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Article

Efficient Synthesis of an Aluminum Amidoborane Ammoniate

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Abstract: A novel species of metal amidoborane ammoniate, $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ has been successfully synthesized in up to 95% via the one-step reaction of $AlH_3{\cdot}OEt_2$ with liquid $NH_3BH_3{\cdot}nNH_3$ (n = 1~6) at 0 °C. This solution based reaction method provides an alternative pathway to the traditional mechano-chemical ball milling methods, avoiding possible decomposition. MAS ^{27}Al NMR spectroscopy confirms the formulation of the compound as an $Al(NH_2BH_3)_6^{3-}$ complex anion and an $Al(NH_3)_6^{3+}$ cation. Initial dehydrogenation studies of this aluminum based M-N-B-H compound demonstrate that hydrogen is released at temperatures as low as 65 °C, totaling ~8.6 equivalents of H_2 (10.3 wt %) upon heating to 105 °C. This method of synthesis offers a promising route towards the large scale production of metal amidoborane ammoniate moieties.

Keywords: aluminum; amidoborane; boranes; dehydrogenation; hydrogen storage; synthetic methods; Nuclear Magnetic Resonance Spectroscopy (NMR)

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1. Introduction

A critical challenge facing the advancement of hydrogen fuel cells for automotive applications is the development of safe and energy efficient hydrogen storage materials. Metal amidoboranes (MNH_2BH_3, MAB) and metal borohydride ammoniates ($MBH_4 \cdot nNH_3$, MBA) are currently among the most promising candidate materials [1–6]. Recent demonstration of the regeneration of ammonia borane derivatives using hydrazine in liquid ammonia point to the feasibility of off-board reversibility [7–9]. Substitution of one protic H atom in the [NH_3] of NH_3BH_3 by a metal atom leads to the formation of MAB complexes.

Aluminum amidoborane ($Al(NH_2BH_3)_3$, AlAB), first synthesized by Hawthorne *et al.* [10], possesses one of the highest theoretical hydrogen capacities among MABs (12.9 wt % H), capable of releasing 6 wt % H_2 at 190 °C and approximately 8 wt % H_2 in the presence of an ionic liquid at lower temperatures [10]. As such, this material has already experienced intensive explorations, although up to now only a few reports have identified its existence owing to its poor stability and spontaneous H_2 loss caused by the chemically vulnerable Lewis-acidic Al^{3+} center [10–12]. The improved dehydrogenation properties of AlAB (Al χ_p = 1.5), relative to ammonia borane [10], makes the Al-N-B-H systems attractive, albeit difficult to synthesize. Recently, Guo *et al.* reported on the stability of $[Al(NH_3)_6](BH_4)_3$ in air, which differs quite significantly from the analogous volatile liquid $Al(BH_4)_3$ [13,14]. Strong $N\text{-}H^{\delta+}\cdots{}^{-\delta}H\text{-}B$ dihydrogen bonds contribute to the stability of this compound resulting in its long term stability in air. Another recently reported Al based amidoborane complex includes $Li_3AlH_6 \cdot n(NH_2BH_3)$ which releases 9 wt % H_2 at a temperature of 130 °C [15].

A variety of B-N amidoborane ammoniates, have previously been synthesized by reacting MAB and NH_3, including $LiNH_2BH_3 \cdot NH_3$ [16], $Mg(NH_2BH_3)_2 \cdot 3NH_3$ [17], and $Ca(NH_2BH_3)_2 \cdot NH_3$ [18]. However, to the best of our knowledge, there has been no prior report of the synthesis of an aluminum analog. Herein we report the first synthesis of aluminum amidoborane ammoniate, $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$.

2. Results and Discussion

The synthesis of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ (according to Equations (1) and (2)) was achieved using a specially-designed polytetrafluoroethylene reactor, which allowed the reactants to be stirred at low temperature under ammonia pressure. Under these conditions, ammonia borane reversibly absorbs up to 6 equivalents of NH_3, forming liquid $NH_3BH_3 \cdot nNH_3$ (n = 1–6) complexes [19]. $AlH_3 \cdot OEt_2$, which is insoluble in $NH_3BH_3 \cdot nNH_3$, was utilized as a highly reactive Al source [20,21]. Immersing the Al source in ammonia borane ammoniate complex permits the selective uptake of ammonia in a one-step synthesis of $Al(NH_2BH_3)_3 \cdot 3NH_3$ as a solid precipitate that can be isolated in up to 95% purity (based on $AlH_3 \cdot OEt_2$) by filtration (Equations (1) and (2), details in Section 3, Experimental Section). It should be emphasized that this method avoids the high-energy impact generally encountered in traditional ball milling methods and further prevents possible decomposition of components. This synthesis strategy may also be effective for other amidoborane ammoniates.

$$NH_3BH_{3(s)} + nNH_{3(g)} \xrightarrow[n = 1\sim6]{0\ ^\circ C} NH_3BH_3 \cdot nNH_{3(l)} \quad (1)$$

$$AlH_3 \cdot OEt_{2(l)} + 3NH_3BH_3 \cdot nNH_{3(l)} \xrightarrow[-3H_2, -Et_2O, -NH_3]{0\ ^\circ C} Al(NH_2BH_3)_3 \cdot 3NH_{3(s)} \quad (2)$$

Figure 1a illustrates the XRD pattern obtained for a sample of $Al(NH_2BH_3)_3 \cdot 3NH_3$ prepared via the method described above. The pattern does not index to any previously reported Al-N-B-H quaternary compound and contains at most, only very minor contributions from unreacted starting material. FTIR analysis of $Al(NH_2BH_3)_3 \cdot 3NH_3$ featured a N-B stretch at 875 cm^{-1} and peaks at 426 and 461 cm^{-1} which were assigned to Al-N lattice vibrations, (Figure S1, Table S1). Attempts were also made to prepare $Al(NH_2BH_3)_3 \cdot 3NH_3$ using ball milling techniques. As shown in Figure 1c, no new species evolved from a mixture of $AlH_3 \cdot OEt_2 + 3NH_3BH_3$, which was ball milled under ammonia atmosphere at 0 °C, at a speed of 150 rpm for at least 2 hours. Moreover, increasing the ball milling energy, such as higher rotational speed or temperature (>40 °C) during the synthesis causes dissociation of the ether adduct, which often leads to the production of γ-AlH_3 (Figure 1b). This alane polymorph incidentally shows much lower reactivity in liquid $NH_3BH_3 \cdot nNH_3$ than pure $AlH_3 \cdot OEt_2$, and inhibits the formation of an Al-N bond [22].

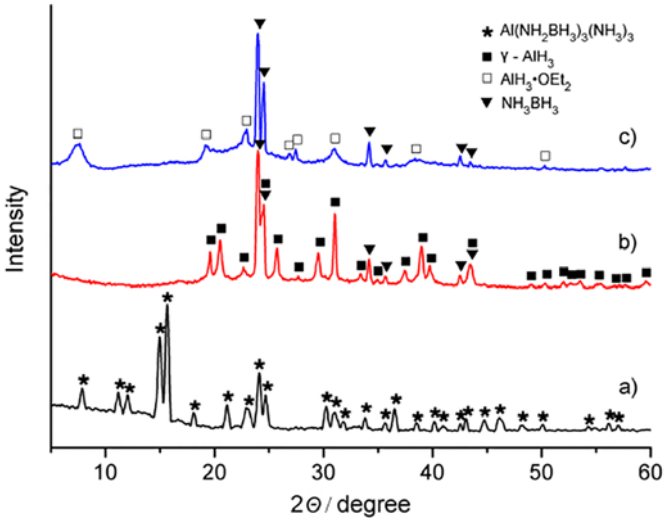

Figure 1. XRD patterns of (**a**) as-prepared $Al(NH_2BH_3)_3 \cdot 3NH_3$; (**b**) mixture of γ-$AlH_3$ + $3NH_3BH_3$; (**c**) ball milled $AlH_3 \cdot OEt_2$ + $3NH_3BH_3$. λ = 1.5406 Å.

The ^{27}Al MAS NMR spectrum (Figure 2b) verifies the formation of $Al(NH_2BH_3)_3 \cdot 3NH_3$ and provides key information about its molecular structure. After reaction, only traces of the characteristic resonance for $AlH_3 \cdot OEt_2$ at 109.9 ppm are observed [23]. Two major resonances at 65.5 ppm and 33.6 ppm dominate the spectrum, clearly indicating that $Al(NH_2BH_3)_3 \cdot 3NH_3$ contains equal amounts of aluminum in two very different coordination environments. The MAS ^{11}B NMR spectrum of the product contains a major resonance for $Al(NH_2BH_3)_3 \cdot 3NH_3$ at 19.6 ppm and a and a minor resonance at −38 ppm which is due the presence of $[(NH_3)_2BH_2^+][BH_4^-]$ DADB or a related decomposition product that was also observed in the starting material [24]. As seen in Figure 2a, the ^{11}B chemical shift of $Al(NH_2BH_3)_3 \cdot 3NH_3$ is 2.7 ppm upfield from the 22.3 ppm shift observed for $NH_3BH_3 \cdot nNH_3$. Similar upfield shifts have been observed for other metal amidoboranes and hence this observation confirms the substitution of an H atom by an Al atom in the ammonia borane molecule [25,26].

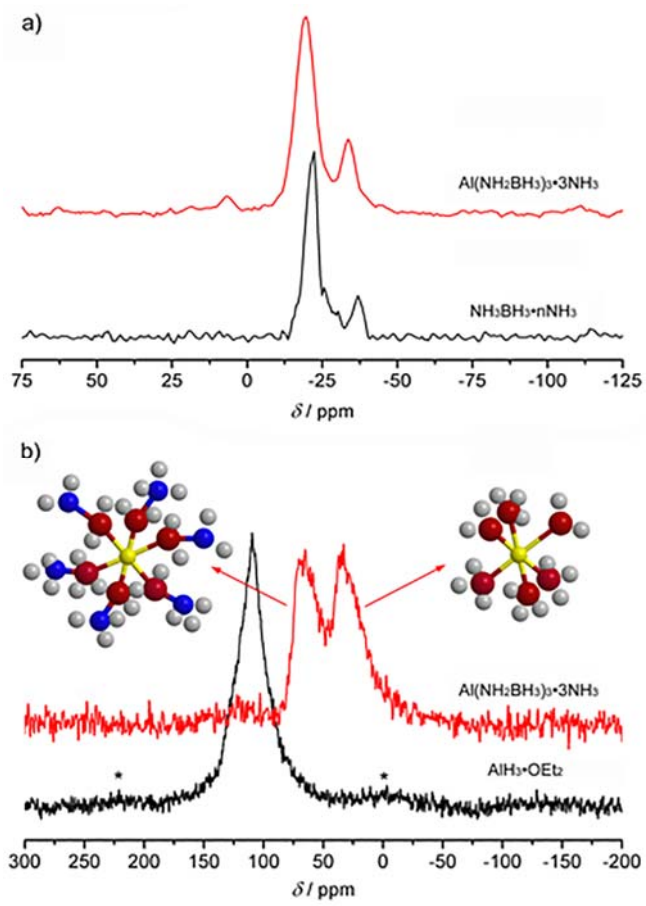

Figure 2. (**a**) ^{11}B MAS NMR spectra of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ and $NH_3BH_3 \cdot nNH_3$; (**b**) ^{27}Al MAS NMR spectra of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ and $AlH_3 \cdot OEt_2$. The molecular structure of the octahedral Al complexes are also depicted (yellow balls represent Al, red for N, blue for B, and grey for H).

Al^{3+} generally has either tetrahedral or octahedral coordination. Thus *a priori* there are four possible coordination geometries for $Al(NH_2BH_3)_3 \cdot 3NH_3$: 1) Al coordinates three $(NH_2BH_3)^-$ anions and three ammonia molecules to give a neutral $Al(NH_3)_3(NH_2BH_3)_3$ complex; 2) Al coordinates octahedrally with only ammonia giving a hexammineraluminum cation [27], $Al(NH_3)_6^{3+}$ and leaving three free $(NH_2BH_3)^-$ anions; 3) Al coordinates tetrahedrally with $(NH_2BH_3)^-$ anions, forming an $Al(NH_2BH_3)_4^-$ anion and three of these anions pair with one $Al(NH_3)_6^{3+}$; and 4) Al octahedrally coordinates with $(NH_2BH_3)^-$ anions giving a $Al(NH_2BH_3)_6^{3-}$ complex anion and ion pairs with the $Al(NH_3)_6^{3+}$ cation. The observation of two peaks with equal intensity in the ^{27}Al MAS NMR spectrum is consistent with only the $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ formulation and as such the ^{27}Al NMR resonances are assigned as follows: $Al(NH_2BH_3)_6^{3-}$ at 65.5 ppm and $Al(NH_3)_6^{3+}$ at 33.6 ppm (Figure 2b). This is quite similar to the reported structure of $Mg(NH_2BH_3)_2 \cdot 3NH_3$ where Mg^{2+} exhibits both tetrahedral and octahedral coordination [17]. Elemental analysis (Table S2) also shows the ratio of Al:N:B is 1:6:3, and supports the $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ formulation.

No apparent reaction was observed after exposure of a sample of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ to dry air for 3 days (Figure S2). The time-programmed-desorption/mass spectroscopy (TPD/MS) results reveal that the thermal decomposition of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ occurs in the temperature range of

65–180 °C, with the release corresponding to 7.5 wt % (Figure 3a,c). The desorbed gaseous product comprises of both H_2 and NH_3.

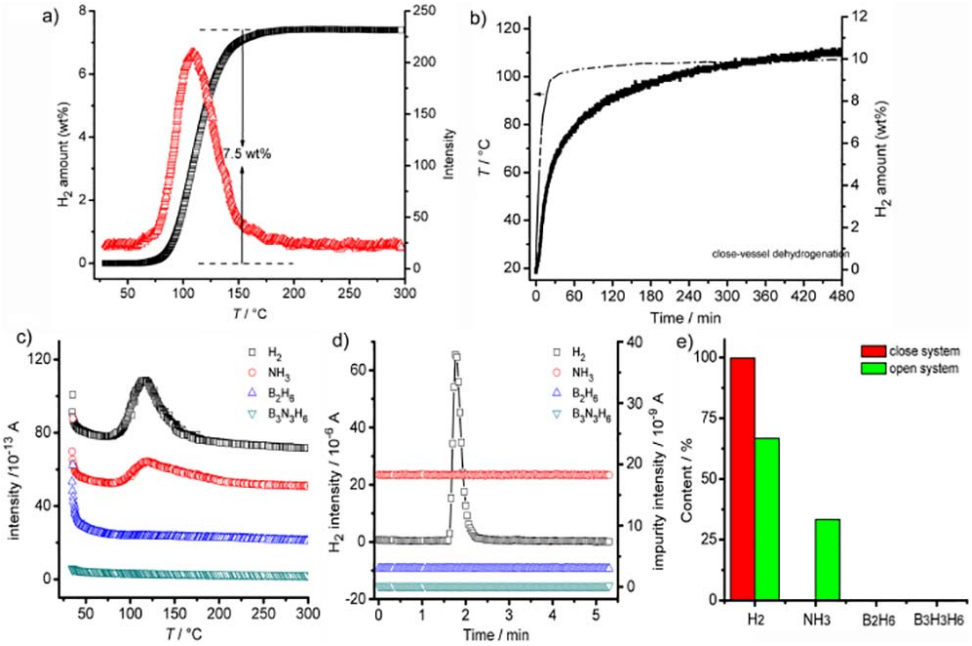

Figure 3. (**a**) TPD (△) and gas release (□) profiles of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ at a heating rate of 5 °C min^{-1} under argon flow; (**b**) Isothermal desorption of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ in a closed vessel; the temperature ramping shown by dash dot line; (**c**) MS signals in (**a**): □ H_2, ○ NH_3, △ B_2H_6, ▽ $B_3N_3H_6$; (**d**) MS signals in (**b**) measured using Calibration Injection Mode: □ H_2, ○ NH_3, △ B_2H_6, ▽ $B_3N_3H_6$; (**e**) H_2 purity comparison between different systems.

Figure 4 shows the N 1s XPS results of $AlAB{\cdot}3NH_3$ before and after thermal decomposition (experimental details described in Supplemental Information). The peaks at ~396.6, ~398.0 and ~399.6 eV are attributed to N-Al, N-B and NH_3, respectively. After decomposition, the evolution of NH_3 and the corresponding peak at ~189.8 eV in B 1s XPS (Figure S3) suggests the formation of an Al-N-B matrix. Combined with the remaining B-H vibrations in micro-FTIR (Figure S4, Table S3), the reaction under dynamic inert gas flow can be described by Equation (3). The anticipated borazine-derivated structure is illustrated in Figure S5 representing $AlN_3B_3H_6$.

$$[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}] \rightarrow 2AlN_3B_3H_3 + 6NH_3 + 12H_2 \quad (3)$$

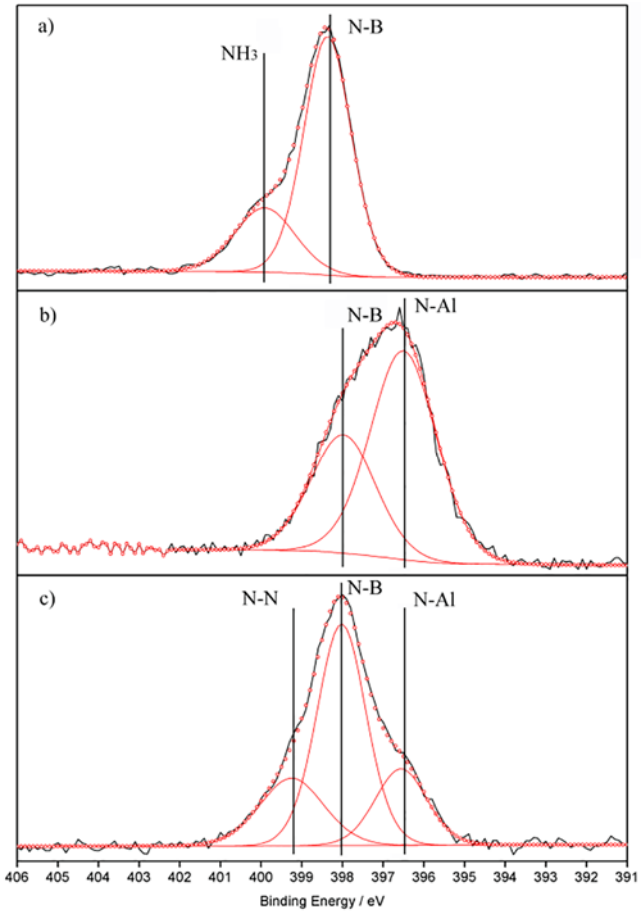

Figure 4. The N 1s XPS results of $Al(NH_2BH_3)_3 \cdot 3NH_3$ (**1**) before (**a**) and after thermal decomposition in an open system (**b**) and in a closed system (**c**). The experiment data are in black, while the fitted ones are in red.

The isothermal desorption in a closed vessel was examined using a Sieverts method at 105 °C (experimental details described in Supplemental Information). The gas evolved is calculated to be 10.3 wt % (Figure 3b), while only 0.05% NH_3 is detectable (Figure 3d). Obviously, the mass difference (Figure 3e) indicates that a significant partial pressure of NH_3 in a closed system suppresses further NH_3 desorption. This phenomenon is in accordance with the decomposition pathways of other metal amidoborane ammoniates [17,28,29]. Element analysis shows that the composition of Al, N, B and H are 15.83%, 48.18%, 18.36% and 3.83%, respectively, indicating an empirical formula of $AlN_6B_3H_{6.5}$*. Similarly, N-H or B-H vibrations are not observed in the micro-FTIR spectrum, while Al-N stretching vibrations and weak H wagging vibrations are apparent (Figure S4 and Table S3). Meanwhile, the peaks at 1367 and 1627 cm^{-1} are typical of N-B stretching in *h*-BN [30]. The N 1s XPS peak ~396.4 eV (Figure 4c) and is attributed to the formation of an Al-N bond, while the two overlapped B 1s XPS peaks in Figure S3 suggests that the decomposed product comprises of not only [AlNBH] but also another B moiety. On the other hand, the ^{11}B MAS NMR spectrum presents at least two overlapping resonances at 6.3 ppm and 18.3 ppm (Figure S6), which is due to the second-order quadrupolar interaction. Thus, the B atoms are likely in a BN_3 or BN_2H environment [31,32]. The N 1s peak at ~399.1 eV is possibly a N-N bond. Clearly, the decomposition mechanism of $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ in a closed system is

much more complicated than that of an open system. On the basis of 8.6 equivalents of H_2, the dehydrogenation process can be briefly described by Equation (4).

$$[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}] \rightarrow AlN_6B_3H_{6.5}^{*} + (8.5\sim9.0)H_2 \quad (4)$$

3. Experimental Section

All starting materials, $LiAlH_4$ 99% (Sigma-Aldrich, Shanghai, China), $AlCl_3$ 99.99%, NH_3BH_3 99% (Sigma-Aldrich), and NH_3 (Alfa Aesar, Shanghai, China), were obtained commercially and used without further purification. All manipulations were carried out under inert atmosphere conditions, either in an argon-filled glovebox or using standard Schlenk line techniques under a nitrogen atmosphere. The organometallic synthesis of $AlH_3 \cdot Et_2O$ is a chemically simple process, but a brief summary is presented. Generally, $AlCl_3$ was reacted with $LiAlH_4$ in diethyl ether with the LiCl precipitate being removed by filtration [21,33]. The excess diethyl ether was then removed under dynamic vacuum. $AlH_3 \cdot Et_2O$ was ground in a mortar with excess NH_3BH_3 and then sealed in a self-designed polytetrafluoroethylene (PTFE) reactor. The reactor was attached to the gas/vacuum manifold and rapidly evacuated/backfilled with 0.3–0.5 MPa NH_3. The system was cooled to −70 °C using acetone and dry ice, and gradually warmed to 0 °C in an ice bath. At this temperature and under the NH_3 atmosphere, ammonia borane reversibly absorbed up to at least 6 equivalents of NH_3, forming liquid $NH_3BH_3 \cdot nNH_3$ (n = 1–6) complexes. $AlH_3 \cdot OEt_2$ was dissolved in liquid $NH_3BH_3 \cdot nNH_3$, and the solution stirred for 2 h until the reaction was complete. The internal temperature and pressure of the reactor and manifold were recorded for the duration of the experiment. The ammonia and reaction produced hydrogen were then removed *in vacuo* at room temperature. Anhydrous diethyl ether was then added to the remaining products, thereby dissolving the excess NH_3BH_3 of which was removed by filtration. The residual solid $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$ was then heated to 45 °C for 12h to remove residual solvent to yield a solid white powder.

4. Conclusions

In summary, a novel aluminum amidoborane ammoniate, $[Al(NH_2BH_3)_6^{3-}][Al(NH_3)_6^{3+}]$, has been successfully synthesized. A reaction vessel has been designed that allows a one-step synthesis from the reaction of $AlH_3 \cdot OEt_2$ with liquid $NH_3BH_3 \cdot nNH_3$ (n = 1~6) at 0 °C. MAS ^{27}Al NMR spectroscopy confirms the formulation of the compound as an $Al(NH_2BH_3)_6^{3-}$ complex anion and a $Al(NH_3)_6^{3+}$ cation. This aluminum based M-N-B-H compound begins to release hydrogen at 65 °C, amounting to ~8.6 equivalents of H_2 (10.3 wt %) upon heating to 105 °C. This method of synthesis offers a promising route towards the large scale production of metal amidoborane ammoniate moieties.

Supplementary Materials

Supplementary materials can be accessed at: http://www.mdpi.com/1996-1073/8/9/9107/s1.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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