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pH-Dependent Transfer Hydrogenation of Water-Soluble Carbonyl Compounds with $[Cp^*Ir^{III}(H_2O)_3]^{2+}$ ($Cp^* = \eta^5$-C_5Me_5) as a Catalyst Precursor and HCOONa as a Hydrogen Donor in Water

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This paper reports a pH-dependent hydrogenation of water-soluble carbonyl compounds by hydrogen transfer from HCOONa as a hydrogen source (transfer hydrogenation) promoted by $[Cp^*Ir^{III}(H_2O)_3]^{2+}$ (**1**, $Cp^* = \eta^5$-C_5Me_5) as a catalyst precursor in water. Complex **1** has been characterized by X-ray structure analysis, ^1H NMR, and potentiometric titration experiments. The active catalyst, a dinuclear μ-hydride complex $[(Cp^*Ir^{III})_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}HCOO)]^+$ (**2**), has been isolated and characterized by ^1H NMR, IR, and electrospray ionization mass spectrometry (ESI-MS). The rate of this transfer hydrogenation shows a sharp maximum at pH 3.2 because the active catalyst **2** is generated from the reaction of **1** with HCOONa at pH 3.2 in the highest yield. The series of the carbonyl compounds consists of a straight chain aldehyde (*n*-butyraldehyde), a cyclic aldehyde (cyclopropanecarboxaldehyde), a ketone (2-butanone), an aldehyde-acid (glyoxylic acid), and a keto-acid (pyruvic acid). Products were determined by ^1H NMR and atmospheric pressure chemical ionization mass spectrometry (APCI-MS). A possible mechanism for this transfer hydrogenation is proposed.

Introduction

In recent years, aqueous organometallic chemistry has been widely studied because of many potential advantages such as industrial applications and alleviation of environmental problems associated with the use of organic solvents.[1] Although a number of water-soluble organometallic complexes containing a variety of water-soluble phosphine ligands are known,[1] few organometallic complexes containing water molecules as the ligands (i.e., organometallic aqua complexes) are known.[2,3] These organometallic aqua complexes have the potential to be pH-selective catalysts since their structures and properties drastically change depending upon pH because of deprotonation of the aqua ligands. We have investigated a pH-dependent hydrogenation of water-soluble carbonyl compounds by hydrogen transfer from HCOONa as a hydrogen source (transfer hydrogenation) promoted by an organometallic aqua complex $[Cp^*Ir^{III}(H_2O)_3]^{2+}$ (**1**, $Cp^* = \eta^5$-C_5Me_5)[2a] as a catalyst precursor in water.[4,5] Herein, we report (i) synthesis and

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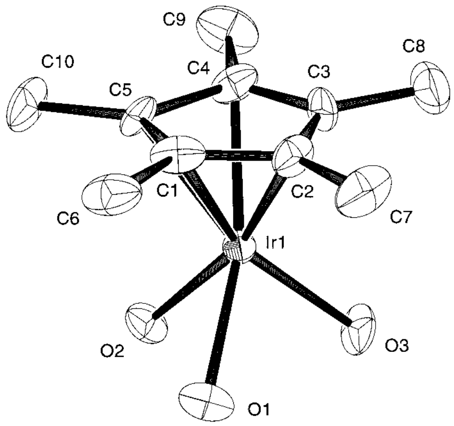

Figure 1. ORTEP drawing of **1**. Hydrogen atoms and the anions omitted for clarity.

characterization of the catalyst precursor **1**, (ii) the pH-dependent transfer hydrogenation, and (iii) isolation and characterization of the active catalyst, a dinuclear μ-hydride complex $[(Cp^*Ir^{III})_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}HCOO)]^+$ (**2**). A possible mechanism for this transfer hydrogenation is also discussed.

Table 1. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for 1·(OTf)$_2$

empirical formula	$C_{12}H_{21}F_6Ir_1O_9S_2$
fw	679.62
cryst color	yellow
cryst dimens (mm)	0.30 × 0.30 × 0.30
cryst syst	orthorhombic
lattice params	
a (Å)	24.094(5)
b (Å)	9.751(3)
c (Å)	18.141(3)
V (Å^3)	4262(1)
space group	$Pna2_1$ (no. 33)
Z value	8
D_{calc} (g cm^{-3})	2.118
F_{000}	2624
μ(Mo Kα) (cm^{-1})	65.71
radiation (Å)	Mo Kα ($\lambda = 0.7107$)
temp (°C)	−100
$2\theta_{max}$ (deg)	55.1
absorp corr method	XABS2[a]
no. of reflns obsd ($I > 3\sigma(I)$)	4577
no. of params	541
R^b	0.042
$R_w{}^c$	0.055
goodness of fit indicator, S^d	1.64
max shift/error in final cycle	0.01
max peak in final diff map (e Å^{-3})	1.25
min peak in final diff map (e Å^{-3})	−2.28

[a] See ref 18. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \sqrt{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2}$. [d] $S = \sqrt{\sum w(|F_o| - |F_c|)^2/(N_o - N_p)}$, where N_o = number of reflections observed, N_p = number of parameters.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1·(OTf)$_2$

Ir1−O1	2.14(1)	Ir2−O4	2.135(9)
Ir1−O2	2.27(1)	Ir2−O5	2.06(1)
Ir1−O3	2.162(9)	Ir2−O6	2.16(1)
Ir1−C1	2.12(1)	Ir2−C11	2.17(1)
Ir1−C2	2.02(1)	Ir2−C12	2.12(1)
Ir1−C3	2.07(1)	Ir2−C13	2.133(9)
Ir1−C4	2.15(1)	Ir2−C14	2.19(1)
Ir1−C5	2.13(1)	Ir2−C15	2.20(1)
O1−Ir1−O2	74.8(4)	O4−Ir2−O5	82.1(4)
O1−Ir1−O3	81.5(4)	O4−Ir2−O6	81.8(4)
O2−Ir1−O3	76.7(4)	O5−Ir2−O6	78.5(5)

Results and Discussion

Catalyst Precursor $[Cp^*Ir^{III}(H_2O)_3]^{2+}$ (1). Complex **1** was quantitatively synthesized from the reaction of $[(Cp^*Ir^{III}Cl)_2(\mu\text{-}Cl)_2]$[6] with Ag_2SO_4 at pH 2.3 in H_2O. Organometallic aqua complexes whose structures are determined by X-ray analysis are unexpectedly rare.[2] Figure 1 shows the structure of **1**.[7] Crystal data, data collection parameters, and structure refinement for **1** are listed in Table 1. Selected bond lengths and angles for **1** are listed in Table 2. Complex **1** adopts a distorted octahedral coordination with a piano stool geometry by coordination of one Cp* and three H_2O ligands. The Ir−O bond length (av 2.15 Å) is close to the Rh−O bond length (av 2.16 Å) observed in $[Cp^*Rh^{III}(H_2O)_3]^{2+}$,[2b] but slightly longer than the Ir−O bond length observed in $[Ir^{III}(H_2O)_6]^{3+}$ (2.041(3) Å) and *trans*-$[Ir^{III}(H_2O)_4Cl_2]^+$ (av 2.04 Å).[8] The existence of the H_2O ligands in **1** was confirmed by ^1H NMR measurements in anhydrous dimethyl sulfoxide (DMSO)-d_6.[2b,9] Complex **1** has high solubility in water (300 mg/mL at 25 °C). When complex **1** was dissolved in water (10 mM), the pH of the solution was found to be 2.7 because of deprotonation of the H_2O ligands of **1**. ^1H NMR experiments show that at pH 3.2 the mononuclear complex **1** (Cp* = 1.61 ppm, D_2O, reference to DSS, 0−25 °C)[10a,b] is reversibly converted to a well-known dinuclear complex $[(Cp^*Ir^{III})_2(\mu\text{-}OH)_3]^+$ (**3**, Cp* = 1.59 ppm).[2c,11] Although there must be at least two distinct deprotonation steps and a dimerization process (not associated with a proton transfer) in the formation of **3** from **1**, intriguingly, potentiometric titration experiments of **1** revealed only one buffer region around pH 3.2.[12] Alternatively, potentiometric titrations of **3** also revealed only one buffer region around pH 3.2.[12] Fish and co-workers have reported a similar equilibrium of the Cp*Rh analogue.[2b]

pH-Dependent Transfer Hydrogenation. $NaBH_4$ is most frequently used as a reducing agent for the stoichiometric (noncatalytic) reduction of carbonyl compounds in aqueous media.[13] Although $NaBH_4$ is rapidly

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(5) Disproportionation of aldehyde into alcohol and acid utilizing $[(Cp^*M)_2(\mu\text{-}OH)_3]^+$ (M = Rh, Ir) in aqueous media has been reported. (a) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2342−2352. (b) Cook, J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 924−925. (c) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1980**, 144−145.

(6) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228−234.

(7) Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-116597. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

(8) (a) Armstrong, R. S.; Beattie, J. K.; Best, S. P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1973−1975. (b) Flenburg, C.; Simonsen, K.; Skov, L. K. *Acta Chem. Scand.* **1993**, *47*, 862−866.

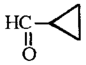
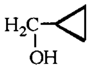
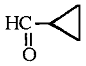
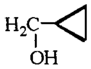
(9) DMSO-d_6 was dried over activated molecular sieves 4A and the samples (10 mM) were prepared in a drybox. The Cp* signal (1.68 ppm, the reference peak was set at 2.50 ppm for the residual proton of DMSO-d_6) and the H_2O signal (3.31 ppm) were found in the ratio Cp*/3H_2O = 15H/6H.

(10) (a) DSS = sodium 2,2-dimethyl-2-silapentane-5-sulfonate. (b) The solution of **1**·SO_4 (10 μmol) in D_2O (1 mL) was titrated with 0.1 M NaOD/D_2O or 0.1 M DOTf/D_2O in the range of pH 1.0−12.0. (c) The solution of **1**·SO_4 (10 μmol) and HCOONa (10 μmol) in D_2O (1 mL) was titrated with 0.1 M NaOD/D_2O or 0.1 M DOTf/D_2O in the range of pH 1.0−12.0.

(11) Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1997−2002.

(12) The solution of **1**·SO_4 (10 μmol) or **3**·OH (10 μmol) in H_2O (1 mL) was titrated with 0.1 M NaOH/H_2O or 0.1 M HOTf/H_2O in the range of pH 1.0−12.0.

Table 3. Transfer Hydrogenation of Water-Soluble Carbonyl Compounds with 1 and HCOONa in Water at pH 3.2[a]

entry	substrates	equiv. of HCOONa[b]	products[c]	TOF[d]
a	$HC(=O)-CH_2CH_2CH_3$	1	$H_2C(OH)-CH_2CH_2CH_3$	0.6
b	$HC(=O)-CH_2CH_2CH_3$	5	$H_2C(OH)-CH_2CH_2CH_3$	1.5
c		1		1.1
d		5		3.2
e	$H_3C-C(=O)-CH_2CH_3$	1	$H_3C-CH(OH)-CH_2CH_3$	0.3
f	$H_3C-C(=O)-CH_2CH_3$	5	$H_3C-CH(OH)-CH_2CH_3$	0.5
g	$HC(=O)-COOH$	1	$H_2C(OH)-COOH$	3.7
h	$HC(=O)-COOH$	5	$H_2C(OH)-COOH$	4.3
i	$H_3C-C(=O)-COOH$	5	no reaction[e]	-

[a] Conditions: $\mathbf{1}\cdot SO_4$ (1 μmol), substrates (10 μmol), HCOONa (10 or 50 μmol), H_2O (or D_2O, 1 mL), 25 °C. The pH of the solution was adjusted to 3.2 by the addition of 0.1 M $HOTf/H_2O$ (or 0.1 M $DOTf/D_2O$) or 0.1 M $NaOH/H_2O$ (or 0.1 M $NaOD/D_2O$). The pH did not change during the course of the reaction. [b] Equivalents of HCOONa toward the substrates. [c] Products were determined by ^1H NMR and APCI-MS. [d] Turnover frequency (TOF): (mol of products/mol of **1**)/h. [e] Only the starting material was observed.

destroyed under acidic conditions, interestingly, $NaBH_3CN$ or n-Bu_4NBH_3CN can be used under acidic conditions (around pH 3).

It is of interest to develop pH-dependent catalytic reduction systems using organometallic catalysts.[3,4] We have studied the pH-dependent transfer hydrogenation of water-soluble carbonyl compounds (10 μmol) with a catalyst precursor of **1** (1 μmol) and a hydrogen donor of HCOONa (10−50 μmol) in water (1 mL). The series of carbonyl compounds includes examples of a straight chain aldehyde (n-butyraldehyde; entries a and b in Table 3), a cyclic aldehyde (cyclopropanecarboxaldehyde; entries c and d), a ketone (2-butanone; entries e and f), an aldehyde-acid (glyoxylic acid; entries g and h), and a keto-acid (pyruvic acid; entry i). Products were determined by ^1H NMR and atmospheric pressure chemical ionization mass spectrometry (APCI-MS). Figure 2 shows a typical pH-dependent profile of this transfer hydrogenation. The rate of this transfer hydrogenation shows a sharp maximum at pH 3.2, which coincides with the pK_a value of HCOOH in the studied concentration. At pH 3.2, the color of the solution changes from yellow to orange during the course of the reaction. The rates of reduction of the aldehydes (entries a−d) are faster than those of the ketone (entries e and f). The cyclic aldehyde (entries c and d) is converted to the corresponding alcohol much more efficiently than the straight chain aldehyde (entries a and b). Interestingly, the reduction of the aldehyde group of glyoxylic acid occurs very easily (entries g and h), but reduction of the ketone

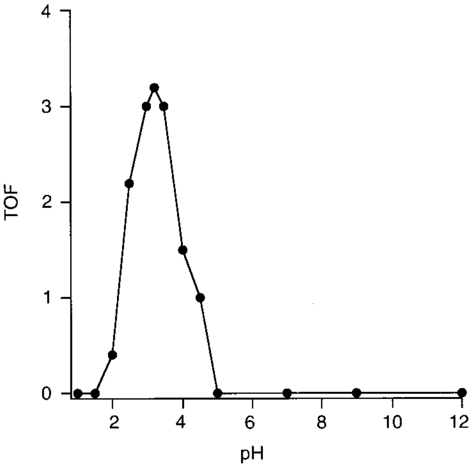


Figure 2. Typical pH-dependent profile of the transfer hydrogenation. Conditions: $\mathbf{1}\cdot SO_4$ (1 μmol), cyclopropanecarboxaldehyde (10 μmol), HCOONa (50 μmol), H_2O (1 mL), 25 °C. Turnover frequency (TOF): (mol of products/mol of $\mathbf{1}\cdot SO_4$)/h.

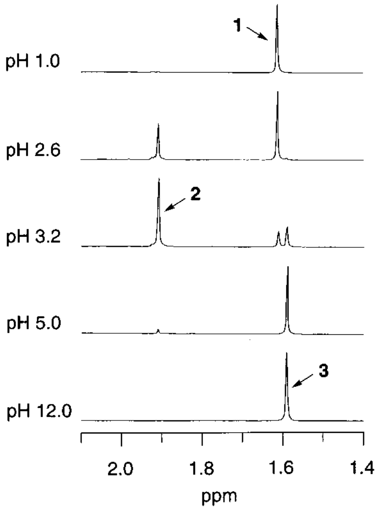


Figure 3. pH-Dependent ^1H NMR spectra of **1** in the presence of HCOONa (hydrogen donor), but in the absence of the carbonyl compounds (hydrogen acceptors). Conditions: $\mathbf{1}\cdot SO_4$ (10 μmol), HCOONa (10 μmol), D_2O (1 mL), pH 1.0−12.0, 25 °C.

group of pyruvic acid does not occur (entry i). It has been confirmed that the reduction does not occur either in the absence of **1** or in the presence of $IrCl_3\cdot(H_2O)_3$. Unfortunately, water-soluble oximes, amides, sulfoxides, alkenes, and alkynes cannot be reduced under these conditions. It is noteworthy that the rate of the transfer hydrogenation with the Cp*Rh analogue is extremely slow at pH 1.0−12.0 compared with that of **1**.

Active Catalyst $[(Cp^*Ir^{III})_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}HCOO)]^+$ (2). To elucidate the active catalyst in this reduction, we have performed ^1H NMR titration experiments of **1** in the presence of HCOONa (a hydrogen donor), but in the absence of the carbonyl compounds (hydrogen acceptors) in the range of pH from 1.0 to 12.0 in D_2O (Figure 3).[10c] At pH 3.2, we have observed a new prominent Cp* signal at 1.92 ppm as well as two small Cp* signals at 1.61 (**1**) and 1.59 ppm (**3**). We have found that the signal at 1.92 ppm corresponds to the dinuclear μ-hydride complex **2**. Complex **2** (which slowly decomposes in water) was isolated as an orange powder.[14] It

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(13) For example: (a) S−Penne, J. In *Reductions by the Alumino- and Borohydrides in Organic Synthesis*; Wiley-VCH: 1997; p 224, and references therein. (b) Lane, C. F. In *Selections from the Aldrichimica Acta*; Aldrich Chemical Co., Inc, 1984; pp 67−74, and references therein.

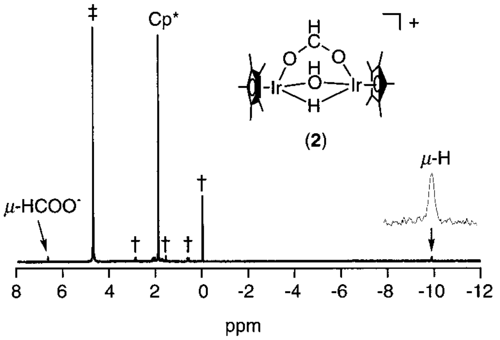


Figure 4. ^1H NMR spectrum of **2** in D_2O at pH 3.2. †: DSS as the internal standard. ‡: water.

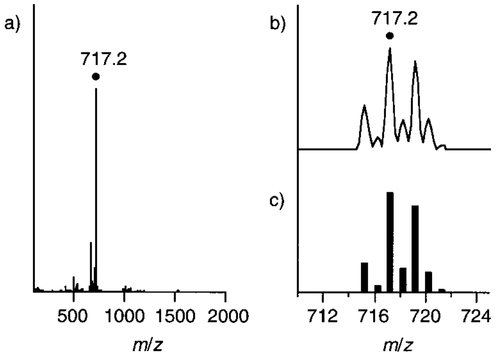
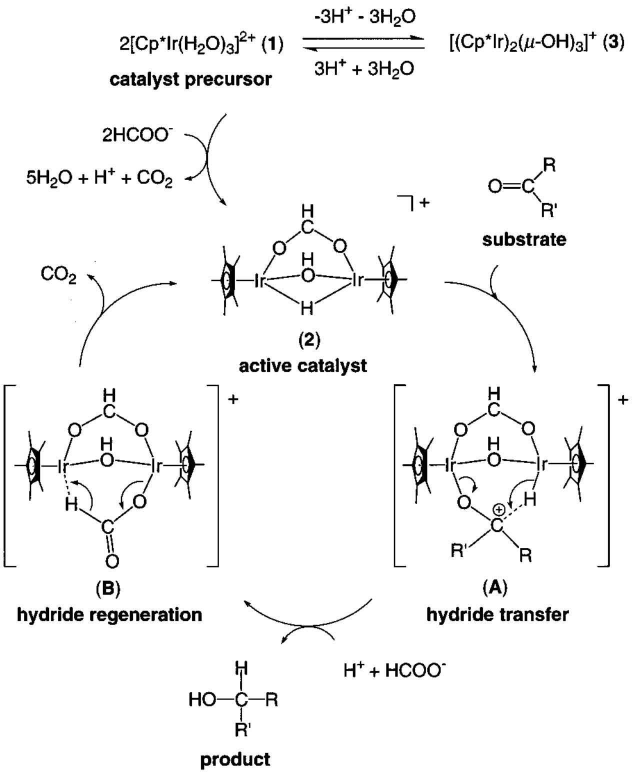


Figure 5. (a) Positive ion ESI mass spectrum of **2** in H_2O at pH 3.2. (b) Signal at *m/z* 717.2 corresponding to $[(Cp^*Ir)_2(H)(OH)(HCOO)]^+$ (**2**). (c) Calculated isotopic distribution for **2**.

has been confirmed that isolated **2** (5 μmol) acts as a reducing agent for a stoichiometric reduction of the carbonyl compounds (5 μmol) in the absence of HCOONa in water (1 mL) at pH 3.2. In addition, isolated **2** (1 μmol) acts as the active catalyst for the transfer hydrogenation of the carbonyl compounds (10 μmol) with HCOONa (50 μmol) in water (1 mL) at pH 3.2.

Complex **2** has been characterized by ^1H NMR, IR, and ESI-MS. The ^1H NMR spectrum (D_2O, reference to DSS, 25 °C, pH 3.2) of **2** provides μ-H (−9.91 ppm), Cp* (1.92 ppm), and μ-$HCOO^-$ (6.71 ppm) signals (Figure 4). The ^{13}C NMR spectrum (D_2O, reference to DSS, 25 °C, pH 3.2) of **2** provides η^5-$C_5(CH_3)_5$ (11.68 ppm), η^5-$C_5(CH_3)_5$ (90.46 ppm), and μ-HCOO (177.25 ppm) signals. The IR spectrum of **2** in mineral oil shows characteristic C−O vibrations of the μ-$HCOO^-$ ligand at 1342.4 and 1556.4 cm^{-1},[14] which respectively shift to 1319.2 and 1510.2 cm^{-1} when $H^{13}COO^-$ is used. The positive-ion ESI mass spectrum of aqueous solution of **2** shows a prominent signal at *m/z* 717.2 (relative intensity (I) = 100% in the range of *m/z* 100−2000) with a characteristic distribution of isotopomers that matches well with the calculated isotopic distribution for $[(Cp^*Ir)_2(H)(OH)(HCOO)]^+$ (Figure 5). To establish the origin of the hydride ligand of **2**, the synthesis of **2** by a reaction of **1** with DCOONa has been carried out. ESI-MS results show that the signal at *m/z* 717.2 ($[(Cp^*Ir)_2(H)(OH)(HCOO)]^+$) shifts to *m/z* 719.2 ($[(Cp^*Ir)_2(D)(OH)(DCOO)]^+$); that is, the labeled hydrogen atoms are incorporated into **2**.

Scheme 1



Mechanism for the Transfer Hydrogenation. We propose a mechanism for the transfer hydrogenation as follows (Scheme 1). At pH 3.2, the catalyst precursor **1** is in equilibrium with the dinuclear complex **3**. The addition of HCOONa to the equilibrium mixture provides the active catalyst **2** through a β-hydrogen elimination with evolution of CO_2. The total number of electrons for **2** (which has a possible vacant site for the incoming substrate) is 34. The evolution of CO_2 has already been confirmed by GC analysis.[15] The active catalyst **2** then reacts with the substrates to provide the products. It has been confirmed by ^1H NMR that the labeled hydrogen atom is incorporated into the product when DCOONa is used as the hydrogen donor in this reaction. We suggest the possibility of hydride transfer to the substrate (**A**) and Ir−H regeneration (**B**) utilizing two Ir centers of the dinuclear unit. Preliminary kinetic studies show that the rate of the formation of **2** from the reaction of **1** with HCOONa in the absence of the substrates at pH 3.2 is very fast compared with the reduction of the substrates by the isolated **2** in the absence of HCOONa at pH 3.2.[16] Furthermore, the rate of this transfer hydrogenation is dependent on the concentration of HCOONa or substrates.[17]

Conclusions

We have demonstrated the potential of the organometallic aqua complex **1** to be a pH-selective catalyst

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(14) The similar structures of **2** have been previously reported. (a) $[(\eta^6\text{-}C_6H_6)_2Ru^{II}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}CH_3COO)]^+$: Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1995**, *496*, 197−205. (b) $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)_2Os^{II}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}HCOO)]^+$: Cabeza, J. A.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1155−1160. (c) $[(Cp^*Ir^{III})_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}CH_3COO)]^+$: White, C.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901−1907.

(15) Shimadzu gas chromatograph, GC-8A with porapac-T column.

(16) The rate of reaction was determined by measurement of the intensity changes of the protons of **1**, **2**, the substrate, and the product in the ^1H NMR spectra.

(17) Concentration ratios to maximize the rate of the formation of the products: [HCOONa]/[**1**] = 50 or [substrate]/[**1**] = 100.

precursor for the transfer hydrogenation of carbonyl groups by HCOONa in water. The reaction rate shows a sharp maximum at pH 3.2 because the active catalyst **2** is formed from the reaction of **1** with HCOONa at pH 3.2 in the highest yield. However, ^{1}H NMR and potentiometric titration experiments suggest that at pH 3.2 complex **1** is in equilibrium with the dinuclear complex **3** via two or more deprotonated species. For a complete understanding of the formation mechanism of **2**, it would be necessary to elucidate the deprotonation process of **1**. Studies of the deprotonation process of **1** by ESI-MS linked with potentiometric titration experiments are currently underway.

Experimental Section

Materials and Methods. All chemicals (highest purity available) were purchased from Aldrich Chemicals Co. and used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on an JEOL JNM-EX 270 spectrometer. The NMR experiments were performed by dissolving the sample in D_2O (reference to DSS), $CDCl_3$ (reference to TMS), or DMSO-d_6 (reference to the residual proton of DMSO-d_6, 2.50 ppm). To determine the exact pH values of the ^{1}H NMR samples, the ^{1}H NMR experiments were also performed by dissolving the samples in H_2O in an NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing DSS (1 mM) dissolved in D_2O (for deuterium lock). The potentiometric titration experiments were performed on a TOA pH meter (model HM-18E) with a TOA pH combination electrode (model GS-5015C). The titration experiments were carried out in the absence of an inert supporting electrolyte to maintain the constant ionic strength because the addition of a large excess of the electrolyte prevents dimerization of the aqua complex **1**. Mass data were obtained by an API 300 triple quadrupole mass spectrometer (PE-Sciex) equipped with ESI or APCI interfaces. The sprayer was held at a potential of +4.5 or −4.5 kV for positive or negative ion detection mode, and compressed N_2 was employed to assist liquid nebulization. Orifice potential was maintained at +25 or −25 V for positive or negative ion detection mode. IR spectra in mineral oil (Merck Paraffin flüssig) were measured on ReactIR 1000 (ASI Applied Systems) and Shimadzu FTIR-8300 spectrometers in the range 4000−400 cm^{-1}.

[Cp*Ir^{III}(H$_2$O)$_3$]$^{2+}$ (1). The pH of a mixture of [(Cp*Ir^{III}Cl)$_2$(μ-Cl)$_2$] (2.40 g, 3.00 mmol) and Ag_2SO_4 (1.87 g, 6.00 mmol) in H_2O (20 mL) is 2.3. The solution was stirred at ambient temperature for 12 h under an argon atmosphere, and the precipitating AgCl was removed by filtration. The solvent was evaporated and dried in vacuo to yield a yellow powder of **1**·SO$_4$ (yield: 98% based on [(Cp*Ir^{III}Cl)$_2$(μ-Cl)$_2$]). ^{1}H NMR (D_2O, reference to DSS, pH 2.3, 25 °C): δ 1.61 (s; Cp*). ^{1}H NMR (DMSO-d_6, reference to the residual proton of DMSO-d_6, 2.50 ppm, 25 °C): δ 1.68 (s; Cp*), 3.31 (br; H_2O). ^{13}C NMR (D_2O, reference to DSS, pH 2.3, 25 °C): δ 11.09 (s; η^5-$C_5(CH_3)_5$), 86.94 (s; η^5-$C_5(CH_3)_5$). Anal. Calcd for **1**·SO$_4$: $C_{10}H_{21}Ir_1O_7S_1$: C, 25.15; H, 4.43. Found: C, 25.39; H, 4.48.

[(Cp*Ir^{III})$_2$(μ-H)(μ-OH)(μ-HCOO)]$^+$ (2). The pH of a solution of **1**·SO$_4$ (95.5 mg, 0.20 mmol) and HCOONa (13.6 mg, 0.20 mmol) in H_2O (5 mL) was adjusted to 3.2 by the addition of 0.1 M NaOH/H_2O. The solution was stirred at ambient temperature for 1 h under an argon atmosphere. The addition of NH_4PF_6 (16.3 mg, 0.10 mmol) gave orange precipitates of **2**·PF$_6$ (yield: 24% based on **1**·SO$_4$). ^{1}H NMR (D_2O, reference to DSS, pH 3.2, 25 °C): δ −9.91 (s, 1H; μ-H), 1.92 (s, 30H; Cp*), 6.71 (br, 1H; μ-HCOO). ^{1}H NMR ($CDCl_3$, reference to TMS, 25 °C): δ −10.5 (s, 1H; μ-H), 1.6 (br, 1H; μ-OH), 1.93 (s, 30H; Cp*), 6.63 (s, 1H; μ-HCOO). ^{13}C NMR (D_2O, reference to DSS, pH 3.2, 25 °C): δ 11.68 (s; η^5-$C_5(CH_3)_5$), 90.46 (s; η^5-$C_5(CH_3)_5$), 177.25 (s; μ-HCOO). ^{13}C NMR ($CDCl_3$, reference to TMS, 25 °C): δ 9.63 (s; η^5-$C_5(CH_3)_5$), 87.20 (s; η^5-$C_5(CH_3)_5$), 173.47 (s; μ-HCOO). IR (in mineral oil, cm^{-1}): μ-HCOO, 1342.4, 1556.4. ESI-MS: **2**: *m*/*z* 717.2 (relative intensity (*I*) = 100% in the range of *m*/*z* 100−2000). Anal. Calcd for $C_{21}H_{33}F_6Ir_2O_3P_1$: C, 29.23; H, 3.85. Found: C, 29.53; H, 3.94.

Transfer Hydrogenation. The reaction was carried out under an argon atmosphere at 25 °C. To a solution of **1**·SO$_4$ (1 μmol) in H_2O (or D_2O, 1 mL) was added carbonyl compounds (10 μmol) and HCOONa (10−50 μmol), then the pH of the solution was adjusted to 3.2 by the addition of 0.1 M HOTf/H_2O (or 0.1 M DOTf/D_2O) or 0.1 M NaOH/H_2O (or 0.1 M NaOD/D_2O). The pH was monitored and did not change during the course of the reaction. The solution was stirred at 25 °C. The color of the solution changed from yellow to orange within 30 min. After 1 h, the products were determined by ^{1}H NMR (internal standard = DSS) and APCI-MS. Turnover frequencies (TOF) are expressed as the number of moles of product formed per mole of catalyst per hour.

X-ray Crystallographic Analysis of 1·(OTf)$_2$. Yellow crystals of **1**·(OTf)$_2$ used in the X-ray structure analysis were obtained by layering the CH_2Cl_2 solution of **1**·(OTf)$_2$ with H_2O, which is a manner similar to that used for the synthesis of the Cp*Rh analogue previously reported by Fish and coworkers.[2b] Crystal data, data collection parameters, and structure refinement for **1** are listed in Table 1. Selected bond lengths and angles for **1** are listed in Table 2. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$) and a rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $28.71° < 2\theta < 30.97°$. The data were collected at a temperature of −100 ± 1 °C using the ω-scan technique to a maximum 2θ value of 55.1°. Scans of $(1.42 + 0.30 \tan \theta)°$ were made at a speed of 8.0°/min (in ω). The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 235 mm. The computer-controlled slits were set to 3.0 mm (horizontal) and 3.0 mm (vertical). Of the 5590 reflections that were collected, 5475 were unique. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. Extinction parameters were not refined. The intensities were corrected for Lorentz−polarization factors, and an empirical absorption correction program XABS2 was applied.[18] The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4577 observed reflections ($I > 3.00\sigma(I)$) and 541 variable parameters and converged (largest parameter shift was 0.01 times its esd). The weighting scheme was based on counting statistics and included a factor ($p = 0.050$) to downweight the intense reflections. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

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Supporting Information Available: Crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53−56.