Hydrogen Storage System | Hot Paper

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Rechargeable Hydrogen Storage System Based on the Dehydrogenative Coupling of Ethylenediamine with Ethanol

*Peng Hu, Yehoshoa Ben-David, and David Milstein**

Abstract: *A novel and simple hydrogen storage system was developed, based on the dehydrogenative coupling of inexpensive ethylenediamine with ethanol to form diacetylethylenediamine. The system is rechargeable and utilizes the same ruthenium pincer catalyst for both hydrogen loading and unloading procedures. It is efficient and uses a low catalyst loading. Repetitive reversal reactions without addition of new catalyst result in excellent conversions in both the dehydrogenation and hydrogenation procedures in three cycles.*

The search for sustainable energy systems to replace the current fossil-fuel-based technologies is an urgent issue.[1,2] Construction of a sustainable energy supply chain requires energy generation, storage, and release. Hence the development of efficient and inexpensive energy storage and liberation systems is needed. Through such systems, energy can be stored during "energy-rich" periods and used during "energy-lean" periods. Hydrogen, which holds the highest energy density by weight, is viewed as an ideal candidate for the future energy supply.[1,2] In fact, the hydrogen-powered fuel cell has been intensively studied in recent years.[3] However, hydrogen storage is a considerable challenge, since its energy density by volume or weight is low when stored as a pressurized gas or cryogenically as a liquid, and safety issues are involved.[1,2,4,5] Hence hydrogen storage materials have attracted much attention in the last decades and many physical and chemical methods for hydrogen storage have been developed. However, most of these methods either suffer from low hydrogen storage capacity or are too expensive for practical use.[1,2,5]

An attractive approach is the storage of hydrogen in chemical bonds, and its release by dehydrogenation reactions, using organic compounds.[2c,6] Especially interesting are organic liquids with considerable hydrogen storage capacity (HSC), which can be easily handled and transported, using the existing infrastructure of the oil or gasoline industry.[6] Recently, methanol reforming catalyzed by metal complexes under relatively mild conditions was reported by Beller, Grützmacher, and us.[7] In these promising systems, aqueous solutions of methanol generate CO_2 and afford three H_2 molecules per one molecule of methanol and water. In addition, a promising formaldehyde–water system was developed for hydrogen production by Prechtl.[8] These approaches are in fact hydrogen- and CO_2-liberation systems, of which the liquid carriers are consumed and cannot readily reload hydrogen. Formic acid has been intensively investigated as a hydrogen carrier; it can be decomposed to hydrogen and CO_2 under mild conditions and has a HSC of 4.4 wt %.[9] The generated CO_2, or mostly carbonates, can be transformed to formic acid under hydrogen pressure. Recently, several rechargeable systems based on formic acid were developed, using the same catalyst for both hydrogenation and dehydrogenation.[9d,e] However, apart from the moderate HSC of formic acid, which is an inherent feature of these systems, a stoichiometric amount of base was usually required to capture the generated CO_2.[10]

Besides formic acid, liquid organic hydrogen carriers (LOHCs), which can unload and load hydrogen through dehydrogenation and hydrogenation reactions, and can be easily transported and stored, were investigated.[5b,6,11–13] Much attention has been devoted to *N*-ethylcarbazole as LOHC,[11] which has a HSC of 5.8 wt %; heterogeneous catalysts were used and different catalytic systems were required for the hydrogenation and dehydrogenation steps. In addition, 2-methyl-1,2,3,4-tetrahydroquinoline[12a] and 2,6-dimethyldecahydro-1,5-naphthyridine[12b] were also reported as hydrogen storage materials. However, these systems suffer from either relatively harsh conditions or high catalyst loadings and both use relatively expensive materials. Until now, most experimental and computational studies about LOHCs emphasize heterocyclic aromatic hydrocarbons, mostly N-heterocycles.[13] Considering this narrow material scope, with its limitations, it is desirable to develop other readily available inexpensive compounds as hydrogen carriers.

Based on Ru pincer catalysts (Figure 1), our group has developed the acceptorless dehydrogenative amidation reaction, using amines and primary alcohols as substrates, resulting in formation of amides and dihydrogen

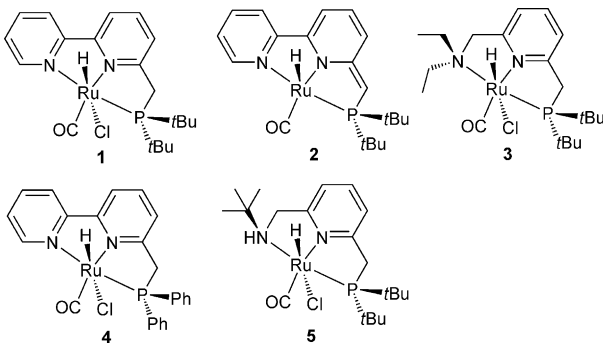

Figure 1. Structures of PNN ruthenium pincer complexes **1**–**5**.

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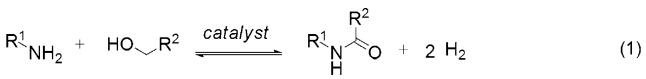
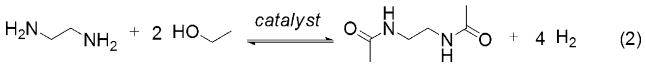
[Eq. (1)].[14,15] In addition, amides can be hydrogenated to the corresponding amines and alcohols under mild hydrogen pressure, catalyzed by the same type of catalysts.[14,16] Very



(1)

recently, we have developed an attractive hydrogen carrier system using 2-aminethanol, which undergoes dehydrogenative cyclization to form glycine anhydride.[17] We now raise the possibility of developing new LOHC systems based on Equation (1), using commercially available, inexpensive, and abundant amines and alcohols as hydrogen carriers. Reported herein is a LOHC system based on the dehydrogenative coupling of ethylenediamine and ethanol, with a HSC of 5.3 wt% [Eq. (2)]. The system is catalyzed by complex **1** in the presence of catalytic base, using low catalyst loading



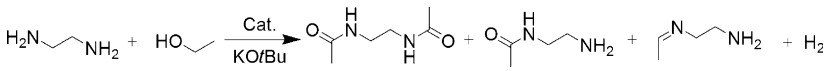
(2)

(0.2 mol%), and exhibits excellent conversions for both the dehydrogenation and hydrogenation reactions.

Initially, we performed the dehydrogenative coupling reaction of ethylenediamine (ED) with ethanol with no added solvent. To a mixture of 10 mmol ED and 24 mmol ethanol, were added 0.01 mmol catalyst **1** (0.1 mol% relative to ED and 0.04 mol% relative to ethanol) and 0.012 mmol KO*t*Bu (1.2 equiv relative to catalyst **1**, for the generation of the actual catalyst **2** in situ; Figure 1). The solution was heated at reflux under argon for 24 h and 47% conversion of ED was achieved, producing the desired product *N*,*N*′-diacetylethylenediamine (DAE) in only 2% yield, the monoamide *N*-(2-aminoethyl)-acetamide (AEA) in 23% yield, and *N*-ethylidenethane-1,2-diamine (EED) in 22% yield, as determined by ^{1}H NMR spectroscopy (Table 1, entry 1). Using ED in excess, higher conversion of both ethanol and ED were achieved, resulting in 17% yield of the desired DAE (Table 1, entry 2). Increasing the amount of ED from 12 mmol to 15 mmol did not significantly improve the results (Table 1, entry 3). Using catalysts **3**–**5** under conditions similar to those of entry 3 resulted in inferior performance relative to that achieved with catalyst **1** (Table 1, entries 4–6). Introducing dioxane as a solvent and increasing the catalyst loading of **1** to 0.4 mol% (based on ED) dramatically improved the reaction. Using 5 mmol of ED, 12 mmol of ethanol, and 2 mL of dioxane resulted in full conversions of ED and ethanol, DAE in 93% yield and AEA in 7% yield (Table 1, entry 7). Lower catalyst loading (0.2 mol% based on ED and 0.08 mol% based on ethanol) did not influence conversions of the reactants and produced DAE in 84% yield (Table 1, entry 8). Note that the employed excess of ethanol (20% relative to ED) releases hydrogen by itself, by self-dehydrogenative coupling to give ethyl acetate as the product.[14,18] Interestingly, when only 1 mL of dioxane was used, full conversions of ethanol and ED were achieved, and 92% yield of DAE was provided (Table 1, entry 9). Moreover, 503 mL of hydrogen was collected, amounting to 95% yield based on full conversion of ethanol and ED, which can produce 5 mmol DAE, 1 mmol ethyl acetate, and 22 mmol H_2. Efforts to decrease the catalyst loading and the amount of solvent were ineffective (Table 1, entries 10–12).

Next we pursued the hydrogenation of *N*,*N*′-diacetylethylenediamine (DAE) to ED and ethanol. Using 1 mol% complex **1**, 1.2 mol% KO*t*Bu, 0.5 mmol DAE in 1 mL dioxane under 40 bar of hydrogen for 24 h resulted in 63% yield of ED and 35% yield of AEA, as determined by ^{1}H NMR spectroscopy (Table 2, entry 1). When 50 bar of hydrogen were applied, 84% yield of ED was obtained (Table 2, entry 2). A longer reaction time of 48 h improved

Table 1: Selected results of optimization studies for dehydrogenative coupling of ethylenediamine with ethanol.[a]

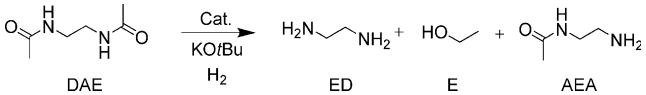


ED E DAE AEA EED

Entry	Cat. [mmol]	ED [mmol]	E [mmol]	Solv. [mL]	ED conv. [%]	E conv. [%]	DAE yield [%]	AEA yield [%]	EED yield [%]
1	**1** (0.01)	10	24	–	47	20	2	23	22
2	**1** (0.01)	12	20	–	74	38	17	48	9
3	**1** (0.01)	15	20	–	74	39	19	49	6
4	**3** (0.01)	15	20	–	30	13	–	7	22
5	**4** (0.01)	15	20	–	27	12	1	13	14
6	**5** (0.01)	15	20	–	40	18	2	24	14
7	**1** (0.02)	5	12	dioxane (2)	100	100	93	7	–
8	**1** (0.01)	5	12	dioxane (2)	100	98	84	16	–
9[b]	**1** (0.01)	5	12	dioxane (1)	100	100	92	8	–
10	**1** (0.01)	10	24	dioxane (2)	51	23	5	29	17
11	**1** (0.01)	5	11	dioxane (1)	98	99	78	20	–
12	**1** (0.02)	10	24	dioxane (1)	77	39	16	44	16

[a] Reaction conditions: Catalyst (as specified), KO*t*Bu (1.2 equiv relative to cat. **1**, **3**, and **4** and 2.4 equiv relative to cat. **5**), 105 °C (oil bath temperature 135 °C), reflux under Ar for 24 h. ED = ethylenediamine, E = ethanol, DAE = *N*,*N*′-diacetylethylenediamine, AEA = *N*-(2-aminoethyl)acetamide, EED = *N*-ethylideneethane-1,2-diamine. [b] 503 mL H_2 was collected, amounting to 95% yield based on full conversion of ethylenediamine and ethanol, which would produce 5 mmol *N*,*N*′-diacetylethylenediamine, 1 mmol ethyl acetate, and 22 mmol H_2.

Table 2: Selected results from the optimization studies for the hydrogenation of *N*,*N*′-diacetylethylenediamine.[a]



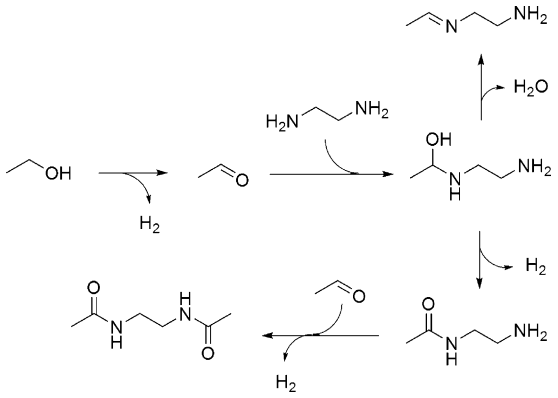
Entry	Cat. [mol%]	KO*t*Bu [equiv to cat.]	DAE [mmol]	*t* [h]	Products [% yield]
1[b,c]	**1** (1)	1.2	0.5	24	ED (63) + AEA (35) + E (55)
2[b]	**1** (1)	1.2	0.5	24	ED (84) + AEA (15) + E (68)
3[b]	**1** (1)	1.2	0.5	48	ED (91) + AEA (9) + E (70)
4[b]	**1** (1)	2.4	0.5	24	ED (89) + AEA (11) + E (71)
5	**1** (0.5)	2.4	1	24	ED (91) + AEA (9) + E (79)
6	**1** (0.2)	2.4	1	48	ED (77) + AEA (22) + E (69)
7	**1** (0.2)	5	1	48	ED (82) + AEA (18) + E (71)
8	**5** (0.2)	2.4	1	48	ED (71) + AEA (28) + E (61)
9[d]	**1** (0.2)	2.4	1	48	ED (92) + AEA (8) + E (73)
10[e]	**1** (1)	2.4	0.5	48	ED (trace) + AEA (14) + E (–)
11[d]	**1** (0.4)	2.4	5	10	ED (>99) + E (89)

[a] Reaction conditions: Catalyst, KO*t*Bu, *N*,*N*′-diacetylethylenediamine, dioxane (2 mL), and H_2 (50 bar) were heated in a 20 mL Parr apparatus at 115 °C (oil bath temperature). Yields were determined by NMR analysis. The relatively lower yields of ethanol are probably due to the evaporation loss during the reaction and workup. [b] 1 mL dioxane was used. [c] 40 bar H_2 was used. [d] 70 bar H_2 was used. [e] 1 mL ethanol was used as solvent, 47% yield of *N*-ethylideneethane-1,2-diamine was observed, the conversion of DAE was 61%.

the yield of ED to 91% and full conversion of DAE was achieved (Table 2, entry 3). A higher amount of base was beneficial (Table 2, entries 4 and 5); full conversion of DAE and excellent yield of ED were obtained even at a lower catalyst loading of 0.5 mol% after 24 h (Table 2, entry 5). Further optimization of the catalyst loading indicated that using 0.2 mol% of catalyst **1** also resulted in good yield of ED after 48 h (Table 2, entry 6). Increasing the amount of base from 2.4 equiv to 5 equiv (relative to catalyst **1**) slightly improved the yield of ED (Table 2, entry 7). Complex **5** also showed good catalytic activity for the hydrogenation reaction, but it was not as efficient as catalyst **1** (Table 2, entry 6 vs. entry 8). When 70 bar of hydrogen and 0.2 mol% of catalyst **1** were applied, full conversion of DAE and 92% yield of ED were achieved after 48 h (Table 2, entry 9). Using ethanol as solvent instead of dioxane resulted in low yields of ED and AEA (Table 2, entry 10). Employing 0.4 mol% catalyst **1**, a larger scale (5 mmol DAE) hydrogenation reaction was tried in less solvent (2 mL) under 70 bar of hydrogen, leading to quantitative yield of ED in just 10 h (Table 2, entry 11).

Repetitive reversal reactions were also tried with no addition of new catalyst, in shorter dehydrogenation and hydrogenation periods of 12 h and 10 h, respectively (Table S1, see the Supporting Information for details). The cycles began with dehydrogenation, using 0.4 mol% catalyst **1**, 0.48 mol% KO*t*Bu, 5 mmol ED, 12 mmol ethanol, and 2 mL dioxane.[19] After the first dehydrogenation reaction, which resulted in 99% conversion of ED, the crude reaction mixture was transferred to a 20 mL Parr apparatus for hydrogenation. The catalytic activity of the system did not decrease and full conversion was observed. Following, the second dehydrogenation step resulted in 92% conversion of ED, while the second hydrogenation step also provided 100% of ED. The performance of the third cycle was also good; even after the catalyst had been used six times, 100% ED was still observed at the end of the third hydrogenation step.

Based on our previous research on dehydrogenation reactions[14–16,20] and the above results, a simplified mechanism for the dehydrogenative amidation of ED and ethanol is shown in Scheme 1. Dehydrogenation of ethanol forms



Scheme 1. Proposed pathway for the dehydrogenation of ethylenediamine and ethanol.

acetaldehyde as an intermediate, which reacts with one amine group of ED to form a hemiaminal intermediate. The latter undergoes competitive elimination of water to produce *N*-ethylidenethane-1,2-diamine[20] and elimination of hydrogen to form *N*-(2-aminoethyl)acetamide. Reaction of *N*-(2-aminoethyl)acetamide with another molecule of acetaldehyde and release of one molecule of hydrogen leads to *N*,*N*′-diacetylethylenediamine as the product.

In conclusion, an efficient and simple homogeneous LOHC system was developed, using ethylenediamine and ethanol as the hydrogen carriers. Employing a low catalyst loading of 0.2 mol%, complex **1** catalyzed both the unloading and the loading of hydrogen in excellent yields; no stoichiometric additives were needed. High concentrations of substrates (5 mol ethylenediamine/mL dioxane and 12 mol ethanol/mL dioxane) could be applied and the efficiency of the reaction did not decrease. The repetitive reactions catalyzed by 0.4 mol% catalyst exhibited excellent conversions in three cycles. Ethylenediamine and ethanol, which are inexpensive and extensively produced by industry, can provide, upon further development, a new simple LOHC system, which is quite different from the existing hydrogen storage systems. Ongoing research will focus on increasing the efficiency of the current system (e.g. using no solvent), and developing other amine–alcohol systems with even higher HSCs (for example, ethylenediamine and methanol).

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