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Communication

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Dehydrogenative Oxidation of Alcohols in Aqueous Media Using Water-Soluble and Reusable Cp*Ir Catalysts Bearing a Functional Bipyridine Ligand

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Supporting Information

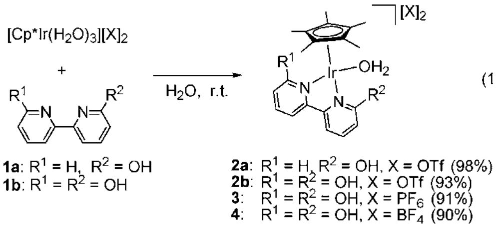
ABSTRACT: A new catalytic system for the dehydrogenative oxidation of alcohols using a water-soluble Cp*Ir complex bearing a bipyridine-based functional ligand as catalyst has been developed. With this catalytic system, a variety of primary and secondary alcohols have been efficiently converted to aldehydes and ketones, respectively, in aqueous media without using any oxidant. Reuse of the catalyst by a very simple procedure has been also accomplished.

The increasing environmental concerns have led chemists to develop cleaner and greener reactions for chemical transformations. It is one of the central subjects in synthetic organic chemistry to develop efficient, selective, and atom-economical reactions which can be performed under safe and mild conditions with the aid of transition metal catalysts.

The oxidation of alcohols to aldehydes and ketones is fundamental transformation in organic chemistry and has profound importance in laboratory and industrial chemistry. Various transition metal catalyzed systems for the oxidation of alcohols have been developed using environmentally acceptable oxidants such as molecular oxygen,[1] hydrogen peroxide,[2] or acetone.[3] Dehydrogenative oxidation accompanied by the release of hydrogen gas without using any oxidant must be superior from the viewpoint of atom economy.[4] To date, several homogeneous catalytic systems for the dehydrogenative oxidation of alcohols using ruthenium,[5] iridium,[6,7] and other transition metal catalysts[5f] have been reported.[8,9] However, all of these catalytic reactions have to be carried out under reflux in organic solvent such as toluene. From the standpoint of green chemistry, it must be very important to develop a new catalytic system which can be performed in a greener solvent such as water.[10]

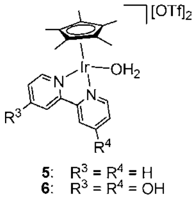
Recently, we have reported the synthesis of a water-soluble Cp*Ir–ammine complex, $[Cp^*Ir(NH_3)_3]^{2+}$, and its high catalytic activity for the N-alkylation of ammonia and organic amines in aqueous media.[11] On the basis of this discovery, we became interested in the design of new water-soluble catalysts and their application to efficient, and atom-economical reactions under environmentally benign conditions. Herein, we report the synthesis of new water-soluble Cp*Ir complexes bearing a bipyridine-based functional ligand and their high catalytic performance for the dehydrogenative oxidation of primary and secondary alcohols in aqueous media. In addition, reuse of the catalyst by a very simple procedure is also demonstrated.

First, we planned to synthesize a new catalyst suitable for the dehydrogenative oxidation of alcohols in aqueous media with respect to stability, solubility in water, and catalytic efficiency. We have previously reported the dehydrogenative oxidation of alcohols under reflux in toluene catalyzed by a Cp*Ir complex bearing 2-hydroxypyridine as a functional ligand, in which "ligand-promoted dehydrogenation" were the most crucial step in the reaction pathway.[6b] On the basis of this concept, we designed a bipyridine-based functional ligand, such as 6-hydroxy-2,2′-bipyridine (**1a**) or 6,6′-dihydroxy-2,2′-bipyridine (**1b**) that should lead to stable catalysts ligated by N,N-chelation. As a Cp*Ir precursor, water-soluble aqua complex, $[Cp^*Ir(H_2O)_3](OTf)_2$, was employed. Thus, treatment of $[Cp^*Ir(H_2O)_3](OTf)_2$ with **1a** and **1b** in water at room temperature gave new dicationic Cp*Ir complexes **2a** and **2b** in 98 and 93% yields, respectively (eq 1).



(1)

The structures of **2a** and **2b** were elucidated by their spectroscopic data and single-crystal X-ray analysis (see the Supporting Information). The complexes **2a** and **2b** were highly soluble in water and stable in air for months. Analogous complexes **3** and **4** having PF_6^- and BF_4^- as counteranions were prepared by the reaction of **1b** with $[Cp^*Ir(H_2O)_3](PF_6)_2$ and $[Cp^*Ir(H_2O)_3](BF_4)_2$, respectively (eq 1). In order to evaluate the catalytic activities of the complexes **2**-**4**, the complexes **5** and **6** having 2,2′-bipyridine and 4,4′-dihydroxy-2,2′-bipyridine as a ligand were prepared, respectively, according to the literature methods.[12]



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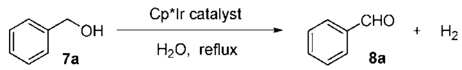
With these water-soluble Cp*Ir complexes in hand, we next examined the dehydrogenative oxidation of benzyl alcohol (**7a**) to benzaldehyde (**8a**) in the presence of a catalytic amount (0.5−1.5 mol % Ir) of the Cp*Ir complexes in water under reflux. The results are summarized in Table 1. The oxidation of **7a** never occurred in the absence of catalyst (entry 1). Water-insoluble $[Cp^*IrCl_2]_2$ (0.5 mol % Ir) showed almost no catalytic activity (entry 2). While the water-soluble aqua complex $[Cp^*Ir(H_2O)_3](OTf)_2$ showed low catalytic activity to give benzaldehyde (**8a**) in 12% yield (entry 3), employment of the complex **2a** bearing the α-monohydroxyl ligand **1a** as a catalyst improved the yield up to 50% (entry 4). The dicationic complex **2b** with the α,α'-dihydroxyl ligand **1b** showed higher activity than **2a** (entry 5, 62% yield). Analogous complexes **3** and **4** having PF_6^- and BF_4^- as counteranions showed lower catalytic activity than **2b** (entries 6 and 7). Other Cp*Ir complexes **5** and **6** were apparently inferior as the catalyst (entries 8 and 9, 25% and 22% yields, respectively), indicating the α-hydroxyl substituent in the ligand was indispensable for high catalytic performance.

Table 1. Dehydrogenative Oxidation of Benzyl Alcohol (7a) to Benzaldehyde (8a) Catalyzed by Cp*Ir Complexes under Various Conditions[a]



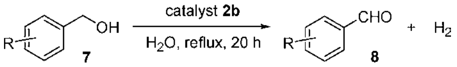
entry	catalyst (mol% Ir)	time (h)	conv. (%)[b]	yield (%)[c]
1	none	20	0	0
2	$[Cp^*IrCl_2]_2$ (0.5)	20	3	3
3	$[Cp^*Ir(H_2O)_3](OTf)_2$ (0.5)	20	12	12
4	**2a** (0.5)	20	51	50
5	**2b** (0.5)	20	63	62
6	**3** (0.5)	20	41	40
7	**4** (0.5)	20	40	39
8	**5** (0.5)	20	25	25
9	**6** (0.5)	20	23	22
10	**2b** (1.5)	20	92	92
11[d]	**2b** (1.5)	20	92	91[e]
12	**2b** (1.5)	6	60	60
13[f]	**2b** (1.5)	20	92	91

[a] Reaction was carried out with **7a** (0.25 mmol) and Cp*Ir catalyst (0.5−1.5 mol % Ir) in water (5 mL) under reflux for 20 h. [b] Conversion of **7a** determined by GC. [c] Yield of **8a** determined by GC. [d] Reaction was carried out with **7a** (0.50 mmol) in water (10 mL). [e] Yield of the evolved hydrogen gas was 89%. [f] Reaction was carried out under air.

The excellent yield was achieved with a slightly larger amount of **2b** (1.5 mol % Ir): **8a** was obtained in 92% yield with complete selectivity (entry 10). Evolution of the hydrogen gas was confirmed by the analysis of the gas phase using a hydrogen sensor. Additionally, quantitative analysis was also carried out: the volume of the evolved hydrogen gas was measured using a gas buret, showing the yield of hydrogen was 89% (entry 11).[13] When the reaction time was reduced to 6 h, the yield of **8a** was moderate (entry 12). It should be noted that the reaction under air gave a similar result to that of the reaction under an argon atmosphere (entry 13), showing the operational advantage of this system because the reaction can be performed under air. Thus, the present catalytic system produces the aldehyde **8a** in high yield with almost complete selectivity using harmless water as a solvent without the formation of any harmful byproducts.

To explore the scope of the present catalytic system, reactions of various alcohols were conducted under the optimized conditions. Results of the dehydrogenative oxidation of primary alcohols to the corresponding aldehydes in water are shown in Table 2.[14] The reactions of benzylic alcohols (**7a–i**) bearing electron-donating and -withdrawing substituents at the aromatic ring proceeded smoothly to give the corresponding aldehydes in good to high yields (entries 1−9). Methoxy-, chloro-, bromo-, trifluoromethyl-, and methoxycarbonyl-substituents were tolerant (entries 2 and 6−9). The reaction of sterically demanding 2-methylbenzyl alcohol also proceeded to give the corresponding aldehyde in high yield (entry 3).[15]

Table 2. Dehydrogenative Oxidation of Primary Alcohols to Aldehydes in Water[a]

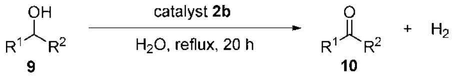


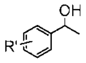
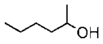
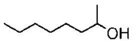
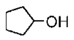
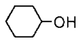
entry	alcohol	cat. 2b (mol%)	product	yield (%)[b]
1	R=H (**7a**)	1.5	**8a**	92
2	4-OMe (**7b**)	1.5	**8b**	93
3	2-Me (**7c**)	2.5	**8c**	91
4	3-Me (**7d**)	1.5	**8d**	86
5	4-Me (**7e**)	1.5	**8e**	94
6	4-Cl (**7f**)	2.0	**8f**	92
7	4-Br (**7g**)	2.0	**8g**	93
8	4-CF_3 (**7h**)	3.0	**8h**	88
9	4-CO_2Me (**7i**)	3.0	**8i**	77

[a] Reaction was carried out with a primary alcohol (0.25 mmol) and **2b** (1.5−3.0 mol %) in water (5 mL) under reflux for 20 h. [b] Determined by GC.

We next investigated the dehydrogenative oxidation of secondary alcohols to ketones in water. As shown in Table 3,[14]

Table 3. Dehydrogenative Oxidation of Secondary Alcohols to Ketones in Water[a]



entry	alcohol	cat. 2b (mol%)	product	yield (%)[b]
				
1	R' =H (**9a**)	1.0	**10a**	92
2	4-OMe (**9b**)	1.0	**10b**	98
3[c]	4-OMe (**9b**)	0.02	**10b**	51 (2550[d])
4	2-OMe (**9c**)	1.0	**10c**	86
5	4-Cl (**9d**)	1.0	**10d**	92
6	4-Br (**9e**)	1.0	**10e**	92
7	4-NO_2 (**9f**)	2.0	**10f**	91
8[e]	 (**9g**)	2.5	**10g**	82
9[e]	 (**9h**)	3.0	**10h**	85
10[e]	 (**9i**)	1.0	**10i**	86
11[e]	 (**9j**)	2.0	**10j**	80

[a] Reaction was carried out with a secondary alcohol (0.25 mmol) and **2b** (0.02−3.0 mol %) in water (5 mL) under reflux for 20 h. [b] Determined by GC (entries 1, 8−11) or ^1H NMR (entries 2−7). [c] Reaction was carried out with **9b** (2.5 mmol) and **2b** (0.02 mol %) in water (50 mL) under reflux for 100 h. [d] Turnover number. [e] Water (4.5 mL) and *tert*-butyl alcohol (0.5 mL) were used as a cosolvent.

the reactions of 1-arylethanols (**9a**−**f**) bearing electron-donating and -withdrawing substituents at the aromatic ring proceeded smoothly to give the corresponding acetophenone derivatives in good to excellent yields (entries 1−7). The highest turnover number (2550) was accomplished when the reaction of **9b** was carried out under reflux in water for 100 h with a very small catalyst loading (0.02 mol %) (entry 3). Reactions of both sterically hindered and unhindered substrates proceeded well (entries 2 and 4). Aliphatic secondary alcohols were also oxidized successfully, although an addition of a small amount of *tert*-butyl alcohol (0.5 mL) was required because of the low solubility of these substrates in water (entries 8−11).

To demonstrate the additional advantage of the present dehydrogenative oxidation system in aqueous media, we turned our attention to reuse of the catalyst. In fact, the use of a water-soluble catalyst **2b** made it easy to separate the organic product from the catalyst by a simple phase separation: after the oxidation of an alcohol catalyzed by **2b** was conducted in water [Figure 1a], hexane was added to the system, and the organic and aqueous phases were separated [Figure 1b]. By this simple procedure, isolation of the carbonyl product in the organic phase and recovery of the **2b** in the aqueous phase were achieved.[16]

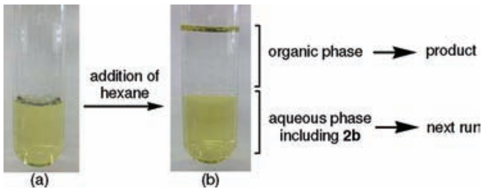
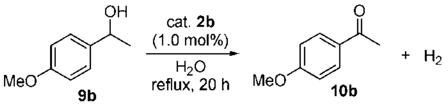


Figure 1. (a) Reaction mixture including the water-soluble catalyst **2b**. (b) Organic phase including the product and the aqueous phase including the catalyst **2b** after phase separation using hexane.

The aqueous phase including the recovered catalyst **2b** could be subjected to the next run, showing that high catalytic activity was still maintained. When the dehydrogenative oxidation of secondary alcohol **9b** was repeated eight times, the recovered catalyst did not lose its high activity until the eighth run (eq 2).[17]



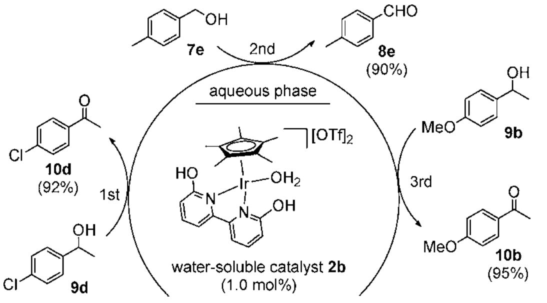
(2)

reuse	1	2	3	4	5	6	7	8
yield of **10b** (%)	98	97	96	95	95	96	95	94

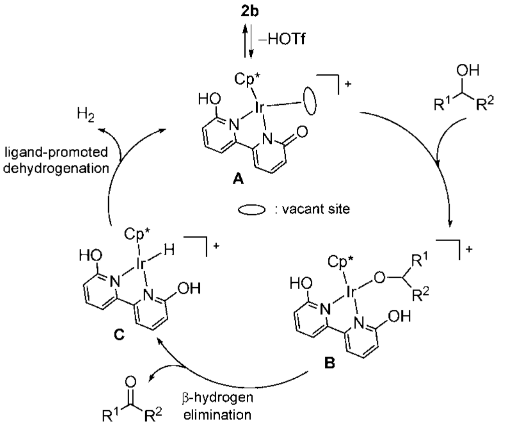
Furthermore, reuse of the catalyst for the dehydrogenative oxidation of different alcohols was accomplished (Scheme 1). In the first run, the oxidation of **9d** was conducted by **2b** (1.0 mol %) to give **10d** in 92%. After the recovery of the catalyst, the second run using **7e** gave **8e** in 90% yield. Finally, the third run using **9b** gave **10b** in 95% yield. Thus it should be very interesting that an efficient reusable catalytic system can be realized not only for oxidation of the same substrate but also for oxidation of different substrates.

A possible mechanism for the present dehydrogenative oxidation of alcohols catalyzed by **2b** is shown in Scheme 2. The mechanism is closely related to the one we have previously proposed for the dehydrogenative oxidation catalyzed by the Cp*Ir complex bearing 2-hydroxypyridine as a functional ligand.[6b] The initial step of the reaction would involve elimination of HOTf from the dicationic catalyst **2b** to afford a monocationic unsaturated species **A** having a 2-pyridonate-based ligand.[18] Then, the activation of an alcohol would occur to afford an alkoxo iridium species **B**. β-Hydrogen elimination of the alkoxo moiety in **B** would occur to give a carbonyl product and a hydrido iridium species **C**. Finally, reaction of the hydride on iridium with the hydroxyl proton on the functional ligand would occur to release dihydrogen (ligand-promoted dehydrogenation) accompanied by the regeneration of **A**.

Scheme 1. Reuse of the Catalyst 2b in the Dehydrogenative Oxidation of Primary and Secondary Alcohols in Aqueous Media



Scheme 2. A Possible Mechanism for the Dehydrogenative Oxidation of Alcohols Catalyzed by 2b



In summary, we have synthesized a new water-soluble Cp*Ir catalyst **2b** bearing a bipyridine-based functional ligand and developed a new catalytic system for the dehydrogenative oxidation of alcohols which can be performed in water under mild conditions with high turnover numbers. To the best of our knowledge, the present catalytic system is the first example of the dehydrogenative oxidation of alcohols in aqueous media.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and X-ray crystallographic data for **2b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) Generated hydrogen gas could be used for the hydrogenation of an alkene (1-decene). Details are shown in Scheme S1 in the Supporting Information.

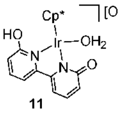
(14) We have also carried out the dehydrogenative oxidation reactions in 0.5 mmol scale with the isolation of the carbonyl products. Results are shown in Table S1 in the Supporting Information.

(15) At present, aliphatic primary alcohols were not efficiently oxidized by the present system: the reaction of 1-octanol in the presence of catalyst **2b** (3.0 mol %) in water under reflux for 20 h gave octanal in 16% yield (conversion of 1-octanol was 17%).

(16) ^{1}H NMR analysis of the aqueous phase revealed that **2b** was quantitatively recovered without decomposition.

(17) We have also carried out the reuse of **2b** in the reactions of a variety of substrates. Results are shown in eq. S1 and Table S2 in the Supporting Information.

(18) In order to support the mechanism proposed, preparation of a monocationic Cp*Ir complex related to **A** was accomplished. Treatment of **2b** with NaO^{t}Bu (1.0 equiv.) in water gave a monocationic complex **11** in 82% yield. Compositional formula of **11** was determined to be $C_{21}H_{24}O_6F_3N_2SIr$ by element analysis, which is consistent with the structure illustrated below. The complex **11** exhibited a high catalytic activity: When the reaction of **7a** was carried out in the presence of **11** (1.5 mol %) in water under reflux for 20 h, **8a** was obtained in 93% yield.



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