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Catalytic Hydrogenation of Carbon Dioxide Using Ir(III)−Pincer Complexes

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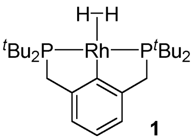
Formic acid is an important chemical product used as a preservative and an insecticide as well as for tanning leathers. In addition, formic acid plays a major role in synthetic chemistry as an acid, a reductant, and a carbon source. In industrial processes, formic acid is mainly synthesized by carbonylation of alcohols using carbon monoxide followed by hydrolysis, which requires a high pressure of toxic carbon monoxide gas.[1] Therefore, development of an alternative route to formic acid or its salt is highly desired.

Hydrogenation of carbon dioxide to generate formic acid is a promising candidate because carbon dioxide is abundant, inexpensive, and a less toxic C1 source. Hydrogenation of carbon dioxide has been widely investigated using transition-metal complexes,[2] especially with rhodium,[3] ruthenium,[4−6] and iridium[7,8] catalysts. Noyori and co-workers carried out the reaction in supercritical carbon dioxide using a Ru(II) catalyst and obtained ammonium formate, alkyl formate, and formamide in high yields.[4] For example, the highest turnover frequency (TOF) (95 000 h^{-1}) has been achieved using RuCl(OAc)(PMe$_3$)$_4$, which is soluble in supercritical CO$_2$.[5] Himeda reported a highly active cationic Cp*Ir(III) catalyst containing phenanthroline derivatives as ligands. The maximum turnover number (TON) of the hydrogenation reached 222 000 (the highest TON reported to date) in a basic aqueous solution.[8] They stated that electron-donating ligands accelerated the reaction.

Pincer ligands are known as multidentate ligands that strongly bind to a metal center to prevent dissociation of the ligand from the metal.[9] The idea that an alkylphosphine-based pincer ligand would be an efficient electron donor prompted us to use a transition-metal−pincer complex as a catalyst for hydrogenation of CO$_2$. Although insertion of CO$_2$ into PCP-ligated rhodium dihydrogen complexes such as **1** and **2** to form formato complexes were intensively studied,[10] catalytic hydrogenation of CO$_2$ with these complexes has never been reported.



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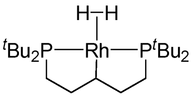

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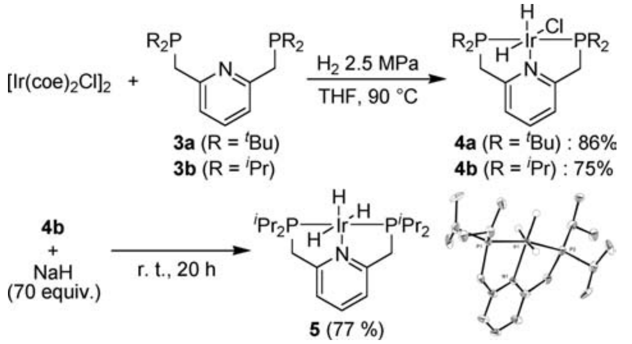
Herein we describe the synthesis of new PNP−Ir(III) hydride complexes and their application to the catalytic hydrogenation of CO$_2$ in aqueous base. The PNP−Ir(III) trihydride complex **5** bearing isopropyl groups on the phosphorus atoms shows higher TON and TOF than reported for any other catalyst to date. Deprotonation of the PNP ligand is proposed to play an essential role in the catalytic cycle.

PNP-ligated chloroiridium(III) dihydride complexes **4a** and **4b** were synthesized by the reaction of an Ir(I) source with an excess amount of alkyl-substituted PNP pincer ligands **3a** and **3b**, respectively, under H$_2$ pressure (Scheme 1). The structures were determined by NMR spectroscopy. In the ^{1}H NMR spectra of **4a** and **4b**, each of the two hydrides is coupled with the two magnetically equivalent phosphorus atoms and with the other hydride. Thus, two hydrides are suggested to occupy positions cis and trans to the nitrogen atom, forming an octahedral structure.

Scheme 1. Synthesis of PNP-Ligated Chloroiridium(III) Dihydride Complexes **4a** and **4b** and PNP-Ligated Iridium(III) Trihydride Complex **5** and ORTEP Drawing of **5** (50% Thermal Ellipsoids, Hydrogen Atoms except Hydrido Ligands Have Been Omitted for Clarity)



PNP-ligated iridium(III) trihydride complex **5** was synthesized from **4b** in 77% yield by addition of an excess amount of NaH. X-ray crystallographic analysis of **5** revealed a meridional coordination mode of the PNP pincer ligand, with three peaks in the Fourier map that could be assigned as hydrides to form the octahedral geometry. The IR spectrum of **5** showed a trans iridium dihydride stretch at 1678 cm^{-1}, which is a much lower wavenumber than that previously reported for *mer*-IrH$_3$(PPh$_3$)$_3$ (1745 cm^{-1}),[11] indicating that the Ir−H bonds in **5** are weakened by the electron-rich PNP pincer ligand. Structural optimization of **5** using B3LYP//6-31G(d)/LANL2DZ calculations reproduced the crystal structure as well as the IR spectrum.

The hydrogenation of carbon dioxide in aqueous KOH was investigated using Ir(III)−PNP pincer complex **4a**, **4b**, or **5** or ^{t}Bu−PCP-ligated iridium(III) complex **6a**[9a] or **6b**[9c] as the catalyst (Table 1). At a reaction temperature of 200 °C, potassium formate was formed even in the absence of catalyst[12] (entry 1), and thus, background corrections to the catalyst TONs based on the data from entry 1 were made. PNP complex **4a** showed higher activity than PCP complex **6a** (entries 2, 3). Changing the ^{t}Bu groups on the phosphorus atoms in **4a** to ^{i}Pr groups in **4b** afforded higher activity, probably because of the higher solubility of **4b** (entries 3, 4). Addition of THF as a cosolvent was necessary because of the poor solubility of **4b** in water (entry 5).

Iridium trihydride complex **5** showed much higher catalytic activity than its chloroiridium dihydride analogue **4b** (entries 4, 7). PCP-ligated iridium dihydride complex **6b** also showed higher activity than its chloroiridium hydride analogue **6a** (entries 2, 6). These results indicate that chloride may suppress the catalytic reaction. Using **5** increased the TON to 150 000 h^{-1} at 200 °C (entry 7),[13] which is 1.5 times as high as the best TOF value in the literature.[5] At 120 °C and lower catalyst loading (100 ppb) (entry 9), the TON of 3 500 000 was 15 times higher and the TOF almost

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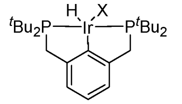
doubled in comparison with the best result at 120 °C reported to date.[8] It should be noted that the use of a weaker base (K_3PO_4 instead of KOH) resulted in a lower yield (entry 10), suggesting that the base plays an essential role in the catalytic cycle.

Table 1. Hydrogenation of Carbon Dioxide Catalyzed by Ir(III)−Pincer Complexes

$$\underset{(1:1)}{H_2 + CO_2} \xrightarrow[\substack{\text{1 M KOH aq.(5.0 mL)} \\ \text{THF (0.1 mL)}}]{\text{Ir cat. (0.010 }\mu\text{mol)}} \text{HCOOK}$$

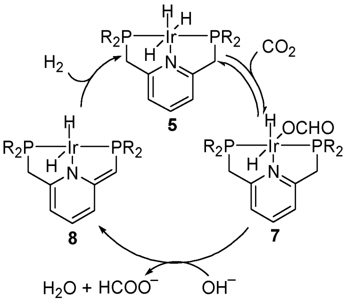
entry	Ir cat.	*T* (°C)	*P* (MPa)[a]	time (h)	yield (%)[b]	TON (×10^3)	TOF (10^2 h^{-1})
1	none	200	5.0	13	4	–	
2	**6a**	200	5.0	13	16	64	49
3	**4a**	200	5.0	13	20	89	68
4	**4b**	200	5.0	13	24	100	77
5[c]	**4b**	200	5.0	13	9	34	26
6	**6b**	200	5.0	2	12	59	300
7	**5**	200	5.0	2	60	300	1500
8	**5**	120	6.0	48	94	470	98
9[d]	**5**	120	6.0	48	70	3500	730
10[e]	**5**	200	5.0	2	8	40	200

[a] Total pressure at room temperature. [b] Yield based on ^1H NMR analysis using sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard. The yield represents conversion of the added base (5 mmol). [c] No THF was added. [d] Catalyst loading was 0.0010 μmol. [e] K_3PO_4 was used instead of KOH.



6a (X = Cl)
6b (X = H)

Scheme 2. Plausible Mechanism for Hydrogenation of CO_2 Using Iridium Trihydride Complex **5**



A catalytic cycle consisting of iridium trihydride **5**, iridium formate **7**, and amidoiridium dihydride **8** (Scheme 2) is proposed on the basis of the following experiments. Treatment of complex **5** with aqueous KOH resulted in no reaction at room temperature in 30 min.[14] On the other hand, exposure of trihydride complex **5** to 1 atm CO_2[15] led to an immediate equilibrium between **5** and dihydridoiridium(III) formate **7** at 25 °C, as observed by ^1H and ^{13}C NMR spectroscopy. Characteristic signals for a formato ligand were observed in the ^1H and ^{13}C NMR spectra ($\delta_H = 7.88$ ppm, $\delta_C = 168$ ppm), although isolation of **7** failed. The two distinct hydride signals of **7** indicated that the formato ligand is located cis to the nitrogen atom of the pyridine moiety. As the next step, elimination of formate anion from **7**, accompanied by deprotonation from $Ar-\underline{CH_2}-P$ and subsequent dearomatization of the pyridine ring, would give amidoiridium dihydride complex **8**.[16] We prepared complex **8** by an alternative method, namely, the addition of $CsOH \cdot H_2O$ to chloroiridium dihydride complex **4b**. Treatment of **8** with hydrogen resulted in the production of **5**. Thus, as shown in Scheme 2, insertion of CO_2 into **5**, deprotonative dearomatization with dissociation of the formato ligand in **7**, and hydrogenation of **8** to regenerate the trihydride complex **5** completes a cycle. The unprecedentedly high catalytic activity performed by catalyst **5** may be attributed to the acceleration of formate dissociation from **7** mediated by the deprotonation of the ligand.

In conclusion, a highly active catalyst, **5**, for hydrogenation of carbon dioxide was developed. The best TOF and TON using **5** reached 150 000 h^{-1} and 3 500 000, respectively. Further mechanistic studies are now in progress.

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Supporting Information Available: Experimental procedures, characterization data, and crystallographic data for **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) For an example of hydrogenation of CO_2 without catalyst in aqueous base, see: Kudo, K.; Sugita, N.; Takezaki, Y. *Nihon Kagaku Kaishi* **1977**, 302. A trace amount of impurities from the autoclave might be responsible for the catalysis. See the Supporting Information for ICP analysis.

(13) High reaction temperature is not always energy-inefficient because heat recovery systems are applied in industry. See: Pilavachi, P. A. *Heat Recovery Syst. CHP* **1993**, *13*, 391.

(14) Treatment of **5** with aqueous KOH at 200 °C for 2 h gave a new signal at 46.6 ppm in the ^{31}P NMR spectrum. Hydride signals were observed at−19.77 and−23.33 ppm in the ^1H NMR (CD_2Cl_2) spectrum.

(15) In the ^{13}C NMR spectrum of CO_2 (2.5 MPa) in a KOH/THF-d_8/D_2O solution, a sole peak was detected at 125.8 ppm, which was identical to the result for CO_2 in THF-d_8. This suggested that CO_2 rather than bicarbonate or carbonate is a major species under the reaction conditions.

(16) Deprotonation from the pyridylmethyl group to dearomatize the pyridine ring has been observed previously. See: (a) Ben-Ari, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 15390. (b) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113. (c) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Milstein, D. *Dalton Trans.* **2007**, 107. (d) Schaub, T.; Radius, U.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2008**, *27*, 1892. (e) Vuzman, D.; Poverenov, E.; Shimon, L. J. W.; Diskin-Posner, Y.; Milstein, D. *Organometallics* **2008**, *27*, 2627. (f) Gunanathan, C.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2009**, *131*, 3146.

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