Bio-Inspired Mn(I) Complexes for the Hydrogenation of CO2 to Formate and Formamide

Bio-Inspired Mn(I) Complexes for Hydrogenation of CO_2 to Formate and Formamide

Abhishek Dubey[a], Luca Nencini[b], Robert Fayzullin[c], Carlo Nervi*[b], and Julia R. Khusnutdinova*[a]

Abstract: *Developing new, efficient catalysts that contain earth-abundant metals and simple, robust ligands for CO_2 hydrogenation is important to create cost effective processes of CO_2 utilization. Inspired by nature, which utilizes secondary coordination sphere interactions in Fe-containing hydrogenases, we developed a novel Mn complex with a simple N-donor ligand, 6,6'-dihydroxy-2,2'-bipyridine, that acts as an efficient catalyst for CO_2 hydrogenation to formate and formamide. We demonstrate that the presence of an ortho-OH group in proximity to the metal is essential for catalytic activity as analogous complexes with 2,2'-bipyridine, para-OH substituted, or ortho-MeO-substituted bipyridine ligands showed significantly lower activity. Turnover numbers (TONs) of 6250 for hydrogenation of CO_2 to formate in the presence of DBU using a 1:1 ratio of CO_2 : H_2 were achieved. Moreover, hydrogenation of CO_2 to formamide was achieved in the presence of a secondary amine. This is the first example of using a Mn complex in CO_2 hydrogenation.*

Catalytic hydrogenation of CO_2 to value-added products is of practical interest for the chemical industry and may find utilization as an energy storage technology since CO_2 provides an abundant and inexpensive carbon source.[1] However, in order to create a cost-efficient and environmentally benign process, the use of non-toxic, earth-abundant metals and robust, simple ligands is required.[1a] Until recently, the majority of efficient catalysts for CO_2 hydrogenation were based on precious metal complexes such as Ir,[2] Rh,[2a, 3] Ru,[4] and other metals.[1a, 2a] Although some of these catalysts show excellent activity, their utilization requires efficient recycling and separation process and poses a problem of possible dissipation of the toxic metal catalyst in the environment.[1a] In contrast, natural systems have evolved to successfully utilize earth-abundant metals (Fe, Ni) in hydrogenases under mild conditions.[5] Another remarkable feature of hydrogenases that is particularly difficult to replicate is the utilization of simple, naturally occurring N- and S-donor ligands.[6] Thus, creating an efficient catalyst based on earth-abundant, non-toxic metals and an inexpensive non-phosphine ligand that mimics hydrogenases' reactivity for hydrogenation would be important both for practical and for environmental reasons.

There are several recent reports on the use of Fe complexes for CO_2 hydrogenation to formate, in all cases supported by polydentate phosphines. [7] On the other hand, complexes of manganese, another earth-abundant and non-toxic metal, have not been reported in CO_2 hydrogenation, and they remain largely underutilized in homogeneous hydrogenation. There were several recent examples by Beller's group on the use of Mn complexes with phosphine pincer ligands in hydrogenation of carbonyl groups.[8] Although Mn complexes with N-donor ligands such as 2,2'-bipyridines were studied in electrocatalytic CO_2 reduction, they have not been used for hydrogenation.[9]

Enzymes in nature successfully employ second coordination sphere interactions in hydrogenases that utilize earth-abundant metals such as Fe and Ni.[5-6] For example, the *ortho*-hydroxypyridine structural fragment present in [Fe]-hydrogenase is proposed to play an important role in H_2 splitting through participation of the adjacent *ortho*-hydroxyl group.[5-6, 10] Pendant amine-assisted H_2 heterolytic splitting in Fe-Fe hydrogenases and in related biomimetic catalysts has been studied in detail.[11] A similar approach led to the development of an efficient iridium catalyst supported by hydroxy-substituted bipyridine or bipyrimidine ligands.[12] Computational and experimental studies confirmed the role of the *ortho*-OH group in these systems, and determined that the OH mediated reactivity was mainly due to two factors.[13] First, hydroxypyridine can undergo facile deprotonation leading to a change in the ligand donor properties by transforming it into a strong π-donor, presumably through a pyridonate-type resonance form.[13] Second, the adjacent oxygen can act as an internal base, assisting in the heterolytic splitting of H_2.[13] Interestingly, recent reports also suggested that a Mn complex containing an OH group in proximity to a metal shows improved catalytic activity for electrochemical CO_2 reduction via Mn hydride intermediates.[14]

Inspired by these developments, we set out to investigate the catalytic reactivity in CO_2 hydrogenation of a series of manganese complexes supported by substituted bipyridine-based ligands containing functional groups that can act as internal bases upon deprotonation (Scheme 1). We were quickly able to develop Mn complexes with a simple, commercially available 6,6'-dihydroxy-2,2'-bipyridine ligand that act as active catalysts for CO_2 hydrogenation to formate, reaching TONs of over 6000. The complexes also catalyze formation of formamide from CO_2 in the presence of a secondary amine. These are the first examples of manganese catalysts for CO_2 hydrogenation. We also found that the presence of *ortho*-OH groups plays a key role in inducing high catalytic activity. Thus, we demonstrate that utilization of hydrogenase-inspired N-donor ligand allows to obtain reactivity in a non-precious metal complex that is competitive with that of the currently known phosphine-based catalysts.[1a]

To investigate the effect of adjacent OH groups on the reactivity of Mn complexes, we synthesized a series of manganese bromotricarbonyl complexes **1**-**5** with substituted 2,2'-bipyridyl ligands (Scheme 1). In addition, abstraction of

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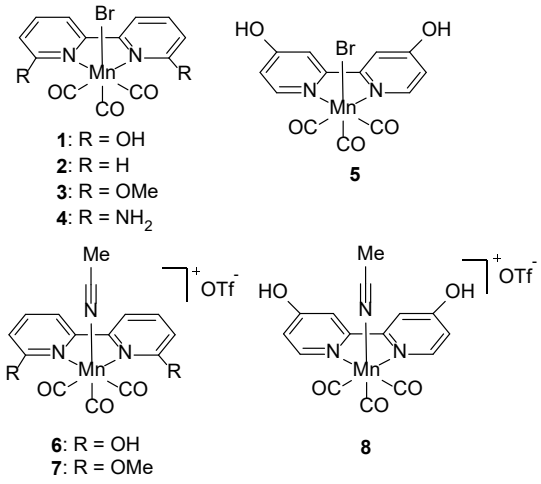
bromide by AgOTf in acetonitrile leads to the formation of the cationic acetonitrile complexes **6**-**8**. All new complexes have been characterized by elemental analysis, NMR, FT-IR spectroscopy, and ESI-MS. Complexes **2** and **5** were previously reported.[15] The structure of **1**, **3**, **4**, **6**, and **7** was confirmed by single crystal X-ray diffraction analysis (Figure 1 and the Supporting Information).[16] All complexes feature octahedral coordination at the Mn center with *fac*-coordinating tricarbonyl motif. The H-atom positions of the OH groups in complexes **1** and **6** were determined from difference electron density maps.



Scheme 1. Manganese complexes used in this study.

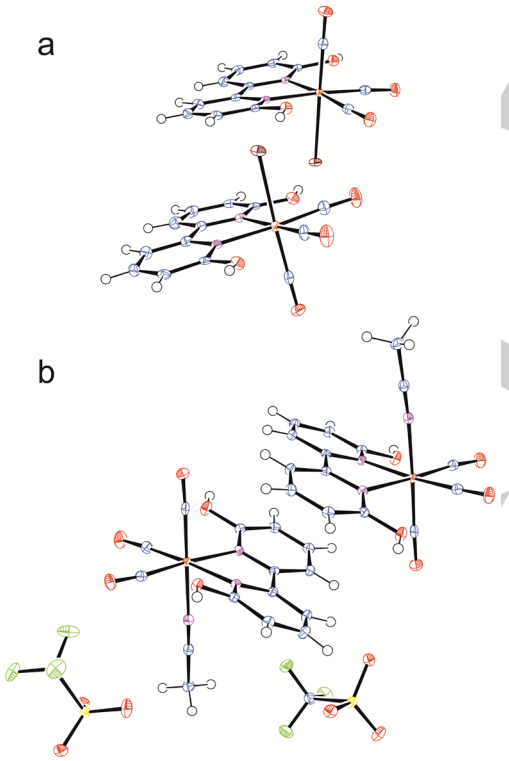
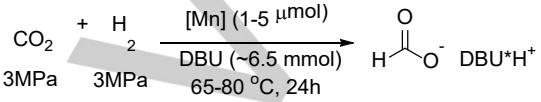


Figure 1. ORTEP representation (ellipsoids at 50% probability) of **1** (a) and **6** (b).For both **1** and **6**, two symmetry-independent molecules are present.

First, we tested catalytic activity of **1** in 1,4-dioxane in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as a base under H_2 : CO_2 (3 MPa : 3 MPa) pressure. To our satisfaction, heating at 80 °C for 24 h lead to formate salt formation, reaching a TON of 1224, corresponding to ~97% yield based on DBU determined by NMR (Table 1, entry 1). Surprisingly, **1** was also efficient when the reaction was carried out in the coordinating solvent MeCN (entry 2) with TOF reaching 238 h^{-1} at 65 °C (see Supp. Info). Since NMR of **1** in MeCN is indicative of bromide dissociation even at room temperature,[17] independently prepared acetonitrile complex **4** was also tested in MeCN, which allowed us to obtain similar results (entry 3). The control experiments using the carbonyl precursor $Mn(CO)_5Br$ and a run without any Mn catalyst did not yield any detectable amounts of formate.

Table 1. [Mn]-catalyzed CO_2 hydrogenation to formate.[a]



Entry	[Mn] (μmol)	Solvent	T (°C)	TON[b]	Yield (%)[c]
1	**1** (5 μmol)	dioxane	80 °C	1224	97
2	**1** (5 μmol)	MeCN	65 °C	1313	96
3	**6** (5 μmol)	MeCN	65 °C	1299	99
4[d]	**1** (5 μmol)	MeCN	65 °C	946	58
5	**1** (2 μmol)	MeCN	65 °C	3445	87
6	**1** (1 μmol)	MeCN	65 °C	6250	98
7	**2** (5 μmol)	MeCN	65 °C	17	<2
8	**3** (5 μmol)	MeCN	65 °C	5	<2
9	**7** (5 μmol)	MeCN	65 °C	88	7
10	**4** (5 μmol)	MeCN	65 °C	20	<2
11	**5** (5 μmol)	MeCN	65 °C	161	10
12	**8** (5 μmol)	MeCN	65 °C	164	12

[a] Typical conditions: [Mn] (1-5 μmol), base (~6.5 mmol), solvent (5 mL), H_2 (3 MPa), CO_2 (3 MPa), 65 °C or 80 °C, 24h. [b] TON = mmol formate/mmol [Mn]; determined as average of three trials; amount of formate was determined by NMR integration relative to DMF standard added to reaction mixture after completion. [c] yield = (mmol formate*100%)/mmol DBU (based on DBU:formate 1:1); determined as average of three trials by integration of formate peak relative to DBU. [d] H_2 1 MPa, CO_2 1 MPa.

DBU was selected for further studies as a model system as it was the most efficient and widely used base for promoting high conversion.[4c, 18] Other amine bases such as Et_3N and DABCO (1,4-diazabicyclo[2.2.2]octane) also showed catalytic turnover using **6**, but ultimately gave lower conversion, and reactions carried out in protic solvents were less efficient (Tables S1-S2 in the SI). Even at reduced pressure, H_2 : CO_2 1 MPa : 1 MPa, a TON of 946 was obtained (entry 4). Overall, further optimization

of reaction conditions led to TON reaching 6250 when **1** was used at low catalytic loading (entry 6).

Notably, when 2,2'-bipyridine complex **2** was used as a catalyst, only a trace amount of formate was detected. Bromide and acetonitrile complexes **3** and **7**, respectively, bearing donating methoxy-substituents in the *ortho*-positions, were significantly less active, showing TONs below 100. These results suggest that the presence of the adjacent OH group that can be easily deprotonated under basic conditions is a key feature required for high catalytic activity. The related complex **4**, which contained amino-groups in the *ortho*-positions showed very low TONs. This could indicate that the pK_a of the *ortho*-substituent needs to be carefully adjusted to allow facile deprotonation.[10]

In order to investigate the positional effect of the OH group, we have examined catalytic activity of complexes **5** and **8** in which the OH group is present in the *para*-positions. In these complexes, deprotonation of OH groups will lead to an analogous electronic contribution. Interestingly, although the catalytic activity of **5** and **8** (entries 11 and 12) was higher than that for bipyridine and methoxy-susbtituted bipyridine complexes, it was still significantly less when compared to the *ortho*-OH substituted **1** and **6**. Therefore, the position of OH groups in proximity to a metal center also plays an important role in enabling efficient catalysis.

These findings resemble the reactivity of iridium complexes with OH-substituted bipyridine or bipyrimidine ligands in which the presence of the OH groups as well as their position were shown to play an important role. As demonstrated in detailed studies of these systems by Himeda, Fujita et al., deprotonation of OH groups in bypiridine ligands leads to the altering of electronic properties in the resulting anionic ligand, leading to improved catalytic activity.[13] Concurrently with the electronic effect, a significantly higher catalytic activity was noted for *ortho*-substituted ligands over the *para*-substituted ones due to the ability of adjacent oxo-groups to participate in H_2 cleavage.[13]

As the presence of the *ortho*-OH group was a key factor in inducing efficient catalysis, we attempted to investigate possible reaction intermediates. The solution of **6** in CD_3CN shows three aromatic multiplets centered at 7.11, 7.83, and 7.95 ppm. Upon addition of 3 equiv of DBU, pyridine proton signals shift upfield and appear at 6.08, 6.72, and 7.18 ppm (Figure S1 in the SI). At the same time, the OH peak originally present at 10.1 ppm disappears, and a new broad peak appears at 12.3 ppm assigned to a DBU*H^+. The upfield shift of aromatic protons suggests increase of electron density at the deprotonated anionic ligand similar to NMR chemical shift observed in dihydroxy-bipyridine Ir complexes in basic media[13]

Interestingly, when a solution of complex **6** in MeCN or THF was reacted with 3 or more equiv of DBU in a similar way, the FT-IR spectrum features a shift of the carbonyl bands to lower energies by *ca.* 40 cm^{-1} (Figure 2a and Figures S7-S8 in the SI). This could also be consistent with generation deprotonated π-donating ligand which increases the electron density at the metal, inducing stronger π-back donation to carbonyls. The absorption bands in UV-vis spectrum of **6** at 329-343 nm attributed to MLCT undergo red-shift by *ca.* 60 nm upon addition of 2 or more equiv of DBU (Figure 2b and Figure S6 in the SI), similar to MLCT band red-shift observed in deprotonated hydroxypyridine iridium complexes due to the increase of the electron density at the metal.[13]

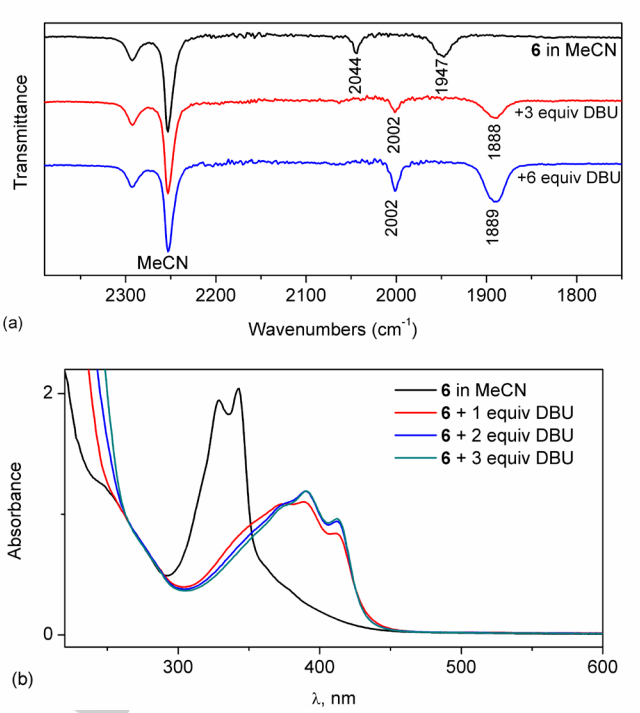


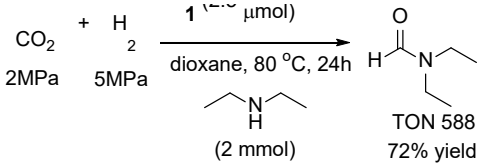
Figure 2. (a) FT-IR spectra changes of complex **6** in MeCN solution upon addition of 3-6 equiv of DBU; .(b) UV-vis spectra changes of complex **6** in MeCN solution upon addition of DBU.

When a CD_3CN solution of **6** in the presence of DBU was exposed to H_2 (5 bar), no hydride signal could be detected by NMR at RT or at -30 °C. However, when the analogous solution was filled with a 1 : 1 mixture of H_2 : CO_2 (5 bar), catalytic formate formation is observed, leading to a TON of 12 after 16h at 50 °C.

Interestingly, when the analogous experiment was performed using a 2,2'-bipyridine complex **2** in CD_3CN solution in the presence of DBU, pressurizing with H_2 : CO_2 1 : 1 mixture led to formation of a dark-colored solution, which features broadened signals in ^1H NMR. Analysis of the resulting solution by UV-vis spectroscopy shows absorption bands at 810, 634 and 390 nm, consistent with reduced Mn(0) dimer $(bipy)_2Mn_2(CO)_6$ reported in the literature.[15a] This observation suggests that the formation of inactive dimer from **2** could be one of the reasons for its lack of catalytic activity. Consistent with this experiment, a previous report suggests that the highly unstable hydride $Mn(bipy)(CO)_3(H)$ decomposes to form the dimer $[Mn_2(bipy)_2(CO)_6]$.[19]

Having observed efficient conversion of CO_2 to formate, we set out to expand the scope of Mn-catalyzed CO_2 hydrogenation to formamide formation in the presence of a secondary amine. CO_2 hydrogenation to formamide was reported previously, catalyzed by precious metal-complexes as well as by

polydentate phosphine-supported Fe and Co complexes.[1a, 7c] To the best of our knowledge however, it has not been reported for Mn catalysts. Using diethylamine and CO_2 : H_2 (2MPa : 5MPa), we obtained a TON of *ca.* 588 after 24h at 80 °C (Scheme 2). While the conditions and the scope of substrates require further optimization, this result shows the versatility of 6,6'-dihydroxy-2,2'-bipyridyl based Mn catalysts in various processes involving CO_2 hydrogenation.



Scheme 2. Hydrogenation of CO_2 to formamide catalyzed by Mn complex **1**.

In conclusion, complexes **1** and **6** are first examples of manganese catalysts that show high activity for CO_2 hydrogenation to formate and formamide at low temperature. In contrast to other first row transition metal hydrogenation catalysts, these complexes do not contain air sensitive phosphine ligands. The complex **1**, for example, can be handled under air without decomposition and can be synthesized without strict exclusion of oxygen. A stoichiometric 1 : 1 mixture of CO_2 : H_2 could be used efficiently to produce formate, without the need to resort to excess H_2 pressure. In the future, we plan to further investigate the reactivity of Mn complexes **1** and **6** in hydrogenation, transfer hydrogenation and hydrogen-borrowing catalytic processes while investigating the role of adjacent OH groups in enabling such reactivity.

Acknowledgements

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Keywords: carbon dioxide fixation • hydrogenation • manganese • N ligands • homogeneous catalysis

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[16] CCDC 1531371 (**1**), 1531372 (**3**), 1531373 (**4**), 1531374 (**6**), 1531375 (**7**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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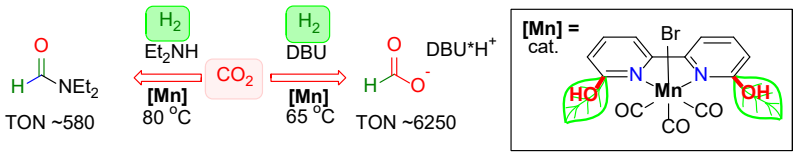

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Simple, earth-abundant, efficient. The manganese catalysts with a simple and robust N-donor ligand, 6,6'-dihydroxy-2,2'-bipyridine, were developed that hydrogenate CO_2 to formate and formamide at 65-80 °C. The presence of the adjacent OH group in proximity to a metal is a key factor to enable such facile reactivity, resembling internal base-assisted reactivity of hydrogenases in Nature. TON over 6000 were obtained for formate formation under mild conditions at 65 °C.