

A New Approach to the Reduction of Carbon Dioxide: CO₂ Reduction to Formate by Transfer Hydrogenation in *i*PrOH

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Summary: A series of four Ir and Ru catalysts have been tested in the reduction of CO_2 to formate in the presence of H_2 . The iridium catalysts containing the basic NHC ligands were the ones to show better catalytic activities, achieving high TON values of up to 1800 TON. The unprecedented reduction of CO_2 with iPrOH through a hydrogen transfer process is also described. TON values of up to 150 were obtained. Two other secondary alcohols, cyclohexanol and 1-phenylethanol, were also used as hydrogen sources for the reduction of carbon dioxide.

Introduction

Highly efficient catalytic activation of CO₂ has become an important research area because of the position of CO₂ as the primary greenhouse gas and its great potential to become an important feedstock and reagent for organic transformations.^{1,2} In the search for a catalyst suitable for the transformation of CO₂, two preliminary issues have to be taken into account: first, the catalyst has to be resistant to the harsh reaction conditions needed for the activation of the stable and inert CO₂, and second, the catalyst requires high-energy d-occupied orbitals to facilitate the interaction with the electron-deficient carbon of the molecule. N-Heterocyclic carbenes (NHCs) may provide a good choice of ligands for the design of this type of catalysts because they are known to be strong electron donors³ and afford highly stable metal complexes.⁴ While the reduction of CO₂ using phosphine-based catalysts has been extensively investigated,^{2,5} there are just a few recent reports describing the use of NHC-containing catalysts for this type of transformation,⁶ but they already illustrate the great potential of this type of ligands.

The homogeneously catalyzed hydrogenation of CO₂ to formic acid⁷ is a well-known reaction that was first reported in 1976.⁸ The reverse reaction (formic acid to CO₂) has also been widely used in the reduction of organic molecules by the hydrogen transfer process in which formic acid is used as the hydrogen source.^{9,10} On the other hand the reversibility of this homogeneously catalyzed process has been proposed as a viable hydrogen storage system.^{11,12} With all this in mind, it may seem clear that effective hydrogen transfer catalysts should also be effective in the reduction of CO_2 , if the right reaction conditions are used.

Some recent reports have shown that "Ir^{III}Cp*" and "Ru^{II}(arene)" complexes constitute valuable catalysts for the hydrogenation of CO_2 to formic acid^{7,13,14} and that the σ -donating power of the coligands determines the activity of the catalysts.^{7,13} In the course of our investigations, we found that "IrCp*(NHC)" fragments are effective catalysts in a wide set of hydrogen-borrowing reactions,^{15,16} including an interesting example of base-free reduction of C=O and C=NR bonds by transfer hydrogenation.¹⁶ On the basis of these results, we decided to see if a more challenging substrate such as CO₂ could be reduced to formate by a transfer

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 Table 1. Comparison of Catalysts 1–4 toward the Hydrogenation of CO₂ to KHCOO^a

entry	catalyst/mM	TON	formate/M
1	1/1.75	67	0.12
2	2/1.75	369	0.65
3	3/1.75	60	0.11
4	4/1.75	180	0.32
6	1/0.17	291	0.05
7	2/0.17	894	0.16
8	4/0.17	516	0.09
9^b	2/0.17	1600	0.28

^{*a*} The reactions were carried out at 60 atm (CO₂/H₂, 1:1) and 80 °C during 18 h in an aqueous KOH solution (1 M). ^{*b*} [KOH] = 2 M.

hydrogenation procedure as an alternative to the ubiquitous reduction with pressurized hydrogen. Here we report the study of the catalytic activity of a set of four Ir and Ru complexes (see Scheme 1) in the reduction of CO_2 using H_2 and in an unprecedented example of a hydrogen transfer reaction using *i*PrOH.

Results and Discussion

We first performed a catalyst screening using the four different catalysts depicted in Scheme 1. The reactions were performed using 60 atm of a CO_2/H_2 mixture (1:1) in an aqueous solution of KOH at 80 °C. As observed by the data shown in Table 1, under these reaction conditions the Ir catalyst **2** afforded the best catalytic performances.

The hydrogenation of CO_2 was affected by the initial concentration of KOH, as can be seen from the reaction outcomes obtained when the reactions were carried out using 1 and 2 M KOH solutions (Table 1, entries 7 and 9, respectively, and Figure S1.2 in the Supporting Information), with a high TON value of 1600 obtained for the reaction performed at the higher concentration of base. A maximum TON of 1800 was obtained when the reaction was allowed to evolve for 64 h in the 2 M aqueous solution.

The results shown for catalysts **3** and **4** are similar to those previously observed for other related half-sandwich species of Ru and Ir with the bipyridine (bpy) ligand.^{10,13} In clear agreement with the results previously described by Himeda and co-workers,¹³ it is observed that the introduction of the electron-donating bis-NHC ligand in catalyst **2** provides an important improvement of the catalytic activity of the IrCp* catalytic system, compared to that shown by **4**. On the other hand, there is a clear difference in the catalytic activity shown by catalysts **1** and **2**. In a previously reported study, we described that the catalytic performance of **1** was far better than that shown by **2** in the catalytic deuteration of several organic molecules.¹⁷ In that case, we attributed this behavior to the need of the catalyst to have two coordination sites available to provide a good catalytic outcome. In accordance



Table 2. Transfer Hydrogenation of CO₂ with Alcohols^a

CO ₂ +	OH R → R'	[cat.]	KUCO		Ö
		0.5M KOH/H ₂ O, 110°C	KHCO ₂ +	+	R R'

entry	alcohol	cat./mM	time (h)	TON ^b
1	<i>i</i> PrOH	1/0.175	16	26
2	iPrOH	2/0.175	16	1
3	iPrOH	3/0.175	16	1
4	<i>i</i> PrOH	4/0.175	16	7
5	<i>i</i> PrOH	5/0.175	72	5
6	<i>i</i> PrOH	$1/1.8 \times 10^{-2}$	16	91
7	<i>i</i> PrOH	$1/1.8 \times 10^{-3}$	16	116
8	<i>i</i> PrOH	$1/1.8 \times 10^{-2}$	72	150
9	cyclohexanol	1/0.175	16	6
10	1-phenylethanol	1/0.175	16	13
11^{c}	iPrOH	1/0.175	16	16

^{*a*} Reactions were carried out at 110 °C in 20 mL of a 0.5 M KOH solution in a mixture of H₂O/*i*PrOH (9:1). $P_{CO2} = 50$ atm. ^{*b*} TONs based on the formation of formate, calculated by ¹HNMR spectroscopy. Average of two experiments. ^{*c*} 0.5 M of K₂CO₃ used instead of KOH.

with recently published mechanistic studies¹⁸ it seems clear that for the reduction of CO_2 to formic acid only one catalytic active site is needed; thus bidentate ligands in half-sandwich Ir and Ru catalyst are perfectly allowed in order to achieve high catalytic performances.

In order to see if the reduction of CO_2 could also be achieved by a transfer hydrogenation procedure, we decided to replace the hydrogen source by iPrOH. iPrOH is an inexpensive and environmentally benign reagent, which may overcome the experimental inconvenience of using H₂. A first screening of the catalytic activity of compounds 1-4was done by using a solution of KOH in a mixture of $H_2O/$ *i*PrOH (9:1) at 110 °C, at a pressure of 50 atm of CO₂. Reactions run at lower temperatures (80 °C) afforded a much lower conversion to the desired formate, while temperatures above 110 °C did not provide any significant improvements on the reaction yields. From the thermodynamic point of view, the reduction of CO₂ in aqueous basic solutions was shown to be the most favorable reaction conditions.¹¹ Together with the formation of formate, the corresponding amount of acetone was also detected by ¹HNMR. For comparative purposes, compound [{IrCp*Cl₂}₂], 5, was also tested under these reaction conditions. Table 2 shows some representative data for this reaction.

These results show that compound 1 affords the best catalytic outcomes from the list of compounds under study. In order to optimize the maximum activity of 1 in terms of TON values, we performed a series of reactions in which the concentration of the catalyst used was gradually lowered to 1.8×10^{-3} mM, for which the TON was 116 after a fixed time of 16 h. For the study of the time course of formate

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Figure 1. Time course of formate formation catalyzed by 1 (1.8 $\times 10^{-2}$ mM). $P_{CO2} = 50$ atm. T = 110 °C.

concentration, we used a catalyst concentration of 1.8×10^{-2} mM; this gave us the best catalytic outcomes when considering both conversions and TONs (Figure 1). Under these reaction conditions, a maximum TON of 150 was obtained after 72 h.

In order to confirm the reliability of our results, several experiments were done. When the reaction is performed in a mixture of $D_2O/iPrOH-d_8$ (9:1), the generation of KDCO₂ could be confirmed by ²DNMR spectroscopy. The general viability of the reaction was evaluated by testing two other secondary alcohols, such as cyclohexanol and 1-phenylethanol (Table 2, entries 9 and 10). Although the reaction outcomes were lower than those obtained with *i*PrOH, both alcohols afforded the formation of formate from CO₂, thus validating the applicability of the hydrogenation transfer process for the reduction of this inert substrate.

Although we have not performed a detailed mechanistic study, we believe that the process starts with the formation of a metal dihydride by reaction of the starting metal complex with *i*PrOH in the presence of the base. We previously proposed the formation of this species to justify the catalytic dehydrogenation of alcohols promoted by 1.19 Then, insertion of a molecule of CO₂ into one Ir-H bond would form a formate complex that may undergo reductive elimination of formic acid, which is then deprotonated by the base. In principle, this simple mechanism should not differ from the very well-known opposite reaction implying the use of formic acid (or formate) as hydrogen source in transfer hydrogenation processes, although we need to carry out studies in order to elucidate the detailed mechanism of interaction between the CO_2 molecule and the metal hydride. Ab initio metadynamics have proved to be a good choice for such studies in the reduction of CO₂ by ruthenium complexes.²⁰

In summary, we have shown that the reduction of CO_2 can be performed by a hydrogen transfer process in which *i*PrOH is used as the hydrogen source. This reaction is unprecedented and should be of great interest if the process can be fully optimized. The reaction is interesting not only because it uses the inexpensive and environmentally benign *i*PrOH as hydrogen source but also because it provides an easy method for the generation of formic acid/sodium formate, a system that has been postulated as a potential hydrogen storage material,^{12,21} capable of producing highly pure hydrogen suitable for all kinds of fuel cells. Given the large library of catalysts available for transfer hydrogenation reactions, a wide catalyst screening may afford promising results. Further studies in the optimization of the reduction of CO_2 with *i*PrOH using other NHC-based catalysts are currently underway in our lab, together with detailed mechanistic studies.

Experimental Section

General Procedures. All the catalysts used $(1, {}^{17}2, {}^{22}3, {}^{23}4, {}^{24}5^{25})$ were prepared according to literature procedures. Solvents and reagents were used as received from commercial suppliers. NMR spectra were recorded on Varian Innova 300 and 500 MHz instruments, using CDCl₃, CD₃OD, and D₂O as solvents.

Catalytic Hydrogenation of CO₂ with H₂. The catalytic reactions were carried out in a Hastelloy Autoclave Mini-Reactor system equipped with a 50 mL cylinder. The catalyst (3.5μ mol for the reactions run with a 0.175 mM concentration of catalyst) was dissolved in a degassed aqueous KOH solution (20 mL). The reactor was pressurized with 60 atm of CO₂/H₂ (1:1) at 80 °C for the appropriate time. After reducing the pressure to 1 atm and cooling to room temperature, the solvent was removed by evaporation, and the residue was dissolved in D₂O. The yield of HCOOK was measured by ¹H NMR in D₂O, using isonicotinic acid as internal standard (100:1 reference: catalyst molar ratio; 43 mg (0.35 mmol) for a 0.175 mM solution of catalyst).

Catalytic Hydrogen Transfer of CO₂ with Alcohol. The reactions were carried out in a Hastelloy Autoclave Mini-Reactor system equipped with a 50 mL cylinder. The catalyst (3.5μ mol for the reactions run with a 0.175 mM concentration of catalyst) and KOH or K₂CO₃ were dissolved in 20 mL of a mixture of H₂O/alcohol (9:1 v/v). The reactor was pressurized with 50 atm of CO₂ at 110 °C for the desired time. After equilibrating to atmospheric pressure and cooling to room temperature, the solvent was removed by evaporation, and the residue was dissolved in D₂O. The yield of HCOOK was measured by ¹H NMR in D₂O, using isonicotinic acid as internal standard (20:1 reference:catalyst molar ratio; 9 mg (0.07 mmol) for a 0.175 mM solution of catalyst).

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Supporting Information Available: Selected NMR spectra are available free of charge via the Internet at http://pubs.acs.org.

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