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Communications

Half-Sandwich Complexes with 4,7-Dihydroxy-1,10-phenanthroline: Water-Soluble, Highly Efficient Catalysts for Hydrogenation of Bicarbonate Attributable to the Generation of an Oxyanion on the Catalyst Ligand

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Summary: Half-sandwich Ru(II), Ir(III), and Rh(III) complexes with 4,7-dihydroxy-1,10-phenanthroline are highly efficient catalysts for hydrogenation of bicarbonate in alkaline aqueous solution without an amine additive. The generation of an oxyanion by deprotonation of the two hydroxy substituents on the catalyst ligand caused a dramatic enhancement of catalytic activity, due to its strong electron-donating ability, as well as imparting water solubility.

The conversion of CO_2 to useful organic products in place of toxic CO still remains an intriguing and challenging subject.[1] From this point of view, the homogeneous catalytic hydrogenation of CO_2 into formic acid catalyzed by transition-metal complexes, usually using phosphine ligand, has been extensively investigated.[2] For example, since 1994, Noyori and co-workers have reported a highly efficient hydrogenation of CO_2 catalyzed by Ru(II) phosphine complexes in supercritical CO_2.[3] On the other hand, some efforts have been devoted to the investigation of CO_2 hydrogenation in aqueous media. In the most effective aqueous systems using the rhodium complexes with sulfonated phosphine ligand at 4 MPa of pressure (CO_2:H_2 = 1:1), a higher temperature (81 °C) resulted in the highest initial turnover frequency (TOF) of 7260 h^{-1}, while a lower temperature (23 °C) resulted in the highest turnover number (TON) of 3439.[4] In both the liquid and supercritical reactions, an amine additive is required for high yields. However, the use of such organic additives should be avoided, because they would eventually prevent separation of product and catalyst for recycling. Recently, Joo and co-workers investigated the hydrogenation of CO_2 and bicarbonate catalyzed by $[Ru(PTA)_4Cl_2]$ (PTA = 1,3,5-triaza-7-phosphaadamantane) in the absence of amines or other organic additives,[5] but this system exhibited a unsatisfactory catalytic efficiency (up to an initial TOF of 807 h^{-1}) compared to systems with an amine additive.

We have studied the highly water-soluble, half-sandwich bipyridine (bpy) complexes [Cp*M(bpy)Cl]Cl (M = Rh, Ir; Cp* = η^5-pentamethylcyclopentadienyl) and $[(C_6Me_6)Ru(bpy)Cl]Cl$ for catalytic transfer hydrogenation, using formic acid as a hydrogen donor in water.[6] In a preliminary experiment, we found that the decomposition of formic acid to CO_2 and H_2 catalyzed by [Cp*Rh(bpy)Cl]Cl proceeded smoothly with a TOF of 238 h^{-1} at 40 °C. The high catalytic activities of the half-sandwich complexes prompted us to investigate the reverse reaction: namely, the hydrogenation of CO_2 or bicarbonate. Herein we report that half-sandwich Ru(II), Ir(III), and Rh(III) complexes with 4,7-dihydroxy-1,10-phenanthroline are highly efficient catalysts for hydrogenation of bicarbonate in alkaline aqueous solution in the absence of an amine additive.

We first examined reactions catalyzed by [Cp*M(phen)Cl]Cl (phen = 1,10-phenanthroline) and [Cp*M(bpy)Cl]Cl in aqueous KOH, which was saturated with CO_2 before the reaction was started,[7,8] under 4 MPa of

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(7) It is known that, in alkaline solution, CO_2 is hydrated almost completely under CO_2-pressurized conditions and exists as the bicarbonate. Indeed, the use of aqueous $KHCO_3$ as an initial reaction solution led to results similar to those in aqueous KOH.

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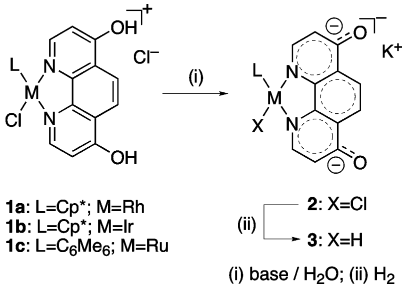
Table 1. Hydrogenation of Bicarbonate in an Aqueous Solution Catalyzed by Rh(III), Ir(III), and Ru(II) Complexes[a]

entry	complex/ concn (mM)	temp (°C)	*p* (MPa)	time (h)	TON	initial TOF (h^{-1})[b]	final concn of formate (M)
1	[Cp*Rh(phen)-Cl]Cl/0.1	80	4	20	220	(11)[d]	0.022
2	[Cp*Ir(phen)-Cl]Cl/0.1	80	4	20	59	(3)[d]	0.006
3	[Cp*Ir(bpy)-Cl]Cl/0.1	80	4	20	140	(7)[d]	0.014
4	**1a**/0.1	80	4	32	2400	270	0.24
5	**1b**/0.1	80	4	116	7300	2600	0.73
6	**1b**/0.1	40	4	236	5300	267	0.53[e]
7	**1b**/0.02	120	6	10	21000	23000	0.42
8	**1b**/0.02	80	1	91	8500	1900	0.17
9	**1b**/0.1	80	0.1	67	800	35	0.08[e]
10[c]	**1c**/0.1	80	4	165	12500	340	1.25
11[c]	**1c**/0.1	120	4	68	12900	1940	1.29
12[c]	**1c**/0.1	120	6	24	15400	3360	1.54
13[c]	**1c**/0.1	100	2	92	10800	600	1.08
14	**4**/0.1	80	4	56	1800	140	0.18
15	**5**/0.1	80	4	20	150	(6)[d]	0.015

[a] A degassed 1 M aqueous KOH solution containing the complex was saturated with CO_2 before introducing H_2. The reaction was carried out under the desired CO_2:H_2 (1:1) pressure. [b] Initial turnover frequencies (initial 20 to 60 min period). [c] The reaction was carried out in 2 M aqueous KOH. [d] Average turnover frequencies in parentheses. [e] The reaction did not reach equilibrium.

Scheme 1



H_2:CO_2 (1:1) (Table 1, entries 1−3). The reactions proceeded without an amine additive, although only small amounts of formate were detected by HPLC. Encouraged by these results, we performed extensive catalyst screening and found that introduction of a hydroxy group into the pyridine ring dramatically improved the catalytic efficiency. Concretely, complexes with 4,7-dihydroxy-1,10-phenanthroline (H_2L^1) exhibited TON and TOF values considerably higher than those for the corresponding unsubstituted phenanthroline complexes (entry 1 vs entry 4, entry 2 vs entry 5). The iridium complex [Cp*Ir(H_2L^1)Cl]Cl (**1b**; Scheme 1) was superior to the corresponding rhodium analogue [Cp*Rh(H_2L^1)Cl]Cl (**1a**) in terms of catalytic activity and equilibrium concentration of formate (entry 4 vs entry 5). The formate concentration−time profiles of the reaction are shown in Figure 1. The highest TOF, 23 000 h^{-1} (initial 20 min period), was obtained when the reaction was carried out with **1b** (0.02 mM) at 6 MPa and 120 °C (entry 7 and Figure 1d). None of the reactions showed a significant induction period. Neither CO nor any other carbon-containing products were detected by GC, LC, or NMR analysis in this system.[9]

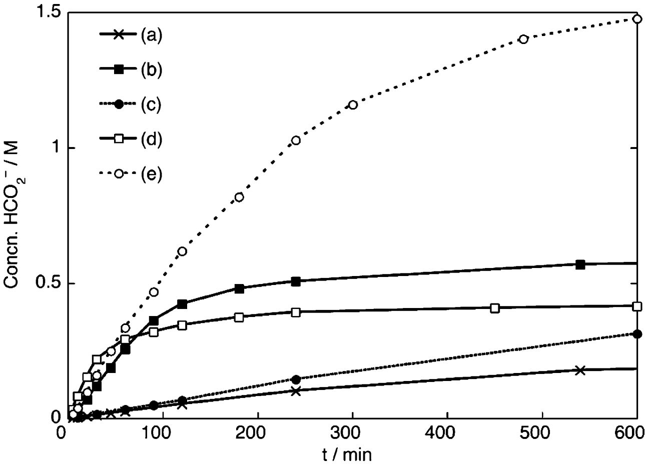


Figure 1. Time course of formate concentration for hydrogenation of bicarbonate catalyzed by (a) **1a**, (b) **1b**, and (c) **1c** (0.1 mM) at 4 MPa and 80 °C, (d) **1b** (0.02 mM) at 6 MPa and 120 °C, and (e) **1c** (0.1 mM) at 6 MPa and 120 °C in 2 M aqueous KOH.

We also found that hydrogenation of bicarbonate catalyzed by **1b** proceeded under ambient pressure at 80 °C to afford formate (TON = 800, initial TOF = 35 h^{-1}; entry 9). Production of formate was observed even at 30 °C (TOF = 5 h^{-1}). To our knowledge, there has been only one other report of homogeneous catalytic hydrogenation occurring under ambient pressure at room temperature: hydrogenation with $Rh(tppts)_3Cl$ (tppts = tris(3-sulfonatophenyl)phosphine) as a catalyst showed a turnover rate of 3 day^{-1} in a water/ethanol-amine mixture.[4]

The use of the (arene)ruthenium complex [(C_6Me_6)-Ru(H_2L^1)Cl]Cl (**1c**), which is isoelectronic with **1a** and **1b**, yielded a higher concentration of formate: the equilibrium concentration depended on the pressure and increased steadily with increasing pressure from 1.08 M at 2 MPa to 1.54 M at 6 MPa. Raising the reaction temperature led to an increase in the initial TOF without degradation of the product yield.

Although catalysts containing certain anionic ($-SO_3H$, $-CO_2H$), cationic ($-NR_2$), and neutral ($-OR$) phosphine ligands have been the subject of much research in the area of aqueous catalysis,[10] other types of water-soluble ligands have hardly been investigated. The ligand H_2L^1 can serve as an anionic water-soluble ligand similar to a carboxylic acid group, because it is known that the hydroxy protons on the pyridine ligand are acidic. In fact, the complex **1b** was highly soluble in a strongly alkaline aqueous solution (over 200 mg/mL in 1 M KOH at 25 °C), albeit slightly soluble below pH 9 (ca. 0.1 mg/mL in 1 M $KHCO_3$ at 80 °C) and insoluble in acidic solution.[11] The pK_a values of the H_2L^1 complexes **1a**−**c** were estimated to be ca. 8.5 by UV−vis spectroscopy.[12]

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(8) Kudo, K.; Sugita, N.; Takezaki, Y. *Nippon Kagaku Kaishi* **1977**, 302−309.

(9) Khan, M. M. T.; Halligudi, S. B.; Shuka, S. *J. Mol. Catal.* **1989**, *57*, 47−60.

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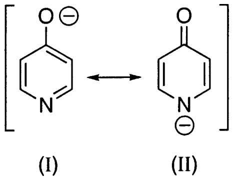
(11) The unsubstituted phenanthroline complex [Cp*Ir(phen)Cl]Cl shows some water solubility under alkaline conditions (ca. 10 mg/mL in 1 M $KHCO_3$ at 25 °C) but is slightly soluble under acidic conditions. In contrast, the water solubility of the unsubstituted bipyridine complex [Cp*Ir(bpy)Cl]Cl is pH independent and high (over 200 mg/mL in aqueous solution at 25 °C).

(12) Giordano, P. J.; Bock, C. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 6960−6965.

Chart 1

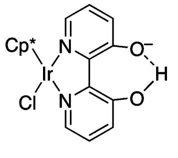


Furthermore, the deprotonated complexes [Cp*Ir(L^1)-Cl]K (**2b**) and [(C_6Me_6)Ru(L^1)Cl]K (**2c**) could be isolated as their potassium salts, whose parent molecular ion peaks were observed by FAB mass spectrometry. The ^{1}H NMR spectra of **2b** in D_2O were nearly identical with those of **1b** in KOD/D_2O, of which the chemical shift of the 2,9-protons on phenanthroline was slightly affected by the pH (the maximum difference was ca. 0.1 ppm). These observations indicate that complexes **1** under the basic reaction conditions certainly exist in the deprotonated forms **2**, which were stable for several weeks and could revert to the protonated complexes **1** by the addition of 6 M HCl.

Interestingly, a solid precipitated from the equilibrium mixture when the reaction was quenched. The precipitate may be a mixture of monoprotonated and fully protonated complexes, because it readily converted to a deprotonated form by addition of an aqueous base. This solid could, of course, also be reused as a catalyst precursor without significant loss of activity. Unfortunately, the complex was not completely recovered; inductively coupled plasma analysis showed that the metal ion concentration in the mother liquor was approximately 10−30 μM even when it was acidified with 6 M HCl. Thus, the complex may decompose partly during the course of the reaction.

When a solution of **2b** was stirred under a positive pressure of H_2, the hydride complexes **3b** were detected by ^{1}H NMR spectroscopy, which showed a singlet at δ −11.10. In addition, owing to the slight difference in the chemical shifts of the aromatic protons in **3b** and **2b** in D_2O, the hydride complex **3b** appeared to still exist in the deprotonated form. Addition of $KHCO_3$ to the aqueous solution of **3b** led to production of formate in high yield under an atmospheric pressure of H_2. This fact suggests that the deprotonated hydride complexes **3** are the actual catalysts and bicarbonate is the substrate.[2a,8] It is reasonable to assume that bicarbonate inserts into the metal−hydride bond to generate the formato intermediate with release of hydroxide ion, as Joo and co-workers suggested in their study.[5b]

The oxyanion generated from the hydroxy substituents on the phenanthroline plays another crucial role in the catalytic efficiency. Giordano suggested that the deprotonated ligand L^1 can act as a π-electron donor,[12] because pyridone form II contributes significantly to the resonance structure of the 4-hydroxypyridine unit[13,14] (Chart 1). When the reaction using deprotonated complex **2b** was conducted without aqueous base under standard conditions (4 MPa, 80 °C), the catalytic activity was low (TON = 122, initial TOF = 160). Apparently, basic conditions were crucial for high catalytic performance, because under such conditions the hydroxy group on the phenanthroline fully deprotonates. Furthermore, the 4,7-methoxy-1,10-phenanthroline complex [Cp*Ir(Me_2L^1)I]I (**4**), which was prepared by methylation of **1b** with MeI,[15] was less active than the hydroxy complex **1b** (entry 14), although it was more active than the unsubstituted phenanthroline complex [Cp*Ir(phen)-Cl]Cl. These results indicated that the catalytic activity is dependent on the electron-donating ability of the substituent on the catalyst ligand (H < OMe < O^-).[16] It has been known that the catalytic performances (i.e. the activity and the selectivity) and the electronic properties of the metal center were affected by the electronic nature of the remote para substituent on the aryl ring of the ligand.[17−20] In the present case, although there has been no direct information concerning the electronic effect of the oxyanion,[21] a dramatic enhancement of catalytic activity can be explained by the strong electron-donating ability of the oxyanion.[2c,22]



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To assess the effect of the substituent position, we adopted 3,3′-dihydroxy-2,2′-bipyridine (H_2L^2) as a ligand instead of H_2L^1. In this complex, [Cp*Ir(HL^2)Cl] (**5**), the presence of a strong intramolecular O−H−O hydrogen bond stabilizes the negative charge on the oxygen atoms and prevents deprotonation of the second hydroxy proton.[23] The catalytic activity of **5** was almost the same as that of the corresponding unsubstituted bipyridine complex [Cp*Ir(bpy)Cl]Cl (Table 1, entry 15 vs entry 3). One of the possible reasons for the poor result could be that its resonance structures cannot increase the π-electron density on the nitrogen atoms. This hypothesis is consistent with the reported data for the nucleophilicity of the nitrogen atom of 3- and 4-hydroxypyridine anions.[13]

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(20) Stechhan, E.; Herrmann, S.; Ruppert, H.; Dietz, E.; Frede, M.; Spika, E. *Organometallics* **1991**, *10*, 1568−1577.

(21) For example, an oxyanion-accelerated, palladium-mediated intramolecular coupling reaction in dimethylacetamide was reported: Hennings, D. D.; Iwasa, S.; Rawal, V. H. *J. Org. Chem.* **1997**, *62*, 2−3.

(22) A theoretical study predicted that an electron-donating ligand is favorable for the hydrogenation of CO_2: Musashi, Y.; Sakaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 7588−7603.

(23) Cargill Thompson, A. M. W.; Jeffery, J. C.; Liard, D. J.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1996**, 879−884.

In conclusion, we have found that half-sandwich Ru(II), Ir(III), and Rh(III) complexes with 4,7-dihydroxy-1,10-phenanthroline can serve as water-soluble, highly efficient catalysts for hydrogenation of bicarbonate without an amine additive. Furthermore, it is noteworthy that the generation of an oxyanion by deprotonation of the two hydroxy substituents on the catalyst ligand caused a dramatic enhancement of catalytic activity, due to its strong electron-donating ability, as well as imparting water solubility. These attractive features may hold significantly broader implications for the design of new water-soluble catalysts.

Supporting Information Available: Text and figures giving details of the preparation of complexes **1**−**5**, ^{1}H NMR spectra of complex **1c** and iridium hydride complex **3b**, catalysis protocol, graphs of the time course of the formate concentration, and the absorption spectrum of **1c** as a function of pH. This material is available free of charge via the Internet at http://pubs.acs.org.

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