Probing the second dehydrogenation step in ammonia-borane dehydrocoupling: characterization and reactivity of the key intermediate, B-(cyclotriborazanyl)amine-borane†

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While thermolysis of ammonia-borane (AB) affords a mixture of aminoborane- and iminoborane oligomers, the most selective metal-based catalysts afford exclusively cyclic iminoborane trimer (borazine) and its B–N cross-linked oligomers (polyborazylene). This catalysed dehydrogenation sequence proceeds through a branched cyclic aminoborane oligomer assigned previously as trimeric B-(cyclodiborazanyl)amine-borane (BCDB). Herein we utilize multinuclear NMR spectroscopy and X-ray crystallography to show instead that this key intermediate is actually tetrameric B-(cyclotriborazanyl)amine-borane (BCTB) and a method is presented for its selective synthesis from AB. The reactivity of BCTB upon thermal treatment as well as catalytic dehydrogenation is studied and discussed with regard to facilitating the second dehydrogenation step in AB dehydrocoupling.

Introduction

The development of clean and efficient technologies for the production, storage and utilization of hydrogen is prerequisite for establishing a hydrogen economy.1 For hydrogen storage,2 chemical hydrides such as methanol,3 formic acid,4 carbazoles,5 hydrazine6 and especially ammonia-borane7 are promising sources that could serve as ‘drop-in’ liquid fuels with the existing fuel delivery infrastructure.

Ammonia-borane (AB, NH3BH3) is an especially attractive hydrogen storage material due to its high gravimetric hydrogen content of 194 g H2 per kg (19.6 wt% H2). Since the molecule contains both hydridic as well as protic hydrogens, hydrogen release can be realized under mild conditions by various means such as thermal treatment,8 acid,9 or base catalysis, or metal-based catalysis.10–13 A number of AB dehydrocoupling mechanisms have been elucidated8,9,10,11,12,13 and metal-based catalysis has been shown to offer the best combination of selectivity and H2 release rate. While many of the very active catalysts afford linear polyaminoborane and a single equivalent of hydrogen,11,12,13,14 the most selective catalysts generate >2 equiv. H2 with concomitant formation of cyclic iminoborane trimer (borazine) and its BN-cross-linked oligomers (polyborazylene; Scheme 1).13b,14† Mechanistic studies of AB dehydrocoupling in ethereal solutions (kinetics, isotope labelling and intermediate trapping) point to the importance of reactive aminoborane, NH2BH3, shown previously to oligomerize above −150 °C.15 It has been suggested that the very active catalysts can retain aminoborane in the first or second coordination sphere and undergo a coordination polymerization-type mechanism (Scheme 1, path B).13e,14 In contrast, the selective catalysts

Scheme 1 Proposed mechanisms for the metal catalyzed dehydrogenation of ammonia-borane.
temperature over several days invariably produced impure samples in low yields (ESI,† p. 3). In contrast, reaction of \( \text{AB} \) with 5 mol% of Schwartz’ reagent, \( \text{Cp}_2\text{ZrHCl} \) (4), at 50 °C afforded much purer samples in fair to good yields (ESI,† p. 4).

As reported previously,\(^{1,3a}\) the \( ^{11}\text{B} \) NMR spectrum of the product consists of doublet, triplet and quartet resonances due to the \( \text{BH}, \text{BH}_2 \) and \( \text{BH}_3 \) groups (Fig. S4†). In previous samples the intensity of the \( \text{BH}_2 \) resonance was often seen to be greater than that of the other two, presumed to be due to differing amounts of the aminoborane cyclic trimer, \( \text{CTB} \) (1). After sublimation (80 °C, 2 × 10 \(^{-6}\) torr for 24 h), however, the desired product was contaminated mostly by a small amount of \( \text{AB} \). Although the \( ^{1}\text{H} \) NMR spectrum confirmed just a trace amount of CTB impurity, the \( \text{BH}_2 \) intensity in the \( ^{11}\text{B} \) NMR spectrum was still approximately twice that of the other two resonances (Fig. S4†). Turning to single crystal X-ray crystallography, crystals from the sublimed product were grown via two different methods and obtained as a glyme solvate and a crown ether adduct.\(^{19}\) Both structures showed the intermediate to be the branched, cyclic aminoborane \( \text{tetramer}, \ \text{B}-(\text{cyclotriborazanyl})\text{-amine-borane} \) (3, BCTB). (Fig. 2 and S7†). As expected, the bond distances and angles within the 6-membered ring (\( \text{B}3-\text{N}3 = 1.572(2) \) Å, \( \text{B}3-\text{N}3-\text{B}2 = 116.8(1) ^{\circ} \) and \( \text{N}1-\text{B}3-\text{N}3 = 107.1(1) ^{\circ} \)) are similar to those in \( \text{CTB} \) (\( \text{B-N}_{\text{avg}} = 1.574(2) \) Å, \( \text{B-N-B}_{\text{avg}} = 115.6(1) ^{\circ} \)). In previous samples the \( \text{BH}_2 \) intensity seen to be greater than that of the other two resonances (Fig. S4†). Turning to single crystal X-ray crystallography, crystals from the sublimed product were grown via two different methods and obtained as a glyme solvate and a crown ether adduct.\(^{19}\) Both structures showed the intermediate to be the branched, cyclic aminoborane \( \text{tetramer}, \ \text{B}-(\text{cyclotriborazanyl})\text{-amine-borane} \) (3, BCTB). (Fig. 2 and S7†). As expected, the bond distances and angles within the 6-membered ring (\( \text{B}3-\text{N}3 = 1.572(2) \) Å, \( \text{B}3-\text{N}3-\text{B}2 = 116.8(1) ^{\circ} \) and \( \text{N}1-\text{B}3-\text{N}3 = 107.1(1) ^{\circ} \)) are similar to those in \( \text{CTB} \) (\( \text{B-N}_{\text{avg}} = 1.574(2) \) Å, \( \text{B-N-B}_{\text{avg}} = 115.6(1) ^{\circ} \)). In previous samples the \( \text{BH}_2 \) intensity seen to be greater than that of the other two resonances (Fig. S4†).

Proton and nitrogen NMR spectra of BCTB, 3

A series of multinuclear NMR studies confirmed the structure of BCTB in solution. In the \( ^{11}\text{B} \) decoupled \( ^{1}\text{H} / ^{1}\text{H} \) COSY NMR spectrum at −15 °C (Fig. 3), the \( \text{BH} \) resonance at \( \delta 2.5 \) ppm is strongly correlated with the \( \text{NH} \) at \( \delta 3.0 \) (a in Fig. 3). A weaker correlation is observed with the other \( \text{NH} \) at \( \delta 3.2 \) (b in Fig. 3), thus confirming the chair configuration of the BCTB molecule at low temperature (i.e., strong axial–axial correlations).

Moreover, two resonances are observed for \( \text{BH}_2 \) groups at \( \delta 18\)
2.1 and 2.2 (in Fig. 3) with integrations close to 1 : 1 (Fig. S6†). These two peaks can be assigned to the axial and equatorial BH2 groups in BCTB. Thus at low temperature separate correlations are observed with axial and equatorial protons of NH2 groups in the ring. On the other hand, the exo-NH2 group (δ 2.7) shows a strong correlation with the BH3 group (δ 1.2) on the side chain (d in Fig. 3). The TOCSY NMR spectrum shows also that the in-ring NH2 resonances are all strongly correlated with each other (e in Fig. 4). As well, the BH2 and BH groups in the ring exhibit strong correlations with the NH2 protons (f in Fig. 4) whereas the BH correlates more weakly with the external NH2 compared with the internal NH2 groups (g in Fig. 4). Variable temperature 1H (14N) NMR spectra of BCTB in THF-d8 show also the sensitivity of the NH chemical shifts to temperature (Fig. S9†), likely due to changes in hydrogen bonding structural motifs. Compared to the literature data for ammonia-borane and CTB,14 we observed similar 15N NMR chemical shifts (Fig. S10†). However, overlapping signals at −362 ppm were assigned to the NH2-groups within the six-membered ring of BCTB (due to correlation with the NH2-protons with an integral of 6) (a in Fig. S10†) and the resonance at −367 ppm was assigned to the exo-cyclic NH2-group (b in Fig. S10†). Finally, the resonance at −377 ppm correlates with the NH3 resonance due to the ammonia-borane impurity in the sample (c in Fig. S10†).

**Reactivity of BCTB, 3**

Reactivity studies demonstrate that thermolysis of 3 yields different products than those derived from its catalytic dehydrogenation. While THF or glyme solutions of AB undergo slow dehydrogenation at 85 °C, thermolysis of CTB does not proceed readily below 125 °C.22 Thermal treatment of BCTB (100 °C, diglyme) led to a mixture of products. After 1 and 3 h CTB, borazine and AB were detected as the main products in a sealed NMR tube experiment (Fig. S11† Scheme 2A). After 20 h almost all BCTB was converted to borazine (as the main product) and CTB (Fig. S11†). Formation of the latter product suggests a 1,3-hydride transfer from the BH3 to the BH group of BCTB, affording CTB and aminoborane, NH2BH2. Indeed, when cyclohexene was used to trap the latter, a clean reaction ensued with predominance formation of CTB and NH2BCy2 (Fig. S12†). In contrast, heating BCTB at 60 °C in the presence of 7.5 mol% [Rh(μ-Cl)(cod)]2 (5, cod = 1,5-cyclooctadiene) afforded exclusively borazine and polyborazylene (Fig. S18†).

In order to probe the second dehydrogenation step of ABA dehydrocoupling in more detail, we investigated a series of metal complexes as precatalysts for the dehydrogenation of BCTB. The complexes [RuCl₂(P^N)₂] (6, P^N: 2-{di-tert-butylphosphino}-ethylamine),24 Ni(IMes)₂ (7, IMes: N,N′-bis{2,4,6-trimethylphenyl}imidazol-2-ylidene),25,26 and [Ru[μ-PMe₃]₂(BH₄)] (8)24,25 have been applied previously as dehydrogenation catalysts for AB. The iron hydride complex [FeH(PPh₃)₅(BH₄)] (9, PPh₃: tris[2-(diphenylphosphino)ethyl]-phosphine)27 has been successfully employed for the catalytic dehydrogenation of formic acid.22 In a typical experiment 20 mg BCTB was heated in THF (60 °C) in the presence of 15 mol% catalyst (with respect to BCTB). The reaction progress was monitored using 11B NMR spectroscopy with samples taken after 1, 3 and 16 h. Based on their reactivity, the catalysts can be divided into three groups (Scheme 2 B-D). Complexes 4 and 8 had little effect and the NMR spectra after 16 h were similar to those obtained from the control experiment (Fig. S13–15†). Complexes 7 and 9, however, converted BCTB to a mixture of CTB, borazine and polyborazylene (Fig. S16 and S17†). The inability of complex 7 to dehydrogenate CTB to borazine was confirmed using isolated CTB (no reaction after 24 h at 60 °C). Most interestingly, a third group of catalysts, complexes 5 and 6, effected the dehydrogenation of both BCTB and CTB after the 16 h reaction time (Fig. S18 and S19†).
Discussion

Synthesis and formation of BCTB, 3

Our new synthesis of BCTB takes advantage of the sluggish reactivity of d⁰ complexes with AB\textsubscript{2} and particularly the inability of C\textsubscript{p}ZrHCl to catalyse the dehydrogenation of BCTB to borazine, as shown above. We propose that the AB dehydrogenation proceeds through the amidoborane complex C\textsubscript{p}ZrCl(NH\textsubscript{2}BH\textsubscript{3}), \textnumero 10, characterized previously by Roesler et al.\textsuperscript{b} \textbeta-elimination of the B–H bond then affords the aminoborane monomer, regenerating the catalyst. In the presence of cyclohexene, all the aminoborane was trapped by cyclohexene and no BCTB formation was observed (Fig. S20†). While we did not observe \textnumero 10 in the \textsuperscript{11}B NMR spectra of these reactions, resonances were observed at −15.8 (quintet, \textit{J}_{B–H} = 86 Hz) (minor) and −7.1 ppm (quintet, \textit{J}_{B–H} = 87 Hz) due to C\textsubscript{p}Zr(BH\textsubscript{4})\textsubscript{2}, 11, and C\textsubscript{p}ZrCl(BH\textsubscript{4}), 12, respectively (Fig. S3†). As these complexes are likely resting states of the Zr hydride catalysts, we also investigated the reaction of complex 11 with 20 equiv. of AB. Poor BCTB selectivity was observed and borazine was detected as the major product (Fig. S21†).

In light of the variety of diverse mechanisms that have been postulated for the thermolytic and catalyzed dehydrogenation of AB, what is the origin of the extremely clean formation of BCTB with selected metal complex catalysts? Substituted primary aminoboranes such as methylaminoborane, NMeH\textsubscript{2}BH\textsubscript{3}, are postulated to oligomerize in solution to the cyclic trimer and, with further heating, to N\textsubscript{x}N\textsubscript{\textgamma}N\textsubscript{\textdelta}-trimethylborazine.\textsuperscript{29} Although the detailed mechanisms of these transformations require additional elucidation, formation of branched oligomers has been confned to reactions of the parent amine-borane, AB. In previous computational studies we\textsuperscript{1} and others\textsuperscript{2} showed that this selective oligomerization could proceed via B–H–B bridged intermediates followed by intramolecular attack of NH\textsubscript{2} on the three-coordinate boron (Scheme 3). The dimerization thus affords unusual (not yet observed) intermediate I with BH and BH\textsubscript{3} groups. Addition of the third aminoborane monomer to I through a similar mechanism then generates intermediate II which was proposed to undergo an additional intramolecular attack of NH\textsubscript{2} on three-coordinate boron to give BCDB, 2 selectively. In this work we find instead that intermolecular reaction of II with a fourth equivalent of aminoborane selectively affords the branched cyclic aminoborane tetramer, BCTB, 3.

On the basis of \textsuperscript{11}B and \textsuperscript{15}N NMR spectroscopy, thermolysis of AB in glyme solvent at 80 °C was proposed to generate both cyclodiborazane and cyclotriborazane in addition to a branched

Scheme 2 Reactivity of BCTB in the presence of complexes 4 to 9 (20 mg BCTB, 15 mol% catalyst, 2.5 mL THF, 60 °C, 16 h).

Scheme 3 Oligomerization of aminoborane through B–H–B bridged intermediates.
aminoborane cyclic oligomer, assigned as BCDB. This product distribution results presumably from the slow thermal generation of the aminoborane monomer, likely catalysed by traces of free BH₃. In the metal-catalysed reaction, however, rapid generation of aminoborane favors selective generation of BCTB, as long as the monomer does not take part in the metal coordination oligomerization pathway to linear polyaminoborane. Further work is thus needed to fully characterize the branched aminoborane cyclic oligomer derived from uncatalysed AB thermolysis.

**Thermal vs. catalysed conversion of BCTB, 3**

The branched aminoborane tetramer, BCTB, 3, is considerably more reactive than the cyclic trimer, CTB, 1, which is believed to undergo competing ring-opening and dehydrogenation pathways. The formation of some borazine and ammonia-borane from the thermolysis of 3 can be attributed to hydrogen transfer processes (eqn (1)) as studied recently by Manners and co-workers. Consistent with this proposal, neither AB nor borazine was observed on thermolysis of 3 in the presence of cyclohexene which effectively traps the aminoborane monomer.

![Thermal vs. catalysed conversion of BCTB, 3](image)

The catalysed reactions of 3 shed additional light on the second H₂ release step from AB. The fact that Ru catalyst precursor 8 is unable to dehydrogenate 3 is consistent with previous studies that showed the sensitivity of 8 to the reaction solvent. While poor selectivity for AB dehydrogenation was observed in THF, formation of insoluble polyaminoborane could be prevented using ionic liquids with nucleophilic anions. Similar observations were made using the Ni(NHC)₃ catalyst that required a mixed benzene–glyme solvent system to release >2 equiv. of H₂. In spite of the short lifetime of this catalyst, the small amount of CTB remaining in Fig. 1(d) supports the greater reactivity seen for 3 vs. CTB using the similar catalyst 7. In contrast, the [RuCl₃(P₃N)₃]KOBu catalyst system 6 that was reported to afford a single equivalent of hydrogen from AB readily converted both CTB and 3 to borazine and polyborazylene. This would thus be a good candidate for further solvent studies to avoid the aminoborane coordination polymerization pathway from AB. Finally, the Rh colloids or clusters derived from the chlororhodium diene catalyst precursor 5 are also effective catalysts for conversion of 3 to borazine and polyborazylene although catalyst lifetime experiments have yet to be performed.

**Conclusions**

Utilization of the Cp₂ZrHCl catalyst precursor has allowed for the isolation and characterization of the key intermediate in the second step of metal-catalysed AB dehydrogenation. In contrast to previous assignments, the intermediate has now been identified as the BN ethylenecyclohexane analog, the branched, cyclic aminoborane tetramer, B-(cyclotriorobazanyl)amine-borane (3). Reactivity studies show that higher yields of 3 would likely be obtained if reaction of the aminoborane monomer with CTB to give borazine and AB (eqn (1)) could be controlled. Testing of several catalysts commonly used for dehydrocoupling reactions for this second dehydrogenation step revealed an important difference in selectivity as some catalysts converted 3, but not CTB, into borazine and polyborazylene. With this information in hand we are now poised to address the challenging third step of AB dehydrogenation – identifying an effective catalyst for the BN cross-linking of borazine to polyborazylene.

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**Notes and references**


33 Note that the BN analogs of cyclohexene and cyclohexadiene have never been observed and may be unstable with respect to formation of borazine and CTB through intermolecular hydrogen transfer reactions.
