The present invention discloses new methods for synthesizing ammonia borane (NH₃BH₃, or AB). Ammonium borohydride (NH₄BH₄) is formed from the reaction of borohydride salts and ammonium salts in liquid ammonia. Ammonium borohydride is decomposed in an ether-based solvent that yields AB at a near quantitative yield. The AB product shows promise as a chemical hydrogen storage material for fuel cell powered applications.

20 Claims, 1 Drawing Sheet
OTHER PUBLICATIONS

Shore, S. G. et al., Large Scale Synthesis of HB(NH)+BH- and HNBH, Inorganic Chemistry, 3 (6), 1964, 914-915.
* cited by examiner
Fig. 1

Fig. 2
PROCESS FOR SYNTHESIS OF AMMONIA BORANE FOR BULK HYDROGEN STORAGE

BACKGROUND OF THE INVENTION

Many research groups around the world are investigating approaches to accelerate the discovery and development of hydrogen storage materials and systems to meet Department of Energy (DOE) 2015 system-based targets. A hydrogen storage system includes all the components required to get hydrogen from a hydrogen storage material and to provide hydrogen for use as an operating fuel. Several processes are described in the literature for synthesizing ammonia borane (AB). In the conventional metathesis approaches, synthesis of AB involves two undesired pathways that involve formation of DADB, the ionic dimer of AB, as shown hereafter:

\[ 2\text{NH}_3\text{BH}_4 \rightarrow 2\text{AB} + \text{H}_2 \]

In pathways (A) and (B), \( \text{NH}_3\text{BH}_4 \) decomposes to form AB with loss of \( \text{H}_2 \) gas. However, as AB is formed, AB can dimerize as in pathway (A) to form DADB or can lose hydrogen and form polymeric polyaminoborane (PAB), a decomposition product. Alternatively, AB can also react with \( \text{NH}_3\text{BH}_4 \) as in pathway (B) to form DADB or PAB. Increasing the AB concentration or temperature increases the likelihood of reactions that form DADB and PAB. In these approaches, DADB is a competing reaction component that can decrease the yield of AB. In an alternative metathesis approach performed in an organic solvent, dilute reactant concentrations were used in an attempt to prevent DADB or PAB formation. However, low yields of AB were obtained. In another approach known in the art, an attempt was made to promote the reaction:

\[ 2\text{AB} + \text{H}_2 \rightarrow \text{DADB} + \text{H}_2 \]

In pathways (A) and (B), \( \text{NH}_3\text{BH}_4 \) decomposes to form AB with loss of \( \text{H}_2 \) gas. However, as AB is formed, AB can dimerize as in pathway (A) to form DADB or can lose hydrogen and form polymeric polyaminoborane (PAB), a decomposition product. Alternatively, AB can also react with \( \text{NH}_3\text{BH}_4 \) as in pathway (B) to form DADB or PAB. Increasing the AB concentration or temperature increases the likelihood of reactions that form DADB and PAB. In these approaches, DADB is a competing reaction component that can decrease the yield of AB. In an alternative metathesis approach performed in an organic solvent, dilute reactant concentrations were used in an attempt to prevent DADB or PAB formation. However, low yields of AB were obtained. In another approach known in the art, an attempt was made to promote the reaction:

\[ 2\text{AB} + \text{H}_2 \rightarrow \text{DADB} + \text{H}_2 \]
In another embodiment, a temperature of ~40° C. and an NH3 partial pressure of 1 atm. are used.

In various embodiments, the borohydride salt can include a constituent selected from: Na, Li, K, Mg, Ca, including combinations of these constituents.

In one embodiment, the ammonium salt includes an anion that is a halide or another anion. In various embodiments, the ammonium salt is selected from, e.g., Cl-, Br-, I-, SO4^2-, CO3^2-, HCO3^-1, PO4^3-, and combinations of these anions.

In one embodiment (sequential addition process), a borohydride salt is mixed with an ammonium salt in liquid ammonia solvent to form ammonium borohydride (NH4BH4). The liquid ammonia (and any NH3 not complexed to the NH4BH4) is removed and a mixture of ammonium borohydride (NH4BH4) and NaCl is isolated as a polycrystalline solid. An ether-based solvent is then subsequently introduced to form the final AB product. NaCl is removed (e.g., by filtering) and the AB is recovered at a high yield.

In another embodiment (parallel addition process), a borohydride salt is mixed with an ammonium salt in liquid ammonia solvent to form ammonium borohydride (NH4BH4). An ether-based (secondary) solvent is then added to the liquid ammonia containing the ammonium borohydride (i.e., NH4BH4) is not recovered (isolated) from the solvent before addition of the ether to form the final AB product at a high yield.

In yet another embodiment (parallel addition process), a borohydride salt reactant (e.g., LiBH4) is introduced in an ether-based solvent (e.g., as LiBH4/THF) to the primary liquid ammonia solvent to form liquid ammonia borohydride (NaBH4). Addition of the ether (THF) to form AB at a high yield and a high purity. Yield of (AB) synthesized in accordance with the invention is near the theoretical yield. In particular, purity of the AB product obtained in accordance with Synthesis (I) that demonstrates the purity of the AB product. Reactant salts can be added sequentially (i.e., one by one) into liquid ammonia. Alternatively, a first salt (MBH4 or NH4X) can be mixed into liquid ammonia followed by addition of a second salt. Alternatively, salts can be added sequentially into liquid ammonia. In short, the invention is not limited by the order at which salts and/or solvents are added. Temperatures for conducting the reactions can be varied. In particular, temperatures can range from ~65°C. to ~25° C. Manner for applying temperature is not limited by the order at which salts and/or solvents are added. For example, temperature can be held constant, altered, or ramped during AB synthesis. Alternatively, one or more temperatures can be applied for each process step. Thus, no limitations are intended. Various ammonia (NH3) pressures can also be used. Ammonia pressures are preferably selected in the range from about 1 atmosphere for the low-temperature syntheses (~80°C. to about 0°C.) up to about 20 atmospheres for near-room temperature syntheses (0°C. to about 25°C.). At a given temperature, pressures are selected above the partial pressure of ammonia so as to maintain the liquid ammonia environment. The method can be performed in a single reaction vessel, i.e., the so-called ‘one-pot’ synthesis. An unexpected result is that e.g., for bulk hydrogen storage, e.g., for fuel cell-powered vehicles and other devices; solvent recycling; and other industrial applications. In the present invention, metathesis reactions that form ammonium borohydride (NH4BH4) are conducted in a liquid ammonia solvent. The ammonium borohydride (NH4BH4) intermediate is stable in the liquid ammonia (NH3). And, liquid ammonia prevents side reactions from occurring during the metathesis reactions that form ammonium borohydride that would normally undermine AB yield.

Addition of an ether-based organic solvent initiates loss of H2 gas from ammonium borohydride and forms AB at a high yield and a high purity. The loss of H2 from the NH4BH4 occurs at a low temperature that eliminates need for a heating step in conventional NH3-only solvent systems. While the present invention is described herein with reference to the preferred embodiments thereof, it should be understood that the invention is not limited thereto, and various alternatives in form and detail may be made therein without departing from the scope of the invention. Two new processes for synthesis of (AB) will now be described.

### Sequential Addition

- Reacting a MBH4 salt and a NH4X salt in liquid ammonia (NH3) at a preselected temperature and pressure to form NH4BH4.
- Removing liquid ammonia solvent (any non-complexed NH3) to recover (isolate) NH4BH4; and
- Adding an ether-based solvent (e.g., THF) to form AB at a high yield and a high purity. Yield of (AB) synthesized in accordance with the invention is near the theoretical yield. In particular, yield of AB is greater than or equal to 99% by weight. More particularly, yield of AB is greater than or equal to 99% by weight. The near quantitative yield of AB (>90% by weight) represents an unexpected result given the low yields of (AB) from metathesis reactions reported in the literature. Purity of the AB product obtained is also high. In particular, purity is greater than or equal to 90%. More particularly, purity is greater than or equal to 99%. FIG. 1 is a 11B-NMR plot of ammonium borane (AB) obtained in accordance with Synthesis 1 that demonstrates the purity of the AB product.

### Synthesis (I)

**Sequential Addition**

In one embodiment of the invention, a new sequential addition process for formation of AB includes the steps of: (1) reacting a MBH4 salt and a NH4X salt in liquid ammonia (NH3) at a preselected temperature and pressure to form NH4BH4; (2) removing liquid ammonia solvent (any non-complexed NH3) to recover (isolate) NH4BH4; and (3) adding an ether-based solvent (e.g., THF) to form AB at a high yield and a high purity. Yield of (AB) synthesized in accordance with the invention is near the theoretical yield. In particular, yield of AB is greater than or equal to 99% by weight. More particularly, yield of AB is greater than or equal to 99% by weight. The near quantitative yield of AB (>90% by weight) represents an unexpected result given the low yields of (AB) from metathesis reactions reported in the literature. Purity of the AB product obtained is also high. In particular, purity is greater than or equal to 90%. More particularly, purity is greater than or equal to 99%. FIG. 1 is a 11B-NMR plot of ammonium borane (AB) obtained in accordance with Synthesis 1 that demonstrates the purity of the AB product. Reactant salts can be added sequentially (i.e., one by one) into liquid ammonia. Alternatively, a first salt (MBH4 or NH4X) can be mixed into liquid ammonia followed by addition of a second salt. Alternatively, salts can be mixed together and then introduced into liquid ammonia. In short, the invention is not limited by the order at which salts and/or solvents are added. For example, temperature can be held constant, altered, or ramped during AB synthesis. Alternatively, one or more temperatures can be applied for each process step. Thus, no limitations are intended. Various ammonia (NH3) pressures can also be used. Ammonia pressures are preferably selected in the range from about 1 atmosphere for the low-temperature syntheses (~80°C. to about 0°C.) up to about 20 atmospheres for near-room temperature syntheses (0°C. to about 25°C.). At a given temperature, pressures are selected above the partial pressure of ammonia so as to maintain the liquid ammonia environment. The method can be performed in a single reaction vessel, i.e., the so-called ‘one-pot’ synthesis. An unexpected result is that...
liquid ammonia (NH₃) suppresses formation of DADB and other competing side reactions that normally decrease the yield of AB. As a result, a greater concentration of the desired (AB) product in the ether-based solvent is achieved, e.g., up to about 2.5 M—a factor 2.5 times greater than maximums reported in the research literature currently. In the present invention, the addition of ether-based solvent, only after NH₃BH₄ is fully and completely formed in liquid ammonia, initiates H₂ loss that converts NH₃BH₄ and provides the AB product at a high yield and a high purity. Use of concentrated liquid ammonia (NH₃) in the metathesis reactions of NH₃X and MBH₄ salts for the synthesis of AB provides at least four beneficial effects. Liquid ammonia stabilizes NH₃BH₄ making it less reactive towards AB. It also facilitates phase separation of NH₃BH₄ from AB, preventing formation of DADB. Liquid ammonia solvent can be removed prior to addition of the ether-based solvent, as described herein. However, some ammonia molecules remain complexed to the NH₃BH₄ solid, which aides in the increased yields obtained by the present invention. These molecules complex with any BH₃ (a likely key intermediate formed during H₂ release from NH₃BH₄) acting as a BH₃ trap, which prevents BH₃ from decomposing to form side products. The ammonia also suppresses AB dimerization that can form DADB, thus allowing greater reactant salt concentrations to be used for AB synthesis. And, results demonstrate that DADB was not found during the metathesis reactions of the present invention in liquid ammonia solvent. In sum, the combination: 1) of forming NH₃BH₄ in liquid ammonia; and 2) adding ether-based solvent to initiate loss of H₂ eliminates the need to heat liquid ammonia to 40°C to evolve H₂ as taught in the prior art, which heating promotes side reactions, yields undesired reaction products, and results in lower yields of AB.

Synthesis (II)
Parallel Addition

In another embodiment of the invention, a parallel addition process for formation of AB includes the steps of: (1) reacting a MBH₄ salt and a NH₃X salt in liquid ammonia (NH₃) at a preselected temperature and pressure to form NH₃BH₄; and (2) adding an ether-based solvent (e.g., THF) to the liquid ammonia containing NH₃BH₄ to form AB at a high yield and a high purity. Yield of (AB) synthesized in accordance with the invention is near the theoretical yield. In particular, yield of AB is greater than or equal to 90% by weight. More particularly, yield of AB is greater than or equal to 99% by weight. Purity of the AB product is also high. In particular, purity is greater than or equal to 99%. More particularly, purity is greater than or equal to 99%. FIG. 2 is an X-ray diffraction (XRD) plot of (AB) synthesized in accordance with Synthesis II that demonstrates the purity of the (AB) product. Melting point determinations showcase the purity of the (AB) product. Impure (AB) melts at temperatures, e.g., below about 100°C, while highly pure (AB) melts at 110°C. The (AB) product obtained from Syntheses I and II both melted at 110°C, indicating a highly pure (AB) product. In the instant process, reactant salts are added together (i.e., in parallel) into liquid ammonia to form ammonium borohydride (NH₃BH₄). Alternatively, the liquid ammonia can be added to the starting salts to form ammonium borohydride (NH₃BH₄). Results demonstrate that the order of addition of the salts and/or solvents does not affect yield of AB. For example, the ether-based solvent [e.g., tetrahydrofuran (THF)] can be added to the liquid ammonia solvent containing (NH₃BH₄) formed in step (1) without removing the liquid ammonia. The process can also be performed in a single reaction vessel, i.e., so-called ‘one-pot’ synthesis. Temperatures for conducting the reactions can be varied. In particular, temperatures can range from about −80°C to about 25°C. More particularly, temperatures can range from about −40°C to about 25°C. Manner for applying temperatures is not limited. For example, temperature can be held constant, altered, or ramped during AB synthesis. Alternatively, one or more temperatures can be applied for each process step. Thus, no limitations are intended. In the present invention, addition of ether-based solvent after NH₃BH₄ is formed in liquid ammonia initiates H₂ loss that converts the NH₃BH₄ to AB product at a high yield and a high purity. The combination: 1) of forming NH₃BH₄ in liquid ammonia and 2) adding ether-based solvent to initiate loss of H₂ eliminates the need to heat liquid ammonia to 40°C to evolve H₂ as taught in the prior art, which heating promotes side reactions, yields undesired reaction products, and results in lower yields of AB. Various ammonia (NH₃) pressures can also be used. Ammonia pressures are preferably selected in the range from about 1 atmosphere for the low-temperature syntheses (−80°C to about 0°C) up to about 20 atmospheres for near-room temperature syntheses (0°C to about 25°C). At a given temperature, pressures are selected above the partial pressure of ammonia so as to maintain the liquid ammonia environment. An unexpected result is that liquid ammonia (NH₃) suppresses formation of DADB and other competing side reactions that normally decrease the yield of AB. As a result, a greater concentration of the (AB) product in the ether-based solvent is achieved, e.g., up to about 2.5 M—a factor 2.5 times greater than maximums currently reported in the research literature. Use of concentrated liquid ammonia (NH₃) in the metathesis reactions of NH₃X and MBH₄ salts for the synthesis of AB provides at least four beneficial effects. Liquid ammonia stabilizes NH₃BH₄ making it less reactive towards AB. It also facilitates phase separation of NH₃BH₄ from AB, preventing formation of DADB. When liquid ammonia solvent is removed prior to addition of the ether-based solvent, some ammonia molecules presumably remain complexed to the NH₃BH₄ solid. The complexed ammonia acts as a BH₃ trap by complexing with any BH₃ (a likely key intermediate formed during H₂ release from NH₃BH₄) which prevents BH₃ from decomposing to form side products. The ammonia also suppresses AB dimerization that can form DADB or PAB, thus allowing use of greater concentrations of reactant salts for synthesis. Neither DADB nor PAB was found during the metathesis reactions in the liquid ammonia solvent. The complexed ammonia thus appears to provide observed enhancements demonstrated by the invention.

The following examples provide further details of the invention.

EXAMPLE 1
Low Salt Concentration

In a first experiment [sequential addition and low salt concentration], anhydrous NH₃ (25 mL) was condensed in an oven dried 100 mL 3-neck round bottom flask fitted with a stir bar. The flask was cooled in a dry-ice/isopropanol bath (−78°C) open to a nitrogen atmosphere. Both NH₃Cl (1 g, 18.6 mmol) and NaBH₄ (0.71 g, 18.6 mmol) were added to the reaction flask using a solids addition funnel. The mixture was stirred for 2 hours under a nitrogen atmosphere at −78°C. Liquid ammonia (NH₃) was removed by vacuum, leaving a
mixture consisting of NaCl and NH₄BH₄ as a white polycrystalline solid. Anhydrous THF (100 mL) was then cannulated in under a nitrogen atmosphere over the white solid at -78°C. After THF addition, the white solid began to foam and release hydrogen. The slurry was stirred at -78°C for 30 minutes and then slowly warmed to room temperature and stirred for an additional 60 minutes when no more gas evolution was observed. The NaCl was filtered and the THF removed by rotary evaporation to yield 0.57 g of a microcrystalline powder. Purity of the product was based on XRD and ¹¹B NMR results. In particular, ¹H NMR showed a quartet -23 ppm (BH₃) and H3 in a slush bath while THF (50 mL) was slowly added to the NH₄Cl. The reaction mixture was stirred for 1 hour under a nitrogen atmosphere over the white solid at -78°C. The flask was then slowly thawed while stirring under N₂, allowing the NH₄ and H₂ gases to evolve slowly. The slurry was stirred at -78°C for 2 hours and then after gas evolution ceased, precipitated NaCl was filtered away through filter paper. THF was removed by rotary evaporation, followed by drying under vacuum overnight. 0.420 g (125% yield) of a mixture of LiBH₄ and NH₄Cl was recovered as a microcrystalline powder at 99% yield of AB after LiBH₄ was removed. Purity of the product was based on XRD and ¹¹B NMR results.

EXAMPLE 2
Sequential Addition (2)
High Salt Concentration

In a second experiment [sequential addition and high salt concentration], NH₄BH₄ was prepared by addition of NaBH₄ and NH₄Cl (18.6 mmol of each reagent) in liquid ammonia at -78°C. The reaction mixture was stirred for 1 hour under a nitrogen atmosphere before warming to -40°C. The dissolved reaction product was filtered and the THF removed by rotary evaporation to yield 0.57 g of a microcrystalline powder. Purity of the product was based on XRD and ¹¹B NMR results. In particular, H NMR showed a slight triplet at 3.8 ppm (NH₃, Jₐₐₐₐ = 45 Hz) and a 1:1:1 quartet centered at 1.5 ppm (BH₃, Jₐₐₐₐ = 94 Hz). ¹¹B NMR showed a quartet ~23 ppm (BH₃, Jₐₐₐₐ = 93 Hz), and a ~99% yield of NH₄BH₄.

EXAMPLE 3
Parallel Addition (1)
High Salt Concentration

In another experiment [parallel addition and high salt concentration], anhydrous NH₄Cl (10 mL) was condensed in an oven dried 100 mL 3-neck round bottom flask fitted with a stir bar. The flask was cooled in a dry-ice/isopropanol bath (~78°C) and open to a nitrogen atmosphere. NH₄Cl (1.06 g, 18.6 mmol) and NaBH₄ (0.71 g, 18.6 mmol) were added by solids addition funnel to the three neck flask and the reaction was stirred for 2 hours under nitrogen at ~78°C. Anhydrous THF (100 mL) was slowly added dropwise to the NH₄Cl and stirred for 1.25 hours under nitrogen atmosphere (~78°C) and open to a nitrogen atmosphere. 9.3 mL of 2 M LiBH₄·THF (18.6 mmol) was added to 50 mL anhydrous THF and loaded in an addition funnel and slowly added dropwise to the NH₄Cl. 0.408 g of NH₄F (11.0 mmol) was loaded in a glove box into a solid addition funnel. The slurry was stirred at ~78°C. The flask was then slowly thawed while stirring under N₂, allowing the NH₄ and H₂ gases to evolve slowly. The slurry was stirred at ~78°C for 2 hours and then after gas evolution ceased, precipitated NaCl was filtered away through filter paper. THF was removed by rotary evaporation, followed by drying under vacuum overnight. 0.420 g (125% yield) of a mixture of LiBH₄ and NH₄Cl was recovered as a microcrystalline powder at 99% yield of AB after LiBH₄ was removed. Purity of the product was based on XRD and ¹¹B NMR results. In particular, H NMR showed a quartet -23 ppm (BH₃) and a pentet ~41 ppm (BH₃, Jₐₐₐₐ = 82 Hz).

EXAMPLE 4
Parallel Addition (2)
Low Salt Concentration

In another experiment [parallel addition; low salt concentration; presence of ether-mixed salt], anhydrous NH₄Cl (25 mL) was condensed in an oven dried 100 mL 3-neck round bottom flask fitted with a stir bar. The flask was cooled in a dry-ice/isopropanol bath (~78°C) and open to a nitrogen atmosphere. 9.3 mL of 2 M LiBH₄·THF (18.6 mmol) was added to 50 mL anhydrous THF and loaded in an addition funnel and slowly added dropwise to the NH₄Cl. 0.408 g of NH₄F (11.0 mmol) was loaded in a glove box into a solid addition funnel. The slurry was stirred at ~78°C. The flask was then slowly thawed while stirring under N₂, allowing the NH₄ and H₂ gases to evolve slowly. The slurry was stirred at ~78°C for 2 hours and then after gas evolution ceased, precipitated NaCl was filtered away through filter paper. THF was removed by rotary evaporation, followed by drying under vacuum overnight. 0.420 g (125% yield) of a mixture of LiBH₄ and NH₄Cl was recovered as a microcrystalline powder at 99% yield of AB after LiBH₄ was removed. Purity of the product was based on XRD and ¹¹B NMR results. In particular, H NMR showed a quartet -23 ppm (BH₃) and a pentet ~41 ppm (BH₃, Jₐₐₐₐ = 82 Hz).
tion, followed by drying under vacuum overnight. The product was dissolved in diethyl ether and recrystallized to remove any residual ammonia. The diethyl ether was then removed by rotary evaporation, followed by drying under vacuum overnight. NH₄BH₄ (9.82 g) was recovered as a microcrystalline powder (0.518 mol, 98% yield). Purity of the product was based on XRD and 11B NMR results. 1H NMR d6-glyme showed a slight triplet at 3.8 ppm (NH₃, J_NH=45 Hz) and a 1:1:1:1 quartet centered at 1.5 ppm (BH₃, J_BH=94 Hz). 11B NMR showed a quartet -23 ppm (BH₃, J_BH=93 Hz).

TABLE 2 compares results from the syntheses detailed in Examples 1-5.

**Lithium borohydride salt was acquired in THF solvent and used without modification.**

In synthesis 1 (sequential addition, Example 1), AB was formed at a near quantitative yield. A borohydride salt was mixed with an ammonium salt in liquid ammonia to form solid ammonium borohydride (NH₄BH₄). A mixture of NaCl and ammonium borohydride (including any complexed NH₃) was recovered (isolated) from liquid ammonia solvent as a polycrystalline solid. Addition of THF to the solid containing NH₄BH₄ produced AB at a near quantitative yield. Low salt concentrations were used. These experiments demonstrated: 1) that the DADB formation pathway is not critical, and 2) decomposition of ammonium borohydride (NH₄BH₄) to DADB does not occur when liquid ammonia is present at a concentration greater than about 10 wt %, a surprising result given previous literature reports. Need for solid reactants, dilute reactant conditions (i.e., high solvent concentrations), and an absence of NH₃ are not required. Further, near-quantitative yields can be obtained from complex mixtures of various reactants. In addition, the secondary (ether-based) solvent can be added simultaneously.

In synthesis 2 (sequential addition, Example 2), a borohydride salt was mixed with an ammonium salt in liquid ammonia to form solid ammonium borohydride (NH₄BH₄). A mixture of NaCl and ammonium borohydride (including any complexed NH₃) was again isolated from liquid ammonia solvent as a polycrystalline solid. Addition of THF to the solid containing NH₄BH₄ produced AB at a near quantitative yield. Results demonstrate that not only is the DADB formation pathway not required, dilute concentrations of reactant salts are not required, another surprising result. Use of concentrated reactant salts will assist industrial-scale production of AB. And, again, undesirable side reactions including, e.g., decomposition of ammonium borohydride (NH₄BH₄) to DADB, is controlled when liquid ammonia is present at a concentration >10 wt %. Finally, results demonstrate that complete removal of ammonia in the reaction synthesis is not required.

In synthesis 3 (parallel addition, Example 3), a borohydride salt was mixed with an ammonium salt simultaneously (i.e., in parallel) in liquid ammonia to form solid ammonium borohydride (NH₄BH₄). Addition of THF to NH₄BH₄ solid in liquid ammonia produced AB at a near quantitative yield. This experiment demonstrates the feasibility of simultaneous reaction processing; one or more reactants can be added to the solvent phase in parallel. Results demonstrate that the ether-based solvent (e.g., THF) does not have to be added only after the metathesis reaction has happened. It can be added at any time during the reaction sequence, e.g., while the ammonia solvent (NH₃) is still present.

In synthesis 4 (parallel addition, Example 4), feasibility of complex parallel processing was demonstrated. In this experiment, a borohydride salt (LiBH₄) that was premixed in THF (the secondary) solvent was added simultaneously (i.e., in parallel) to liquid ammonia solvent containing a different ammonium salt (NH₄F). Results demonstrated a near-quan-itative yield of AB, a very surprising result given previous literature reports. Need for solid reactants, dilute reactant conditions (i.e., high solvent concentrations), and an absence of NH₃ are not required. Further, near-quantitative yields can be obtained from complex mixtures of various reactants. In addition, the secondary (ether-based) solvent can be added simultaneously.

In synthesis 5 (parallel addition, Example 5), a borohydride salt was mixed with an ammonium salt simultaneously (i.e., in parallel) under a positive partial pressure of NH₃ (about 100 psia) that allowed the salts to be mixed at a higher temperature (15.5° C.) in a liquid ammonia solvent. Addition of THF produced AB at a near quantitative yield. Results demonstrate that low reaction temperatures are not required, an additional finding demonstrating the advantages and utility of the processes of the present invention. Presence of the liquid ammonia solvent prevents side reactions such as formation of DADB and other unwanted polymeric products such as PAB that would be expected to lower the yield of AB product. Results indicate that formation of DADB is eliminated by the present invention. Findings further show that a yield of AB product can be obtained in ether and ammonia/THF solvent mixtures at concentrations 2.5 times those reported in the research literature, a new finding.

What is claimed is:

1. A method for preparing ammonia borane, characterized by the steps of:

   reacting a preselected quantity of a borohydride salt with an ammonium salt in liquid ammonia at a preselected temperature and pressure to form ammonium borohydride (NH₄BH₄); and
adding a preselected quantity of an ether-based solvent to said ammonium borohydride to form ammonia borane (NH₃BH₃) at a yield greater than 90 percent by weight and a purity greater than 90 percent.

2. The method of claim 1, wherein said ether-based solvent is selected from the group consisting of: glyme; diglyme; ether; tetrahydrofuran, and combinations thereof.

3. The method of claim 2, wherein said liquid ammonia is not removed.

4. The method of claim 2, wherein said liquid ammonia is not removed prior to addition of said ether-based solvent.

5. The method of claim 2, wherein said ether-based solvent is added prior to addition of said liquid ammonia.

6. The method of claim 1, wherein said temperature is about 15° C. and said pressure is an ammonia partial pressure of about 7.0 atm.

7. The method of claim 1, wherein said temperature is about -40° C. and said pressure is a partial pressure of ammonia of about 1 atm.

8. The method of claim 1, wherein said temperature is selected in the range from about -80° C. to about 25° C.

9. The method of claim 1, wherein said temperature is selected in the range from about -40° C. to about 25° C.

10. The method of claim 1, wherein said pressure is a partial pressure of ammonia selected in the range from about 1 atm to about 20 atm.

11. The method of claim 1, wherein said temperature is in the range from about 0° C. to about 25° C. and said pressure is a partial pressure of ammonia selected in the range from about 100 psia to about 500 psia.

12. The method of claim 1, wherein said temperature is the same for said reacting step and for said adding step.

13. The method of claim 1, wherein said temperature is held constant for said reacting step and for said adding step.

14. The method of claim 1, wherein said borohydride salt includes a constituent selected from the group consisting of: Na, Li, K, Mg, Ca, and combinations thereof.

15. The method of claim 1, wherein said ammonium salt includes an anion selected from the group consisting of: Cl−, Br−, I−, SO₄²−, CO₃²−, HCO₃⁻, PO₄³−, and combinations thereof.

16. The method of claim 1, further including the steps of refluxing ammonia and continuously venting H₂ gas during formation of said ammonium borohydride intermediate.

17. The method of claim 1, wherein yield of AB is greater than or equal to about 99%.

18. The method of claim 1, further including the step of isolating said AB product.

19. The method of claim 17, wherein the step of isolating said AB product includes filtering said AB product.

20. The method of claim 1, wherein said method is performed in a continuous reaction process.

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