Heterogeneous Dehydrocoupling of Amine–Borane Adducts by Skeletal Nickel Catalysts

Alasdair P. M. Robertson,[†] Riccardo Suter,[†,‡] Laurent Chabanne,[†] George R. Whittell,[†] and Ian Manners[†,*]

[†]School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS United Kingdom

[‡]Department of Chemistry and Applied Biosciences, ETH, Hönggerberg, 8093 Zürich, Switzerland

Ⓢ *Supporting Information*

ABSTRACT: Skeletal Ni, produced by the selective leaching of Al from a Ni/Al alloy, has been successfully employed in the catalytic dehydrogenation of various amine–borane adducts. The combination of low cost and facile single-step synthesis make this system a potentially attractive alternative to the previously described precious metal and other first-row metal catalysts. The heterogeneous nature of the catalyst facilitates convenient product purification, and this is the first such system to be based on a first-row transition metal. Catalytic dehydrocoupling of $Me_2NH \cdot BH_3$ (**1**) and $Et_2NH \cdot BH_3$ (**5**) was demonstrated using 5 mol % skeletal Ni catalyst at 20 °C and produced $[Me_2N{-}BH_2]_2$ (**2**) and $[Et_2N{-}BH_2]_2/Et_2N{=}BH_2$ (**6**), respectively. The related adduct $iPr_2NH \cdot BH_3$ (**7**) was also dehydrogenated to afford $iPr_2N{=}BH_2$ (**8**) but with significant catalyst deactivation. Catalytic dehydrocoupling of $MeNH_2 \cdot BH_3$ (**9**) was found to yield the cyclic triborazane $[MeNH{-}BH_2]_3$ (**10**) as the major product, whereas high molecular weight poly-(methylaminoborane) $[MeNH{-}BH_2]_n$ (**11**) ($M_w = 78\,000$ Da, PDI = 1.52) was formed when stoichiometric quantities of Ni were used. Similar reactivity was also observed with $NH_3 \cdot BH_3$ (**12**), which produced cyclic oligomers and insoluble polymers, $[NH_2{-}BH_2]_x$ (**14**), under catalytic and stoichiometric Ni loadings, respectively. Catalyst recycling was hindered by gradual poisoning. A study of possible catalyst poisons suggested that BH_3 was the most likely surface poison, in line with previous work on colloidal Rh catalysts. Catalytic dehydrogenation of amine–borane adducts using skeletal Cu and Fe was also explored. Skeletal Cu was found to be a less active dehydrogenation catalyst for amine–borane adducts but also yielded poly(methylaminoborane) under stoichiometric conditions on reaction with $MeNH_2 \cdot BH_3$ (**9**). Skeletal Fe was found to be completely inactive toward amine–borane dehydrogenation.
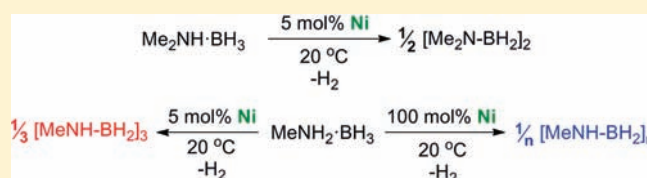
■ INTRODUCTION

Interest in amine–borane adducts, which are commonly applied as reducing and hydroborating reagents in organic synthesis,[1,2] has increased dramatically over the past decade. This increased attention has, in part, resulted from their potential application in hydrogen storage and transfer[3–6] and also as precursors to new materials.[7–10] Catalytic dehydrocoupling/dehydrogenation of amine–borane adducts is of key importance in this respect, and a plethora of catalytic systems have now been reported, which are based on various transition metals[5,11–25] and main group elements.[26,27] In general, however, the reported catalyst systems are based on 4d and 5d metals, including Rh, Ir, Re, and Ru, where the cost is particularly high relative to their 3d counterparts (Supporting Information, Figure SI 2). With regard to first-row metal-catalyzed processes, homogeneous systems based on Ni and Ti have been reported,[15,17,28–30] as have those containing Cr, Mn and Fe,[15,18,19,31,32] although most of the compounds of the latter required photoirradiation to produce a catalytic effect. Stoichiometric and catalytic amine–borane dehydrocoupling/dehydrogenation has also been achieved using frustrated Lewis pair (FLP) chemistry, although this work is currently in its infancy.[33–35] The development of novel first-row amine–borane dehydrocoupling catalysts is therefore of significant
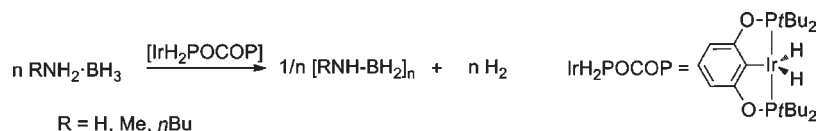
interest, due to the low cost of these metals relative to those of the second and third row.

The analogy between C–C bonds and B–N bonds is well-known,[36] and amine–borane adducts and aminoboranes can be considered as inorganic analogues of alkanes and olefins, respectively. This relationship has guided catalyst discovery within the amine–borane dehydrogenation field, where the alkane dehydrogenation catalyst IrH_2POCOP (POCOP = η^3-1,3-$(OPtBu_2)_2$-C_6H_3)[37] has been successfully applied to ammonia–borane and various primary amine–borane adducts as substrates to yield a variety of dehydrogenated products,[21,38] including the first soluble polyaminoboranes (Scheme 1).[20] Similarly, Schneider and Fagnou have also successfully applied Ru catalysts to amine–borane dehydrocoupling,[12,14] following previous reports of their use in alcohol redox processes and ketone hydrogenation.[39–41] The screening of such catalysts was initially attempted due to the similarities in both polarity and electronic structure between ammonia–borane and methanol.

Based upon a combination of the C–C/B–N bonding analogy and the previous reports of amine–borane dehydrogenation by

Scheme 1. Catalytic Amine−Borane Dehydropolymerization by IrH$_2$POCOP[20,21,38]

$$n \ RNH_2 \cdot BH_3 \xrightarrow{[IrH_2POCOP]} 1/n \ [RNH\text{-}BH_2]_n \ + \ n \ H_2$$

$$R = H, \ Me, \ n\text{Bu}$$

$$IrH_2POCOP =$$

Scheme 2. Generalized Aqueous Synthesis of Skeletal Ni from Ni/Al Alloy

$$2 \ Ni/Al \ + \ 2 \ NaOH \ + \ 6 \ H_2O \longrightarrow 2 \ Ni \ + \ 2 \ Na[Al(OH)_4] \ + \ 3 \ H_2$$

Scheme 3. Catalytic Dehydrogenation of 1 with Ni$_{T50}$ To Produce the Cyclic Diborazane 2

$$Me_2NH \cdot BH_3 \xrightarrow[\text{Toluene, 20 °C}]{\text{5 mol\% Ni}_{T50}} \frac{1}{2} \ [Me_2N\text{-}BH_2]_2 \ + \ H_2$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

C=C hydrogenation catalysts, we postulated that skeletal first-row transition metals may be effective amine−borane dehydrogenation catalysts. Skeletal first-row metals are well-known olefin hydrogenation catalysts, with their activity first reported in patents by Raney in 1925 and 1927.[42,43] These catalysts are generally produced by the selective leaching of Al or Si content from an alloy with the relevant metal,[44] and skeletal forms of Ni,[43,45,46] Cu,[46−50] Co,[51] and Fe[52] have been reported. These highly reactive, high surface area systems are attractive due partly to their heterogeneous nature, which facilitates product separation, and perhaps more importantly due to their relatively low cost and ease of synthesis.

The potential for skeletal first-row metals to act as cheap, readily available heterogeneous catalysts provided us with a strong impetus to investigate their use in the dehydrocoupling of amine−borane adducts. In this paper we report our studies on the catalytic dehydrogenation of amine−borane adducts using skeletal Ni, Cu, and Fe.

■ RESULTS AND DISCUSSION

Skeletal Ni Catalysts. A representative example of skeletal Ni was prepared in deaerated aqueous solution via a modification of literature methods (Scheme 2).[53] This approach effectively involved the base leaching of Al from a commercial 50:50 wt % alloy of Ni and Al at 50 °C. The solid product was isolated by decantation of the aqueous solution and then washed successively with deaerated ethanol and diethyl ether, before the remaining volatile species were removed under high vacuum. The catalyst produced under these conditions is henceforth referred to as Ni$_{T50}$, where the subscript denotes the leaching temperature.

Although skeletal Ni catalysts are often employed in aqueous or protic media and indeed are often supplied as aqueous slurries,[54−56] this would clearly be inappropriate for the non-hydrolytic amine−borane dehydrogenation of interest in this work. Furthermore, catalytic hydrolysis and alcoholysis of amine−boranes using various heterogeneous catalysts, including skeletal Ni, have previously been reported.[57,58] In initial experiments, toluene was therefore utilized as an alternative solvent, and the adduct Me$_2$NH·BH$_3$ (**1**) selected due to its well-defined dehydrogenation chemistry, which yields the cyclic diborazane [Me$_2$N−BH$_2$]$_2$ (**2**) as the final product. Treatment of a toluene solution of **1** with 5 mol % Ni$_{T50}$ produced vigorous bubbling, with ^{11}B NMR spectroscopy indicating complete consumption of the adduct within 6 h. The sole product was demonstrated by ^{11}B NMR spectroscopy to be the expected diborazane **2**
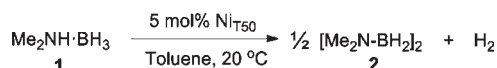
(Scheme 3), which appeared as a triplet with a chemical shift of 4.5 ppm (J_{BH} = 113 Hz).[11] The quantitative nature of the dehydrogenation in this case was confirmed through the use of an internal NMR standard.[59] Analysis of the peak integrals in the ^{11}B NMR spectrum of the resulting mixture confirmed ∼100% yield of aminoborane **2**.

Ni Catalyst System Optimization. The properties of skeletal Ni catalysts and their resulting hydrogenation activity can be strongly attenuated by the conditions used during their synthesis and the catalytic conditions subsequently employed. With respect to tuning the structure of the skeletal metal, the temperature utilized during the Al leaching process has been shown to have a significant effect with the catalyst produced at 50 °C exhibiting the highest activity for hydrogenation reactions.[60] Temperatures in excess of 50 °C have been shown to produce lower surface area materials as a result of particle sintering, which creates larger pore volumes and reduces catalytic activity.[44] At lower temperatures, the base leaching reaction is markedly slower, and it has also been suggested that the Ni/Al ratio at the surface is lower in the resulting catalysts, leading to reduced hydrogenation activity.[46,61]

With a view to investigating a range of Ni catalysts for amine−borane dehydrogenation, we therefore prepared two further batches of skeletal Ni, leaching the Al content at 20 and 100 °C, respectively, to produce a total of three catalysts henceforth referred to as Ni$_{T20}$, Ni$_{T50}$, and Ni$_{T100}$. Somewhat conflicting reports exist concerning the sensitivity of the catalyst synthesis to oxygen, with some preparations not describing the use of deaerated solvents.[53] A sample of Ni$_{T50}$ was therefore also prepared using aerated solvents (denoted Ni$_{T50}$*) for comparative purposes. The degree of Al leaching was quantified in the cases of Ni$_{T20}$, Ni$_{T50}$, and Ni$_{T100}$ by atomic absorption spectroscopy (AAS), which indicated negligible differences between the three samples with respect to their Ni/Al contents.[62]

Studies of the rate of dehydrogenation of **1**, using the range of Ni catalysts with a 5 mol % catalyst loading, indicated clearly that the catalyst produced at 50 °C under anaerobic conditions (Ni$_{T50}$) led to the most rapid conversion to **2** (Figure 1). This result is what would be expected based upon the reported surface areas of the materials produced at the different temperatures. At this stage, investigations utilizing Ni$_{T20}$ and Ni$_{T100}$ were discontinued, and subsequent reactions were carried out using Ni$_{T50}$. The effect of using aerated solvents in the synthesis of skeletal Ni upon the rate of dehydrogenation of **1** was found to be significant. Ni$_{T50}$* produced a significantly slower dehydrogenation reaction under the same conditions employed for Ni$_{T50}$,
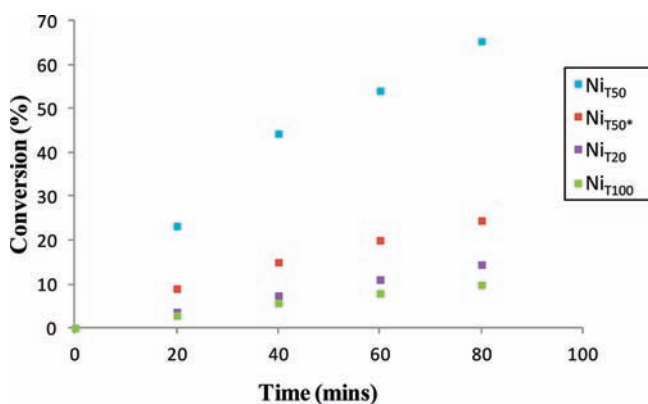
Figure 1. Conversion of **1** to **2** with time for 5 mol % loadings of various skeletal Ni formulations in toluene solution at 20 °C. Conversions based on integration of ^{11}B NMR spectra.
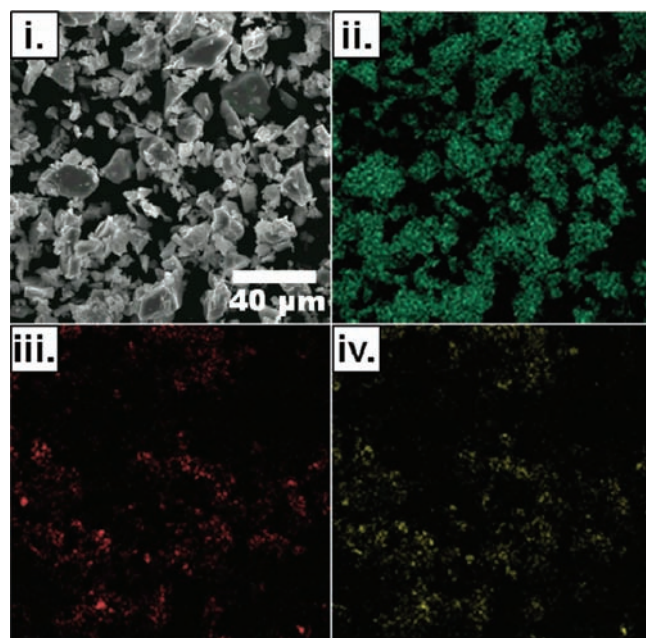

Figure 2. (i) SEM micrograph of Ni_{T50} as prepared. (ii) EDX spectroscopic Ni mapping. (iii) EDX spectroscopic Al mapping. (iv) EDX spectroscopic O mapping.

which was presumably due to partial deactivation of the Ni surface by oxidation. Deactivation by oxidation was also suggested by the complete catalytic inactivity of a sample of Ni_{T50} toward **1** in toluene solution after exposure of the solid catalyst to air over 12 h.

Characterization of all catalyst formulations was performed using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. All catalysts showed the expected surface composition, which was dominated primarily by Ni with lower levels of Al detected. Oxygen was also detected and was believed to occur as a result of the unavoidable exposure of the samples to the atmosphere during introduction to the microscope (Figure 2). (For related data for other catalysts see Supporting Information, Section 5).

*Effect of Solvent on the Rate of Dehydrogenation of **1** with Ni_{T50}.* It was important to elucidate the effect of solvent on the

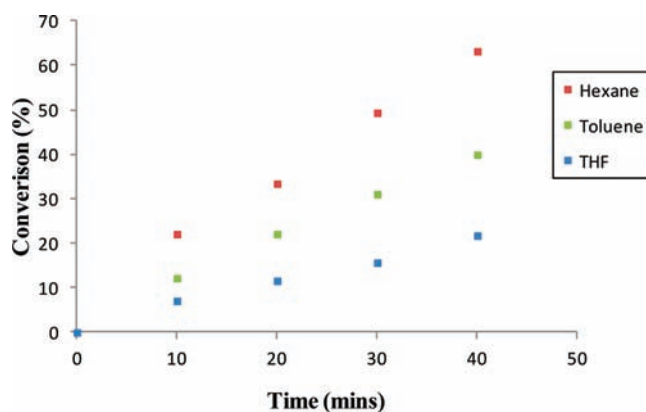**Figure 3.** Conversion of **1** to **2** with time in various solvents at 20 °C and with 5 mol % Ni_{T50}. Conversions based on integration of ^{11}B NMR spectra.

activity of the skeletal Ni. As previously discussed, skeletal Ni is often used in aqueous or protic media, with fewer literature reports documenting its use in common organic solvents. Kishida and Teranishi, however, investigated the direct hydrogenation of acetone using skeletal Ni in various organic solvents, demonstrating decreasing rates of hydrogenation in the order *n*-hexane > cyclohexane > methanol and isopropanol.[63] We therefore screened the reaction of **1** with 5 mol % Ni_{T50} in a variety of common organic solvents and studied the initial rate of dehydrogenation in each case (Figure 3).

The rate of dehydrogenation was shown to depend strongly upon the reaction solvent with the least polar, hexane, producing the most rapid dehydrogenation and reaching complete conversion of **1** to **2** after 1.5 h. As the solvent polarity increased from toluene to tetrahydrofuran (THF), the activity dropped, which is presumably due to an increased level of competition in the binding of solvent and amine—borane adduct at the Ni surface. Although this screening indicated that the use of hexane resulted in the most rapid reaction, it was considered inappropriate for further investigations as it was a poor solvent for adduct **1**. Furthermore, other potential substrates, i.e. $MeNH_2 \cdot BH_3$ and $NH_3 \cdot BH_3$, are completely insoluble in this solvent, which would make a comparison of reaction rates difficult. Toluene was therefore accepted as the most effective solvent for further studies, providing a compromise between catalyst activity and substrate solubility.

*Investigation of the Heterogeneous Nature of Ni_{T50} in the Catalytic Dehydrogenation of **1***. Although skeletal metals are accepted heterogeneous catalysts for various processes, it was conceivable that the metal could be leached into solution, thereby serving as a precursor to an active homogeneous species. To confirm the presence of a solely heterogeneous system, the effects of filtration and Hg poisoning on the catalytic dehydrogenation of **1** were investigated. Both procedures are accepted tests for heterogeneous catalysts, with literature precedent for their use.[64−66] Three parallel reactions of **1** with 5 mol % Ni_{T50} were preformed at 20 °C, and ^{11}B NMR spectra were recorded for each reaction every 10 min over 2 h. After 55 min, one mixture was filtered through glass fiber paper, the second was treated with a large excess of Hg, and the final mixture was preserved as a control. Upon filtration, all visible bubbling in the solution stopped and conversion of **1** to **2** was shown to cease immediately by ^{11}B NMR spectroscopy (Figure 4a). These results are
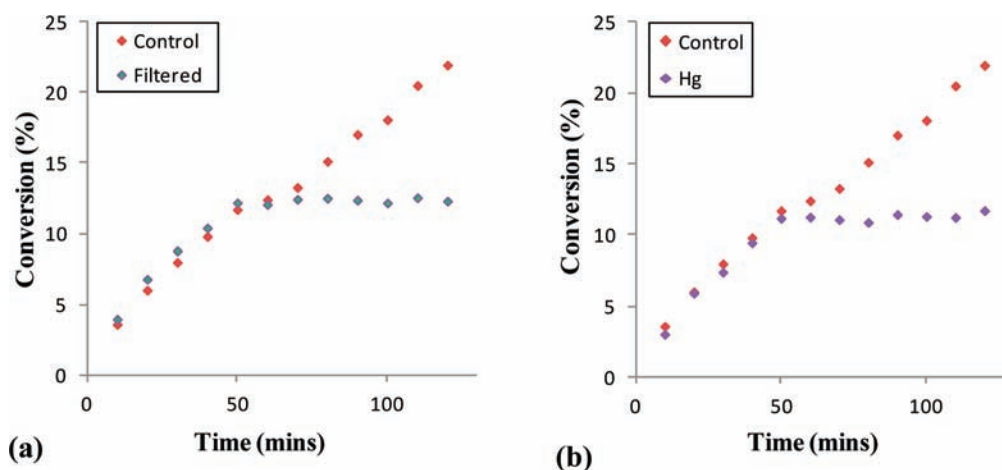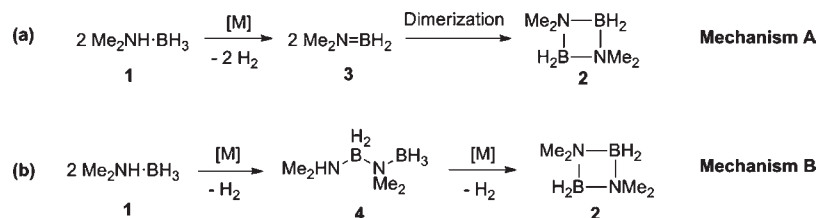
Figure 4. Effects of (a) filtration and (b) Hg poisoning (after 55 min) on the Ni$_{T50}$ catalyzed dehydrogenation of **1** in toluene at 20 °C. Conversions based on integration of ^{11}B NMR spectra.

Scheme 4. Possible Mechanisms for the Metal-Catalyzed Dehydrogenation of 1

consistent with a catalyst which is insoluble and heterogeneous. Addition of Hg to the reaction mixture provided almost identical results, completely halting catalysis (Figure 4b). The effect of excess Hg pointed further toward a heterogeneous catalyst system, as Hg is known to form amalgams with heterogeneous metal catalysts but has little effect on most homogeneous systems.[65,67,68]

*Mechanism of Catalytic Dehydrogenation of **1** with Ni$_{T50}$.* With respect to the mechanism of dehydrogenation of **1** to form **2** by Ni$_{T50}$, two likely pathways appear possible. Initial hydrogen release may occur either via an intra- or intermolecular process, to form either dimethylaminoborane, Me$_2$N=BH$_2$ (**3**) (Scheme 4a, mechanism A), or the linear diborazane, Me$_2$NH—BH$_2$—NMe$_2$—BH$_3$ (**4**) (Scheme 4b, mechanism B). These intermediates may then undergo cycloaddition or dehydrogenative cyclization reactions, respectively, to afford the cyclic diborazane **2**. In the case of mechanism A, H$_2$ release occurs at the metal center to produce two molecules of **3**, which subsequently dimerize in an off-metal process. In the case of mechanism B, H$_2$ release occurs in two distinct steps, both of which occur at the metal center. In an initial step, one equivalent of H$_2$ is lost in an intermolecular fashion to form **4**, with a subsequent intramolecular process releasing a further equivalent of H$_2$ and forming the cyclic dimer **2**.

Both mechanisms A and B have been reported experimentally for metal and FLP-induced amine—borane dehydrogenation, with route A perhaps the most commonly observed,[15,16,18,19,33,34,69−72] with significant support from computational studies.[12,73−75] Route B is less common but has been postulated as the mechanism for thermal dehydrocoupling of amine—boranes[11,76,77] and has been implicated in various catalytic systems, most convincingly in the

case of that based on titanocene, "Cp$_2$Ti".[17,28] In the latter system, experimental and computational evidence for mechanism B was elucidated, although a previous computational study favored mechanism A.[78] It has also been shown that in some systems, most notably in that based on Ru reported by Schneider and co-workers, that both mechanisms may operate in parallel.[13]

During the dehydrogenation of **1** using Ni$_{T50}$ at 20 °C, there was evidence for the formation of small quantities (<2%) of **3** within the reaction mixture, as evidenced by ^{11}B NMR spectroscopy [δ_B = 37.0 (t, $^1J_{BH}$ = 130 Hz)].[13,19] The presence of this species suggested that dehydrogenation via mechanism A was likely to operate, with **3** known to dimerize in a spontaneous fashion.[69] To probe the mechanism further, a catalytic loading of 50 mol % was employed, in an attempt to increase the quantity of **3** observed in the early stages of reaction. ^{11}B NMR spectroscopic analysis, however, indicated not only an increase in the magnitude of the signal attributed to **3** but also the appearance of a new peak consistent with the bridging BH$_2$ environment in the linear diborazane **4** [δ_B = 1.16 (t, J_{BH} = 106 Hz, BH$_2$)][13,79] (Figure 5). It is likely that the signal due to the terminal BH$_3$ moiety in the linear diborazane **4** overlaps with that of unreacted **1**, from which it is indistinguishable in toluene.[17]

The unexpected appearance of peaks consistent with **4** implied that dehydrogenation via mechanism B was also occurring to some extent. To probe the contribution of this mechanism, a sample of pure, independently prepared **4** was reacted with 5 mol % Ni$_{T50}$. This led to 20% conversion to **2** over 6 h at 20 °C, as evidenced by ^{11}B NMR spectroscopy (Scheme 5a), during which time **1** was found to react to completion under the same conditions (Scheme 5b).
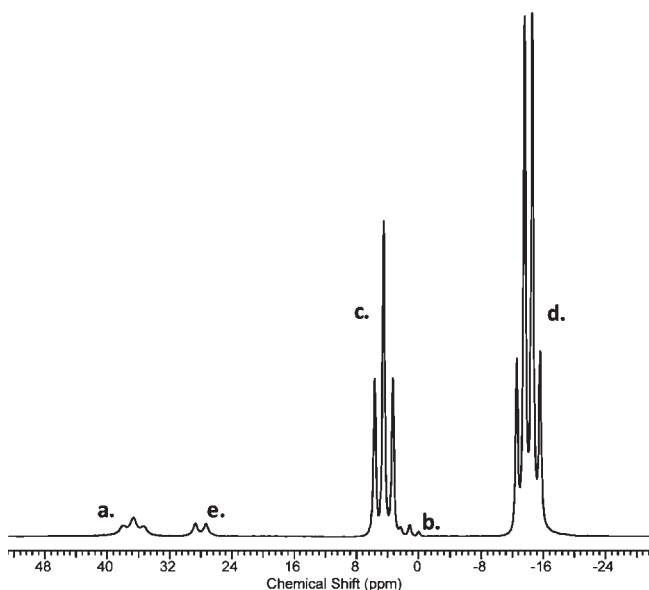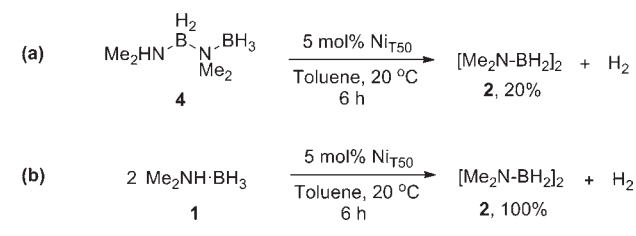
Figure 5. ^{11}B NMR spectrum after 5 min of the reaction of **1** with 50 mol % Ni_{T50} in toluene: (a) $Me_2N=BH_2$ (**3**); (b) $Me_2NH-BH_2-NMe_2-BH_3$ (**4**); (c) $[Me_2N-BH_2]_2$ (**2**); (d) $Me_2NH\cdot BH_3$ (**1**) and $Me_2NH-BH_2-NMe_2-\underline{BH_3}$ (**4**); and (e) $HB(NMe_2)_2$.

Scheme 5. Reactions of (a) $Me_2NH-BH_2-NMe_2-BH_3$ (4) and (b) $Me_2NH\cdot BH_3$ (1) with Ni_{T50} at 20 °C in Toluene


It is likely, based on the reactivity of isolated **4** with Ni_{T50}, that both mechanisms A and B operate in parallel during the reaction of **1** with Ni_{T50} (Scheme 6). However, the rate of reaction of **1** via mechanism A is significantly greater than that via mechanism B, as evidenced by the absence of peaks corresponding to **4** in the ^{11}B NMR spectra under catalytic conditions. It is also conceivable, however, that at higher catalyst loadings, an increased concentration of **3** leads to an appreciable reaction with remaining amine−borane adduct **1**, in which the metal may or may not be involved, thereby forming **4** as discussed by Schneider and Weller, respectively (Scheme 6).[13,69] The thermodynamics of the reaction between **3** and **1** have also been elucidated computationally by Schneider and co-workers with a reaction enthalpy of −2.3 kcal mol^{−1}, suggesting a thermodynamically feasible process under ambient conditions.[13]

Reactions of Ni_{T50} with Other Secondary Amine−Borane Adducts. Following the successful catalytic dehydrocoupling of **1** with Ni_{T50}, the reactivity of this catalyst with other amine−borane substrates was also investigated. Reaction with the closely related $Et_2NH\cdot BH_3$ (**5**) with 5 mol % Ni_{T50} led to catalytic dehydrocoupling over 60 h, to yield a 1:48 mixture of $Et_2N=BH_2$ (**6a**) $[\delta_B\ 36.5\ (t,\ J_{BH} = 125\ Hz)\ ppm]$ and $[Et_2N-BH_2]_2$ (**6b**) $[\delta_B\ 1.5\ (t,\ J_{BH} = 112\ Hz\ ppm)]$,[80] respectively (Scheme 7). The

Scheme 6. Proposed Mechanism of Dehydrogenation of 1 by Skeletal Ni
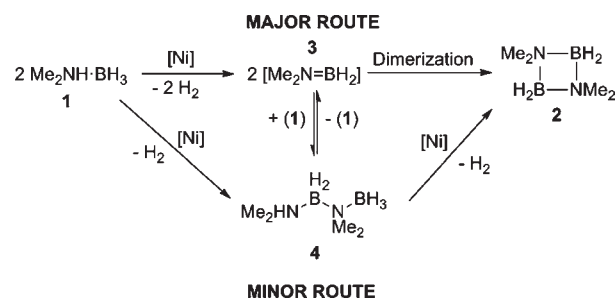
Scheme 7. Catalytic Dehydrogenation of 5 with 5 mol % Ni_{T50} in Toluene at 20 °C
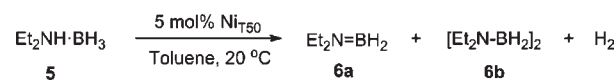
reduced rate of the dehydrogenation reaction relative to that of **1** was initially postulated to be due to the increased steric bulk of this adduct. The ratio of **6a** to **6b**, at 1:48 differed from the values previously published,[31,80] where the ratios vary from 40:60 to 10:90. However, the reaction solvents and methods of preparation vary widely, and this may account for the difference in the observed product ratios.

To provide further insight into the origins of both the rate reduction and the product ratios observed for **5**, catalytic dehydrogenation of the sterically encumbered adduct $iPr_2NH\cdot BH_3$ (**7**) was attempted. Upon reaction of **7** with 5 mol % Ni_{T50} at 20 °C, vigorous bubbling was observed which quickly ceased, with only ∼5% conversion to $iPr_2N=BH_2$ (**8**) $[\delta_B\ 34.6\ (t,\ J_{BH} = 127\ Hz,\ BH_2)\ ppm]$ being detected after 16 h. No further increase in conversion was observed even after 120 h, however, increasing the catalyst loading to stoichiometric quantities yielded complete conversion of **7** to the expected aminoborane **8**, as evidenced by ^{11}B NMR spectroscopy. The limited extent of the dehydrogenation of **7** with 5 mol % of Ni_{T50} is not easily explained solely on steric grounds, as although a reduced rate of conversion to **8** would be expected, the reaction would also be anticipated to ultimately reach completion. With a view to probing the chemistry further, the stoichiometric reaction of **7** with Ni_{T50} was repeated in C_6D_6, facilitating study of the final reaction mixture by ^{1}H and ^{13}C NMR spectroscopies. In this solvent ^{11}B NMR spectroscopy again indicated **8** as the sole boron-containing product. However, the ^{1}H NMR spectrum contained 2 sets of isopropyl resonances in a 7:3 ratio, with the larger pair being assigned to aminoborane **8** $[\delta_H\ 3.16\ (2H,\ septet,\ J_{HH} = 6.79\ Hz,\ CH)\ and\ 1.04\ (12H,\ d,\ J_{HH} = 6.79\ Hz,\ CH_3)\ ppm]$. The second set of isopropyl resonances corresponded to those of iPr_2NH in the same solvent $[\delta_H\ 2.81\ (2H,\ septet,\ J_{HH} = 6.24\ Hz,\ CH)\ and\ 0.95\ (12H,\ d,\ J_{HH} = 6.24\ Hz,\ CH_3)\ ppm]$, suggesting B−N bond cleavage had occurred. Addition of $B(OiPr)_3$ as an internal NMR standard enabled quantification of the [11]B content of the solution and indicated the loss of ∼30% of the initial boron present.[59] It is highly likely, therefore, that B−N bond cleavage in **7** or **8** leads to coordination of a borane moiety to the Ni surface, liberating

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Scheme 8. Ni-Catalyzed Dehydrogenation of 7 in Toluene Solution at 20 °C[a]

$$iPr_2NH \cdot BH_3 \xrightarrow[\substack{\text{Toluene, 20 °C} \\ -Ni_{T50}BH_x{}^a}]{Ni_{T50}} iPr_2N=BH_2 + iPr_2NH + H_2$$
$$\qquad\qquad 7 \qquad\qquad\qquad\qquad 8, 70\% \quad\quad 30\%$$
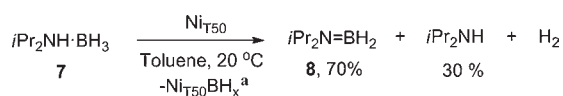
[a] $Ni_{T50}BH_x$ is postulated based on stoichiometry of other reagents/products.

Scheme 9. Dissociation of 7 To Produce Free Amine and BH_3

$$iPr_2NH \cdot BH_3 \rightleftharpoons iPr_2NH + BH_3$$
$$\qquad 7$$

free amine into solution. Such a process may be responsible for the low catalytic activity of Ni_{T50} toward this substrate, with BH_3 poisoning the catalyst by irreversibly binding to the metal surface (Scheme 8).

To probe the source of the free amine, isolated **8** was reacted with a stoichiometric quantity of Ni_{T50} over 16 h at 20 °C in C_6D_6. Over this time period, ^{1}H NMR spectroscopic analysis of the reaction mixture indicated 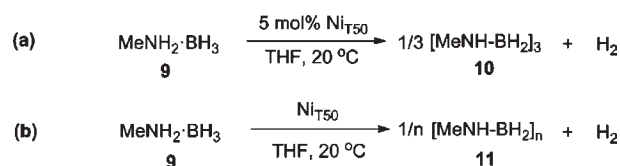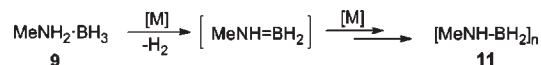very minor elimination (~1%) of iPr_2NH into solution, with the vast majority of **8** remaining unreacted under these conditions. It is therefore probable that the source of the free amine in solution is the initial adduct **7** and that iPr_2NH is liberated to solution through the dissociative equilibrium present in the adduct (Scheme 9).[81,82] In this process, an equal quantity of BH_3 must also be released to the solution, which could then be removed from the equilibrium by irreversible coordination to Ni.[83] The fact that **7** reacts significantly in this fashion may be explained to some degree by the relative bond strengths in the three secondary amine–borane adducts studied. Various studies, both experimental and computational,[84,85] have suggested that increasing steric bulk at nitrogen leads to a reduction in bond enthalpy for the N–B σ-bond in an amine–borane adduct. This is exemplified by the bond enthalpies that are believed to decrease in the following series in the following order: $Et_2NH \cdot BH_3 > nPr_2NH \cdot BH_3 > nBu_2NH \cdot BH_3$.[84] The weaker B–N bond in the case of **7** is likely therefore to favor dissociation, with a greater proportion of free amine and BH_3 in solution than in the case of **5** or **1**. The reduced rate of dehydrogenation of **5** relative to **1** may possibly be explained by a similar argument, although an increase in steric encumbrance is also likely to reduce the rate of reaction such that the order of adduct reactivity is **1** > **5** > **7**.

*Reactions of Ni_{T50} with $MeNH_2 \cdot BH_3$ (**9**) and $NH_3 \cdot BH_3$ (**12**).* The dehydrocoupling of primary amine–borane adducts was also explored, with that of $MeNH_2 \cdot BH_3$ (**9**) attempted using 5 mol % Ni_{T50} at 20 °C. This reaction was performed in THF due to the low solubility of **9** in toluene. On catalyst addition, the reaction mixture was observed to bubble vigorously over 5 min, and after 16 h ~15% conversion to two new products was observed by ^{11}B NMR spectroscopy. Allowing the reaction to stir for a further 100 h allowed the conversion to products to reach 70%, with the major peak (with an upfield shoulder) at −5.1 ppm now dominating as a triplet in the proton-coupled ^{11}B NMR spectrum (J_{BH} = 96 Hz). Upon isolation, this product was identified on the basis of ^{11}B, ^{1}H, and ^{13}C NMR spectroscopies as the cyclic triborazane $[MeNH-BH_2]_3$ (**10**) (Scheme 10a), a postulated intermediate in the catalytic dehydrocoupling of **9**

Scheme 10. Reaction of 9 with (a) Catalytic and (b) Stoichiometric Quantities of Ni_{T50} in THF at 20 °C

$$(a) \quad MeNH_2 \cdot BH_3 \xrightarrow[\text{THF, 20 °C}]{5\ mol\%\ Ni_{T50}} 1/3\ [MeNH-BH_2]_3 + H_2$$
$$\qquad\qquad 9 \qquad\qquad\qquad\qquad\qquad\qquad 10$$

$$(b) \quad MeNH_2 \cdot BH_3 \xrightarrow[\text{THF, 20 °C}]{Ni_{T50}} 1/n\ [MeNH-BH_2]_n + H_2$$
$$\qquad\qquad 9 \qquad\qquad\qquad\qquad\qquad\qquad 11$$

Scheme 11. Proposed Mechanism of Polymerization of 9 to Produce 11[20]

$$MeNH_2 \cdot BH_3 \xrightarrow[-H_2]{[M]} \big[MeNH=BH_2 \big] \xrightarrow{[M]} [MeNH-BH_2]_n$$
$$\qquad 9 \qquad\qquad\qquad\qquad\qquad\qquad\qquad 11$$

using Rh complexes.[11,86,87] In contrast, however, treatment of an identical solution of **9** in THF with a stoichiometric quantity of Ni_{T50} at 20 °C for 2 h led to a very broad peak in the ^{11}B NMR spectrum at −6 ppm, which was consistent with the formation of poly(methylaminoborane), $[MeNH-BH_2]_n$ (**11**).[20] The product was purified from the catalyst by filtration of the reaction mixture through glass fiber paper, followed by precipitation into hexanes at −78 °C. This procedure furnished a fine white solid in 60% yield (Scheme 10b). Multinuclear NMR spectra of the product were consistent with those previously reported for poly(methylaminoborane),[20] and GPC analysis confirmed the macromolecular nature of the material $[M_w = 78\,000\ Da, PDI\ (M_w/M_n) = 1.52]$.

Previous attempts to produce high molecular weight polyaminoboranes using heterogeneous Rh catalysts resulted in relatively low molecular weight polymers. For example, polymerization of **9** using Rh/Al_2O_3 resulted in a material with $M_w = 26\,000\ Da$ and a PDI = 8.5.[20] The formation of high molecular weight polymers with this heterogeneous Ni system is therefore particularly significant, due to the facile polymer purification that is possible as a result of the insoluble nature of the catalyst. When homogeneous catalysts are employed, unless extensive purification is performed, small amounts of the metal complex remain, as evidenced by the color of the isolated polymers, which results in the slow degradation of the material. When Ni_{T50} is used, perfectly white powders can be obtained, due to the absence of residual metal catalyst. In addition and to the best of our knowledge, this is only the second report of the synthesis of high molecular weight polyaminoboranes by a non-precious metal catalyst.[19]

The fact that the products of the reaction of **9** with Ni_{T50} can be tuned by altering the catalyst loading is significant. This observation reinforces the previously reported assertion that metal-catalyzed polymerization of **9** by IrH_2POCOP occurs via an aminoborane intermediate, $MeNH=BH_2$, which is the true monomer for the polymerization (Scheme 11).[20] In this Ni-based system, where the kinetics of dehydrogenation are markedly slower, catalytic quantities of metal are likely to produce only low concentrations of this monomer in solution, hence favoring the formation of cyclic oligomers or short chain polymers. By increasing the catalyst loading to stoichiometric quantities, the rate of dehydrogenation should be significantly increased. This would be expected to increase the concentration of monomer in solution, allowing for the formation of longer polymer chains.

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Scheme 12. Summary of (a) Catalytic and (b) Stoichiometric Dehydrocoupling of 12 with Ni$_{T50}$ at 20 °C in THF

Scheme 13. Dehydrocoupling Reactivity of Skeletal Cu (a) Catalytic Dehydrogenation of 1; (b) Stoichiometric Dehydrogenation of 1; and (c) Stoichiometric Dehydropolymerization of 9

Table 1. Effect of BH$_3$·THF on Ni$_{T50}$-Catalyzed (5 mol %) Dehydrocoupling of 1 To Form 2 at 20 °C in Toluene

equiv of BH$_3$·THF	conversion 1 h (%)	conversion 6 h (%)	conversion 24 h (%)
0	54	100	N/A
0.1	12	60	100
10	0	0	0

The attempted dehydrogenation of the related and intensively studied adduct, ammonia—borane, NH$_3$·BH$_3$ (12),[3,4,88] led to slow catalytic dehydrogenation over 7 days at 20 °C using 5 mol % Ni$_{T50}$ to produce ~32% conversion to a single product. The product was assigned on the basis of ^{11}B NMR spectroscopy as the cyclolinear aminoborane trimer, B-(cyclodiborazanyl)-aminoborohydride (13) [δ_B −5.5 (d, J_{BH} = 108 Hz, BH), −11.9 (t, J_{BH} = 98 Hz, BH$_2$),[89] −24.4 (br. s, BH$_3$) (Scheme 12a).[19,72] The use of stoichiometric quantities of Ni$_{T50}$, however, resulted in the significant precipitation of a white solid over 24 h, with only small amounts of soluble boron-containing products apparent after 7 days by ^{11}B NMR spectroscopy. The solid, due to its complete insolubility in common organic solvents, proved to be inseparable from the catalyst. The solid-state IR spectrum of the product, however, contained peaks corresponding to N—H (3290 and 3246 cm^{-1}) and B—H (2323 cm^{-1}) stretching modes, all of which correlated well with those described for [NH$_2$—BH$_2$]$_n$ (14) prepared by an Ir-catalyzed dehydrogenation of 12.[7,20] Based on the similarity in the IR spectrum and the complete insolubility in common organic solvents, the product was therefore tentatively assigned as the polyaminoborane 14 (Scheme 12b), analogous to the soluble [MeNH—BH$_2$]$_n$ (11) produced from MeNH$_2$·BH$_3$ (9).[90]

Catalyst Poisoning and Recycling Studies. The limited catalytic effect of Ni$_{T50}$ with respect to the dehydrogenation of 7 (vide supra) suggested the possibility of catalyst poisoning by BH$_3$. To probe this postulate, the effect of BH$_3$·THF on the catalytic dehydrogenation of 1 was investigated. To stirred suspensions of Ni$_{T50}$ at 20 °C was added 0.1 and 10 equiv of BH$_3$·THF, and the mixtures stirred at 20 °C for 16 h before the addition of 20 equiv of 1 (to produce an effective 5 mol % catalyst loading). In both cases, addition of BH$_3$·THF was found to significantly reduce the activity of Ni$_{T50}$ toward the dehydrogenation of 1 at 20 °C, with a partial poisoning effect being observed with 0.1 equiv of BH$_3$·THF and a complete loss of catalytic activity with 10 equiv (Table 1).

The behavior of BH$_3$·THF as a surface poison for heterogeneous metal catalyst systems has been previously demonstrated for a related colloidal Rh system,[83] wherein treatment with BH$_3$·THF led to irreversible binding of boron at the metal surface as a metal boride (M—B) or metal boryl (M—BH$_2$),[83] formed by catalytic decomposition of BH$_3$. It is highly likely therefore that Ni$_{T50}$ is poisoned by BH$_3$ in much the same way, as implicated in the catalytic dehydrogenation of 7 and by the significantly reduced catalytic activity observed on addition of BH$_3$·THF. For completeness, Ni$_{T50}$ was also treated, under identical conditions, with representative examples of the remaining components of a dehydrogenation reaction mixture, specifically H$_2$ and iPr$_2$NH. These species were found to have only a minor effect on the rate of dehydrogenation of 1 at 20 °C when used in 10-fold excess with respect to the catalyst.

Attempts to recycle Ni$_{T50}$ through multiple catalytic dehydrogenations using adduct 1 were only partially successful, with a significant loss in activity apparent after the initial dehydrogenation cycle. On completion of the dehydrogenation of 1 in toluene at 20 °C using a 5 mol % loading of Ni$_{T50}$, the catalyst was isolated and dried under high vacuum, and a further equivalent of 1 was added following resuspension in toluene. No bubbling was observed in solution upon addition of 1, with almost negligible dehydrocoupling detected by ^{11}B NMR spectroscopy after 72 h at 20 °C. When the reaction was repeated without isolation of the catalyst, some catalytic activity was preserved with 16% conversion to 2 possible over 6 h; the time period over which fresh catalyst completely dehydrogenates 1. It is therefore clear that the catalytic activity of Ni$_{T50}$ is significantly reduced after the completion of a single catalytic run, suggesting a gradual surface poisoning effect either during or after the dehydrogenation reaction.

Skeletal Catalysts of Other First-Row Transition Metals. Among the other reported skeletal catalysts of first-row transition metals, Cu and Fe potentially provide even more environmentally benign and cheaper alternatives to skeletal Ni. Skeletal Cu, which has received more attention than skeletal Fe, can provide increased selectivity in catalytic hydrogenation in some cases,[50] although the surface area of such catalysts are reported to be up to an order of magnitude smaller than those of skeletal Ni.[46] Complexes of these metals have only been briefly reported with respect to catalytic amine—borane dehydrogenation chemistry.[15,19]

Treatment of 1 with 5 mol % of skeletal Cu[91] in toluene solution at 20 °C was shown to produce 5% conversion to the expected aminoborane 2 over 16 h, with no further reaction apparent over 3 days under the same conditions (Scheme 13a). Attempted dehydrogenation using a stoichiometric quantity of Cu did however yield complete conversion to 2 over 4 days at 20 °C, with no loss of boron content (Scheme 13b).[59] Reaction of 7 with 5 mol % Cu over 16 h produced less than 1% conversion to the corresponding aminoborane 8, with 10% conversion over the same period when Cu was employed in stoichiometric quantities and 20% after 4 days.

Reaction of skeletal Cu with **9** in stoichiometric quantities over 16 h furnished **11**, which was identified by multinuclear NMR spectroscopy (Scheme 13c). GPC analysis of this product confirmed the formation of low molecular weight polymer, with an estimated M_w of ~10 000 Da. A more precise molecular weight, however, could not be determined, as the peak was outside the low end of the calibrated range for the GPC columns. Nonetheless, ESI-MS of the product in THF/acetonitrile did confirm formation of a linear polymer, containing the expected [MeNH$-$BH$_2$] repeat unit (43.05 Da) and consistent with authentic samples of the same material (Supporting Information, Scheme SI 7).[20] This technique, however, can also be problematic in providing accurate molecular weight values for polyaminoboranes[20] and was used in this context solely to confirm the polymeric nature of the product.

Synthesis of the analogous skeletal Fe species was achieved by base leaching of the Al content from FeAl$_2$ under identical conditions to those used to produce Ni$_{T50}$ (vide supra). This catalyst, however, was found to be completely inactive toward amine$-$borane dehydrocoupling in either catalytic or stoichiometric quantities even at 50 °C.

■ CONCLUSIONS

Skeletal Ni metal has been demonstrated to be an effective amine$-$borane dehydrogenation catalyst at 20 °C and is of immediate interest due to the low cost and ready availability of this metal. The catalyst was shown to be heterogeneous and could be simply removed from complete reactions by filtration, facilitating the ready purification of products. To the best of our knowledge, this is the first example of a heterogeneous, non-hydrolytic first-row amine$-$borane dehydrogenation catalyst.

The dehydrogenation of Me$_2$NH·BH$_3$ (**1**) to form [Me$_2$N$-$BH$_2$]$_2$ (**2**) with 5 mol % skeletal Ni reached completion over 6 h at 20 °C and was shown to occur primarily via the monomeric aminoborane Me$_2$N$=$BH$_2$ (**3**) as the major intermediate, although the linear diborazane Me$_2$NH$-$BH$_2$$-NMe_2$$-BH_3$ (**4**) was also observed in lower concentrations. Catalytic dehydrogenation of Et$_2$NH·BH$_3$ (**5**) was demonstrated at 20 °C, although due to catalyst poisoning, the related adduct iPr$_2$H·BH$_3$ (**7**) was only completely dehydrogenated by employing the Ni in stoichiometric quantities. Reaction of MeNH$_2$·BH$_3$ (**9**) with skeletal Ni was shown to produce either the cyclic triborazane [MeNH$-$BH$_2$]$_3$ (**10**) at 5 mol % catalyst loading or the high molecular weight poly(methylaminoborane), [MeNH$-$BH$_2$]$_n$ (**11**) (M_w = 78 000 Da, PDI = 1.52) when employing stoichiometric quantities of Ni. This observation provided some interesting mechanistic insight into the polymerization process, suggesting that, as previously postulated, the transient amino-borane, MeNH$=$BH$_2$, is the true monomer in the polymeriza-tion. Although polymerizations of **9** with heterogeneous Rh catalysts have been reported,[20] this is the first heterogeneous system to provide access to high molecular weight polyamino-boranes with comparatively low PDIs.

Recycling of the Ni-based catalysts was found to be difficult, with catalytic activity rapidly lost due to poisoning. An investiga-tion of various potential poisons suggested that BH$_3$ was the likely surface poison, as has been observed previously for heterogeneous Rh systems. Extending the study to include skeletal Cu and Fe was less successful. Skeletal Cu was found to exhibit a similar pattern of reactivity to Ni, although with vastly reduced rates, and skeletal Fe was found to be inactive toward amine$-$borane dehydrogenation.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of nitrogen gas using standard vacuum line and Schlenk techniques or under an atmosphere of argon within an MBraun glovebox. All solvents were dried via a Grubbs' type solvent purification system.[92] Deuterated solvents were purchased from Sigma Aldrich and distilled from potas-sium (C$_6$D$_6$) or CaH$_2$ (CDCl$_3$). Ni/Al alloy (50 wt %), skeletal Cu aqueous slurry, and Me$_2$NH·BH$_3$ (**1**) were purchased from Sigma Aldrich, with the latter sublimed prior to use. NaOH was purchased from Fisher Scientific. MeNH$_2$·BH$_3$ (**9**), Me$_2$NH$-$BH$_2$$-NMe_2$$-BH_3$ (**4**), and iPr$_2$NH·BH$_3$ (**7**) were synthesized according to literature proce-dures, with the former two compounds sublimed prior to use.[11] iPr$_2$N$=$BH$_2$ (**8**) was synthesized via literature method and purified by distillation prior to use.[80] FeAl$_2$ was synthesized via the method of Johnston and co-workers[52] using 99.7% Al powder supplied by Strem Chemicals, Inc. and 99.99% Fe powder supplied by ABCR-Chemicals.

NMR spectra were recorded using JEOL JNM-ECP300/400 or JNM-LA300 spectrometers. Chemical shifts were reported relative to residual solvent peaks (^{1}H and ^{13}C) or to external standards: BF$_3$·OEt$_2$ ([11]B). Atomic absorption spectroscopy (AAS) was performed on a Unicam 919 AA spectrometer following initial dissolution of the samples in aqua regia over 5 min. Al analysis was carried out using a nitrous oxide/acetylene flame and Ni, Fe, and Cu analysis using an air/acetylene flame. GPC samples were dissolved in the eluent (0.5 mg/mL) and filtered (Acrodisc, PTFE membrane, 0.45 mm) before analysis. GPC chroma-tography was performed on a Viscotek VE2001 instrument, using a flow rate of 1 mL/min of THF containing 0.1 w/w % nBu$_4$NBr, calibrated using polystyrene standards. The columns used were of grade GP5000HHR followed by GP2500HHR (Viscotek) at a constant temperature of 30 °C, and a VE 3580 refractometer was employed. IR spectra were measured using a Perkin-Elmer FT-IR spectrometer. SEM was performed on a JEOL JSM 5600LV microscope with an accelerating voltage of 30 kV and working distance of 15 mm. The instrument was fitted with an Everhardt-Thornley secondary electron detector and an Oxford Instruments ISIS 310 system with silicon detector and an atmospheric thin window (ATW) for energy-dispersive X-ray analysis (EDX). Samples were prepared in the glovebox, by mounting ~5 mg of skeletal metal onto a graphite disk, and were rapidly transferred to the microscope to minimize the exposure to air. ESI mass spectra were recorded using a cone potential of +150 V in a THF/acetonitrile mixture on a Bruker Daltonics Apex IV Fourier transform ion cyclotron mass spectrometer.

Synthesis of Skeletal Ni$_{T50}$. To a suspension of 50:50 wt % Ni/Al (2.5 g) in deaerated distilled water at 50 °C was added, over the course of 45 min, a 6 M deaerated aqueous solution of NaOH (23.16 mL, 139.0 mmol), producing vigorous bubbling. Following the addition, the mixture was stirred at 50 °C for a further 2 h before cooling to 20 °C and removing the stirrer bar. The dark solid product of the reaction was isolated by decantation and washed with distilled water under a nitrogen flow until the washings were neutral. The solid was then washed with deaerated EtOH (30 mL) and finally deaerated Et$_2$O (30 mL), before drying under high vacuum for 1 h and transferring to an inert atmo-sphere glovebox for storage. Yield: 1.2 g, 96%.

Preparation of Ni$_{T20}$ and Ni$_{T100}$ was carried out in an identical fashion, using leaching temperatures of 20 and 100 °C, respectively. The leaching of Ni$_{T20}$ was, however, carried out over 72 h due to the reduced rate of this reaction.

Synthesis of Skeletal Fe. To a suspension of FeAl$_2$ (1 g, 9.10 mmol) in deaerated distilled water (10 mL) was added, over 30 min, a 6 M deaerated aqueous solution of NaOH (10 mL) at 50 °C. Following the addition, the mixture was stirred at 50 °C for a further 1.5 h before cooling to 20 °C, removing the stirrer bar and isolating the solid products via decantation. The product was then washed with deaerated

distilled H_2O until the washings became neutral and subsequently with deaerated EtOH (30 mL) and Et_2O (30 mL), before drying under high vacuum for 2 h. Yield: 0.47 g, 92%.

Drying of Skeletal Cu. An aqueous slurry of skeletal Cu, purchased from Sigma Aldrich, was dried under the same regime described for skeletal Ni and transferred to the glovebox for storage.

Catalytic Dehydrogenation of $Me_2NH \cdot BH_3$ (1) with Ni_{T50}. To a solution of **1** (100 mg, 1.70 mmol) in toluene (4 mL) was added 5 mol % Ni_{T50} (5 mg, 0.09 mmol), producing immediate and vigorous bubbling. The solution was then stirred at 20 °C for 6 h, producing complete conversion to $[Me_2N-BH_2]_2$ (**2**). The product was not isolated, but the reaction was shown to be quantitative through the addition of $B(OiPr)_3$ (49 μL, 0.21 mmol) to the filtered 0.5 mL NMR sample. Integration of the signal arising from **2** relative to the borate (δ_B +18 ppm) indicated that 100% of the initial boron content was present as this species. ^{11}B NMR (96 MHz, toluene): δ_B 4.5 (t, J_{BH} = 113 Hz) ppm. Repeating the reaction in C_6D_6 enabled the recording of further NMR data: ^{1}H NMR (300 MHz, C_6D_6): δ 3.03 (br. q, J_{BH} = 113 Hz, BH_2), 2.23 (s, NMe_2), ^{13}C NMR (76 MHz, C_6D_6): δ 52.0 (s, NMe_2).

Effect of Solvent on the Ni_{T50} Catalyzed Dehydrogenation of 1. Reaction mixtures were prepared, as for the dehydrogenation described above, using a 1.70 mmol quantity of **1** in tetrahydrofuran and hexane. A 5 mol % loading of Ni_{T50} was added at 20 °C, and the mixtures monitored every 20 min by ^{11}B NMR spectroscopy. In the case of the hexane reaction, it was necessary to add a stoichiometric quantity of $B(OiPr)_3$ (29.4 μL) to each 0.3 mL NMR sample to quantify the conversion, due to the limited solubility of **1** in this solvent.

Tests for Catalyst Heterogeneity. To three separate solutions of **1** (0.1 g, 1.7 mmol) in toluene (4 mL) were added 5 mol % Ni_{T50} (5 mg, 0.09 mmol), the solution stirred rapidly, and ~0.7 mL of each sample transferred to a J. Youngs NMR tube. The reactions were then allowed to proceed as open systems, by opening to an atmosphere of N_2 on a Schlenk line, so that the H_2 formed could easily escape. ^{11}B NMR spectra were recorded every 10 min for 50 min, and conversion to products calculated based upon integration of the resonances. After 55 min, one of the reactions was filtered through glass fiber filter paper (Fisher MF-100 grade), before transferring to a fresh J. Youngs NMR tube, while to the second excess (a drop) mercury was added. The third reaction was left unchanged. ^{11}B NMR spectra were subsequently recorded every 10 min for a further 1 h.

Synthesis of $Et_2NH \cdot BH_3$ (5). A mixture of $[Et_2NH_2]Cl$ (7.50 g, 68.4 mmol) and $NaBH_4$ (2.61 g, 68.9 mmol) was cooled to −78 °C, and THF (200 mL), which was also cooled to −78 °C, was added dropwise over 15 min. The reaction was then stirred for 30 min before removing the cooling bath and allowing to mixture to warm to 20 °C. During the warming process, vigorous gas evolution was observed, and after stirring for a further 2 h, the reaction mixture was filtered though Celite. Volatiles were then removed under high vacuum, and the mixture was filtered through glass fiber filter paper to yield the product as a colorless oil. Yield: 3.55 g, 60%. ^{11}B NMR (96 MHz, $CDCl_3$): δ −17.9 (q, J_{BH} = 94 Hz, BH_3); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.55 (1H, br. s, NH), 2.76 (4H, dq, J_{HH} = 7.34 Hz, J_{HH} = 6.00, CH_2), 1.40 (3H, br. q, BH_3), 1.19 (6H, t, J_{HH} = 7.34 Hz, CH_3); ^{1}H{^{11}B} NMR (300 MHz, $CDCl_3$): δ 3.55 (1H, br. s, NH), 2.76 (4H, dq, J_{HH} = 7.34 Hz, J_{HH} = 6.00, CH_2), 1.40 (3H, br. s, BH_3), 1.19 (6H, t, J_{HH} = 7.34 Hz, CH_3); ^{13}C NMR (76 MHz, $CDCl_3$): δ 48.9 (s, CH_3), 11.3 (s, CH_2).

Catalytic Dehydrogenation of 5 with Ni_{T50}. To a solution of **5** (0.15 g, 1.7 mmol) in toluene (4 mL) was added 5 mol % Ni_{T50} (5.0 mg, 0.09 mmol) at 20 °C, which initially produced vigorous bubbling. The reaction was then stirred for 60 h at 20 °C before sampling for ^{11}B NMR spectroscopic analysis. ^{11}B NMR (96 MHz, toluene): δ 36.5 (t, J_{BH} = 125 Hz, $Et_2N=BH_2$), 1.5 (t, J_{BH} = 111 Hz, $[Et_2N-BH_2]_2$).

Attempted Catalytic Dehydrogenation of $iPr_2NH \cdot BH_3$ (7) with Ni_{T50}. To a solution of **7** (0.19 g, 1.7 mmol) in toluene (4 mL) was added 5 mol % Ni_{T50} (5.0 mg, 0.09 mmol) at 20 °C, which initially produced vigorous bubbling. The reaction mixture was then stirred for 16 h at 20 °C before analysis by ^{11}B NMR spectroscopy indicated ~5% conversion to $iPr_2N=BH_2$ (**8**), with no further conversion apparent after 120 h at 20 °C. ^{11}B NMR (96 MHz, toluene): δ 34.6 (t, J_{BH} = 127 Hz, $iPr_2N=BH_2$), −21.2 (q, J_{BH} = 96 Hz, $iPr_2NH \cdot BH_3$).

Stoichiometric Dehydrogenation of 7 with Ni_{T50}. To a solution of **7** (0.19 g, 1.7 mmol) in C_6D_6 (4 mL) was added 100 mol % Ni_{T50} (0.10 g, 1.7 mmol) at 20 °C, which initially produced vigorous bubbling. The reaction mixture was then stirred for 6 h at 20 °C before analysis by ^{11}B NMR spectroscopy indicated 100% conversion of the soluble boron content to **8**. Addition of a stoichiometric quantity of $B(OiPr)_3$ to the NMR samples however indicated that at least 30% of the initial boron was not present in solution. ^{1}H and ^{13}C NMR spectroscopies indicated the presence of iPr_2NH (~30%) in solution, suggesting cleavage of either the adduct or the aminoborane product. ^{11}B NMR (96 MHz, C_6D_6): δ 34.5 (t, J_{BH} = 125 Hz, $iPr_2N=BH_2$); ^{1}H NMR (300 MHz, C_6D_6): δ 3.16 (2H, septet, J_{HH} = 6.79 Hz, $iPr_2N=BH_2$), 2.81 (2H′, septet, J_{HH} = 6.24, iPr_2NH), 1.04 (6H, d, J_{HH} = 6.79 Hz, $iPr_2N=BH_2$), 0.95 (6H′, d, J_{HH} = 6.24 Hz, iPr_2NH) (The apostrophes used in the above assignments denote the two different compounds present within the reaction mixture, for which the resonances were integrated separately); ^{13}C NMR (76 MHz, C_6D_6): δ 52.8 (s, $iPr_2N=BH_2$ (CH)), 45.7 (s, iPr_2NH, (CH)), 25.4 (s, $iPr_2N=BH_2$ (CH_3)), 24.1 (s, iPr_2NH, (CH_3)).

Catalytic Dehydrogenation of $MeNH_2 \cdot BH_3$ (9) with Ni_{T50}. To a solution of **9** (0.20 g, 4.46 mmol) in THF (2 mL) was added 5 mol % Ni_{T50} (0.013 g, 0.22 mmol) which produced significant bubbling, which gradually subsided over 5 min. The mixture was stirred at 20 °C for 120 h before analysis by ^{11}B NMR spectroscopy study indicated 70% conversion of the starting material to $[MeNH-BH_2]_3$ (**10**). The volatiles were then removed under high vacuum to yield an oily white solid, which was redissolved in CD_2Cl_2 for further analysis, by ^{1}H and ^{13}C NMR spectroscopies. ^{11}B NMR (96 MHz, CD_2Cl_2): δ −5.7 (t, J_{BH} = 106 Hz, $[MeNH-BH_2]_3$, e,e,a) −6.7 (t, J_{BH} = 107 Hz, $[MeNH-BH_2]_3$, e,e,e), −19.6 (q, J_{BH} = 97 Hz, $MeNH_2 \cdot BH_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.42 (t, J_{HH} = 6.42 Hz, $MeN\underline{H}_2 \cdot BH_3$), 2.28 (d, J_{HH} = 6.42 Hz, $[MeNH-BH_2]_3$), 2.12 (d, J_{HH} = 6.06, $[MeNH-BH_2]_3$); ^{13}C NMR (76 MHz, CD_2Cl_2): δ 38.6 (s, $[MeNH-BH_2]_3$, e,e,a), 36.4 (s, $[MeNH-BH_2]_3$, e,e,a), 35.3 (s, $[MeNH-BH_2]_3$, e,e,e), 34.8 (s, $MeNH_2 \cdot BH_3$). The terms e,e,e and e,e,a used in the above assignments refer to the orientation of the Me groups on the six-membered ring which adopts a chair conformation: e,e,e denotes the triply equatorial isomer, and e,e,a the second isomer where two Me groups are found equatorial and the third axial.

Polymerization of 9 with Ni_{T50}. To a solution of **9** (0.50 g, 11.1 mmol) in THF (6 mL) was added Ni_{T50} (0.65 g, 11.1 mmol), which produced vigorous bubbling. The mixture was stirred at 20 °C for 2 h before filtering through a glass fiber filter paper and subsequently precipitating into hexanes (100 mL) at −78 °C. The solids so formed were isolated via filter cannula and washed twice with hexanes (50 mL), before drying under high vacuum for 4 h, to yield the product, $[MeNH-BH_2]_n$ (**11**), as a white solid. Yield: 0.29 g, 60%, ^{11}B NMR (96 MHz, $CDCl_3$): δ −6.5 (br. s, BH_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.87 (1H, br. s, NH), 2.26 (3H, br. s, Me), 1.75 (2H, br. s, BH_2); ^{13}C NMR (76 MHz, $CDCl_3$): δ 36.0 (s, CH_3), GPC: M_w = 78 000 Da, PDI = 1.52.

Catalytic Dehydrogenation of $NH_3 \cdot BH_3$ (12) with Ni_{T50}. To a solution of **12** (0.2 g, 6.4 mmol) in THF (16 mL) was added 5 mol % Ni_{T50} (0.02 g, 0.32 mmol) which produced significant bubbling, which gradually subsided over 5 min. The mixture was stirred at 20 °C for 7 days before the clear solution was analyzed by ^{11}B NMR spectroscopy, which indicated 32% conversion to B-(cyclodiborazanyl)aminoborohydride (**13**). ^{11}B NMR (96 MHz, THF): δ −5.5

(d, 108 Hz, BH), −11.9 (t, J_{BH} = 98 Hz, BH$_2$),[89] −22.8 (q, J_{BH} = 97 Hz, NH$_3$·BH$_3$), −24.4 (br. s, BH$_3$).

Polymerization of 12 with Ni$_{T50}$. To a solution of **12** (0.2 g, 6.5 mmol) in THF (16 mL) was added 100 mol % Ni$_{T50}$ (0.38 mg, 6.5 mmol), which produced vigorous initial bubbling. The rapid formation of a white precipitate was observed, and the mixture was stirred at 20 °C over 7 days. After this time, minimal **12** (or other soluble species) was apparent in the ^{11}B NMR spectrum of the supernatant liquid. The liquid was decanted from the reaction mixture, and the solid mixture of product and catalyst dried under high vacuum over 16 h. The solid components proved to be inseparable due to its complete insolubility in all common organic solvents. Solid-state IR of the product/catalyst mixture however indicated a close correlation with $[NH_2−BH_2]_n$ (**14**), previously identified via reaction of **12** with IrH$_2$POCOP. FT-IR: 3290, 3246 (N−H), 2323 (B−H) cm^{-1}.

Attempted Recycling of Ni$_{T50}$. To a solution of **1** (0.1 g, 1.7 mmol) in toluene (4 mL) was added Ni$_{T50}$ (5 mg, 0.09 mmol), and the mixture was stirred at 20 °C for 16 h. The mixture was then analyzed by ^{11}B NMR spectroscopy, which indicated complete conversion of the starting material to yield the cyclic aminoborane **2**. The solution was then removed via syringe, and the solid catalyst was dried under high vacuum over 4 h. The solid was then resuspended in toluene (4 mL), and further **1** (0.1 g, 1.7 mmol) was added. The mixture was then stirred at 20 °C over 72 h, with no evidence of conversion of **1** by ^{11}B NMR spectroscopy over this period.

An alternative methodology for recycling was then attempted, with dehydrogenation of **1** (0.1 g, 1.7 mmol) again run to completion over 16 h. In this case, however, the catalyst was not isolated from the mixture, and solid **1** (0.1 g, 1.7 mmol) was then added. This resulted in 16% conversion of the second batch of **1** over a period of 6 h.

Ni$_{T50}$ Poisoning Studies. To suspensions of Ni$_{T50}$ (5 mg, 0.09 mmol) in toluene (4 mL) was added 0.9 mmol of iPr$_2$NH, BH$_3$·THF (1 M in THF), and the mixtures were stirred for 16 h at 20 °C. Solid **1** (0.1 g, 1.70 mmol) was then added, and each mixture was sampled after 6 and 24 h for analysis by ^{11}B NMR spectroscopy. An identical experiment using 0.009 mmol of BH$_3$·THF was also carried out under the same conditions. In the case of poisoning with H$_2$, the gas was bubbled through a toluene suspension of Ni$_{T50}$ over 16 h before addition of **1**.

Attempted Catalytic and Stoichiometric Dehydrogenation of 1 with Skeletal Cu. To a solution of **1** (0.1 g, 1.7 mmol) in toluene (4 mL) was added 5 or 100 mol % skeletal Cu (5.3 mg, 0.09 mmol or 0.11 g, 1.7 mmol), and the mixture was stirred at 20 °C for 16 h before analysis by ^{11}B NMR spectroscopy. Over this period, the catalytic reaction was found to yield 5% **2**, whereas the stoichiometric reaction produced 37%. The catalytic reaction produced no further conversion by ^{11}B NMR spectroscopy over 4 d, with the stoichiometric reaction reaching complete conversion to **2** over the same period.

Polymerization of 9 with Skeletal Cu. To a solution of **9** (0.20 g, 4.46 mmol) in THF (10 mL) was added skeletal Cu (0.28 g, 4.46 mmol), and the mixture was stirred at 20 °C for 16 h. The mixture was then analyzed by ^{11}B NMR spectroscopy, indicating 80% conversion of the starting material (δ_B = −19.4 ppm) to a new product (δ_B = −5.7 ppm). The mixture was added to rapidly stirred hexanes (100 mL) at −78 °C, and the resulting solids were isolated by filter cannula. The product was then dried under high vacuum for 4 h and subsequently identified as **11**. Yield: 68 mg, 36%, ^{11}B NMR (96 MHz, CDCl$_3$): δ −5.7 (br. s, $[MeNH−BH_2]_n$), −19.4 (q, J_{BH} = 96 Hz, MeNH$_2$·BH$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.87 (br. s, NH$_2$), 2.57 (s, MeNH$_2$·BH$_3$), 2.25 (br. s, Me), 1.70 (br. s, BH$_2$); ^{13}C NMR (76 MHz, CDCl$_3$): δ 35.8 (s, CH$_3$), GPC: M_w ~10 000 Da (see Supporting Information, Figure SI 6).

Attempted Dehydrogenation of 1 with Skeletal Fe. Using an identical procedure to that described above for Cu-catalyzed dehydrogenation of **1**, skeletal Fe-catalyzed reactions were attempted on the

same scale using 5 and 100 mol % skeletal Fe (5 mg, 0.09 mmol, and 100 mg, 1.7 mmol). Under catalytic and stoichiometric Fe loadings, no evidence of dehydrogenation of the adduct was apparent by ^{11}B NMR spectroscopy over 4 days at 20 °C or at 50 °C.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Supporting information contains selected spectra, SEM/EDX characterization of the various catalyst formulations and also details of additional experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: ian.manners@bristol.ac.uk.

■ ACKNOWLEDGMENT

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