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pH-Dependent Catalytic Activity and Chemoselectivity in Transfer Hydrogenation Catalyzed by Iridium Complex with 4,4′-Dihydroxy-2,2′-bipyridine

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Abstract: Transfer hydrogenation catalyzed by an iridium catalyst with 4,4′-dihydroxy-2,2′-bipyridine (DHBP) in an aqueous formate solution exhibits highly pH-dependent catalytic activity and chemoselectivity. The substantial change in the activity is due to the electronic effect based on the acid–base equilibrium of the phenolic hydroxyl group of DHBP. Under basic conditions, high turnover frequency values of the DHBP complex, which can be more than 1000 times the value of the unsubstituted analogue, are obtained (up to 81000 h^{-1} at 80 °C). In addition, the DHBP catalyst exhibits pH-dependent chemoselectivity for α,β-unsaturated carbonyl compounds. Selective reduction of the C=C bond of enone with high activity are observed under basic conditions. The ketone moieties can be reduced with satisfactory activity under acidic conditions. In particular, pH-selective chemoselectivity of the C=O versus C=C bond reduction was observed in the transfer hydrogenation of cinnamaldehyde.

Keywords: ligand design · pH-dependent catalyst · substituent effects · transfer hydrogenation · water chemistry

Introduction

The use of water as a reaction medium is of great interest for organometallic catalysis.[1] Among various solvents, water is the most preferred solvent, because it is inexpensive, safe, clean, and abundant.[2] Moreover, owing to the amphoteric behavior in the Brønsted sense, the reaction rates and the selectivities can be varied by changing the pH of the solution.[3–8] Extensive studies by Joó on pH-switchable chemoselective hydrogenation of cinnamaldehyde are intriguing.[3,9–12]

Transfer hydrogenation (TH) reaction using a formate as a hydrogen donor in water has received much attention, because it avoids the use of explosive molecular hydrogen and harmful organic solvents.[6–8,13–20] Although highly efficient TH catalysts in *i*PrOH have been reported recently,[21–25] aqueous TH reactions, which usually require high reaction temperatures and low substrate/catalyst (S/C) ratios, seem to be sluggish except for an iridium complex with monotosylated ethylenediamine (turnover frequency (TOF) up to 132000 h^{-1} at 80 °C).[26] On the other hand, attempts have been made at the chemoselective TH of α,β-unsaturated carbonyl compounds in *i*PrOH.[27–31] The pH-dependent chemoselective TH of α,β-unsaturated carbonyl compounds in an aqueous formate solution was reported by Frost for the first time in 2007.[32] However, further improvements in catalyst efficiency, selectivity, and versatility are required.

Recently, we have reported two important developments in aqueous catalysis. First, the half-sandwich bipyridine complexes [MCp*(bpy)Cl]Cl (Cp* = C_5Me_5; M = Rh, Ir; bpy = 2,2′-bipyridine) serve as efficient catalysts for the TH of ketones in an acidic formate solution.[6,33] Although it is known that the rhodium complex shows poor activity in TH (TOF = 0.2 h^{-1}) under neutral formate conditions,[34] we have revealed that the reactivity toward ketones is strongly pH-dependent (TOF = 66 h^{-1} at pH 2.5). Second, remarkable catalytic activation has been achieved by the introduction of a hydroxyl group into the pyridine ligand (i.e., 4,4′-

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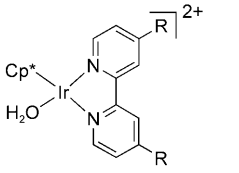
dihydroxy-2,2′-bipyridine (DHBP) and 4,7-dihydroxy-1,10-phenanthroline (DHPT)) for the hydrogenation of bicarbonates.[35] This is attributed to the strong electron-donating ability of the oxyanion generated by deprotonation of the phenolic hydroxy group under basic conditions.[36,37] In particular, the iridium series is most strongly affected by the electronic substituent effect among ruthenium, rhodium, and iridium complexes. In fact, in comparison with the initial TOF of the unsubstituted bipyridine complex, the TOF of the iridium–DHBP complex is increased about 1300 times.

These two findings have prompted us to develop efficient and chemoselective TH by using DHBP complexes. Herein, we report that the catalytic activity and chemoselectivity of the TH catalyzed by an iridium–DHBP complex in an aqueous formate solution is strongly pH-dependent. The catalytic activity is discussed on the basis of the acid–base equilibrium of the hydroxyl group of the ligand and the Hammett rule under acidic and basic conditions. The pH-dependent chemoselective TH of α,β-unsaturated carbonyl compounds is also investigated.

Results and Discussion

pH-Dependent TH of 2-cyclohexen-1-one: To probe the effect of pH, the TH of a water-soluble cyclic enone, 2-cyclohexen-1-one, was selected as the model reaction. The TH of 2-cyclohexen-1-one (2 mmol) was carried out with the water-soluble iridium aqua catalyst **1**-SO_4 (0.5 μmol) at 40 °C in 1 M formate solution (20 mL) at various pH values by adjusting the HCO_2H/HCO_2Na/NaOH [formate/substrate/catalyst (F/S/C) mole ratio = 40000:4000:1]. The initial TOFs of TH were measured after 10 min (Figure 1a). From pH 6.7 to 9.0, cyclohexanone was exclusively formed with high TOFs ($>4000\ h^{-1}$) through 1,4-reduction, but the substrate was not consumed completely under these conditions (turnover number (TON) > ca. 3500). An almost quantitative yield was obtained under an S/C ratio of 2000.[38] However, the activity of the chemoselective TH of 2-cyclohexen-1-one is far superior to earlier studies.[28,29]



1: R=OH, **2**: R=H, **3**: R=Me, **4**: R=OMe, **5**: R=CO_2H

At pH 4 and below, the TOFs decreased below $1400\ h^{-1}$. After 8 h, a mixture of cyclohexanone, cyclohexanol, and a small amount of 2-cyclohexen-1-ol as a 1,2-reduction product was obtained. An analysis of the progress of the reaction by GC showed that cyclohexanone was generated at first and then the amount of cyclohexanol increased gradually with a TOF of up to $700\ h^{-1}$. After 24 h, 2-cyclohexen-1-one was consumed completely at pH 2.6, and a mixture of cyclohexanol (94%) and 2-cyclohexen-1-ol (6%) was obtained.

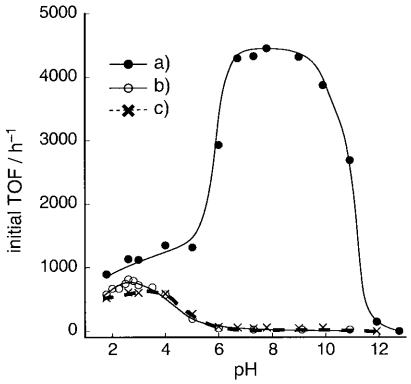


Figure 1. pH-Dependent profile of initial TOFs for the TH of a) 2-cyclohexen-1-one (2.0 mmol) with **1**-SO_4 (0.5 μmol), b) cyclohexanone (2.0 mmol) with **1**-SO_4 (1.0 μmol), and c) 2-cyclohexen-1-one (2.0 mmol) with **4**-SO_4 (2.0 μmol) in an aqueous 1 M formate solution (20 mL) at 40 °C.

The pH of the reaction solution changed during the course of the reaction, due to the consumption of HCO_2H as a hydrogen donor and/or the generation of CO_2, which produces bicarbonates and carbonates under basic conditions.[4,38] For example, the initial pH values changed from 7.3 and 2.6 to 8.5 and 2.8, respectively, at the end of the reaction. The TH in air without inert gas protection proceeded with high initial TOF at the beginning of the reaction. However, the catalyst degraded gradually and lower yields were obtained.[26] The use of an excess of formate was required to obtain a high yield of the desired reduction product.

Correlation with the Hammett substituent constant (σ_p^+) at pH 2.6 and 7.3: Next, we systematically examined the electronic substituent effect on the TH of 2-cyclohexen-1-one by using a series of iridium complexes **1**–**5** at pH 2.6 and 7.3. As expected, the catalytic activities were strongly affected by the substituents in the bipyridine ligand. At pH 2.6, the TOF of **1** was 19 and 1.9 times higher than the TOFs of **2** and **4**, respectively. Figure 2a shows a good correlation between log TOF and the σ_p^+ value[39] of the respective sub-

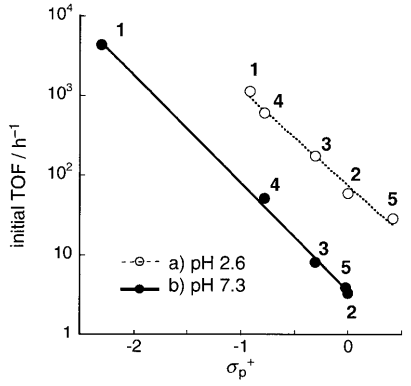


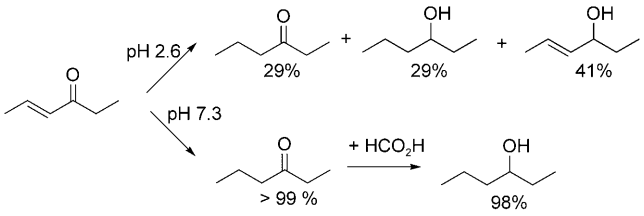
Figure 2. Plot for the correlation between σ_p^+ and the initial TOF for the TH of 2-cyclohexen-1-one at pH 2.6 and 7.3 with catalyst **1**–**5** (20–0.5 μmol) at 40 °C.

stituents (R). A similar result was observed for the TH of cyclohexanone at pH 3.0.

At pH 7.3, although the TOF of **1** was approximately three times higher than that at pH 2.6, the TOFs of **2**–**5** were decreased significantly. Although the correlation among the TOFs of **2**–**4** was unchanged, **1** and **5** showed a different correlation due to the deprotonation of the acidic substituents. Namely, the σ_p^+ values for **1** and **5** are regarded as −2.30 (-O^-) and −0.02 (-CO_2^-), respectively.[37] The Hammett plot according to the interpretation shows a good correlation (Figure 2b). In addition, high reaction constants ($\rho = -1.3$ and −1.2 at pH 2.6 and 7.3, respectively) of the Hammett plots were observed, which were similar to those observed for the hydrogenation of bicarbonates ($\rho = -1.3$).[37] The strong electronic substituent effect has never been observed in other catalyst ligands (e.g., phosphorus ligands and 1,2-dephenylethylendiamine).[30,40–42] It is apparent that the remarkable activation of **1** can be attributed to the strong electron-donating ability of the oxyanion (i.e., low σ_p^+ value) and the strong substituent effect (i.e., high ρ value).

TH with various substrates: The scope of TH using **1** was examined with various substrates at pH 2.6 and 7.3, and the results are summarized in Table 1. In the TH of all the enones at pH 7.3, the 1,4-reduction proceeded exclusively with high TOFs to give ketones (entries 1–3 at pH 7.3). The generated ketones were tolerated under basic conditions. Equilibrium, which was dependent on reaction conditions, seems to exist.[38] Lowered S/C ratio led to increased yield.

On the other hand, although at pH 2.6 the substrates were consumed completely, the distributions of 1,4- and 1,2-reduction products were influenced by a steric hindrance at the β-position of the enones. While 2-cyclohexen-1-ol was generated in 6% yield from 2-cyclohexen-1-one (entry 1 at pH 2.6), no 1,2-reduction product was observed in the case of methyl vinyl ketone (entry 2 at pH 2.6). The TH of 4-hexen-3-one (entry 3 at pH 2.6) yielded a mixture of 1,4-reduction products (58%) and 1,2-reduction product (41%; Scheme 1). To avoid the formation of the mixed product, the reaction was carried out in 1 M HCO_2Na solution at first, followed by the addition of formic acid to give 3-hexanol exclusively.

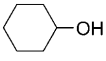
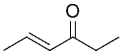
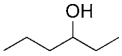
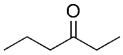
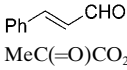
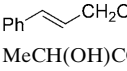
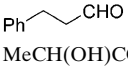
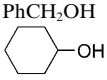
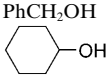


Scheme 1. TH of 4-hexen-3-one catalyzed by **1**.

The TH of cinnamaldehyde at pH 2.6 afforded cinnamyl alcohol as the major 1,2-reduction product in 85% yield (entry 4). The minor 1,4-reduction product was further reduced to give 3-phenyl-1-propanol in 15% yield. On the other hand, the TH at pH 7.3 showed highly selective 1,4-reduction with high TOF, and the product distributions and the yields were temperature-dependent (Table 2). The generated hydrocinnamaldehyde was tolerated at 40°C (entry 1), while the aldehyde moiety was smoothly reduced at 80°C (entry 3). It is interesting that the pH-dependent product distribution is the inverse of that of biphasic hydrogenation using ruthenium complexes with sulfonated phosphine ligands.[9] Unfortunately, the C=C bond in ethyl crotonate was not reduced.

Next, other substrates were examined. The TH of α-keto acid, pyruvic acid, gave lactic acid under both acidic and basic conditions (entry 5 in Table 1).[43,44] The reduction of benzaldehyde proceeded with a high TOF at pH 7.3 (entry 6 in Table 1). The highest TOF of 81000 h^{-1} and almost quantitative yield were obtained at 80°C. However, high sub-

Table 1. TH catalyzed by **1**[a]

	Substrate	t [h]	TOF [h^{-1}]	pH 2.6 Yield [%]	Product	t [h]	TOF [h^{-1}]	pH 7.3 Yield [%]	Product
1		24	1100	94[b]		2[c]	4300	>99	
2		24[c]	1500	72[d]		0.5[c]	5300	>99	
3		24[c]	700	29[e]		3	2700	>99	
4		8[c]	1200	85[f]		0.2[c]	4100	17[g]	
5	MeC(=O)CO_2H	8	620	>99	MeCH(OH)CO_2H	8	1100	>99	MeCH(OH)CO_2H
6	PhCHO	6	1400	>99	$PhCH_2OH$	0.2[h]	81000	>99	$PhCH_2OH$
7		8[c]	820	>99		8[c]	15	6	
8	PhCOMe	8[c]	480	>99	PhCH(OH)Me	6[c]	80	7	PhCH(OH)Me

[a] The reaction was carried out at 40°C in an aqueous 1 M formate solution (20 mL) with a substrate (2 mmol) and **1**-SO_4 (0.5 μmol); F/S/C = 40000:4000:1; yields were determined by a GC or HPLC analysis. The initial TOF was measured after 10 min. [b] 2-Cyclohexenol (6%) was formed. [c] The reaction was carried out by using **1**-SO_4 (1 μmol); F/S/C = 20000:2000:1. [d] 2-Butanone (28%) was formed. [e] 4-Hexen-3-ol (41%) and 3-hexanone (29%) were formed. [f] 3-Phenyl-1-propanol (15%) was formed. [g] The reaction reached equilibrium. [h] The reaction was carried out at 80°C in an aqueous 2 M formate solution (20 mL) with a substrate (4 mmol) and **1**-SO_4 (0.5 μmol); F/S/C = 80000:8000:1] The initial TOF was measured after 5 min.

Table 2. TH of cinnamaldehyde[a]

	T [°C]	TOF [h^{-1}]	Ph⟋CHO	Ph⟋CHO	Ph⟋CH$_2$OH	Ph⟋CH$_2$OH
1	40	5000	79	19	1	<1
2	60	17000	35	48	16	1
3[b]	80	28000	0	27	72	1
4[c]	40	1200	0	0	15	85

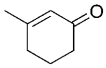
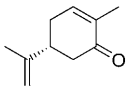
[a] The reaction was carried out in an aqueous 2 M HCO_2Na solution (20 mL) with a substrate (2 mmol) and **1**-SO_4 (0.5 μmol) for 3 h; F/S/C = 80000:4000:1; yields were determined by a GC and ^{1}H NMR analyses. The initial TOF was measured after 5 min. [b] The reaction was carried out for 8 h. [c] The reaction was carried out in an aqueous 1 M formate solution (pH 2.6) with a substrate (2 mmol) and **1**-SO_4 (1 μmol) for 8 h; F/S/C = 20000:2000:1.

strate concentration led to decreased TOF and yield due to phase separation.[38] In the TH of the water-soluble cyclohexanone and insoluble acetophenone at pH 2.6, the TOFs improved significantly compared with that of unsubstituted analog **2** (entries 7, 8 in Table 1). The high TOF of 4000 h^{-1} at pH 2.6 was obtained in the TH of acetophenone at 80 °C. On the other hand, the TH at pH 7.3 showed poor activities toward ketones. The pH-dependent profiles for the TH of cyclohexanone with **1**, in which the TOFs improved significantly compared with the TOFs of unsubstituted analog **2** under acidic conditions, are consistent with a previous observation (Figure 1b).[6] The pH dependence of the reduction of ketones can be explained by the activation of the carbonyl moiety by protons.[44] Consequently, the order of the reactivity at pH 2.6 is aldehyde > C=C bond of α,β-unsaturated carbonyl compounds > ketone, while that at pH 7.3 is C=C bond of α,β-unsaturated carbonyl compounds > aromatic aldehyde ≫ ketone.

Next, the reactivities of substituted cyclic eneones at pH 7.3 were investigated (Table 3). The TH of 2-cyclopenten-1-one showed high activity similar to that of 2-cyclohexen-1-one (entry 1). While the activity for 2-metlyl-2-cyclopenten-1-one somewhat decreased (entry 2), the THs of 3-methyl-substituted analogues were sluggish (entries 3 and 4). The decrease in activity due to steric hindrance in TH is known.[28,29] Since the influence of α-substituted enone was relatively small, (*R*)-(−)-carvone could be efficiently converted to dihydrocarvone as a *trans*/*cis* mixture (entry 5).

Effect of acid-base equilibrium of DHBP: The acid–base equilibrium of **1**, which has two types of proton-donating groups (i.e., two phenolic hydroxyl groups and an aqua ligand), was examined using absorption spectra as a function of pH adjusted by H_2SO_4/KOH (Figure 3). Figure 4a shows the percentage change in the optical density of **1** at 265 nm against the pH. From our previous studies, the change from pH 3 to 6 can be attributed to the acid–base equilibrium of the hydroxy groups in **1**.[36] On the other hand, the change from pH 8 to 10 may be attributed to that of the aqua ligand.[46] Thus, the complex seems to exist as a protonated form **1** at pH 2.6, a deprotonated form **6** at pH 7.3, and a hydoxo complex **7** at pH above 10 (Scheme 2).

Table 3. TH of cyclic enones into ketones at pH 7.3[a]

Entry	Substrate	t [h]	TOF [h^{-1}]	Yield [%]
1		2	3600	>99
2		6	2200	>99
3		8	130	14
4		8	560	31
5		1.5	2000	>99[b]

[a] The reaction was carried out at 40 °C in an aqueous 1 M formate solution (20 mL) with a substrate (2 mmol) and **1**-SO_4 (0.5 μmol); F/S/C = 40000:4000:1; yields were determined by a GC analysis. [b] The reaction was carried out using a substrate (1 mmol) and **1**-SO_4 (1 μmol); F/S/C = 20000:1000:1; dihydrocarvone was isolated as a mixture (*trans*/*cis* = 1.7:1).[45]

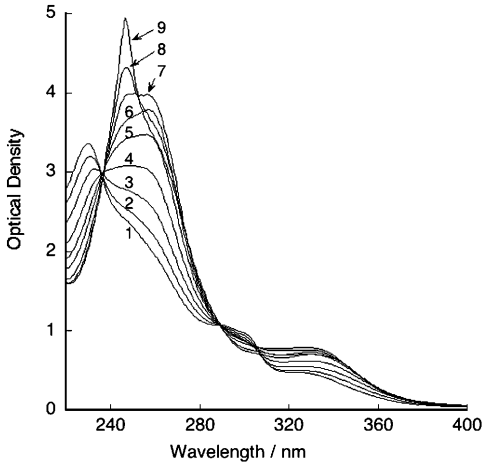


Figure 3. Absorption spectra of **1** (0.1 mM) in an aqueous solution as a function of pH. Curves 1, 2, 3, 4, 5, 6, 7, 8, and 9 were obtained at pH 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, 8.0, 9.0, and 10.0, respectively.

The degree of pH dependence of the catalytic activation of **1** was examined by comparing it with the methoxy analogue **4**, in which the electronic effect of the methoxy group was independent of pH. The pH-dependent profile for the TH of 2-cyclohexen-1-one with **4**, the trend for which is opposite compared to **1**, is shown in Figure 1c. The TOF ratio of **1**/**4** on a logarithmic scale as a function of pH is shown in Figure 4b. A sharp increase of the TOF ratio from 2 to 85 times was observed from pH 3 to 7. Interestingly, the curve overlapped appreciably with the above-mentioned curve of the absorbance change. This result strongly suggests that the increase in activity can be attributed to the increase in the electron-donating effect due to the deprotonation of the hydroxyl group.

The observations made at various pH values can be explained by the reaction path depicted in Scheme 2. In the pH range from 2 to 10, the iridium complex reacted easily with formate to generate the corresponding hydride com-

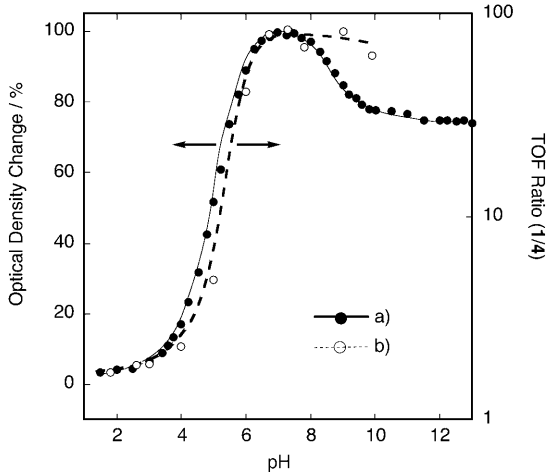
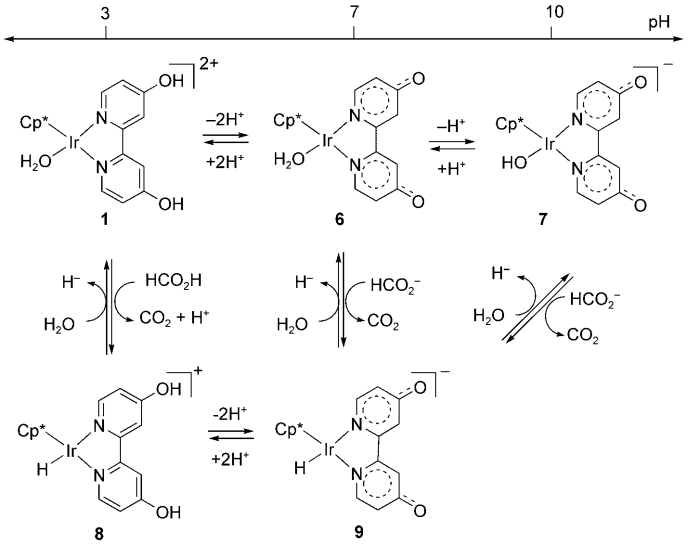


Figure 4. a) Absorbance change of **1** at 265 nm as a function of pH. b) TOF ratio of **1** vs. **4** as a function of pH on a logarithmic scale.



Scheme 2. Behavior of **1** at various pH values.

plexes **8** or **9** as active species. It is worth noting that the formation of hydride complex **9** may be unaffected by the hydroxo complex **7**.[44] The generated hydride complexes showed catalytic activities that were dependent on the electronic effect of the substituent in the bipyridine ligand. Although the catalytic activities decreased significantly under basic conditions due to the increase in the protonic character of the hydride,[4447] the activation of **9** by the strong electronic effect of the oxyanion surpassed the inherent deactivation.

Conclusion

The results clearly showed that the reaction activity and chemoselectivity in the TH catalyzed by the iridium–DHBP complex **1** were controlled by pH. We demonstrated that catalyst activation by the electronic effect of the oxyanion was applicable to TH in an aqueous formate solution. It was confirmed that the substantial change in the catalytic activity of **1** was due to the electronic effect based on the acid–base equilibrium of the hydroxyl group by means of the comparison with that of methoxy analogue **4**. The TOF values of **1** at pH 7.3 can be more than 1000 times the value of the unsubstituted analogue **2**. The highest TOF of 81 000 h^{-1} was obtained in the TH of benzaldehyde at 80 °C. In addition, the DHBP catalyst exhibited pH-dependent chemoselectivity for α,β-unsaturated carbonyl compounds. Selective reductions of the C=C bond of enone with high TOF were observed under basic conditions. The ketone moieties can be reduced with satisfactory activity under acidic conditions. In particular, pH-selective chemoselectivity of the C=O versus C=C bond reduction was observed in the TH of cinnamaldehyde. From the viewpoint of green chemistry, we believe that TH, through improvement in reaction efficiency, has the potential to be a safe and innocuous alternative to the hydrogenation reaction.

Experimental Section

General considerations: All manipulations were carried out under an argon atmosphere. All aqueous solutions were degassed prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 spectrometer using sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as an internal standard. Mass spectra were recorded on Waters ZQ2000 (ESI). Elemental analyses were carried out on an Eager 200 instrument. FT-IR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer. The pH values were measured on an Orion Model 290 A pH meter with a glass electrode after calibration to standard buffer solutions. [IrCp*-$(H_2O)_3$][SO_4] was prepared according to the literature procedure.[48] The 4,4′-dihydroxy-2,2′-bipyridine[49] and **4**-SO_4[50] were prepared according to the literature procedures.

DHBP complex (1-SO_4): A aqueous solution (30 mL) of [IrCp*$(H_2O)_3$]-[SO_4] (400 mg, 0.84 mmol) and 4,4′-dihydroxy-2,2′-bipyridine (158 mg, 0.84 mmol) was stirred at 40 °C for 12 h. The solution was filtered. The volume of the filtrate was reduced to ≈5 mL in vacuo. The solution was placed in a refrigerator to give a yellow solid **1**-SO_4 (370 mg, 70 %). ^{1}H NMR (400 MHz, D_2O): δ = 8.77 (d, J = 6.4 Hz, 2H), 7.77 (brs, 2H), 7.24 (dd, J = 6.4, 2.6 Hz, 2H), 1.66 ppm (s, 15H); ^{13}C NMR (100 MHz, D_2O): δ = 170.37, 160.38, 154.94, 119.13, 114.41, 90.94, 10.48 ppm; ^{1}H NMR (400 MHz, D_2O/KOD): δ = 8.25 (d, J = 6.6 Hz, 2H), 7.13 (d, J = 2.7 Hz, 2H), 6.63 (dd, J = 6.6, 2.7 Hz, 2H), 1.56 ppm (s, 15H); ^{13}C NMR (100 MHz, D_2O/KOD): δ = 178.61, 159.76, 152.91, 121.50, 115.95, 87.47, 10.23 ppm; IR (KBr): $\tilde{\nu}$ = 1622, 1498, 1457, 1027 cm^{-1}; ESIMS: m/z: 515 $[M-SO_4-H_2O-H]^+$; elemental analysis calcd (%) for $C_{20}H_{25}IrN_2O_7S$: C 38.15, H 4.00, N 4.45, S 5.09; found: C 38.16, H 4.09, N 4.42, S 5.03.

4,4′-Dimethyl-2,2′-bipyridine complex (3-SO_4): This compound was prepared from [IrCp*$(H_2O)_3$][SO_4] (192 mg, 0.4 mmol) and 4,4′-dimethyl-2,2′-bipyridine (74 mg, 0.4 mmol) according to the procedure described for the preparation of **1**-SO_4. Recrystallization from water gave yellow powder; yield 200 mg (80 %). ^{1}H NMR (400 MHz, D_2O): δ = 8.92 (d, J = 5.9 Hz, 2H), 8.35 (brs, 2H), 7.71 (dd, J = 5.9, 1.0 Hz, 2H), 2.64 (s, 3H), 1.66 ppm (s, 15H); ^{13}C NMR (100 MHz, D_2O): δ = 158.31, 157.56, 153.38, 132.56, 127.53, 91.60, 23.44, 10.43 ppm; IR (KBr): $\tilde{\nu}$ = 1621, 1484, 1452, 1031 cm^{-1}; ESIMS: m/z: 511 $[M-SO_4-H_2O-H]^+$; elemental analysis calcd (%) for $C_{22}H_{29}IrN_2O_5S$: C 42.23, H 4.67, N 4.48, S 5.12; found: C 42.14, H 4.72, N 4.50, S 5.29.

4,4′-Dicarboxy-2,2′-bipyridine complex (5-SO_4): This compound was prepared from $[IrCp^*(H_2O)_3][SO_4]$ (192 mg, 0.4 mmol) and 4,4′-dicarboxy-2,2′-bipyridine (98 mg, 0.4 mmol) according to the procedure described for the preparation of **1**. Purification by chromatography over Sephadex LH-20 with water gave yellow powder; yield 145 mg (53%). ^{1}H NMR (400 MHz, D_2O): $\delta = 9.38$ (d, $J = 5.7$ Hz, 2H), 9.18 (d, $J = 1.6$ Hz, 2H), 8.44 (dd, $J = 5.7$, 1.7 Hz, 2H), 3.7–3.4 (br s, 2H), 1.78 ppm (s, 15H); ^{13}C NMR (100 MHz, D_2O): $\delta = 169.32$, 159.41, 155.38, 146.59, 131.54, 126.93, 92.83, 10.48 ppm; ^{1}H NMR (400 MHz, D_2O/KOD): $\delta = 9.05$ (d, $J = 5.7$ Hz, 2H), 8.80 (d, $J = 1.6$ Hz, 2H), 8.10 (dd, $J = 5.7$, 1.6 Hz, 2H), 1.65 ppm (s, 15H); ^{13}C NMR (100 MHz, D_2O/KOD): $\delta = 173.14$, 158.72, 154.12, 150.62, 130.23, 125.51, 90.24, 10.14 ppm; IR (KBr): $\tilde{\nu} = 1725$, 1560, 1454, 1408 cm^{-1}; ESIMS: m/z: 571 $[M-SO_4-H_2O-H]^+$; elemental analysis calcd (%) for $C_{22}H_{25}IrN_2O_9S \cdot H_2SO_4 \cdot H_2O$: C 32.95, H 3.65, N 3.49, S 8.00; found: C 32.71, H 3.46, N 3.46, S 8.20.

General procedure for transfer hydrogenation: A solution of complex (0.5 μmol) in water (0.1 ml) was added to a degassed aqueous 1 M formate solution (20 mL) of a substrate (2 mmol). The reaction was carried out at 40 °C in an argon atmosphere with vigorous stirring. The reaction solution was analyzed by GC (PEG-HT 5%, Uniport HT 60/80, 2 m packed column, 100 °C) or HPLC (Tosoh TSKgel SCX(H^+)).

UV studies of acid–base equilibrium: Stock solutions of **1**-SO_4 (0.1 mM) in 0.05 M H_2SO_4 and 0.1 M KOH were prepared. The pH of the solutions was adjusted by mixing. The UV/Vis spectra were measured after reading the pH value.

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