Molecular Catalysis of the Electrochemical and Photochemical Reduction of CO_2 with Earth-Abundant Metal Complexes. Selective Production of CO vs HCOOH by Switching of the Metal Center

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S *Supporting Information*

ABSTRACT: Molecular catalysis of carbon dioxide reduction using earth-abundant metal complexes as catalysts is a key challenge related to the production of useful products—the "solar fuels"—in which solar energy would be stored. A direct approach using sunlight energy as well as an indirect approach where sunlight is first converted into electricity could be used. A Co^{II} complex and a Fe^{III} complex, both bearing the same pentadentate N5 ligand (2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2,12,14,16-pentaene), were synthesized, and their catalytic activity toward CO_2 reduction was investigated. Carbon monoxide was formed with the cobalt complex, while formic acid was obtained with the iron-based catalyst, thus showing that the catalysis product can be switched by changing the metal center. Selective CO_2 reduction occurs under electrochemical conditions as well as photochemical conditions when using a photosensitizer under visible light excitation ($\lambda > 460$ nm, solvent acetonitrile) with the Co catalyst. In the case of the Fe catalyst, selective HCOOH production occurs at low overpotential. Sustained catalytic activity over long periods of time and high turnover numbers were observed in both cases. A catalytic mechanism is suggested on the basis of experimental results and preliminary quantum chemistry calculations.

Considering CO_2 as a source of valuable chemicals is an attractive way to deal with massive industrial release of CO_2 and could lead, in particular, to the production of fuels or precursors to fuels,[1] like CO, an intermediate in the production of liquid fuels through the classical dihydrogen-reductive Fischer−Tropsch chemistry.[2] However, reducing CO_2 is a highly energy-demanding process, requiring the use of appropriate catalysts. Molecular homogeneous catalysis, under electrochemical or photochemical conditions, has essentially, but not exclusively, involved reduced states of transition metal complexes. Following the pioneering work on Ni and Co macrocyclic complexes as potential catalysts for electrochemical CO_2 reduction,[3] various metal complexes have been used in this purpose, including mainly Re, Ru, Ir, Rh, Os, Pd, Mo, Cu, Co, Ni,

Mn, and Fe.[1a,4] The reduction products may be oxalate, carbon monoxide, or more rarely formic acid. Only one example has been shown to catalyze CO_2 reduction with more than two electrons under electrochemical conditions (formaldehyde production).[5] There is also an essential need for new catalysts based on benign, nontoxic, and earth-abundant materials instead of noble metals, for the development of practical devices that would ultimately lead to economically viable applications. Another general issue related to the catalysis of CO_2 reduction is the catalyst's long-term stability as well as its selectivity. In particular, competition with hydrogen evolution is a general issue for molecular catalysis of the CO_2-to-CO conversion, as confirmed by recent findings concerning catalysts derived from terpyridine complexes of first-row transition metals in (90:10, v:v) DMF/H_2O mixtures.[6]

Among molecular catalysts for the CO_2-to-CO conversion, iron porphyrins reduced electrochemically[7] or photochemically[8] to the Fe(0) state have proved to be particularly selective, efficient, and robust. In this class of compounds, cyclic voltammetry (CV) as a main mechanistic analysis tool has allowed scientists to establish the reduction mechanism in detail, in particular the exact sequencing of electron transfers, proton transfers, and breaking of the C−O bond, as well as their degree of concertedness.[7f,9] CV also allowed researchers to relate the turnover frequency (TOF) to the overpotential for catalysis (catalytic Tafel plots), leading to a rational benchmarking of the various homogeneous catalysts.[4c,7g,h] Mechanistic insights have been gained recently too with Re-,[10] Mn-,[11] and Ni-based[12] catalysts through electrochemical and spectroscopic analyses and quantum chemistry calculations. The reduction of CO_2 to formate has been more rarely observed using molecular catalysts, under electrochemical conditions with Fe-, Ni-, Co-, Ru-, Rh-, or Ir-based catalysts[13] (see also Tables 2 and 3 in ref 4a) and under photochemical conditions[4g,h,14] with mainly Re, Ru, and Ir and very recently Mn complexes.[14d] Accordingly, mechanistic studies have been scarce. In some cases, formate is deemed to result from the insertion of CO_2 by a metal-hydride donor intermediate (before or after the hydride is further reduced), as found with Re, Ru, and Ir[13j,14a,b] as well as with Fe complexes,[13i,k] but this may
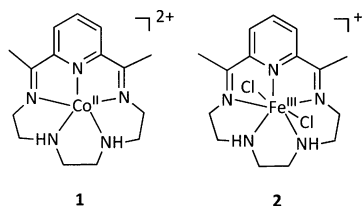
not be always the case, and the active metal-based catalyst may bind to CO_2 through one of the oxygen atoms without intermediacy of a hydride species.[13e]

We have discovered that two complexes, $[Co^{II}(L)](ClO_4)_2$ (**1**, $(ClO_4)_2$) and $[Fe^{III}(L)Cl_2](ClO_4)$ (**2**, ClO_4), both bearing a pentadentate N5 ligand (Scheme 1), reduce CO_2 to CO and

Scheme 1. $[Co^{II}(L)]^{2+}$ (1) and $[Fe^{III}(L)Cl_2]^+$ (2) Cationic Complexes Investigated

HCOOH, respectively, under electrochemical and photochemical conditions (using visible light, a photosensitizer (PS), and a sacrificial electron donor). Cyclic voltammograms of **1** and **2** are shown in Figure 1. The first reduction of $[Co^{II}(L)]^{2+}$
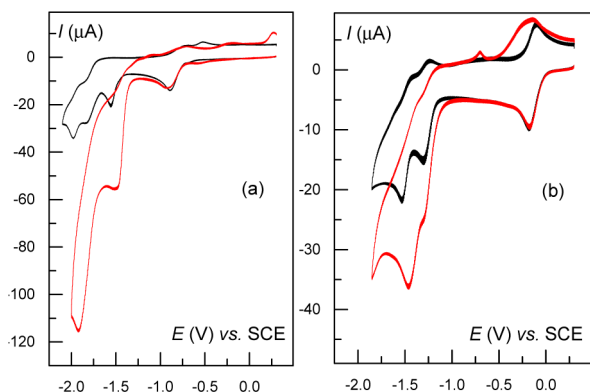
Figure 1. CV ($v = 0.1\ V\ s^{-1}$ in DMF, 0.1 M NBu$_4$PF$_6$) at a glassy carbon electrode under argon (black trace) and with 0.23 M CO_2 (red trace) of (a) **1** (1 mM) and (b) **2** (1 mM).

(Figure 1a) is most likely metal-centered to produce $[Co^I(L)]^+$, while the second reduction is ligand-centered to generate $[Co^I(L^{•-})]$, both waves being reversible (see Figure S1 in Supporting Information (SI) and Table 1). Similar behavior was

Table 1. Standard Redox Potentials of Complexes Determined by CV (V vs SCE, at 0.1 V s^{-1})

complex	$M^{III/II}$	$M^{II/I}$	ligand$^{0/•-}$
$[Co^{II}(L)]^{2+}$	–	−0.89	−1.52
$[Fe^{III}(L)Cl_2]^+$	−0.14	−1.26	−1.49

recently obtained with a related tetraaza Co complex.[15] In the case of $[Fe^{III}(L)]^+$ (Figure 1b), three distinct monoelectronic, reversible reduction waves were observed (Table 1), corresponding respectively to the formation of $[Fe^{II}(L)]$, $[Fe^I(L)]^-$, and finally $[Fe^I(L^{•-})]^{2-}$. The standard redox potential value for the $[Fe^I(L)]^-/[Fe^I(L^{•-})]^{2-}$ couple matches closely the value obtained for the $[Co^I(L)]^+/[Co^I(L^{•-})]$ redox couple (Table 1), confirming that the charge resides on the ligand. CVs of both **1** and **2** in a CO_2-saturated solution ($[CO_2]$ = 0.23 M) show strong catalytic currents at the level of the $[Co^I(L)]^+/[Co^I(L^{•-})]$ wave in the case of the cobalt complex and at the level of the

$[Fe^{II}(L)]/[Fe^I(L)]^-$ wave in the case of the iron complex. In the latter case, catalytic current starts flowing at ca. −1.15 V vs SCE, while in the former case, catalysis occurs at potentials negative to ca. −1.35 V vs SCE, corresponding to remarkably small overpotential values (see below).

Electrolysis experiments were then performed at a glassy carbon electrode. In 1 h, electrolysis of **1** ($E_{electrolysis}$ = −1.5 V vs SCE, j = 0.4 mA/cm^2) led to the exclusive formation of CO with high faradaic yield (82%). These conditions correspond to an overpotential of 566 mV ($E^0(CO_2/CO)$ = −0.934 V vs SCE in DMF).[7e] Current could be sustained over several hours, with a non linear increase of the passed charge, thus showing slow deactivation of the catalyst over long-term experiments (see Figure S2; further investigation will shed light on these deactivation mechanisms). Encouraged by the selective CO_2-to-CO conversion, we then performed photocatalytic experiments under visible light ($\lambda > 460$ nm) using a PS as co-reactant and a sacrificial electron donor (triethylamine, TEA). We started our investigation with fac-tris(2,2′-phenylpyridine) iridium(III) (Ir(ppy)$_3$, see SI) as PS, since it has recently been used for CO_2 reduction with iron porphyrin as catalyst.[8b] PS* is very efficiently quenched by the cobalt catalyst ($k_{quenching}$ = 0.68 × 10^{10} L mol^{-1} s^{-1}) and reduce the cobalt catalyst $[Co^{II}(L)]^{2+}$ with two electrons to its active state, $[Co^I(L^{•-})]$ (see Scheme S1). As shown in Figure 2, the catalytic system is highly selective and efficient
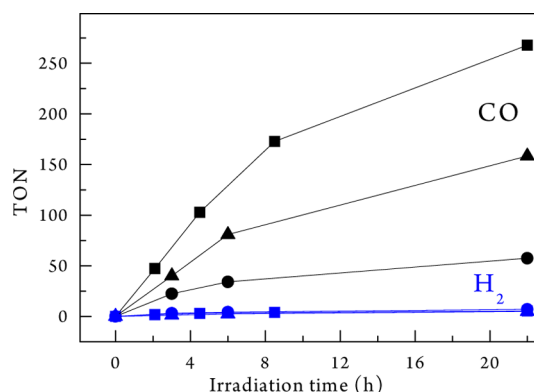
Figure 2. Comparison of photocatalytic activity of **1** (■) with $[Co(CR)Cl_2]^+$ (●)[15] and $[Co(TPA)Cl]^+$ (▲)[16] for CO (black trace) and H$_2$ (blue trace) production. Conditions: 4 mL of MeCN saturated with CO_2, containing 0.05 mM catalyst, 0.2 mM Ir(ppy)$_3$, and TEA (MeCN/TEA 4:1, v/v).

toward CO_2 reduction, with only a very minor amount of H$_2$ detected by gas chromatography (GC; a catalytic selectivity in CO of ca. 97% was repeatedly measured), and a turnover number (TON, calculated as the number of moles of CO divided by the number of moles of catalyst) up to 270 was obtained after 22 h of irradiation. TON evolution vs time remains linear over 8 h (TOF = 21.9 h^{-1}), showing the good stability of the system. Figure 2 also shows the photocatalytic activity obtained in similar conditions with related macrocyclic Co complexes, including the catalysts recently studied by Peters et al. ($[Co(CR)Cl_2]^+$,[15] see complex structure in SI) and Chan et al. ($[Co(TPA)Cl]^+$,[16] see complex structure in SI), showing that **1** is the most efficient and active catalyst. TON and TOF values obtained in this study are comparable to or higher than values obtained with more expensive photocatalysts (see ref 8b and references cited therein). Control experiments also showed that all components are necessary to get CO_2-to-CO conversion, since no carbon

monoxide is formed in the absence of the sensitizer, the catalyst, or CO_2. It was also verified that no Co particles were formed upon long irradiation time (22 h) by dynamic light scattering (see Figure S3). Experiment in the presence of Hg(0) gave similar TON (220 vs 270, 22 h irradiation, see Figure S4), leaving little doubt that the CO_2 reduction proceeds thanks to a homogeneous molecular catalyst.

CV of **2** in a saturated CO_2 solution also leads to a catalytic increase of the current, as noted above (Figure 1b). That current enhancement is due to CO_2 reduction was proved by controlled potential electrolysis at −1.25 V vs SCE. Constant current for about 3 h was repeatedly obtained (j = 0.09 mA/cm^2), highlighting the stability of the catalytic system. Gas-phase analysis of the headspace above the solution by GC showed no traces of H_2 and CO, contrary to the case with **1**. Likewise, analysis of the liquid solution by ionic chromatography revealed the formation of a large amount of formic acid, with high faradaic efficiency (ca. 75−80%). Addition of a weak acid (e.g., H_2O or PhOH) does not affect the catalyst activity. Blank experiments in the absence of catalyst did not produce any HCOOH. The electrolysis potential corresponds to a remarkably low over-potential value of η = 310 mV (η = $E^0(CO_2/HCOOH)$ − $E_{electrolysis}$ = −0.940 − $E_{electrolysis}$; see SI for an estimation of the standard potential).

From the averaged electrolysis current and considering a two-electron process, a catalytic rate k_{cat} = 0.29 s^{-1} was calculated from eq 1,[4c,17] where S is the active surface during electrolysis

$$i = \frac{FSC^0_{cat}\sqrt{D_{cat}}\sqrt{2k_{cat}}}{1 + \exp\left[\frac{F}{RT}(E - E^0_{cat})\right]} \quad (1)$$

(13.9 cm^2), D_{cat} is the catalyst diffusion coefficient (10^{-5} cm^2 s^{-1}), C^0_{cat} is the catalyst concentration (1 mM), E is the electrolysis potential (−1.25 V vs SCE), E^0_{cat} is the catalyst standard potential (−1.26 V vs SCE, see Table 1), T is the temperature (298 K), and i is the averaged electrolysis current (1.3 mA). Since the catalyst remains stable during electrolysis, a TON could be calculated from the intrinsic catalytic rate constant (eq 2),[4c] leading to a value of 1260. Molecular

$$TON = \frac{k_{cat}}{1 + \exp\left[\frac{F}{RT}(E - E^0_{cat})\right]} \times t \quad (2)$$

complexes catalyzing the CO_2-to-HCOOH conversion remain scarce, in particular those based on earth-abundant metals. The nickel cyclam is one of these, showing faradaic efficiency up to 75% (460 mV overpotential, 5 h electrolysis in neat DMF) and a TON (based on the catalyst concentration) of 3.[13e] The iron complex of 2,9-bis(2-hydroxyphenyl)-1,10-phenanthroline is another example, leading to a faradaic efficiency of 74% in a 1 h electrolysis in DMSO at large overpotential ($E_{electrolysis}$ = −1.76 V vs SCE).[13k] Finally, a recent example related to an iron cluster complex gave CO_2-to-HCOOH conversion in acetonitrile (MeCN) at an overpotential comparable to that in **2**, the formic acid being identified by ^{13}C NMR spectroscopy.[13i] Going to more expensive metals, an example concerns the use an iridium pincer immobilized at the surface of a carbon electrode and has led to high selectivity and activity toward CO_2-to-HCOOH conversion in water at overpotentials larger than 510 mV.[18] Ru(bpy)$_2$(CO)$_2$$^{2+}$ (bpy = 2,2′-bipyridine) also furnishes formic

acid during electrolysis at mercury pool with current density of ca. 3 mA/cm^2 in MeCN, and at −1.3 V vs SCE.[13c,d]

This latter Ru compound also proved to be very active and selective in photochemical conditions (DMF/TEOA 4:1 mixtures, v/v) as well, with photon wavelengths above 500 nm, leading to TON as high as 671.[19] Finally, a manganese-based catalyst (*fac*-Mn(bpy)(CO)$_3$Br) has recently shown good activity in the same photochemical conditions with TON in HCOOH up to 157 over 12 h irradiation.[14d] Photocatalytic experiments with **2** in the same experimental conditions as with **1** (irradiation with visible light (λ > 420 nm), using Ir(ppy)$_3$ (0.2 mM) as PS and TEA (50 mM) as sacrificial electron donor) led to the selective formation of HCOOH. A TON of ca. 5 was measured with a 20 μM solution of **2** in a 20 h experiment. Only traces of H_2 and CO were found.

While both **1** and **2** thus proved to be selective, efficient catalysts of the two-electron reduction of CO_2, changing the metal from Co to Fe allows switching of catalysis product. Coordination between CO_2 and the metal plays an important role in the reactivity. In the case of **1**, CO_2 likely binds to the metal through the carbon atom (η_1-CO_2 coordination), before protonation and reduction with a second electron in association with the cleavage of a C−O bond finally furnishes an OH$^-$ and a CO molecule, along with a sequencing and a degree of concertedness that remain to be precisely determined. A general catalytic mechanism is proposed in Scheme 2, and preliminary

Scheme 2. Proposed Mechanisms for the Reduction of CO_2 with (a) $[Co^{II}(L)]^{2+}$ (1) and (b) $[Fe^{III}(L)Cl_2]^+$ (2)
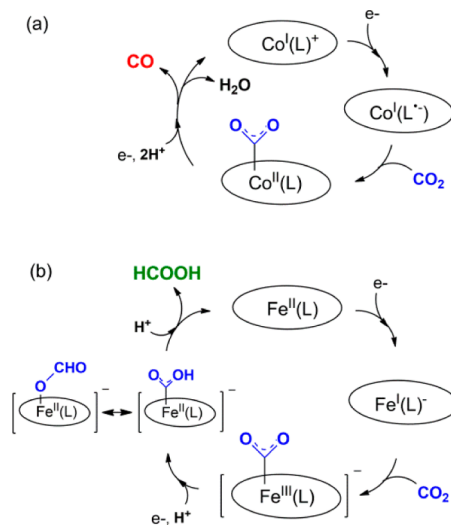
DFT calculations are detailed in the SI. In the case of **2**, quantum chemistry calculations (see SI) also suggest that an η_1-CO_2 coordination is preferred, but the reduced and protonated adduct does not undergo C−O cleavage and rather evolves to an η_1-OCOH-coordinated complex, finally releasing a formate molecule (Scheme 2). In the case of Co-CO_2H intermediate, π-back-bonding from the electron-rich, formally Co^{II} center to π^* orbitals of CO_2 will weaken the C−O bond and hence facilitate its cleavage to give CO product. On the other hand, in the case of the Fe-CO_2H intermediate, since the formally Fe^{III} is a poor π-donor, C−O cleavage is slow and hence isomerization is more facile, finally leading to HCOOH formation. This argument is in line with the electrocatalytic reduction of CO_2 by $[Ru(bpy)(CO)_2]_n$ films, where electron-donating substitu-

ents on the 4,4′ positions of the bpy ligand favor CO formation, while electron-withdrawing substituents favor $HCOO^-$ formation.[20]

In conclusion, **1** and **2** show remarkable catalytic properties toward CO_2 reduction, with high selectivity and good efficiency at low overpotential. While carbon monoxide is obtained with the cobalt complex **1** under both electrochemical and photochemical conditions with visible light, the iron analogue **2** leads to clean formation of formic acid.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06535.

> Structures of $Ir(ppy)_3$, $[Co(CR)Cl_2](ClO_4)$, and $[Co-(TPA)Cl]Cl$; experimental details and additional data (synthesis of complexes and characterization, photolysis, CV, electrolysis); estimation of the standard redox potential for $CO_2/HCOOH$; DFT calculations for the reactions of **1** and **2** with CO_2 (PDF)

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Notes
The authors declare no competing financial interest.

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