

## Ambient Temperature, Tandem Catalytic Dehydrocoupling–Hydrogenation Reactions Using Rh Colloids and Me<sub>2</sub>NH·BH<sub>3</sub> as a Stoichiometric H<sub>2</sub> Source

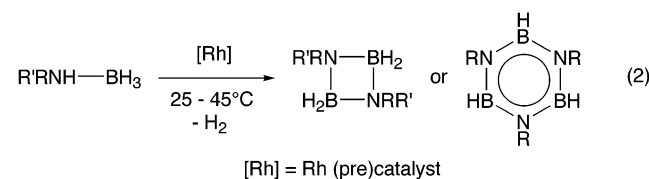
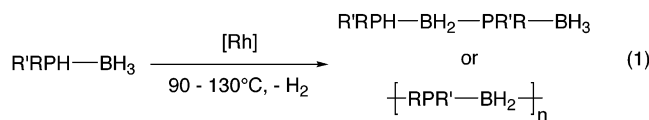
Cory A. Jaska and Ian Manners\*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

Received November 19, 2003; E-mail: imanners@chem.utoronto.ca

The use of soluble, transition metal nanoclusters and colloids as highly active catalysts has been the focus of considerable research efforts in the last 15 years.<sup>1</sup> While nanoclusters and colloids can be formed by a variety of methods, which include electrochemical reduction<sup>2</sup> and metal vapor deposition,<sup>3</sup> the chemical reduction of transition metal salts in the presence of stabilizing agents is an efficient and facile route.<sup>4,5</sup> This method can also provide some degree of control over particle size, which is important for high activity and selectivity in catalytic applications.<sup>6</sup> This field has benefitted from recent kinetic and mechanistic studies that show slow, continuous nucleation is followed by rapid autocatalytic surface growth, which results in either soluble monodisperse nanoclusters or insoluble bulk metal formation.<sup>7</sup> Over the past decade, nanoclusters and colloids have been utilized as catalysts in alkene and arene hydrogenation,<sup>8</sup> Heck<sup>9</sup> and Suzuki<sup>10</sup> coupling and silylation<sup>11</sup> reactions, and ring-opening polymerization.<sup>12</sup> In this communication, we have utilized highly active and in situ generated Rh colloids as a heterogeneous catalyst in a tandem dehydrocoupling–hydrogenation reaction that operates at room temperature.

Our group has shown that phosphine–borane adducts RR'PH·BH<sub>3</sub> undergo Rh-catalyzed dehydrocoupling to afford phosphinoborane rings, chains, and high-molecular weight polymers [RR'P–BH<sub>2</sub>]<sub>n</sub> (eq 1).<sup>13</sup> We have recently extended this work to the catalytic dehydrocoupling of amine–borane adducts RR'NH·BH<sub>3</sub>, which provides a mild and convenient route to cycloaminoboranes [RR'N–BH<sub>2</sub>]<sub>2</sub> and borazines [RN–BH]<sub>3</sub> (eq 2).<sup>14,15</sup> In the latter case, we provided some evidence for the operation of a heterogeneous mechanism involving colloidal Rh(0) metal.<sup>15,16</sup>



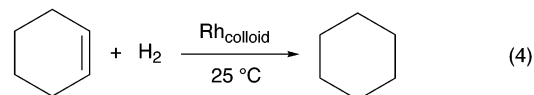
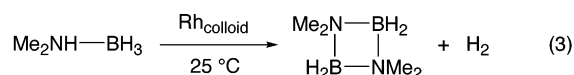
During the course of our studies on the catalytic dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub> with the precatalyst [{Rh(cod)(μ-Cl)}<sub>2</sub>], the formation of small quantities of cyclooctane was consistently observed in the reaction mixtures. This presumably resulted from the catalytic hydrogenation of cod (1,5-cyclooctadiene), which was present in solution upon reduction of the precatalyst to Rh colloids. Thus, it was apparent that the active catalyst for the dehydrocoupling reaction also acted as an active catalyst for alkene hydrogenation, without the need for an external H<sub>2</sub> source (e.g., an atmosphere of H<sub>2</sub>). To test for quantitative hydrogenation of alkenes via this

**Table 1.** Tandem Catalytic Dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub>–Hydrogenation of Various Substrates with (Pre)catalysts at 25 °C

	substrate	(pre)catalyst	dehydro. (%) <sup>a</sup>	hydrog. (%) <sup>a</sup>	time (h)
1 <sup>b</sup>	cyclohexene	[[Rh(cod)(μ-Cl)] <sub>2</sub> ]	100	65	24
2	cyclohexene	[[Rh(cod)(μ-Cl)] <sub>2</sub> ]	72	38	8
3	cyclohexene	[[Rh(cod)(μ-Cl)] <sub>2</sub> ]	100	100	24
4	cyclohexene	RhCl <sub>3</sub>	100	100	24
5	cyclohexene	Rh/Al <sub>2</sub> O <sub>3</sub> (5 wt %)	98	98	24
6	cyclohexene	Rh <sub>colloid</sub> /[Oct <sub>4</sub> N]Cl	99	81	24
7	cyclohexene	Pd/C (10 wt %)	95	10	72
8	1-octene	[[Rh(cod)(μ-Cl)] <sub>2</sub> ]	100	99	24
9	1/2 cod	[[Rh(cod)(μ-Cl)] <sub>2</sub> ]	0	0	24
10	1/2 cod	RhCl <sub>3</sub>	100	100	24
11 <sup>c</sup>	2 cyclohexene	[[Rh(cod)(μ-Cl)] <sub>2</sub> ]	73	68	72
12 <sup>d</sup>	cyclohexene	[[Rh(cod)(μ-Cl)] <sub>2</sub> ]	99	97	24

<sup>a</sup> % Dehydro(coupling) and hydrog(enation) were determined via integration of <sup>1</sup>H NMR spectra. <sup>b</sup> Reaction performed in an *open* vessel under an N<sub>2</sub> atmosphere. <sup>c</sup> Using MeNH<sub>2</sub>·BH<sub>3</sub>. <sup>d</sup> Using (1,4-C<sub>4</sub>H<sub>8</sub>)NH·BH<sub>3</sub>.

method, stoichiometric reactions were performed using commercially available Me<sub>2</sub>NH·BH<sub>3</sub> and cyclohexene in the presence of colloidal Rh as a catalyst (eqs 3 and 4).



In a typical experiment, Me<sub>2</sub>NH·BH<sub>3</sub> (1 equiv), cyclohexene (1 equiv) and [{Rh(cod)(μ-Cl)}<sub>2</sub>] (ca. 2 mol % Rh) were dissolved in C<sub>6</sub>D<sub>6</sub> in an *open* vessel under N<sub>2</sub>. The mixture was stirred for 24 h at 25 °C, and the contents were analyzed by <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR spectroscopy. Integration of the <sup>1</sup>H NMR resonances indicated complete conversion of Me<sub>2</sub>NH·BH<sub>3</sub> to [Me<sub>2</sub>N–BH<sub>2</sub>]<sub>2</sub>, but only 65% conversion of cyclohexene to cyclohexane, presumably due to partial H<sub>2</sub> loss (Table 1). When the reaction was performed in a *closed* vessel, after 8 h the dehydrocoupling reaction had reached 72% conversion and the hydrogenation reaction had reached 38% conversion. However, when the mixture was left to stir for 24 h in a closed vessel, the dehydrocoupling and hydrogenation conversions were both quantitative.<sup>17</sup> A blank reaction between Me<sub>2</sub>NH·BH<sub>3</sub> and cyclohexene in the absence of precatalyst indicated no evidence of dehydrocoupling–hydrogenation reactivity. In addition, no evidence for hydroboration of the alkene was observed by <sup>11</sup>B NMR.

This tandem reaction is not limited to [{Rh(cod)(μ-Cl)}<sub>2</sub>] as the precatalyst. For example, RhCl<sub>3</sub>, Rh/Al<sub>2</sub>O<sub>3</sub> (5 wt % Rh) and [Oct<sub>4</sub>N]Cl (Oct = *n*-octyl) stabilized Rh colloids<sup>4</sup> are all effective (pre)-catalysts for the dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub>. For RhCl<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub>, the catalytic hydrogenations of cyclohexene were both

quantitative after 24 h. However, for  $[\text{Oct}_4\text{N}]\text{Cl}$ -stabilized Rh colloids the hydrogenation reached only 81% after 24 h. This may be due to the Rh colloids having a lower activity due to increased aggregation, thereby increasing the reaction time beyond 24 h. Pd/C can also be used as a dehydrocoupling catalyst but was found to be a poor hydrogenation catalyst in this study.

Acyclic substrates can also be hydrogenated via this method. For example, 1-octene was quantitatively converted to octane after 24 h. However, no dehydrocoupling was observed when a near stoichiometric quantity of cod (0.5 equiv) was tested as a substrate using  $[\{\text{Rh}(\text{cod})(\mu\text{-Cl})\}_2]$  as a precatalyst. This is probably due to inhibited dissociation of the bound cod ligand in the precatalyst, which consequently prevents reduction to form catalytically active Rh colloids. However, the use of  $\text{RhCl}_3$  as a precatalyst resulted in quantitative conversion for both dehydrocoupling and hydrogenation reactions. The possibility of selective hydrogenation of cod to cyclooctene was also partially realized, with the formation of 80% cyclooctene using 1 equiv of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  and  $\text{Rh}/\text{Al}_2\text{O}_3$  or  $\text{Rh}_{\text{colloid}}/[\text{Oct}_4\text{N}]\text{Cl}$  as catalysts.

Other amine–borane adducts can also be utilized for this tandem reaction. For example, the primary adduct  $\text{MeNH}_2\cdot\text{BH}_3$  has been shown to undergo Rh-catalyzed dehydrocoupling to afford the borazine  $[\text{MeN}-\text{BH}]_3$  via a two-step dehydrocoupling process, with the formation of  $[\text{MeNH}-\text{BH}_2]_3$  as an intermediate species.<sup>14,15</sup> Thus, reaction of  $\text{MeNH}_2\cdot\text{BH}_3$  with 2 equiv of cyclohexene and the precatalyst  $[\{\text{Rh}(\text{cod})(\mu\text{-Cl})\}_2]$  was found to result in 73% dehydrocoupling (73%  $[\text{MeN}-\text{BH}]_3$ , 27%  $[\text{MeNH}-\text{BH}_2]_3$ ) and 68% hydrogenation after 3 d at 25 °C. The secondary adduct  $(1,4\text{-C}_4\text{H}_8)\text{NH}\cdot\text{BH}_3$  also underwent dehydrocoupling to give the dimer  $[(1,4\text{-C}_4\text{H}_8)\text{N}-\text{BH}_2]_2$ , while cyclohexene was hydrogenated in high yield (97%) after 24 h.

We have found that the initially formed Rh colloids used in amine–borane dehydrocoupling reactions eventually aggregate and form bulk metal.<sup>16</sup> However, this bulk metal is still catalytically active toward dehydrocoupling, albeit with slightly reduced activity presumably due to decreased surface area. A potential concern for the aforementioned tandem reactions is the activity of bulk metal for catalytic hydrogenation. To test this, bulk Rh metal was formed by aging the colloids for 3 d in solution followed by removal of the solvent to give a black powder. Addition of fresh  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  and cyclohexene was found to result in nearly quantitative dehydrocoupling (98%) and hydrogenation conversion (96%) after 24 h. Thus, bulk Rh metal is also a competent catalyst for hydrogenation.<sup>18</sup>

Although catalytic transfer hydrogenations<sup>19</sup> are well-known, relatively few operate at room temperature with a stoichiometric hydrogen source. This new method, therefore, offers potential advantages for cases involving thermally sensitive substrates or where selective reductions are desirable. In addition, as  $[\text{Me}_2\text{N}-\text{BH}_2]_2$  does not react with hydrogen to re-form  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ , the hydrogenation reaction is not reversible, solving a problem which is encountered in some systems.<sup>19c</sup> Isolation of the hydrogenated products can also be facilitated by the choice of amine–borane adduct and catalyst used. For example,  $[\text{Me}_2\text{N}-\text{BH}_2]_2$  can be easily removed under vacuum at 25 °C (bp 76–77 °C at 760 mmHg), whereas  $[(1,4\text{-C}_4\text{H}_8)\text{N}-\text{BH}_2]_2$  can be left as an involatile solid. Thus, for involatile hydrogenated products, the use of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  and  $\text{Rh}/\text{Al}_2\text{O}_3$  would allow removal of  $[\text{Me}_2\text{N}-\text{BH}_2]_2$  by vacuum and the catalyst by filtration. For volatile products, the use of  $(1,4\text{-C}_4\text{H}_8)\text{NH}-\text{BH}_3$  and any catalyst would allow removal of the desired product directly by distillation.

In summary, we have demonstrated that  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  acts as both a reducing agent to generate catalytically active Rh colloids and as a stoichiometric hydrogen source (via catalytic dehydrocoupling) for the hydrogenation of alkenes in a one-pot procedure at 25 °C. This is a promising new method, as a variety of readily available amine–borane adducts, substrates, and (pre)catalysts can be used to tailor these transformations. Future work will involve the expansion of this method to the catalytic hydrogenation of species with polar multiple bonds.

**Acknowledgment.** C.A.J. is grateful for a NSERC scholarship (2002–2004) and I.M. thanks NSERC for a Discovery Grant and the Canadian Government for a Canada Research Chair. We thank Prof. R. H. Morris (University of Toronto) and Prof. P. G. Jessop (Queen's University) for helpful discussions.

## References

- (1) (a) Aiken, J. D., III; Finke, R. G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 1. (b) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757. (c) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638.
- (2) (a) Reetz, M. T.; Quaiser, S. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2240. (b) Reetz, M. T.; Helbig, W. *J. Am. Chem. Soc.* **1994**, *116*, 7401.
- (3) Vitulli, G.; Evangelisti, C.; Pertici, P.; Caporusso, A. M.; Panziera, N.; Salvadori, P.; Faga, M. G.; Manfredotti, C.; Martra, G.; Coluccia, S.; Balerna, A.; Colonna, S.; Mobilio, S. *J. Organomet. Chem.* **2003**, *681*, 37.
- (4) Bönneman, H.; Brijoux, W.; Brinkmann, R.; Dinjus, E.; Jousen, T.; Korall, B. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1312.
- (5) For a "green" synthesis of Ag nanoparticles, see: Raveendran, P.; Fu, J.; Wallen, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13940.
- (6) Grunes, J.; Zhu, J.; Somorjai, G. A. *Chem. Commun.* **2003**, 2257.
- (7) (a) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382. (b) Widregren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10301.
- (8) (a) Bönneman, H.; Braun, G. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1992. (b) Weddle, K. S.; Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653. (c) Schulz, J.; Roucoux, A.; Patin, H. *Chem. Eur. J.* **2000**, *6*, 618. (d) Dyson, P. J. *Chem. Commun.* **2003**, 2964. (e) Doyle, A. M.; Shaikhutdinov, S. K.; Jackson, S. D.; Freund, H.-J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5240.
- (9) (a) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, 1921. (b) Rahim, E. H.; Kamounah, F. S.; Frederiksen, J.; Christensen, J. B. *Nano Lett.* **2001**, *1*, 499. (c) Caló, V.; Nacci, A.; Monopoli, A.; Detomaso, A.; Iliade, P. *Organometallics* **2003**, *22*, 4193.
- (10) (a) Reetz, M. T.; Breinbaur, R.; Wanninger, K. *Tetrahedron Lett.* **1996**, *37*, 4499. (b) Biffis, A.; Sperotto, E. *Langmuir* **2003**, *19*, 9548. (c) Narayanan, R.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 8340.
- (11) Chauhan, B. P. S.; Rathore, J. S.; Chauhan, M.; Krawicz, A. *J. Am. Chem. Soc.* **2003**, *125*, 2876.
- (12) (a) Wu, X.; Neckers, D. C. *Macromolecules* **1999**, *32*, 6003. (b) Temple, K.; Jäkle, F.; Sheridan, J. B.; Manners, I. *J. Am. Chem. Soc.* **2001**, *123*, 1355.
- (13) (a) Dorn, H.; Singh, R. A.; Massey, J. A.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 3321. (b) Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669.
- (14) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Chem. Commun.* **2001**, 962.
- (15) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424.
- (16) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 1334.
- (17) A typical experiment was performed as follows: In a  $\text{N}_2$  filled glovebox,  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  (0.105 g, 1.78 mmol), cyclohexene (0.146 g, 1.78 mmol) and a catalytic amount of  $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$  (0.008 g, 0.02 mmol, ca. 2 mol % Rh) were dissolved in  $\text{C}_6\text{D}_6$  (1 mL) in a screw-cap vial. The vial was sealed, and the mixture was rapidly stirred for 24 h. The contents of the vial were analyzed by  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR spectroscopy. From the  $^1\text{H}$  NMR spectrum, conversion of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  to  $[\text{Me}_2\text{N}-\text{BH}_2]_2$  and cyclohexene to cyclohexane were both 100%.
- (18) A reviewer suggested the possibility for size reduction of large particles to smaller particles upon the addition of  $\text{Me}_2\text{NH}\cdot\text{BH}_3$ . However, a TEM study of the heterogeneous Rh catalyst before and after the tandem dehydrocoupling–hydrogenation reaction showed no apparent change in the particle size or morphology. Only large, extensively aggregated particles were observed in both instances.
- (19) (a) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129. (b) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (c) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.

JA039696X