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Selective formic acid dehydrogenation catalyzed by Fe-PNP pincer complexes based on the 2,6-diaminopyridine scaffold

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ABSTRACT: Fe(II) hydridocarbonyl complexes supported by PNP pincer ligands based on the 2,6-diaminopyridine scaffold were studied as homogeneous, non-precious metal based catalysts for selective formic acid dehydrogenation to hydrogen and carbon dioxide, reaching quantitative yields and high TONs under mild reaction conditions.

Keywords: iron pincer complexes; formic acid dehydrogenation; hydrogen production; Liquid Organic Hydrogen Carriers

INTRODUCTION

A global issue that scientists worldwide are called to answer is to provide solutions for sustainable energy production, by cleaner and renewable alternatives to fossil fuels. Hydrogen has been identified as an important energy vector, as its chemical bond energy can be converted into electricity using mature fuel cell technology.¹ One of the major limitations to widespread use of hydrogen for energy applications remains its efficient handling and storage, to overcome safety issues and improve cost-effectiveness.^{2,3} As a possible answer, a great deal of research has been carried out to identify suitable hydrogen-rich molecules from which hydrogen can be extracted reversibly under mild conditions of temperature and pressure.

Among several candidates,^{4,6} liquid organic hydrogen carriers (LOHC),⁷ from which hydrogen can be released on-demand by catalytic dehydrogenation, are receiving increasing attention. Among these, formic acid (FA), a liquid at ambient conditions having 4.4% in weight of hydrogen, can be safely handled, stored, and transported easily. Formic acid can be dehydrogenated under mild conditions in the presence of a suitable catalyst to afford fuel cell grade H₂ and CO₂ as the sole by-product. In principle, CO₂ can be rehydrogenated to HCOOH, so a zero-carbon emission energy storage cycle can be contemplated.⁸

In recent years, many different heterogeneous and homogeneous catalyst systems for the dehydrogenation of formic acid have been studied. In the case of homogeneous catalysts, the best results were obtained with noble metal-based complexes, such as Ru⁹ and Ir.¹⁰ At present, an important target in organometallic catalysis is the replacement of noble metal-based catalysts with non-precious metal catalysts of comparable activity. Beller's group reported the efficient hydrogen generation from formic acid catalyzed either by the in situ catalytic system obtained from Fe(BF₄)₂·6H₂O and PP₃ ligand (PP₃ = tris[2-(diphenylphosphino)ethyl]phosphine) or the well-defined complexes [FeH(PP₃)]BF₄, [FeH(η²-H₂)(PP₃)]BF₄,

[FeH(η²-H₂)(PP₃)]BPh₄ and [FeCl(PP₃)]BF₄ in propylene carbonate (PC) as solvent, without the need for an additional base. Except for [FeCl(PP₃)]BF₄, excellent activities were observed for all these systems, with a maximum TOF of 1942 h⁻¹ after 3 h at 40 °C using Fe(BF₄)₂·6H₂O/PP₃. Remarkably, this system showed a good performance¹¹ in continuous hydrogen production at 80 °C with TON = 92000 and TOF = 9425 h⁻¹. Lately, some of us reported hydrogen generation from formic acid catalyzed by iron complexes bearing the linear tetraphosphine 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1), under mild reaction conditions with good activities.¹² Laurenczy and co-workers described the first Fe-based catalyst for the formic acid dehydrogenation in aqueous solution, using Fe(II) salts together with the water soluble *meta*-trisulfonated analogue of PP₃, namely PP₃TS.¹³ Recently, Milstein and co-workers described the iron dihydride pincer complex *trans*-[Fe(tBuPNP)(H)₂(CO)] (tBuPNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) which showed an outstanding activity and selectivity in formic acid dehydrogenation at 40 °C in the presence of trialkylamines, with TONs up to 100000.¹⁴ Finally, Schneider, Hazari, and co-workers reported a new pincer-type iron catalyst that, without the need of added base or free ligand, in the presence of a Lewis acid (LA) as co-catalyst (10 mol%) at 60 °C, achieves the highest TON (ca. 1000000) reported for formic acid dehydrogenation using a first-row transition metal catalyst.¹⁵

In recent times, some of us synthesized new transition metal complexes containing PNP pincer ligands based on the 2,6-diaminopyridine scaffold containing NH and NR linkers between the aromatic pyridine ring and the phosphine moieties.¹⁶ In particular, the iron complexes *trans*-[Fe(PNP^H-iPr)(H)(CO)(Br)] (**1**) and *trans*-[Fe(PNP^{Me}-iPr)(H)(CO)(Br)] (**2**), proved to be active catalysts for ketones and aldehydes hydrogenation.^{16c,h} Very recently we used complexes **1** and **2** (Chart 1) as catalysts for CO₂ and NaHCO₃ hydrogenation obtaining good results even under very mild conditions of temperature and pressure.¹⁷ A key role in catalysis was played by

the *in-situ* formed complex *trans*-[Fe(PNP^{Me}-iPr)(H)₂(CO)] (3). Encouraged by these results, we decided to explore the possible application of these complexes as catalysts for formic acid dehydrogenation. Hereby we present a series of experimental results including detailed screening of reaction conditions and mechanistic considerations based on stoichiometric NMR reactions, which allowed for the description of a proposed catalytic cycle for these systems.

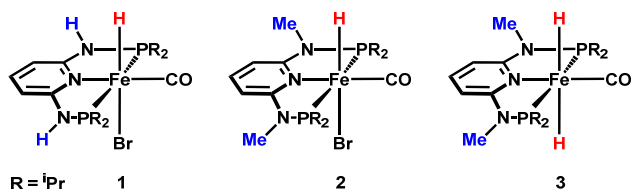


Chart 1. Fe-PNP pincer complexes 1-3.

RESULTS AND DISCUSSION

Formic acid dehydrogenation tests.

We have tested complexes 1 and 2 for catalytic formic acid dehydrogenation under isobaric conditions at atmospheric pressure in the presence of added bases and additives, different solvents, temperatures and catalyst loadings. The development of gas during the catalytic tests was measured with a manual gas buret. Aliquots of the gas mixtures produced were analyzed off-line by FT-IR, showing the absence of CO for all tests (see Experimental Section).

Initially, we checked the activity of complex 1 and 2 using formic acid without added base, but no activity was observed under these conditions, in contrast to the iron phosphine-based systems reported in the literature.^{11,12,15}

We therefore applied the reaction conditions previously described by Milstein *et al.*¹⁴ for a similar pincer complex, i.e. adding 50 mol% NEt₃ (0.5 equiv. to FA) as base. To our delight, complex 1 and 2 were found to be catalytically active under these reaction conditions. Using 0.1 mol% of catalysts at 60 °C, formic acid dehydrogenation took place with TOF_{1h} (turnover frequency at 1h) of 95 h⁻¹ and 276 h⁻¹ and TONs (turnover numbers) of 200 and 653 within 3h in the case of 1 and 2, respectively (Table 1, entries 1,2).

The presence of a base appeared to be mandatory for the reaction to occur. Initially, we tested the effect of different amounts of NEt₃ as base on the catalytic activity was studied (Table 1). For complex 2, lowering the amount of NEt₃ to 25 mol% led to a significant decrease of the catalytic activity (TON = 204, entry 3). On the other hand, better performances were obtained in the presence of 100 mol% (1 equiv. to FA) of NEt₃ (TON = 816, entry 4). Noteworthy, under these conditions the activity shown by 2 was comparable to Milstein's catalyst.¹⁴ A further increase of amine content to 200 mol% did not lead to a significant improvement (TON = 827, entry 5). The catalytic activity of complex 1 also increased using 100 mol% of NEt₃ (entry 6 vs. 1) albeit also under these conditions catalyst 1 performed less efficiently than 2 (TON = 369, entry 6).

Substrate concentration effects were then studied (entries 4 to 9). For catalyst 2, increasing FA concentration from 2.5 mol/L to 10.0 mol/L resulted in an increase of TOF_{1h} from 398 h⁻¹ to 770 h⁻¹ (entry 4 vs. 8), and full conversions were achieved with FA concentrations of 5.0 mol/L and 10.0 mol/L

(entries 7 and 8). Interestingly, catalyst 2 achieved complete conversion using a FA concentration of 5.0 mol/L, showing in this case a faster initial rate than 1 with a TOF_{1h} of 716 h⁻¹ (entry 9). A comparison of reaction profiles at various NEt₃ and FA concentrations is shown in Figure 1.

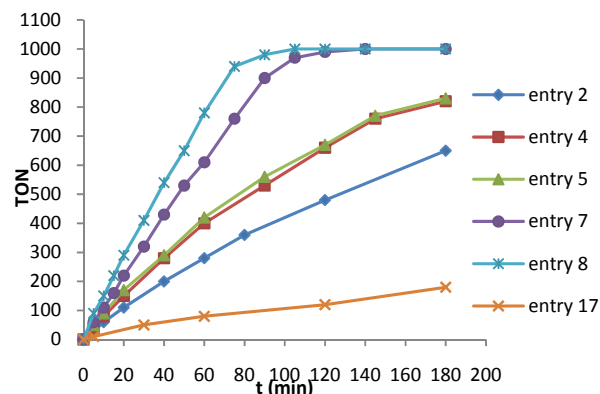


Figure 1. Reaction profiles of selected FA dehydrogenation tests run at 60 °C with 2 (0.1 mol%) at increasing amounts of NEt₃ (50 mol%, entry 2; 100 mol%, entry 4, 200 mol%, entry 5), increasing FA amounts (5.0 mol/L, entry 7; 10.0 mol/L, entry 8) and at a different temperature (40 °C, 5.0 mol/L FA, 100 mol% NEt₃, entry 17). Other details in Table 1 footnote.

Based on these results, the effect of different amines and solvents on the catalytic activity was examined (entries 10 to 12), showing that replacement of NEt₃ with other bases did not lead to any remarkable improvement.^{14,18} Using complex 2, with 50 mol% dimethyloctylamine (DMOA), TON was unchanged compared to NEt₃ albeit TOF_{1h} slightly increased from 593 h⁻¹ to 673 h⁻¹ (entry 10 vs 11). With DBU as base, the catalytic performance dropped with a TON of 571 and TOF_{1h} of 459 h⁻¹ (entry 12). Complex 1 showed no activity with DBU and was almost inactive with DMOA (entry 13).

The results of solvent screening showed that the highest catalytic activity was achieved in aprotic solvents such as THF (TOF_{1h} = 612 h⁻¹, entry 7), propylene carbonate (PC, TOF_{1h} = 500 h⁻¹, entry 14) and 1,4-dioxane (TOF_{1h} = 378 h⁻¹, entry 15), whereas the use of a protic solvent such as EtOH resulted in significantly lower reaction rates (TOF_{1h} = 165 h⁻¹, entry 16). The same order THF > PC > 1,4-dioxane > EtOH was observed for TONs and FA conversions at 3h reaction time.

The effect of Lewis acid as co-catalysts was then tested. As recently reported by Hazari *et al.* for other Fe-pincer based systems,¹⁵ such additives can accelerate FA dehydrogenation dramatically. This was however not the case for our systems, as no FA conversion was observed under standard reaction conditions in the presence of LiBF₄ (10 mol%) instead of bases using complex 1-3.

The effect of temperature was then evaluated for 2 (entries 17 to 19). A TON = 180 and TOF_{1h} = 79 h⁻¹ were obtained at 40 °C using a 2 : FA ratio of 1:1000 (entry 17) after 3h. To test higher temperature conditions, PC was used as solvent. In this case, complete conversion (TON = 1000) was achieved at 80 °C after 30 min only, with a high TOF_{1h} = 1000 h⁻¹ (entry 19).

The effect of catalyst loading was studied in the case of reactions catalyzed by 2.

Table 1. Formic acid dehydrogenation using Fe-PNP complexes **1-3** screening FA/base ratios, FA concentrations, nature of base, solvent, temperature, catalyst concentration effects.^[a]

Entry	Catalyst	[FA] (mol/L)	Solvent	Base (mol%)	T (°C)	TOF _{1h} (h ⁻¹) ^[c]	TON ^[d]	Conversion (%)
1	1	2.5	THF	NEt ₃ (50)	60	95	200 (3)	20
2	2	2.5	THF	NEt ₃ (50)	60	276	653 (3)	65
3	2	2.5	THF	NEt ₃ (25)	60	102	204 (3)	20
4	2	2.5	THF	NEt ₃ (100)	60	398	816 (3)	82
5	2	2.5	THF	NEt ₃ (200)	60	418	827 (3)	83
6	1	2.5	THF	NEt ₃ (100)	60	174	369 (3)	37
7	2	5.0	THF	NEt ₃ (100)	60	612	1000 (2.5)	100
8	2	10.0	THF	NEt ₃ (100)	60	770	1000 (2)	100
9	1	5.0	THF	NEt ₃ (100)	60	716	1000 (2)	100
10	2	5.0	THF	NEt ₃ (50)	60	593	980 (3)	98
11	2	5.0	THF	DMOA (50)	60	673	980 (3)	98
12	2	5.0	THF	DBU (50)	60	459	571 (3)	57
13	1	5.0	THF	DMOA (50)	60	51	76 (3)	2
14	2	5.0	PC	NEt ₃ (100)	60	500	1000 (3)	100
15	2	5.0	1,4-dioxane	NEt ₃ (100)	60	378	878 (3)	88
16	2	5.0	EtOH	NEt ₃ (100)	60	165	650 (3)	65
17	2	5.0	THF	NEt ₃ (100)	40	79	180 (3)	18
18	2	5.0	PC	NEt ₃ (100)	60	500	1000 (3)	100
19 ^[e]	2	5.0	PC	NEt ₃ (100)	80	1800	1000 (0.6)	100
20 ^[b]	2	10.0	THF	NEt ₃ (100)	60	918	2245 (6)	22
21 ^[b]	2	10.0	PC	NEt ₃ (100)	80	2635	10000 (6)	100
22 ^[b]	2	5.0	PC	NEt ₃ (100)	80	1714	6286 (6)	63
23	3	5.0	THF	-	60	0	0 (3)	0
24	3	5.0	THF	NEt ₃ (100)	60	633	1000 (2)	100

^[a] Reaction conditions: 10.0 μmol catalyst; 10.0 mmol FA, specified amount of base, specified solvent. ^[b] 5.0 μmol catalyst; 50.0 mmol FA, specified amount of base, specified solvent. Gas evolution measured by manual gas buret. ^[c] Defined as mmol_{H₂} produced / mmol_{catalyst} · h⁻¹, calculated after 1h. ^[d] Defined as mmol_{H₂} produced / mmol_{catalyst}. Run time (h) in parenthesis. ^[e] TOF calculated after 20 min due to fast reaction. All tests were repeated at least twice to check for reproducibility (error ± 10%).

When a catalyst to substrate ratio of 1:10000 was used at 60 °C with a FA concentration of 10.0 mol/L in THF, a TON = 2245 was achieved after 6 h with a 22% conversion (entry 20). Running the test in PC at 80 °C, full conversion was reached within the same period giving a rewarding TON of ca. 10000 (entry 21). Decreasing FA concentration to 5.0 mol/L led to a significant decrease in the catalyst activity with a TON of 6286 and a conversion of 63% at 80 °C (entry 22).

Complex **3** was inactive in FA dehydrogenation in the absence of amine (entry 23), similarly to Milstein's catalyst,¹⁴

whereas it gave comparable activity to **1** and **2** in the presence of NEt₃ under the same test conditions (entry 24 vs. 7 and 9).

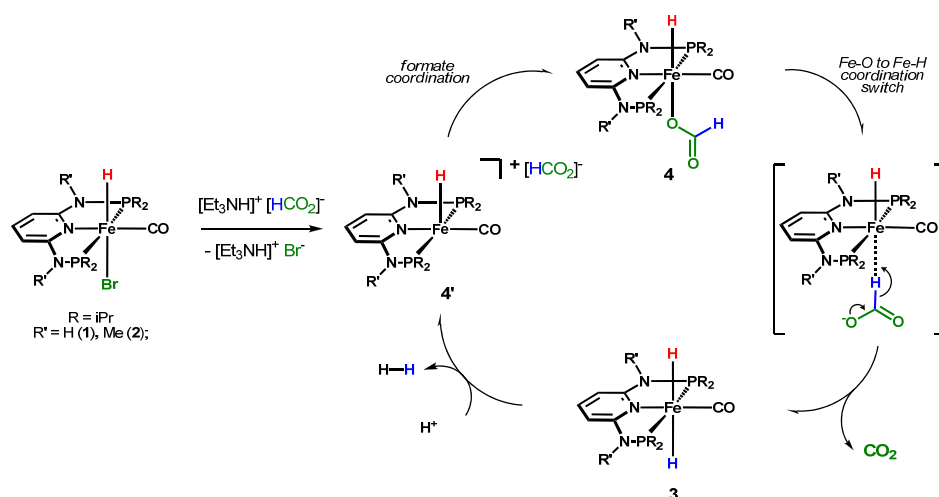
Then, a series of experiments with **2** were carried out to test catalyst deactivation vs. product inhibition, by adding neat HCOOH aliquots (0.47 mL each) after the first run had reached 50% substrate conversion (see Experimental Section). Using this procedure, an overall TON = 12170 was reached after ca. 8.5 h with an initial catalyst to substrate ratio of 1:5000 running the test in PC at 80 °C. A decrease in activity was observed after the fourth addition. At an initial catalyst to substrate ratio of 1:1000, a higher number of consecutive

cycles (11) was possible, reaching however a lower overall TON = 5574 after 4.5 h (see Table S7 and Figure S7 in Supporting Information). Complex **3** (1:5000 catalyst to substrate ratio) gave comparable results to **2** under otherwise identical conditions (overall TON = 12300 after ca 9h).

Mechanistic Studies.

A plausible mechanism for the catalytic dehydrogenation of formic acid with our complexes is outlined in Scheme 1. Based on our recent studies¹⁷ related to carbon dioxide hydrogenation, *i.e.* the reverse reaction of FA dehydrogenation, using catalysts **1** and **2**, we envisage that the latter proceeds via a

very similar but reverse reaction pathway. The pre-catalysts (**1** or **2**) are activated by bromide abstraction giving the coordinatively unsaturated cationic intermediate $[\text{Fe}(\text{PNP}^{\text{Me}}\text{-iPr})(\text{H})(\text{CO})]^+$ (**4'**). Subsequently, the formate ion may coordinate the iron metal center on the vacant site via the O atom, resulting in neutral *trans*- $[\text{Fe}(\text{PNP}^{\text{Me}}\text{-iPr})(\text{H})(\text{CO})(\eta^1\text{-OCO})]$ (**4**). Then, the formate ligand switches from $\eta^1\text{-O}$ to $\eta^1\text{-H}$ coordination to Fe. Facile carbon dioxide elimination occurs yielding **3** which, upon hydride protonation, releases H_2 to give back **4'**.

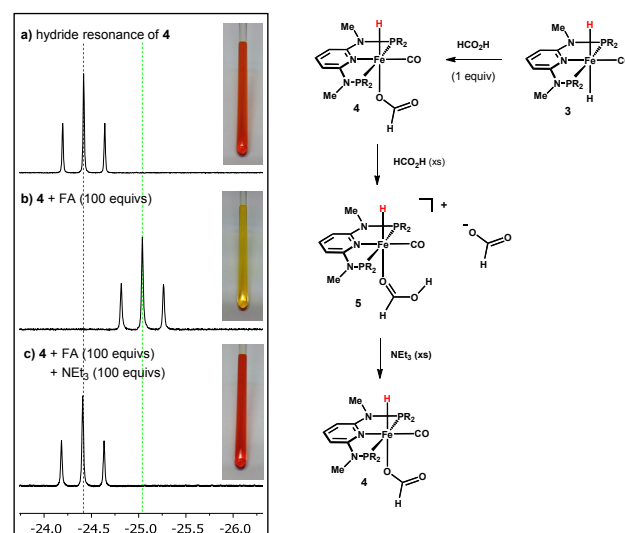


Scheme 1. Proposed simplified catalytic cycle for FA dehydrogenation catalysed by **1** and **2**. (R = iPr; R' = H or Me)

To understand the role of the base in the mechanism, we performed a series of stoichiometric NMR experiments on the reactivity of precatalyst **2** with FA. No reaction could be observed after the addition of 10 equiv. of neat FA to a solution of **2** in THF (with 20% C_6D_6 for deuterium lock), even upon heating the NMR tube to 60 °C for 1 h. On the other hand, when the experiment was repeated adding also 10 equiv. of NEt_3 under otherwise identical conditions, the spectra revealed partial formation complex **4** (ca. 25% based on integration) and conversion of the substrate, as demonstrated by the decrease of the signals due to free formate. These observations confirm that a base is needed to activate the pre-catalyst, facilitating bromide dissociation and freeing a coordination site on the metal center.

It was observed experimentally (see above) that another role of amine is to promote catalytic turnover. This was confirmed by NMR experiments showing that addition of FA (1 equiv.) to a solution of **3** in THF/ C_6D_6 (20%) caused immediate formation of **4**, as demonstrated by the disappearance of the ^1H NMR triplet at -8.76 ppm ($J_{\text{PH}} = 42.9$ Hz) due to **3** and the appearance of the new triplet due to **4** at -24.4 ppm. Under these conditions, **4** showed to be stable in solution without evolving further. In a separate NMR experiment, addition of a known excess of FA (100 equiv.) led to a slight shift of the hydride resonance of **4** in the ^1H NMR spectrum (-25.1 ppm), along with a significant colour change of the respective solution from orange to bright yellow (Scheme 2). When NEt_3 (1 equiv. to FA) was added to the NMR tube, the hydride resonance shifted back to its initial value and also the colour of the reaction solution turned back to orange.

We attribute this upfield shift of the hydride resonance to the change from an anionic (formate) to a neutral (FA) oxygen ligand coordinated *trans* to it. An excess of FA might thus lead to substitution/re-protonation of the formate ligand resulting in the cationic complex *trans*- $[\text{Fe}(\text{PNP}^{\text{Me}}\text{-iPr})(\text{H})(\text{CO})(\eta^1\text{-HCOOH})](\text{HCO}_2)$ (**5**), which in turn gives back **4** in the presence of added base.



Scheme 2. Effect of excess FA and added base on the shift of the ^1H NMR hydride resonance of **4**.

The trend of the hydride resonances to shift towards more negative values is known for similar systems.^{16c,16h,19} In our case, DFT calculations confirmed the chemical shift trend (see Scheme S1 in Supporting Information). Thus, the role of the base in this step is to deprotonate the formic acid ligand in **5** to give back **4**, which in turn eliminates CO₂ and regenerates **3** by beta-hydride elimination closing the catalytic cycle.

CONCLUSIONS

In summary, we have shown that Fe(PNP) pincer-type complexes bearing the easily accessible and tunable 2,6-diaminopyridine scaffold are efficient catalysts for selective formic acid dehydrogenation, in the presence of added base, under mild reaction conditions. Studies are in progress to fine-tune the structure of the complexes in order to obtain more robust catalysts allowing for improved long-term stability and more efficient recycling.

EXPERIMENTAL SECTION

General Methods and Materials

Complexes **1-3** were prepared according to recently reported procedures.^{16c} Formic acid, triethylamine, dimethylcetylamine and DBU were purchased from commercial suppliers and degassed under nitrogen prior to use. All manipulations were carried out using standard Schlenk and glovebox techniques. Solvents were freshly distilled over appropriate drying agents, collected over Linde type 3Å or 4Å molecular sieves under nitrogen, and degassed with nitrogen or argon gas. Deuterated solvents for NMR measurements were purchased from commercial suppliers and stored onto activated 4Å molecular sieves under Ar before use. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker AVANCE-250 spectrometer (operating at 250.13, 101.26, and 62.90 MHz, respectively), on a Bruker Avance II 300 spectrometer (operating at 300.13, 75.47, and 121.50 MHz, respectively) and on a Bruker Avance II 400 spectrometer (operating at 400.13, 100.61, and 161.98 MHz, respectively) at room temperature. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (¹H) or the deuterated solvent multiplet (¹³C). ³¹P{¹H} NMR were referenced to 85% H₃PO₄, with the downfield shift taken as positive.

Typical procedure for FA dehydrogenation tests: In a typical experiment, a solution of catalyst (typically 0.010 mmol) in THF (2.0 mL) was placed under a nitrogen atmosphere in a magnetically stirred glass reaction vessel thermostated by external liquid circulation and connected to a reflux condenser and gas-buret (2 mL scale). After heating to the desired temperature, NEt₃ (1.38 mL, 0.01 mol) and FA (0.38 mL, 0.01 mol) were added and the experiment started. The gas evolution was monitored throughout the experiment by reading the values of liquid displacement reached on the burets. The gas mixtures were analyzed off-line by FTIR spectroscopy using a 10 cm gas cell (KBr windows) to check for CO formation (detection limit 0.02%).²⁰ Each test was repeated at least twice for reproducibility.

Typical procedure for slow substrate feed experiments: In a typical experiment carried out with the experimental setup described above, using either **2** or **3** (0.005 mmol), FA (initial amount 50 mmol) and NEt₃ (50 mmol) at a set temperature of 80 °C in PC as solvent, once 50% of the initial amount of FA had converted, neat FA (0.47 mL, 12.5 mmol) was added by

syringe to the reaction vessel. The procedure was repeated until no further gas evolution was observed.

ASSOCIATED CONTENT

Supporting Information

Additional tables for catalytic tests for various effects screening and corresponding reaction profiles; computational details for **4'** and **5** and corresponding .xyz files. 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.

Notes

The authors declare no competing financial interests.

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REFERENCES

- (1) (a) Züttel, A.; Bogschulte, A.; Schlapbach, L. eds. Hydrogen as a future energy carrier. John Wiley & Sons, **2011**. (b) Kaveh, M.; Gomes, C. *Renewable and Sustainable Energy Reviews* **2012**, *16*, 3024-3033. (c) Turner, J. A. *Science* **2004**, *305*, 972-974.
- (2) Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V.; *Physics Today* **2004**, *57*, 39-44.
- (3) (a) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353-358. (b) Eberle, U.; Felderhoff, M.; Schüth, F. *Angew. Chem. Int. Ed.* **2009**, *121*, 6732-6757.
- (4) (a) Lamari Darkrima, F.; Malbrunota, P.; Tartaglia, G.P. *Int. J. Hydrogen Energy* **2002**, *27*, 193-202. (b) Ströbel, R.; Garche, J.; Moseley, P.T.; Jörissen, Wolf, L. G. *J. Power Sources* **2006**, *159*, 781-801.
- (5) (a) Billur, S.; Lamari-Darkrim, F.; Hirscher M. *Int. J. Hydrogen Energy* **2007**, *32*, 1121-1140. (b) Morten, L.; Jepsen, B.; Lars, H.; Young-Su, L.; Young-Whan, C.; von Colbe, B.; Dornheim, J. M.; Rokni, M.; Jensen, M.; Sloth, J. O.; Filinchuk, M.; Jørgensen, Y.; Besenbacher, J. E.; Jensen, F.; Torben, R. *Mat. Today* **2014**, *17*, 122-128.
- (6) Langmi, H. W.; Ren, J.; North, B.; Mathe, M.K.; Bessarabov, D. *Electrochim. Acta* **2014**, *128*, 368-392.
- (7) (a) Okada, Y.; Sasaki, E.; Watanabe, E.; Hyodo, S.; Nishijima, H. *Int. J. Hydrogen Energy* **2006**, *31*, 1348-1356. (b) Wang, Z.; Tonks, I.; Belli, J.; Jensen, C. M. *J. Organomet. Chem.* **2009**, *694*, 2854-2857. (c) Wang, J.; Zhang, X. B.; Wang, Z.-L.; Wang, L.-M.; Zhang, Y. *Energy Environ. Sci.* **2012**, *5*, 6885-6888; (d) Johnson, T. C.; Morris, D. J.; Wills, M. *Energy Environ. Sci.* **2010**, *3*, 1207-1217. (e) Alsabeh, P. G.; Mellmann, D.; Junge, H.; Beller, M. *Top. Organomet. Chem.* **2014**, *48*, 45-80. (f) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.-J.; Junge, H.; Gladiali, S.; Beller, M. *Nature* **2013**, *495*, 85-89. (g) Zeng, G.; Sakaki, S.; Fujita, K. I.; Sano, H.;

Yamaguchi, R. *ACS Catal.* **2014**, *4*, 1010-1020. (h) Polukeev, A.V.; Petrovskii, P.V.; Peregodov, A.S.; Ezernitskaya, M. G.; Koridze, A.A. *Organometallics* **2013**, *32*, 1000-1015. (i) Kawahara, R.; Fujita, K. I.; Yamaguchi, R. *J. Am. Chem. Soc.* **2012**, *134*, 3643-3646. (j) Spasyuk, D.; Smith, S.; Gusev, D.G. *Angew. Chem. Int. Ed.* **2012**, *51*, 2772-2775. (l) Putignano, E.; Bossi, G.; Rigo, P.; Baratta, W. *Organometallics* **2012**, *31*, 1133-1142. (m) Bertoli, M.; Choualeb, A.; Lough, A.J.; Moore, B.; Spasyuk, D.; Gusev, D. G. *Organometallics* **2011**, *30*, 3479-3482. (n) Baratta, W.; Boss, G.; Putignano, E.; Rigo, P. *Chem. Eur. J.* **2011**, *17*, 3474-3481. (o) Alberico, E.; Sponholz, P.; Cordes, C.; Nielsen, M.; Drexler, H. J.; Baumann, W.; Junge, H.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 14162-14166.

(8) (a) Joó, F. *ChemSusChem* **2008**, *1*, 805-808. (b) Enthaler, S.; von Langermann, J.; Schmidt, T. *Energy Environ. Sci.* **2010**, *3*, 1207-1217. (c) Loges, B.; Boddien, A.; Gärtner, F.; Junge, H.; Beller, M. *Top. Catal.* **2010**, *53*, 902-914.

(9) (a) Gao, Y.; Kuncheria, J.; Puddephatt, R. J.; Yap, G. P. A. *Chem. Commun.* **1998**, 2365-2366. (b) Fellay, C.; Dyson, P. J.; Laurency, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 1-4. (c) Loges, B.; Boddien, A.; Junge, H.; Beller, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 3962-3965. (d) Boddien, A.; Loges, B.; Junge, H.; Beller, M. *ChemSusChem* **2008**, *1*, 751-758. (e) Maiewsky, A.; Morris, D. J.; Kendall, K.; Wills, M. *ChemSusChem* **2010**, *28*, 4133-4140. (f) Boddien, A.; Loges, B.; Junge, H.; Gärtner, F.; Noyes, J. R.; Beller, M. *Adv. Synth. Catal.* **2009**, *351*, 2517-2520. (g) Li, X.; Ma, X.; Shi, F.; Deng, Y. *ChemSusChem* **2010**, *3*, 71-74. (h) Boddien, A.; Gärtner, F.; Federsel, C.; Sponholz, P.; Mellmann, D.; Jackstell, R.; Junge, H.; Beller, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 6411-6414. (i) Boddien, A.; Federsel, C.; Sponholz, P.; Mellmann, D.; Jackstell, R.; Junge, H.; Laurency, G.; Beller, M. *Energy Environ. Sci.* **2012**, *5*, 8907-8911. (j) Rodriguez-Lugo, R. E.; Trincado, M.; Vogt, M.; Tewes, F.; Santiso-Quinones, G.; Grützmacher, H. *Nat. Chem.* **2013**, *5*, 342-347. (k) Mellone, I.; Peruzzini, M.; Rosi, L.; Mellmann, D.; Junge, H.; Beller, M.; Gonsalvi, L. *Dalton Trans.* **2013**, *42*, 2495-2501. (l) Sponholz, P.; Mellmann, D.; Junge, H.; Beller, M. *ChemSusChem* **2013**, *6*, 1172-1176. (m) Czaun, M.; Goepfert, A.; Kothandaraman, J.; May, R. B.; Haiges, R. G.; Prakash, K. S.; Olah, G. A. *ACS Catal.* **2014**, *4*, 311-320. (n) Filonenko, G. A.; Putten, R. V.; Schulp, E. N.; Hensen, M. E. J.; Pidko, E. A. *ChemCatChem* **2014**, *6*, 1526-1530. (o) Pan, Y.; Pan, C.-L.; Zhang, Y.; Li, H.; Min, S.; Guo, X.; Zheng, B.; Chen, H.; Anders, A.; Lai, Z.; Zheng, J.; Huang, K.-W. *Chem. Asian. J.* **2016**, *11*, 1357-1360.

(10) (a) Himeda, Y.; *Green Chem.* **2009**, *11*, 2018-2022. (b) Tanaka, R.; Yamashita, M.; Chung, L. W.; Morokuma, K.; Nozaki, K. *Organometallics* **2011**, *30*, 6742-6750. (c) Hull, J. F.; Himeda, Y.; Wang, W. H.; Hashiguchi, B.; Periana, R.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. *Nat. Chem.* **2012**, *4*, 383-388. (d) Maenaka, Y.; Suenobu, T.; Fukuzumi, S. *Energy Environ. Sci.* **2012**, *5*, 7360-7367. (e) Barnard, J. H.; Wang, C.; Berry, N. G.; Xiao, *Chem. Sci.* **2013**, *4*, 1234-1244. (f) Fukuzumi, S.; Kobayashi, T.; Suenobu, T. *J. Am. Chem. Soc.* **2010**, *132*, 1496-1497. (g) Oldenhof, S.; de Bruin, B.; Lutz, M.; Siegler, M. A.; Patureau, F. W.; van der Vlugt, J. I.; Reek, J. N. H. *Chem. Eur. J.* **2013**, *19*, 11507-11511. (h) Suna, Y.; Ertem, M.

Z.; Wang, W. H.; Kambayashi, H.; Manaka, Y.; Muckerman, J. T.; Fujita, E.; Himeda, Y. *Organometallics* **2014**, *33*, 6519-6530. (i) Wang, W. H.; Xu, S.; Manaka, Y.; Suna, Y.; Kambayashi, H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. *ChemSusChem* **2014**, *7*, 1976-1983. (j) Wang, Z.; Lu, S.-M.; Li, J.; Wang, J.; Li, C. *Chem. Eur. J.* **2015**, *21*, 12592-12595. (k) Papp, G.; Olveti, G.; Horváth, H.; Kathó, Á.; Joó, F. *Dalton Trans.* **2016**, DOI: 10.1039/c6dt01695b. (l) Celaje, J. J. A.; Lu, Z.; Kedzie, E. A.; Terrile, N. J.; Lo, J. N.; Williams, T. J. *Nat. Commun.* **2016**, *7*, 11308.

(11) Boddien, A.; Mellmann, D.; Gaertner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurency, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733-1736.

(12) Bertini, F.; Mellone, I.; Ienco, A.; Peruzzini, M.; Gonsalvi, L. *ACS Catal.* **2015**, *5*, 1254-1265.

(13) Montandon-Clerc, M.; Dalebrook, A. F.; Laurency, G. *J. Catal.* **2016**, in press. DOI: 10.1016/j.jcat.2015.11.012.

(14) Zell, T.; Butschke, B.; Ben-David, Y.; Milstein, D. *Chem. Eur. J.* **2013**, *19*, 8068-8072.

(15) Bielinski, E.A.; Lagaditis, P.O.; Zhang, Y.; Mercado, B.Q.; Würtele, C.; Bernskoetter, W.H.; Hazari, N.; Schneider, S. *J. Am. Chem. Soc.* **2014**, *136*, 10234-10237.

(16) a) Bichler, B.; Glatz, M.; Stöger, B.; Mereiter, K.; Veiros, L. F.; Kirchner, K. *Dalton Trans.* **2014**, *43*, 14517-15419; b) de Aguiar, S. R. M. M.; Öztöpcü, Ö.; Stöger, B.; Mereiter, K.; Veiros, L. F.; Pittenauer, E.; Allmaier, G.; Kirchner, K. *Dalton Trans.* **2014**, *43*, 14669-14679; c) Gorgas, N.; Stöger, B.; Veiros, L. F.; Pittenauer, E.; Allmaier, G.; Kirchner, K. *Organometallics* **2014**, *33*, 6905-6914; d) Bichler, B.; Holzacker, C.; Stöger, B.; Puchberger, M.; Veiros, L. F.; Kirchner, K. *Organometallics* **2013**, *32*, 4114-4121; e) Benito-Garagorri, D.; Becker, E.; Wiedermann, J.; Lackner, W.; Pollak, M.; Mereiter, K.; Kisala, J.; Kirchner, K. *Organometallics* **2006**, *25*, 1900-1913; f) Benito-Garagorri, D.; Wiedermann, J.; Pollak, M.; Mereiter, K.; Kirchner, K. *Organometallics* **2007**, *26*, 217-222; g) Benito-Garagorri, D.; Puchberger, M.; Mereiter, K.; Kirchner, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 9142-9145; h) Gorgas, N.; Stöger, B.; Veiros, L. F.; Kirchner, K. *ACS Catal.* **2016**, *6*, 2664-2672.

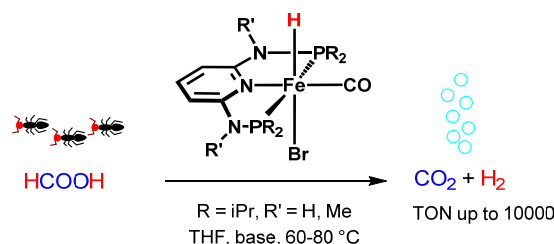
(17) Bertini, F.; Gorgas, N.; Stöger, B.; Peruzzini, M.; Veiros, L. F.; Kirchner, K.; Gonsalvi, L. *ACS Catal.* **2016**, *6*, 2889-2893.

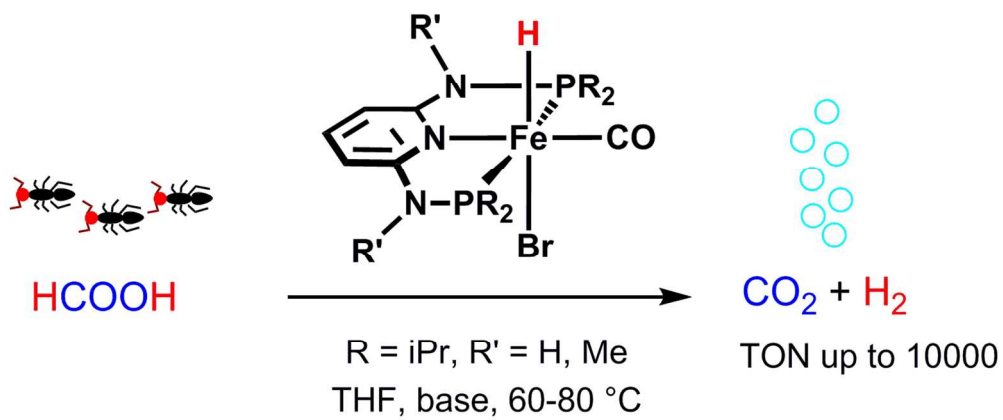
(18) Junge, H.; Boddien, A.; Capitta, F.; Loges, B.; Noyes, J. R.; Gladiali, S.; Beller, M. *Tetrahedron Lett.* **2009**, *50*, 1603-1606.

(19) Langer, R.; Iron, M. A.; Konstantinovskii, L.; Diskin-Posner, Y.; Leitens, G.; Ben-David, Y.; Milstein, D., *Chem. Eur. J.* **2012**, *18*, 7196-7209.

(20) Gas mixture analyses were carried out by FTIR spectroscopic methods described in previous publications. For details see: (a) Morris, D. J.; Clarkson, G. J.; Wills, M. *Organometallics* **2009**, *28*, 4133-4140. (b) Guerriero, A.; Bricout, H.; Sordakis, K.; Peruzzini, M.; Monflier, E.; Hapiot, F.; Laurency, G.; Gonsalvi, L. *ACS Catal.* **2014**, *4*, 3002-3012.

Table of Contents artwork





TOC graphic

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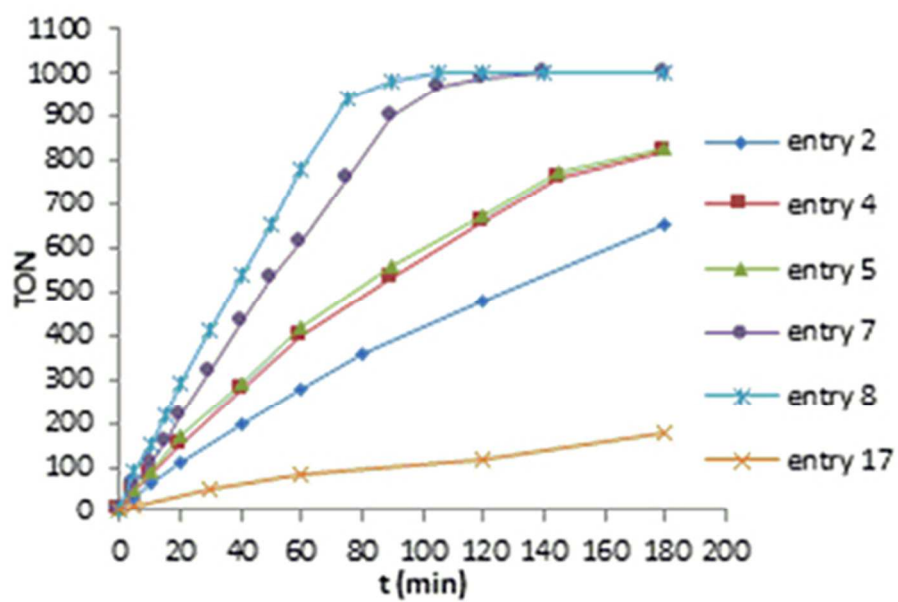
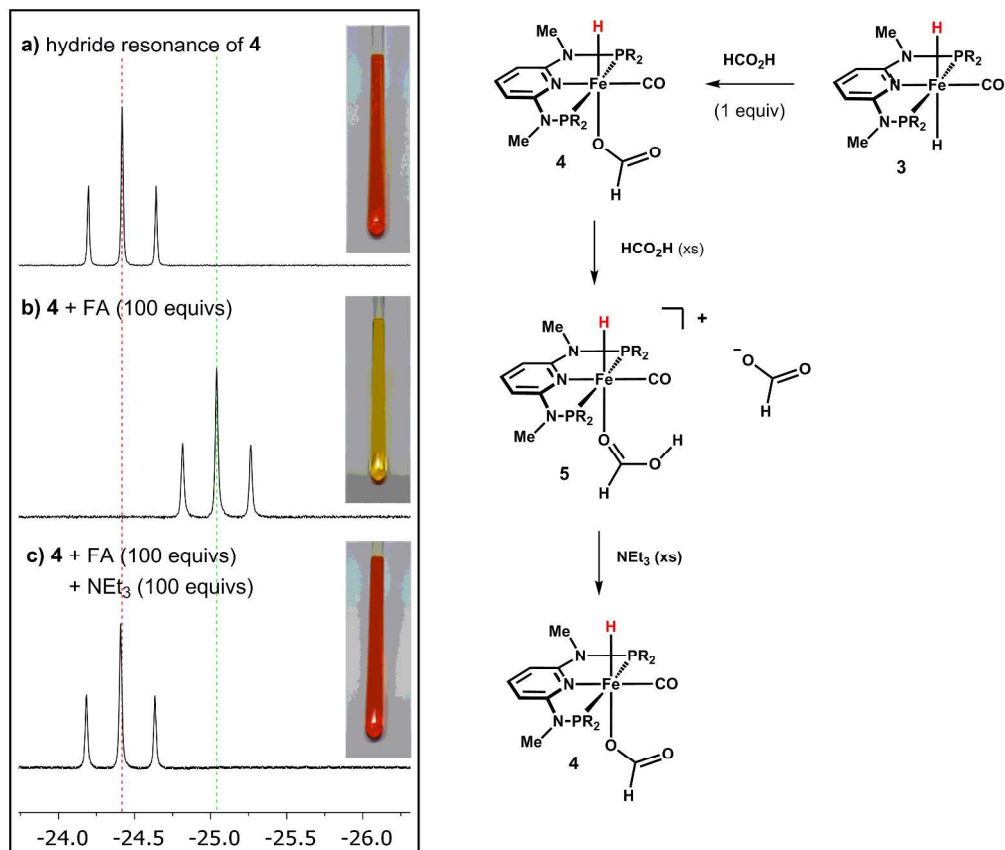


Figure 1

39x26mm (300 x 300 DPI)



Scheme 2

270x246mm (300 x 300 DPI)