Dehydrogenation

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Cooperative Catalysis by Iridium Complexes with a Bipyridonate Ligand: Versatile Dehydrogenative Oxidation of Alcohols and Reversible Dehydrogenation–Hydrogenation between 2-Propanol and Acetone**

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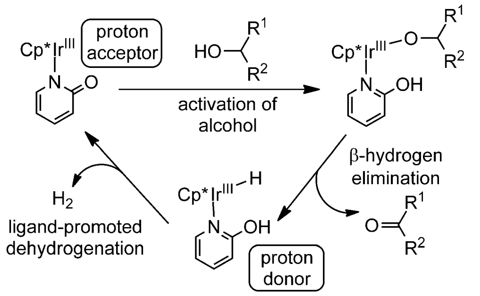
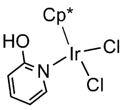
The oxidation of alcohols to carbonyl compounds is one of the most important and fundamental reactions in organic chemistry. Conventionally, this reaction is carried out by using stoichiometric amounts of harmful oxidants, for example, a chromium reagent.[1] Recently, a number of transition-metal-catalyzed oxidation reactions of alcohols have been developed using environmentally acceptable oxidants, such as molecular oxygen,[2] hydrogen peroxide,[3] or acetone.[4] However, oxidant-free or acceptor-free oxidation based on the catalytic dehydrogenation of alcohols accompanied by the evolution of hydrogen gas must be desirable from the standpoint of atom economy and environmental concerns. Dehydrogenative oxidation of alcohols is important for the production of synthetically useful aldehydes and ketones from readily available alcohols with high atom efficiency,[5] and also for the production of hydrogen gas, which is one of the most promising energy carriers in energy plans for the future.[6,7] Up to now, various homogeneous catalytic systems have been reported for the dehydrogenative oxidation of alcohols to carbonyl compounds.[8,9] Most of these catalytic reactions have to be carried out under reflux in organic solvent at high temperature (> 100 °C).[10] Additionally, most of these systems can be utilized only for the oxidation of secondary alcohols, and the systems that effectively oxidize primary alcohols to aldehydes are rare.[8j,11] Currently, there is no catalytic system that is able to dehydrogenatively oxidize a wide variety of both primary and secondary alcohols at relatively low temperatures (< 90 °C).

We have previously reported the dehydrogenative oxidation of alcohols catalyzed by Cp*Ir complexes **1**–**3**, which bear functional ligands with an α-hydroxypyridine skeleton.[12] Regarding the mechanisms of these catalytic systems, it has been proposed that the crucial steps are the intramolecular reaction of hydride on the metal with protic hydrogen on the α-hydroxypyridine-based ligand (ligand-promoted dehydrogenation), and the activation of the alcohol with the intermediate α-pyridonate species.[12] Therefore, an α-pyridonate-based ligand could act as a proton acceptor in the activation step and as a proton donor in the dehydrogenation step, and thus play a dual role in cooperative catalysis (Scheme 1). Moreover, bidentate functional ligands that form stable five-membered chelate structures in **2** and **3** are important for the dehydrogenation of both primary and secondary alcohols.[12b,c]



Scheme 1. Dual role of α-pyridonate ligand in cooperative catalysis.

On the basis of these assumptions, we designed new catalysts **4** and **5** bearing α,α′-bipyridonate ligands, anticipating that the activation of alcohols would be much accelerated and lead to high catalytic performance in the dehydrogenative oxidation of various kinds of alcohols.



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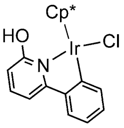

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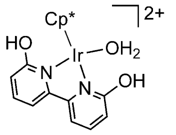

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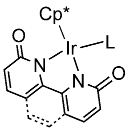

4, **5**

Here, we report the synthesis of a series of new Cp*Ir complexes that bear bipyridonate ligands and a study of their catalytic activity in the dehydrogenative oxidation of alcohols. Oxidation of alcohols under extremely mild conditions was accomplished by using a new Cp*Ir catalyst that bears a bipyridonate and an aquo ligand, and oxidations under solvent-free conditions were also achieved. Furthermore, the reversible transformation between 2-propanol and acetone by catalytic dehydrogenation and hydrogenation as a prototype for hydrogen storage is also described.

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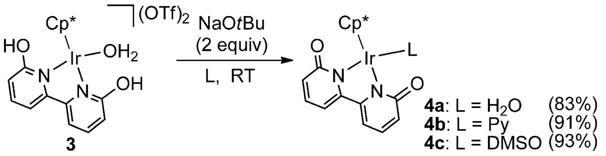
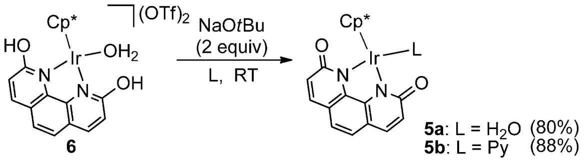
First, we planned to prepare a series of new Cp*Ir catalysts by the reaction of the dicationic complex **3** with base. Treatment of **3** with two equivalents of NaO*t*Bu in water gave neutral complex **4a** bearing a *N*,*N*-chelated α,α′-bipyridonate ligand and an aquo ligand in 83 % yield [Eq. (1)]. Similarly,



(1)

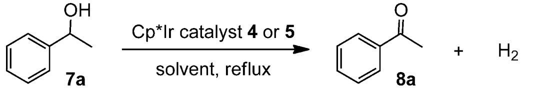
complexes **4b** and **4c** were prepared by reaction of **3** with NaO*t*Bu in dichloromethane in the presence of pyridine and dimethylsulfoxide, respectively. Complexes **4** were soluble in various organic solvents (alkanes, aromatic solvents, ethers, haloalkanes, esters, amides, or alcohols) and sparingly soluble in water. Related complexes **5a** and **5b**, which bear a phenanthroline-based functional ligand, were also prepared from dicationic complex **6** [Eq. (2)].



(2)

With the new Cp*Ir complexes **4** and **5** in hand, we investigated their catalytic performance in the dehydrogenation of 1-phenylethanol (**7a**; Table 1).[13] When the reaction of **7a** was carried out in the presence of **4a** (0.5 mol %) under reflux in pentane (36 °C) for 5 h, acetophenone (**8a**) was obtained quantitatively (Table 1, entry 1), showing an extremely high catalytic activity of **4a** for the dehydrogenative oxidation of an alcohol at very low temperature. Other catalysts **4b** and **4c**, which bear pyridine or dimethylsulfoxide as a ligand, showed lower activity (Table 1, entries 2 and 3), thus indicating the superiority of the labile aquo ligand in **4a**. Employment of catalysts **5a** and **5b** with a phenanthroline-based functional ligand gave inferior results (Table 1, entries 4 and 5). The loading of highly active catalyst **4a** could be reduced to 0.01 mol % (Table 1, entry 7), while maintaining an excellent yield of **8a**. The turnover number (TON) reached up to 9500, even at 36 °C. Performance of the reaction under air did not influence the outcome of the reaction at all (Table 1, entry 8), thus showing the operational advantage of this system. The evolution of hydrogen gas was confirmed by analysis of the gas phase using a hydrogen sensor. Additionally, the volume of the evolved hydrogen gas was measured using a gas burette, giving a 96 % yield of hydrogen gas (Table 1, entry 9).[14] When the reaction of **7a** was carried out under reflux in *p*-xylene (b.p. 138 °C) in the presence of 0.0002 mol % of **4a** for 48 h, the TON reached up to 275 000 (Table 1, entry 10). To the best of our knowledge, this is the highest TON that was reported thus far for a catalytic system for the dehydrogenative oxidation of alcohols.

Table 1: Dehydrogenative oxidation of 1-phenylethanol (**7a**) to acetophenone (**8a**) under various conditions.[a]



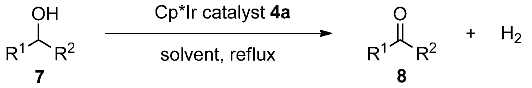
Entry	Catalyst (mol %)	Solvent	(b.p.)	*t* [h]	Yield [%][b] (TON)
1	**4a** (0.5)	pentane	(36 °C)	5	100
2	**4b** (0.5)	pentane	(36 °C)	5	7
3	**4c** (0.5)	pentane	(36 °C)	5	16
4	**5a** (0.5)	pentane	(36 °C)	5	36
5	**5b** (0.5)	pentane	(36 °C)	5	8
6	**4a** (0.1)	pentane	(36 °C)	20	96
7[c]	**4a** (0.01)	pentane	(36 °C)	48	95 (9500)
8[d]	**4a** (0.5)	pentane	(36 °C)	5	100
9[e]	**4a** (0.5)	pentane	(36 °C)	5	100[f]
10[d,g]	**4a** (0.0002)	*p*-xylene	(138 °C)	48	55 (275 000)

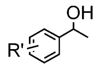
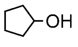
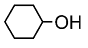
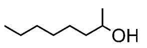
[a] Reaction was carried out with **7a** (1.0 mmol) and Cp*Ir catalyst (0.1–0.5 mol %) in pentane (3 mL). [b] Determined by GC analysis. Selectivity toward the formation of **8a** was higher than 95 %. [c] Reaction was carried out with **7a** (10.0 mmol) and **4a** (0.01 mol %) in pentane (30 mL). [d] Reaction was carried out under air. [e] Reaction was carried out with **7a** (5.0 mmol) in pentane (15 mL). [f] Yield of the evolved hydrogen gas was 96 %. [g] Reaction was carried out with **7a** (500 mmol) and **4a** (0.0002 mol %) in *p*-xylene (500 mL).

Results of the dehydrogenative oxidation of various secondary alcohols to the corresponding ketones catalyzed by **4a** are shown in Table 2. The reactions of 1-arylethanols (**7a**–**f**) bearing electron-donating and electron-withdrawing substituents at the aromatic ring proceeded smoothly under reflux in pentane to give the corresponding acetophenone derivatives in good to excellent yields (Table 2, entries 1–6). The reaction of a sterically hindered substrate **7c** also proceeded well (Table 2, entry 3). Aliphatic secondary alcohols could be oxidized successfully, although a slightly higher reaction temperature (reflux in hexane) led to better results (Table 2, entries 7–12).

Having established the unprecedented high catalytic performance of **4a** for the dehydrogenative oxidation of secondary alcohols, we next investigated the reactions of primary alcohols. In order to find optimum conditions for primary alcohols, the dehydrogenative oxidation of benzyl alcohol (**9a**) was conducted under various conditions (Table 3). When the reaction of **9a** was carried out in the presence of **4a** (1.5 mol %) under reflux in benzene (b.p. 80 °C) for 20 h, benzaldehyde (**10a**) was obtained in excellent yield (96 %, Table 3, entry 1). Employment of *t*BuOH (b.p. 82 °C) as a 'greener' solvent also led to a high yield of **10a** (92 %, Table 3, entry 2).[15] The TON reached up to 3100, when the reaction of **9a** was carried out in the presence of 0.01 mol % of **4a** for 48 h (Table 3, entry 3).[16] The presence of air did not affect the reaction at all (Table 3, entry 4). Quantitative analysis showed that the yield of evolved hydrogen gas was 89 % (Table 3, entry 5).[14] The reaction proceeded at much lower temperature under reflux in THF (b.p. 66 °C), although the yield of **10a** was moderate (54 %, Table 3, entry 6). The highest TON (47 500) was obtained when the reaction of **9a** was carried out under reflux in

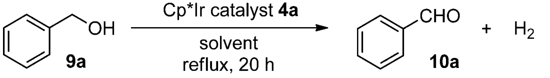
Table 2: Dehydrogenative oxidation of various secondary alcohols to ketones catalyzed by **4a** under mild reaction conditions.[a]



Ent.	Alcohol		Cat. [mol %]	Solvent	(b.p.)	Prod.	*t* [h]	Yield [%][b]
								
1	R′ = H	(**7a**)	0.5	pentane	(36 °C)	**8a**	5	100 (98)
2	R′ = 4-OMe	(**7b**)	0.5	pentane	(36 °C)	**8b**	5	100 (99)
3	R′ = 2-OMe	(**7c**)	1.0	pentane	(36 °C)	**8c**	5	92
4	R′ = 4-Cl	(**7d**)	1.0	pentane	(36 °C)	**8d**	5	92 (89)
5	R′ = 4-Br	(**7e**)	1.0	pentane	(36 °C)	**8e**	5	90 (88)
6	R′ = 4-NO$_2$	(**7f**)	2.0	pentane	(36 °C)	**8f**	20	85
7		(**7g**)	1.0	hexane	(69 °C)	**8g**	20	100
8			2.0	pentane	(36 °C)		20	93
9		(**7h**)	1.0	hexane	(69 °C)	**8h**	20	94
10			2.0	pentane	(36 °C)		20	82
11		(**7i**)	2.0	hexane	(69 °C)	**8i**	20	88 (84)
12			3.0	pentane	(36 °C)		20	80

[a] Reaction was carried out with a secondary alcohol (1.0 mmol) and **4a** (0.5–3.0 mol %) in solvent (3 mL) under reflux. [b] Determined by GC analysis (entries 1, 7–12) or ^{1}H NMR spectroscopy (entries 2–6). Selectivity toward the formation of **8** was higher than 99 %. Yield of isolated product is in parenthesis.

Table 3: Dehydrogenative oxidation of benzyl alcohol (**9a**) to benzaldehyde (**10a**) catalyzed by **4a** under various conditions.[a]



Entry	Cat. [mol %]	Solvent	(b.p.)	Yield [%][b] (TON)
1	1.5	benzene	(80 °C)	96
2	1.5	*t*BuOH	(82 °C)	92
3[c]	0.01	*t*BuOH	(82 °C)	31 (3100)
4[d]	1.5	*t*BuOH	(82 °C)	92
5[e]	1.5	*t*BuOH	(82 °C)	92[f]
6	1.5	THF	(66 °C)	54
7[d,g]	0.002	toluene	(110 °C)	95 (47 500)

[a] Reaction was carried out with **9a** (0.25 mmol) and **4a** (1.5 mol %) in solvent (5 mL). [b] Determined by GC analysis. Selectivity toward the formation of **10a** was higher than 97 %. [c] Reaction was carried out with **9a** (10 mmol) and **4a** (0.01 mol %) in *t*BuOH (200 mL) under reflux for 48 h. [d] Reaction was carried out under air. [e] Reaction was carried out with **9a** (2.0 mmol) in *t*BuOH (40 mL). [f] Yield of the evolved hydrogen gas was 89 %. [g] Reaction was carried out with **9a** (80 mmol) and **4a** (0.002 mol %) in toluene (270 mL) under reflux for 48 h.

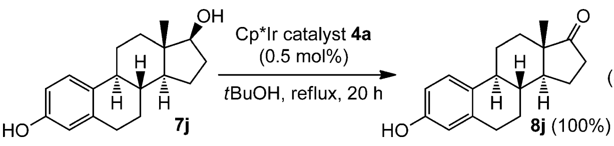
toluene (b.p. 110 °C) for 48 h with a very small catalyst loading (0.002 mol %; Table 3, entry 7).[16]

Results of the dehydrogenative oxidation of various primary alcohols to the corresponding aldehydes under mild conditions are summarized in Table 4. Reactions of benzylic alcohols (**9a–k**) bearing electron-donating and electron-withdrawing substituents at the aromatic ring proceeded smoothly to give the corresponding aldehydes (**10a–k**) in good to high yields (Table 4, entries 2–11). A variety of functional groups were tolerated (Table 4, entries 2 and 6–10). The reaction of **9j**, which has a phenolic hydroxy group, gave the corresponding aldehyde **10j** in 79 % yield at higher temperature (reflux in toluene, Table 4, entry 10). While dehydrogenative oxidation of aliphatic primary alcohols to aldehydes has been known to be very difficult,[17] this reaction proceeded smoothly using **4a** as the catalyst under reflux in toluene (Table 4, entries 12 and 13).

The present catalytic system was also applicable to the dehydrogenative transformation of biologically important and complex molecules. When the reaction of β-estradiol (**7j**) was conducted in the presence of **4a** (0.5 mol %) under reflux in *t*BuOH for 20 h, the selective dehydrogenation proceeded to give estrone (**8j**) quantitatively [Eq. (3)].

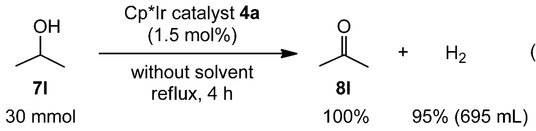
The reaction of pregnenolone (**7k**) proceeded with concomitant isomerization of C=C bond and quantitatively afforded progesterone (**8k**), which has an α,β-unsaturated ketone moiety (see Eq. (S1) in the Supporting Information).

We next studied the solvent-free dehydrogenative oxidation of alcohols (Table S2 in the Supporting Information). When the reaction of **7a** was carried out in the presence of **4a** (3.0 mol %) at 60 °C for 20 h, **8a** was obtained in 93 % yield (Table S2, entry 1). Reactions of other secondary alcohols (**7g** and **7i**) proceeded at 90 °C to give the corresponding ketones in good yields (Table S2, entries 2 and 3), while the reaction of a primary alcohol **9a** resulted in a low yield of aldehyde **10a** (Table S2, entry 4).



(3)

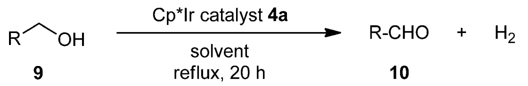
Anticipating the possibility of an efficient hydrogen gas production from alcohols, we next investigated the dehydrogenation of 2-propanol [**7l**; Eq. (4)]. The reaction of **7l** (1.4 mL; 30 mmol) in the presence of **4a** (1.5 mol %) under reflux for 4 h gave acetone (**8l**) quantitatively with the evolution of 695 mL (95 % yield) of hydrogen gas.[14] It is worth noting that an efficient production of hydrogen gas was achieved under neutral and mild reaction conditions from easily handled and readily available 2-propanol as a starting material.[7f–h]

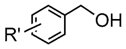
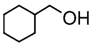
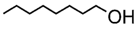


(4)

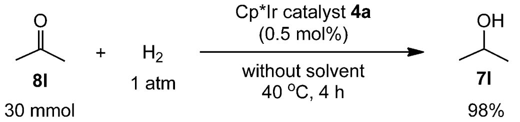
Interestingly, the reverse reaction, that is, the hydrogenation of **8l** to **7l** could be accomplished using the same catalyst **4a** [Eq. (5)]. When the hydrogenation of **8l** was carried out in the presence of **4a** (0.5 mol %) at 40 °C for 4 h

Table 4: Dehydrogenative oxidation of various primary alcohols to aldehydes catalyzed by **4a** under mild reaction conditions.[a]



Ent.	Alcohol		Cat. [mol%]	Solvent	(b.p.)	Prod.	Yield [%][b]
							
1	R′ = H	(**9a**)	1.5	*t*BuOH	(82°C)	**10a**	92
2	R′ = 4-OMe	(**9b**)	1.5	*t*BuOH	(82°C)	**10b**	98 (96)
3	R′ = 2-Me	(**9c**)	2.5	*t*BuOH	(82°C)	**10c**	85
4	R′ = 3-Me	(**9d**)	1.5	*t*BuOH	(82°C)	**10d**	91
5	R′ = 4-Me	(**9e**)	1.5	*t*BuOH	(82°C)	**10e**	96 (94)
6	R′ = 4-Cl	(**9f**)	1.5	*t*BuOH	(82°C)	**10f**	90 (87)
7	R′ = 4-Br	(**9g**)	1.5	*t*BuOH	(82°C)	**10g**	88 (86)
8	R′ = 4-CF_3	(**9h**)	3.0	heptane	(98°C)	**10h**	88
9	R′ = 4-CO_2Me	(**9i**)	5.0	*t*BuOH	(82°C)	**10i**	80
10	R′ = 4-OH	(**9j**)	1.0	toluene	(110°C)	**10j**	79
11	R′ = 4-Ph	(**9k**)	1.5	*t*BuOH	(82°C)	**10k**	93 (91)
12		(**9l**)	2.5	toluene	(110°C)	**10l**	81
13		(**9m**)	5.0	toluene	(110°C)	**10m**	87

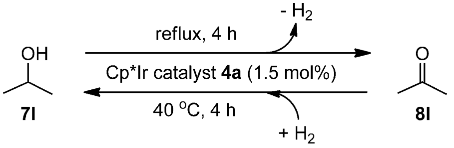
[a] Reaction was carried out with a primary alcohol (0.5 mmol) and **4a** (1.0–5.0 mol%) in solvent (10 mL) under reflux for 20 h. [b] Determined by GC analysis (entries 1–8, 11–13) or ^{1}H NMR spectroscopy (entries 9 and 10). Selectivity toward the formation of **10** was higher than 97%. Yield of isolated product is in parenthesis.



(5)

under a hydrogen atmosphere (1 atm), **7l** was obtained almost quantitatively (98%).

Table 5: Reversible transformation between 2-propanol (**7l**) and acetone (**8l**) in one flask by dehydrogenation and hydrogenation reactions catalyzed by **4a**.[a]



Cycle	Dehydrogenation yield of **8l** [%][b]	Dehydrogenation yield of H_2 [%][c]	Hydrogenation yield of **7l** [%][b]
1	100	95	100
2	99	94	98
3	98	94	98
4	96	92	97
5	97	93	95
6	96	92	94
7	95	91	96
8	95	91	96

[a] The dehydrogenation was carried out with **7l** (30.0 mmol), **4a** (1.5 mol%), and internal standard (*p*-xylene, 1.0 mmol) under reflux for 4 h. Next, the atmosphere of the flask was replaced with hydrogen, and a balloon filled with hydrogen gas was connected to the flask. The mixture was stirred for 4 h at 40°C. [b] Determined by GC analysis. [c] Yield of hydrogen gas that was collected in a gas burette.

On the basis of the above-mentioned results, we designed a new prototype for a hydrogen storage system,[18] based on the interconversion between **7l** and **8l** (Table 5). First, the dehydrogenation of **7l** was conducted under the same conditions as those in Eq. (4) to afford **8l** (100%) and hydrogen gas (95%). Next, a balloon filled with hydrogen gas (1 atm) was attached to the flask and the solution was stirred at 40°C for 4 h. This simple procedure transformed **8l** back to **7l** in 100% yield. Moreover, the reversible transformation between **7l** and **8l** could be repeated eight times without loss of the high catalytic activity of **4a**, thus demonstrating a promising prototype for a hydrogen storage system using 2-propanol, a simple and harmless molecule, as storage material.[19]

In summary, we have developed a new, efficient, and versatile catalytic system for the dehydrogenative oxidation of primary and secondary alcohols under extremely mild conditions (reflux in pentane for secondary alcohols and reflux in *t*BuOH for primary alcohols) by using the new Cp*Ir catalyst **4a**, which bears a functional bipyridonate ligand. The TONs reached up to 9500 (275000 at 138°C) for alcohol **7a**, and 3100 (47500 at 110°C) for alcohol **9a**, which are the highest TONs reported for known homogeneous catalysts, thus demonstrating a high catalytic performance of **4a**. Furthermore, reversible and repetitive transformations between 2-propanol (**7l**) and acetone (**8l**) by dehydrogenation–hydrogenation catalyzed by **4a** were achieved, providing a promising prototype for a hydrogen storage system.

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[13] Detailed results of the optimization for the dehydrogenative oxidation of **7a**, including the reaction using other catalysts and various solvents, are shown in Table S1 in the Supporting Information.

[14] Generated hydrogen gas could be used for the hydrogenation of an alkene. Details are shown in Scheme S1 in the Supporting Information.

[15] We have also carried out the reaction of **9a** under reflux in *t*BuOH in the presence of dicationic catalyst **3** (1.5 mol%), which resulted in the formation of **10a** in only 40% yield accompanied by the formation of benzyl *tert*-butyl ether as a by-product. This result indicates the superiority of the new catalyst **4a**.

[16] To the best of our knowledge, the TONs presented here are among the highest reported thus far for known homogeneous catalysts for the dehydrogenative oxidation of primary alcohols to aldehydes.

[17] While reports of a homogeneous catalytic system that exhibits high activity for the dehydrogenative oxidation of aliphatic primary alcohols to aldehydes do not exist, a few heterogeneous systems have been reported (see references [9a and e]).

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[19] It should be noted that the present dehydrogenation and hydrogenation can be carried out without solvent, resulting in a high hydrogen content of the system. Although there have been a few reports of hydrogen storage based on homogeneously catalyzed reversible dehydrogenation and hydrogenation reactions, those reactions have to be conducted using a solvent; a) R. Yamaguchi, C. Ikeda, Y. Takahashi, K. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 8410; b) A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, *Angew. Chem.* **2011**, *123*, 6535; *Angew. Chem. Int. Ed.* **2011**, *50*, 6411; c) G. Papp, J. Csorba, G. Laurenczy, F. Joó, *Angew. Chem.* **2011**, *123*, 10617; *Angew. Chem. Int. Ed.* **2011**, *50*, 10433; d) J. F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.* **2012**, *4*, 383.