Multiple metal-bound oligomers from Ir-catalysed dehydropolymerisation of H$_3$B·NH$_3$ as probed by experiment and computation†

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Multiple metal-bound oligomers in the dehydropolymerisation of H$_3$B·NH$_3$ have been observed by electrospray-ionisation mass spectrometry and NMR spectroscopy using the catalytic metal fragment (Ir(PCy$_3$)$_2$(H)$_2$)$^+$. A computational study suggests that stericity may control which metal-bound oligomers are formed. In contrast to H$_3$B-NNMe$_2$H, higher oligomeric products are observed with H$_3$B-NNMe$_3$H. Direct mechanistic insight into the dehydropolymerisation process has been obtained from computational studies. These results suggest that the selectivity for the formation of a given metal-bound oligomer is dependent on both steric factors and the metal/ligand combination.

Introduction

The dehydropolymerisation of amine-boranes H$_3$B·NRH$_2$ (R = H, Me) is a promising methodology for the synthesis of new B-N materials, for example, polymeric materials that are isoelectronic with the inherently polyolefinic C-C bond. 1-2 Catalysis of these processes by a transition metal fragment offers potential for control of kinetics and final product distributions, and various systems have been shown to promote dehydropolymerisation. 3-12 Non-metal catalysed processes have also been discussed. 13,14

The mechanism of catalytic dehydropolymerisation of H$_3$B·NH$_3$ or H$_3$B·NNMeH$_2$ has been suggested to be based upon dehydrogenation followed by a metal-mediated coordination polymerisation step. 5,8,10,12,15,16 In particular, there is growing evidence to suggest that transient amino-boranes (e.g. H$_3$B·NH$_2$ or H$_3$B·NNMeH), that arise from dehydrogenation of the precursor amino-borane, remains associated with the metal. 17 If liberated these unsaturated fragments form the corresponding borazine by oligomerisation (Scheme 1), or can be trapped by hydroboration of exogenous cyclohexene – assuming such reactions are faster than polymerisation (i.e. B-N bond formation leading to a growing polymer chain). In addition bulky primary amine-boranes, H$_3$B·N’Bu$_2$H$_2$, 18 or secondary amine-boranes, e.g. H$_3$B·NMe$_2$H, 19,20 give simple amino-borane products rather than extensive oligomerisation. Adding to the complexity, different metal/ligand combinations likely lead to subtly different mechanisms. 8,10,12

Direct mechanistic insight into the dehydropolymerisation process through the observation of intermediates has been sparse. Recently we reported the isolation of the product of the first oligomerisation event in such a process by reaction of [Ir(PCy$_3$)$_2$(H)$_2$][BArF$_4$], 1, with 2 equivalents of H$_3$B·NNMeH$_2$ to form [Ir(PCy$_3$)$_2$(H)$_2$](η$^3$-H$_3$B·NNMe$^*$H$_2$·NNMe$_2$H)][BArF$_4$], 5b, (Scheme 2). 21 This reaction is slow and does not produce higher oligomers, and a tentative mechanism was suggested to account for this selectivity. With bulkier H$_3$B·NNMe$_2$H only dehydrogenation to form the bound amino-borane (i.e. 4a*) is observed. 19

We now report that with H$_3$B·NH$_2$, H$_3$B·NNMeH$_2$, and that, in contrast to H$_3$B·NNMe$_2$H, higher oligomeric products bound to the metal centre (6a-e; Scheme 2) can be observed by electrospray ionisation mass spectrometry (ESI-MS) and NMR spectroscopy. ESI-MS provides the ideal analytical platform to study these processes as it allows for the convenient analysis of mixtures of products under inert conditions. 22,23 Computational studies 19,24-27 offer a mechanistic rationale for oligomerisation that explains both the difference in the degree of oligomerisation with increasing steric bulk between the amine-boranes H$_3$B·NNMe$_3$H, H$_3$B·NNMe$_2$H, and H$_3$B·NNMe$_2$H$_2$.

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1** Dehydrogenation and dehydropolymerisation of amine-boranes; full pathways not shown.

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and H$_3$B·NMe$_2$H and the previously noted requirement for additional amine-borane to promote this process.$^{21}$

**Results and discussion**

Addition of one equivalent of H$_3$B·NH$_3$ to 1$^{18}$ in C$_6$H$_5$F solvent results in the immediate formation of the sigma amine-borane complex [Ir(PC$_3$)$_3$(H)$_2$($n^2$−H$_3$B·NH$_3$)][BarF$_4^{-}$] 6a in quantitative yield by NMR spectroscopy. There is no onward dehydrogenation after 4 hours under these conditions, but addition of further H$_3$B·NH$_3$ (10 equivalents total) results in the formation of higher oligomers, [Ir(PC$_3$)$_3$(H)$_2$($n^2$−H$_3$B·NH$_3$)$_4$·NH$_3$)][BarF$_4^{-}$] $n = 1$−4. This requirement for additional amine-borane to promote dehydrogenation has been noted before in these systems, although its role has only been speculated upon.$^{21}$ Fig. 1 shows the ESI-MS spectra of the reaction of 1 with the amine-boranes H$_3$B·NMe$_2$H$_x$ (x = 0−3) demonstrating the increasing degrees of dehydrogenation and oligomerisation with decreasing steric bulk of the amine-borane. Under these conditions H$_3$B·NMe$_2$H undergoes dehydrogenation with no subsequent B−N coupling (4a$^+$),$^{19}$ while H$_3$B·NMeH$_2$ gives the product of one dehydrocoupling event (5b).$^{21}$ By contrast for H$_3$B·NH$_3$ metal-bound oligomers arising from up to four of these dehydrocoupling events are observed by ESI-MS (6b−e), which all show excellent fits with calculated isotopomer patterns, with 6d,e ($n = 4, 5$; Scheme 2) observed as [M−H$_2$]$^+$ cations. In the $^1$H($^{11}$B) NMR spectrum of this mixture three distinct pairs of Ir−···H−B and Ir−H environments are observed in an approximate 1 : 10 : 10 ratio (see ESI†), which are assigned to 6a, 6b and 6c respectively (vide infra), consistent with the major species observed by ESI-MS (6a−c). The $^{11}$B($^1$H) NMR spectrum of this mixture shows broad, potentially overlapping, signals in the Ir−···H−B and [BH$_2$] regions, and the $^{31}$P($^{1}$H) NMR spectrum shows two tightly-coupled AB doublets in approximately equal ratio, the third species (i.e. 6a) being too low in intensity to be observed. The identity of these complexes has been confirmed by the independent synthesis of 6b and 6c from the preformed borazanes H$_3$B·NH$_3$BH$_2$·NH$_3$, and H$_3$B·(NH$_3$BH$_2$)$_2$·NH$_3$ respectively. Scheme 3 shows the solid-state structure (as the [BarF$_4^{-}$]$^-$ salts$^{30}$ from [Ir(PC$_3$)$_3$(H)$_2$][BarF$_4^{-}$], 2) of 6c, alongside that of 6a, which confirm formation, being closely related to analogous complexes 3a, 4a, 5a and 5b.$^{21}$ Over time (24 h) these mixtures of products degrade to give bimetallic products identified by ESI-MS as [[Ir(PC$_3$)$_3$(H)$_2$][H$_2$B(NH$_3$BH$_2$)$_2$H]]$^+$ 7a−d ($n = 0$ to 3 respectively), presumably in which the anionic amino-boranes [H$_3$B(NH$_3$BH$_2$)$_2$H]$^{-}$ bridge between two cationic metal fragments. Recrystallisation of this mixture afforded small amounts of the borohydride complex$^{41}$ [[Ir(PC$_3$)$_3$(H)$_2$($n^2$−H$_3$B·NMeH)$_2$]][BarF$_4^{-}$] 7a (see ESI† for a solid-state structure). We were unable to definitely characterise the other byproducts of this decomposition.

Borazine was also observed during the oligomerisation of H$_3$B·NH$_3$ (<10%) by $^{11}$B NMR spectroscopy relative to [BarF$_4^{-}$]$^-$, which might suggest free amino-borane is formed as a transient intermediate during the reaction.$^{15,18}$ Addition of excess cyclohexene to the reaction did not result in the observation of any hydroboration product, Cy$_2$B·NH$_3$, a trapping reaction that...
has previously been suggested to be indicative of free amino-
borane in dehydrocoupling reactions.\textsuperscript{15} As recently noted,
however, this process relies on hydroboration being kinetically
competitive with oligomerisation, which might not necessarily
be the case.\textsuperscript{16}

Although these data are consistent with a growing oligo-
meric chain at the $\{\text{Ir(PCy}_3)_2(\text{H})_2\}^+$ fragment, similar to those
observed by ESI-MS for olefin polymerisation,\textsuperscript{32,33} these observations
cannot discount a scenario where metal-catalysed
dehydrogenation forms the free amino-borane, $\text{H}_2\text{B} = \text{NH}_3$,
which then polymerises off-metal,\textsuperscript{13} with the most soluble
short-chain oligomers then coordinating to the metal fragment.
However, as computation suggests (\textit{vide infra}) that the first
dehydrogenation has a significantly higher barrier than subsequent
oligomerisation we propose that this scenario is less
likely. To probe further the oligomerisation process, three
sequential additions of 1.1 equivalents of $\text{H}_2\text{B} = \text{NH}_3$ to 1 gave
progressively longer oligomer chains (\textit{i.e.} $6a$–$6c$) as measured by
ESI-MS (see ESI\textsuperscript{f}), although this mixture was biased towards $6a$
and $6b$, suggesting that the sigma-bound oligomeric units, \textit{e.g.}
$6b$ or $6c$, are only weakly bound with the metal centre and can
be displaced by excess $\text{H}_2\text{B} = \text{NH}_3$. Confirming this, addition of
two equivalents of $\text{H}_2\text{B} = \text{NH}_3$ to $6c$ immediately results in a
mixture of $6a$–c and free $\text{H}_2\text{B} = (\text{NH}_2\text{BH}_3)_2 = \text{NH}_3$, with $6c$
the major observed product. After 4 hours this has developed into a
mixture of $6a$–c with $6b$ and $6c$ the major products. Addition of 2
equals of $\text{H}_2\text{B} = (\text{NH}_2\text{BH}_3)_2 = \text{NH}_3$ to $6a$ results in the formation of
$6b$ and relatively smaller amounts of $6c$–$6e$ (by ESI-MS), the latter
presumably derived from further dehydrocoupling events
from $6b$ with $\text{H}_2\text{B} = \text{NH}_3$ (Scheme 4). Overall this suggests a
mechanism in which the formed sigma-bound oligomer can be
displaced by other amine-boranes, \textit{i.e.} reversible chain transfer
can occur. At the end of the reaction (24 h) a white solid is
recovered that shows an IR spectrum essentially identical to
polyaminoborane.\textsuperscript{34} Use of 5 equivalents each of $\text{H}_2\text{B} = \text{NH}_3$ and
$\text{H}_2\text{B} = \text{NMMe}_2\text{H}$ gave a mixture of metal-bound co-oligomers
$[\text{Ir(PCy}_3)_2(\text{H})_2(\text{H}(\text{H}_2\text{BNNH}_2)\text{H})_2(\text{H}_2\text{B} = \text{NMMe}_2\text{H})_2)]^+ (x = 0, 1, y = 1, 2; x = 1, y = 0; x = 2, y = 1)$.

Density functional theory (DFT) calculations\textsuperscript{35} have been
used to study the mechanism of the dehydrocoupling of
$\text{H}_2\text{B} = \text{NH}_3$ at $6a$ with particular focus on (i) the requirement for
additional $\text{H}_2\text{B} = \text{NH}_3$ to induce dehydrogenation, (ii) the mecha-
nism of the $\text{B} = \text{N}$ coupling step and (iii) the varying affinities of
the different amine-boranes toward oligomerisation. These
calculations employed PMe$_3$ ligands, with $[\text{Ir(PMe}_3)_2(\text{H})_2(\eta^1$–$
\text{H}_2\text{B} = \text{NMMe}_2\text{H}_3, x)]^+$ (denoted $6a'$, $x = 0$, $6a''$, $x = 1$ and $4a''$, $x = 2$)
the model initial reactants, and use a BP86-D3(C$_6$H$_5$F) protocol.

We report free energies derived from gas-phase BP86-optimi-
sations, corrected for dispersion and solvation effects. Each key
step in the dehydrocoupling process (B–H/N–H bond activation
and B–N bond coupling) presented more than one possible
transition state and the most accessible of these are presented
here, with alternative structures given in the ESI.\textsuperscript{f}

We have previously modelled the dehydrogenation of
$\text{H}_2\text{B} = \text{NMMe}_2\text{H}$ in $[\text{Ir(PMe}_3)_2(\text{H})_2(\eta^1$–$\text{H}_2\text{B} = \text{NMMe}_2\text{H})]^+$ ($4a''$) to form
the corresponding amino-borane adduct (\textit{i.e.} $4a''$*, a model of
$4a''$ in Scheme 2) and defined a mechanism based on sequential
B–H activation, H loss and rate-limiting N–H activation.\textsuperscript{36}

Applying this mechanism to $\text{H}_2\text{B} = \text{NH}_3$ dehydrogenation in $6a$
reveals a barrier of 33.8 kcal mol$^{-1}$ in which the N–H activation
step is again rate-limiting (see Fig. S1–3, ESI\textsuperscript{f}). With an added
$\text{H}_2\text{B} = \text{NH}_3$ molecule a related mechanism can be characterised
but with a significantly reduced barrier of 26.7 kcal mol$^{-1}$
(Fig. 2). In this process the second $\text{H}_2\text{B} = \text{NH}_3$ molecule first adds to
$6a'$ to give $[\text{Ir(PMe}_3)_2(\text{H})_2(\eta^1$–$\text{H}_2\text{B} = \text{NH}_3)]^+$, $16a'$, with a binding energy of 5.0 kcal mol$^{-1}$. This stabilisation is in part
due to a BH($\delta^-$–H($\delta^+$)$\text{N}$ dihydrogen interaction between the
two $\text{H}_2\text{B} = \text{NH}_3$ ligands.\textsuperscript{36,37} B–H activation in $16a'$, entails a

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Computed free energy reaction profile (kcal mol$^{-1}$, BP86-
D3(C$_6$H$_5$F)) for dehydrogenation of $\text{H}_2\text{B} = \text{NH}_3$ in $6a'$ in the presence of
added $\text{H}_2\text{B} = \text{NH}_3$.}
\end{figure}
barrier of 16.6 kcal mol\(^{-1}\) via TS\(_{6a,HN1}\) and proceeds with concomitant reductive coupling of the two hydride ligands to give \([\text{Ir}(\text{PMe}_3)_2(\text{BH}_2\text{NH}_3)](\text{H}(\text{H})(\eta^2-\text{H}_2\text{BH}-\text{NH}_3))\), 16a’\(_2\) (\(G = +15.9\) kcal mol\(^{-1}\)). \(\text{H}_2\) loss then leads to 16a’\(_3\) (\(G = +10.7\) kcal mol\(^{-1}\)) from which rate-limiting N–H activation occurs via TS\(_{6a,HN1}\) (\(G = +26.7\) kcal mol\(^{-1}\)) to give 16a’\(_4\) in which both an amine- and an amino-borane are bound to the metal centre.

The computed geometry of TS\(_{6a,HN1}\) is shown in Fig. 3a and shows transfer of H\(^4\) from the BH\(_2\)NH\(_3\) ligand to Ir (\(\text{N}^1-\text{H}^4 = 1.42\) Å; \(\text{Ir}^-\text{H}^4 = 1.74\) Å) while a dihydrogen bonding interaction is maintained with the spectator H\(_2\)BH-NH\(_3\) ligand (H\(^{24}\)-\(\text{H}^1\) = 1.80 Å). This feature stabilises both TS\(_{6a,HN1}\) and its precursor 16a’\(_3\) and so contributes to a reduction in the overall barrier to dehydrogenation of 7.1 kcal mol\(^{-1}\) compared to the reaction direct from 6a’ without added amine-borane. An alternative transition state, TS\(_{6a,HN1}\) (Alt 1), in which the second H\(_2\)B-NH\(_3\) ligand adopts an \(\eta^2\)-(B,H) bonding mode (similar to the amino-borane ligand in TS\(_{6a,H2}\); see Fig. 3b and below) is comparable in energy (\(G = +26.9\) kcal mol\(^{-1}\), see Fig. S6(b)‡). Both forms of TS\(_{6a,HN1}\) are consistent with dehydrogenation being facilitated by the addition of amine-borane to 6a’.

For the subsequent B–N coupling step a total seven different pathways have been characterised. Four of these stem from intermediate 16a’\(_4\) and entail B–H activation in the H\(_2\)B-NH\(_3\) ligand to produce a Lewis acidic \([\text{H}_2\text{BNH}_3]\) moiety that then couples with H\(_2\)B\(\equiv\text{NH}_2\). In most cases these processes occur in one step. Two further pathways have been characterised for the direct reaction of free H\(_2\)B\(\equiv\text{NH}_2\) with either 6a’ or its B–H activated form. All of these pathways, however, have computed barriers in excess of 28 kcal mol\(^{-1}\), and as this is higher than the barrier to dehydrogenation these pathways would be inconsistent with the lack of any bound amino-borane intermediates being observed experimentally. Full details of these alternative pathways are given in the ESI (see Fig. S12†).

A significantly more accessible B–N coupling route was characterised that involved the direct reaction of two H\(_2\)B\(\equiv\text{NH}_2\) units. This process therefore requires the prior dehydrogenation of a second H\(_2\)B\(\equiv\text{NH}_3\) molecule and a pathway for this, analogous to that shown in Fig. 2, has been defined starting from 16a’\(_4\) and forming \([\text{Ir}(\text{PMe}_3)_2(\text{H})(\eta^2-\text{H}_2\text{BH}=\text{NH}_3))\] (16a’\(_2\)) and free H\(_2\)B\(\equiv\text{NH}_2\) (see also Fig. S7–9†). 16a’\(_2\) is closely related to that calculated for the product of dehydrogenation of H\(_2\)B\(\equiv\text{NH}_3\) by the same fragment.\(^{19}\) The key N–H activation transition state in this process, TS\(_{6a,HN12}\) (Fig. 3b), has a free energy of +24.2 kcal mol\(^{-1}\) and features a spectator \(\eta^2\)-(B,H)-H\(_2\)B\(\equiv\text{NH}_3\) ligand\(^{20}\) that stabilises the metal centre. Oligomerisation then proceeds through the reaction of 16a’\(_2\) with H\(_2\)B\(\equiv\text{NH}_2\) and the associated reaction profile (Fig. 4) shows B–N coupling via TS\(_{6a,HN2}\) at only +17.9 kcal mol\(^{-1}\). The structure of this transition state (Fig. 5) shows that the Ir-bound amino-borane has rearranged to an \(\eta^2\)-(B,H) mode that exposes the pendant \(\text{NH}_2\) moiety to attack by the second, incoming amino-borane (N\(^1\)-B\(^2\) = 2.37 Å). As this occurs a hydride transfers from Ir onto N\(^2\) (Ir^-H\(^2\) = 1.63 Å; H\(^{24}\)-N\(^2\) = 1.64 Å) to generate an \(\eta^2\)-(B,H)-H\(_2\)B\(\equiv\text{NH}_2\)-BH\(_2\text{NH}_3\) ligand in the resultant intermediate 16a’\(_6\) (\(G = +1.6\) kcal mol\(^{-1}\)).\(^{21}\) Addition of H\(_2\) (16a’\(_6\), \(G = +7.3\) kcal mol\(^{-1}\)) and facile B–H reductive coupling gives the final model product, \([\text{Ir}(\text{PMe}_3)_2(\text{H})(\eta^2-\text{H}_2\text{BH}=\text{NH}_2\text{BH}_2\text{NH}_3)]\), 6b’ (\(G = -10.9\) kcal mol\(^{-1}\)).\(^{22}\) This coupling process is similar to that suggested by
Schneider and co-workers in bifunctional Ru(H)2(PMe3)(PNP) catalysis [PNP = HN(CH2CH2P3Bu)2], in which an N–H activated H3B·NH3 group undergoes B–N coupling with H2B=NH2 during dehydropolymerisation.10

Reaction profiles analogous to those in Fig. 2 and 4 were also computed for the dehydrocoupling of H3B·NMe2H at 5a′ and H3B·NMe2H at 4a′. Similar dehydrogenation barriers are found in each case (5a′/H3B·NMe2H: 25.2 kcal mol–1; 4a′/H3B·NMe2H: 26.2 kcal mol–1) and in the absence of a second amine-borane molecule these barriers increase to above 33 kcal mol–1, reiterating the promotional effect of added amine-borane on this process. In contrast the B–N coupling transition states are more substrate-dependent and increase significantly in energy with the size of the amine-borane (6a′/H3B·NMe2H: 17.9 kcal mol–1; 5a′/H3B·NMe2H: 19.9 kcal mol–1; 4a′/H3B·NMe2H: 26.5 kcal mol–1). This trend is consistent with oligomerisation being accessible for both H3B·NH3 and H3B·NMe2H, but this step becoming significantly more difficult for the larger H3B·NMe2H. Indeed oligomerisation is not seen experimentally for 4a′/H3B·NMe2H under the conditions used here.41

An analogous mechanism based on dehydrocoupling of H3B·NH3 and H3B·NH2BH2·NH3 can account for the formation of the H3B·(NH2BH2)2·NH3 trimer seen in 6c (modelled by 6c′). The key energetics are similar to those computed in the pathway for the formation of 6b′: dehydrogenation of H3B·NH3 (in the presence of H3B·NH2BH2·NH3) has an overall barrier of 26.3 kcal mol–1, then dehydrogenation of H3B·NH2BH2·NH3 (now in the presence of H2N=BNH2) has a barrier of 24.3 kcal mol–1. The order of dehydrogenation is important, however, as the alternative initial dehydrogenation of H3B·NH2BH2·NH3 (in the presence of H3B·NH3) has a higher barrier of 28.1 kcal mol–1 (see Fig. S15†). The subsequent B–N coupling transition state is again more accessible than dehydrogenation, TS6b′_BNA (Fig. 6a) having a computed energy of 21.2 kcal mol–1. In this case there are two possible B–N coupling outcomes, depending on whether H2B=NH3 (as in TS6b′_BNA) or H2B=NH2BH2·NH3 (TS6b′_BNa, Fig. 6b) is bound to Ir in the transition state. The former case leads to a straight chain oligomer product, and is 2.3 kcal mol–1 more stable than the alternative that gives a branched chain product. The barrier for this second oligomerisation step is close to that for the B–N coupling of H2B·NMe2H (19.9 kcal mol–1), highlighting the similar behaviour of these two mono-substituted amine-boranes. This in turn suggests that subsequent chain growth with further H2B·NH3 may proceed via transition states related to TS6b′_BNa in which the growing oligomer chain extends away from the metal centre with minimal additional steric impact. By the same token, H2B·NMe2H trimerisation is more difficult with the equivalent transition state, TS5b′_BNA, equating to a higher barrier of +24.8 kcal mol–1 (Fig. 6c). This trend towards higher oligomerisation barriers as the size of the amine-borane increases is consistent with the experimental observations (i.e. 5a giving 5b alone whereas 6a can undergo multiple oligomerisation steps to give 6b–e).

A potential side reaction within this mechanistic picture involves the cyclisation of two aminoborane fragments, either directly at the metal (e.g. via reaction of H2B=NH3 with [Ir(PMe3)2(H)2(η5-H2B=NH3)]+, 16a′) or via an off-metal process13,44 involving two free aminoboranes. In fact for H2B·NH3 both these processes are computed to be competitive with B–N coupling via TS6a′_BNA, dimerisation at 16a′ having a transition state energy of +15.4 kcal mol–1 while the off-metal process has a barrier of 16.2 kcal mol–1 (see Fig. S16†). Some dimerisation (and trimerisation) may therefore be anticipated, and indeed evidence of this is seen in the small amount of borazine that is observed as minor products in the oligomerisation processes.

Overall the proposed dehydrogenation/oligomerisation mechanism captures the key trends observed experimentally by ESI-MS and NMR spectroscopy. In particular the promotional effect of added amine-borane on dehydrogenation for all three H3B·NMe2H, H3B·NH2BH2·NH3 (x = 0–2) species and the decreasing propensity toward oligomerisation as the size of the amine-borane increases are reproduced. However, some issues do remain: (i) the absolute barriers computed for the dehydrogenation are ca. 26 kcal mol–1 and so are rather high for a (albeit slow) room temperature process; (ii) once dehydrogenation has occurred, the competing H2B=NH2 dimerisation processes are computed to be slightly more favourable than oligomerisation. One reason for these discrepancies may be the use of a model system in the present study, where PMe3 is used in place of PCy3 ligands. However, an additional factor may be that both the key N–H activation (e.g. TS6a′_NH1) and B–N coupling (e.g. TS6a′_BN)
transition states exhibit a vacant site that offers the potential for further stabilisation. Indeed a third $\text{H}_3\text{B}_x\text{NH}_3$ molecule was found to promote both of these steps (see Scheme 5 and Fig. 7). Starting from $\text{H}_3\text{B}_x\text{NH}_3$ dehydrogenation proceeds with a reduced overall barrier of $22.4 \text{ kcal mol}^{-1}$ to give $\text{H}_3\text{B}_x\text{AB}$ at $-4.9 \text{ kcal mol}^{-1}$ and from here $\text{B}$–$\text{N}$ coupling has a barrier of only $9.4 \text{ kcal mol}^{-1}$. Moreover, $\text{B}$–$\text{N}$ coupling (and the completion of the oligomerisation process) are now kinetically preferred over dimer formation. Therefore several substrate molecules may cooperate to promote the oligomerisation process. Alternatively a solvent molecule may interact with the unsaturated metal centre and so promote the oligomerisation step, although we have not attempted to explicitly model this here.

Conclusions

In summary, we report the observation and characterisation of multiple metal-bound oligomers in the dehydrocoupling of $\text{H}_3\text{B}_x\text{NH}_3$. This contrasts with only a single oligomerisation event being observed for $\text{H}_3\text{B}$–$\text{NMeH}_2$ and none for $\text{H}_3\text{B}$–$\text{NMeH}_2$. Interrogation of the likely mechanism using computational methods reveals that initial dehydrogenation of $\text{H}_3\text{B}$–$\text{NH}_3$ is a higher energy process than both the subsequent dehydrogenation of a second amine-borane and metal-promoted $\text{B}$–$\text{N}$ bond formation to form an oligomeric borazane bound to the metal centre. Steric factors play an important role in determining the barrier to $\text{B}$–$\text{N}$ coupling which increases with $x$ in the $\text{H}_3\text{B}_x\text{NMe}_x\text{H}_{3-x}$ series ($x = 0$–$2$). These studies also suggest a role for additional amine- or amino-borane in promoting dehydrocoupling processes through the formation of adduct species and complementary $\text{N}$–$\text{H}$…$\text{H}$–$\text{B}$ interactions, an observation we noted from experimental studies both here and previously and recently from computational studies on related systems.

An overall mechanism that captures these observations is shown in Scheme 6. For $\text{H}_3\text{B}$–$\text{NH}_3$ initial dehydrogenation of the amine-borane (step 1) has the highest barrier (+26.7 kcal mol$^{-1}$), with the subsequent dehydrogenation of a second amine-borane (step 2) proceeding through a slightly lower energy transition state at +24.2 kcal mol$^{-1}$. The transition state for the $\text{B}$–$\text{N}$ coupling of the resultant amino-boranes (step 3) is then most accessible of all (+17.9 kcal mol$^{-1}$). The rather high barrier to dehydrogenation (step 1) means that these systems turnover rather slowly, especially compared to others that rapidly promote dehydropolymerisation.$^{5,12}$ However, the corollary is that intermediates such as $\text{H}_3\text{B}_x\text{NH}_3$ can be observed, allowing for direct mechanistic insight. For subsequent oligomerisations (e.g. to form $\text{H}_3\text{B}_x\text{NH}_3$, Scheme 6) the key transition state energies retain the same pattern, thus promoting formation of a growing oligomeric chain at the metal centre. When the amine-borane is changed to $\text{H}_3\text{B}$–$\text{NMeH}_2$ the same computed pattern still holds for the initial oligomerisation, but the second $\text{B}$–$\text{N}$ coupling transition state (+24.8 kcal mol$^{-1}$) does becomes very close in energy to those for the two dehydrogenation steps (+25.4 kcal mol$^{-1}$ and +24.0 kcal mol$^{-1}$). Clearly $\text{B}$–$\text{N}$ coupling is disfavoured by the greater bulk and experimentally only 5b is observed to be formed. For $\text{H}_3\text{B}$–$\text{NMe}_2\text{H}$ no $\text{B}$–$\text{N}$ bond formation to give a linear diborazane is observed under these experimental conditions, with $\text{H}_3\text{B}_x\text{NH}_3$ formed only.

$\text{B}$–$\text{N}$ coupling is also calculated to be competitive with amino-borane cyclisation, consistent with the observation of a small amount of borazine. However, coupling must be faster than reaction of exogenous cyclohexene with amino-borane as no hydroborated product is observed under these conditions. Our mechanism therefore has some similarities to those recently proposed for the catalytic dehydropolymerisation of $\text{H}_3\text{B}$–$\text{NH}_3$ using a bifunctional Ru-based catalyst$^{18}$ and of $\text{H}_3\text{B}$–$\text{NMeH}_2$ using Ir$^3$BuPOCOPBu$^2$.$^{12}$ Although the intimate mechanistic details of these two systems likely differ, both propose dehydrogenation to form an amino-borane, that then must undergo fast metal-mediated $\text{B}$–$\text{N}$ coupling, as neither system promotes hydroboration when exogenous cyclohexene is added.
Amine-borane dehydrocoupling presents a high degree of mechanistic complexity that is additionally highly catalyst specific. Although the precise mechanism outlined here might be rather system specific, the observations and suggested pathways presented might help guide future work on developing and understanding this challenging transformation. Ultimately the goal is the design of improved catalysts for this important process that have the potential to produce B-N materials “to order”.

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Notes and references

2 A. Staubitz, A. P. M. Robertson, M. E. Sloan and I. Manners, Chem. Rev., 2010, 110, 4023–4078.
34 ESI-MS has been used to analyse the metal-free product of dehydropolymerisation. See, for example, mass spectra reported in ref. 4, 6 and 12.
35 Calculations were run with the Gaussian suite of programs and employed the BP86 functional. Rh and P centres described with the Stuttgart RECPs and associated basis set with added d-orbital polarisation on P (\(\gamma = 0.387\)) and 6-31G** basis sets for all other atoms. Free energies are reported in the text, based the gas-phase values, incorporating corrections for dispersion effects using.
Grimme’s D3 parameter set (i.e. BP86-D3) and solvent (C₆H₅F, PCM approach). See ESI† for references and full details.

40 Experimentally, addition of sequential equivalents of H₃BNMe₂H to 1 under a sparge of Ar to remove H₂ resulted in a reduced yield of 5b with significant amounts of unidentified decomposition products formed.
41 When H₃B·NMe₂H is added to the amino-borane complex 4a⁺ significant (~35%) quantities of the corresponding linear diborazane are observed, suggesting that under these conditions of a high local concentration of H₂B·NMe₂ the B–N bond forming reaction is kinetically competent. See ref. 19. This experimental observation is consistent with the essentially similar barriers to dehydrogenation and B–N coupling calculated here for the secondary amine-borane. At lower concentrations of amine-borane used in this study dimerisation to form [H₂B·NMe₂]₂ dominates and the diborazane is not observed.