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Base-free dehydrogenation of aqueous and neat formic acid with Iridium(III)Cp*(dipyridylamine) catalysts

Shengdong Wang,^{[a]‡} Haiyun Huang,^{[a]‡} Thierry Roisnel,^[b] Christian Bruneau,^[a] Cédric Fischmeister^{*[a]}

Abstract: The selective dehydrogenation of formic acid by Iridium(III)Cp*(dipyridylamine) catalysts is reported. The electron enriched catalyst **Ir6** led to the best performances enabling the base free dehydrogenation of aqueous and neat formic acid. In both cases the reaction was selective with no carbon monoxide detectable. The latent behavior of **Ir6** was demonstrated which may be of practical utility. Experimental results suggest an outer-sphere interaction with the ligand.

Hydrogen will undoubtedly become an essential source of energy for future generations provided some issues related to large scale utilization of this energy vector are solved. In particular hydrogen storage and availability on demand are of major importance. Many options have received attention and are still attracting interest of researchers. Among them, the chemical storage of hydrogen in the form of formic acid is gaining increasing importance. Indeed, formic acid is a stable liquid without important safety and hazard issue, it is therefore easy to handle and transport. Considering the reversibility of formic acid dehydrogenation, i.e. CO₂ hydrogenation, a carbon neutral energy cycle is in theory accessible.^[1] A number of heterogeneous^[2] and homogeneous catalysts^[3] have been reported for the dehydrogenation of formic acid. Heterogeneous catalysts are essentially based on palladium. They are in general reusable but they display low activity. Although the dehydrogenation of formic acid with homogeneous catalysts has been known for more than fifty years,^[4] it is only recently after the reports by Beller and Laurenczy that formic acid has been intensively investigated as a hydrogen reservoir.^[5] Iridium-based complexes are the most studied and efficient homogeneous catalysts reported to date. In 2015, Li reported a TOF value of 487 500 h⁻¹ obtained with a cationic iridium complex, which to the best of our knowledge is still the highest reported TOF. This catalyst, as most iridium catalysts is a 5-membered iridacycle operating in water, which is one of the prerequisite for this transformation considering potential application in fuel cells. Another important issue to consider is the use of additives, in

particular basic additives such as alkylamines. Such additives would complicate an overall fuel cell process since an additional hydrogen post-purification step would be necessary for their removal. To date, only a few catalysts able to promote formic acid dehydrogenation under base-free conditions have been reported.^[6] It must be noted that most of these results were obtained using a solvent, in general water. Only few examples of pure formic acid dehydrogenation have been reported. In 2013, Xiao described a series of cyclometallated iridium complexes operating without solvent with an azeotropic mixture of formic acid and triethylamine. The highest initial TOF obtained was 2570 h⁻¹ but when studying the continuous formic acid dehydrogenation they observed extremely high initial activity (TOF 147 000 h⁻¹) upon reloading formic acid.^[7] In 2016, Williams reported the efficient formic acid dehydrogenation under neat conditions using an iridium catalyst bearing a *P,N*-chelate. A TOF of 3000 h⁻¹ was obtained in the presence of a base.^[8] Some reports briefly mention attempts to perform the base-free dehydrogenation of pure formic acids but very low activities were obtained.^[6a, 9]

Herein, we report a new iridium catalyst operating under base free conditions. The catalyst is active in water and under neat conditions and owing to a very good stability it can be used in a semi-continuous mode leading to high cumulative TONs.

Recently, our group has been investigating the reduction of levulinic acid into γ -valerolactone using new ruthenium and iridium complexes bearing dipyridylamine ligands.^[10] This type of catalyst was earlier identified as efficient transfer hydrogenation catalysts of ketones in water.^[11] In particular, we have demonstrated that the transfer hydrogenation of levulinic acid with formic acid was in fact proceeding essentially by hydrogenation resulting from a very fast initial formic acid dehydrogenation under base-free conditions. We have also reported that iridium catalysts were very efficient for this transformation contrary to a related dipyridylamine-ruthenium catalyst.^[12] These results prompted us to investigate in more details the dehydrogenation of formic acid with these 6-membered iridacycles bearing dipyridylamine ligands. We have thus studied some previously reported complexes and also prepared new complexes featuring dimethylamino electron donating substituents (Figure 1) considering previous reports^[13] and the studies on aqueous hydricity of late metal catalysts by Miller.^[14] **Ir1-4** and the new complexes **Ir5-7** were prepared according to a previously reported procedure (see supporting information).

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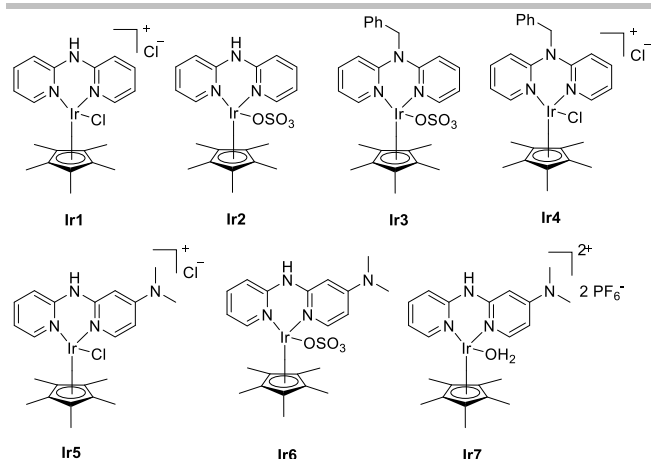


Figure 1. Iridium complexes used in this study

Crystals suitable for X-Ray diffraction for molecular structure determination were obtained for **Ir5** (Figure 2). Analysis of bond lengths and bond angles in **Ir5** revealed no significant differences with those of the parent dimethylamino-free complex **Ir1** reported earlier (see supporting information). Hence, without important alteration of the steric properties, the catalytic properties of the new complexes **Ir5-7** should find their origin in the variation of the electronic properties of the ligand in particular in their stronger electron donation.

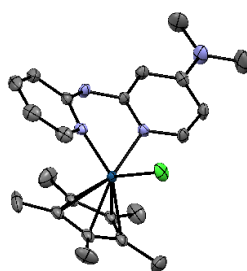


Figure 2. Molecular structure of **Ir5** represented at 70% ellipsoid probability. H atoms, Cl⁻, and solvent are omitted for clarity.

In order to gauge the electronic properties of the ligands, complexes **Ir1**, **Ir2**, **Ir4**, **Ir5** and **Ir6** were analyzed by cyclic voltammetry. In addition, the iridium-bipyridine complex [Cp*Ir(bpy)OSO₃]^[12] **Ir8** closely related to **Ir2** was also studied as a reference. All these complexes display a non-reversible reduction process (see SI). Their E_{pc} was measured in acetonitrile vs ferrocene (Table 1). Several important information can be obtained from these results. Due to the possible exchange of the sulphato-ligand for acetonitrile in the zwitterionic complexes **Ir2** and **Ir6**, information should only be extracted by comparing complexes with the same X-ligand (X = -Cl, -OSO₃).

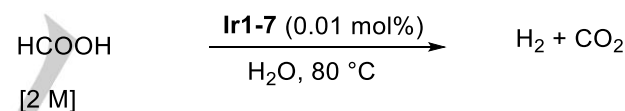
Table 1 Cyclic voltammetry analyses^a

Entry	Complex	E _{pc} (V) ^b
1	Ir1	-1.67
2	Ir2	-2.03
3	Ir4	-2.14
4	Ir5	-1.95
5	Ir6	-2.17
6	Ir8	-1.63

^aComplex 0.0025 M in acetonitrile, Bu₄NPF₆ (0.25 M), v = 100 mV.s⁻¹. ^b Cathodic (reduction) potentials are reported in V vs FeCp₂/FeCp₂⁺ as an internal standard.

First of all, comparing entries 2 and 6, it clearly appears that the dipyriddyamine ligand makes **Ir2** more electron rich than its bipyridine analogue **Ir8**. Comparing data within the dipyriddyamine-iridium complexes also brings key information. As observed upon comparing the reduction potentials of **Ir1** (NH) and **Ir4** (NBz) (Table 1, entries 1,3), the functional modification of the bridging nitrogen in the dipyriddyamine ligand also translates in a lower reduction potential. As expected, the introduction of a dimethylamino- group in the 4-position of one pyridine led to more electron rich complexes; **Ir1** vs **Ir5** (Table 1, entries 1 and 4) and **Ir2** vs **Ir6** (Table 1, entries 2 and 5).

Complexes **Ir1-7** were evaluated in the base-free dehydrogenation of formic acid in water at 80 °C with a low catalyst loading (Scheme 1). All the complexes were fully soluble under the experimental conditions. The gas evolution was measured with a digital flowmeter from which the catalyst activity was determined after 10 minutes.



Scheme 1 Base-free formic acid dehydrogenation

As depicted in Table 2, the best result was obtained with the most electron rich **Ir6** catalyst (Table 2, entry 6). These results also demonstrate the inhibition or low activity of chloro- complex **Ir1** as compared to the more electron rich and zwitterionic sulfato-complex **Ir2**. This is further evidenced by comparing the results obtained with catalysts **Ir5** and **Ir6** (Table 2, entries 5 and 6). The low lability of the chloride ligand is a reasonable hypothesis for explaining the poor activity of chloride complexes. The substitution pattern of the bridging nitrogen atom is also a key factor as both **Ir3** and **Ir4** displayed very low activity (Table 2, entries 3 and 4). In particular, **Ir3** displayed a much lower activity than the unsubstituted **Ir2** catalyst. All together, these results indicate the three main trends for an efficient catalyst: i) Ir-chloride complexes are the least active catalysts. ii) The highest activity is obtained with an electron rich complex. iii) the substitution pattern of the remote bridging amine strongly influences the catalyst efficiency hence suggesting the potential involvement of this bridging N-H group in the catalytic mechanism.

Table 2 Dehydrogenation of FA with **Ir1-7**^a

Entry	Catalyst	TOF (h ⁻¹) ^b
1	Ir1	3047
2	Ir2	8705
3	Ir3	3382
4	Ir4	2980
5	Ir5	4319
6	Ir6	12321
7	Ir7	10781

Conditions: ^aFA (4 mmol), catalyst (0.01 mol%), H₂O (2 mL), 80 °C, 10 min.
^bbased on gas volume released (see SI)

Ir6 was further investigated in order to determine the optimum conditions of use. We first inspected the influence of the reaction pH. Reactions were thus conducted with varying ratio of formic acid and sodium formate. Interestingly, **Ir6** delivered the best performance at pH 1.8 (i. e. no added sodium formate) (Table 3). This is in sharp contrast with other iridium complexes bearing bipyridine or bis-*N*-heterocyclic ligands.^[6d,g,13a-15] for which the best TOFs were obtained at pH 3.5 - 4 (i.e. ~ pK_a of formic acid). This characteristic makes catalyst **Ir6** very interesting since, as explained earlier, it is highly desirable to run the dehydrogenation of FA under additive-free conditions in order to eliminate a post-purification of H₂ when volatile bases such as trialkylamine are used. Furthermore, it opens the way towards the base-free dehydrogenation of neat formic acid which, to the best of our knowledge, has only been scarcely reported with low efficiency (TOF < 800 h⁻¹).^[6a,9] Henceforth, we have investigated the influence of formic acid concentration on the reaction outcome (Figure 3).

Table 3. Influence of the pH on the catalyst performances.^a

Entry	pH	HCOOH/HCOONa ^[b]	TOF ^[c]
1	1.8	4/0	12321
2	3.2	3/1	11584
3	3.7	2/2	8940
4	4.2	1/3	4821
5	7.6	0/4	2276

^a**Ir6**: 0.01 mol%; H₂O: 2 mL, 80 °C, 10 min. ^bmol ratio maintaining total mole number = 4 mmol. ^cTOF calculated from the released gas volume at 10 min.

The dehydrogenation of FA was conducted with **Ir6** at different concentrations ranging from neat formic acid (26.5 M) to a 1 M aqueous solution. TOF higher than 11384 h⁻¹ were obtained with concentrations ranging from 2 M to 8 M with a maximum TOF of 13058 h⁻¹ obtained for a concentration of 3 mol.L⁻¹. Lower concentration (1 M) led to a decrease of the activity to 5800 h⁻¹. Interestingly, the reaction performed in neat formic acid displayed a TOF of 4800 h⁻¹. Although this result is

lower than those obtained in water, it demonstrates the feasibility of a base-free dehydrogenation of neat formic acid, a process of high interest for hydrogen production. To the best of our knowledge, this is the highest TOF reported for the base free dehydrogenation of neat formic acid.

Ideally, for practical utility, formic acid should be stored with a catalyst and produce hydrogen on demand by application of a stimuli (T, light,). Catalyst exhibiting this property are quoted as latent or dormant catalysts and should also display another important property, which is a long term stability in the presence of the reactant. To address this question, a stock solution of **Ir6** (0.08 mol%) in 2 mL of FA was prepared and stored in a fridge (T ± 4 °C). After 2 days, an aliquot was taken and subjected to dehydrogenation by heating at 80 °C. This operation was repeated after 10 days. In both cases, TOFs of 4687 and 4583 h⁻¹ were obtained, respectively, hence corresponding to a slight decrease when compared to 4800 h⁻¹ obtained under the standard conditions. These results demonstrate that the catalyst **Ir6** is stable in pure formic acid.

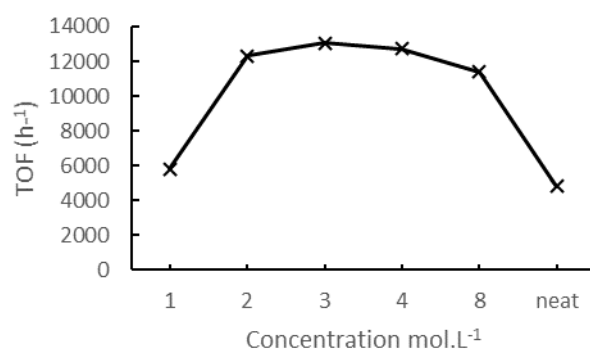


Figure 3 Influence of the concentration on the efficiency of the base-free dehydrogenation of FA. FA (4 mmol), **Ir6** (0.01 mol%), H₂O, 80 °C, 10 min.

The temperature dependence of the catalyst activity was investigated over a range of temperature going from 60 °C to 100 °C in aqueous solution of FA and neat FA (Table 4). It was demonstrated that in both cases, the catalyst remained active even at 60 °C albeit TOF values were low. Highest TOF were obtained at 100 °C and noteworthy, a TOF of 13292 h⁻¹ was obtained for the base-free dehydrogenation of neat FA.

Table 4. Catalyst activity vs T

Entry	T (°C)	TOF (h ⁻¹) FA (3 M in H ₂ O) ^a	TOF (h ⁻¹) Pure FA ^b
1	60	3214	1774
2	70	5825	2678
3	80	13058	4821
4	90	23805	9174
5	100	38236	13292

^aFA: 0.184 g (4 mmol); **Ir6**: 0.01 mol%; H₂O: 1.3 mL, 80 °C, 10 min. ^bFA: 0.184 g (4 mmol); **Ir6**: 0.01 mol%, 80 °C, 10 min

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With these results in hands, we turned our attention to the continuous use of the catalyst in water in order to investigate the productivity of the catalyst. This process was investigated by adding 40 mmol of FA to a solution of **Ir6** (0.001 mol%) in 13.3 mL of water until gas evolution ceased. A new load a FA was then added until no more catalytic activity was observed. After 10 days a cumulative TON of 710 000 could be obtained.

As mentioned earlier, the H₂ purity is of prime importance for application in fuel cells. In particular carbon monoxide resulting from formic acid dehydration is strongly undesired as it is not compatible with platinum electrodes.^[16] The purity of the released gas for the reactions performed with **Ir6** catalyst in H₂O (FA 3M) and in neat FA was measured by gas chromatography using a catharometer detector. In both cases, CO content was below the detection limit of the measuring equipment (< 1 ppm, see supporting information).

Different mechanisms have been proposed for the dehydrogenation of formic acid.^[17] The formation of a metal hydride M-H may occur *via* the formation of a metal-formate followed by a β -hydride elimination. However, this mechanism should require the presence of an external base. Another pathway involves a concerted mechanism where the ligand plays the role of the base through outer-sphere interactions. H-bonding interactions with remote ligands have been proposed in many examples as key features for the formation of metal-hydrides species as well as for the elimination of H₂.^[17,18]

In order to get more insight into the key steps of the mechanism, Kinetic Isotope Effect measurements were performed. As depicted in Table 5, the rate of the reaction performed with formic acid in D₂O was not strongly impacted contrary to reaction performed with deuterated formic acid in H₂O or D₂O. These results clearly demonstrate that cleavage of the H-CO₂H bond to form an Ir-H species constitutes the rate determining step of the reaction. Of note the same study performed in neat FA did not reveal any significant KIE. In this case the rate determining step is not the Ir-H formation and could rather be the elimination of H₂ since water-assisted H₂ elimination has been proposed for reactions conducted in water.^[13a, 19]

Table 5 KIE in the dehydrogenation of FA^a

Entry	Source	Solvent	TOF (h ⁻¹)	KIE
1	HCOOH	H ₂ O	13058	-
2	HCOOH	D ₂ O	8337	1.6
3	DCOOD	H ₂ O	3314	3.9
4	DCOOD	D ₂ O	2980	4.4
5	HCOOH	neat	5122	-
6	DCOOD	neat	4952	1.0(3)

^a Source (4 mmol), **Ir6** (0.01 mol%), H₂O or D₂O (1.3 mL), 80 °C, 10 min. ^b based on gas volume released

Based on these results and the involvement of the remote bridging NH in the dipyrildamine ligand, a tentative catalytic mechanism in water is proposed in Figure 4. An initial displacement of the OSO₃ ligand by water in **Ir6** generates the aquo-complex **a**. A concerted mechanism involving the bridging NH (**b**) and SO₄²⁻ acting as a base then releases CO₂ and the hydride species **c**. An Iridium-hydride species compatible with

the structure of **c** was observed by ¹H NMR in d⁶-DMSO (see supporting information). This NMR did not reveal any protonation of the bridging NH or dimethylamino-group. An outer-sphere interaction with H₂O acting as a proton shuttle then releases H₂ with regeneration of **a**. In the case of the dehydrogenation of neat formic acid, the situation is more intricate since the formation of **a** is not certain, albeit the formic acid used is not anhydrous. Hence the activation of formic acid may follow a different pathway under neat conditions. As explained earlier, the absence of water may also influence the hydrogen release. Further experimental and theoretical calculations will be necessary to clarify this mechanism both in water and neat conditions.

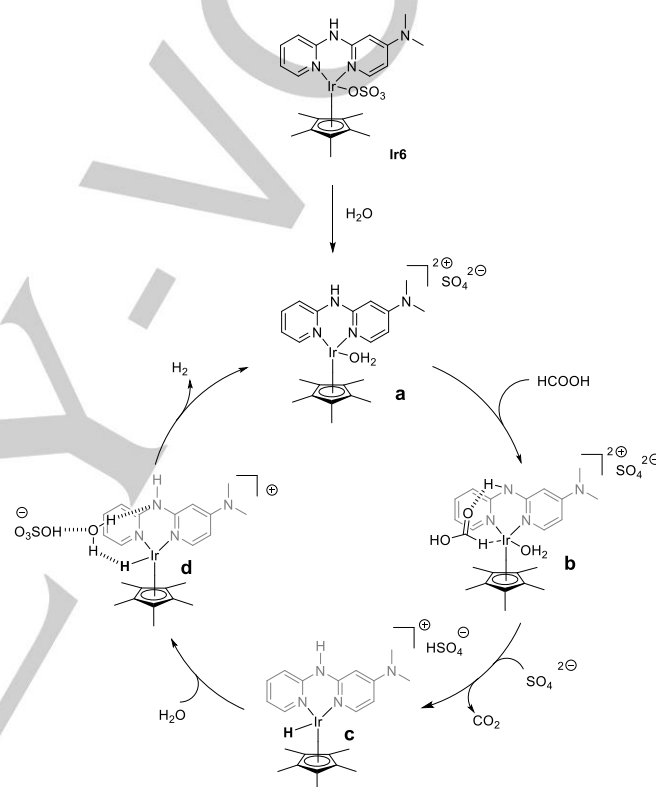


Figure 4 Mechanism proposal

In conclusion, we have prepared a new catalyst bearing an electron enriched dipyrildamine ligand. This catalyst performs the base-free dehydrogenation of aqueous formic acid with high efficiency at temperatures equal or below 100 °C. The base-free dehydrogenation of neat formic acid was also achieved with a TOF of 13292 h⁻¹ obtained at 100 °C. In both cases carbon monoxide was not detected in the released gas. The versatile and tunable dipyrildamine ligands appear as promising ligands possibly operating via outer-sphere interactions. Further investigations will be necessary to elucidate the catalytic mechanism. The latent behavior of the catalyst highlighted in this article will also require deeper investigations to fully assess its potential and utility.

Experimental Section

Full experimental details available as supporting information

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Keywords: Formic acid • Hydrogen • Energy • Iridium • Dipyrindylamine

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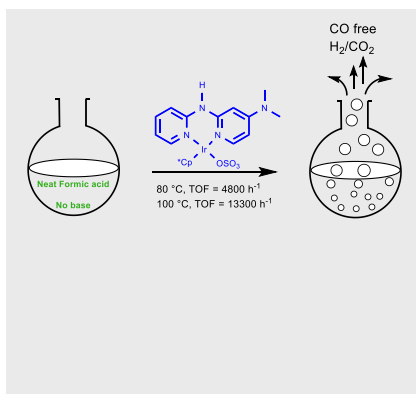
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