

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 H₂ 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 CO₂ hydrogenation.

Several approaches are currently under investigation to replace fossil fuels as energy vectors.¹ For example, H₂ 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 H₂ 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 CO₂ hydrogenation and is a potential liquid CHS material.³ Several heterogeneous^{3,4} and homogeneous⁵ catalysts have been reported that can dehydrogenate FA to a mixture of H₂ and CO₂, 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% NEt₃.^{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 CO₂ hydrogenation⁸ and Ru catalysts for ammonia borane dehydrogenation,⁹ supported by pincer ligands of the type HN{CH₂CH₂(P^RPr₂)₂}₂ (^RPN^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 ester¹² and ketone¹³ 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{CH₂CH₂(PR₂)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 d⁶ 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

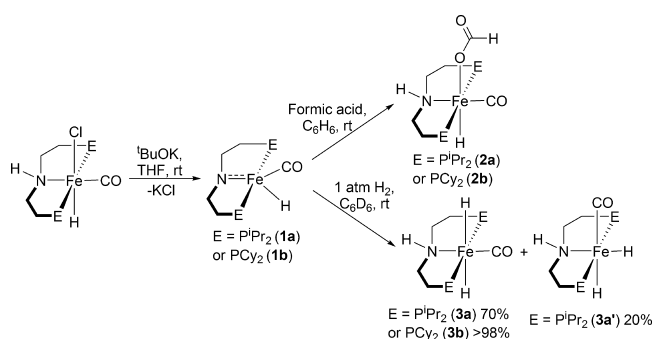
The reaction of FA with both **1a** and **1b** results in addition across the iron amide bond to generate (ⁱPrPN^HP)Fe(CO)H(COOH) (**2a**) and (CyPN^HP)Fe(CO)H(COOH) (**2b**) (Scheme 1). The ¹H NMR resonances at 9.10 (**2a**) and 9.20 ppm (**2b**) are characteristic of coordinated formate ligands, while 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% NEt₃ 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

Received: May 25, 2014

Published: July 7, 2014

Scheme 1. Synthesis and Reactivity of Five-Coordinate Iron Amido Species

Table 1. FA Dehydrogenation Using 1a, 1b, 2a, and 2b^a

$$\text{HCO}_2\text{H} \xrightarrow{\text{cat. (0.1 mol\%), 50 mol\% NEt}_3} \text{H}_2 + \text{CO}_2$$

cat.	THF, 40 °C		dioxane, 80 °C	
	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)

^aReaction conditions: FA (110 μL , 2.91 mmol), catalyst (2.91 μmol , 0.10 mol%), 50 mol% NEt₃, 5 mL solvent. ^bTurnover frequencies (TOF) were measured after the first hour. ^cTurnover 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 H₂ and CO₂ with less than 0.5% CO (see SI). This is comparable to the amount of CO observed in Beller's best iron system.^{5f}

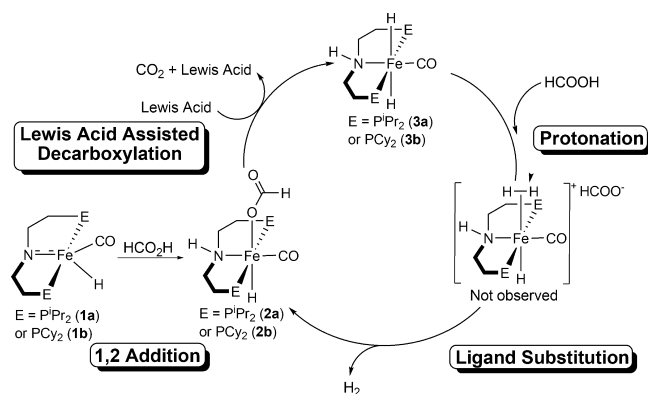
Further information about catalysis was obtained through stoichiometric reactions. The reaction of 1a/1b with a 1:1 mixture of 1 atm H₂ and CO₂ at room temperature results in clean formation of the formate compounds 2a/2b. This reaction most likely proceeds via initial heterolytic cleavage of H₂, followed by CO₂ insertion into the Fe–H bond. Accordingly, in the absence of CO₂, 1a/1b rapidly adds H₂ (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 H₂ loss. The *trans*-H₂ configuration is supported by the characteristic ¹H 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*-H₂ 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 ¹H EXSY NMR spectroscopy indicates intramolecular hydride exchange within 3a' and intermolecular exchange of 3a and 3a'. Besides these main products, minor quantities of free ⁱPrPN^HP (7%) and the Fe(0) complex (ⁱPrPN^HP)Fe(CO)₂^{10a} (3%) are immediately formed. Over the course of several days, 3a and 3a' slowly convert to (ⁱPrPN^HP)Fe(CO)₂, free ⁱPrPN^HP, and an intractable precipitate. In contrast, presumably due to steric factors, the reaction of 1b with H₂ 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^HP, (^{Cy}PN^HP)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 H₂ and CO₂. Accordingly, 3a/3b are formed in high yield upon heating 2a/2b at 80 °C in dioxane under H₂ (1 atm) (Schemes 3 and S2). In the absence of H₂, complete conversion to (^RPN^HP)Fe(CO)₂ (R = ⁱPr 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 H₂. In our proposed cycle, regeneration of 2a/2b and liberation of H₂ occur through the reaction of 3a/3b with FA (see SI). This reaction may involve the formation of molecular H₂ 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* ³¹P NMR spectroscopy. This observation is consistent with decarboxylation being the turnover-limiting step.

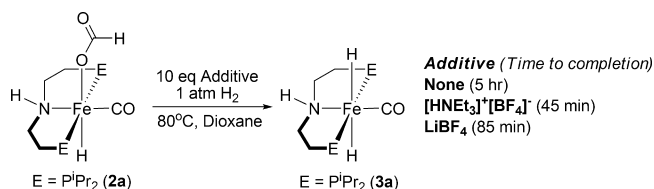
The stoichiometric studies confirm the feasibility of each step in the absence of NEt₃, yet the presence of base greatly increases catalyst activity (Table 2, entry 1). A variety of other bases, including pyridine and ^tBuOK, also promote the catalytic reaction (Table S3). In the case of NEt₃, this is presumably through the action of HNEt₃⁺ formed under the catalytic conditions via the reaction of NEt₃ with excess FA. Accordingly, the rate of decarboxylation of 2a/2b, the proposed turnover-limiting step, is significantly increased in the presence of [HNEt₃]⁺[BF₄][−] (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 CO₂ 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 HNEt₃⁺, 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

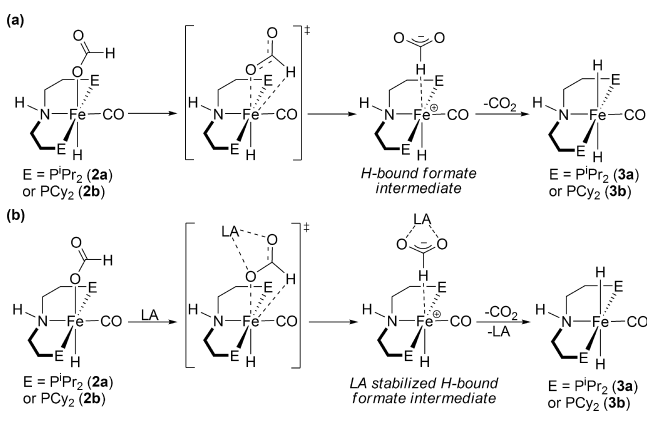
Table 2. LA Screening for FA Dehydrogenation Using 2a^a

$\text{HCO}_2\text{H} \xrightarrow[80^\circ\text{C, dioxane}]{2\text{a (0.1 mol\%), 10 mol\% LA}} \text{H}_2 + \text{CO}_2$

entry	LA	TOF (h ⁻¹) ^b	TON (time, h) ^c
1	no additive ^d	—	182 (48 h)
2	$\text{B}(\text{C}_6\text{F}_5)_3$	231	639 (12.5)
3	HCOONa^e	255	>999 (7.5)
4	NaPF_6	147	449 (9)
5	NaBAR_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)

^aReaction 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. ^bTurnover frequencies (TOF) were measured after the first hour. ^cTurnover numbers (TON) were measured using a gas buret. All numbers are an average of two runs. ^dReaction performed in the absence of LA or base. ^e9:1 FA:HCOONa. ^f $\text{BAR}_4 = \text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4^-$.

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 TON⁵¹ and TOF^{5d,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 $[\text{HNET}_3]^+[\text{BF}_4]^-$ 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, $[(\text{PP}_3)\text{FeH}]^+[\text{BF}_4]^-$ ($\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_3)_3$),^{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_4^f 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

$\text{HCO}_2\text{H} \xrightarrow[80^\circ\text{C, dioxane}]{2\text{a, 10 mol\% LA}} \text{H}_2 + \text{CO}_2$

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

^aReaction conditions: FA (110 μL , 2.91 mmol), 2a, LA (0.291 mmol, 10 mol%), 5 mL dioxane, 80 °C. ^bTurnover frequencies (TOF) were measured after the first hour. ^cTurnover numbers (TON) were measured using a gas buret. All numbers are an average of two runs. ^dAverage 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 CO₂ 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.

■ ACKNOWLEDGMENTS

We acknowledge support from the National Science Foundation through the “Center for the Capture and Conversion of CO₂” (CHE-1240020) and from the Deutsche Forschungsgemeinschaft (SCHN 950/4-1). We thank Daniel DeCiccio and Dr. Christoph Rose-Petruck for help with GC.

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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 H₂ heterolysis, as assumed for **3a** (see SI).

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