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On Water and in Air: Fast and Highly Chemoselective Transfer Hydrogenation of Aldehydes with Iridium Catalysts**

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The use of water as a solvent for organic reactions has emerged as one of the most interesting fields for organic chemists, both in the laboratory and in industry, because of substantial economical and ecological gains.^[1] Recently, Sharpless and co-workers demonstrated the benefits of performing C–C bond-formation reactions “on water”.^[2] We recently discovered that water is an excellent solvent for the asymmetric transfer hydrogenation of ketones.^[3,4] Herein, we disclose that $[(\text{Cp}^*\text{IrCl}_2)_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) in combination with monotosylated ethylenediamine is a good catalyst system for highly chemoselective transfer hydrogenation (TH) of aldehydes.^[5] The reduction works in air and appears to occur on water.

TH reactions have been studied for more than one century. The reduction of ketones and aldehydes by the Meerwein–Ponndorf–Verley reaction was first described in 1925,^[6] and since then a great deal of progress has been made in TH chemistry.^[7–10] However, aldehydes are difficult to reduce by catalysts commonly used for TH, and controlling the chemoselectivity of the reaction presents a further challenge.^[7b,11,12] To date, the most efficient TH catalyst appears to be the iridium complex of an N-heterocyclic carbene, which affords a turnover frequency (TOF) of up to 3000 h^{-1} in refluxing 2-propanol.^[12a] With most other metal catalysts, the TOFs range from a few to several hundred per hour.^[7–12] In fact, few catalysts have been reported that enable fast, selective, and productive TH of aldehydes with inexpensive, eco-friendly reductants, and that can tolerate the presence of synthetically useful functional groups.^[7]

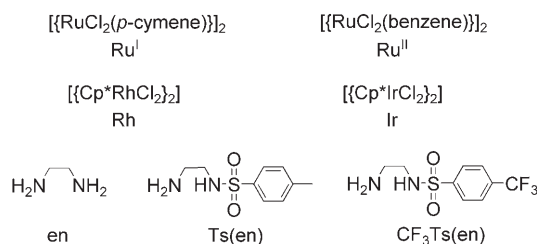
In continuing our investigation into aqueous TH reactions,^[5] we examined the TH of benzaldehyde with HCOONa

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in water, initially using metal complexes with no additional ligands (Scheme 1). After the complexes had been stirred in water at 65 °C for 1 h, HCOONa and benzaldehyde (10.0 mmol) were introduced to start the reduction. As



Scheme 1. Metal precursors and ligands screened in this study. Ts = toluene-4-sulfonyl.

shown in Table 1, the reaction was slow for all four complexes. However, the introduction of the readily available ethylenediamine (en) brought about a significant ligand-acceleration effect on the rates and, most remarkably, the monotosylated analogue Ts(en) led to around a 1000-fold increase in rate (Table 1, entries 3, 11, and 14).^[13]

Table 1: Optimization of the TH reaction of benzaldehyde by HCOONa in water.^[a]

| Entry | Catalysts | <i>t</i> [h] | Conv. [%] ^[b] | TOF ^[c] [mol mol ⁻¹ h ⁻¹] |
|-------|--|--------------|--------------------------|--|
| 1 | Ru ^I | 25 | 32 | 2 |
| 2 | Rh | 25 | 35 | 3 |
| 3 | Ir | 25 | 70 | 20 |
| 4 | Ru ^{II} | 25 | 20 | 0.6 |
| 5 | Ru ^I -en | 1 | 1.2 | 12 ^[d] |
| 6 | Rh-en | 1 | 74 | 900 |
| 7 | Ir-en | 1 | 99 | 1800 |
| 8 | Ru ^{II} -en | 1 | 0.8 | 8 ^[d] |
| 9 | Ru ^I -Ts(en) | 2 | 99 | 1000 |
| 10 | Rh-Ts(en) | 0.33 | 99 | 6000 |
| 11 | Ir-Ts(en) | 0.08 | > 99 | 12 000 |
| 12 | Ir-Ts(en), IPA ^[e] | 1 | 2.6 | 26 ^[d] |
| 13 | Ir-Ts(en), F/T ^[f] | 1 | 1.5 | 15 ^[d] |
| 14 | Ir-Ts(en) ^[g] | 1.5 | > 99 | 20 400 |
| 15 | Ir-Ts(en) ^[h] | 0.9 | > 99 | 28 800 |
| 16 | Ir-CF ₃ Ts(en) ^[h] | 0.3 | > 99 | 42 000 |
| 17 | Ir-CF ₃ Ts(en) ^[i] | 1 | 98 | 132 000 |

[a] 65 °C, HCOONa (5 equiv) at S/C 1000:1 in water (10 mL). [b] Determined by GC. [c] Based on conversion after 5 min. [d] Based on conversion after 1 h. [e] 2-propanol (IPA) was used as hydrogen source and solvent, 3.2% conversion after 8 h. [f] HCOOH/Et₃N (F/T) azeotrope used, 9% conversion after 8 h. [g] S/C 1 × 10⁴:1. [h] 80 °C, S/C 1 × 10⁴:1. [i] 80 °C, S/C 5 × 10⁴:1.

The precatalyst (M–ligand) was generated by simply reacting the precursor complex with the ligand in water at 65 °C for 1 h. It is apparent from Table 1 that the Ir^{III} catalysts with en and Ts(en) ligands proved to be the most active. For instance, benzaldehyde was reduced with almost complete conversion in 5 min using Ir–Ts(en) with a substrate/catalyst (S/C) ratio of 1000:1 at 65 °C (Table 1, entry 11). When the

same reaction was carried out in 2-propanol or the azeotropic formic acid/triethylamine mixture, which are the two most commonly used solvents for TH reactions, the conversion was less than 3 % (Table 1, entries 12 and 13). These results show the remarkable benefit of carrying out the reduction in the aqueous phase.

The effectiveness of using the Ir^{III} catalysts in synthesis was tested by carrying out the TH reaction at higher S/C ratios. At an S/C ratio of 1 × 10⁴:1, Ir–Ts(en) led to a TOF of 28 800 h⁻¹ at 80 °C (Table 1, entry 15), and with the more electron-deficient Ir–CF₃Ts(en), a higher TOF of 42 000 h⁻¹ was achieved (Table 1, entry 16). Using Ir–CF₃Ts(en), the S/C ratio could be increased to 5 × 10⁴:1 and a TOF as high as 1.3 × 10⁵ h⁻¹ was attained. Under these conditions, benzaldehyde (5.30 g) was reduced to give phenylmethanol in 98 % yield (5.28 g after 1 h using 0.4 mg of [(Cp*IrCl₂)₂]), demonstrating the superior activity,^[7] robustness, and easy scalability of the aqueous Ir^{III} catalytic system. However, as seen with the TH of ketones using ruthenium catalysts,^[1c,3b,14] the reduction is also pH dependent, with neutral conditions being most favorable (Figure 1).

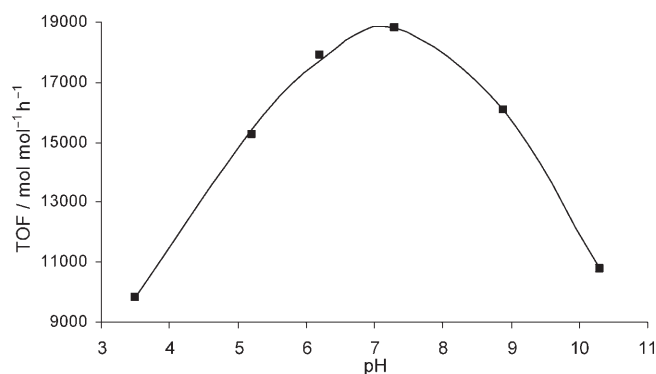




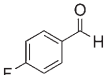

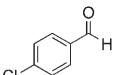

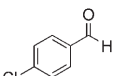

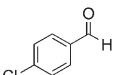
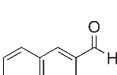
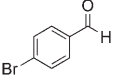

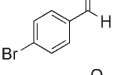

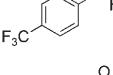
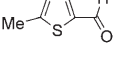
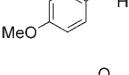
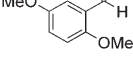
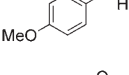
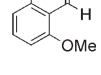
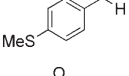
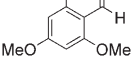

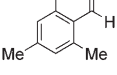

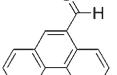

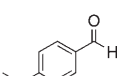

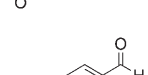


Figure 1. Plot showing the TOF against the initial solution pH values in the reduction of benzaldehyde (10 mmol), using Ir–Ts(en) and HCOONa (5 equiv) in water (10 mL) at 80 °C and S/C 5000:1. The initial pH value was determined by varying the HCOOH/NaOH molar ratios.

With these findings in hand, we were interested in extending this reduction system to a wider range of aldehydes. The results on the TH of aromatic aldehydes with Ir–Ts(en) at S/C 5000:1 and with Ir–CF₃Ts(en) at S/C 10000:1 are shown in Table 2. To our delight, most of the reactions were complete in a short time, and gave high yields. For example, the reductions of 4-halo- and 4-methoxybenzaldehyde with the Ir–Ts(en) catalyst both achieved over 99 % conversion within 1 h (Table 2, entries 3, 4, 5, 7, and 10). With the more active Ir–CF₃Ts(en) catalyst, similar results were obtained at a higher S/C ratio (10000:1; Table 2, entries 6, 8, and 11). An exception to these results is the reduction of sulfur-containing substrates, probably because of coordination between sulfur and iridium. However, reduction of these substrates can be performed using a lower S/C ratio (1000:1; Table 2, entries 12, 25, and 26). The reduction also works well for sterically demanding substrates such as trisubstituted benzaldehydes (Table 2, entries 29 and 30) and significantly, the reduction

Table 2: The TH reaction of aromatic aldehydes with HCOONa.^[a]

| Entry | Substr. | t [h] | Conv. [%] ^[b] | Entry | Substr. | t [h] | Conv. [%] ^[b] |
|-------|---|---------------------|--------------------------|-------|---|--------------------|--------------------------|
| 1 |  | 0.6 | > 99 (98) | 18 |  | 1.5 | 99 |
| 2 |  | 0.6 ^[c] | > 99 | 19 |  | 1.8 ^[d] | 99 (97) |
| 3 |  | 0.5 | > 99 | 20 |  | 7 | 99 |
| 4 |  | 0.6 | > 99 | 21 |  | 1.5 | > 99 |
| 5 |  | 0.67 ^[c] | > 99 (98) | 22 |  | 1.5 | > 99 |
| 6 |  | 0.9 ^[d] | > 99 | 23 |  | 1.5 | > 99 |
| 7 |  | 0.67 | 99 | 24 |  | 0.25 | 98 |
| 8 |  | 1.2 ^[d] | 99 | 25 |  | 0.5 ^[f] | > 99 |
| 9 |  | 3 | 98 | 26 |  | 2 ^[e] | 99 |
| 10 |  | 0.5 | > 99 | 27 |  | 2 | 98 (97) |
| 11 |  | 0.6 ^[d] | > 99 | 28 |  | 3 | 96 (94) |
| 12 |  | 0.5 ^[e] | > 99 | 29 |  | 1.5 ^[h] | 99 (97) |
| 13 |  | 0.8 | > 99 | 30 |  | 0.7 ^[i] | 99 (97) |
| 14 |  | 1 | > 99 | 31 |  | 1.5 | 99 (98) |
| 15 |  | 0.5 | 98 | 32 |  | 0.5 | 99 (95) |
| 16 |  | 0.5 | 91 | 33 |  | 0.6 | > 99 |

tolerates a variety of functionalities. Of particular note is the reduction of 4-acetylbenzaldehyde, proceeding in 95 % yield after 0.5 h, with no sign of ketone reduction (Table 2, entry 32). The results shown in Table 3 also prove that the aqueous Ir^{III} system is the most efficient, chemoselective catalyst for aldehyde reduction thus far reported. In addition, these TH reactions can be carried out in air without inert gas protection (Table 3, entries 2, 5, and 22).

Interestingly, under the same conditions, neither the water-soluble 4-carboxybenzaldehyde nor its sodium salt could be reduced. However, the ester analogue, methyl 4-formylbenzoate, was reduced with > 99 % conversion in 40 min (compare entries 33 and 34, Table 2). These results suggest that the catalysis takes place on water rather than in water in these biphasic reactions. This supposition is supported by the observation that the catalyst is more soluble in the organic phase and that the aqueous phase remains almost colorless during the reduction.

A further test of the chemoselectivity of the catalyst system is the TH of α,β -unsaturated aldehydes. Few catalysts are available that enable highly chemoselective TH of the carbonyl groups without reduction of the C=C bonds.^[5,9] As shown in Table 3, various α,β -unsaturated aldehydes were selectively reduced on the formyl group. Notably, these include the acetylated cinnamaldehydes, in which both the alkenyl and acetyl groups remained intact during the reduction (Table 3, entries 7 and 8). To the best of our knowledge, no catalysts have been reported for the TH of these substrates.^[15]

Surprisingly, when aliphatic aldehydes (for example, octanal) were subjected to TH under the conditions reported in Table 2, conversions were very low, even after prolonged reaction times. This reduction in the rate does not appear to result from product inhibition, as the TH of benzaldehyde was not affected by the presence of 1-octanol or 1-butanol as additives. Rather it is more likely related to the presence of α protons in these substrates. Thus, trimethylacetaldehyde was reduced in 3 h [Eq. (1)]. In sharp contrast, under the same conditions, the reduction of octanal proceeded in only 3 %

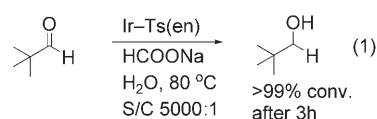
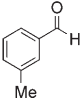
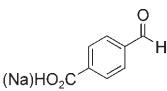
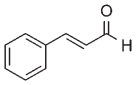
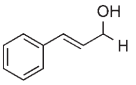
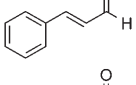
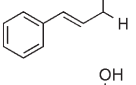
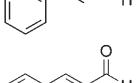
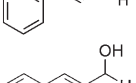
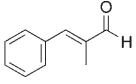
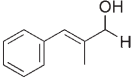
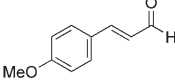
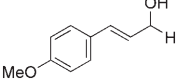
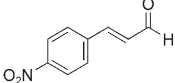
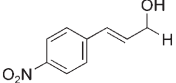
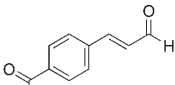
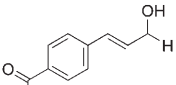
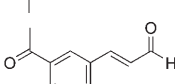
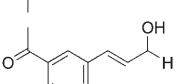
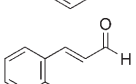
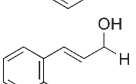
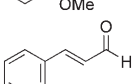
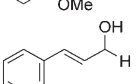
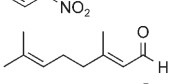
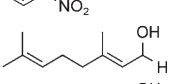
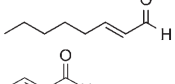
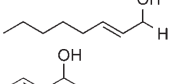
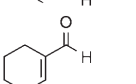
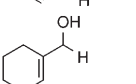
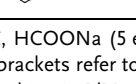
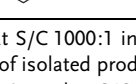


Table 2: (Continued)

| Entry | Substr. | <i>t</i> [h] | Conv. [%] ^[b] | Entry | Substr. | <i>t</i> [h] | Conv. [%] ^[b] |
|-------|---|--------------|--------------------------|-------|---|--------------|--------------------------|
| 17 |  | 1.3 | > 99 | 34 |  | 1 | na ^[j] |

[a] 80 °C, HCOONa (5 equiv) at S/C 5000:1 in water (15 mL). [b] Numbers in brackets refer to yields of isolated products. [c] The reaction was performed in air. [d] Ir-CF₃Ts(en), S/C 1 × 10⁴:1. [e] S/C 1000:1; 48 % conversion after 8 h at S/C 5000:1. [f] S/C 1000:1; 30 % conversion after 5 h at S/C 5000:1. [g] S/C 1000:1; 32 % conversion after 19 h at S/C 5000:1. [h] S/C 1000:1; 98 % conversion after 12 h at S/C 5000:1. [i] S/C 1000:1; 99 % conversion after 8 h at S/C 5000:1. [j] Not applicable (na); initial pH 6.8; no product was detected by NMR spectroscopy after 1 h.

Table 3: The TH reaction of α,β-unsaturated aldehydes with HCOONa.^[a]

| Entry | Aldehyde | Product | <i>t</i> [h] | Conv. [%] ^[b] |
|-------|---|---|------------------|--------------------------|
| 1 |  |  | 3 | 99 (97) |
| 2 |  |  | 3 ^[c] | > 99 |
| 3 |  |  | 3 ^[d] | 98 |
| 4 |  |  | 0.2 | > 99 (98) |
| 5 |  |  | 0.3 | > 99 (98) |
| 6 |  |  | 0.5 | 99 (98) |
| 7 |  |  | 1.5 | 98 (96) |
| 8 |  |  | 3 | 99 (97) |
| 9 |  |  | 0.4 | > 99 (98) |
| 10 |  |  | 0.7 | 99 (98) |
| 11 |  |  | 4 | 98 (97) |
| 12 |  |  | 4.5 | 97 |
| 13 |  |  | 1 | > 99 |
| 14 |  |  | 9 | 98 |

[a] 80 °C, HCOONa (5 equiv) at S/C 1000:1 in water (10 mL). [b] Numbers in brackets refer to yields of isolated products. [c] The reaction was performed in air. [d] Ir-CF₃Ts(en) used at S/C 5000:1.

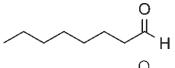
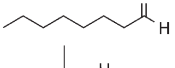
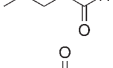


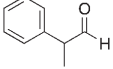
yield after 18 h. One explanation is that under the reaction conditions, the α position in the aldehydes is deprotonated, leading to aldol products that might inhibit the iridium catalysis. The NMR and mass spectra of the reaction mixture

arising from the reduction of octanal indeed show the presence of aldol and enol products.

If one assumes that the reduction is retarded by the aldol condensation,^[1c,12a] lowering the concentration of substrates should disfavor the aldol reaction and enable TH of the aldehydes. Indeed, various aldehydes with α-hydrogen atoms could be reduced at S/C 2000:1 when the aldehyde was slowly added portionwise over the times shown in Table 4. Under such

conditions, however, these aldehydes are still more difficult to reduce than aryl aldehydes. Thus, a competitive reduction of a mixture of benzaldehyde (30 mmol) and phenylacetaldehyde

Table 4: The TH reaction of aliphatic aldehydes using Ir-CF₃Ts(en) with HCOONa.^[a]

| Entry | Substrate | <i>t</i> [h] | Conv. [%] |
|-------|--|-------------------|-----------|
| 1 |  | 13 ^[b] | 95 |
| 2 |  | 7 | 97 |
| 3 |  | 4 | 95 |
| 4 |  | 3.7 | 96 |
| 5 |  | 3.6 | 98 |
| 6 |  | 5 ^[c] | 90 |

[a] HCOONa (5 equiv) at 80 °C in water (10 mL). The aldehyde (20.0 mmol) was added dropwise in ten portions; 1-octanol (2.0 mmol) as a diluting agent was added initially; HCOOH was added to keep the pH neutral after the fifth addition. [b] Without diluting reagent. [c] S/C 1600:1.

(6 mmol) with Ir-Ts(en) (0.01 mmol) gave a 98 % conversion in 20 min for the former but required 5 h for the latter; as expected, when the concentration of phenylacetaldehyde was increased, the reduction rate decreased for both (equal molar mixture and total S/C 5000:1 gave 70 % conversion for the former and 16 % for the latter after 24 h).

In summary, we have demonstrated that Ir-Ts(en) and Ir-CF₃Ts(en) are highly active and chemoselective catalysts for the aqueous-phase TH of aldehydes. The catalytic reduction can be carried out with S/C ratios as high as 5 × 10⁴:1, the initial TOFs near 1.3 × 10⁵ h⁻¹, and an inert atmosphere is not required. Of significant practical importance is that the catalyst tolerates a wide variety of synthetically useful functional groups including nitro groups, halogens, ketones, esters, and olefins. To the best of our knowledge, this on-water Ir^{III}-diamine catalysis represents the most efficient, simple,

and environmentally friendly catalytic system for the reduction of aldehydes to date.

Experimental Section

[[Cp*IrCl₂]₂] (1.6 mg, 0.002 mmol) and Ts(en) (1.2 mg, 0.0048 mmol) were suspended in degassed distilled water (15 mL). After the reaction mixture had been stirred at 80 °C for 1 h,^[16] HCOONa (6.8 g, 0.1 mol) and benzaldehyde (2.1 g, 20 mmol) were added to the resulting solution. The reaction mixture was rapidly degassed three times through vacuum-nitrogen cycles and then heated at 80 °C for 0.6 h. The workup and analysis were conducted as previously reported.^[3a]

Representative of a TH reaction (S/C ratio of $5 \times 10^4:1$): An aqueous solution of the catalyst Ir–CF₃Ts(en) (0.001 M, 1 mL) was added to degassed distilled water (30 mL), and the mixture was stirred at 80 °C for 10 min. HCOONa (17 g, 0.25 mol) and benzaldehyde (5.30 g, 50.0 mmol) were then introduced. A conversion of 98 % was achieved after 1 h, and following workup, phenylmethanol was obtained as a colorless liquid (5.28 g, 98 % yield).

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- [16] The iridium compound isolated is consistent with [Cp*IrCIL] (L = Ts(en) or CF₃Ts(en) without the amido hydrogen atom) with a structure probably similar to the related, structurally characterized Ir–Ts(dpen) compound (dpen = 1,2-diphenylethylenediamine).^[17] Analytical data for the Ir–CF₃Ts(en) catalyst: ¹H NMR (400 MHz, CDCl₃/TMS): δ = 8.04 ppm (d, J = 8.1 Hz, 2H) 7.63 (d, J = 8.1 Hz, 2H), 4.07 (brs, 2H), 2.74 (2H, m), 2.66 (m, 2H), 1.75 (s, 15H). HRMS (ES) for C₁₉H₂₆ClF₃IrN₂O₂S ([M+H]⁺): calcd: 631.0932 (Ir¹⁹¹Cl³⁷) and 631.0985 (Ir¹⁹³Cl³⁵); found: 631.0950; for C₁₉H₂₅F₃IrN₂O₂S ([M–Cl]⁺): calcd: 595.1218 (Ir¹⁹³) and 593.1195 (Ir¹⁹¹); found: 595.1190 and 593.1222. Elemental analysis: calcd for C₁₉H₂₅ClF₃IrN₂O₂S: C 36.21, H 4.00, N 4.45; found: C 36.40, H 4.12, N 4.31.
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