

Catalytic Redistribution and Polymerization of Diborazanes: Unexpected Observation of Metal-Free Hydrogen Transfer between Aminoboranes and Amine-Boranes

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S Supporting Information

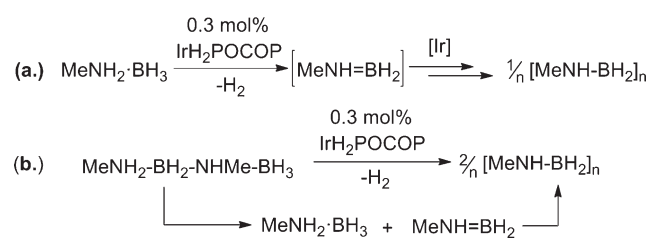
ABSTRACT: Ir-catalyzed (20 °C) or thermal (70 °C) dehydrocoupling of the linear diborazane MeNH₂-BH₂-NHMe-BH₃ led to the formation of poly- or oligoaminoboranes [MeNH-BH₂]_x (x = 3 to >1000) via an initial redistribution process that forms MeNH₂·BH₃ and also transient MeNH=BH₂, which exists in the predominantly metal-bound and free forms, respectively. Studies of analogous chemistry led to the discovery of metal-free hydrogenation of the B=N bond in the “model” aminoborane *i*Pr₂N=BH₂ to give *i*Pr₂NH·BH₃ upon treatment with the diborazane Me₃N-BH₂-NHMe-BH₃ or amine-boranes RR'NH·BH₃ (R, R' = H or Me).

Amine-boranes RR'NH·BH₃ (R, R' = alkyl, aryl, or H) are well-known main-group species that have recently become the focus of intense interest as a result of their use in hydrogen storage and transfer and as precursors to new materials.^{1,2} For example, soluble polyaminoboranes, inorganic analogues of polyolefins, have been prepared from the dehydrocoupling of RNH₂·BH₃ (R = Me or *n*Bu) in the presence of catalysts such as IrH₂POCOP [POCOP = κ³-1,3-(OP*t*Bu)₂C₆H₃].^{3,4} In addition, NH₃·BH₃ has attracted attention as a precursor to “white graphene”, monolayer films of hexagonal boron nitride, on Cu surfaces.⁵ The increasing importance of metal-mediated processes in these fields has led to the rapid emergence of a new area of coordination chemistry involving amine-boranes and aminoboranes, RR'N=BH₂, as reactive ligands.⁶ A key challenge for hydrogen storage applications is the rehydrogenation of “spent fuel” dehydrogenation products.⁷ Recent advances in this area have involved the use of hydrazine to regenerate NH₃·BH₃ following metal-catalyzed hydrogen release.^{7b}

Linear diborazanes, RR'₂N-BH₂-NRR'-BH₃ (R, R' = Me or H) have recently attracted attention, partly as a consequence of their role as intermediates in a range of metal-catalyzed dehydrogenations of amine-boranes.⁸ In this paper, we report a series of unexpected results that emerged from our recent studies of the catalytic dehydrocoupling of a series of linear diborazanes MeR₂N-BH₂-NMeR-BH₃ (R = H or Me).

We previously showed that dehydrocoupling of MeNH₂·BH₃ in THF with 0.3 mol % IrH₂POCOP at 20 °C yields high-molecular-weight poly(methylaminoborane), [MeNH-BH₂]_n (M_w = 160 000 Da, PDI = 2.90).^{3b} A mechanism was tentatively proposed that involves two metal-catalyzed steps: initial generation of the monomeric aminoborane MeNH=BH₂, and subsequent

Scheme 1. Proposed Mechanism of Polymerization of (a) MeNH₂·BH₃ and (b) MeNH₂-BH₂-NHMe-BH₃ with 0.3 mol % IrH₂POCOP

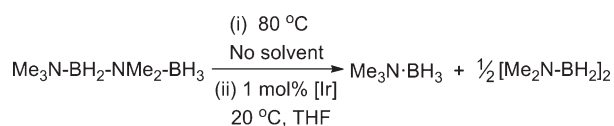
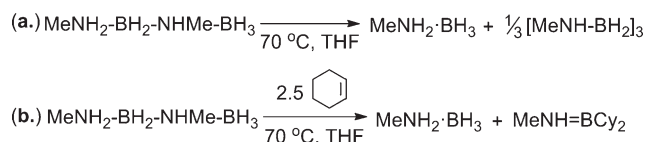


polymerization of this species (Scheme 1a). Surprisingly, reaction of the linear diborazane MeNH₂-BH₂-NHMe-BH₃ with 0.3 mol % IrH₂POCOP under the same conditions over 1.5 h yielded a spectroscopically identical product, as determined by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS) (86% yield; M_w = 97 000 Da, PDI = 1.44) (see Figures SI-1 and SI-2 in the Supporting Information). During this reaction, an apparent intermediate was detected by ¹¹B NMR spectroscopy (δ_B = -18.7 ppm) that split into a quartet (J_{BH} = 94 Hz) upon proton coupling and was assigned as MeNH₂·BH₃.^{8f} The detection of this species suggested that a redistribution reaction of the diborazane precursor may have taken place (Scheme 1b). On the basis of the substrate stoichiometry, such a process would also yield MeNH=BH₂, the proposed precursor to [MeNH-BH₂]_n in the dehydrocoupling of MeNH₂·BH₃ by IrH₂POCOP.^{3b}

Significantly, Burg and Randolph previously reported that thermolysis of the unsymmetrical diborazane Me₃N-BH₂-NMe₂-BH₃ at 80 °C in the solid state leads to the formation of Me₃N·BH₃ and [Me₂N-BH₂]₂ (Scheme 2),⁹ where the latter species was presumably formed by the cyclodimerization of the monomeric aminoborane Me₂N=BH₂. To explore whether this redistribution process could occur in a catalytic manner at 20 °C, we prepared Burg's diborazane, Me₃N-BH₂-NMe₂-BH₃, via the reaction of Me₃N with [H₂B(μ-H)(μ-NMe₂)₂BH₂] in THF solution at -78 °C using an approach developed recently by Shore.^{8h} Subsequent treatment of a THF-*d*₈ solution of Me₃N-BH₂-NMe₂-BH₃ with 1 mol % IrH₂POCOP (20 °C, 4 h) indeed led to rapid redistribution of the substrate and clean formation of Me₃N·BH₃ and [Me₂N-BH₂]₂, which were

Received: September 16, 2011

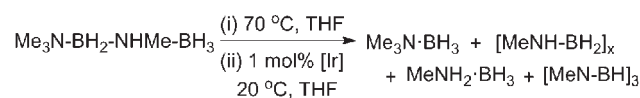
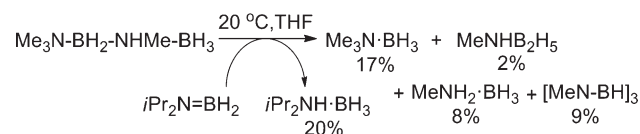
Published: October 28, 2011

Scheme 2. (i) Thermal and (ii) Catalytic Redistribution of $\text{Me}_3\text{N}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$

Scheme 3. (a) Thermolysis of $\text{MeNH}_2-\text{BH}_2-\text{NHMe}-\text{BH}_3$ (b) with Cyclohexene Trapping


identified by multinuclear NMR spectroscopy (Scheme 2 and Figure SI-3). An intermediate, the monomeric aminoborane $\text{Me}_2\text{N}=\text{BH}_2$, was also observed in small amounts during the catalytic redistribution as a triplet in the ^{11}B NMR spectrum at 37.0 ppm ($J_{\text{BH}} = 130$ Hz).^{8d}

To provide further evidence for the proposed steps in the Ir-catalyzed redistribution/polymerization of our diborazane, $\text{MeNH}_2-\text{BH}_2-\text{NHMe}-\text{BH}_3$, we attempted to demonstrate the presence of the transient monomeric aminoborane $\text{MeNH}=\text{BH}_2$ within the reaction mixture [the other redistribution product, $\text{MeNH}_2\cdot\text{BH}_3$, was identified by ^{11}B NMR spectroscopy (see above)]. Although $\text{MeNH}=\text{BH}_2$ has neither been observed directly nor isolated through trapping reactions, the trapping of the related species $\text{NH}_2=\text{BH}_2$ as $\text{NH}_2=\text{BCy}_2$ using excess cyclohexene has recently been described.^{6d,8g,10} We therefore explored the reaction of $\text{MeNH}_2-\text{BH}_2-\text{NHMe}-\text{BH}_3$, with 0.3 mol % IrH_2POCOP (20 °C, THF, 3 h) in the presence of 2.5 equiv of cyclohexene. Significantly, the reaction appeared to be unperturbed by the presence of the olefin and yielded the polyaminoborane $[\text{MeNH}-\text{BH}_2]_n$ with no evidence for the formation of $\text{MeNH}=\text{BCy}_2$, which appears at $\delta_{\text{B}} = 44.9$ ppm in the ^{11}B NMR spectrum in THF solution (see below and Supporting Information). We believe that the inability to trap $\text{MeNH}=\text{BH}_2$ despite the formation of $[\text{MeNH}-\text{BH}_2]_n$ indicates that the aminoborane remains bound to the metal center during both the redistribution and polymerization^{8a} and hence may not be free in solution for sufficiently long to allow reaction with cyclohexene.¹¹

To probe this postulate further, we also studied the thermolysis of the diborazane $\text{MeNH}_2-\text{BH}_2-\text{NHMe}-\text{BH}_3$ (70 °C, THF, 18 h) in the absence of the Ir catalyst. Under these conditions, in the absence of cyclohexene, the diborazane was shown to be almost quantitatively converted to $\text{MeNH}_2\cdot\text{BH}_3$ and $[\text{MeNH}-\text{BH}_2]_3$ together with a small amount of the borazine $[\text{MeN}-\text{BH}]_3$ (Scheme 3a). The formation of $[\text{MeNH}-\text{BH}_2]_3$ is again consistent with elimination of $\text{MeNH}=\text{BH}_2$, which then may cyclotrimerize. In striking contrast to the Ir-catalyzed process, repeating the metal-free reaction in the presence of 2.5 equiv of cyclohexene yielded both $\text{MeNH}_2\cdot\text{BH}_3$ and the trapped product $\text{MeNH}=\text{BCy}_2$ in an approximately 1:1 ratio (Scheme 3b and Figure SI-4). The latter trapping product was characterized by multinuclear NMR spectroscopy and high-resolution chemical ionization MS (CI-MS).

Scheme 4. (i) Thermal and (ii) Catalytic Redistribution of $\text{Me}_3\text{N}-\text{BH}_2-\text{NHMe}-\text{BH}_3$

Scheme 5. Reaction of $\text{Me}_3\text{N}-\text{BH}_2-\text{NHMe}-\text{BH}_3$ with $i\text{Pr}_2\text{N}=\text{BH}_2$


The ^{11}B NMR spectrum of $\text{MeNH}=\text{BCy}_2$ consisted of a broad singlet at 44.7 ppm (C_6D_6) that showed no splitting upon ^1H coupling. The isolation of this species strongly implicates the presence of free $\text{MeNH}=\text{BH}_2$ in the thermal redistribution of the diborazane $\text{MeNH}_2-\text{BH}_2-\text{NHMe}-\text{BH}_3$ and is in contrast with observations in the Ir-catalyzed redistribution/polymerization of the same substrate.

To probe the catalytic redistribution chemistry further, we prepared another, unsymmetrical diborazane, $\text{Me}_3\text{N}-\text{BH}_2-\text{NHMe}-\text{BH}_3$. On the basis of the aforementioned results, we predicted that Ir-catalyzed redistribution of this diborazane would yield $\text{Me}_3\text{N}\cdot\text{BH}_3$ and oligomeric or polymeric products derived from $\text{MeNH}=\text{BH}_2$. Treatment of $\text{Me}_3\text{N}-\text{BH}_2-\text{NHMe}-\text{BH}_3$ with 1 mol % IrH_2POCOP in THF solution over 6 h led to complete consumption of the initial diborazane and formation of a mixture containing, as expected, $\text{Me}_3\text{N}\cdot\text{BH}_3$ (51%) and oligomeric/polymeric species $[\text{MeNH}-\text{BH}_2]_x$ (28%) (see Figure SI-5).^{11b} Somewhat surprisingly, however, we also observed the formation of $[\text{MeN}-\text{BH}]_3$ (13%) and $\text{MeNH}_2\cdot\text{BH}_3$ (8%)^{11b} (Scheme 4). These products are indicative of an additional mode of reactivity. Interestingly, essentially the same product distribution was obtained when the thermolysis of $\text{Me}_3\text{N}-\text{BH}_2-\text{NHMe}-\text{BH}_3$ was performed under metal-free conditions (70 °C, THF, 16 h). This result indicated that the Ir catalyst does not play a role in the unexpected chemistry.

Perhaps the most likely route to $[\text{MeN}-\text{BH}]_3$ and $\text{MeNH}_2\cdot\text{BH}_3$ involves the highly reactive aminoborane $\text{MeNH}=\text{BH}_2$. However, because of the transient nature of $\text{MeNH}=\text{BH}_2$, it was not easy to probe the reactivity of this species directly in further studies. Instead, we therefore chose to explore the reactivity of $i\text{Pr}_2\text{N}=\text{BH}_2$, a sterically encumbered "model" aminoborane that is stable in its monomeric form at ambient temperature.¹²

Following treatment of $\text{Me}_3\text{N}-\text{BH}_2-\text{NHMe}-\text{BH}_3$ with $i\text{Pr}_2\text{N}=\text{BH}_2$ (20 °C, THF, 18 h), analysis of the reaction mixture by ^{11}B NMR spectroscopy indicated partial conversion of the reactants. The products identified showed ca. 20% hydrogenation of $i\text{Pr}_2\text{N}=\text{BH}_2$ to $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ together with significant redistribution of the diborazane to yield products including $\text{Me}_3\text{N}\cdot\text{BH}_3$ (17%) and also $[\text{MeN}-\text{BH}]_3$ (9%), $\text{MeNH}_2\cdot\text{BH}_3$ (8%), and a trace of $[\text{H}_2\text{B}(\mu\text{-H})(\mu\text{-NMeH})\text{BH}_2]$ (2%)^{11b} (Scheme 5). This room temperature experiment clearly indicated that aminoboranes generated from the redistribution of linear diborazanes are capable of surprising reactivity, and this can even involve their hydrogenation. This process apparently occurs with the

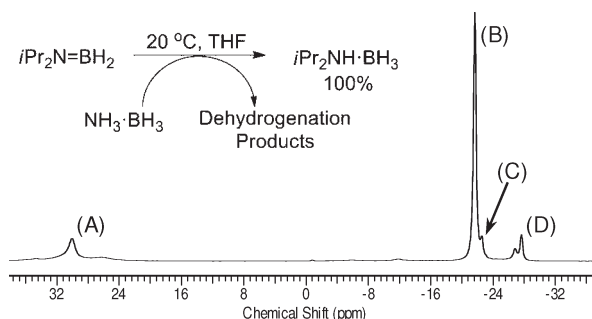


Figure 1. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum for the reaction of $i\text{Pr}_2\text{N}=\text{BH}_2$ and $\text{NH}_3\cdot\text{BH}_3$ after 18 h: (A) $[\text{NH}-\text{BH}]_3$, (B) $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$, (C) $\text{NH}_3\cdot\text{BH}_3$, (D) $\text{NH}_2\text{B}_2\text{H}_5$.

formation of side products such as $[\text{MeN}-\text{BH}]_3$ and $\text{MeNH}_2\cdot\text{BH}_3$, which were also identified in the aforementioned reaction in the presence of the Ir catalyst.

The highly unexpected observation of aminoborane hydrogenation detected with diborazanes inspired us to conduct a further investigation of related reactions of $i\text{Pr}_2\text{N}=\text{BH}_2$ with simpler substrates under metal-free conditions. The reaction of $i\text{Pr}_2\text{N}=\text{BH}_2$ with $\text{NH}_3\cdot\text{BH}_3$ (20 °C, THF) in either a sealed or open system led to a clear reaction solution from which a colorless solid rapidly began to precipitate. Analysis of the reaction mixture by ^{11}B NMR spectroscopy after 18 h (Figure 1) indicated the complete consumption of $i\text{Pr}_2\text{N}=\text{BH}_2$ ($\delta_{\text{B}} = 34.6$ ppm) to form the amine-borane hydrogenation product $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ ($\delta_{\text{B}} = -21.7$ ppm). A trace quantity of $\text{NH}_3\cdot\text{BH}_3$ remained in solution, with $[\text{H}_2\text{B}(\mu\text{-H})(\mu\text{-NH}_2)\text{BH}_2]^{8\text{h}}$ and $[\text{NH}-\text{BH}]_3$ identified as the only other soluble products. However, these species accounted for a total of only ca. 50% of the initial boron present as $\text{NH}_3\cdot\text{BH}_3$.^{11b} The colorless precipitate from the reaction mixture was collected via decantation but proved to be entirely insoluble in common organic solvents. Characterization by FT-IR spectroscopy showed both N–H and B–H stretching modes at frequencies consistent with those of the insoluble polyaminoborane $[\text{NH}_2-\text{BH}_2]_x$, which has been previously prepared via the Ir-catalyzed dehydrogenation of $\text{NH}_3\cdot\text{BH}_3$.^{3b}

These results indicate that, remarkably, $i\text{Pr}_2\text{N}=\text{BH}_2$ is quantitatively hydrogenated by $\text{NH}_3\cdot\text{BH}_3$ to form $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ and $\text{NH}_2=\text{BH}_2$. The transient aminoborane $\text{NH}_2=\text{BH}_2$ presumably then spontaneously oligomerizes to form insoluble $[\text{NH}_2-\text{BH}_2]_x$. The presence of the free aminoborane $\text{NH}_2=\text{BH}_2$ was confirmed by repeating the reaction in the presence of 2.5 equiv of cyclohexene. Under these conditions, only a small amount of $[\text{NH}_2-\text{BH}_2]_x$ was observed to form as an insoluble white precipitate, and 75% conversion to $\text{NH}_2=\text{BCy}_2$ ($\delta_{\text{B}} = 46.9$ ppm) was apparent by ^{11}B NMR spectroscopy.^{13,11b}

To investigate the generality of this hydrogen transfer process, we also investigated the reactions of $i\text{Pr}_2\text{N}=\text{BH}_2$ with $\text{MeNH}_2\cdot\text{BH}_3$ and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ at 20 °C in THF.¹⁴ The reaction of $i\text{Pr}_2\text{N}=\text{BH}_2$ and $\text{MeNH}_2\cdot\text{BH}_3$ (20 °C, 21 h) resulted in 90% hydrogenation of $i\text{Pr}_2\text{N}=\text{BH}_2$ to $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$, accompanied by 75% dehydrogenation of $\text{MeNH}_2\cdot\text{BH}_3$ to form various products including $[\text{H}_2\text{B}(\mu\text{-H})(\mu\text{-NHMe})\text{BH}_2]$ (6%), $[\text{MeN}-\text{BH}]_3$ (4%), and $[\text{MeNH}-\text{BH}_2]_x$ (Scheme 6; also see Figures SI-6 and SI-7). The formation of the latter would be anticipated on the basis of the isolation of $[\text{NH}_2-\text{BH}_2]_x$ in the case of the reaction between $\text{NH}_3\cdot\text{BH}_3$ and $i\text{Pr}_2\text{N}=\text{BH}_2$ (see above).

Scheme 6. Reaction of $\text{MeNH}_2\cdot\text{BH}_3$ with $i\text{Pr}_2\text{N}=\text{BH}_2$

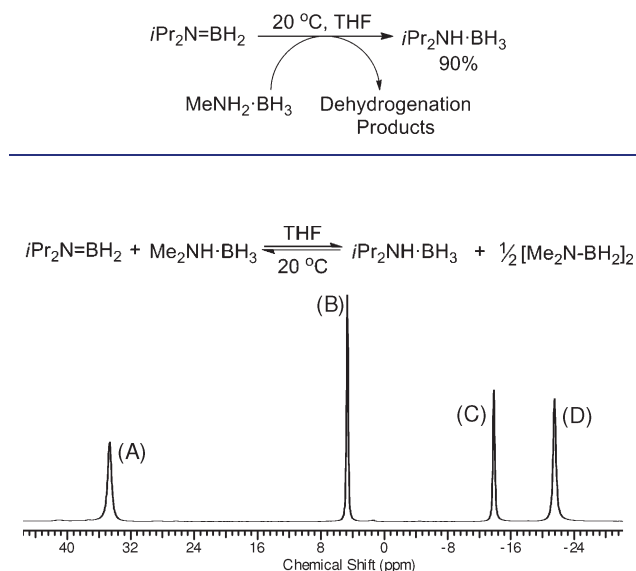


Figure 2. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the reaction of $i\text{Pr}_2\text{N}=\text{BH}_2$ and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ after 48 h: (A) $i\text{Pr}_2\text{N}=\text{BH}_2$, (B) $[\text{Me}_2\text{N}-\text{BH}_2]_2$, (C) $\text{Me}_2\text{NH}\cdot\text{BH}_3$, (D) $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$.

Allowing this reaction to stir for a further 30 h produced no further conversion of $i\text{Pr}_2\text{N}=\text{BH}_2$ or $\text{MeNH}_2\cdot\text{BH}_3$. This suggested that the system may be at equilibrium under the conditions studied. Once again, the formation of $\text{MeNH}=\text{BH}_2$ in the reaction was confirmed by the addition of cyclohexene to the initial reaction mixture, with 45% $\text{MeNH}=\text{BCy}_2$ formed over 18 h.^{11b}

The reaction of $i\text{Pr}_2\text{N}=\text{BH}_2$ with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (20 °C, 18 h) yielded 54% hydrogenation of $i\text{Pr}_2\text{N}=\text{BH}_2$ and 58% dehydrogenation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ to furnish $[\text{Me}_2\text{N}-\text{BH}_2]_2$ cleanly. Again in this case, even though the reaction was allowed to stir for a further 30 h, complete conversion of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ to $[\text{Me}_2\text{N}-\text{BH}_2]_2$ could not be achieved, which also suggested that the system reached an equilibrium under these conditions (Figure 2 and Figure SI-8).

To explore the existence of an equilibrium further, the “reverse” reaction between $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ and $[\text{Me}_2\text{N}-\text{BH}_2]_2$ (20 °C, THF) was also studied. Although notably slower, this reaction also reached equilibrium after 190 h, and the equilibrium mixture contained comparable quantities of $i\text{Pr}_2\text{N}=\text{BH}_2$ / $i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ and $[\text{Me}_2\text{N}-\text{BH}_2]_2$ / $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (Figure SI-9). The observation that the degree of hydrogenation of $i\text{Pr}_2\text{N}=\text{BH}_2$ with amine-boranes appears to decrease in the order $\text{NH}_3\cdot\text{BH}_3 > \text{MeNH}_2\cdot\text{BH}_3 > \text{Me}_2\text{NH}\cdot\text{BH}_3$ is consistent with the calculated dehydrogenation enthalpies for the latter species.¹⁵

For comparison, we also investigated the reaction of $i\text{Pr}_2\text{N}=\text{BH}_2$ and $\text{Me}_2\text{ND}\cdot\text{BD}_3$ (20 °C, THF). Analysis by ^{11}B NMR spectroscopy after 2 h was consistent with initial transfer of D_2 to $i\text{Pr}_2\text{N}=\text{BH}_2$ to give $i\text{Pr}_2\text{ND}\cdot\text{BH}_2\text{D}$, which possessed a broad triplet characteristic of a BH_2D group (Figures SI-10 and SI-11). As expected, this reaction proceeded more slowly than that with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ under the same conditions, consistent with cleavage of N–H/D and/or B–H/D bonds in the rate-determining step. In addition, scrambling of deuterium into all of the hydrogen environments was detected as the reaction progressed.

In summary, Ir-catalyzed dehydrocoupling of diborazanes such as $\text{MeNH}_2-\text{BH}_2-\text{NHMe}-\text{BH}_3$ proceeds with redistribution and

subsequent polymerization/oligomerization reactions of the aminoborane $\text{MeNH}=\text{BH}_2$, which appears to be present as a metal-bound species. Thermal treatment leads to similar reactions in the absence of the Ir catalyst, but the aminoborane is “free” in solution and can be trapped with cyclohexene. The observation of other side products led to the interesting discovery that the model aminoborane $i\text{Pr}_2\text{N}=\text{BH}_2$ can be hydrogenated in reactions with diborazanes and amine-boranes in the absence of a metal catalyst. The facile, room temperature hydrogenation of the $\text{B}=\text{N}$ bond in aminoboranes is of fundamental significance¹⁶ and also has other potential implications, such as in the regeneration of amine-borane hydrogen storage materials and the use of $\text{B}-\text{N}$ compounds in metal-free catalysis. These results are also important with respect to the mechanistic considerations associated with metal-catalyzed group 13–15 dehydrocoupling reactions, as to date the focus has been almost entirely on the role of the metal. Further studies in this intriguing area are in progress in our group.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental data and relevant spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

A.P.M.R., E.M.L., and I.M. acknowledge the EPSRC for funding. We thank Dr. George R. Whittell for useful discussions.

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