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Heterogeneous or Homogeneous Catalysis? Mechanistic Studies of the Rhodium-Catalyzed Dehydrocoupling of Amine-Borane and Phosphine-Borane Adducts

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Abstract: In depth, comparative studies on the catalytic dehydrocoupling of the amine-borane adduct $Me_2NH \cdot BH_3$ (to form $[Me_2N-BH_2]_2$) and the phosphine-borane adduct $Ph_2PH \cdot BH_3$ (to form $Ph_2PH-BH_2-PPh_2-BH_3$) with a variety of Rh (pre)catalysts such as $[\{Rh(1,5\text{-}cod)(\mu\text{-}Cl)\}_2]$, Rh/Al_2O_3, $Rh_{colloid}/[Oct_4N]Cl$, and $[Rh(1,5\text{-}cod)_2]OTf$ have been performed in order to determine whether the dehydrocoupling proceeds by a homogeneous or heterogeneous mechanism. The results obtained suggest that the catalytic dehydrocoupling of $Me_2NH \cdot BH_3$ is heterogeneous in nature involving Rh(0) colloids, while that of $Ph_2PH \cdot BH_3$ proceeds by a homogeneous mechanism even when starting with Rh(0) precursors such as Rh/Al_2O_3. The catalytic dehydrocoupling reactions are thought to proceed by different mechanisms due to a combination of factors such as (i) the greater reducing strength of amine-borane adducts, (ii) the increased ease of dissociation of phosphine-borane adducts, and (iii) phosphine ligation and/or poisoning of active catalytic sites on metal colloids.

Introduction

Transition metal catalysis plays a profound role in organic synthesis. Drug, natural product, and polymer syntheses all utilize metal-catalyzed reactions to provide alternative or improved routes to the desired end products. Thus, the formation of new C−C, C−N, C−O, and C−H bonds can be facilitated by a ready arsenal of metal-catalyzed routes, allowing for precise control over factors such as chemo-, regio-, and stereoselectivity while being performed under mild reaction conditions with increased efficiency, minimal waste generation, and decreased energy consumption. In contrast, the use of transition metal-catalyzed processes for the preparation of inorganic molecules and polymers is relatively unexplored. The development of facile catalytic processes for the synthesis of inorganic compounds would be highly desirable, as currently available synthetic strategies are often haphazard, of limited scope, or are restricted to salt metathesis reactions. In particular, detailed mechanistic studies of the catalytic cycles would allow for the development of generalized reactions, which should help to advance this promising field.[1]

Recently, we have shown that the heterodehydrocoupling of phosphine-borane adducts RR′PH·BH₃ can be catalyzed by a variety of Rh complexes, providing facile routes to phosphino-borane rings, chains, and high molecular weight polymers $[RR'P-BH_2]_n$.[2,3] We have recently extended this work to the catalytic dehydrocoupling of amine-borane adducts RR′NH·BH₃, which provides a mild and convenient route to cycloamino-

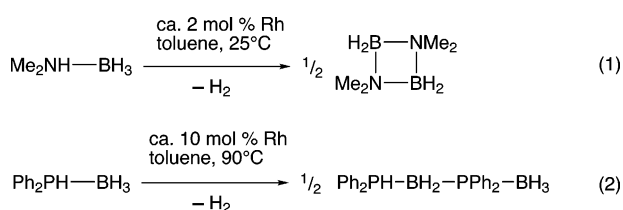boranes $[RR'N-BH_2]_2$ and borazines $[RN-BH]_3$.[4] Based on the catalytic chemistry displayed by amine-borane adducts, a tandem catalytic dehydrocoupling−hydrogenation reaction involving a variety of Rh (pre)catalysts and Me₂NH·BH₃ as a stoichiometric hydrogen source for the hydrogenation of alkenes at 25 °C has been recently developed.[5] Interestingly, the catalytic dehydrocoupling of phosphine-borane and amine-borane adducts using the common precatalyst $[\{Rh(1,5\text{-}cod)(\mu\text{-}Cl)\}_2]$ (cod = cyclooctadiene) were observed to afford dramatically different reaction mixtures: a clear, dark red solution for the former but a black, opaque solution with a precipitate for the latter. These initial visual observations led us to investigate the possibility that different mechanisms (homogeneous or heterogeneous) may be operating for the two different systems.[6]

Distinguishing between true homogeneous catalysis and soluble or insoluble metal-particle heterogeneous catalysis is a problem that has attracted much recent attention.[7] For example, many catalytic processes such as hydrosilation,[8] alkene or arene

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hydrogenation,[9] ring-opening polymerization,[10] and cross-coupling reactions[11] have been studied in detail with respect to the presence of a homogeneous or heterogeneous mechanism. Since catalytic issues such as selectivity, activity, stability, and recovery are influenced differently for homogeneous and heterogeneous catalysts, the problem of distinguishing between the two is of key significance. In an important contribution, Finke and co-workers have developed a general approach to address this problem by performing a series of tests involving reaction kinetics, transmission electron microscopy (TEM) imaging, UV−visible spectroscopy, poisoning experiments, filtration experiments, catalyst isolation, etc.[7b] In this paper, we report full details of our studies in which we have utilized this approach to address the question of the potential presence of homogeneous or heterogeneous catalysis for the dehydrocoupling of the adducts $Me_2NH \cdot BH_3$ (eq 1) and $Ph_2PH \cdot BH_3$ (eq 2) using a series of different Rh (pre)catalysts such as $[\{Rh(1,5\text{-}cod)(\mu\text{-}Cl)\}_2]$, Rh/Al_2O_3, $[Oct_4N]Cl$ stabilized Rh colloids (hereafter referred to as $Rh_{colloid}/[Oct_4N]Cl$; Oct = n-octyl), and $[Rh(1,5\text{-}cod)_2]OTf$.[6]

$$Me_2NH—BH_3 \xrightarrow[{-H_2}]{\substack{\text{ca. 2 mol \% Rh} \\ \text{toluene, 25°C}}} \frac{1}{2} \begin{array}{c} H_2B—NMe_2 \\ | \quad\quad | \\ Me_2N—BH_2 \end{array} \quad (1)$$

$$Ph_2PH—BH_3 \xrightarrow[{-H_2}]{\substack{\text{ca. 10 mol \% Rh} \\ \text{toluene, 90°C}}} \frac{1}{2} \ Ph_2PH–BH_2—PPh_2–BH_3 \quad (2)$$

Results and Discussion

"Homogeneous vs Heterogeneous" Tests Performed: For the comparative studies between $Me_2NH \cdot BH_3$ and $Ph_2PH \cdot BH_3$, the following series of tests were performed:

(i) Analysis by TEM. This is commonly used as a preliminary test for the presence of metal particles in catalytically active solutions.[7b] However, this test suffers from the drawback that if metal particles are observed, they might not be the actual species responsible for the catalysis.[8c]

(ii) Analysis by UV−visible spectroscopy. The presence of metal colloids in solution can be deduced using UV−visible spectroscopy. For example, 10 nm Rh colloids exhibit a continuous absorption in the visible range due to a surface plasmon resonance, with a steep rise in absorbance at short wavelengths.[12]

(iii) Analysis of the reaction kinetics. The presence of a sigmoidal-shaped kinetic curve strongly suggests a heterogeneous catalyst. It has been shown that slow, continuous nucleation followed by rapid autocatalytic surface growth can result in soluble monodisperse nanoclusters[13] or insoluble bulk metal formation.[9b] It is suggested that the presence of such a

kinetic curve is a "compelling single piece of evidence" for the formation of a heterogeneous catalyst.[7b,14]

(iv) Mercury poisoning experiments. Mercury is a well-known poison of heterogeneous catalysts through the formation of an amalgam or adsorption onto the catalyst surface.[15] If the addition of Hg is found to suppress catalytic activity, a heterogeneous catalyst can be assumed, given that proper control experiments were performed.

(v) Fractional poisoning experiments. The addition of strongly coordinating ligands (such as PPh_3) can help distinguish between homogeneous and heterogeneous catalysis.[7b] A heterogeneous catalyst can be completely poisoned by <1 equiv of ligand (per metal atom) because only a fraction of the metal atoms are on the surface, whereas a homogeneous catalyst would require >1 equiv of ligand to completely poison the active site.

(vi) Filtration experiments. Filtration of the reaction mixture using small pore membrane filters can distinguish between soluble and insoluble catalysts.[7b] If the activity is lowered upon filtration, an insoluble catalyst is assumed.

Analysis of Catalytically Active Solutions by TEM: For the catalytic dehydrocoupling of $Me_2NH \cdot BH_3$ and $Ph_2PH \cdot BH_3$ using the precatalyst $[\{Rh(1,5\text{-}cod)(\mu\text{-}Cl)\}_2]$, initial TEM images were obtained in order to test for the presence of metal particles. For $Me_2NH \cdot BH_3$, analysis of the catalytically active solution by TEM (using an accelerating voltage of $V_{acc.} = 75$ kV) revealed the presence of ca. 2 nm Rh particles (Figure 1a). For a $Ph_2PH \cdot BH_3$ reaction solution, the presence of small Rh particles was also observed (Figure 1b). However, a solution of the *precatalyst only* was also found to contain small Rh particles by TEM (Figure 1c). These results suggest that the precatalyst underwent decomposition under the high energy TEM electron beam to form metal particles. Electron beam induced degradation effects such as this are relatively rare but have been previously described in the literature. For example, Schmid has reported that the characterization of gold clusters by high-resolution TEM was hampered by the continual growth of larger clusters as the electron beam damaged the protective ligand shell.[16] More recently, high-resolution TEM investigations of copper(I) bisphenanthroline nanoscaffolds have led to the formation of crystalline copper nanoparticles as a result of radiation damage to the supramolecular precursor.[17] *Fortunately, this electron-beam-induced degradation was prevented when the samples were analyzed by a lower energy electron beam which used an accelerating voltage of $V_{acc} = 30$ kV.* For catalytically active $Me_2NH \cdot BH_3$ solutions, extensive aggregation was observed with the presence of large particles (Figure 1d). Significantly, the analogous case of $Ph_2PH \cdot BH_3$ (Figure 1e) and the precatalyst $[\{Rh(1,5\text{-}cod)(\mu\text{-}Cl)\}_2]$ alone showed only the presence of an amorphous film with no indication of any Rh particles. These results suggest that the catalytic dehydrocoupling of $Me_2NH \cdot BH_3$ is heterogeneous involving Rh metal while that of $Ph_2PH \cdot BH_3$ is homogeneous.

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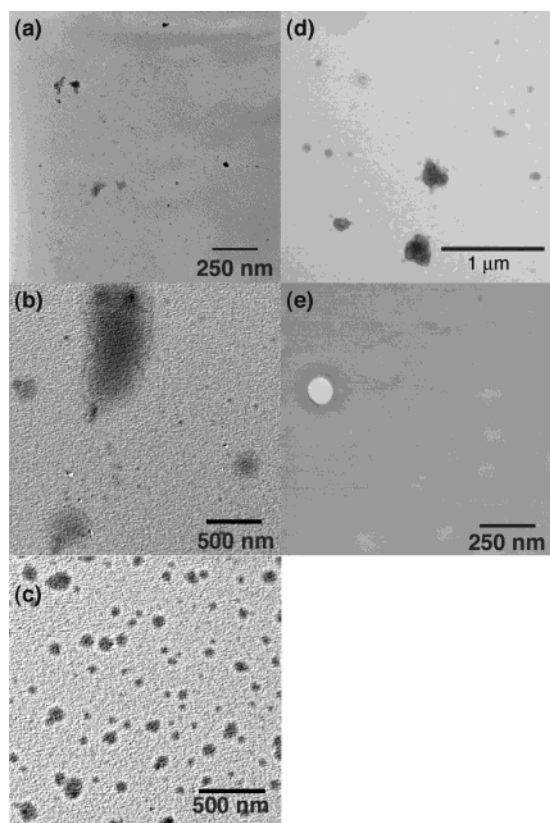
Figure 1. TEM micrographs obtained using V_{acc} of 75 kV: (a) Me$_2$NH·BH$_3$ + [{Rh(1,5-cod)(μ-Cl)}$_2$] reaction mixture; (b) Ph$_2$PH·BH$_3$ + [{Rh(1,5-cod)(μ-Cl)}$_2$] reaction mixture; (c) the precatalyst [{Rh(1,5-cod)(μ-Cl)}$_2$] only. TEM micrographs obtained using V_{acc} of 30 kV: (d) Me$_2$NH·BH$_3$ + [{Rh(1,5-cod)(μ-Cl)}$_2$] reaction mixture; (e) Ph$_2$PH·BH$_3$ + [{Rh(1,5-cod)-(μ-Cl)}$_2$] reaction mixture. The white spot in micrograph (e) is a hole in the TEM grid.

Clearly, the use of TEM analysis to provide evidence for the presence of metal particles should be performed with extreme care and with the knowledge that the electron beam may be of sufficient energy to induce degradation of the sample. In particular, when TEM images are used to identify potential active species in catalytic applications, it is highly suggested that control experiments with the precatalyst are performed in order to eliminate the possibility of beam degradation effects that may induce metal nanoparticle formation.

Analysis of Catalytically Active Solutions by UV−vis Spectroscopy: For the dehydrocoupling of both Me$_2$NH·BH$_3$ and Ph$_2$PH·BH$_3$ with the precatalyst [{Rh(1,5-cod)(μ-Cl)}$_2$], the UV−vis spectra of catalytically active solutions were obtained. For Me$_2$NH·BH$_3$, a broad plasmon absorption characteristic of Rh colloids was observed (Figure S1, Supporting Information).[12] This spectrum was compared against the UV−vis spectrum of the well-defined colloids Rh$_{colloid}$/[Oct$_4$N]Cl, which gave a similar broad absorption. However, the spectrum of Ph$_2$PH·BH$_3$ showed only a large absorption at short wavelengths. The spectrum of the precatalyst [{Rh(1,5-cod)(μ-Cl)}$_2$] also showed a large absorption at short wavelengths with a λ_{max} at 351 nm, which has been previously assigned as metal-to-ligand charge transfer.[18] From these spectra, we can conclude that catalytically active Me$_2$NH·BH$_3$ solutions appear to contain Rh colloids, while those of Ph$_2$PH·BH$_3$ do not.

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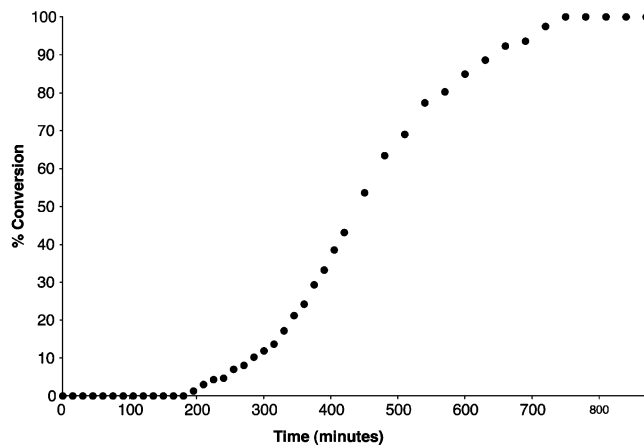
Figure 2. Graph of % conversion vs time for the catalytic dehydrocoupling of Me$_2$NH·BH$_3$ using [{Rh(1,5-cod)(μ-Cl)}$_2$] (ca. 2 mol % Rh, toluene, 25 °C).

Kinetic Curves and Poisoning Experiments for the Catalytic Dehydrocoupling of Me$_2$NH·BH$_3$ with the Precatalyst [{Rh(1,5-cod)(μ-Cl)}$_2$]: The treatment of Me$_2$NH·BH$_3$ with a catalytic amount of [{Rh(1,5-cod)(μ-Cl)}$_2$] (ca. 2 mol % Rh) was found to result in a gradual color change from orange to black over about 2 h. With increasing time, the slow formation of a black precipitate and the presence of a "Rh mirror" on the sides of the flask were observed. By monitoring of the dehydrocoupling reaction using ^{11}B NMR, a variable length (45−200 min) induction period was consistently observed.[19] Following this induction period, a dramatic surge of catalytic activity was observed resulting in a sigmoidal-shaped kinetic curve (Figure 2). This sigmoidal kinetic curve has been shown to be characteristic for the metal-particle formation reactions A → B (nucleation) and A + B → 2B (autocatalytic surface growth).[9,13] Mercury poisoning experiments performed on this catalytic system also supported the presence of heterogeneous catalysis. For dehydrocoupling trials initiated in the presence of excess mercury, no catalytic activity and no color change to black was observed (Figure 3, curve ◆). When excess mercury was added to a partially dehydrocoupled sample, the catalytic activity was completely suppressed and no further dehydrocoupling was observed (Figure 3, curve ■). In addition, test reactions between mercury and [{Rh(1,5-cod)(μ-Cl)}$_2$] eliminated the possibility of any complicating side reactions that may have led to catalyst deactivation.[20]

Upon complete conversion of Me$_2$NH·BH$_3$, the addition of fresh adduct to the catalytically active solution was found to result in immediate dehydrocoupling without an induction period (Figure 4, curve ●). When a catalytically active solution was treated with the ligand poison PPh$_3$ (0.5 equiv) and fresh Me$_2$NH·BH$_3$ added, a substantial reduction in the dehydrocoupling rate was found to result (Figure 4, curve ◆). The observed partial catalytic activity is likely due to incomplete surface coverage by PPh$_3$, resulting in residual active sites where dehydrocoupling could still occur. Filtration of a catalytically

(19) The variability in the length of the induction period may arise from a number of different factors. For example, solvent and Me$_2$NH·BH$_3$ purity, stirring rate, reaction temperature (inside a glovebox), and the use of different batches of [{Rh(1,5-cod)(μ-Cl)}$_2$] may all affect the length of the induction period observed for a given trial. However, irreproducible induction periods are not unexpected for the in situ formation of a heterogeneous catalyst. See ref 7b for further details.

(20) See the Experimental Section for a complete description of the test reactions involving Hg and the precatalyst [{Rh(1,5-cod)(μ-Cl)}$_2$].

Figure 3. Graph of % conversion vs time for the catalytic dehydrocoupling of $Me_2NH \cdot BH_3$ using $[\{Rh(1,5\text{-cod})(\mu\text{-Cl})\}_2]$ (ca. 2 mol % Rh, toluene, 25 °C). At ca. 35% conversion, ex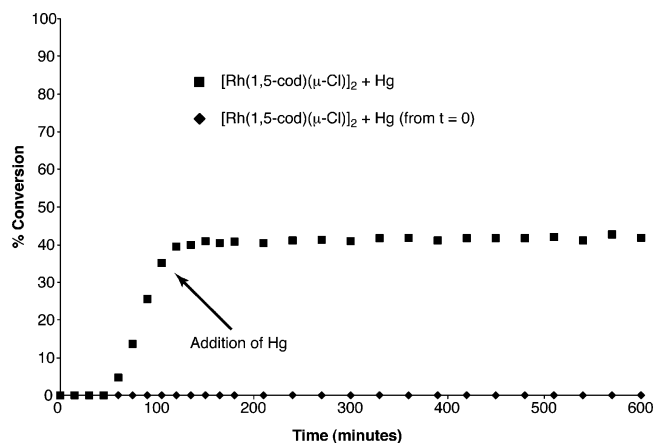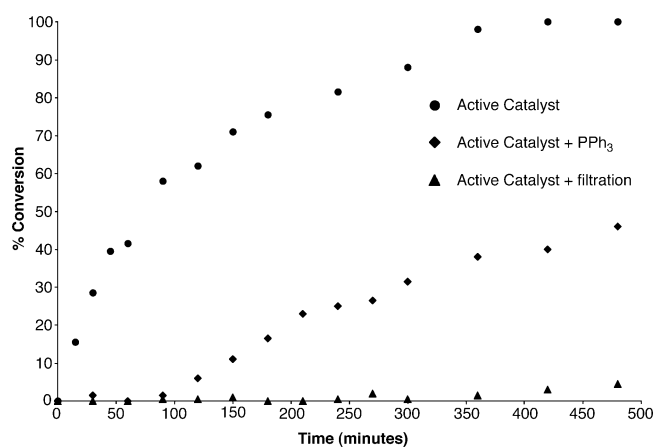cess Hg was added to the reaction mixture (curve ■). The dehydrocoupling reaction was initiated in the presence of excess Hg (curve ◆).

Figure 4. Graph of % conversion vs time for the catalytic dehydrocoupling of $Me_2NH \cdot BH_3$ using $[\{Rh(1,5\text{-cod})(\mu\text{-Cl})\}_2]$ (ca. 2 mol % Rh, toluene, 25 °C). Upon complete conversion, $Me_2NH \cdot BH_3$ was added to the catalytically active solution (curve ●). Upon complete conversion, the catalytically active solution was treated with 0.5 equiv of PPh_3 and more $Me_2NH \cdot BH_3$ was added (curve ◆). Upon complete conversion, the catalytically active solution was filtered and more $Me_2NH \cdot BH_3$ was added (curve ▲).

active solution through a 0.5 μm filter and the addition of fresh $Me_2NH \cdot BH_3$ were found to result in almost complete suppression of catalytic activity (Figure 4, curve ▲). All of these tests performed on the $Me_2NH \cdot BH_3/[\{Rh(1,5\text{-cod})(\mu\text{-Cl})\}_2]$ system suggest the operation of an insoluble, heterogeneous catalyst.

Evolution of the Precatalyst $[\{Rh(1,5\text{-cod})(\mu\text{-Cl})\}_2]$ during the Dehydrocoupling of $Me_2NH \cdot BH_3$: The decomposition of the precatalyst $[\{Rh(1,5\text{-cod})(\mu\text{-Cl})\}_2]$ in the presence of $Me_2NH \cdot BH_3$ was conveniently monitored by ^{1}H NMR. The hydrogenation of precatalyst-derived 1,5-cyclooctadiene to cyclooctane was consistently observed as $[\{Rh(1,5\text{-cod})(\mu\text{-Cl})\}_2]$ evolved into the catalytically active Rh colloids during the dehydrocoupling of $Me_2NH \cdot BH_3$. During the induction period (colloid nucleation, from $t = 0-60$ min), evidence for cyclooctane or even free 1,5-cyclooctadiene was not detected (Figure S2, Supporting Information). At 15% conversion of $Me_2NH \cdot BH_3$ ($t = 120$ min), rapid decomposition of the precatalyst was evident as autocatalytic surface growth occurred. This resulted in nearly 50% conversion of the catalytic amounts of 1,5-cyclooctadiene present. At $t = 180$ min, 1,5-cyclooctadiene

conversion was nearly complete (ca. 90%) while $Me_2NH \cdot BH_3$ conversion had reached only 60%. It is important to note that the curve of 1,5-cyclooctadiene conversion also adopted a sigmoidal shape, characteristic of heterogeneous catalysis. These results indicate that the precatalyst underwent rapid decomposition and was fully converted to the active catalyst Rh(0) metal before the dehydrocoupling reaction was complete.

Following complete conversion of $Me_2NH \cdot BH_3$, bulk Rh metal was isolated as the active catalyst in ca. 90% yield after removal of all volatile components of the reaction mixture. The resulting black powder was insoluble in common organic solvents such as THF and toluene, but the washings were found to contain $[Me_2NH_2]Cl$ by ^{1}H and ^{13}C NMR. The presence of $[Me_2NH_2]Cl$ likely arises from the reaction of free Me_2NH (from dissociation of the adduct) and HCl, which may be generated during the reduction step.[21] It is likely that small, nanometer sized Rh colloids may be initially formed in solution, with $[Me_2NH_2]Cl$ acting as an electrostatic stabilizing agent which helps to slow aggregation of the colloids.[22] However, evolution of these colloids via aggregation still occurred to form the observed bulk Rh metal, which is a kinetically competent catalyst. For example, use of the isolated active catalyst resulted in dehydrocoupling of $Me_2NH \cdot BH_3$ (ca. 9 h, 25 °C) without a detectable induction period.

Catalytic Dehydrocoupling of $Me_2NH \cdot BH_3$ with the (Pre)-Catalyst Rh/Al_2O_3: As the dehydrocoupling of $Me_2NH \cdot BH_3$ can be achieved using a variety of catalysts,[4b] a selection of other Rh species was subject to the "homogeneous vs heterogeneous" tests. For these catalysts, only the kinetic curves, Hg poisoning, and filtration tests were performed. For Rh/Al_2O_3 (5 wt. % Rh), the dehydrocoupling of $Me_2NH \cdot BH_3$ proceeded immediately without the presence of an induction period and with high activity (Figure S3, Supporting Information). The lack of an induction period was expected as the catalysis was performed using preformed metal particles attached to a solid support. The addition of excess Hg was found to have no effect on the dehydrocoupling, as poisoning of the active catalyst was not observed. This implies that mercury poisoning of Rh, in this case, does not occur by adsorption to the metal surface but rather by amalgam formation which is more difficult for metals attached to a solid support. Filtration of the solution to remove the insoluble Rh/Al_2O_3 was found to completely suppress the catalytic activity. These results suggest that Rh/Al_2O_3 is an insoluble, heterogeneous catalyst for the dehydrocoupling of $Me_2NH \cdot BH_3$.

Catalytic Dehydrocoupling of $Me_2NH \cdot BH_3$ with the (Pre)-Catalyst $Rh_{colloid}/[Oct_4N]Cl$: For $Rh_{colloid}/[Oct_4N]Cl$, the dehydrocoupling of $Me_2NH \cdot BH_3$ proceeded immediately without the presence of an induction period (Figure S4, Supporting Information). However, the addition of excess Hg was found to suppress the dehydrocoupling, as poisoning of the active catalyst was observed. Filtration of the solution through a 0.5 μm filter was found to have only a small effect on the catalytic activity. This was expected as these colloids (ca. 2 nm) are soluble in organic solvents such as THF and toluene, and thus filtration would only remove a minor insoluble component. This

(21) The reaction of HCl with $Me_2NH \cdot BH_3$ has been shown to give $Me_2NH \cdot BH_2Cl$ and H_2: Jaska, C. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **2004**, *43*, 1090. Therefore, HCl must react with free Me_2NH in order to give the observed $[Me_2NH_2]Cl$.
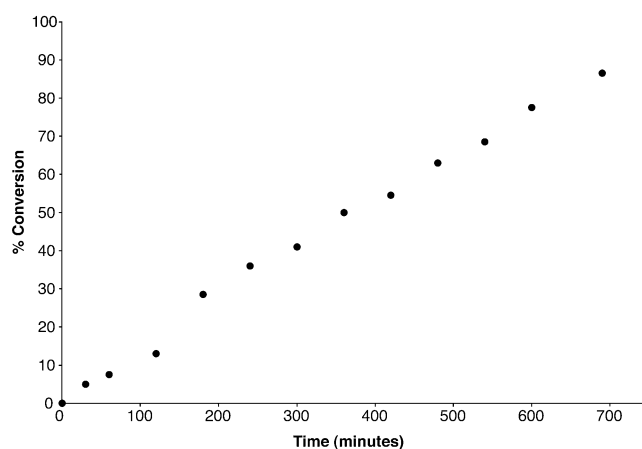(22) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757.

insoluble component may make a small contribution to the overall catalytic activity, as a slight reduction in the rate was observed compared to the unfiltered sample. These results indicate that $Rh_{colloid}$/[Oct$_4$N]Cl is a soluble, heterogeneous catalyst[23−25] for the dehydrocoupling of Me$_2$NH·BH$_3$.

Catalytic Dehydrocoupling of Me$_2$NH·BH$_3$ with the Pre-catalyst [Rh(1,5-cod)$_2$]OTf: For [Rh(1,5-cod)$_2$]OTf, the dehydrocoupling of Me$_2$NH·BH$_3$ involved the presence of a short induction period (30−45 min) followed by rapid dehydrocoupling to give a sigmoidal-shaped conversion curve (Figure S5, Supp. Info.). A small amount of conversion (<5%) was observed when the catalytic dehydrocoupling was initiated in the presence of excess Hg, whereas the addition of excess Hg to a partially converted sample was found to suppress the dehydrocoupling activity. Upon complete conversion of Me$_2$NH·BH$_3$, the addition of fresh adduct to the catalytically active solution was found to result in immediate dehydrocoupling without an induction period (Figure S6, Supporting Information). Filtration of a catalytically active solution and addition of fresh Me$_2$NH·BH$_3$ to the filtrate was found to result in only moderate suppression of catalytic activity. This may be due to a highly active soluble component[23] or continued generation of the active catalyst after filtration. These results indicate that [Rh(1,5-cod)$_2$]-OTf is a heterogeneous catalyst for the dehydrocoupling of Me$_2$NH·BH$_3$.

These results indicate that the dehydrocoupling of Me$_2$NH·BH$_3$ with the four different Rh (pre)catalysts [{Rh(1,5-cod)(μ-Cl)}$_2$], Rh/Al$_2$O$_3$, Rh$_{colloid}$/[Oct$_4$N]Cl, and [Rh(1,5-cod)$_2$]OTf involved a heterogeneous mechanism. For [{Rh(1,5-cod)(μ-Cl)}$_2$] and [Rh(1,5-cod)$_2$]OTf, an initial reduction reaction was required to give Rh colloids, which underwent significant aggregation to yield bulk Rh metal. This reduction step accounted for the observed induction period, whereas Rh/Al$_2$O$_3$ and Rh$_{colloid}$/[Oct$_4$N]Cl did not display an induction period because the heterogeneous catalyst was not formed in situ.

Kinetic Curves and Poisoning Experiments for the Catalytic Dehydrocoupling of Ph$_2$PH·BH$_3$ with the Precatalyst [{Rh(1,5-cod)(μ-Cl)}$_2$]: The treatment of Ph$_2$PH·BH$_3$ with a catalytic amount of [{Rh(1,5-cod)(μ-Cl)}$_2$] (ca. 10 mol % Rh) at 90 °C was found to result in a color change from orange to dark red after ca. 10 min. Over numerous repeat trials, the presence of a black color or a black precipitate characteristic of colloidal or metallic rhodium was never observed. When monitoring the extent of reaction by ^{11}B NMR, the presence of an induction period was not observed even after 15 min of

(23) While the term "soluble heterogeneous catalyst" may initially appear to be an oxymoron, we have adopted the definition of homogeneous and heterogeneous as proposed by Schwartz. See ref 24. Accordingly, Finke and co-workers have suggested a revised classification of homogeneous and heterogeneous catalysis, which can be divided into four categories: (1) soluble homogeneous (e.g., Wilkinson's catalyst), (2) insoluble homogeneous (e.g., zeolites), (3) soluble heterogeneous (e.g., soluble metal nanoclusters or colloids; see ref 25), and (4) insoluble heterogeneous (e.g., oxide-supported metals). For further details, see: Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891. The catalyst used in this particular case ([Rh$_{colloid}$/[Oct$_4$N]Cl) falls into category 3.
(24) Schwartz has proposed alternative definitions of homogeneous and heterogeneous that do not depend on solubility. He has suggested that a homogeneous catalyst possesses only one type of active site, whereas a heterogeneous catalyst may have multiple types of active sites. See: Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302. By this definition, the catalyst used is heterogeneous.
(25) For examples of "soluble heterogeneous" catalysts, see the following and references therein: (a) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335. (b) Aiken, J. D., III; Lin, Y.; Finke, R. G. *J. Mol. Catal. A: Chem.* **1996**, *114*, 29. (c) Aiken, J. D., III; Finke, R. G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 1.

Figure 5. Graph of % conversion vs time for the catalytic dehydrocoupling of Ph$_2$PH·BH$_3$ using [{Rh(1,5-cod)(μ-Cl)}$_2$] (ca. 10 mol % Rh, toluene, 90 °C).
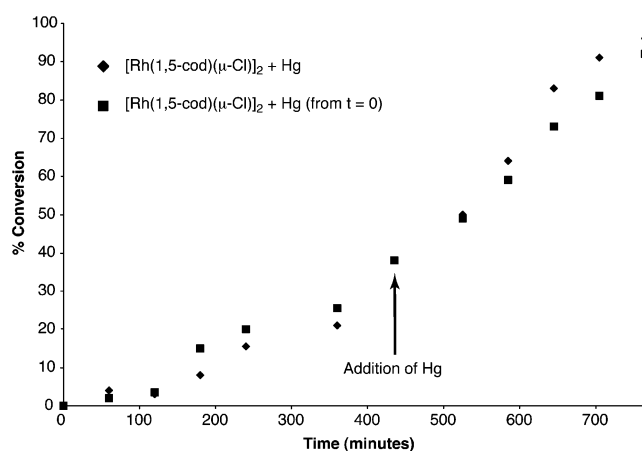
Figure 6. Graph of % conversion vs time for the catalytic dehydrocoupling of Ph$_2$PH·BH$_3$ using [{Rh(1,5-cod)(μ-Cl)}$_2$] (ca. 10 mol % Rh, toluene, 90 °C). At ca. 35% conversion, excess Hg was added to the reaction mixture (curve ◆). The dehydrocoupling reaction was initiated in the presence of excess Hg (curve ■).

reaction time. Thus, a sigmoidal kinetic curve was not observed. Instead, nearly linear conversion with respect to time was consistently observed over many repeat trials (Figure 5). Catalytic dehydrocoupling involving initiation in the presence of excess mercury was found to have no significant effect on the dehydrocoupling activity (Figure 6, curve ■). Similarly, the addition of excess Hg to a partially converted sample was also found to have no effect on the dehydrocoupling, which indicated that poisoning had not occurred (Figure 6, curve ◆). When a catalytically active solution was treated with the ligand poison PPh$_3$ (0.5 equiv), the addition of fresh Ph$_2$PH·BH$_3$ (Figure 7, curve ●) was found to have little effect on the dehydrocoupling rate compared to an untreated sample (Figure 7, curve ◆). Filtration of a catalytically active solution followed by the addition of more Ph$_2$PH·BH$_3$ was also found to have little effect on the dehydrocoupling activity (Figure 7, curve ▲).

Catalytic Dehydrocoupling of Ph$_2$PH·BH$_3$ with the (Pre)-Catalyst Rh/Al$_2$O$_3$: The dehydrocoupling of Ph$_2$PH·BH$_3$ with Rh/Al$_2$O$_3$ (5 wt. % Rh) was observed to proceed slowly, the reaction reaching completion after ca. 60 h at 90 °C (Figure S7, Supporting Information). The addition of excess Hg was found to have no effect on the dehydrocoupling. Surprisingly, filtration of the reaction mixture did not suppress the catalytic

Figure 7. Graph of % conversion vs time for the catalytic dehydrocoupling of Ph$_2$PH·BH$_3$ using [{Rh(1,5-cod)(μ-Cl)}$_2$] (ca. 10 mol % Rh, toluene, 90 °C). Upon complete conversion, Ph$_2$PH·BH$_3$ was added to the catalytically active solution (curve ◆). Upon complete conversion, the catalytically active solution was treated with 0.5 equiv of PPh$_3$ and more Ph$_2$PH·BH$_3$ was added (curve ●). Upon complete conversion, the catalytically active solution was filtered and more Ph$_2$PH·BH$_3$ was added (curve ▲).

activity, as the reaction proceeded to completion even after the insoluble Rh/Al$_2$O$_3$ was removed. The filtered solution was orange in color, which suggested that leaching of Rh metal from the insoluble precatalyst to give a soluble species might have occurred. The leaching of metal from an insoluble, heterogeneous catalyst is a known phenomenon,[26] in which the catalytic activity may reside with the leached metal.[11a] To test which phase was catalytically active, both the soluble and insoluble (residual Rh/Al$_2$O$_3$) fractions from a completely converted sample were isolated. The addition of Ph$_2$PH·BH$_3$ to the soluble fraction resulted in further dehydrocoupling activity after 3 d at 90 °C. Conversely, the addition of Ph$_2$PH·BH$_3$ to the insoluble fraction showed no dehydrocoupling activity after 5 d at 90 °C.[27] Analysis of the Rh/Al$_2$O$_3$ particles by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) before catalysis indicated an average Rh content of 3.35 wt %. Analysis of the particles after catalysis indicated a small decrease in the average Rh content to 2.74 wt %. This suggested that a small quantity of Rh had leached out from the solid support during the catalysis. The ^{31}P NMR spectrum of the soluble fraction contained two resonances not associated with dehydrocoupling products, two doublets centered at δ 34.0 and -23.8 ppm, both with the same coupling constant of $J = 220$ Hz that may be due to Rh$-$P coupling. The ^{1}H coupled ^{31}P NMR spectrum did not show any further coupling, eliminating the possibility of P$-$H groups. In addition, the hydride region of the ^{1}H NMR spectrum showed a broad doublet at δ -7.6 ppm ($J = 150$ Hz). This strongly suggests that the active catalyst is not insoluble Rh/Al$_2$O$_3$ but is possibly a soluble, homogeneous Rh hydride complex containing PPh$_2$ groups.

(26) (a) Wang, Q.; Lui, H.; Han, M.; Li, X.; Jiang, D. *J. Mol. Catal. A: Chem.* **1997**, *118*, 145. (b) De Blasio, N.; Wright, M. R.; Tempesti, E.; Mazzocchia, C.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1998**, *551*, 229. (c) Arena, F.; Giovenco, R.; Torre, T.; Venuto, A.; Parmaliana, A. *Appl. Catal. B* **2003**, *45*, 51. (d) Carlini, C.; Di Girolamo, M.; Macinai, A.; Marchionna, M.; Noviello, M.; Galletti, A. M. R.; Sbrana, G. *J. Mol. Catal. A: Chem.* **2003**, *204−205*, 721.

(27) The observation that the residual Rh/Al$_2$O$_3$ catalyst displays no dehydrocoupling activity suggests that no further Rh(0) is leached from the solid support. It is likely that the initial leaching process involves primarily exposed surface Rh atoms, which are easily accessible. However, subsequent leaching might be inhibited for the more inaccessible Rh atoms in the interior of the alumina particles, even over long reaction times.

Catalytic Dehydrocoupling of Ph$_2$PH·BH$_3$ with the (Pre)-Catalyst Rh$_{colloid}$/[Oct$_4$N]Cl: The treatment of Ph$_2$PH·BH$_3$ with Rh$_{colloid}$/[Oct$_4$N]Cl resulted in no dehydrocoupling activity after 21 h at 25 °C or after 62 h at 90 °C. In addition, the soluble colloids were observed to form bulk, insoluble Rh metal over the course of the reaction at 90 °C. Therefore, both soluble Rh colloids and insoluble bulk Rh metal are not effective catalysts for the dehydrocoupling of Ph$_2$PH·BH$_3$.

Catalytic Dehydrocoupling of Ph$_2$PH·BH$_3$ with the (Pre)-Catalyst [Rh(1,5-cod)$_2$]OTf: The treatment of Ph$_2$PH·BH$_3$ with [Rh(1,5-cod)$_2$]OTf at 90 °C resulted in the formation of a dark red solution with no visible evidence of black colloidal Rh. Similar to the case of [{Rh(1,5-cod)(μ-Cl)}$_2$], an induction period was not observed and catalytic dehydrocoupling trials initiated in the presence of excess Hg, and the addition of excess Hg to a partially converted sample, were found to have little effect on the dehydrocoupling activity (Figure S8, Supporting Information). Filtration of a catalytically active solution through a 0.5 μm filter also resulted in little change in the dehydrocoupling rate (Figure S9, Supporting Information).

Attempted Dehydrocoupling of Me$_2$NH·BH$_3$ Using the Active Catalyst Obtained from the Catalytic Dehydrocoupling of Ph$_2$PH·BH$_3$ and Vice Versa: It was of interest to test if the active catalyst obtained from the catalytic dehydrocoupling of Ph$_2$PH·BH$_3$ was active with respect to the dehydrocoupling of Me$_2$NH·BH$_3$. A catalytically active Ph$_2$PH·BH$_3$/[{Rh(1,5-cod)(μ-Cl)}$_2$] reaction mixture was formed at 90 °C for 14 h. Treatment of this solution with Me$_2$NH·BH$_3$ was found to result in no dehydrocoupling activity (3 d, 25 °C). Heating this reaction mixture to 70 °C was found to result in only moderate dehydrocoupling activity, with ca. 6% conversion (24 h). In addition, the active catalyst obtained from the catalytic dehydrocoupling of Me$_2$NH·BH$_3$ was also tested for catalytic activity with respect to the dehydrocoupling of Ph$_2$PH·BH$_3$. Treatment of a catalytically active Me$_2$NH·BH$_3$/[{Rh(1,5-cod)-(μ-Cl)}$_2$] reaction mixture (formed at 25 °C for 4 d) with Ph$_2$PH·BH$_3$ was found to result in no dehydrocoupling activity (7 d, 90 °C).

Discussion of the Factors which Influence the Mechanism of Catalytic Dehydrocoupling: It remains an intriguing problem to explain why the catalytic dehydrocoupling is heterogeneous in the case of amine-borane adducts but homogeneous in the case of phosphine-borane analogues. The main factors that may be responsible for this contrasting behavior include (i) the reducing strength of the adduct, (ii) the extent of dissociation of the adduct, and (iii) potential ligation and poisoning of the active catalyst.

With respect to factor (i), amine-borane and phosphine-borane adducts would be expected to possess different strengths as reducing agents, which are likely related to the hydridic character of the B$-$H substituents. Thus, Me$_2$NH·BH$_3$ might be expected to be sufficiently hydridic to facilitate reduction of the Rh(I) precatalyst to colloidal Rh(0) metal, while Ph$_2$PH·BH$_3$ might not. Calculations have shown that there is more substantial charge transfer from N to B in NH$_3$·BH$_3$ (0.314e) than from P to B in PH$_3$·BH$_3$ (0.299e) (E$^{\delta+}$$-$$^{\delta-}$B; E = N, P).[28] Due to the larger electronegativity of H (2.20 for H vs 2.04 for B), the negative charge will be further transferred from B to H by inductive effects. Calculations performed on NH$_3$·BH$_3$ support

(28) Chaillet, M.; Dargelos, A.; Marsden, C. J. *New J. Chem.* **1994**, *18*, 693.

this increase in electron density on the hydrogen atoms in BH$_3$ upon adduct formation.[29] The enhanced hydridic nature of the B−H hydrogen substituents in amine-borane adducts would be expected to promote reduction of the precatalyst, leading to behavior as a "borohydride type" reducing agent. Borohydrides such as Na[BH$_4$] or Li[BEt$_3$H] have been commonly used as reducing agents in the synthesis of transition metal colloids from metal halide precursors.[22,30] For example, Me$_2$NH·BH$_3$ has been used to generate Pt and Au colloids by reduction of H$_2$PtCl$_6$[31] and HAuCl$_4$,[32] respectively. This difference in reducing strength was demonstrated by reacting the precatalyst [{Rh(1,5-cod)(μ-Cl)}$_2$] with the tertiary adducts Me$_3$E·BH$_3$ (E = N, P), as no complications could arise from catalytic dehydrocoupling.[33] Treatment of a [{Rh(1,5-cod)(μ-Cl)}$_2$] solution with Me$_3$N·BH$_3$ was found to result in the formation of a black solution characteristic of colloidal Rh and the chlorinated adduct Me$_3$N·BH$_2$Cl (24 h, 25 °C). However, treatment with Me$_3$P·BH$_3$ under similar conditions was found to result in no observable reaction, as the Rh(I) complex was not reduced and the solution remained yellow-orange in color. Further evidence for the enhanced hydridic nature of B−H hydrogen substituents in amine-boranes can also be illustrated by the reaction with acids, such as HCl. For example, we have found that Me$_2$NH·BH$_3$ reacts readily with HCl (1 equiv) to form the chlorinated adduct Me$_2$NH·BH$_2$Cl and H$_2$.[21] However, treatment of Ph$_2$PH·BH$_3$ with HCl (1 equiv) was found to result in no reaction, likely due to the fact that the B−H bonds are less polar than those in amine-borane adducts.

With respect to factor (ii), amine-borane and phosphine-borane adducts also possess different dissociation energies. In general, phosphine-borane adducts will have lower dissociation energies as they have weaker dative bonds than amine-borane adducts. For example, the dissociation energy of PH$_3$·BH$_3$ has been calculated to be 21.8 kcal mol^{-1} (91.2 kJ mol^{-1}), while NH$_3$·BH$_3$ has a value of 27.8 kcal mol^{-1} (116 kJ mol^{-1}).[34] In addition, the high temperatures (90 °C and above) required for the catalytic dehydrocoupling of Ph$_2$PH·BH$_3$ may facilitate this dissociation process. However, variable temperature ^{1}H NMR studies on Me$_2$NH·BH$_3$ and Ph$_2$PH·BH$_3$ in toluene-d_8 showed no evidence for dissociation even at elevated temperatures of 85 °C. A further possibility to consider is that transition metal-assisted P−B bond cleavage might take place in these reactions. Indeed, the treatment of the adducts Ph$_2$PH·BH$_3$ and Ph$_3$P·BH$_3$ with Rh$_{colloid}$/[Oct$_4$N]Cl in THF (or toluene) at 25 °C was found to result in the formation of the free phosphines Ph$_2$PH and Ph$_3$P, respectively. Conversely, significant metal-assisted N−B bond cleavage of Me$_2$NH·BH$_3$ or Me$_3$N·BH$_3$ was not evident as the appreciable formation of free Me$_2$NH, or Me$_3$N was not observed upon treatment with Rh$_{colloid}$/[Oct$_4$N]Cl in C$_6$D$_6$. The presence of free Ph$_2$PH and BH$_3$ (as B$_2$H$_6$) in the reaction

mixture may favor alternative reaction pathways such as ligation or oxidative addition of the phosphine over reduction of the metal center. Indeed, the oxidative addition of P−H bonds in PhPRH·BH$_3$ (R = H, Ph) at Pt(0) centers has been previously observed by our group.[3] In addition, the P−H bonds of uncoordinated phosphines can also undergo oxidative addition reactions at metal centers.[35]

With respect to factor (iii), the presence of free phosphine in solution may result in ligation and/or catalyst poisoning of either a homogeneous metal center or a heterogeneous metal surface. For cases involving a homogeneous metal center, the ligation of phosphines would have two effects: (1) the transition metal center would become more electron rich, thereby making reduction even more difficult than for the original precatalyst,[36] and (2) poisoning of the active catalyst could occur, which may only be disrupted at high temperatures by forcing ligand dissociation. Point 2 can be used to rationalize the observation that significantly elevated temperatures are required for the catalytic dehydrocoupling of phosphine-borane adducts, as ligand dissociation to generate a vacant coordination site probably does not occur at lower temperatures. For cases involving a heterogeneous metal surface, ligation of phosphines to the surface atoms would effectively poison the catalytically active sites (vide supra). For example, pretreatment of Rh$_{colloid}$/ [Oct$_4$N]Cl with either Ph$_2$PH or Ph$_2$PH·BH$_3$ followed by addition of Me$_2$NH·BH$_3$ was found to result in no catalytic dehydrocoupling activity due to poisoning by Ph$_2$PH. Interestingly, pretreatment of Rh$_{colloid}$/[Oct$_4$N]Cl with Me$_2$NH followed by addition of Me$_2$NH·BH$_3$ was found to result in 90% dehydrocoupling (3 h, 25 °C). Significantly, this implies that even if Me$_2$NH·BH$_3$ dissociation does occur, Me$_2$NH does not act as a catalyst poison.

A combination of the aforementioned factors can explain the contrasting dehydrocoupling mechanisms for both amine-borane and phosphine-borane adducts. For amine-borane adducts, reduction of the precatalyst appears to be favored to give a heterogeneous catalyst that is not poisoned by any free amine that might be generated. For phosphine-borane adducts on the other hand, the B−H hydrogen substituents do not appear to be hydridic enough to promote reduction of the precatalyst. Instead, metal-assisted P−B bond cleavage or adduct dissociation may occur to give free phosphine, which could favor alternative reaction pathways such as ligation and/or oxidative addition. Phosphine ligation to a homogeneous metal center would (i) disfavor reduction of the precatalyst to elemental metal and (ii) inhibit dehydrocoupling unless forcing conditions were utilized, such as high temperatures. We have shown that phosphine ligation at a heterogeneous metal surface results in poisoning of the active site which results in no dehydrocoupling activity.

While the results of this study indicate a heterogeneous process for amine-borane dehydrocoupling and a homogeneous process for phosphine-borane dehydrocoupling, the details of the individual reaction steps that comprise the catalytic cycle

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(32) Esumi, K.; Hosoya, T.; Suzuki, A.; Torigoe, K. *J. Colloid Interface Sci.* **2000**, *229*, 303.
(33) H$_2$ gas is commonly used as a reducing agent for the synthesis of transition metal nanoclusters and colloids starting from molecular precursors. See ref 22.
(34) Rablen, P. R. *J. Am. Chem. Soc.* **1997**, *119*, 8350.

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(36) For example, [{Ir(1,5-cod)(μ-Cl)}$_2$] can be reduced to Ir colloids at 4 atm of H$_2$, whereas, in the presence of a bidentate phosphine ligand, no reduction of the [Ir(phosphine)Cl] complex was observed at 70 atm of H$_2$. See ref 7b.

are still unknown and further mechanistic investigations are certainly required. For example, the microscopic reversal of the well-accepted Horiuti−Polanyi mechanism[37] for olefin hydrogenation at a metal surface might be considered as a distinct possibility for amine-borane dehydrocoupling.[38] However, previous studies have indicated that the thermal dehydrocoupling of $Me_2NH \cdot BH_3$ is an intermolecular process involving two adduct molecules,[4b,39] which may be complicated by a complex reaction chemistry at metal surfaces. In the case of phosphine-borane adducts, the potential reaction steps in the homogeneous catalytic cycle have been briefly investigated using Pt complexes in which the initial reaction step involved oxidative addition of the P−H bond of the adduct.[3] However, subsequent coupling chemistry to form new P−B bonds at the metal center were not observed. Further investigations are clearly needed.

Summary

Our results indicate that a seemingly subtle change on substrate from an amine-borane adduct to a phosphine-borane adduct led to a fundamental change from a heterogeneous mechanism to a homogeneous mechanism for Rh-catalyzed dehydrocoupling. Furthermore, the differences are not just a result of the relative ability of the adducts to reduce the Rh(I) precatalyst, as efficient dehydrocoupling of phosphine-borane adducts was not detected using Rh metal as a potential catalyst. Differences in the extent of dissociation, or perhaps the ease of transition metal-assisted adduct bond cleavage, resulted in phosphine ligation and poisoning of heterogeneous Rh catalysts when phosphine-borane adducts were employed. In addition, dehydrocoupling of phosphine-borane adducts may require higher reaction temperatures in order to induce phosphine ligand dissociation from a transition metal center to generate an active homogeneous catalyst. Unless transition metal complexes are utilized in which phosphine ligand dissociation is a more facile process, the dehydrocoupling of phosphine-borane adducts may be limited to higher reaction temperatures. In contrast, for amine-borane adducts, the reduction of metal complexes to colloidal metal is facile, and free amine, even if it is formed, does not poison the heterogeneous catalyst. The observation that the active catalyst for phosphine-borane dehydrocoupling is not active for amine-borane adducts suggests that fundamentally different chemistry occurs at the metal center. This is not unexpected, as N-ligands differ in many key respects from P-donor analogues.

The results described also demonstrate the importance of performing a thorough, critical analysis of catalytic systems on a case-by-case approach, as even structurally analogous species may display fundamentally different reactivity and behavior. Further work is aimed at understanding the detailed mechanisms for the P−B and N−B bond formation processes via the study of appropriately designed model complexes as well as the use of this new chemistry in molecular[5] and polymer[2] synthesis.

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 a MBraun glovebox filled with dry nitrogen unless otherwise specified. Toluene was dried over Na/benzophenone and distilled prior to use. Rh/Al_2O_3 (5 wt. % Rh), Me_3N, Me_2NH (2.0 M in THF) (Aldrich), Mercury (99.998%), [Rh(1,5-cod)$_2$]-OTf (Strem Chemicals), and PPh_3 (BDH) were purchased and used as received. $Me_2NH \cdot BH_3$ (Strem) was purified by sublimation at 25 °C. $[\{Rh(1,5\text{-}cod)(\mu\text{-}Cl)\}_2]$,[40] $Ph_2PH \cdot BH_3$,[41] $Me_3P \cdot BH_3$,[42] and $Rh_{colloid}$/$[Oct_4N]Cl^{30a}$ were synthesized by literature procedures. $Ph_3P \cdot BH_3$ and $Me_3N \cdot BH_3$ were prepared by reaction of Ph_3P or Me_3N with a solution of $BH_3 \cdot THF$ in THF at 0 °C, followed by solvent removal that afforded white solids of sufficient purity by NMR.

Equipment: NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are reported relative to residual protonated solvent peaks (^1H, ^{13}C) or external $BF_3 \cdot Et_2O$ (^{11}B) or H_3PO_4 (^{31}P). NMR spectra were obtained at 300 MHz (^1H), 96 MHz (^{11}B), 75 MHz (^{13}C), or 121 MHz (^{31}P). TEM images were obtained on either a Hitachi model 600 electron microscope with an accelerating voltage of 75 kV (Figure 1a−c) or on a Hitachi S-5200 electron microscope with an accelerating voltage of 30 kV (Figure 1d and e). EDX data were obtained on a Hitachi S-5200 electron microscope. Elemental analyses were obtained on a Perkin-Elmer Series 2400 CHNS analyzer maintained by the Analest facility at the University of Toronto. Millex Millipore filters (PTFE membrane, pore size 0.5 μm) were obtained from Aldrich. UV−visible spectra were obtained on a Perkin-Elmer Lambda 900 spectrometer.

Catalytic Dehydrocoupling of $Me_2NH \cdot BH_3$: In a typical reaction, the appropriate Rh catalyst (ca. 2 mol % Rh) was added to a solution of $Me_2NH \cdot BH_3$ (ca. 0.200 g) in toluene (3 mL) in a 10 mL vial with a small stir bar. The mixture was rapidly stirred at 25 °C, and small aliquots were removed periodically for analysis. The aliquots were dissolved in CH_2Cl_2, and the ^{11}B NMR spectrum was immediately obtained. Integration of the product ($^B\delta$ 5 ppm) and reactant ($^B\delta$ −14 ppm) resonances was used to calculate the percent conversion of the reaction. For the tests, two general methods were used.

Method **BN-1**: A typical dehydrocoupling reaction was initiated by addition of catalyst and monitored until a desired % conversion was reached. At this point, the solution was treated (e.g., addition of poison, filtered), and monitoring was continued until the reaction reached completion.

Method **BN-2**: A typical dehydrocoupling trial was allowed to proceed to 100% completion by stirring overnight for 18 h. At this point, the solution was treated (e.g., addition of poison, filtered), and additional $Me_2NH \cdot BH_3$ was added to the mixture. A small aliquot was immediately removed for ^{11}B NMR analysis. The integration of product and reactant resonances were then treated as the zero % conversion mark for the new dehydrocoupling trial.[43] Monitoring was continued until the reaction reached completion.

Catalytic Dehydrocoupling of $Ph_2PH \cdot BH_3$: In a typical reaction, the appropriate Rh catalyst (ca. 10 mol % Rh) was added to a solution of $Ph_2PH \cdot BH_3$ (ca. 0.100 g) in toluene (3 mL) in a 25 mL Schlenk flask equipped with a small stir bar. The mixture was rapidly stirred and heated to 90 °C to commence the dehydrocoupling reaction. At set times, the reaction mixture was cooled quickly to room temperature using ice water which effectively quenched the dehydrocoupling reaction. Test reactions show that the *dehydrocoupling does not occur at room temperature, only at elevated temperatures*. The contents of the mixture were transferred to an NMR tube and analyzed by ^{11}B NMR

(37) Horiuti, I.; Polanyi, M. *Trans. Faraday Soc.* **1934**, *30*, 1164.
(38) For example, adsorption of the amine-borane adduct to the metal surface followed by N−H and B−H bond cleavage could give adsorbed aminoborane (R′RN=BH$_2$) and H moieties. Formation of H$_2$ and dissociation of the aminoborane followed by dimerization would give the observed products and regenerate the catalytic metal surface.
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(43) The formula for determining the corrected % conversion of the product is given by %($t)_{corr}$ = (%(t) − %(0)) × (100 ÷ [100 − %(0)]) where %(t) is % conversion of the product at time t as obtained from the ^{11}B NMR spectrum before correction and %(0) is the % conversion of product at time t = 0. Example: If %(0) = 45% and %(60 min) = 60%, %($t)_{corr}$ = (60% − 45%) × (100 ÷ [100−45%]) = 27%.

via integration of the reactant ($^B\delta$ −39) and product ($^B\delta$ −33 and −37) resonances. After NMR analysis, the solution was returned to the flask and the heating was continued to resume the dehydrocoupling. For the tests, two general methods were used.

Method **BP-1**: A typical dehydrocoupling reaction was initiated by heating to 90 °C and monitoring until a desired % conversion was reached. At this point, the solution was treated (e.g., addition of poison, filtered) and monitoring continued until the reaction reached completion.

Method **BP-2**: A typical dehydrocoupling trial was allowed to proceed to 100% completion by heating overnight at 90 °C for 18 h. At this point, the solution was cooled to 25 °C and treated (e.g., addition of poison, filtered) and additional Ph₂PH·BH₃ was added to the mixture. The solution was analyzed by ¹¹B NMR with the integration of product and reactant resonances being treated as the zero % conversion mark for the new dehydrocoupling trial.[43] The dehydrocoupling reaction was resumed by heating to 90 °C, and monitoring was continued until the reaction reached completion.

TEM Analysis of Catalytically Active Solutions: For each of the three experiments, TEM images were obtained using two different accelerating voltages of 75 and 30 kV. (a) A typical dehydrocoupling reaction involving Me₂NH·BH₃ and [{Rh(1,5-cod)(μ-Cl)}₂] was allowed to react for 6 h to give a black, catalytically active solution. A small aliquot was removed, deposited on a carbon-coated TEM grid, and evaporated to dryness to obtain a TEM image. (b) A typical dehydro-coupling reaction involving Ph₂PH·BH₃ and [{Rh(1,5-cod)(μ-Cl)}₂] was allowed to react for 6 h to give a dark red, catalytically active solution. A small aliquot was removed, deposited on a carbon-coated TEM grid, and evaporated to dryness to obtain a TEM image. (c) Blank: A solution of [{Rh(1,5-cod)(μ-Cl)}₂] in toluene was deposited on a carbon-coated TEM grid and evaporated to dryness to obtain a TEM image.

UV−vis Analysis of Catalytically Active Solutions: (a) A typical dehydrocoupling reaction involving Me₂NH·BH₃ and [{Rh(1,5-cod)-(μ-Cl)}₂] was allowed to react for 6 h to give a black, catalytically active solution. A small aliquot was removed, diluted with CH₂Cl₂, filtered, and analyzed using CH₂Cl₂ as a background reference. (b) Rh$_{colloid}$/[Oct₄N]Cl was dissolved in THF/toluene (50/50), filtered, and analyzed using THF/toluene as a background reference. (c) A typical dehydrocoupling reaction involving Ph₂PH·BH₃ and [{Rh(1,5-cod)(μ-Cl)}₂] was allowed to react for 6 h to give a dark red, catalytically active solution. A small aliquot was removed, diluted with toluene, filtered, and analyzed using toluene as a background reference. (d) [{Rh(1,5-cod)(μ-Cl)}₂] was dissolved in toluene, filtered, and analyzed using toluene as a background reference.

Catalytic Dehydrocoupling of Me₂NH·BH₃. (A) Induction Experiment: Method **BN-2** was used without treatment of the solution.

(B) Hg Poisoning Experiments: (a) Method **BN-1** was used. Prior to catalyst addition, excess Hg (ca. 70−75 equiv per Rh atom) was added to the reaction mixture. (b) Method **BN-1** was used. At approximately 30−50% conversion, excess Hg (ca. 70−75 equiv per Rh atom) was added to the reaction mixture. (c) Blank reaction: A solution of [{Rh(1,5-cod)(μ-Cl)}₂] (0.034 g, 0.069 mmol) in toluene (3 mL) was stirred in the presence of excess Hg (1.028 g, 5.125 mmol, ca. 75 equiv) for 24 h. The solution was decanted/filtered to remove the Hg, divided into two equal parts, and used in dehydrocoupling experiments with Me₂NH·BH₃ and Ph₂PH·BH₃. Both samples showed evidence of the expected catalytic dehydrocoupling activity after 6 h.

(C) PPh₃ Poisoning Experiment: Method **BN-2** was used. The solution was treated with a substoichiometric amount of PPh₃ (ca. 0.5 equiv per Rh atom).

(D) Filtration Experiment: Method **BN-2** was used. The solution was filtered through a 0.5 μm filter into a *new vial with a new stir bar*. Typically, the solution changed in color from black to pale yellow-brown or colorless.

[{Rh(1,5-cod)(μ-Cl)}₂] Precatalyst Decomposition into Rh Colloids: In a small vial, Me₂NH·BH₃ (0.10 g, 1.7 mmol) was dissolved in C₆D₆ (1.5 mL) and [{Rh(1,5-cod)(μ-Cl)}₂] (0.02 g, 0.04 mmol, ca.

5 mol % Rh) was added as a solid. The mixture was stirred, and small aliquots were removed periodically in order to obtain ¹H, ¹¹B, and ¹³C NMR spectra. Upon complete reaction, the following major products were identified: cyclooctane ($^H\delta$ 1.49; $^C\delta$ 27.3), (μ-NMe₂)B₂H₅ ($^H\delta$ 2.62; $^B\delta$ −17.5 (td, J_{BHb} = 29 Hz, J_{BHt} = 129 Hz); $^C\delta$ 52.1); lit. $^B\delta$ −17.0 (td, J_{BHb} = 30 Hz, J_{BHt} = 130 Hz),[44] [Me₂NH₂]Cl ($^H\delta$ 9.92, 2.70; $^C\delta$ 34.8). In addition, many unassigned resonances were observed: $^H\delta$ 7.64, 2.62; $^C\delta$ 43.0; $^B\delta$ 37.7 (t, J_{BH} = 129 Hz), $^B\delta$ 32.7 (d, J_{BH} = 161 Hz), $^B\delta$ 28.7 (d, J_{BH} = 132 Hz), $^B\delta$ 3.7 (s), $^B\delta$ 2.0 (t, J_{BH} = 65 Hz) and $^B\delta$ −1.3 (s).

Preparation and Isolation of Rh(0) Colloids from [{Rh(1,5-cod)-(μ-Cl)}₂] and Me₂NH·BH₃: Me₂NH·BH₃ (1.0 g, 17 mmol) and [{Rh(1,5-cod)(μ-Cl)}₂] (0.10 g, 0.20 mmol) were combined and heated at 45 °C for 18 h. The sublimed [Me₂N−BH₂]₂ was removed, and the residue was evacuated at 45 °C for 3 h to give a black solid. Successive washings with CH₂Cl₂ (5 × 3 mL) were found to completely remove the ammonium chloride salts from the insoluble Rh metal. Yield (prior to washing): 0.067 g (90% assuming 1 equiv [Me₂NH₂]Cl per Rh atom). ¹H NMR (CDCl₃): δ 9.92 (br, [Me₂N*H*₂]Cl, ca. 12%), 7.64 (br, ca. 0.8%), 2.69 (t, J_{HH} = 5.7 Hz, [*Me*₂NH₂]Cl, ca. 80%), 2.62 (d, J_{HH} = 5.1 Hz, ca. 7%), 1.25 (s, ca. 0.5%). ¹³C NMR (CDCl₃): δ 43.0 (s, 34.8 (s, [Me₂NH₂]Cl). Elemental analysis calcd (%) for Rh([Me₂-NH₂]Cl)$_x$ (x = ²/₃): C, 10.18; H, 3.42; N, 5.94. Found: C, 10.93; H, 3.32; N, 4.83.

Catalytic Dehydrocoupling of Ph₂PH·BH₃. (A) Induction Experiment: Method **BP-2** was used without treatment of the solution.

(B) Hg Poisoning Experiments: (a) Method **BP-1** was used. Prior to catalyst addition, excess Hg (ca. 150 equiv per Rh atom) was added to the reaction mixture. (b) Method **BP-1** was used. At approximately 50% conversion, excess Hg (ca. 150 equiv per Rh atom) was added. (c) Blank reaction: See "Hg Poisoning of Me₂NH•BH₃" (vide supra).

(C) PPh₃ Poisoning Experiment: Method **BP-2** was used. The solution was treated with a sub-stoichiometric amount of PPh₃ (ca. 0.5 equiv. per Rh atom).

(D) Filtration Experiment: Method **BP-2** was used. The solution was filtered through a 0.5 μm filter into a *new flask with a new stir bar* containing additional Ph₂PH·BH₃.

Catalytic Dehydrocoupling of Ph₂PH·BH₃ with Rh/Al₂O₃: To a solution of Ph₂PH·BH₃ (0.078 g, 0.39 mmol) in toluene (3 mL) Rh/Al₂O₃ (0.080 g, ca. 10 mol % Rh) was added, and the mixture was stirred for 2.5 d at 90 °C. The mixture was filtered through Celite, and the yellow solution was evacuated to dryness to give a yellow oil. Analysis of the oil by NMR (C₆D₆) indicated the presence of Ph₂PH−BH₂−PPh₂−BH₃ (lit. $^P\delta$ −3.3 (Ph₂PH), −17.7 (PPh₂); $^B\delta$ −33.2 (BH₂), −37.3 (BH₃),[2b] ca. 10%), Ph₂PH ($^P\delta$ −40.7 (d, J_{PH} = 215 Hz); $^H\delta$ 5.2 (d, J_{HP} = 215 Hz), ca. 6%), Ph₂P(=O)H ($^P\delta$ 17.6 (d, J_{PH} = 477 Hz), ca. 83%) and unassigned resonances: $^P\delta$ 34.0 (d, J_{PRh} = 220 Hz, ca. 0.5%), $^P\delta$ −23.8 (d, J_{PRh} = 220 Hz, ca. 0.5%); $^H\delta$ −7.6 (br d, J = 150 Hz).

Reaction of Ph₂PH·BH₃ with Rh/Al₂O₃; Catalytic Dehydro-coupling Activity of Soluble and Insoluble Fractions: Ph₂PH·BH₃ (0.013 g, 0.065 mmol) was dissolved in toluene (5 mL), and Rh/Al₂O₃ (0.096 g, 0.047 mmol) was added. Ph₂PH·BH₃ was completely consumed after 22 h at 90 °C as indicated by ¹¹B and ³¹P NMR. The orange solution was decanted and filtered into a new flask. The black residue was washed with toluene (2 × 5 mL), and the washings were filtered and combined with the soluble fraction. (i) To the soluble fraction Ph₂PH·BH₃ (0.030 g, 0.15 mmol) was added, and the mixture was heated at 90 °C. After 3 d, complete conversion to Ph₂PH−BH₂−PPh₂−BH₃ was observed. (ii) To the insoluble residue Ph₂PH·BH₃ (0.101 g, 0.505 mmol) in toluene (3 mL) was added, and the mixture was heated at 90 °C. After 5 d, only unreacted Ph₂PH·BH₃ was observed by ¹¹B and ³¹P NMR.

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Analysis of Rh/Al$_2$O$_3$ Before and After Catalytic Dehydrocoupling of Ph$_2$PH·BH$_3$: Prior to catalysis, Rh/Al$_2$O$_3$ particles were analyzed by SEM/EDX: wt % (average of 2 particles) 32.69% Al, 63.96% O, 3.35% Rh. To a solution of Ph$_2$PH·BH$_3$ (0.063 g, 0.31 mmol) in toluene (3 mL) Rh/Al$_2$O$_3$ (0.074 g, ca. 10 mol % Rh) was added, and the mixture was stirred for 66 h at 90 °C. The orange solution was decanted, and the black residue was washed with toluene (2 × 5 mL). The insoluble residue was evacuated to dryness giving a black powder (0.044 g). The insoluble residue was then analyzed by SEM/EDX: wt % (average of 4 particles) 31.39% Al, 65.87% O, 2.74% Rh.

Attempted Catalytic Dehydrocoupling of Ph$_2$PH·BH$_3$ using Rh$_{colloid}$/[Oct$_4$N]Cl: Ph$_2$PH·BH$_3$ (0.099 g, 0.49 mmol) and Rh$_{colloid}$/[Oct$_4$N]Cl (0.008 g, ca. 10 mol % Rh) were dissolved in toluene (5 mL) to give a black solution. After 62 h at 90 °C, only unreacted Ph$_2$PH·BH$_3$ was observed in the ^{11}B NMR spectrum. The initially soluble colloids were also observed to aggregate to form bulk Rh metal, which was deposited as a black film on the sides of the flask.

Attempted Dehydrocoupling of Me$_2$NH·BH$_3$ Using the Active Catalyst from Ph$_2$PH·BH$_3$ Dehydrocoupling: (a) A solution of Ph$_2$PH·BH$_3$ (0.100 g, 0.500 mmol) and [{Rh(1,5-cod)(μ-Cl)}$_2$] (0.012 g, 0.024 mmol, ca. 10 mol % Rh) in toluene (3 mL) was reacted for 14 h at 90 °C. The solution was filtered, Me$_2$NH·BH$_3$ (0.158 g, 2.68 mmol) was added, and the mixture stirred at 25 °C. After 3 d, no evidence of dehydrocoupling activity was observed by ^{11}B NMR. (b) A solution of Ph$_2$PH·BH$_3$ (0.109 g, 0.545 mmol) and [{Rh(1,5-cod)-(μ-Cl)}$_2$] (0.013 g, 0.026 mmol, ca. 10 mol % Rh) in toluene (3 mL) was reacted for 18 h at 90 °C. The solution was filtered, and Me$_2$NH·BH$_3$ (0.200 g, 3.39 mmol) was added. Heating the mixture at 70 °C for 24 h was found to result in ca. 6% conversion to [Me$_2$N—BH$_2$]$_2$ by ^{11}B NMR. Raising the temperature to 85 °C for 24 h was shown to have little effect, as the conversion only increased to 15%.

Attempted Dehydrocoupling of Ph$_2$PH·BH$_3$ Using the Active Catalyst from Me$_2$NH·BH$_3$ Dehydrocoupling: A solution of Me$_2$NH·BH$_3$ (0.150 g, 2.54 mmol) and [{Rh(1,5-cod)(μ-Cl)}$_2$] (0.012 g, 0.024 mmol, ca. 2 mol % Rh) in toluene (3 mL) was stirred at 25 °C for 4 d. The volatiles were removed, and the residue was washed with toluene (5 mL) and dried in vacuo to give the active catalyst as a black powder. To this catalyst a solution of Ph$_2$PH·BH$_3$ (0.097 g, 0.48 mmol) in toluene (3 mL) was added, and the mixture was heated to 90 °C. After 7 d, no evidence of dehydrocoupling activity was observed by ^{11}B NMR.

Reduction of [{Rh(1,5-cod)(μ-Cl)}$_2$] to Rh(0) with Me$_3$E·BH$_3$ (E = N, P): (a) A solution of Me$_3$N·BH$_3$ (0.079 g, 1.1 mmol) and [{Rh(1,5-cod)(μ-Cl)}$_2$] (0.006 g, 0.012 mmol) in toluene (3 mL) was stirred at 25 °C. After 24 h, the solution had turned black in color and the presence of a thin black film was observed on the sides of the flask. The ^{11}B NMR spectrum of the mixture indicated the formation of a small amount of Me$_3$N·BH$_2$Cl ($^B\delta$ −0.1 ppm (t, J_{BH} = 125 Hz); lit. $^B\delta$ −0.5 (J_{BH} = 121 Hz)^{45}). (b) A solution of Me$_3$P·BH$_3$ (0.033 g, 0.37 mmol) and [{Rh(1,5-cod)(μ-Cl)}$_2$] (0.002 g, 0.004 mmol) in toluene (3 mL) was stirred at 25 °C. After 24 h, the solution remained yellow-orange in color with no visual evidence for a black precipitate.

Attempted Reaction of Ph$_2$PH·BH$_3$ with HCl: A solution of HCl in Et$_2$O (0.07 mL, 0.1 mmol) was added to a solution of Ph$_2$PH·BH$_3$ (0.027 g, 0.13 mmol) in Et$_2$O (2 mL) at 0 °C. No reaction was observed in the ^{11}B and ^{31}P NMR spectra even upon warming to 25 °C.

Variable-Temperature NMR Studies on the Dissociation of Me$_2$NH·BH$_3$ and Ph$_2$PH·BH$_3$: Separate solutions of Me$_2$NH·BH$_3$ and Ph$_2$PH·BH$_3$ in toluene-d_8 were analyzed at various temperatures (25, 40, 55, 70, and 85 °C). The ^{1}H NMR spectra of both samples were acquired at the corresponding temperature after equilibration for 15 min. There was no indication of dissociation into free Me$_2$NH or Ph$_2$PH even at 85 °C.

Reaction of Ph$_2$PR·BH$_3$ (R = H, Ph) with Rh$_{colloid}$/[Oct$_4$N]Cl: (a) Rh$_{colloid}$/[Oct$_4$N]Cl (0.010 g, 0.052 mmol Rh, ca. 2 mol % Rh) and

Ph$_2$PH·BH$_3$ (0.110 g, 0.550 mmol) were dissolved in THF (3 mL) and stirred at 25 °C. After 21 h, free Ph$_2$PH (ca. 4%) was observed in the ^{31}P NMR spectrum (δ −40.8 ppm). Similar results were obtained using toluene. (b) Rh$_{colloid}$/[Oct$_4$N]Cl (0.002 g, 0.01 mmol Rh, ca. 11 mol % Rh) and Ph$_3$P·BH$_3$ (0.025 g, 0.091 mmol) were dissolved in THF (3 mL) and stirred at 25 °C. After 24 h, free Ph$_3$P (ca. 1%) was observed in the ^{31}P NMR spectrum (δ −5.4 ppm). Similar results were obtained using toluene.

Reaction of Me$_2$NR·BH$_3$ (R = H, Me) with Rh$_{colloid}$/[Oct$_4$N]Cl: (a) Rh$_{colloid}$/[Oct$_4$N]Cl (0.002 g, 0.01 mmol Rh, ca. 1 mol % Rh) and Me$_2$NH·BH$_3$ (0.066 g, 1.1 mmol) were dissolved in C$_6$D$_6$ (1 mL) and stirred at 25 °C in a sealed vial. After 24 h, no evidence for the presence of free Me$_2$NH was observed in the ^{1}H and ^{13}C NMR spectra. (b) Rh$_{colloid}$/[Oct$_4$N]Cl (0.001 g, 0.005 mmol Rh, ca. 1 mol % Rh) and Me$_3$N·BH$_3$ (0.034 g, 0.47 mmol) were dissolved in C$_6$D$_6$ (1 mL) and stirred at 25 °C in a sealed vial. After 24 h, no evidence for the presence of free Me$_3$N was observed in the ^{1}H and ^{13}C NMR spectra.

Attempted Dehydrocoupling of Me$_2$NH·BH$_3$ with Rh$_{colloid}$/[Oct$_4$N]Cl after Ph$_2$PH·BH$_3$ or Ph$_2$PH Pretreatment: (a) Rh$_{colloid}$/[Oct$_4$N]Cl (0.010 g, 0.052 mmol Rh, ca. 2 mol % Rh) and Ph$_2$PH·BH$_3$ (0.110 g, 0.550 mmol) were dissolved in THF (3 mL) and stirred for 21 h at 25 °C. The presence of free Ph$_2$PH was observed in the ^{31}P NMR spectrum. Me$_2$NH·BH$_3$ (0.150 g, 2.54 mmol) was added, and the solution was stirred at 25 °C for 24 h. No evidence for dehydrocoupling was observed in the ^{11}B NMR spectrum of the reaction mixture. (b) Rh$_{colloid}$/[Oct$_4$N]Cl (0.006 g, 0.05 mmol Rh, ca. 2 mol % Rh) and Ph$_2$PH (0.010 g, 0.054 mmol) were dissolved in THF (3 mL) and stirred for 6 h at 25 °C. Me$_2$NH·BH$_3$ (0.149 g, 2.53 mmol) was added, and the solution was stirred at 25 °C for 18 h. No evidence for dehydrocoupling was observed in the ^{11}B NMR spectrum of the reaction mixture.

Attempted Dehydrocoupling of Me$_2$NH·BH$_3$ with Rh$_{colloid}$/[Oct$_4$N]Cl after Me$_2$NH Pretreatment: A solution of Me$_2$NH in THF (0.1 mL, 0.2 mmol, 5 equiv per Rh) was added to a solution of Rh$_{colloid}$/[Oct$_4$N]Cl (0.009 g, 0.04 mmol Rh, ca. 2 mol % Rh) in toluene (3 mL) and stirred at 25 °C. After 1 h, Me$_2$NH·BH$_3$ (0.145 g, 2.46 mmol) was added to the reaction mixture. After 3 h, the ^{11}B NMR spectrum indicated 90% conversion to [Me$_2$N—BH$_2$]$_2$. Similar results were observed when a large excess of Me$_2$NH (125 equiv per Rh) was used.

Supporting Information Available: UV−vis spectra of Me$_2$NH·BH$_3$ and Ph$_2$PH·BH$_3$ dehydrocoupling mixtures, Rh$_{colloid}$/[Oct$_4$N]Cl and [{Rh(1,5-cod)(μ-Cl)}$_2$] solutions; graph of % conversion vs time for the catalytic dehydrocoupling of Me$_2$NH·BH$_3$ and the hydrogenation of 1,5-cyclooctadiene using [{Rh(1,5-cod)(μ-Cl)}$_2$]; graph of % conversion vs time for the catalytic dehydrocoupling of Me$_2$NH·BH$_3$ or Ph$_2$PH·BH$_3$ using the (pre)catalysts Rh/Al$_2$O$_3$, Rh$_{colloid}$/[Oct$_4$N]Cl, or [Rh(1,5-cod)$_2$]OTf along with their respective poisoning and filtration studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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