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

Robert J. Less,* Raúl García-Rodríguez, Hayley R. Simmonds, Lucy K. Allen, Andrew D. Bond and Dominic S. Wright

The presence of 18-crown-6 in the Lewis acid-promoted dehydrocoupling reaction of ammonia borane permits isolation of [(THF)BH₂NH₃]⁺ and [BH₂(NH₃)₂]⁺ cations. [(THF)BH₂NH₃]⁺ 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, BH₃N₂H₂ (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. %.³,⁴

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 [BH₂(NH₃)]⁺ 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 [BH₂(NH₃)₂]⁺ and H₂B(μ-H)(μ-NH₂)BH₂.⁵ The structure of the Lewis-based stabilised boronium cation [(Et₂O)BH₂NH₂Me]⁺ has been reported recently, along with its reactivity with sterically-hindered amines.⁶ So far no structural data on the parent cation [BH₂(NH₃)]⁺ 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’.⁷

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 [(THF)BH₂NH₃]⁺ (1-THF) and [BH₂(NH₃)₂]⁺ (2).

The effects of the presence of a crown ether during reaction are demonstrated by preliminary ¹B 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), H₂B(μ-H)(μ-NH₂)BH₂ (-27.5 ppm) and THF-BH₂ (-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 \(\text{AlCl}_3\) is required for complete conversion of ammonia-borane starting material, in contrast to Brønsted acids which only need stoichiometric quantities.\(^{48}\) \(\text{In situ}\) \(\text{H}, \text{B}^\text{11}\) and \(\text{Al}^\text{27}\) 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 \(\text{H}_2\) and a range of Al species (such as \(\text{AlCl}_3\text{2THF}, [\text{AlCl}_4]^+\text{4THF}], [\text{AlCl}_4]\) and \(\text{AlH}_2\text{Cl}_2\text{2THF}\)) (see ESI, Figure S13).\(^6\)

The new boronium salt \([\text{THF}]\text{BH}_2\text{NH}_3\text{(18-C-6)}][\text{AlCl}_4]\) ([1-THF(18-C-6)][AlCl4]) (Figure 2) is easily crystallised in 38% yield from the 4:1 reaction mixture of \(\text{AlCl}_3\) with \(\text{AB}\) by filtration and layering with \(\text{Et}_2\text{O}\) (see ESI). The boron atom of the cation has a tetrahedral environment (as predicted by Baker\(^{45}\)) and is coordinated to a THF molecule. The B-N bond length \([1.54(2) \text{ Å}]\) is similar to that seen in the previously reported N-methyl derivative \([\text{Et}_2\text{O}]\text{BH}_2\text{NH}_3\text{Me}^+\) \([1.60(2) \text{ Å}]\).\(^6\) The NH\(_3\) group of the cation [1-THF(18-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 \(\text{AlCl}_3\) at reflux was also investigated in order to determine the final products formed. After 16 h the \(\text{B}^\text{11}\) NMR spectrum shows the same products as found by Baker in the Bronsted and Lewis acid-catalysed dehydrocoupling of \(\text{AB}\) using \(\text{B(OCF}_3)_3\), \(\text{HOSO}_2\text{CF}_3\) or \(\text{HCl}\), consisting of a mixture of borazine (\(\text{B}_2\text{N}_3\text{H}_6\), 30.3 ppm, d, \(\text{I}^\text{b} = 137 \text{ Hz}\)) and BN polymers (25 - 35 ppm), as well as borazine \(\text{[BH}_2\text{NH}_3]^+\), \(\text{[BH}_2\text{(NH}_3\text{)}]^+\), \(\text{H}_2\text{B}^\text{5}\text{(µ-H)(µ-NH}_3\text{)}^+\text{BH}_2\) and THF-BH\(_3\) (see ESI, Figure S1). The new complex \(\text{[BH}_2\text{(NH}_3\text{)}_2\text{(18-C-6)}][\text{AlCl}_4]\) \([2\text{(18-C-6)}][\text{AlCl}_4]\) could be isolated in low crystalline yield from this reaction after filtration and layering with \(\text{Et}_2\text{O}\). However, this compound can be prepared directly and more efficiently simply by introducing \(\text{NH}_3\text{Cl}\) in the reaction. Heating \(\text{AB}\), \(\text{NH}_3\text{Cl}\) and \(\text{AlCl}_3\) (1:1:1 eq.) in refluxing THF for 16 h gave exclusively \([\text{BH}_2\text{(NH}_3\text{)}_2][\text{AlCl}_4]\) ([2][AlCl4]) (see ESI, Figure S7). 18-crown-6 can be added either before or after the reaction to form \(\text{[2(18-C-6)]}[\text{AlCl}_4]\) (61% yield). The presence of \(\text{AlCl}_4\) is essential to the reaction which appears to proceed via the intermediate \(\text{CIBH}_2\text{NH}_3\) with subsequent displacement of \(\text{Cl}^-\) by \(\text{NH}_3\) generated in \(\text{situ}\) from deprotonation of \(\text{NH}_3\text{Cl}\) (the established route to the \(\text{BH}_2\text{(NH}_3\text{)}_2]^+\) cation uses \(\text{CIBH}_2\text{NH}_3\) as a starting material, reacting with \(\text{NH}_3\text{(l)}\) to give the salt \([2][\text{Cl}^-]\)).\(^5\)

The solid state structure of \([2\text{(18-C-6)}][\text{AlCl}_4]\) contains a ‘trapped’, \(\text{bis}\)-(18-C-6)-coordinated \([\text{BH}_2\text{(NH}_3\text{)}_2]^+\) cation where the \(\text{NH}_3\) groups are both H-bonded to 18-C-6 O-atoms (Figure 3). The \(\text{mono}\)-(18-C-6)-coordinated cation \([2\text{(18-C-6)}]\) was reported previously in the salt \([2\text{(18-C-6)}][\text{B}_2\text{H}_4]\).\(^{32}\) Bond lengths and angles within the \([\text{BH}_2\text{(NH}_3\text{)}_2]^+\) cation unit of the \(\text{bis}\)-coordinated cation \(2\text{(18-C-6)}\) are similar to those previously reported in the cation \(2.\(^5\)

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**Figure 1** in situ \(\text{B}^{	ext{11}}\) NMR spectrum of reaction mixture of \(\text{AB}\) with 4 eq. of \(\text{AlCl}_3\) (THF, 16 h, room temperature) (top) and the same reaction in the presence of 1 eq. 18-crown-6 (bottom).

**Figure 2** Structure of the cation of \([1\text{-THF}(18\text{-C-6})][\text{AlCl}_4]\). Selected bond lengths (Å) and angles (°): 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 \([2\text{(18-C-6)}][\text{AlCl}_4]\) found in the solid-state structure. Selected bond lengths (Å) and angles (°): 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 \(\text{AlCl}_3\) with \(\text{AB}\) (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 \(\text{AB}\) and with Lewis bases. Interestingly, the reaction of 10 mole % of \([1\text{-THF}(18\text{-C-6})][\text{AlCl}_4]\) with \(\text{AB}\) at reflux in THF leads to complete consumption of \(\text{AB}\) after 16 h and a mixture of products that is identical to that found in the reaction of \(\text{AlCl}_3\) with \(\text{AB}\) (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 \([1\text{-THF}(18\text{-C-6})][\text{AlCl}_4]\) with the relatively unhindered base \(\text{Et}_3\text{N}\) in \(\text{CH}_2\text{Cl}_2\) results in simple substitution of the \(\text{B}\)-bonded THF ligand to give the new species.
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 [BH$_{3}$NH$_{3}$]$^{+}$ ion 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 Et$_{3}$N, 1 is also a potentially highly useful starting material for the preparation of a range of ligand-substituted ammonia boranes [L-BH$_{3}$NH$_{3}$]$^{+}$ (L = ligand). Further studies are underway to determine the precise mechanisms of hydride abstraction of AB and reaction pathways following deprotonation of [BH$_{3}$NH$_{3}$]$^{+}$.

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NOTES AND REFERENCES


