Efficient and Mild Carbon Dioxide Hydrogenation to Formate Catalyzed by Fe(II)-Hydridocarbonyl Complexes bearing 2,6-(diaminopyridyl)diphosphine Pincer Ligands.

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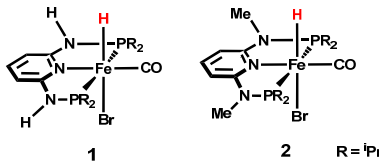
ABSTRACT: Fe(II) hydridocarbonyl complexes supported by PNP pincer ligands based on the 2,6-diaminopyridine scaffold were found to promote the catalytic hydrogenation of CO_2 and $NaHCO_3$ to formate in protic solvents in the presence of bases, reaching quantitative yields and high TONs under mild reaction conditions, with pressures as low as 8.5 bar and temperature as low as 25 °C. NMR and DFT studies highlighted the role of dihydrido and hydridoformate complexes in catalysis.

KEYWORDS . CO_2 hydrogenation • iron pincer complexes • homogeneous catalysis • mechanistic studies • DFT calculations.

INTRODUCTION

The use of CO_2 as a C1-source is a matter of great interest due to its high abundance, availability and low cost. In particular, its reduction to HCOOH or derivatives has attracted significant attention in recent years, since it holds the potential for reversible hydrogen storage.[1] The reduction of $NaHCO_3$ is also of interest, as CO_2 can be easily trapped in basic solutions and reversible hydrogen storage cycles based on bicarbonate and formate have been proposed.[2] The most efficient catalysts for CO_2 hydrogenation are typically based on expensive noble metals such as ruthenium or iridium.[3] In the quest for cheaper alternatives, the preparation of well-defined earth abundant metal catalysts of comparable activity is highly desirable and important progresses have been made recently.[4] Efficient iron based catalysts supported by tetraphosphine ligands have been reported by Beller[4a,b] and some of us,[4c] whereas Milstein reported that the iron pincer complex [Fe(PNP)$(H)_2$(CO)] (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) catalyzes CO_2 hydrogenation at low pressure.[4d] More recently, Hazari and co-workers achieved impressive catalytic activities in Fe-catalyzed CO_2 hydrogenation reaching turnover numbers (TONs) up to 79600 using iron PNP pincer complexes in the presence of Lewis acid (LA) co-catalysts.[4e] In recent years, some of us developed a new class of PNP pincer complexes based on the 2,6-diaminopyridine scaffold where the PR_2 moieties of the PNP ligand are connected to the pyridine ring via NH, N-alkyl or N-aryl spacers.[5] Among these, iron hydrido carbonyl complexes [Fe(PNP^H-*i*Pr)(H)(CO)(Br)] (**1**) and [Fe(PNP^{Me}-*i*Pr)(H)(CO)(Br)] (**2**) shown in Scheme 1 were shown to be active catalysts for hydrogenation reactions.[5c] Mechanistic studies showed that the N–H spacer of the PNP ligand in **1** can work as a bifunctional catalyst promoting metal-ligand cooperation,[5c,d] while the N–Me spacer in complex **2** prevents such a possibility. In addition, the presence of a labile bromide and strong σ-donating H and CO ligands, could give the ideal donor set suitable for catalytic CO_2 hydrogenation.[4d] Thus, we investigated the activities of these complexes for CO_2 and $NaHCO_3$ hydrogenation reactions.



1 **2** R = ^{i}Pr

Scheme1. Fe-PNP pincer complexes **1** and **2**.

RESULTS AND DISCUSSION

Catalytic Studies. Initially, the catalytic activities of **1** and **2** in $NaHCO_3$ hydrogenation were tested in different solvents using 0.05 mol% catalyst at 80 °C, 90 bar H_2, 24 h (Table S1). The best results were obtained in H_2O/THF (4:1) mixtures which ensure good solubility of both catalysts and substrate, reaching 98% formate yield and TON = 1964 for **1** and 52% formate yield and TON = 1036 for **2**, respectively. In MeOH, TONs and yields decrease by ca. 50% with both catalysts, whereas the reaction does not proceed in neat THF indicating the need of a protic solvent. In all cases, **1** performed better than **2** under analogous conditions (see SI for details). Based on the solvent screening results, the hydrogenation of $NaHCO_3$

in H_2O/THF was then studied with **1** under different conditions of temperature, pressure and catalyst loading (Table 1). In the presence of only 0.005 mol% of **1**, TONs up to 4560 could be achieved at 80 °C, 90 bar H_2 after 24h (entry 2). Either higher or lower temperatures resulted in lower turnover numbers (entries 3,4). Noteworthy, the reaction proceeds *even at room temperature* giving a TON = 188 after 72h (entry 5). Reducing the H_2 pressure resulted in a drop of TONs (entries 6,7), yet at higher catalyst loadings (0.1 mol%) sodium formate was obtained (14% yield) with a TON of 140 at only 8.5 bar H_2 (Milstein's conditions)[4d] after 16h (entry 8).

Table 1. Hydrogenation of $NaHCO_3$ to $NaHCO_2$ with **1** at different catalyst loadings, temperatures and pressures.[a]

Entry[a]	Cat.**1** [mol%]	T [°C]	P [bar]	TON[b]	t[h]	Yield[c] [%]
1	0.05	80	90	1964	24	98
2	0.005	80	90	4560	24	23
3	0.005	100	90	400	24	2
4	0.005	60	90	2360	24	12
5	0.05	25	90	188	72	9
6	0.005	80	60	640	24	3
7	0.005	80	30	80	24	<1
8	0.1	80	8.5	140	16	14

[a] General reaction conditions: 20 mmol $NaHCO_3$, 0.01 - 0.001 mmol catalyst, 25 mL H_2O/THF 4:1, 80 °C, 90 bar, 24h. [b] TON = (mmol of formate)/(mmol of catalyst). [c] Yields calculated from the integration of ^{1}H NMR signals due to $NaHCO_2$, using DMF as internal standard.

Next, the hydrogenation of CO_2 to formate in H_2O/THF (4:1) in the presence of **1** and NaOH as base was studied (Table 2), reaching TONs up to 1220 with nearly quantitative yield under optimized conditions (catalyst/NaOH = 1/1250, CO_2/H_2 = 40/40 bar, 80°C, 21h).

Table 2. Hydrogenation of CO_2 to formate with **1** using different solvents and bases.[a]

Entry	Cat. **1** [mol%]	Base	Solvent	TON[e]	Yield[f] [%]
1	0.08	NaOH	H_2O/THF	1220	98
2[b]	0.04	NaOH	H_2O/THF	608	24
3[c]	0.008	NaOH	H_2O/THF	120	1
4[d]	0.04	NaOH	H_2O/THF	656	26
5	0.08	DBU	EtOH	0	0
6	0.08	DMOA	EtOH	0	0
7	0.08	NEt_3	EtOH	288	23
8	0.08	-	EtOH	0	0
9	0.08	DBU	THF	0	0

[a] General reaction conditions: 12.5 mmol base, 0.01 mmol catalyst, 25.0 mL solvent, 80 °C, 80 bar total pressure, 21 h. [b] 25.0 mmol base. [c] 0.001 mmol catalyst. [d] 0.005 mmol catalyst. [e] TON = (mmol of formate)/(mmol of catalyst). [f] Yields calculated from the integration of ^{1}H NMR signals due to $NaHCO_2$, using DMF as internal standard.

Higher NaOH/catalyst ratios gave worse results regardless of concentrations (entries 2-4). We then tested the hydrogenation of CO_2 with **1** in EtOH in the presence of different amine bases. Quite surprisingly, formate was not formed using either DBU (1,8-diaza-bicyclo[5.4.0]undec-7-ene) or DMOA (N,N-dimethyloctylamine), whereas in the presence of NEt_3 formate was obtained only in low yields (entries 5-7). The observation that complex **1** fails to catalyze the hydrogenation of CO_2 in EtOH in the presence of amine bases such as DBU or DMOA may be attributed to the fact that EtOH appears to prevent the formation of dihydrides,[5c] which are expected to be the catalytically active species in this reaction. No reaction occurred in EtOH in the absence of base (entry 8), nor in THF with DBU as base due to catalyst decomposition (entry 9).

A complete screening of the effects of catalyst concentration, nature of base, solvent and temperature for CO_2 hydrogenation in the presence of **2** was then carried out (Table 3).

Table 3. Hydrogenation of CO_2 to formate with **2** using different solvents and bases.[a]

Entry	Cat. **2** [mol%]	Base	Solvent	T [°C]	TON[i]	Yield[j] [%]
1	0.08	NaOH	H_2O/THF	80	680	54
2[b]	0.04	NaOH	H_2O/THF	80	372	15
3	0.08	NaOH	MeOH	80	220	18
4	0.08	NaOH	EtOH	80	654	53
5	0.08	DBU	EtOH	80	1153	92
6	0.08	DMOA	EtOH	80	452	36
7	0.08	NEt_3	EtOH	80	686	55
8	0.08	-	EtOH	80	0	0
9	0.08	DBU	THF	80	0	0
10[c,d]	0.1	DBU	EtOH	80	480	48
11[c]	0.1	DBU	EtOH	25	856	86
12[c,e]	0.1	DBU	EtOH	25	1032	103
13[c,f]	0.01	DBU	EtOH	80	9840	98
14	0.01	DBU	EtOH	25	465	5
15	0.005	DBU	EtOH	80	10275	21
16[c,g]	0.001	DBU	EtOH	80	5000	5
17[c,f,h]	0.01	DBU	EtOH	80	620	6
18[a]	-	DBU	EtOH	80	0	0
19[k]	0.08	DBU	EtOH	80	1163	93

[a] General reaction conditions: 12.5 mmol base, 0.01 mmol catalyst, 25.0 mL solvent, 21 h. [b] 25.0 mmol base. [c] 10.0 mmol base. [d] 8.5 bar (CO_2/H_2 = 1:1) total pressure. [e] 72 h. [f] 0.001 mmol catalyst. [g] 0.0001 mmol catalyst. [h] In the presence of LiOTF as Lewis Acid additive, DBU:LiOTf = 7.5. [i] TON = (mmol of formate)/(mmol of catalyst). [j] Yields calculated from the integration of ^{1}H NMR signals due to $NaHCO_2$, using DMF as internal standard. [k] As for [a], Hg(0) added.

As for $NaHCO_3$ hydrogenation, catalyst **2** showed poorer performance compared to **1** in the hydrogenation of CO_2 in H_2O/THF (4:1) in the presence of NaOH (Table 3, entries 1,2 *vs* Table 2, entries 1,2). Among alcohols, reactions in EtOH gave comparable activity to what observed in H_2O/THF (entry 4), whereas worse performance was achieved in MeOH (entry 3). Based on the solvent screening results, amine screening

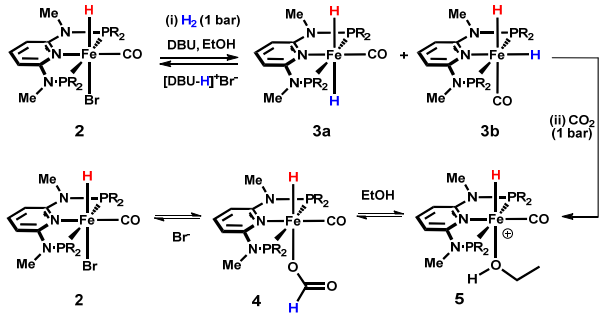
was then studied for CO_2 hydrogenation with **2** in EtOH. To our delight, using DBU as base gave nearly quantitative formate yield (>90%) with a TON of 1153 at 80 °C under 80 bar total pressure (entry 5). Using either DMOA or NEt_3 instead of DBU resulted in lower TONs (entries 6,7) and no reaction occurred in the absence of base (entry 8) or with DBU in THF (entry 9) under otherwise analogous conditions.

The potential of catalyst **2** was then further explored under milder reaction conditions. At first, the effect of lower total pressure was determined. In the presence of 0.1 mol% of **2** a TON of 480 was reached after 21h at 80 °C under only 8.5 bar H_2/CO_2 (1:1) (entry 10), an activity comparable to that of other known iron pincer catalysts.[4d,f] Then, temperature effects were studied. At 25 °C, catalyst **2** manifested a remarkable catalytic activity, affording sodium formate in high yields[6] with a TON of 856 after 21h and of 1032 after 72h under 80 bar initial pressure (entries 11,12) in the presence of 0.1 mol% catalyst. To the best of our knowledge, these are *the highest TONs obtained for Fe-catalyzed CO_2 hydrogenation at room temperature* to date.

Finally, the effect of catalyst loading was studied. At lower catalyst loading (0.01 mol%) sodium formate was still obtained in excellent yield (98%) with a TON of 9840 after 21h at 80 °C (entry 13), whereas a TON of 465 was achieved at 25 °C after 21h at 80 bar (entry 14). Reducing further the catalyst loading to 0.005 mol%, CO_2 formate was still achieved with a high TON of 10275 albeit in low yield respect to the base (21%, entry 15). Lowering further the catalyst amount (0.001 mol%) under the same conditions resulted in a lower TON of 5000 (entry 16). We also tested the effect of additives at high substrate to catalyst ratios. Surprisingly, in contrast to what observed by Hazari *et al.*,[4e] the use of a LA co-catalyst such as LiOTf affected negatively the performance (entry 17). Colloidal metal catalysis was ruled out by carrying out Hg poisoning test which gave comparable results to what observed in the original run (entry 19 vs. 5).

Mechanistic Studies. In order to gain insights in the reaction mechanism, the reactivity of complex **2** was investigated in stoichiometric reactions by NMR techniques. Exposure of an EtOH solution of **2** to H_2 (1 bar) in the presence of KO*t*Bu resulted in the quantitative formation of dihydrides **3a** and **3b** (*cis* and *trans* isomers).[5c,7] The $^{31}P\{^1H\}$ NMR spectrum exhibits two singlets at 187.5 ppm (**3a**) and 189.9 ppm (**3b**), while the ^1H NMR exhibits a triplet at -9.57 ppm for **3a** and a broad resonance at -13.86 ppm for **3b**. Upon cooling to -50 °C, the broad signal starts to split into two separate triplets centered at -8.82 ppm and -17.64 ppm.[7] Using DBU as base, NMR analysis revealed that only 40% of **2** was converted into the Fe(II) dihydrides **3**, even after prolonged standing under an hydrogen atmosphere, suggesting that **2** and **3** are in equilibrium with each other (Scheme 2, step i). This may be explained by the lower pK_a value of $[DBU\text{-}H]^+$ in comparison to tBuOH.[8]

Next, the EtOH/base solution containing *in situ* formed **3** was stirred under an atmosphere of CO_2 for 30 min. Regardless of the base used, we observed the formation of the hydridoformate complex [Fe(PNP^{Me}-*i*Pr)(H)(CO)(η^1-O_2CH)] (**4**, Scheme 2, step ii) characterized by a triplet at -24.71 ppm for the hydride and a singlet at 7.96 ppm for the proton of the formate ligand, which both integrate to 1 in the ^1H NMR spectrum (see SI).



Scheme 2. Stepwise reaction of **2** with H_2 (i) and CO_2 (ii) in the presence of DBU as base in EtOH.

Under these reaction conditions, **4** is in equilibrium with **2** due to the presence of bromide anions in solution. As a result, a broad signal at 8.65 ppm due to free formate salt appeared in the corresponding ^1H NMR spectrum. In addition, the cationic hydride complex [Fe(PNP^{Me}-*i*Pr)(H)(CO)(EtOH)]$^+$ (**5**) was present (Scheme 2), exhibiting a ^1H NMR triplet resonance at -25.57 ppm. The $^{31}P\{^1H\}$ NMR chemical shift of **5** is very close to that of formate complex **4**. However, no signal for the free formate counteranion could be found in the ^1H spectrum of **5**. Noteworthy, complex **5** was independently synthesized by treatment of **2** with silver salts in EtOH.[7] In a separate experiment, stirring a mixture of **2** and sodium formate (4 equiv.) in EtOH for 1h also affords a mixture of **2**, **4** and **5**. In another experiment, this time starting from *isolated* **3**, the reaction with CO_2 in EtOH afforded **5** with minor traces of **4**. Evidently, the formate ligand is easily displaced by an excess of solvent under these conditions.

Single crystals of **4** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a concentrated solution of the complex in THF under an atmosphere of CO_2. The solid state structure of **4** confirms the geometry proposed on the basis of NMR data. A structural view is depicted in Figure 1 with selected bond distances given in the caption. Complex **4** adopts a distorted octahedral geometry around the metal center with the fomate and hydride ligands trans to each other and in *cis* position to the CO ligand. The hydride could be unambiguously located in the difference Fourier maps. The Fe-H distance was refined to 1.46(2) Å.

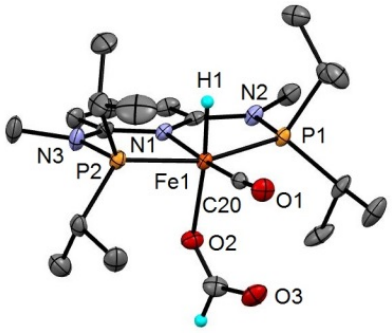
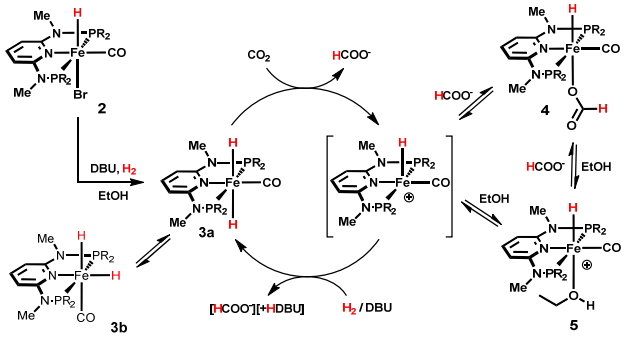


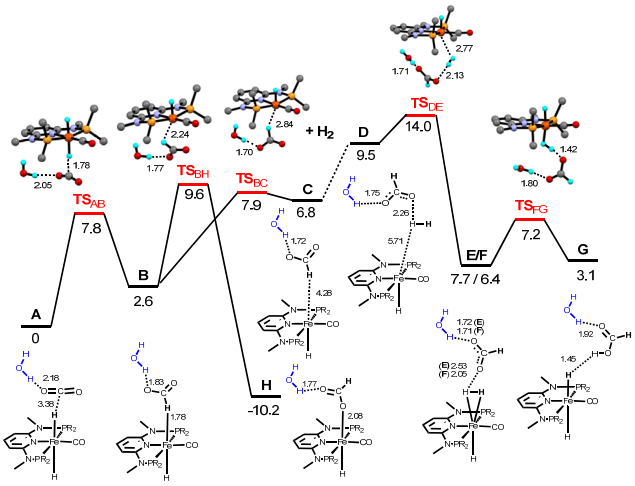
Figure 1. Structural view of **4** showing 50% thermal ellipsoids (most H atoms and a second independent complex omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1-P1 2.1765(7), Fe1-P2 2.1789(7), Fe1-N1 2.004(2), Fe1-C20 1.737(2), Fe1-O2 2.032(2), Fe1-H1 1.46(2), P1-Fe1-P2 162.57(2), N1-Fe1-C20 175.58 (8).

Based on the experimental evidence, a catalytic cycle for CO_2 hydrogenation starting from **2** can be proposed, encompassing formation of dihydrides **3**, CO_2 insertion to give the hydrido formate complex **4** followed by hydrogenolysis and formate elimination giving back **3** in the presence of base. Solvent-assisted formate decoordination in **4** may occur to leave a highly reactive, unobserved pentacoordinate cationic Fe(II) hydridocarbonyl species, which can be stabilized by EtOH coordination to give **5**, observed by NMR (Scheme 3).

Further mechanistic details on CO_2 hydrogenation mechanism were obtained by DFT calculations using **3a** as the initial active species. The free energy profile is shown in Scheme 5. Computational details are presented as SI. The model used in the calculations included one explicit water molecule that provides H-bond stabilization of the intermediates. The highlights of the calculated mechanism are presented in Scheme 4 with relevant intermediates and the corresponding free energy values.[9]



Scheme 3. Proposed catalytic cycle for CO_2 hydrogenation with **3a.**



Scheme 4. Free energy profile calculated (DFT) for the hydrogenation of CO_2 catalyzed by **3a** (denoted as **A**). The free energy values (kcal/mol) are referred to the initial reactants and relevant distances (Å) are indicated.

In the first step of the calculated mechanism, from **A** to **B**, the hydride attack from complex **3a** to a CO_2 molecule results in a H-bonded formate complex. This is a facile process with a barrier of 7.8 kcal/mol. In the resulting intermediate (**B**) the formate ion is stabilized by a H-bond with the water molecule. From **B**, formate can coordinate the metal giving complex **4** (**H** in Scheme 5), where the formate ligand is bonded through the O-atom. This intermediate represents the potential well of the mechanism, thus it may be viewed as the catalyst resting state. Alternatively, the formate ion dissociates from the metal in **B** to give **C**, opening one coordination position that is occupied by a molecule of H_2 in the following step. Both processes are competitive with barriers within 2 kcal/mol. The reaction pathway proceeds with H_2 addition to **C** yielding the dihydrogen complex **F**. This process has an energy barrier of 14 kcal/mol, corresponding to the highest of the entire mechanism. In the final step, the formate ion is protonated by **F**, regenerating the initial complex **3a** and producing formic acid. Giving the excess of base present in the reaction medium under experimental conditions, formed acid will be then deprotonated in an acid-base reaction that provides the final driving force for the entire process. Importantly, the free formate ion (the reaction product under the experimental conditions) is stabilized by a H-bond with the nearby water molecule in intermediates **E**/**F**.[9] This facilitates the opening of the coordination position that will be used by H_2 in the following step of the mechanism, justifying the need of a protic solvent in the catalytic reaction. A similar reaction mechanism was recently proposed for the selective hydrogenation of aldehydes in EtOH with **3** as catalyst[7] and by other authors on related systems.[10]

CONCLUSIONS

In conclusion, selected Fe(II) pincer-type complexes of 2,6-diaminopyridyl-bis(diisopropylphosphine) gave high activities as catalysts for CO_2 and $NaHCO_3$ reduction to formate under very mild to moderate conditions, even at room temperature. Mechanistic details were obtained by NMR techniques highlighting the role of dihydride and hydridoformate complexes. DFT calculations indicate an outer sphere mechanism with a hydridoformate complex as catalyst resting state and suggest that the overall reaction is pushed forward by the acid-base reaction between the product (formic acid) and the excess base present in solution. Protic solvents promote catalysis by stabilizing the reaction intermediates and assisting formate elimination from the coordination sphere of the metal.

ASSOCIATED CONTENT

Supporting Information. General materials and methods, synthetic procedures, NMR experiments and spectra, cartesian coordinates of the computed structures, crystallographic data for the X-ray structure of **4**, additional catalytic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All authors have given approval to the final version of the manuscript.

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Fe(II) hydrido carbonyl complexes supported by PNP pincer ligands based on 2,6-diaminopyridine scaffold promote CO_2 and $NaHCO_3$ catalytic hydrogenation to formate in the presence of bases and protic solvents, with quantitative yields and high TONs even at room temperature.