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Ir(III)-PC(*sp*³)P Bifunctional Catalysts for Production of H₂ by Dehydrogenation of Formic Acid: Experimental and Theoretical Study

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ABSTRACT Reversible storage of hydrogen in the form of stable and relatively harmless chemical substances such as formic acid (FA) is one of the corner-stones of fossil fuels-free economy. Recently, Ru(III)-PC(sp^3)P (where PC(sp^3)P = modular dibenzobarrelene-based pincer ligand possesing a pendant functional group) complex **1** has been reported as a mild and *E*selective catalyst in semihydrogenation of alkynes with stoichiometric neat formic acid. Discovery of the additive-free protocol for dehydrogenation of FA launched further studies aiming at the rational design of highly efficient catalysts for this reaction operating under neutral conditions. We now report the results of our investigation on a series of bifunctionl PC(sp^3)P complexes equipped with different outer-sphere auxiliaries, that allowed to identify an aminefunctionalized Ir(III)-PC(sp^3)P complex **3**, as a clean and efficient catalyst for the FA dehydrogenation. The catalyst is suitable for fuel cells applications demonstrating TON up to 5*10⁵ and TOF up to 2*10⁴ h⁻¹ (3.8*10⁵ and 1.2*10⁴ h⁻¹ with no additives). In addition to the practical value of the catalyst, experimental and computational mechanistic studies provide rationale for the design of improved next-generation catalysts.

KEYWORDS. ligand-metal cooperation, dehydrogenation, formic acid, hydrogen, pincer complexes.

Introduction

Efficient hydrogen-based fuel technology is an important concept for the development of future global energy markets. However, successful realization of the environmentally benign fuel solutions is conditioned upon finding a way to reversibly store hydrogen under ambient conditions. Dehydrogenation of formic acid (FA) is among the favorites on the list of potential hydrogen storage-release systems, especially, for fuel cell applications because formic acid is sustainable (as it maybe produced chemically or biotechnologically from naturals stocks on million tonnes/year scale on demand),¹ it is stable in transportation and relatively harmless in storage. Finally yet importantly, FA is technologically convenient for engineering fuel cells, as only one gaseous by-product (CO_2) is co-produced upon hydrogen liberation.

Dehydrogenation of neat FA under relatively harsh reaction temperatures using either heterogeneous or heterogenized catalysts was known for a long time.² However, dehydration of FA leading to the formation of carbon monoxide often accompanies high-temperature processes, which complicates any fuel cell applications.³ Homogeneous catalysis brought a significant progress in the CO-free dehydrogenation. The most efficient catalytic systems based on Ir, Ru, Au, Ag, Pd and Fe complexes have been reported to dehydrogenate FA selectively to H₂ and CO₂.⁴ Some of these catalysts demonstrate exceptionally high stability (TONs up to 5*10⁶), high conversion rates (TOFs up to 5*10⁵ h⁻¹), but some require the presence of over- or slightly substoichiometric bases. For example, FA/amine azeotropes are often employed to achieve the desired conversions;^{4c, 4m, 4q, 5} iodide ions were found to enhance the rate of

the dehydrogenation even further.⁶ However, such mixtures are less attractive for the fuel cell applications because they are characterized by a lower hydrogen content, on the one hand, and because of the complicated waste treatment, on the other.

More recently, iridium complexes bearing hydroxypyridine ligands were spotted as efficient catalysts for the dehydrogenation of FA to H₂ and CO₂ in aqueous medium without amine additives. However, pH adjustment with buffers might be needed to achieve highest performance.⁷ In addition, hydrogen production in water poses engineering problems in the design of fuel cells. New Fe-based catalysts demonstrate good TONs under additive-free conditions (although, an excess of the ligand is required),^{4p} while excellent performance is achieved when catalytic Lewis acids are added.⁸ Although these recent developments are encouraging and exciting, the TON and TOF characteristics of the truly additive-free systems^{4a, 9} still require improvement that may come only from new catalysts operating via less traditional mechanistic schemes.^{4h, 10}

We previously reported several iridium, rhodium, palladium and platinum bifunctional catalysts mimicking naturally occurring [FeFe]-hydrogenase enzymes capable of promoting reversible activation and fixation of small molecules in outer coordination sphere with the aid of the pendant sidearm (Scheme 1).¹¹



Scheme 1. Previously reported bifunctional catalysts.

With the hypothesis that these polyfunctional complexes are also capable of catalyzing hydrogen transfer from formic acid via outer-sphere mechanism, we have investigated FA dehydrogenation cycle coupled with hydrogenation of unsaturated hydrocarbons. Their catalytic performances have been tested under a variety of conditions. We discovered that the carbometalated Ru complex (1) equipped with a pendant hydroxyl arm in the secondary coordination sphere acts as a mild and *E*-selective catalyst in semihydrogenation of alkynes with formic acid.¹² In this ruthenium-catalyzed reaction, the FA dehydrogenation and the alkyne hydrogenation steps are well-synchronized driving the reaction to completion under nearly stoichiometric FA/alkyne ratio (Scheme 2).



Scheme 2. Previously reported bifunctional catalysts.

Our brief mechanistic studies revealed that the presence of the OH group in the outer coordination sphere was crucial for the described catalytic activity. Even more importantly, the reaction proceeded in neat FA obviating employment of additives of any kind, which also can be attributed to the assistance of the pendant functionality spotting this class of compounds as attractive candidates for the development of efficient and "clean" catalysts for the FA dehydrogenation suitable for fuel cells applications. Obviously, structural modification of the ligands at the secondary coordination sphere will likely affect their catalytic performance. This prompted us to study the potential influence of the pendent functionality on the mechanism and efficiency of FA dehydrogenation with these multifunctional complexes.

Here, we present studies on new and known iridium pincer-type compounds possessing different functional groups and their use as catalysts for the dehydrogenation of FA under neutral conditions including an example without external additives.

Results and discussion

After preliminary optimization studies (for details, please, see SI), we decided to focus on a series of iridium-based complexes bearing ligands with different pendant groups: a neutral OH-containing **2**, a basic NH₂-containing **3** and an acidic CO₂H-containing **4**.

The compounds are easily accessed in a three-step protocol in good yields from common and readily available precursors: i) quantitative Diels-Alder cycloaddition of 1,8-bis-(diphenylphosphino)anthracene and a dienophile of choice (dimethyl fumarate or fumaronitrile, correspondingly); ii) hydrogenation or hydrolysis, correspondingly, and iii) metalation with [IrCl(COE)]₂ (Scheme 3).



Scheme 3. Synthesis of the ligands used in this study.

The compound **2** was depicted by us in the past.^{11f} Complexation of the amino- and carboxylic acid-containing ligands with $[IrCl(COE)]_2$ led to the formation of bright, airand moisture-stable solids **3** and **4** that were identified as the corresponding carbometalated pincer complexes.

³¹P{1H} and ¹H-NMR patterns of the new complexes were quite similar and showed an expected set of doublets (14.4 and 14.9 ppm with J = 12 Hz for **3** and 21.8 and 28.8 ppm with J = 14 Hz for **4**) due to the presence of two different phosphine groups, while the hydride signals appeared as virtual double doublet or triplet (-9.6 ppm with J = 28 Hz for **3** and -18.3 ppm J = 14 Hz for **4**) indicating non-equivalence of the phosphine groups. Remarkably, the hydride signals of the complexes **2** and **4** gradually disappear if the complexes left in solution.¹³

The decomposition of 2^{11d} and 4 proceeds via stoichiometric extrusion of the molecular hydrogen which apparently originates from intramolecular iridium hydride– carboxylic/hydroxyl proton interactions (Scheme 4). We cannot completely rule out an intermolecular pathway,¹⁴ however, isolation and full structural assignment of the suggested intermediates - the alkoxide-iridium species $2^{,11d}$ and of the carboxylateiridium species $4^{,}$ strongly support this hypothesis.

Hydrogen formation, however, proceeds in a different rate according to ¹H NMR: while hydride signals of **2** disappear after 30 min heating to 60 $^{\circ}$ C, this process with **4** occurs at room temperature. This reactivity trend is most likely dictated by the acidity of the corresponding protons in **2** and **4**, as well as thermodynamic stability of the resultant **2**' and **4**'. Expectedly, a reversed process followed the opposite trend: when **2**' and **4**' were

pressurized with 500 kPa of hydrogen at 100 $^{\circ}$ C in CDCl₃ side by side, the parent compound **2** was regenerated after 3 hours, while only ca. 5% of **4** re-formed.



Scheme 4. Hydrogen formation step in 2-4.

On the other hand, the amine-containing **3** is stable in solution and no hydrogen formation was observed unless external acids (e.g. *p*-toluenesulfonic, acetic or formic acid) are added. In this case, the hydride signal quickly disappears followed by hydrogen

liberation independently of the strength of the acid.¹⁵ We, therefore, assume that H_2 originates from intramolecular (rather than intermolecular) protonolysis of the Ir-H bond with the aid of the protonated sidearm in **3'** leading to the formation of a cationic intermediate stabilized by the amine chelation (**3"** in the Scheme 4, bottom). Expectedly, utilization of DCO₂D results in the formation of HD as was detected by IR-MS.¹⁶ The presumed formation of **3"** is supported by a significant low-field P NMR shift characteristic of the formation of cationic species of this type observed in the stoichiometric reaction between **3** and FA.¹⁷

With these compounds in hand (2-4), we performed a new series of structure-reactivity relationship studies of decomposition of formic acid in different formulations: HCO₂H/TEA, HCO₂H/Na₂CO₃ and HCO₂H/HCO₂Na in DME (1,2-dimethoxyethane) at 70 °C using the constant 1:2000 catalyst:FA ratio. Formic acid degrades to hydrogen and carbon dioxide without contamination of carbon monoxide as was monitored by GC-TCD, and the TON was determined by monitoring the amount of gaseous products using the standard gas burette measurements (please, see ESI). The results are listed in the Table 1.

Table 1. Representative results of FA dehydrogenation using the catalysts 2-4.

N	Cat	Conditions ^a	TON ^b	TOF $(h^{-1})^c$
1	2	HCO ₂ H/TEA (5:3), DME, 70 °C	318500	13710
2	3	HCO ₂ H/TEA (5:3) , DME, 70 °C	35080	1200
3	4	HCO ₂ H/TEA (5:3) , DME, 70 °C	1452	ND
4	2	HCO ₂ H/Na ₂ CO ₃ (1:0.3) , DME, 70 °C	258800	9380

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5	3	HCO ₂ H/Na ₂ CO ₃ (1:0.3) , DME, 70 °C	468690	18630
6	4	HCO ₂ H/Na ₂ CO ₃ (1:0.3) , DME, 70 °C	1660	ND
7	2	HCO ₂ H/HCO ₂ Na (1:0.3), DME, 70 °C	189500	9460
8	3	HCO ₂ H/HCO ₂ Na (1:0.3) , DME, 70 °C	498190	18390
9	3	HCO ₂ H/HCO ₂ Na (1:0.05), DME, 70 °C	473950	18890 ^d
10	3	HCO ₂ H, neat, 70 °C	383000	11760
11	4	HCO ₂ H/HCO ₂ Na (1:0.3), DME, 70 °C	560	ND

^aCatalyst:FA = 1:2000, 70 °C under air. ^bMaximal TON. ^cInitial TOF (average of 2 runs). ^dAfter repetitious injections of FA.

We found that the carboxylic acid-functionalyzed **4** was the least active catalyst under all sets of conditions (Table 1, entries 3, 6 and 11). Decomposition of FA catalyzed by this compound was negligible at 30-100 °C, although some activity (TONs up to 2000) was observed at 140 °C after replacing DME with analogous diglyme. On the contrary, complexes **2** and **3** decomposed FA in different formulations, albeit with different efficacy and in opposite reactivity trends.¹⁸

Thus, when the reaction was performed in 5M DME solution of HCO_2H/TEA (5:3) at 70 °C, the initial TOF of 13710 h⁻¹ (Table 1, entry 1) was achieved by the OH-modified **2** showing $3.18*10^5$ turnovers (after repetitious injections of FA). Under the same conditions, **3** was about one order of magnitude less reactive (Table 1, entry 2). Azeotropes with other amines (trioctylamine or TMEDA) did not lead to a significant improvement.

An opposite reactivity trend was observed under the amine-free conditions. Thus, using the complex **2**, 1:0.2 mixture of HCO_2H/Na_2CO_3 (5M in DME) can be completely dehydrogenated, giving an initial TOF of 9380 h⁻¹ and 2.58*10⁵ turnovers (Table 1, entry

4). Under the same conditions, the reaction with the amine-containing 3 provides a significantly higher TOF of 18390 h⁻¹ and TON of 4.68*10⁵ (Table 1, entry 5). A practically similar reactivity was obtained when sodium carbonate was replaced with 30 mol% of sodium formate: the amine-containing 3 was superior over the hydroxylcontaining 2 with almost doubled TON and TOF - 4.98×10^5 (3) versus 1.89×10^5 (2) and h^{-1} (3) versus 9460 h^{-1} (2), correspondingly.¹⁹ Furthermore, we found that 3 was equally active in the presence of only 5 mol% of sodium formate (Table 1, entry 9) and even in neat formic acid (Table 1, entry 10). This performance in neat FA is comparable to or exceeding the state-of-the-art catalysts operating under amine-free conditions and in the absence of exotic additives.^{4i, 4p, 5d, 8, 10a, 20} Noteworthy, our attempts to employ **2** under the solvent-less and base-free conditions failed, emphasizing the difference between the catalysts. Obveously, protonation of the amine groups facilitates solubilization of the catalyst. A relatively short induction period of ca. 2-3 minutes was typically observed. To rule out a possibility that the induction is due to decomposition of the homogenous catalysts and that the FA cleavage is practically catalyzed by the metal particles, we carried out a catalytic experiment in the presence of mercury - no diminished catalytic performance was detected.

We further evaluated the performance of the catalyst under high-pressure conditions. The experiment was performed in the sealed 100 mL Parr bomb in the presence of 0.05 mol% of the catalyst **3** (conversion of FA was determined by ¹H-NMR using DMF as an internal standard). Full conversion of 130 mmol of formic acid free of additives to the 1:1 mixture of CO₂ and H₂ was obtained within 14 h corresponding to the total pressure of 978 kPa.^{4r, 21}

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On the basis of the stoichiometric and catalytic studies, we suggested a plausible sequence of mechanistic events for the decomposition of FA by **3** (Scheme 5). As the first step, we propose that immediate protonation of the pre-catalyst **3** takes place in the presence of diluted or neat formic acid forming actual catalytic species **3'**. Next, the activated **3'** starts a turnover by releasing dihydrogen via intramolecular protonolysis of the Ir-H bond with the subsequent formation of a cationic 16-electron intermediate **3"**. Unlike the traditional and generally accepted mechanism, where protonolysis of such metal-hydride intermediates by FA may be mediated intermolecularly by water or external amines,^{4b, 4f, 4i, 4n, 7b, 10I} we believe that the intramolecular interaction with a highly acidic pendant ammonium group greatly facilitates hydrogen liberation from **3'**. Formation of a coordinatively saturated iridium formate complex **3"**. Finally, extrusion of CO₂ from **3"** and regeneration of **3'** locks the catalytic cycle.

Taking into account the steric hindrance of the iridium center in **3**", the last step may be rate-determining because β -H elimination from coordinatively saturated complexes requires either additional ligand dissociation step or coordination switch from an O-bound formate to an H-bound formate prior to CO₂ elimination. Since the dissociation of, for example, a chloride ligand from the protonated **3**" is highly unlikely, rearrangement of the O-bound formate intermediate is hypothesized, despite that such reorganization is usually energetically disfavoured^{5a} and/or requires assistance of external agents.⁸



Scheme 5. Plausible mechanism of the FA dehydrogenation using **3**.

To confirm this assumption and to validate the suggested mechanism, we performed quantum chemical calculations. Figure 1 represents the free energy profile for the catalytic cycle. The computations confirmed that the first step in the cycle proceeds via polar 1,2-Ir-H^{...}₃HN-elimination of dihydrogen from **3'** via a **TS3-I** located only 10.8 kcal mol⁻¹ above **3'** resulting in the formation of the cationic iridium intermediate **3"**. This step is chelation-assisted, which makes it exergonic by 11.9 kcal mol⁻¹. The next step of the catalytic cycle is the concert 1,2-addition of FA across the N-Ir coordination bond of **3"** toward the formation of the O-bound iridium formate intermediate **3"** with a protonated ligand side-arm. Finally, we concentrated on the most questionable and apparently rate-determining step – the β -H elimination of carbon dioxide from the coordinatively saturated

3^{"'} to regenerate catalytically active **3**[']. The identified TS3-II is located 34.0 kcal mol⁻¹ above the Ir-formate intermediate **3**^{"''} with the cleaved Ir-O bond and non-classical $^{-}O_2C^{-}H^{-}Ir$ contact. Clearly, the stabilizing interactions between the positively charged ammonium site and the negatively charged carboxylate make the β -H elimination of CO₂ at the coordinatively saturated metal center possible via intramolecular outer-sphere mechanism (see also Scheme 5). In order to verify the obtained TS, we have computed the frequencies and we calculated the Intrinsic Reaction Coordinate (IRC) pathway using Damped Velocity-Verlet integrator²² forward, to the product, and backward, to the reactant species. The normal mode analysis yielded one imaginary frequency confirming the transition state nature of TS3-II. Further, the IRC connected **3**["] and **3**['] via TS3-II providing additional evidence for β -H elimination of CO₂ (the animation of the IRC can be found in the ESI).

This arguable point was experimentally probed by the KIE experiments. Thus, when HCO₂H was replaced with fully deuterated DCO₂D, the initial reaction rate measured over the first 6 min decreased strongly showing the KIE of 2.5. Less expectedly, employment of both partially deuterated HCO₂D and DCO₂H demonstrated a lower KIE (1.7 and 2.1, correspondingly). This observation, consistent with a scenario when both proton and hydride participate in a single bottleneck step, also supports relevance of the transition state TS3-II.

Figure 1. Calculated mechanism (BP86/def2-TZVP/W06) of the FA dehydrogenation using **3** (left) and **2** (right). The free energy values are given below in kcal/mol.

To stress differences between the catalysts equipped with different functional groups, we attempted evaluation of the free energy profiles for **2** (Figure 1, right). It turned out that hydrogen formation step for a less acidic OH-containing catalyst is highly endergonic by 15.6 kcal mol⁻¹ with a more significant barrier of 18.6 kcal mol⁻¹ (Figure 1, right). This is consistent with experimentally observed spontaneous H₂ extrusion from **3** in contrast to **2** (pls, see Scheme 4). We also attempted to compute a free energy profile of the decarboxylation step via O-bound/H-bound formate switch for this catalyst. We failed to locate the corresponding transition state using various techniques. The lack of this TS may indicate a different decarboxylation mechanism, for example, the one that proceeds via dissociation of the chloride ligand to provide a vacant coordination site essential for a more conventional β -H elimination of carbon dioxide.

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Conclusions

In conclusion, we have described a highly efficient Ir catalyst for the selective decomposition of formic acid to hydrogen and carbon dioxide operating under amine-free conditions and in the absence of exotic additives. According to our studies, dihydrogen liberation proceeds via intramolecular protonolysis of the Ir-hydride species with the aid of acidic remote functionality. Regeneration of the active hydride catalyst is also achieved via non-classical outer-sphere intramolecular β -H elimination of CO₂, as we deduced from the experimental studies and quantum chemical calculations. Nevertheless, the most important ramification of this work is that unique topology of this family of compounds and flexibility in their synthesis offer essentially unlimited opportunities for the fine-tuning of the catalytic activity in many classical reaction schemes, as well as render new reactivity to many classical organometallic catalysts. Further mechanistic and catalytic studies are under way.

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Author Contributions

All authors have given approval to the final version of the manuscript. ‡SC performed all experimental work; VB performed all theoretical investigations.

ASSOCIATED CONTENT

Computational details

All geometries were optimized using the BP86 functional²³ in conjunction with the def2-TZVP basis set²⁴ and W06 auxiliary basis set for density fitting²⁵ in Gaussian 09²⁶ program package. In addition we have benchmarked three different density functionals using a smaller basis set def2-SVP (see Figure S35 in the ESI). To account for the longrange dispersion interaction, Grimme's dispersion with Becke-Johnson damping (GD3BJ) was included.²⁷ To simulate the solvent effects, the conductor-like continuum model (C-PCM)²⁸ was used. The transition states (TSs) were obtained using the QST3 algorithm. The initial guess for the TS-II was obtained by interpolation of the geometries of the product and reactant. All transition states we confirmed by a normal mode analysis that showed a single imaginary frequency in all cases. The Intrinsic Reaction Coordinate (IRC) calculation was carried out starting from the transition state (TS3-II) towards the reactant (backward) and the product (forward). The Damped Velocity Verlet²² (DVV) algorithm was utilized for the IRC computation.

Supporting Information

The Supporting Information including spectral data, experimental protocols and computational details, is available free of charge on the ACS Publications website at DOI:

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13. A suitable crystal of 2 can only be obtained in the CO atmosphere; otherwise it loses hydrogen to form the previously observed 2'. Attempts to crystallize 4 failed even in the presence of CO and the crystal of 4' was analyzed (please see ESI for details).

14. A crossover experiment staring from the stoichiometric mixture of 2 and a fully deuterated 2 (ESI), resulted in the formation of statistically distributed H₂, D₂ and HD according to IR-MS analysis. However, the H-D exchange may also originate from the presence of a spectator hydroxyl group.

15. In principle, intramolecular protonolysis of transition metal hydrides with strong acids is well known (e.g. Dobson, A.; Robinson, S. D. *J. Organomet. Chem.*, **1975**, *87*, C52-53). Therefore, we tested a similar reaction with **2**. Fast decomposition of **2** along with the formation of H_2 was observed after one hour heating with *p*-toluenesulfonic acid in CDCl₃. The same experiment with formic acid, revealed decomposition only after 24 hours, showing a clear acid strength dependence in contrast to **3**.

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18. The FA/TEA (5:3) decomposition rate in the presence of 1-7 was evaluated at temperatures between 30 and 100 °C showing the expected temperature dependence. In both of the cases, an activation period of ca. 3-5 minutes was required for the catalysts to initiate gas evolution at temperatures below 70 °C, while essentially immediate reaction took place when the reactor was immersed into the preheated oil bath at the temperatures above 70 °C (See supporting information).

19. Remarkably, all catalyst manipulations and the experiments were performed in air stressing out the robustness of the catalytic systems.

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