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# Bio-Inspired Mn(I) Complexes for Hydrogenation of CO<sub>2</sub> to Formate and Formamide

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**ABSTRACT:** Developing new, efficient catalysts that contain earth-abundant metals and simple, robust ligands for CO<sub>2</sub> hydrogenation is important to create cost effective processes of CO<sub>2</sub> utilization. Inspired by nature, which utilizes an *ortho*-OH substituted pyridine motif in Fe-containing hydrogenases, we developed a Mn complex with a simple N-donor ligand, 6,6'-dihydroxy-2,2'-bipyridine, that acts as an efficient catalyst for CO<sub>2</sub> hydrogenation. Turnover numbers of 6250 for hydrogenation of CO<sub>2</sub> to formate in the presence of DBU were achieved. Moreover, hydrogenation of CO<sub>2</sub> to formamide was achieved in the presence of a secondary amine. This is the first example of a homogeneous Mn complex for CO<sub>2</sub> hydrogenation.

**KEYWORDS:** Manganese, Carbon Dioxide Hydrogenation, Homogeneous Catalysis, Second Coordination Sphere, Non-Phosphine Ligand, Formate, Formamide

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Catalytic hydrogenation of CO<sub>2</sub> to value-added products is of practical interest for the chemical industry and may find utilization as an energy storage technology since CO<sub>2</sub> provides an abundant and inexpensive carbon source.<sup>1</sup> 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.<sup>1a</sup> Until recently, the majority of efficient catalysts for CO<sub>2</sub> hydrogenation were based on precious metal complexes such as Ir,<sup>2</sup> Rh,<sup>2a, 3</sup> Ru,<sup>4</sup> and other metals.<sup>1a, 2a</sup> 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.<sup>1a</sup> In contrast, natural systems have evolved to successfully utilize earth-abundant metals (Fe, Ni) in hydrogenases under mild conditions.<sup>5</sup> Another remarkable feature of hydrogenases that is particularly difficult to replicate is the utilization of simple, naturally occurring N- and S-donor ligands.<sup>6</sup> Thus, creating an efficient catalyst based on earth-abundant, non-toxic metals and an inexpensive non-phosphine ligand that mimics hydrogenases' reactivity would be important both for practical and for environmental reasons.

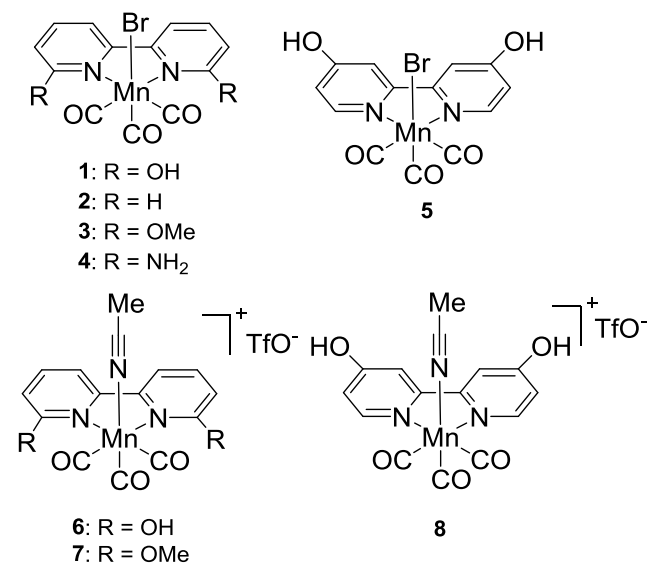
There are several recent reports on the use of Fe complexes for CO<sub>2</sub> hydrogenation to formate, in all cases supported by polydentate phosphines.<sup>7</sup> On the other hand, complexes of manganese, another earth-abundant and non-toxic metal, have not been reported in homogeneous CO<sub>2</sub> hydrogenation, and they remain largely underutilized in homogeneous hydrogenation.<sup>8</sup> There were several

recent examples on the use of Mn complexes with phosphine pincer ligands in hydrogenation of carbonyl groups.<sup>9</sup> Although homogeneous Mn complexes with N-donor ligands such as 2,2'-bipyridines were studied in electrocatalytic CO<sub>2</sub> reduction, they have not been used for hydrogenation of CO<sub>2</sub>.<sup>10</sup>

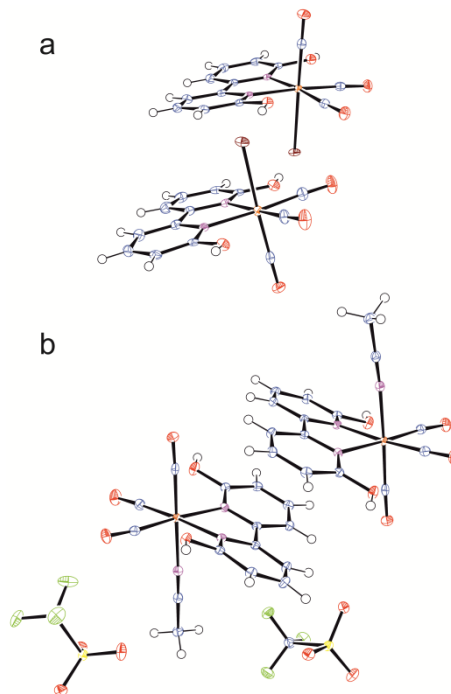
Enzymes in nature successfully employ second coordination sphere interactions in hydrogenases that utilize earth-abundant metals such as Fe and Ni.<sup>5-6</sup> For example, the *ortho*-hydroxypyridine structural fragment present in [Fe]-hydrogenase is proposed to play an important role in H<sub>2</sub> splitting through participation of the adjacent *ortho*-hydroxyl group.<sup>5-6, 11</sup> H<sub>2</sub> heterolytic splitting in Fe-Fe hydrogenases and in related biomimetic catalysts that is assisted by a pendant amine have been studied in detail.<sup>12</sup> A similar approach led to the development of an efficient iridium catalyst supported by hydroxy-substituted bipyridine or bipyrimidine ligands.<sup>13</sup> Computational and experimental studies confirmed the important role of the *ortho*-OH group in promoting bond scission.<sup>14</sup> Interestingly, recent reports also suggested that a Mn complex containing an OH-functionalized ligand as a "local proton source" shows improved catalytic activity for electrochemical CO<sub>2</sub> reduction to HCOOH via transient Mn hydride intermediates that were confirmed by detailed spectroscopic studies.<sup>15</sup> Therefore, the presence of proton-responsive functional groups in the secondary coordination sphere of a complex, that resemble the ligand motif present in [Fe]-hydrogenase, may play an important role in improving catalytic activity for CO<sub>2</sub> reduction.

Inspired by these developments, we set out to investigate the catalytic reactivity of a series of manganese complexes supported by substituted bipyridine-based ligands containing proton-responsive functional groups (Chart 1) in CO<sub>2</sub> hydrogenation. We were quickly able to identify Mn complexes with a simple, commercially available 6,6'-dihydroxy-2,2'-bipyridine ligand as active catalysts for CO<sub>2</sub> hydrogenation to formate, reaching TONs of over 6000. The complexes also catalyze formation of formamide from CO<sub>2</sub> in the presence of a secondary amine. These are the first examples of a manganese catalysts for homogeneous CO<sub>2</sub> hydrogenation. During our study, we proved that the presence of *ortho*-OH groups play a key role in inducing high catalytic activity. Thus, we demonstrate that utilization of a hydrogenase-inspired N-donor, non-phosphine ligand gives rise to reactivity in a non-precious metal complex competitive with some of the currently reported phosphine-based catalysts.<sup>1a</sup>

We synthesized a series of manganese bromotricarbonyl complexes **1-5** with substituted 2,2'-bipyridyl ligands (Chart 1). Afterwards, abstraction of bromide by silver triflate AgOTf in acetonitrile led 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 (electrospray ionization mass spectrometry). Complexes **2** and **5** were previously reported.<sup>16</sup> Bromide complexes **1-5** are moderately sensitive to ambient light; however, they can be stored for at least 2 days under ambient light without significant changes. Complexes **6-8** need to be stored in the dark to avoid decomposition, but they can be safely handled under ambient light for limited periods, such as the time required for reaction setup. The structures of **1**, **3**, **4**, **6**, and **7** were confirmed by single crystal X-ray diffraction analysis (Figure 1 and the Supporting Information). All complexes feature octahedral coordination at the Mn center with a *fac*-coordinating tricarbonyl motif. The H-atom positions of the OH groups in complexes **1** and **6** and NH<sub>2</sub> groups in complex **4** were determined from difference electron density maps.



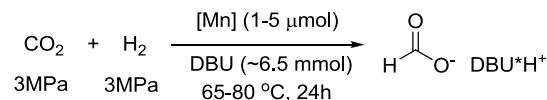
**Chart 1.** Manganese complexes used in this study.



**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<sub>2</sub> : CO<sub>2</sub> (3 MPa : 3 MPa) pressure. To our satisfaction, heating at 80 °C for 24 h led to formate salt formation, reaching a TON of 1224, corresponding to ~97% yield based on DBU determined by NMR spectroscopy (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<sup>-1</sup> at 65 °C (see Supp. Info, Table S3). Since NMR spectrum of **1** in MeCN is indicative of bromide dissociation even at room temperature (RT),<sup>17</sup> 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)<sub>5</sub>Br and a run without any Mn catalyst did not yield any detectable amounts of formate. ICP-MS analysis of Mn(CO)<sub>5</sub>Br as well as complexes **1** and **6** do not show the presence of detectable amounts of platinum group metals (see Supp. Info for details).

**Table 1.** [Mn]-catalyzed CO<sub>2</sub> hydrogenation to formate.<sup>a</sup>



entry	[Mn] (μmol)	solvent	T (°C)	TON <sup>b</sup>	yield (%) <sup>c</sup>
1	<b>1</b> (5 μmol)	dioxane	80	1224	97
2	<b>1</b> (5 μmol)	MeCN	65	1313	96
3	<b>6</b> (5 μmol)	MeCN	65	1299	99

4 <sup>d</sup>	<b>1</b> (5 $\mu$ mol)	MeCN	65	946	58
5	<b>1</b> (2 $\mu$ mol)	MeCN	65	3445	87
6	<b>1</b> (1 $\mu$ mol)	MeCN	65	6250	98
7	<b>2</b> (5 $\mu$ mol)	MeCN	65	17	<2
8	<b>3</b> (5 $\mu$ mol)	MeCN	65	18	<2
9	<b>7</b> (5 $\mu$ mol)	MeCN	65	88	7
10	<b>4</b> (5 $\mu$ mol)	MeCN	65	20	<2
11	<b>5</b> (5 $\mu$ mol)	MeCN	65	161	10
12	<b>8</b> (5 $\mu$ mol)	MeCN	65	164	12

<sup>a</sup>Typical conditions: [Mn] (1-5  $\mu$ mol), base (~6.5 mmol), solvent (5 mL), H<sub>2</sub> (3 MPa), CO<sub>2</sub> (3 MPa), 65 °C or 80 °C, 24h. <sup>b</sup>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. <sup>c</sup>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. <sup>d</sup>H<sub>2</sub> 1 MPa, CO<sub>2</sub> 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.<sup>4c, 18</sup> Other amine bases such as Et<sub>3</sub>N 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<sub>2</sub> : CO<sub>2</sub> 1 MPa : 1 MPa, a TON of 946 was obtained (entry 4). Overall, further optimization of reaction conditions led to the 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. 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 in turn indicates that the pK<sub>a</sub> of the *ortho*-substituent needs to be carefully adjusted to allow facile deprotonation.<sup>11</sup>

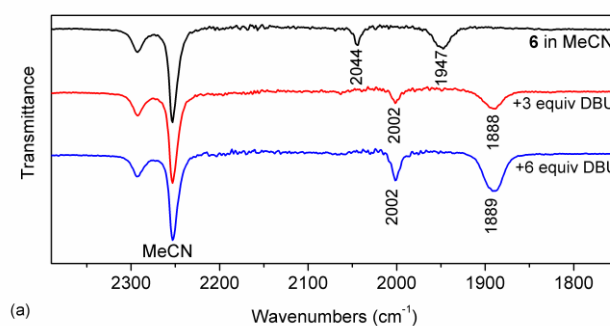
In order to investigate the positional effect of the OH group, we have examined catalytic activity of complexes **5** and **8** in which the OH group is present in the *para*-positions. Although the catalytic activity of **5** and **8** (entries 11 and 12) was higher than that for bipyridine and methoxy-substituted bipyridine complexes, it was still significantly less when compared to the *ortho*-OH substituted **1** and **6**.

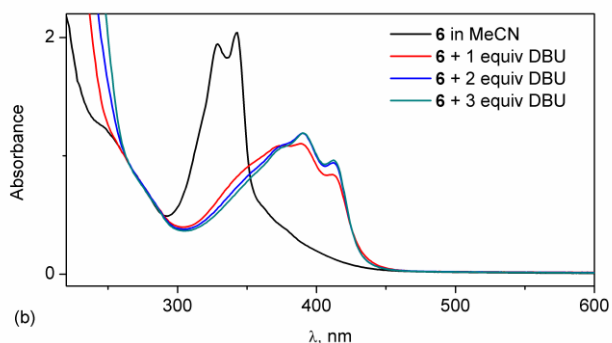
These findings resemble the reactivity of iridium complexes with OH-substituted bipyridine or bipyrimidine ligands in which the presence of the OH groups as well as their position were shown to play an important role. As demonstrated in detailed studies of these systems by Himeda, Fujita et al., deprotonation of OH groups in bi-

pyridine ligands leads to the altering of electronic properties in the resulting anionic ligand, leading to improved catalytic activity.<sup>14</sup> 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<sub>2</sub> cleavage.<sup>14</sup>

As the presence of the *ortho*-OH group was a key factor in inducing efficient catalysis, we attempted to investigate possible reaction intermediates in the presence of a base. The solution of **6** in CD<sub>3</sub>CN shows three aromatic multiplets centered at 7.11, 7.83, and 7.95 ppm (Figure S14 in the SI). 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). 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<sup>+</sup>. 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.<sup>14</sup> Similarly, pyridine protons of *para*-OH substituted complex **8** undergo upfield shift by ca. 1 ppm upon addition of 3 equiv of DBU.

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 peaks to lower energies by ca. 40 cm<sup>-1</sup> (Figure 2a and Figures S7-S8 in the SI). This is also consistent with the generation of a deprotonated anionic ligand which increases the electron density at the metal, inducing stronger  $\pi$ -back donation. The absorption bands in UV-vis spectrum of **6** at 329-343 nm attributed to MLCT are red-shifted by ca. 60 nm upon addition of 2 or more equiv of DBU (Figure 2b and Figure S6 in the SI), similar to the MLCT band red-shift observed in deprotonated di-hydroxy-bipyridine iridium complexes due to the increase of the electron density at the metal.<sup>14</sup>



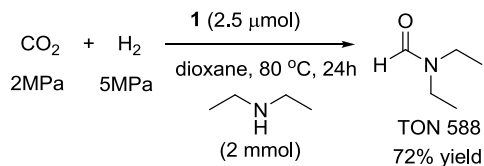


**Figure 2.** (a) FT-IR spectra changes of complex **6** in MeCN solution upon addition of 3-6 equiv of DBU; (b) UV-vis spectra changes of complex **6** in MeCN solution upon addition of DBU.

When a  $\text{CD}_3\text{CN}$  solution of **6** in the presence of DBU was exposed to  $\text{H}_2$  (5 bar), no hydride signal could be detected by NMR spectroscopy at RT or at  $-30^\circ\text{C}$  (Figure S2). However, when the analogous solution was filled with a 1 : 1 mixture of  $\text{H}_2$  :  $\text{CO}_2$  (5 bar), catalytic formate formation is observed, leading to a TON of 12 after 16h at  $50^\circ\text{C}$  (Figure S4).

Interestingly, when the analogous experiment was performed using a 2,2'-bipyridine complex **2** in  $\text{CD}_3\text{CN}$  solution in the presence of DBU, pressurizing with  $\text{H}_2$  :  $\text{CO}_2$  1 : 1 mixture led to formation of a dark-colored solution, which features broadened signals in  $^1\text{H}$  NMR spectrum. Analysis of the resulting solution by UV-vis spectroscopy shows absorption bands at 810, 634 and 390 nm, consistent with reduced Mn(0) dimer  $(\text{bipy})_2\text{Mn}_2(\text{CO})_6$  reported in the literature.<sup>16a</sup> 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  $\text{Mn}(\text{bipy})(\text{CO})_3(\text{H})$  decomposes to form the dimer  $[\text{Mn}_2(\text{bipy})_2(\text{CO})_6]$ .<sup>19</sup> Recent computational studies suggested that  $\text{Mn}(\text{bipy})(\text{CO})_3(\text{H})$  may form through the reaction of **6** with  $\text{H}_2$  and  $\text{Me}_2\text{NH}$  as a base.<sup>20</sup>

Having observed efficient conversion of  $\text{CO}_2$  to formate, we set out to expand the scope of Mn-catalyzed  $\text{CO}_2$  hydrogenation to formamide formation in the presence of a secondary amine.  $\text{CO}_2$  hydrogenation to formamide was reported previously, catalyzed by precious metal-complexes as well as by polydentate phosphine-supported Fe and Co complexes.<sup>1a, 7c</sup> To the best of our knowledge however, it has not been reported for Mn catalysts. Using diethylamine and  $\text{CO}_2$  :  $\text{H}_2$  (2MPa : 5MPa), we obtained a TON of ca. 588 after 24h at  $80^\circ\text{C}$  (Scheme 1). A series of control experiments: in the absence of Mn catalyst, in the presence of  $\text{Mn}(\text{CO})_5\text{Br}$ , or in the presence of complex **2**, all indicated that either no reaction occurs, or only trace product is formed under the reaction conditions (see Supp. Info). 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  $\text{CO}_2$  hydrogenation.



**Scheme 1.** Hydrogenation of  $\text{CO}_2$  to formamide catalyzed by **1**.

In conclusion, complexes **1** and **6** are first examples of manganese catalysts that show high activity for  $\text{CO}_2$  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  $\text{CO}_2$  :  $\text{H}_2$  could be used efficiently to produce formate, without the need to resort to excess  $\text{H}_2$  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.

## ASSOCIATED CONTENT

**Supporting Information.** The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>. General information, experimental details, and characterization data.

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### Notes

The authors declare no competing financial interest.

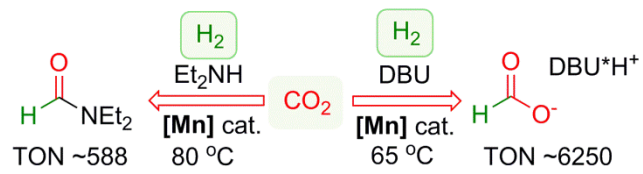
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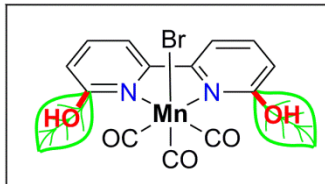
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