Hydrides

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Air-Stable (CAAC)CuCl and (CAAC)CuBH$_4$ Complexes as Catalysts for the Hydrolytic Dehydrogenation of BH$_3$NH$_3$**

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Abstract: *The first stable copper borohydride complex [(CAAC)CuBH$_4$] [CAAC = cyclic(alkyl)(amino)carbene] bearing a single monodentate ligand was prepared by addition of NaBH$_4$ or BH$_3$NH$_3$ to the corresponding [(CAAC)CuCl] complex. Both complexes are air-stable and promote the catalytic hydrolytic dehydrogenation of ammonia borane. The amount of hydrogen released reaches 2.8 H_2/BH_3NH_3 with a turnover frequency of 8400 $mol_{H_2} mol_{cat}^{-1} h^{-1}$ at 25 °C. In a fifteen-cycle experiment, the catalyst was reused without any loss of efficiency.*

Metal borohydride M(BH$_4$)$_n$ (n = 1, 2, and 3)[1] and ammonia borane (BH$_3$NH$_3$) are known as excellent hydrogen storage materials because of their high hydrogen capacity.[2] Among M(BH$_4$)$_n$ complexes, CuBH$_4$ is unstable,[3] and only a few copper(I) borohydride complexes stabilized by two or three ligands (L),[4] such as the commercially available [(Ph$_3$P)$_2$CuBH$_4$], have been isolated. So far, all attempts to isolate CuBH$_4$ complexes supported by a single monodentate ligand have failed, as exemplified by the rapid decomposition of [(Ph$_3$P)CuBH$_4$] at −20 °C.[5] Releasing H$_2$ at room temperature with a high hydrogen generation rate is vital to making significant use of BH$_3$NH$_3$.[6] Rh,[7] Ru,[8] Pd,[9] and Ir[10] complexes are representative catalysts for the pyrolytic dehydrogenation, whereas Pt[11] and Au[12] are the most efficient for the hydrolytic dehydrogenation of BH$_3$NH$_3$. Developing catalysts based on cheap transition metals,[13,14] especially earth-abundant metals such as Fe[15] and Cu,[16] is one of the most important steps for the large-scale application of these dehydrogenation reactions. Additionally, because of decomposition or particle agglomeration, most of the catalysts (both noble and non-noble metal catalysts) suffer from a short lifetime and are hardly recyclable.[2]

Herein, we report the isolation of a copper borohydride complex supported by a single ligand. We also describe the serendipitous discovery that [(CAAC)CuCl] complexes [CAAC = cyclic(alkyl)(amino)carbene][17] are highly efficient and recyclable catalysts for the hydrolytic dehydrogenation of BH$_3$NH$_3$.

In the course of our ongoing search for the preparation of a hitherto unknown stable monomeric copper hydride,[18] we attempted the reduction of the [(CAAC^{Et})CuCl] (**1**) with NaBH$_4$ (Figure 1). The ^{11}B NMR spectrum of the resulting

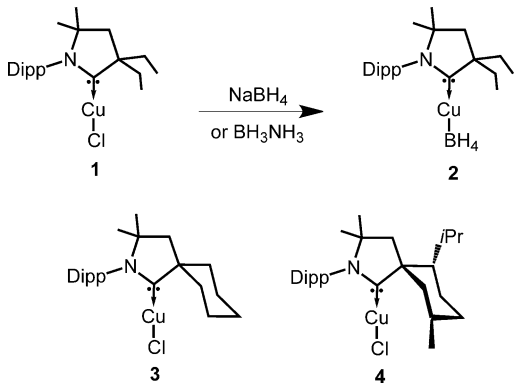

Figure 1. Synthesis of the [(CAAC^{Et})CuBH$_4$] complex **2** and the [(CAAC)CuCl] complexes **1**, **3**, and **4** used in this study. Dipp = 2,6-diisopropylphenyl.

product showed a quintet at $\delta = -38.2$ ppm, thus indicating the presence of a BH$_4$ fragment, which is different from NaBH$_4$ (δ^{11}B: −43.5 ppm). After work up, the complex **2** was isolated as a white solid in 58% yield, and its structure was confirmed by a single-crystal X-ray diffraction study (Figure 2).[19] Two hydrogen atoms of BH$_4$ interact with the metal, with Cu···H distances of 1.679(2) and 1.717(18) Å. The Cu···C$_{carbene}$ distance [1.8879(15) Å] is comparable to that of **1** [1.8752(13) Å]. The complex **2** is air stable at room temperature, both in solution and in the solid state, and decomposes only above 162 °C. Surprisingly, we found that **2** could also be prepared in 91% yield by addition of excess ammonia borane to the copper chloride complex **1**. In this case, the formation of **2** might result from an ion exchange between **1** and [(NH$_3$)$_2$BH$_2$]$^+$[BH$_4$]$^-$, a postulated unstable intermediate in the dehydrogenation of BH$_3$NH$_3$.[2f,g,20]

Since the copper chloride **1** cleanly reacts at room temperature with BH$_3$NH$_3$ to produce **2**, we wondered whether **1** could be an efficient catalyst for the hydrolytic dehydrogenation of BH$_3$NH$_3$.[21] When a 1 mol% acetone/water solution (20 wt% of water) of **1** was added to BH$_3$NH$_3$,

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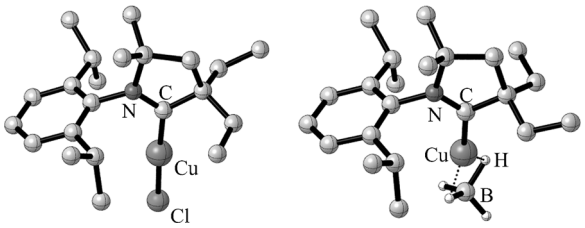

Figure 2. X-ray structure of **1** (left) and **2** (right). All hydrogen atoms, except those bonded to boron, are omitted for clarity.

2.6 moles of H_2 were released per mole of BH_3NH_3 over 5 minutes, and corresponds to a turnover frequency (TOF) of 3100 $mol_{H_2} mol_{cat}^{-1} h^{-1}$ (Figure 3). As observed with other catalysts, NH_4BO_2 is produced as the hydrolytic byproduct.[2,11,12]

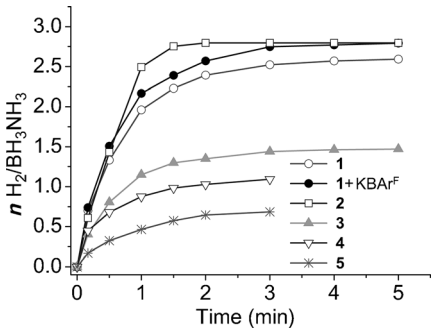

Figure 3. Amount of H_2 released in the hydrolytic dehydrogenation of BH_3NH_3 using 1 mol% **1**, **1** + $KBAr^F$, **2**, **3**, **4**, and **5** at 25 °C.

The TOF for **1** is about 500 times higher than that reported using 30 mol% of $CuCl_2$.[16] We found that $[(Ph_3P)_2CuCl]$ (**5**) was also a poor catalyst (TOF = 850), which is not surprising since this complex does not react with BH_3NH_3 when the reaction is carried out at room temperature. These observations prompted us to try optimizing the structure of the CAAC-supported copper catalyst. Introducing bulkier substituents on the α-carbon atom of the CAAC ligand, as shown by **3** and **4** (Figure 1), resulted in a decrease of activity (TOF = 1770 and 1340, respectively).

We then focused on the smallest CAAC ligand. Having already shown that the presence of a chloride scavenger often enhances the reactivity of CAAC-coinage metal complexes,[22] we sought to augment the reactivity of **1** by first using a 1:1 mixture of **1** and potassium tetrakis(pentafluorophenyl)borate ($KBAr^F$). The amount of H_2 released increased to 2.8 moles, with a TOF of 3360. Then, we realized that **2** was probably either the active catalytic species or the resting state of the catalyst. Indeed, by using 1 mol% of **2**, the hydrolytic dehydrogenation reaction of BH_3NH_3 was finished within 2 minutes at 25 °C, with 2.8 moles of H_2 released per mole of BH_3NH_3, thus giving a TOF of 8400. These results compared well with those obtained in the hydrolytic dehydrogenation of ammonia borane promoted by noble metal catalysts.[11,12]

Other than the TOF, an important aspect for the large-scale application of catalysts is their robustness in recycling processes. The 1:1 mixture of **1** and $KBAr^F$ was reused 15 times without any noticeable loss of catalytic activity (Figure 4). For each cycle, the dehydrogenation reaction was

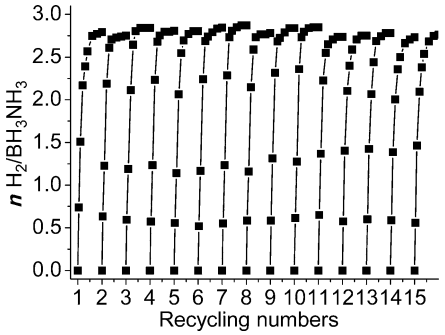

Figure 4. Recycling of catalyst in the BH_3NH_3 dehydrogenation at 25 °C. Catalyst: 1 mol% (**1** + $KBAr^F$). Reaction time for each cycle: 5 min.

finished within 5 minutes and the release of H_2 fluctuated around 2.8 moles. The procedure for recycling the catalyst is straightforward. After the dehydrogenation reaction was over, the suspension was filtered and the solution was directly reused without any treatment. The recyclability of the catalyst solution greatly enhances the hydrogen storage capacity when taking solvent into consideration.[2b]

In summary, the peculiar electronic properties of CAACs allow the isolation of the first monoligated $CuBH_4$ complex. Both [(CAAC)$CuBH_4$] and their precursors [(CAAC)CuCl] efficiently promote the hydrolytic dehydrogenation of BH_3NH_3. TOFs reach 8400 at 25 °C, and compare well with those reported for noble-metal-based catalysts. Additionally, the catalytic solution can be handled in air and be recycled without significant loss of activity.

Experimental Section

Synthesis of **1**: Diethyl cyclic iminium tetrafluoroborate salt (1204 mg, 3.00 mmol), potassium hexamethyldisilazide (628 mg, 3.15 mmol), and copper(I) chloride (312 mg, 3.15 mmol) were loaded in a Schlenk tube under argon. THF (40 mL) was added to the solids at −78 °C and the mixture was stirred for 1 h at the same temperature. The mixture was warmed to room temperature and stirred for another 5 h. The volatiles were removed under vacuum and the residue was washed with hexanes (30 mL). After removing the volatiles, the residue was extracted with benzene (40 mL). The solution was evaporated and dried under vacuum, affording **1** as a white solid (963 mg, 78% yield). Single crystals were obtained from a diethyl ether solution stored at −38 °C. m.p. 241–242 °C; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 250.26$ ($C_{carbene}$), 145.03 (C_{aro}), 134.59 (C_{aro}), 129.72 (CH_{aro}), 124.74 (CH_{aro}), 81.04 (C_q), 62.55 (C_q), 42.39 (CH_2), 31.11 (CH_2), 29.28 (CH_3), 29.19 (CH_3), 27.30 (CH), 22.37 (CH_3), 9.64 ppm (CH_3); HRMS (*m*/*z*): $[M+NH_4]^+$ calcd for $[C_{22}H_{35}NCuCl{\cdot}NH_4]^+$: 429.2092, found 429.2084.

Synthesis of **2**: *Method A*: The complex **1** (411 mg, 1.00 mmol) and $NaBH_4$ (151 mg, 4.00 mmol) were loaded in a Schlenk tube under argon. THF (30 mL) was added and the mixture was stirred for 24 h at room temperature. The suspension was filtered under argon. The

filtrate was evaporated under vacuum and the residue was extracted with ether (50 mL). The solution was evaporated and dried under vacuum, thus affording **2** as a white solid (225 mg, 58% yield). *Method B*: Compound **1** (411 mg, 1.00 mmol) and BH_3NH_3 (185 mg, 6.00 mmol) were loaded in a Schlenk tube under argon. THF (30 mL) was added to the solids and the mixture was stirred for 24 h at room temperature. The suspension was filtered under argon. The filtrate was evaporated under vacuum and the residue was extracted with ether (50 mL). The solution was evaporated and dried under vacuum, thus affording **2** as a white solid (356 mg, 91% yield). Single crystals were obtained at −38 °C from an ether solution. m.p. 162–163 °C (dec.); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.12$ (t, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 2H), 2.75 (sept, $J = 6.0$ Hz, 2H), 1.65 (m, 2H), 1.56 (m, 2H), 1.43 (s, 2H), 1.36 (d, $J = 6.0$ Hz, 6H), 1.09 (d, $J = 6.0$ Hz, 6H), 0.88 (br, 12H), 0.56 ppm (m, $J = 83.0$ Hz, 4H); ^{11}B NMR (96 MHz, $CDCl_3$): $\delta = -38.21$ (quint, $J = 83.0$ Hz).

Syntheses of **3** and **4** can be found in the Supporting Information.

Procedure for the hydrolytic dehydrogenation of BH_3NH_3 catalyzed by **1**, **3**, **4**, or **5:** The dehydrogenation reactions were carried out at 25 °C under air. BH_3NH_3 (15.4 mg, 0.5 mmol) was loaded in a tube equipped with a magnetic stirrer. A solution of catalyst (1 mol% based on BH_3NH_3) in 1.0 mL of acetone/water (20 wt% of water) was quickly added by a syringe. The amount of H_2 released was measured with a water-filled burette.

Procedure for the hydrolytic dehydrogenation of BH_3NH_3 catalyzed by **2**: The dehydrogenation reaction was carried out at 25 °C under air. BH_3NH_3 (15.4 mg, 0.5 mmol) and **2** (2.0 mg, 0.005 mmol) was loaded in a tube equipped with magnetic stirrer. 1.0 mL of acetone/water (20 wt% of water) was quickly added to the tube by a syringe. The amount of H_2 released was measured by a water-filled burette.

Keywords: boranes · carbenes · copper · hydrides · structure elucidation

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