

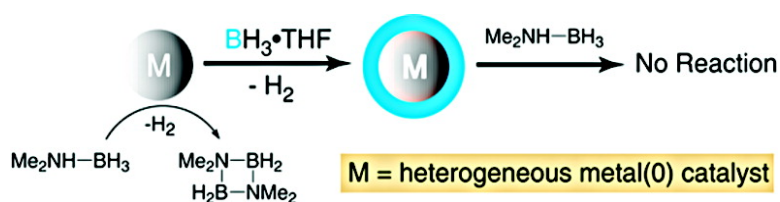
Article

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## Poisoning of Heterogeneous, Late Transition Metal Dehydrocoupling Catalysts by Boranes and Other Group 13 Hydrides

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**Abstract:** Borane reagents are widely used as reductants for the generation of colloidal metals. When treated with a variety of heterogeneous catalysts such as colloidal Rh, Rh/Al<sub>2</sub>O<sub>3</sub>, and Rh(0) black, BH<sub>3</sub>·THF (THF = tetrahydrofuran) was found to generate H<sub>2</sub> gas with the concomitant formation of a passivating boron layer on the surface of the Rh metal, thereby acting as a poison and rendering the catalyst inactive toward the dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub>. Analogous poisoning effects were also detected for (i) colloidal Rh treated with other species containing B–H bonds such as [HB–NH]<sub>3</sub>, or Ga–H bonds such as those present in GaH<sub>3</sub>·OEt<sub>2</sub>, (ii) colloidal Rh that was generated from Rh(I) and Rh(III) salts using borane or borohydrides as reductants, and (iii) for other metals such as Ru and Pd. In contrast, analogous poisoning effects were not detected for the catalytic hydrogenation of cyclohexene using Rh/Al<sub>2</sub>O<sub>3</sub> or the Pd-catalyzed Suzuki cross-coupling of PhB(OH)<sub>2</sub> and PhI. These results suggest that although this poisoning behavior is not a universal phenomenon, the observation that such boron layers are formed and surface passivation may exist needs to be carefully considered when borane reagents are used for the generation of metal colloids for catalytic or materials science applications.

### Introduction

In recent years, studies of the synthesis and catalytic activity of stable transition metal colloids and nanoclusters have attracted intense interest.<sup>1</sup> A multitude of synthetic strategies can now be employed to afford these types of heterogeneous species that find applications primarily as catalysts for a number of different bond-forming reactions.<sup>2</sup> For example, nanoclusters and colloids can be synthesized by electrochemical<sup>3</sup> or chemical reduction<sup>4</sup> methods employing either electrostatic (e.g. polyoxoanions),<sup>4a</sup> steric (e.g. polymers, dendrimers, or microgels)<sup>5,6</sup> or electrosteric (e.g. R<sub>4</sub>N<sup>+</sup> where R is a long chain alkyl group)<sup>4b</sup> stabilization in order to prevent aggregation. The chemical reduction of transition metal salts can be performed by a variety of reducing agents such as alcohols, dihydrogen, borohydrides, or boranes and is probably the most common synthetic route to colloids.<sup>2</sup> Nanoclusters and colloids have found extensive use as catalysts

in synthetic transformations, including alkene and arene hydrogenation,<sup>7</sup> Heck<sup>8,9</sup> and Suzuki<sup>9,10</sup> couplings, Ullmann-type aminations,<sup>11</sup> ring-opening polymerization,<sup>12</sup> silylation,<sup>13</sup>

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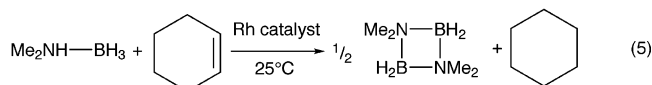
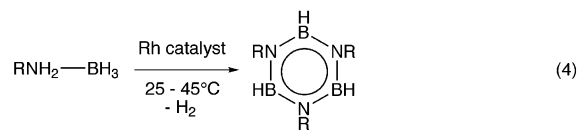
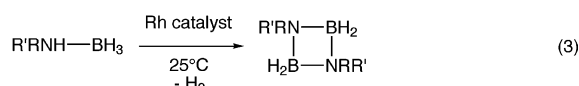
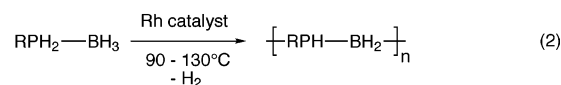
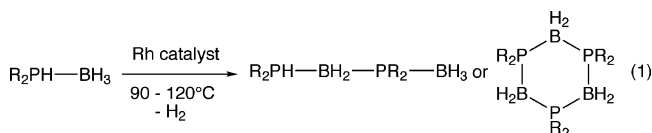
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and allylic alkylation<sup>14</sup> reactions. However, one disadvantage of colloids and nanoclusters (and heterogeneous catalysts in general) is their ability to be poisoned by substoichiometric quantities of reagent, which correspondingly reduces or inhibits their catalytic activity. For example, mercury is a well-known poison of heterogeneous catalysts through the formation of an amalgam or adsorption onto the catalyst surface.<sup>15</sup> Strongly coordinating ligands such as PPh<sub>3</sub><sup>16</sup> or CS<sub>2</sub><sup>17</sup> can also be used in fractional poisoning experiments.<sup>18</sup> Interestingly, these types of ligands can also function as colloid and nanocluster stabilizers,<sup>19a,20</sup> however this is generally accompanied by a corresponding reduction of their catalytic activity.<sup>21</sup> In some cases, this poisoning effect can be used as a reliable and reproducible test to differentiate between homogeneous and heterogeneous catalysis.<sup>16</sup>

Our group is interested in the development of catalytic routes for the formation of new bonds between inorganic elements. Recent work has focused on the catalytic dehydrocoupling of primary and secondary phosphine–borane R'RPH·BH<sub>3</sub> and amine–borane adducts R'RNH·BH<sub>3</sub> using primarily Rh (pre)-catalysts.<sup>22</sup> For example, the catalytic dehydrocoupling of phosphine–borane adducts has been shown to provide access to oligomeric chains R<sub>2</sub>PH–BH<sub>2</sub>–PR<sub>2</sub>–BH<sub>3</sub> (R = Ph, <sup>t</sup>Bu; eq 1), six- and eight-membered rings [R<sub>2</sub>P–BH<sub>2</sub>]<sub>x</sub> [R = Ph, x = 3, 4; eq 1], and high molecular weight polymers [RPH–BH<sub>2</sub>]<sub>n</sub> (R = Ph, <sup>t</sup>Bu, *p*-BuC<sub>6</sub>H<sub>4</sub>; eq 2).<sup>23,24</sup> For amine–borane adducts, catalytic dehydrocoupling was found to provide a mild and convenient route to cycloaminoboranes [R<sub>2</sub>N–BH<sub>2</sub>]<sub>2</sub> (R = Me, 1,4-C<sub>4</sub>H<sub>8</sub>; eq 3) and borazines [RN–BH]<sub>3</sub> (R = H, Me, Ph; eq 4).<sup>25</sup> In addition, a tandem catalytic dehydrocoupling–hydrogenation reaction involving a variety of Rh (pre)catalysts and Me<sub>2</sub>NH·BH<sub>3</sub> as a stoichiometric hydrogen source for the hydrogenation of alkenes at 25 °C has been recently developed

(eq 5).<sup>26</sup> In all cases involving amine–borane adducts, evidence has been found that the catalytic dehydrocoupling reactions involve some form of heterogeneous catalyst species, whether it be oxide-supported metals (e.g. Rh/Al<sub>2</sub>O<sub>3</sub>), transition metal colloids (e.g. [Oct<sub>4</sub>N]Cl stabilized Rh colloids hereafter referred to as Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl; Oct = *n*-octyl) or the in situ formation of elemental metal (e.g. Rh(0)) from homogeneous precursors.<sup>27,28</sup> Interestingly, the analogous catalytic dehydrocoupling of phosphine–borane adducts was found to proceed via a homogeneous mechanism only. It was reasoned that one of the contributing factors for this disparate behavior may involve adduct dissociation and subsequent poisoning of heterogeneous catalysts by free phosphine.<sup>28</sup> However, another potential interfering species is the other dissociation product “BH<sub>3</sub>”. Thus, in this paper we report on our further investigations of adduct dissociation and discuss, in particular, our findings on the poisoning behavior of BH<sub>3</sub>·THF (THF = tetrahydrofuran) and other related group 13 hydride species with heterogeneous transition metal catalysts used for the dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub>.



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## Results and Discussion

**Evidence for Metal-Assisted Dissociation of Me<sub>3</sub>E·XH<sub>3</sub> (E = N, P; X = B, Al, Ga) and the Effect on Catalytic Dehydrocoupling Activity.** During our earlier studies, evidence was provided supporting the metal-assisted dissociation of phosphine–borane adducts such as Ph<sub>2</sub>PR·BH<sub>3</sub> (R = H, Ph) in the presence of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl.<sup>28</sup> These dissociation reactions would generate free phosphine, a well-known poison for heterogeneous colloidal metal catalysts.<sup>16</sup> To establish the generality of this adduct dissociation chemistry, reactions involving Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl with the series of phosphine adducts Me<sub>3</sub>P·BH<sub>3</sub> and Me<sub>3</sub>P·GaH<sub>3</sub> and amine adducts Me<sub>3</sub>N·BH<sub>3</sub>, Me<sub>3</sub>N·AlH<sub>3</sub>, and Me<sub>3</sub>N·GaH<sub>3</sub> were performed. We also probed for catalyst poisoning effects by evaluating the subsequent catalytic activity of the Rh colloids toward the dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub> (eq 3, R = R' = Me). As a control,

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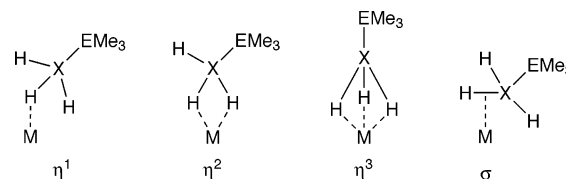
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the stability of the adducts in  $C_6D_6$  solution was first verified. Indeed, no dissociation of any of the species was observed by NMR spectroscopy after 24 h at 25 °C.

For the adducts  $Me_3P \cdot BH_3$  and  $Me_3P \cdot GaH_3$ , slight (ca. 7%) and complete (100%) dissociation was observed, respectively, to generate free  $PMe_3$  upon treatment with  $Rh_{colloid}/[Oct_4N]Cl$  (24 h, 25 °C,  $C_6D_6$ ). Subsequent treatment of these mixtures with  $Me_2NH \cdot BH_3$  resulted in no catalytic dehydrocoupling activity to form  $[Me_2N-BH_2]_2$ . Based on the detection of adduct dissociation, the poisoning effect observed presumably arises from ligation of the  $PMe_3$  groups to the surface of the  $Rh(0)$  colloids, which blocks the active catalytic sites. We have previously shown that free phosphine is a potent, substoichiometric poison for colloidal  $Rh$ -catalyzed dehydrocoupling reactions.<sup>28</sup> In addition, in the case of  $Me_3P \cdot BH_3$ , the  $^{31}P\{^1H\}$  NMR spectrum of the reaction mixture showed the presence of a cluster of signals centered at  $\delta -10$  ppm that can be assigned to the surface ligated  $PMe_3$  groups (e.g.  $\{Rh_{colloid}(PMe_3)/[Oct_4N]Cl\}$ ). Indeed, treatment of  $Rh_{colloid}/[Oct_4N]Cl$  with  $PMe_3$  showed a similar cluster of signals in the  $^{31}P\{^1H\}$  NMR spectrum ( $\delta$  ca.  $-10$  ppm), which were shifted downfield relative to free  $PMe_3$  ( $\delta$  ca.  $-61$  ppm). Previous work by Chaudret and co-workers support this  $^{31}P$  NMR assignment of  $\{Rh_{colloid}(PMe_3)/[Oct_4N]Cl\}$ , as they have also observed a general downfield shift for  $PPh_3$  on the surface of  $Pt$ ,  $Pd$ , and  $Cu$  particles compared to the free phosphine.<sup>19,29</sup>

Previous work on the dissociation of  $Me_2NR \cdot BH_3$  ( $R = H, Me$ ) in the presence of colloidal  $Rh(0)$  metal has suggested that cleavage of the adduct  $N-B$  bonds either does not occur or occurs to a very small extent.<sup>28</sup> Thus, treatment of the series of adducts  $Me_3N \cdot XH_3$  ( $X = B, Al, Ga$ ) with  $Rh_{colloid}/[Oct_4N]Cl$  was found to result in partial (ca. 6 and 31%) dissociation for the borane and alane, respectively, and complete (100%) dissociation for the gallane as indicated by the  $^1H$  NMR spectra (24 h, 25 °C,  $C_6D_6$ ). Subsequent treatment of these mixtures with  $Me_2NH \cdot BH_3$  was found to result in catalytic dehydrocoupling to yield  $[Me_2N-BH_2]_2$  for the borane case only, while the analogous alane and gallane treated  $Rh$  colloids did not show any significant catalytic activity. One possible explanation to consider is that in the latter cases  $NMe_3$  might be poisoning the catalyst in a manner similar to that of  $PMe_3$ . Significantly, treatment of  $Rh_{colloid}/[Oct_4N]Cl$  with a variety of amines (e.g.  $NEt_3$ ,  $Me_2NH$ , and pyridine) did not show any suppression of catalytic activity toward the dehydrocoupling of  $Me_2NH \cdot BH_3$ . This suggested that the species responsible for the poisoning of the catalyst might be the group 13 hydride species “ $XH_3$ ” instead. Further detailed experiments were therefore performed to test this hypothesis (vide infra). However, first we conclude this section with some further considerations concerning the metal-assisted adduct bond cleavage process.

One might expect that the degree of adduct dissociation in the presence of colloidal metal would be significantly affected by the dissociation energy of the individual adducts, with weaker dative bonds being more prone to dissociation in the presence of elemental metal. For example, the calculated dissociation energies follow the trend:  $Me_3P \cdot GaH_3$  (82.7 kJ/mol) <  $Me_3N \cdot GaH_3$  (102.1 kJ/mol) <  $Me_3N \cdot AlH_3$  (129.2 kJ/mol) <  $Me_3N \cdot$



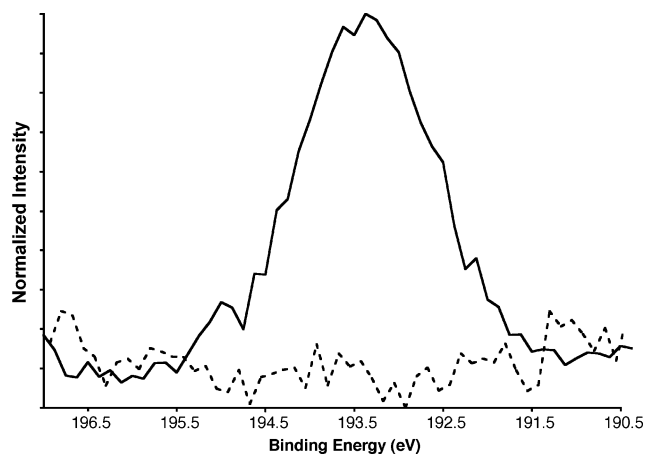
**Figure 1.** Possible coordination modes for  $Me_3E \cdot XH_3$  adducts ( $E = N, P$ ;  $X = B, Al, Ga$ ) with transition metal ( $M$ ) centers.

$BH_3$  (145.6 kJ/mol) <  $Me_3P \cdot BH_3$  (159.4 kJ/mol).<sup>30–33</sup> The extent of dissociation of these adducts was indeed observed to broadly follow the same general trend, with weaker adducts undergoing a higher degree of dissociation in  $C_6D_6$  at 25 °C over 24 h in the presence of  $Rh_{colloid}/[Oct_4N]Cl$ :  $Me_3P \cdot GaH_3$  (100%) =  $Me_3N \cdot GaH_3$  (100%) >  $Me_3N \cdot AlH_3$  (31%) >  $Me_3N \cdot BH_3$  (6%)  $\approx$   $Me_3P \cdot BH_3$  (7%). This dissociation process may proceed via coordination of the  $XH_3$  ( $X = B, Al, Ga$ ) moiety to the surface  $Rh$  atoms by means of the hydridic hydrogen atoms (e.g.  $H^{\delta-}$ ). This coordination might involve the formation of a transient  $\eta^1$ ,  $\eta^2$ , or  $\eta^3$  complex or alternatively by the formation of a  $\sigma$  complex (Figure 1). These types of coordination modes are all well-established in the literature, including, for example, complexes that contain amine- and phosphine-borane adducts.<sup>34</sup> Coordination in this manner may then weaken the adduct dative bond (e.g.  $E \rightarrow X$ ), thereby leading to displacement of the Lewis base and adduct dissociation.<sup>35</sup>

**Treatment of  $Rh_{colloid}/[Oct_4N]Cl$  with  $BH_3 \cdot THF$  and Analysis of the Subsequent Catalytic Dehydrocoupling Activity.** To further explore the potential poisoning effects by “ $BH_3$ ” generated in metal-assisted adduct dissociation reactions, a series of experiments involving colloidal  $Rh$  and  $BH_3 \cdot THF$  were performed. Treatment of  $Rh_{colloid}/[Oct_4N]Cl$ <sup>36</sup> in  $THF$  with excess  $BH_3 \cdot THF$  (ca. 5 equivalents per  $Rh$  atom) was found to result in an immediate reaction as indicated by the release of a gas, which was determined to be  $H_2$  ( $H^{\delta}$  4.46; lit.  $H^{\delta}$  4.46).<sup>37</sup>

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- (34) For  $\eta^1$  complexes, see: (a) Shimoi, M.; Nagai, S. I.; Ichikawa, M.; Kawano, Y.; Katoh, K.; Uruichi, M.; Ogino, H. *J. Am. Chem. Soc.* **1999**, 121, 11704. (b) Kakizawa, T.; Kawano, Y.; Shimoi, M. *Organometallics* **2001**, 20, 3211. (c) Bajko, Z.; Daniels, J.; Gudat, D.; Hap, S.; Nieger, M. *Organometallics* **2002**, 21, 5182. For  $\eta^2$  complexes, see: (d) Khan, K.; Raston, C. L.; McGrady, J. E.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, 16, 3252. (e) Ingleson, M.; Patmore, N. J.; Ruggiero, G. D.; Frost, C. G.; Mahon, M. F.; Willis, M. C.; Weller, A. S. *Organometallics* **2001**, 20, 4434. (f) Volkov, O.; Macfas, R.; Rath, N. P.; Barton, L. *Inorg. Chem.* **2002**, 41, 5837. For  $\eta^3$  complexes, see: (g) White, J. P., III; Deng, H.; Shore, S. G. *Inorg. Chem.* **1991**, 30, 2337. (h) Gozum, J. E.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1992**, 114, 9483. For  $\sigma$  complexes, see: (i) Hartwig, J. F.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. *J. Am. Chem. Soc.* **1996**, 118, 10936. (j) Muhoro, C. N.; He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, 121, 5033. (k) Schlecht, S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, 122, 9435.
- (35) (a) Cowley, A. H.; Mills, J. L. *J. Am. Chem. Soc.* **1969**, 91, 2911. (b) Toyota, S.; Futawaka, T.; Asakura, M.; Ikeda, H.; Oki, M. *Organometallics* **1998**, 17, 4155. (c) In the case of  $Me_3P \cdot BH_3$ , we have recently found evidence for this process in the model reaction with the  $Co(0)$  complex  $Co_2(CO)_8$  which affords first  $Me_3P \cdot Ga[Co(CO)_4]_3$  and subsequently  $Co_2(CO)_6(PMe_3)_2$ . Unpublished results.
- (36) It should be noted that the preparation of  $Rh_{colloid}/[Oct_4N]Cl$  (and the analogous  $Ru$  colloids) involves the use of  $[Oct_4N][BEt_3H]$  as the reducing agent. Thus,  $BEt_3$  is formed as a byproduct, which is fully removed upon workup as indicated by the lack of a  $B(1s)$  peak in the XPS spectrum of the colloidal product. See Figure 2.
- (37) Bohm, V. P. W.; Brookhart, M. *Angew. Chem., Int. Ed.* **2001**, 40, 4694.

(29) In our case, the parts per million difference between free and complexed phosphine amounts to a  $\Delta\delta$  of ca. 48 ppm for  $PMe_3$  on  $Rh$  colloids. For  $PPh_3$  on  $Pt$  and  $Cu$  colloids,  $\Delta\delta$  values of ca. 51–56 and 34 ppm have been observed, respectively. See ref 19.



**Figure 2.** XPS spectra (B(1s) region) of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  before treatment (dashed line) and after treatment with  $\text{BH}_3\cdot\text{THF}$  (solid line).

The  $^{11}\text{B}$  NMR spectrum of the reaction mixture indicated the presence of unreacted  $\text{BH}_3\cdot\text{THF}$  and the formation of the monochlorinated adduct  $\text{BH}_2\text{Cl}\cdot\text{THF}$  ( $\delta$  4.3 ppm), which may arise from reaction with the colloid stabilizing agent  $[\text{Oct}_4\text{N}]\text{Cl}$  as it is the only source of chlorine. Upon subsequent treatment of the solution with  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ , no evidence for any catalytic dehydrocoupling activity was observed by  $^{11}\text{B}$  NMR. Thus, it was apparent that the  $\text{BH}_3\cdot\text{THF}$  was reacting with the Rh colloids to effectively act as a catalyst poison. This poisoning cannot be attributed to a solvent effect in which the THF molecules may block access to the active sites, as removal of the volatiles after the  $\text{BH}_3\cdot\text{THF}$  addition was still found to result in an inactive catalyst when the dehydrocoupling reaction with  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was attempted in toluene. The colloidal catalyst was examined by X-ray photoelectron spectroscopy (XPS) before and after treatment with  $\text{BH}_3\cdot\text{THF}$ . The XPS spectrum of the colloids before treatment showed essentially no boron content as indicated by the lack of a B(1s) peak (Figure 2, dashed line). However, the colloids after treatment with  $\text{BH}_3\cdot\text{THF}$  showed a B(1s) peak at 193.4 eV (Figure 2, solid line) in addition to the expected  $\text{Rh}(3d_{5/2})$  peak at 308.0 eV. Both of these peaks are characteristic of oxide species as they fall into the region typical for  $\text{B}_2\text{O}_3$  (ca. 192–193.5 eV) and  $\text{Rh}_2\text{O}_3$  (ca. 308.5–309 eV).<sup>38</sup> Neglecting the other elements present (e.g. C, Cl, O, and N), the relative atomic concentrations of Rh and B were determined to be approximately in a ratio of 1 to 2.5, respectively. After sputtering the surface with  $\text{Ar}^+$ , it was found that the relative atomic concentrations of Rh increased while that of B decreased, giving a ratio of approximately 1 to 1. This is indicative of a higher concentration of boron on the surface of the colloids and suggests the formation of a passivated surface layer. For example, if the Rh colloids simply catalyzed the decomposition of  $\text{BH}_3\cdot\text{THF}$  into bulk boron (e.g.  $\text{B}_{12}$ ), segregated domains of Rh and B would result. Sputtering with  $\text{Ar}^+$  might then be expected to remove equal quantities of both Rh and B from the surface of these domains, and thus the relative atomic concentrations would not be affected to a great extent. However, this was not observed as there was a substantial decrease in the concentration of B from the surface. Upon sputtering, the B(1s) peak was unchanged but the  $\text{Rh}(3d_{5/2})$  peak was observed at slightly lower energy (307.6 eV), which is

(38) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer: Eden Prairie, MN, 1992.

characteristic of metallic rhodium (cf.  $\text{Rh}(0)$  ca. 307.3 eV)<sup>38</sup> (Figure S1, Supporting Information). It is likely that Rh and B both form oxide layers when the treated colloids were exposed to the atmosphere during preparation of the sample for XPS. However, sputtering with  $\text{Ar}^+$  ions would remove the oxide layer from Rh, resulting in a different binding energy. No change was observed for the B peak, likely due to the fact that an extremely thin film of boron may be formed, which could be entirely converted to boric oxide upon exposure to air.

As to the nature of the passivating boron layer on the surface of the Rh colloid, the formation of rhodium boride may be a distinct possibility. For example, the structure of rhodium boride ( $\text{RhB}$ ) has been determined<sup>39</sup> and metal borides are well-known materials.<sup>40</sup> This boride layer may be formed from a catalyzed decomposition of “ $\text{BH}_3$ ”, similar to a reaction that has been previously reported involving Co particles and  $\text{B}_2\text{H}_6$  in which elemental boron and  $\text{H}_2$  are formed.<sup>41</sup> Another possibility might involve the formation of a metal boryl layer (e.g.  $\text{M}-\text{BH}_2$ )<sup>42</sup> or a bridging structure with a residual terminal hydrogen (e.g.  $\text{M}-\text{B}(\text{H})-\text{M}$ ). However, we were unable to confirm the presence of B–H bonds on the colloids by IR spectroscopy.

**Poisoning of Other Heterogeneous Transition Metal Catalysts by Treatment with  $\text{BH}_3\cdot\text{THF}$ .** To determine the scope of this poisoning behavior toward the catalytic dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ , a variety of heterogeneous transition metal catalysts were pretreated with  $\text{BH}_3\cdot\text{THF}$  and the resulting catalytic dehydrocoupling activities were then explored. For all the metal catalysts tested, their activity toward the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was first verified by performing control experiments. Significantly, the stabilized colloids  $\text{Ru}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$ , the supported species  $\text{Rh}/\text{Al}_2\text{O}_3$  and  $\text{Pd}/\text{C}$  and  $\text{Rh}(0)$  black all displayed a reaction with  $\text{BH}_3\cdot\text{THF}$  (ca. 5 equiv) with the elimination of  $\text{H}_2$  gas. Subsequent addition of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was found to result in the absence of catalytic dehydrocoupling activity for all of the samples, as the expected cyclic dimer  $[\text{Me}_2\text{N}-\text{BH}_2]_2$  was not observed by  $^{11}\text{B}$  NMR. In addition,  $\text{Rh}(0)$  metal prepared using borane or borohydride reducing agents also showed similar poisoning effects. For example, two separate samples of  $\text{Rh}(0)$  metal were prepared from the reaction of  $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]_2$  with  $\text{BH}_3\cdot\text{THF}$  and the reduction of  $\text{RhCl}_3$  with  $\text{Na}[\text{BH}_4]$ . The subsequent addition of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  to each of these potential catalysts was found to result in no observable dehydrocoupling activity (24 h, 25 °C), suggestive of poisoning by the reduction byproduct species  $\text{BH}_2\text{Cl}\cdot\text{THF}$  or  $\text{B}_2\text{H}_6$ . It is likely that poisoning of these catalysts is similar to that observed for  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$ , in which a passivated boron surface layer was formed, thereby preventing subsequent dehydrocoupling.

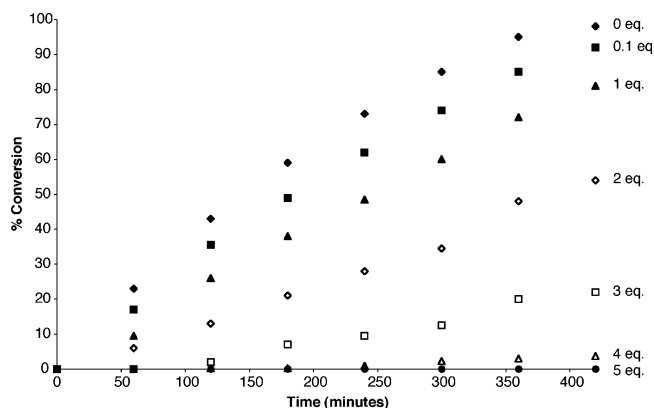
A series of fractional poisoning experiments involving  $\text{Rh}/\text{Al}_2\text{O}_3$  and  $\text{BH}_3\cdot\text{THF}$  were also performed in order to determine how much borane was required to completely passivate the catalyst surface toward catalytic dehydrocoupling over 7 h at

(39) Aronsson, B.; Aselius, J.; Stenberg, E. *Nature* **1959**, *183*, 1318.

(40) Hoard, J. L.; Hughes, R. E. In *The Chemistry of Boron and Its Compounds*; Muettteries, E. L., Ed.; Wiley: New York, 1967; p 25.

(41) Glavee, G. N.; Klabunde, K. J.; Sorensen, C. M.; Hadjippanayis, G. C. *Inorg. Chem.* **1993**, *32*, 474.

(42) For examples involving reactions of B–H bonds at Rh centers, see: (a) Baker, R. T.; Ovenall, D. W.; Harlow, R. L.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *Organometallics* **1990**, *9*, 3028. (b) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350. For a review on metal-boryl complexes see: (c) Braunschweig, H. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1786.



**Figure 3.** Graph of percent conversion vs time for the catalytic dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  using  $\text{Rh}/\text{Al}_2\text{O}_3$  without treatment (◆) or after treatment with 0.1 (■), 1 (▲), 2 (◇), 3 (□), 4 (△) or 5 (●) equiv of  $\text{BH}_3\cdot\text{THF}$  (Rh atom).

25 °C. Thus,  $\text{Rh}/\text{Al}_2\text{O}_3$  was treated with varying quantities of  $\text{BH}_3\cdot\text{THF}$  (0, 0.1, 1, 2, 3, 4, or 5 equiv/(Rh atom)), which was followed by the addition of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  and monitoring of the subsequent dehydrocoupling reaction by  $^{11}\text{B}$  NMR. Figure 3 shows the resulting percent conversion versus time curves. These studies demonstrate that for increasing amounts of  $\text{BH}_3\cdot\text{THF}$  added to the catalyst, there is a corresponding decrease in the dehydrocoupling rate. Thus, it is evident that a significant excess of borane (5 equiv) is required to completely poison the catalyst surface toward dehydrocoupling activity under these conditions. This implies that if a small amount of amine–borane adduct dissociation occurred during dehydrocoupling, the generated free  $\text{BH}_3$  might not affect the catalytic activity to a significant extent. This result can then explain the previous observation that the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  proceeds efficiently using  $\text{Me}_3\text{N}\cdot\text{BH}_3$  treated  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$ , despite there being ca. 6% free  $\text{BH}_3$  present in solution.

**Poisoning of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  by Treatment with Various Other Species Containing B–H Bonds.** The use of other borane species containing B–H bonds was also investigated to determine if they react with heterogeneous metal surfaces to inhibit the catalytic dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ . For example, treatment of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  with 5 equiv of ( $\mu\text{-NMe}_2$ ) $\text{B}_2\text{H}_5$ ,  $[\text{HB-NH}]_3$ ,  $[\text{HB-NMe}]_3$  or 9-BBN (BBN = borabicyclo[3.3.1]nonane) followed by addition of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was found to result in no catalytic dehydrocoupling activity after 20 h. The boranes  $^i\text{Pr}_2\text{N}=\text{BH}_2$  or  $[\text{H}_2\text{B-MeNH}]_3$  were observed to only partially poison the catalyst, with 74 and 61% conversion after the same time period, respectively. The catalyst poisoning may result from reaction with, or adsorption to, the surface Rh atoms and the formation of a protective layer. For example, the boranes ( $\mu\text{-NMe}_2$ ) $\text{B}_2\text{H}_5$ ,  $[\text{HB-NH}]_3$ , and  $[\text{H}_2\text{B-MeNH}]_3$  were all observed to form  $\text{H}_2$  when reacted with the Rh colloids, whereas  $[\text{HB-NMe}]_3$ , 9-BBN, and  $^i\text{Pr}_2\text{N}=\text{BH}_2$  showed no evidence of  $\text{H}_2$  formation. This suggests that the former group may react with the metal surface to poison catalytic activity, while the latter group may simply adsorb to the surface and block the substrate from accessing the active sites. The results involving  $[\text{HB-NH}]_3$ ,  $[\text{HB-NMe}]_3$ , and  $[\text{H}_2\text{B-MeNH}]_3$  are significant as they may explain why the catalytic dehydrocoupling of  $\text{NH}_3\cdot\text{BH}_3$  or  $\text{MeNH}_2\cdot\text{BH}_3$  requires longer reaction times (ca. 3 days) and higher temperatures (45 °C) compared to that of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (ca. 8 h, 25 °C) using identical (pre)-

catalysts.<sup>25</sup> Again, reaction of the B–H bonds at the catalyst surface may effectively poison the active sites and inhibit or suppress the catalytic activity.<sup>43</sup> As partial dehydrocoupling activity was observed for the intermediate  $[\text{H}_2\text{B-MeNH}]_3$ , this implies that the borazine  $[\text{HB-NMe}]_3$  is more effective as a catalyst poison.

We also considered the possibility that the above boranes might poison the active catalyst by adsorption to the surface, rather than reacting at the surface to form a passivated layer. This was investigated by treating  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  with ( $\mu\text{-NMe}_2$ ) $\text{B}_2\text{H}_5$ ,  $[\text{HB-NH}]_3$ , 9-BBN,  $[\text{HB-NMe}]_3$ , or  $^i\text{Pr}_2\text{N}=\text{BH}_2$  followed by removal of these and all other volatile components of the reaction mixture. The results obtained suggested that the poisoning mechanism involved reaction at the surface, as the Rh colloids treated with ( $\mu\text{-NMe}_2$ ) $\text{B}_2\text{H}_5$ ,  $[\text{HB-NH}]_3$ , or 9-BBN displayed no catalytic activity. The dehydrocoupling results involving  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  are identical to those obtained when the excess borane was left in solution (vide supra). For the case of  $[\text{HB-NMe}]_3$  and  $^i\text{Pr}_2\text{N}=\text{BH}_2$ , partial dehydrocoupling (66 and 33%, respectively) was observed, which might imply that the surface reaction is slow or that adsorption to the surface is more significant for these species.

The formation of the borane byproduct  $\text{BEt}_3$  may also be anticipated to affect the catalytic activity of metal colloids that are prepared using “superhydride” reducing agents such as  $\text{M}[\text{BEt}_3\text{H}]$  ( $\text{M} = \text{Li}, [\text{R}_4\text{N}]$ ). Indeed, treatment of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  with  $\text{BEt}_3$  followed by addition of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was found to result in no observable dehydrocoupling. However, when the volatiles were removed prior to adduct addition, partial dehydrocoupling (35%) was observed, suggesting that this may be a surface adsorption phenomenon in this particular case.

**Poisoning of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  by Treatment with  $\text{GaH}_3\cdot\text{OEt}_2$ .** With the poisoning behavior of  $\text{BH}_3\cdot\text{THF}$  and heterogeneous metal catalysts now established for the dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ , it was of interest to examine if similar poisoning behavior would occur with other types of group 13 hydrides species. After  $\text{BH}_3\cdot\text{THF}$ , the next two simplest congener group 13 hydrides are  $\text{AlH}_3\cdot\text{THF}$  and  $\text{GaH}_3\cdot\text{THF}$ . However, both alane and gallane adducts containing oxygen donors such as THF and  $\text{Et}_2\text{O}$  tend to be unstable species.<sup>44</sup> Nevertheless, modification of an existing literature preparation<sup>45</sup> allowed us to synthesize  $\text{GaH}_3\cdot\text{OEt}_2$ . Thus, treatment of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  with  $\text{GaH}_3\cdot\text{OEt}_2$  (ca. 5 equiv) was observed to result in the immediate release of  $\text{H}_2$  gas and the slow formation of Ga metal. Addition of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  to this treated catalyst was found to result in no dehydrocoupling activity after 24 h, as only unreacted starting material was observed in the  $^{11}\text{B}$  NMR spectrum. Again, it is likely that the gallane reacts at the metal surface to form a protective layer that prevents any catalytic dehydrocoupling activity. The gallium metal observed in the reaction mixture

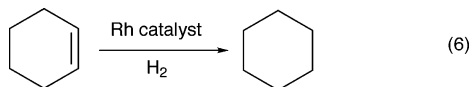
(43) An alternative explanation is that the formation of the dehydrocoupling product (e.g.  $[\text{HB-NH}]_3$ ) may actually block the active catalytic sites by binding to the surface Rh atoms, in a fashion similar to the well-known case of  $(\text{CO})_3\text{Cr}(\text{RB-NR}')_3$  in which the borazine ring is bound to the metal center through the nitrogen atoms. See: Lagowski, J. J. *Coord. Chem. Rev.* **1977**, *22*, 185. However, dissociation of the bound borazine may require higher reaction temperatures in order to generate an active site where dehydrocoupling could occur. An equilibrium between bound and unbound borazine on the Rh surface might help to suppress the catalysis, resulting in much longer dehydrocoupling times for  $\text{NH}_3\cdot\text{BH}_3$ .

(44) Unfortunately, attempts to prepare stable solutions of  $\text{AlH}_3\cdot\text{OEt}_2$  in our laboratory have been unsuccessful to date, and thus the reactivity of this species with heterogeneous metal catalysts could not be investigated.

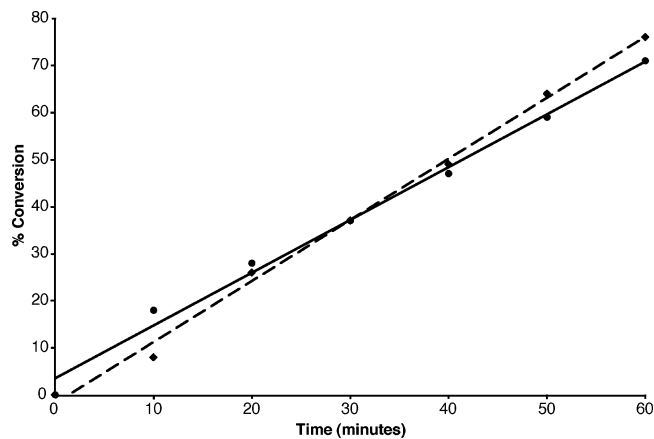
(45) Shriver, D. F.; Parry, R. W.; Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorg. Chem.* **1963**, *2*, 867.

may arise from the thermal (25 °C) decomposition of GaH<sub>3</sub>·OEt<sub>2</sub> over time or from a metal-catalyzed decomposition process as the gallane–etherate is prone to decompose in the presence of trace impurities.<sup>46</sup>

**Influence of Borane Treatment on the Activity of Heterogeneous Catalysts for Other Transformations. (i) Catalytic Hydrogenation with Borane Treated, Heterogeneous Rh Catalysts.** It has been previously demonstrated that colloids or nanoclusters and oxide-supported metals are very efficient heterogeneous catalysts for the hydrogenation of olefins.<sup>2</sup> It was of interest to determine if treatment of these catalysts with BH<sub>3</sub>·THF would lead to surface passivating boron layers, which could poison the catalyst surface and inhibit hydrogenation reactivity. This type of poisoning behavior might be of profound significance, as one of the most common routes to heterogeneous metal colloids or nanoclusters used in catalysis involves the reduction of transition metal salts using borohydride reducing agents such as Na[BH<sub>4</sub>], Li[BH<sub>4</sub>], or [R<sub>4</sub>N][BEt<sub>3</sub>H] (R = long-chain alkyl group).<sup>5e,f,7a,8b,c,e,10c,47c,48</sup> If the byproducts from these reduction reactions (e.g. B<sub>2</sub>H<sub>6</sub> or BEt<sub>3</sub>) react with the generated metal catalyst to form a passivated layer, a significant reduction in the observed catalytic activity might result. Thus, the hydrogenation of cyclohexene to cyclohexane (eq 6) under H<sub>2</sub> was monitored using untreated and BH<sub>3</sub>·THF treated (5 equiv) Rh/Al<sub>2</sub>O<sub>3</sub> as a catalyst at 25 °C. However, it was found that the relative rate of hydrogenation was comparable for trials involving both untreated and treated catalysts after 1 h of reaction time (Figure 4). Thus, it can be concluded that treatment of Rh/Al<sub>2</sub>O<sub>3</sub> with BH<sub>3</sub>·THF does not poison the surface of the catalyst toward catalytic hydrogenation, in stark contrast to the case of catalytic dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub>.<sup>49</sup>

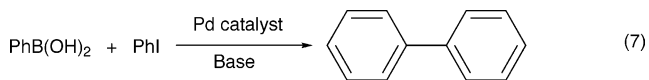


**(ii) Suzuki Coupling with Borane Treated, Heterogeneous Pd Catalysts.** Pd colloids and nanoclusters have been previously shown to be excellent catalysts in C–C bond forming reactions such as Suzuki cross-coupling.<sup>10e,50</sup> It was of interest to determine if treatment of these types of catalysts with BH<sub>3</sub>·THF could poison the catalyst surface and inhibit the cross-



**Figure 4.** Graph of percent conversion vs time for the catalytic hydrogenation of cyclohexene under H<sub>2</sub> using Rh/Al<sub>2</sub>O<sub>3</sub> without treatment (◆, dashed line) or after treatment with 5 equiv of BH<sub>3</sub>·THF (Rh atom) (●, solid line).

coupling reactivity. This was tested by using Pd(0) metal formed by three different reducing agents (BH<sub>3</sub>·THF, EtOH, and H<sub>2</sub>) followed by an evaluation of the catalytic activity in a Suzuki reaction involving phenylboronic acid and iodobenzene at 100 °C (eq 7). For example, treatment of H<sub>2</sub>PdCl<sub>4</sub> with BH<sub>3</sub>·THF resulted in the formation of a black precipitate of Pd(0) metal. Use of this precipitate as a catalyst was found to result in the formation of biphenyl in an isolated yield of 45%. However, similar yields were observed for Pd(0) catalysts formed via EtOH and H<sub>2</sub> reduction methods (44 and 52%, respectively). This implies that there is no poisoning effect by BH<sub>3</sub>·THF for this particular catalytic reaction.



## Summary

Metal-assisted dissociation reactions of group 13 – group 15 adducts have been shown to generate both well-known heterogeneous catalyst poisons, such as free phosphines (e.g. PMe<sub>3</sub>), and also the group 13 hydride species EH<sub>3</sub> (E = B, Al, Ga) via the formation of a passivating boron/boride layer. Analogous poisoning effects were noted in the cases of heterogeneous Ru and Pd catalysts. These results explain the need for higher temperatures and longer reaction times for the synthesis of certain borazines such as [HB–NH]<sub>3</sub> from NH<sub>3</sub>·BH<sub>3</sub> by catalytic dehydrocoupling as this product also exhibits a significant poisoning effect. The results also strongly imply that catalyst poisoning/surface passivation effects need to be carefully considered in catalytic reactions in which heterogeneous transition metal catalysts are prepared using the commonly applied borane or borohydride reduction procedures. Although no analogous poisoning effects were observed for the hydrogenation and Suzuki coupling reactions we studied using colloidal metal treated with, or prepared using BH<sub>3</sub>·THF, the formation of boron layers and the potential for surface passivation is likely of direct relevance for many other reactions and in materials science applications.<sup>51,52</sup>

## 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

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dry nitrogen unless otherwise specified. THF and Et<sub>2</sub>O were dried over Na/benzophenone and distilled prior to use. Toluene was dried via the Grubb's method.<sup>53</sup> ACS grade EtOH, pentane, and CH<sub>3</sub>CN were used without further purification. PhB(OH)<sub>2</sub>, PhI, sodium acetate, NEt<sub>3</sub>, NMe<sub>3</sub>, Me<sub>2</sub>NH (2.0 M in THF) BH<sub>3</sub>·THF (1.0 M in THF), PMe<sub>3</sub> (1.0 M in toluene), Rh/Al<sub>2</sub>O<sub>3</sub> (5 wt % Rh), Pd/C (10 wt % Pd), 9-BBN (0.5 M in THF), BEt<sub>3</sub> (1.0 M in THF), GaCl<sub>3</sub>, Me<sub>3</sub>N·BH<sub>3</sub> (Aldrich), Rh(0) black (Strem), and PdCl<sub>2</sub> (Pressure) were purchased and used as received. Pyridine (Aldrich) was dried over Na and distilled prior to use. Me<sub>2</sub>NH·BH<sub>3</sub> (Strem) was purified by sublimation at 25 °C. Li-[AlH<sub>4</sub>] (Aldrich) was purified by dissolving a sample in Et<sub>2</sub>O, followed by filtration and solvent removal to afford a white powder. Me<sub>3</sub>P·GaH<sub>3</sub>,<sup>54</sup> Me<sub>3</sub>N·AlH<sub>3</sub>,<sup>55</sup> Me<sub>3</sub>P·BH<sub>3</sub>,<sup>56</sup> Me<sub>3</sub>N·GaH<sub>3</sub>,<sup>57</sup> M<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl (M = Rh, Ru),<sup>4b</sup> (μ-NMe<sub>2</sub>)<sub>2</sub>B<sub>2</sub>H<sub>5</sub>,<sup>58</sup> [HB-NH]<sub>3</sub>,<sup>59</sup> iPr<sub>2</sub>N=BH<sub>2</sub>,<sup>25b</sup> [MeN-BH]<sub>3</sub>,<sup>25b</sup> [MeNH-BH<sub>2</sub>]<sub>3</sub>,<sup>60</sup> and [Rh(1,5-cod)(μ-Cl)]<sub>2</sub><sup>61</sup> 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 (<sup>1</sup>H, <sup>13</sup>C) or external BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B) or H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) references. NMR spectra were obtained at 300 MHz (<sup>1</sup>H), 96 MHz (<sup>11</sup>B), 75 MHz (<sup>13</sup>C) or 121 MHz (<sup>31</sup>P). Silicon(100) substrates were purchased from Wafer World Inc. and cleaned by successive sonication treatments in CH<sub>2</sub>Cl<sub>2</sub>, 2-propanol, piranha solution (H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>, 1:3 vol. %; *caution: extremely corrosive!*), and deionized water followed by drying in air. XPS samples were solution deposited onto a clean silicon substrate and analyzed on a PHI 5500 ESCA system. A Mg Kα source with a photon energy of 1253.6 eV was used and recorded at a photoelectron takeoff angle of 45°. The peak positions were aligned and corrected for charge effects based on an adventitious C(1s) peak position at 284.8 eV. For depth profiling analysis, an Ar<sup>+</sup> ion beam of 3 keV was used for 15 min and the spectra were reacquired.

**Treatment of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl with Me<sub>3</sub>E·XH<sub>3</sub> (E = N, P; X = B, Al, Ga).** A typical reaction was performed as follows: A solution of Me<sub>3</sub>E·XH<sub>3</sub> (ca. 0.03 g) in C<sub>6</sub>D<sub>6</sub> (0.75 mL) was stirred at 25 °C for 18 h. The presence or absence of free EMe<sub>3</sub> was determined by <sup>1</sup>H NMR (i). Solid Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl (ca. 0.002 g) was then added, and the mixture was stirred for 24 h. Again, the presence or absence of free EMe<sub>3</sub> was determined by <sup>1</sup>H NMR (ii). Solid Me<sub>2</sub>NH·BH<sub>3</sub> (ca. 0.05 g) was then added, and the mixture was stirred for 24 h. Integration of the product ([Me<sub>2</sub>N-BH<sub>2</sub>]<sub>2</sub>, <sup>δ</sup> 5 ppm) and reactant (Me<sub>2</sub>NH·BH<sub>3</sub>, <sup>δ</sup> -13 ppm) resonances in the <sup>11</sup>B NMR spectrum was used to determine the extent of the catalytic dehydrocoupling reaction (iii).

For Me<sub>3</sub>N·BH<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 2.4$  (br q,  $J_{\text{HB}} = 98$  Hz, BH<sub>3</sub>), 2.01 (s, NMe<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -7.7$  (s). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 53.9$ . (i) 0% dissociation. (ii) 6% dissociation into NMe<sub>3</sub>. (iii) 95% [Me<sub>2</sub>N-BH<sub>2</sub>]<sub>2</sub>, 5% unreacted Me<sub>2</sub>NH·BH<sub>3</sub>, and Me<sub>3</sub>N·BH<sub>3</sub>.

For Me<sub>3</sub>N·AlH<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 4.01$  (br, AlH<sub>3</sub>), 1.84 (s, NMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 47.7$ . (i) 0% dissociation. (ii) 31% dissociation into NMe<sub>3</sub>. (iii) 100% unreacted Me<sub>2</sub>NH·BH<sub>3</sub>.

(51) One example may be metal-catalyzed hydroboration reactions, which also involve the use of reactants with B-H bonds. See ref 52. Interestingly, the metal-catalyzed hydroboration of 1-octene has been recently reported using Rh(0) metal formed in situ by the reaction of RhCl<sub>3</sub> with BH<sub>3</sub>·THF. Morrill, T. C.; D'Souza, C. A. *Organometallics* **2003**, *22*, 1626. However, to date, the exact nature of the active catalyst was not determined, and our results suggest that a homogeneous catalyst may need to be considered as the actual species responsible for the catalysis.

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For Me<sub>3</sub>N·GaH<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 5.00$  (br, GaH<sub>3</sub>), 1.84 (s, NMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 49.8$ . (i) 0% dissociation. (ii) 100% dissociation. (iii) 89% unreacted Me<sub>2</sub>NH·BH<sub>3</sub>, 9% Me<sub>3</sub>N·BH<sub>3</sub> (via amine exchange) and 2% [Me<sub>2</sub>N-BH<sub>2</sub>]<sub>2</sub>.

For Me<sub>3</sub>P·BH<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.32$  (qd,  $J_{\text{HB}} = 95$  Hz,  $J_{\text{HP}} = 15$  Hz), 0.64 (d,  $J_{\text{HP}} = 10.5$  Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -36.9$  (d,  $J_{\text{BP}} = 62$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 12.7$  (d,  $J_{\text{CP}} = 37$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -2.15$  (q,  $J_{\text{PB}} = 59$  Hz). (i) 0% dissociation. (ii) 7% dissociation into PMe<sub>3</sub>. (iii) 92% unreacted Me<sub>2</sub>NH·BH<sub>3</sub>, 8% [Me<sub>2</sub>N-BH<sub>2</sub>]<sub>2</sub> and Me<sub>3</sub>P·BH<sub>3</sub>.

For Me<sub>3</sub>P·GaH<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 4.30$  (br, GaH<sub>3</sub>), 0.59 (d,  $J_{\text{HP}} = 7.5$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 11.7$ . <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -40.2$  (s). (i) 0% dissociation. (ii) 100% dissociation into PMe<sub>3</sub>. (iii) 100% unreacted Me<sub>2</sub>NH·BH<sub>3</sub>.

For NMe<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 2.06$  (s). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 48.1$ .

For PMe<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.78$  (s). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 15.3$ . <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -61$  (s).

**PMe<sub>3</sub> Ligation to Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl; Preparation of {Rh<sub>colloid</sub>-(PMe<sub>3</sub>)/[Oct<sub>4</sub>N]Cl}.** (a) To a solution of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl (0.012 g, ca. 0.058 mmol Rh) in THF (1 mL), a solution of PMe<sub>3</sub> in toluene (0.12 mL, 0.12 mmol, ca. 2 equiv/(Rh atom)) was added, and the mixture was stirred for 7 h at 25 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (THF):  $\delta = -10$  (m, {Rh<sub>colloid</sub>(PMe<sub>3</sub>)/[Oct<sub>4</sub>N]Cl}), -61 (s, PMe<sub>3</sub>). Treatment of this solution with Me<sub>2</sub>NH·BH<sub>3</sub> (ca. 0.1 g) was found to result in no dehydrocoupling activity (24 h, 25 °C), indicative of PMe<sub>3</sub> poisoning.

(b) To a solution of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl (0.002 g, ca. 0.01 mmol of Rh) in THF (1 mL), a solution of Me<sub>3</sub>P·BH<sub>3</sub> (0.016 g, 0.18 mmol) in THF (1 mL) was added, and the mixture was stirred for 18 h at 25 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (THF):  $\delta = -0.7$  (q, Me<sub>3</sub>P·BH<sub>3</sub>), -10 (m, {Rh<sub>colloid</sub>-(PMe<sub>3</sub>)/[Oct<sub>4</sub>N]Cl}), -61 (s, PMe<sub>3</sub>).

**Attempted Poisoning of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl by the Nitrogen Donors Me<sub>2</sub>NH, NEt<sub>3</sub>, and Pyridine.** A typical reaction was performed as follows: To a solution of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl (0.005 g, ca. 0.02 mmol of Rh) in THF (1 mL), a solution of Me<sub>2</sub>NH in THF (1.5 mL, 3.0 mmol, ca. 150 equiv/(Rh atom)) was added at 25 °C. The mixture was stirred for 6 h, and then Me<sub>2</sub>NH·BH<sub>3</sub> (0.109 g, 1.85 mmol) was added as a solid. After 18 h, only unreacted Me<sub>2</sub>NH·BH<sub>3</sub> was observed in the <sup>11</sup>B NMR spectrum. Similar results were obtained using NEt<sub>3</sub> and pyridine.

**Reaction of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl with BH<sub>3</sub>·THF.** To a solution of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl (0.045 g, ca. 0.22 mmol of Rh) in THF (1 mL), a solution of BH<sub>3</sub>·THF (1.0 mL, 1.0 mmol, ca. 5 equiv/(Rh atom)) was added at 25 °C. An immediate reaction was observed with the formation of bubbles and the release of a gas. <sup>11</sup>B NMR (THF):  $\delta = 4.3$  (t,  $J_{\text{BH}} = 139$  Hz; lit. 4.6,  $J_{\text{BH}} = 135$  Hz;<sup>62</sup> BH<sub>2</sub>Cl·THF, ca. 11%), 0.6 (q, BH<sub>3</sub>·THF, ca. 85%), -30.0 (s, unidentified product, ca. 4%). The gas was identified as being H<sub>2</sub> by <sup>1</sup>H NMR ( $\delta$  4.46). After 2 h, the reaction mixture was evaporated to dryness, and the black residue was washed with toluene (2 × 10 mL). The toluene washings were found to contain [Oct<sub>4</sub>N]Cl by <sup>1</sup>H NMR (<sup>1</sup>H  $\delta = 3.95$  (m), 1.59 (m), 1.34 (m), 0.93 (m)). The residue was dried *in vacuo* to yield a black powder (0.048 g) that was only slightly soluble in THF. XPS: Rh (308.0 eV, relative atomic concentration = 28.3%), B (193.4 eV, relative atomic concentration = 71.7%). After Ar<sup>+</sup> sputter: Rh (307.6 eV, relative atomic concentration = 42.7%), B (193.4, relative atomic concentration = 57.3%).

**Attempted Catalytic Dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub> Using BH<sub>3</sub>·THF Treated Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl.** To a solution of Rh<sub>colloid</sub>/[Oct<sub>4</sub>N]Cl (0.008 g, ca. 0.04 mmol Rh) in THF (1 mL), a solution of BH<sub>3</sub>·THF (0.18 mL, 0.18 mmol) in THF was added at 25 °C. After 2 h, solid Me<sub>2</sub>NH·BH<sub>3</sub> (0.087 g) was added and the mixture was left to stir at 25 °C. After 18 h, only unreacted Me<sub>2</sub>NH·BH<sub>3</sub> was observed in the <sup>11</sup>B NMR spectrum. In a repeat trial, the volatiles were removed after the addition of BH<sub>3</sub>·THF. The addition of solid Me<sub>2</sub>NH·BH<sub>3</sub> was found to result in no dehydrocoupling activity.



**Treatment of Heterogeneous Transition Metal Catalysts with  $\text{BH}_3\cdot\text{THF}$  and Attempted Catalytic Dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .** (a) A typical reaction was performed as follows: To a solution of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  (0.008 g, ca. 0.06 mmol of Ru) in THF (1 mL), a solution of  $\text{BH}_3\cdot\text{THF}$  (0.30 mL, 0.30 mmol, ca. 5 equiv/(Ru atom)) was added at 25 °C. An immediate reaction was observed with the formation of bubbles and the release of a gas ( $\text{H}_2$ ,  $^1\text{H}$   $\delta$  4.46). After 4 h,  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (0.050 g, 0.85 mmol) was added and the mixture was stirred at 25 °C. After ca. 20 h, only unreacted  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was observed in the  $^{11}\text{B}$  NMR spectrum. Other heterogeneous catalysts tested were  $\text{Rh}/\text{Al}_2\text{O}_3$ , Pd/C and Rh(0) black which all showed similar poisoning behavior.

(b) Blank reactions of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$ ,  $\text{Rh}/\text{Al}_2\text{O}_3$ , Pd/C, and Rh(0) black were performed to verify their catalytic activity toward  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  dehydrocoupling. In all cases, complete dehydrocoupling was observed after 24 h at 25 °C.

**Preparation of Rh(0) Metal by Reaction of  $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$  with  $\text{BH}_3\cdot\text{THF}$  and Attempted Catalytic Dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .** To a solution of  $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$  (0.020 g, 0.041 mmol) in THF (1 mL), a solution of  $\text{BH}_3\cdot\text{THF}$  in THF (0.41 mL, 0.41 mmol) was added at 25 °C. The solution immediately turned black, and the evolution of a gas and the formation of a black precipitate were both observed.  $^{11}\text{B}$  NMR (THF):  $\delta = 7.2$  (d,  $J_{\text{BH}} = 164$  Hz; lit. 7.0,  $J_{\text{BH}} = 162$  Hz;  $\text{BHCl}_2\cdot\text{THF}$ , ca. 15%),<sup>63</sup> 4.3 ( $\text{BH}_2\text{Cl}\cdot\text{THF}$ , ca. 85%).<sup>62</sup> Solid  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (0.054 g, 0.92 mmol) was added, and the mixture was stirred at 25 °C overnight. After 24 h, the  $^{11}\text{B}$  NMR spectrum of the reaction mixture indicated only the presence of unreacted  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .

**Preparation of Rh(0) Metal by Reaction of  $\text{RhCl}_3$  with  $\text{Na}[\text{BH}_4]$  and Attempted Catalytic Dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .** To a solution of  $\text{RhCl}_3$  (0.050 g, 0.24 mmol) in THF (2 mL), a solution of  $\text{Na}[\text{BH}_4]$  (0.027 g, 0.73 mmol) in THF (2 mL) was added at 25 °C. The solution turned black over ca. 5 min, and the evolution of a gas and the formation of a black precipitate were both observed. After 24 h,  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (ca. 0.1 g) was added and stirred. The  $^{11}\text{B}$  NMR spectrum indicated no dehydrocoupling activity after 24 h at 25 °C.

**Treatment of  $\text{Rh}/\text{Al}_2\text{O}_3$  with  $\text{BH}_3\cdot\text{THF}$  and Effect on the Rate of Catalytic Dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .** To a suspension of  $\text{Rh}/\text{Al}_2\text{O}_3$  (ca. 0.05 g) in toluene (2 mL), a solution of  $\text{BH}_3\cdot\text{THF}$  (0, 0.1, 1, 2, 3, 4, or 5 equiv) was added via microsyringe. The solution was stirred for 18 h at 25 °C, and then  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (ca. 0.15 g) was added as a solid. The dehydrocoupling reaction was monitored by removing a small aliquot of solution, diluting with toluene, and obtaining the  $^{11}\text{B}$  NMR spectrum. The percent conversion was calculated from the integration of the product ( $^{\text{B}}\delta$  5 ppm) and reactant ( $^{\text{B}}\delta$  -13 ppm) resonances.

**Treatment of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  with Various Boranes and Attempted Catalytic Dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .** (a) A typical reaction was performed as follows: To a solution of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  (0.008 g, ca. 0.06 mmol of Rh) in THF (1 mL), a solution of  $(\mu\text{-NMe}_2)\text{B}_2\text{H}_5$  (0.025 g, 0.35 mmol, ca. 5 equiv/(Rh atom)) in THF (1 mL) was added at 25 °C. When the reaction was repeated in  $\text{C}_6\text{D}_6$ , the presence of  $\text{H}_2$  was detected in solution by  $^1\text{H}$  NMR. The mixture was stirred 4 h; then  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (0.053 g, 0.90 mmol) was added as a solid. After ca. 20 h, only unreacted  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was observed in the  $^{11}\text{B}$  NMR spectrum.

For  $[\text{HB}-\text{NH}]_3$ :  $\text{H}_2$  observed; no dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .

For  $[\text{MeN}-\text{BH}]_3$ : no  $\text{H}_2$  observed; no dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .

For  $[\text{MeNH}-\text{BH}_2]_3$ :  $\text{H}_2$  observed; 61% dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .

For 9-BBN: no  $\text{H}_2$  observed; no dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .

For  $^i\text{Pr}_2\text{N}=\text{BH}_2$ : no  $\text{H}_2$  observed; 74% dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .

For  $\text{BEt}_3$ : no dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .

(b) The above experiments were repeated by treating  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  with the appropriate borane, followed by removal of volatiles. The residue was redissolved in THF,  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was added and the mixture stirred for 24 h. For  $(\mu\text{-NMe}_2)\text{B}_2\text{H}_5$ ,  $[\text{HB}-\text{NH}]_3$ , and 9-BBN, no dehydrocoupling was observed. For  $[\text{HB}-\text{NMe}]_3$ ,  $^i\text{Pr}_2\text{N}=\text{BH}_2$ , and  $\text{BEt}_3$ , only 66, 33, and 35% dehydrocoupling were observed, respectively.

**Preparation of  $\text{GaH}_3\cdot\text{OEt}_2$ .**  $\text{GaH}_3\cdot\text{OEt}_2$  was prepared by a modified literature procedure.<sup>45</sup> A solution of  $\text{GaCl}_3$  (0.167 g, 0.948 mmol) in  $\text{Et}_2\text{O}$  (5 mL) was added dropwise to a solution of  $\text{Li}[\text{AlH}_4]$  (0.109 g, 2.87 mmol, 3 equiv) in  $\text{Et}_2\text{O}$  (10 mL) at 0 °C. The formation of a white precipitate was observed. The mixture was stirred for 2 h at 0 °C and then stored overnight at -20 °C in order to completely decompose the proposed intermediate mixed hydride  $[\text{Ga}(\text{AlH}_4)_3]$ .<sup>46</sup> The solution was quickly filtered cold to afford a colorless solution of  $\text{GaH}_3\cdot\text{OEt}_2$  (ca. 0.059 M based on 100% yield) that was stored at -55 °C to prevent decomposition. An NMR sample was prepared by removing the solvent at -78 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 4.01$  (br s,  $\text{GaH}_3$ ), 3.30 (s,  $\text{OCH}_2$ ), 1.05 (s,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 66.5$  ( $\text{OCH}_2$ ), 15.6 ( $\text{CH}_3$ ). Note: The  $^1\text{H}$  NMR spectrum did not give acceptable integration values, as a small amount of decomposition into  $\text{Ga}(\text{s})$ ,  $\text{H}_2$ , and  $\text{Et}_2\text{O}$  was consistently observed.

**Treatment of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  with  $\text{GaH}_3\cdot\text{OEt}_2$  and Attempted Catalytic Dehydrocoupling of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ .** To a solution of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  (0.005 g, ca. 0.03 mmol Rh) in THF (1 mL), a solution of  $\text{GaH}_3\cdot\text{OEt}_2$  (2.5 mL, ca. 0.15 mmol, ca. 5 equiv/(Rh atom)) in  $\text{Et}_2\text{O}$  was added at 25 °C. The formation of bubbles and the release of a gas ( $\text{H}_2$ ,  $^1\text{H}$   $\delta$  4.46) was immediately observed. The slow formation of a gray powder was also observed, which was attributed to gallium metal. The mixture was stirred for 2 h; then  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (0.098 g, 1.7 mmol) was added. Upon stirring at 25 °C for 24 h, only unreacted  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  was observed in the  $^{11}\text{B}$  NMR spectrum.

**Treatment of  $\text{Rh}/\text{Al}_2\text{O}_3$  with  $\text{BH}_3\cdot\text{THF}$  and Evaluation of the Catalytic Hydrogenation Activity.** To a suspension of  $\text{Rh}/\text{Al}_2\text{O}_3$  (ca. 0.05 g) in THF (2 mL) in a 10 mL vial, a solution of  $\text{BH}_3\cdot\text{THF}$  (5 equiv/(Rh atom)) was added via syringe. The solution was stirred for 2 h at 25 °C, and the volatiles were removed. A solution of cyclohexene (ca. 0.15 g) in  $\text{C}_6\text{D}_6$  (1 mL) was added to the black residue, and the vial was capped with a septum. The solution was frozen using liquid nitrogen, and the headspace of the vial was evacuated. The vial was refilled with pressurized  $\text{H}_2$  gas (ca. 0.1 atm) to commence the hydrogenation reaction. The reaction was monitored by periodically removing a small aliquot of solution (50  $\mu\text{L}$ ) and running the  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  via integration of the product and reactant signals. A control experiment was performed in a similar manner, except that the catalyst was not treated with  $\text{BH}_3\cdot\text{THF}$ .

For cyclohexene.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 5.69$  (s,  $\text{CH}=\text{CH}$ ), 1.90 (m,  $\text{CH}_2$ ), 1.51 (m,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 127.7$  ( $\text{CH}=\text{CH}$ ), 25.8 ( $\text{CH}_2$ ), 23.3 ( $\text{CH}_2$ ).

For cyclohexane.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 1.40$  (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 27.6$ .

**Evaluation of Boron Content by XPS for Poisoned  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  Catalyst after Hydrogenation.** To a solution of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  (0.082 g, ca. 0.26 mmol Rh) in THF (2 mL), a solution of  $\text{BH}_3\cdot\text{THF}$  (1.3 mL, 1.3 mmol, ca. 5 equiv/(Rh atom)) was added and stirred overnight at 25 °C. The solution was split equally into two fractions. The first fraction was pumped to dryness, washed with toluene (5 mL), and dried *in vacuo*. The black residue was suspended in toluene and deposited onto a clean Si substrate, and the volatiles were removed under vacuum for 16 h. The second fraction was stirred under a hydrogen atmosphere for 3 h, followed by the same workup procedure for the above blank sample. The XPS spectra for both fractions showed the presence of boron on the surface of the catalyst.

**Evaluation of Catalytic Dehydrocoupling Activity for Poisoned  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  Catalyst after Hydrogenation.** To a solution of

(63) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1976**, *98*, 1798.

$\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  (0.004 g, ca. 0.013 mmol Rh) in THF (2 mL), a solution of  $\text{BH}_3\cdot\text{THF}$  (0.65 mL, 0.65 mmol, ca. 5 equiv/(Rh atom)) was added. The volatiles were removed after 1 h; the black residue redissolved in toluene (2 mL) and stirred under a hydrogen atmosphere for 3 h. Solid  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (0.120 g, 2.04 mmol) was then added, and the reaction was stirred under  $\text{N}_2$  at 25 °C. After 16 h, the  $^{11}\text{B}$  NMR spectrum showed that only 4% of the dehydrocoupling product  $[\text{Me}_2\text{N}-\text{BH}_2]_2$  was present.

**Preparation of Pd(0) Metal via  $\text{BH}_3\cdot\text{THF}$ , EtOH, or  $\text{H}_2$  Reduction and Evaluation of Suzuki Coupling Activity.** A solution of  $\text{H}_2\text{PdCl}_4$  (0.002 M) was prepared by the addition of 0.2 M HCl (6 mL) to a solution of  $\text{PdCl}_2$  (0.090 g) in water (100 mL), followed by dilution to 250 mL in air.<sup>9e</sup> The solvent was removed from a 15 mL portion of this to give a red solid, which was redissolved in THF (15 mL). To this solution under  $\text{N}_2$ , a solution of  $\text{BH}_3\cdot\text{THF}$  in THF (0.45 mL) was added dropwise via syringe at 25 °C. A black precipitate of Pd(0) was formed immediately. After 1 h, the solution was decanted and the precipitate washed with THF (10 mL) and dried under vacuum. A solution of  $\text{PhB}(\text{OH})_2$  (6 mmol),  $\text{PhI}$  (2 mmol), and sodium acetate (7 mmol) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3:1, 35 mL) was added to the Pd(0) residue. The mixture was sonicated for 1 min to give a fine dispersion of Pd(0), and the mixture was refluxed at 100 °C for 16 h under air. The product was extracted with pentane and dried over  $\text{MgSO}_4$  and the solvent removed to give biphenyl as a white solid in 45% yield (crude).

For the reduction of  $\text{H}_2\text{PdCl}_4$  with EtOH, EtOH (10 mL) was added to the THF solution of  $\text{H}_2\text{PdCl}_4$  and the mixture was refluxed at 100 °C for 16 h. A similar procedure was followed for the Suzuki coupling, with an isolated yield of 44%. For the reduction of  $\text{H}_2\text{PdCl}_4$  with  $\text{H}_2$ , the THF solution of  $\text{H}_2\text{PdCl}_4$  was stirred under a  $\text{H}_2$  atmosphere for 1 h at 25 °C. A similar procedure was followed for the Suzuki coupling, with an isolated yield of 52%.

For Ph–Ph.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.71$  (m), 7.54 (m), 7.45 (m).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 141.5, 129.0, 127.5, 127.4$ .

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**Supporting Information Available:** XPS spectrum (Rh region) of  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  after treatment with  $\text{BH}_3\cdot\text{THF}$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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