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COMMUNICATION

Use of Crown Ethers to Isolate Intermediates in Ammonia-Borane Dehydrocoupling Reactions

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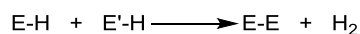
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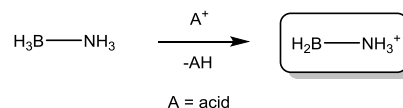
The presence of 18-crown-6 in the Lewis acid-promoted dehydrocoupling reaction of ammonia borane permits isolation of $[(\text{THF})\text{BH}_2\text{NH}_3]^+$ and $[\text{BH}_2(\text{NH}_3)_2]^+$ cations. $[(\text{THF})\text{BH}_2\text{NH}_3]^+$ reacts with Lewis bases to give either boron adducts or by deprotonation at nitrogen to give borazine and ammonia-borane.

In the past few decades there has been continuing interest in the applications of transition metals¹ and, more recently, main group metals² in the dehydrocoupling reactions in a range of bond-forming reactions (Scheme 1). A major focus in this area has been the use of amine-boranes as H₂ fuel sources. As a cheap, environmentally-benign and air-stable compound ammonia borane, BH₃NH₃ (AB), is one of the most promising H₂-storage compounds, potentially capable of releasing three moles of H₂ per molecule and containing a very high H-content of 19.6 wt. %.^{1,2}



Scheme 1 Hydrogenic coupling of two element-H bonds to form a new element-element bond.

Of primary concern in this field is the development of catalysts which can effect H₂ release from AB efficiently under mild conditions. Our interest lies in main group metal-based catalysts which so far have been molecular, homogeneous systems in which activation of AB is proposed *via* a basic pathway involving N-H deprotonation and metal-hydride catalytic intermediates.¹⁻³ However, Brønsted or Lewis acid catalysis of AB dehydrogenation is also known.⁴ The first step in the catalytic process is B-H hydride abstraction to form the boronium cation $[\text{BH}_2\text{NH}_3]^+$ active species (scheme 2) which then undergoes further reaction with AB. The subsequent reaction steps have been probed computationally and experimentally. Like base catalysis, the ultimate reaction products of acid catalysis are normally borazine (B₃N₃H₆) and BN polymers.



Scheme 2 Generation of the ammonia-boronium cation.

Other side products which have been structurally characterised are $[\text{BH}_2(\text{NH}_3)_2]^+$ and $\text{H}_2\text{B}(\mu\text{-H})(\mu\text{-NH}_2)\text{BH}_2$.⁵ The structure of the Lewis-based stabilised boronium cation $[(\text{Et}_2\text{O})\text{BH}_2\text{NH}_2\text{Me}]^+$ has been reported recently, along with its reactivity with sterically-hindered amines.⁶ So far no structural data on the parent cation $[\text{BH}_2\text{NH}_3]^+$ have been reported. However, it has been noted that 'Isolation of this initiator [in acid-catalysed AB dehydrocoupling] will be invaluable for future studies of reaction kinetics and isotope effects'.^{4a}

There are several examples where crown ethers have assisted in the isolation of products from ammonia borane reactions, where they strongly coordinate N-H protons.⁷ In these cases, however, crowns have been added *after* completion of reactions, merely as a way of assisting crystallisation of the final products. Here we report that the presence of crown ethers *during* reaction has a profound effect on the course of reaction and allows the selective isolation of the boronium cations $[(\text{THF})\text{BH}_2\text{NH}_3]^+$ (**1**·THF) and $[\text{BH}_2(\text{NH}_3)_2]^+$ (**2**).

The effects of the presence of a crown ether during reaction are demonstrated by preliminary ¹¹B NMR spectroscopic studies of the products of the Lewis acid-induced reaction of AlCl₃ with AB in THF at room temperature, with and without 18-crown-6 (Figure 1). In the absence of 18-crown-6 (18-C-6), AB reacts sluggishly to form **1**·THF (broad peak at ca. 0.5 ppm), which further reacts with AB to give a number of products, including **2** (-13.6 ppm), $\text{H}_2\text{B}(\mu\text{-H})(\mu\text{-NH}_2)\text{BH}_2$ (-27.5 ppm) and THF·BH₃ (-1.0 ppm). In contrast, in the presence of one equivalent of 18-crown-6, AB reacts rapidly (5 min at room temp.) to give only the H-bonded adduct [**1**·THF(18-C-6)], in which crown ether

coordination effectively blocks the $[\text{BH}_2\text{NH}_3]^+$ cation intermediate from deprotonation. It should be noted in this case that a large excess (4 eq.) of AlCl_3 is required for complete conversion of ammonia-borane starting material, in contrast to Brønsted acids which only need stoichiometric quantities.^{4a} *In situ* ^1H , ^{11}B and ^{27}Al NMR spectroscopic studies of the reaction mixture after initial mixing of the reactants suggest that a complicated series of reactions is involved in the formation of **1**, which includes the formation of H_2 and a range of Al species (such as $\text{AlCl}_3\cdot 2\text{THF}$, $[\text{AlCl}_2\cdot 4\text{THF}]^+$, $[\text{AlCl}_4]^-$ and $\text{AlH}_2\text{Cl}\cdot 2\text{THF}$) (see ESI, Figure S13).⁸

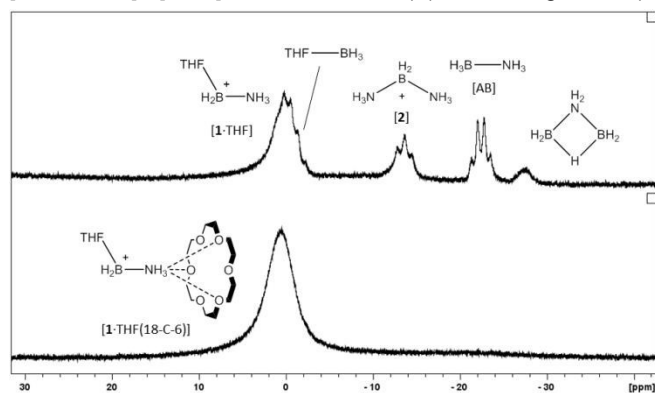


Figure 1 *In situ* ^{11}B NMR spectrum of reaction mixture of AB with 4 eq. of AlCl_3 (THF, 16h, room temperature) (top) and the same reaction in the presence of 1 eq. 18-crown-6 (bottom).

The new boronium salt $[(\text{THF})\text{BH}_2\text{NH}_3(18\text{-C-6})][\text{AlCl}_4]$ ($[\mathbf{1}\cdot\text{THF}(18\text{-C-6})][\text{AlCl}_4]$) (Figure 2) is easily crystallised in 38% yield from the 4:1 reaction mixture of AlCl_3 with AB by filtration and layering with Et_2O (see ESI). The boron atom of the cation has a tetrahedral environment (as predicted by Baker^{4a}) and is coordinated by a THF molecule. The B-N bond length [1.54(2) Å] is similar to that seen in the previously reported N-methyl derivative $[(\text{Et}_2\text{O})\text{BH}_2\text{NH}_2\text{Me}]^+$ [1.602(8) Å].⁶ The NH_3 group of the cation $[\mathbf{1}\cdot\text{THF}(18\text{-C-6})]$ is hydrogen bonded to the 18-crown-6 O-atoms through N-H...O interactions [N-H...O range 1.97 - 2.03 Å, N...O range 2.87(1) - 2.94(1) Å].

The same reaction using 1 eq. of AlCl_3 at reflux was also investigated in order to determine the final products formed. After 16h the ^{11}B NMR spectrum shows the same products as found by Baker in the Brønsted and Lewis acid-catalysed dehydrocoupling of AB using $\text{B}(\text{C}_6\text{F}_5)_3$, HOSO_2CF_3 or HCl , consisting of a mixture of borazine ($\text{B}_3\text{N}_3\text{H}_6$, 30.3 ppm, d, $^1J_{\text{BH}} = 137$ Hz) and BN polymers (25 - 35 ppm), as well as borazane (BH_2NH_2), $[\text{BH}_2(\text{NH}_3)_2]^+$, $\text{H}_2\text{B}(\mu\text{-H})(\mu\text{-NH}_2)\text{BH}_2$ and $\text{THF}\cdot\text{BH}_3$ (see ESI, Figure S1). The new complex $[\text{BH}_2(\text{NH}_3)_2(18\text{-C-6})_2][\text{AlCl}_4]$ ($[\mathbf{2}(18\text{-C-6})_2][\text{AlCl}_4]$) could be isolated in low crystalline yield from this reaction after filtration and layering with Et_2O . However, this compound can be prepared directly and more efficiently simply by introducing NH_4Cl in the reaction. Heating AB, NH_4Cl and AlCl_3 (1:1:1 eq.) in refluxing THF for 16h gave exclusively $[\text{BH}_2(\text{NH}_3)_2][\text{AlCl}_4]$ ($[\mathbf{2}][\text{AlCl}_4]$) (see ESI, Figure S7). 18-crown-6 can be added either before or after the reaction to form $[\mathbf{2}(18\text{-C-6})_2][\text{AlCl}_4]$ (61% yield). The presence of AlCl_3 is essential to the reaction which appears to proceed *via* the intermediate ClBH_2NH_3 with subsequent displacement of Cl^- by NH_3 generated

in situ from deprotonation of NH_4Cl (the established route to the $[\text{BH}_2(\text{NH}_3)_2]^+$ cation uses ClBH_2NH_3 as a starting material, reacting with $\text{NH}_3(\text{l})$ to give the salt $[\mathbf{2}][\text{Cl}]$).⁹

The solid state structure of $[\mathbf{2}(18\text{-C-6})_2][\text{AlCl}_4]$ contains a 'trapped', *bis*-(18-C-6)-coordinated $[\text{BH}_2(\text{NH}_3)_2]^+$ cation where the NH_3 groups are both H-bonded to 18-C-6 O-atoms (Figure 3). The *mono*-(18-C-6)-coordinated cation $[\mathbf{2}(18\text{-C-6})]$ was reported previously in the salt $[\mathbf{2}(18\text{-C-6})][\text{B}_3\text{H}_8]$.^{5c} Bond lengths and angles within the $[\text{BH}_2(\text{NH}_3)_2]^+$ cation unit of the *bis*-coordinated cation $\mathbf{2}(18\text{-C-6})_2$ are similar to those previously reported in the cation $\mathbf{2}$.⁵

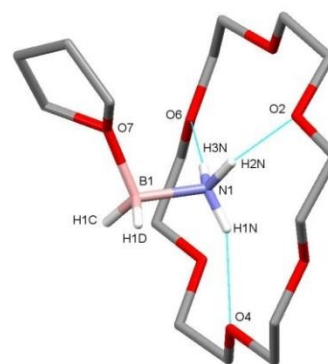


Figure 2 Structure of the cation of $[\mathbf{1}\cdot\text{THF}(18\text{-C-6})][\text{AlCl}_4]$. Selected bond lengths (Å) and angles ($^\circ$): B1-N1 1.54(2), B1-O7 1.53(2), N-H...O range 1.97 - 2.03 [N...O range 2.87(1) - 2.94(1)]; O7-B1-N1 108(1).

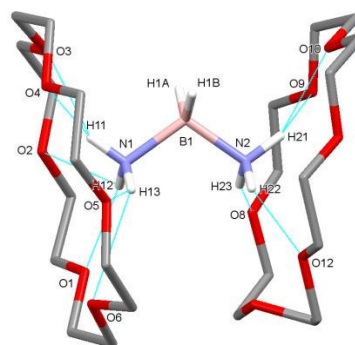


Figure 3 One of the two independent cation units of $[\mathbf{2}(18\text{-C-6})_2][\text{AlCl}_4]$ found in the solid-state structure. Selected bond lengths (Å) and angles ($^\circ$): B-N mean 1.58(1), N-H...O range 2.04 - 2.64 [N...O range 2.872(8) - 3.284(7)]; N-B-N range 110.0(6) - 110.8(6).

The cation **1** is not only an apparent intermediate in the formation of the ultimate products of the reaction of AlCl_3 with AB (borazine and BN polymers) but a potentially useful starting material in its own right. With these features in mind, we explored its reaction characteristics with AB and with Lewis bases. Interestingly, the reaction of 10 mole % of $[\mathbf{1}\cdot\text{THF}(18\text{-C-6})][\text{AlCl}_4]$ with AB at reflux in THF leads to complete consumption of AB after 16h and a mixture of products that is identical to that found in the reaction of AlCl_3 with AB (see ESI, Figure S11). This strongly supports the conclusion that the cation **1** is a catalytic intermediate in the formation of borazine.

The reaction of $[\mathbf{1}\cdot\text{THF}(18\text{-C-6})][\text{AlCl}_4]$ with the relatively unhindered base Et_3N in CH_2Cl_2 results in simple substitution of the B-bonded THF ligand to give the new species

[1-Et₃N(18-C-6)][AlCl₄], the solid state structure of which is shown in Figure 4. There is no apparent change in the B-N(H₃) bond length [1.579(4) Å] compared to that in the [1-THF(18-C-6)] cation. The reactivity of the THF-coordinated boronium ion towards Et₃N contrasts with ClBH₂NH₃, which undergoes displacement of NH₃ rather than the Cl⁻ to form ClBH₂NEt₃.⁹ The reaction of the [1-THF(18-C-6)] cation with the sterically bulkier base ⁱPr₂EtN, however, gives a mixture of borazine, AB and H₂B(μ-H)(μ-NH₂)BH₂ as the major products (Figure 5). This product mixture is distinctly different from that produced with AlCl₃ and probably occurs by a mechanism involving the deprotonation of the [BH₂NH₃]⁺ to give the amino-borane monomer H₂N=BH₂, followed by disproportionation and trimerisation to form borazine and AB. Although H₂N=BH₂ could not be observed in the low-temperature (-40°C) ¹¹B NMR spectrum the fact that the related MeHN=BH₂ monomer has been detected under similar reaction conditions suggests a similar pathway is likely.⁶

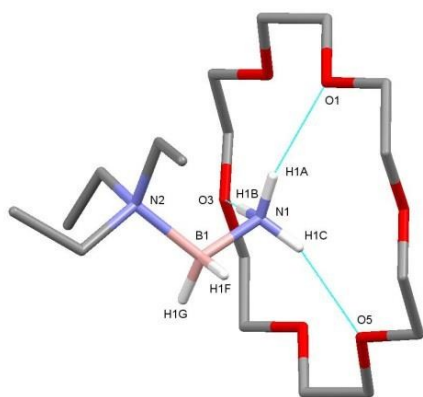


Figure 4 Structure of the cation of [1-Et₃N(18-C-6)][AlCl₄]. Selected bond lengths (Å) and angles (°): B1-N1 1.579(4), B1-N2 1.621(4), N-H...O range 2.09 - 2.21 [N...O range 2.949(4) - 3.092(4)].

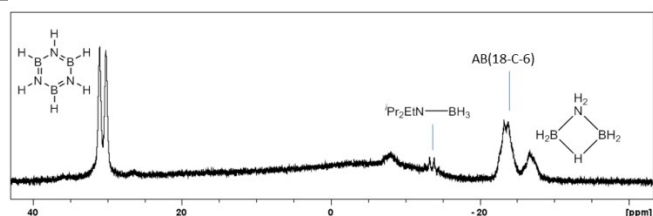


Figure 5 Room temperature *in situ* ¹¹B NMR spectrum of [1-THF(18-C-6)][AlCl₄] + ⁱPr₂EtN (2 eq.) in CD₂Cl₂.

In summary, we have demonstrated the usefulness of crown ethers in trapping and stabilising intermediates from reactions involving AB, obtaining the solid state structure of the [BH₂NH₃]⁺ ion **1** for the first time. Our results support the view that this cation is a key intermediate in the Lewis acid-catalysed dehydrocoupling of AB. As demonstrated by its reaction with Et₃N, **1** is also a potentially highly useful starting material for the preparation of a range of ligand-substituted ammonia boranes [L-BH₂NH₃]⁺ (L = ligand). Further studies are underway to determine the precise mechanisms of hydride abstraction of AB and reaction pathways following deprotonation of [BH₂NH₃]⁺.

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NOTES AND REFERENCES

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