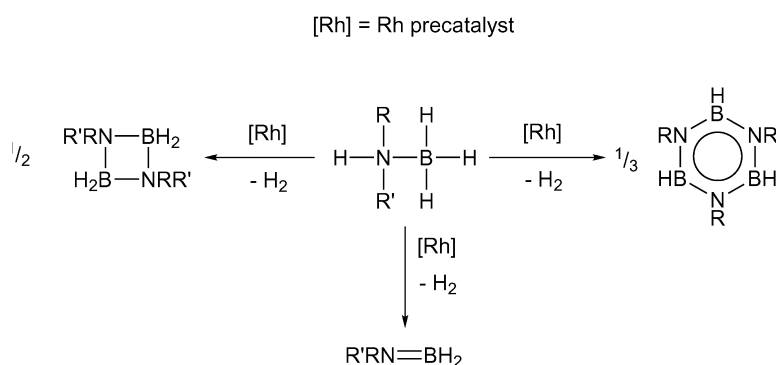Article

Transition Metal-Catalyzed Formation of Boron–Nitrogen Bonds: Catalytic Dehydrocoupling of Amine-Borane Adducts to Form Aminoboranes and Borazines

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Transition Metal-Catalyzed Formation of Boron−Nitrogen Bonds: Catalytic Dehydrocoupling of Amine-Borane Adducts to Form Aminoboranes and Borazines

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Abstract: A mild, catalytic dehydrocoupling route to aminoboranes and borazine derivatives from either primary or secondary amine-borane adducts has been developed using late transition metal complexes as precatalysts. The adduct $Me_2NH \cdot BH_3$ thermally eliminates hydrogen at 130 °C in the condensed phase to afford $[Me_2N-BH_2]_2$ (**1**). Evidence for an intermolecular process, rather than an intramolecular reaction to form $Me_2N=BH_2$ as an intermediate, was forthcoming from "hot tube" experiments where no appreciable dehydrocoupling of gaseous $Me_2NH \cdot BH_3$ was detected in the range 150−450 °C. The dehydrocoupling of $Me_2NH \cdot BH_3$ was found to be catalyzed by 0.5 mol % $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ in solution at 25 °C to give **1** quantitatively after ca. 8 h. The rate of dehydrocoupling was significantly enhanced if the temperature was raised or if the catalyst loading was increased. The catalytic activity of various other transition metal complexes (Ir, Ru, Pd) for the dehydrocoupling of $Me_2NH \cdot BH_3$ was also demonstrated. This new catalytic method was extended to other secondary adducts $RR'NH \cdot BH_3$ which afforded the dimeric species $[(1,4\text{-}C_4H_8)N-BH_2]_2$ (**2**) and $[PhCH_2(Me)N-BH_2]_2$ (**3**) or the monomeric aminoborane $^iPr_2N=BH_2$ (**4**) under mild conditions. A new synthetic approach to the linear compounds $R_2NH-BH_2-NR_2-BH_3$ (**5**: R = Me; **6**: R = $1,4\text{-}C_4H_8$) was developed and subsequent catalytic dehydrocoupling of these species yielded the cyclics **1** and **2**. The species **5** and **6** are postulated to be intermediates in the formation of **1** and **2** directly from the catalytic dehydrocoupling of the adducts $R_2NH \cdot BH_3$. The catalytic dehydrocoupling of $NH_3 \cdot BH_3$, $MeNH_2 \cdot BH_3$, and $PhNH_2 \cdot BH_3$ at 45 °C to give the borazine derivatives $[RN-BH]_3$ (**10**: R = H; **11**: R = Me; **12**: R = Ph) was demonstrated. TEM analysis of the contents of the reaction solution for the $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ catalyzed dehydrocoupling of $Me_2NH \cdot BH_3$ together with Hg poisoning experiments suggested a heterogeneous catalytic process involving Rh(0) colloids.

Introduction

The application of transition metal catalysis to organic synthesis is of profound current importance. Many industrial processes depend on metal-mediated routes (e.g., the production of polyolefins via Ziegler−Natta polymerization) and transition metal complexes are increasingly used to provide alternative routes to specialty organic polymers with controlled architectures and in synthetic transformations leading to the total synthesis of new organic molecules.[1] In contrast, the development of analogous methods for the formation of homonuclear or heteronuclear bonds between main group elements is relatively unexplored. Traditional methods in synthetic main group chemistry have utilized metathesis reactions such salt elimination

to provide a pathway for the formation of new bonds. However, the discovery in the mid 1980s that group 4 metallocene complexes catalytically dehydrocouple primary silanes to afford polysilanes[2] has led to the development of a range of new catalytic routes toward molecular and polymeric main group species.[3,4] Transition metal-catalyzed dehydropolymerization routes to polygermanes[5] and polystannanes[6] have been described in detail, while the dehydrocoupling method has been extended to include reactions that form new P−P,[7] B−Si,[8] B−C,[9] Si−

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(1) For some recent examples, see: (i) Atom Transfer Radical Polymerization (ATRP): (a) Matyjaszewski, K. *Curr. Org. Chem.* **2002**, *6*, 67. (ii) Olefin Metathesis reactions such as Ring Opening Metathesis Polymerization (ROMP) and Ring Closing Metathesis (RCM): (b) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (c) Fürstner, A. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3012. (iii) Cross-coupling reactions: (d) Luh, T.-Y.; Leung, M.-K.; Wong, K.-T. *Chem. Rev.* **2000**, *100*, 3187. (e) *Metal Catalyzed Cross-Coupling Reactions*, Diederich, F.; Stang, P. J. Eds., Wiley-VCH: New York, 1998. (iv) Asymmetric synthesis: (f) *Asymmetric Catalysis in Organic Synthesis*; Noyori, R., Wiley: New York, 1994.

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(3) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.

(4) For metal-catalyzed routes to transition metal-containing polymers, see for example: (a) Steffen, W.; Köhler, B.; Altmann, M.; Scherf, U.; Stitzer, K.; zur Loye, H.-C.; Bunz, U. H. F. *Chem. Eur. J.* **2001**, *7*, 117. (b) Gómez-Elipe, P.; Resendes, R.; Macdonald, P. M.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 8348. (c) Knapp, R.; Velten, U.; Rehahn, M. *Polymer* **1998**, *39*, 5827. (d) Kelch, S.; Rehahn, M. *Macromolecules* **1997**, *30*, 6185.

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(6) (a) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607. (b) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931. (c) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 12481.

C,[10] Sn–Te,[11] Si–P,[12] Si–N,[13] and Si–O[14] bonds. Our group has recently reported a novel catalytic route toward B–P bond formation, which involves the dehydrocoupling of primary or secondary phosphine-borane adducts in the presence of late transition metal catalysts to afford linear and cyclic oligomeric species and also high molecular weight polyphosphinoboranes.[15] On the basis of this discovery, extension of the catalytic dehydrocoupling method to systems comprised of other combinations of Group 13–Group 15 elements was of key interest.

Amine-borane adducts are well-known[16] and can be readily synthesized from the free amine and commercially available borane sources or from the appropriate ammonium chloride salt and $LiBH_4$. In addition, primary and secondary amine-borane adducts have been shown to undergo thermally induced dehydrocoupling at elevated temperatures (> 100 °C) to yield cyclic aminoborane $[R_2B-NR'_2]_x$ ($x = 2$ or 3) and borazine [RB–

NR']_3 derivatives.[17] If the dehydrocoupling could be achieved under milder conditions using a transition metal-catalyst, improved routes to boron–nitrogen rings and chains would be possible. Moreover, the formation of polyaminoboranes under the appropriate conditions might be achieved with a suitable choice of monomer.[18]

As a follow up to our preliminary communication,[19] in this paper, we present full details of our studies of the metal-catalyzed dehydrocoupling of primary and secondary amine-borane adducts.[20]

Results and Discussion

Hot Tube Reactions Involving $Me_2NH\cdot BH_3$: Evidence for Intermolecular Thermally-Induced Dehydrocoupling. The adduct $Me_2NH\cdot BH_3$ undergoes thermally induced dehydrocoupling at 130 °C in the melt to form the cyclic aminoborane dimer $[Me_2N-BH_2]_2$ (**1**).[21] Prior to commencing catalytic studies, some mechanistic information on this thermal process was desired. To explore whether the dehydrocoupling is intermolecular or intramolecular in nature, and to investigate the possible formation of the multiply bonded species $Me_2N=BH_2$ as a transient reactive intermediate, we studied the behavior of $Me_2NH\cdot BH_3$ under "hot tube" conditions in the gas phase under vacuum. If the dehydrocoupling is an intermolecular process, then there should be little or no hydrogen elimination as reactions between gas phase molecules are minimized. If the dehydrocoupling is an intramolecular process, then hydrogen elimination should occur readily with the formation of $Me_2N=BH_2$, which may undergo addition polymerization[22] to afford $[Me_2N-BH_2]_n$. Volatile $Me_2NH\cdot BH_3$ was passed through a heated quartz tube under vacuum and the thermolysis products were trapped at -196 °C. Thermolysis temperatures of 150 °C, 250 °C, 350 °C, and 450 °C were used in four separate experiments which were each performed over 2–3 h. Lower temperatures of 150 °C and 250 °C resulted in the recovery of only unreacted $Me_2NH\cdot BH_3$, whereas higher furnace temperatures of 350 °C and 450 °C resulted in unreacted $Me_2NH\cdot BH_3$ as the major product, and a trace amount ($<5\%$) of $[Me_2N-BH_2]_2$ (**1**). With only minor amounts of **1** obtained in these gas-phase experiments, our results support the conclusion that hydrogen loss from $Me_2NH\cdot BH_3$ at 130 °C is an intermolecular process. This result is consistent with earlier work performed in the condensed phase at lower temperatures (100 °C) where labeling experiments led to the same conclusion.[23] The probability of two $Me_2NH\cdot BH_3$ molecules encountering one another to facilitate dehydrocoupling in the gas phase is low, and thus the formation of **1** is minimized even at elevated temperatures. However, in the molten liquid state at 130 °C, the molecules are free to interact and dehydrocoupling occurs quite readily to yield **1**.[21]

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(20) To the best of our knowledge, three brief previous reports of transition metal-catalyzed dehydrocoupling routes to B–N bonds exist. (a) Primary or secondary amine-borane adducts have been briefly reported to undergo dehydrocoupling to yield cyclic aminoboranes $[R_2N-BH_2]_2$ or borazines using $M(CO)_6$ (M = Cr, W) under photolytic conditions. No experimental conditions were reported. Shimoi, M.; Katoh, K.; Uruichi, M.; Nagai, S.; Ogino, H. *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; 1994, 293. (b) The dehydrocoupling of the secondary amine-borane adduct ^{t}Bu(Me)NH·BH_3 to give a cyclic dimer has been reported using Pd/C as a catalyst. However, fairly harsh reaction conditions (120 °C, partial vacuum of *ca.* 200 Torr, 2.5 h) were employed which are close to those generally needed for uncatalyzed dehydrocoupling. Green, I. G.; Johnson, K. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1963. (c) A patent claims the catalytic formation of partially characterized mixtures of B–N compounds (including borazines) and insoluble polymeric products by the dehydrocoupling of mixtures of primary amines and $Me_3N\cdot BH_3$ over extended periods of time at elevated temperatures. The conditions reported typically involve reaction times of 30–80 h at 60 °C using $Ru_3(CO)_{12}$ as a catalyst. Blum, Y. D.; Laine, R. M. *US Pat.* 4801439, **1989**.

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(23) Labeling experiments have previously suggested that H_2 elimination from $Me_2NH\cdot BH_3$ is an intermolecular process: Ryschkewitsch, G. E.; Wiggins, J. W. *Inorg. Chem.* **1970**, *9*, 314.

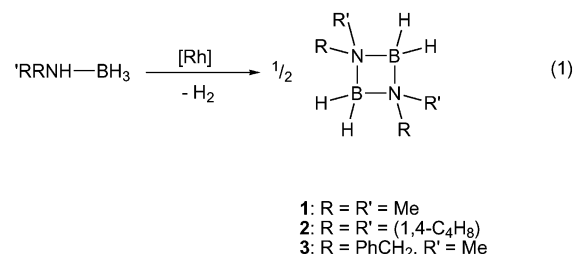**Table 1.** Dehydrocoupling of Me$_2$NH·BH$_3$ to Yield **1** Using Various Transition Metal-Catalysts and Conditions[a]

	catalyst	T (°C)	mol % catalyst	T (h)	yield (%)[b]
1	none	45		168	0
2	[Rh(1,5-cod)(μ-Cl)]$_2$	25	0.5	8	100
3	[Rh(1,5-cod)(μ-Cl)]$_2$	45	0.5	2	90
4	[Rh(1,5-cod)(μ-Cl)]$_2$	45[c]	0.5	2	55[d]
5	[Rh(1,5-cod)(μ-Cl)]$_2$	25	5.0	<2	100
6	[Rh(1,5-cod)(μ-Cl)]$_2$	45	5.0	<2	100
7	[Rh(1,5-cod)(μ-Cl)]$_2$	45[c]	5.0	0.8	30[d]
8	[Ir(1,5-cod)(μ-Cl)]$_2$	25	0.5	136	95
9	RhCl$_3$	25	0.5	22.5	90
10	RhCl$_3$·3H$_2$O	25	0.5	64	90
11	IrCl$_3$	25	0.5	160	25
12	RhCl(PPh$_3$)$_3$	25	0.5	44	95
13	[Cp*Rh(μ-Cl)Cl]$_2$	25	0.5	112	100
14	[Rh(1,5-cod)$_2$]OTf	25	0.5	7.5	95
15	[Rh(1,5-cod)(dmpe)]PF$_6$	25	0.5	112	95
16	HRh(CO)(PPh$_3$)$_3$	25	0.5	160	5
17	*trans*-RuMe$_2$(PMe$_3$)$_4$	25	0.5	16	100
18	*trans*-PdCl$_2$(P(*o*-tolyl)$_3$)$_2$	25	0.5	160	20
19	Pd/C (10%)	25	0.5	68	95
20	Cp$_2$TiMe$_2$	25	0.5	160	0
21	B(C$_6$F$_5$)$_3$	25	0.5	96	0

[a] Reactions were performed using ~0.20 g of Me$_2$NH·BH$_3$ in toluene (2 mL) and were monitored periodically by ^{11}B NMR spectroscopy. [b] On the basis of the integration of ^{11}B NMR spectrum of the reaction mixture. [c] Performed in the absence of solvent. Time corresponds to time required for **1** to completely sublime out of reaction flask. [d] Isolated yield of **1** via sublimation.

The intermolecular dehydrocoupling of Me$_2$NH·BH$_3$ is likely favored by the presence of protic (H$^{\delta+}$) and hydridic (H$^{\delta-}$) hydrogen substituents at nitrogen and boron, respectively, which promotes thermally induced H$_2$ elimination. Next, we proceeded with attempts to catalyze this process under mild conditions.

Catalytic Dehydrocoupling of Secondary Amine-Borane Adducts: Synthesis of the Cyclic Dimers [Me$_2$N−BH$_2$]$_2$ (1), [(1,4-C$_4$H$_8$)N−BH$_2$]$_2$ (2), and [PhCH$_2$(Me)N−BH$_2$]$_2$ (3). When a solution of Me$_2$NH·BH$_3$ in toluene was treated with a catalytic amount (0.5 mol % catalyst) of [Rh(1,5-cod)(μ-Cl)]$_2$ (1,5-cod = 1,5-cyclooctadiene) and stirred at 25 °C, evolution of hydrogen gas and the formation of [Me$_2$N−BH$_2$]$_2$ (**1**) was observed after 8 h (Equation 1, Table 1). The conversion to **1** appeared to be quantitative as indicated by the ^{11}B NMR spectrum of the reaction mixture, as the starting material (δ −13.5 ppm) was completely consumed and the only new signal observed was a triplet at δ 4.75 ppm (J_{BH} = 110 Hz). ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction were employed to further confirm the structure of **1**. Due to the extreme volatility of **1**, removal of the solvent in vacuo from the reaction mixture also resulted in the removal of the product itself. Repeated attempts to recrystallize **1** from the reaction mixture also failed, and thus isolated yields could not be obtained for the reactions performed in solution at 25 °C. Raising the temperature to 45 °C allowed the dehydrocoupling reaction to be performed as a neat mixture of the catalyst and the molten adduct (mp of Me$_2$NH·BH$_3$ is 36 °C). This led to a reduction in the conversion time to 2 h and allowed volatile **1** to sublime directly out of the neat mixture, thereby facilitating isolation and purification steps. As the isolated yield of this neat reaction was found to be only 55%, (which improved to 77% upon scale-up), a similar dehydrocoupling trial performed in a toluene solution at 45 °C indicated the complete conversion to **1** after the same time period (2 h). This implied that while the catalytic dehydrocoupling reactions do proceed to completion

in the neat reaction mixture, some of the volatile product is still lost, thereby decreasing the isolated yield. Further reductions in reaction time were observed if the catalyst loading was increased to 5 mol %, with full conversion occurring in less than 2 h at 25 °C, or in 0.8 h (neat) or 2 h (solution) at 45 °C. To confirm that a catalytic effect indeed existed, prolonged heating (168 h, 45 °C) of neat Me$_2$NH·BH$_3$ in the absence of any catalyst resulted in the exclusive recovery of unreacted adduct. This clearly demonstrates the activity of the Rh precatalyst toward the dehydrocoupling of Me$_2$NH·BH$_3$.

$$'RRNH-BH_3 \quad \xrightarrow[\text{- H}_2]{\text{[Rh]}} \quad 1/2 \quad \text{(1)}$$

1: R = R' = Me
2: R = R' = (1,4-C$_4$H$_8$)
3: R = PhCH$_2$, R' = Me

We found that the active catalyst can be recycled for further reactions. After **1** had been completely removed by sublimation from the neat reaction mixture at 45 °C, additional Me$_2$NH·BH$_3$ was added to the residual catalyst. The catalytic activity was retained, and this process was successfully repeated numerous (5) times to give a high overall yield of 72%. The only limitation is an increase in the reaction time caused by a slow deactivation of the catalytic species.

The use of other late transition metal-catalysts for the solution dehydrocoupling of Me$_2$NH·BH$_3$ at 25 °C was also examined (Table 1). [Ir(1,5-cod)(μ-Cl)]$_2$ was found to be a less active catalyst than its Rh counterpart, requiring much longer reaction times (136 h) for appreciable conversion to **1**. The Rh(III) salts RhCl$_3$ and RhCl$_3$·3H$_2$O were also found to be catalytically active, whereas the activity of IrCl$_3$ was much lower. The neutral complexes [Cp*Rh(μ-Cl)Cl]$_2$ (Cp* = η^5-C$_5$Me$_5$) and RhCl-(PPh$_3$)$_3$ as well as the cationic Rh(I) complexes [Rh(1,5-cod)$_2$]-OTf (OTf = SO$_3$CF$_3$) and [Rh(1,5-cod)(dmpe)]PF$_6$ (dmpe = bis(dimethylphosphino)ethane) were also found to be active catalysts. Interestingly, the hydride species HRh(CO)(PPh$_3$)$_3$ was found to have low catalytic activity, with only 5% conversion after 160 h. The complex *trans*-RuMe$_2$(PMe$_3$)$_4$, which is a known catalyst for the demethanative coupling of arylgermanes,[5c] shows a high catalytic activity with 100% conversion after 16 h. The catalytic dehydrocoupling of ^{t}Bu(Me)NH·BH$_3$ to give the corresponding cyclic dimer has been briefly noted by Roberts and co-workers using Pd/C at 120 °C, a temperature at which uncatalyzed dehydrocoupling may occur.[20b] We found that the use of Pd/C resulted in 95% conversion of Me$_2$NH·BH$_3$ to **1** after 68 h. However, the palladium complex *trans*-PdCl$_2$(P(*o*-tolyl)$_3$)$_2$ showed a low catalytic activity with only 20% conversion to **1** after 160 h. As group 4 metallocene complexes are excellent catalysts[3] for the dehydrocoupling of silanes, stannanes, and germanes, Cp$_2$TiMe$_2$ was also tested for catalytic activity. However, no dehydrocoupling was observed after 160 h. Recently, Denis and co-workers have reported that B(C$_6$F$_5$)$_3$ can dehydropolymerize PhPH$_2$·BH$_3$ to yield [PhPH−BH$_2$]$_n$.[24] However, no dehydrocoupling of Me$_2$NH·BH$_3$ was observed when B(C$_6$F$_5$)$_3$ was tested as a catalyst.

(24) Denis, J.-M.; Forintos, H.; Szelke, H.; Toupet, L.; Pham, T.-N.; Madec, P.-J.; Gaumont, A. C. *Chem. Commun.* **2003**, 54.
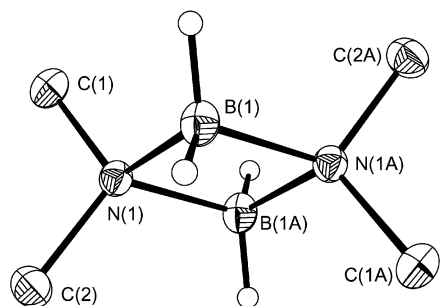
Figure 1. Molecular structure of **1**. All hydrogen atoms bonded to carbon are omitted for clarity. Selected bond lengths and angles are presented in Table 2.
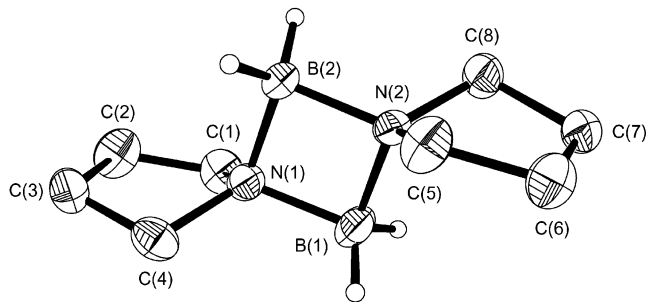

Figure 2. Molecular Structure of **2**. All hydrogen atoms bonded to carbon are omitted for clarity. Selected bond lengths and angles are presented in Table 2.
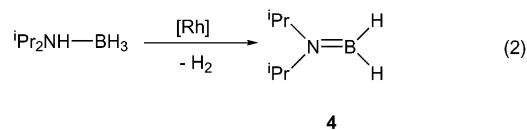
One important factor that was found to drastically affect the rate of dehydrocoupling was the purity of $Me_2NH \cdot BH_3$. Generally, adduct of lower purity (e.g., 97% as purchased) required much longer reaction times for complete conversion to **1** than multiply sublimed samples with a purity of >99%. For example, $Me_2NH \cdot BH_3$ of greater than 99% purity was catalytically dehydrocoupled to **1** in ca. 8 h at 25 °C, whereas 97% pure $Me_2NH \cdot BH_3$ required ca. 36 h under the same conditions.

This catalytic dehydrocoupling strategy can also be generalized to other secondary amine-borane adducts. For example, when pyrrolidine-borane $(1,4\text{-}C_4H_8)NH \cdot BH_3$ was treated with 0.5 mol % of $RhCl_3 \cdot 3H_2O$ or $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ and stirred at 25 °C in toluene for 24 h, the cyclic dimer $[(1,4\text{-}C_4H_8)N{-}BH_2]_2$ (**2**) was isolated as a white powder in 73% yield. The unsymmetrically substituted adduct $PhCH_2(Me)NH \cdot BH_3$ was also found to similarly undergo catalytic dehydrocoupling in the presence of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (1.2 mol %) to give the cyclic dimer $[PhCH_2(Me)N{-}BH_2]_2$ (**3**) in 79% yield. A 1:1 mixture of cis and trans isomers were obtained, as two sets of signals for the CH_3 groups were observed in the ^1H and ^{13}C NMR spectra.

The identity of the aminoboranes **1** and **2** was confirmed by single-crystal X-ray diffraction studies and the molecular structures are shown in Figures 1 and 2, respectively. Both **1** and **2** were found to be dimeric and contained four membered B−N rings. The structure of **1** was found to have B−N bond lengths of 1.596(4)Å and 1.595(4)Å, which are similar to those found in the structure of the analogous cyclic trimer $[Me_2N{-}BH_2]_3$ [1.61(4)Å].[25] The N−B−N and B−N−B angles were found to deviate quite significantly from the ideal tetrahedral geometry, with values of 93.7(2)° and 86.3(2)°, respectively. The structure of **2** was found to have four independent molecules

(25) Trefonas, L. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1959**, *81*, 4435.

in the unit cell, with values of the B−N bond lengths in the range 1.584(5)Å − 1.609(5)Å. The average N−B−N and B−N−B angles were found to be 92.9(3)° and 86.9(3)°, respectively.

Catalytic Dehydrocoupling of a Secondary Amine-Borane Adduct with Bulky Substituents on Nitrogen: Synthesis of the Monomeric Aminoborane $^iPr_2N{=}BH_2$ (4). When a secondary amine-borane adduct with bulky substituents on nitrogen was subject to catalytic dehydrocoupling, formation of the cyclic dimer was not observed and a monomeric species was formed. Thus, treatment of $^iPr_2NH \cdot BH_3$ with a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ led to the formation of $^iPr_2N{=}BH_2$ (**4**) which was isolated in 49% yield (Equation 2). The ^{11}B NMR spectrum of **4** displayed a triplet at δ 34.7 (J_{BH} = 123 Hz; lit. δ 34.2).[26] Previous studies on monomer−dimer equilibria of $R_2N{=}BH_2$ species by ^{11}B NMR indicate a general trend for the chemical shifts of both monomers ($\delta \approx 37$ ppm) and dimers (δ 1.9−5.4 ppm).[27] Thus, based on the chemical shift observed (δ 34.7 ppm) we can conclude that the aminoborane **4** is monomeric in nature, with dimerization being prevented by the steric bulk of the *N* substituents.

$$^iPr_2NH{-}BH_3 \xrightarrow[{-H_2}]{[Rh]} \begin{array}{c} ^iPr \\ \diagdown \\ N{=}B \\ \diagup \quad \diagdown \\ ^iPr \qquad H \end{array} \quad H \qquad (2)$$

4

If the catalytic dehydrocoupling of $^iPr_2NH \cdot BH_3$ is an intermolecular process similar to that for the thermal reaction of $Me_2NH \cdot BH_3$ (vide supra), then the formation of the monomeric **4** may result as a combination of intermolecular dehydrocoupling and dissociation reactions. The potential intermediate species in the catalytic cycle are considered in the next section.

Synthesis, Characterization and Catalytic Dehydrocoupling of the Linear Amine-Borane Dimers $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (5) and $(1,4\text{-}C_4H_8)NH{-}BH_2{-}N(1,4\text{-}C_4H_8){-}BH_3$ (6). The thermally induced dehydrocoupling of $Me_2NH \cdot BH_3$ is an intermolecular process (vide supra). It is reasonable to propose that at a catalytic site, two molecules of $Me_2NH \cdot BH_3$ could react in an intermolecular fashion to form the linear dimer $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (**5**) and 1 equiv of hydrogen. This linear dimer **5** could then interact with the catalyst again, but now in an intramolecular fashion to afford the cyclic dimer **1** and another equivalent of hydrogen.[28] This inter/intramolecular reactivity is a more favorable process than an inter/intermolecular reaction sequence. Consecutive intermolecular reactions would result in the formation of higher linear oligomers, which were not detected during any of the catalytic dehydrocoupling studies performed. Another potential reaction sequence involves the initial formation of **5**, followed by dissociation of both Me_2-NH and BH_3 to give $Me_2N{=}BH_2$, which could then dimerize to afford **1**. Free Me_2NH and BH_3 could also then reform Me_2-$NH \cdot BH_3$ and re-enter the catalytic cycle. To gain further mechanistic insight, the potential linear intermediates **5** and **6** were prepared and their catalytic dehydrocoupling chemistry was studied.
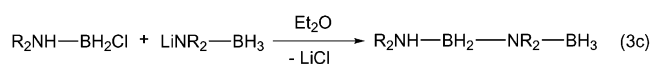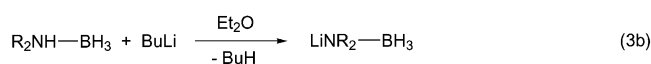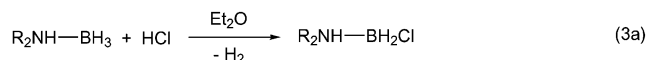
(26) Kanjolia, R. K.; Krannich, L. K.; Watkins, C. L. *J. Chem. Soc., Dalton Trans.* **1986**, 2345.
(27) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1967**, *100*, 3353.
(28) It has been suggested that the thermal dehydrocoupling of $Me_2NH \cdot BH_3$ to give $[Me_2N{-}BH_2]_2$ proceeds by the linear dimer intermediate **5**. See ref 23 and also Beachley Jr., O. T. *Inorg. Chem.* **1967**, *6*, 870.

The reaction of $R_2NH \cdot BH_2Cl$ with $Li[R_2N \cdot BH_3]$ afforded the linear dimers $R_2NH-BH_2-NR_2-BH_3$ (**5**: R = Me; **6**: R = 1,4-C_4H_8) in 34% and 23% yield, respectively (equations 3a–c). The observed low yields for the preparation of **5** and **6** occur as a result of the formation of the cyclics **1** and **2** as byproducts. Characterization of **6** was achieved by ^1H, ^{11}B, and ^{13}C NMR, mass spectrometry, elemental analysis and single-crystal X-ray diffraction (vide infra). Species **5** afforded spectroscopic data that was identical to that of samples prepared previously via an alternative route.[29]

$$R_2NH-BH_3 + HCl \xrightarrow[-H_2]{Et_2O} R_2NH-BH_2Cl \quad (3a)$$

$$R_2NH-BH_3 + BuLi \xrightarrow[-BuH]{Et_2O} LiNR_2-BH_3 \quad (3b)$$

$$R_2NH-BH_2Cl + LiNR_2-BH_3 \xrightarrow[-LiCl]{Et_2O} R_2NH-BH_2-NR_2-BH_3 \quad (3c)$$

5: R = Me
**6**: R = 1,4-C_4H_8

When a solution of **5** in toluene was treated with a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (1.5 mol %), gas evolution was observed and the formation of **1** was confirmed by ^{11}B NMR. Full conversion to **1** occurred after 2 d at 25 °C (equation 4). Treatment of **6** with a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (1.6 mol %) in toluene at 45 °C also led to intramolecular dehydrocoupling, with the formation of **2** in 100% yield after 24 h (Equation 4). These results clearly indicate that the chain ends prefer to dehydrocouple in an intramolecular fashion, rather than intermolecularly. This may be due to the flexibility of the B−N−B−N backbone, which would allow for the molecule to backbite when interacting with the catalyst. An intriguing mechanistic implication of these results is that the formation of the monomer **4** from the catalytic dehydrocoupling of $^iPr_2NH \cdot BH_3$ apparently occurs via the formation of a linear dimer, followed by cyclization and/or dissociation. As linear B−N−B−N chains were not detected spectroscopically as intermediates, their cyclization or dissociation is more rapid than their formation.

$$R_2NH-BH_2-NR_2-BH_3 \xrightarrow[-H_2]{[Rh]} \text{(cyclic)} \quad (4)$$
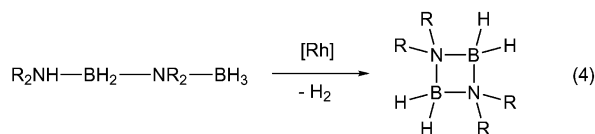
5: R = Me
6: R = 1,4-C_4H_8

1: R = Me
2: R = 1,4-C_4H_8

An X-ray crystallographic study was performed on **6**, the molecular structure of which is shown in Figure 3a. Structure **6** represents the second example of a crystallographically characterized linear dimer, the first being **5** recently reported by Nöth.[29] The terminal B−N bonds have equal lengths of 1.595(4) Å and 1.598(5) Å, whereas the central B−N bond is slightly shorter at 1.576(2) Å (Table 3). The B−N−B and N−B−N angles around the central nitrogen and boron atoms were found to be 111.4(2)° and 112.7(3)°, respectively. An interesting feature is the association of the chains in the solid state, which form a dimeric structure through two short H···H

(29) Nöth, H.; Thomas, S. *Eur. J. Inorg. Chem.* **1999**, 1373.
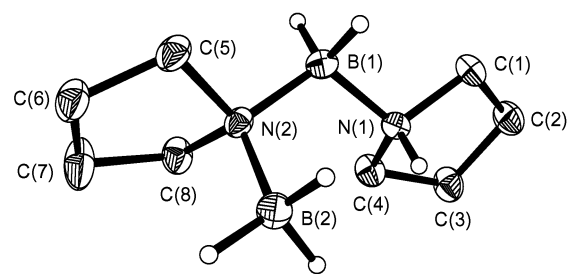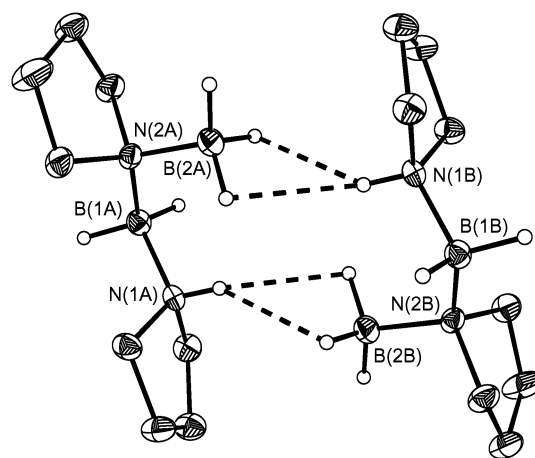
Figure 3. (a) Molecular Structure of **6**. (b) Association of two molecules of **6** via H···H interactions. All hydrogen atoms bonded to carbon are omitted for clarity. Selected bond lengths and angles are presented in Table 3.

interactions (2.253 Å and 2.382 Å) between the B−H and N−H hydrogen atoms (Figure 3b). To minimize the errors associated with X−H bond lengths as determined by X-ray diffraction, normalized values (1.21 Å for B−H; 1.03 Å for N−H) as established by neutron diffraction[30] were used. This resulted in H···H distances of 2.13 Å and 2.27 Å, which are shorter than the sum of the van der Waals radii for two hydrogen atoms (2.4 Å). The H···H−B angles were found to be 96.3° and 89.7°, whereas the H···H−N angles were 141.5° and 144.3°. This type of linear N−H···H and bent B−H···H geometry is consistent with other examples of close $H^{\delta+} \cdots ^{\delta-}H$ contacts for crystallographically characterized amine-borane species.[30] Nonclassical hydrogen bonding interactions were also observed in the structure of **5**.[29]
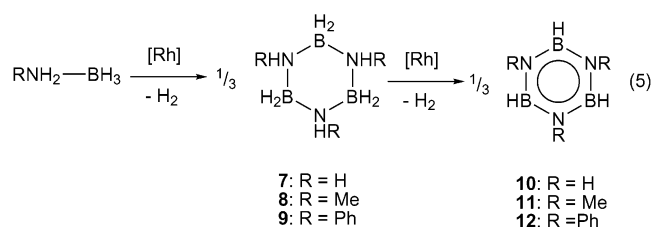
Catalytic Dehydrocoupling of Primary Amine-Borane Adducts and Ammonia-Borane: Synthesis of the Borazines [HN−BH]₃ (10), [MeN−BH]₃ (11), and [PhN−BH]₃ (12). Next, we attempted to extend the catalytic dehydrocoupling chemistry to the analogous primary amine-borane adducts and to $NH_3 \cdot BH_3$. The catalytic dehydrocoupling of $MeNH_2 \cdot BH_3$ was of particular interest following a brief report on the synthesis of poly(methylaminoborane) from the addition polymerization of in situ generated $MeNH=BH_2$.[22a,31] Catalytic dehydrocoupling trials were performed on ammonia-borane ($NH_3 \cdot BH_3$) and

(30) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337.
(31) This polymer was reported to be insoluble and thermodynamically unstable, with reversion to the cyclic trimer [MeNH−BH₂]₃ in the presence of free Me₂NH.

the primary adducts $MeNH_2 \cdot BH_3$ and $PhNH_2 \cdot BH_3$. In all cases, catalytic dehydrocoupling was observed with the formation of the borazines $[HB-NR]_3$ (**10**: R = H, **11**: R = Me, **12**: R = Ph). For example, when ammonia-borane was treated with a catalytic amount (0.6 mol %) of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ in either diglyme or tetraglyme at 45 °C, the evolution of gas was observed along with the formation of borazine **10** as identified by its ^{11}B NMR spectrum, which occurs as a doublet at δ 30.2 (J_{BH} = 141 Hz) (equation 5). Reaction times varied over several repeat trials, with 100% conversion detected after ca. 48−84 h. In addition, two intermediate products were consistently observed in the ^{11}B NMR spectra of the reaction mixtures. Resonances at δ −11.2 and −26.8 (td, J_{BHt} = 128 Hz, J_{BHb} = 33 Hz) have been identified as the cyclic trimer $[H_2B-NH_2]_3$ (**7**) (lit. δ −11.2, t, J_{BH} = 97 Hz)[32] and the μ-aminodiborane ((μ-NH_2)B_2H_5) (lit. δ −26.7, td, J_{BHt} = 130 Hz, J_{BHb} = 30 Hz),[33] respectively. These species have also been detected as intermediates in the thermal decomposition of $NH_3 \cdot BH_3$ at 130 °C in ether solvents in the stepwise loss of hydrogen to yield borazine.[34]

$$RNH_2{-}BH_3 \xrightarrow[-\,H_2]{[Rh]} \tfrac{1}{3} \underset{\text{HR}}{\overset{H_2B}{\underset{N}{\overset{B}{\underset{}{}}}}} \begin{array}{c} H_2 \\ B \\ RHN \quad NHR \\ \\ BH_2 \end{array} \xrightarrow[-\,H_2]{[Rh]} \tfrac{1}{3} \begin{array}{c} H \\ B \\ RN \quad NR \\ HB \quad BH \\ N \\ R \end{array} \quad (5)$$

7: R = H
8: R = Me
9: R = Ph

10: R = H
11: R = Me
12: R = Ph

Isolation of pure samples of **10** from the reaction mixture proved to be difficult. Vacuum fractionation techniques involving a three temperature trap system[35] routinely yielded only a ca. 10% yield of **10**. ^{11}B NMR analysis of the nonvolatile residue showed the presence of several broad signals in the region δ 26−36 ppm, which suggested that further intermolecular dehydrocoupling reactions occur to give oligomeric and/or polymeric B−N species. This is not an unreasonable assumption, as Sneddon and co-workers have reported that the thermal (70 °C) dehydrocoupling of borazine yields poly(borazylene) along with small amounts of the dimers diborazine (1,2′-($B_3N_3H_5$)$_2$) and borazanaphthalene ($B_5N_5H_8$).[18b] A mixture of poly(borazylene) (δ 31 ppm), diborazine (δ 32.5, 32.1, 31.2, 29.7 ppm) and borazanaphthalene (δ 35.5, 31.1, 25.8 ppm) and other low molecular weight oligomers would account for the abundance of resonances observed in the ^{11}B NMR spectrum. In addition, there is also the possibility of dehydrocoupling of the cyclic trimer **7**, an intermediate in the formation of **10**, to give nonvolatile, intermolecularly coupled species.

When $MeNH_2 \cdot BH_3$ was treated with a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (1.0 mol %) in monoglyme at 45 °C, the formation of the cyclic trimer $[MeNH-BH_2]_3$ (**8**) was initially detected (^{11}B NMR: δ −5.1, t, J_{BH} = 108 Hz; lit. δ −5.4, t, J_{BH} = 107 Hz).[36] Full conversion of the adduct to **8** was found to take between 4 and 6 h, and was followed by further loss of

(32) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1963**, *85*, 3592.
(33) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1964**, *86*, 1505.
(34) Wang, J. S.; Geanangel, R. A. *Inorg. Chim. Acta* **1988**, *148*, 185.
(35) For an example of the trap-to-trap vacuum fractionation setup for product purification, see: Wideman, T.; Fazen, P. J.; Lynch, A. T.; Su, K.; Remsen, E. E.; Sneddon, L. G. *Inorg. Synth.* **1998**, *32*, 232.
(36) Narula, C. K.; Janik, J. F.; Duesler, E. N.; Paine, R. T.; Schaeffer, R. *Inorg. Chem.* **1986**, *25*, 3346.

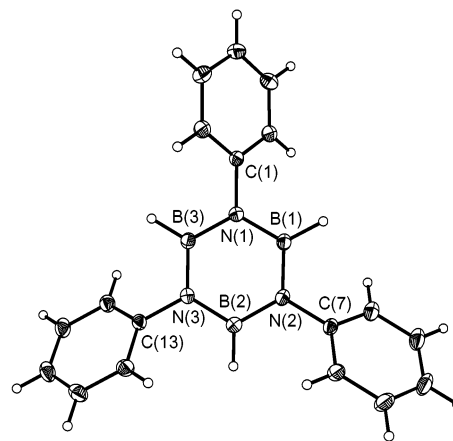**Figure 4.** Molecular Structure of **12**. Selected bond lengths and angles are presented in Table 4.

hydrogen to give *N*-trimethylborazine $[MeN-BH]_3$ (**11**). The second dehydrocoupling step was relatively slow, with full conversion of **8** to **11** requiring 48−72 h. Vacuum fractionation of the reaction mixture yielded pure samples of **11** in moderate yields (40%). Again, yields may be limited by undesirable intermolecular dehydrocoupling of the intermediate **8** to give involatile, coupled species.

Catalytic dehydrocoupling trials performed on the trimer **8** also demonstrated the slow loss of hydrogen to give **11** after 40 h at 45 °C (equation 5). The difference in dehydrocoupling rates in the stepwise elimination of hydrogen from $MeNH_2 \cdot BH_3$ is also reflected in the high temperature, uncatalyzed thermal route to **11**. Initial pyrolysis at 100 °C in the absence of catalyst gives **8**, which then has to be heated to 200 °C in order to eliminate the second equivalent of hydrogen to afford **11**.[37]

In the case of $PhNH_2 \cdot BH_3$, catalytic dehydrocoupling to give *N*-triphenylborazine $[PhN-BH]_3$ (**12**) was observed to occur rapidly in monoglyme (0.8 mol % $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$, 16 h, 25 °C). However, several byproducts were also formed (^{11}B NMR: δ 24, 17 and −3.8), which reduce the isolated yields to 56%. The minor resonances at δ 24 and 17 are unidentified, whereas the small resonance at δ −3.8 may be due to the intermediate trimer $[PhNH-BH_2]_3$ (**9**) which has not been previously reported. A single-crystal X-ray analysis of **12** was performed, with the molecular structure shown in Figure 4. As expected, the B_3N_3 ring is planar, with B−N bond lengths in the range 1.429(2)Å to 1.431(2)Å and B−N−B and N−B−N angles which are all close to 120° (Table 4). The phenyl groups are not coplanar with the B_3N_3 ring but are slightly twisted, with angles between the two planes of 48.8°, 43.7° and 42.3°. This type of ring twisting is also present in the structure of hexaphenylborazine $[PhB-NPh]_3$, which has angles between the ring planes in the range of 62.5° to 71.4°.[38]

Identification of the Active Catalyst: TEM Imaging and Catalyst Poisoning Experiments with Hg. The observation that all catalytic trials involving Rh precatalysts resulted in the formation of a black, opaque solution raised the often discussed problem about whether the catalysis is homogeneous or

(37) Bissot, T. C.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 3481.
(38) Lux, D.; Schwarz, W.; Hess, H. *Crystal. Struct. Commun.* **1979**, *8*, 33.
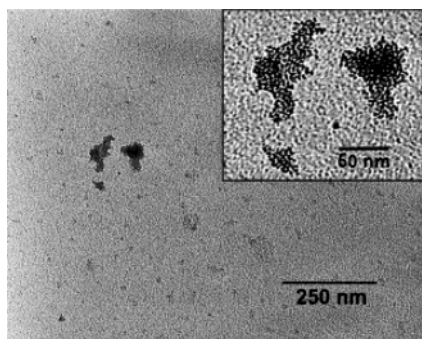
Figure 5. TEM image of an evaporated extract of the reaction mixture involving the catalytic dehydrocoupling of Me$_2$NH·BH$_3$ in the presence of [Rh(1,5-cod)(μ-Cl)]$_2$.
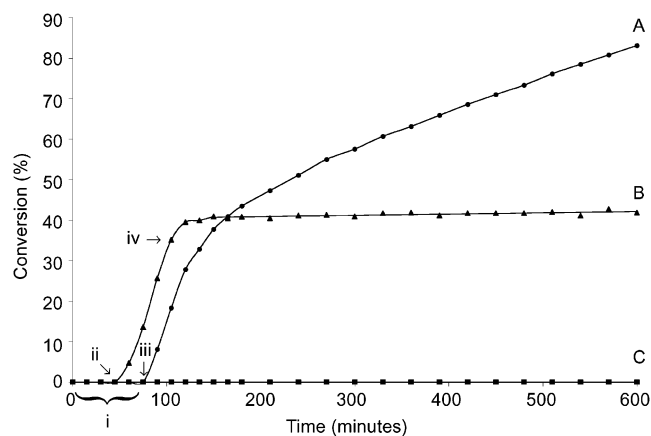

Figure 6. Graph of percent conversion versus time for the catalytic dehydrocoupling of Me$_2$NH·BH$_3$ to **1** using 0.5 mol % [Rh(1,5-cod)(μ-Cl)]$_2$ in toluene at 25 °C. (A) Control reaction. (B) Dehydrocoupling for first 105 min, then 68 equivalents of Hg were added at point iv. (C) Dehydrocoupling initiated in the presence of 71 equivalents of Hg. Region i represents the induction period for the dehydrocoupling of trials A and B. Points iii and ii indicate the visual formation of colloidal Rh for trials A and B, respectively.

heterogeneous.[39] Heterogeneous catalysis involving Rh colloids was immediately considered. In an attempt to more directly detect the colloidal species, a catalytic dehydrocoupling experiment involving Me$_2$NH·BH$_3$ and [Rh(1,5-cod)(μ-Cl)]$_2$ in toluene was initiated and an extract was removed from the reaction mixture after 6 h and evaporated to dryness. Analysis of this sample by transmission electron microscopy (TEM) showed the presence of small ($\sim$2 nm) Rh clusters (see Figure 5).

Another method to probe the nature of the catalytic species involves mercury poisoning experiments. Mercury is a well-known poison of heterogeneous catalysts, owing to its adsorption onto the catalyst surface or the formation of an amalgam.[40] Three parallel experiments were performed involving the dehydrocoupling of Me$_2$NH·BH$_3$ (0.5 mol % of catalyst, 25 °C, toluene): (A) a control reaction, (B) partial conversion of Me$_2$NH·BH$_3$ to **1** followed by the addition of 68 equiv of Hg and (C) dehydrocoupling initiated in the presence of 71 equiv of Hg (see Figure 6). Monitoring the extent of reaction by ^{11}B NMR initially indicated the presence of an induction period

(region i in Figure 6), in which no dehydrocoupling occurs. During this induction period, the trials (A) and (B) showed no formation of colloidal metal by visual inspection. However, at points ii and iii (Figure 6), the formation of a black, opaque solution was observed and the dehydrocoupling reaction was found to proceed immediately following this color change. This induction period is apparently a result of the time that is required for the formation of colloidal Rh(0) metal from the Rh(I) precatalyst complex. The dehydrocoupling of trial (A) indicated rapid conversion to **1** from 0 to 38% in 60 min after the induction period, followed by a general decrease in the rate over time. The subsequent reduction in the dehydrocoupling rate most likely results from a decrease in the concentration of Me$_2$NH·BH$_3$ in the reaction mixture. The dehydrocoupling of trial (B) also proceeds very rapidly for the first 60 min after the induction period. However, at $t = 105$ min (point iv in Figure 6), 68 equiv of Hg were added to the reaction mixture. After this point, very little further conversion ($<$5%) to **1** was observed as the added Hg had poisoned the active catalytic species. The dehydrocoupling trial (C) was initiated in the presence of a catalyst poison. Subsequently, no formation of Rh colloids and no conversion to **1** were observed. This verifies that the addition of mercury inhibits the catalytic dehydrocoupling and suggests the operation of a heterogeneous process involving Rh(0) colloids as the true active catalyst.

Summary

The first well-characterized examples of transition metal-catalyzed boron−nitrogen bond formation under mild reaction conditions have been demonstrated. Secondary amine-borane adducts dehydrocouple in the 25−45 °C temperature range in the presence of Rh, Ir, Ru, and Pd precatalysts to give either monomeric or cyclodimeric aminoboranes, whereas the primary adducts or NH$_3$·BH$_3$ afford borazine derivatives. This new, mild synthetic method represents a significant improvement over the previously reported thermal routes to these species, which typically require forcing, high temperature (100−200 °C) conditions to facilitate the dehydrogenation reactions. A drawback of the catalytic method, noted in some cases, is the lowering of product yields due to intermolecular coupling reactions of either intermediate species or the products themselves. The linear dimers **5** and **6** were shown to catalytically dehydrocouple to form cyclic aminoboranes, indicating that backbiting and the formation of a ring represent limitations to extended chain formation. However, the incorporation of either a rigid or a longer spacer unit between boron and nitrogen may allow for polymer formation. Transition metal-catalyzed routes to boron−nitrogen compounds are potentially of significant importance. For example, borazines with hydrogen or organic substituents have been shown to be useful precursors to cyclolinear polymers,[18a,b] boron nitride ceramics,[18b,41] and boron nitride nanotubes.[42] The mechanism of the transition metal-catalyzed dehydrocoupling is of key interest. Our studies of the Rh-catalyzed dehydrocoupling reactions suggest that the active catalyst is colloidal metal.

(39) (a) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693. (b) Weddle, K. S.; Aiken III, J. D.; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653.
(40) For previous examples of Hg poisoning of heterogeneous Rh catalysts, see: (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Young Jr., R. J.; Grushin, V. V. *Organometallics* **1999**, *18*, 294. (c) See ref 39b.

(41) (a) Wideman, T.; Sneddon, L. G. *Chem. Mater.* **1996**, *8*, 3. (b) Toury, B.; Miele, P.; Cornu, D.; Vincent, H.; Bouix, J. *Adv. Funct. Mater.* **2002**, *12*, 228.
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Experimental Section

General Procedures and Materials. All reactions and product manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in an Innovative Technologies or MBraun glovebox filled with dry nitrogen unless otherwise specified. All solvents were dried over the appropriate drying agents such as Na/benzophenone (toluene, hexanes, THF, Et_2O) or Na/K/benzophenone (monoglyme, diglyme, tetraglyme) and distilled prior to use. $BH_3 \cdot SMe_2$, $BH_3 \cdot$ THF (1.0 or 2.0 M in THF), HCl (1.0 or 2.0 M in Et_2O), BuLi (1.6 M in hexanes), $PhCH_2(Me)NH$, $MeNH_2$, NH_3, $HRh(CO)$- $(PPh_3)_3$, Pd/C (10 wt. %), Mercury (Aldrich), $Me_2NH \cdot BH_3$, $RhCl(PPh_3)_3$, *trans*-$PdCl_2(P(o\text{-}tolyl)_3)_2$, $[Rh(1,5\text{-}cod)_2]OTf$ (Strem Chemicals), $RhCl_3$, $RhCl_3 \cdot 3H_2O$, $IrCl_3$ (Pressure Chemical Co.) were purchased and used as received. $Me_2NH \cdot BH_3$ was further purified by sublimation at 25 °C. 1,5-cyclooctadiene, $^iPr_2NH$ (Aldrich), $PhNH_2$ (BDH), and $(1,4\text{-}C_4H_8)NH$ (Acros) were dried over CaH_2 and distilled prior to use. $B(C_6F_5)_3$ (Aldrich) was dried with Me_3SiCl and sublimed prior to use. **5**,[43b] **8**,[36] [Rh-(1,5-cod)(μ-Cl)]$_2$,[44] [Ir(1,5-cod)(μ-Cl)]$_2$,[45] Cp_2TiMe_2,[46] [Cp*Rh-(μ-Cl)Cl]$_2$,[47] *trans*-$RuMe_2(PMe_3)_4$,[48] and [Rh(1,5-cod)(dmpe)]-PF_6[49] were synthesized by literature procedures.

Equipment. NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are reported relative to residual protonated solvent peaks (^{1}H, ^{13}C) or external $BF_3 \cdot Et_2O$ (^{11}B). NMR spectra were obtained at 300 MHz (^{1}H), 96 MHz (^{11}B) or 75 MHz (^{13}C). Mass spectra were obtained with a VG 70–250S mass spectrometer operating in electron impact (EI) mode. Transmission electron micrographs were obtained on a Hitachi model 600 electron microscope after evaporation of the solution onto a carbon film. Melting points were performed in sealed capillary tubes and are uncorrected. Tube furnace experiments were performed using a ThermCraft pyrolysis oven. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

X-ray Structural Characterization. Diffraction data were collected on a Nonius Kappa-CCD using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The data were integrated and scaled using the Denzo-SMN package.[50] The structures were solved and refined with the SHELXTL-PC V5.1 software package.[51] Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Molecular structures are presented with thermal ellipsoids at a 30% probability level and all hydrogen atoms attached to carbon are omitted for clarity. In all structures, hydrogen atoms bonded to carbon were included in calculated positions and treated as riding atoms, whereas those attached to boron or nitrogen were located and refined with isotropic thermal parameters. For the structure **1**, the hydrogen atoms attached to boron were located and included in calculated positions and treated as riding atoms. For

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Table 2. Selected Bond Lengths (Å) and Angles (°) for Structures **1** and **2**

1			
N(1)−B(1)	1.596(4)	B(1)−N(1)−B(1A)	86.3(2)
N(1)−B(1A)	1.595(4)	N(1)−B(1)−N(1A)	93.7(2)
B(1)−N(1A)	1.595(4)	C(1)−N(1)−C(2)	109.0(3)
N(1)−C(1)	1.478(4)	B(1)−N(1)−C(1)	115.4(3)
N(1)−C(2)	1.474(4)	B(1)−N(1)−C(2)	115.6(3)

2			
N(1)−B(1)	1.587(6)	B(1)−N(1)−B(2)	86.7(3)
N(1)−B(2)	1.593(5)	B(1)−N(2)−B(2)	86.6(3)
N(2)−B(1)	1.600(6)	N(1)−B(1)−N(2)	93.1(3)
N(2)−B(2)	1.584(5)	N(1)−B(2)−N(2)	93.5(3)
N(1)−C(1)	1.485(5)	C(1)−N(1)−C(4)	101.8(3)
N(1)−C(4)	1.483(5)	B(1)−N(1)−C(1)	116.7(4)
N(2)−C(5)	1.471(5)	B(2)−N(1)−C(1)	118.3(3)
N(2)−C(8)	1.475(4)		

Table 3. Selected Bond Lengths (Å) and Angles (°) for Structure **6**

N(1)−B(1)	1.595(4)	B(1)−N(2)−B(2)	111.4(2)
N(2)−B(1)	1.576(5)	N(1)−B(1)−N(2)	112.7(3)
N(2)−B(2)	1.598(5)	C(1)−N(1)−C(4)	104.0(2)
N(1)−C(1)	1.501(4)	C(5)−N(2)−C(8)	101.8(2)
N(1)−C(4)	1.494(4)	C(1)−N(1)−B(1)	109.9(3)
N(1)−H(1N)	0.89(3)	C(4)−N(1)−B(1)	118.5(2)
N(2)−C(5)	1.502(4)	C(5)−N(2)−B(1)	106.6(2)
N(2)−C(8)	1.499(4)	C(5)−N(2)−B(2)	110.7(3)
B(2)−H(3B)	1.14(3)	C(8)−N(2)−B(1)	114.9(2)
B(2)−H(4B)	1.14(3)	C(8)−N(2)−B(2)	110.9(3)
H(1N)−H(3B*)	2.13	H(1N)−H(3B*)−B(2*)	96.3
H(1N)−H(4B*)	2.27	H(1N)−H(4B*)−B(2*)	89.7
		N(1)−H(1N)−H(3B*)	141.5
		N(1)−H(1N)−H(4B*)	144.3

Table 4. Selected Bond Lengths (Å) and Angles (°) for Structure **12**

N(1)−B(1)	1.429(2)	B(1)−N(1)−B(3)	121.14(15)
N(1)−B(3)	1.429(3)	B(1)−N(2)−B(2)	121.10(16)
N(2)−B(1)	1.431(3)	B(2)−N(3)−B(3)	120.60(16)
N(2)−B(2)	1.437(2)	N(1)−B(1)−N(2)	118.74(17)
N(3)−B(2)	1.430(3)	N(2)−B(2)−N(3)	119.00(17)
N(3)−B(3)	1.432(3)	N(1)−B(3)−N(3)	119.35(17)
N(1)−C(1)	1.445(2)		
N(2)−C(7)	1.439(2)		
N(3)−C(13)	1.443(2)		

the structure of **2**, four independent molecules were found in the unit cell, one of which is presented in Figure 2. The bond lengths and angles of this particular molecule are presented in Table 2. Crystallographic data and the summary of data collection and refinement for structures **1**, **2**, **6**, and **12** are presented in Table 5. CCDC-160965 (**1**), CCDC-204991 (**2**), CCDC-204992 (**6**), and CCDC-204993 (**12**) are contained in the Supporting Information.

Synthesis of RR′NH·BH₃. General Procedure for Liquid Amines. To a solution of the appropriate amine in THF cooled to −30 °C, a solution of $BH_3 \cdot$THF in THF was added via syringe (or a dropping funnel for larger scale preparations). The reaction mixture was warmed to 25 °C and stirred overnight. The solvent was removed in vacuo to give either white solids or colorless oils. Further purification was achieved via sublimation of the solids or distillation of the liquids.

For $(1,4\text{-}C_4H_8)NH \cdot BH_3$: White solid. Yield: 85%; mp 31– 35 °C; ^{1}H NMR (CDCl₃): δ 4.53 (br, NH), 3.23 (m, NCH₂), 2.65 (m, NCH₂), 1.89 (m, CH₂), 1.80 (m, CH₂), 1.8–0.9 (q, br,

Table 5. Crystallographic Data and Summary of Data Collection and Refinement for Structures **1**, **2**, **6**, and **12**

	1	2	6	12
emp. formula	$C_4H_{16}B_2N_2$	$C_8H_{20}B_2N_2$	$C_8H_{22}B_2N_2$	$C_{18}H_{18}B_3N_3$
formula wgt.	113.81	165.88	167.90	308.78
T (K)	103(1)	150(1)	150(1)	150(1)
λ (Å)	0.71070	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	orthorhombic	orthorhombic
space group	P$\bar{1}$	Pc	Pbca	Pna2$_1$
crystal size (mm)	0.30 × 0.30 × 0.25	0.15 × 0.12 × 0.10	0.40 × 0.36 × 0.06	0.32 × 0.30 × 0.16
a (Å)	5.8330(7)	12.5679(6)	9.1701(9)	7.7831(16)
b (Å)	6.0290(10)	13.5569(7)	11.9879(5)	19.919(4)
c (Å)	6.2400(10)	12.6790(6)	20.1229(17)	10.965(2)
α (°)	80.372(8)	90	90	90
β (°)	81.533(10)	100.634(3)	90	90
γ (°)	65.942(8)	90	90	90
V (Å^3)	196.80(5)	2123.17(18)	2212.1(3)	1699.9(6)
Z	1	8	8	4
D_C (g/cm^3)	0.960	1.038	1.008	1.207
μ (mm^{-1})	0.055	0.059	0.057	0.070
F(000)	64	736	752	648
θ range (°)	3.32−27.51	2.58−25.06	2.97−22.50	2.81−25.07
index ranges	$0 \leq h \leq 7$	$0 \leq h \leq 14$	$0 \leq h \leq 9$	$0 \leq h \leq 9$
	$-6 \leq k \leq 7$	$0 \leq k \leq 16$	$0 \leq k \leq 12$	$-23 \leq k \leq 0$
	$-7 \leq l \leq 8$	$-15 \leq l \leq 14$	$0 \leq l \leq 21$	$0 \leq l \leq 13$
reflns collected	3782	20933	10559	8712
ind. reflns.	895	3737	1436	1572
R_{int}	0.069	0.034	0.157	0.032
GoF on F^2	1.162	1.027	1.098	1.069
$R1^a$ ($I > 2\sigma(I)$)	0.0963	0.0507	0.0647	0.0292
$wR2^b$ (all data)	0.3002	0.1363	0.1776	0.0719
peak/hole (eÅ^3)	0.499/−0.261	0.173/−0.140	0.216/−0.232	0.118/−0.111

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

BH$_3$); ^{11}B NMR (CDCl$_3$): δ −17.0 (q, J_{BH} = 94 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 54.1 (NCH$_2$), 24.5 (CH$_2$).

For ^{i}Pr$_2$NH·BH$_3$: Colorless oil. Yield: 90%; bp 50 °C (0.01 mmHg); ^{1}H NMR (CDCl$_3$): δ 3.23 (m, CH), 2.93 (br, NH), 1.31 (d, J_{HH} = 3 Hz, CH$_3$), 1.29 (d, J_{HH} = 3 Hz, CH$_3$), 2.0−1.0 (q, br, BH$_3$); ^{11}B NMR (CDCl$_3$): δ −21.1 (q, J_{BH} = 97 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 52.3 (CH), 21.3 (CH$_3$), 19.2 (CH$_3$).

For PhNH$_2$·BH$_3$: White solid. Yield: 91%; ^{1}H NMR (CDCl$_3$): δ 7.4−7.0 (m, Ph), 5.38 (br, NH), 2.5−1.5 (q, br, BH$_3$); ^{11}B NMR (CDCl$_3$): δ −15.5 (q, J_{BH} = 97 Hz).

For PhCH$_2$(Me)NH·BH$_3$: White solid. Yield: 67%; mp 75.5−77.5 °C; ^{1}H NMR (CDCl$_3$): δ 7.41 (m, Ph), 7.28 (m, Ph), 4.39 (br, NH), 4.28 (dd, $^4J_{HH}$ = 3 Hz, $^2J_{HH}$ = 13.8 Hz, CH$_a$H$_b$), 3.50 (dd, $^4J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 13.8 Hz, CH$_a$H$_b$), 2.42 (d, $^3J_{HH}$ = 6 Hz, CH$_3$), 2.2−1.2 (q, br, BH$_3$); ^{11}B NMR (CDCl$_3$): δ −14.0 (q, J_{BH} = 97 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 134.2 (*ipso*-C), 129.6 (Ar), 129.1 (Ar), 128.9 (Ar), 60.9 (CH$_2$), 40.2 (CH$_3$).

General Procedure for Gaseous Amines. For MeNH$_2$·BH$_3$, the anhydrous amine was bubbled through a solution of BH$_3$·THF in THF at −78 °C for 10−20 min, depending on the scale. For NH$_3$·BH$_3$, the amine was bubbled through a solution of BH$_3$·SMe$_2$ in Et$_2$O at −20 °C for 10−20 min, depending on the scale. The solution was then warmed to 25 °C and stirred overnight. The solvent was removed in vacuo to give white solids, which were purified by sublimation.

For MeNH$_2$·BH$_3$: Yield: 89%; mp 55−57 °C; ^{1}H NMR (CDCl$_3$): δ 3.80 (br, NH), 2.54 (t, J_{HH} = 6 Hz, CH$_3$), 2.0−1.0 (q, br, BH$_3$); ^{11}B NMR (CDCl$_3$): δ −18.8 (q, J_{BH} = 94 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 34.8.

For NH$_3$·BH$_3$: Yield: 86%; mp 111−114 °C; ^{1}H NMR

(CDCl$_3$): δ 3.37 (t, br, NH$_3$), 1.60 (q, br, BH$_3$); ^{11}B NMR (CDCl$_3$): δ −21.6 (q, J_{BH} = 95 Hz).

Tube Furnace Reactions involving Me$_2$NH·BH$_3$: Me$_2$NH·BH$_3$ (2.934 g, 49.78 mmol) was placed in a round-bottom flask, which was attached to a horizontal quartz tube (4 cm diameter, 91 cm length) filled with pieces of broken quartz. The other end of the tube was connected to a specially designed receiving flask, which was connected to a high vacuum pump. The tube was placed inside a tube furnace reactor and heated to 150 °C while applying a dynamic vacuum (0.035 mmHg). Gentle heating (~50 °C) was used to volatilize the Me$_2$NH·BH$_3$ over ca. 2−3 h, and the thermolysis products were trapped at −196 °C. A colorless oil and a white solid were obtained, but were shown to be unreacted Me$_2$NH·BH$_3$ by ^{1}H and ^{11}B NMR. Higher thermolysis temperatures of 250 °C, 350 °C and 450 °C were also used. Unreacted Me$_2$NH·BH$_3$ was obtained at 250 °C, whereas temperatures of 350 °C and 450 °C also resulted in unreacted Me$_2$NH·BH$_3$ with a very minor amount (<5%) of **1**.

Synthesis of [Me$_2$N−BH$_2$]$_2$ (1). (a) Me$_2$NH·BH$_3$ (3.836 g, 65.08 mmol) and a catalytic amount of [Rh(1,5-cod)(μ-Cl)]$_2$ (0.125 g, 0.254 mmol, 0.4 mol %) were combined and heated to 45 °C to form a melt. The mixture turned black almost immediately and vigorous gas evolution was observed. The mixture was stirred for 24 h, during which time colorless crystals of **1** sublimed to the top of the flask. X-ray quality crystals of **1** were obtained by sublimation at 25 °C under N$_2$ onto a 0 °C coldfinger. Yield: 2.847 g, 77%; mp 74−76 °C; ^{1}H NMR (CDCl$_3$): δ 3.2−2.0 (q, br, BH$_2$), 2.42 (s, CH$_3$); ^{11}B NMR (CDCl$_3$): δ 4.75 (t, J_{BH} = 110 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 52.0; EI-MS (70 eV): 114 (M$^+$, 4%), 57 (M$^+$/2, 100%). (b) Blank reaction: Heating of neat Me$_2$NH·BH$_3$ at 45 °C in the

absence of catalyst resulted in no dehydrocoupling products after 168 h by ^{11}B NMR.

Reuse of Initial Active Catalyst for the Formation of 1. Me$_2$NH·BH$_3$ (0.203 g, 3.44 mmol) and a catalytic amount of [Rh(1,5-cod)(μ-Cl)]$_2$ (0.012 g, 0.024 mmol, 0.7 mol %, 1.4 mol % Rh) were combined and heated to 45 °C. After 2 h, sublimed crystals of **1** were obtained (0.110 g, 56%). A second amount of Me$_2$NH·BH$_3$ (0.325 g) was added to the residual catalyst. The dehydrocoupling reaction was performed under identical conditions as the original trial to give **1** (0.242 g, 77%) after 10.5 h. Three more repeat trials were performed with Me$_2$NH·BH$_3$ (0.268, 0.287 and 0.385 g) using the original catalyst, yielding **1** (0.235 g (91%), 0.185 g (67%) and 0.261 g (70%)) after 17, 17.5, and 43 h, respectively.

Synthesis of [(1,4-C$_4$H$_8$)N−BH$_2$]$_2$ (2). (a) To a solution of (1,4-C$_4$H$_8$)NH·BH$_3$ (1.714 g, 20.17 mmol) in toluene (5 mL), a catalytic amount of [Rh(1,5-cod)(μ-Cl)]$_2$ (0.050 g, 0.10 mmol, 0.5 mol %) was added. The solution darkened immediately and vigorous gas evolution was observed. The solution was stirred at 25 °C for 24 h, then filtered through charcoal under air to yield a colorless solution. The solvent was removed in vacuo to afford **2** as a white powder. Purification via sublimation under static vacuum at 25 °C gave colorless crystals of X-ray quality. Yield: 1.220 g, 73%; mp 30−32 °C; ^{1}H NMR (CDCl$_3$): δ 3.2−2.0 (q, br, BH$_2$), 2.84 (t, br, NCH$_2$), 1.70 (m, CH$_2$); ^{11}B NMR (CDCl$_3$): δ 2.56 (t, J_{BH} = 110 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 60.1 (NCH$_2$), 23.7 (CH$_2$); EI−MS (70 eV): 165 (M$^+$−H, 12%), 82 ((M$^+$/2) − H, 100%); elemental analysis calcd (%) for C$_4$H$_{10}$BN (82.94): C 57.93, H 12.15, N 16.89; found: C 58.18, H 12.19, N 17.29. (b) Blank reaction: Neat (1,4-C$_4$H$_8$)-NH·BH$_3$ was stirred at 45 °C in the absence of catalyst. After 24 h, the formation of dehydrocoupling products was not observed by ^{11}B NMR.

Synthesis of [PhCH$_2$(Me)N−BH$_2$]$_2$ (3). (a) To a solution of PhCH$_2$(Me)NH·BH$_3$ (0.597 g, 4.42 mmol) in toluene (10 mL), a catalytic amount of [Rh(1,5-cod)(μ-Cl)]$_2$ (0.026 g, 0.05 mmol, 1.2 mol %) was added. The mixture was stirred at 45 °C for 18 h. The solution was filtered through charcoal under air to give a colorless solution, and the solvent was removed in vacuo to yield **3** as a white powder. Colorless crystals of **3** were obtained from slow evaporation of a CH$_2$Cl$_2$/hexanes (2:1) solution at 25 °C. Yield: 0.465 g, 79%; mp 98−101 °C; ^{1}H NMR (1:1 cis/trans isomers, CDCl$_3$): δ 7.39 (m, Ph), 7.33 (m, Ph), 3.96 (s, CH$_2$), 2.42 (s, CH$_3$), 2.41 (s, CH$_3$); ^{11}B NMR (CDCl$_3$): δ 4.21 (s, br); ^{13}C{^{1}H} NMR (1:1 cis/trans isomers, CDCl$_3$): δ 136.7 (*ipso*-C), 136.5 (*ipso*-C), 130.0 (Ar), 129.7 (Ar), 128.5 (Ar), 128.4 (Ar), 127.9 (Ar), 127.8 (Ar), 66.9 (NCH$_2$), 66.4 (NCH$_2$), 48.6 (CH$_3$), 47.9 (CH$_3$); EI−MS (70 eV): 266 (M$^+$, 2%), 133 (M$^+$/2, 100%); elemental analysis calcd (%) for C$_8$H$_{12}$BN (133.00): C 72.25, H 9.09, N, 10.53; found: C 71.39, H 8.70, N 10.52. (b) Blank reaction: A solution of PhCH$_2$(Me)NH·BH$_3$ in toluene was stirred at 45 °C for 20 h. No dehydrocoupling products were observed in the ^{11}B NMR spectrum.

Synthesis of ^{i}Pr$_2$N=BH$_2$ (4). (a) ^{i}Pr$_2$NH·BH$_3$ (2.171 g, 18.87 mmol) and a catalytic amount of [Rh(1,5-cod)(μ-Cl)]$_2$ (0.091 g, 0.19 mmol, 1.0 mol %) were combined. The neat mixture was frozen at −196 °C, and the flask was evacuated. The mixture was stirred vigorously at 25 °C and periodically degassed every 12−24 h to remove any hydrogen gas that had

formed. After 4 d, a mixture of **4** (92%) and unreacted ^{i}Pr$_2$-NH·BH$_3$ (8%) were observed in the ^{11}B NMR spectrum. Partial pressure (15−20 mmHg) distillation of the reaction mixture at 25 °C gave **4** as a colorless liquid. Yield: 1.038 g, 49%; bp 38−39 °C (60 mmHg); ^{1}H NMR (CDCl$_3$): δ 4.32 (br q, J_{BH} = 125 Hz, BH$_2$), 3.39 (septet, J_{HH} = 6.6 Hz, CH), 1.17 (d, J_{HH} = 6.6 Hz, CH$_3$); ^{11}B NMR (CDCl$_3$): δ 34.7 (t, J_{BH} = 126 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 52.5 (CH), 25.3 (CH$_3$); EI-MS (70 eV): 114 (M$^+$ + H, 14%); HR-MS (EI): calcd for C$_6$H$_{15}$^{11}BN (M$^+$ − H) 112.129755; found 112.129756. (b) Blank reaction: Stirring of neat ^{i}Pr$_2$NH·BH$_3$ under static vacuum in the absence of catalyst resulted in no dehydrocoupling products after 18 d at 25 °C.

Synthesis of (1,4-C$_4$H$_8$)NH−BH$_2$−N(1,4-C$_4$H$_8$)−BH$_3$ (6). (1,4-C$_4$H$_8$)NH·BH$_2$Cl was prepared from the reaction of (1,4-C$_4$H$_8$)NH·BH$_3$ (1.119 g, 13.17 mmol) in Et$_2$O (15 mL) and HCl in Et$_2$O (6.8 mL, 13.6 mmol) at 0 °C. To a solution of (1,4-C$_4$H$_8$)NH·BH$_3$ (1.122 g, 13.20 mmol) in Et$_2$O (15 mL) cooled to 0 °C, a solution of BuLi in hexanes (8.4 mL, 13 mmol) was added dropwise. The mixture was stirred for 30 min, then warmed to 25 °C for 1 h. The solution was recooled to −78 °C, and the solution of (1,4-C$_4$H$_8$)NH·BH$_2$Cl was added dropwise. The mixture was warmed to 25 °C slowly and stirred overnight. The solution was filtered to remove LiCl and the solvent removed in vacuo. The resulting oil was dissolved in monoglyme and cooled to −55 °C, which afforded colorless crystals of **6**. X-ray quality crystals were obtained by sublimation at 45 °C. Yield: 0.498 g, 23%; mp 66.5−68.5 °C. ^{1}H NMR (CDCl$_3$): δ 5.66 (s, br, NH), 3.19 (m, NCH$_2$), 2.94 (m, NCH$_2$), 2.77 (m, NCH$_2$), 2.22 (m, CH$_2$), 1.68 (m, CH$_2$), 1.06 (m, CH$_2$); ^{11}B NMR (CDCl$_3$): δ 0.5 (t, J_{BH} = 112 Hz, BH$_2$), −16.0 (q, J_{BH} = 100 Hz, BH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 60.5 (NCH$_2$), 52.1 (NCH$_2$), 24.4 (CH$_2$), 23.6 (CH$_2$); EI-MS (70 eV): 167 (M$^+$, 2%), 153 (M$^+$ − BH$_3$, 18%); elemental analysis calcd (%) for C$_4$H$_{11}$BN (83.95): C 57.23, H 13.21, N 16.68; found: C 57.27, H 13.05, N 16.54.

Synthesis of Me$_2$NH−BH$_2$−NMe$_2$−BH$_3$ (5). Compound **5** was prepared with a method similar to **6**, substituting Me$_2$NH·BH$_3$ as the amine-borane. Yield: 34%. The product was identified from its literature ^{1}H, ^{11}B and ^{13}C NMR shifts.[29]

Catalytic Dehydrocoupling of 5. (a) To a solution of **5** in toluene (2 mL), [Rh(1,5-cod)(μ-Cl)]$_2$ (1.5 mol %) was added and the mixture was stirred for 48 h at 25 °C. Conversion of **5** to the cyclic dimer **1** was 100% as indicated by ^{11}B NMR. (b) Blank reaction: A solution of **5** in CDCl$_3$ was stirred at 25 °C for 8 d. No dehydrocoupling products were observed in the ^{11}B NMR spectrum.

Catalytic Dehydrocoupling of 6. (a) To a solution of **6** in toluene (2 mL), [Rh(1,5-cod)(μ-Cl)]$_2$ (1.6 mol %) was added and the mixture was stirred for 24 h at 45 °C. Conversion of **6** to the cyclic dimer **2** was 100% as indicated by ^{11}B NMR. (b) Blank reaction: A solution of **6** in CDCl$_3$ was stirred at 45 °C for 2 d. No dehydrocoupling products were observed in the ^{11}B NMR spectrum.

Synthesis of [HB−NH]$_3$ (10). (a) To a solution of NH$_3$·BH$_3$ (7.36 g, 238 mmol) in tetraglyme (20 mL), a catalytic amount of [Rh(1,5-cod)(μ-Cl)]$_2$ (0.75 g, 1.5 mmol, 0.6 mol %, 1.2 mol % Rh) was added and the solution heated to 45 °C. Almost immediately, the solution turned black and vigorous gas evolution was observed. After 48 h, the ^{11}B NMR spectrum

confirmed that the reaction had reached 100% conversion of $NH_3 \cdot BH_3$. The reaction flask was connected to a series of three U-tubes that were cooled to -196 °C, and the system was placed under a dynamic vacuum to isolate **10** (in the first trap) as a colorless liquid.[35] Pure **10** was obtained by a second vacuum fractionation through a series of U-tubes held at -45, -78, and -196 °C, with retention of **10** in the -78 °C trap. Yield: 0.57 g, 10%; ^{1}H NMR (C_6D_6): δ 5.54 (t, br, NH), 4.45 (q, br, BH); ^{11}B NMR (C_6D_6): δ 30.2 (d, $J_{BH} = 141$ Hz). (b) Blank reaction: A solution of $NH_3 \cdot BH_3$ in diglyme was stirred at 45 °C in the absence of catalyst. After 3 d, the ^{11}B NMR spectrum indicated the presence of unreacted $NH_3 \cdot BH_3$ and the initial formation of a small amount (ca. 5%) of **7**. After 6 d, the predominant product was still unreacted $NH_3 \cdot BH_3$ but now the formation of a small amount (ca. 5%) of **10** was also observed.

Synthesis of [HB−NMe]₃ (11). (a) To a solution of $MeNH_2 \cdot BH_3$ (1.967 g, 43.80 mmol) in monoglyme (5 mL), a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (0.217 g, 0.440 mmol, 1.0 mol %) was added and heated at 45 °C for 72 h. The contents of the flask were removed under vacuum and collected into a series of U-tubes held at -45 °C and -196 °C, with **11** being retained in the -45 °C trap.[35] Pure **11** was obtained by a second vacuum fractionation through -45 °C and -196 °C traps. Yield: 0.716 g, 40%; ^{1}H NMR (C_6D_6): δ 4.65 (q, br, BH), 2.96 (s, CH_3); ^{11}B NMR (C_6D_6): δ 33.2 (d, $J_{BH} = 132$ Hz); ^{13}C{^{1}H} NMR (C_6D_6): δ 38.5 (CH_3); EI−MS (70 eV): 122 ($M^+ - H$, 100%). (b) Blank reaction: A solution of $MeNH_2 \cdot BH_3$ in monoglyme was stirred at 45 °C in the absence of catalyst. No dehydrocoupling products were observed after 3 d by ^{11}B NMR.

Catalytic Dehydrocoupling of [MeNH−BH₂]₃ (8). To a solution of **8** (0.102 g, 0.793 mmol) in monoglyme (5 mL), a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (0.004 g, 0.008 mmol, 1.0 mol %) was added. The solution was heated at 45 °C and monitored periodically by ^{11}B NMR. Formation of borazine **11** was observed to reach 95% completion after 40 h. Isolation of **11** from the reaction mixture was not performed.

Synthesis of [HB−NPh]₃ (12). (a) To a solution of $PhNH_2 \cdot BH_3$ (1.190 g, 11.12 mmol) in monoglyme (5 mL), a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (0.045 g, 0.091 mmol, 0.8 mol %) was added. A color change to black was observed, along with vigorous gas evolution. After stirring for 16 h at 25 °C, the volatiles were removed and the black residue was sublimed at 100 °C to give a white powder. X-ray quality crystals of **12** were obtained after 1 month upon cooling a solution in monoglyme to -30 °C. Yield: 0.642 g, 56%; mp 96−100 °C; ^{1}H NMR ($CDCl_3$): δ 7.41 (m, Ph), 7.29 (m, Ph), 5.10 (br, BH); ^{11}B{^{1}H} NMR ($CDCl_3$): δ 32.8 (br); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.2 (*ipso*-C), 129.1 (Ar), 125.5 (Ar), 124.9 (Ar); EI-MS (70 eV): 309 (M^+, 38%), 91 (NPh, 100%). (b) Blank reaction: A solution of $PhNH_2 \cdot BH_3$ in monoglyme was stirred at 25 °C in the absence of catalyst. After 16 h, no dehydrocoupling products were detected by ^{11}B NMR.

Catalyst Poisoning Experiments involving Hg. For all three experiments, $Me_2NH \cdot BH_3$ ($\sim$0.50 g, $\sim$8.5 mmol) in toluene (3 mL) and a catalytic amount of $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ (ca. 0.5 mol %) were vigorously stirred at 25 °C. At set times (15−30 min), a small amount of solution was removed from the reaction mixture and the ^{11}B NMR spectra were obtained in CH_2Cl_2. The percent conversion of $Me_2NH \cdot BH_3$ to **1** was based upon the integration of product and reactant signals in the ^{11}B NMR spectrum. For trial (B), Hg (0.551 g, 68 equiv) was added after 35% conversion (105 min). For trial (C), Hg (0.579 g, 71 equiv) was added prior to catalyst addition.

Supporting Information Available: CCDC-160965 (**1**), CCDC-204991 (**2**), CCDC-204992 (**6**), and CCDC-204993 (**12**) crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

JA030160L