The Catalytic Dehydrocoupling of Amine– and Phosphine–Boranes

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Abstract Mechanistic studies into the catalysed dehydrocoupling of amine– and phosphine–boranes have seen a rapid development over the last 5 years. The primary driver for this intense research effort has been the development of catalysts that might offer significant benefits with regard to the kinetics of hydrogen release, for potential use when linked with a fuel cell. Secondary to this, although becoming increasingly important, is the use of dehydrocoupling approaches to afford well–defined polymeric materials with B–N or B–P backbones that offer potential as high–performance polymers, pre–ceramic materials and as precursors to white graphene. There have been many systems studied, using catalysts incorporating metals from across the periodic table. This review attempts to bring together the insight revealed from these studies, which shows a rich and complex mechanistic landscape for the dehydrocoupling of phosphine– and amine–boranes.

Keywords: Amine–Borane; Phosphine–Borane; Mechanism; Dehydrocoupling; Catalysis
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Acknowledgments
1 Introduction

The transition metal catalysed dehydrocoupling of amine-boranes and, to a lesser extent phosphine-boranes, has received much attention in recent years [1, 2]. For amine-boranes, the parent compound, H$_3$B·NH$_3$, is an air-stable solid containing a high weight percentage of hydrogen (19.6%), and thus has been explored extensively as a potential candidate for chemical hydrogen storage vectors [3]. Although H$_3$B·NH$_3$ can release dihydrogen on heating to temperatures above 120 °C, leading to mixtures of products including polyborazylene and polyaminoboranes, metal catalysts have led to more efficient and controlled dehydrogenation [4]. Amine–boranes have also been studied with respect to the formation of BN–based materials. In particular polyaminoboranes, which are isoelectronic with societally and technologically ubiquitous polyolefins, have potential applications as piezoelectric materials or as precursors to BN-based ceramics[5] or white graphene [6]. Likewise the analogous dehydrocoupling of phosphine-boranes produces oligomeric and polymeric materials that show promise as electron beam resists and precursors to semi-conducting boron-phosphide. [7].

In this review we outline recent developments to elucidate, and thus harness, the mechanism of catalytic dehydrocoupling of amine– and phosphine–boranes. Although there is yet to be developed a common, detailed, overarching mechanism that encompasses all catalysed systems, we hope that this contribution serves to mark the current state–of–the–art in the field and provide a background to aid future developments in the area. It is the control of these processes, to either afford well–defined final products, or the maximum rate and yield of hydrogen evolution, that makes catalytic routes attractive for dehydrocoupling. This is not the first time that dehydrocoupling of amine– and phosphine–boranes has been reviewed, and there
have been recent overviews dealing with their general chemistry and properties,[1, 2] role in hydrogen storage applications,[4, 8, 9] as well as dehydrocoupling processes [5, 7, 10, 11]. We do not attempt to review the extensive literature on the catalysed hydrolysis of amine–boranes to produce H_2 as the principal product of interest [3]

2. Transition metal catalysed dehydrocoupling of amine–boranes

2.1 General considerations

A generalised scheme for the products observed from amine–borane dehydrocoupling is shown in Scheme 1. The parent H_3B·NH_3 can also lose over 2 equivalents of hydrogen to form polyborazylene as well as often insoluble oligomeric and polymeric materials that arise from loss of less than two equivalents of H_2 [8]. Primary amine–boranes, H_3B·NRH_2, can undergo loss of one equivalent of hydrogen during dehydrocoupling to afford polyaminoboranes [H_2BNRH]_n (R = H, Me, ⁷Bu); while borazines, [HBNR]_3 (R = H, Me, ⁷Bu), can result from the loss of 2 equivalents of dihydrogen and should be considered to be the thermodynamic product of the dehydrocoupling of primary amine–boranes. Secondary amine-boranes H_3B·NR_2H can lose one equivalent of dihydrogen and dehydrocouple through soluble and well-defined intermediates; for H_3B·NMe_2H, the most commonly observed are the aminoborane H_2B=NMMe_2 and the linear diborazane H_3B·NMMe_2BH_2·NMMe_2H (see Section 2.2). Consequently, H_3B·NMMe_2H is often used as a model for dehydrocoupling of H_3B·NH_3 and H_3B·NMMeH_2,[12, 13] the products of which are often insoluble or poorly defined polymeric or oligomeric materials [14]. The cyclic dimer [H_2BNR]_2 (R = e.g. Me, Et) is generally formed as the major dehydrocoupling
product of $H_3B\cdot NR_2H$. With bulky N-substituents, e.g. $^i$Pr or Cy, dimerisation is prevented and instead the aminoborane $H_2B=NR_2$ results [15, 16].

Scheme 1 Simplified dehydrocoupling pathway for $H_3B\cdot NMe_2H$, $H_3B\cdot NMeH_2$ and $H_3B\cdot NH_3$. The generation of intermediate aminoboranes is not shown, but is implicit for many processes.

2.2 Aminoboranes: observation and trapping

The dehydrocoupling of amine-boranes is often proposed to proceed via formation of aminoboranes $H_2B=NR'\cdot$ that arise from initial dehydrogenation; and aminoboranes such as e.g. $H_2B=N^t$BuH and $H_2B=NMe_2$ have been directly observed as intermediates in catalytic dehydrocoupling of their respective amine-boranes [17, 18]. The kinetics for the ‘off-metal’ dimerisation of $H_2B=NMe_2$ to form $[H_2B\cdot NMe_2]_2$ have been explored, and found to be a second order process with a large negative entropy of activation [19]. Interestingly, a significant solvent effect on the relative rate of dimerisation has also been noted, with acetonitrile accelerating the process [13, 20]. The less bulky congeners $H_2B=NH_2$[21] and $H_2B=NMeH_2$[22, 23] however, have not been directly observed as intermediates in dehydrocoupling, although they have been isolated coordinated to a transition metal fragment, being formed from dehydrogenation of the corresponding amine–borane [24]. In 2008, Baker, Dixon and
coworkers proposed that $\text{H}_2\text{B}=\text{NH}_2$ liberated from the metal results in the eventual production of borazine, whereas $\text{H}_2\text{B}=\text{NH}_2$ (or derivatives thereof) remaining bound to the metal results in oligomeric or polymeric products [25]. To detect free aminoborane, cyclohexene was added to reaction mixtures, as cyclohexene can be hydroborated by $\text{H}_2\text{B}=\text{NRH}$ ($\text{R} = \text{H}, \text{Me}$), forming $\text{Cy}_2\text{B}=\text{NRH}$ (Scheme 2) thereby acting as a useful marker for free aminoboranes.

Scheme 2 Trapping of aminoboranes by cyclohexene. $\text{R} = \text{Me}, \text{H}$.

Accordingly, when cyclohexene was added to a reaction mixture of $\text{H}_3\text{B} \cdot \text{NH}_3$ and $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})]_2$, $\text{Cy}_2\text{B}=\text{NH}_2$ was the major product observed instead of the expected borazine (see Section 2.4[26]). However, upon addition of cyclohexene to a solution of $\text{H}_3\text{B} \cdot \text{NH}_3$ and catalyst $\text{Ir}([\text{BuPOCOPBu}](\text{H}))_2$[27] the same oligomeric products were observed as in the absence of cyclohexene, i.e. no hydroboration product was observed (Section 2.8.3). Although cyclohexene trapping is still regarded as a useful method for detecting free aminoboranes, more recent studies have suggested that the absence of hydroboration does not necessarily reflect an absence of free aminoborane. It has been suggested that, if borazine formation (from aminoborane trimerisation/dehydrogenation) or hydroboration of cyclohexene are not kinetically competitive with metal-based BN oligomerisation/polymerisation processes, $\text{Cy}_2\text{B}=\text{NH}_2$ will not be observed even if $\text{H}_2\text{B}=\text{NH}_2$ is present [21, 28, 29].

2.3 Linear diborazanes
Another intermediate often observed in the dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ is the linear diborazane $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ [15]. Schneider has calculated that the pathway for B—N bond cleavage of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ to generate $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ and $\text{H}_2\text{B} \equiv \text{NMe}_2$ is close to thermoneutral ($\Delta G = -2.3$ kcal mol$^{-1}$) [30]. Therefore if this process is reversible the position of the equilibrium (and hence whether $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ is observed in catalysis) is likely to be dependent upon their relative concentrations and rates of formation with a particular catalyst. A general pathway for the dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ with Schneider’s ruthenium catalysts (see Section 2.8.4) was developed (Scheme 3), suggesting that the formation of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ is a metal–based process. The role of this diborazane in the dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ has been further discussed by others [15, 19, 28, 31, 32].

Scheme 3 Schneider’s early model for dehydrocoupling $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ to form $[\text{H}_2\text{BNMe}_2]_2$.

Weller and Manners have since reported that the diborazane $\text{H}_3\text{B} \cdot \text{NMeHBH}_2 \cdot \text{NMeH}_2$, the product of one dehydrooligomerisation of $\text{H}_3\text{B} \cdot \text{NMeH}_2$, can be formed by catalytic methods [33] and its role as a possible intermediate in dehydropolymerisation has been further explored (see Section 2.8.3) [28]. Shore and co-workers have also reported the synthesis by stoichiometric methods of the $\text{H}_3\text{B} \cdot \text{NH}_3$ analogue,
H₃B·NH₂BH₂·NH₃,[34] while Sneddon and co-workers have reported the synthesis of triborazanes, such as H₃B·(NH₂BH₂)₂·NH₃,[35] which are implicated in dehydropolymerisation processes [36].

2.4 Early examples of metal-catalysed dehydrocoupling

The first example of transition metal catalysed dehydrocoupling was reported in 1989 by Roberts and co-workers. The amine-borane H₃B·N'BuMeH was dehydrogenated at 120 °C by 10% Pd on charcoal to form the aminoborane H₂B·N'BuMe, which dimerised to form [H₂BN'BuMe]₂ [37]. In 2001 Manners and co-workers reported that Rh¹ or Rh³ precursors catalytically dehydrocoupled secondary amine-boranes H₃B·NR₂H (R₂ = Me₂, cyclo-C₄H₈) to yield the corresponding cyclic dimer [H₂BNR₂]₂ (Scheme 4). The Rh¹ precursor was also an effective catalyst for the dehydrocoupling of H₃B·NH₃ and H₃B·NMe₂H to form their respective borazines, although in both cases insoluble material, indicative of oligomeric chains, was also observed in the reaction mixtures [26].

Scheme 4 Dehydrocoupling of amine-boranes by [Rh(1,5-cod)(µ-Cl)]₂ and RhCl₃·3H₂O.
2.5 Heterogeneous catalysts for the dehydrocoupling of amine-boranes

Various systems act as heterogeneous catalysts for amine-borane dehydrocoupling by the formation in situ of catalytically active nanoparticles, although the nature of the actual catalytic component can be the subject of debate. Nonetheless, heterogeneous catalysis is attractive due to facile separation of the products and catalyst. The dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ by $[\text{Rh}(1,5\text{-cod})(\mu-\text{Cl})]_2$ showed a reaction profile with an induction period, during which a black precipitate was observed to form. Tests, originally developed by Finke,[38] were performed to probe for heterogeneous catalysis. For example, both filtration and catalyst poisoning with mercury halted catalysis (Figure 1), suggesting a heterogeneous system in which the dehydrocoupling is catalysed by rhodium nanoparticles [39].

![Figure 1](image.png)

**Figure 1** Left: Addition of mercury to the reaction mixture. Right: The effect of filtration and poisoning with PPh$_3$. Both figures reprinted (adapted) with permission from C. A. Jaska and I. Manners, *J. Am. Chem. Soc.*, 2004, **126**, 9776-9785. Copyright 2004 American Chemical Society.

Later EXAFS studies by Autrey and co-workers suggested that, instead, soluble Rh$_6$ clusters are responsible for the dehydrocoupling activity in this system [40].
Interestingly, the catalytic dehydrocoupling of H$_3$B·PPh$_2$H with [Rh(1,5-cod)(µ-Cl)]$_2$ to form H$_3$B·PPh$_2$BH·PPh$_2$H was reported by Manners as homogeneous (see Section 3.2) [39]

Some heterogeneous systems are among the fastest reported dehydrocoupling catalysts. A system using [Fe(NCMe)$_2$(PNPN)][BF$_4$]$_2$/KO'Bu [PNPN = (PPh$_2$C$_6$H$_4$CH=NCH$_2$)$_2$], reported by Morris and co–workers, was highly active the dehydrogenation of H$_3$B·NH$_3$. At 2.5 mol% catalyst loading, an equivalent of H$_2$ is released within a minute, representing a turnover frequency (TOF) of approximately 2400 h$^{-1}$, to yield a mixture of products: borazine, polyborazylene, and B-N oligomers or partially cross-linked polyborazylene, as well as unreacted H$_3$B·NH$_3$ [41]. The active species is proposed to be iron(0) nanoparticles stabilised by PNPN ligands. Catalysis slowed after the initial fast dehydrogenation, and free PNPN ligand was observed by $^{31}$P{$^1$H} NMR spectroscopy, implying that catalyst deactivation was occurring and active sites on the iron nanoparticle were being blocked. Consistent with this, attempts to recycle the catalyst resulted in slower dehydrocoupling.

Systems based upon ruthenium nanoparticles have been explored by Ozkar et al. for the dehydrocoupling of H$_3$B·NMe$_2$H to yield [H$_2$BNMe$_2$]$_2$, and show good activities. Oleylamine-stabilised ruthenium(0) nanoparticles (generated in situ from RuCl$_3$) effects dehydrocoupling of this amine–borane with a TOF of 137 h$^{-1}$,[42] while ruthenium(0) nanoparticles stabilised by 3-aminopropyltriethoxysilane gave a TOF of 55 h$^{-1}$ [43]. Ozkar also obtained turnover frequencies of ~ 60 h$^{-1}$ for the dehydrocoupling of H$_3$B·NMe$_2$H when using rhodium(0) nanoclusters (~ Rh$_{90}$–Rh$_{460}$), produced from [(C$_5$H$_{11}$CO$_2$)$_2$Rh]$_2$ [44]. Zahmakiran and co-workers dehydrogenated H$_3$B·NH$_3$ to form [H$_2$BNH$_2$]$_n$ and polyborazylene (average TOF ~ 24 h$^{-1}$) with a ruthenium nanocatalyst that is formed from the in situ hydrogenation of
Poisoning experiments suggested subnanometer Ru\textsubscript{n} clusters as the dominant catalytically active species, rather than Ru(0) nanoparticles [45]. Iron-doped H\textsubscript{3}B·NH\textsubscript{3} (5 mol\%) has been shown to produce crystalline [H\textsubscript{2}BNH\textsubscript{2}]\textsubscript{n} on heating the solid to 60 °C, the mechanism being proposed to operate via an FeB alloy [46].

A skeletal nickel catalyst, produced from base-leaching a Ni/Al alloy, for the heterogeneous dehydrocoupling of amine-boranes was reported by Manners and co-workers [22]. Although the dehydrocoupling is relatively slow (TOF ~3 h\textsuperscript{-1} for H\textsubscript{3}B·NMe\textsubscript{2}H, 5 mol\% Ni), mechanistic insight into heterogeneous dehydrocoupling was obtained. The major route for dehydrocoupling H\textsubscript{3}B·NMe\textsubscript{2}H was proposed to be dehydrogenation to afford the aminoborane H\textsubscript{2}B=NMe\textsubscript{2}, which dimerises off-metal to form the final product [H\textsubscript{2}BNMe\textsubscript{2}]\textsubscript{2}. A minor pathway was also suggested, involving the on-metal formation of the linear dimer H\textsubscript{3}B·NMe\textsubscript{2}BH\textsubscript{2}·NMe\textsubscript{2}H, followed by on-metal dehydrocyclisation to form [H\textsubscript{2}BNMe\textsubscript{2}]\textsubscript{2}. (Scheme 5).

\begin{center}
\textbf{Scheme 5} Suggested dehydrocoupling pathway for the dehydrocoupling of H\textsubscript{3}B·NMe\textsubscript{2}H by skeletal Ni (5 mol\%, toluene).
\end{center}

Dehydrocoupling of the primary amine-borane H\textsubscript{3}B·NMeH\textsubscript{2} was also investigated with this system. At a catalyst loading of 5 mol\%, slow conversion (TOF ~ 0.2 h\textsuperscript{-1}) to
form the cyclic triborazane \([\text{H}_2\text{BNMeH}]_3\) resulted. Interestingly at 100 mol\% Ni, polyaminoborane \([\text{H}_2\text{BNMeH}]_n\) was formed \((M_n = 51300 \text{ g mol}^{-1}, \text{ PDI} = 1.5)\), Scheme 6. This effect of catalyst loading on the identity of the final product was attributed to initial dehydrogenation of \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) to form the monomer \(\text{H}_2\text{B} \cdot \text{NMeH}\), which is formed in higher concentrations with higher catalyst loadings, and under such a kinetic regime polymerisation is favoured over cyclisation. Similarly, in the dehydrocoupling of \(\text{H}_3\text{B} \cdot \text{NH}_3\), 5 mol\% of Ni produced B-(cyclodiborazanyl)-aminoborohydride, whereas stoichiometric quantities of Ni formed polyaminoborane \([\text{H}_2\text{BNH}_2]_n\).

**Scheme 6** Dehydrocoupling of \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) with skeletal Ni.

An important result for the potential development of amine-boranes as hydrogen storage materials originated from Liu and coworkers using a heterogenous system. The cyclic amine-borane BN-methylcyclopentane (1, Scheme 7), an air and moisture stable liquid at room temperature, was shown to release 2 equivalents of \(\text{H}_2\) (4.7 wt\%) at 80 °C to cleanly generate the trimer 2, also a liquid, using 5 mol\% FeCl\(_2\) (TOF 120 h\(^{-1}\)) in a neat solution of 1 [47]. The reaction profile showed an induction period, and a black powder was produced during the reaction, with mercury experiments suggesting a heterogeneous catalyst as the active species. The catalyst was recyclable, with three successive experiments all showing similar activities. Significantly 2 could be treated with MeOH (to form 3), followed by LiAlH\(_4\) to regenerate 1 (Scheme 7) in
92% yield. Although a more efficient regeneration method is desirable, these results illustrate the potential of this system as a hydrogen storage candidate, with the additional benefit of using cheap and abundant iron as the catalyst. The properties of the materials produced by this process have been described (e.g. viscosity, thermal stability, purity) [48]. A related system was recently reported in which MeH₂B·NMeH₂ is dehydrogenated by CoCl₂ (5 mol%, 80 °C, diglyme) to form the borazine product [MeBNMe]₃ in 71% yield. Subsequent treatment of [MeBNMe]₃ with HCOOH and then LiAlH₄ regenerated MeH₂B·NMeH₂ in a 46% yield [49].

Scheme 7 Dehydrogenation of 1 to yield 2, and regeneration of 1 from 2.

Manners and co-workers recently illustrated that subtle changes in the ligand set can have significant effects on whether the catalysis is homogeneous or heterogeneous. [CpFe(CO)₂]₂ (5 mol%) dehydrocouples the amine-boranes H₃B·NMe₂H, H₃B·NMeH₂ and H₃B·NH₃ under photoirradiation (Scheme 8). With H₃B·NMeH₂, high molecular weight [H₂BNMeH]ₙ was produced (Mₙ = 64300 g mol⁻¹, PDI = 1.8) after 3 hours (90% conversion), although after 16 hours of irradiation, the borazine [HBNMe]₃ was the major product [50].
Scheme 8 Catalytic dehydrocoupling of H₃B·NMe₂H, H₃B·NMeH₂ and H₃B·NH₃ with 5 mol% [FeCp(CO)]₂₂.

Further mechanistic investigations were undertaken with a range of iron carbonyl cyclopentadienyl complexes and H₃B·NMe₂H [51]. When using [CpFe(CO)]₂₂ under photoirradiation, and Cp₂Fe₂(CO)₃(NCMe) (no photoirradiation), H₂B=NMe₂ was observed as the sole intermediate during the dehydrocoupling. With CpFe(CO)₂I however, under photoirradiation the linear diborazane H₃B·NMe₂BH₂·NMe₂H was observed as an intermediate, with H₂B=NMe₂ observed in no significant quantities. Investigations into the nature of the reaction mixtures showed that [CpFe(CO)]₂₂ and Cp₂Fe₂(CO)₃(NCMe) were producing iron nanoparticles as the active catalyst, thought to form via the loss of CO and NCMe, respectively. The heterogeneous mechanism is thought to involve initial dehydrogenation of H₃B·NMe₂H on the nanoparticle surface to form H₂B=NMe₂, which then dimerises off-metal. By contrast, CpFe(CO)₂I appeared to be acting as a homogeneous catalyst, and this mechanism is discussed in more detail in Section 2.8.3.
2.6 Transition metal catalysed dehydrocoupling of H$_3$B·NH$_3$ promoted by ionic liquids

In 2006 Sneddon and co-workers noted that dissolving H$_3$B·NH$_3$ in ionic liquids increased the rate and extent of thermal dehydrocoupling relative to that of solid H$_3$B·NH$_3$ [52, 53]. In 2011 Baker and Sneddon sought to utilise this enhancement by combining transition metal catalysts with ionic liquid solvents. A range of transition metal catalysts were screened for the dehydrocoupling of H$_3$B·NH$_3$ in the ionic liquid [bmim][Cl] (bmim = 1-butyl-3-methylimidazol),[54] all at 5 mol% loading, including [Rh(1,5-cod)(µ-Cl)]$_2$, Ru(1,5-cod)Cl$_2$, RhCl$_3$, Ni(1,5-cod)$_2$ and NiCl$_2$. All showed enhanced dehydrocoupling activity at 65 °C compared with the analogous reaction in [bmim][Cl] in the absence of catalyst. However, increasing the temperature to 85 °C with the catalyst [Rh(1,5-cod)(µ-Cl)]$_2$ led to lower total H$_2$ release than that in the absence of catalyst. Similar effects were observed with [RuCl$_2$(PMe$_3$)$_4$] (0.78 mol%) in [emim][O$_3$SOEt] (emim = 1-ethyl-3-methylimidazole), implying that transition metal catalysts can enhance the rate of H$_2$ release in ionic liquids, but the advantage is most apparent below 85 °C. Moreover, different products were observed with changing the ionic liquid: catalysis with [RuCl$_2$(PMe$_3$)$_4$] in [emim][O$_3$SOEt] resulted in borazine and polyborazylene, whereas the same reaction in [bmim][NTf$_2$] resulted in [H$_2$BNH$_2$]$_n$ (Scheme 9).

![Scheme 9 Different product distributions for the Ru-catalysed dehydrocoupling of H$_3$B·NH$_3$ with different ionic liquids.](image-url)
This selectivity could have useful implications in the future design of chemical hydrogen storage systems, and was exploited by Baker in the dehydrocoupling of mixtures of \( \text{H}_3\text{B}\cdot\text{NH}_3 \) and \( \text{sec-} \text{butylamine–borane} \), \( \text{H}_3\text{B}\cdot\text{N}^\text{sec} \text{BuH}_2 \) [55]. \( \text{H}_3\text{B}\cdot\text{N}^\text{sec} \text{BuH}_2 \) can solubilise \( \text{H}_3\text{B}\cdot\text{NH}_3 \), resulting in liquid fuel mixtures that have an upper limit for \( \text{H}_2 \) release of 12.8 wt%. With the [RuCl\(_2\)(PMe\(_3\))\(_4\)] catalyst (~ 1 mol%), the system released over 5.0 wt% of hydrogen in 1 hour at 80 °C, affording \( \text{HBN}^\text{sec} \text{Bu} \), \( \text{[HBNH]}_3 \) and polyborazylene. However, insoluble \( \text{[H}_2\text{BNH}_2]_n \) was also observed in the reaction mixture, which is undesirable for a liquid fuel cell, which prevailed on testing diglyme and sulfolane as co-solvents (Scheme 10). Addition of \([\text{emim}][\text{O}_3\text{SOEt}]\) as the co-solvent, however, released 3.6 wt% \( \text{H}_2 \) at 80 °C over 18 hours (a lower overall storage capacity due to the ionic liquid) with no insoluble \( \text{[H}_2\text{BNH}_2]_n \) observed, making \( \text{H}_3\text{B}\cdot\text{N}^\text{sec} \text{BuH}_2/\text{H}_3\text{B}\cdot\text{NH}_3 \) mixtures more appealing as potential liquid fuels cells.

![Scheme 10 Products resulting from the dehydrogenation of H₃B·N'BuH₂ / H₃B·NH₃ with [RuCl₂(PMe₃)]₄ (~ 1 mol%) with and without [emim][O₃SOEt] as co-solvent.](attachment:scheme10.png)

2.7 **Homogeneous dehydrocoupling of amine-boranes**
Although heterogeneous catalysts can produce high turnover numbers, homogeneous catalysts are more readily studied due to the well-defined coordination sites that can allow for control of catalytic processes by modification of the metal and ligand environment. Homogeneous catalysts can operate via inner sphere or outer sphere mechanisms. Outer sphere mechanisms allow dehydrogenation of amine-boranes without the direct coordination to the metal centre, by using metal–ligand cooperativity [21, 30, 56-59]. By contrast, inner sphere mechanisms involve initial coordination of the amine-borane to the metal forming a sigma complex, followed by dehydrogenation of the amine-borane (Scheme 11). Various mechanistic scenarios have been implicated for the mechanism of dehydrogenation and will be discussed in detail in Section 2.8.

Scheme 11 Simplified pathway for inner-sphere dehydrogenation.

2.7.1 Sigma complexes of amine-boranes

Inner sphere mechanisms for the dehydrocoupling of amine-boranes often invoke coordination of an amine-borane to the metal via 3 centre–2 electron M-H-B interactions,[60] forming a sigma complex, \([L_nM-H_3B\cdot NR_3]\). These weak interactions
arise primarily from donation from the $\sigma$ B—H orbital to the metal; the B—H $\sigma^*$ orbital is high in energy, meaning that back-donation from the metal is negligible [11, 61]. Often, sigma complexes are isolated using tertiary amine-boranes, e.g. H$_3$B·NM$_3$, as the lack of N—H bonds generally prevents further reactivity. The first example of a simple amine-borane coordinated to a metal was reported by Shimoi and coworkers in 1999, in which $[\text{M(CO)}_6(\eta^1\text{H}_3\text{B} \cdot \text{NM}_3)]$ (M = Cr, Mo, W) is formed through photolysis of $[\text{M(CO)}_6]$ in the presence of H$_3$B·NM$_3$ [61]. This ‘end-on’ $\eta^1$ binding of the amine-borane occurs through one B—H bond, and various other $\eta^1$ sigma complexes of amine-boranes have since been reported (a selection shown in Figure 2) [61-63].

![Figure 2](image)

**Figure 2** Examples of $\eta^1$ sigma amine-borane complexes. M = Cr, Mo or W. NRR’H = N′BuH$_2$, NM$_2$H or NH$_3$. [BArF$_4$] anions not shown.

Amine-boranes can also bind to the metal centre through two B—H sigma bonds, resulting in $\eta^2$ complexes [19, 64, 65]. Oligomeric species such as H$_3$B·NM$_2$BH$_2$·NM$_2$H have also been observed to bind in this manner (Figure 3) [31, 66, 67].
Examples have also been isolated in which multiple amine-borane moieties are bound to a metal centre, similar to intermediates often invoked for dimerisation and polymerisation mechanisms \((\textit{vide infra})\) \cite{12, 62, 68-70}. In 2010, Weller and co-workers reported a bimetallic hydrido-boryl species formed from two \(\{\text{Rh(PR)}_3\}^+\) \((R = \text{i} \text{Pr, Cy})\) fragments bridged by three \(\text{H}_2\text{B}·\text{NMe}_3\) ligands, two of which have undergone \(\text{B}—\text{H}\) activation (Figure 4) \cite{71}. The same group also reported cationic rhodium species with two amine-boranes bound to one rhodium centre, \([\text{Rh}\{\text{P}(\text{C}_5\text{H}_9)_2(\eta^2-\text{C}_5\text{H}_7)\}((\eta^2-\text{H}_3\text{B}·\text{NMeRR'})((\eta^1-\text{H}_3\text{B}·\text{NMeRR'})][\text{BAR}_4^\text{F}]\) \((R, R' = \text{Me, H})\) \cite{72}

\[
\begin{align*}
\text{Figure 3} & \quad \text{Examples of } \eta^2 \text{ sigma amine-borane complexes. } [\text{BAR}_4^\text{F}]^- \text{ anions not shown. } \\
\text{IMes} & = N,N\text{'-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene}, n = 1 - 3.
\end{align*}
\]

\[
\begin{align*}
\text{Figure 4} & \quad \text{Examples of multiple amine-borane bonding to transition metal fragments. } \\
R & = \text{i} \text{Pr, Cy. Cyp = cyclopentyl. } R = \text{Me, H. } R' = \text{Me, H. } [\text{BAR}_4^\text{F}]^- \text{ not shown.}
\end{align*}
\]
In 2013, Weller and MacGregor reported the first well-characterised example of the B—B homocoupling of an amine-borane to yield the diborane(4) Me₃N·BH₂BH₂·NMe₃ ligand sigma bound to rhodium [62]. B—B homocoupling of boranes has been otherwise limited to B—B bond formation in polyhedral boranes,[73, 74] guanidine bases,[75] and catechol- and pinacolboranes [76-78]. Pd^{II} catalysts have been demonstrated to rapidly (TOF ~ 2000 h⁻¹) dehydrocouple H₃B·NH₃ to yield poorly defined materials proposed to contain B—B bonds [79].

Addition of excess H₃B·NMe₃ to the sigma complex [Rh(κ²-(p,p-Xantphos)(η²-H₂B(CH₂CH₂Bu)·NMe₃)][BAr₄F] (4) yielded [Rh(κ²-(p,p-Xantphos)(η²-H₄B₂·2NMe₃)][BAr₄F] (5) alongside the Rh^{III} complex [Rh(κ³-(p,o,p-Xantphos)(H)₂(η¹-H₃B·NMe₃)][BAr₄F] (6) in an approximate 50:50 ratio (Scheme 12).

**Scheme 12** B—B homocoupling using the [Rh(Xantphos)]⁺ fragment. [BAr₄F]⁻ not shown.

The homocoupling mechanism was probed by DFT calculations. Starting from the putative complex [Rh(κ²-(p,p-Xantphos)(η²-H₃B·NMe₃)][BAr₄F], a low energy initial B—H activation of the coordinated H₃B·NMe₃ is followed by coordination of a second H₃B·NMe₃ molecule, with a higher energy combined second B—H activation/B—B coupling step. Addition of excess cyclohexene to the reaction
mixture resulted in nearly quantitative yields of 5 by reducing 6 to \([\text{Rh}(\kappa^2_{-p,p-}\text{Xantphos})(\eta^2\text{H}_3\text{B}\cdot\text{NMe}_3)][\text{BAr}_4^\text{F}])\), enabling further homocoupling at a Rh$^1$ centre.

Sigma complexes of aminoboranes have also been isolated, where donation from the B—H bonds into a vacant metal orbital is reinforced by $\pi$ back-donation from the metal into the $\pi^*$ B-N orbital of the aminoborane [80]. Various examples have been characterised with rhodium,[13, 66, 80, 81] iridium[17, 19, 80, 82] and ruthenium[24, 80, 83, 84] and a selection are presented in Figure 5. Sabo-Etienne and Alcaraz have recently reported an unusual aminoborane complex exhibiting adjacent agostic B—H and C—H interactions (Figure 6) [85]. The isolation of aminoborane complexes is of interest mechanistically, as aminoboranes bound to the metal centre have been implicated in dehydrocoupling mechanisms, although often not observed directly (\textit{vide infra}) [12, 70, 86]. These aminoborane complexes are also closely related to transition metal complexes of three-coordinate boranes, e.g. H$_2$BR or HBR$_2$ [87].

**Figure 5** Aminoborane complexes. (PR$_3$)$_2$ = (Ph$_3$P)$_2$ or (Cy$_2$PCH$_2$CH$_2$PCy)$_2$. M = Ru, R$’$ = ‘Pr, Me, H; M = Rh$^+$ or Ir$^+$, R$’$ = ‘Pr, Me. [BAr$_4^\text{F}$] not shown.

**Figure 6** Sabo-Etienne and Alcaraz’s bis(agostic) phosphinobenzyl-(amino)borane ruthenium complex.
2.8 Mechanistic Studies on Homogeneous Dehydrocoupling Systems

2.8.1 Early Transition Metals

In 2006, Manners demonstrated the first well-defined homogeneous catalytic dehydrocoupling of H₂B·NMe₂H to form [H₂BNMe₂]₂ by using the [Cp₂Ti] fragment, generated in situ from Cp₂TiCl₂/nBuLi [88]. After this initial report, calculations by Ohno and Luo suggested a stepwise mechanism for dehydrocoupling in which N—H bond activation is followed by B—H activation to form H₂B=NMe₂, which dimerises off-metal [89]. A more detailed kinetic mechanistic study by Manners, Lloyd-Jones and coworkers on the [Cp₂Ti] system contradicted this mechanism; significantly, the linear diboraza H₃B·NMe₂BH₂·NMe₂H was identified as an intermediate in the dehydrocoupling reaction (2 mol% [Cp₂Ti], TOF = 12.5 h⁻¹) [69]. The proposed mechanism (Scheme 13) involves two cycles. Initial coordination of H₂B·NMe₂H to [Cp₂Ti] to form [Cp₂Ti(η²-H₂B·NMe₂H)] is suggested to be followed by N—H activation of the protic hydrogen with the Tiᴵᴵ centre to yield the amido–borane [Cp₂Ti(H)(NMe₂·BH₂)], 7. A second equivalent of H₂B·NMe₂H reacts with 7 resulting in B—N formation to give Cp₂TiH₂ with loss of H₂B·NMe₂BH₂·NMe₂H. The second cycle invokes reaction of H₂B·NMe₂BH₂·NMe₂H with [Cp₂Ti] to form 8, which undergoes on-metal dehydrocyclisation to form [H₂BNMe₂]₂ and Cp₂TiH₂. The proposed scheme is consistent with experimental and kinetic observations, in particular that reaction of independently prepared H₂B·NMe₂BH₂·NMe₂H with [Cp₂Ti] resulted in complete consumption of H₂B·NMe₂BH₂·NMe₂H to form [H₂BNMe₂]₂, with only negligible amounts of H₂B=NMe₂ observed. This implies that H₂B·NMe₂BH₂·NMe₂H is the sole intermediate in the formation of [H₂BNMe₂]₂ in this case, contrary to Luo and Ohno’s mechanism. Interestingly, the same system was unreactive towards H₂B·NMeH₂ (20 °C) and H₂B·PPh₂H (up to 40 °C). Zirconium
analogues of amido–boranes such as 7 have been synthesised and structurally characterized by Roesler and co–workers [90]

\[ \text{Scheme 13} \] Mechanism proposed by Manners and Lloyd-Jones for the dehydrocoupling of \( \text{H}_3\text{B} \cdot \text{NMe}_2\text{H} \).

More recent work has found that paramagnetic Ti\(^{III}\) species may play a significant role in the [\( \text{Cp}_2\text{Ti} \)] system. Following the report of the isolation of the Ti\(^{III}\) complex [\( \text{Cp}_2\text{Ti} (\text{NH}_2 \cdot \text{BH}_3) \)] by McGrady,[91] the analogous complexes [\( \text{Cp}_2\text{Ti} (\text{NMe}_2 \cdot \text{BH}_3) \)] (9) and [\( \text{Cp}_2\text{Ti} (\text{PPh}_2 \cdot \text{BH}_3) \)] (10) (Figure 7) were synthesised and employed as catalysts under the same conditions as with the titanocene fragment (2 mol%, toluene) [92] 9 and 10 were shown to be effective catalysts, promoting 83% and 97% consumption of \( \text{H}_3\text{B} \cdot \text{NMe}_2\text{H} \) after 2 hours, respectively. Similar to [\( \text{Cp}_2\text{Ti} \)], both reaction profiles showed \( \text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H} \) as an intermediate, followed by formation of [\( \text{H}_2\text{BNMe}_2 \cdot \text{2} \)], with 9 showing comparable activity to [\( \text{Cp}_2\text{Ti} \)] (TOF of 10.7 h\(^{-1}\) for 9, cf. 12.5 h\(^{-1}\) for [\( \text{Cp}_2\text{Ti} \)]). Analysis by UV/Vis and EPR spectroscopies of reaction solutions using [\( \text{Cp}_2\text{Ti} \)] and 9 as precatalysts resulted in spectra comparable with those of isolated 9. These results imply that the Ti\(^{III}\) complex 9 may
be of importance in the catalytic dehydrocoupling by titanocene, in contrast to the Ti\textsuperscript{II} and Ti\textsuperscript{IV} cycle depicted in Scheme 13. The zirconocene analogue of 10, [Cp\textsubscript{2}Zr(PPh\textsubscript{2}·BH\textsubscript{3})], was a far less active catalyst, achieving negligible consumption of H\textsubscript{3}B·NMe\textsubscript{2}H after 2 hours. Related work on metallocene complexes by Rosenthal and co-workers using the alkyne complex [Cp\textsubscript{2}M(η\textsuperscript{2}·Me\textsubscript{3}SiCCSiMe\textsubscript{3})(L)] (M = Ti, Zr; L = pyridine for Zr, no L for Ti) as a source of [Cp\textsubscript{2}M] showed turnover frequencies of 3 h\textsuperscript{-1} and 1 h\textsuperscript{-1} for M = Ti and M = Zr, respectively, for the dehydrocoupling of H\textsubscript{3}B·NMe\textsubscript{2}H [93]. The closely related precatalyst [(η\textsuperscript{5}·C\textsubscript{5}H\textsubscript{4}·iPr)\textsubscript{2}Ti(η\textsuperscript{2}·Me\textsubscript{3}SiCCSiMe\textsubscript{3})] was explored shortly afterwards and showed improved dehydrocoupling activity (TOF = 32 h\textsuperscript{-1} at 40 °C, 6 h\textsuperscript{-1} at 24 °C) [94]. The Cp* analogue, however, showed no dehydrocoupling activity, highlighting the importance of steric effects in designing systems for dehydrocoupling with early transition metal systems [93]

![Figure 7 Ti\textsuperscript{III} complexes 9 and 10.](image)

The fastest group IV systems reported include Chirik’s Ti\textsuperscript{II} complex 11 (Figure 8), which dehydrocoupled H\textsubscript{3}B·NMe\textsubscript{2}H with a TOF of 420 h\textsuperscript{-1} [95]. Based on kinetic and isotopic labelling experiments a mechanism was proposed that involved reversible B–H oxidative addition followed by β-H elimination. A rapid Zr\textsuperscript{IV} catalyst based on a frustrated Lewis pair (TOF ~ 600 h\textsuperscript{-1}) published by Wass is discussed further in Section 2.8.4.
Nishibayashi and co-workers reported the heterobimetallic group 4/8 complex [ZrMe(μ-η^5:η^1-C₅H₄PEt₂):RuCp*], 12, and showed that it was a slow catalyst for the dehydrocoupling of H₃B·NMe₂H to form [H₂BNMe₂]₂ (2 mol% 12, TOF ~ 8 h⁻¹, 50 °C) (Scheme 14) [96]. The system was less active for the dehydrocoupling of H₃B·NMeH₂ and H₃B·NH₃, reaching 92% and 56% completion, respectively, after 24 hours (10 mol% 12 at 50 °C) to form B-N oligomeric materials. Accordingly, mechanistic studies were conducted with H₃B·NMe₂H, and the proposed catalytic cycle is presented in Scheme 15.

**Scheme 14** Dehydrocoupling of H₃B·NMe₂H using 12.
Scheme 15 Proposed mechanism for the dehydrocoupling of H₃B·NMe₂H with 12.

The initial conversion of 12 to 13 is proposed to occur via ligand exchange of the hydride on H₃B·NMe₂H with the methyl group at Zr, forming MeH₂B·NMe₂H and 13, which is suggested to be the true catalyst. The thus formed MeH₂B·NMe₂H undergoes dehydrogenation to afford MeHB=NMe₂ (observed) in an analogous manner to the subsequent catalytic dehydrogenation of H₃B·NMe₂H. From 13, the dehydrogenation of H₃B·NMe₂H proceeds via initial N—H activation of H₃B·NMe₂H on the Zr centre, forming the amidoborane dihydride 14. Bimetallic reductive elimination of H₂ forms 15; and B—H activation by the Ru centre can then occur (16), releasing H₂B=NMe₂, which yields [H₂BNMe₂]₂ upon dimerisation, reforming 13. This cycle highlights that the cooperative effect of two metals in close proximity
could be of potential use in designing future catalysts, although the activity of 12 is only moderate compared with some other homogeneous systems [12, 21, 59, 65]. Rousseau has also explored multimetallic dehydrocoupling of H$_3$B·NMe$_2$H with Rh$_4$ clusters [97].

2.8.2 Mid–transition metals

Shimoi and co-workers have shown that photoactivated [M(CO)$_6$] (M = Cr, Mo, W) act as dehydrocoupling catalysts yielding [H$_2$BNMe$_2$]$_2$ from H$_3$B·NMe$_2$H (TOF 19 h$^{-1}$ when M = Cr), and a mixture of [HBNMe]$_3$ and [H$_2$BNMeH]$_n$ from H$_3$B·NMeH$_2$ [98]. The mechanism of dehydrocoupling H$_3$B·NMe$_2$H with [Cr(CO)$_6$] was investigated by DFT calculations, and suggested that the active species is the 14–electron [Cr(CO)$_4$] fragment, which can coordinate H$_3$B·NMe$_2$H to form the sigma complex 17 (Scheme 16). From this, N—H activation to form an amido–borane (18) precedes B—H activation to release H$_2$B=NMe$_2$ from 19. [Cr(CO)$_4$] is regenerated from [Cr(CO)$_4$(H)$_2$] (20) (Scheme 16). Interestingly, although the sigma complex [Cr(CO)$_5$(η$^1$-H$_3$B·NMe$_2$H)] was observed in the reaction mixture it was calculated to sit outside the cycle, acting simply as a source of [Cr(CO)$_4$].
Scheme 16 Shimoi’s proposed mechanism for the dehydrocoupling of H$_3$B·NMe$_2$H. [Cr] = [Cr(CO)$_4$].

In 2009, Berke and co-workers explored a range of nitrosyl rhenium catalysts for the dehydrocoupling of H$_3$B·NMe$_2$H to form [H$_2$BNMe$_2$]$_2$ [86]. The most active catalysts were 22, 23 and 24 (Figure 9), showing turnover frequencies of 77, 100 and 92 h$^{-1}$, respectively. All three catalysts were also active for the transfer hydrogenation of n-octene using H$_3$B·NMe$_2$H as the hydrogen source. Two possible mechanisms for the dehydrocoupling reaction using 22 were suggested (Scheme 17). Cycle A involves coordination of H$_3$B·NMe$_2$H to the vacant coordination site in 22, forming the sigma complex 25. Loss of a PCy$_3$ ligand reveals a vacant coordination site, allowing B—H activation to form the base–stabilised boryl species 26. Reductive elimination of H$_2$ forms 27, from which a β-H elimination yields free H$_2$B=NMe$_2$ and reforms 22. An alternative pathway (B) involves the formation of the sigma compound 28, followed by N—H protonation of Re—H to form 29. B—H cleavage then forms H$_2$B=NMe$_2$ and 22. During catalysis, a dihydrogen complex [ReBr(PCy$_3$)$_2$(H)(H$_2$)(NO)] was the
observed resting state in the presence of hydrogen, being in equilibrium with the active species 22.

![Figure 9](image_url)

**Figure 9** Rhenium catalysts for the dehydrocoupling of H$_3$B·NMe$_2$H.

![Scheme 17](image_url)

**Scheme 17** Suggested mechanisms for dehydrocoupling of H$_3$B·NMe$_2$H using 22.

### 2.8.3 Late Transition Metals

Many studies regarding the mechanisms of catalytic dehydrocoupling have used late transition metal systems. Early reports by Manners on Rh systems indicated that these were operating as heterogeneous catalysts (see Section 2.4) [15, 26]. In 2006
Heinekey and Goldberg used Brookhart’s catalyst \( \text{Ir}^{(\text{BuPOCOP}^\text{Bu})\text{H}_2} \)
\( (\text{BuPOCOP}^\text{Bu} = \kappa^3-\text{PCP}-1,3-\text{OP}^\text{Bu}_2)\text{C}_6\text{H}_3) \) catalyst (30) to efficiently
dehydrocouple \( \text{H}_3\text{B} \cdot \text{NH}_3 \) to form the purported cyclic pentamer \( [\text{H}_2\text{BNH}_2]_5 \) ([27]
although this product was later reassigned by Manners and co-workers as \( [\text{H}_2\text{BNH}_2]_n \) \( (n \sim 20) \) [23]
At 1 mol% an impressive ToF of 1500 h\(^{-1} \) was recorded. At long
reaction times a dormant new species is formed, assigned as the sigma–borane complex \( \text{Ir}^{(\text{BuPOCOP}^\text{Bu})\text{H}_2(\text{BH}_3)} \) (31) (Figure 10),[99]
which can be regenerated to form a catalytically active species on addition of \( \text{H}_2 \).
Related sigma complexes of 30 bound to pinacol borane and 9-BBN have also been reported.
Various kinetic data of the hydrogen release process using this catalyst have been determined, and all follow
a first order dependence on amine-borane, for \( \text{H}_3\text{B} \cdot \text{NH}_3 \) and \( \text{H}_3\text{B} \cdot \text{NMeH}_2 \) [100].
Interestingly, for this system, dehydrocoupling of \( \text{H}_3\text{B} \cdot \text{NMe}_2\text{H} \) is sluggish at best.
Calculations suggest a concerted process for \( \text{B}–\text{H}/\text{N}–\text{H} \) activation at the Ir–centre
[101].

![Figure 10 The structure of \( \text{Ir}^{(\text{BuPOCOP}^\text{Bu})(\text{H})_2(\text{BH}_3)} \) (31)](image)

In 2007 Baker reported that \( \text{Ni(NHC)}_2 \) systems were active catalysts for the
dehydrogenation of ammonia–borane [102]. A variety of NHC ligands were used,
with Enders’ carbene \( (1,3,4\text{-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene}) \)
affording the most active catalyst (Scheme 18). First order rate constants were
determined, and KIE experiments indicated that both \( \text{B}–\text{H} \) and \( \text{N}–\text{H} \) bonds were being
broken in the rate determining step(s). This report generated considerable interest with regard to mapping the processes occurring using computational methods [103-107]. In particular the non–innocent role of the NHC ligands, by mediating hydrogen transfer from the amine–borane to the Ni–centre, and the role of free carbene in dehydrogenation was revealed.

Scheme 18 Dehydrocoupling of H$_3$B·NH$_3$ with Ni(cod)$_2$ and Enders’ carbene.

In 2009, Weller and Hall conducted a detailed experimental and computational study[66] on the dehydrocoupling of H$_3$B·NMe$_2$H by the latent low-coordinate complex [Rh(P$^\text{i}$Bu$_3$)$_2$][BAr$_4^-$][108] (5 mol%, TOF = 34 h$^{-1}$) to afford [H$_2$BNMe$_2$]$_2$. Coordination of H$_3$B·NMe$_2$H to [Rh(P$^\text{i}$Bu$_3$)$_2$][BAr$_4^-$] forms the sigma complex [Rh(P$^\text{i}$Bu$_3$)$_2$(η$^2$-H$_3$B·NMe$_2$H)][BAr$_4^-$] (32, Scheme 19). A complex pathway was calculated for the lowest energy dehydrogenation of 32. Either initial B—H activation and N—H transfer, or initial N—H activation and B—H transfer, occurs to yield the aminoborane complex [Rh(P$^\text{i}$Bu$_3$)$_2$(H$_2$)(η$^2$-H$_2$B=NMMe$_2$)][BAr$_4^-$] (33). N—H activation was calculated to be rate-limiting in either pathway. Then, H$_2$ loss followed by dissociation of H$_2$B=NMMe$_2$, or vice versa, forms [H$_2$BNMe$_2$]$_2$ and regenerates the Rh$^\text{I}$ fragment. A constant oxidation state Rh$^\text{III}$ cycle was also proposed. Experimentally H$_3$B·NMe$_2$BH$_2$·NMe$_2$H was observed as an intermediate during catalytic dehydrocoupling and its role probed further. The linear diborazane complex [Rh(P$^\text{i}$Bu$_3$)$_2$(η$^2$-H$_3$B·NMe$_2$BH$_2$·NMe$_2$H)][BAr$_4^-$] was stable in 1,2-C$_6$H$_4$F$_2$ solution
but upon addition of excess $\text{H}_3\text{B} \cdot \text{NMe}_2 \text{BH}_2 \cdot \text{NMe}_2 \text{H}$, formed $[\text{H}_2\text{BNMe}_2]_2$ with $\text{H}_2\text{B} = \text{NMe}_2$ also observed, suggesting that $\text{B} - \text{N}$ cleavage is occurring rather than a simple intramolecular dehydrocyclisation.

**Scheme 19** Initial dehydrogenation of 32. $[\text{BAR}^4]$ anions not shown.

The first example of well-defined homogeneous catalytic dehydropolymerisation of amine-boranes was reported by Manners and co-workers in 2008 [14]. The dehydropolymerisation of $\text{H}_3\text{B} \cdot \text{NRH}_2$ ($R = \text{H, Me, }^{\text{t}}\text{Bu}$) mediated by 30 formed $[\text{H}_2\text{BNRH}]_n$ (Scheme 20). With $R = \text{Me}$, high molecular weight $[\text{H}_2\text{BMeH}]_n$ was isolated ($M_n = 55200 \text{ g mol}^{-1}$, PDI = 2.9, Figure 11c). The $^{11}\text{B}$ NMR spectrum of the polymer shows a broad resonance consistent with multiple $^{11}\text{B}$ environments within the polymer chain (Figure 11b).

**Scheme 20** Catalytic dehydropolymerisation of amine-boranes using 30.
In a detailed follow-up paper, on the basis of molecular weight versus conversion experiments alongside other markers, a modified chain growth mechanism was proposed for this system, in which a slow initial dehydrogenation of H₃B·NMeH₂ is followed by fast insertion of the resulting H₂B=NMeH [23]. Manners also demonstrated that a variety of other catalysts based on rhodium and ruthenium were active in dehydropolymerisation [23]. A recent computational study explored the mechanism of the polymerisation of H₂B=NH₂ by 30 (although concomitant dehydrogenation of the amine–borane was not probed) and also implicated a chain growth mechanism, as suggested experimentally by Manners. The proposed mechanism for propagation involves end chain growth; the lone pair on the NH₂ end of the chain interacts with the Lewis acidic BH₂ group of the entering H₂B=NH₂ molecule [29]. This suggested mechanism contrasts with a coordination insertion mechanism, in which a transient aminoborane inserts into a growing polymer chain at the metal centre, similar to Zielger–Natta olefin polymerisation.
Scheme 21 Hydrogen redistribution reaction of H$_3$B·NMe$_2$BH$_2$·NMe$_3$.

The role of 30 in the redistribution of linear diborazanes has also been probed. The diborazane H$_3$B·NMe$_2$BH$_2$·NMe$_3$ was prepared to act as a ‘model’ diborazane as it does not have a functional N—H group. This can undergo both thermal (70 °C, THF) and metal catalysed (20 °C, 1 mol% [Ir], THF) redistribution reactions to form H$_3$B·NMe$_3$ and [H$_2$BNMe$_2$]$_2$ (Scheme 21). Kinetic analyses and simulations were used to probe the metal-catalysed pathway. The model suggested that 30 reacts with H$_3$B·NMe$_2$BH$_2$·NMe$_3$ to form a proposed sigma complex 34, from which a direct redistribution reaction gives H$_2$B=NMe$_2$ and a sigma complex 35 (Scheme 22). Dimerisation of H$_2$B=NMe$_2$ affords [H$_2$BNMe$_2$]$_2$, and the kinetic simulations showed that, as well as the expected off-metal dimerisation, the dimerisation was also being catalysed by 35, or a closely related fragment. Related to this, the pincer complex [Pd(‘BuPCP’Bu)(OH$_2$)][PF$_6$] (‘BuPCP’Bu = 2,6-C$_6$H$_3$(CH$_2$P‘Bu)$_2$) has been shown to release one equivalent of H$_2$ on reaction with H$_3$B·NH$_3$, and DFT modelling also suggested an on-metal cyclodimerisation to form [H$_2$BNH$_2$]$_2$ [109].
Scheme 22 Model suggested for the metal-catalysed hydrogen redistribution reaction.

The redistribution chemistry of the more complex (i.e. containing N—H groups) linear diborazane $\text{H}_3\text{B} \cdot \text{NMeHBH}_2 \cdot \text{NMeH}_2$, first noted by Weller and Manners as the product of a single oligomerisation of $\text{H}_3\text{B} \cdot \text{NMeH}_2$, was also explored by Manners and co–workers. Treatment of $\text{H}_3\text{B} \cdot \text{NMeHBH}_2 \cdot \text{NMeH}_2$ with 0.6 mol% yielded high molecular weight $[\text{H}_2\text{BNMeH}]_n$ ($M_n = 67400$, PDI = 1.4), with the parent amine-borane $\text{H}_3\text{B} \cdot \text{NMeH}_2$ observed as an intermediate. Hydroboration trapping experiments with cyclohexene (Section 2.2) did not lead to $\text{Cy}_2\text{B} = \text{NMeH}$. Nonetheless, the observation of $\text{H}_3\text{B} \cdot \text{NMeH}_2$ suggests that $\text{H}_2\text{B} = \text{NMeH}$ is formed, either remaining on-metal, or polymerising rapidly relative to the rate of hydroboration. By contrast, metal-free thermolysis of $\text{H}_3\text{B} \cdot \text{NMeHBH}_2 \cdot \text{NMeH}_2$ at 70 °C in THF led to the formation of $\text{H}_3\text{B} \cdot \text{NMeH}_2$ and the cyclic trimer $[\text{H}_2\text{BNMeH}]_3$, presumed to arise from trimerisation of $\text{H}_2\text{B} = \text{NMeH}$. Addition of cyclohexene resulted in the formation of the trapping product $\text{Cy}_2\text{B} = \text{NMeH}$, implying free $\text{H}_2\text{B} = \text{NMeH}$ is present in solution and that hydroboration is kinetically competitive with trimerisation [28, 110]
Scheme 23 Proposed mechanism for the metal-catalysed redistribution of H$_3$NMeHBH$_2$·NMeH$_2$.

In 2011, Weller and Manners reported that the dehydrocoupling of H$_3$NMeHBH$_2$·NMeH$_2$ with the cationic rhodium chelating phosphine system [Rh(Ph$_2$P(CH$_2$)$_x$PPh$_2$)(η$^6$-C$_6$H$_5$F)][BAR$_4$] (x = 3 – 5) produced high molecular weight and narrow polydispersity polyaminoborane [H$_2$BNMeH]$_n$ (when x = 4, $M_n$ = 144000 g mol$^{-1}$, PDI = 1.3) (Scheme 24) [65]

Scheme 24 Dehydropolymerisation by [Rh(Ph$_2$P(CH$_2$)$_x$PPh$_2$)(η$^6$-C$_6$H$_5$F)][BAR$_4$] (x = 3 – 5). [BAR$_4$] not shown.

These catalysts were also efficient in dehydrocoupling H$_3$B·NMe$_2$H to form [H$_2$BNMe$_2$]$_2$ (fastest TOF ~ 1250 h$^{-1}$ when x = 3) following an induction period of approximately five minutes. The bite angle correlated with binding strength in the related sigma complexes [Rh(Ph$_2$P(CH$_2$)$_x$PPh$_2$)(η$^2$-H$_3$B·NMe$_3$)][BAR$_4$] (x = 3 – 5); the smallest bite angle (x = 3) has the weakest sigma binding of H$_3$B·NMe$_3$ and the
fastest dehydrocoupling activity of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$. Tests indicated a homogeneous catalyst, and, although the reason for the induction period is yet to be deduced, it was speculated on the basis of ESI-MS experiments that this temporal profile was due to the formation of an initial inactive dimeric species, possibly in a slow equilibrium with an active monomeric species. Independent computational work on this system has suggested dimerisation forms an inactive hydridoboryl species, and the active catalyst is monomeric [111].

One of the fastest dehydrocoupling catalysts that has been reported is the Ni$^+$ species $[\text{Ni}(\text{trop}_2\text{NH})(\text{OOCCF}_3)]$ (trop$_2$NH = bistropylidenylamine) (36, Scheme 25) [112]. At 0.3 mol% of 36 one molar equivalent of hydrogen is released from a solution of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ in less than 1 minute (TOF $\sim$ 20000 h$^{-1}$) to form $[\text{H}_2\text{BNMe}_2]_2$. Interestingly the amidoborane $\text{K}[\text{NMe}_2\text{BH}_3]$ is used as co-catalyst (1 – 3 mol%) and, although its role was not commented upon, it is tempting to speculate that the active species is a Ni–amidoborane. During dehydrocoupling, the aminoborane $\text{H}_2\text{B}=\text{NMe}_2$ is observed as an intermediate, although further mechanistic details were not reported.

Scheme 25 Dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ with 36.

Alcaraz and Sabo-Etienne reported the novel dehydrogenative cyclisation of the diamine-monoboranes 37-Me, 37-iPr and 39 leading to cyclic diaminoboranes 38-Me, 38-iPr and 40, respectively, using the $[\text{Ru}(\text{PCy}_3)_2(\text{H})_2(\text{H}_2)_2]$ catalyst at 2.5 mol%
loading (Scheme 26) [113]. The reaction was slower in the presence of bulkier N-substituents (3 hours for complete formation of \textit{38-Me versus} 8 hours for complete formation of \textit{38-iPr}), but lengthening the alkyl chain length of the starting amine-borane (\textit{37-Me versus 39}) did not significantly affect the rate. [Ru(PCy$_3$)$_2$(H)$_2$(H$_2$)$_2$] remained the resting state throughout catalysis, and could be reused twice.

\textbf{Scheme 26} Dehydrocyclisation of amine-boranes using [Ru(PCy$_3$)$_2$(H)$_2$(H$_2$)$_2$]. R = Me, iPr.

In 2013, Weller explored the mechanism of the dehydrocoupling of H$_3$B·NMe$_2$H with the neutral rhodium catalyst Rh(PCy$_3$)$_2$(H)$_2$Cl after its catalytic activity had been implicated in an earlier study with [Rh(PCy$_3$)$_2$][BAr$_{4}$$^\text{F}$] (\textit{vide infra}) [13, 32]. Investigations showed that Rh(PCy$_3$)$_2$(H)$_2$Cl is a moderate catalyst for dehydrogenation of H$_3$B·NMe$_2$H (2 mol\% [Rh], TOF = 28 h$^{-1}$) to form H$_2$B=NMe$_2$, which dimerises to form [H$_2$BNMe$_2$]$_2$ (Scheme 27) [32].
Scheme 27 Dehydrocoupling of H₃B·NMe₂H with Rh(PCy₃)₂(H)₂Cl.

Mechanistic investigations indicated that N—H activation (either preceding or following B—H activation) is turnover-limiting in this system, indicated by a large primary kinetic isotope effect observed using H₃B·NMe₂D.

The {Ir(PCy₃)₂(H)₂}⁺ fragment has proved a useful, albeit slow (10-20 mol%, TOF ~ 0.1 h⁻¹), catalyst for the dehydrogenation and dehydrocoupling of H₃B·NMe₂H,[19] H₃B·NMeH₂,[33] and H₃B·NH₃,[70] in which metal-bound products and intermediates can be observed, allowing direct comparisons between the different amine-boranes. Reaction of the bis-dihydrogen complex [Ir(PCy₃)(H)₂(H₂)]₂[BAr₅F₄], a source of {Ir(PCy₃)₂(H)₂}⁺, with H₃B·NMe₂H forms ultimately [H₂BNMe₂]₂, and the major metal-containing product is the bound aminoborane complex [Ir(PCy₃)₂(H)₂(η²-H₃B=NMMe₂)][BAr₅F₄] (41). The mechanism of dehydrogenation of [Ir(PCy₃)₂(H)₂(η²-H₃B·NMMe₂H)][BAr₅F₄] to form 41 has been suggested by calculation to be sequential B—H activation, H₂ loss from the metal, and rate-limiting N—H activation [19]. By contrast, H₃B·NMeH₂ catalytically undergoes an on–metal oligomerisation event to yield the diborazane H₃B·NMMeBH₂·NMeH₂, with the sigma complex [Ir(PCy₃)₂(H)₂(η²-H₃B·NMMeBH₂·NMeH₂)][BAr₅F₄] (42) observed during the dehydrocoupling. Furthermore, H₃B·NH₃ undergoes further oligomerisation events, yielding insoluble [H₂BNH₂]ₙ. During the dehydrocoupling,
various species with bound oligomeric units, \([\text{Ir} \left( \text{PCy}_3 \right)_2 \left( \text{H}_2 \right)_2 (\eta^2 - \text{H}_3 \text{B} \cdot (\text{NH}_2 \text{BH}_2)_n \cdot \text{NH}_3) \right] \left[ \text{BAR}^F_4 \right] \) \((43_n)\) \((n = 0 - 4)\), were observed using ESI–MS techniques (Scheme 28).

Scheme 28 Metal-bound products in the reaction of excess amine-borane with \(\{\text{Ir} \left( \text{PCy}_3 \right)_2 \left( \text{H}_2 \right)_2 \}^+\). [BAR\(^F_4\)] not shown.

Calculations conducted on the model system \(\{\text{Ir} \left( \text{PMe}_3 \right)_2 \left( \text{H}_2 \right)_2 \}^+\) for the dehydrogenation and oligomerisation of \(\text{H}_3 \text{B} \cdot \text{NH}_3\) propose a pathway (Scheme 29) involving: (i) initial dehydrogenation of the amine-borane; (ii) dehydrogenation of a second amine-borane; and (iii) B—N coupling. Step (i) was calculated to have the highest barrier, and the B—N coupling step (iii) had the lowest barrier. Calculations showed that subsequent oligomerisations were also viable for this system, as observed experimentally. With \(\text{H}_3 \text{B} \cdot \text{NMeH}_2\), the B—N coupling barrier for subsequent oligomerisations was significantly raised, consistent with the experimental observations of a single oligomerisation event. With the more sterically encumbered \(\text{H}_3 \text{B} \cdot \text{NMe}_2\text{H}\), the calculated B—N coupling barrier was prohibitively high, consistent with no experimental observation of linear diborazane. Although likely systems-
specific, this selectivity illustrates the potential importance of steric in the dehydrocoupling of amine-boranes. Moreover, the calculations point to outer sphere N–H···H–B interactions as being important to lowering barriers to dehydrogenation processes, as has been reviewed by others more generally for amine–boranes [114].

Scheme 29 Calculated pathway by MacGregor and Weller for the dehydrogenation and coupling of H₃B·NH₃. R = H (first oligomerisation), R = BH₂NH₂ (second oligomerisation). [Ir] = {Ir(PR’₃)₂}⁺ (R’ = Cy, experiment; Me, computation).

As introduced in Section 2.5, Manners and co-workers recently found that [CpFe(CO)₂I], under conditions of photoirradiation, acts as a homogeneous catalyst in the dehydrocoupling of H₃B·NMe₂H to form [H₂BNMe₂]₂ [51]. A two-stage
mechanism was proposed for this system to account for the formation of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ and the on-metal dehydrocyclisation to yield $[\text{H}_2\text{BNMe}_2]_2$ (Scheme 30), similar to that invoked for Cp$_2$Ti systems [69].

Scheme 30 Proposed two stage mechanism for the homogeneous dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ using CpFe(CO)$_2$I.

Experimental evidence and DFT calculations support initial coordination of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ to the photogenerated $[\text{FeCp(CO)}]^+$ fragment, forming the sigma complex 44. Addition of a second equivalent of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ results in a B—N bond formation process to yield the bound $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ complex 45. $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ and dihydrogen are displaced by $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ to reform 44. The second cycle proposes that the just formed $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ displaces $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ in 44 to form the chelate sigma complex 46, not unrelated to Rh—
complexes crystallographically characterised with this motif [31]. Subsequent on-metaldidehydrocyclisation occurs to form \([\text{H}_2\text{BNMe}_2]_2\) sigma bound to the metal (47). \([\text{H}_2\text{BNMe}_2]_2\) and dihydrogen are displaced by \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\), reforming 44. It was speculated that the electronegative iodide ligand enables heterolytic Fe—I cleavage under photoirradiation, maintaining an Fe\(\text{II}\) species. However, the dimeric complexes \([\text{CpFe(CO)}_2]_2\) and \(\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{NCMe})\) formally are in the lower Fe\(\text{I}\) oxidation state and already have Fe—Fe interactions; these factors aid nanoparticle formation, and hence heterogeneous catalysis is observed (Section 2.5).

![Scheme 31](image)

**Scheme 31** Dehydrocoupling of \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\) and \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) using 4. \([\text{BAR}_4]^–\) not shown.

A recent report by Weller, Manners and Lloyd-Jones has explored in detail the catalytic dehydrocoupling of \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\) and \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) with 4 (Scheme 31) [12]. Open to argon, thus allowing for release of \(\text{H}_2\), complex 4 (0.2 mol%) dehydrocouples \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\) rapidly, forming \([\text{H}_2\text{BNMe}_2]_2\) (TOF ~ 1000 h\(^{-1}\)), following an induction period of approximately 5 minutes. \(\text{H}_2\text{B} = \text{NMe}_2\) was observed as an intermediate with only negligible amounts of \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}\) detected, a similar reaction profile to the closely related \([\text{Rh}(\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2)(\eta^6\text{-C}_6\text{H}_5\text{F})][\text{BAR}_4]^–\) system (TOF ~ 1250 h\(^{-1}\) for \(x = 3\)). Under these conditions, the decay of \([\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}]\) appeared pseudo-zero order at high \([\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}]\) (approximately 0.1 M), becoming pseudo-first order
at lower $[\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}]$. This suggested saturation kinetics were operating, corroborated by kinetic modelling. By contrast, under closed conditions, in which a pressure of $\text{H}_2$ can build, the reaction profile appeared pseudo-first order over the entire concentration range (post induction period). With $\text{H}_3\text{B} \cdot \text{NMeH}_2$, in an open system, 0.2 mol% 4 catalysed the formation of $[\text{H}_2\text{BNMeH}]_n$ ($M_n = 22700 \text{ g mol}^{-1}$, PDI = 2.1) in 1,2-C$_6$H$_4$F$_2$ solution within 2 hours, also with an induction period observed. Similar to $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$, saturation kinetics were apparent. Molecular weight versus conversion experiments indicated a chain growth mechanism; in particular, high molecular weights were achieved at less than 20% conversion. In THF solvent, the catalysis was slower (85% completion, 19 hours) but produced higher molecular weight $[\text{H}_2\text{BNMeH}]_n$ ($M_n = 52200 \text{ g mol}^{-1}$, PDI = 1.4). Conversely, in a sealed system, the molecular weight was significantly lower ($M_n = 2800 \text{ g mol}^{-1}$, PDI = 1.8) and took approximately 24 hours to reach ~95% completion. $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy of the product isolated from the closed system provided evidence for the presence of shorter chain oligomers (Figure 12).
Figure 12  (a) $^{11}$B{$^1$H} NMR spectrum of [H$_2$BNMeH]$_n$ ($\delta \sim$ -5) isolated after dehydropolymerisation of H$_3$B·NMeH$_2$ (4, 0.2 mol%) under open conditions (signal at $\delta$ -17 is unreacted H$_3$B·NMeH$_2$). (b) $^{11}$B{$^1$H} NMR spectrum of material isolated after reaction under sealed conditions (4, 0.2 mol%). H. C. Johnson, E. M. Leitao, G. R. Whittell, I. Manners, G. C. Lloyd-Jones and A. S. Weller, *J. Am. Chem. Soc.*, 2014, **134**, 1520. Copyright 2014 American Chemical Society.

Exploring the rationale behind the induction period, heterogeneous catalysis was ruled out. Additionally, the authors noted that the induction period was approximately twice as long using H$_3$B·NMe$_2$D compared with H$_3$B·NMe$_2$H, whereas no change was observed using D$_3$B·NMe$_2$H. This implied that N—H activation was rate-limiting in the formation of the active species, which is proposed to be an amido-boryl complex 48. These, and other, observations led to a proposed catalytic cycle applicable for both the dehydropolymerisation of H$_3$B·NMeH$_2$ and dehydrogenation of H$_3$B·NMe$_2$H (Scheme 32).
**Scheme 32** Suggested cycle for the dehydropolymerisation of H$_3$B·NMe$_2$H (R’ = H or growing polymer chain; R = H) and dehydrogenation of H$_3$B·NMe$_2$H (R’ = H, R = Me). [Rh] = {Rh(Xantphos)}$^+$. 

Stoichiometric reactions of 4 with 2 equivalents of H$_3$B·NMe$_2$H or H$_3$B·NMeH$_2$ led to the immediate formation of the Rh$^{III}$ dihydride [Rh$(\kappa^3$·P,O,P-Xantphos)(H)$_2$(η$^1$-H$_3$B·NMeRH)][BAr$^F$$_4$] (R = Me, H), and it was speculated that these species were the starting points in the catalytic cycle. The induction period (i.e. initiation) occurs, involving N—H activation, to yield 48. Complex 48 as written would have a vacant site, allowing the reversible binding of another equivalent of amine-borane, forming 48-AB, as implicated by saturation kinetics. From 48-AB, dehydrogenation (with H$_3$B·NMe$_2$H) or chain propagation (with H$_3$B·NMeH$_2$) occurs, for the latter leading to a growing polymer from the metal centre. At high [amine-borane], the turnover limiting step occurs after formation of 48-AB, resulting in a pseudo-zero order decay of [amine-borane], but at lower [amine-borane], the formation of 48-AB is dependent upon [amine-borane], giving pseudo-first order kinetics. Chain termination can arise from H$_2$ binding to 48 and undergoing heterolytic H$_2$ cleavage,[115] consistent with the observations of shorter polymer chains, and first order decay of [H$_3$B·NMe$_2$H], under an atmosphere of H$_2$. THF can also bind competitively with H$_2$ and H$_3$B·NMeH$_2$, slowing catalysis but attenuating chain termination, resulting in higher molecular weight [H$_2$BNMeH]$_n$. This tuning of molecular weight has provided valuable insight into methods of controlling polyaminoborane formation.

### 2.8.4 Dehydrocoupling of Amine-Boranes Involving Ligand Cooperativity
In 2008, Fagnou and co-workers reported the rapid dehydrogenation of H₃B·NH₃ to form [H₂BNH₂]ₙ with 0.03 mol% loadings of the catalyst [Ru(PᵢPr₂CH₂CH₂NH₂₂Cl₂] (49), activated by 0.9 mol% KO'Bu (TOF ~ 20000 h⁻¹) [59]. Furthermore, 0.5 mol% of 49 could promote release of two equivalents of H₂ from H₃B·NMeH₂ within ten minutes. An outer sphere mechanism was proposed using DFT calculations on the model complex [Ru(PMe₂CH₂CH₂NH₂)(PMe₂CH₂CH₂NH)₂H] (50-Me), the product of activation of [Ru(PMe₂CH₂CH₂NH₂₂Cl₂] (49-Me) with KO'Bu (Scheme 33). The mechanism proposed invokes protonation of the ligand by the amine (51-Me), loss of H₂B=NH₂ to form 52-Me, and rate-limiting formation of the dihydrogen complex 53-Me.

Scheme 33 Proposed mechanism for the dehydrogenation of H₃B·NH₃ by 50-Me.

In 2009, Schneider and co-workers reported that the related bifunctional catalyst [Ru(PNP)(H)(PMe₃)] {Figure 13, PNP = N(CH₂CH₂PᵢPr₂)₂} (54) was extremely active in the dehydrocoupling of H₃B·NH₃ to release approximately one equivalent of dihydrogen (TOF ~ 12000 h⁻¹ at 0.1 mol% 54) to form [H₂BNH₂]ₙ, with small
amounts of borazine also observed [57]. H$_3$B·NMe$_2$H was also rapidly dehydrocoupled by 54 (2 mol%), forming [H$_2$BNMe$_2$]$_2$, until approximately 70% conversion (initial TOF $\sim$ 3600 h$^{-1}$); after this point, a much slower regime operates (TOF $\sim$ 1.5 h$^{-1}$), suggesting a change in mechanism [30]. During the fast regime, the species trans-[Ru(PNP$^H$)(H)$_2$(PMe$_3$)] (55) was observed as the resting state and, indeed, starting catalysis with 55 showed very similar kinetics as with 54. However, a new species evolved throughout the dehydrocoupling, [Ru(PNP$^B$)(H)$_2$(PMe$_3$)] (PNP$^B$ = NMe$_2$BH$_2$N(CH$_2$CH$_2$PPr$_2$)$_2$) (56), containing a four membered bora-metallacycle. The use of isolated 56 as the dehydrocoupling catalyst gave essentially the same catalytic activity as for the slow regime.

Figure 13 Schenider’s bifunctional ruthenium complexes.

A more detailed study published in 2013 focused on the catalytic dehydrocoupling of H$_3$B·NH$_3$ with 54, 55 and [Ru($^{Me}$PNP)(H)(PMe$_3$)] (PNP$^{Me}$ = MeN(CH$_2$CH$_2$PPr$_2$)$_2$) (57) [21]. The methylation of the pincer nitrogen atom in 57 prevents the bifunctional reactivity that is thought to be key in rationalising the high activities of these complexes. Accordingly, catalysis using 57 exhibited a rate of H$_2$ evolution two orders of magnitude lower than with 54 or 55, confirming the importance of amine cooperativity in these systems.
In contrast to the previous results, in which 54 and 55 appeared to operate within the same catalytic cycle,[30] on closer examination differences were found between the two, suggesting different mechanisms for each [21]. Both catalysts demonstrated first order kinetics for H₂ evolution on dehydrocoupling H₃B·NH₃. On using the N-deuterated analogue H₃B·ND₃, first order kinetics were retained with 55. However, the H₂ evolution became zero order with 54, implying a change in the turnover limiting step upon deuteration for this system. Additionally, some cross-linking of [H₂BNH₂]ₙ was observed with 55, which was not detected in [H₂BNH₂]ₙ produced with 54.

For catalysis with 55, a combination of DFT (using a PMe₂-truncated model) and experimental methods led to a proposed mechanism for the formation of [H₂BNH₂]ₙ from H₃B·NH₃, depicted in Scheme 34.

**Scheme 34** Dehydrogenation and dehydrocoupling pathways proposed by Schneider and co-workers.
The mechanism involves dehydrogenation of \( \text{H}_3\text{B} \cdot \text{NH}_3 \), via initial \( \text{N}—\text{H} \) activation, to form \( \text{H}_2\text{B}=\text{NH}_2 \) (Pathway A), which undergoes oligomerisation by catalytic insertion of \( \text{H}_2\text{B}=\text{NH}_2 \) into the \( \text{N}—\text{H} \) bond of the substrate (Pathway B). Experiments with \( \text{H}_3\text{B} \cdot \text{NMe}_3 \) and \( \text{Et}_3\text{B} \cdot \text{NH}_3 \) in the presence of 1 mol\% 55 showed that ‘head-to-tail’ coupling to yield \( \text{Et}_3\text{B} \cdot \text{NH}_2\text{BH}_2 \cdot \text{NMe}_3 \) did not occur, indicating that proton and hydride transfer from the same substrate molecule to the catalyst is required in this system, as suggested in the proposed mechanism.

Further mechanistic insight into dehydropolymerisation of amine–boranes was also obtained by Gordon, Baker, et al. in the dehydrocoupling of \( \text{H}_3\text{B} \cdot \text{NH}_3 \) to selectively form \( \text{[H}_2\text{BNH}_2]_n \) using \([\text{Fe(PCy}_2\text{CH}_2\text{CH}_2\text{PCy}_2](\text{NPhCH}_2\text{CH}_2\text{NPh})] \) (58) at 5 mol\% loading (TOF ~ 80 h\(^{-1}\)) (Scheme 35) [68]. The catalyst could not be recycled; during catalysis, a black precipitate – presumed to be iron metal – was observed, indicating catalyst decomposition during dehydrocoupling. \textit{In situ} NMR spectroscopy suggested de-coordination of one of the chelating phosphine arms during catalysis, possibly responsible for the observed induction period (ca. 2 minutes). Two mechanisms were proposed to account for experimental observations, one of which is shown in Scheme 36.

![Scheme 35 Dehydrocoupling of H3B-NH3 by 58.](image-url)
Scheme 36 A proposed mechanism for the dehydropolymerisation of H$_3$B·NH$_3$ by 58.

Initial dissociation of a phosphine arm enables coordination of H$_3$B·NH$_3$ to form 59. Protonation of one arm of the amido ligand by the amine-borane (affording a bound amido-borane, 60) follows, and the resulting amino arm of the ligand can dissociate, allowing ligation of a second equivalent of H$_3$B·NH$_3$ (61). From this, successive dehydrogenation and insertion steps yield [H$_2$BNH$_2$]$_n$. Throughout the proposed mechanism, no free H$_2$B=NH$_2$ is implicated, and experimentally H$_2$B=NH$_2$ was neither detected directly nor with cyclohexene trapping. This is consistent with previous work by some of the authors,[25] and others,[17] suggesting that H$_2$B=NH$_2$ must remain bound to the metal to oligomerise (Section 2.2), although other work has suggested that cyclohexene trapping does not necessarily rule out the presence of free H$_2$B=NH$_2$ if the hydroboration is not kinetically competitive with oligomerisation [21, 28].
Scheme 37 Dehydrocoupling of H₃B·NH₃ by 62.

Williams also reported ligand cooperativity in the dehydrocoupling of H₃B·NH₃ to yield borazine using Shvo’s ruthenium catalyst, 62 (Scheme 37). The catalyst showed reasonable activity at 5 mol% 62 and 2 mol% EtOH (TOF ~ 18 h⁻¹ for release of 2 eq. H₂ at 70 °C) [58]. H₂ release measurements (total 2 eq.) produced a kinetic profile with three regimes evident: (i) initiation period; (ii) fast catalysis showing a zero order decay of [H₃B·NH₃]; (iii) slow catalysis showing a first order decay of [H₃B·NH₃]. The induction period was attributed to the dissociation of 62 into 63 and 64 (Scheme 38). Fast dehydrogenation follows, in which H—H bond formation is the rate determining step, similar to Fagnou’s mechanism [59] and 63 is the resting state observed during catalysis [58]. At high [borazine], the third regime dominates. This is attributed to hydroboration of 64 by borazine, to form 66 (Figure 14). H₃B·NH₃ is required to convert 66 back into 63, which is the rate-limiting step in this slow regime, and thus the reaction becomes first order in [H₃B·NH₃] [116].
Scheme 38 Suggested catalytic cycle for the catalyst initiation and fast dehydrocoupling of H$_3$B·NH$_3$.

Figure 14 Complexes 66 and 67.

To avoid deactivation by borazine, the same group developed a catalyst with an oxygen atom already borylated, 67 (Figure 12). 67 catalysed the dehydropolymerisation of H$_3$B·NH$_3$ to form a mixture of borazine and polyborazylene (2 mol%, 70 °C, TOF ~ 25 h$^{-1}$ for release of 2 equivalents of H$_2$ in a tetraglyme slurry). Significantly for potential practical applications, the catalysis could be conducted under air and the catalyst could be reused; four successive runs in
a single reactor produced similar rates and quantities of H₂ loss in each run (2.1 – 2.3 eq.). To date, mechanistic details have not been unravelled, although a mechanism involving dual-site cooperativity is likely [117].

Phillips and co-workers recently reported the fast dehydrocoupling of H₃B·NH₃ and H₃B·NMe₂H (TOF ~ 400 h⁻¹ for H₃B·NMe₂H at 42 °C in THF) using 0.5 mol% of the bifunctional Ru(II) β-diketiminato complex, 68 (Scheme 39) [118]. Mechanistic studies focused on H₃B·NMe₂H as, under these reaction conditions, H₃B·NH₃ can thermally release H₂ in the absence of catalyst. The proposed mechanism for initial dehydrogenation is that of hydride coordination from BH₃ by the Ru(II) centre, forming 69. The acidic NMe₂H proton can then protonate the β-carbon position of the β-diketiminato ligand, resulting in 70. 68 had been previously shown to reversibly heterolytically cleave H₂ to yield 70 [119]. An induction period was observed in the dehydrocoupling, thought to be the slow initial formation of 70, which is the active catalyst for subsequent dehydrogenations. An experiment performed using a THF solution that had been saturated with H₂ resulted in faster dehydrogenation and a reduced induction period compared with the N₂-flushed THF used as the normal reaction solvent, demonstrating the rate is dependent on the rate of formation of 70.
Scheme 39 Proposed mechanism for the initial dehydrogenation of H$_3$B·NMe$_2$H using 68. [OTf]$^-$ anions not shown.

Wass and co-workers reported a fast dehydrocoupling catalyst based upon a ‘frustrated’ Lewis pair, but where the Lewis acid (typically a fluorinated aryl borane) was replaced with an electrophilic Zr$^{IV}$ centre. The species [Cp$_2$ZrOC$_6$H$_4$P$^i$Bu$_2$][B(C$_6$F$_5$)$_4$] (71) dehydrocoupled H$_3$B·NMe$_2$H rapidly (1 mol% 71, TOF ~ 600 h$^{-1}$), being the fastest reported Group IV catalyst to our knowledge (Scheme 40) [120]. Wass’ proposed mechanism (Scheme 41) is different from those of other Group IV metallocene catalysts (Section 2.8.1). Following sigma coordination of H$_3$B·NMe$_2$H to the Zr$^{IV}$ centre to form 72, ligand-assisted dehydrogenation yields H$_2$B=NMe$_2$ and 73. The loss of hydrogen from 73 is facile, regenerating 71. The reaction using [Cp$_2$ZrO$^i$Bu][B(C$_6$F$_3$)$_4$] did not dehydrogenate H$_3$B·NMe$_2$H, illustrating the importance of the phosphine in this cooperative system.
Scheme 40 Dehydrocoupling of H$_3$B·NMe$_2$H with 71. [B(C$_6$F$_5$)$_4$]$^-$ anion not shown.

Scheme 41 Suggested mechanism for dehydrocoupling of H$_3$B·NMe$_2$H by 71. [Zr] = Cp$_2$Zr. [B(C$_6$F$_5$)$_4$]$^-$ anions not shown.

Ligand cooperatively in Ni(NHC) systems has been discussed in Section 2.8.3.

2.8.5 The role of solvent in dehydrocoupling using late transition metals.

Many dehydrocoupling reactions of amine-boranes are conducted in THF due to good solubility of H$_3$B·NMeH$_2$ and H$_3$B·NH$_3$ in this solvent [23]. A recent report by Conejero and López-Serrano, using [Pt(I'Bu')(I'Bu)][BAR$_4$], 74 (Scheme 42) (I'Bu = 1,3-di-tert-butylimidazol-2-ylidene, I'Bu' = cyclometalated I'Bu), showed that THF is
intimately involved in the dehydrocoupling mechanism of H$_3$B·NMe$_2$H to form [H$_2$BNMe$_2$]$_2$ [121].

Scheme 42 Dehydrocoupling of H$_3$B·NMe$_2$H with 74.

The suggested mechanism (Scheme 43), supported by DFT calculations (in which H$_3$B·NH$_3$ is used as the model amine-borane), involves the initial reaction of 74 with H$_3$B·NMe$_2$H to form a sigma complex, 75. In the presence of NMe$_2$H (thought to arise from B—N cleavage of H$_3$B·NMe$_2$H[27, 32, 95]), 75 rearranges to form the neutral 76 with expulsion of the boronium cation [(NMe$_2$H)$_2$BH$_2$]$^+$. Calculations indicated that dehydrogenation of bound H$_3$B·NH$_3$ to yield an aminoborane has a prohibitively high barrier of 42.5 kcal mol$^{-1}$. However, addition of a Lewis base such as THF or NMe$_2$H (Me$_2$O and NH$_3$ used as model analogues in the calculations) lowers the barrier to B—H activation. In THF solution, [(NMe$_2$H)$_2$BH$_2$]$^+$ and [(NMe$_2$H)BH$_2$(THF)]$^+$ are in an equilibrium. The THF adduct reacts with 76 to reform 74 and H$_2$B=NMe$_2$ with H$_2$ loss. Stoichiometric experiments showed that [(NMe$_2$H)$_2$BH$_2$]$^+$ reacted slowly with 76, leading to unidentified products, whereas [(NMe$_2$H)BH$_2$(THF)]$^+$ reacted rapidly, producing H$_2$B=NMe$_2$, supporting the proposed cycle.
Many dehydrocoupling reactions involving cationic complexes are studied in essentially non-coordinating solvents such as C₆H₅F or 1,2-C₆H₄F₂, enabling the observation of weakly sigma-bound intermediates [13, 66, 70]. Weller and co-workers have shown that sigma bound amine-boranes can be displaced by excess THF (Scheme 44) [12].

**Scheme 43** Proposed catalytic cycle. [BAR₄]⁻ not shown.

**Scheme 44** Equilibrium between [Rh(κ³-P₃O₃P-Xantphos)(H)₂(η¹-H₃B·NMe₃)][BAR₄]⁻ and [Rh(κ³-P₃O₃P-Xantphos)(H)₂(THF)][BAR₄]. [BAR₄]⁻ anions not shown.
As mentioned in Section 2.8.3, however, the formation of $[\text{H}_2\text{BNMeH}]_n$ using the cationic rhodium species 4 produced higher molecular weight material in THF than C$_6$H$_5$F, although the polymerisation took longer to reach completion. It was suggested that THF can bind to the Rh centre competitively with both amine-borane (slowing catalysis) and H$_2$ (hindering chain transfer). Solvent effects have also been noted by Manners and Weller in the off-metal dimerisation of H$_2$B=NM$_2$, with the rate of dimerisation being accelerated in MeCN [19, 20].

2.9 Generic mechanisms for dehydrocoupling of H$_3$B·NM$_2$H using transition metals

In 2012, Weller and Lloyd-Jones conducted a thorough mechanistic study on the dehydrocoupling of H$_3$B·NM$_2$H to form $[\text{H}_2\text{BNMe}_2]_2$ using the $\{\text{Rh(PCy})_3\text{L}_n\}^+$ fragment (Scheme 45) [13]. During catalysis (5 mol\% [Rh], TOF 10 h$^{-1}$), both the aminoborane H$_2$B=NM$_2$ and the linear diborazane H$_3$B·NM$_2$BH$_2$·NM$_2$H were observed by $^{11}$B NMR spectroscopy. Several important observations were noted for this system. Addition of 2 equivalents of H$_3$B·NM$_2$H to $\{\text{Rh(PCy}}_3\text{L}_n\}^+$ led first to the Rh$^I$ sigma complex $[\text{Rh(PCy}}_3\text{)}_2(\eta^2\text{-H}_3\text{B·NM}_2\text{H})][\text{BAR}_4]^+$, which then rapidly formed the Rh$^{III}$ species $[\text{Rh(PCy}}_3\text{)}_2(\text{H})_2(\eta^2\text{-H}_3\text{B·NM}_2\text{H})][\text{BAR}_4]^+$ with concomitant loss of H$_2$B=NM$_2$ (Scheme 46). This species does not lose H$_2$ easily, implying the active catalyst is a Rh$^{III}$ complex, operating at a constant oxidation state, after the initial dehydrogenation.
**Scheme 45** Catalytic dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ by $[\text{Rh}(\text{PCy}_3)_2\text{L}_n][\text{BArF}_4]$.

**Scheme 46** Stoichiometric reactivity of $\{\text{Rh}(\text{PCy}_3)_2\text{L}_n\}^+$ with $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$. $[\text{BArF}_4]^-$ not shown.

However, addition of the product $[\text{H}_2\text{BNMe}_2]_2$ to the $\text{Rh}^{\text{III}}$ species $[\text{Rh}(\text{PCy}_3)_2(\text{H})_2(\eta^2-\text{H}_2)]_2[\text{BArF}_4]$ resulted in the immediate formation of the $\text{Rh}^{\text{I}}$ complex $[\text{Rh}(\text{PCy}_3)_2(\eta^2-(\text{H}_2\text{BNMe}_2)_2)][\text{BArF}_4]$, indicating that $[\text{H}_2\text{BNMe}_2]_2$ can drive the reductive elimination of $\text{H}_2$ to reform a $\text{Rh}^{\text{I}}$ species (Scheme 47). Consistent with this, under catalytic conditions, $[\text{H}_2\text{BNMe}_2]_2$ was found to have an autocatalytic role in the dehydrocoupling catalysis by acting as a modifier to produce kinetically significant amounts of a $\text{Rh}^{\text{I}}$ catalytically active species alongside the $\text{Rh}^{\text{III}}$ species. Thus, the dehydrocoupling was shown to exist in both a constant oxidation state $\text{Rh}^{\text{III}}/\text{Rh}^{\text{III}}$ cycle (slow), and a $\text{Rh}^{\text{I}}/\text{Rh}^{\text{III}}$ cycle (faster).
Scheme 47 Reduction from Rh$^{\text{III}}$ to Rh$^{1}$ by addition of [H$_2$BNMe$_2$]$_2$. [BAr$_4$]$^-$ not shown.

Kinetic simulations indicated the presence of an additional catalyst present in constant (low) concentrations that promoted the first order dehydrogenation of H$_3$B·NMe$_2$H to give H$_2$B=NMe$_2$. Due to a constant concentration of chloride ions in solution (arising from the catalyst preparation method), it was determined that the active catalyst was the neutral species Rh(PCy$_3$)$_2$(H)$_2$Cl, whose catalytic activity was separately examined (see Section 2.8.3) [32].

The observations led to a generalised mechanistic scenario (Scheme 48) simplified into several parts: (i) dehydrogenation of H$_3$B·NMe$_2$H with a change in the oxidation state of the catalyst; (ii) dehydrogenation of H$_3$B·NMe$_2$H with no change in the oxidation state of the catalyst; (iii) the formation and cleavage of H$_3$B·NMe$_2$BH$_2$·NMe$_2$H; (iv) dehydrocyclisation of H$_3$B·NMe$_2$BH$_2$·NMe$_2$H; (v) the off-metal dimerisation of H$_2$B=NMe$_2$ to give [H$_2$BNMe$_2$]$_2$. This cycle, or parts thereof, is generally applicable to various homogeneous transition-metal catalysed systems reported. For example, dehydrogenation with a change in oxidation state has been implicated for systems based upon Ti,[69, 92] Re,[86] Cr[98] and Rh [65]. Systems remaining in a constant oxidation state, however, include cationic Rh[66] and Ir[19, 70] systems as well as bifunctional Ru catalysts [21, 59]. The formation of H$_3$B·NMe$_2$BH$_2$·NMe$_2$H from H$_3$B·NMe$_2$H and H$_2$B=NMe$_2$ has been observed with Ti,[69] Rh[66], Ir[19] and Ru[30] systems. These systems also catalyse the dehydrocyclisation of H$_3$B·NMe$_2$BH$_2$·NMe$_2$H to form [H$_2$BNMe$_2$]$_2$. 

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**Scheme 48** General mechanistic cycle for the dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$. $\text{M} =$ metal catalyst.

Manners and co-workers have suggested closely related, but alternate, schemes for the processes occurring in the dehydrogenation and dehydrocoupling of ammonia-borane and primary and secondary amine–boranes, as shown in Scheme 49 [5, 122].

2.10 Main Group Element Catalysed Dehydrocoupling of Amine-Boranes

2.10.1 Main Group Amidoboranes, Stoichiometric Studies

The use of amine-boranes as a means of chemical hydrogen storage prompted great interest in the dehydrogenation of these species. However, in the case of the parent ammonia-borane, which has the highest weight percentage of hydrogen, some of the
dehydrocoupling products are insoluble and poorly characterised. A promising avenue of study was that of group 1 and 2 amidoboranes [123, 124]. Characterised as having the general formula \([M(NH_2 \cdot BH_3)_n]\) (M = group 1 or 2 metal; n = 1 for group 1, n = 2 for group 2), these simple amidoboranes were found to have a lower release temperature for two equivalents of dihydrogen than parent ammonia-borane (90 °C for lithium and sodium amidoborane and 120-170 °C for calcium bis(amidoborane) compared to 110-200 °C for ammonia-borane). The dehydrogenation of the amidoboranes also proceeds more cleanly with little formation of borazine and other by-products observed for ammonia-borane. The structure of the calcium analogue \([Ca(NH_2 \cdot BH_3)_2(THF)_2]\) was determined by X-ray crystallography, and the molecules were found to form long chains with intermolecular sigma interactions between the B-H bonds and the calcium centres of adjacent molecules. The tetrahydrofuran solvent could be removed under vacuum at room temperature to form \([Ca(NH_2 \cdot BH_3)_2]\) [124]. The first example of a monomeric calcium amidoborane was reported by Harder et al. who used the bulky \(\beta\)-diketiminate ligand \(\{(2,6-^iPr_2C_6H_3)NC(Me)C(H)C(Me)N(2,6-^iPr_2C_6H_3) = DIPP-nacnac\}\) to stabilise the calcium centre. Reaction of the dimeric calcium hydride starting material \([(DIPP-nacnac)CaH(THF)]_2\), with ammonia-borane in a mixture of toluene and THF led to elimination of dihydrogen and formation of the amidoborane complex \([(DIPP-nacnac)Ca(NH_2 \cdot BH_3)(THF)_2]\) (77), Scheme 50. In THF solution this complex was stable, even at elevated temperatures, but in benzene solution hydrogen loss was observed and dimerisation occurred. The product was the dinuclear species \([(DIPP-nacnac)Ca(THF)];(HNBHNH \cdot BH_3)]_2\) (78) with a dianionic \((HNBHNH \cdot BH_3)^{2-}\) fragment bridging the calcium centres [125]. If a bulky substituent was attached to the nitrogen centre of the amine-borane (e.g. DIPP), a similar
monomeric amidoborane complex was formed initially. This complex lost dihydrogen, but did not dimerise to form a dinuclear species, and remained mononuclear with a borylamide ligand at the calcium centre (79), being a deprotonated analogue of an aminoborane (Scheme 50) [126]

Scheme 50 Dehydrogenation of [(DIPP-nacnac)Ca(NRH·BH3)(THF)2] (77). DIPP = 2,6-di(isopropyl)phenyl.

This ligand system was also used in an attempt to form a zinc amidoborane complex. Reaction of [(DIPP-nacnac)ZnCl] with the amidoborane salt K[H3B·NPrH] did not give the amidoborane complex as expected but a hydride species was formed, [(DIPP-nacnac)ZnH], along with oligomeric aminoborane species. The authors postulated that an amidoborane complex did form but underwent rapid β-hydride elimination of a B-H bond to form the zinc hydride and free, reactive aminoborane which quickly formed oligomers (Scheme 51) [127]. Although this reaction was not catalytic, it did suggest main group metals could be used to dehydrogenate amine-boranes.

Scheme 51 Formation of [(DIPP-nacnac)ZnH]. DIPP = 2,6-di(isopropyl)phenyl.
2.10.2 Group 2 Metal Catalysed Dehydrocoupling of Amine-Boranes

The first catalytic use of a main group metal for the dehydrogenation of an amine-borane also came from the group of Harder who used the same bulky β-diketiminate ligand DIPP-nacnac on a magnesium centre to dehydrocouple $\text{H}_3\text{B} \cdot \text{N(DIPP)H}_2$ to form a diaminoborane $\text{HB}\{\text{N(DIPP)H}\}_2$ and BH$_3$ (detected as B$_2$H$_6$). The authors were able to improve the atom efficiency of the system by using a 2:1 ratio of N(DIPP)H$_2$ and H$_3$B·SMe$_2$ as the substrates and commercially available Mg$n$Bu$_2$ (2.5 mol%) as the precatalyst. Heating this mixture to 60 °C for 14 h led to complete conversion to the diaminoborane product [128]

The first stage of the reaction involves the formation of the amidoborane complex 80, Scheme 52. The authors then propose that B–N coupling occurs at the metal centre, followed by either a β-hydride elimination to form a magnesium hydride species 81 or a 1,3-hydride shift from one boron centre to the other to form a magnesium borohydride species 82. Evidence for this latter mechanism was obtained by isolation of the [(DIPP-nacnac)Mg(BH$_4$)$_2$] species as a product of the reaction, although the first mechanism could not be ruled out as a reactive Mg-H bond could react with the BH$_3$ released to form a borohydride species. In a follow up report the authors suggested that the β-hydride elimination mechanism was the most likely to occur with formation of the metal hydride and aminoborane. The reactivity of these intermediates then depends on the metal and the nitrogen substituents of the aminoborane [129]
Scheme 52 Suggested mechanism for the dehydrocoupling of \( \text{H}_3\text{B} \cdot \text{N} \cdot \text{DIPP} \cdot \text{H}_2 \) to form bis(amine)borane and BH\(_3\). DIPP = 2,6-di(isopropyl)phenyl.

A more general route to a variety of diaminoboranes, including unsymmetrical ones, was reported by Hill and co-workers. Using the group 2 metal catalysts \([\text{M}\{\text{N} \cdot \text{SiMe}_3\}_2]\) (M = Mg, Ca) a mixture of primary and secondary amines and amine-boranes in a 1:1 ratio could be dehydrocoupled to form the \([\text{RR}' \cdot \text{NBHNR''R'''}]\) (R, R', R'', R''' = H, alkyl or aryl) species with little or no formation of the symmetrical products. The mechanism of formation of these species is proposed to proceed via the formation of an amidoborane complex which undergoes \(\beta\)-hydride elimination to give an aminoborane and a metal hydride. The free amine then reacts with the metal hydride releasing H\(_2\) and the aminoborane inserts into the M-NRR' bond. A further \(\beta\)-hydride elimination regenerates the metal hydride and releases the diaminoborane product (Scheme 53) [130]
Scheme 53 Suggested mechanism for the formation unsymmetrical bis(amine)borane from H₃B·NRR'H and HNR''R'''.

The first example of a main group catalyst which formed a product with an equal B:N ratio was also from the group of Hill [131]. Stoichiometric reactions between either Mg⁶Bu₂ or [Mg{CH(SiMe₃)₂}₂(THF)] and four equivalents of H₃B·NMe₂H produced H₂ and [Mg(NMe₂BH₂NMe₂BH₃)₂(THF)] in which the amine-borane units have formed anionic linear diborazane coordinated to the Mg centre through an amide bond and an η²-agostic interaction from the terminal BH₃. Heating this species to 60 °C led to formation of the cyclic [H₂BNMe₂]₂ dimer, however, the corresponding metal species was not able to be identified. In order to attempt to create a soluble, stable metal species, the same bulky β-diketiminate ligand used by Harder et al [128] was employed to synthesise [(DIPP-nacnac)Mg⁶Bu]. Reaction of this complex with two equivalents of H₃B·NMe₂H again produced hydrogen and the product with bound linear diborazane was isolated [(DIPP-nacnac)Mg(NMe₂BH₂NMe₂BH₃)]. Heating this
species to 60 °C resulted in a slower reaction but the cyclic \([\text{H}_2\text{BNMe}_2]_2\) dimer was again observed and the metal–ligand species formed could be identified as \([(\text{DIPP-nacnac})\text{MgH(THF)}_2]\). The formation of the metal hydride means reaction with a further two equivalents of amine-borane could again form the bound linear diborazane species and the reaction could turn over in a catalytic sense. This hypothesis was tested by heating 5 mol% of \([\text{Mg}\{\text{CH(SiMe}_3)\}_2\}_2(\text{THF})_2]\) with \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\). Although the reaction was slow, taking 72 h for 80% conversion, \([\text{H}_2\text{BNMe}_2]_2\) was produced along with a small amount of the diaminoborane \(\text{HB(NMe}_2\text{)}_2\). The proposed reaction mechanism is detailed in Scheme 54.

**Scheme 54** Proposed mechanism of group 2 catalysed dehydrocoupling of \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\).

Hill and co-workers also employed a calcium \(\beta\)-diketiminate ligand system to dehydrocouple a primary amine-borane \(\text{H}_3\text{B} \cdot \text{N}^\text{iBu}\text{H}_2\). 5 mol% of
[(DIPP-nacnac)Ca{N(SiMe₃)₂}(THF)] was heated to 60 °C in the presence of the substrate to form a mixture of boron–containing compounds. After 24 h 68% of the H₃B·N'BuH₂ remained unreacted and the products were found to be [H₂BN'BuH]₂ (5%), H₂B=N'BuH (1%), HB(N'BuH)₂ (13%), H₃B·N'BuHBH₂ (7%) and [Ca(BH₄)₂] (6%). Heating of this reaction mixture for a further 5 days led to formation of the borazine product [HBN'Bu]₃ (20%) and an increased amount of [H₂BN'BuH]₂ (45%) although 14% of the starting substrate remained unreacted [132].

Sicilia and co-workers performed a computational DFT analysis on the group 2 metal β-diketiminate catalysed dehydrocoupling of secondary amine-boranes [133]. Using magnesium as the metal they found that the calculated mechanism was broadly the same at that proposed by Hill et al [131] (Scheme 54) in which the amidoborane undergoes β-hydride elimination to form the metal hydride and free aminoborane. The aminoborane inserts into the M-N bond of a metal bound amidoborane to form the bound diborazane. The rate determining step of the reaction was found computationally to be the δ-hydride elimination to form [H₂BNMe₂]₂. In contrast, when a DFT analysis was carried out on the analogous calcium system the β-hydride elimination from the amidoborane species was not found to occur. In order for dehydrogenation to take place a further equivalent of amine-borane must also coordinate to the metal centre and the interaction of the N-H of the bound amine-borane with the B-H of the amidoborane releases H₂ and aminoborane, regenerating the amidoborane. This difference in mechanism was ascribed to the larger ionic radius of the calcium ion and the calculated relative instability of the calcium hydride species compared to the amidoborane complex.
2.10.3 Group 3 Metal Catalysed Dehydrocoupling of Amine-Boranes

Hypothesising that an increase in charge density at the metal centre would increase the dehydrocoupling activity, Hill and co-workers used group 3 metals as catalysts for the dehydrocoupling of amine-boranes. Reaction of 3 mol% of \( [Y\{N(SiMe_3)_2\}_3] \) with \( H_3B\cdot NMe_2 H \) at 60 °C led to complete consumption of the substrate and formation of \( [H_2BNMe_2]_2 \) dimer (90%) and \( HB(NMe_2)_2 \) (10%) in 12 h. The first stage of the reaction was observed to be protonation of the amide ligands with formation of amidoborane ligands as seen with the group 2 metals. Use of the more reactive scandium starting material \( [Sc\{N(SiHMe_2)_2\}_3(THF)_2] \) (3 mol%) provided a much faster reaction with complete consumption of the amine-borane and near quantitative conversion to \( [H_2BNMe_2]_2 \) in 1 h at 60 °C. In an attempt to elucidate the active species, when 4 equivalents of \( H_3B\cdot NMe_2 H \) was reacted with \( [Sc\{N(SiHMe_2)_2\}_3(THF)_2] \) the dehydrocoupling product \( [Sc\{N(SiHMe_2)_2\}(NMe_2BH_2NMe_2BH_3)] \) (83) was isolated (Scheme 55). The linear diborazane species coordinates in a similar fashion to the group 2 metal complexes with a metal-amido bond from the deprotonated nitrogen centre and a \( \eta^2-B \)-agostic interaction from the terminal \( BH_3 \) [134]

![Scheme 55 Formation of \([Sc\{N(SiHMe_2)_2\}(NMe_2BH_2NMe_2BH_3)]\) (83).](image)

The increased activity of the rare earth metals in oxidation state (III) was further exploited by Chen et al. who used an yttrium complex with two unusual 1-methyl
boratabenzene ligands to catalyse the dehydrocoupling of a secondary amine-borane [135]. \([\text{(MeBC}_5\text{H}_5)\text{Y}\{\text{CH(SiMe}_3\text{)}\}_2}\)] (0.5 mol%) was used to dehydrocouple \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\) at 50 °C with the reaction reaching completion in \(\text{ca. 12 minutes}\) (Scheme 56). The products of the reaction observed after this were \([\text{H}_2\text{BNMe}_2]_2\) (98%) and a small portion of as yet undimerised aminoborane \(\text{H}_2\text{B}=\text{NMe}_2\) (2%). A turnover frequency of 1015 h\(^{-1}\) is by far the largest observed for the main-group catalysts and comparable with some of the best transition metal catalysts. The reaction using the lutetium analogue of this system reached completion in 29 minutes with a similar product distribution.

![Scheme 56](image)

**Scheme 56** Catalytic dehydrocoupling of \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\) using \([\text{(MeBC}_5\text{H}_5)\text{Y}\{\text{CH(SiMe}_3\text{)}\}_2}\]).

The extremely high activity of this system was ascribed to either the electron withdrawing nature of the ligand or a possible interaction between the electron deficient boron centre of the 1–methyl boratabenzene ligand and the hydridic B-H bonds of the substrate. An analogous complex with an electron donating substituent (NEt\(_2\)) on the boratabenzene \([\text{(Et}_2\text{NBC}_5\text{H}_5)\text{Y}\{\text{CH(SiMe}_3\text{)}\}_2}\]) proved to be much less active in catalysis indicating either the electron withdrawing nature of the ligand or the Lewis acidic centre were important for high activity. While the authors were unable to elucidate the mechanism of the reaction, they did observe free diborazane \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}\) as an intermediate in the reaction mixture, suggesting the
mechanism is different than those reported by Harder and Hill in which free linear diborazane was never observed [129, 136]

Rare earth metal catalysts were used by Okuda et al. for which the hydride tetramers \([(1,7-\text{Me}_2\text{TACD})\text{MH}]_4\) (\(M = \text{La, Y}; 1,7-\text{Me}_2\text{TACD} = 1,7\text{-dimethyl}-1,4,7,10\text{-tetraazacyclododecane}\)) were used to catalyse the dehydrocoupling of \(\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}\) (2.5 mol\%, 60 °C, THF), with the lanthanum complex giving full conversion to \([\text{H}_2\text{BNMe}_2]_2\) (79%) and diaminoborane (21%) in 2 h, Scheme 57. The yttrium analogue took significantly longer with 95% conversion reached after 48 h to form a similar product ratio. Stoichiometric reactivity of \([(1,7-\text{Me}_2\text{TACD})\text{LaH}]_4\) demonstrated the non-innocent behaviour of the ligand in reactivity with the secondary amine-borane. The basic amido-groups of the 1,7-\text{Me}_2\text{TACD} ligand were shown to deprotonate the acidic amine protons of the amine-borane to form coordinated amidoborane species. The lone pair of these amido groups was also able to provide stabilisation for the boron centre of a coordinated aminoborane by acting as a Lewis base [137]
Scheme 57 Catalytic dehydrocoupling of H$_3$B·NMe$_2$H using 
[\{(1,7-Me$_2$TACD)LaH\}$_4$].

2.10.4 P-Block Catalysed Dehydrocoupling of Amine-Boranes

Wright et al. reported that reaction of [Al(NMe$_2$)$_3$] with H$_3$B·NMe$_2$H led to formation of [AlH{H$_2$B(NMe$_2$)$_2$}] (Scheme 58) by formation of an amidoborane complex and migration of the NMe$_2$ amido ligands to the boron centre. This complex (at 5 mol%) was able to catalyse the dehydrocoupling of H$_3$B·NMe$_2$H at 50 °C to give [H$_2$BNMe$_2$]$_2$ and HB(NMe$_2$)$_2$ in a 6:1 molar ratio after 48 h [138]. In a follow up report [Al(N$i$Pr$_2$)$_3$] was used to catalytically form the aminoborane H$_2$B=N$i$Pr$_2$ from the corresponding secondary amine-borane (10 mol%, 60 °C, 2 h). As with the system reported by Okuda et al., the amido ligands of the starting material were found to be non-innocent, and if [Al(NMe$_2$)$_3$] was used instead, by-products containing the NMe$_2$ moiety were observed. Extending this investigation to a primary amine-borane, the precatalyst [Al(NMe$_2$)$_3$] was able to slowly dehydrocouple H$_3$B·N$i$BuH$_2$ to form first the cyclic trimer borazane [H$_2$BN$i$BuH]$_3$ which was then further dehydrogenated to the borazine product [HBN$i$Bu]$_3$. That the borazine can be observed early in the reaction suggests the rate of formation of borazine from borazane is comparable to the rate of initial dehydrocoupling to form the borazane from the monomers. However, overall this reaction was slow with only 30% conversion of the amine-borane after 4 days at 20 °C [139]. Wright et al. have also found that Li[AlH$_4$] can be used as a catalyst to dehydrocouple H$_3$B·NMe$_2$H to give [H$_2$BNMe$_2$]$_2$ along with HB(NMe$_2$)$_2$ as a minor product [140]. Stoichiometric reactions of amine-boranes with aluminium
species has revealed possible reaction intermediates although the mechanism of the dehydrocoupling has not been unambiguously determined [138-141].

**Scheme 58** Formation of $[\text{AlH}_2\text{B(NMe}_2)_2\text{]}_2$.

The group 4 metal tin, in both II and IV oxidation states, was utilised by Waterman *et al.* to catalyse the dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$, $\text{H}_3\text{B} \cdot \text{N}^\text{t} \text{BuH}_2$ and $\text{H}_3\text{B} \cdot \text{NH}_3$. The majority of the catalytic reactions occurred slowly with most taking at least 24 h and producing a range of BN containing products. The best performing was the $\text{SnCl}_2$–catalysed (10 mol%) dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NH}_3$ to borazine (87%) in 1 h at 65 °C (Scheme 59). Attempts to identify the active species in catalysis were not successful as no tin–containing intermediates could be characterised or isolated. NMR spectroscopic investigations could not determine whether the active species was a Sn$^\text{II}$ or Sn$^\text{IV}$ complex, although several different active species could be present. It was determined that the likely method of catalyst deactivation was by reduction to Sn$^0$ [142]

**Scheme 59** $\text{SnCl}_2$ catalysed dehydrocoupling of $\text{H}_3\text{B} \cdot \text{NH}_3$ to give borazine (87%).

Sneddon has reported that Verkade’s Base (VB) acts as an initiator for base–promoted anionic dehydropolymerisation of $\text{H}_3\text{B} \cdot \text{NH}_3$ to form anionic aminoborane chain growth products, such as the structurally characterised
[VBH]⁺[H₂BNH₂BH₂NH₂BH₃]⁻ [9]. The mechanism proposed for this dehydrocoupling invokes initial deprotonation of H₃B·NH₃ by VB to form [VBH]⁺[BH₃NH₂]⁻, which then reacts with further H₃B·NH₃ to form the borane-capped [VBH]⁺[BH₃NH₂BH₃]⁻ and NH₃. Subsequent, sequential, dehydrocoupling affords the longer chain oligomers. Such steps are suggested to be facilitated by N–H···H–B dihydrogen bonding as informed by a solid–state structural analysis. This result builds upon earlier studies in which Proton Sponge was used as the base initiator,[36] as well as work by Girolami and co-workers that reported mild thermal conversion of Na[NH₂BH₃] leads to NaNH₂ and Na[NH₂(BH₃)₃] [143]. By contrast, Baker and Dixon have reported that the strong Lewis–acid, B(C₆F₅)₃, or Brønsted–acid, HOSO₂CF₃, promotes dehydrocoupling of amine borane by a hydride abstraction pathway to form a boronium cation [102]. This is not dissimilar to the mechanism suggested for the Pt–catalysed dehydrocoupling of H₃B·NMe₂H (Scheme 43).

2.10.5 Frustrated Lewis Pair Dehydrogenation of Amine-Boranes

Since the discovery that frustrated Lewis pairs can activate dihydrogen, interest has focussed on activation of other small molecules [144, 145]. The abstraction of dihydrogen from amine-boranes, particularly if it could be performed catalytically, would provide an alternative method to the traditional metal based catalysis. The first to the dehydrogenation of H₃B·NMe₂H using frustrated Lewis pairs were Miller and Bercaw who used a stoichiometric combination of P′Bu₃ and B(C₆F₅)₃ to ultimately form [H₂BNMe₂]₂ along with trace amounts of other BN containing products. However, this reaction could not be carried out catalytically and heating the reaction
mixture in an attempt to release hydrogen gas from \([\text{HP}^3\text{Bu}_3][\text{HB}(\text{C}_6\text{F}_5)_3]\) and regenerate the frustrated Lewis pair was unsuccessful. Ammonia-borane could also be dehydrocoupled by a stoichiometric amount of these reagents to give polyaminoborane \([\text{H}_2\text{B}N\text{H}_2]_n\) and \([\text{HP}^3\text{Bu}_3][\text{HB}(\text{C}_6\text{F}_5)_3]\). Addition of further \(\text{P}^3\text{Bu}_3\) and \(\text{B}(\text{C}_6\text{F}_5)_3\) did not appear to result in further dehydrogenation to form borazine or other products. The authors suggested the mechanism of dehydrogenation was likely to proceed via hydride abstraction by \(\text{B}(\text{C}_6\text{F}_5)_3\) followed by rapid deprotonation by \(\text{P}^3\text{Bu}_3\) to form the aminoborane. This then undergoes rapid oligomerisation to form the products [146]. The group of Manners used a variety of less expensive frustrated Lewis pairs to dehydrocouple \(\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}\), with a combination of \([\text{Me}_3\text{SiO}_3\text{SCF}_3]\) and 2,2,6,6-tetramethylpiperidine performing best in forming \([\text{H}_2\text{BNMe}_2]_2\), with only traces of side products observed. The reaction could only be performed by a stoichiometric amount of Lewis pair and therefore the reaction was not catalytic. Attempts to dehydrogenate the primary amine-borane \(\text{H}_3\text{B} \cdot \text{NMeH}_2\) did not result in readily characterised products [147].

The first example of use of a frustrated Lewis pair to catalytically dehydrocouple an amine-borane was reported by Uhl et al. who used a compound containing both a Lewis basic bulky phosphine and a Lewis acidic aluminium centre (Scheme 60). Stoichiometric reaction between this compound and ammonia-borane led to dehydrogenation and formation of the aminoborane adduct. However, this final complex was thermally stable and the aminoborane could not be liberated to regenerate the original Lewis Pair. Computational analysis of this reaction gave a mechanism contrasting that suggested by Miller and Manners where the first step of the reaction is now deprotonation of the N-H by the phosphine centre and formation of an Al-N bond. Rearrangement followed by loss of \(\text{H}_2\) from the complex gives the
aminoborane and the 5-membered cyclic product quickly forms. The forced proximity of the Lewis acid and base in this compound may be the cause of this alternative mechanism. When the secondary amine-borane \( \text{H}_3\text{B} \cdot \text{NMe}_2\text{H} \) was used, dihydrogen was again produced, and the five-membered cyclic species was formed but this was found to only be stable below -30 °C. Above this temperature the aminoborane \( \text{H}_2\text{B} = \text{NMe}_2 \) is released, which quickly dimerises to form \([\text{H}_2\text{BNMe}_2]_2\) and the frustrated Lewis pair catalyst is regenerated. A melt reaction of \( \text{H}_3\text{B} \cdot \text{NMe}_2\text{H} \) (45 °C then 90 °C) with 9.3 mol% of catalyst produced \([\text{H}_2\text{BNMe}_2]_2\) in 71% isolated yield after 45 minutes. A lower catalyst loading (0.4 mol%) gave 77% \([\text{H}_2\text{BNMe}_2]_2\) in 44 h under similar conditions [148]

![Scheme 60](image)

**Scheme 60** Reaction of the FLP with \( \text{H}_3\text{B} \cdot \text{NH}_3 \) (top) and catalytic dehydrocoupling of \( \text{H}_3\text{B} \cdot \text{NMe}_2\text{H} \) (bottom).

3. **Dehydrocoupling of Phosphine-Boranes**

3.1 **Transition Metal Catalysed Dehydrocoupling of Phosphine-Boranes**

Phosphine-boranes were first found to undergo thermal dehydrocoupling in the 1950s when monomers were heated to 150 °C and released hydrogen to form a mixture of
cyclic trimer and tetramers [149]. Some polymerisation was reported at higher temperature but the products were ill–defined (Scheme 61) [150]

Scheme 61 Thermal dehydrocoupling of dimethyl phosphine-borane.

The breakthrough in catalytic dehydrocoupling came at the turn of the century when the group of Manners reported dehydrocoupling of both secondary and primary phosphine-boranes to give a variety of products. The precatalysts used were initially simple rhodium (I) species [Rh(1,5-cod)(µ-Cl)]$_2$ or the salt [Rh(1,5-cod)$_2$][O$_3$SCF$_3$]. The secondary phosphine-borane H$_3$B·PPh$_2$H was found to selectively form the linear diboraphosphine species at 90 °C in the presence of 0.3 mol% of the rhodium(I) precatalyst in the absence of solvent (melt conditions) after 14 h. Heating a similar reaction mixture to 120 °C for 15 h gave cyclic trimer and tetramers as the sole products (Scheme 62) [151, 152]. Analysis of this reaction mixture after 4 h showed complete consumption of the H$_3$B·PPh$_2$H starting material and a mixture of diborophosphine, H$_3$B·PPh$_2$BH$_2$·PPh$_2$H, and the cyclic species, and it was suggested that H$_3$B·PPh$_2$BH$_2$·PPh$_2$H is an intermediate in formation of the cyclic oligomers.

Scheme 62 Rhodium (I) catalysed dehydrocoupling of secondary phosphine-borane.
When the primary phosphine-borane $\text{H}_3\text{B} \cdot \text{PPhH}_2$ was used, 0.3 mol% of 
$[\text{Rh}(1,5\text{-cod})_2][\text{O}_3\text{SCF}_3]$ in refluxing toluene (15 h) gave an air and moisture stable, 
off-white solid product found to be low molecular weight 
polyphenylphosphinoborane ($M_w = 5600$). If melt conditions were used with $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$ as the catalyst a similar product could be made with a higher molecular 
weight ($M_w = 31000$) (Scheme 63 and Figure 15) [151]

Scheme 63 Catalytic formation of polyphosphinoboranes.

![Scheme 63 diagram]

Figure 15 $^{31}\text{P}$ NMR spectrum of $[\text{H}_2\text{BPPhH}]_n$ in CDCl$_3$ (121 MHz): (a) $^1\text{H}$-decoupled; (b) 1H-coupled, $J_{\text{PH}} = 360$ Hz. Reprinted (adapted) with permission from H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2000, 122, 6669-6678. Copyright 2000, American Chemical Society.
In a follow up report Manners et al. screened a range of precatalysts for the dehydrocoupling of H₃B·PPh₂H. In addition to the species tested above, the best performing precatalysts under melt conditions were found to be either Rh¹ or Rh³ compounds, with species containing other metals (Ir, Pd, Pt) giving lower conversions and slower turnover. The scope of the polymerisation of primary phosphine-boranes was also expanded to the alkyl-substituted H₃B·P'BuH₂, which was dehydrocoupled in 13 h at 120 °C [152]

The alkyl substituted secondary phosphine-borane H₃B·P'Bu₂H could be dehydrocoupled by similar rhodium–based precatalysts under melt conditions at elevated temperatures. Full conversion of the phosphine-borane was not achieved for any of the catalysts and although the major product formed was the diborophosphine, H₃B·P'Bu₂BH₂·P'Bu₂H. Other products were also observed including in some cases the chloride–terminated diborophosphine (ClH₂B·P'Bu₂BH₂·P'Bu₂H) with the chloride provided by the precatalyst. One of the best catalysts was found to be [Rh(1,5-cod)(µ-Cl)]₂ which had also been used for the previous systems [153]. Another report from Manners and co–workers focussed on the formation of polymers from the dehydrocoupling of primary phosphine-boranes; Aryl–substituted phosphine-boranes H₃B·P(p–Bu-C₆H₄)H₂ and H₃B·P(p–(C₁₂H₂₅)-C₆H₄)H₂ were polymerised by [Rh(1,5-cod)(µ-Cl)]₂ under melt conditions [154]

3.2 Determination of the Active Catalytic Species: Hetero or Homogeneous
In all of these reports from the group of Manners the active catalytic species and mechanism of polymerisation was not investigated in detail. While in general rhodium–based precatalysts under melt conditions performed best, precatalysts with different oxidation states and ligands could all give catalytic turnover for dehydrocoupling. Since formation of rhodium nanoparticles had been found to be an important step in the catalytic dehydrocoupling of amine-boranes, Manners et al. investigated whether the phosphine-borane catalysis operated in a hetero- or homogeneous mode. Addition of 10 mol% of [Rh(1,5-cod)(µ-Cl)]₂ to a toluene solution of H₃B·PPh₂H at 90 °C resulted in a colour change from orange to red but no evidence of black material was observed, which is often characteristic of nanoparticle formation [155]. In addition to this no induction period was observed and filtration and mercury poisoning experiments also suggested the catalyst was a heterogeneous species. Similar results were found for the ion–separated precatalyst [Rh(1,5-cod)₂][O₃SCF₃] (Figure 16).
**Figure 16** Left: Graph of % conversion vs time for the catalytic dehydrocoupling of H$_3$B·PPh$_2$H using [Rh(1,5-cod)(µ-Cl)]$_2$ (ca. 10 mol% Rh, toluene, 90 °C). Right: Graph of % conversion vs time for the catalytic dehydrocoupling of H$_3$B·PPh$_2$H using [Rh(1,5-cod)(µ-Cl)]$_2$ (ca. 10 mol % Rh, toluene, 90 °C). At ca. 35% conversion, excess Hg was added to the reaction mixture (curve ♦). The dehydrocoupling reaction was initiated in the presence of excess Hg (curve ■). Reprinted (adapted) with permission from C. A. Jaska and I. Manners, *J. Am. Chem. Soc.*, 2004, 126, 9776-9785. Copyright 2004, American Chemical Society.

Dehydrocoupling was attempted using the heterogeneous Rh/Al$_2$O$_3$ (5 wt. % Rh) precatalyst and, interestingly, catalysis was found to occur. However, filtration of the solution showed the soluble portion to be orange suggesting some rhodium had leached into solution to form a homogeneous catalytically active species. Addition of further H$_3$B·PPh$_2$H to both soluble and insoluble portions showed them to be active and inactive respectively, confirming the homogeneous nature of the catalyst. While the authors were unable to identify the true catalytic species, they were able to speculate that the phosphine-boranes were not reducing enough to form Rh$^0$ from the Rh$^1$ precatalyst. In addition to this the relative weakness of the P-B bond (compared to the N-B bond in amine-boranes) allowed dissociation and formation of free phosphine which could act as ligands for solubilising heterogeneous species. However, an excess of free phosphine could act as a catalyst poison and they suggest higher temperatures required for phosphine-borane dehydrocoupling might be needed to create a vacant site at the metal centre which is often required in polymerisation catalysis [39].

### 3.3 Sigma-Complexes and B-agostic Interactions of Phosphine-Boranes

An important step in the dehydrocoupling of amine-boranes is thought to be the formation of σ-complexes where the metal centre interacts with the H—B bond of the
borane moiety (Section 2.7.1). Similarly, in phosphine-borane dehydrocoupling, the creation of a vacant site at the metal centre to which the phosphine-borane can bind, or displacement of a ligand by a phosphine-borane, is likely to be an important step [39]. The initial interaction between the metal centre and the substrate is likely through formation of a $\sigma$–complex with the hydridic B–H bonds. A number of phosphine-borane $\sigma$-complexes and B–agostic interactions (where the phosphine-borane is further tethered to the metal centre) have been reported in the literature. An early example of a $\sigma$-complex was reported in 1984 in which zinc is complexed with diphosphine-diborane(4), $[\text{ZnCl}_2\{\text{B}_2\text{H}_4\cdot(\text{PMe}_3)_2}\}]$,[156] and a phosphidoborane complex with a $\beta$-B-agostic interaction $[\text{CpMo(CO)}_2(\text{P}\{\text{N}((\text{SiMe}_3)_2}\cdot\text{Ph}\cdot\text{BH}_3)]$ was published two years later [157]. The first $\sigma$-complex with a monomeric phosphine-borane was synthesised by the photolysis of $[\text{M(CO)}_6]$ (M = Cr, Mo, W) in the presence of $\text{H}_3\text{B}\cdot\text{PR}_3$ (R = Me, Ph) to form the $\eta^1$-complexes $[\text{M(CO)}_5(\text{H}_3\text{B}\cdot\text{PR}_3)]$ [61]. There are a number of reports of similar compounds[158-160] including examples of $\eta^2$-B-agostic interactions in rhodium complexes [161-163]

An interesting observation came from Whittlesey et al. who reported that reaction of $[\text{RuH(Xantphos)}(\text{PPh}_3)(\text{OH}_2)][\text{BAR}_4]$ with amine-boranes produced $\sigma$-complexes by displacement of the water ligand, but reaction with the phosphine-borane $\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}$ gave only the P—B cleavage product $[\text{RuH(Xantphos)}(\text{PPh}_2\text{H}_2)][\text{BAR}_4]$. This shows the relative weakness of the P—B bond compared to the N—B bond in amine-boranes and suggests P—B cleavage is likely to play a role in metal catalysed dehydrocoupling of phosphine-boranes [63]

In 2013 Weller et al. described an attempt to form a $\sigma$-complex from the reaction between $[\text{RhCl(PPh}_3]_3$ and $\text{Na}[\text{BAR}_4]$ in the presence of a secondary phosphine-borane $\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}$. However, this reaction led to dehydrocoupling and the formation
of the complex \([\text{Rh}(\text{PPh}_3)_2(\text{PPh}_2\text{BH}_2\cdot\text{PPh}_3)][\text{BArF}_4]\) (Scheme 64). One triphenylphosphine ligand has migrated to the boron centre and a B-H bond has formed a \(\beta\)-B-agostic interaction with the rhodium centre. While the mechanism of this transformation was not determined, it was postulated that the reaction could occur either via P-H activation, B-H activation or by the formation of a transient phosphinoborane intermediate \(\text{H}_2\text{B}=\text{PPh}_2\) at the metal centre [164]. Aminoboranes, their nitrogen containing analogues, have been shown to be crucial if often short lived intermediates in the metal catalysed dehydrocoupling of amine-boranes \(\text{vide supra}\) yet free phosphinoboranes have yet to be observed during phosphine-borane dehydrocoupling.

![Scheme 64](image)

Scheme 64 Formation of \([\text{Rh}(\text{PPh}_3)_2(\text{PPh}_2\text{BH}_2\cdot\text{PPh}_3)][\text{BArF}_4]\) from dehydrogenation of \(\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}\). [\text{BArF}_4]^- anion not shown.

There are examples of group 10 phosphido–boranes that have been synthesized by reaction of a metal fragment with \(\text{H}_3\text{B}\cdot\text{PR}_3\text{H}\) and oxidative addition of the P–H bond [165, 166]. These examples, however, are not active in dehydrocoupling either stoichiometric or catalytic, although, as will be shown in Section 3.6, such motifs can be strongly implicated in the dehydrocoupling process with different metal–ligand fragments.

### 3.4 Stabilised Phosphinoboranes
Although not directly observed during dehydrocoupling, there are phosphinoboranes which have been synthesised that rely on stabilisation by the presence of bulky substituents or by coordination of a Lewis acid or a Lewis base. Those with large substituents do not oligomerise due to the steric crowding of the phosphorus and boron centres [167]. However, those with Lewis acid or base stabilisation can undergo further reactivity [168, 169]. The Lewis base stabilised unsubstituted phosphinoborane Me$_3$N·H$_2$BPH$_2$ was synthesised by Scheer et al. and was found to oligomerise in the presence of [Cp$_2$Ti(Me$_3$SiCCSiMe$_3$)], with different products observed depending on the temperature and stoichiometry. The first step of the reaction is coordination of the stabilised phosphinoborane through the lone pair at the phosphorus centre to form [Cp$_2$Ti(Me$_3$SiCCSiMe$_3$)(PH$_2$BH$_2$·NMe$_3$)] (84) (Scheme 65). This complex is only stable below –80 °C in solution and above this temperature the alkyne dissociates and oligomerisation occurs in both head-to-tail and head-to-head fashion, along with some Lewis base dissociation. The complexes formed are oligomeric chains of 3 (85), 4 (86) and 6 (87) phosphinoborane monomers stabilised by coordination of the [Cp$_2$Ti] fragment [170].

Scheme 65 [Cp$_2$Ti] catalysed oligomerisation of Me$_3$N·H$_2$BPH$_2$. [Ti] = Cp$_2$Ti.
3.5 Group 8 Catalysed Dehydrocoupling of Phosphine-Boranes

Complexes based on group 8 metals were first used in 2008 as precatalysts for dehydrocoupling when Manners et al. reported the use of [CpM(CO)2(PPh2·BH3)] (M = Fe, Ru) to form diborophosphate, H3B·PPh2BH2·PPh2H, from the secondary phosphine-borane H3B·PPh2H under both melt conditions and in solution. The phosphidoborane precatalyst complexes were synthesised by a reaction of [CpMI(CO)2] (M = Fe, Ru) with (H3B·PPh2)Li. In toluene solution at 110 °C the Fe complex performed poorly only converting 50% of H3B·PPh2H at 25 mol% catalyst loading. However, under melt conditions (120 °C) the iron and ruthenium complexes were able to convert 65% and 60% of the starting material to linear diboraphosphate respectively (1.5 mol%, 15 h). Under the same melt conditions Fe2(CO)9 was also found to catalyse the dehydrocoupling of H3B·PPh2H to form the same product (80% conversion in 15 h). The authors postulated that the loss of a carbonyl ligand at high temperatures allowed dehydrocoupling to occur in the vacant coordination site created [171]. This is closely related to the mechanism proposed for amine–borane dehydrocoupling using the same metal–ligand system, Scheme 30.

3.6 Mechanistic Investigations into the Rhodium Catalysed Dehydrocoupling of Secondary Phosphine-Boranes

The first detailed investigation into the mechanism of the rhodium catalysed dehydrocoupling of phosphine-boranes was reported by Huertos and Weller in 2012. The precatalyst used was [Rh(1,5-cod)2][BARF4] similar to the
[Rh(1,5-cod)₂][O₃SCF₃] complex used previously by Manners and co-workers [7]. Heating 5 mol% of the precatalyst with H₃B·P'Bu₂H under melt conditions (140 °C) for 20 h led to formation of H₃B·P'Bu₂BH₂·P'Bu₂H (65%) along with a bisphosphine-boronium salt [H₂B(P'Bu₂H)₂][BH₄] (10%) as a side product from P-B cleavage. Interrogation of the melt reaction by addition of 1,2-difluorobenzene solvent and analysis by ³¹P NMR spectroscopy and ESI mass spectrometry revealed the organometallic species present to be [Rh(P'Bu₂H)₂(η²-H₃B·P'Bu₂BH₂·P'Bu₂H)]⁺ (88) and [Rh(P'Bu₂H)₂(η⁶-C₆H₅F₂)]⁺. The secondary phosphine ligands at the rhodium centre originate from the phosphine-borane having undergone P—B cleavage and the rest of the coordination sphere of the Rhᴵ centre is filled by a solvent molecule or the σ-bound linear phosphine-borane diboraphosphine. These observations suggested that the [Rh(P'Bu₂H)₂]⁺ fragment was the active species in catalysis. [Rh(P'Bu₂H)₂(η⁶-C₆H₅F)][BArF₄] was independently synthesised and was found to catalyse the dehydrocoupling of H₃B·P'Bu₂H under melt conditions to form the same intermediates and final products as [Rh(1,5-cod)₂][BArF₄]. This provided further evidence that the [Rh(P'Bu₂H)₂]⁺ fragment is the active catalyst and a simple mechanism was postulated (Scheme 66) [172]
Scheme 66 Proposed mechanism for rhodium catalysed formation of linear diboraphosphine from \( \text{H}_3\text{B} \cdot \text{P}^\dagger \text{Bu}_2\text{H} \). [\( \text{BAr}^F \_4 \)] omitted for clarity.

In an attempt to find a more stable catalytic fragment, [\( \text{Rh}(\text{P}^\dagger \text{Bu}_3)_2(\eta^6\cdot\text{C}_6\text{H}_5\text{F})][\text{BAr}^F \_4 \)] which had been shown to be an effective dehydrocoupling catalyst for amine-boranes, was used as a precatalyst for dimerisation of \( \text{H}_3\text{B} \cdot \text{P}^\dagger \text{Bu}_2\text{H} \). However, analysis of the reaction mixture found a mixture of organometallic species with the tri-\( i \)-butylphosphine ligand replaced on the rhodium centre by \( \text{P}^\dagger \text{Bu}_2\text{H} \) ligands, presumably from P-B cleavage of the substrate. In a further development of this system Huertos and Weller were able to form a more stable catalytic fragment by replacement of the monodentate phosphine ligands with a chelating phosphine ligand 1,3-bis(diphenylphosphino)propane (\( \text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2 \), dppp) [173]. Under the harsh melt conditions required for catalysis to occur, the chelating ligand was not displaced by any free phosphine formed from P-B cleavage of the substrate, allowing further investigation into the [\( \text{Rh}(\text{dppp}) \)] fragment as the active catalytic species. A stoichiometric reaction between the precatalyst [\( \text{Rh}(\text{dppp})(\eta^6\cdot\text{C}_6\text{H}_5\text{F})][\text{BAr}^F \_4 \)] and \( \text{H}_3\text{B} \cdot \text{P}^\dagger \text{Bu}_2\text{H} \) led to formation of the \( \sigma \)-complex [\( \text{Rh}(\text{dppp})(\eta^2\cdot\text{H}_3\text{B} \cdot \text{P}^\dagger \text{Bu}_2\text{H})][\text{BAr}^F \_4 \)] by displacement of the labile fluorobenzene ligand (Scheme 67). In the presence of another equivalent of \( \text{H}_3\text{B} \cdot \text{P}^\dagger \text{Bu}_2\text{H} \), the complex was found to undergo dehydrocoupling at 70 °C in 1,2-difluorobenzene to form the \( \sigma \)-bound linear diboraphosphine product [\( \text{Rh}(\text{dppp})(\text{H}_3\text{B} \cdot \text{P}^\dagger \text{Bu}_2\text{BH}_2 \cdot \text{P}^\dagger \text{Bu}_2\text{H}) \)]\(^+\) although the reaction produced several side products.
Extending the study to H$_3$B·PPh$_2$H, quite different complexes were isolated from these stoichiometric studies. Reaction of [Rh(dppp)(η$^6$-C$_6$H$_5$F)][BAr$_4^+$] with 2 equivalents of H$_3$B·PPh$_2$H in 1,2-difluorobenzene gave a Rh$^{III}$ complex in which one phosphine-borane unit had undergone P—H activation to form a rhodium hydride and a β-B-agostic phosphidoborane and the second molecule was σ-bound through one hydrogen atom of the borane moiety. The two phosphine-borane units on this complex were found to cleanly dehydrocouple in a first order process at room temperature to form a linear diboraphosphine product which is also P-H activated and the remainder of the Rh$^{III}$ coordination sphere is filled by two β-B-agostic interaction from the terminal BH$_3$ moiety (Scheme 68, Figure 17). These data, when combined with H/D labelling experiments, allowed for the rate determining step for dehydrocoupling to be suggested to lie in the second B–H activation and ligand reorganisation step(s). In catalysis the turnover–limiting step, however, is substitution of the chelating linear diboraphosphine by another molecule of H$_3$B·PPh$_2$H (Scheme 69).
Scheme 68 Formation of $[\text{RhH(dppp)(PPh}_2\cdot\text{BH}_3)(\eta^1\cdot\text{H}_3\text{B}\cdot\text{PPh}_2\text{H})]^+$ and dehydrocoupling. $[\text{BAR}_{4}]^-$ omitted for clarity.

Figure 17 First order plots and Eyring analysis of dehydrocoupling of $[\text{RhH(dppp)(PPh}_2\cdot\text{BH}_3)(\eta^1\cdot\text{H}_3\text{B}\cdot\text{PPh}_2\text{H})][\text{BAR}_{4}]^-$ to $[\text{RhH(dppp)(PPh}_2\cdot\text{BH}_2\text{PPh}_2\cdot\text{BH}_3)][\text{BAR}_{4}]$. Reprinted (adapted) with permission from M. A. Huertos and A. S. Weller, Chem. Sci., 2013, 4, 1881-1888. Copyright 2014, Royal Society of Chemistry.

The substituents at the phosphorus position of the phosphine-borane unit were found to have an effect on the reactivity both stoichiometrically and in catalysis. The phosphine-borane with the bulky, electron-donating $t$-butyl substituent was found to dehydrocouple slowly (16 h at 140 °C, 60% conversion) and complexes with this ligand where observed in the Rh$^1$ oxidation state. Contrastingly, when the phosphine-borane with the electron-withdrawing phenyl substituent was used, dehydrocoupling proceeded faster (4 h at 90 °C) while Rh$^{	ext{III}}$ complexes were favoured. The difference in oxidation state of the rhodium centre in these cases is likely due to the acidity of
the P—H bond. When electron-withdrawing substituents are present on phosphorus the P—H bond more readily undergoes P—H oxidative addition making Rh$^{III}$ species favoured [173].

Scheme 69 Detailed mechanism for the dehydrocoupling of secondary phosphine-borane by the [Rh(dppp)]$^+$ fragment. [BAR$_4^-$] omitted for clarity.

In a follow up report secondary phosphine-boranes bearing fluorinated substituents, H$_3$B·P(p-F$_3$C-C$_6$H$_4$)$_2$H and H$_3$B·P(m-(F$_3$C)$_2$C$_6$H$_3$)$_2$H were found to dehydrocouple at a faster rate than H$_3$B·PPh$_2$H using the same [Rh(dppp)]$^+$ system [174]. However, stoichiometric reactions showed the weakening of the P—B bond by the presence of the electron-withdrawing groups caused P—B bond cleavage and hence catalyst deactivation by formation of [Rh(dppp)(PR$_2$H)$_2$]$^+$. The faster dehydrocoupling of
fluorinated phosphine-boranes is in agreement with Manners et al. who found these substrates could be catalytically dehydrocoupled at lower temperature than the non-fluorinated aryl analogues (*vide infra*). Conversely, the presence of an electron donating group H₃B·P(ρ–MeO-C₆H₄)₂H at the phosphorus centre was found to reduce the rate of dehydrocoupling. However, the increased strength of the P—B bond meant cleavage and hence catalyst deactivation was largely avoided. Fluorinated phosphine-boranes can be also catalytically dehydrocoupled using different catalyst systems. The secondary phosphine-borane H₃B·P(p-F₃C-C₆H₄)₂H was converted to the corresponding linear diboraphosphine product by heating with [Rh(1,5-cod)(μ-Cl)]₂ (2 mol% based on Rh) to 60 °C for 15 h under melt conditions [175]. The cyclic trimer and tetramer species observed for the high temperature dehydrocoupling of H₃B·PPh₂H were also formed at lower temperature (100 °C, 15 h). The fluorinated primary phosphine-borane H₃B·P(p-F₃C-C₆H₄)H₂ was found to form high molecular weight polymer under similar conditions; [Rh(1,5-cod)(μ-Cl)]₂ precatalyst (2.5 mol% based on Rh), 60 °C, 9 h in melt conditions. The lowering of the reaction temperature was ascribed to the increased acidity of the P—H bond due to the electron-withdrawing substituents and therefore its ability to react more readily with the hydridic B—H bonds to dehydrocouple.

3.7 Mechanistic Investigation into the Rhodium Catalysed Dehydrocoupling of Primary Phosphine-Boranes

The mechanism of dehydrocoupling of primary phosphine-boranes using the [Rh(dpdp)(η⁶-C₆H₅F)][BArF₄] has also been reported. H₃B·PCyH₂ was used as the substrate and under stoichiometric conditions it reacted in a similar way to
H₃B·PPh₂H with formation of a Rh^{III} complex with a hydride, a phosphidoborane and a σ-bound η¹-H₃B·PCyH₂ (Scheme 70). This complex was found to exist as an approximately 1:1 mixture of two diastereomers (89a and 89b) due to the P—H activation at the prochiral phosphorus centre. As with the secondary aryl phosphine-boranes this complex underwent dehydrocoupling, although faster than the secondary analogues, being complete in 1 h at room temperature. The dehydrocoupled complex formed was again equivalent to the H₃B·PPh₂H reaction with the linear diboraphosphine having undergone P—H activation and chelating via 2 β-B-agostic bonds from the terminal borane moiety. The complex is formed as a mixture of two, unresolved, diastereomers (90a and 90b) because of P—H activation at the prochiral phosphorus centre although the diastereomers are present as a 6:1 mixture with one thermodynamically favoured. This complex can also be synthesised by reaction of the preformed linear diboraphosphine with [Rh(dppp)(η⁶-C₆H₅F)][BARF₄], which initially forms a kinetic 1:1 diastereomeric mixture, and over 18 h reaches the 6:1 ratio observed from dehydrocoupling. This provides evidence for the mechanism proposed in Scheme 69 in which the Rh¹ σ-bound linear diboraphosphine complex in is equilibrium with the P—H activated Rh^{III} octahedral complex as such a process would allow interconversion of the Rh^{III} diastereomers. Such a diastereomeric bias may afford some control of polymer tacticity in dehydropolymerisation reactions [174]. Interestingly, the use of a chiral chelating phosphine ligand on rhodium resulted in a further bias towards one diastereoisomer, but the absolute configuration was not determined.
Scheme 70 Reaction of \([\text{Rh(dppp)}(\eta^6-\text{C}_6\text{H}_5\text{F})][\text{BAR}^5_4]\) with primary phosphine-borane \(\text{H}_3\text{B} \cdot \text{PCyH}_2\). \([\text{BAR}^5_4]\) omitted for clarity.

The \([\text{Rh(dppp)}]^+\) fragment performed competently as a catalyst for the polymerisation of the more reactive primary phosphine-borane \(\text{H}_3\text{B} \cdot \text{PPhH}_2\) under melt conditions. Heating 5 mol% of precatalyst \([\text{Rh(dppp)}(\eta^6-\text{C}_6\text{H}_5\text{F})][\text{BAR}^5_4]\) with neat \(\text{H}_3\text{B} \cdot \text{PPhH}_2\) to 90 °C for 4 h led to a peak in the \(^{31}\text{P}\) NMR spectrum matching previous literature reports for polyphenylphosphinoborane along with minor signals thought to be short-chain oligomers and cyclic species [152]

An expansion of the scope of dehydrocoupling of primary phosphine-boranes was reported in 2014 when ferrocenylphosphine-boranes were dehydrocoupled to form polymeric material. Using the catalytic system developed by Manners et al. \(\text{H}_3\text{B} \cdot \text{P}\{(\text{CH}_2)_x\text{Fc}\}_2\text{H}_2\) (Fc = ferrocenyl, \(x = 0\) or \(1\)) was dehydrocoupled using 0.6 mol% \([\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})]_2\) (based on Rh) with the products characterised by NMR spectroscopy (Figure 18). Low molecular weight polymer was formed when the
reaction was carried out in toluene solution (110 °C) but in melt conditions higher molecular weights could be obtained (Scheme 71) [176]

![Scheme 71 Rh Idaho catalysed dehydrocoupling of primary ferrocenyl phosphine-boranes.](image)

Figure 18 $^{31}$P NMR spectra of monomer H$_3$B·P(CH$_2$Fc)H$_2$ (A, B) and polymer [H$_2$BP(CH$_2$Fc)H]$_n$ (C, D) in CDCl$_3$ (161.9 MHz): (A) $^1$H-coupled, $^1$J$_{PH}$ = 358 Hz; (B) $^1$H-decoupled; (C) $^1$H-coupled, $^1$J$_{PH}$ = 352 Hz; (D) $^1$H-decoupled. Reprinted (adapted) with permission from S. Pandey, P. Lönnecke and E. Hey-Hawkins, Eur. J. Inorg. Chem., 2014, 2456-2465. Copyright 2014, John Wiley and Sons.

The same group reported the dehydrocoupling of secondary phosphine-boranes bearing ferrocenyli substituents. The H$_3$B·P'Bu(Fc)H substrate could be dehydrocoupled to form the linear diboraphosphine under melt conditions (160 °C) using [Rh(1,5-cod)(µ-Cl)]$_2$ as the catalyst. The product was found to be a mixture of H$_3$B·P'Bu(Fc)H$_2$B·P'Bu(Fc)H and ClH$_2$B·P'Bu(Fc)H$_2$B·P'Bu(Fc)H (Scheme 72), which is a similar observation to that made by Manners et al. in the dimerisation of H$_3$B·P'Bu$_2$H where the terminal chloride was thought to originate from the precatalyst
Interestingly, the authors were able to couple two different phosphine-boranes to form a mixed diboraphosphine, the first time this had been achieved. If a mixture of H_3B·P^tBu(Fc)H and a slight excess of either H_3B·P^tBu(″Bu)_2H or H_3B·PPh(″Bu)_2H was heated under melt conditions (160 °C) with a [Rh(1,5-cod)_2][O_3SCF_3] precatalyst (4 mol%), the linear diboraphosphines could be synthesised in moderate isolated yield with the tertiary phosphine in the terminal position due to its lack of P—H functionality (Scheme 72) [177]

Scheme 72 Catalytic dehydrocoupling of secondary phosphine-boranes bearing ferrocenyl substituents.

### 3.8 Lewis Acid Catalysed Dehydrocoupling of Phosphine-Boranes

In 2003 came the first report of a non-transition metal catalysed dehydrocoupling of primary phosphine-boranes. The strong Lewis acid B(C_6F_5)_3 was used as the catalyst and heating a solution of H_3B·PPhH_2 to 90 °C in toluene (0.5 mol% catalyst) for 3 h resulted in short oligomers and cyclic species characterised by $^{31}$P NMR spectroscopy and size exclusion chromatography. Alternatively, a longer reaction time at a lower temperature (3 d at 20 °C) resulted in high molecular weight polymeric material. This catalyst was also found to dehydropolymerise H_3B·PH_3 (formed from bubbling PH_3 and B_2H_6 through dichloromethane) to form oligomers at 70 °C and polymer at 90 °C
The mechanism of polymerisation was thought to involve an initial exchange reaction of the strong Lewis acid with the BH$_3$ of one phosphine-borane to form (C$_6$F$_5$)$_3$B·PPh$_2$. The coordination of the electron-withdrawing group thus increased the acidity of the P—H bond allowing reaction with the hydridic B—H bond on another phosphine-borane. This argument is similar to that made by Manners et al. for the reason phosphine-boranes with fluorinated substituents dehydrocouple at lower temperatures than simple aryl phosphine-boranes [178].

Scheme 73 Formation of polyphosphinoboranes using Lewis acid B(C$_6$F$_5$)$_3$ as a precatalyst along with a suggested mechanism.


It is clear from this review that the mechanistic studies into the dehydrocoupling of amine– and phosphine–boranes has seen a rapid development over the last 5 years, with many systems studied, using catalysts based on metals from across the whole periodic table. The primary driver for this intense research has been the development of catalysts that might offer significant benefits with regard to the kinetics of hydrogen release, for potential use when this gaseous product is linked with a fuel cell. Although it is unlikely that any of these sometimes elegant and well–defined molecular systems would be capable of delivering a truly practicable system for long–
term commercial use (i.e. with the constraints of total system weight, cost, extended recyclability, stability, operating conditions), although notable examples do exist of systems that show promise,[117] this overarching goal has provided a focus for the elucidation of the mechanism of dehydrocoupling. More likely is that any commercial catalyst will be based around heterogeneous processes that utilise relatively cheap metal/ligand precursors – such as first row transition metals [47]. More recently, attention is turning to the use of molecular single–site catalysts for the closely related dehydropolymerisation of amine–boranes. In this process the end product of value is the aminoborane, rather than the hydrogen released. It is probable that many of the major developments will likely arise from this area in the near future, as polyaminoboranes (and their closely related polyphosphinoboranes) have an essentially untapped potential with regard to their use as high–performance polymeric materials, pre–ceramics or as precursors to extended B–N materials, such as white graphene.

Although complex and nuanced, with different catalysts and amine–borane starting materials offering a variety of final products, intermediates, and observed catalyst resting states, a number of mechanistic scenarios are now becoming apparent for dehydrocoupling. The intermediate role of aminoboranes is now becoming clear, but whether such species remain associated with the metal centre once formed or are released into solution is still to be completely resolved. This is important as free aminoborane oligomerises to form cyclic products (i.e. borazines), whereas if B—N bond formation at the metal centre is fast then polymerisation can occur. In some systems aminoborane formation and B—N bond forming reactions may be closely correlated. Likewise, the propagating species in dehydropolymerisation and
dehydroooligomerisation still remain to be fully resolved. Given the regular occurrence of amido– (and phopshido–) boranes with supporting β–B–agostic interactions in many of these mechanistic studies, such species are perhaps likely candidates as key intermediates. If the current pace of discovery continues over the next 5 years it is likely that the resulting mechanistic insight will lead to the production of catalysts that can dehydrocouple amine– and phosphine–boranes “to order” to provide high–value bespoke materials such as polyaminoboranes, or pre–ceramics in an atom efficient process, recognising that hydrogen is the only by–product. Indeed, linking such bond–forming processes with hydrogen transfer reactions might prove profitable if it generates two products of value with true 100% atom economy [86]. As recently enunciated,[5] the formation of main group element–element bonds using catalytic techniques lags behind those developed for carbon–carbon bond forming reactions that are so important for the synthesis of state-of-the-art organic molecules and macromolecules. The development of robust, and scalable, catalysts for amine– and phosphine–borane dehydrocoupling is thus one promising area to develop with regard to opening up the field to all those interesting in main–group element–element bond forming reactions; whether ultimately interested in the release of gaseous hydrogen from such processes, or the products and functional materials that arise directly from such events. It will certainly be interesting to see how the field develops.

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