

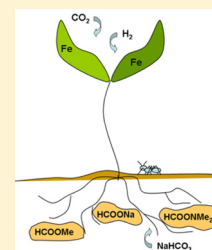
Well-Defined Iron Catalyst for Improved Hydrogenation of Carbon Dioxide and Bicarbonate

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S Supporting Information

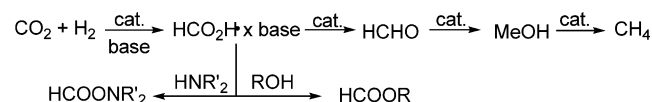
ABSTRACT: The most efficient, stable, and easy-to-synthesize non-noble metal catalyst system for the reduction of CO₂ and bicarbonates is presented. In the presence of the iron(II)-fluoro-tris(2-(diphenylphosphino)phenyl)phosphino]tetrafluoroborate complex **3**, the hydrogenation of bicarbonates proceeds in good yields with high catalyst productivity and activity (TON > 7500, TOF > 750). High-pressure NMR studies of the hydrogenation of carbon dioxide demonstrate that the corresponding iron-hydridodihydrogen complex **4** is crucial in the catalytic cycle.



INTRODUCTION

The usage and storage of CO₂ is of fundamental interest for chemistry and energy technologies.¹ Clearly, refinement of carbon dioxide to more valuable chemical products will not solve the global problem of increasing CO₂ emissions. Nevertheless, CO₂ constitutes already today an important C1-source for the chemical industry, for example, for the production of urea. It is likely its use in the future will significantly increase as a result of the lower toxicity and abundant availability in comparison with the widely employed CO.² In addition, with respect to energy storage, interesting applications for carbon dioxide are hydrogen storage and release technologies.³ Here, CO₂ is reversibly transformed with hydrogen into valuable secondary energy carriers, such as methane, methanol, or formic acid (Scheme 1).

Scheme 1. Hydrogenation of CO₂ and Selected Products



Notably, the first reduction step of carbon dioxide to formic acid proceeds under comparably mild conditions and does not produce any water as a side product, which lowers the energy efficiency in the cases of methanol and methane. Since the pioneering work of Graf and Leitner,⁴ Jessop and Noyori and co-workers,⁵ as well as Joó,⁶ various organometallic catalysts have been developed in the past decade. Recently, high catalyst turnover numbers for this hydrogenation were achieved by the groups of Nozaki,⁷ and Himeda.⁸ Moreover, interesting process improvements were reported by Schaub and Paciello at BASF.⁹ Despite an increasing scientific interest in the hydrogenation of carbon dioxide, the use of biorelevant metals such as iron, nickel or cobalt as catalysts has still scarcely been investigated

compared with noble metal-based complexes. Although some recent catalyst improvement was reported by us¹⁰ as well as Milstein and co-workers,¹¹ basically, all the non-noble metal catalyst systems show still lower activity.¹²

In addition to carbon dioxide, the reduction of bicarbonate is of considerable interest, too, because CO₂ can be easily trapped from waste streams in basic solution. On the basis of this principle, recently we developed a reversible energy storage system in which bicarbonate is hydrogenated to sodium formate and the latter releases hydrogen on demand to form again bicarbonate without losing CO₂.¹³ Unfortunately, as a catalyst a special ruthenium complex has to be applied for this process. In fact, only a few reports using iron or cobalt catalysts for the hydrogenation of bicarbonate are known.^{10,11}

In continuation of our work to develop "real" iron-catalyzed hydrogenation/dehydrogenation reactions,¹⁴ here, we present the most active and productive Fe catalyst for the reduction of carbon dioxide and bicarbonates known to date.

RESULTS AND DISCUSSION

Synthesis of Tetradentate Ligands. Molecular-defined iron complexes with tri- and tetradentate ligands show remarkable behavior in catalytic hydrogenations and hydrosilylations.¹⁵ Parallel to other groups, we also initiated a program to synthesize iron complexes of multidentate phosphorus ligands. More specifically, we had the idea to use tris(2-(diarylphosphino)aryl)phosphines as ligands.

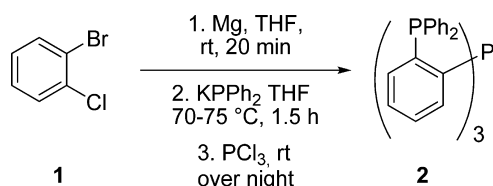
Although the preparation of most multidentate ligands involves several reaction steps and tedious purification, advantageously the respective phenyl ligand **2** is synthesized in a one-pot reaction! By improving a known literature protocol,¹⁶ 1,2-bromochlorobenzene is converted with magne-

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sium into the corresponding aryne reagent in minutes. In situ reaction with potassium diphenylphosphide and final quenching of the metalated 2-diphenylphosphinophenyl with PCl_3 gave the desired ligand **2** straightforward in 42% isolated yield (Scheme 2). The structure of the ligand was confirmed by common analytical methods and X-ray crystallography (Supporting Information Figure S1).

Scheme 2. Synthesis of the Tetradentate Ligand **2**



Synthesis of Iron Complexes. Next, we set out to prepare iron complexes of **2**. Although reaction of $\text{Fe}(\text{acac})_3$ with **2** did not result in any defined complex, to our delight, the combination of **2** and $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ gave the corresponding complex **3** $\{[\text{FeF}(\text{2})]\text{BF}_4\}$. Crystals suitable for X-ray analysis were grown from a solution of **3** in THF. The coordination geometry at the iron center is distorted trigonal bipyramidal, and selected bond lengths and angles are given below in Figure 1. Interestingly, this complex exhibits one fluorine ligand

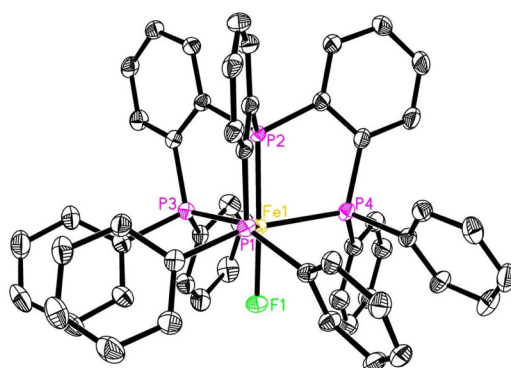


Figure 1. Molecular structure of the complex **3** $\{[\text{FeF}(\text{2})]\text{BF}_4\}$. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms as well as the counterion BF_4^- are omitted for clarity. Selected bond lengths (Å) and angles (°): F1–Fe1, 1.849(2); P1–Fe1, 2.2892(9); P2–Fe1, 2.1915(9); P3–Fe1, 2.2672(9); P4–Fe1, 2.2921(9). F1–Fe1–P1, 97.11(6); P1–Fe1–P2, 84.18(3); P1–Fe1–P3, 120.06(3); P1–Fe1–P4, 116.95(3); P3–Fe1–P4, 119.54(3).

derived from the original BF_4^- anion. Although different metal complexes of ligand **2** have been analytically characterized,¹⁷ to the best of our knowledge, no catalytic experiments have yet been reported.

Optimization of the Reaction Conditions the Bicarbonate Reduction. In initial catalytic experiments on the hydrogenation of sodium bicarbonate to sodium formate, either a combination of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and the ligand **2** or the defined complex **3** were used. Similar results were obtained when comparing the in situ-generated catalyst with the defined complex, demonstrating the immediate formation of the same active catalyst species (Table 1, entry 2 vs entry 7). In both cases, good yields (80–83%) and with respect to iron high turnover numbers (around 1500) are achieved. Already, these results represent the best catalyst productivities ever reported

Table 1. Iron-Catalyzed Hydrogenation of Sodium Bicarbonate and Sodium Methylcarbonate to Sodium Formate^a

entry	substrate	T [°C]	P _{H₂} [bar] ^b	yield [%] ^c	TON
1	NaHCO ₃	80	60	86	1597
2	NaHCO ₃	100	60	80	1485
3	NaHCO ₃	60	60	47	873
4	NaHCO ₃	120	60	15	279
5	NaHCO ₃	100	85	85	1579
6	NaHCO ₃	100	30	52	966
7 ^d	NaHCO ₃	100	60	83	1541
8 ^e	NaHCO ₃	100	60	77	7546
9 ^f	NaHCO ₃	100	60	77	3850
10 ^g	NaHCO ₃	80	60	84	1600
11 ^h	NaHCO ₃	80	60	48	914
12 ⁱ	NaHCO ₃	80	60	85	1619
13 ^j	NaHCO ₃	80	60	80	1524
14	NaCO ₃ Me	100	60	71	1352

^aReaction conditions, entries 1–13: 40 mmol of substrate, 0.021 mmol of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, 0.021 mmol of **2**, 40 mL of MeOH, 20 h. ^bPressure at room temperature. ^cEntries 1–13: yields based on the ratio of ¹H NMR signals of sodium formate to THF (internal standard). ^d0.021 mmol of the defined complex **3** (Figure 1). ^e49 mmol of substrate, 0.005 mmol of catalyst loading of **3**, 30 mL of MeOH. ^fReaction time, 5 h; TOF, 770. ^g0.021 mmol of $\text{Fe}(\text{acac})_3$. ^h0.021 mmol of FeCl_2 . ⁱ0.021 mmol of $\text{Fe}(\text{acac})_2$. ^j0.021 mmol of FeF_2 .

for any iron-catalyzed hydrogenation of carbon dioxide and its derivatives. It is important to note that the catalyst is stable to >100 °C, which is an advantage to the previously known more sensitive ethyl-bridged ligand.^{10b} At higher and lower temperatures, the yield of formate decreased (Table 1, entries 3 and 4). Hence, for further optimization, we decided to choose 100 °C as the standard temperature. Variation of the hydrogen pressure had no significant influence on the activity of the catalyst, but it does affect the equilibrium of bicarbonate and formate (Figure 2). Pressure higher than 60 bar resulted in

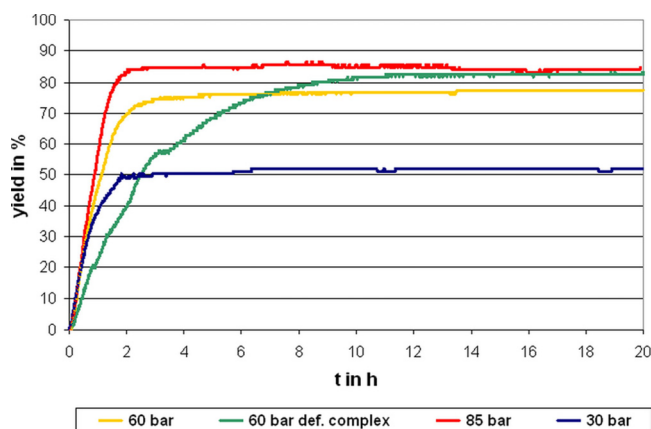


Figure 2. Yield of formate as a function of pressure.

slightly increased yields (Table 1, entry 5), whereas only 52% of formate was obtained at 30 bar hydrogen pressure (Table 1, entry 6). The improved efficiency of the iron complex **3** was confirmed by lowering the catalyst loading to 0.01 mol % Fe, which still resulted in good yields and an excellent TON of >7500 (Table 1, entry 8). With respect to the iron precursor, it is noteworthy that apart from iron tetrafluoroborate, very

inexpensive $\text{Fe}(\text{acac})_3$, $\text{Fe}(\text{acac})_2$, FeF_2 , and even simple FeCl_2 showed significant catalytic reactivity (Table 1, entries 10–13).

Next, we studied the hydrogenation of sodium methylcarbonate (Table 1, entry 14) which might be an intermediate in the hydrogenation of carbon dioxide to methyl formate. For this purpose, CO_2 was passed into a solution of sodium methanolate in methanol to give sodium methylcarbonate. Hydrogenation of the resulting white precipitate gave 71% yield of sodium formate.

Hydrogenation of Carbon Dioxide. The hydrogenation of carbon dioxide in methanol was also investigated in the presence of amines. Without any further optimization the direct hydrogenation of CO_2 in the presence of triethylamine led to a mixture of formic acid and methyl formate with a conversion of carbon dioxide of around 15% (Table 2, entry 1). Addition of

Table 2. Iron-Catalyzed Hydrogenation of Carbon Dioxide^a

entry	product	yield product [%] ^c	yield HCOOH [%] ^d	$P_{\text{H}_2/\text{CO}_2}$ [bar] ^b	TON ^e
1	HCO_2Me	7.0	7.9	30/30	1692
2 ^f	HCO_2Me	0	16.7	30/30	1897
3	DMF	70	2.9	30/30	2329
4 ^g	DMF	74	7.7	70/30	5104
5	HCONEt_2	39	9.1	30/30	2114

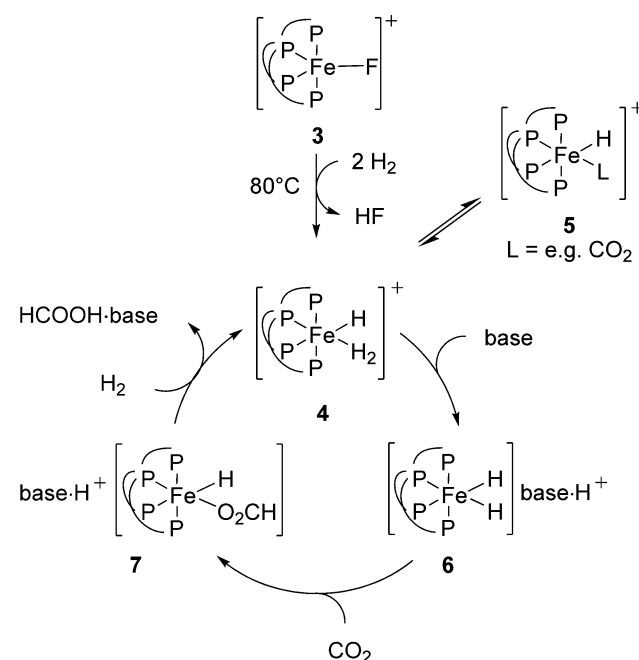
^aReaction conditions: 0.014 mmol of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, 0.014 mmol of 2, 20 mL of MeOH, 159 mmol of CO_2 , 100 °C, 20 h. Entries 1–2: 36 mmol of NEt_3 . Entries 3–5: 40 mmol of dialkylamine, 5 mL of THF.

^bPressure at room temperature. ^cEntries 1–2: GC-yield based on CO_2 with diglyme as internal standard. Entries 3–5: GC-yield based on the dialkylamine with diglyme as internal standard. ^dHPLC-yield of formic acid based on CO_2 with benzoic acid as internal standard. ^eMillimoles of converted CO_2 /mmol catalyst. ^fAddition of 2.9 mL of water. ^g80 mmol of HNMe_2 (2 M in MeOH).

water suppressed the formation of methyl formate (Table 2, entry 2). When using dialkylamines as the base, the formation of formamides is observed. As an example, dimethylamine led to 74% yield of dimethylformamide (DMF) (with respect to the amine) and 7.7% of formic acid, which corresponds to a turnover number >5100 (Table 2, entries 3 and 4). In agreement with the work of Sugita,¹⁸ Inoue,^{12c} and our previous reported iron system,^{10b} longer alkyl chains resulted in lower yields. Nevertheless, the achieved turnover numbers are at least 1 order of magnitude higher in comparison with any previously reported iron system.^{10–12}

Proposed Mechanism. To understand the mechanism of these Fe-catalyzed hydrogenations in more detail, in situ nuclear magnetic resonance (NMR) measurements of different catalytic experiments were performed. As shown in Scheme 3, in the catalytic cycle an initial formation of an iron-hydridodihydrogen complex 4 is proposed. Indeed, in situ NMR spectroscopy of a solution of 3 under 23 bar hydrogen pressure showed that complex 4 is formed from the Fe–F complex 3 at 80 °C within a few hours. Notably, complex 3 is paramagnetic and has therefore been identified using MS and X-ray, Figure 1), whereas 4 is characterized by two ³¹P NMR signals (142.5 ppm, rel. intensity 1, and 87.0 ppm, rel. intensity 3, $J_{\text{P,P}}$ = 37 Hz) and one broad ¹H signal at –9.18 ppm, representing both the hydride and the dihydrogen ligand. Complex 4 behaves similarly to its known analogue with the tris[2-(diphenylphosphino)ethyl]phosphine (tetrphos) ligand,¹⁹ (see the Supporting Information). When CO_2 was added to the reaction solution (up to 30 bar total pressure at 80

Scheme 3. Postulated Mechanism for the Iron-Catalyzed Hydrogenation of Carbon Dioxide



°C), a second hydride signal (–12.10 ppm) appeared, together with three phosphorus signals (135.8 ppm, rel. intensity 1, 86.2 ppm, rel. intensity 2, 82.8 ppm, rel. intensity 1) at the expense of the resonances of complex 4. However, no formation of formic acid or formate is observed in the proton NMR after several hours. We explain this observation with equilibrium between complexes 4 and 5, in which the hydrogen ligand is exchanged either with solvent molecules or carbon dioxide. Only after addition of base (triethylamine) did we immediately observe a product signal, $\delta(1\text{H})$ 8.95 ppm, and the complete disappearance of complex 4. Apparently, the presence of base is necessary to transform 4, which constitutes the resting state in the catalytic cycle, into a more active reduction catalyst 6. Subsequent insertion of carbon dioxide into the Fe–H bond forms the corresponding iron formate complex. Final protonation of 7 and coordination of hydrogen closes the catalytic cycle, and formic acid and methyl formate can be detected by NMR. Detailed information on the NMR experiments under pressure is compiled in the Supporting Information.

CONCLUSION

In conclusion, we present the most active and productive iron-based catalyst system for hydrogenation of bicarbonates and carbon dioxide to formates and formamides. The key to success is the tetradentate phosphorus ligand 2, which is easily accessible in a one-pot procedure. The resulting iron complexes, such as 3, are air- and temperature-stable and give similar catalytic results compared with the in situ generated catalysts. It can be expected that this novel iron complex will also be of value for other catalytic reductions, such as hydrogenation of nitroarenes²⁰ and carbonyl compounds.

ASSOCIATED CONTENT

Supporting Information

Further information for ligand synthesis, reaction parameters and mechanistic investigations are included in the Supporting

Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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