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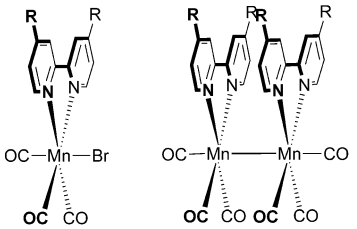
Electrocatalysis

[Mn(bipyridyl)$(CO)_3$Br]: An Abundant Metal Carbonyl Complex as Efficient Electrocatalyst for CO_2 Reduction**

Marc Bourrez, Florian Molton, Sylvie Chardon-Noblat, and Alain Deronzier**

Decrease of the massive amount of carbon dioxide that is released into the atmosphere is of vital importance for the environment. In complement or in parallel to the sequestration and storage of this greenhouse gas its chemical transformation into valuable organics and fuels could prove a potential answer to the CO_2 issues and also to the shortage of fossil fuels.[1] However, the transformation of CO_2 requires a large amount of energy because CO_2 has the most oxidized state of carbon. Among various possible methods to "sustainably" transform CO_2, efficient and selective electrochemical reduction appears to be important and promising. This route may produce carbon-based fuels and chemicals utilizing CO_2 as an unlimited, cheap, and nontoxic renewable carbon source.[2] The electrochemically driven reaction can be accomplished at bulk metallic electrodes, however it needs large overpotentials. Electrode poisoning often occurs and the selectivity is generally poor.[3] These problems can be addressed by using molecular catalysts. Metal complexes are good candidates because their reduction is accompanied by the appearance of a vacant coordination site which is able to bind CO_2 and thus activate its reduction in the metal coordination sphere.[4] Numerous metal complexes have been shown to be active electrocatalysts[5] and they can be conveniently grouped into three main families: metal complexes with 1) macrocyclic, 2) phosphine, and 3) polypyridyl ligands. For the latter class of catalysts, carbonyl complexes of Re^{I},[5d,6] Ru^{II},[7] and Os^{II}[8] exhibit outstanding performances and the metal–metal-bound polymers of Ru and Os carbonyl complexes operate in pure aqueous electrolyte.[9] However, in terms of practical application the use of abundant first-row transition-metal complexes instead of unsustainable rare and noble metal complexes is advantageous.[10] Surprisingly, there are no reports about the use of carbonyl polypyridyl manganese complexes as electrocatalysts for the reduction of CO_2 although manganese is the third most abundant transition metal (0.1 % of the Earth's crust[11]). Moreover only a few studies have been devoted to the redox behavior of manganese complexes.[12]

Herein, we demonstrate for the first time that [Mn(L)$(CO)_3$Br] complexes (**1**: L = 2,2′-bipyridine (bpy); **2**: L = 4,4′-dimethyl-2,2′-bipyridine (dmbpy); Scheme 1), synthesized according to a known procedure,[13] exhibit an excellent efficiency, selectivity, and stability for reducing CO_2 to CO, and the process occurs at a moderate overpotential.



1 : R = H
2 : R = Me
3 : R = H
4 : R = Me

Scheme 1. Chemical structures of the manganese carbonyl complexes.

The electrochemical behavior of **1** and **2** in MeCN with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) are similar to that previously reported for **1** in tetrahydrofuran (THF) electrolyte.[12b] On the initial reduction scan, both Mn complexes undergo two successive irreversible reduction reactions (Figure 1 a and Figures S1a (**1**) and S2a (**2**) in the Supporting Information) corresponding to the respective formation of the dimer $[Mn(L)(CO)_3]_2$ and the mononuclear $[Mn(L)(CO)_3]^-$. Equations (1)–(4) summarize the probable mechanism. The formation of dimers has already been shown for **1** by IR and UV/Vis spectroelectrochemical experiments in THF electrolyte.[12b]

$$[Mn(L)(CO)_3Br] + e^- \rightarrow [Mn(L)(CO)_3Br]^- \quad (1)$$

$$[Mn(L)(CO)_3Br]^- \rightarrow [Mn(L)(CO)_3] + Br^- \quad (2)$$

$$[Mn(L)(CO)_3] \rightarrow {}^1\!/_2\,[Mn(L)(CO)_3]_2 \quad (3)$$

$$[Mn(L)(CO)_3]_2 + 2\,e^- \rightarrow 2\,[Mn(L)(CO)_3]^- \quad (4)$$

A third reversible redox system not discussed here is also observed (Figure 1 a). All potential values measured by cyclic voltammetry (CV) are reported in Table 1.

One-electron reduction reactions of **1** and **2** at −1.65 and −1.70 V, respectively, (Figures S1b and S2b in the Supporting Information) result in exhaustive formation of soluble dimers

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[*] M. Bourrez, F. Molton, Dr. S. Chardon-Noblat, Dr. A. Deronzier
Université Joseph Fourier-Grenoble1/CNRS
Département de Chimie Moléculaire UMR 5250
Laboratoire de Chimie Inorganique Redox
Institut de Chimie Moléculaire de Grenoble FR-CNRS-2607
BP53, 38041 Grenoble cedex 09 (France)
E-mail: sylvie.chardon@ujf-grenoble.fr
alain.deronzier@ujf-grenoble.fr

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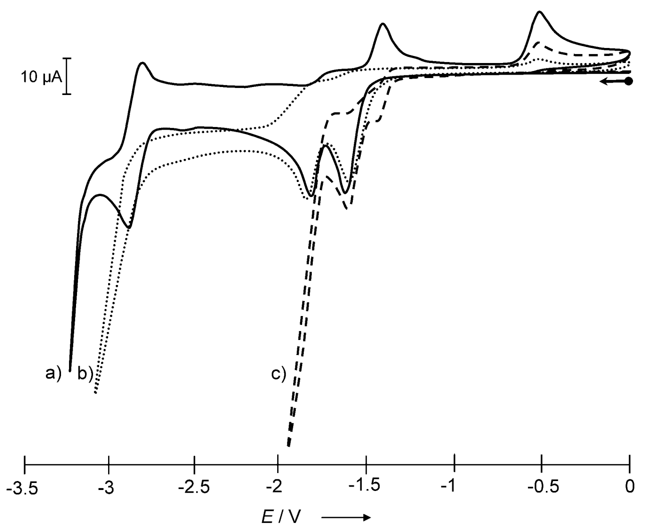

Figure 1. CVs of **1** at a concentration of 1 mM in MeCN with 0.1 M TBAP versus a vitreous carbon electrode of 3 mm diameter, $v = 100\ \text{mV s}^{-1}$ at room temperature a) under Ar and under CO_2, b) without and c) with 5% of H_2O.

$[Mn(L)(CO)_3]_2$ (**3**: L = bpy; **4**: L = dmbpy; Scheme 1). UV/Vis spectra recorded during the bulk reductive electrolysis in MeCN (insets of Figures S1 and S2 in the Supporting Information) show the progressive growth of characteristic and intense absorption bands of $[Mn(L)(CO)_3]_2$ species in good agreement with those previously reported for the electro-[12b] and photo-[14] generated dimer **3** in THF.

The radical ligand-localized transient species ($[Mn(L^{\bullet -})(CO)_3Br]^-$) has not been detected in MeCN under argon. This is most likely due to its short lifetime at RT. This contrasts with the Re radical anion $[Re(bpy^{\bullet -})(CO)_3Cl]^-$ which has been electrochemically produced and spectroscopically characterized in MeCN.[15]

The dimers show in turn an irreversible two-electron oxidation leading to the corresponding acetonitrile monomer complexes $[Mn(L)(CO)_3(MeCN)]^+$ (Table 1; Figures S1b and S2b in the Supporting Information ; [Eq. (5)]). On the reverse scan new reduction peaks are located at around 150 mV before the potential where $[Mn(L)(CO)_3Br]$ species are reduced. These new peaks are attributed to the reduction of the solvent-coordinated complexes $[Mn(L)(CO)_3(MeCN)]^+$ formed during the oxidation processes.

$$[Mn_2(L)_2(CO)_6] + 2\,MeCN \rightarrow 2\,[Mn(L)(CO)_3(MeCN)]^+ + 2\,e^- \tag{5}$$

The electrogeneration of Mn acetonitrile complexes has been proved by comparison of the spectroscopic and electrochemical properties (Table 1) of the electrolyte solutions obtained after exhaustive two-electron oxidation of dimers **3** and **4** with those of the two authentic samples of $[Mn(L)(CO)_3(MeCN)](PF_6)$ (L = bpy and dmbpy), synthesized following an adapted literature procedure (see the Supporting Information).[16]

Exhaustive electrochemical formation of $[Mn(L)(CO)_3]^-$ (second irreversible reduction process of **1** and **2**) has been also evidenced by in situ UV/Vis spectroscopy. During the bulk reduction reactions of **3** and **4** new intense bands appear in the visible range (around 560 nm; Table 1) which are in agreement with those observed in THF.[12b,17] However, these anionic species are moderately stable (see Figures S3 and S4 in the Supporting Information). The $[Mn(L)(CO)_3]^-$ species are oxidized at less negative potentials (around 0.40 V) than those of the parent dimer reduction reactions and lead mainly to the recovery of the dimers [Eq. (6)].

$$2\,[Mn(L)(CO)_3]^- \rightarrow [Mn(L)(CO)_3]_2 + 2\,e^- \tag{6}$$

When an acetonitrile solution of **1** is saturated with CO_2 (Figure 1 b) no significant difference is observed in the first two reduction peaks, while the addition of H_2O induces a dramatic change (Figure 1 c) with a strong enhancement of the cathodic current at the second reduction system [Eq. (4)]. This indicates the involvement of the reduced Mn dimer as the active species in the electrocatalytic process. In addition, with the presence of water under CO_2, a new reduction peak appears at a potential that is 150 mV less negative than the first reduction peak of **1** (Figure 1 c). This peak is attributed to the reduction of $[Mn(bpy)(CO)_3(S)]^+$ (S = MeCN or/and H_2O) resulting from partial solvolysis of **1**. This has been confirmed by analysis of UV/Vis absorption spectra and CV evolutions under Ar of an acetonitrile solution of **1** containing 5% of slightly acidified H_2O (pH 4), which mimics the acidity effect brought about by CO_2 (see Figures S5 and S6 in the Supporting Information). The fact that water is needed to obtain a significant catalytic activity is consistent with the activity observed with other electrocatalysts based on metal carbonyl complexes.[7,9,18] In the case of rhenium it has been reported that the addition of a weak Brønsted acid, including water, stabilizes the rhenium–carbon dioxide intermediate most likely through protonation and thus facilitates the cleavage of one of the C–O bonds of CO_2 to

Table 1: Redox potentials[a] and UV/Vis data of manganese carbonyl complexes in MeCN with 0.1 M TBAP.

Complexes	$E(\text{Red}_1)$ [V][b]	$E(\text{Ox})$ [V][b]	$E(\text{Red}_2)$ [V][b]	λ [nm]
$[Mn(bpy)(CO)_3Br]$ (**1**)	−1.56		−1.80	366 (sh), 416
$[Mn(bpy)(CO)_3(MeCN)]$[c]	−1.42		−1.80	376
$[Mn(dmbpy)(CO)_3Br]$ (**2**)	−1.64		−1.89	360 (sh), 412
$[Mn(dmbpy)(CO)_3(MeCN)]$[c]	−1.50		−1.89	375
$[Mn(bpy)(CO)_3]_2$ (**3**)	−1.80	−0.51	–	394, 461, 633, 806
$[Mn(bpy)(CO)_3]^-$	–	−1.39	–	370, 560, 626 (sh)
$[Mn(dmbpy)(CO)_3]_2$ (**4**)	−1.89	−0.59	–	404, 445, 538 (sh), 638, 817
$[Mn(dmbpy)(CO)_3]^-$	–	−1.48	–	374, 561

[a] Determined by CV ($v = 100\ \text{mV s}^{-1}$); Mn complexes of around 1 mM; CV disk working electrode (diameter of 3 mm) and 10 mM Ag/Ag^+ reference electrode. [b] Successive cathodic (Red_x) and anodic (Ox) peak potentials of redox systems. [c] Synthesized complexes.

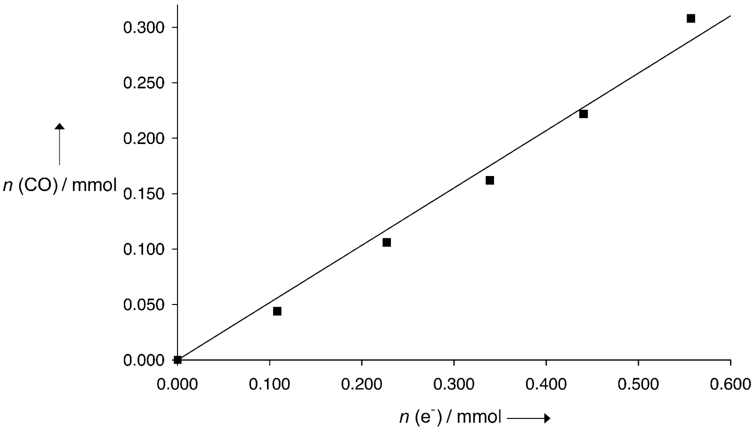

Figure 2. Number of CO moles produced during the reduction of CO_2 at −1.70 V in MeCN with 0.1 M TBAP and 5% H_2O under CO_2 containing 2.5×10^{-2} mmol of **1** versus the number of electrons consumed.

yield CO.[19] A similar situation was previously reported by Saveant and co-workers for the electrocatalytic reduction of CO_2 with iron porphyrin.[20] Some complementary experiments will be done with Mn complexes to precisely determine the mechanism of the electrocatalytic process.

To confirm the catalytic activity of **1** and to determine the selectivity of the CO_2 reduction we have carried out preparative-scale electrolysis. Controlled potential electrolysis at −1.70 V (the foot of the catalytic reduction peak) of a solution containing the complex at a concentration of 1 mM in MeCN/H_2O (95/5) under CO_2, which was followed by gas chromatography (GC). The product analysis shows that the amount of CO produced is directly proportional to the number of consumed electrons (Figure 2; turnover number: TON = 13 for 4 h).

For an electrolysis time of 4 h there is a quantitative Faradic efficiency for production of CO without generation of hydrogen. Because of the formation of electrocatalytic species the current density decreases at first during the consumption of the first 0.1 mmole of electrons (0.5 h) and then is perfectly stable (0.2 mA cm^{-2}) for a further 3.5 h, indicating that the concentration of electrogenerated catalytic intermediates remains stable in solution. After 4 h of electrolysis we have confirmed by CV that **1** is totally stable. However, after longer electrolysis times at −1.70 V the current starts to decrease (0.07 mA cm^{-2}h^{-1}) until it reaches a perfectly stable value (0.06 mA cm^{-2}). Finally, after 22 h ($Q = 130$ C) CO production ($\rho = 85\%$) is associated with H_2 production ($\rho = 15\%$). The catalytic activity of **2** is better in terms of selectivity and even for long electrolysis times ($Q = 138$ C) at −1.70 V CO is solely quantitatively formed (see Figure S7 in the Supporting Information; TON = 34 after 18 h) with no detectable byproducts and no deactivation of the catalyst. For this complex in MeCN with 5% H_2O under CO_2, a significant catalytic current is already observed at the first reduction wave indicating that the initial one-electron-reduced species ($[Mn(L)(CO)_3Br]^-$, $[Mn(L)(CO)_3]$) or the dimer **4** produced by reactions (1)–(3) are involved in the catalytic process, while a stronger catalytic effect is observed on the reduction peak of **4** (see Figure S8c in the Supporting Information). The observation of this additional catalytic peak indicates that for **2**, formation of CO can proceed through two distinct pathways (the one- and two-electron pathways, respectively). Studies are currently underway, including those using spectroelectrochemical techniques during bulk electrolysis, to identify the details of the two processes. Preliminary results show that it is more probable that dimer **4** and not the transient radical species is responsible for the catalytic effect. For both molecular catalysts (**1** and **2**), electrolysis under CO_2 conducted at a more negative applied potential (−1.80 V) decreases the selectivity because of the production of a small amount of H_2 (around 10% for **1** and **2** after 4 h of electrolysis; $TON_{(H_2)} = 1.3$ after 4 h) in addition to CO. Finally for **1** or **2** in MeCN with 5% H_2O under Ar, H_2 was not produced when preparative electrolysis was performed at an applied potential less negative than −2.10 V.

Our results are comparable in terms of selectivity, stability, and efficiency with those reported by Meyer and co-workers[21] who studied Re complexes. They obtained around 85% current efficiencies for the production of CO with $[Re(L)(CO)_3Cl]$ (L = bpy) using a dimethylformamide (DMF) electrolyte at an applied potential of −1.80 V versus a saturated calomel electrode (SCE), namely, −2.10 V versus Ag/$AgNO_3$ at 10 mM,[22] and 98% with L = dmbpy in MeCN at −1.85 V versus SCE.

In conclusion, beyond the fact that manganese is an abundant metal another advantage over rhenium complexes is that manganese catalysts reduce CO_2 at markedly less overpotential (a gain of 0.40 V), while selectivity and Faradic efficiency for the production of CO are almost identical. A similar selective electrocatalytic activity (compared to **2**) can be obtained (0.2 mA cm^{-2}; TON = 13 after 4 h) by simply mixing $[Mn(CO)_5Br]$ with the dmbpy ligand in a 1:1 molar ratio in MeCN with 5% water under CO_2, thus generating the catalyst in situ. This last approach is very promising as it combines both simplicity and mild conditions to afford efficient electrocatalysts based on manganese carbonyl complexes. A change of the ligand may also afford better catalytic performances. We are currently investigating this important new strategy.

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