



**Solution-Based Routes to Ammine Metal Borohydrides:
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Complete List of Authors:	Mostajeran, Mehdi; University of Ottawa, Chemistry and Biomolecular Sciences and CCRI Wolstenholme, David; University of New Brunswick, Department of Chemistry Frazee, Chris; University of New Brunswick, Department of Chemistry McGrady, Sean; University of New Brunswick, Baker, R; University of Ottawa, Department of Chemistry



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Solution-Based Routes to Ammine Metal Borohydrides: Formation of Ammonia-Borane

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Mehdi Mostajeran,^a David J. Wolstenholme,^b Chris Frazee,^b G. Sean McGrady^{b,c,*} and R. Tom Baker^{a,*}

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Ammine metal borohydrides (AMBs) have recently commanded attention as low-temperature hydrogen sources. As an alternative to widely used mechanochemical synthesis that affords mixtures with salt co-products, we have been investigating solution synthesis routes to obtain pure AMBs. Here we show that reactions of $MCl_n + nNaBH_4$ with ammonia in thf afford ammonia-borane (AB) via borane abstraction from M-coordinated borohydride. The amount of AB formed correlates roughly with the metal ion electronegativity and AMB thermal stability, except for reducible metals such as Ti, which affords nearly 3 equiv. of AB per Ti.

Development of the hydrogen economy will be enhanced by safe and efficient H_2 storage methods and materials.¹ Lightweight metal borohydrides, $[M(BH_4)_m]$, contain large amounts of hydrogen (10–15 wt.%), but are plagued by high desorption temperatures and, in some cases, formation of toxic and potentially explosive diborane.² These shortcomings led to the development of ammine metal borohydrides $[M(BH_4)_m \cdot nNH_3; AMBs]^{3-14}$ that exploit protic N–H and hydridic B–H bonds to reduce the energy barriers to low temperature hydrogen release.¹⁵ Currently, the majority of AMBs are synthesised through ball-milling of $MCl_m \cdot nNH_3$ with Li/NaBH₄. One drawback of this method is the retention of Li/NaCl in the mixture, which decreases the efficiency of the material to serve as a hydrogen source by imposing “dead mass”¹⁶ and perhaps also introducing additional reaction pathways to volatile contaminants such as diborane and ammonia. In this paper we show that solution synthesis of AMBs in tetrahydrofuran (thf) can be accompanied by formation of ammonia-borane (NH_3BH_3 ; AB).

We began our investigation with the yttrium AMB, $Y(BH_4)_3(NH_3)_4$, **1**, prepared initially by Yu *et al.* by ball-milling a

mixture of $YCl_3(NH_3)_4$ and 3 equiv. $LiBH_4$.¹³ In order to avoid formation of ‘ate’ complexes and to facilitate separation of the salt co-product, we prepared the known complex, $Y(BH_4)_3(thf)_3$ ¹⁷ from YCl_3 and 3 equiv. of $NaBH_4$ in thf solution (Fig. S1). Subsequent treatment of a thf solution of this complex with ammonia gas produced immediate precipitation of a colourless solid, **2**. After filtration, the ¹¹B NMR spectrum of the filtrate contained two resonances in a 1:1 ratio (Fig. S2†). The quintet resonance at –26.6 ppm ($J_{BH} = 85$ Hz) is due presumably to an unidentified yttrium borohydride complex (*cf.* $Y(BH_4)_3(thf)_3$ in thf is at –23.6 ppm, 85 Hz), whereas the quartet at –22.3 ppm ($J_{BH} = 93$ Hz) can be assigned to AB (ca. 0.2 equiv. per Y using an external $BF_3 \cdot Et_2O$ standard). The FT-IR spectrum of **2** (Fig. S26†) shows minor differences when compared to a pure sample of **1** (prepared by treatment of $Y(BH_4)_3(thf)_3$ with liquid NH_3 at –50 °C). The ¹¹B{¹H} MAS NMR spectrum of **2** consists of a minor amount of AB at –22.6 ppm and two Y–BH₄ resonances at –27.9 and –37.9 ppm in a 26:1 ratio (Fig. S14†). Although Yu *et al.* assigned two similar resonances at –28.6 and –39.0 ppm to Y-coordinated and outer-sphere borohydrides in the tetra-ammoniate salt, $[Y(BH_4)_2(NH_3)_4]BH_4$ (2:1 ratio),¹³ a more recent study by Jensen *et al.* reports these resonances to arise from the tetra- and hepta-ammoniates, respectively.¹⁸ In concert with this assignment, we found that the pure solid product obtained from reaction of $Y(BH_4)_3(thf)_3$ with liquid ammonia gave rise to a single ¹¹B NMR resonance at –27.3 ppm due to **1** (Fig. S15†).

We next investigated the generality of AB formation accompanying the synthesis of most known AMBs in thf solution (Table 1). A solution or suspension of the metal chloride and $NaBH_4$ was treated with ammonia, and the resulting solid and filtrate were then characterised by IR and NMR spectroscopy. Note that under these reaction conditions, both thf and ammonia adducts of the metal halides will be reacting with the borohydride salt. For the yttrium reaction, a mixture of 223 mg anhydrous YCl_3 and 135 mg $NaBH_4$ in 30 g of dry thf was treated with excess ammonia to afford 405 mg of a colourless solid, **3**. The ¹¹B NMR spectrum (Fig. S3†) of the filtrate shows formation of AB and a small amount of unreacted $NaBH_4$ but none of the soluble Y–BH₄ by-product observed above. Integration of the spectrum vs. the $BF_3 \cdot Et_2O$ standard indicated ca. 99% conversion of $NaBH_4$ and the formation of 0.28 mmol AB (0.25

^a Department of Chemistry and Biomolecular Sciences and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, ON K1N 6N5 Canada. Email: rbaker@uottawa.ca.

^b Department of Chemistry, University of New Brunswick, P.O. Box 4400, Fredericton, NB E3B 5A3 Canada.

^c Department of Chemistry, Binghamton University, State University of New York, Binghamton, NY 13902, USA. Email: gmcgrady@binghamton.edu.

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equiv. vs. Y). Comparison of the FT-IR spectra of solids **2** and **3** (Fig. S27†) again suggests contamination of the desired Y AMB product **1**.

Table 1. Formation of Ammonia-Borane During Synthesis of AMBs

Element	Ionic radius, Å ^a	Zhang Electronegativity ^b	Zhang Lewis acidity ^c	Amount of AB formed (equiv./metal)
Li ^d	0.92	0.94	1.97	0.02
Na ^d	1.18	0.96	1.38	0.01
Mg	0.89	1.21	1.40	0.37
Ca	1.12	1.03	1.59	0.20
Zn	0.74	1.43	0.66	0.01
Al	0.53	1.50	3.04	0.47
Ti ^e	0.67	1.41	1.69	3.10
V ^e	0.78	0.61	1.09	1.35
Y	1.02	1.21	1.47	0.25
La ^d	1.17	1.21	0.85	0.09

^a ref. 19a. ^b ref. 19b. ^c ref. 20. ^d See the section S1† in the supporting information for synthesis details. ^e Oxidation state: 3+.

Reactions of divalent metal chlorides with NaBH₄ and ammonia afforded varying amounts of AB. In the case of Mg, in addition to the resonance for unreacted NaBH₄ (at -42.7 ppm), the resonance centred at -38.2 ppm in the solid-state ¹¹B MAS NMR (Fig. S17†) could be assigned to the tetra-ammoniate, Mg(BH₄)₂(NH₃)₄ **4**, on the basis of the estimated ammonia uptake (Table S1).²¹ The ¹¹B NMR spectrum of the filtrate yielded an estimate of 0.37 equiv. of AB vs. Mg. In contrast, the Ca reaction afforded Ca(BH₄)₂(NH₃)₂ **5** (sharp singlet at -35.1 ppm vs. -34.7 ppm in the literature).^{7a} While only 0.2 equiv. of AB (vs. Ca) were produced in this reaction, a new Ca-coordinated BH₄ resonance was observed in the solution ¹¹B NMR spectrum at -36.9 ppm (J_{BH} = 82 Hz) (Fig. S5†). For the heavier divalent metal, Zn(BH₄)₂(NH₃)₂^{10b} is reported to exhibit a ¹¹B MAS NMR resonance at -44.1 ppm. However, in our reaction this is only a minor product (-44.3 ppm), with the major product **6** giving rise to two resonances at -36.8 ppm and -38.5 ppm in a ratio of 1:2 (Fig. S19†). We have observed this AMB with formula Zn₃(BH₄)₆(NH₃)₈ previously from treatment of isolated Zn(BH₄)₂(thf)₂ with liquid ammonia; full characterization will be published elsewhere. In this reaction only 0.01 equiv. of AB (vs. Zn) were formed (Fig. S6†), indicating the potential to prepare a pure sample of **6** using the thf solution method.

Reactions with trivalent metal chlorides shed additional light on the factors leading to AB formation. The ¹¹B MAS NMR spectrum of the colourless solid obtained from the Al reaction showed two overlapping resonances centred at -35.8 and -37.0 ppm in a ratio of ca. 2.5:1 that can be assigned to a mixture of Al(BH₄)₃(NH₃)₄^{6d} (-36.9 ppm) and Al(BH₄)₃(NH₃)₆^{6c} (-36.7 ppm). Analysis of the reaction filtrate gave an estimate of 0.47 equiv. of AB (vs. Al) (Fig. S7†). As seen for yttrium, the lanthanum reaction afforded one major product **7** with a ¹¹B MAS NMR resonance at -24.1 ppm which matches that of the product obtained from reaction of La(BH₄)₃(thf)₃ with liquid ammonia. In contrast to Y, however, the La reaction in thf produced less than 0.1 equiv. of AB (vs. La).

The most remarkable results were obtained from the V and Ti reactions. ¹¹B MAS NMR spectroscopic analysis of the brown solid

8 obtained from the reaction of 1:3 VCl₃:NaBH₄ with ammonia in thf gave a series of broad peaks between -13.7 and 38.1 ppm that includes resonances typical of 3-coordinate boron (Fig. S22†).²² While the paramagnetic d² V³⁺ ion likely prevents observation of V-coordinated borohydride NMR resonances, the spectrum suggests that the reaction also involves some dehydrocoupling. In this reaction 1.35 equiv. of AB (vs. V) were produced. In the remarkable reaction of TiCl₃ + 3 NaBH₄ with ammonia, formation of nearly 3 equiv. of AB (vs. Ti) was observed along with colourless solid **9**. Indeed, evaporation of the filtrate and drying *in vacuo* afforded 72 mg of colourless solid (*cf.* 2.53 mmol AB = 78 mg). The FT-IR spectrum of solid **9** clearly indicates the presence of B-H units although only a weak, broad feature is observed in the N-H stretching region (Fig. S29†). Both tetra- and tricoordinate boron environments are clearly observed in the ¹¹B MAS NMR spectrum of solid **9** (Fig. 1). Three different environments can be identified: a major broad peak spans 1.8 to 13.9 ppm, indicative of 3-coordinate boron, a weak resonance at -27.6 ppm may be due to a BH₃ unit, and a major BH₄ resonance appears at -44.2 ppm, i.e., upfield of NaBH₄. Ti³⁺ is a paramagnetic d¹ ion, and ¹¹B NMR spectra of its monomeric borohydride derivatives are not typically observed.²³ Formation of colourless solid **9** and the presence of a sharp borohydride resonance are both suggestive of accompanying redox chemistry. EPR spectroscopy is currently being applied to investigate this reaction further, and the results will be published in due course.

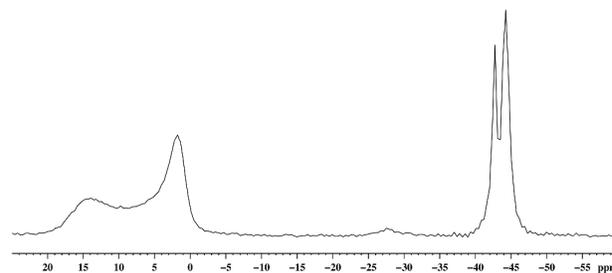


Fig. 1. ¹¹B{¹H} MAS NMR spectrum (128 MHz) of solid **9** obtained from TiCl₃/3NaBH₄ and NH₃ in thf.

In these one-pot reactions, ammonia adducts of MCl_n appear to react more readily with NaBH₄ than do the pure MCl_n reagents in thf.^{10b} Nonetheless, the results described above indicate that formation of AB usually accompanies attempts to prepare pure AMBs using thf solution routes. Reactions of Cp₂Zr(BH₄)₂ with an amine base to afford amine-borane and Cp₂ZrH(BH₄) were reported by Bird and Wallbridge *et al.*,²⁴ and Nöth *et al.* noted that dissolution of Ti(BH₄)₃ in pyridine afforded pyridine-borane.²⁵ However, this reaction pathway has not been recognised in recent work investigating AMBs as hydrogen storage media.⁸ As can be seen in Figure 2a, the amount of AB formed with the s- and p-block metals correlates roughly with the Zhang electronegativity^{19b} with the exception of Zn, which shows the least tendency to produce the amine-borane adduct. In this respect, the electronegativity of the metal centre in a series of AMBs was also recently correlated with their thermal decomposition.²⁶ This suggests that AB may be formed as an intermediate in the decomposition of these hydrogen storage candidates, possibly through generation of M-NH₂BH₃ units derived from dehydrocoupling of M-H + AB. In contrast, little correlation is

found with the metal ion Lewis acidity as calculated by Zhang^{20a} (Figs. S33† and S34†).

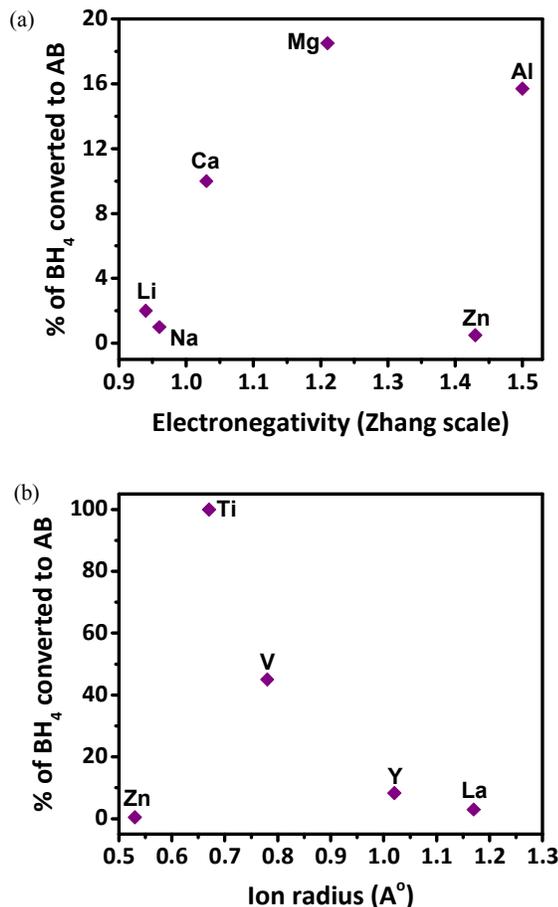


Fig. 2. Correlation between the amount of AB produced in reactions of $MCl_n + n NaBH_4$ with NH_3 vs. (a) Zhang electronegativity of the s- and p-block metal ions, and (b) Ionic radius of the d-block metal ions.

As can be seen in Fig. 2b, the ionic radii for the d-block metal derivatives display a strong correlation with the amount of AB formed in these reactions, with the exception of $[Zn_3(BH_4)_6(NH_3)_8]$. This indicates a pronounced increase in the formation of AB as the ionic radius decreases. Closer inspection of this behaviour shows that the redox-inactive d^0 and d^{10} complexes yield small amounts of AB (< 0.25 equiv.), whereas the d^1 (Ti) and d^2 (V) derivatives engage in a competitive dehydrocoupling process, leading to appreciable quantities of the amine-borane adduct. If we consider the reaction as a nucleophilic abstraction of borane from the coordinated borohydride ligand, the relative stability of the metal borohydride vs. metal hydride should be one thermodynamic factor to be considered. While we do not yet fully understand this trend, it is interesting to consider that these are the only redox active metals on the list. The presence of these non-bonding electrons may also confer a kinetic advantage by increasing the lability of the ligands within their metal coordination sphere.

At the request of a referee, the experimental thermal stability (T_{dec}) of some of the AMBs is plotted against the amount of AB obtained for each metal (Fig. 3). The strong correlation suggests that more stable AMBs are less susceptible to AB formation. As above, Zn and the reducible transition metals (*i.e.* Ti and V) are exceptions to this trend.

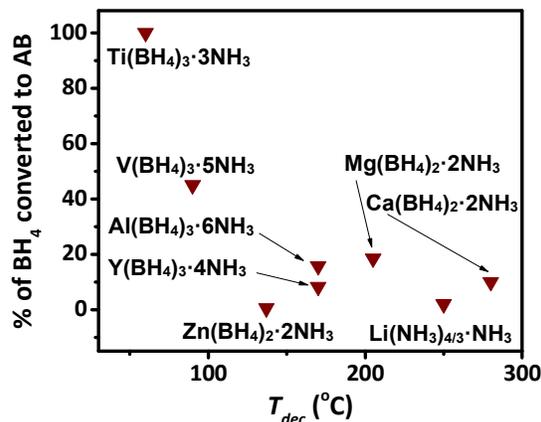


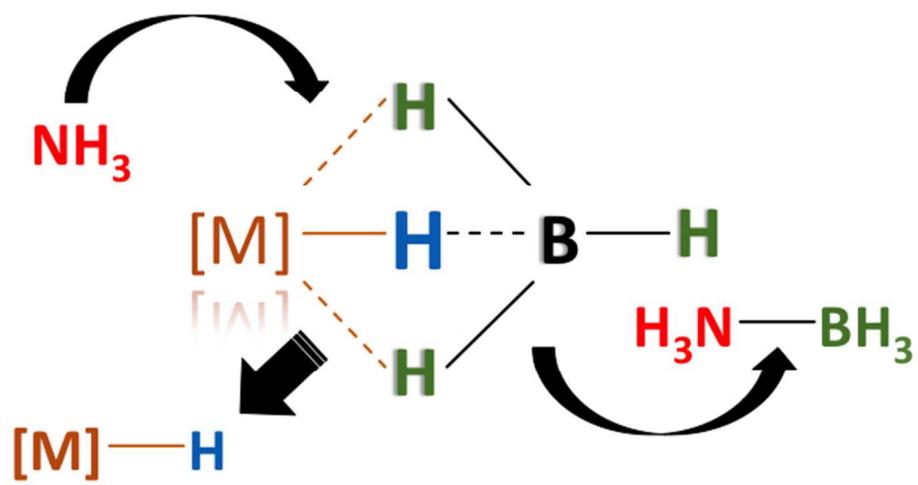
Fig. 3. Correlation between the amount of AB produced vs. the decomposition onset temperature (T_{dec}) of each AMB.

To consider the effect of solvent polarity on the formation of AB, YCl_3 was treated with 3 equivalents of $NaBH_4$ in dichloromethane (DCM, $\epsilon = 9.1$), pyridine (py, $\epsilon = 12.3$) and dimethyl sulfoxide (DMSO, $\epsilon = 46.7$). Only 0.1 equivalents of AB were formed in DCM while 1.6 equivalents were obtained in DMSO (Figs S11† and S13†). Notably, ¹¹B NMR spectroscopy indicated that the hepta-ammoniate Y-AMB, $Y(BH_4)_3 \cdot 7NH_3$,¹⁸ is favored in DCM (*vs.* the tetra-ammoniate in thf; Fig. S25†). The result in pyridine solvent is complicated by formation of pyridine-borane that could arise from both direct reaction with a Y-BH₄ group or its known reaction with ammonia-borane.²⁷ A total of 0.24 equivalents/Y of AB was formed in this reaction (Fig. S12†). The increased amount of AB formation observed in DMSO *vs.* thf may be attributed to the stronger donor power of the former that could facilitate the borane abstraction.

In summary, we have shown that solution synthesis of ammine metal borohydrides in thf is accompanied by formation of ammine-borane via ammonia abstraction of borane from a metal-coordinated borohydride ligand. An inspection of ¹¹B MAS NMR spectra for a number of AMBs prepared by mechanochemical means also provides evidence for AB formation.^{6b, 13, 6f} Although AB is observed as a by-product for each metal studied here, the solution method offers a potentially efficient route to prepare the desired AMBs directly and cleanly from their corresponding metal borohydrides in liquid ammonia or dimethylsulfide¹⁸ solvents at low temperatures. Further investigations along these lines are in progress in our labs. We thank NSERC H2CAN network for support of this research and the University of Ottawa, Canada Foundation for Innovation and Ontario Ministry of Economic Development and Innovation for essential infrastructure. We also thank a referee for valuable suggestions.

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