}X_n$, $n = 0-2$), from which $Mg(BH_4)_2$ ($n = 0$) is difficult to separate (or even to identify); (ii)

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quantitative reactions in which $Mg(BH_4)_2$ is the prevalent product (generally based on the insertion of BH_3 into Mg−C or Mg−H bonds) have been carried out in donor solvents (O or N Lewis bases); this implies the formation of stable $Mg(BH_4)_2 \cdot L$ Lewis complexes (hard acid−hard bases) from which complete, and controlled, dissociation of L is almost impossible, even under extreme conditions of high temperature and high vacuum.

Aiming at overcoming these difficulties, we have identified two efficient synthetic methods (methods a and b), based on the following considerations: (i) noncoordinating solvents (such as aliphatic or aromatic hydrocarbons) are to be used; (ii) if the only insoluble species in the reaction medium is $Mg(BH_4)_2$, then separation of the desired product by filtration can easily be achieved. Thus, a high-yield reaction in which all reactants and side products are soluble is required.

Method a consists of a metathesis reaction schematized as

$$3Mg(C_4H_9)_2 + 2Al(BH_4)_3 \rightarrow 3Mg(BH_4)_2 + 2Al(C_4H_9)_3 \quad \text{(a)}$$

$Mg(C_4H_9)_2$ is a commercial product available as an *n*-heptane solution and is also highly soluble in toluene; at variance, a toluene solution of $Al(BH_4)_3$ can be easily prepared by the following reaction:

$$AlCl_3 + 3LiBH_4 \rightarrow Al(BH_4)_3 + 3LiCl$$

This reaction[7] takes place quantitatively and generates the (soluble) $Al(BH_4)_3$ species and a colorless precipitate, LiCl. Because of its high volatility, $Al(BH_4)_3$ cannot be easily separated from its original toluene solution; however, distillation of the pristine solution affords a toluene/$Al(BH_4)_3$ mixture exempt of any Li^+ and Cl^- ions; significantly, the actual concentration of $Al(BH_4)_3$ in the distilled fraction can be easily determined by classical analytical methods, using, for example, ethylenediaminetetraacetic acid as a titrating agent. The direct use of $Al(BH_4)_3$ solutions is definitely preferable to that of neat (liquid) $Al(BH_4)_3$, with the latter material being air- or moisture-sensitive, volatile, flammable, and, thus, very dangerous.

The capability of $Al(BH_4)_3$ in exchanging its BH_4^- groups with the R groups of other organometallic compounds (e.g., LiC_2H_5) has already been reported.[8] Because our preliminary experiments had shown the sought, thus appealing, poor solubility of $Mg(BH_4)_2$ in toluene [in which, inter alia, $Al(C_4H_9)_3$ and the reaction products are easily dissolved], this solvent was chosen as the ideal reaction medium. Thus, the mixing of $Mg(C_4H_9)_2$ and $Al(BH_4)_3$ (in 3:2 molar ratio) in toluene solutions causes the progressive formation of a colorless precipitate. After stirring overnight, the powdery precipitate was filtered, washed with toluene [in order to remove completely residual $Al(C_4H_9)_3$], and dried under vacuum. The chemical and crystallographic purities of this $Mg(BH_4)_2$ material were tested through elemental analysis, ^{11}B NMR spectroscopy of a diethyl ether solution, and powder X-ray diffraction measurement of crude samples sealed in Lindemann capillaries (see Figures 1 and 2).

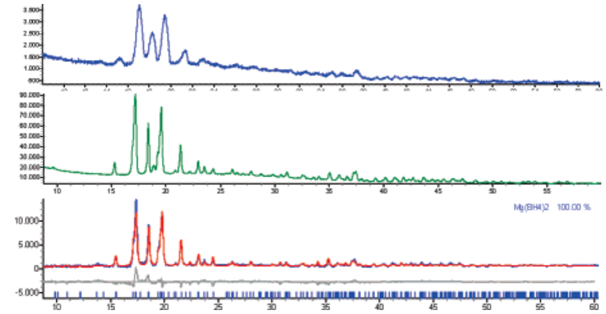

Figure 1. Powder X-ray diffraction traces of $Mg(BH_4)_2$ isolated from methods a (top) and b (center). The bottom plot shows the simulated trace (in red, coordinates from ref 3a), matching the observed data (in blue).

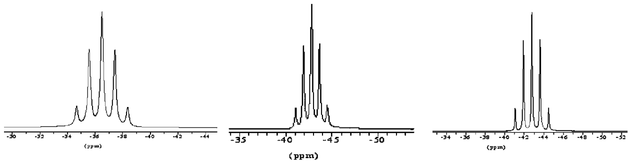

Figure 2. ^{11}B NMR spectra of the reaction intermediates and products: $Al(BH_4)_3$ (left trace: δ −36.50 ppm; $J_{B-H} = 88.8$ Hz) and $Mg(BH_4)_2$ for methods a (center trace) and b (right trace) (δ −42.80 ppm; $J_{B-H} = 83.1$ Hz).

Method b represents a modification and improvement with respect to the previously reported[5] reactions involving the stepwise BH_3 insertion into Mg−C bonds. Also, in this case, an *n*-heptane solution of $Mg(C_4H_9)_2$ was used as the Mg-containing starting material and toluene as the main solvent. At variance, the $BH_3 \cdot S(CH_3)_2$ borane adduct (in toluene) was employed as a source of the borohydride species. The reaction scheme may be represented as

$$3Mg(C_4H_9)_2 + 8BH_3 \cdot S(CH_3)_2 \rightarrow 3Mg(BH_4)_2 \cdot 2S(CH_3)_2 + 2B(C_4H_9)_3 \cdot S(CH_3)_2 \quad \text{(b)}$$

On employment of an excess of the borane species, a colorless product precipitates and, thus, can be easily isolated by filtration, washed, and dried in vacuo. The reaction product contains $Mg(BH_4)_2$ complexed by $S(CH_3)_2$. However, it must be observed that, in contrast to many other $Mg(BH_4)_2 \cdot L$ complexes (L = O and N donor ligands, such as ethers or amines, hard enough to make their dissociation rather difficult or nearly impossible), $S(CH_3)_2$ is a much softer Lewis base, allowing the recovery of a pure, uncomplexed $Mg(BH_4)_2$ form by breaking the weak bonds between the thioether and the hard Mg^{2+} acceptor. The only other reaction product, $B(C_4H_9)_3 \cdot S(CH_3)_2$, is highly soluble in toluene and, therefore, can be easily eliminated. The precipitate, $Mg(BH_4)_2 \cdot nS(CH_3)_2$ (likely, $n = 2$), can be easily vacuum-dried at room temperature (at 10^{-1} mbar for 6 h), followed by diffusive vacuum (10^{-5} mbar, at 75 °C, for 13 h). Worthy of note, the reaction requires a large excess of $BH_3 \cdot S(CH_3)_2$ to be complete (and selective), thus avoiding the formation of partially substituted species of the $Mg[BH_{4-n}(C_4H_9)_n]_2$ type. Characterization of the final product, performed as described in method a, demonstrated that

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the colorless powders isolated by this procedure correspond to the same crystalline product, $Mg(BH_4)_2$.

The comparison between the powder X-ray diffraction traces reported in Figure 1 indicates that the powders, derived from two independent reaction pathways, contain the very same polycrystalline species. Well before the recent structural determinations,[3] we succeeded in indexing the first 23 peaks by TOPAS-R (GOF = 25.8) by a hexagonal unit cell of approximate dimensions $a = 10.33$ Å, $c = 37.09$ Å, and $V = 3430$ Å^3, later confirmed by a structureless whole-pattern profile fitting by the Le Bail method. These experimentally derived lattice metrics and the X-ray diffraction pattern simulation (using the coordinates published in ref 3a) allowed us to confirm once more that our powders are a monophasic material, i.e., pure $Mg(BH_4)_2$, the complex crystal structure of which has been very recently determined from synchrotron data by two leading groups in the field.[3a,b]

Our crystalline magnesium tetrahydroborate powders are highly reactive. In particular, when in contact with a moist atmosphere, pure $Mg(BH_4)_2$ gives rise to a highly exothermic reaction with violent effervescence. In addition, this material is very interesting as a hydrogen storage material because it possess as rather exceptional (nominal) hydrogen content of about 14.9 wt %. The hydrogen desorption of the product has already been beautifully reported in ref 3c and will not be discussed here any further.

Furthermore, additional interesting applications of the pure, crystalline $Mg(BH_4)_2$ prepared by our methods may arise from its use as a starting material (of controlled stoichiometry and physicochemical properties) in chemical vapor deposition processes of magnesium diboride, MgB_2. Indeed, this superconducting material, discovered in 2001,[9] is presently actively studied and widely engineered in a variety of fields;[10] in particular, for electronic applications, thin films are required, and actually the best results have been obtained mainly by hybrid physical−chemical deposition of toxic gaseous borane species.[11]

In summary, this contribution has presented two relatively cheap, rapid, alternative (but equally efficient) synthetic methods for obtaining the (for long-time, elusive) $Mg(BH_4)_2$ material, which can be isolated in a very pure and (poly)-crystalline form. The operations described in these chemical recipes do not require sophisticated handling systems (apart from vacuum lines or dry boxes) or hazardous materials, like gaseous BH_3, which is often supplied in high-pressure vessels. Here, cheap and commercially available starting materials are used, and the whole sequence of manipulation processes can be easily carried out within an efficient drybox system under a controlled, inert, atmosphere.

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Supporting Information Available: Details of the two synthetic methods, analytical data, and a description of the instrumentation used. This material is available free of charge via the Internet at http://pubs.acs.org.

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