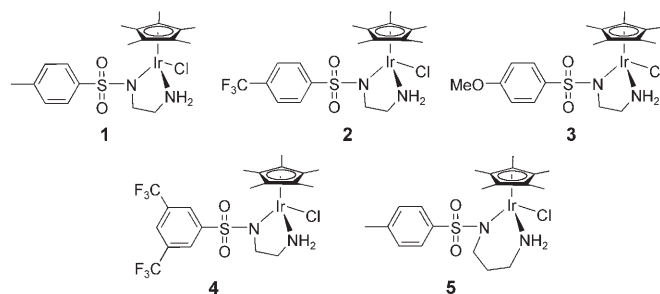# A Versatile Iridium Catalyst for Aldehyde Reduction in Water

Xiaofeng Wu, Charlotte Corcoran, Shujie Yang, and Jianliang Xiao*[a]

Catalysis in water has attracted increasing attention over the last several years in response to calls for sustainable chemistry.[1] Recently, we and other groups explored the asymmetric transfer hydrogenation (ATH) of ketones and imines in neat water with a range of catalysts and found that the reaction generally affords fast rates and good to excellent enantioselectivities.[1b,2,3] We also demonstrated that aldehydes can be reduced to alcohols under transfer hydrogenation (TH) conditions in water with an iridium catalyst in a fast, highly chemoselective, and productive manner.[2a,4] Herein, we disclose that the same catalyst works efficiently for the hydrogenation of aldehydes in water as well. Although TH and hydrogenation catalysis can share the same hydridic intermediate, when, for example, the latter activates H_2 heterolytically, few catalysts are effective for both reactions.[5–9] Very recently, during the course of this study, Noyori, Ohkuma, and co-workers reported that the Ru-TsDPEN (TsDPEN = (1R,2R)-N-(p-toluenesulfonyl)-1,2-diphenylethylenediamine) catalyst, one of the best catalysts for the ATH of ketones and imines,[10] can be applied to the hydrogenation of ketones in methanol under slightly acidic conditions.[5]

Our study started with the reduction of benzaldehyde as a model reaction using tosylated Ir^{III} catalysts 1–5 in neat water.

zaldehyde, an additive, and H_2. The results are summarized in Table 1. As can be seen, complex 1 catalyzes the hydrogena-

Table 1. Hydrogenation of benzaldehyde with different catalysts in water.[a]

Entry	[Ir]	H_2 [bar]	KOH [equiv]	S/C	Conv. [%][b]
1	1	20	none	200	80
2	1	20	5	200	>99
3	1	10	5	200	>99
4	1	10	5	1000	45
5	1	20	5	1000	78
6	1	20	10	1000	88
7	1	20	20	1000	32
8	1	20	CF_3COOH	1000	17
9	2	20	10	1000	>99
10	3	20	10	1000	48
11	4	20	10	1000	99
12	5	20	10	1000	20

[a] Conditions: 2 or 10 mmol substrate, S/C = 200 or 1000, aq. KOH (5–20 equiv relative to catalyst) or acid (5 equiv relative to catalyst), 10 mL water, 80 °C, 2 h. [b] Determined by GC.

1   2   3

4   5

These catalysts have previously been shown to be highly effective in the TH of aldehydes in water.[2a] Expecting that the H_2 pressure, base, and acid would have an impact on the formation of Ir–H from H_2, we first examined a range of conditions for 1-catalyzed hydrogenation. Following generation of the catalyst in situ by reacting [Cp*IrCl$_2$]$_2$ (Cp* = pentamethylcyclopentadienyl) and N-(p-toluenesulfonyl)ethylenediamine (TsEN) in water for 1 h, the reduction was started by introducing ben-

tion of benzaldehyde in water under neutral conditions (Table 1, entry 1). Most interestingly, the reduction becomes faster in the presence of base (Table 1, entries 2 and 3), although a further increase in the pH of the solution is detrimental to the conversion (entry 6 vs 7). Contrary to the effect of base, the introduction of acid led to a significantly lower conversion (Table 1, entry 8 vs 5). A faster rate was also achieved at a higher H_2 pressure (Table 1, entries 4 and 5).[11] By analogy to the mechanism proposed by Ikariya and co-workers for ketone hydrogenation with a Ru^{II}-diamine catalyst,[12] the effect of the base may be explained as facilitating the generation of the Ir–H species from Ir–(H$_2$) [Eq. (1)].
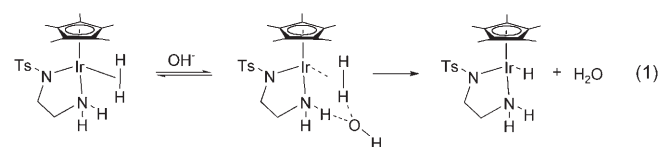

$$\text{(1)}$$

Table 1 also shows that a more electron-deficient ligand affords faster reduction rates, reminiscent of the observations made in the TH of aldehydes in water.[2a] Thus, benzaldehyde was reduced in the presence of 2 with over 99% conversion, whilst the conversion was only 48% with 3, at a substrate/catalyst (S/C) ratio of 1000 in 2 h (Table 1, entries 9 and 10). The

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higher activity of the former catalyst could be attributed to its ligand, in which the CF$_3$ group is expected to increase the acidity of the dihydrogen species shown in Equation (1). However, the more electron-deficient catalyst **4** did not give better rates of conversion in comparison with **2** (Table 1, entry 11).
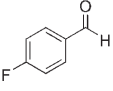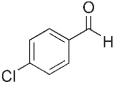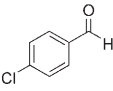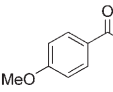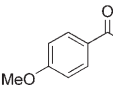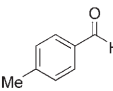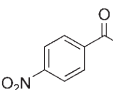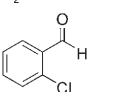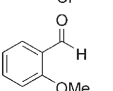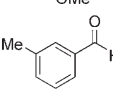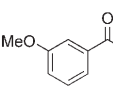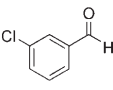
With these findings in hand, we subsequently extended the chemistry to other aldehydes. Aromatic aldehydes were first examined and the reaction was carried out at a S/C ratio of 1000 (Table 2). As can be seen, for most substrates, reduction in the presence of **2** was complete in a few hours, affording the primary alcohols in excellent yields. There appears to be no significant steric effect of substrates on the reaction, which was completed in comparable reaction times in the case of *para*-, *meta*-, and *ortho*-substituted aldehydes. Of practical significance is that the reduction is highly chemoselective toward the formyl group. Thus, 4-acetylbenzaldehyde was only reduced to 4-acetylphenylmethanol in 97% yield, and the ketone functionality was tolerated (Table 2, entry 16). This observation is similar to that seen in the TH of aldehydes with the same catalyst in water.[2a] However, the rates of TH were faster: for instance, the hydrogenation of 4-chloro- and 4-methoxybenzaldehydes afforded 94% conversion in 4 h and 99% conversion in 3 h, respectively, at 80 °C at S/C = 1000 (Table 2, entries 3 and 5); however, under TH conditions with formate as the hydrogen source, the same reactions went to completion within 1 h at a S/C = 10 000 at 80 °C in water.[2a]

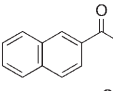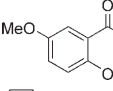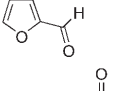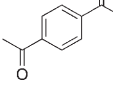Attempts were made to run the hydrogenation with **2** at higher S/C ratios. Under the same conditions as described above, benzaldehyde was reduced at a S/C = 2000 in 2 h; however, only 50% conversion was obtained in 3 h at a still higher S/C ratio of 5000. For other substrates, for example, 3-methoxybenzaldehyde, 2-naphthylaldehyde, and 2-furylaldehyde, full conversion was again observed at S/C = 2000 in a slightly longer time.

As with TH by the same catalyst in water, hydrogenation of α,β-unsaturated aldehydes in water is also highly chemoselective. Thus, as shown in Table 3, a range of α,β-unsaturated aldehydes were readily reduced with exclusive selectivity towards the formyl group. For instance, cinnamaldehyde was hydrogenated in 3.5 h to furnish the cinnamyl alcohol in an excellent yield of 98% (Table 3, entry 1). Similarly, in the reduction of citral in water, the C=C double bonds were tolerated (Table 3, entry 6). Few homogeneous catalysts are available that enable highly chemoselective hydrogenation of carbonyl groups without saturating the C=C double bonds.[1h, 13] With [RuH$_2$(mTPPMS)$_4$] (mTPPMS = (meta-sulfonatophenyl)diphenylphosphane) at high pH (pH > 8), cinnamaldehyde can be selectively reduced to cinnamyl alcohol under atmospheric H$_2$ pressure;[13h] [RuClH(mTPPMS)$_3$] affords a mixture of cinnamyl alcohol and dihydrocinnamaldehyde depending on the H$_2$ pressure.[11] A mixture of products was also obtained in the aqueous-phase hydrogenation of citral with related [M(mTPPMS)] (M = Ru, Rh) catalysts.[13j,k]

Aliphatic aldehydes can also be hydrogenated in the presence of **2** under the conditions described above. However, the reaction was slower than that of aromatic and α,β-unsaturated aldehydes (Table 4). The reduction took longer to complete at

Table 2. Hydrogenation of aromatic aldehydes in the presence of **2** in water.[a]

Entry	Aldehyde	t [h]	Conv. [%][b]
1	4-fluorobenzaldehyde	5	90 (89)
2	4-chlorobenzaldehyde	1.5[c]	>99 (98)
3	4-chlorobenzaldehyde	4	94
4	4-methoxybenzaldehyde	1.5[c]	>99 (99)
5	4-methoxybenzaldehyde	3	99
6	4-methylbenzaldehyde	3	98 (96)
7	4-nitrobenzaldehyde	5	92 (90)
8	2-chlorobenzaldehyde	5	>99 (98)
9	2-methoxybenzaldehyde	3	98 (96)
10	3-methylbenzaldehyde	3	95 (93)
11	3-methoxybenzaldehyde	2	>99 (98)
12	3-chlorobenzaldehyde	3	>99 (99)
13	2-naphthaldehyde	3	>99 (99)
14	2,5-dimethoxybenzaldehyde	5	92 (89)
15	2-furaldehyde	2	>99 (97)
16	4-acetylbenzaldehyde	3	99 (97)

[a] Conditions: 10 mmol substrate, 10 mL water, 20 bar H$_2$, 80 °C, S/C = 1000, 5–10 equiv KOH. [b] Determined by GC; the number in parentheses refers to the yield of isolated product. [c] S/C = 200.

Table 3. Hydrogenation of α,β-unsaturated aldehydes.[a]
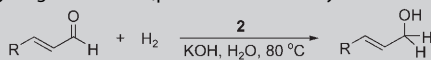
Entry	Substrate	t [h]	Conv. [%][b]
1		3.5	>99 (98)
2		5	99 (97)
3		5	>99 (98)
4		6	98 (95)
5		7	97 (95)
6		5	98 (93)

[a] Conditions: 5 mmol substrate, 10 mL water, 20 bar H_2, 80 °C, S/C = 500, 5–10 equiv KOH. [b] Determined by GC; the number in parentheses refers to the yield of isolated product.

Table 4. Hydrogenation of aliphatic aldehydes with **2**.[a]

Entry	Substrate	t [h]	Conv. [%][b]
1		5	96 (87)
2		5	99 (97)
3		5	97 (90)
4		7	93 (83)
5		7	95 (90)
6[c]		3	>99 (98)

[a] Conditions: 2 mmol substrate, 10 mL water, 20 bar H_2, 80 °C, S/C = 200, 5 equiv KOH. [b] Determined by GC; the number in parentheses refers to the yield of isolated product. [c] S/C = 1000.

a lower S/C ratio of 200. Thus, the hydrogenation of phenylacetaldehyde afforded 96% conversion in 5 h (Table 4, entry 1), and octanal was hydrogenated with 93% conversion in 7 h. As in the case of TH in water, the slow reaction of this class of substrates results probably from the presence of acidic α protons, which may give rise to aldol condensation under the basic conditions employed.[14, 15] The condensation products could inhibit catalysis by coordination to Ir[III]. In line with this

reasoning, trimethyl acetaldehyde, which has no α protons, was fully hydrogenated at a higher S/C ratio of 1000 in 3 h (Table 4, entry 6).

Together with our previous study of **2**-catalyzed aqueous-phase TH reactions,[2a] the results presented in this report show that Ir complex **2** is a versatile catalyst that allows a wide range of aldehydes, including aromatic, aliphatic, heterocyclic, and α,β-unsaturated aldehydes, to be readily reduced in water under H_2 or with formate. As with the TH in water, the hydrogenation is efficient and chemoselective and proceeds in neat water with no need for the addition of an organic cosolvent, thus providing an atom-economic and ecologically benign means for aldehyde reduction.

Experimental Section

[Cp*IrCl$_2$]$_2$ (4 mg, 0.005 mmol) and N-(p-trifluoromethyltoluenesulfonyl)ethylenediamine (5 mg, 0.018 mmol) were stirred in distilled water (10 mL) at 80 °C for 1 h, presumably forming **2**. The resulting mixture was then transferred to an autoclave equipped with a glass liner containing a stirrer bar. After adding KOH (1 M aq., 5–10 equiv relative to the catalyst) and aldehyde (10 mmol; S/C = 1000), the autoclave was degassed with hydrogen three times and then heated with stirring at 20 bar hydrogen pressure and 80 °C for a period of time. After cooling to room temperature and carefully releasing the hydrogen, the mixture was extracted with Et$_2$O (3× 5 mL) and passed through a short silica gel column before GC analysis (Chirasil Dex CB 25 m × 0.25 mm). For isolation, the combined organic layer was dried over Na$_2$SO$_4$, concentrated, and purified by silica gel column chromatography to give the product.

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