Lewis Acid-Assisted Formic Acid Dehydrogenation Using a Pincer-Supported Iron Catalyst

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Ⓢ *Supporting Information*

ABSTRACT: Formic acid (FA) is an attractive compound for H_2 storage. Currently, the most active catalysts for FA dehydrogenation use precious metals. Here, we report a homogeneous iron catalyst that, when used with a Lewis acid (LA) co-catalyst, gives approximately 1,000,000 turnovers for FA dehydrogenation. To date, this is the highest turnover number reported for a first-row transition metal catalyst. Preliminary studies suggest that the LA assists in the decarboxylation of a key iron formate intermediate and can also be used to enhance the reverse process of CO_2 hydrogenation.

Several approaches are currently under investigation to replace fossil fuels as energy vectors.[1] For example, H_2 gas can be directly or electrochemically combusted within a proton-exchange membrane fuel cell.[2] However, as a result of problems with the storage of gaseous H_2 and its low volumetric energy density, chemical hydrogen storage (CHS) based on the reversible hydrogenation/dehydrogenation of small molecules is an attractive alternative.[3] Formic acid (FA) can be obtained renewably from biomass oxidation or CO_2 hydrogenation and is a potential liquid CHS material.[3] Several heterogeneous[3,4] and homogeneous[5] catalysts have been reported that can dehydrogenate FA to a mixture of H_2 and CO_2, which is directly suitable as a feed for fuel cells.[6] The most active systems are based on expensive precious metals such as Ir, Ru, Au, Ag, and Pd. In addition, many of the best homogeneous catalysts either require the addition of base or have a complicated pendant base attached to the ligand framework in order to achieve a high turnover number (TON).[5a−k,m]

Recently, the first homogeneous iron-based systems for FA dehydrogenation were reported.[5f,k,7] Milstein and co-workers reported TONs of up to 100,000 using a pincer-supported system, in the presence of 50 mol% NEt_3 as an additive.[5k] Additionally, Beller et al. described an iron catalyst which requires an extra equivalent of the tetradentate auxiliary ligand and gives a TON of approximately 92,000.[7] Although these results with first-row transition metal catalysts are promising, the TONs and turnover frequencies (TOFs) are still inferior to those achieved with precious metal catalysts, and the role of the additives in the catalytic reactions is unclear.

Previously, we described Ir catalysts for CO_2 hydrogenation[8] and Ru catalysts for ammonia borane dehydrogenation,[9] supported by pincer ligands of the type $HN\{CH_2CH_2(P^iPr_2)\}_2$ ($^{iPr}PN^HP$). We also reported the synthesis of iron complexes with the same ligand,[10] which are related to catalysts for methanol dehydrogenation with strong base,[11] ester[12] and ketone[13] hydrogenation, and the hydrogenation/dehydrogenation of N-heterocycles.[14] Here, we present the synthesis and characterization of a series of $Fe(^RPN^HP)$ compounds and their use as catalysts for FA dehydrogenation without additional base or ligand. We explain instead the strong effect of Lewis acid (LA) co-catalysts, which enable TONs of almost 1,000,000.

The five-coordinate amido complexes **1a** and **1b** were synthesized through the dehydrohalogenation of $(^RPN^HP)Fe(CO)H(Cl)$[10a] ($^RPN^HP = HN\{CH_2CH_2(PR_2)\}_2$; R = ^iPr or Cy) with 1.2 equiv of ^tBuOK (Scheme 1). The molecular structures of **1a** and **1b** in the solid state are shown in Figures S1 and S2. In both cases the coordination of the metal ion can best be described as *pseudo*-trigonal bipyramidal, with the phosphorus atoms in the apical position. There is a Y-shape distortion, as a consequence of strong N→Fe π-donation, which is typical for five-coordinate d^6 ions with one strongly π-donating ligand.[15] Hence, **1a** and **1b** are 18-valence-electron compounds with low-spin ground states, which is a prerequisite for the formation of stable hydrides.[16]

The reaction of FA with both **1a** and **1b** results in addition across the iron amide bond to generate $(^{iPr}PN^HP)Fe(CO)H(COOH)$ (**2a**) and $(^{Cy}PN^HP)Fe(CO)H(COOH)$ (**2b**) (Scheme 1). The ^1H NMR resonances at 9.10 (**2a**) and 9.20 ppm (**2b**) are characteristic of coordinated formate ligands, while signals assignable to the hydride ligands are found at −25.71 (**2a**) and −25.82 ppm (**2b**).

Both the amides (**1a/1b**) and the formate complexes (**2a/2b**), as well as a series of previously reported $^RPN^HP$-supported iron complexes,[10] were tested for the catalytic dehydrogenation of FA (Tables 1 and S2). The reaction conditions described by Milstein with 50 mol% NEt_3 as an additive were utilized. At a relatively high catalyst loading (0.1 mol%), **1a**, **1b**, **2a**, and **2b** gave activity comparable to that of the iron systems reported by Beller[5f,7] and Milstein,[5k] particularly at 80 °C in dioxane. In all cases, the gas mixture produced from catalysis was analyzed by

Scheme 1. Synthesis and Reactivity of Five-Coordinate Iron Amido Species
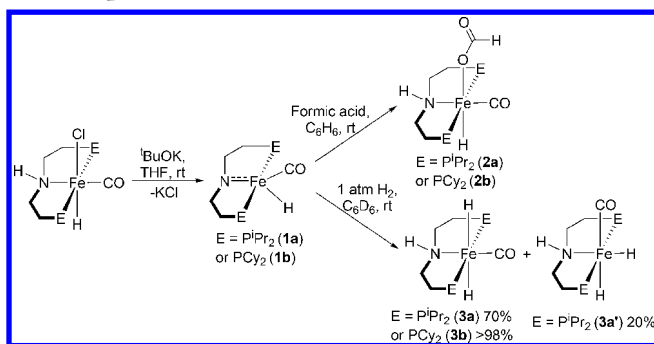
Table 1. FA Dehydrogenation Using 1a, 1b, 2a, and 2b[a]

$$HCO_2H \xrightarrow{\text{cat. (0.1 mol\%), 50 mol\% NEt}_3} H_2 + CO_2$$

	THF, 40 °C		dioxane, 80 °C	
cat.	TOF (h^{-1})[b]	TON (time, h)[c]	TOF (h^{-1})[b]	TON (time, h)[c]
1a	173	346 (5.5)	527	910 (4.5)
1b	220	270 (6)	572	885 (2.5)
2a	238	463 (6)	622	>999 (3)
2b	181	904 (7.5)	739	994 (2.5)

[a]Reaction conditions: FA (110 μL, 2.91 mmol), catalyst (2.91 μmol, 0.10 mol%), 50 mol% NEt$_3$, 5 mL solvent. [b]Turnover frequencies (TOF) were measured after the first hour. [c]Turnover numbers (TON) were measured using a gas buret. All numbers are an average of two runs.

GC and found to be a 1:1 mixture of H$_2$ and CO$_2$ with less than 0.5% CO (see SI). This is comparable to the amount of CO observed in Beller's best iron system.[5f]

Further information about catalysis was obtained through stoichiometric reactions. The reaction of **1a/1b** with a 1:1 mixture of 1 atm H$_2$ and CO$_2$ at room temperature results in clean formation of the formate compounds **2a/2b**. This reaction most likely proceeds via initial heterolytic cleavage of H$_2$, followed by CO$_2$ insertion into the Fe–H bond. Accordingly, in the absence of CO$_2$, **1a/1b** rapidly adds H$_2$ (1 atm) to give the *trans*-dihydride complexes **3a/3b** as the main products (Scheme 1). This reaction is fully reversible, which prevents isolation of **3a/3b** due to facile H$_2$ loss. The *trans*-H$_2$ configuration is supported by the characteristic ^{1}H NMR chemical shifts (−9.57 and −9.69 ppm for **3a** and −9.29 and −9.37 ppm for **3b**) and the mutual coupling constant of the hydride signals ($^2J_{HH}$ = 9.7 Hz for **3a** and 9.5 Hz for **3b**).[13] In the case of **1a**, smaller amounts of the *cis*-H$_2$ complex **3a′** (Scheme 1) are also observed, based on the hydride chemical shifts (−8.63 and −21.13 ppm), hyperfine structure ($^2J_{HH}$ = 15 Hz), and NOESY pattern.[17] ^{1}H EXSY NMR spectroscopy indicates intramolecular hydride exchange within **3a′** and intermolecular exchange of **3a** and **3a′**. Besides these main products, minor quantities of free ^{iPr}PN^{H}P (7%) and the Fe(0) complex (^{iPr}PN^{H}P)Fe(CO)$_2$[10a] (3%) are immediately formed. Over the course of several days, **3a** and **3a′** slowly convert to (^{iPr}PN^{H}P)Fe(CO)$_2$, free ^{iPr}PN^{H}P, and an intractable precipitate. In contrast, presumably due to steric factors, the reaction of **1b** with H$_2$ results in the formation of only the *trans*-dihydride **3b** (Scheme 1). **3b** is also only moderately stable and slowly decomposes to free ^{Cy}PN^{H}P, (^{Cy}PN^{H}P)Fe(CO)$_2$, and an intractable precipitate.

Based on these results, a mechanism for FA dehydrogenation is proposed (Scheme 2). The five-coordinate complexes **1a/1b** can enter the catalytic cycle through addition of FA (Scheme 1) to give the formate complexes **2a/2b**, which are part of the cycle. Subsequent decarboxylation forms dihydrides **3a/3b**, in part the reverse of stoichiometric formation of **2a/2b** from **1a/1b** with H$_2$ and CO$_2$. Accordingly, **3a/3b** are formed in high yield upon heating **2a/2b** at 80 °C in dioxane under H$_2$ (1 atm) (Schemes 3 and S2). In the absence of H$_2$, complete conversion to (^{R}PN^{H}P)Fe(CO)$_2$ (R = ^{i}Pr or Cy), the appropriate free ligand, and an unidentified precipitate were observed (Scheme S1). These products are consistent with the initial formation of **3a/3b** and subsequent decomposition in the absence of H$_2$. In our proposed cycle, regeneration of **2a/2b** and liberation of H$_2$ occur through the reaction of **3a/3b** with FA (see SI). This reaction may involve the formation of molecular H$_2$ complexes, but species of this type were not observed spectroscopically. The catalyst resting state was identified as the formate complexes **2a/2b** using *in situ* ^{31}P NMR spectroscopy. This observation is consistent with decarboxylation being the turnover-limiting step.

The stoichiometric studies confirm the feasibility of each step in the absence of NEt$_3$, yet the presence of base greatly increases catalyst activity (Table 2, entry 1). A variety of other bases, including pyridine and ^{t}BuOK, also promote the catalytic reaction (Table S3). In the case of NEt$_3$, this is presumably through the action of HNEt$_3^+$ formed under the catalytic conditions via the reaction of NEt$_3$ with excess FA. Accordingly, the rate of decarboxylation of **2a/2b**, the proposed turnover-limiting step, is significantly increased in the presence of [HNEt$_3$]$^+$[BF$_4$]$^-$ (Schemes 3 and S2). Although the decarboxylation is a formal β-hydride elimination reaction, the absence of a vacant coordination site on iron requires an indirect pathway. Recently, Milstein and co-workers suggested that decarboxylation in a related iron pincer system proceeds via intramolecular rearrangement to an H-bound formate followed by CO$_2$ elimination.[5k] DFT studies on **2a** support this mechanism (see Scheme 4 and SI), with rate-determining initial rearrangement. Analysis of the transition state for intramolecular rearrangement and the H-bound formate intermediate indicates significant buildup of negative charge on the carboxylate group. Hence, Brønsted acids, like HNEt$_3^+$, can presumably stabilize these species through hydrogen bonding.

Recently, we demonstrated that LAs facilitate β-hydride elimination in nickelalactones by stabilizing negatively charged

Scheme 2. Proposed Mechanism of FA Dehydrogenation
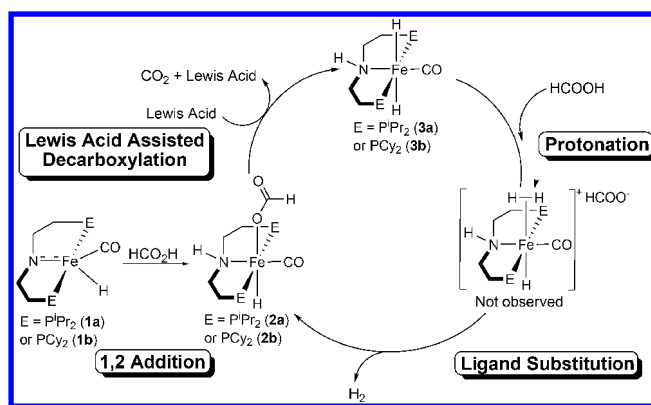
**Scheme 3. Effect of Additive on Decarboxylation of 2a**
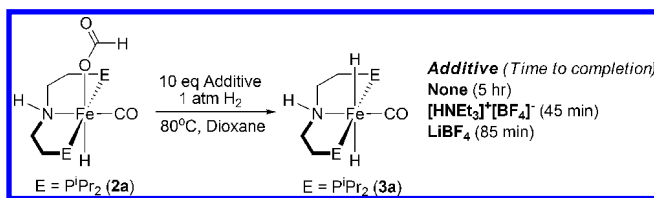
Table 2. LA Screening for FA Dehydrogenation Using 2a[a]

$$HCO_2H \xrightarrow[\text{80 °C, dioxane}]{\text{2a (0.1 mol%), 10 mol% LA}} H_2 + CO_2$$

entry	LA	TOF (h^{-1})[b]	TON (time, h)[c]
1	no additive[d]	–	182 (48 h)
2	$B(C_6F_5)_3$	231	639 (12.5)
3	$HCOONa$[e]	255	>999 (7.5)
4	$NaPF_6$	147	449 (9)
5	$NaBAr^F_4$[f]	193	994 (8)
6	$NaBF_4$	323	>999 (6.5)
7	$NaCl$	263	>999 (7.5)
8	$LiCl$	274	>999 (7)
9	KCl	132	674 (8.5)
10	$CsCl$	112	>999 (7)
11	$CaCl_2$	133	386 (23)
12	$MgCl_2$	260	>999 (8)
13	$LiBF_4$	231	>999 (4 h)

[a]Reaction conditions: FA (110 μL, 2.91 mmol), **2a** (2.91 μmol, 0.10 mol %), LA (0.291 mmol, 10 mol %), 5 mL dioxane, 80 °C. [b]Turnover frequencies (TOF) were measured after the first hour. [c]Turnover numbers (TON) were measured using a gas buret. All numbers are an average of two runs. [d]Reaction performed in the absence of LA or base. [e]9:1 FA:HCOONa. [f]$BAr^F_4 = B\{3,5\text{-}(CF_3)_2C_6H_3\}_4^-$.

Scheme 4. Proposed Pathway for Decarboxylation of 2a/2b in the Absence (a) and Presence (b) of a LA
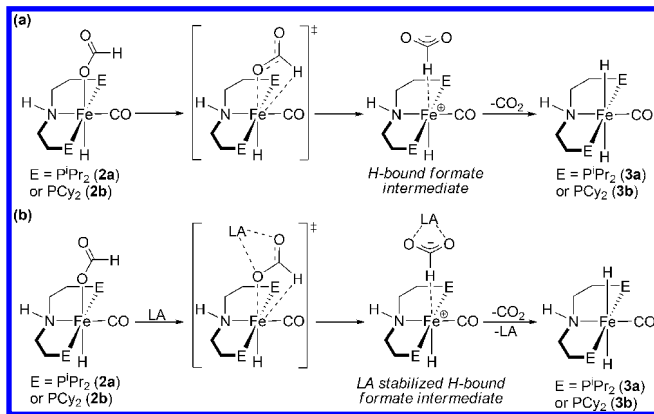
carboxylate groups.[18] Similarly, LA addition in catalytic amounts (10 mol%) promotes FA dehydrogenation with catalysts **2a/2b** (Tables 2 and S4). In general, the highest TON and TOF are achieved with alkali or alkali earth metal salt co-catalysts. Importantly, the enhancement of activity correlates with the chemical affinity for carboxylate, with the best results obtained for Li$^+$ (entries 7–12). Weakly coordinating anions, such as BF$_4^-$, are preferred as anions (entries 3–7). LiBF$_4$ (entry 13) results in the most rapid completion of the reaction; however, full conversion is also obtained with much cheaper additives, such as NaCl. The optimal loading of LA is 10 mol%, with a decrease in efficiency at both lower and higher loadings

(Table S5). A series of standard tests suggest that homogeneous catalysis is occurring (see SI).

A major drawback of NEt$_3$ as an additive with **2a/2b** is the lower yield at low catalyst loading (Table S6). In contrast, complete substrate conversion was obtained using 0.01 mol% **2a**/10 mol% LA (NaCl, NaBF$_4$, or LiBF$_4$), with LiBF$_4$ again giving the fastest time to completion (Table 3). In fact, with catalyst loadings as low as 0.0001 mol% **2a**, a TON of 983,642 and TOF of 196,728 h^{-1} are obtained. These are comparable with the highest TON[Sl] and TOF[Sd,g,h,j] obtained with precious metal systems, without the need for a complicated ligand or external base (see Table S7 for a full comparison).

The LA effect was examined by monitoring the rate of decarboxylation of **2a/2b**, the proposed turnover-limiting step in catalysis, in the presence of 10 equiv of LiBF$_4$ (Scheme 3 and S2). A large rate increase was observed compared to that of reaction without an additive. However, a slightly slower rate was observed compared to when [HNEt$_3$]$^+$[BF$_4$]$^-$ was present, consistent with faster catalysis using NEt$_3$. We propose that the LA increases the rate by stabilizing the transition state to the H-bound formate (Scheme 4). The utility of LA-promoted FA dehydrogenation for other catalysts was also examined. For example, with Beller's best catalyst, [(PP$_3$)FeH]$^+$[BF$_4$]$^-$ (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$),[5f] poor catalytic activity was obtained under our conditions (80 °C, dioxane) in the absence of a co-catalyst (Table S8). The addition of 10 mol% LiBF$_4$ or NaBAr$^F_4$ results in enhancement under our and Beller's conditions (80 °C, propylene carbonate) and eliminates the need for excess ligand to achieve high activity (Table S8).

The utilization of FA as a CHS material requires both H$_2$ liberation and sequestration, which prompted preliminary examination of the LA effect on CO$_2$ hydrogenation. Treatment of **1b** with 300 equiv of 1,8-diazabicycloundecene (DBU) and a 1:1 mixture of 69 atm H$_2$ and CO$_2$ at 80 °C for 12 h gave a modest yield of formate (62%, TON 186). However, the analogous reaction in the presence of 150 equiv of LiBF$_4$ gave nearly full conversion to formate (96%, TON 289) in only 4 h. Thus, LAs enhance both directions of the potential FA utilization cycle.

In conclusion, we have shown that, in the presence of a LA co-catalyst, a new pincer-supported iron catalyst system achieves the highest TON reported for FA dehydrogenation using a first-row transition metal catalyst. Stoichiometric experiments indicate the LA co-catalyst assists in the

Table 3. Optimization of Catalytic Dehydrogenation of FA Using 2a[a]

$$HCO_2H \xrightarrow[\text{80 °C, dioxane}]{\text{2a, 10 mol% LA}} H_2 + CO_2$$

entry	LA	mol% 2a	TOF (h^{-1})[b]	TON (time, h)[c]
1	CsCl	0.01	1 440	7 495 (15)
2	NaCl	0.01	2 142	>9 999 (7)
3	NaBF$_4$	0.01	1 580	>9 999 (6)
4	LiBF$_4$	0.01	1 756	>9 999 (5.5)
5	LiBF$_4$	0.001	21 150	93 600 (6.5)
6	LiBF$_4$	0.0001	196 728[d]	983 642 (9.5)[d]

[a]Reaction conditions: FA (110 μL, 2.91 mmol), **2a**, LA (0.291 mmol, 10 mol%), 5 mL dioxane, 80 °C. [b]Turnover frequencies (TOF) were measured after the first hour. [c]Turnover numbers (TON) were measured using a gas buret. All numbers are an average of two runs. [d]Average of four runs.

decarboxylation of an iron formate intermediate, obviating the need for base or excess ligand. Preliminary experiments indicate that this LA promotion is general for other catalysts for FA dehydrogenation, as well as the reverse process of CO_2 hydrogenation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, X-ray information for **1a** and **1b**, and details about DFT calculations. 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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(17) At room temperature, the hydride peaks are broadened and sharpen below 260 K. The NOESY pattern indicates an *anti* configuration of the H-N-Fe-H moiety, which suggests that **3a′** is not formed directly by H_2 heterolysis, as assumed for **3a** (see SI).

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