A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO₂ Reduction to CO

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Abstract: We report here the first purely organometallic fac-[Mn(CO)₃(bis-MNHC)Br] complex with unprecedented activity for the selective electrocatalytic reduction of CO₂ to CO, exceeding 100 turnovers with excellent faradic yields (ηCO ≈ 95 %) in anhydrous CH₂CN. Under the same conditions, a maximum turnover frequency (TOFₘₚ) of 2100 s⁻¹ was measured by cyclic voltammetry, which clearly exceeds the values reported for other manganese-based catalysts. Moreover, the addition of water leads to the highest TOFₘₚ value (ca. 320000 s⁻¹) ever reported for a manganese-based catalyst. A Mn(I) tetracarbonyl intermediate was detected under catalytic conditions for the first time.

The large-scale production of value-added chemicals and fuels from renewable energy and CO₂ as a feedstock would contribute to increasing the sustainability of our society.[1] Despite the increasing number of homogeneous catalysts based on earth-abundant transition metals that are able to reduce CO₂,[2] further catalyst development is needed not only to achieve high catalytic rates, better selectivity for a specific product, and long durability, but also to better understand the operative mechanisms for CO₂ reduction.

Among the different families of molecular catalysts reported to be active for selective electrochemical 2e⁻ reductions of CO₂ to CO, metal-based porphyrins and polypyridine complexes show promising results in terms of their activity and stability.[1–3] In particular, Mn fac-tricarbonyl derivatives with polypyridyl moieties are able to catalyse the production of CO from CO₂ with high faradaic efficiencies (ηCO) in the presence of Bronsted or Lewis acids (Figure 1).[4] However, their further improvement is mainly limited to the functionalization of the bipyridyl,[5,6] or pyridyl[7] ligands, whereas reported examples of catalysts with non-pyridyl diimine units are still rare and usually inefficient.[7]

In this regard, N-heterocyclic carbenes (NHCs) are attractive for catalysis[8] owing to their strong σ-donor and weak σ-acceptor properties, which lead to unique stability. However, several NHC-based molecular complexes show low efficiency in CO₂ reduction and low catalyst stability,[9] such as tricarbonyl pyridyl-NHC Mn complexes (Figure 1).[10]

Herein, we explore the electrocatalytic CO₂ reduction properties of the new manganese complex [Mn(CO)₃(ps-MNHC)Br] (1), bearing the readily available bidentate methylene bis(N-methylimidazol) ligand bis-MNHC (Figure 1). For comparative reasons, we also evaluated the catalytic properties of the [Mn(CO)₃(py-MNHC)] complex (py-MNHC = N-methyl-2-pyridylimidazol; 2) under the same reaction conditions.

Figure 1. Selected Mn¹ catalysts for electrocatalytic CO₂-to-CO reduction with N²N and N²C ligands reported in the literature and complexes 1 and 2.
Cyclic voltammetry (CV) analysis of 1 revealed a main reduction event at $E_{p,\text{red}} = -2.30$ V (all reduction potentials are reported vs. Fe$^{3+}$/Fe$^{2+}$ unless otherwise specified), which is approximately 300 mV cathodically shifted with respect to the corresponding redox wave found for complex 2 ($E_{p,\text{red}} = -1.97$ V), reflecting the stronger electron-donating properties of the bis-M$_3$NHC ligand. In agreement with FTIR-SEC data (see below) and previous studies,[4,10,11] the observed redox events involve a $2e^-$ reduction of 1 (or 2) to generate a five-coordinate anion, [Mn(CO)$_3$(bis-M$_3$NHC)]$^-$(1$^-$) (or [Mn(CO)$_3$(py-M$_3$NHC)]$^-$, 2$^-$), after loss of the axial Br$^-$ (or I$^-$). An additional minor feature in the CVs of 1 ($E_p = -2.47$ V) merges with the main wave at high scan rates. CVs at different scan rates indicate reductive diffusion-limited processes for 1 (Figures S8–S10).

Under CO$_2$ atmosphere, CVs of 1 show a dramatic current increase at the first reduction wave (ca. 35-fold) with an onset potential at approximately $-2.12$ V and a current plateau at about $-2.60$ V (Figure 2B). This is in sharp contrast to the behaviour of 2, which displays only a very small increase in current with a maximum at comparable reduction potentials ($-2.56$ V; Figures 2B and S9). Furthermore, it is worth noting that there are only a few examples of molecular Mn$^+$ complexes that are able to electrocatalytically activate CO$_2$ in anhydrous CH$_3$CN, and those reported have considerably lower activity than 1.[8a,11]

For complex 1, the S-shaped catalytic wave, independent of the scan rate, is indicative of a purely kinetic regime for catalytic CO$_2$ reduction. This behaviour results in a maximum turnover frequency (TOF$_{\text{max}}$) of 2100 s$^{-1}$ under CO$_2$ atmosphere in neat CH$_3$CN estimated from CV (see Figures S11 and S12).[21] Notably, the calculated TOF$_{\text{max}}$ is more than 2000 times higher than the values reported for analogous pyridyl-NHC catalysts under more favourable conditions (CH$_3$CN + 5% H$_2$O).[8c] and about 50 times higher than the highest CO$_2$ reduction TOF ever reported for an NH-containing Mn$^+$ catalyst.[19] Moreover, the TOF$_{\text{max}}$ value of 1 is of about the same order of magnitude as the ones calculated for common bpy-based Mn$^+$ complexes (Table S1).[19] The linear increase in the catalytic current with the Mn complex concentration is also consistent with the molecular nature of the catalyst (Figure S13).

Controlled potential electrolysis (CPE) of 1 (1 mM) under a constant CO$_2$ flow (30 mL min$^{-1}$) in anhydrous CH$_3$CN was performed to study its durability and selectivity (Figures S14–S18). On-line gas chromatography (GC-TCD) analysis of the headspace allowed for quantification of the gaseous products. At an applied potential of $-2.32$ V, an average electrocatalytic current of about 2.5 mA cm$^{-2}$ and linear variation of charge over time were observed throughout the experiment, leading to catalytic CO production with a high faradaic efficiency ($\eta_{\text{CO}} \approx 92\%$), without any detectable traces of H$_2$ (Figures 2C,D). A charge of 50 C passed over 4 h corresponds to a TON$_{\text{CO}}$ value of 56, without any substantial decrease in catalytic activity. Electrolysis for extended periods of time revealed prolonged catalyst durability, exceeding turnovers of 100 after 8 h with an excellent selectivity to CO. Catalytically active nanoparticles were discarded by the negligible current observed after a “rinse test” performed after CPE. Remarkably, at a 250 mV more cathodic applied potential ($E_{\text{app}} = -2.57$ V), the reference compound 2 showed a significantly lower electrocatalytic current (ca. 0.5 mA cm$^{-2}$) than 1 under the same experimental conditions (CO$_2$ in dry CH$_3$CN). Moreover, the average faradaic efficiency of 2 was fairly low (after 3.5 h, $\eta_{\text{CO}} \approx 22\%$, TON$_{\text{CO}} \approx 2.5$; Figures 2C, S19, and S20).

We employed FTIR-SEC to gain insight into the main species involved in the reduction catalysed by 1. Under Ar atmosphere, when the applied potential matched the reduction wave of 1 (ca. $-2.30$ V), the bands belonging to 1 ($\nu_{\text{CO}} = 2007, 1922, 1887$ cm$^{-1}$) started to disappear, giving rise to new CO stretches at 1827, 1731, and 1713 cm$^{-1}$, which can be assigned to the doubly reduced 1$^-$ anion.[44] This assignment is corroborated by the excellent correlation between the experimental and DFT-calculated IR spectra of 1. The growth of a broad visible band ($\lambda_{\text{max}} = 527$ nm) in a UV/Vis SEC experiment is in agreement with the formation of 1$^-$ as the main species (Figures S22–S24 and Table S2).[44–46]

Taken together, these results account for the direct conversion of the initial species, 1, into five-coordinate 1$^-$. 

Figure 2. A) X-ray crystal structure of 1. B–D) Electrochemical behaviour of 1 and 2 (1 mM) in anhydrous 0.1 m TBAPF$_6$/CH$_3$CN electrolyte. B) CVs under Ar atmosphere (1 and 2; solid and dashed black lines, respectively) and under CO$_2$-saturated atmosphere (1; red; 2; blue) at $\nu = 0.1$ V s$^{-1}$. The green dotted line represents the blank electrolyte under CO$_2$. C) The amount of CO formed during CPE experiments under CO$_2$ atmosphere with 1 and 2 at $E_{\text{app}} = -2.32$ V (red) and $-2.57$ V (blue), respectively. D) Linear correlation between the number of moles of produced CO and the electrons consumed during CPE of 1.
which is the predominant product formed upon reduction. Importantly, the low-energy nature of the experimental CO stretches of 1 indicates a strongly localized negative charge on the Mn atom, which is consistent with the redox innocence of the bis-MeNHC ligand. Indeed, comparison of the Kohn–Sham orbitals of 1 to those of [Mn(CO)₅(bis-MeNHC)]⁺ (1') and 1 shows that the reduction takes place exclusively over the metal centre. The HOMO orbital of 1', unlike that of 2', is clearly accessible to engage in a nucleophilic attack (Figure S34).

This is reflected by the thermodynamics of the reactions with CO₂, which are exergonic for 1 but endergonic for 2' (Scheme 1 and Figures S35–S41). Moreover, the rate-determining step for the catalytic cycle is the C–O cleavage, with an energy barrier as low as 20.1 kcal mol⁻¹ for 1 and a higher one for 2 (26.8 kcal mol⁻¹), in good agreement with the catalytic activity.

When a solution of 1 was saturated with CO₂, bands at 1685 and 1646 cm⁻¹, related to free HCO₃⁻/CO₃²⁻, rapidly increased in intensity at the onset potential of the catalytic wave. Sustained CO evolution prevents further monitoring of the reaction. During the reduction, the CO stretches of the initial complex 1 decreased in intensity, with concomitant growth of a new set of low-intensity bands at 2090, 2002, and 1969 cm⁻¹, without any evidence for 1' formation. Differential IR spectra confirmed the formation of a new species, which was assigned to the tetracarbonyl intermediate [Mn(CO)₅(bis-MeNHC)]⁺ (1-CO), as corroborated also by the theoretical IR spectrum (Figures S23–S26). This is the first direct evidence for this type of intermediate under catalytic conditions. An analogous νCO pattern has recently been found for a structurally similar complex, which was synthesized under CO atmosphere with a bpy-based Mn³⁺ catalyst.[44]

The addition of a relatively small amount of water (0.09 M) to a CO₂-saturated solution of 1 significantly boosted the catalytic response, providing a peak-shaped CV with a maximum at −2.61 V (Figure S27). Titration with different aliquots of added water to a CH₃CN solution of 1 highlighted two distinct regimes. At low water concentrations ([H₂O] ≈ 0.09–0.56 M), the current tends to increase linearly with [H₂O], reaching a maximum activity (>150-fold) for [H₂O] = 0.56 M (Figure 3A). At high scan rates (ν > 50 Vs⁻¹), plateau-shaped catalytic voltammograms were progressively achieved,[45] leading to a TOF max value of 3.2 × 10⁸ s⁻¹ for 1 in wet CH₃CN ([H₂O] = 0.56 M, Figure 3B). In contrast, the pyridyl-NHC complex 2 displayed only a modest increase in the catalytic current upon increasing the water content in CH₃CN under CO₂ atmosphere, in agreement with previous reports.[10] Nevertheless, a further increase in the water concentration rapidly reduced the catalytic current ([H₂O] > 0.56 M, Figure 3A). The inhibiting effect of Brønsted
acids on Mn\textsuperscript{II} electrocatalysts has recently been highlighted elsewhere.\textsuperscript{[4a–e]} No electrocatalytic wave was observed with 1 under an Ar atmosphere, over a wider range of H\textsubscript{2}O/CH\textsubscript{3}CN mixtures ([H\textsubscript{2}O] = 0.09–2.60 m), suggesting selective CO\textsubscript{2} over H\textsuperscript{+} reduction (Figure S28). In this regard, CPE ($E_{onset}$ = −2.32 V) of 1 (1 mm) in aqueous CH\textsubscript{3}CN (0.22 m H\textsubscript{2}O) results in quantitative CO production ($\eta_{CO} = 98\%$) for more than 6 h (Figures S31–S33), without formation of H\textsubscript{2}. Nevertheless, catalyst deactivation appears to be significantly faster than under anhydrous conditions.

In summary, we have reported the first family of purely organometallic NHC-based tricarbonyl Mn\textsuperscript{II} complexes that are active in the electrocatalytic reduction of CO\textsubscript{2} to CO. The replacement of a pyridine ring with an NHC unit had a significant effect on the catalytic performance, substantially improving the TOF\textsubscript{max} and selectivity for CO production of well-established C,N-ligand-based Mn systems. Furthermore, the novel bis-NHC catalyst efficiently and selectively converted CO\textsubscript{2} into CO in anhydrous aprotic organic solvents, whereas the majority of classical bpy-based systems are reported to be inactive without an explicit proton source.\textsuperscript{[4a–e]}

The estimated TOF\textsubscript{max} for 1 upon addition of moderate amounts of water is several orders of magnitude higher than those commonly reported for Mn complexes containing functionalized poly(pyridyl) motifs under considerably more acidic conditions.\textsuperscript{[4a–e]}

Complementary FTIR-SEC measurements and computational data suggest that the strongly nucleophilic character of the Mn atom is likely responsible for the positive ligand effect on catalysis. We believe that the unique aspects exhibited by this novel family of CO\textsubscript{2} reduction complexes, together with the synthetic viability of ligand modification, open new perspectives for the design of more efficient molecular catalysts.

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Conflict of interest

The authors declare no conflict of interest.

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