Coordination of aminoborane, NH_2BH_2, dictates selectivity and extent of H_2 release in metal-catalysed ammonia borane dehydrogenation†

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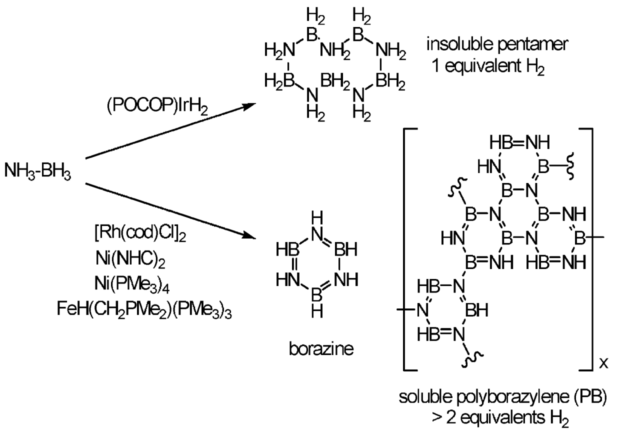
In situ **^{11}B NMR monitoring, computational modeling, and external trapping studies show that selectivity and extent of H_2 release in metal-catalysed dehydrogenation of ammonia borane, NH_3BH_3, are determined by coordination of reactive aminoborane, NH_2BH_2, to the metal center.**

Over the last few years, the scientific community has expressed an increasing interest in ammonia borane (NH_3BH_3, AB, **1**) due to its remarkable hydrogen storage potential (19.6 wt% H).[1] While AB dehydrogenation in the solid state[2] and in solution[3] has been studied previously in some detail, new reports have shown that metal-complex-catalysed reactions allow greater extent of hydrogen release at lower temperatures.[4–9] The observation of different products and rates obtained for various catalysts prompted us to investigate the mechanism(s) involved in determining the selectivity in AB dehydrogenation (Scheme 1).

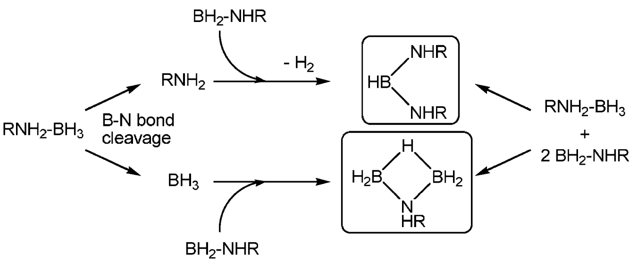
Manners and others have shown that metal-catalysed dehydrogenation of alkylamineboranes RR′NHBH$_3$ affords dialkylaminoborane RR′NBH$_2$ (R, R′ = ^{i}Pr, Cy)[4,10–12] that in some cases undergoes oligomerisation to cyclic dimers (R, R′ = Me) or trimers (R = H; R′ = Me). For primary amineboranes and parent AB, further dehydrogenation yields borazines and even B–N linked borazine (polyborazylene, PB). We have reinvestigated this chemistry at different temperatures in several solvents using *in situ* ^{11}B NMR monitoring.§ Dehydrogenation of more sterically demanding primary amineboranes, RNH$_2$BH$_3$ (R = ^{t}Bu, Cy), using $[Rh(cod)Cl]_2$ as precatalyst reveals, in addition to oligomeric cyclic aminoboranes, (RNH–BH$_2$)$_n$ (n = 1–3), formation of both diaminoborane, HB(NRH)$_2$ (25 ppm), and aminodiborane, B$_2$H$_5$(NHR) (−18 ppm) (Fig. S1 and S2, ESI†). Analogous products were also observed for secondary amineboranes (R = Me, R′ = ^{n}Bu).[13] These products result presumably from metal-mediated B–N bond cleavage (Scheme 2).



Scheme 1 Selectivity in metal catalysed AB dehydrogenation. (POCOP = 2,6-(^{t}Bu$_2$POCH$_2$)C$_6$H$_3$, NHC = *N*-heterocyclic carbene, cod = 1,5-cyclooctadiene).

In contrast, while aminodiborane, B$_2$H$_5$(NH$_2$),[14] has been observed as a minor by-product of metal-catalysed AB dehydrogenations,[15] discussion of product selectivity has focused on formation of borazine, PB, and the cyclic pentamer, (BH$_2$NH$_2$)$_5$ (Scheme 1). If AB dehydrogenation follows similar pathways as those observed for alkylamineboranes, is monomeric aminoborane, NH_2BH_2, formed? While direct observation is unlikely (preparation in low-temperature matrices showed oligomerisation even below −155 °C),[16] we now employ *in situ* monitoring to provide indirect evidence for its formation.

Monitoring AB dehydrogenation by ^{11}B NMR spectroscopy at 25 °C using 10 mol% Ni(NHC)$_2$ reveals three prominent resonances at −5.3 (doublet, $J_{B\text{–}H}$ = 114 Hz), −11.3 (triplet, $J_{B\text{–}H}$ = 104 Hz) and −24 ppm (quartet, $J_{B\text{–}H}$ = 93 Hz) (Fig. 1). Further reaction at 60 °C in the NMR probe showed simultaneous decay of these signals and



Scheme 2 Alkylamineborane B–N bond cleavage products.

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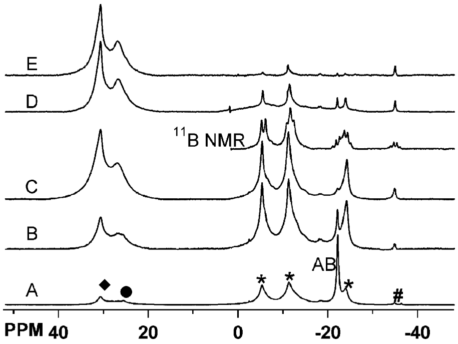
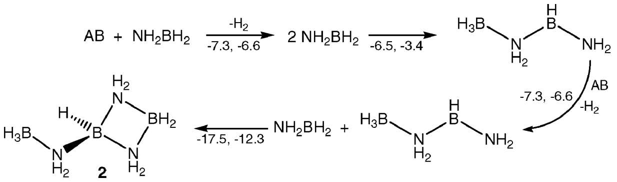


Fig. 1 Evolution of the $^{11}B\{^1H\}$ NMR spectra of AB dehydrogenation (400 MHz, diglyme, 5 mol% $Ni(NHC)_2$) ● PB; ◆ borazine; * **2**; # NHC–BH_3. Spectrum A was recorded after 12 h reaction time at 25 °C, B after 10 min equilibration in the NMR probe at 60 °C, and C–E at 60 °C after additional intervals of 20, 40 and 120 min.



Scheme 3 Trapping of NH_2BH_2 by AB. G3MP2, B3LYP/DZVP2 gas phase enthalpies at 298 K. The highly accurate CCSD(T)/CBS (complete basis set) result for the first step is -5.1 kcal mol^{-1}.[20]

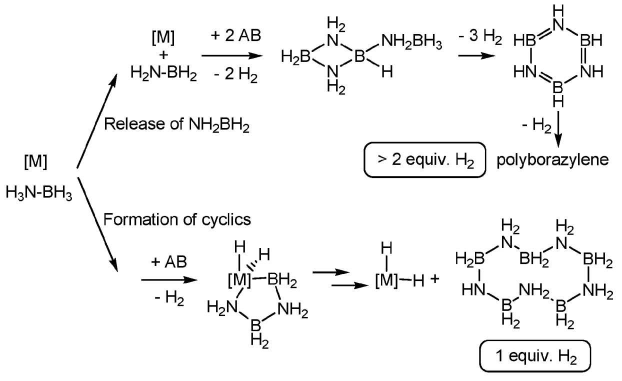
formation of borazine and PB (28–35 ppm). After completion of the reaction, two weak signals remain at -11 and -35 ppm. They are assigned respectively to a small amount of aminoborane oligomer and NHC–BH_3.

Using $\{^1H–^{11}B\}$ HETCOR NMR spectroscopy, we were able to assign the three types of BH resonances to intermediate **2** shown in Scheme 3.[17] The IR spectrum shows broad NH (3263 cm^{-1}) and BH stretches at 2361 and 2371 cm^{-1}. Given the highly reactive nature of aminoborane, this intermediate **2**, B-(cyclodiborazanyl)aminoborohydride, may be formed by trapping reactions with AB (Scheme 3).[18]

Calculations at the B3LYP/DZVP2 level were performed to map out possible reaction pathways. In complementary results to those found previously for BH_3 and AB,[19] NH_2BH_2 can either weakly catalyse the unimolecular loss of H_2 from AB or the BH_2 of NH_2BH_2 interacts with AB in a complex transition state leading to H_2 loss (Fig. S6A, ESI†). In both cases, two NH_2BH_2 molecules are formed and the chain structure $BH_3NH_2BHNH_2$ can only be formed by an unfavorable high-energy pathway (there is a slightly higher energy structure where the BH_3 forms a bridging H to the BH group, Fig. S6B, ESI†).[20] The $BH_3NH_2BHNH_2$ chain can be generated in a slightly exothermic reaction by the dimerisation of the two weakly interacting NH_2BH_2 molecules with a low barrier of 10.5 kcal mol^{-1}. We found no evidence for formation of the other chain isomer $NH_3BH_2NHBH_2$ in the dimerisation process even though it is only 2.3 kcal mol^{-1}higher in energy at the G3MP2 level.[21] The $BH_3NH_2BHNH_2$ chain can then catalyse H_2 loss from AB leading to formation of NH_2BH_2 which subsequently adds to the $BH_3NH_2BHNH_2$ chain to form an NH_2BH_2 trimer (with a BHB terminal bond) with a low barrier of 5.0 kcal mol^{-1} (Fig. S6C and D, ESI†). Finally, this trimer chain can rearrange in an exothermic process with a small barrier (<6 kcal mol^{-1}) to form the ring compound $B_2N_2H_7NH_2BH_3$ (NH_2BH_3 side chain bonded to B) as observed. The other ring compound, $B_2N_2H_7BH_2NH_3$, which is higher in energy (G3MP2 calculations: $\Delta\Delta H_{298}$ = 2.3 kcal mol^{-1}, $\Delta\Delta G_{298}$ = 2.7 kcal mol^{-1}) was never formed in any of our simulations. The H_2 elimination barriers that have been found so far for the isolated molecules are comparable to the B–N bond energy in BH_3NH_3 suggesting a potential role for solvent or coordination to the catalyst.[19] These results are consistent with the DFT B3LYP/6-311+G(2d,p) calculations of Nutt and McKee.[22] Further work is in progress to understand the detailed thermochemistry and reaction pathways of **2** as well as more details on its generation.[3b] Preliminary results show no change after heating diglyme solutions of **2** for 24 hours at 70 °C, whereas addition of rhodium catalyst to these solutions yields PB and borazine even at 25 °C.

To further support our mechanistic proposal involving formation of reactive NH_2BH_2 in metal-catalysed AB dehydrogenation, we performed external trapping reactions with cyclohexene. Using $[Rh(cod)Cl]_2$ as precatalyst and a large excess of cyclohexene in diglyme solvent at 25 °C, the expected resonances for borazine and PB were not observed. Instead, a broad signal observed at 48 ppm is assigned to Cy_2BNH_2[23] arising from cyclohexene hydroboration using both BH bonds of aminoborane. Remarkably, use of $Ir(POCOP)H_2$ under the same reaction conditions *still* afforded $(BH_2NH_2)_5$ as *the sole product*. However, at 60 °C, a mixture of Cy_2BNH_2 and insoluble pentamer was observed. In keeping with our proposal, the same Ir-catalysed reaction in the absence of cyclohexene at 60 °C now forms a significant amount of borazine along with $(BH_2NH_2)_5$. Finally, in the presence of 20 equivalents of cyclohexene–AB and 10 mol% $Ni(NHC)_2$, NH_2BH_2 is not trapped at 25 °C, PB and borazine are still observed after the reaction goes to completion (Table S1, ESI†). Based on the trapping results using rhodium and iridium catalysts, we can propose that formation of cyclic $(BH_2NH_2)_n$ species results from strong coordination of aminoborane to the iridium center; partial dissociation at 60 °C results in some trapping (Scheme 4).[24] Details of the proposed metal-mediated dehydrocyclisation are currently under investigation.

While AB dehydrogenation has appeared at first glance to be more complex than that of alkylamineboranes, we have



Scheme 4 Metal-catalysed AB dehydrogenation mechanism.

now shown that the diversity of dehydrogenation products from AB can be attributed to the high reactivity of aminoborane. Further catalyst development in our laboratories focuses on efficient and exclusive release of aminoborane, rapid conversion of intermediate **2** to borazine and subsequent cross-linking to polyborazylene.[25]

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Notes and references

§ Caution should be exercised in managing pressure build-up in these reactions. They were typically conducted in evacuated J-Young NMR tubes, in regular NMR tubes with minimally perforated rubber septa, or in sealed polyether ether ketone cells designed for pressure work.

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17 Crude samples of **2** were obtained from Ni-catalyzed AB dehydrogenation reactions after filtration, solvent removal and washing with toluene to remove PB. DFT GIAO calculations of the ^{11}B NMR chemical shifts of **2** performed by R. Butterick, III and L. G. Sneddon show BH, BH_2 and BH_3 signals at −4.4, −11.2, −23.8 ppm, respectively.

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24 While AB reacts with cyclohexene at 60 °C (but not at 25 °C), this side reaction is slow enough to be neglected in the metal-catalysed trapping of NH_2BH_2 and formation of Cy_2BNH_2.

25 Efficient catalysis of cross-linking will prevent build-up of volatile borazine that could contaminate the H_2 stream and poison the fuel cell catalyst.