

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

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

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1637916> since 2017-05-24T13:19:21Z

Published version:

DOI:10.1021/acscatal.7b00943

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

Bio-Inspired Mn(I) Complexes for Hydrogenation of CO₂ 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 CO₂ hydrogenation is important to create cost effective processes of CO₂ 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 CO₂ 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 CO₂ to formate in the presence of DBU using a 1:1 ratio of CO₂ : H₂ were achieved. Moreover, hydrogenation of CO₂ to formamide was achieved in the presence of a secondary amine. This is the first example of using a Mn complex in CO₂ hydrogenation.

Catalytic hydrogenation of CO₂ to value-added products is of practical interest for the chemical industry and may find utilization as an energy storage technology since CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 H₂ splitting through participation of the adjacent *ortho*-hydroxyl group.^[5-6, 10] Pendant amine-assisted H₂ 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 H₂.^[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 CO₂ reduction via Mn hydride intermediates.^[14]

Inspired by these developments, we set out to investigate the catalytic reactivity in CO₂ 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 CO₂ hydrogenation to formate, reaching TONs of over 6000. The complexes also catalyze formation of formamide from CO₂ in the presence of a secondary amine. These are the first examples of manganese catalysts for CO₂ 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]

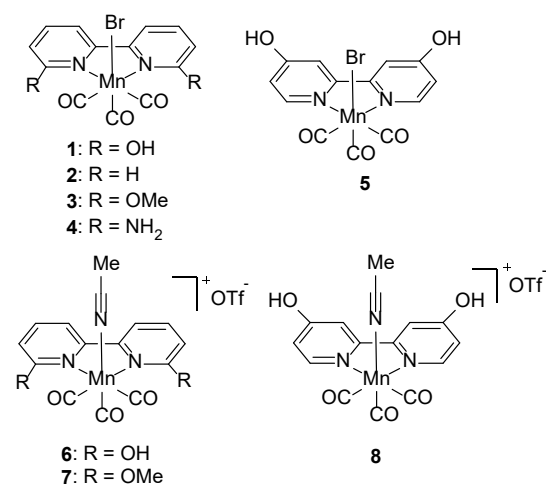
To investigate the effect of adjacent OH groups on the reactivity of Mn complexes, we synthesized a series of manganese bromotricarbonyl complexes **1-5** with substituted 2,2'-bipyridyl ligands (Scheme 1). In addition, abstraction of

[a] Dr. A. Dubey, Prof. J. R. Khusnutdinova
Coordination Chemistry and Catalysis Unit,
Okinawa Institute of Science and Technology,
1919-1 Tancha, Onna-son, Okinawa, Japan
E-mail: juliak@oist.jp

[b] L. Nencini, Prof. C. Nervi
Dipartimento di Chimica, Università di Torino
Via Pietro Giuria 7, 10125, Torino, Italia
Email: carlo.nervi@unito.it

[c] Dr. R. R. Fayzullin
A.E. Arbusov Institute of Organic and Physical Chemistry,
Kazan Scientific Center, Russian Academy of Sciences,
Arbusov Street 8, Kazan 420088, Russian Federation

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.

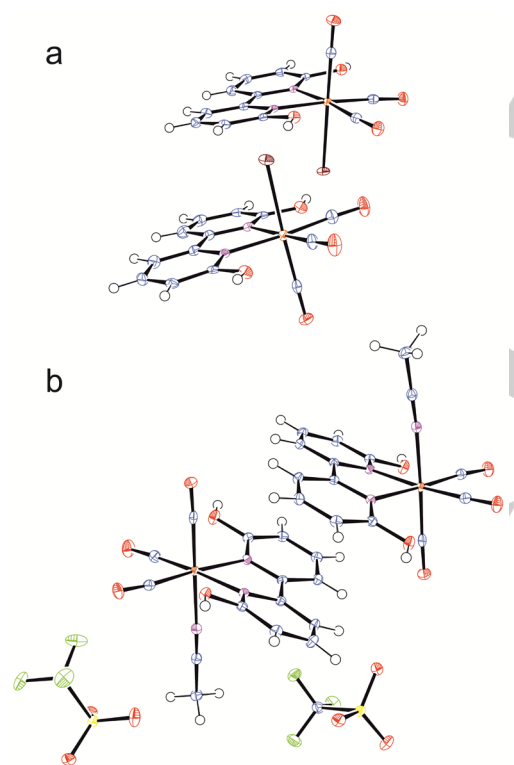
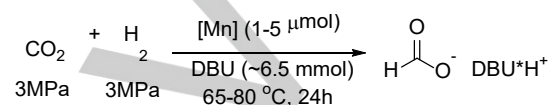


Figure 1. ORTEP representation (ellipsoids at 50% probability) of **1** (a) and **6** (b). For both **1** and **6**, two symmetry-independent molecules are present.

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 H₂ : CO₂ (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 CO₂ 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), H₂ (3 MPa), CO₂ (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] H₂ 1 MPa, CO₂ 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 Et₃N 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, H₂ : CO₂ 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-substituted 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 bipyridine 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 H₂ 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 CD₃CN 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]

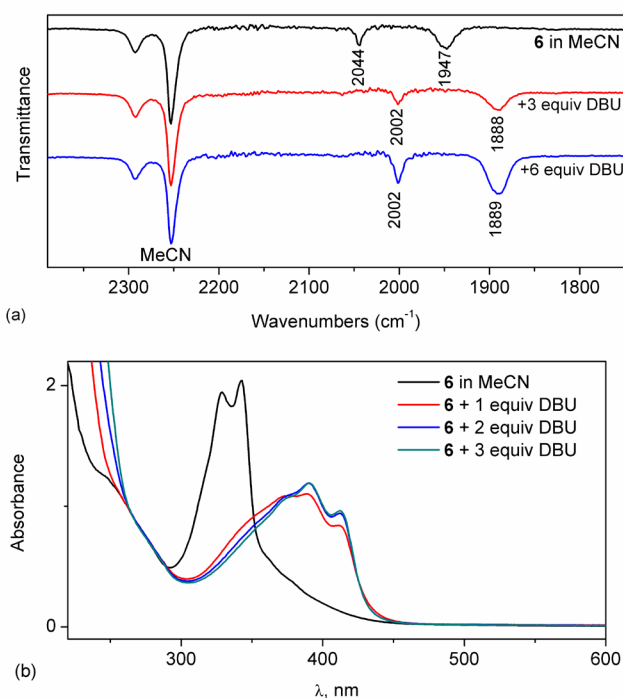


Figure 2. (a) FT-IR spectra changes of complex **6** in MeCN solution upon addition of 3-6 equiv of DBU; (b) UV-vis spectra changes of complex **6** in MeCN solution upon addition of DBU.

When a CD₃CN solution of **6** in the presence of DBU was exposed to H₂ (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 H₂ : CO₂ (5 bar), catalytic formate formation is observed, leading to a TON of 12 after 16h at 50 °C.

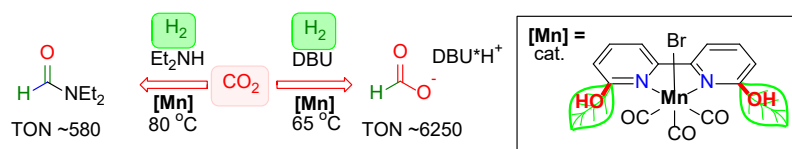
Interestingly, when the analogous experiment was performed using a 2,2'-bipyridine complex **2** in CD₃CN solution in the presence of DBU, pressurizing with H₂ : CO₂ 1 : 1 mixture led to formation of a dark-colored solution, which features broadened signals in ¹H NMR. Analysis of the resulting solution by UV-vis spectroscopy shows absorption bands at 810, 634 and 390 nm, consistent with reduced Mn(0) dimer (bipy)₂Mn₂(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 [Mn₂(bipy)₂(CO)₆].^[19]

Having observed efficient conversion of CO₂ to formate, we set out to expand the scope of Mn-catalyzed CO₂ hydrogenation to formamide formation in the presence of a secondary amine. CO₂ hydrogenation to formamide was reported previously, catalyzed by precious metal-complexes as well as by

Entry for the Table of Contents

Layout 2:

COMMUNICATION



Abhishek Dubey, Luca Nencini, Robert R. Fayzullin, Carlo Nervi*, and Julia R. Khusnutdinova*

Page No. – Page No.

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

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 CO₂ 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.