Low-Pressure Hydrogenation of Carbon Dioxide Catalyzed by an Iron Pincer Complex Exhibiting Noble Metal Activity

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Owing to its high abundance, low price and relatively low toxicity, the use of carbon dioxide as a C\textsubscript{1} source in chemical reactions and processes is an attractive alternative to common C\textsubscript{1} starting compounds, such as carbon monoxide and phosgene. For example, the direct, low-pressure hydrogenation of carbon dioxide to formic acid and its derivatives is a desirable transformation, considering that formic acid is highly active catalysts with rhodium, importantly as carbon source. Forms of carbon dioxide are obtained with this catalytic system when carbon dioxide is hydrogenated in the presence of a secondary amine under total pressure of 90 bar of a 1:2 mixture of carbon dioxide and hydrogen (TON = 727, TOF = 36.4 h\textsuperscript{-1}).

Encouraged by the recent development of iron pincer complexes for the hydrogenation of ketones, and the hydrogenation of carbon dioxide with iridium pincer complexes, we investigated the application of iron pincer complexes in this catalytic transformation. Calculations for Ru\textsuperscript{II} complexes predict that strong donor ligands facilitate the insertion of carbon dioxide into the ruthenium–hydride bond. In addition, the trans-influence of the ligand opposite the hydride was shown to have a major effect on the favorability of CO\textsubscript{2} insertion into Ir–H bonds. Owing to the strongly \(\sigma\)-donating properties of carbon monoxide and hydride ligands, the trans-dihydride carbonyl complexes of the type \([\{\text{PPN}\}\text{Fe}(\text{H})\text{2(CO)}]\) seemed to be promising candidates for this goal (PNP = 2,6-bis(dialkylphosphinomethyl)-pyridine). However, our previously reported complex \([\{\text{PPN}\}\text{Fe}(\text{H})\text{2(CO)}]\) with isopropyl groups bound to the phosphorus atoms was too unstable to allow for its isolation.

Herein we report the synthesis and characterization of the iron(II) pincer complex \([\{\text{tBu-PNP}\}\text{Fe}(\text{H})\text{2(CO)}]\) (4). The dihydride complex 4 is the most active iron catalyst reported to date for the hydrogenation of carbon dioxide and sodium bicarbonate to formate salts and displays similar activity to known noble metal catalysts. Carbon dioxide and sodium bicarbonate are efficiently hydrogenated in aqueous media at 80 \(^\circ\)C under remarkably low pressures (6–10 bar), with turnover numbers up to 788 and turnover frequencies up to 156 h\textsuperscript{-1}. The hydrido formate complex \([\{\text{tBu-PNP}\}\text{Fe}(\text{H})(\text{CO})(\text{η}^1\text{-OOC})]\) (5) was characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. Based on these observations a possible reaction mechanism is discussed.

Reaction of the \(\text{tBu-PNP}\) ligand with \(\text{FeBr}_3\) in a 1:1 acetonitrile/ethanol mixture and one or more equivalents of sodium borohydride cleanly results within minutes in formation of the hydride complex 1 (Scheme 1). Complex 1 exhibits a triplet resonance at \(\delta = -13.65\) ppm in the \(^1\text{H}\) NMR spectrum and a singlet resonance at \(\delta = 102.7\) ppm in the \(^{31}\text{P}[\^1\text{H}]\) NMR spectrum, indicating equivalence of the two phosphorus atoms. Complex 1 is isolated by exchanging the counter ion with tetraphenylboron. The crystal structure of 1 shows that a cationic hydride complex is formed under these conditions.
conditions, in which the iron(II) center exhibits a distorted octahedral environment formed by the pincer ligand, the hydride and two acetonitrile ligands. One of the two acetonitrile ligands is located in the apical position trans to the hydride ligand, while the second one coordinates to the iron center trans to the pyridine nitrogen.\[^{15}\]

Performing the above mentioned reaction with an excess of NaBH\(_4\) (\(>2\) equiv) followed by evaporation of the volatiles leads to the loss of the coordinated acetonitrile ligands and formation of the hydrido borohydride complex 2.\[^{15}\]

Treatment of a solution of 1 with carbon monoxide in a 1:1 mixture of acetonitrile and ethanol results in a color change from deep red to orange within two hours. The \(^{31}\)P\{1H\} NMR spectrum of the product exhibits a singlet resonance at \(\delta = 107.22\) ppm (slightly shifted compared to 1) and a triplet at \(\delta = -5.98\) ppm for the hydride ligand in the \(^1\)H NMR spectrum, indicating that a stronger \(\sigma\)-donor ligand is now bound trans to the hydride. The appearance of a strong band at 1951 cm\(^{-1}\) in the IR spectrum supports the formation of an iron carbonyl complex. The molecular structure of 3 shows the iron(II) center of the cationic complex in an octahedral environment with the carbon monoxide ligand trans to the hydride and the remaining acetonitrile trans to the pyridine nitrogen.\[^{15}\] Owing to the strong trans effect of the hydride ligand the acetonitrile ligand in the apical position in 1 is exclusively substituted.

The trans-dihydride complex 4 is obtained by solvent evaporation after two hours stirring under an atmosphere of carbon monoxide, followed by addition of tetrahydrofuran to the residue and stirring of the suspension for 24 to 48 h. The treatment of complex 3 with THF was necessary for the reaction to proceed. It is likely that the coordinated acetonitrile is slowly released during this period and a borohydride counter ion becomes coordinated. The corresponding hydrido borohydride complex could not be detected, indicating that one signal at \(\delta = 1.44\) ppm for the tert-butyl groups and one signal at \(\delta = 3.04\) ppm for the benzyl positions of the coordinated \(\text{Bu-PNP}\) ligand. The infrared spectrum of 4 exhibits a strong carbonyl band centered at 1865 cm\(^{-1}\), consistent with an electron-rich iron(II) center. In accordance with the NMR spectra, the crystal structure of 4 displays an iron(II) center with a distorted octahedral environment (Figure 1). The CO ligand and the \(\text{Bu-PNP}\) ligand form a plane, while the two hydride ligands occupy the apical positions.

Initially, the trans-dihydride complex 4 was investigated as a catalyst for the hydrogenation of sodium bicarbonate under various conditions. Significant activity was observed only when water was used as solvent, with small amounts of THF as co-solvent (Table 1). Experiments at different temperatures were conducted using 8.3 bar of hydrogen pressure (entries 1–5). The highest activities of complex 4 in the hydrogenation of sodium bicarbonate are observed at 60°C (entry 3, TON = 200) and 80°C (entry 4, TON = 320), while at 100°C turnover numbers of only 70 are achieved (entry 5).

\[
\begin{array}{cccc}
\text{Entry} & \rho(\text{H}_2) & T & \text{Yield} & \text{TON} \\
\text{[bar]} & {^\circ}\text{C} & \% & \\
1 & 8.3 & 23 & 0.2 & 2 \\
2 & 8.3 & 40 & 3.2 & 32 \\
3 & 8.3 & 60 & 20.0 & 200 \\
4 & 8.3 & 80 & 32.0 & 320 \\
5 & 8.3 & 100 & 7.0 & 70 \\
6 & 6.2 & 80 & 26.7 & 267 \\
7 & 10 & 80 & 13.9 & 139 \\
8\[{^e}\] & 8.3 & 80 & 1.5 & 15 \\
\end{array}
\]

\[^{a}\] Reaction conditions: 4 (0.005 mmol), NaHCO\(_3\) (5 mmol), H\(_2\)O/THF (10:1), \(0.1\) mol\% 4, \(16\) h. \[^{b}\] Pressure at room temperature. \[^{c}\] Based on \(^1\)H NMR analysis using dimethylformamide as internal standard. \[^{d}\] Mol of sodium formate per mol of catalyst. \[^{e}\] Na\(_2\)CO\(_3\) (5 mmol) was used instead of NaHCO\(_3\).

\[\text{NaHCO}_3 + \text{H}_2 \rightarrow \text{NaOOCH} + \text{H}_2\text{O}\]

Figure 1. Molecular structure of 4, selected bond lengths [Å] and angles [°]: Fe1–P1 2.1777(4), Fe1–P2 2.1802(4), Fe1–N1 2.0155(11), Fe1–C1 1.7062(18), Fe1–H1 1.42(2), Fe1–H2 1.57(2), C1–O1 1.705(18) (thermal ellipsoids set at 50% probability, the hydrogen atoms of the \(\text{Bu-PNP}\) ligand are omitted for clarity).

Table 1: Iron-catalyzed hydrogenation of bicarbonate.\[^{a}\]
Interestingly, even at ambient temperature the formation of sodium formate is still observed (entry 1, TON = 2) and activity is significantly increased at 40°C (entry 2, TON = 32).

When NaOH is employed under the same conditions instead of NaHCO₃, the reaction proceeds very slowly and only very low conversion is obtained (Table 1, entry 8, TON = 15). With turnover numbers of 320 at 8.3 bar hydrogen pressure, complex 4 is a considerably more efficient catalyst for the hydrogenation of bicarbonates than the most active previously reported iron catalyst, which achieved a turnover number of 112 at 30 bar of hydrogen pressure.[2] Catalyst 4 can also compete with known noble metal catalysts, such as [RuCl₂(tppms)₂]_2/tppms (TON = 108, p(H₂) = 10 bar)[7] or [HRu(ac)(tppms)]_2/tppms (TON = 284, p(H₂) = 10 bar) (ppms = sodium 3-sulfonatophenyldiphosphine).[8]

When a 1:1 mixture of carbon dioxide and hydrogen with aqueous sodium hydroxide is utilized instead of sodium bicarbonate under the same total pressure of 8.3 bar, sodium formate was formed with a similar turnover number of 337 after 14 h (Table 2, entry 1). Changing the ratio of hydrogen to carbon dioxide from 1:1 to 2:1 resulted in significantly increased turnover numbers of 480 and turnover frequencies of 60 h⁻¹ (entry 2). In contrast to the case of bicarbonate, in which increased hydrogen pressure (10 bar, Table 1, entry 7) did not result in greater efficacy, the hydrogenation of carbon dioxide at a total pressure of 10 bar gave a turnover number of 458 with a 1:1 ratio of hydrogen and carbon dioxide (entry 3) and 532 with 2:1 ratio (entry 4).

Next, we examined the effect of base concentration on the reaction. Typically, base concentrations of 1 molL⁻¹ or less are used in transition-metal-catalyzed hydrogenations of carbon dioxide. When the reaction is carried out in a 0.5 m NaOH solution lower turnover numbers are observed (Table 2, entry 5). With increasing sodium hydroxide concentration the activity of catalyst 4 steadily increased and resulted in the highest activity observed so far in 2 m NaOH solutions, with a turnover number of 788 and a turnover frequency of 156 h⁻¹ (entries 4–7). In comparison with state-of-the-art noble metal catalysts for the hydrogenation of carbon dioxide, complex 4 displays a surprisingly similar activity. For example, one of the most active catalysts reported to date is the iridium(III) complex [Cp*Ir(dhpt)-Cl]Cl (Cp* = η⁵-pentamethylcyclopentadienyl, dhpt = 4,7-dihydroxy-1,10-phenanthroline), which is capable of hydrogenating CO₂ in aqueous KOH with turnover numbers of 8500 under a total pressure of 10 bar.[9] Although the turnover number is approximately one order of magnitude higher than with complex 4, significantly lower turnover frequencies (93.4 h⁻¹) and lower yields of the formate salt (17%) were achieved under these conditions with the iridium catalyst. Hazari and co-workers achieved turnover numbers of 3932 and turnover frequencies of 164 h⁻¹ with the iridium(III) pincer complex [(PNP)IrH₂(OOCH)], employing 13.8 bar of total pressure at 185°C (yield = 1%; PNP = HN(CH₂CH₂PPr₂)₂).[10]

In order to gain mechanistic understanding of the iron-catalyzed hydrogenation of carbon dioxide, complex 4 was investigated in stoichiometric reactions. Exposure of a pentane solution of 4 to carbon dioxide resulted in the immediate formation of an orange precipitate (Scheme 2).

### Table 2: Iron-catalyzed hydrogenation of CO₂[4]

<table>
<thead>
<tr>
<th>Entry</th>
<th>p(H₂)[b]</th>
<th>p(CO₂), p(H₂)[b]</th>
<th>ωNaOH</th>
<th>t</th>
<th>Yield[3]</th>
<th>TON[d]</th>
<th>TOF[h⁻¹]</th>
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<tr>
<td>1</td>
<td>4.15</td>
<td>4.15</td>
<td>1</td>
<td>14</td>
<td>33.7</td>
<td>337</td>
<td>24</td>
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<td>2</td>
<td>5.52</td>
<td>2.76</td>
<td>1</td>
<td>8</td>
<td>48.0</td>
<td>480</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>10</td>
<td>45.8</td>
<td>458</td>
<td>46</td>
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<tr>
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<td>6.66</td>
<td>3.33</td>
<td>1</td>
<td>10</td>
<td>53.2</td>
<td>532</td>
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</tr>
<tr>
<td>5</td>
<td>6.66</td>
<td>3.33</td>
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<tr>
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<td>3.33</td>
<td>2</td>
<td>5</td>
<td>39.4</td>
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<td>3.33</td>
<td>3</td>
<td>5</td>
<td>19.9</td>
<td>597</td>
<td>119</td>
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</table>

[a] Reaction conditions: 4 (0.005 mmol), NaOH, H₂O (5 mL), THF (0.5 mL). [b] Pressure at room temperature. [c] Based on 1H NMR analysis using dimethylformamide as internal standard. [d] Mol of sodium formate per mol of catalyst.

The NMR spectrum of the newly formed compound exhibits a singlet at δ = 109.51 ppm in and the H NMR spectrum a triplet resonance for the hydride ligand is observed at δ = −22.64 ppm that integrates to one. Appearance of two virtual triplets for the tert-butyl groups and a ABX spin system for the benzyl protons of the pincer ligand indicate reduced symmetry in comparison to 4. In addition, a singlet resonance at δ = −8.41 ppm is observed in the H NMR spectrum which correlates to a singlet resonance at δ = 172.35 ppm in the 31C[1]H NMR spectrum (by 1H–13C HSQC NMR), suggesting that the corresponding hydrido formate complex [(Bu-PNP)Fe(H)(CO)(η⁵-OOCH)] (5) is formed in the reaction with carbon dioxide. The IR spectrum exhibits a strong absorption centered at 1885 cm⁻¹, confirming that carbon monoxide is bound to the iron(II) center in this complex. The formate ligand gives rise to a strong absorption at 1613 cm⁻¹ for asymmetric stretching vibration and at 1319 cm⁻¹ for symmetric stretching vibration in IR spectrum. Finally, the molecular structure is confirmed by single-crystal X-ray diffraction (Figure 2). The iron(II) center adopts a distorted octahedral coordination by the pincer ligand, carbon monoxide, a hydride and a formate ligand, with the hydride ligand located trans to the formate ligand.

This stoichiometric reaction suggests that reduction of carbon dioxide proceeds through a direct attack on the trans-dihydrido complex 4 followed by formation of the oxygen-bound hydrido formate complex 5. When 5 is dissolved in D₂O, or when 4 is reacted with NaHCO₃ in D₂O, a new
formate ligand in resonance at $d_{\text{res}}$.

Scheme 3. Following direct attack of CO$_2$ on the hydride

ligand of $A$ is replaced by a weaker donor ligand in the new

complex. It is likely that a cationic water-coordinated com-

plex $[(tBu-PNP)Fe(H)(CO)(H_2O)]^+$ is formed under these

conditions. Upon addition of an excess of KOH (20 equiv) no change in the NMR spectra was detected.

Based on these observations, a possible reaction mech-

anism for the hydrogenation of carbon dioxide is outlined in

Scheme 3. Following direct attack of CO$_2$ on the hydride

ligand of $A$, the oxygen-bound formate complex $B$ is formed.

The formate ligand in $B$ is easily replaced by a water mole-

cule, to give the cationic complex $C$. Under hydrogen pressure the dihydrogen-coordinated species $A$ is possibly formed, which

regenerates complex $A$ by heterolytic cleavage of the coordi-

nated H$_2$ by $\cdot$OH ($B$) or by dearomatization and subsequent

proton migration ($C$). Recently, similar catalytic cycles have

been postulated in computational studies on iridium, cobalt

and iron pincer complexes using density functional

theory.[10,17]

In conclusion we have developed an efficient iron catalyst,

which is capable of hydrogenating carbon dioxide under

remarkably low pressures and with high turnover numbers.

The reaction likely proceeds through direct attack of the iron

hydride to the carbon dioxide, followed by replacement of the

resulting formate ligand by water. Dihydrogen coordination,

prior to heterolytic cleavage of H$_2$ by hydroxide or dearoma-

tization and subsequent proton migration are plausible path-

ways for the regeneration of the trans-dihydride complex $A$.

The observed activity is comparable to known noble metal

catalysts and highlights the enormous potential of iron-based

catalysts for possible applications in the future.

The reaction of the trans-dihydride complex $[(tBu-PNP)-

Fe(H)(CO)]$ (4) with carbon dioxide in aprotic solvents such

as pentane resulted in the formation of the isolable hydrido

formate complex $[(tBu-PNP)Fe(H)(CO)(\eta^1-\text{OOCH})]$ (5). NMR investigations show that the formate ligand is easily

replaced by a water ligand in aqueous solution.

**Experimental Section**

General procedure for catalytic hydrogenation of NaHCO$_3$: A 90 mL

Fischer–Porter tube was charged under nitrogen with the catalyst $1$ (0.005 mmol) dissolved in 0.5 mL THF and NaHCO$_3$ (5 mmol) dissolved in 5 mL H$_2$O. The tube was pressurized at ambient temperature with hydrogen and the solution was stirred at the specified temperature for 16 h (Table 1). After the reaction, the Fischer–Porter tube was cooled to room temperature with water and the pressure was released. Dimethylformamide (1 mmol) was added to the reaction mixture as an internal standard and 0.05 mL of the mixture were dissolved in D$_2$O for determination of the yield by $^1$H NMR spectroscopy.

General procedure for catalytic hydrogenation of CO$_2$: A 90 mL

Fischer–Porter tube was charged under nitrogen with the catalyst $1$ (0.005 mmol) dissolved in 0.5 mL THF and 5 mL of an aqueous NaOH solution with the specified concentration (Table 2). The tube was pressurized with CO$_2$ and allowed to equilibrate for 5 min. After this period the specified hydrogen amount was added to the tube and the reaction mixture was heated to 80°C. After the reaction, the Fischer–Porter tube was cooled with water and the pressure was released. Dimethylformamide (1 mmol) was added to the reaction mixture as an internal standard and 0.05 mL of the mixture were dissolved in D$_2$O for determination of the yield by $^1$H NMR spectroscopy.

CCDC 830169 (1), 830170 (2), 830171 (3), 830172 (4), and 830173 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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