

Catalytic Dehydrocoupling of Amine-Borane and Phosphine-Borane Adducts: The Mechanism Is Heterogeneous in One Case and Homogeneous in the Other

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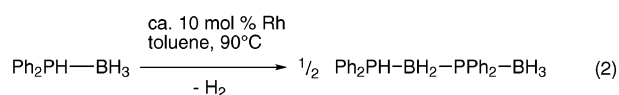
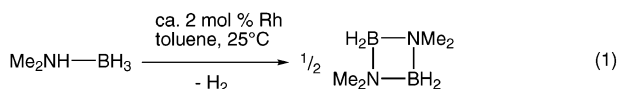
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The development of metal-catalyzed reactions revolutionized synthetic organic chemistry in the latter part of the 20th century. In contrast, metal-catalyzed processes are still relatively unexplored in inorganic chemistry but are highly desirable, as currently available synthetic strategies are often haphazard, of limited scope, or are restricted to salt elimination reactions. The long-term development of new catalytic chemistry involving inorganic elements is likely to benefit from mechanistic studies, which should help to advance this promising field.¹

Recently, we have shown that the heterodehydrocoupling of phosphine-borane adducts $RR'PH\cdot BH_3$ can be catalyzed by a variety of Rh complexes, providing facile routes to phosphinoborane rings, chains, and high molecular weight polymers $[RR'P-BH_2]_n$.² We have recently extended this work to the Rh-catalyzed dehydrocoupling of amine-borane adducts $RR'NH\cdot BH_3$, which provide a mild and convenient route to cycloaminoboranes $[RR'N-BH_2]_2$ and borazines $[RN-BH]_3$.³ In the latter case, we provided some evidence for the operation of a heterogeneous mechanism involving colloidal Rh(0) metal.^{3b} In this Communication, we present detailed comparative studies of the catalytic dehydrocoupling of a phosphine-borane adduct and an amine-borane adduct which, remarkably, suggest that the mechanism for the former involves homogeneous catalysis.

The problem of distinguishing true homogeneous catalysis from soluble or insoluble metal-particle heterogeneous catalysis has attracted much recent attention.⁴ In particular, platinum-catalyzed hydrosilylation,⁵ alkene or arene hydrogenation,⁶ ring-opening polymerization,^{7a} and cross-coupling reactions^{7b} have been studied in detail. Finke and co-workers have proposed a general approach to address this problem by performing a series of tests involving reaction kinetics, transmission electron microscopy (TEM) imaging, poisoning experiments, filtration, catalyst isolation, etc.⁸ We have used this approach to address the question 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 $[Rh(1,5-cod)(\mu-Cl)]_2$ as the most frequently used precatalyst.



As noted previously, treatment of $Me_2NH\cdot BH_3$ with catalytic amounts of $[Rh(1,5-cod)(\mu-Cl)]_2$ (ca. 2 mol %) resulted in a color change from orange to black, with the slow formation of a black precipitate. Analysis by TEM revealed the presence of ca. 2 nm

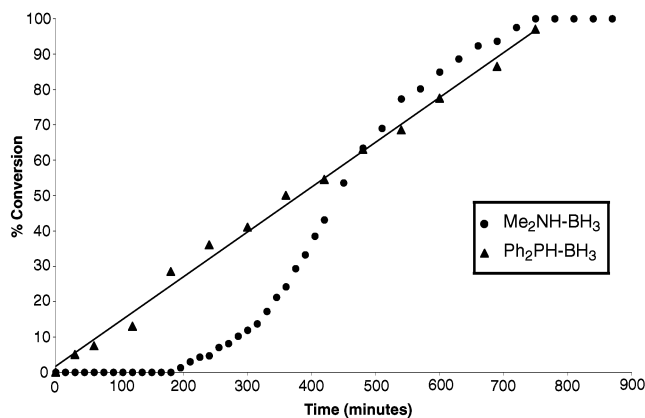


Figure 1. Graph of % conversion versus time for the catalytic dehydrocoupling of $Me_2NH\cdot BH_3$ (●, 2 mol % Rh, toluene, 25 °C) and $Ph_2PH\cdot BH_3$ (▲, 10 mol % Rh, toluene, 90 °C) using $[Rh(1,5-cod)(\mu-Cl)]_2$ as a precatalyst.

Rh particles.⁹ Following catalyst addition, a variable length (45–200 min) induction period was observed followed by a rapid increase in catalytic activity resulting in a sigmoidal kinetic curve (Figure 1), which is characteristic for the metal-particle formation reactions $A \rightarrow B$ (nucleation) and $A + B \rightarrow 2B$ (autocatalytic surface growth).^{6b,10} The presence of such a kinetic curve is a compelling piece of evidence for the formation of a heterogeneous catalyst.^{8,10} Additional experiments involving mercury, a well-known poison for heterogeneous catalysts through the formation of an amalgam or adsorption onto the catalyst surface, were also explored.^{8,11} Complete suppression of all catalytic activity was detected when excess mercury was added to dehydrocoupling trials involving $Me_2NH\cdot BH_3$. Test reactions between mercury and the Rh precatalyst eliminated the possibility of any complicating side reactions that may have led to catalyst deactivation.

We have now performed a series of additional experiments to provide further support for a heterogeneous mechanism in the Rh-catalyzed dehydrocoupling of $Me_2NH\cdot BH_3$. The addition of the strongly coordinating ligand PPh_3 in fractional poisoning experiments can also help distinguish between homogeneous and heterogeneous catalysis.¹² When 0.5 equiv of PPh_3 was added to dehydrocoupling trials involving $Me_2NH\cdot BH_3$, a strong reduction in the dehydrocoupling rate was observed. It was likely that surface coverage by PPh_3 was incomplete, resulting in residual active sites where dehydrocoupling could still occur.

Filtration using small pore membrane filters can also distinguish between soluble and insoluble catalysts.⁸ If the activity is lowered upon filtration, an insoluble catalyst is assumed. For the case of $Me_2NH\cdot BH_3$, filtration through a 0.5 μm filter resulted in almost complete suppression of the catalytic activity as compared to an unfiltered sample. These results suggest an insoluble heterogeneous

catalyst. The residual catalytic activity may arise from continued generation of the active heterogeneous catalyst after filtration.

In the case of $\text{Me}_2\text{NH}\cdot\text{BH}_3$, black Rh metal was isolated as the active catalyst in ca. 90% yield and was shown by ^1H and ^{13}C NMR to also contain $[\text{Me}_2\text{NH}_2]\text{Cl}$. Rh colloids may be initially formed in solution, with $[\text{Me}_2\text{NH}_2]\text{Cl}$ acting as an electrostatic stabilizing agent which helps to slow the aggregation.¹³ However, evolution of these colloids via aggregation still occurred to form the observed bulk Rh metal, which is a kinetically competent catalyst. Significantly, use of the isolated active catalyst resulted in dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ without a detectable induction period.

In striking contrast to the case of $\text{Me}_2\text{NH}\cdot\text{BH}_3$, our studies on the dehydrocoupling of $\text{Ph}_2\text{PH}\cdot\text{BH}_3$ with catalytic amounts of $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$ showed only a color change from orange to dark red. Over numerous repeat trials, the presence of a black color or a black precipitate characteristic of colloidal or metallic rhodium was never observed. In addition, induction periods were never observed even on short time scales (15 min) and a sigmoidal kinetic curve was noticeably absent (see Figure 1). Instead, a nearly linear relationship was consistently observed over many repeat trials. These kinetic results are suggestive of homogeneous catalysis.

For $\text{Ph}_2\text{PH}\cdot\text{BH}_3$ dehydrocoupling trials, the addition of either excess mercury or 0.5 equiv of PPh_3 was found to have no detectable effect on the catalytic activity. When a catalytically active solution was filtered through a 0.5 μm filter, no change in the dehydrocoupling rate was observed. All of these experimental results strongly suggest the operation of a soluble homogeneous catalyst for the case of $\text{Ph}_2\text{PH}\cdot\text{BH}_3$.

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. As amine-borane and phosphine-borane adducts have different strengths as reducing agents, one explanation is that the former are sufficiently reducing to generate colloidal rhodium.¹⁴ Thus, $\text{Me}_2\text{NH}\cdot\text{BH}_3$ may function as a "borohydride type" reducing agent, of the type commonly used to prepare transition metal colloids from metal halide precursors.¹⁵ For example, $\text{Me}_2\text{NH}\cdot\text{BH}_3$ has been used to generate Pt and Au colloids by reduction of H_2PtCl_6 and HAuCl_4 , respectively.¹⁶ A byproduct of the reduction step may be HCl, which could react with free Me_2NH (generated from the dissociation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$) to form the observed $[\text{Me}_2\text{NH}_2]\text{Cl}$. However, in the case of phosphine-borane adducts, an alternative (albeit unknown) homogeneous mechanism is favored over reduction.

Despite the fact that the generation of Rh metal was not detected in the catalytic dehydrocoupling of $\text{Ph}_2\text{PH}\cdot\text{BH}_3$ with $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$, it was interesting to investigate whether preformed Rh metal would function as an active catalyst. Thus, when isolated Rh metal (formed from the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$) was used in $\text{Ph}_2\text{PH}\cdot\text{BH}_3$ dehydrocoupling trials, very low catalytic activity was observed as compared with the precatalyst $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$. For example, 90% conversion was achieved after 144 h using Rh metal, whereas similar conversions were obtained after 9–10 h using $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$ under the same conditions (toluene, 90 °C). This is indicative of fundamental differences in reactivity between phosphine-borane and amine-borane adducts at the catalytic surface.

In summary, our results indicate that a seemingly subtle change in substrate from an amine-borane adduct to a phosphine-borane adduct leads 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 bulk Rh metal was found to be a poor catalyst in the dehydrocoupling of phosphine-borane adducts. These results suggest that both homogeneous and heterogeneous catalysis offer excellent opportunities for performing useful transformations in synthetic inorganic chemistry. We are now pursuing studies with well-defined colloids and model complexes to provide detailed insight into the mechanism of the dehydrocoupling processes.

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Supporting Information Available: Experimental details, TEM images, and graphs for the filtration and Hg and PPh_3 poisoning experiments (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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