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Communication

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Selective Hydrogenation of Cyclic Imides to Diols and Amines and its Application in the Development of a Liquid Organic Hydrogen Carrier.

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Supporting Information Placeholder

ABSTRACT: Direct hydrogenation of a broad variety of cyclic imides to diols and amines using a ruthenium catalyst is reported here. We have applied this strategy towards the development of a new Liquid Organic Hydrogen Carrier (LOHC) system based on the hydrogenation of *bis*-cyclic imide that is formed by the dehydrogenative coupling of 1,4-butanediol and ethylenediamine using a new ruthenium catalyst. The rechargeable system has a maximum gravimetric hydrogen storage capacity of 6.66 wt%.

Catalytic hydrogenation of polar bonds, in particular organic carbonyl groups, offers a green and sustainable strategy to access synthetically important building blocks such as alcohols and amines. We and others have previously reported the catalytic hydrogenation of ketones, esters, acids, anhydrides, amides and even more challenging carbonyl groups, such as of carbonates, carbamates and urea derivatives, to the corresponding alcohols and amines, as reviewed.[1-9] Much attention has also been paid to the hydrogenation of cyclic imides; Ikariya[10-11] and Bergens[12] have reported the partial hydrogenation of cyclic imides to hydroxyamides. Hydrogenative C-O bond cleavage of cyclic imides to form lactams or cyclic amines has also been reported independently by Drago,[13] Bruneau,[14] Beller[15] and Agbossou-Niedercorn.[16] However, selective hydrogenation of cyclic imides to diols and amines has been hitherto limited to a single substrate (N-benzylphthalimide), recently reported by Lv and Zhang.[17]

Hydrogenation/Dehydrogenation of small organic molecules has also attracted significant interest in recent years because of its potential application in the development of Liquid Organic Hydrogen Carriers (LOHCs).[18-20] Taking advantage of the favorable thermodynamics in amide bond formation by dehydrogenating coupling of alcohols and amines,[21] we recently reported LOHC systems based on the formation of amide bonds from cheap and easily available starting materials such as ethanolamine or ethanol/ethylenediamine and their hydrogenation under mild conditions (Figure 1).[22-23]

Herein we report the first example of selective hydrogenation of a broad variety of cyclic imides to diols and amines, using a ruthenium catalyst under mild conditions. The rare selectivity of this hydrogenation reaction allowed us to develop a new reversible hydrogen storage system based on the formation of *bis*-cyclic imides (spent fuel) from inexpensive and easily available starting materials 1,4-butanediol and ethylenediamine (charged fuel). Using ruthenium complexes **3** and **4** we show that both the dehydrogenation and hydrogenation processes can occur to make a reversible hydrogen storage system with the high theoretical hydrogen storage capacity of 6.66 wt %.

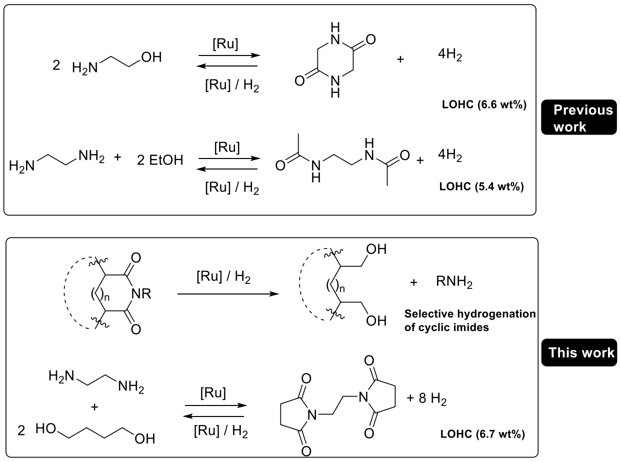


Figure1. LOHCs reported by us based on the amide bond formation and hydrogenation (top), selective hydrogenation of cyclic imides to diols and amines; and the LOHC based on the formation of *bis*-cyclic imide and its hydrogenation as described in this work (bottom).

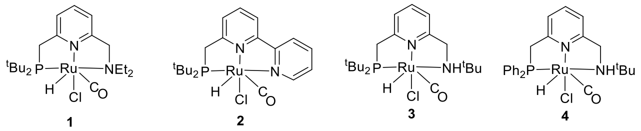
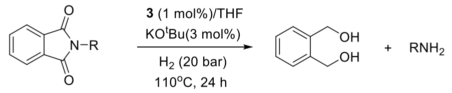
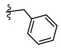
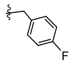
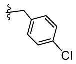
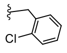
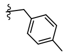
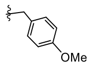
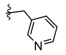
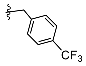
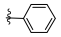


Figure 2. Ruthenium complexes used in this report.

We commenced our investigation by exploring the catalytic utility of complexes **1**-**3** (Figure 2) for the hydrogenation of N-benzylphthalimide. Under the catalytic conditions of complex **1** (1 mol%), KO^tBu (1 mol%) in THF under 20 bar H_2 at 110°C, 67% conversion of N-benzylphthalimide was observed in 24 h with the concomitant formation of benzylamine in 65% yield and 1,2-benzenedimethanol in 60% yield. Formation of the cyclic ester phthalide was also observed in 5% yield by ^1H NMR spectroscopy and GC-MS (See Table S1 for the optimization details). Under the same conditions, precatalyst **2**, which has been previously used for the efficient hydrogenation of amides gave similar yields of the products as that of precatalyst **1**.[24] Interestingly, employing complex **3** (1 mol%) in presence of 1 mol% KO^tBu under the same reaction conditions as used for **1** resulted in better conversion of N-benzylphthalimide (84% conversion) to 1,2-benzenedimethanol and benzylamine. Finally, when the amount of base was raised to 3 mol%, complex **3** gave almost complete conversion of N-benzylphthalimide, with quantitative formation of 1,2-benzenedimethanol and benzylamine as detected by GC and NMR spectroscopy. We believe that the higher catalytic activity of complex **3** relative to **1** and **2** is due to its ability to exhibit dual modes of metal-ligand cooperation *i.e.* via H-M/N-H and via aromatization/dearomatization of the lutidine backbone. We have previously demonstrated that addition of two equivalents of base or more to complex **3** results in the formation of a double deprotonated monoanionic enamido complex which serves as a highly active catalyst for the unprecedented hydrogenation of ester at room temperature and low pressure (5at.).[25]

Table 1. Catalytic hydrogenation of phthalimides using complex **3**.[a]



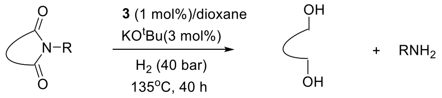
Entry	R	phthalimide conversion[b]	yield of amine[c]	yield of diol[b]
1		99%	99%	95%
2		99%	99%	99%
3		95%	95%	93%
4		90%	90%	88%
5		95%	95%	93%
6		98%	96%	95%
7		94%	90%	90%
8		85%	85%	84%
9		99%	99%	99%
10		99%	99%	99%

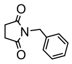
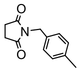
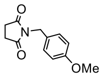
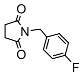
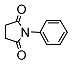
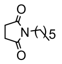
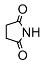
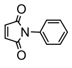
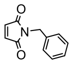
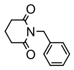
[a]Conditions: phthalimide (1 mmol), complex **3** (0.01 mmol), KO^{t}Bu (0.03 mmol), THF (2 mL), H$_2$ (20 bar), 110^{o}C, 24 h. [b]Conversion of phthalimide and yield of diol are detected by ^{1}H NMR spectroscopy using mesitylene as an internal standard. Yield of amine is detected by GC and ^{1}H NMR spectroscopy using toluene/mestitylene as an internal standard.

Upon optimizing the catalytic conditions for efficient hydrogenation of N-benzylphthalimide, we explored the hydrogenation of other phthalimde substrates. As shown in Table 1, phthalimdes of benzylamines bearing both electron withdrawing and electron donating substituents were efficiently hydrogenated. N-phenylphthalimide and N-hexylphthalimde were also completely hydrogenated to afford 1,2-benzenedimethanol and the corresponding amine in quantitative yield.

Encouraged by the efficient catalytic hydrogenation of N-substituted phthalimides, we screened other cyclic imides towards hydrogenation. However, under the catalytic conditions described in Table 2, only 30% conversion of N-benzylsuccinimide to 1,4-butanediol and benzylamine was observed. Increasing the reaction temperature to 135°C improved the hydrogenation yield such that 75% conversion of N-benzylsuccinimide to 1,4-butanediol and benzylamine was observed. Finally, changing the reaction time from 24 h to 40 h and using 1,4-dioxane as a solvent resulted in almost complete hydrogenation of N-benzylsuccinimide and the quantitative formation of 1,4-butanediol and benzylamine was observed by ^{1}H NMR spectroscopy and GC. Other succinimides bearing either electron rich or electron deficient benzyl groups, phenyl and hexyl groups were successfully hydrogenated to afford 1,4-butanediol and the corresponding amines in excellent yield (Table 2, entries 1-6). Unsubstituted succinimide was also hydrogenated in good yield and 78% of 1,4-butanediol was observed by ^{1}H NMR spectroscopy (entry 7). Under the same conditions, hydrogenation of N-phenylmaleimide and N-benzylmaleimide resulted in high yields of aniline and benzylamine, respectively, in addition to 1,4-butanediol yields (entries 8,9); both C=O and C=C hydrogenation took place. N-benzylglutarimide was also successfully hydrogenated to afford 1,6-hexanediol and benzyl amine in 90% yield (entry 10).

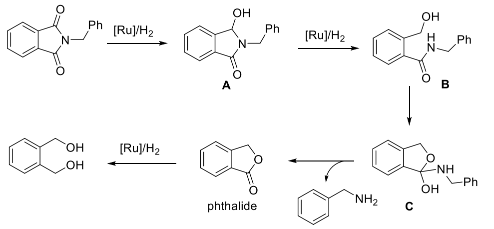
Table 2. Catalytic hydrogenation of cyclic imides using complex **3**.[a]



Entry	cyclic imide	cyclic imide conversion[b]	yield of amine[c]	yield of diol[b]
1		99%	99%	97%
2		99%	97%	98%
3		90%	90%	88%
4		95%	95%	95%
5		99%	99%	99%
6		96%	95%	95%
7		82%	-	78%
8		99%	99%	99%
9		95%	90%	88%
10		90%	90%	90%

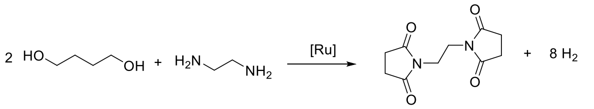
[a]Conditions: cyclic imide (0.5 mmol), complex **3** (0.005 mmol), KO^{t}Bu (0.015 mmol), 1,4-dioxane (2 mL), H$_2$ (40 bar), 135^{o}C, 40 h. [b]Conversion of cyclic imide and yield of diol are detected by ^{1}H NMR spectroscopy using mesitylene as an internal standard. Yield of amine is detected by GC and ^{1}H NMR spectroscopy using mesitylene/toluene as an internal standard.

In order to gain mechanistic insight into the hydrogenation process, we carried out the hydrogenation of N-benzylphthalimide under conditions described in Table 1, except that the catalysis was stopped after 6 h. Analysis of the reaction mixture by ^{1}H NMR spectroscopy and GC showed approximately 50% conversion of N-benzylphthalimide. Other than the expected 1,4-benzenedimethanol and benzylamine, phthalide was observed in approximately 15% yield. We suggest that the hydrogenation process takes place as outlined in Scheme 1. In presence of the ruthenium catalyst, the cyclic imide first undergoes hydrogenation of one of the carbonyl groups to form intermediate **A**, followed by C-N hydrogenolysis forming the hydroxyamide **B.** Upon intramolecular cyclization, **B** forms a hemiaminal intermediate **C** which can eliminate the amine and form a lactone (phthalide). The lactone then undergoes ruthenium catalyzed hydrogenation to form the corresponding diol product. Indeed, the catalytic hydrogenation of phthalide under the reaction conditions described in Table 1 resulted in complete conversion to 1,2-benzenedimethanol in quantitative yield.



Scheme 1. Proposed mechanism for the hydrogenation of cyclic imides to diols and amines.

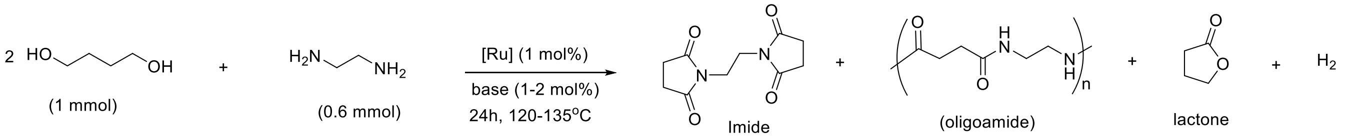
The unique selectivity of the catalytic hydrogenation of succinimides inspired us to develop an LOHC system based on the formation of butanediol and ethylenediamine. Hong has reported the synthesis of cyclic imides from simple diols and amines using a ruthenium catalyst.[26] We envisioned that the *bis*-cyclic imide formed from the dehydrogenative coupling of 1,4-butanediol and ethylenediamine can serve as a potentially clean reversible LOHC if the spent fuel, i.e. *bis*-cyclic imide can be hydrogenated back to the charged fuel, i.e. 1,4-butanediol and ethylenediamine (Scheme 2). The proposed system would have a maximum hydrogen capacity of 6.67 wt% which is higher than the current DOE target for 2020 of 5.5 wt%.[27]



Scheme 2. Dehydrogenative coupling of 1,4-butanediol and ethylenediamine.

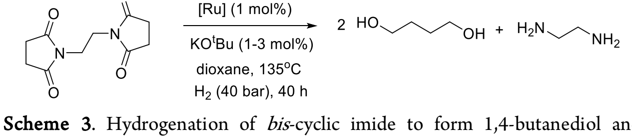
We started our investigation by screening ruthenium catalysts for the dehydrogenative coupling of 1,4-butanediol (1 mmol) and ethylenediamine (0.6 mmol). Using 1 mol% of complex **1** and 1 mol% KO^{t}Bu, almost complete conversion of 1,4-butanediol was observed in 24 h but the *bis*-cyclic imide was formed in only 55% yield as observed by ^{1}H NMR spectroscopy (Table 3, entry 1). Remaining side products were characterized as lactone (20% yield) and linear oligoamides[28] (See SI for characterization details). 70 mL of hydrogen gas was also collected using a gas-burette method. Analysis of the gas evolved during the dehydrogenation reaction by GC showed the presence of only H_2 gas. CO which is harmful for the fuel cell was not detected. Under similar reaction conditions, complexes **2** and **3** gave slightly lower yields of H_2 and *bis*-cyclic imide (Table 3, entry 2-3). We then synthesized a new complex **4,** which is the PPh_2 analogue of complex **3** (See SI for the synthesis and characterization details). Interestingly, use of complex **4** under identical reaction conditions as that of **3** resulted in 70% formation of *bis*-cyclic imide (isolated yield 60%) with the concomitant release of 82 mL of hydrogen gas, corresponding to 3.36 mmol at 25°C, i.e. 84% of the expected 4 mmol H_2 for quantitative formation of the imide (Table 3, entry 4). Considering the yield of the imide (70%), formation of the lactone and oligoamide contributes to approximately 14% of the produced H_2. Decreasing the solvent amount from 2 mL to 1 mL lowered the yield of hydrogen gas (Table 3, entry 5). When the reaction was carried out without adding any solvent under the reaction conditions of entry 4 (Table 3), 5 mmol of 1,4-butanediol and 3 mmol of ethylenediamine produced only 150 mL of hydrogen gas resulting in only 30% efficiency of the hydrogen storage capacity. Changing the solvent from dioxane to toluene and base from KO^{t}Bu to KH also resulted in the lower amount of hydrogen gas production (Table 3, entries 7 and 8).

Table 3. Dehydrogenative coupling of butanediol with ethylene diamine using ruthenium catalysts[a]



Entry	Cat	Base (mol%)	Solvent (mL)	temp	H_2 (mL)	Diol conversion	Product yield
1	**1**	KOtBu (1 mol%)	Dioxane (2 mL)	120°C	70 mL	95%	Imide (55%) + lactone (20%) + oligoamide
2	**2**	KOtBu (1 mol%)	Dioxane (2 mL)	120°C	62 mL	90%	Imide (40%) + lactone (25%) + oligoamide
3	**3**	KOtBu (2 mol%)	Dioxane (2 mL)	120°C	58 mL	99%	Imide (34%) + lactone (30%) + oligoamide
4	**4**	KOtBu (2 mol%)	Dioxane (2 mL)	120°C	82 mL	99%	Imide (70%) + lactone (12%) + oligoamide
5	**4**	KOtBu (2 mol%)	Dioxane (1 mL)	120°C	81 mL	99%	Imide (63%) + lactone (24%) + oligoamide
6	**4**	KOtBu (2 mol%)	Dioxane (1 mL)	135°C	82 mL	99%	Imide (60%) + lactone (20%) + oligoamide
7	**4**	KH (2 mol%)	Dioxane (2 mL)	120°C	68 mL	99%	Imide (58%) + lactone (27%) + oligoamide
8	**4**	KH (2 mol%)	Tol (2 mL)	120°C	74 mL	99%	Imide (65%) + lactone (15%) + oligoamide

After successful dehydrogenative synthesis of *bis*-cyclic imide, we explored the reverse reaction i.e. the hydrogenation of *bis*-cyclic imide to 1,4-butanediol and ethylenediamine. Under the catalytic conditions described in Table 2, 99% conversion of *bis*-cyclic imide was observed and the corresponding 1,4-butanediol and ethylenediamine were detected by ^{1}H NMR in more than 90% yield (Scheme 3). Using complex **4** under identical catalytic conditions resulted in only 65% conversion of the bis-cyclic imide and the desired 1,4-butanediol was detected in only 50% yield. Use of complexes **1** and **2** also resulted in a lower yield of 1,4-butanediol and ethylenediamine as detected by the ^{1}H NMR spectroscopy (See SI, Table S3).



Scheme 3. Hydrogenation of *bis*-cyclic imide to form 1,4-butanediol and ethylene diamine.

Furthermore, we explored the interconversion cycle between the spent fuel bis-cyclic imide and the charged fuel i.e. 1,4-butanediol/ethylenediamine mixture. As mentioned above, the bis-cyclic imide (1 mmol) was hydrogenated using 1 mol% **3** and 3 mol% KO^{t}Bu in 2 mL of 1,4-dioxane using 40 bar H_2 to produce 1,4-butanediol and ethylenediamine in more than 90% yield. The resulting reaction mixture was charged with 1 mol% **4** and 3 mol% KO^{t}Bu and refluxed at 120°C. 78 mL of hydrogen gas was collected after 24 h of reflux and ^{1}H NMR spectroscopy showed complete conversion of 1,4-butanediol and ethylenediamine. The desired product *bis*-cyclic imide was obtained in 68% yield, the remaining products were detected as lactone (10% yield) and oligoamide. The reaction mixture obtained here was then subjected to a second hydrogenation/dehydrogenation cycle. Hydrogenation of the reaction mixture obtained from the first cycle resulted in the formation of 1,4-butanediol and ethylenediamine in almost 88% and 85% yields respectively under the catalytic conditions of 2 mol% **3**, 6 mol% KO^{t}Bu, 50 bar hydrogen and the reaction time of 40 h (See SI, Table S4 for optimization details). A further dehydrogenation step (conditions: Table 3, entry 4) resulted in the formation of 71 mL hydrogen gas and the expected bis-cyclic imide in ~64% yield.

In conclusion, we have reported a rare, efficient and selective catalytic hydrogenation of a broad variety of cyclic imides to synthetically and industrially useful diols and amines building blocks. The unique selectivity of succinimide hydrogenation allowed to pursue a fundamentally new LOHC system based on the hydrogenation of *bis*-cyclic imide and its formation from the dehydrogenative coupling of 1,4-butanediol and ethylenediamine, which are inexpensive and extensively produced by industry. This hydrogen storage system has a theoretically high gravimetric storage capacity of 6.66 wt%. Further studies are aimed at increasing the efficiency of this novel LOHC system.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectroscopic details of the catalytic reactions. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

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