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Cobalt-catalyzed ammonia borane dehydrocoupling and transfer hydrogenation under aerobic conditions†

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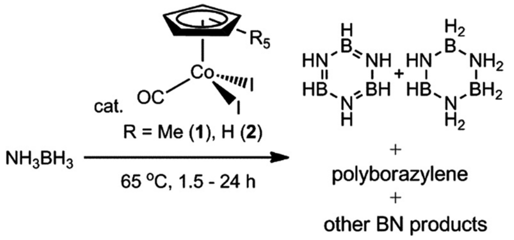
Two cobalt compounds, $Cp^*Co(CO)I_2$ (1) and $CpCo(CO)I_2$ (2) ($Cp^* = \eta^5\text{-}C_5Me_5$, $Cp = \eta^5\text{-}C_5H_5$), catalyze the dehydrogenation of ammonia borane under either anaerobic or aerobic conditions and are also effective hydrogenation catalysts for alkenes and alkynes using ammonia borane as a hydrogen source, also in the presence of air.

The dehydrocoupling of amine boranes by heterogeneous and homogenous catalysts has been extensively studied due to the potential use of amine boranes as hydrogen storage materials and potential applications of polyaminoboranes in materials science.[1] Manners discovered the first example of metal-catalyzed ammonia borane dehydrocoupling using rhodium precatalysts,[2] which initiating aggressive study of this reaction.[1b,3] It has been noted that rhodium catalysts have exhibited higher activity towards amine borane dehydrocoupling when these reactions were performed in open *versus* sealed vessels, which is attributed to more facile H_2 loss from the system.[3f,4] However, many amine borane dehydrocoupling catalysts must operate under anaerobic conditions.[1b] Indeed, a highly active and well-studied NH_3BH_3 dehydrocoupling catalyst, (POCOP)-$Ir(H)_2$ (POCOP = $[\eta^3\text{-}1,3\text{-}(OP^tBu_2)_2C_6H_3]$),[5] is known to be air sensitive.[6] The high interest in heavier group 9 metals suggests that cobalt catalysts may be a promising, sustainable alternative. Additionally, ammonia borane has been a challenging substrate with fewer examples of catalytic dehydrocoupling, which is often attributed to the poor solubility of NH_3BH_3 in most organic solvents and the difficulty in removing water from NH_3BH_3.[1b,c] The value of air-stable catalysts for organic transformations is well established,[7] and if amine boranes are to be used has a hydrogen source in devices, air-stable catalysts may be a consideration in those applications.

While catalyst stability is an important consideration, a focus on earth-abundant elements will allow for growth in this area as supplies of platinum-group metals dwindle.[8] Many catalysts for amine borane dehydrogenation feature 4d and 5d metals.[2,5c,9] While strides have been made in using earth-abundant metal catalysts, such as those of iron,[3b] nickel,[10] tin,[11] group 4 metals,[3d] and even some acid-catalyzed[12] and metal-free systems,[3c] continued efforts to investigate first-row transition-metal complexes for this reactivity are warranted. Despite the apparent ubiquity of catalysts for the dehydrogenation of ammonia borane, Peters has reported the only example of a cobalt compound that can participate in this reactivity.[13]

Treatment of ammonia borane in a THF solution with 1 mol% of $Cp^*Co(CO)I_2$ (**1**) resulted in rapid gas evolution immediately followed by a color change of the solution from dark red to light green. Minor conversion to dehydrocoupling products was observed by $^{11}B\{^1H\}$ NMR spectroscopy after *ca.* 15 min at ambient temperature. Heating the reaction mixture to 65 °C increased gas evolution and formation of dehydrocoupling products as evidenced by ^{11}B NMR spectroscopy (Table 1). Under these conditions, it was found that **1** failed to give appreciable dehydrocoupling of Me_2NHBH_3 or $^tBuNH_2BH_3$ over three days. Therefore, only NH_3BH_3 is included in this study.



(1)

Notably, the catalyst loading did not seem to greatly affect consumption of NH_3BH_3, indicating that **1** may be a particularly useful catalyst for dehydrocoupling at relatively low loadings (Table 1). Even at the lowest catalyst loading, the dehydrocoupling of ammonia borane to a variety of products

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Table 1 Initial optimization of reaction conditions for ammonia borane dehydrocoupling by **1**[a]

Loading (mol%)	1.0	1.0	0.5	0.5	0.1	0.1
Temperature (°C)	23	65	23	65	23	65
Time (h)	72[b]	24	72[b]	24	72[b]	24
Conversion (%)	12	98	11	98	8	97

[a] Reaction conditions: 5.0 mg **1**, 32.4 mg, 64.9 mg, or 324.0 mg NH_3BH_3 for 1.0, 0.5, and 0.1 mol% loading in THF, respectively, 65 °C, 2 freeze–pump–thaw cycles were performed prior to heating and every 2 h thereafter. [b] Reactions did not reach completion after 72 h.

Table 2 Dehydrocoupling of NH_3BH_3 using **1** under anaerobic and aerobic conditions[a]

Reaction	Rxn atm.	*t*/h	Conv./%	Major products[b]/%
Anhydrous THF, loaded in N_2	N_2 [c]	2	99	Borazine (48), polyborazylene (28)
Anhydrous THF, loaded in N_2	Air[d]	1.5	98	Borazine (50), polyborazylene (29)
Anhydrous THF, loaded in air	N^2	2.5	96	Borazine (59)
Anhydrous THF, loaded in air	Air	2.5	97	Borazine (50), polyborazylene (30)
Wet THF, loaded in air[e]	Air	24	4	

[a] Reaction conditions: 0.20 mL **1** (2.0 mM in THF), 0.20 mL NH_3BH_3 (2.0 M in THF), 65 °C. [b] The borazine resonance appears to have a slight downfield shoulder, which has not been definitively assigned.[16] Integrations are not corrected for this feature. [c] Reactions were performed under a back pressure of N_2 gas. [d] Reactions were fitted with a rubber septum and needle to allow free H_2 evolution. [e] Reaction was fitted with a rubber septum and needle and *ca.* 0.5 mL H_2O was added.

was nearly complete after 24 h at 65 °C in all cases. Concentration did not appear to play a significant role in activity as well (Table S-1†). When $CpCo(CO)I_2$ (**2**) was screened as a potential catalyst, similar results were obtained (Table S-2†). Both catalysts yielded similar products including primarily borazine ($^{11}B\{^1H\}$ NMR = s, δ 31.1), borazane ($^{11}B\{^1H\}$ NMR = s, δ −10.8), and small quantities of polyborazylene ($^{11}B\{^1H\}$ NMR = s, δ 27.2).[1b,14] Control reactions demonstrated that 65 °C is the highest temperature for cobalt-catalyzed dehydrocoupling, and reactions in the presence of cobalt run at higher temperatures were complicated by competitive thermal dehydrocoupling of the substrate.

Because cobalt does not form an amalgam with mercury,[15] a filtration test was undertaken to asses homogeneity. A standard reaction mixture (2.0 mM catalyst, 2.0 M NH_3BH_3) was allowed to react for 1 h at 65 °C, after which the reaction was filtered through a 0.22 μm syringe filter and heated for an additional 2 h.[3f] Monitoring the reactions before and after the filtration showed no significant change in activity, consistent with, though not evidence of, a homogeneous process.

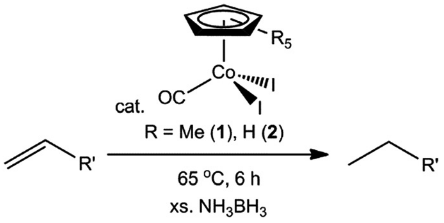
Due to the robust nature of compounds **1** and **2**, the potential for aerobic NH_3BH_3 dehydrocoupling was a tantalizing target. Indeed, when dehydrocoupling reactions were run under aerobic conditions, successful dehydrocoupling was observed (Table 2). However, under these conditions, the distribution of products more heavily favored polyborazylene over borazine in comparison to reactions run in PTFE-sealed tubes based on relative integration in ^{11}B NMR spectra. Most notably, reactions run under an open atmosphere (N_2 or air) proceeded to completion significantly faster than those in NMR tubes under reduced atmosphere (Table 1), similar to reported rhodium catalysts.[3f,4] These observations demonstrate significant inhibition of catalysis by hydrogen.

While aerobic conditions were tolerated well, addition of excess water to the reaction resulted in almost no conversion (Table 2). The volume of H_2 evolved during catalysis was 1.91 equiv. of H_2 per equiv. of NH_3BH_3, giving an average turnover number (TON) of 1924 and a turnover frequency (TOF) of 496 h^{-1} as an average of three trials (see ESI for details†). These values are modest when compared to platinum group catalysts.[5c] However, **1** and **2** utilize cobalt, a more abundant and less expensive transition metal than heavier group 9 congeners and are supported by simple cyclopentadienyl ligands.

Investigation of the fate of the cobalt after the reaction yielded evidence for the preservation of **1**. After completion, only a single resonance for a cyclopentadienyl ligand was observed by ^1H NMR spectroscopy (either THF-d_8 or benzene-d_6), which appeared unchanged as compared to authentic samples of **1**. Infrared spectra of the completed reactions were uninformative regarding the fate of the catalyst because broad and intense ν_{BH} bands centered around 2500 cm^{-1} obstructed possible carbonyl stretches.[17] No evidence for lost cyclopentadienyl ligands was observed in these studies. Further study to establish the exact identity of the catalyst is required.

Given the air stability of **1** and **2** and their activity under aerobic conditions, this catalysis appeared rife for use in benchtop organic transformations. Despite the importance of transfer hydrogenation,[18] relative little attention has been paid to amine boranes as sacrificial hydrogen sources.[18b,19] Indeed, many processes that utilize amine boranes as hydrogen sources use dimethylamine borane as a sacrificial hydrogen donor as opposed to ammonia borane, which could deliver up to two additional equivalents of hydrogen. Thus, the full potential of amine boranes as sacrificial hydrogen sources in transfer hydrogenation is perhaps unrealized, and further study using NH_3BH_3 as a hydrogen source has merit.

Therefore, the transfer hydrogenation of styrene, 2-vinylpyridine, *tert*-butylethylene, *cis*-cyclooctene, phenylacetylene, and diphenylacetylene utilizing NH_3BH_3 as a hydrogen source were attempted. All substrates were reduced to give the hydrogenation products ethylbenzene, 2-ethylpyridine, 2,2-dimethylbutane, cyclooctane, styrene, and *cis*/*trans*-stilbene, respectively. Nearly complete conversion of the unsaturated substrates to other products was observed in all cases as observed by $^{13}C\{^1H\}$ NMR spectroscopy and GC. It should be noted that competitive hydroboration is a known process in reactions where NH_3BH_3 is utilized as a sacrificial hydrogen source.[18a,20] For most substrates, some boron-containing byproducts were observed in a region of the ^{11}B NMR spectrum associated with hydroboration (δ 45–55 ppm), but most boron-containing products were similar to those seen in the dehydrocoupling catalysis (*vide supra*). Hydroboration products were not detected by ^{13}C NMR spectroscopy or identified by GC/MS, which suggests these are minor byproducts. With respect to competitive hydroboration, the best substrate in this proof-of-concept trial was 2-vinylpyridine, where only dehydrocoupling products were observed by ^{11}B{^{1}H} NMR spectroscopy, and complete conversion of the substrate to 2-ethylpyridine was measured within the detection limits of ^{13}C{^{1}H} NMR spectroscopy and GC. All hydrogenation reactions gave nearly identical results whether they were performed in a PTFE-sealed reaction tube or in an open Schlenk flask fitted with a condenser. A control reaction of 2 mM of **1** in THF with 50 equiv. of styrene was heated to 65 °C under one atmosphere of H_2. No detectible reaction occurred even after reaction times up to 7 days, which is consistent with transfer hydrogenation rather than hydrogenation from ambient H_2 generated by dehydrocoupling of NH_3BH_3. Peters's PBP-supported cobalt compound also engages in transfer hydrogenation and uses dimethylamine borane as the hydrogen.[13] It should be noted that yields of hydrogenated products were nearly quantitative in that study, showing more selective reactivity than the systems described here. However, that catalyst and reaction are not reported to be air stable.



(2)

In conclusion, two half sandwich cobalt complexes **1** and **2** were shown to be effective catalysts for the dehydrogenation of ammonia borane. These represent two rare examples of homogeneous cobalt complexes that can catalyze this reactivity. In addition, these catalysts are able to effectively transfer hydrogenate unsaturated organic substrates using NH_3BH_3 as a sacrificial hydrogen source. Finally, these compounds display unique robustness with respect to aerobic conditions for both dehydrogenation and transfer hydrogenation reactions.

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