Inorg. Chem. **2007**, *46*, 7522–7527

Inorganic Chemistry
Article

Highly Efficient Colloidal Cobalt- and Rhodium-Catalyzed Hydrolysis of $H_3N·BH_3$ in Air

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Received April 27, 2007

The compound $H_3N·BH_3$ (**1**) is currently attracting considerable attention as a potential hydrogen storage material. Group 9 catalysts which rapidly and conveniently hydrolyze aqueous **1** in air are described. When treated with 1 mol % [{Rh(μ-Cl)(1,5-cod)}$_2$] (cod = cyclooctadiene) in air, aqueous **1** undergoes rapid hydrolysis to afford the ionic species $[NH_4][BO_2]$ in ∼40 s. Higher catalyst loadings (3 mol %) result in a reduction in reaction time to 10 s. Quantification of the hydrogen evolved revealed that, on average, 2.8 of a maximum possible 3.0 equivalents (93%) were generated during the course of the reaction. Rh(0) species (e.g., Rh black, Rh stabilized on alumina, aqueous Rh colloids) were also found to be active hydrolysis catalysts, and evidence for a heterogeneous mechanism is provided. Significantly, although Ir(0) colloids are less active, aqueous Co(0) colloids are also effective catalysts for this process. This result is particularly important as Co, a first-row metal, is considerably more economical than the precious metal catalysts typically employed.

Introduction

Transition metal-catalyzed dehydrocoupling and dehydrogenation reactions are of growing interest as a preparative route to rings, chains, polymers, and materials based on main group elements.[1,2] Further impetus to this area has recently been provided by the realization that the catalytic dehydrogenation of hydrogen-rich inorganic compounds may play a key role in their utility as hydrogen storage materials. Thus, as environmental concerns over carbon-based emissions grow, the search for an alternative vehicle fuel to petroleum has become increasingly critical.[3] To this end, hydrogen storage materials have attracted significant attention, as they can potentially store H_2 safely and efficiently.[4] The most studied materials, metal hydrides, suffer from drawbacks such as low hydrogen storage densities and slow reaction kinetics.[5] Ammonia−borane, $H_3N·BH_3$ (**1**), is now being studied extensively, as it possesses one of the highest densities of hydrogen available (19.6 wt % H_2).[6]

Our group has previously investigated the catalytic dehydrogenation of a variety of amine−borane adducts, including **1** (Scheme 1). Our results have shown that both heterogeneous (e.g., Rh(0))[7,8] and homogeneous (e.g., Ti)[9] catalysts effectively promote amine−borane dehydrocoupling with useful scope and activity. Other groups have recently reported key advances in the area of thermal[10] or catalytic[11] elimina-

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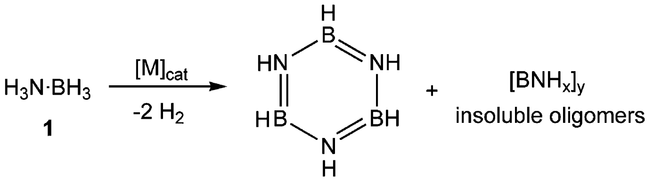
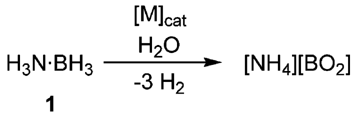
10.1021/ic700806b CCC: $37.00

Scheme 1



Scheme 2



tion of H_2 from **1** and other high-hydrogen-content amine−borane adducts. Regeneration of the hydrogen storage material is a key issue, and although multistep processes can be considered, the recent observation of reversible H_2 release from a phosphonium−borate species is particularly noteworthy in this regard.[12,13]

Hydrolysis reactions provide an additional method for H_2 release from hydrogen-rich amine−borane adducts such as **1** (Scheme 2). For example, Xu and Chandra have described the metal-catalyzed hydrolysis of **1** under an inert atmosphere of Ar with various late transition metals; Pt(0) gave the most impressive results with complete reaction being observed in ca. 2−10 min with 20 wt % Pt on C.[11a] In addition, these workers investigated the addition of undissolved Rh catalysts and observed slightly reduced reactivity and the elimination of 2.5 of a possible 3.0 equiv of H_2 in ∼15 min. Of particular relevance to this paper is their recent observation that supported non-noble metals (e.g., Ni, Co) are also effective catalysts for this process.[11e]

Sneddon and co-workers have recently described the acid- and metal-mediated hydrolysis of ammonia−triborane, $NH_3B_3H_7$ (**2**).[11d] For example, **2** was reported to rapidly release H_2 in aqueous solution with moderately high loadings of Rh-based catalysts (ca. 7 mol %) in 1.5 min. Although the use of **2** can potentially yield more equivalents of H_2 per molecule compared to **1**, the wt % H_2 per molecule of **2** (17.8 wt %) is actually less than that of **1**. Furthermore, unlike **1**, it is not a commercially available material but must be prepared in four steps.[11d,14] In this paper, we report our studies on the metal-promoted hydrolysis of **1**, which can be synthesized in one step or purchased, using relatively low loadings of both bulk and colloidal Group 9 metals as catalysts in water. Moreover, we show that these efficient catalytic reactions proceed under very convenient conditions in air.

Experimental Section

General Procedures and Materials. All reactions and manipulations were performed in air unless stated otherwise. As H_2 is released during dehydrogenation reactions and is a flammable gas, these experiments should be conducted in a fumehood. Distilled water and ACS grade tetrahydrofuran were used without any further purification. $H_3N{\cdot}BH_3$, $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (cod = cyclooctadiene), Rh black, and Rh/Al_2O_3 were purchased and used as received. $[Co_2(CO)_8]$ was sublimed immediately before use. Aqueous colloidal Rh(0)[15] and Ir(0)[16] solutions were prepared according to literature procedures. Generally, a solution of the $MCl_3{\cdot}xH_2O$ (M = Rh, Ir) salt in H_2O was treated, with vigorous stirring, with an aqueous mixture of the reductant $Li[BH_4]$ and surfactant *N*-hexadecyl-*N*-(2-hydroxyethyl)-*N*-dimethylammonium bromide, giving a black suspension in both cases.

Equipment. NMR spectra were recorded on a Jeol ECP 300 spectrometer operating at 96 MHz (^{11}B). Chemical shifts are reported relative to external $BF_3{\cdot}Et_2O$.

Catalytic Hydrolysis of (1) by $[\{Rh(\mu\text{-}Cl)(1{,}5\text{-}cod)\}_2]$. To a solution of **1** (0.050 g, 1.62 mmol) in H_2O (ca. 5 mL), $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (0.004 g, 0.0081 mmol, 1 mol %) in THF (ca. 1 mL) was added at 20 °C resulting in the immediate release of a gas as evidenced by vigorous bubbling and a color change to black. After ∼40 s, the bubbling ceased, an aliquot of the reaction mixture was removed and the ^{11}B NMR spectrum obtained showing a single resonance at 9 ppm corresponding to $[BO_2]^-$.[11a,17]

Increasing the $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ catalyst loading for the above reaction to 3 mol % (0.012 g) resulted in complete conversion to $[BO_2]^-$ in 10 s as judged by the cessation of H_2 evolution using a gas burette.

Hydrogen Gas Volumetric Measurements. A solution of **1** (0.034 g, 1.10 mmol) in H_2O (ca. 5 mL) was prepared as above in a two-necked round-bottom flask with one neck used for catalyst solution injection through a rubber septum and the other neck connected via plastic tubing to a 100 mL gas burette containing H_2O. To the above solution, $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (0.009 g, 0.019 mmol, 3 mol %) in THF (ca. 1 mL) was added, causing 73 mL of H_2O (of a maximum 79.5 mL based on the maximum of 3 mol of H_2 that can be eliminated by the complete dehydrogenation of **1**) to be displaced in the gas burette. A repeat trial resulted in 75 mL being displaced.

Testing Rh Catalyst Recyclability. To a solution of **1** (0.050 g, 1.62 mmol) in H_2O (ca. 5 mL), $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (0.004 g, 0.0081 mmol, 1 mol %) in THF (ca. 1 mL) was added at 20 °C resulting in the immediate release of a gas as evidenced by vigorous bubbling and a color change to black. After ∼40 s, the bubbling ceased, an aliquot of the reaction mixture was removed, and the ^{11}B NMR spectrum obtained showing a single resonance at 9 ppm

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Table 1. Reaction Times Required for the Complete Catalytic Hydrolysis of Additional Equivalents of **1** by the Rh Catalyst Derived from [{Rh(μ-Cl)(1,5-cod)}$_2$]

no. of equiv of **1**	reaction time
1	40 s
2	6 min
3	15 min
4	35 min

corresponding to $[BO_2]^-$.[11a,17] Subsequent equivalents of **1** (0.050 g, 1.62 mmol) were added and the reactions monitored by ^{11}B NMR spectroscopy in order to determine the amount of time required for complete consumption of **1** (results summarized in Table 1).

Catalytic Hydrolysis of (1) by Rh(0) Species. To a solution of **1** (0.050 g, 1.62 mmol) in H_2O (ca. 5 mL), Rh/Al_2O_3 (0.033 g, 0.032 mmol, 1 mol %) was added at 20 °C resulting in the immediate release of a gas as evidenced by vigorous bubbling. After ~1 min, the bubbling ceased and an aliquot of the reaction mixture was removed. The ^{11}B NMR spectrum obtained showed a single resonance at 9 ppm corresponding to $[BO_2]^-$.[11a,17]

Similar results were obtained for Rh black.

Catalytic Hydrolysis of (1) by Aqueous Colloidal Rh(0). To a solution of **1** (0.050 g, 1.62 mmol) in H_2O (ca. 18 mL), a 4.74×10^{-3} M solution of colloidal Rh(0) (3.40 mL, 0.0161 mmol, 1 mol %) in H_2O was added at 20 °C resulting in the immediate release of a gas as evidenced by vigorous bubbling. The reaction was monitored by ^{11}B NMR spectroscopy in order to determine the amount of time required for complete consumption of **1** (25 min).

Treatment of Aqueous Colloidal Rh(0) with Hg Prior to Addition of (1). To a 4.74×10^{-3} M solution of colloidal Rh(0) (3.40 mL, 0.0161 mmol, 1 mol %) in H_2O, Hg (4.50 g, 22.43 mmol) was added and stirred rapidly for 45 min. *IMPORTANT: Good stirring is known to be needed to ensure contact of the catalyst with Hg(0), a condition required to avoid false negatives in this experiment.*[18] To this mixture, **1** (0.050 g, 1.62 mmol) in H_2O (ca. 18 mL) was added at 20 °C and the reaction monitored by ^{11}B NMR spectroscopy. After 25 min, an aliquot of the reaction mixture was removed and the ^{11}B NMR spectrum obtained showing only 35% conversion of **1** to $[BO_2]^-$.

Filtration Experiment: Catalytic Hydrolysis of (1) by Aqueous Colloidal Rh(0). To a solution of **1** (0.050 g, 1.62 mmol) in H_2O (ca. 4 mL), a 4.74×10^{-3} M solution of Rh(0) (3.40 mL, 0.0161 mmol, 1 mol %) in H_2O was added at 20 °C resulting in the immediate release of a gas as evidenced by vigorous bubbling. After 25 min, the reaction was judged to be complete by ^{11}B NMR. The reaction mixture was then filtered through a 200 nm porous filter giving a black solution. To this solution, a second equivalent of **1** (0.050 g, 1.62 mmol) was added. After 25 min, an aliquot of the reaction mixture was taken and the ^{11}B NMR spectrum was obtained showing the presence of 58% $[BO_2]^-$ and 42% unreacted **1**.

A blank reaction, where the reaction mixture *was not filtered* prior to addition of the second equivalent of **1**, showed a single resonance in the ^{11}B NMR spectrum at 9 ppm corresponding to $[BO_2]^-$ after 25 min.[11a,17]

Testing Aqueous Colloidal Rh(0) Catalyst Recyclability. To a solution of **1** (0.050 g, 1.62 mmol) in H_2O (ca. 5 mL), a 4.74×10^{-3} M solution of Rh(0) (3.40 mL, 0.0161 mmol, 1 mol %) in H_2O was added at 20 °C resulting in the immediate release of a gas as evidenced by vigorous bubbling. After 25 min, the reaction was judged to be complete by ^{11}B NMR. Subsequent equivalents of **1** (0.050 g, 1.62 mmol) were added and the reactions monitored by ^{11}B NMR spectroscopy in order to determine the amount of time required for complete consumption of **1** (results summarized in Table 2).

Table 2. Reaction Times Required for the Complete Catalytic Hydrolysis of Additional Equivalents of **1** by Aqueous Colloidal Rh(0)

no. of equiv of **1**	reaction time (min)
1	25
2	25
3	25
4	35
5	40

Catalytic Hydrolysis of (1) by Aqueous Colloidal Ir(0). To a solution of **1** (0.049 g, 1.59 mmol) in H_2O (ca. 4 mL), a 9.33×10^{-4} M solution of colloidal Ir(0) (17 mL, 0.0159 mmol, 1 mol %) in H_2O was added at 20 °C resulting in the immediate release of a gas as evidenced by bubbling. The reaction was monitored by ^{11}B NMR spectroscopy in order to determine the amount of time required for complete consumption of **1** (105 min). A repeat trial took 110 min.

Treatment of $Me_2NH{\cdot}BH_3$ (3) with a Catalytic Amount of Co(0). This reaction was carried out in an argon-filled glovebox. To a solution of **3** (0.250 g, 4.24 mmol) in toluene (ca. 3 mL), a catalytic amount of bulk Co(0) powder (0.005 g, 0.085 mmol, 2 mol %) was added and stirred in an open vessel for 16 h. After this time, an aliquot of the reaction mixture was removed and an ^{11}B NMR spectrum obtained showing only unreacted **3** ($^{B}\delta$ −14 ppm).

No reaction was observed when the same procedure was carried out with $[Co_2(CO)_8]$.

Treatment of (1) with a Catalytic Amount of Co(0). To a solution of **1** (0.200 g, 6.48 mmol) in H_2O (ca. 5 mL), bulk Co(0) powder (0.004 g, 0.068 mmol, 1 mol %) was added and stirred for 5 h. After this time, an aliquot of the reaction mixture was removed and an ^{11}B NMR spectrum obtained showing the presence of 10% $[BO_2]^-$ and 90% unreacted **1**.

Preparation of Aqueous Colloidal Co(0). Under an atmosphere of dry N_2, lithium borohydride (0.032 g, 1.47 mmol) was added to a deoxygenated aqueous solution (ca. 120 mL) of *N*-hexadecyl-*N*-(2-hydroxyethyl)-*N*-dimethylammonium bromide (0.360 g, 0.91 mmol). This solution was added all at once to a vigorously stirred, deoxygenated aqueous solution (ca. 6 mL) of $CoCl_2{\cdot}6H_2O$ (0.077 g, 0.32 mmol) to give a black Co(0) colloidal suspension (126 mL).

Catalytic Hydrolysis of (1) by Aqueous Colloidal Co(0). To a solution of **1** (0.050 g, 1.62 mmol) in H_2O (ca. 18 mL), a 4.71×10^{-3} M solution of colloidal Co(0) (3.40 mL, 0.0160 mmol, 1 mol %) in H_2O was added at 20 °C resulting in the immediate release of a gas as evidenced by bubbling. The reaction was monitored by ^{11}B NMR spectroscopy in order to determine the amount of time required for complete consumption of **1** (60 min). A repeat trial also took 60 min.

Results and Discussion

i. Rhodium-Catalyzed Hydrolysis of 1. We have previously shown that **1** undergoes catalytic dehydrocoupling in diglyme with Rh (pre)catalysts such as [{Rh(μ-Cl)(1,5-cod)}$_2$] at 45 °C under N_2 to afford borazine $[HN{-}BH]_3$ and insoluble oligomeric/polymeric products over 48−84 h (Scheme 1).[7a,b] Notably, when an aqueous solution of **1** is treated with a 1 mol % THF solution of the same Rh (pre)catalyst in air, an instantaneous color change to black

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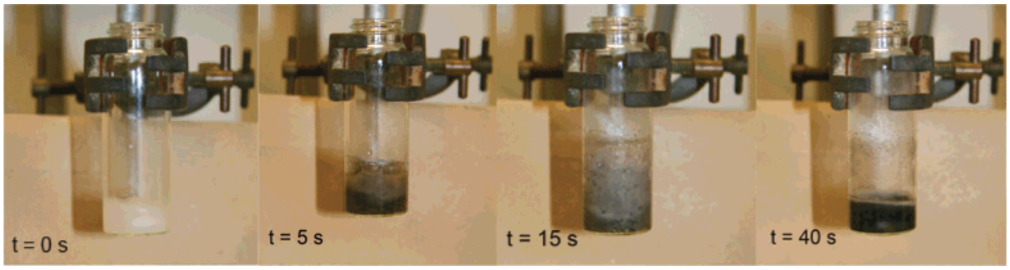
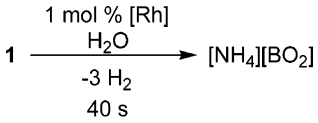


Figure 1. Photographs depicting an aqueous solution of **1** before 1 mol % Rh catalyst addition ($t = 0$ s) and at various stages of reaction after Rh addition until completion at $t = 40$ s.

Scheme 3



$$\mathbf{1} \xrightarrow[\substack{-3\ H_2 \\ 40\ s}]{\substack{1\ mol\ \%\ [Rh] \\ H_2O}} [NH_4][BO_2]$$

consistent with the formation of colloidal Rh(0) was observed along with vigorous gas evolution (Figure 1). After 40 s, the bubbling subsided and ^{11}B NMR spectroscopy confirmed that the starting material had been completely consumed by the absence of a resonance at −24.5 ppm and revealed a new resonance at 9 ppm. We assign this chemical shift to the borate species $[NH_4][BO_2]$ (Scheme 3).[11a,17] This remarkably short reaction time was further reduced to 10 s upon increasing the Rh catalyst loading to 3 mol %. As noted above, Chandra and Xu have recently studied the late metal-catalyzed hydrolysis of **1** under an inert atmosphere.[11a] By comparison, they reported that 1.8 mol % $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$, added in the solid state, catalytically hydrolyzed **1** in 15 min under an Ar atmosphere. Here, our results indicate that over repeat trials, the addition of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ as a solution in air significantly decreases the reaction time.

In order to quantify the amount of H_2 gas eliminated during the course of the reaction, we measured the displacement of water in a gas burette. Over two runs, an average 74 mL of a maximum 79.5 mL of H_2 were released, which equates to 2.8 out of a possible 3.0 equivalents of H_2 (93%), confirming the stoichiometry shown in Scheme 3. The extent of H_2 release from **1** here, particularly in such a short period of time at room temperature, makes this catalytic system, which operates in air, highly promising.

The recyclability of the Rh catalyst was also explored. Immediately following a hydrolysis reaction with **1**, another equivalent of **1** was added leading to further hydrogen evolution from the reaction mixture. However, the time needed to completely consume **1** increased to 6 min, which can still be regarded as a short reaction time although significantly lengthened relative to the 40 s required for the initial equivalent. Subsequent treatment with a third and fourth equivalent of **1** resulted in further increases in reaction time to 15 and 35 min, respectively (Table 1). This apparent decrease in catalytic activity may be attributed to aggregation of the Rh(0) particles over time resulting in a decrease in catalyst surface area. Another potential contributing factor could be that species with B−H functionalities inhibit hydrolytic activity by slowly poisoning the catalyst surface. We have previously reported that heterogeneous catalysts treated with Group 13 hydrides, as well as colloidal metals prepared by the reduction of transition metal salts by borane or borohydride species, exhibit reduced activity toward the dehydrocoupling of amine−borane adducts.[19] This was attributed to a passivating layer of the Group 13 element on the metal surface blocking access of the substrate to catalyst active sites.

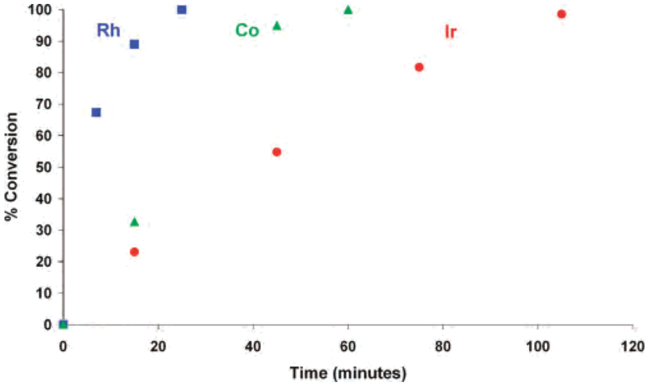


Figure 2. Graph of % conversion (as determined by ^{11}B NMR) versus time for the catalytic hydrolysis of **1** employing 1 mol % of colloidal Co (green triangles), Rh (blue squares), and Ir (red circles) aqueous solutions.

The observed color change to black along with the formation of visible dark precipitate is presumably due to reduction of the Rh(I) (pre)catalyst $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ to catalytically active Rh(0) metal. Although it is likely that the catalyst is heterogeneous, a homogeneous metal species cannot be completely ruled out at this stage.[18] This is supported by our previous studies on late metal-catalyzed dehydrocoupling of amine−borane adducts under an inert atmosphere, where a variable-time induction period was observed as the catalytically active heterogeneous species is formed prior to dehydrogenation of the adduct.[7b,c]

Consequently, we turned our attention to Rh(0) catalysts in an effort to investigate and compare their catalytic activity toward **1**. Treatment of an aqueous solution of **1** in air with 1−2 mol % Rh black or Rh/Al_2O_3 again resulted in immediate gas evolution and complete conversion to $[NH_4][BO_2]$ by ^{11}B NMR spectroscopy in ca. 1−4 min. As the reaction appeared to be heterogeneous and is performed in water, an aqueous colloidal Rh solution was also prepared[15] and its catalytic activity examined. Upon treatment of **1** with a 1 mol % aqueous solution of colloidal Rh(0) in air, bubbling was again observed and complete reaction was detected after 25 min (Figure 2, blue squares). This increase

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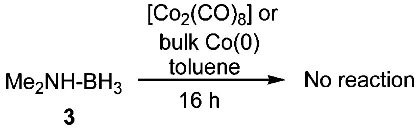
in reaction time relative to the previously mentioned Rh systems may be due to the dilute solutions required in order to prevent aggregation of the colloids to give insoluble bulk Rh metal.[20] An alternative possibility is that the surfactant, while stabilizing the colloidal Rh(0) against aggregation, may also be hindering the access of **1** to catalyst active sites. Significantly, rapid stirring of the Rh(0) solution with a large excess of Hg followed by similar treatment with **1** resulted in only 35% conversion to $[NH_4][BO_2]$ after 25 min. This decrease in rate is likely caused by poisoning of the Rh(0) catalyst by Hg; a well-known heterogeneous catalyst poison.[18,21] The heterogeneity of the process was further supported by filtration experiments, which indicate an insoluble catalyst is the active species if the activity is lowered upon filtering through small (ca. 200 nm) pore membrane filters.[18] Two hydrolysis reactions of **1** were carried out simultaneously with the aqueous colloidal Rh(0) solution; after 25 min both reactions were complete by ^{11}B NMR. A second equivalent of **1** was added to one of the reactions and stirred, while the other reaction mixture was filtered through a 200 nm porous filter giving a black solution prior to addition of a second equivalent of **1**. After a further 25 min, ^{11}B NMR revealed complete reaction had occurred in the case of the former, while in the latter case, only 58% of the second equivalent had formed $[NH_4][BO_2]$. This strongly supports the assertion that the key active catalytic species in this process is heterogeneous.

The recyclability of the aqueous colloidal Rh(0) catalyst was also tested in a similar manner to that used for the above Rh catalyst. In contrast to the Rh catalyst derived from $[\{Rh(\mu\text{-}Cl)(1,5\text{-cod})\}_2]$, the activity of the aqueous colloidal Rh(0) catalyst does not decrease appreciably until the addition of a fourth equivalent of **1**, as the initial three equivalents all took 25 min to be completely converted to $[NH_4][BO_2]$, the fourth taking 35 min (Table 2). By comparison, a fourth equivalent of **1** also required 35 min for complete conversion to $[NH_4][BO_2]$ with the Rh catalyst derived from $[\{Rh(\mu\text{-}Cl)(1,5\text{-cod})\}_2]$; however, the first equivalent only took 40 s. We attribute this significant difference in catalyst recyclability to the surfactant stabilizing the aqueous colloids, which likely hinders aggregation resulting in reasonably constant reaction times. Another possibility is that the high surface area of the colloidal Rh(0) catalyst may also prevent appreciable surface passivation by species containing B−H bonds.[19]

ii. Iridium-Catalyzed Hydrolysis of 1. Other aqueous Group 9 metal colloid solutions were examined in order to determine whether they exhibit catalytic activity toward the hydrolysis of **1**. An aqueous solution of colloidal Ir(0)[16] in air was found to be effective, although not as efficient as Rh(0), as complete conversion was found to have taken place after 105 min (Figure 2, red circles). These findings are analogous to our previous observations on the catalytic dehydrocoupling of $Me_2NH{\cdot}BH_3$ (**3**) in organic solvents under an inert atmosphere which yields the cyclic dimer $[Me_2N{-}BH_2]_2$. In particular, we reported that the room-temperature reaction with $[\{Rh(\mu\text{-}Cl)(1,5\text{-cod})\}_2]$ took 8 h while that of $[\{Ir(\mu\text{-}Cl)(1,5\text{-cod})\}_2]$ took 136 h.[7b] Although in the case described here the difference in reaction time is not as dramatic, the same trend is observed.

Scheme 4



iii. Cobalt-Catalyzed Hydrolysis of 1. As noted by Baker and co-workers in a recent report detailing their Ni-catalyzed dehydrocoupling of **1** (at 60 °C in diglyme over 4 h),[11i] there is a general desire not just for greater catalyst activity and stability but also for catalysts comprising more abundant, economical first-row metals. In this context, our studies of the Group 9 metal-catalyzed hydrolysis of **1** were extended to Co. We found that treatment of **3** with 2 mol % of the Co(0) source $[Co_2(CO)_8]$ or bulk Co(0) powder did not result in dehydrocoupling and formation of the cyclic dimer $[Me_2N{-}BH_2]_2$ after 16 h as determined by ^{11}B NMR spectroscopy (Scheme 4). Furthermore, treatment of an aqueous solution of **1** with 2 mol % bulk Co(0) powder resulted in only 10% conversion to $[NH_4][BO_2]$ after 5 h as judged by ^{11}B NMR spectroscopy. These results contrast with those of Chandra and Xu who reported that **1** was completely consumed by various insoluble, supported Co(0) catalysts including Co/Al_2O_3, Co/SiO_2, and Co/C.[11e]

In contrast to our studies employing molecular Co(0) species and bulk Co metal, an aqueous solution of colloidal Co(0) (1 mol %) was found to be an active hydrolysis catalyst for **1**, as the reaction was found to be complete in only 60 min (Figure 2, green triangles). The distinct difference in catalytic activity apparent in these results and our observations involving bulk and colloidal Co(0) is of importance and underscores the change in behavior that can be observed upon shifting to smaller particle sizes. By comparison, Chandra and Xu reported that **1** undergoes complete hydrolysis when treated with 1.8 mol % of Co/C over the same period of time, reflecting reasonably consistent reaction times for the Co(0) catalyzed reaction. They also detailed that Co/C catalysts gave the best results as other Co(0) systems such as Co/Al_2O_3 took longer to catalyze the hydrolysis of **1** (70 min) under the same conditions.[11e] This difference in reactivity was attributed to particle size effects as the Co/C particles were found to be smaller than that of Co/Al_2O_3 as determined by powder X-ray diffraction. Significantly, both our results on colloids and those of Chandra and Xu on supported systems demonstrate that the cheaper and more abundant first-row metal Co exhibits greater reactivity toward **1** than the precious metal Ir.

Summary

As part of our continuing research on the catalytic dehydrocoupling and dehydrogenation of amine−borane

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(20) The various reaction times for the bulk or colloidal metal catalysts are uncorrected for the different surface areas and number of active sites of these different heterogeneous catalysts.

(21) (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

adducts, we have explored the bulk or colloidal Group 9 metal-catalyzed hydrolysis of the promising hydrogen storage material **1**. We have shown that the aqueous Rh-catalyzed hydrolysis of **1** in air can occur at 25 °C at rates that significantly exceed those of other reported catalysts, with 2.8 of a maximum possible 3.0 equivalents H_2 eliminated in seconds in some cases. Furthermore, we have studied the extension of this method to aqueous solutions of other colloidal Group 9 metals such as Co, a cheap and abundant first-row transition metal. Thus, Co(0) colloids also efficiently and conveniently catalyze the hydrolysis of **1** in air at 25 °C. Future work is directed toward exploring the efficient multistep regeneration of **1** from the hydrolysis products and analogous studies of other amine−borane adducts. The role of air in the promotion of the heterogeneous catalytic dehydrogenation chemistry relative to corresponding reactions under an inert atmosphere is also under investigation.

Acknowledgment. T.J.C. thanks the Ontario Government for a Graduate Scholarship (OGS). I.M. thanks the European Union for a Marie Curie Chair and the Royal Society for a Wolfson Research Merit Award.

IC700806B