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Local proton source in a [Mn(bpy-R)(CO)₃Br]-type redox catalyst enables CO₂ reduction even in absence of Brønsted acids†

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The effect of a local proton source on the activity of a bromotricarbonyl Mn redox catalyst for CO₂ reduction has been investigated. The electrochemical behaviour of the novel complex [*fac*-Mn(dhbpy)(CO)₃Br] (dhbpy = 4-phenyl-6-(1,3-dihydroxybenzen-2-yl) 2,2'-bipyridine), containing two acidic OH groups in the proximity of the metal centre, under CO₂ atmosphere showed a sustained catalysis in homogeneous solution even in absence of Brønsted acids.

An efficient transformation of carbon dioxide into higher energy carbon products would make a remarkable impact on global economy, as an environmentally friendly decrease of CO₂ content in the atmosphere could be coupled with a sustainable way to gain useful chemicals (e.g. CO, HCOOH and CH₃OH).[1] A possible approach to reduce the large overpotentials required for this multi-electron process is the use of organometallic molecular compounds, able to catalyze CO₂ reduction through proton-assisted processes.[2] Two series of Re(I) and Mn(I) *fac*-tricarbonyl complexes of the type [M(bpy-R)(CO)₃X] (M = Re(I), Mn(I); bpy-R = 2,2'-bipyridine or its 4,4'-disubstituted derivatives; X = Cl, Br), have been shown to have not only the capability of providing high selective conversion of CO₂ into CO at relatively low negative potentials, but also long durability in solution.[3,4a] Albeit structurally similar, the electrochemical behaviour of these two classes of catalysts is different. In [Re(bpy-R)(CO)₃X] a reversible 1e reduction is usually followed by an irreversible 1e process; CO₂ can reacts slowly with the one electron reduced species (giving CO and CO₃²⁻) and in a catalytically much faster way with the 2e reduced species (that gives no CO₃²⁻), even in absence of an external proton source.[3a] Electrochemistry of Mn(bpy-R)(CO)₃X, instead, shows a 1e reduction, followed by rapid loss of X⁻ that leads to the formation of the Mn-Mn dimer; its subsequent irreversible reduction gives the active species [Mn(bpy-R)(CO)₃]⁻. In the case of Mn catalysts the selective catalytic reduction of CO₂ to CO occurs only in the presence of a Brønsted acid.[4a] This discrepancy was suggested to be due to the less negative potentials (~300 mV) required for the 2e reduction of the Mn(I) complexes for the formation of the catalytically active species, [M(bpy-R)(CO)₃]⁻ (M = Re, Mn).[4b] Recent detailed experimental studies on [Mn-(dmbpy)CO)₃Br] (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) have elu-

cidated two main pathways for electrocatalytic reduction of CO₂ to CO:[4] in addition to the 2e route involving the previously mentioned active species, a second pathway based on the formation of the dimer [Mn(dmbpy)(CO)₃]₂ was proposed. Under CO₂, H⁺ rapidly reacts with the substrate, giving the experimentally observed hydroxyl-carbonyl low-spin complex [Mn(dmbpy)(CO)₃(COOH)]⁺,[4c] an intermediate similar to the neutral one found for Re.[4e] Furthermore, in absence of Brønsted acids, CO₂ is not reduced by the anionic Mn active species even if the dimer formation in Mn(I) complexes is suppressed by using bulky bipyridine.[4f] These experimental data clearly demonstrate that for [Mn(bpy-R)(CO)₃Br], unlike the Re(I) based catalysts, both the mechanisms for selective CO₂ reduction to CO are proton-dependent.

In Fe(III) porphyrins, availability of local proton sources is known to greatly enhance the selectivity and the redox catalytic activity for CO₂ reduction to CO.[5] To our knowledge there are rare examples of local proton source applied to polypyridyl ligands.[6] Herein we report the synthesis and the electrochemical behaviour towards CO₂ reduction of [Mn(dhbpy)(CO)₃Br] (dhbpy = 4-phenyl 6-(1,3-dihydroxybenzen-2-yl)-2,2'-bipyridine) (**1**), a Mn(I) tricarbonyl complex that contains two hydroxylic groups.

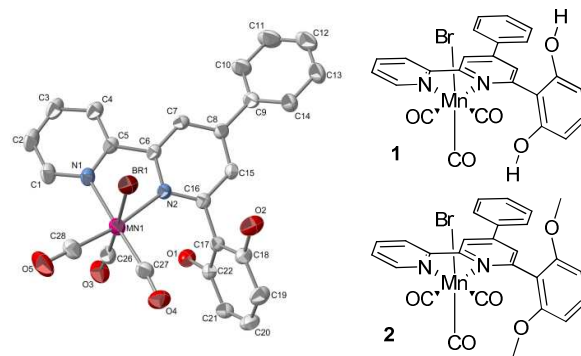

Fig. 1 Sketch of **1** and **2**. Molecular structure of **1** in the solid state. The hydrogen atoms are omitted for clarity. One of the two molecules of the unit cell is represented, with the thermal ellipsoid set at 30% probability level.

Compound **1** was obtained by refluxing the ligand (see ESI) and Mn-(CO)$_5$Br for 4 hours in diethyl ether. Yellow prismatic crystals of **1** suitable for X-ray structural analysis were grown by slow evaporation under dark conditions from a diethyl ether solution. **1** crystallizes in triclinic P-1 space group, with two molecules and two disordered solvent molecules in the unit cell. The metallic centre has a slightly distorted octahedral geometry. The phenyl group in 4' is almost coplanar with the aromatic bpy system, but the ellipsoids show a weak barrier to rotation. The diphenolic ring in 6' position is instead nearly perpendicular to the α,α'-diimine plane (dihedral angle of 109.5(2)°). This portion is more ordered because of the presence of hydrogen bond interactions with a bromine of the nearest molecule (2.714(4) Å) and with the oxygen of the diethyl ether (1.943(8) Å). Fig. 1 shows the structure of **1** obtained from X-ray diffraction data.
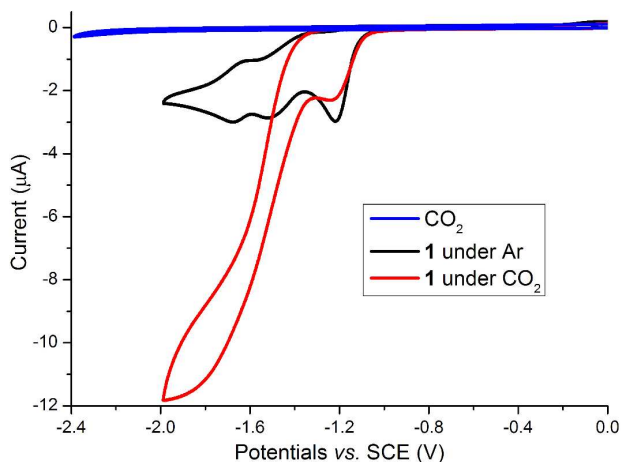

Fig. 2 CVs of a 1 mM dry acetonitrile solution of **1** at 100 mV s^{-1} (GC working electrode, TBAPF$_6$ 0.1 M) under Ar (black) or CO$_2$ (red). The blue CV is the CO$_2$ saturated background.

The electrochemical behaviour of **1** is quite different from that of other Mn(bpy-R)(CO)$_3$Br (R = H, t-Bu) derivatives.[4a,4b] Cyclic Voltammetry (CV) of **1** under Ar shows three subsequent reductions, 0/1$^-$ and 1$^-$/2$^-$ irreversible, and 2$^-$/3$^-$ reversible (Fig. 2). The irreversibility of the 0/1$^-$ process (E_p=–1.20 V vs. SCE) is due to the fast dissociation of Br$^-$ followed by the formation of the dimer [Mn-(dhbpy)(CO)$_3$]$_2$ (which is reoxidized at E_p=–0.1 V giving [Mn(dhbpy)(CO)$_3$(MeCN)]$^+$, Fig. S3). The dimer itself is then irreversibly reduced at E_p=–1.51 V, producing the purported catalytically active species [Mn(CO)$_3$(dhbpy)]$^-$, analogously to Mn(bpy)CO$_3$Br.[4a,4b] At a scan rate of 0.1 V/s an unexpected reversible reduction appears at $E_{1/2}$(2$^-$/3$^-$)=–1.66 V, E_p=–1.69 V. However, the intensity of the current peaks decreases in the order 0/1$^-$>>1$^-$/2$^-$>2$^-$/3$^-$. This order is maintained by increasing the scan rate (up to 1 V/s), but both 1$^-$/2$^-$ and 2$^-$/3$^-$ processes further decrease their peak currents with respect to the 0/1$^-$ reduction peak, and 2$^-$/3$^-$ retains its reversibility (Fig. S4). This is a clear indication that homogeneous chemical reactions follow the electron transfer. The overall mechanism can be explained assuming that the dimer is relatively slowly formed, at least slower than in Mn(bpy)CO$_3$Br, and another species is produced after the dimer reduction, that undergoes the further 2$^-$/3$^-$ reversible reduction. Indeed, bulkiness of the 1,3-dihydroxyphenyl substituent may slow down the dimer formation, as seen in the case of similar bulky substituent.[4f] To account for the unusual behaviour, we performed geometry optimization of **1** and its radical anion **1**$^-$ by DFT calculation at B3LYP/6-31G(d,p) level using acetonitrile as solvent within the CPCM method (see ESI). An

atypical intramolecular OH⋯Br interaction (2.391 Å), analogue to the intermolecular OH⋯Br one observed in the solid, stabilizes the Mn-Br bond (2.614 Å), while the second OH group interacts with the nitrogen of the bpy unit (2.881 Å). The optimized geometry of the radical anion **1**$^-$ shows that while the Mn-Br bond is elongated (2.731 Å) as expected, the other two interactions are even strengthened (OH⋯N and OH⋯Br distances are now 2.870 and 2.371 Å, respectively), thus supporting the hypothesis of partial stabilization of the radical anion **1**$^-$. In order to investigate the nature of the newly formed species responsible of the observed 2$^-$/3$^-$ reversible reduction, it is worth noting that during exhaustive electrolysis we produced a not negligible amount of formate (see below). Metal hydrides of Fe[7a], Ir[7b-c] and Rh[7c-d] are catalytically active, in anhydrous solvents, towards the reduction of CO$_2$ to formate. Moreover, electro-induced formation of Ir,[8a-c] Rh[8d] and Ru[8e] metal hydrides are known. In a similar way, we propose to assign the 2$^-$/3$^-$ reduction to the Mn hydride anion; this intermediate can be originated from [Mn(dhbpy)(CO)$_3$]$^-$ via proton transfer from the local OH group of dhbpy to the metal. DFT calculations show that the structures of Mn hydride anion and the corresponding dianion are relatively stable and very similar (Mn-H = 1.598, 1.609, Mn⋯HO = 2.870, 2.865 and OH⋯N = 2.039, 1.918 Å for the anion and the dianion, respectively), suggesting that a reversible reduction of the Mn hydride anion is feasible (see ESI).

CO$_2$ saturated solutions of **1** provided a strong catalytic effect at the 1$^-$/2$^-$ reduction wave, with an onset potential at –1.30 V. In particular, although in total absence of an external proton source, a significant increase in current intensity resulted in the characteristic sigmoidal shape for the catalytic current, essentially independent by the scan rate (Fig. S5). Controlled potential electrolysis (CPE) was carried out at –1.8 V on a 1 mM dry acetonitrile solution of **1** under a 20 ml/min constant flow of CO$_2$. Sustained electrocatalysis was monitored for 4 hours, showing a stable current density of about 0.6 mA/cm^2 during the first minutes of experiment, followed by deactivation of the catalyst (Fig. S6). The protons required for the catalytic process are supposed to be supplied by the Hofmann degradation of the supporting electrolyte,[7b] or by hydrogen abstraction from CH$_3$CN.[7d,8a] Gas chromatographic measurements revealed that CO was produced with a faradic efficiency of 70% (Fig. 3), reaching a TON$_{CO}$ ~ 19 (Fig. S7) after four hours. Traces of hydrogen were found, with a mean CO/H$_2$ ratio of about 65. CPE data gave a TOF$_{CO}$ = 1.4 s^{-1}, corresponding to a value of the homogeneous rate constant k of about 5 M^{-1}s^{-1}.[2,5] Such value, obtained in the absence of Brønsted acids, is comparable with that of
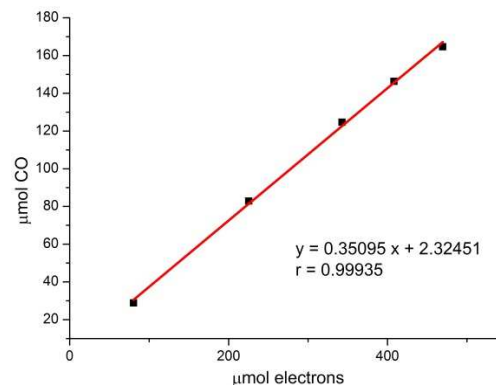

Fig. 3 CO production against the charge passed during bulk electrolysis at −1.8 V vs. SCE of a 1 mM solution of **1**. The slope of about 0.35 corresponds to a faradic efficiency of 70%.

Mn(bpy)(CO)$_3$Br in CH$_3$CN containing 5% of H$_2$O,[5] even though **1** undergoes a more rapid deactivation. This is likely due to the poor efficiency of the degradation reactions into restoring protons. Surprisingly, ion chromatography performed at the end of the experiment revealed a considerable amount of HCOOH (TON$_{HCOOH}$ around 6) with a faradic yield of 22% (Fig. S2). No other detectable products were found in solution. Bulk electrolysis of **1** repeated at –1.50 V gave almost identical data, with only slightly reduced catalytic activity (TON ~ 14) and no appreciable difference in catalyst deactivation. Hydrogen traces and production of HCOOH after CPE support the hypothesis of hydride formation.

To proof the catalytic role of the local proton source we synthesized the complex *fac*-Mn(dmobpy)(CO)$_3$Br (dmobpy = 4-phenyl 6-(1,3-dimethoxybenzen-2-yl) 2,2'-bipyridine), **2**, analogue to **1**, but with the two OH groups converted into the corresponding methyl ethers (Figure 1). CV of **2** shows only two overlapped irreversible reductions, indicating, as expected, a lower stability of the dimer due to the presence of a bulkier ligand. For this compound no catalytic activity towards CO$_2$ reduction is observed in the absence of Brønsted acids (Fig. S8). Furthermore, the lack of the third reduction is in agreement with the impossibility of forming the Mn hydride species because no protons close to the metal centre are available.

In summary, the electrochemical behaviour of a novel polypyridyl Mn(I) catalyst **1** containing two acidic OH groups in proximity of the purported metal binding site for CO$_2$ redox catalysis is reported. **1** showed a substantial catalytic activity in anhydrous media induced by the presence of a local proton source. Single crystal X-ray diffraction analysis on **1** confirmed the bent orientation of the diphenol group substituted in 6' position of the 2,2'-bipyridyl ligand. The electrochemical data for **1** highlighted two crucial issues: 1) CV exhibited a strong catalytic effect on the current of the 1$^-$/2$^-$ reduction when the solution was saturated with CO$_2$, so that the 2e pathway was supposed to be favoured for **1**. This represents the first reported experimental evidence of an intramolecular proton-assisted catalytic process for a Mn(I) catalyst, in which the key factor is the spatial closeness of protons to the active site rather than their bulk concentration in solution. 2) Bulk electrolysis at the end of the catalytic plateau (–1.8 V) under CO$_2$ showed an unusual change of selectivity for CO$_2$ reduction by the Mn(I) catalyst, giving a mixture of CO and HCOOH. Recently, a photocatalytic system based on the use of Mn(bpy)(CO)$_3$Br as catalyst precursor and [Ru(dmb)$_3$]$^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine) as redox photosensitizer revealed to be able to efficiently reduce CO$_2$ to formic acid (as major product) and CO with TON$_{HCOOH}$ = 149; although the mechanism is not fully understood yet, the simultaneous formation of CO and HCOOH are suggested to occur via two distinct competing pathways.[9] A similar behaviour has been found also in some Fe(III) molecular catalysts for CO$_2$ reduction containing bidentate ligands structurally similar to dhbpy.[6] In particular, **1** highlighted a remarkable production of CO (70%) in anhydrous conditions, comparable with that obtained for other analogous Mn catalysts in the presence of 5% H$_2$O, and a non negligible amount of HCOOH (22%). After 4 hours of CPE, a very small quantity of hydrogen was produced (~1%). CPE at a less negative potential (–1.50 V) revealed that the selectivity of the catalyst did not vary significantly. Based on previous literature data,[3,6,7] it seems reasonable to propose that two distinct molecular intermediates operate using **1** as precursor: while the anion [Mn(dhbpy)(CO)$_3$]$^-$ activates the reduction of CO$_2$ to CO, the Mn hydride anion, produced by an intramolecular rearrangement of the former catalyst, would lead to HCOOH. The effect of water on efficiency and selectivity of **1** towards CO$_2$ reduction and the design of new experiments to better understand the mechanistic details for this class of Mn catalysts are currently under study. We are also focusing onto the synthesis of novel OH-containing α,α'-diimine ligands in order to explore the reasons for the selectivity in CO$_2$ reduction towards CO or formate of Mn-based catalysts.

Notes and references

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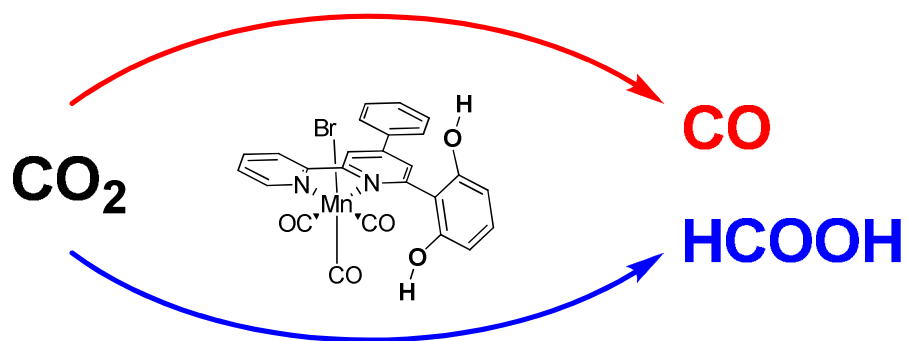
A novel bromotricarbonyl Mn(I) complex with local proton source shows strong redox catalytic properties in acetonitrile homogeneous solution even in the absence of Brønsted acids. After 4 hours of electrolysis the catalyst is still active, with an overall very efficient conversion of CO_2 to CO (70%) and HCOOH (22%).