

Catalysis | Hot Paper |

Cobalt-Catalyzed Aqueous Dehydrogenation of Formic Acid

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Dedicated to Professor Gabor Laurenczy on the occasion of his 65th birthday

Abstract: Among the known liquid organic hydrogen carriers, formic acid attracts increasing interest in the context of safe and reversible storage of hydrogen. Here, the first molecularly defined cobalt pincer complex is disclosed for the dehydrogenation of formic acid in aqueous medium under mild conditions. Crucial for catalytic activity is the use of the specific complex **3**. Compared to related ruthenium and manganese complexes **7** and **8**, this optimal cobalt complex showed improved performance. DFT computations support an innocent non-classical bifunctional outer-sphere mechanism on the triplet state potential energy surface.

With the ever-increasing energy demand and ongoing depletion of fossil fuels, the development of renewable and environmentally friendly sources of energy is imperative. In this respect, hydrogen is considered as a promising, secure and clean energy carrier for enabling a more sustainable future.^[1] However, the so-called “hydrogen economy” still faces many problems. For example, hydrogen is a highly volatile gas and consequently possesses a very low gravimetric energy density. Hence, the development of efficient hydrogen storage systems is highly desired. In this regard, liquid organic chemicals, such as methanol and formic acid (FA), constitute an attractive choice.^[2] Specifically, FA is interesting because it is easily obtained either from non-edible biomass or carbon dioxide and hydrogen. Furthermore, it can undergo selective decomposition to hydrogen and carbon dioxide at mild conditions in the presence of suitable catalysts.

Thus, during the past decades, major efforts have focused on the development of catalysts for dehydrogenation of formic acid, especially in the presence of noble metals. More

specifically, a number of highly active homogeneous and heterogeneous catalysts based on Ir, Ru, Au, Pd have been developed by Fukuzumi, Himeda, Laurenczy, Xu, Tsang, our group, and many others.^[3]

Due to the limitations and price of noble metals, in recent years more and more attention has focused on the development of more abundant 3d metal systems because of their low cost and toxicity. In 2010, our group introduced the first iron-based catalyst for FA dehydrogenation under irradiation conditions.^[4a] Notably, in 2011, a much more efficient iron complex has been reported, which allowed for catalyst turnover numbers of > 90 000.^[4b] Based on that work, also a water-soluble derivative of this complex was applied by Laurenczy and co-workers in aqueous solution.^[4c] Milstein and co-workers have reported another iron catalyzed dehydrogenation of FA,^[4d] whereas Hazari and Schneider have developed a Lewis acid assisted FA dehydrogenation by using an iron pincer complex.^[4e] In addition to iron, copper and nickel catalysts have been also disclosed to be active for this transformation.^[5]

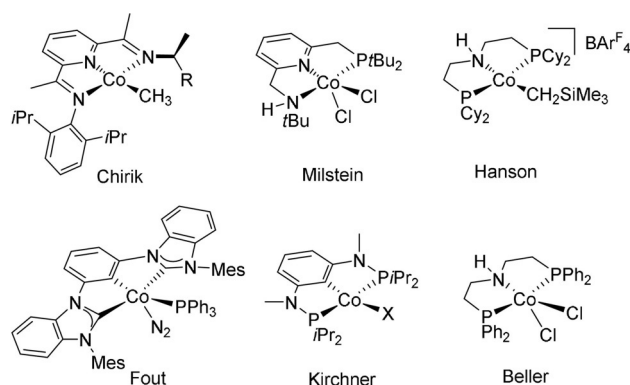


Figure 1. Selected cobalt pincer complexes for (transfer)hydrogenation and dehydrogenative coupling reactions.

Alternatively, cobalt-catalyzed decomposition of formic acid into hydrogen and carbon dioxide is relatively unknown, although it is an essential 3d element for living organisms, which has received much attention during the past decade for its diverse activities in polymerization,^[6] C–H bond functionalization,^[7] (transfer)hydrogenation,^[8] hydrofunctionalization^[9] and dehydrogenative coupling reactions.^[10] For example, in 2012 Hanson and co-workers have reported a new aliphatic PNP pincer Co^{II} complex for the hydrogenation of olefins, ke-

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tones, aldehydes, and imines.^[8a] Later, Milstein and co-workers have developed another Co^{II} system with pyridine-based PNN pincer ligand for the hydrogenation of esters and nitriles.^[8c,d] Very recently, the group of Fout has showed that Co^I complexes with monoanionic bis(carbene) ligands can also promote olefin hydrogenation through a Co^I/Co^{III} redox cycle (Figure 1).^[8f]

Although cobalt catalyzed hydrogenation of carbon dioxide into formic acid/formate or alcohols, has already been reported,^[11] the reverse processes, that is, hydrogen generation from FA is scarcely known.^[12] A known nanocobalt catalyst for the selective dehydrogenation of formic acid has been reported by our group last year,^[13] however, the relatively harsh reaction conditions and comparably low activity under mild conditions stimulated us to look for improved molecularly-defined systems. Based on our long standing interest in non-noble metal catalyzed dehydrogenation reactions,^[14] here we report the first cobalt PNP complex for FA dehydrogenation reaction in aqueous medium.

Initially, a series of Co^{II} complexes which were active for the hydrogenation of esters in our previous report^[8k] was tested for the dehydrogenation of formic acid under various conditions. Unfortunately, none of these complexes showed activity for the dehydrogenation reaction (see Supporting Information). Looking at previous hydrogenation systems, we realized that Co^I species might constitute the active catalyst under reductive conditions. However, these Co^I species cannot be easily formed under dehydrogenative conditions. Based on this assumption, Co^I complexes 1–3 were synthesized and characterized by NMR, combustion analysis and X-ray diffraction. Indeed, when complex 1 (Figure 2) was employed, hydrogen evolution was observed from a formic acid/amine mixture at 80 °C, albeit with very low efficiency. Its bromide analogue 2 showed a similar activity. To our delight, the phenyl substituted PNP pincer complex 3 exhibited much higher activity, in which case formic acid was almost fully decomposed into hydrogen and carbon dioxide within 90 minutes, reaching a catalyst turnover number (TON) of 2260.

Encouraged by these results, we further tested the performance of Co^I complex 3 under aqueous conditions with potassium formate as base. Under these conditions, still high activity was observed (Table 1, entry 1), whereas lowering the temperature to 60 °C significantly slowed down the gas evolution rate (Table 1, entry 2). Due to the highly air-sensitive nature of 3, which makes the handling inconvenient, we also tried to apply the precursor complex 4 instead of 3 and performed an in situ activation by sodium triethylborohydride.^[15] However, treating 4 with one equivalent of sodium triethylborohydride as an activator prior to the dehydrogenation reaction, resulted in a lower activity compared to the preformed Co^I complex 3 (Table 1, entries 2 and 3). This might be due to the uncompleted reduction of Co^{II} precursor, considering that we observed a pink solution of the aqueous phase which indicates the existence of Co^{II} species. Interestingly, when two equivalents of sodium triethylborohydride were used, a slightly higher activity than that of the preformed complex 3 was observed (Table 1, entry 4). Further optimization showed that the

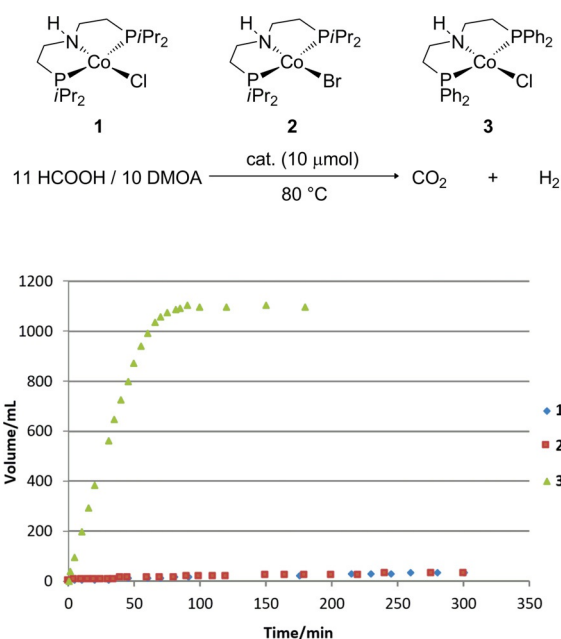


Figure 2. Cobalt(I) pincer complexes catalyzed dehydrogenation of formic acid. conditions: HCOOH/DMOA 11:10 (5 mL, containing 1.075 g of FA); DMOA: *N,N*-dimethyloctylamine.

Table 1. Catalytic dehydrogenation of formic acid under aqueous conditions.^[a]

$\text{HCOOH} \xrightarrow[\text{HCOOK, H}_2\text{O, 60 } ^\circ\text{C}]{\text{cat. (10 } \mu\text{mol), NaBEt}_3\text{H}} \text{CO}_2 + \text{H}_2$							
Entry	Complex	NaBEt ₃ H [μmol]	HCO ₂ H [mmol]	HCO ₂ K [mmol]	V _{1h} [mL]	V _{3h} [mL]	
1 ^[b]	3	–	10	40	388	n.d.	
2	3	–	10	40	131	396	
3	4	10	10	40	64	220	
4	4	20	10	40	134	426	
5	4	20	10	20	133	448	
6	4	20	10	10	125	436	
7	4	20	10	5	71	200	
8	4	20	20	20	102	292	
9	4	20	10	0	14	26	
10	4	20	0	10	12	22	
11	3	10	10	10	118	432	
12	5	20	10	10	100	300	
13	6	–	10	10	0	0	
14	7	–	10	10	0	0	
15	8	–	10	10	6	18	

[a] In all cases, the total volume of formic acid and water was 4 mL; catalyst loading was based on metal complex; gas evolution was measured by using a manual burette with correction by blank value. 100 mL gas evolution corresponds to a catalyst turnover number of 205 for CO₂/H₂ = 1:1. CO was not detected by GC measurement. [b] The reaction was performed at 80 °C. n.d.: not determined.

amount of formate can be reduced to 1:1 ratio regarding the amount of formic acid without a significant loss of the activity. Contrary, an increased FA concentration leads to a slight decrease in activity (Table 1, entries 5–8). When pure formic acid or formate were used as substrate, only very slow gas evolution was observed (Table 1, entries 9 and 10). To understand the different activity between complex **3** and the in situ activated complex **4** with two equivalents of sodium triethylborohydride, we also performed an experiment using **3** in the presence of one equivalent of sodium triethylborohydride. The result showed it exhibits the same activity as complex **4** with two equivalents of reductant (Table 1, entries 6 and 11), which suggests that the same active species is generated in both systems. The bromide analogue of complex **4**, showed a slightly decreased activity. In addition, the commercially available Co^I complex **6** was also tested. However, no gas evolution was observed underlining the importance of the pincer ligand in this system. Finally, we compared the activity of these new complexes with other well-known pincer complexes, which are active in methanol and/or FA dehydrogenation.^[14b,16] Surprisingly, the manganese complex **7** was completely inactive under these aqueous conditions, and even the ruthenium benchmark complex **8** gave only marginal hydrogen production. Obviously, Co^I complex **3** is a superior catalyst for the dehydrogenation of formic acid under aqueous conditions.

With the optimized conditions in hand, we further tested the stability of the system. As shown in the supporting information (Figure S14, Supporting Information), gas evolution ceased after 70 hours, and a maximum TON of 7166 was obtained.

To gain more mechanistic insight into the catalytic system, kinetic isotope effect (KIE) studies were performed. In the formic acid/amine system as well as under aqueous conditions, primary KIE values of 2.91 and 2.05 for HCOOH/DCOOH, respectively, were observed, whereas the KIE value of HCOOH/HCOOD in formic acid/amine is only 1.34. These results indicate the decarboxylation step should be involved as the rate determining step. To understand the deactivation of the system, Co^I-carbonyl complexes **9** and **10** were synthesized from complex **3** and were fully characterized (Figure 3). Neither complex **9** nor **10** showed any activity under optimized conditions, and this suggests that carbon monoxide coordination to cobalt might be responsible for the deactivation process (Fig-

ure S19). Notably, formic acid can also undergo dehydration process to give H₂O and CO.^[17] This observation is quite different from previously reported 3d metal catalysts, such as iron and manganese complexes, in which the catalyst needs carbonyl groups as co-ligands to be active.

Along with our experimental work, we further computed the potential energy surface to elucidate the reaction mechanism at the level of B3PW91 density functional theory. All computational details are given in the Supporting Information. On the basis of the recent study for structures and stability^[8k] as well as of the catalytic activity of cobalt PNP pincer in acetophenone hydrogenation,^[18] we tested B3PW91 and M06L methods on the basis of the reaction from complex **9** to monocarbonyl complex **10** in Figure 3. It is found that M06L favours the dicarbonyl amido complex (**10a**, trigonal bipyramidal) instead of the monocarbonyl complex **10** (square planar) [**10a** = **10** + CO] both in gas phase and solution by 6.09 and 8.94 kcal mol^{−1}, respectively, and this disagrees with the experiment. In contrast, B3PW91 prefers complex **10** instead of the dicarbonyl complex **10a** by 2.90 and 1.20 kcal mol^{−1} in gas phase and in solution, respectively, and this agrees with the experiment. Indeed, such monocarbonyl complex has been found for the *i*Pr and *t*Bu substituted counterpart.^[19]

In agreement with the experiment, complex **10** has a square planar structure in singlet state which is more stable than the triplet state by 2.36 kcal mol^{−1} and stable towards CO dissociation to form **3C** (18.48 kcal mol^{−1}). The square planar structure and the stability of the singlet state over the triplet state of complex **10** explain the amido coordination 18-valence-electron configuration. On the basis of this result as well as our previous results on other PNP pincer metal complexes regarding stability and catalytic activity,^[20] we present the B3PW91 results for discussion, while the M06L-SCRF results are given in Supporting Information for comparison. It is noted that all species actively involved on the Gibbs free energy surface have triplet ground states and the corresponding singlet states are higher in energy and less stable. Importantly, there are no crossing points between the triplet and singlet states. Therefore, all states refer to their triplet states if no noted otherwise. The free energy potential energy surface is shown in Figure 4.

The first step of the reaction is the substitution of the chloro ligand in complex **3** by formate resulting in the formation of complex **3A1**. In **3A1**, apart from the O-coordination (Co–O = 1.983 Å), there is H-bonding between the second O atom and the H atom of the N–H group (O–H = 1.850 Å). Such coordination mode has been found also in other transition-metal PNP pincer complexes.^[2,3] Both **3** and **3A1** have trigonal pyramidal configuration, since the sum of the two Cl–Co–P and one P–Co–P angles in **3** is 359.9° and the sum of the two O–Co–P and one P–Co–P angles in **3A1** is 359.7°. The corresponding singlet state of **3** and **3A1** is less stable than the corresponding triplet state by 23.39 and 38.59 kcal mol^{−1}, respectively.

Apart from the O-coordination, we located the complex of C–H coordination **3A2**, which is responsible for the activation and dissociation of the C–H bond,^[20c,d] and higher in energy than **3A1** by 25.28 kcal mol^{−1}. In **3A2**, the H–C distance is 1.235 Å, the Co–H distance is 1.805 Å and the H–to–O H-bond-

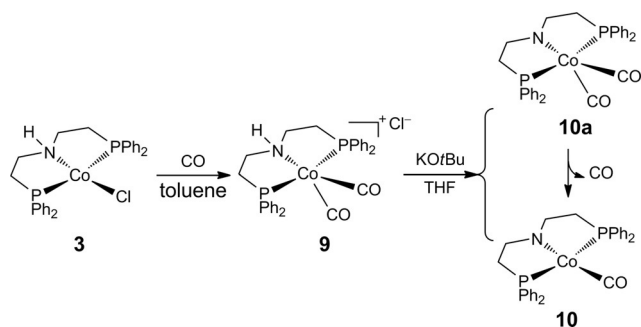


Figure 3. Synthesis of Co^I-carbonyl complexes **9** and **10**.

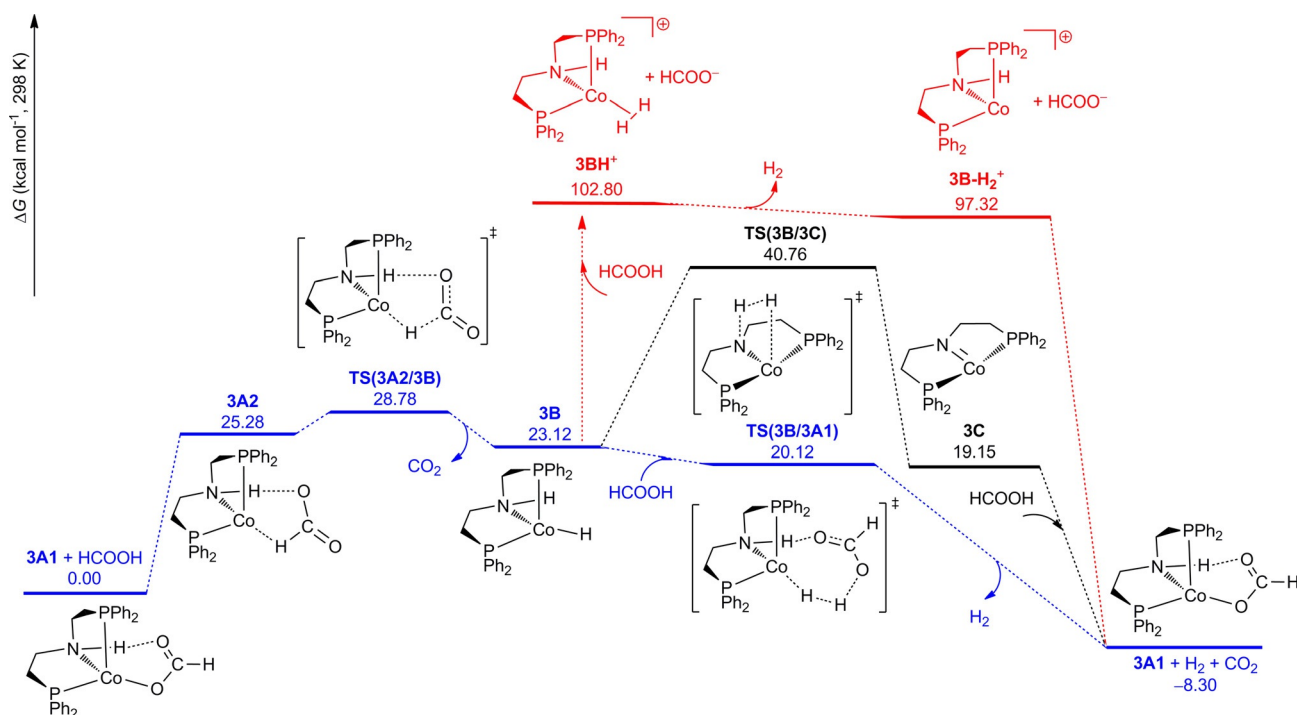


Figure 4. Gibbs free energy profile for formic acid dehydrogenation at B3PW91/TZVP level.

ing distance is 1.822 Å. Next, we located the corresponding transition state for the C–H activation and dissociation, **TS(3A2/3B)**, which leads to CO₂ release and the formation of the parent amine complex (**3B**). In **TS(3A2/3B)**, the breaking C–H distance is 1.914 Å, and the forming Co–H distance is 1.659 Å; and the distance of the N–H to O–H-bonding distance is 2.064 Å. As expected, **3B** has trigonal pyramidal configuration on the basis of the sum of the two H–Co–P and one P–Co–P angles (359.9°). Starting from **3A1**, this step has free energy barrier of 28.78 kcal mol^{−1} and is endergonic by 23.12 kcal mol^{−1}. In addition, the singlet state of **3B** is less stable than the triplet state by 33.10 kcal mol^{−1}.

Starting from the parent amine complex **3B**, there are three possible routes for H₂ release (Figure 4). The first one (black line for the classical bifunctional outer-sphere mechanism) is the direct way from the combination of the N–H and Co–H groups via the so-called non-innocent mechanism with the formation of the amido complex **3C**. In the transition state **TS(3B/3C)**, the forming H–H distance is 0.974 Å; and the distance of dissociating N–H and Co–H bonds is 1.451 and 1.757 Å, respectively. This step has free energy barrier of 17.64 kcal mol^{−1} and is exergonic by 3.97 kcal mol^{−1}. In addition, the singlet state of **3C** is less stable than the triplet state by 24.80 kcal mol^{−1}. Formic acid addition to the amido complex **3C** leads to the starting point of complex **3A1**. The second route (blue line for the non-classical bifunctional outer-sphere mechanism) involves the formic acid assisted mechanism, where H₂ formation results from the Co–H group and the acid proton, whereas the N–H group simultaneously stabilizes the transition state through H-bonding. In the transition state **TS(3B/3A1)**, the forming H–H distance is 0.934 Å; and the dis-

sociating Co–H and H–O distances are 1.699 and 1.360 Å, respectively, whereas the distance of the O–H H-bonding is 1.753 Å. This step has negative Gibbs free energy barrier (−3.00 kcal mol^{−1}) and is highly exergonic (−31.42 kcal mol^{−1}). The third one (red line) involves the protonation of the Co–H group by formic acid and this step is very endergonic by 102.80 kcal mol^{−1} and can be discarded.

On the basis of the computed free energy potential surface, all species have formal Co^I oxidation states and triplet states; and the rate-determining step is the C–H activation accompanied by CO₂ release. The simplified catalytic cycle is shown in Figure 5. Starting from complex **3A1**, the first step is C–H activation resulting in CO₂ release and the formation of amine complex (**3B**); and the second step is the formic acid assisted H₂ formation and the regenerating of complex **3A1** through the innocent mechanism. In contrast to the classical bifunctional outer-sphere mechanism in which both M–H and N–H are involved directly in H₂ formation, our system shows a non-classical bifunctional outer-sphere mechanism in which the N–H functional is not directly involved in H₂ formation, and instead the N–H functional actively stabilizes the transition state for H₂ formation. This is different from the proposed non-bifunctional inner-sphere mechanism for Hanson's Co^{II} system.^[21]

In summary, we have developed the first molecularly defined cobalt complex for catalytic dehydrogenation of formic acid under aqueous conditions. The system features mild conditions and good activity. Preliminary results suggested that carbonyl coordination to cobalt results in deactivation of the catalyst. On the potential energy surface, all species actively involved have formal Co^I oxidation states in triplet states. The first step, which is also the rate-determining step, is the C–H activation

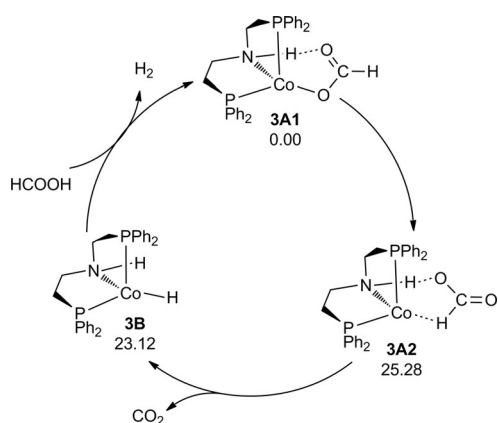


Figure 5. Proposed mechanism for cobalt-catalyzed dehydrogenation of formic acid.

resulting in CO₂ release and formation of the amine complex. The second step is the formic acid assisted H₂ release from the amine complex through a non-classical bifunctional outer-sphere mechanism. We believe that these results will be interesting for the further development of non-noble metal catalyzed hydrogenation/dehydrogenation reactions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cobalt • dehydrogenation • formic acid • pincer complexes • synthetic methods

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