

An update on Formic Acid Dehydrogenation by Homogeneous Catalysis

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Abstract: Formic acid (FA) has been extensively studied as one of the most promising hydrogen energy carriers today. The catalytic decarboxylation of FA ideally leads to the formation of CO₂ and H₂ that can be applied in fuel cells. A large number of transition-metal based homogeneous catalysts with high activity and selectivity have been reported for the selective FA dehydrogenation.

In this review, we discussed the recent development of C,N/N,N,N-ligand and pincer ligand-based homogeneous catalysts for the FA dehydrogenation reaction. Some representative catalysts are further evaluated by the CON/COF assessment (catalyst on-cost number)/(catalyst on-cost frequency). Conclusive remarks are provided with the future challenges and opportunities.

Keywords: formic acid • hydrogen energy carrier • homogeneous catalysis

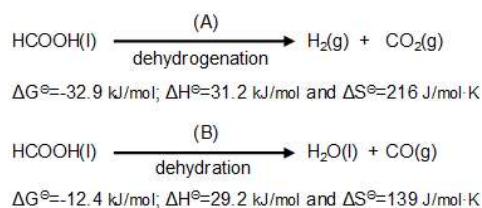
1. Introduction

The social progress of humankind is highly related to the utilization of energy. Since the industrial revolution in 1850, the world's fossil fuels energy consumption has increased dramatically, in the forms of coal, oil, and gas.^[1] On one hand, the energy security concern is on the horizon due to the overusing of the non-renewable energy sources. On the other hand, the use of fossil fuels has resulted in carbon dioxide (CO₂) emission that is believed to contribute to increasing of the global temperature.^[2] Therefore, the urgent developments of suitable and renewable carbon-free or low-carbon energy technology are needed. Hydrogen (H₂) is considered a promising bridge between the power generation plants and end-users for mobile applications. In combination with lower-temperature proton-exchange membrane fuel cells, H₂ can be efficiently converted into electricity, producing only water (H₂O) as a byproduct.^[3] However, the practical use of H₂ is limited due to the associated issues in delivery and storage.^[4] In this regard, formic acid (FA) has gained much attention because it is convenient to ship and store, and it has a high volumetric hydrogen content 53 g-H₂/L under ambient conditions.^[5]

The decomposition of FA proceeds via two main pathways: (A) decarboxylation/dehydrogenation resulting in CO₂ and H₂ and (B) decarbonylation/dehydration resulting in carbon monoxide (CO) and equivalent H₂O (Scheme 1). FA can be selectively decomposed to pressurized H₂/CO₂ using an appropriate homogeneous or heterogeneous catalyst. The most important requirement of an FA dehydrogenation catalyst is that it must be highly selective for the production of H₂ and CO₂ and should not catalyze the formation of CO through dehydration as it would poison the fuel cells. Thus far, a large number of efficient heterogeneous^[6] and homogeneous^[7] catalytic systems for FA dehydrogenation have been reported. Although heterogeneous catalysts are best known for easy separation and recycling,^[6b] homogeneous catalysts are generally more efficient and highly selective. The best performances for FA dehydrogenation were achieved using homogeneous metal catalysts such as Ir^[8], Ru^[9], Rh^[10], and Fe^[11] complexes. Since there was no unified standard to evaluate the potential of catalysts in practical usage, we have proposed the concept of CON and COF, the dimension-free key parameters based on TON and TOF for normalizing catalysts' performance and costs.^[5] In this review, the recent advances of homogeneous catalysts for FA decomposition will be summarized, focusing on the complexes with a different type of ligands. Moreover, some of these representative catalysts will be evaluated

by our assessment system of CON/COF. Conclusive remarks will be provided on future challenges and opportunities.

Scheme 1. Decomposition pathways of FA dehydrogenation (A) and dehydration (B).



2. The advent and development of homogeneous FA decomposition reactions

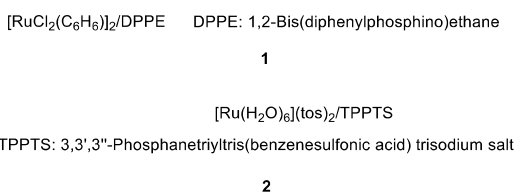
The first description of FA dehydrogenation was reported by Coffey in 1967. The result showed that IrH₂Cl(PPh₃)₃ gave the best TOF of 1187 h⁻¹ at an elevated temperature over 100°C during the decomposition process.^[12] In 1982, Paonessa and co-workers published a platinum dihydride complex (PtH₂L₂; L=PEt₃) for the FA dehydrogenation, and the process was strongly influenced by the solvent and sodium formate.^[13] In 1996, Noyori and co-workers developed the prototype [Ru(η⁶-arene)(N-tosylated 1,2-diamine)] complexes for the transfer hydrogenation reaction in the presence of FA/ triethylamine(5:2).^[14] In 2000, the Puddephatt group reported extensive studies on the use of a diruthenium catalyst [Ru₂(μ-CO)(CO)₄(μ-dppm)₂] for the conversion of FA to H₂ and CO₂ and hydrogenation of CO₂.^[15] As early as 1979, FA was also used as a H₂ donor for the rapid removal of benzyl-type protecting group from peptides via transfer hydrogenation.^[16]

In 2003, Himeda and co-workers demonstrated a half sandwich Rh(III) complex of [Cp*Rh(bpy)Cl]Cl, (Cp* = pentamethylcyclopentadienyl, bpy = 2,2-bipyridine) for reduction of ketones where FA was used as the H₂ donor.^[17] Willis and co-workers also focused on this strategy of using FA as the H₂ source for asymmetric transfer hydrogenations reaction in the presence of Ru(II) complex with a tethered ligand.^[18] Although these reports for utilization of FA came with moderate activities, these discoveries pave the way towards the development of more efficient homogeneous catalysts for the FA dehydrogenation.

It was not until 2008 that FA started to gained more attention after independent works by Beller and Laurency. Various

catalysts were widely investigated by the Beller group under mild reactions with the evolution of H₂ and CO₂. The catalytic activity could be increased significantly in the presence of some adducts such as Et₃N.^[9b, 9c, 19] The influence of different phosphine ligands on catalytic activity and durability was studied,^[9c, 19] which provided insights on the specific electronic and steric environment for the stabilization of the metal center. [Ru(H₂O)₆]²⁺ or commercial RuCl₃·xH₂O coordinated with two equivalents of meta-trisulfonated triphenylphosphine (mTPPTS) could selectively decompose FA to H₂ and CO₂ (1:1). The activity can be increased by additional HCOONa (SF) to the aqueous FA solution (FA/SF=9:1).^[9a, 20] In particular, Ru catalyst system **1** (Scheme 2) allows continuous FA dehydrogenation to CO₂/H₂ to give a TON over 1 million.^[9g] Laurency *et al.* reported an aqueous catalytic system of FA/SF by a Ru complex **2** with a water-soluble phosphine ligand tppts (tris(3-sulfonatophenyl)phosphine) to give a TOF of 460 h⁻¹ at 120 °C (Scheme 2).^[9a, 21] With continuous feeding of FA, a total TON of over 40 000 was obtained, and the gas was produced up to 750 bar in a closed system. The plausible mechanism suggested that the formate was firstly coordinated to the Ru center, and a stable [Ru(H)(H₂O)(η²CO₂)(tppts)₃] intermediate was generated via β-hydride elimination. Protonation to form a H₂ intermediate proceeded with the releases of H₂ to complete the catalytic cycle.^[22] They also investigated a series of water-soluble phosphine ligands in the dehydrogenation of FA such as oligocationic, and ammoniomethyl-substituted triarylphosphines Ru catalysts.^[23] The TOF of 1950 h⁻¹ was received under the Ru complex supported by tppts with the ratios of 2:1 and 3:1 at 120 °C. Moreover, the system of tppts/Ru (2:1) could continue to work over 10 hours at 90 °C providing a total TON of 10,000. The Laurency group further investigated Ru(II) and Ru(III) metal precursors supported by various sulfonated phosphines with monodentate aryl and specific tetrasulfonated diphosphines and identified that higher basicity and stronger σ-donating ligands showed better FA dehydrogenation activity.^[9i]

Scheme 2. The catalysts reported by Beller's and Laurency's groups for FA dehydrogenation.

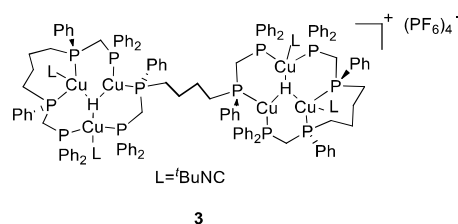


Subsequent studies by Himeda, Fujita and co-workers described plenty of water-soluble catalysts, like Ir, Ru, Rh complexes with bipyridine moieties.^[8b, 8d, 8f, 8n, 8s, 24] The detail of these catalysts with N, N-type ligand will be discussed in section 3. In 2011, Nozaki introduced an Ir-PNP complex to demonstrate the reversible FA dehydrogenation providing TOF of 120,000 h⁻¹ in *tert*-butanol during the first minute at 80 °C.^[8a] A great number of catalysts bearing pincer type ligands were also investigated in the selective FA decomposition under different conditions.^[9h, 9m, 9q, 9r, 11d, 11e, 11g, 25] These studies are described in section 4.

Many noble metals catalysts give outstanding performances for FA decomposition. Meanwhile, several complexes containing earth-abundant metals have also been developed.^[11, 25b, 26] In 2009,

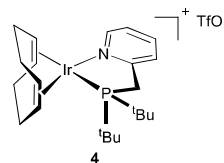
the catalytic performances of different nonprecious metal chlorides, such as Fe, Co, and Ni, are reported by Wills in FA/Et₃N at 120 °C.^[26b] Beller reported *in situ* catalysts formed from Fe₃(CO)₁₂, pyridine or 1,10-phenanthroline, triphenylphosphine, which could decompose FA to H₂/CO₂ (1:1) with the observed TON of over 100 under visible light irradiation at room temperature.^[11b] In 2011, another *in situ* iron catalytic system for FA dehydrogenation was demonstrated in propylene carbonate without additives or light to provide a TON of 100,000 and TOF nearly 10 000 h⁻¹ without any CO released.^[11c] Both the kinetic measurement and the DFT studies indicated that β-hydride elimination of the Fe formate complex for the release of CO₂ is the rate-determining step. In 2014, more extensive studies were conducted on the iron-catalyzed system in which the active catalytic species were formed *in situ* from different cationic Fe^{II}/Fe^{III} precursors in the presence of PPh₃. The results suggested that the activity of catalytic system was highly associated with the solvent, the water content, and the ligand-metal ratio. Accordingly, the best TON of 8117 was obtained by using [FeH(PP₃)BF₄]/PPh₃ in propylene carbonate with trace water.^[27]

Scheme 3. Selected non-precious catalyst reported by Tanase's group



More recently, hexanuclear copper hydride complex **3**, [Cu₆(μ₃-H)₂(meso-L₄)₃(RNC)₄](PF₆)₄ (R = 'Bu), was developed by Tanase and co-workers for FA dehydrogenation (Scheme 3).^[26g] This Cu complex [Cu(CH₃CN)₄]PF₆ coupled with 'BuNC (2 eq) and NEt₃ (0.4 eq) provided a TON of 1500 per Cu at 70 °C for 8 h. Although the intention is to use cheap copper metal to reduce costs, the complicated ligands also increase the over cost of the entire catalyst. The economic efficiency of this system will be analyzed by CON/COF in section 5.

Scheme 4. Selected catalyst for neat FA dehydrogenation reported by William's group.

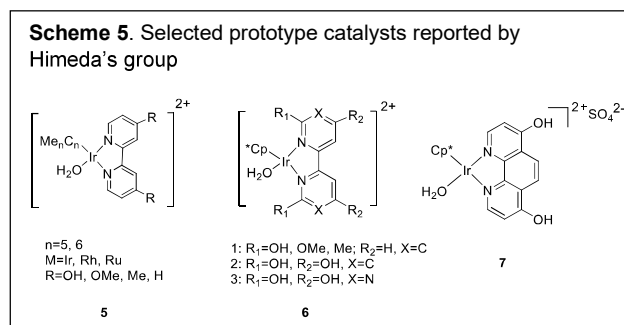


Neat FA decomposition gains attention because it allows the maximum use of FA at its full volumetric capacity. This can also directly produce high-pressure H₂ under very acidic conditions. Williams's group described an iridium-NP complex **4** (Scheme 4), which can continue to work up to 4 months and provide a TON of 2,160,000 under the neat FA condition.^[8j] Fischmeister and co-workers also reported an iridium complex with Cp*(dipyridylamine) ligand to selective decompose aqueous and neat FA under the base-free conditions to give TOF of 13,292 h⁻¹ at 100 °C.^[8l] More discussions will be provided in section 3.

3. Catalysts with bidentate C, N/N, N-type ligands

In 2008, Fukuzumi and co-workers described selective FA/SF dehydrogenation in the presence of water with $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})(\text{BPY})]^{2+}$ complex at 25 °C, giving the highest TOF of 28 h⁻¹ at pH of 3.8.^[10a] Further, improved TOF of 426 h⁻¹ was achieved with the heterodinuclear iridium–ruthenium complex of $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})(\text{BMP})\text{Ru}(\text{bpy})_2](\text{SO}_4)_2$ (BMP: 2,2'-bipyrimidine).^[9d] More recently, they also developed a monometallic phenylpyrazolyl organoiridium complex containing a proton-responsive carboxylic acid for FA dehydrogenation, with an optimal TOF of 1880 h⁻¹ at pH 2.8 at room temperature.^[28]

After the introduction of Cp* ligand as an electron-donating group, different electron-donating functionalities such as OH, OMe, and Me to bipyridine ligands were employed in this type of catalysts **5**, $[(\text{C}_n\text{Me}_n)\text{M}(4,4'\text{-R}_2\text{-BPY})\text{Cl}]^+$ by Himeda's group (Scheme 5).^[10b, 17] The chloro ligand of these complexes could readily go through water ligand substitution in aqueous solutions to give the corresponding aqua complexes. Moreover, when the solution pH was increased from 5.0–6.0, hydroxyl substituted bipyridine ligands are deprotonated.^[29] Such diamine ligands containing pyridinol moiety are widely recognized as proton-responsive ligands with pH-switchable properties.^[30] Furthermore, the polarity and electron-donating ability could be modified, tailoring the water-solubility and catalytic activity of the complexes.^[31]

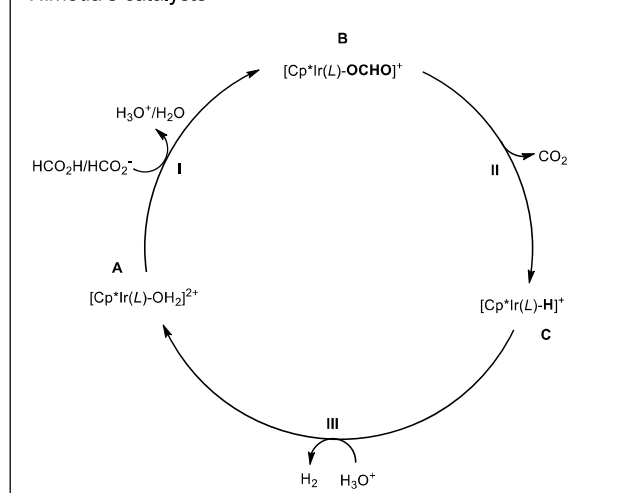


Complexes with OH moieties are particularly of interest. In 2012, Himeda, Fujita and co-workers reported another pH-dependent iridium-bipyridine dimer catalysts bearing four hydroxyl groups with a TOF 12,000 h⁻¹ at 60 °C under the base and additive-free conditions. Moreover, the improved TOF of 31,600 h⁻¹ was obtained in the FA/SF(1:1) aqueous solution.^[8b] The reason for the significant increase in catalyst activity was proposed to be attributed to the strong electron-donating effect of aryloxy anions. The activity of catalyst $[\text{Cp}^*\text{Ir}(4\text{-DHBP})\text{OH}_2]^{2+}$ (4-DHBP: 4,4'-dihydroxy-2,2'-bipyridine) with hydroxyl substituents at 4 and 4' positions showed 90 times higher activity than that of its unsubstituted analog $[\text{Cp}^*\text{Ir}(\text{bpy})\text{OH}_2]^{2+}$.^[24a]

Imidazole, pyrazole, and imidazoline ligands with electron-donating properties were also introduced in the Cp*Ir system.^[8f] Himeda, Fujita and co-workers also reported an iridium biimidazole complex with a TOF of 34,000 h⁻¹ at 80 °C in water without bases and additives.^[8f] The electron-donating ability of azole ligands is sufficient for activating the catalyst in the FA decomposition. Complexes supported by OH substituted bipyridine ligands again offer more opportunities to tune activity under different pH conditions. The markedly different performances were found

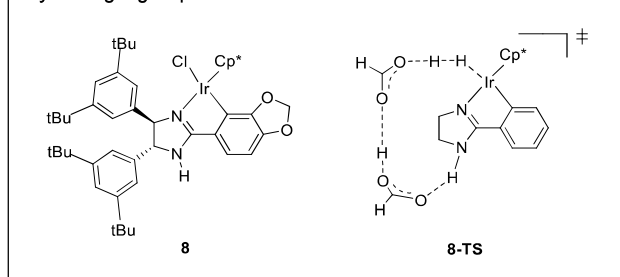
among the complexes $[\text{Cp}^*\text{Ir}(6\text{-DHBP})\text{OH}_2]^{2+}$ (6-DHBP: 6,6'-dihydroxy-2,2'-bipyridine), $[\text{Cp}^*\text{Ir}(\text{TH4BPM})\text{OH}_2]^{2+}$ (TH4BPM: 2,2',6,6'-tetrahydroxy-4,4'-bipyrimidine) and $[(\text{Cp}^*\text{IrCl})_2(\text{THBPM})]^{2+}$ (THBPM: 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine) with all OH group at the ortho position.^[8b, 24d] The best performance of catalyst's activity was found with pH at around 4.0 using $[(\text{Cp}^*\text{IrCl})_2(\text{THBPM})]^{2+}$. It was proposed that the deprotonation of OH groups on the ligands and the ionization of FA occurred at higher pH values of the solution. The deprotonation of OH groups helps to generate more electron-donating O⁻ at a higher pH, which may improve the catalytic activity of complexes **6** (Scheme 5).^[24d] Meanwhile, different substituted groups may suggest different catalytic mechanisms. In general, the catalytic cycle (Scheme 6) starts from the formation of formate complexes followed by the release of CO₂ via β-hydride elimination to form the Ir-H species. The production of H₂ from the reaction of Ir-H and proton proceeds to regenerate the active species.^[24e] It is noteworthy that in order to achieve a goal for practical application, Kawanami and Himeda designed an iridium complex **7**, $[\text{Cp}^*\text{Ir}(\text{PHEN-diol})\text{H}_2\text{O}]\text{SO}_4$, which can continue work 2600 hours to give a TON of 5 million (Scheme 5).^[8j]

Scheme 6. General mechanism for FA dehydrogenation by Himeda's catalysts

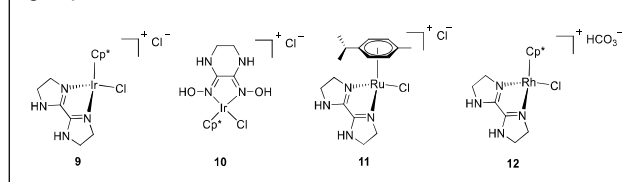


In 2013, Xiao's group reported a well defined bifunctional $\text{Cp}^*\text{IrCl}(\text{N}^{\wedge}\text{C})$ complex **8** bearing cyclometallated 2-aryl-imidazoline ligands for FA dehydrogenation in the presence of Et₃N, providing the initial TOF of 147,000 h⁻¹ at 40 °C for 10 seconds without CO formation (Scheme 7).^[8c] Mechanistic studies suggest

Scheme 7. Selected C,N-prototype catalyst **8** reported by Xiao's group and important transition state **8-TS** calculated by Zhang's group.



Scheme 8. Selected catalysts reported by Li's and Huang's groups



the long-range metal-ligand cooperation between FA and the distal NH functional group from the imidazole moiety. The subsequent computational study by Zhang's group^[32] corroborated the reaction mechanism involving two FA molecules, where one acts as a H₂ source, and the other participates as a proton shuttle to favor the long-range activation (**8-TS**, Scheme 7).

In 2015, Li's group reported a new iridium catalyst **9** bearing an N,N'-diimine ligand for the FA dehydrogenation (Scheme 8).^[8f] Different from the previously reported iridium catalysts with aromatic bipyridine, bipyrimidine, and biimidazole ligands, the N, N'-diimine ligand was used in this system to achieve a TOF of up to 487,500 h⁻¹ (90 °C) and an unprecedented TON of 2,400,000 (80 °C). The conjugated diimine ligand showed desirable properties,^[33] such as air- and water-stability. Moreover, the electron-donating ability could enhance the catalytic activity.^[34] Within a short induction period, the pre-catalysts can be rapidly converted to monomeric active species [Ir-catalyst-HCO₂]. When pure FA was used, no dehydrogenation reaction could be observed, due to the absence of hydronium ion or/and HCOO⁻. KIE experiments for complex **9** showed that the formate is involved in the rate determining step (RDS). As the Ir-H was not detected in the acidic solution by NMR, the generation of Ir-H is proposed to be the RDS in the catalytic cycle. In 2018, Li continuously developed another new type of diaminoglyoxime derived iridium catalyst (**10**) to reach a TON of 5,020,000 at 70 °C for the FA dehydrogenation. It is worth noting that these robust catalysts can be prepared *in situ* from the Ir precursor and dioxime ligands without any purification.^[8f]

The Huang group also reported a ruthenium complex (**11**) bearing (η⁶)*p*-cymene, chloride, and N, N'-diimine ligands (Scheme 8).^[9f] The best TOF of 12,000 h⁻¹ was reached in the first 10 minutes at 90 °C with an SF/FA ratio of 5. No CO was detected during the FA dehydrogenation process, even under pressurized conditions (>260 bar). In addition to the excellent selectivity, the catalyst could continue to work for over 35 hours, reaching a TON of 350,000. A rhodium complex (**12**) containing the 2,2-biimidazole ligand and Cp* ligands was also prepared and examined for the FA dehydrogenation as suggested by the initial DFT screening.^[10g] Although complex **12** provided a higher TOF of 20,000 h⁻¹ at 90 °C under the optimized FA/SF ratio than that of Ru **11** as predicted, the catalyst decomposed quickly and rearranged to an inactive species containing a Rh₂H₂ core bridged by an N,N'-ligand based on the NMR and HRMS analysis. It was concluded that while DFT guided design of new catalysts is a very powerful tool, cautions should be paid.

Since the commercial FA sources usually contain 5-15% of water, the high activity and good stability of the water-soluble catalysts with N, N or N, C-type ligands make H₂ generation from FA more feasible for potential applications. These N, N or N, C-

type ligands work very well with precious metals, but the cost of these metals may limit the practical usage in a large scale. How to balance the efficiency and cost should be considered further. More discussions will continue in section 5.

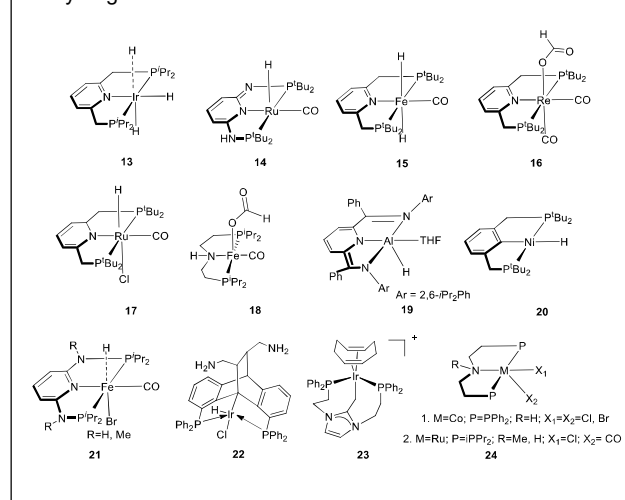
4. Catalysts with a pincer-type ligand

Recently, various metal complexes supported by pincer ligands were reported to show high activity in the selective FA decomposition. In 2011, Nozaki and co-workers first investigated the PNP-ligated iridium trihydride complex **13** dehydrogenation behavior in the idea of reversible H₂ fixation, and the H₂ gas was measured by water replacement to provide a TON of 890 (Scheme 9).^[8a]

As the hydrogen transfer of ketones was demonstrated using the Ru-PN³(P) pincer complexes,^[35] it was not a surprise that the FA dehydrogenation could also proceed.^[9m, 9r, 36] This well-defined PN³-Pincer Ru catalytic system (**14**) can efficiently and selectively liberate H₂ from FA under mild conditions without CO and reached a TOF of 7,000 h⁻¹ and a TON more than 1.1 million during a long lifetime over 150 hours.^[9m] Mechanistic studies suggested the imine arm participates in the FA activation via deprotonation/reprotonation step,^[9f] and the N-H arms may play a role to enhance the stability.^[8q] It is worth noting that this Ru catalyst can be even used for the production of high-pressure H₂ in the presence of organic solvents. The highest pressure of 20 Mpa can be achieved when using 1,4-dioxane as solvent at 80 °C.^[37] The first self-sustained FA-based H₂ fuel cell electricity generating device was developed by Huang and Zheng accordingly in 2015.^[38]

In 2013, the PNP-Fe complex **15** was employed to efficiently and selectively catalyze the FA dehydrogenation by Milstein's group, giving the activity in 1,4-dioxane of TOF=653 h⁻¹ at 40 °C in the presence of Et₃N. A TON of 100,000 was accomplished in ten days.^[11d] In 2014, the PNP-Re analog **16** was reported by the same group showing the catalytic dehydrogenation behavior under base-free conditions.^[25a] The isotope experiments were carried out to explore a possible reaction mechanism, suggesting that FA protonates the dearomatized PNP-Re (*cis*-[Re(PNP^tBu)(CO)₂]) to generate the formate complex *cis*-[Re(PNP^tBu)(CO)₂(OOCH)] (**16**)

Scheme 9. Selected pincer-type catalysts reported for FA dehydrogenation



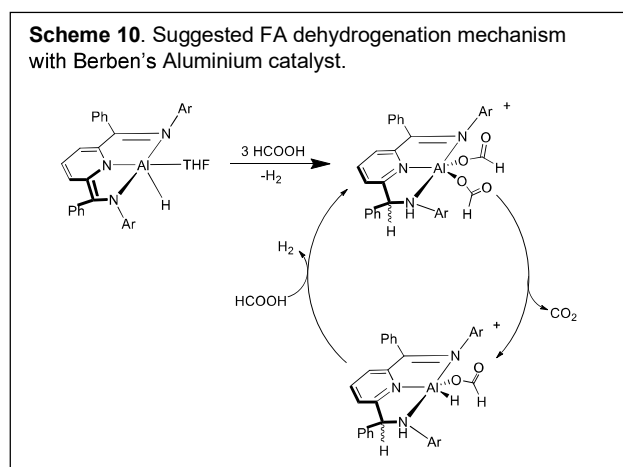
which subsequently undergoes decarboxylation and dehydrogenation to produce H₂ and CO₂.

In 2014, Pidko and co-workers investigated FA dehydrogenation using complex **17**, [Ru(PNP^tBu)H(CO)Cl]. The optimized conditions with the trihexylamine as additive was employed in DMF to offer a high TOF of 256,000 h⁻¹ and a TON of 706,500 at 90 °C without any CO formation. Interestingly, when DBU was used, the TOF decreased dramatically to 93,100 h⁻¹.^[9h] With continuous feeding of FA at 90 °C, both DBU and Et₃N could assist the H₂ formation. It was proven that the temperature (65-90 °C) is the key to controlling the reaction rate in the presence of DBU, showing first order kinetics on the FA concentration. In the presence of a weaker base, NEt₃, the release of H₂ through the reaction of a metal-hydride intermediate and a proton was favored compared to the C-H bond cleavage of the formate group. However, with the stronger base, DBU, the initial base-assisted H₂ process is rate-limiting. This catalytic system holds a promise for the development of H₂ storage, an integrated and compact 25 kW FA-to-power system was developed recently.^[39]

Hazari and Schneider reported PNP iron complex **18** of Fe(^RPNHP) (^RPNHP = HN[CH₂CH₂(PR₂)₂]; R = ⁱPr) in dioxane.^[11e] The presence of Lewis acid (LA) interacted with the proposed active iron formate species provided the high of 196,700 and a TON of 1 million at 80°C in 9.5 hours. However, these high TONs can only be realized at low catalyst loadings (0.0001 mol%), limiting its potential in the practical applications.

Berben's group established aluminum complex **19** to expand the scope of pincer ligand by using phenyl-substituted bis(imino)pyridine ligands to achieve a high initial TOF of 5,200 h⁻¹ in THF using a 5FA/2Et₃N substrate at 65 °C.^[26d] According to the analysis of NMR, IR, and X-ray, a plausible mechanism was proposed to proceed via an Al-(OOCH)₂ species (unlike other monoformate intermediates) followed by β-hydride elimination and FA-enabled protonation (Scheme 10). Further insights about these mechanistic pathways have been scrutinized computationally by

Scheme 10. Suggested FA dehydrogenation mechanism with Berben's Aluminium catalyst.



Yu and Fu.^[40]

Enthaler's group reported the first Ni-based PCP pincer complex **20** for the FA decomposition to CO₂ and H₂ with the TON of up to 626 (Scheme 9).^[25b] However, the efficiency is not as good as those of others complexes.^[11d] The corresponding nickel

hydride and nickel formate complexes were found to be the intermediates in the catalytic cycle.

In 2016, Gonsalvi and Kirchner also reported PN³P-Fe pincer complexes **21** for the FA dehydrogenation.^[11g] The influences of various factors, such as bases, additives, temperatures and catalyst loadings were systematically studied. The results showed that the highest TOF of 2,635 h⁻¹ and a full conversion were obtained with a low catalyst loading of 0.01 mol% in an aprotic solvent at 80 °C after 6 hours.

In 2017, Gelman and Schapiro investigated an amine-functionalized Ir(III)-PC(sp³)P complex **22**, which gave a TON of 500,000 and a TOF of 20,000 h⁻¹, respectively. According to the experimental and theoretical results, H₂ is released by intramolecular metal-ligand cooperation via Ir-hydride and acidic remote functionality.^[41] Oro's group also reported an iridium complex **23** that bearing a PCP and an N-heterocyclic olefin ligand. This catalyst can work both in water and under solvent-free conditions, demonstrating a TOF of 11,590 h⁻¹ using a low catalyst loading of 0.001 mol%.^[42]

In 2019, PNP-Co complexes **24** catalyzed FA dehydrogenation in an aqueous solution was reported by Beller's group.^[43] It was demonstrated that the optimized system afforded a maximum TON of 7,166 by PNP-Co complexes. The carbonyl coordination to the cobalt center led to the deactivation of the catalyst. In contrast to the bifunctional out-sphere mechanism,^[11e] the PNP-Co system showed that although N-H functional group was not directly involved in the H₂ formation. While the N-H group can assist the elimination of Co-H via hydrogen bonding of N-H...OOCH, the team found the catalytic activity was improved by replacing N-H with N-Me in a PNP-Ru analog **24**.^[44]

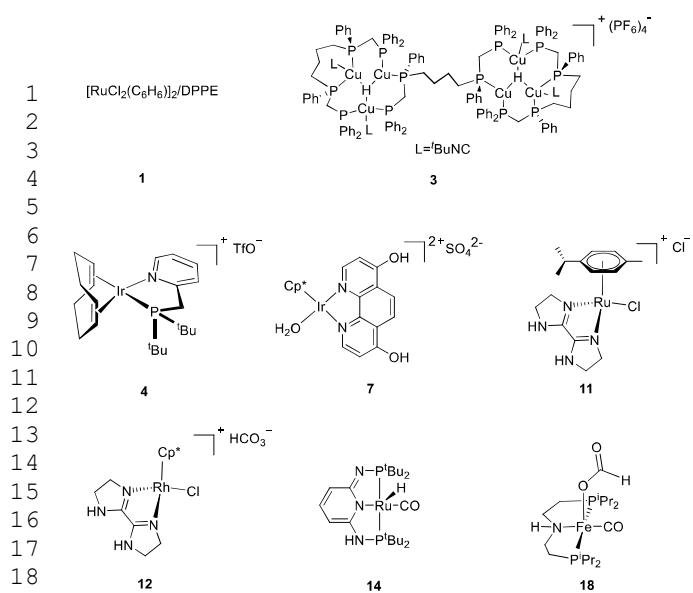
5. The assessment of representative catalysts using the CON/COF system

$$\text{CON} = \frac{1}{\text{TON}} \times \frac{\text{Mw (product)}}{\text{Mw (catalyst)}} \times \frac{\text{Price/kg (catalyst)}}{\text{Price/kg (product)}} \quad (1)$$

$$\text{COF} = \frac{1}{\text{TOF}} \times \frac{\text{Mw (product)}}{\text{Mw (catalyst)}} \times \frac{\text{Cost/kg (catalyst)}}{r_{\text{FC}}(\text{H}_2)/C_s} \quad (2)$$

$$d_{\text{service}} = 0.2 \text{ km/s} \times \frac{\text{TON}}{\text{TOF}} [\text{S}^{-1}] \quad (3)$$

Some of the representative catalysts with different types of ligands mentioned above may be developed for practical usages in the dehydrogenation of FA. Specific technical requirements have to be met if they are used in a H₂ fuel cell in electric vehicles.^[5] The parameters for considerations include the selectivity for the FA dehydrogenation, the activity of the catalyst (generally measured as the TOF at a given temperature, the lifetime of catalyst (typically characterized by TONs), and the cost of the catalyst. While the importance of these key factors are widely recognized, there was no relatively unified standard to evaluate different catalytic systems. We have thus proposed the concept of CON (eq 1), COF (eq 2), $r_{\text{FC}}(\text{H}_2) = 0.713 \text{ mmol} \cdot (\text{s} \cdot \text{kW})^{-1}$, $C_s =$ and d_{service} (eq 3), to offer dimension-free key parameters with process-specifics based on TON and TOF for normalizing catalysts costs.^[5] Herein, eight



homogeneous catalysts were selected for assessment under this evaluation system.

Table 1. Selected recent catalysts for evaluation.

catalyst	operation conditions	cost (\$/mol) ^a	TON ($\times 10^3$)	TOF (h^{-1})
1	in DMOA at 25 °C	60,000	>1,000	1,000
3	in CD ₃ CN/NEt ₃ at 70 °C	90,000	1.5	188 ^b
4	solvent free at 90 °C	141,000	2,160	13,320
7	in H ₂ O at 60 °C	98,000	5,000	1,900
11	in H ₂ O at 90 °C	85,000	350	12,000
12	in H ₂ O at 90 °C	286,000	0.75	20,000
14	in DMSO/NEt ₃ at 90 °C	35,000	1,100	7333 ^b
18	in Dioxane/LiBF ₄ at 80 °C	11,000	984	196,728

^aThe price estimation was based on the reference 5i. ^bAn average over the catalyst lifetime.

The CON and COF analysis is summarized in Figure 1. Catalysts **1** and **7** have potential for practical usage because they have high enough TONs, and therefore lower CONs, even though the costs per mole are higher for catalysts containing precious metals. However, due to the slow TOFs, they may be more suitable for stationary applications. While catalyst **3** uses cooper, the ligand is expensive, resulting in a final catalyst price even exceeding those of the precious metal complexes **1**, **11**, and **14**. Its small TON of 1,500 thus makes it an unrealistic choice for FA dehydrogenation. Catalyst **12** is extremely unlikely to be used for practical applications due to the high price and low service miles. Ir catalyst **4** and Ru catalyst **14** both have reasonable CONs and COFs making them a good candidate as the catalyst for applications in

transportation with fuel cells. Complex **18** has been discussed previously.^[5i] While the cost factor CON is low enough, due to the requirement of a low catalyst loading (0.0001 mol%), the need for reactor volume to meet the H₂ production rate is deemed too large to be practical.

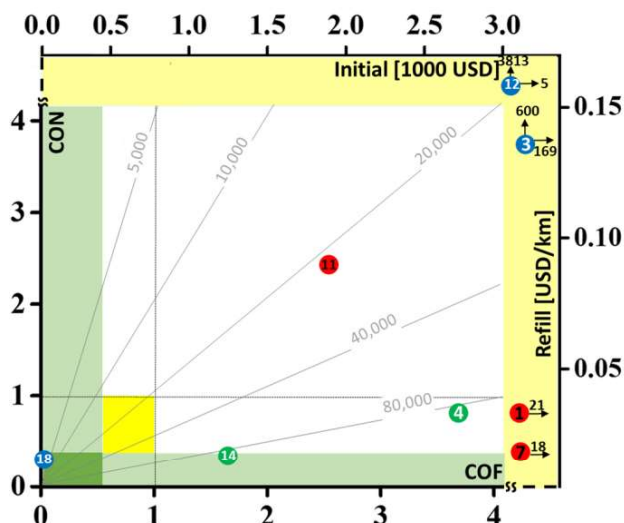


Figure 1. Graphical representation for the selected catalysts evaluated by CON/COF system.

6. Challenges and Opportunities

FA has now been known and considered as a promising candidate for H₂ energy carrier for H₂ fuel cell applications. In principle, infrastructures for fossil fuels may be easily adapted for the FA distribution after minimum modifications against the corrosiveness issues.^[5i] FA-based electricity generation has been demonstrated by several groups. For example, at the ICEF 2016, a 400 W model car that can carry 45 kg at a speed of 8 km/h was introduced to a formic acid workgroup by Huang and Zheng.^[45] Launczy and co-workers also developed a power generator using FA as a H₂ source providing 800W power output.^[7a, 46] A scale-up system at 25 kW for a bus was also built by "Team FAST" and the Pidko group.^[39] From these contributions, utilization of FA can be conceived to play an important role in the future global energy scheme.

However, although the great potential is foreseen, there are still many challenges needed to be addressed before large-scale deployment is possible. For onboard applications, a moderate TOF of 5,000-10,000 h⁻¹ is sufficient, so the search for more economic catalysts with high TON (multi-millions) should be continued. To be coupled with renewable or low-carbon energy sources to utilize the FA technology for energy storage and delivery, more energy efficient ways of formic acid production from hydrogenation or electrochemical reduction of CO₂ are needed. Comprehensive techno-economic analysis employing the CON/COF factors shall assist the identification of a practical catalyst system. Engineering efforts have to be invested to examine the potential and limitation for future improvements. In summary, it is conceivable that FA dehydrogenation system can contribute to the hydrogen energy future and the journey just starts. It is time to transform the challenges into opportunities

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References

- [1] The International Energy Outlook 2019 (IEO2019), <https://www.eia.gov/outlooks/ieo/> (2019).
- [2] World Energy Outlook; International Energy Agency, 2019.
- [3] a) J. A. Turner, *Science* **2004**, *305*, 972-974. b) N. S. Lewis and D. G. Nocera, *Proc Natl Acad Sci U S A* **2006**, *103*, 15729-15735. c) G. M. Whitesides and G. W. J. S. Crabtree, *Science* **2007**, *315*, 796-798. d) P. Moriarty and D. Honnery, *Int. J. Hydrogen Energy* **2009**, *34*, 31-39. e) P. Moriarty and D. Honnery, *Int. J. Hydrogen Energy* **2010**, *35*, 12374-12380.
- [4] a) M. Felderhoff, C. Weidenthaler, R. von Helmolt and U. Eberle, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2643-2653. b) N. Armaroli and V. J. C. Balzani, *ChemSusChem* **2011**, *4*, 21-36.
- [5] a) S. Fukuzumi, *Eur. J. Inorg. Chem.* **2008**, *2008*, 1351-1362; b) S. Enthaler, J. von Langermann and T. Schmidt, *Energy Environ. Sci.* **2010**, *3*, 1207-1217; c) T. C. Johnson, D. J. Morris and M. Wills, *Chem. Soc. Rev.* **2010**, *39*, 81-88; d) B. Loges, A. Boddien, F. Gärtner, H. Junge and M. Beller, *Top. Catal.* **2010**, *53*, 902-914; e) S. Fukuzumi, Y. Yamada, T. Suenobu, K. Ohkubo and H. Kotani, *Energy Environ. Sci.* **2011**, *4*, 2754-2766; f) S. Enthaler and B. Loges, *ChemCatChem* **2012**, *4*, 323-325; g) M. Yadav and Q. Xu, *Energy Environ. Sci.* **2012**, *5*, 9698-9725; h) W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck and E. Fujita, *Chem. Rev.* **2015**, *115*, 12936-12973; i) J. Eppinger and K.-W. Huang, *ACS Energy Lett.* **2017**, *2*, 188-195. j) A. K. Singh, S. Singh and A. Kumar, *Catal. Sci. Technol.* **2016**, *6*, 12-40; k) M. Iglesias and L. A. Oro, *Eur. J. Inorg. Chem.* **2018**, 2125-2138.
- [6] a) X. Zhou, Y. Huang, W. Xing, C. Liu, J. Liao and T. Lu, *Chem. Commun.* **2008**, 3540-3542; b) Y. Huang, X. Zhou, M. Yin, C. Liu and W. Xing, *Chem. Mater.* **2010**, *22*, 5122-5128; c) X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita and Q. Xu, *J. Am. Chem. Soc.* **2011**, *133*, 11822-11825; d) K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. W. Smith and S. C. E. Tsang, *Nat. Nanotechnol.* **2011**, *6*, 302-307; e) Q.-Y. Bi, X.-L. Du, Y.-M. Liu, Y. Cao, H.-Y. He and K.-N. Fan, *J. Am. Chem. Soc.* **2012**, *134*, 8926-8933; f) K. Mori, M. Dojo and H. Yamashita, *ACS Catal.* **2013**, *3*, 1114-1119. g) Z.-L. Wang, J.-M. Yan, Y. Ping, H.-L. Wang, W.-T. Zheng and Q. Jiang, *Angew. Chem. Int. Ed.* **2013**, *52*, 4406-4409; h) S. Zhang, Ö. Metin, D. Su and S. Sun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3681-3684; i) K. Jiang, K. Xu, S. Zou and W.-B. Cai, *J. Am. Chem. Soc.* **2014**, *136*, 4861-4864; j) Q.-L. Zhu, N. Tsumori and Q. Xu, *Chem. Sci.* **2014**, *5*, 195-199; k) Y. Chen, Q.-L. Zhu, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.* **2015**, *137*, 106-109.
- [7] a) M. Grasmann and G. Laurenczy, *Energy Environ. Sci.* **2012**, *5*, 8171-8181; b) D. Mellmann, P. Sponholz, H. Junge and M. Beller, *Chem. Soc. Rev.* **2016**, *45*, 3954-3988; c) K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller and G. Laurenczy, *Chem. Rev.* **2017**, *118*, 372-433; d) L. Wang, R. Kanega, H. Kawanami and Y. Himeda, *Chem. Rec.* **2017**, *17*, 1071-1094; e) N. Onishi, M. Iguchi, X. Yang, R. Kanega, H. Kawanami, Q. Xu and Y. Himeda, *Adv. Energy Mater.* **2018**, 1801275; f) N. Onishi, G. Laurenczy, M. Beller and Y. Himeda, *Coord. Chem. Rev.* **2018**, *373*, 317-332.
- [8] a) R. Tanaka, M. Yamashita, L. W. Chung, K. Morokuma and K. Nozaki, *Organometallics* **2011**, *30*, 6742-6750; b) J. F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman and E. Fujita, *Nat. Chem.* **2012**, *4*, 383-388; c) J. H. Barnard, C. Wang, N. G. Berry and J. Xiao, *Chem. Sci.* **2013**, *4*, 1234-1244; d) E. Fujita, J. T. Muckerman and Y. Himeda, *Biochim. Biophys. Acta* **2013**, *1827*, 1031-1038; e) S. Oldenhof, B. de Bruin, M. Lutz, M. A. Siegler, F. W. Patureau, J. I. van der Vlugt and J. N. Reek, *Chem. Eur. J.* **2013**, *19*, 11507-11511; f) Y. Manaka, W.-H. Wang, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita and Y. Himeda, *Catal. Sci. Technol.* **2014**, *4*, 34-37; g) A. Matsunami, Y. Kayaki and T. Ikariya, *Chem. Eur. J.* **2015**, *21*, 13513-13517; h) S. Oldenhof, M. Lutz, B. de Bruin, J. I. van der Vlugt and J. N. Reek, *Chem. Sci.* **2015**, *6*, 1027-1034; i) Z. Wang, S. M. Lu, J. Li, J. Wang and C. Li, *Chem. Eur. J.* **2015**, *21*, 12592-12595; j) J. J. A. Celaj, Z. Lu, E. A. Kedzie, N. J. Terrile, J. N. Lo and T. J. Williams, *Nat. Commun.* **2016**, *7*, 11308; k) M. Czaun, J. Kothandaraman, A. Goeppert, B. Yang, S. Greenberg, R. B. May, G. A. Olah and G. S. Prakash, *ACS Catal.* **2016**, *6*, 7475-7484; l) M. Iguchi, Y. Himeda, Y. Manaka and H. Kawanami, *ChemSusChem* **2016**, *9*, 2749-2753; m) M. Iguchi, Y. Himeda, Y. Manaka, K. Matsuoka and H. Kawanami, *ChemCatChem* **2016**, *8*, 886-890; n) N. Onishi, M. Z. Ertem, S. Xu, A. Tsurusaki, Y. Manaka, J. T. Muckerman, E. Fujita and Y. Himeda, *Catal. Sci. Technol.* **2016**, *6*, 988-992; o) C. Broicher, S. R. Foit, M. Rose, P. J. Hausoul and R. Palkovits, *ACS Catal.* **2017**, *7*, 8413-8419; p) M. Iguchi, H. Zhong, Y. Himeda and H. Kawanami, *Chem. Eur. J.* **2017**, *23*, 17788-17793; q) A. Matsunami, S. Kuwata and Y. Kayaki, *ACS Catal.* **2017**, *7*, 4479-4484; r) S.-M. Lu, Z. Wang, J. Wang, J. Li and C. Li, *Green Chem.* **2018**, *20*, 1835-1840; s) N. Onishi, R. Kanega, E. Fujita and Y. Himeda, *Adv. Synth. Catal.* **2019**, *361*, 289-296; t) S. Wang, H. Huang, T. Roisnel, C. Bruneau and C. Fischmeister, *ChemSusChem* **2019**, *12*, 179-184.
- [9] a) C. Fellay, P. J. Dyson and G. Laurenczy, *Angew. Chem. Int. Ed.* **2008**, *47*, 3966-3968; b) B. Loges, A. Boddien, H. Junge and M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3962-3965; c) A. Boddien, B. Loges, H. Junge, F. Gärtner, J. R. Noyes and M. Beller, *Adv. Synth. Catal.* **2009**, *351*, 2517-2520; d) S. Fukuzumi, T. Kobayashi and T. Suenobu, *J. Am. Chem. Soc.* **2010**, *132*, 1496-1497; e) M. Czaun, A. Goeppert, J. Kothandaraman, R. B. May, R. Haiges, G. S. Prakash and G. A. Olah, *ACS Catal.* **2013**, *4*, 311-320; f) I. Mellone, M. Peruzzini, L. Rosi, D. Mellmann, H. Junge, M. Beller and L. Gonsalvi, *Dalton Trans.* **2013**, *42*, 2495-2501; g) P. Sponholz, D. Mellmann, H. Junge and M. Beller, *ChemSusChem* **2013**, *6*, 1172-1176; h) G. A. Filonenko, R. van Putten, E. N. Schulpen, E. J. Hensen and E. A. Pidko, *ChemCatChem* **2014**, *6*, 1526-1530; i) A. Guerriero, H. Bricout, K. Sordakis, M. Peruzzini, E. Monflier, F. Hapiot, G. Laurenczy and L. Gonsalvi, *ACS Catal.* **2014**, *4*, 3002-3012. j) K. Sordakis, M. Beller and G. Laurenczy, *ChemCatChem* **2014**, *6*, 96-99; k) K. Sordakis, A. F. Dalebrook and G. Laurenczy, *ChemCatChem* **2015**, *7*, 2332-2339; l) C. Guan, D.-D. Zhang, Y. Pan, M. Iguchi, M. J. Ajitha, J. Hu, H. Li, C. Yao, M.-H. Huang and S. Min, J. Zheng, Y. Himeda, H. Kawanami and K.-W. Huang, *Inorg. Chem.* **2017**, *56*, 438-445; m) Y. Pan, C. L. Pan, Y. Zhang, H. Li, S. Min, X. Guo, B. Zheng, H. Chen, A. Anders and Z. Lai, J. Zheng and K.-W. Huang, *Chem. Asian J.* **2016**, *11*, 1357-1360; n) V. Henricks, I. Yuranov, N. Autissier and G. Laurenczy, *Catalysts* **2017**, *7*, 348; o) S. Siek, D. B. Burks, D. L. Gerlach, G. Liang, J. M. Tesh, C. R. Thompson, F. Qu, J. E. Shankwitz, R. M. Vasquez and N. Chambers, *Organometallics* **2017**, *36*, 1091-1106; p) C. Fink, L. Chen and G. Laurenczy, *Z. Anorg. Allg. Chem.* **2018**, *644*, 740-744; q) Y. Nakahara, T. Toda, A. Matsunami, Y. Kayaki and S. Kuwata, *Chem. Asian J.* **2018**, *13*, 73-80; r) X. Wang, E. A. P. Ling, C. Guan, Q. Zhang, W. Wu, P. Liu, N. Zheng, D. Zhang, S. Lopatin, Z. Lai and K.-W. Huang, *ChemSusChem* **2018**, *11*, 3591-3598; s) Z. Xin, J. Zhang, K. Sordakis, M. Beller, C. X. Du, G. Laurenczy and Y. Li, *ChemSusChem* **2018**, *11*, 2077-2082; t) Y. Zhang, X. Chen, B. Zheng, X. Guo, Y. Pan, H. Chen, H. Li, S. Min, C. Guan, K.-W. Huang and J. Zheng, *Proc Natl Acad Sci U S A* **2018**, *115*, 12395-12400; u) A. Frenklah, Z. Treigerman, Y. Sasson and S. Kozuch, *Eur. J. Org. Chem.* **2019**, *2019*, 591-597; v) C. Prichatz, M. Trincado, L. Tan, F. Casas, A. Kammer, H. Junge, M. Beller and H. Grützmacher, *ChemSusChem* **2018**, *11*, 3092-3095.
- [10] a) S. Fukuzumi, T. Kobayashi and T. Suenobu, *ChemSusChem* **2008**, *1*, 827-834; b) Y. Himeda, S. Miyazawa and T. Hirose, *ChemSusChem* **2011**, *4*, 487-493; c) A. Nova, D. J. Taylor, A. J. Blacker, S. B. Duckett, R. N. Perutz and O. Eisenstein, *Organometallics* **2014**, *33*, 3433-3442; d) L. Jongbloed, B. De Bruin, J. Reek, M. Lutz and J. Van der Vlugt, *Catal. Sci. Technol.* **2016**, *6*, 1320-1327; e) C. Fink and G. Laurenczy, *Dalton Trans.* **2017**, *46*, 1670-1676; f) J. Fidalgo, M. Ruiz-Castañeda, G. García-Herbosa, A. Carbayo, F. I. A. Jalón, A. M. Rodríguez, B. R. Manzano and G. Espino, *Inorg. Chem.* **2018**, *57*, 14186-14198; g) C. Guan, D.-D. Zhang, T. Zhang, M.-H. Huang, P. Chakraborty, H. Li, C. Yao, C. Zhou, J. Hu and K.-W. Huang, *Int. J. Hydrogen Energy* **2019**, *44*, 28421-28429.
- [11] a) A. Boddien, F. Gärtner, R. Jackstell, H. Junge, A. Spannenberg, W. Baumann, R. Ludwig and M. Beller, *Angew.*

- Chem. Int. Ed.* **2010**, *49*, 8993-8996; b) A. Boddien, B. r. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig and M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 8924-8934; c) A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science* **2011**, *333*, 1733-1736; d) T. Zell, B. Butschke, Y. Ben-David and D. Milstein, *Chem. Eur. J.* **2013**, *19*, 8068-8072; e) E. A. Bielinski, P. O. Lagaditis, Y. Zhang, B. Q. Mercado, C. Würtele, W. H. Bernskoetter, N. Hazari and S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 10234-10237; f) F. Bertini, I. Mellone, A. Ienco, M. Peruzzini and L. Gonsalvi, *ACS Catal.* **2015**, *5*, 1254-1265; g) I. Mellone, N. Gorgas, F. Bertini, M. Peruzzini, K. Kirchner and L. Gonsalvi, *Organometallics* **2016**, *35*, 3344-3349.
- [12] R. S. Coffey, *ChemComm* **1967**, 923-924.
- [13] R. S. Paonessa and W. C. Troglor, *J. Am. Chem. Soc.* **1982**, *104*, 3529-3530.
- [14] A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 2521-2522.
- [15] a) Y. Gao, J. Kuncheria, G. P. A. Yap and R. J. Puddephatt, *ChemComm* **1998**, 2365-2366; b) Y. Gao, J. K. Kuncheria, H. A. Jenkins, R. J. Puddephatt and G. Payap, *J. Chem. Soc., Dalton Trans* **2000**, 3212-3217.
- [16] B. ElAmin, G. M. Anantharamaiah, G. P. Royer and G. E. Means, *J. Org. Chem.* **1979**, *44*, 3442-3444.
- [17] a) Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa and K. Kasuga, *J. Mol. Catal. A: Chem.* **2003**, *195*, 95-100; b) Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara and K. Kasuga, *J. Photochem. Photobiol. A: Chem.* **2006**, *182*, 306-309.
- [18] A. M. Hayes, D. J. Morris, G. J. Clarkson and M. Wills, *J. Am. Chem. Soc.* **2005**, *127*, 7318-7319.
- [19] a) A. Boddien, B. Loges, H. Junge and M. Beller, *ChemSusChem* **2008**, *1*, 751-758. b) H. Junge, A. Boddien, F. Capitta, B. Loges, J. R. Noyes, S. Gladiali and M. Beller, *Tetrahedron Lett.* **2009**, *50*, 1603-1606.
- [20] J. Kovács, F. Joó, A. C. Bényei and G. Laurenczy, *Dalton Trans.* **2004**, 2336-2340.
- [21] C. Fellay, N. Yan, P. J. Dyson and G. Laurenczy, *Chem. Eur. J.* **2009**, *15*, 3752-3760.
- [22] A. Thevenon, E. Frost-Pennington, G. Weijia, A. F. Dalebrook and G. Laurenczy, *ChemCatChem* **2014**, *6*, 3146-3152.
- [23] W. Gan, D. J. M. Snelders, P. J. Dyson and G. Laurenczy, *ChemCatChem* **2013**, *5*, 1126-1132.
- [24] a) Y. Himeda, *Green Chem.* **2009**, *11*, 2018-2022. b) W. H. Wang, J. F. Hull, J. T. Muckerman, E. Fujita, T. Hirose and Y. Himeda, *Chem. Eur. J.* **2012**, *18*, 9397-9404; c) W.-H. Wang, J. F. Hull, J. T. Muckerman, E. Fujita and Y. Himeda, *Energy Environ. Sci.* **2012**, *5*, 7923-7926; d) W.H. Wang, S. Xu, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita and Y. Himeda, *ChemSusChem* **2014**, *7*, 1976-1983; e) M. Z. Ertem, Y. Himeda, E. Fujita and J. T. Muckerman, *ACS Catal.* **2016**, *6*, 600-609.
- [25] a) M. Vogt, A. Nerush, Y. Diskin-Posner, Y. Ben-David and D. Milstein, *Chem. Sci.* **2014**, *5*, 2043-2051; b) S. Enthaler, A. Brück, A. Kammer, H. Junge, E. Irran and S. Gülak, *ChemCatChem* **2015**, *7*, 65-69; c) T. Zell and D. Milstein, *Acc. Chem. Res.* **2015**, *48*, 1979-1994.
- [26] a) J. H. Shin, D. G. Churchill and G. Parkin, *J. Organomet. Chem.* **2002**, *642*, 9-15; b) D. J. Morris, G. J. Clarkson and M. Wills, *Organometallics* **2009**, *28*, 4133-4140; c) T. P. Rieckborn, E. Huber, E. Karakoc and M. H. Prosenc, *Eur. J. Inorg. Chem.* **2010**, *2010*, 4757-4761; d) T. Myers and L. Berben, *Chem. Sci.* **2014**, *5*, 2771-2777; e) N. Scotti, R. Psaro, N. Ravasio and F. Zaccheria, *RSC Adv.* **2014**, *4*, 61514-61517; f) M. C. Neary and G. Parkin, *Dalton Trans.* **2016**, *45*, 14645-14650; g) T. Nakajima, Y. Kamiryo, M. Kishimoto, K. Imai, K. Nakamae, Y. Ura and T. Tanase, *J. Am. Chem. Soc.* **2019**, *141*, 8632-8736.
- [27] D. Mellmann, E. Barsch, M. Bauer, K. Grabow, A. Boddien, A. Kammer, P. Sponholz, U. Bentrup, R. Jackstell, H. Junge, G. Laurenczy, R. Ludwig and M. Beller, *Chem. Eur. J.* **2014**, *20*, 13589-13602.
- [28] Y. Maenaka, T. Suenobu and S. Fukuzumi, *Energy Environ. Sci.* **2012**, *5*, 7360-7367.
- [29] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara and K. Kasuga, *Organometallics* **2007**, *26*, 702-712.
- [30] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara and K. Kasuga, *J. Am. Chem. Soc.* **2005**, *127*, 13118-13119.
- [31] C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* **1991**, *91*, 165-195.
- [32] Y. Li, J. Li, D. Zhang and C. Liu, *ACS Catal.* **2016**, *6*, 4746-4754.
- [33] S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1204.
- [34] a) S. Xu, N. Onishi, A. Tsurusaki, Y. Manaka, W.-H. Wang, J. T. Muckerman, E. Fujita and Y. Himeda, *Eur. J. Inorg. Chem.* **2015**, *2015*, 5591-5594; b) L. Wang, N. Onishi, K. Murata, T. Hirose, J.T. Muckerman, E. Fujita and Y. Himeda, *ChemSusChem*, **2017**, *10*, 1071-1075.
- [35] a) K.-W. Huang, T. Chen, L. He, D. Gong, W. Jia and L. Yao. U.S. Patent No. 8,598,351 B2, 2013; b) H. Li, B. Zheng and K.-W. Huang, *Coord. Chem. Rev.* **2015**, *293*, 116-138; c) H. Li, T. P. Gonçalves, D. Lupp, K.-W. Huang, *ACS Catal.* **2019**, *9*, 1619-29.
- [36] a) C. Guan, Y. Pan, E. P. L. Ang, J. Hu, C. Yao, M.-H. Huang, H. Li, Z. Lai and K.-W. Huang, *Green Chem.* **2018**, *20*, 4201-4205; b) K.-W. Huang, Y. Pan, C. Guan, P. Chakraborty, H. Li and C. Zhou, *Dalton Trans.* **2019**, *48*, 12812-12816. c) K.-W. Huang, C. Pan and Y. Pan. U.S. Patent No. 10,300,469 B1, 2019.
- [37] M. Iguchi, C. Guan, K.-W. Huang and H. Kawanami, *Int. J. Hydrogen Energy* **2019**, *44*, 28507-28513.
- [38] K.-W. Huang and J. Zheng. E. P. Patent No. 3,391,447 B1, 2019.
- [39] R. van Putten, T. Wissink, T. Swinkels and E. A. Pidko, *Int. J. Hydrogen Energy* **2019**, *44*, 28533-28541.
- [40] Q.-Q. Lu, H.-Z. Yu and Y. Fu, *Chem. Eur. J.* **2016**, *22*, 4584-4591.
- [41] S. Cohen, V. Borin, I. Schapiro, S. Musa, S. De-Botton, N. V. Belkova and D. Gelman, *ACS Catal.* **2017**, *7*, 8139-46.
- [42] A. Iturmendi, M. Iglesias, J. Munarriz, V. Polo, V. Passarelli, J. J. Pérez-Torrente and L. A. Oro, *Green Chem.* **2018**, *20*, 4875-4879.
- [43] W. Zhou, Z. Wei, A. Spannenberg, H. Jiao, K. Junge, H. Junge and M. Beller, *Chem. Eur. J.* **2019**, *25*, 8459-8464.
- [44] A. Agapova, E. Alberico, A. Kammer, H. Junge and M. Beller, *ChemCatChem* **2019**, *11*, 1910-1914.
- [45] Innovation for Cool Earth Forum. <http://www.icef-forum.org/> (2016).
- [46] EPFL news. <https://actu.epfl.ch/news/the-world-s-first-formic-acid-based-fuel-cell/> (2018)