# Dalton Transactions

## PAPER



Cite this: Dalton Trans., 2015, 44, 753

# Reductive dechlorination of BCl<sub>3</sub> for efficient ammonia borane regeneration<sup>+</sup>

This paper reports a complete ammonia borane (AB) regeneration process in which Bu<sub>3</sub>SnH was utilized

as a reductant for the reductive dechlorination of BCl<sub>3</sub>, and Et<sub>2</sub>PhN was selected as a 'helper ligand' to

generate Et<sub>2</sub>PhN·BH<sub>3</sub>, which gives rise to a high yield of AB by a base-exchange reaction at ambient

Yingbin Tan, Lijun Zhang, Xiaowei Chen and Xuebin Yu\*

Received 29th May 2014, Accepted 31st October 2014 DOI: 10.1039/c4dt01592d

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## Introduction

As the demand for clean and renewable sources of energy grows, attention has increasingly been focused on using hydrogen as an alternative to fossil fuels.<sup>1</sup> However, the application of hydrogen in on-board transportation systems still confronts us with some scientific and technical problems, in which the development of safe and efficient hydrogen-storage materials is widely regarded as one of the greatest challenges.<sup>2–5</sup> Recently, extensive efforts have been focused on boron–nitrogen (B–N)-based hydride materials, primarily due to the light constitutional boron element and their resulting high hydrogen storage capacities.<sup>6–10</sup> Among them, ammonia borane (AB) has quickly dominated as one appealing material, especially because of its satisfactory air stability, relatively low hydrogen-release temperature (<100 °C) and remarkably high gravimetric hydrogen capacity (19.6 wt%).<sup>11–15</sup>

temperature.

However, due to the thermodynamics of AB dehydrogenation, direct hydrogenation of  $H_2$ -depleted AB is unfeasible.<sup>16-19</sup> Previous efforts have demonstrated that a more feasible approach would be to perform the regeneration off-board in a series of reactions that are more thermodynamically reasonable.<sup>20-24</sup> A three-step regeneration strategy of AB based on the digestion of  $H_2$ -depleted AB (BNH<sub>x</sub>) by the formation of a series of B–X species (*i.e.* B–O, B–S, B–Cl, B–Br), the reduction of these compounds with the yielding of Lewis base borane adducts, and the replacement of these 'helper ligands' with ammonia has been widely accomplished for the implementation of the schemed regeneration strategies still face a grand challenge: non-recyclablability of the reductants

(e.g. CH<sub>3</sub>OH-LiAlH<sub>4</sub>, HCl-MgH<sub>2</sub> or Et<sub>3</sub>SiH and HBr-Et<sub>3</sub>SiH systems) (Table S1<sup>†</sup>), which has thus far limited their success as an industrially viable process for H<sub>2</sub> storage. In general, an acceptable and complete regeneration scheme must be (1) appropriate for a variety of spent fuel types, (2) high yielding and (3) highly energy efficient.<sup>21</sup> Recently, a new regeneration strategy has been presented by Mertens and Reller, who applied HCl-AlCl3-CS2 to digest the H2-depleted AB (polyaminoborane  $(BH_2NH_2)_x$ , borazine and crosslinked polyborazylene) with 90% yield of BCl3, which gave rise to 60% overall yield of AB via H2-Ni3B-Et3N reduction and the base-exchange steps.<sup>23</sup> The new process is quite attractive due to the optimization of the reduction step. However, the relatively low yield, low energy efficient and high-temperature ammoniation reaction do not make the current process appear favorable on an industrial scale.<sup>21</sup> Therefore, the development of new strategies that are high-yielding and energy-efficient for the recycling of AB is still an important issue.

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Herein we recommend a complete recycling scheme for the reductive dechlorination of BCl<sub>3</sub> (Scheme 1), in which Bu<sub>3</sub>SnH



Scheme 1 Hydrogen cycle and regeneration of  $\mathsf{NH}_3\mathsf{BH}_3$  based on  $\mathsf{SnBu}_3\mathsf{H}.$ 

Department of Materials Science, Fudan University, Shanghai 200433, China.

*E-mail: yuxuebin@fudan.edu.cn; Fax: +86-21-5566 4581; Tel: +86-21-5566 4581* †Electronic supplementary information (ESI) available: Experimental details, <sup>11</sup>B NMR, XRD, FTIR, schematic illustration and theoretically calculated results. See DOI: 10.1039/c4dt01592d

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was employed as a reduction reagent which avoids the formation of thermodynamically stable Cl–M products (no efficient recycling pathway has been demonstrated to recycle them), and Et<sub>2</sub>PhN was selected as a 'helper ligand' of boron intermediates to maximize the overall efficiency of the AB regeneration process. Our results demonstrated that ammoniation of the generated  $Et_2PhN \cdot BH_3$  gives rise to a high yield of AB at ambient temperature.

## **Experimental**

#### Sample preparation

The source materials BCl<sub>3</sub> (1.0 M in methylene chloride), CH<sub>2</sub>Cl<sub>2</sub> 99.8%, Bu<sub>3</sub>SnH 97%, Et<sub>3</sub>N 99.5%, Et<sub>2</sub>PhN 99.5%, THF $d_8$  99.5% (Sigma-Aldrich, USA) and NH<sub>3</sub> 99.99% (Alfa Aesar, China) were obtained commercially. NH<sub>3</sub> was purified by passing the gas through a column of soda lime prior to use. All samples were handled in a N<sub>2</sub>-filled glove box equipped with a recirculation system to keep H<sub>2</sub>O and O<sub>2</sub> levels below 1 ppm.

#### Reaction of BCl<sub>3</sub> with Bu<sub>3</sub>SnH in the presence of Et<sub>3</sub>N

Bu<sub>3</sub>SnH (2 mL, 2.196 g) and triethylamine (5 mL) were added to BCl<sub>3</sub> (2.5 mL, 0.293 g) in an ice-water bath and loaded into a closed vessel. This mixture was reacted for 12 h at RT or 60 °C with stirring. The <sup>11</sup>B NMR spectra presented that BCl<sub>3</sub> was converted into the Et<sub>3</sub>NBC<sub>12</sub>H species, which was the major product ( $\delta = -4.5$  ppm).

#### A two-step reaction to generate NEt<sub>3</sub>·BH<sub>3</sub>

Bu<sub>3</sub>SnH (4 mL, 4.392 g) was added dropwise into to BCl<sub>3</sub> (5 mL, 0.586 g) at the molar ratio of 3:1 in the ice-water bath. The reaction mixture was stirred for 12 h and no BCl<sub>3</sub> was detected by <sup>11</sup>B NMR. The released gas (B<sub>2</sub>H<sub>6</sub>) was bubbled through a trap filled with Et<sub>3</sub>N to form Et<sub>3</sub>N·BH<sub>3</sub>, which was identified by <sup>11</sup>B NMR. A schematic diagram of the experiment is shown in Fig. S1.<sup>†</sup>

#### Reaction of BCl<sub>3</sub> with Bu<sub>3</sub>SnH in the presence of Et<sub>2</sub>PhN

Bu<sub>3</sub>SnH (2 mL, 2.196 g) and Et<sub>2</sub>PhN (5 mL) were added to BCl<sub>3</sub> (2.5 mL, 0.293 g) and loaded into a closed vessel. This mixture was reacted for 12 h at RT or 60 °C with stirring. The <sup>11</sup>B NMR spectra presented only one boron species resonating at -13.3 ppm, corresponding to BH<sub>3</sub> units ( $J_{BH} = 97.656$  Hz), which were confirmed for Et<sub>2</sub>PhN·BH<sub>3</sub> by comparison of the <sup>11</sup>B NMR spectrum with synthetic Et<sub>2</sub>PhN·BH<sub>3</sub>. Et<sub>2</sub>PhN·BH<sub>3</sub> was exposed in a closed vessel to ammonia gas at a pressure of 1 bar for 3 h.

#### A two-step reaction to generate Et<sub>2</sub>PhN·BH<sub>3</sub>

Bu<sub>3</sub>SnH (4 mL, 4.392 g) was added dropwise into to BCl<sub>3</sub> (5 mL, 0.586 g) at the molar ratio of 3:1 in the ice-water bath. The reaction mixture was stirred for 12 h and no BCl<sub>3</sub> was detected by <sup>11</sup>B NMR. The released gas (B<sub>2</sub>H<sub>6</sub>) was bubbled through a trap filled with Et<sub>2</sub>PhN to form Et<sub>2</sub>PhN·BH<sub>3</sub>, which

was identified by <sup>11</sup>B NMR. A schematic diagram of experiment is shown in Fig. S1.† Et<sub>2</sub>PhN·BH<sub>3</sub> was exposed in a glass tube to ammonia gas at a pressure of 1 bar for 3 h. Afterwards, this mixture was filtered and washed three times with CH<sub>2</sub>Cl<sub>2</sub>. Finally, AB (0.137 g, 89%) [<sup>11</sup>B NMR (THF-*d*<sub>8</sub>):  $\delta$  = -23.5 ppm, *J*<sub>BH</sub> = 92 Hz] was afforded by removing the CH<sub>2</sub>Cl<sub>2</sub> in a vacuum at room temperature.

#### Synthesis of Et<sub>2</sub>PhN·BH<sub>3</sub>

 $BH_3$ ·THF (2 mL) was added to  $Et_2PhN$  (2.5 mL) in the ice-water bath and loaded into a glass tube. This mixture was reacted for 12 h. The <sup>11</sup>B NMR spectra demonstrated that  $BH_3$ ·THF was completely converted into the  $Et_2PhN$ ·BH<sub>3</sub> species.

#### Materials characterization

Solid-state infrared spectra of the samples (as KBr pellets) were recorded using a Nicolet Nexus 470 FTIR instrument in the range of 500–4000 cm<sup>-1</sup>. During the IR measurement (KBr pellets), samples were loaded into a closed tube with CaF<sub>2</sub> windows. The <sup>11</sup>B NMR spectra were recorded using a Bruker Avance III 500 MHz spectrometer, and the <sup>11</sup>B shifts were referenced to BF<sub>3</sub>·OEt<sub>2</sub> ( $\delta = 0$  ppm). For all samples the spectra were measured with and without decoupling. NMR solvents were used without further purification.

#### Powder X-ray diffraction measurement

In-house powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements using CuK $\alpha$  radiation at 50 kV and 150 mA were also conducted to confirm the phase composition of the samples. During the XRD measurements, amorphous polymer tape was used to cover the surface of the powder to avoid oxidation.

## **Results and discussion**

Employing the appropriate reductants is critical for obtaining the optimal chemical yield and energy efficiency of the recycling of these reducing agents, and thus the overall energy efficiency of the AB regeneration cycle.<sup>21</sup> Thus, the reductants must not only be competent for the digested products, but also have a realizable, relatively low energy recycling pathway.<sup>21</sup> By systematic screening experiments, we employed Bu<sub>3</sub>SnH as a reducing reagent, which has been extensively employed in organic reactions.<sup>24-26</sup> In the pre-existing reports, Bu<sub>3</sub>SnH could completely convert BCl3 into gaseous diborane at ambient temperature and the formed Cl-Sn product is easily recycled through an efficient pathway.<sup>27,28</sup> Recently, Gordon et al. have demonstrated that polyborazylene, one form of spent AB fuel, can be regenerated efficiently by the stepwise addition of appropriate digesting-  $(C_6H_4(SH)_2)$  and reducingagents (Bu<sub>3</sub>SnH).<sup>19</sup> Therefore, Bu<sub>3</sub>SnH, as a commercially available reagent, would be a good starting point.

Given that diborane is easy to coordinate with Lewis bases, our initial reductive dechlorination of BCl<sub>3</sub> using Bu<sub>3</sub>SnH was carried out in Et<sub>3</sub>N solution at room temperature. As shown in

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Fig. 1  $^{11}$ B NMR (THF- $d_8$ ) spectra of the products of BCl<sub>3</sub> after reduction using Bu<sub>3</sub>SnH in the presence of Et<sub>3</sub>N at RT and 60 °C, respectively.



**Fig. 2** <sup>11</sup>B NMR (THF- $d_8$ ) spectra of (a) BCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, and the products (b) after reduction using Bu<sub>3</sub>SnH, and (c) Et<sub>3</sub>N coordinated with the released B<sub>2</sub>H<sub>6</sub>.

Fig. 1, the <sup>11</sup>B NMR spectra demonstrated that BCl<sub>3</sub> was converted into Et<sub>3</sub>NBCl<sub>2</sub>H.<sup>23</sup> However, the unreacted Et<sub>3</sub>NBCl<sub>3</sub> ( $\delta$  = 9.7 ppm) was still retained as determined by <sup>11</sup>B NMR. After elevating the temperature to 60 °C, Et<sub>3</sub>NBCl<sub>3</sub> disappeared completely (Fig. 1) and a yield of more than 95% Et<sub>3</sub>NBCl<sub>2</sub>H was obtained, while only a small amount of Et<sub>3</sub>NBClH<sub>2</sub> was observed, which agrees well with the results that active MgH<sub>2</sub> and Et<sub>3</sub>SiH reduced BCl<sub>3</sub> in the presence of Et<sub>3</sub>N, respectively.<sup>29</sup> This suggests that the reductive dechlorination of BCl<sub>3</sub> in the presence of Et<sub>3</sub>N may be unfavorable for the reduction reaction.

To improve the reduction efficiency, we employed a twostep reaction to generate Et<sub>3</sub>N·BH<sub>3</sub> (Fig. S1†). In a typical experiment, a solution of Bu<sub>3</sub>SnH (2 mL) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added into BCl<sub>3</sub> (2.5 mL) with stirring at ambient temperature. After 24 h, no BCl<sub>3</sub> ( $\delta$  = 9.9 ppm) was observed as detected by <sup>11</sup>B NMR (Fig. 2b). The released gas was bubbled through the Et<sub>3</sub>N-solution with the formation of Et<sub>3</sub>N·BH<sub>3</sub> ( $\delta$  = -14.4 ppm,  $J_{BH}$  = 98.877 Hz) (Fig. 2c).<sup>23</sup> An advantage of the two-step process is that it is achieved at ambient temperature with the formation of a high yield of Et<sub>3</sub>N·BH<sub>3</sub> (95%). However, the high ammoniation reaction temperature (for the conversion of Et<sub>3</sub>N·BH<sub>3</sub> into NH<sub>3</sub>BH<sub>3</sub> at 80 °C) was inadvisable to the overall efficiency of an AB regeneration process.<sup>23</sup> Consequently, it



**Fig. 3** (a) <sup>11</sup>B NMR (THF- $d_8$ ) spectra of the products of Et<sub>2</sub>PhN coordinated with B<sub>2</sub>H<sub>6</sub> and then ammoniation; (b) X-ray diffraction patterns of the neat AB and the regenerated AB, respectively.



Fig. 4 <sup>11</sup>B NMR (THF-*d*<sub>8</sub>) spectra of the synthetic Et<sub>2</sub>PhN·BH<sub>3</sub> and the reaction products between BCl<sub>3</sub> and Bu<sub>3</sub>SnH in the presence of Et<sub>2</sub>PhN.

could be expected that a base of medium strength, *e.g.*  $Et_2PhN$ , could be suitable.<sup>29</sup>

We then replaced Et<sub>3</sub>N with Et<sub>2</sub>PhN as the 'helper ligand', and the reaction was carried out at room temperature in a two-step reaction. As shown in Fig. 3a, the <sup>11</sup>B NMR spectra presented only one boron species resonating at –13.3 ppm, corresponding to the BH<sub>3</sub> units ( $J_{BH}$  = 97.656 Hz). By comparison of the <sup>11</sup>B NMR spectrum with the synthesized Et<sub>2</sub>PhN·BH<sub>3</sub>, the formation of the desired product, Et<sub>2</sub>PhN·BH<sub>3</sub>, was confirmed (Fig. 4). Indeed, exposing Et<sub>2</sub>PhN·BH<sub>3</sub> to dry ammonia gas at a pressure of 1 bar at 0 °C for 3 h resulted in quantitative conversion to the BH<sub>3</sub>-containing species. <sup>11</sup>B NMR spectroscopic investigation of the white



Fig. 5 FTIR spectra of neat AB and the regenerated products, respectively.

solid after removal of the remaining  $Et_2PhN$  by filtering and washing with  $CH_2Cl_2$  revealed the quantitative conversion to AB with a yield of >95% (Fig. 3a). XRD and FTIR analyses on the formed AB by this method afforded identical results to those performed on an authentic sample of AB (Fig. 3b and 5).

Inspired by the above results, we performed the reaction of  $Bu_3SnH$  and  $BCl_3$  in the presence of  $Et_2PhN$  at room temperature and 60 °C, respectively. Both reactions were converted into species that mainly contained  $Et_2PhN\cdot BH_3$  (Fig. 6). However, the replacement of  $Et_2PhN$  by ammonia leads to a small amount of AB (5%), which could be due to the fact that some by-products have influence the base-exchange reaction. This indicates that the two-step reaction is favourable for



**Fig. 6** <sup>11</sup>B NMR (THF- $d_8$ ) spectra of the products of BCl<sub>3</sub> after reduction using Bu<sub>3</sub>SnH in the presence of Et<sub>2</sub>PhN at RT and 60 °C, respectively (a), and then ammoniation at ambient temperature (b).

improving the overall efficiency of an AB regeneration process in terms of the enhanced AB yield and the modified reaction conditions. The regeneration reaction of  $BCl_3$  can be speculated as eqn (1)–(3):

$$6Bu_3SnH + 2BCl_3 \rightarrow B_2H_6 + 6Bu_3SnCl$$
(1)

$$B_2H_6 + 2Et_2PhN \rightarrow 2Et_2PhN \cdot BH_3$$
 (2)

$$Et_2PhN \cdot BH_3 + NH_3 \rightarrow Et_2PhN + NH_3BH_3.$$
 (3)

Recycling of the reductants is crucial for an efficient regeneration scheme. Recently, a report from Gordon *et al.* has achieved the recycling of the by-product  $Bu_3SnCl$  *via* multistep reactions as shown in Scheme 1.<sup>27</sup> In a typical reaction,  $Bu_3SnCl$  can be converted into  $Bu_3SnCOOH$  *via* reaction with formic acid in the presence of  $Et_3N$ . In the thermolysis process,  $Bu_3SnCOOH$  was decomposed to release  $CO_2$  and form  $Bu_3SnH$  in 60% isolated yield, in which  $Bu_3SnH$  can reenter the AB regeneration process.<sup>29</sup> In addition,  $Et_2PhN$  was able to be recycled with 90% isolated yield by dynamic vacuum for the removal of  $CH_2Cl_2$  at 0 °C. Thus, we have successfully achieved a complete regeneration cycle for AB as illustrated in Scheme 1. Using the energetic efficiency developed by eqn (4),<sup>19</sup>

$$\frac{(\text{equiv. H}_2 \text{ stored})(57.8)}{(\text{equiv. H}_2 \text{ used})(57.8) + \sum (\Delta H_{\text{endo}}) - (\% \text{ heat recovery}) \sum (-\Delta H_{\text{endo}})}$$
(4)

our regeneration process is estimated to be 43% efficient with regard to the energy input required, which is a little higher than the estimated 38% efficiency in recovering AB using the  $HCl-H_2/Ni_3B$  strategy (Table 1 and Table S1–S6, see the ESI<sup>†</sup> for complete equations).<sup>23</sup> To test the overall procedure, including all separation steps, we obtained an overall yield of 89% isolated AB on the first attempt, which is higher than most of the previously reported regeneration systems (*e.g.* the  $HCl-H_2$  system, 60% isolated yield;  $CH_3OH-LiAlH_4-NH_4Cl$  system, 81% isolated yield; and  $C_6H_6S_2-Bu_3SnH$  system, 67% isolated yield).<sup>19,23,30</sup>

Table 1	Research	status	of a	ll the	reported	regenera	ation	schemes

Regeneration scheme	Complete recycling	Efficiency (20% heat recovery) (%)	Yield (%)
CH <sub>3</sub> OH-LiAlH <sub>4</sub> -NH <sub>4</sub> Cl	No	50	81
C <sub>6</sub> H <sub>6</sub> S <sub>2</sub> -Bu <sub>3</sub> SnH-Bu <sub>2</sub> SnH <sub>2</sub>	No	65	67
HCl-MgH <sub>2</sub> or Et <sub>3</sub> SiH	No	_	_
HBr-Et <sub>3</sub> SiH	No	_	84
C <sub>6</sub> H <sub>6</sub> S <sub>2</sub> -Bu <sub>3</sub> SnH	Yes	55	_
N <sub>2</sub> H <sub>4</sub> -NH <sub>3</sub>	Yes	_	95
HCl-H <sub>2</sub> /Ni <sub>3</sub> B	Yes	38	60
HCl-Bu <sub>3</sub> SnH	Yes	43	89
$\begin{array}{l} C_{6}H_{6}S_{2}{-}Bu_{3}SnH{-}Bu_{2}SnH_{2} \\ HCl{-}MgH_{2} \ or \ Et_{3}SiH \\ HBr{-}Et_{3}SiH \\ C_{6}H_{6}S_{2}{-}Bu_{3}SnH \\ N_{2}H_{4}{-}NH_{3} \\ HCl{-}H_{2}/Ni_{3}B \\ HCl{-}Bu_{3}SnH \end{array}$	No No Yes Yes Yes Yes	65 	67 — 84 — 95 60 89

## Conclusions

In summary, we have successfully developed a complete regeneration cycle for AB based on Bu<sub>3</sub>SnH as a reductant for the reductive dechlorination of BCl<sub>3</sub>, and Et<sub>2</sub>PhN as a 'helper ligand' to generate Et<sub>2</sub>PhN·BH<sub>3</sub>, resulting in a high yield of AB by base-exchange reaction at ambient temperature. Using this methodology, an overall yield of 89% isolated AB was achieved, which is higher than most of the previously reported regeneration systems. All of the by-products in the regeneration scheme are feasible to be converted into main reactants without generating any new undesired products. As one of the most potentially viable chemical hydrogen storage materials, our results on the chemical regeneration of AB provide new insights into B–N hydrogen storage materials moving toward their practical application.

## Acknowledgements

This work was partially supported by the National Natural Science Foundation of China (21271046, 51471053), the Ph.D. Programs Foundation of Ministry of Education of China (20110071110009), and the Science and Technology Commission of Shanghai Municipality (11JC1400700). DFT calculations were carried out at the Multi-modal Australian ScienceS Imaging and Visualisation Environment (MASSIVE) facility.

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