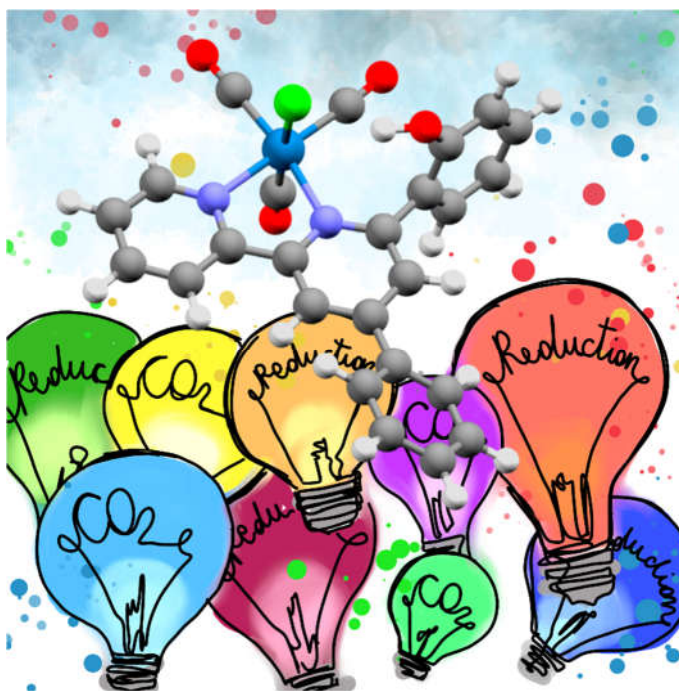




Università degli Studi di Torino

Doctoral School of Sciences and Innovative Technologies
PhD Programme in Chemical and Materials Sciences XXXIII Cycle

Electro- and photoreduction of carbon dioxide by Re (I) and Mn (I) bipyridine complexes



Laura Rotundo

Supervisor:
Prof. Carlo Nervi



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Candidate: **Laura Rotundo**

Supervisor: Prof. **Carlo Nervi**

Jury Members: Prof. **Silvia Bordiga**
University of Turin
Department of Chemistry

Prof. **Kim Daasbjerg**
Aarhus University
Department of Chemistry

Prof. **Angela Dibenedetto**
University of Bari
Department of Chemistry

Head of the Doctoral School: Prof. Alberto Rizzuti
PhD Programme Coordinator: Prof. Bartolomeo Civalieri

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CHAPTER 1. The challenging approaches for CO₂ conversion

1.1 Why does CO₂ get more attention rather than other gases?

Climate change is primarily a problem of too much carbon dioxide in the atmosphere. Since the first industrial revolution, fossil fuels like natural gas, coal and oil played a significant role in response to an overwhelming, worldwide energy demand. The key chemical process, mainly combustion, of these carbon-based fossil fuels inevitably generates carbon dioxide, which is the major responsible for global warming and associated events, such as rising of sea levels, ocean acidification and other environmental concerns. Moreover, the parallel trend existing for the growth of population alongside with the increase of energy consumption and atmospheric concentration of CO₂ is rising serious concerns about the potential climate change of our Planet¹; amongst other issues, overpopulation has also strengthened water scarcity issues across the globe. A target level of 450 ppm CO₂ equivalent concentration has been predicted by many models as the concentration needed to stabilize the global average temperature increase to 2 °C at the end of 21st century.^{2,3} As can be noticed from Figure 1, carbon dioxide concentration measured at Mauna Loa Observatory, Hawaii, is constantly increasing: the latest CO₂ reading in August 2020 is about 415 ppm, that is, almost nearing the established target value. To limit the CO₂-equivalent concentration to 450 ppm, between 40% to 70% of the total anthropogenic emissions need to be reduced by 2050, compared to 2010 emissions, and no anthropogenic emissions by 2100, as it has been reported in the Paris agreement.⁴⁻⁶

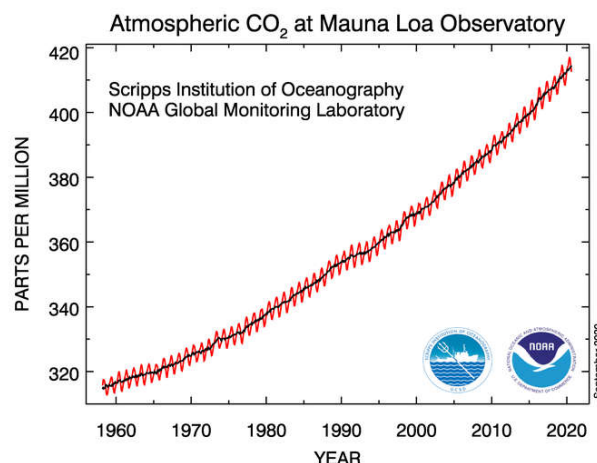


Figure 1.1. Full record of combined CO₂ concentration data from Scripps Institution of Oceanography and NOAA (National Oceanic and Atmospheric Administration).⁷

It is worthwhile to note how government policies during the COVID-19 pandemic have dramatically altered patterns of energy demand around the world. Whilst many international borders were closed and populations were confined to their homes, daily CO₂ emissions decreased by 17% by early April 2020 compared with the mean 2019 levels,^{8,9} just under half from changes in surface transport. Government actions and economic incentives postcrisis will likely influence the global CO₂ emission path for decades. Nevertheless, it was a temporary reduction of CO₂ emissions as a direct consequence of the lockdown regime.

Generally, the carbon overload is mainly due to anthropogenic activities, i.e. burning of fossil fuels, cutting down and burning forests. There are many heat-trapping gases (methane and water vapor), but CO₂ puts us at the greatest risk of irreversible changes if it continues to accumulate undiminished: CO₂ remains in the atmosphere longer than the other major heat-trapping gases emitted as a result of human activities. It has been established in a IPCC (Intergovernmental Panel on Climate Change)¹⁰ report, that CO₂ itself accounts for nearly 77% of the Global Greenhouse Gas Emissions. The dependence of our world on the use of fossil fuels for energetic purposes results into two urgent problems which needed to be solved:

- 1) Economic issues due to the NON-SUSTAINABILITY of fossil fuels since their depletion is constantly increasing.
- 2) Environmental issues caused by accumulation of CO₂ in the atmosphere and consequential warnings for the planet's climate; as the globe warms, we experience more extreme weather and climate events.

Global energy consumption is expected to increase by over 48% reaching 815 quadrillions Btu by 2040 vs. the 2012 baseline (549 quadrillions Btu), as reported in Figure 1.2.¹¹ Hence, the current practice of using fossil fuels as energy source must not continue. On the other hand, it must be taken in account that generating energy from renewable sources (solar energy, wind energy, tidal energy, geothermal energy...) suffers from their intermittent nature, because of the dependence on geographic location as well as the seasonal and nocturnal variations. The scientific community is striving towards the transition to a sustainable future¹²: all our energy and all our carbon must be renewable. Sustainability is defined as "the ability to meet the current needs without compromising the ability of future generations to meet their needs"¹³. How do we achieve this goal? Through chemistry and chemical engineering by understanding basic chemistry and then applying it to complex real systems, navigating the energy maze.¹⁴

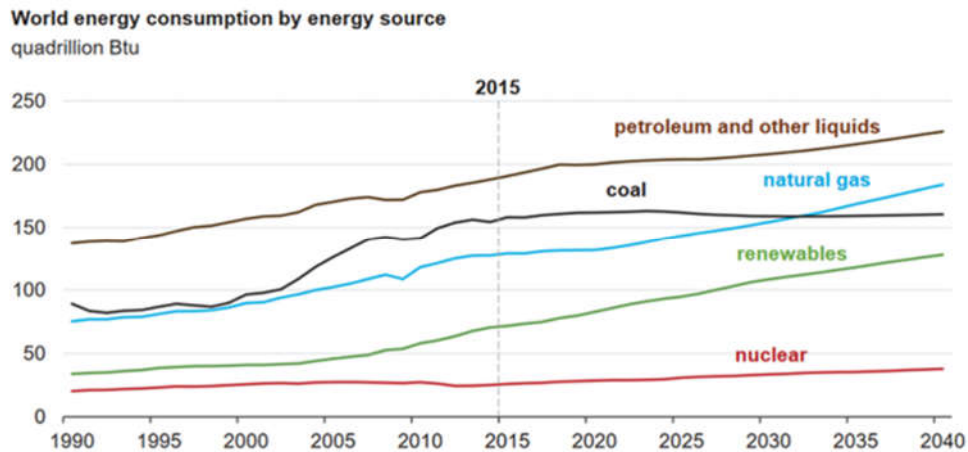


Figure 1.2. Total world energy consumption from different energy sources (reproduced from the International Energy Outlook, 2016).¹⁵

1.2 The CO₂ problem “management”

Carbon dioxide in the atmosphere can also be viewed as carbon that is “out of place”. Within this perspective, it is possible to think of moving that carbon elsewhere, such as underground for deep storage. At the same time, the emerging concept of “carbon to value” circular economy, frames carbon dioxide as a useful waste. The term waste is a complex and multivalent term. CO₂ as waste means something dangerous which must be disposed safely; in view of “CO₂ recycling”, waste is no longer a by-product, but an opportunity of the resource frontier.^{16–18} The “Circular Economy” attempts to mimic Nature¹⁹ which does not produce waste: within this perspective, goods are recycled in order to lower both the extraction of natural resources and the environmental liability of human activities. C-recycling means building a man-made C-cycle that can integrate the natural one and provide goods that are commonly employed. The exploitation of such ability will ensure longer availability of the limited natural resources.

Different approaches have been proposed in order to reduce the global carbon dioxide emissions:

- Improvement of process efficiencies to reduce energy consumption
- Utilization of alternative energy sources (e.g. solar energy, wind power and geothermal) and renewable (e.g. biomass and biofuel)
- Application of carbon dioxide capture, sequestration or storage, and utilization (CCS & U) technologies

Few words should be spent underlining the difference between renewable and regenerative carbon sources.²⁰ Biomass is a renewable carbon containing energy. Conversely, regenerative

carbon fuels are produced from CO₂ hydrogenation and any other suitable reduction process. A rational integrated approach of the three above-listed needs would be hoped for. Nevertheless, economic feasibility should be also addressed.

1.2.1 CARBON CAPTURE AND STORAGE (CCS)

CCS consists of separation of CO₂ from industrial and energy-related sources, transportation to a storage location, and long-term isolation from the atmosphere. CCS is widely recognized as an effective CO₂ fixation technology.^{21–23} Among the technologies to capture CO₂ from the atmosphere at different stages, pre-combustion, oxy-combustion and post-combustion are well-established techniques.²⁴ The main difference among these processes lies in the amount of CO₂ that is captured from a stationary source and at what stage. Physical and chemical phenomena including absorption, adsorption (solvents/sorbents), membrane separations, cryogenic methods, metal organic frameworks (MOFs) may be used as mass transfer practices for CO₂ sequestration. CO₂ capture in post-combustion energy schemes is currently believed as the most mature and viable way for decarbonization. The state-of-the-art removal from post-combustion flue gases is provided by aqueous amine solutions, namely amine-scrubbing processes.^{25,26} However, this practice deals with high-regeneration costs issues (e.g. the high energy consumption related to the use of water as a solvent). Adsorption by porous solids potentially allows for a weaker bonding with CO₂. Moreover, typical properties of solid-adsorbents – zeolites, active carbons or metal organic frameworks (MOFs)- offer the possibility to reduce the energetic cost of the recovery step.^{24,25,27–31} Particularly, MOFs are one class of crystalline adsorbent materials that are believed to be of huge potential in CO₂ capture applications because of their advantages such as ultrahigh porosity, boundless chemical tunability, and surface functionality over traditional porous zeolites and activated carbon.^{31,32} Once CO₂ is captured and pressurized, it must be transported to storage tanks or injected into underwater formations and other underground options. Geological and ocean storage are the two most discussed alternatives.

The majority of the nineteen large-scale CCS facilities capture CO₂ for natural gas processing^{11,33} and they globally had an annual storage capacity between 37.1 and 37.8 metric million tons¹ in 2019 (Figure 1.3).³⁴ Considering that CO₂ emissions in 2019 almost remained unchanged with respect to 2018 (about 35 Gt)³⁵, CCS alone does not seem to effectively solve the problem, but literally buries it underground. CCS is functional to a linear economy, whereas utilization of carbon dioxide is at the hearth of a circular economy and its strategic role will grow in the future.²³

¹ Metric ton: a unit of weight equal to 1000 kg or about 2205 pounds.

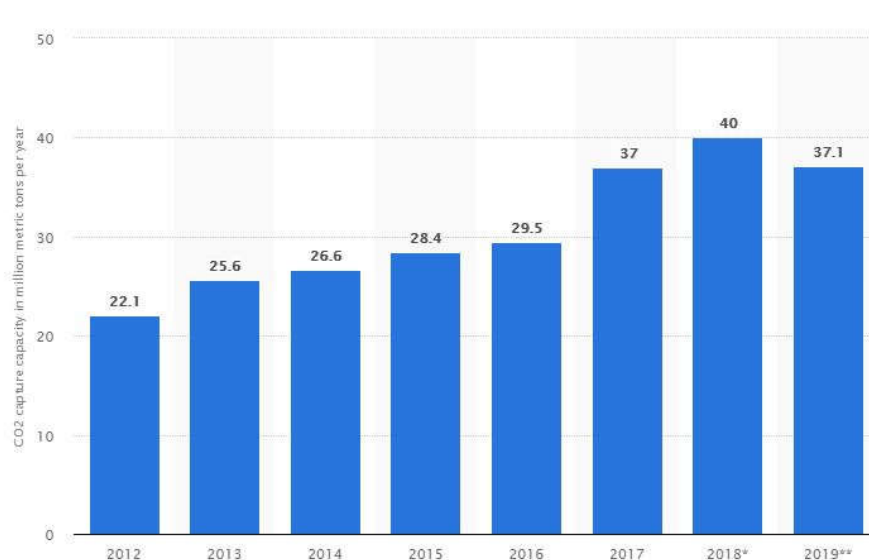


Figure 1.3. Capacity of operational large-scale CCS facilities worldwide from 2012 to 2019. Reproduced from ref.³⁴

To some extent, CCS is merely a temporary solution for the CO₂ problem, since CO₂ is simply relocated from the atmosphere to long-term storage places. Additionally, some of the major drawbacks of CO₂ deployment are represented by energy requirement, capture cost, transport infrastructure availability, geological storage availability, technical and integration risks. Clearly, there is the need to shift towards CCU (Carbon Capture and Utilization), because of its advantages over CCS, which will be further addressed, within its related challenges.

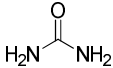
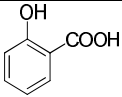
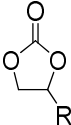
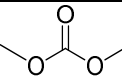
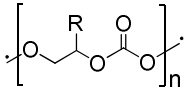
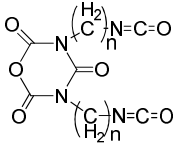
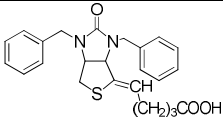
1.2.2 CARBON CAPTURE UTILIZATION (CCU)

This option aims at the core part of the CO₂ management process.³⁶ The utilization of CO₂ and its conversion to chemical products, including fuels, would allow reduction of its concentration in the atmosphere and reduction of the extraction of fossil-C, part of which would be substituted by recycled-C. Utilization itself should be divided into two parts: the former accounts for the use of CO₂ without any conversion, such as enhanced oil recovery by CO₂ flooding or physical solvent applications; the latter provides for conversion to chemicals and fuels via carboxylation^{37,38} or reduction routes.³⁹ For instance, carboxylation of glycerol into added value chemicals has grown interest: the synthesis of glycerol carbonate plays a prominent role as the monomer could be used for the synthesis of new functionalized polymers that might have interesting new applications.^{40,41}

CO₂ as a building-block, or feedstock for the chemical industry has already made significant achievements. Among the most common products from CO₂, urea, formic acid, methanol, cyclic carbonates, polycarbonates, and salicylic acid may be listed. Today, around 230 million tons (Mt) of CO₂ are used each year. The largest consumer is the fertilizer industry, where

around 130 Mt CO₂ per year is used in urea manufacturing, followed by the oil sector, with a consumption of 70 to 80 MtCO₂ for enhanced oil recovery (EOR).⁴² CO₂ is also widely used in food and beverage production, the fabrication of metal, cooling, fire suppression and in greenhouses to stimulate plant growth. Table 1.1 shows some of the chemicals produced from CO₂.^{39,43} Interestingly, another useful intermediate for pharmaceutical industries can be produced: when CO₂ reacts with phenolate anion through electrophilic substitution via the Kolbe-Schmitt reaction, salicylic acid is afforded. This is the progenitor of other valuable fine chemicals like acetylsalicylic acid (aspirin), salicylic amide and phenyl salicylates.⁴⁴

Table 1.1 Some of the chemicals that can be possibly produced from CO₂.

Chemical	Molecular Formula	Annual production	Utilized CO ₂ as feedstock per year
Urea		150 million tons	112 million tons
Methanol	CH ₃ OH	100 million tons	2 million tons
Salicylic acid		70 thousand tons	30 thousand tons
Formaldehyde		9.7 million tons	
Formic acid		700 thousand tons	
Cyclic carbonates		80 thousand tons	40 thousand tons
Ethylene carbonate			
Di-methyl carbonate		10 million tons	
Copolymers			
Polymer building blocks			
Fine chemicals (for instance biotin)			

CO₂ conversion reactions can be classified into two main categories^{19,36,39}:

- 1) Low energy processes: reactions which do not require substantial amount of external energy. Products formed contain the C-atom with the redox state unchanged (+4) or slightly diminished (+3) with respect to CO₂ itself. Such reactions are often named as carboxylation reactions and produce -amongst others- carboxylates, carbamates, lactones, carbonates, ureas and isocyanates. This kind of reactions efficiently proceed thermally or upon catalyst addition. The presence of a co-reactant (usually a strong base) is often needed.
- 2) High energy processes: reactions which produce reduced forms of CO₂. These reduction reactions need considerable amount of external energy. These processes lead to the formation of chemicals with strongly reduced C atom (+2 oxidation state or lower). They include products like HCOO⁻ (+2) (formates), [C(O)O]₂²⁻ (+3) (oxalates), H₂CO (0) (formaldehyde), CO (+2), CH₃OH (-2), CH₄ (-4) and C₂H₄ (-2). All these molecules possess a significant energy content; therefore, they can be used as fuels themselves (e.g. HCOO⁻, CH₃OH, CH₄...) or are directly involved in fuel synthesis processes (e.g. CO via Fischer-Tropsch process). The external energy required by this group of reactions can be supplied as: (i) heat, (ii) electrons and (iii) irradiation/photons. Hence, processes are called as thermal, electrochemical, and photochemical, respectively. Energy carriers, electrons, photons, or hydrogen (hydrogenation reactions) are mandatory to transfer energy to the system allowing the reaction to occur. Henceforth, catalysts are generally needed to obtain acceptable rates for these reactions.

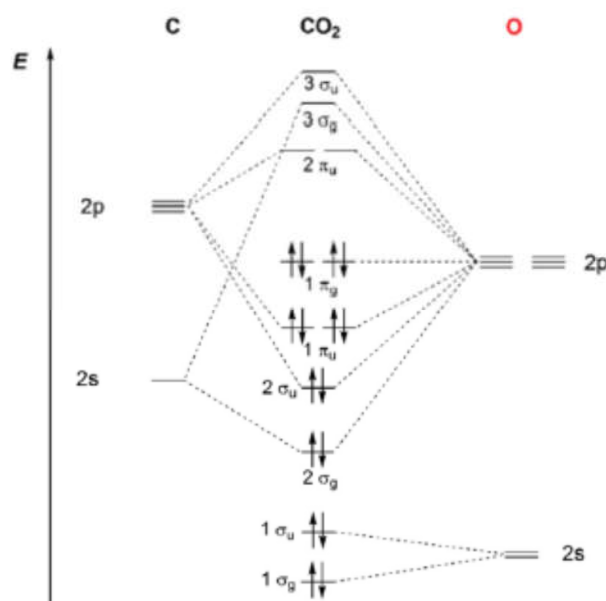
Electrochemical, photochemical and photoelectrochemical techniques for reducing CO₂ require energy from perennial sources, directly or indirectly. Therefore, the application of biocatalysts, such as enzymes and microorganisms for CO₂ utilization is highly desirable. Biocatalysts and enzymes are known from natural CO₂ reduction processes, for which they yield high efficiencies and selectivity under mild reaction conditions (e.g., ambient temperature and pressure, aqueous media at neutral pH). For the direct reduction of CO₂, dehydrogenase enzymes can convert CO₂ into alcohols directly under ambient conditions and in aqueous environments. Nonetheless, such processes need electrons and proton donors or co-factors, which in nature are represented by nicotinamide adenine dinucleotide. An integration of electrochemical and photoelectrochemical approaches would allow to directly inject electrons into enzymes without the requirement of any co-factors.^{45,46}

Carbon dioxide capture and utilization is a challenging contemporary issue having multi-aspects. Conversion of CO₂ to useful products by different processing routes is limited by the

lack of knowledge about the products that can be made by converting CO₂, about the catalyst that may be needed and the associated reaction kinetics.¹¹ As a result of this, carbon dioxide conversion processes have been restricted to the production of bulk chemicals like methanol, syngas or dimethyl carbonate (DMC), although in principle, hundreds of chemicals can be generated through carbon dioxide conversion reactions.⁴⁷ Most of carbon dioxide technologies are currently in their early stage of development. Industrially, conversion processes have been used to produce urea and carbonates and for methanol production, which is one of the most mature technology, considering that some plants for the CO₂ to CH₃OH conversion already exist in Iran⁴⁸, Qatar⁴⁹ and Iceland⁵⁰.

1.3 CO₂ energetics: thermodynamics vs. kinetics

Before getting into specifics of the CO₂ conversion, it is worthwhile to start with some considerations about the molecular properties of carbon dioxide itself. The carbon atom of CO₂ shows the most oxidized state of carbon (+4) and a high energy input is necessary for its transformation, considering that it is a thermodynamically stable molecule ($\Delta G_f^\circ = -396$ kJ/mol). CO₂ is a 16e⁻ molecule with a linear equilibrium structure in its electronic ground state, therefore belonging to the D_{∞h} symmetry group. Since the first ionization potential (I_p) of CO₂ is 13.8 eV and the electron affinity (E_a) is -0.6 eV, CO₂ is rather an electron acceptor than a donor^{51,52}, and the reactivity is strongly dependent on the electrophilicity of the carbon atom which is surrounded by empty antibonding 2π_u orbitals. Reactivity of the molecule results from the weak electrophilicity of the carbon atom, the lone pairs of electrons on the oxygen atoms, or the presence of the π electron density of the C–O double bonds. The qualitative molecular orbitals (MO) energy diagram of CO₂ is depicted in Scheme 1.1.



Scheme 1.1. Qualitative molecular orbital diagram. Reproduced from ref.⁵².

The most relevant molecular orbitals (MOs) are $1\pi_g$ and $2\pi_u$ which play the role of HOMO and LUMO, respectively. The doubly occupied nonbonding $1\pi_g$ MOs are mainly localized at the terminal oxygen atoms, whereas the empty antibonding $2\pi_u$ orbitals are mostly centered on the carbon atom. Therefore, CO_2 can be considered as an amphoteric molecule, where the oxygen atoms display a Lewis basic character, and the carbon atom behaves as a Lewis acid center. The one-electron reduction of CO_2 occurs at a very negative potential (-1.90 V vs. normal hydrogen electrode NHE at pH 7 in aqueous media).^{17,53,54} When the LUMO orbitals are filled via an electron transfer, the linear CO_2 molecule changes itself in the bent radical anion $\text{CO}_2^{\bullet-}$, displaying C_{2v} symmetry. The injection of an electron into the CO_2 molecule is highly unfavorable, due to the thermodynamic instability of the radical anion species. Moreover, the kinetic contribution due to the difficult and large reorganizational energy between linear and bent molecule gives reason of the overpotential (100-600 mV) required for this direct one-electron reduction.^{51,55} The efficient reduction of CO_2 into chemicals requires that both thermodynamic and kinetic barriers are overcome. More promising pathways than the single-electron route for CO_2 reduction are represented by *proton-coupled electron transfer* (PCET).⁵⁶ As it is reported in Table 1.2, the involvement of protons in the redox reactions leading to the desired chemicals (which are much more stable than $\text{CO}_2^{\bullet-}$) significantly lowers the thermodynamic barrier. On the other hand, products like CH_3OH and CH_4 , are thermodynamically more feasible than $2e^-$ reduction products (CO and HCOOH), but the latter processes are more favored than the former ones, which involve 6 and 8 e^- respectively, because of kinetic reasons. Furthermore, it must be also taken in account that side production

of hydrogen becomes a competitive process in presence of protic acid in solution (entry 7, Table 1.2).

Table 1.2. Formal potential $E^{0'}$ for competing reduction processes of CO_2 to C1 chemicals. Both values vs. NHE and SCE are referred to standard conditions in aqueous solutions: pH = 7, T = 25°C, p = 1 atm and [solutes] = 1M.

Redox reaction	$E^{0'}$ (V) vs. NHE	$E^{0'}$ (V) vs. SCE
1) $\text{CO}_2 + 1\text{e}^- \rightarrow \text{CO}_2^{\bullet-}$	− 2.14	− 1.90
2) $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	− 0.77	− 0.53
3) $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	− 0.85	− 0.61
4) $\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	− 0.72	− 0.48
5) $\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	− 0.62	− 0.38
6) $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	− 0.48	− 0.24
7) $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	− 0.65	− 0.41

The formation of the CO_2 radical anion by accepting one electron is viewed as the rate determining step for CO_2 reduction: catalytic strategies are indispensable to avoid the radical anion intermediate as well as to lower the energetic cost of the reductive process. The choice of an efficient and selective catalyst is mandatory and crucial, considering the variety of competitive processes and the challenge between thermodynamic and kinetic feasibility.

1.4 Molecular catalysts for CO_2 reduction

Transition metal complexes are good candidates to act as molecular catalysts for CO_2 reduction, since they possess multiple redox state, which can optimally activate proton-coupled, multi-electron reactions.⁵⁶ Since they possess partially filled d orbitals they are believed to have the capability to facilitate the bonding with CO_2 , forming active intermediates. Among various advantages the use of molecular catalysts, such as defined transition metal–ligand complexes, allows for fine-tuning of the chelating abilities and the steric, electronic and electrostatic effects of the ligands, thus opening a wide door towards thorough mechanistic and spectroscopic studies. Notably, abundant transition metals such as iron, manganese, cobalt, copper, or nickel with activity for CO_2 catalytic reduction were already investigated in the early 1970s, starting with phthalocyanines and porphyrins, as well as polypyridyl, phosphine, cyclam and aza-macrocylic ligands.^{57–64} There are complicated pathways to convert CO_2 into chemicals or fuels, including (i) electrochemical, (ii) thermocatalytic, (iii)

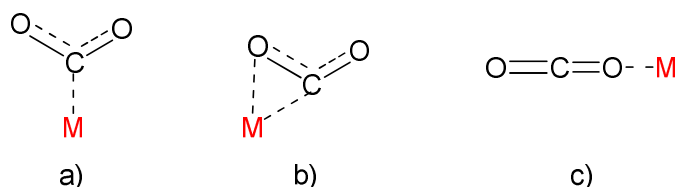
photochemical, (iv) biochemical and (v) hybrid methods.⁶⁵ The most challenging task is the choice of a robust, selective and efficient catalyst: even if an enormous body of work have been conducted in the last 15 years, molecular catalysts able to go beyond the 2-electron 2-proton traditional reduction products (CO and formic acid) remain scarce. Among the external factors affecting the efficiency of the catalytic process, the purity grade and solubility of CO₂ in the reaction medium must be considered: CO₂ has a relatively low solubility in water (0.038 M), whereas it displays much higher solubility in organic solvents (0.28 M in acetonitrile and 0.2 M in dimethylformamide, respectively). To conclude, the latter ones are better solvents for CO₂ reduction experiments, although water would be highly desirable for a green chemistry optics.

1.4.1 CO₂ COORDINATION TO METAL CENTERS

One of the critical steps in the catalytic mechanism is the formation of a CO₂-catalyst adduct, in which the substrate binds to a vacant coordination site at the metal center of a reduced catalyst. The CO₂ catalyst adduct should be stable enough to activate the catalytic cycle, but stability of the adduct should not limit the release of the reduction product. As depicted in Scheme 1.2, there are three common binding modes for CO₂ coordination^{51,66–68}:

- end-on $\eta^1\text{-C}$
- side-on $\eta^2(\text{C,O})$
- end-on $\eta^1\text{-O}$

The first one (Scheme 1.2a) is preferred with electron-rich metals normally forming a carboxylate adduct. When the CO₂ molecule is also bent and coordinated through the carbon and one of the oxygen atoms, via the $\eta^2(\text{C,O})$ binding mode, it is the so called side-on π bonding (Scheme 1.2b). Differently, in rare cases CO₂ binds to the metal center as a Lewis base via its oxygen atoms. The end-on $\eta^1\text{-O}$ coordination (Scheme 1.2c) is preferred with electron poor metals and the CO₂ molecule can keep its linearity or be weakly bent.



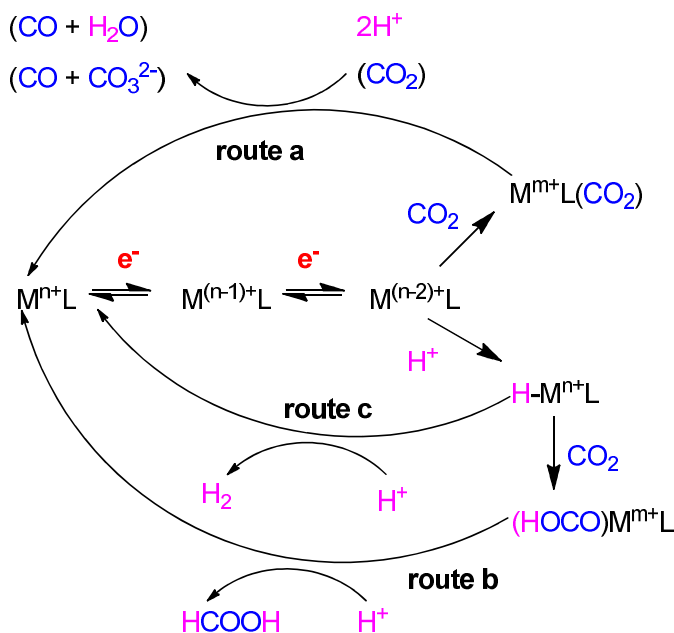
Scheme 1.2. CO₂ coordination mode to a single metal center.

1.4.2 MOLECULAR CATALYSTS BENCHMARK: SELECTIVITY FOR CO₂ REDUCTION PRODUCTS

It could be noted that many of the molecular catalysts currently studied and published are similar or even identical to those that have been thoroughly investigated in the 1980s and 1990s, during the first wave of CO₂ reduction studies. As it has been mentioned before, most of the molecular catalysts are able to efficiently reduce CO₂ to CO and HCOOH. The selectivity issue is partially due to the reaction product's close thermodynamics and to the greater ease of transferring two rather than four, six, or eight electrons, thus forming high energy molecules like CH₂O, CH₃OH and CH₄. On the industrial scale, CO is widely employed in mixtures with H₂ (syngas) then used for producing liquid fuel through the Fischer-Tropsch process⁶⁹, for the production of methanol and in the hydroformylation of olefins to aldehydes and alcohols.⁷⁰ Differently, formic acid can be spent for fuel cells⁷¹ or as a potential hydrogen storage material.⁷²

Since this PhD thesis is entirely focused on CO₂ reduction to CO and HCOOH, an overview of the commonly proposed reductive pathways leading to CO and HCOOH is reported in Scheme 1.3. The original catalyst, Mⁿ⁺L, needs to be doubly reduced to get the electrogenerated catalyst, M⁽ⁿ⁻²⁾⁺L, which can selectively bind both CO₂ or H⁺. Focusing on **route a**, the electrophilic carbon of the substrate reacts with the nucleophilic metal center of the catalyst, leading to the formation of a carboxylate CO₂-metal adduct, Mⁿ⁺L(CO₂). The subsequent electron transfer from the metal ion towards CO₂ induces a C-O bond cleavage and is generally accompanied by a concomitant proton transfer: CO is formed by dissociation of M-CO bond and the original catalyst is regenerated. As the catalytic CO₂ reduction is a proton-assisted process, water is formally written as the co-product of the catalytic reaction. However, in some cases, another molecule of CO₂ can formally act as an oxide O₂²⁻ unit acceptor, leading to CO₃²⁻. Alternatively, if protonation of the nucleophilic metal center of the catalyst occurs, a hydride intermediate, H-Mⁿ⁺L is formed. This species is responsible for competitive HCOOH (**route b**) and H₂ (**route c**) productions. The former mechanism is based on insertion of CO₂ into the metal-hydride bond, with a subsequent release of HCOO⁻ ion and catalyst regeneration. Insertion of CO₂ into M-H bonds has been shown to follow two major pathways affording either the M-OCHO and M-COOH moieties. These two methods of insertion are known as normal (i) and abnormal (ii), respectively. This classification originates by the concept that in M-H bond, the metal center usually bears the fraction of the positive charge while the negative is accumulated on H. Therefore, it is expected that during the insertion of CO₂ into a M-H bond, one of the nucleophilic oxygen atoms should interact with the metal atom and the electrophilic carbon atom with the hydride ligand, affording M-OCHO intermediate. Nevertheless, formation

of a M–COOH moiety via reaction of a metal carbonyl species M–(CO) with a hydroxide anion or via protonation of a M–(η^1 -C)–CO₂ complex represents the more common scenarios.⁵¹ Catalysts are highly specific compounds, capable of steering the reaction to yield a particular product: this is termed as catalyst's selectivity. For common molecular catalysts for CO₂ reduction, selectivity towards HCOOH, CO or H₂ is often largely affected by the experimental conditions, such as pH of the solution, electrolyte, and properties of the catalyst itself. Metal and ancillary ligand play a significant role in tuning the selectivity.^{73,74}



Scheme 1.3. Competitive mechanisms for CO₂ reduction to CO (**route a**) and HCOOH (**route b**) and for side H₂ catalytic production from H⁺ (**route c**). M = metal center, L = generic ligand, n⁺ = initial oxidation state of the metal, m⁺ = oxidation state of the CO₂-catalyst intermediate. Adapted from ref.⁷⁵

1.5 Catalytic strategies for CO₂ reduction

As it has been mentioned, different catalytic strategies can be adopted to activate CO₂. Three main viable processes, which have been extensively exploited until today, are herein listed: i) *chemical catalysis* ii) *electrocatalysis* iii) *photocatalysis*. The former approach requires the presence of a reducing agent: when H₂ is employed, reactions are known as *catalytic hydrogenation* processes.^{72,73} Being hydrogenation and chemical catalysis beyond the scope of this PhD thesis, no detailed investigations will be further delivered.

1.5.1 ELECTROCATALYSIS

The interest on this topic grew up exponentially during the last years, as it is also testified by the increasing number of reviews present in literature.^{51,52,54,56–61,75,78–80} Electrocatalysis can be divided in homogeneous and heterogeneous approach. Most electrocatalytic studies in this field originally focused on the catalyst/substrate interaction in homogeneous solution. Nowadays, a reasonable amount of work has been dedicated on the heterogeneous electrochemical catalysis.^{79,81–90}

Within this optics, the aim is to obtain an efficient catalytic device capable of being part of an industrial process. Furthermore, the perspective of using the electricity produced by green technologies (e.g. photovoltaic) to accomplish the desired catalytic processes is even more appealing.

The reducing equivalents needed to generate the active form of a catalyst are directly provided by an electrode surface. The electron uptake during the catalytic reaction is controlled by a potentiostat and is dependent on the diffusion-adsorption phenomena occurring at the interface between solution and electrode surface that rule the electrochemical processes. The catalyst simply shuttles electrons between the electrode and the substrate. The electrocatalytic CO₂ reduction reaction (CO₂RR) may undergo several multi-electron, multi-proton pathways, leading to a wide range of carbon-based products. Reminding the standard redox potentials (E^0) of Table 1.2, it is important to emphasize how those values merely represent the thermodynamics of the final reaction, which may be composed by several intermediate steps, responsible for the overall kinetic of the whole process. Such proton-coupled electron multi-electron reactions are relatively favorable, since they lead to products which are thermodynamically similar or more stable when compared to CO₂. However, in the practical case the kinetics of direct CO₂ electroreduction are slow, which leads to a demand for potentials more negative than the thermodynamic requirement in order to obtain reasonable reaction rates. This additional driving force, the overpotential required for catalysis (η_{cat}),^{51,57} is defined as the difference between the potential that is required to drive a reaction $A \rightarrow B$ at a specific rate and the standard potential E^0 (A/B) for the formation of product B from substrate A. The reduction potential of the electrocatalyst (E^0_{cat} , Figure 1.4) should fit within the appropriate range, minimizing the overpotential: catalysts which can be rapidly and reversibly reduced are preferred over those with slow electron kinetics.

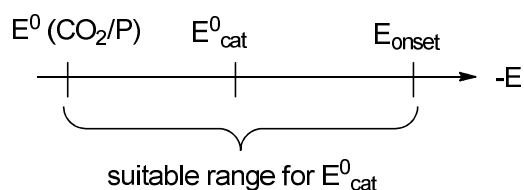


Figure 1.4. Prerequisite relative positions of potentials for establishing a catalytic cycle. E^0 (CO_2/P) refers to the potential of the reduction of CO_2 to a certain product (P), E^0_{cat} is the reduction potential of the catalyst and E_{onset} is the potential value of the direct CO_2 reduction at the electrode. Adapted from ref.⁵¹

Additionally, rate constants (k_{cat}) for conversion of CO_2 into the product must be also considered, since only fast reactions provide efficient electrocatalysis.⁵⁴

The use of electrochemical techniques, in particular cyclic voltammetry (CV), has been proven to be particularly fruitful to benchmark the intrinsic properties of the catalysts. A typical example of CV results is depicted in Figure 1.5. Firstly, it is possible to study the redox behavior without CO_2 , which enables to determine whether a catalyst can be reduced within the appropriate potential range and at which potential a possible electrocatalytic reaction can proceed. Finally, observing changes of the shape of recorded cyclic voltammograms (CVs), according to certain diagnostic criteria, catalytic activity can be detected. Comparing the peak currents under inert atmosphere (i_p) and under CO_2 (i_{cat}), the ratio i_{cat}/i_p is an indicator of the catalyst activity. The catalyst's redox couple typically gives a reversible (or quasi-reversible) wave under Ar (black CV in figure 1.5) but loses its reversibility in CO_2 -saturated conditions (red CV in figure 1.5) due to fast interaction between the catalyst and the substrate. The peaked shape of the catalytic wave (red line) represents a special case where consumption of CO_2 is competing with its diffusion to the electrode, the latter process limiting the current response at higher potentials. In order to extract kinetic data, experimental conditions led by pure kinetic control should be met. By increasing the scan rate, a transition from the peak-shaped profile (red curve in figure 1.5) to a sigmoidal-shaped response, can be reached. This behavior reflects a situation where the concentration of CO_2 in bulk solution is equal to its concentration on the surface throughout the entire potential regime. In other words, substrate depletion on the electrode surface is suppressed by shortening the time scale of the CV experiment, which allows for observation of the voltammetric response under kinetic control without substrate consumption.

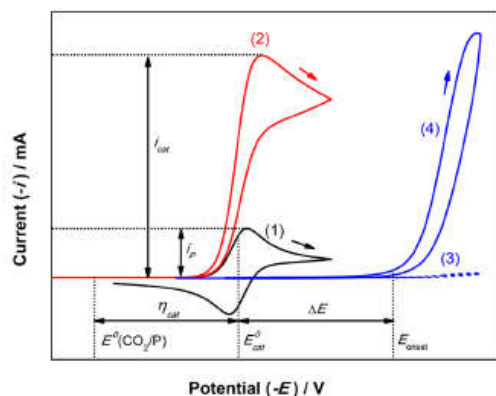


Figure 1.5. Example of voltammetric analysis of a CO₂ electrocatalyst. (1) CV of the catalyst under Ar, (2) CV of the catalyst under CO₂, (3) blank under Ar, (4) blank under CO₂. Reproduced from ref. ⁵¹

There are five fundamentals parameters to compare for evaluation of the performance of electrocatalysts for CO₂ reduction^{51,54,57,79,91}:

- 1) The above-mentioned catalysts selectivity (CS) see Paragraph 1.4.2.
- 2) The overpotential required for catalysis η_{cat} (see above), which is the thermodynamic cost for catalysis.
- 3) Turnover Number (TON) and Turnover Frequency (TOF); TON is the total number of molecules of substrate that a catalyst converts into product molecules, and TOF is the TON in the unit time. The term TOF_{max} is frequently used as a synonymous of the apparent rate constant (k_{app}) which represents the overall rate of the catalyzed reaction.
- 4) Faradaic Efficiency (FE); FE is defined as the percentage of electrons employed to generate the desired product. This parameter not only refers to product selectivity but also to energetic efficiency.
- 5) The Tafel slope; the Tafel plot is built by the logarithm of the current density vs. overpotential. A lower Tafel slope value indicates better performance of electrocatalysts, see Figure 1.6. The TOF is indeed dependent on η_{cat} since the amount of active catalysts in the reaction layer increases when η_{cat} increases, reaching a plateau value equal to k_{cat} (or k_{app}), the pseudo-first-order rate constant of the limiting step of the catalytic process (provided the experimental conditions allow reaching the pure kinetic regime).

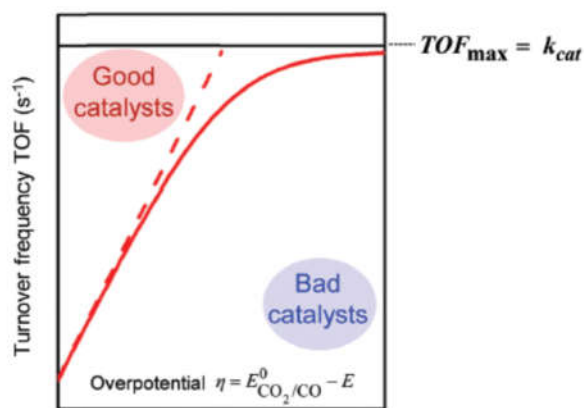


Figure 6. Benchmarking of molecular catalyst intrinsic properties for the CO₂-to-CO reduction through the catalytic Tafel plot. Reproduced from ref.⁵⁷

Spectroelectrochemical (SEC) studies, combined with optical spectroscopies (UV-Vis and IR) and electrochemical techniques, represent a complementary approach for an in-depth investigation of the intermediate or transient species formed during an electrochemical process. Lastly, long-term performances of molecular electrocatalysts are studied by means of bulk-electrolysis experiments coupled to analytical measurements (for both gas and solution products) to gain information about the catalyst selectivity and durability over time.

In homogenous electrocatalysis, soluble electrocatalysts act as the electron transfer agents to facilitate and accelerate the reaction differently from heterogeneous electrocatalysis where the electrode itself also performs as the electrocatalyst. A large number of potential advantages of the latter approach with respect to the former can be identified: easier recovery of products and catalysts, small amounts of catalyst necessary for efficient electrolysis, deactivation pathways often hindered or suppressed and elimination of solubility problems. Furthermore, in a heterogeneous system the electron transfer is generally more efficient when the catalyst is attached or chemically bonded on the electrode surface instead to diffuse in solution, lowering the limitation of the electron transfer in the catalytic cycle. Transition metal complexes immobilized on electrode surfaces can represent promising catalysts to be utilized in a large-scale process for CO₂ reduction, particularly if non-precious metals like manganese, cobalt, iron, nickel, copper, and zinc are involved.

At this outset, it is useful to distinguish between *inner-sphere* and *outer-sphere* electron-transfer reactions at electrodes (Figure 1.7). In an *outer-sphere* electron reaction, the reactant and product do not interact strongly with the electrode surface, and they are generally at a distance of at least a solvent layer from the electrode. Conversely, in an *inner-sphere electrode reaction*, there is a strong interaction of the reactant, intermediates, or products with the

electrode; that is, such reactions involve specific adsorption of species involved in the electrode reaction.

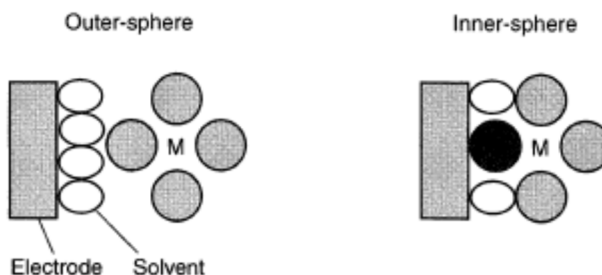
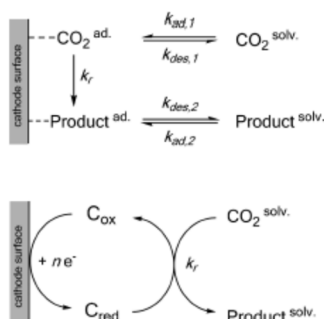


Figure 1.7. Outer-sphere and inner-sphere reactions. Reproduced from ref.⁹¹

Most of the homogeneous electrocatalysts experience *outer-sphere* reactions, although it is worthwhile to note that inner-sphere electron transfers between a homogeneous catalyst and CO₂ may occur. In this scenario, the reduced form of the catalyst (C_{red}) can experience a binding interaction with the substrate prior to the electron transfer from C_{red} to CO₂.⁵¹

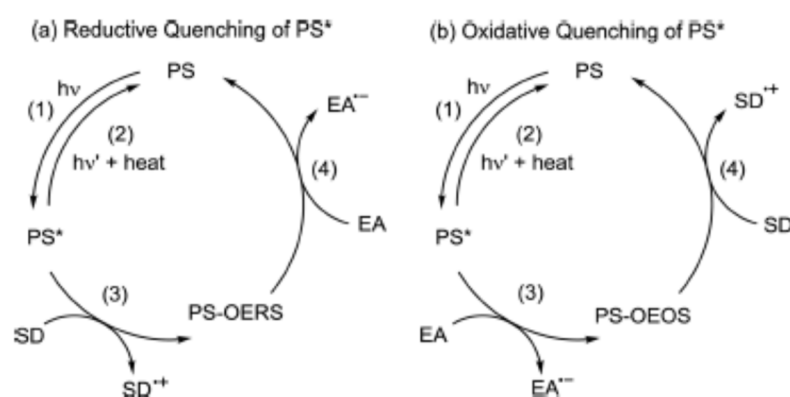
Many materials provide the possibility for bond-forming interactions (chemisorption) prior to the electron transfer ("*inner-sphere* electrodes") thereby lowering the activation barrier and influencing the selectivity of the reaction (scheme 1.4). Massive efforts have been undertaken in order to develop the catalytically active electrodes for CO₂ reduction. A vast number of different materials has been studied and reviewed. These materials can be classified into four different categories: metals, metal alloys, transition metal oxides/chalcogenides, and metal organic frameworks.^{92–94} Efficient homogenous electrocatalytic reduction of CO₂ which can be employed on an industrial scale still remains challenging, essentially due to low performances of currently employed electrocatalysts, in terms of stability and selectivity. More promising results are achieved by the heterogenous electroreduction.



Scheme 1.4. Electrochemical CO₂ Reduction via Heterogeneous (top) and Homogeneous Catalysis (bottom). Reproduced from ref.⁵¹

1.5.2 PHOTOCATALYSIS

Many of the catalysts investigated in electrochemical conditions have also been investigated in photochemical conditions. The general trend is that the best molecular catalysts in electrochemical conditions are also efficient in photochemical conditions, although there are some exceptions. The reasons could be found in the similarities of the high energy intermediates found in electrocatalytic and photocatalytic approaches: both involves an electron formally located in the LUMO orbital, but with different charge. Catalytic CO_2 photoreduction is a light-driven redox catalytic process in which the electron transfer to the molecular catalyst is mediated by a chemical species (instead of a solid electrode surface) acting as an electron source. A photocatalytic system typically comprises a catalyst (CAT) for CO_2 reduction and a redox photosensitizer (PS) that can photochemically mediate the transfer of one electron from a sacrificial donor (SD) to the catalyst (CAT).^{57,60,80,95–97} Developing photocatalytic systems for CO_2 reduction will provide useful and energy-rich compounds and would be one of the most important focuses in the field of “artificial photosynthesis” and “solar fuels”. The photocatalytic reduction of CO_2 gained interest as an artificial means of photosynthesis since the oil crisis of the 1970s until the 1990s. Most of the reported photocatalytic reactions using transition metal complexes have combined systems containing PS, which photochemically induces a one-electron transfer from a reductant SD to CAT. Once CAT accepts the electron from the PS, “accumulates” two electrons, and introduces them to the CO_2 molecule, producing CO and/or HCOOH .^{60,95} There are two types of initiation reactions in the photosensitized reactions: i) reductive quenching and ii) oxidative quenching (scheme 1.5).⁶⁰ In the former reaction, the excited PS (PS^*) is quenched by SD to the OERS (One Electron Reduced Species), in the latter one PS^* is oxidatively quenched by CAT or a mediator, which transfers the electron to CAT via the subsequent process. Reductive quenching is the most common mechanism for photocatalytic CO_2 reduction.



Scheme 1.5. Reductive and oxidative quenching of the excited state of PS. Reproduced from ref.⁶⁰

The PS for CO₂ reduction is required to meet the following photophysical and electrochemical properties:

- 1) Stronger absorption at an excitation wavelength than the other coexisting materials, such as D and CAT, preferably in visible region.
- 2) Long emission lifetimes, because of the requirement of an efficient reductive quenching process.
- 3) Strong oxidation power in the excited state, to capture an electron from SD.
- 4) High stability of the OERS produced after the electron transfer.

Differently from electrocatalytic reactions, in photocatalytic reactions only a stepwise electron injection from the PS^{•-} to the CAT is possible because one-photon excitation of the PS can induce only one-electron transfer in the photosensitized reactions. Under steady-state irradiation conditions, both the compounds with high reduction power OERS of the PS and the CAT, and those with high oxidation power, e.g., the OEOS (one electron oxidized species) of SD and PS* exist together in the reaction solution. This situation often leads to undesirable electron transfer.

The selection of SD is also crucial and drastically affects the photocatalytic abilities of the systems. Once OERS of PS is produced, OEOS of SD is formed, SD^{•+}. Its stability strongly influences the efficiency of photocatalytic systems, since back electron transfer from PS^{•-} to SD^{•+} can occur. Hence back electron transfer must be suppressed and SD^{•+} should be sacrificially decomposed.

Among the characteristics for benchmarking photocatalysts, the ones required for electrochemical conditions are still valid, Quantum Yield (ϕ) must be included; it reflects the conversion of photons to products formed and to some extent it ought to be used as a measure of system efficiency. It can be determined by comparing quantified product (mol) with the molar quantity of monochromatic photons incident on the sample during photocatalysis.^{80,96}

Electro-and-photo-reduction of CO₂ are very closed and complementary techniques, which are experiencing an intense and thorough study. Both approaches have their drawbacks; difficulties can be encountered regarding catalyst stability, conversion efficiency, product selectivity. Simple uncatalyzed proton assisted CO₂ reduction can lead to competitive H⁺ reduction reaction producing H₂ as an unwanted by-product. The catalyst is the key component in the chase of overpotential decrease, considering that CO₂ reduction is energetically costly.

1.5.3 TOWARDS ARTIFICIAL PHOTOSYNTHESIS (AP)

The photosynthetic approach occurs in nature in various forms of life such as plants and algae. The process consists in capturing energy from sunlight, a renewable energy source, to carry out conversion of CO_2 and H_2O into glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and O_2 , which are essential to life. This is an excellent model of direct chemical storage of solar energy.

Artificial photosynthesis, which is described as “Chemistry's Greatest Challenge” attempts to replicate the natural processes of photosynthesis, and, at least in near future, the goal of artificial photosynthesis is to use sunlight energy to make high-energy chemicals to store energy. A challenge in artificial photosynthesis is to use cheap and environmentally friendly compounds. Many components currently proposed for use in artificial photosynthetic systems are expensive, toxic, inefficient, or nondurable. Mimicking the photosynthesis process means harvesting natural sunlight and in turn convert CO_2 into fuels like hydrogen and carbon-based ones. The hydrogen is produced from water splitting while carbon-based fuels like methanol, methane, or CO are usually produced from the reduction of CO_2 in the presence of water.^{1,98}

In this perspective, the most attractive challenge is represented by the photoelectrochemical cell (PEC), based on coupling the catalytic and photosensitized CO_2 reduction and water oxidation processes: in this way, the reducing equivalents and the protons needed to convert CO_2 into carbon products are provided by water oxidation. PEC cells are based on a light-harvesting material (typically a semiconductor) able to convert the incident photons into electron-hole pairs, which activate redox processes leading to final production of fuels. On one side, photogenerated holes can oxidize water to oxygen. On the other hand, the photogenerated electrons and the protons co-produced upon water oxidation are employed for reduction of CO_2 to higher-energy chemicals, represented by the well-known equations reported in Table 1.2.

The widespread configuration mode for a PEC cell consists of two distinct photoactive electrodes on which the catalytic water oxidation and CO_2 reduction reactions occur. They are confined within two separate compartments divided by a proton exchange membrane in order to reduce recombination and back-electron transfer processes. Both the electrodes are connected through an external circuit for electron flow (Figure 1.8). Furthermore, molecular catalysts for water oxidation and CO_2 reduction are usually supported onto the corresponding photoelectrodes. In a typical PEC cell, upon light absorption the photoanode promotes the excited electrons towards the photocathode through the external circuit. For an efficient electron transfer, the conduction band of the former should be more negative than the valence

band of the latter. The energy gap between these two bands is an important parameter that can be tuned to optimize the cell performance.

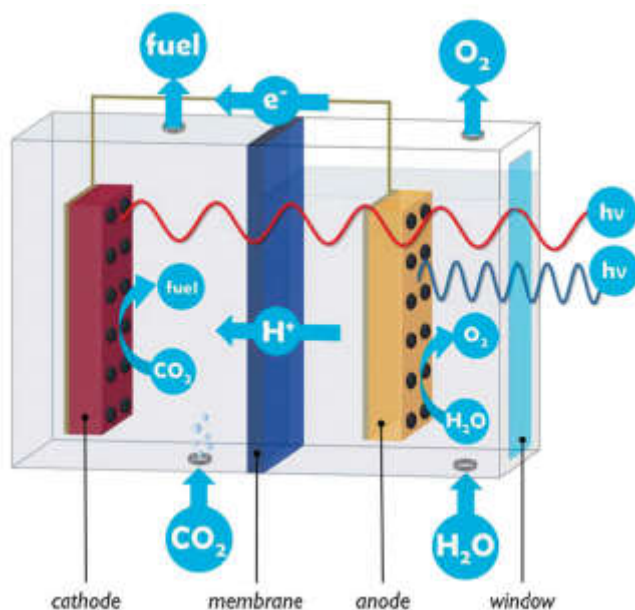


Figure 1.8. A double-compartment PEC cell for solar fuel production. Reproduced from ref.¹²

Given the strong complexity of the overall process, a common strategy to design PEC cells relies on an independent optimization of the properties of the desired half reactions. In this regard, the study of the electrocatalytic and photocatalytic CO_2 reduction processes under homogeneous conditions represents a crucial research step, enabling an in-depth investigation of the molecular catalyst properties avoiding (or limiting) undesired phenomena, like back-electron currents and adventitious side-reactions.

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CHAPTER 2. Molecular electrocatalysts timeline

2.1 Introduction

This chapter will be entirely referred to the state-of-the-art of the wide variety of transition metal-based complexes which have been proposed as precursors of electrocatalysts, particularly focusing on Re and Mn tricarbonyl bipyridine complexes.

Molecular electrocatalysts can be summarized and classified into three major categories depending on the ligand type (Chart 2.1)^{1,2}:

- 1) Metal catalysts with macrocyclic ligands, e.g. porphyrins, phthalocyanines, corroles and cyclams.
- 2) Metal catalysts with polydentate ligands, e.g. 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen); 2,2'; 6',2''-terpyridine (tpy), 2,2':6',2'',2'''-quaterpyridine (qtpy); 2,4,6-tri(pyridine-2-yl)-1,3,5-triazine (tptz); 2,3,5,6-tetra(pyridine-2-yl)pyrazine (tppz); diaza-1,2,4,5(2,6)-tetrapyridinacyclo-hexaphane (hamc-bpy); diaza-1,3(2,9)-diphenantrolinacyclobutaphane (hamc-phen) ligands.
- 3) Phosphine metal complexes containing 1,2-bis(diphenylphosphino)ethane (dppe) and triphenylphosphine (PPh₃) ligands.

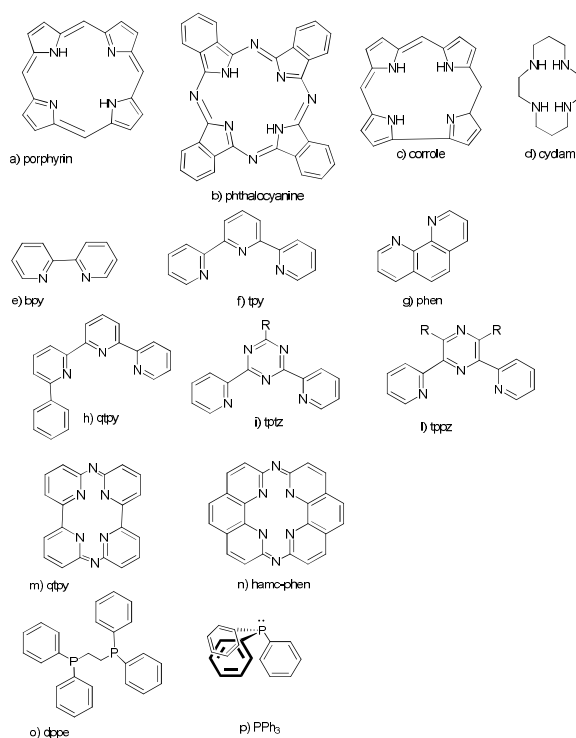


Chart 2.1. Common unsubstituted ligands in metal electrocatalysts for CO₂ reduction: macrocyclic ligands (a-d), polypyridyl ligands (e-n) and phosphine ligands (o, p).

Electrocatalysts can be also classified in terms of the selectivity for CO₂ conversion, whether they produce CO or HCOOH and depending on the metal involved. Nowadays, literature in this field is widespread and comprises a huge number of different catalysts that have been developed modifying the backbone of the ligand and/or tuning the metal center. This reminds us the non-negligible role of homogeneous electrocatalysis seeking for the discovery of better performing catalysts and for heterogenization by attachment to the electrode surface.

2.2 Non-porphyrinic macrocyclic complexes of Cobalt and Nickel

Early significative work in the field of molecular electrocatalysis has been achieved by Meshitsuka³ and Eisenberg⁴ during 1970s and 1980s. Meshitsuka originally reported the capability of Co and Ni phthalocyanines as CO₂ electrocatalysts, but the first reported transition metal catalysts with high current efficiencies and TONs were tetraazomacrocycles of Co and Ni (Chart 2.2), as published by the pioneer work of Eisenberg⁵ and Sauvage⁶. In the following years other authors like Tinnemans⁷ and Che⁸ investigated structurally similar and strictly related Co and Ni tetraazaomacrocycles, both in electro- and photocatalysis.

Complexes depicted in Chart 2.2 could reduce CO₂ to CO or afford a combination of CO and H₂ at potentials ranging from -1.3 to -1.6 V vs. SCE on a mercury pool electrode in aqueous or water-acetonitrile solutions². Complex **6** was also able to yield high current efficiencies (98%) but displayed low TOFs.

Sauvage and co-workers extensively exploited the reaction of CO₂ with Ni^{II}(cyclam) complexes.^{6,9,10} One of the most popular macrocyclic ligands used for decades in coordination chemistry is 1,4,8,11-tetraazatetradecane, universally known as cyclam. Ni^{II}(cyclam) (complex **5** Chart 2.2) is a remarkable example for which the CO₂ to CO conversion occurs very efficiently and selectively (high TON and high FE) in water (pH 4 to 5) at a mercury electrode. Additionally, the anion of the supporting electrolyte has been shown to be crucial: the fastest observed rates were obtained with KNO₃ and KClO₄. Conversely, CO₂ reduction in an aprotic solvent (DMF) led to the production of formic acid mainly (75% FE) and a TON of 3.2.¹⁰ Concerning the mechanism, it was postulated that in DMF, the Ni^I reduced active species binds CO₂ and after further reduction and protonation a Ni^{II}-OCHO intermediate is formed rather than Ni^{II}-COOH which would have furnished CO and H₂ (Scheme 2.1). Later, it was also found that Ni^I reduced complex strongly binds to CO affording Ni(cyclam)(CO)⁺ which deposited on the electrode surface; they concluded that catalysis is kinetically controlled by the CO loss from this Ni^I-CO adduct.^{9,11,12} Replacing the mercury pool by an inert glassy carbon electrode, a good catalytic activity for CO production was reached in a 1:4 water-acetonitrile solution, although with a slower rate.

Typically, nickel and cobalt macrocycle are very sensitive to pH: in the absence of any proton source, they are reduced to the monovalent state but there is no further reaction with CO₂, hence protons are necessary to yield reasonable TONs for CO.

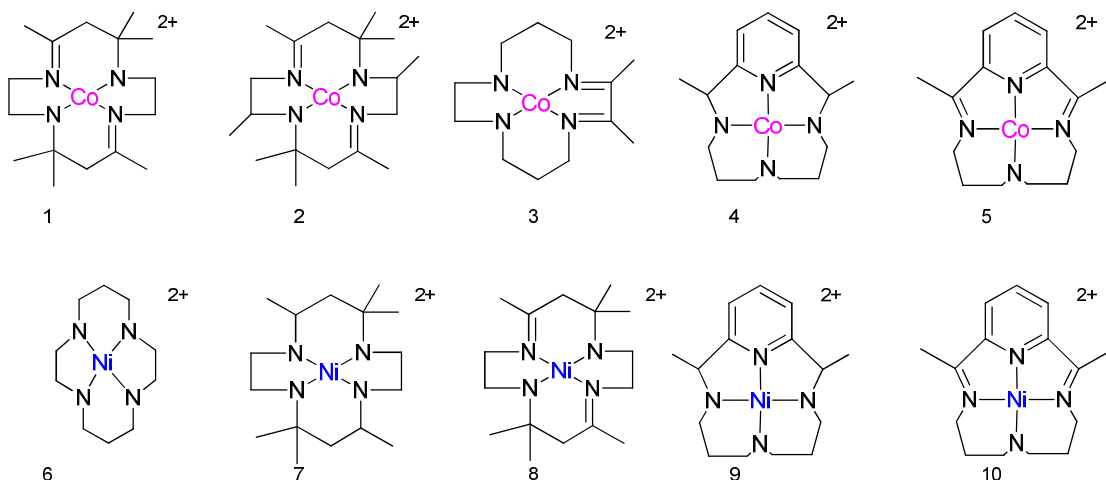
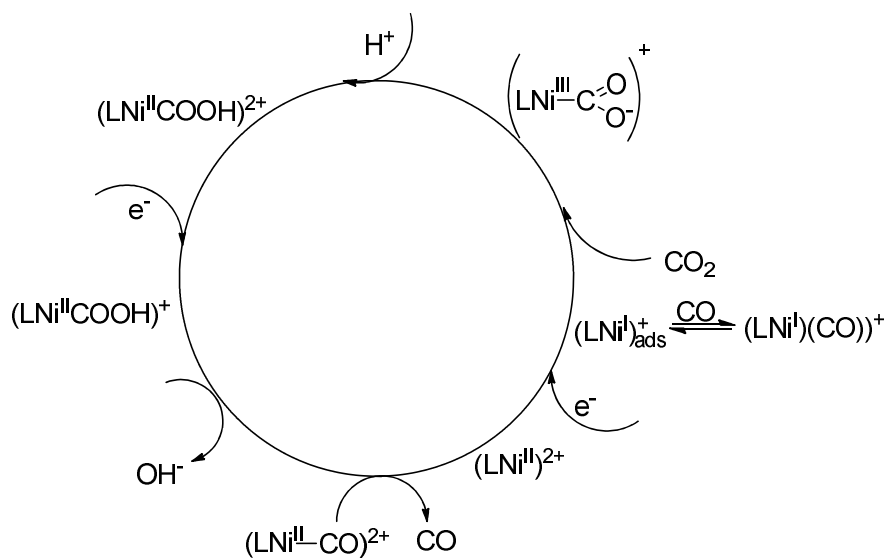


Chart 2.2. Co and Ni tetraazamacrocyclic catalysts for CO₂ reduction to CO.



Scheme 2.1. Proposed reductive pathway for Ni^{II}(cyclam) following a general ECEC mechanism. L = cyclam.

2.3 Phthalocyanines and Porphyrins

Properties of metallophthalocyanines and metalloporphyrins (MPc's and MPs, respectively) include a rich redox chemistry derived from a rich 18 π -electron arrangement. MPc's and MPs have been investigated for many years employing different metal centers and various substituents on the heterocyclic ring. The catalytic activity have been attributed to the relative

energy of the metal since metal *d* orbital energies may be positioned between the HOMO and the LUMO of the ligand ring¹³. The first paper related to electrocatalytic reduction of CO₂ mediated by Ni and Co phthalocyanines (PCs) was published, as mentioned before, by Meshitsuka in the early 1970s.³ The electrocatalyst **Co1** (Chart 2.3) was deposited onto a graphite electrode by dip coating. This communication did not report TONs or FEs and it was not clear which products were formed. In 1977, tetra-sulphonated PCs, **Co2** were described by other Japanese researchers as the first example of water-soluble PCs electrocatalysts.¹⁴

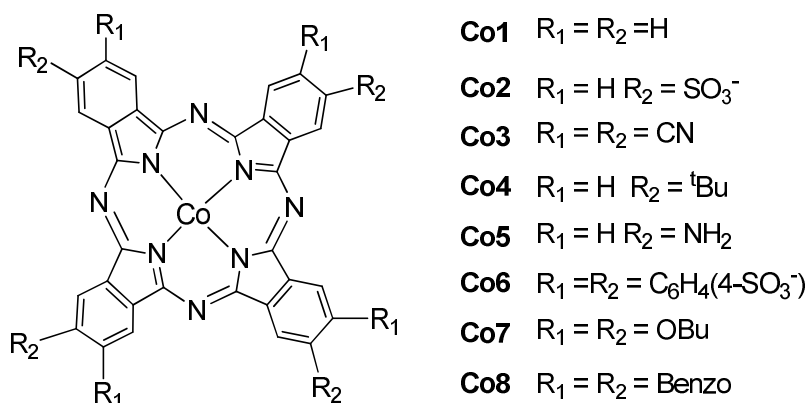


Chart 2.3. Co phthalocyanines studied as CO₂ reduction catalysts.¹⁵

One of the major drawbacks of the employment of metal PCs as homogenous electrocatalysts is their scarce solubility in organic solvents and water, hence their utilization is more directed towards adsorption onto electrodes.^{15,16} The most reactive metal PCs for CO₂ reduction are CoPCs and derivatives.^{17–20} These systems have produced high turnover numbers for CO in electrocatalytic experiments under constant applied potentials. CoPCs modified with -NH₂ groups were dispersed on carbon nanotubes and have been found to catalyze the electrochemical conversion of carbon dioxide to methanol.²¹

With regard to MPs, Co porphyrins were identified as effective catalysts in 1979²² but no catalytic activity was noticed at that time for Fe and Cu porphyrins. In a very recent work, cobalt porphyrin catalyst was adhered on a carbon nanotube (CNT) supporting material, which greatly enhances the reactivity and enables catalysis in water, which is otherwise impossible.²³ However, variously substituted Fe tetraphenyl porphyrin have been shown some years later to be the most active homogenous catalysts for CO₂ to CO conversion in aprotic solvents (DMF, CH₃CN) reported in the literature (Chart 2.4).^{24–32} Under some experimental conditions, they have also been able to afford formate as reduction product.^{33–35} **Fe1** was reported by the Savéant group in 1991 to reduce CO₂ to CO at -1.8 V vs. SCE in DMF.^{36,37} At early stages, Fe porphyrins were unstable and degraded after few catalytic cycles. Later Savéant found that **Fe1** was able to catalyze the reduction of CO₂ to CO in the presence of weak Brønsted acids

such as water, trifluoroethanol and phenol or with added Lewis acids like the hard Mg^{2+} electrophile.³⁸ Figure 2.1a shows the CV of **Fe1** in DMF. In absence of CO_2 , three reduction waves are observed; typically, the catalyst precursor undergoes three electrochemical reductions to form $\text{Fe}(0)$, the real active catalytic species. Figure 2.1b depicts two possible scenarios (red and blue arrows) to produce CO depending on the experimental conditions: in presence of Brønsted acids or Lewis acids. Figure 2.1c schematically reveals how formate can be produced by involvement of a metal hydride (path 1) or a metal carboxylate (path 2). The latter has been shown to be the mechanism followed by **Fe1** in presence of tertiary amines, e.g. NEt_3 , in DMF solutions. The role of either weak Brønsted acids or Lewis acids as co-substrates is to stabilize the Fe-CO_2 adduct and foster CO cleavage. A significant improvement of the catalytic performance of **Fe1** was reached with **Fe2** which bears phenolic groups in ortho and ortho' positions of the arene substituents. These acidic functions ensured proton availability (both for H-bonding stabilization properties of the Fe-CO_2 adduct and proton relay assistance for protonation steps) and fast kinetics. Conversely, introduction of electron withdrawing fluorine moieties on the phenyl rings of the ligand (**Fe8**, **Fe9** and **Fe10**) allowed decreasing the overpotential, but at the expense of a lower activity. This lower activity is the effect of a smaller electron density on the $\text{Fe}(0)$ center produced by the fluorine withdrawing group and hence a less stabilized metal- CO_2 adduct. Water soluble porphyrins³⁹, **Fe5** and **Fe6**, bearing four positive charges (trimethylammonium groups) at the para and ortho-positions of the phenyl rings respectively show high activity at very low overpotential. The opposite is true for **Fe7**, whose four anionic sulfonates in the para position destabilize the primary catalytic intermediate, resulting in detrimental catalytic activity. Many different substituents exerting the through-structure and through-space effect have been explored on the porphyrin ring: the latter, exemplified by electrostatic and hydrogen bonding interactions can afford marked improvements in the catalysis of electrochemical conversion of CO_2 mediated by Iron porphyrins.²⁷ Both effects reflects a trade-off between activity and overpotential and it has been the object of a thorough investigation.⁴⁰

The discovery of a strongly enhanced catalytic effect promoted by ligand modifications in this kind of catalysts has opened interesting new perspectives for design of new efficient molecular catalysts for CO_2 reduction, not only applied to Iron porphyrins class.^{41,42}

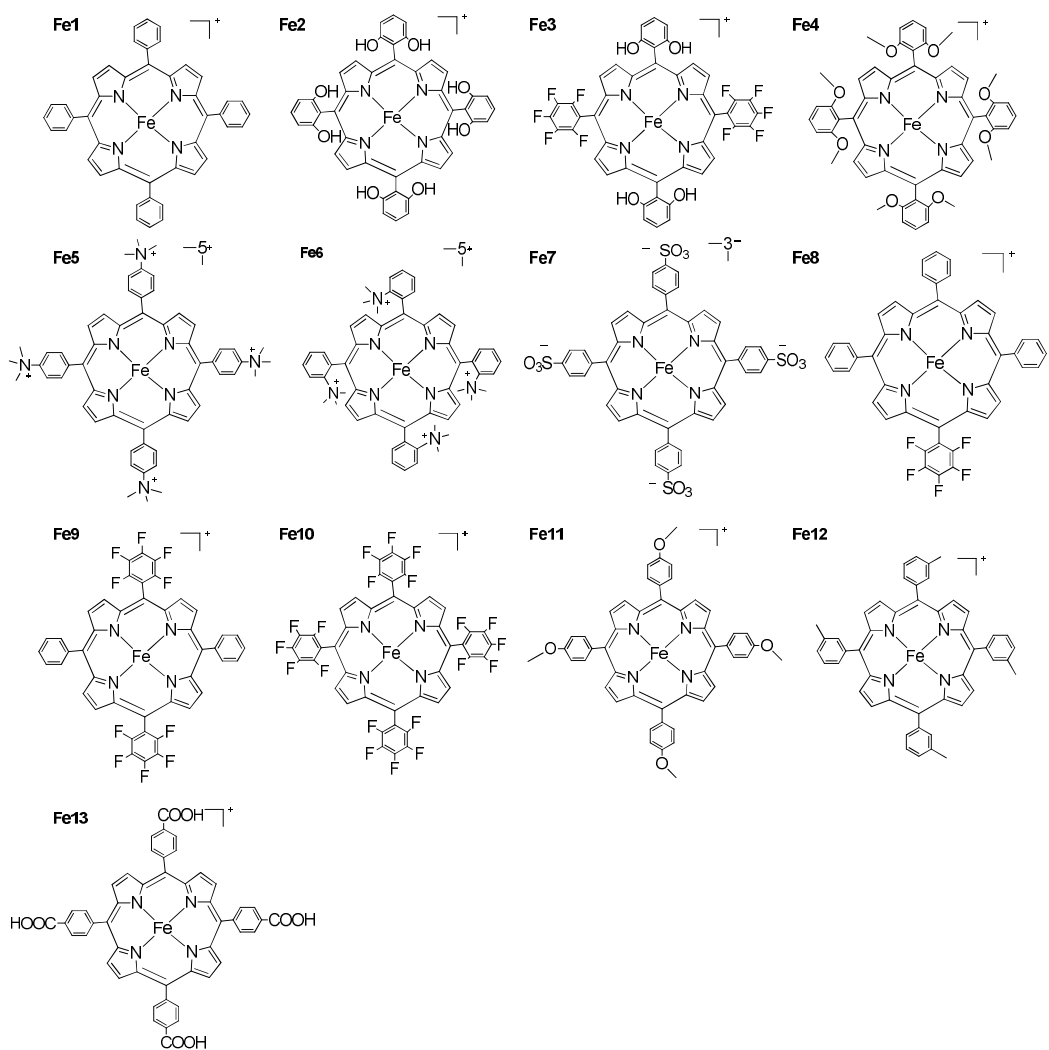


Chart 2.4. Iron porphyrins pre-catalysts developed by Saveant's group.

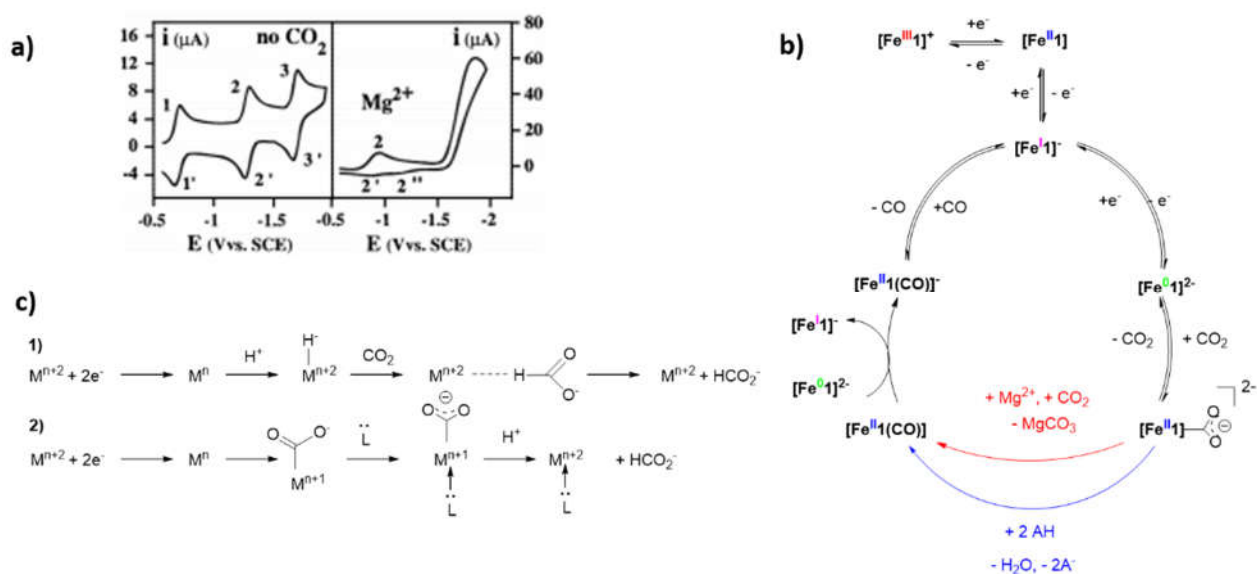


Figure 2.1. a) Cyclic voltammetry of 1 mM **Fe1** in DMF + 0.1 M NET_4ClO_4 (100 mV s^{-1}) in the absence of CO_2 (left) and in the presence of CO_2 and Mg^{2+} (right). Adapted from ref.³⁸ **b)** Mechanistic insight of CO_2 electroreduction by **Fe1** in the presence of Mg^{2+43} and Brønsted acids³⁸. **c)** (1 and 2) Pathways for the two-electron CO_2 reduction to formate involving a metal-hydride (1) or a metal carboxylate (2) as an intermediate.^{24,44}

In 2002 Fujita and co-workers published the ability of cobalt and iron corroles to catalyze the reduction of CO_2 to CO. Most of the analytical studies of the products for this reaction were done during photochemical reduction, but it was found that the major product of reduction was CO.⁴⁵

2.4 Transition metal phosphine complexes

The first reported transition metal electrocatalyst with phosphine ligand was $\text{Rh}(\text{dppe})_2\text{Cl}$ complex reported by Wagenknecht group.⁴⁶ Reduction products were found to be the formate anion with small percentages of cyanoacetate. Since a clear mechanism insight was missing, it was hypothesized that a hydride species is formed and subsequently CO_2 insertion into M-H bond occurs. Another proposed pathway is formation of a CO_2 -adduct followed by abstraction of the proton from acetonitrile.

Nevertheless, the most extensively studied catalyst bearing phosphine ligands is represented by the class of Pd complexes firstly reported in 1991 by the Dubois group (Chart 2.5).^{47–49}

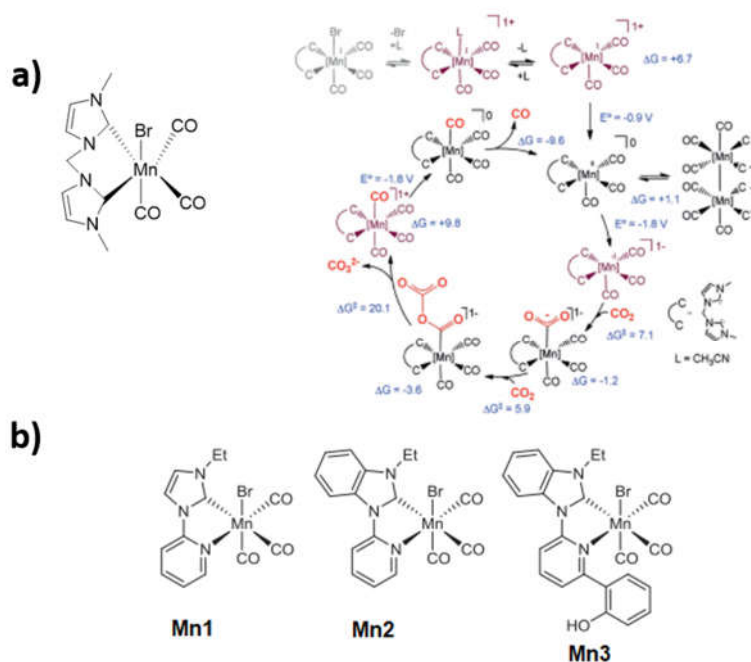
The typical catalyst system is based on a tridentate phosphine ligand that was initially coordinated to Co, Fe, or Ni. $[\text{Pd}(\text{triphos})(\text{PR}_3)](\text{BF}_4)_2$, the first reported Pd phosphine complex (**Pd1**), was able to catalyze the reduction of CO_2 to CO in acidic acetonitrile solutions.

Mechanistic studies determined that once the Pd(II) complex gains an electron to form a Pd(I) intermediate, a reaction with CO_2 occurs to afford a five-coordinate CO_2 adduct. Up to the second electron transfer, the Pd intermediate dissociated the solvent. Protonation of one of the oxygen atoms of coordinated CO_2 provides a metallo-carboxylic acid intermediate, Pd-COOH. It is believed that the metallo-carboxylic acid is protonated again to form a "dihydroxy carbene", and that CO is then formed by dehydration of the dihydroxy carbene. CO dissociation and solvent association regenerates the initial complex. This proposed catalytic cycle is depicted in Scheme 2.2.

Binding of CO_2 to the metal center and the C-O bond cleavage to form CO and water are the key steps in the proposed mechanism for CO_2 electrochemical reduction catalyzed by $[\text{Pd}(\text{triposphine})(\text{CH}_3\text{CN})]^{2+}$ complexes.⁵⁰ In particular, the latter process, which is closely

2.5 N-heterocyclic carbenes

N-Heterocyclic carbenes (NHCs) also represent an important class of organic molecules effectively employed to improve the CO₂RR catalytic performances owing to the strong σ -donor and weak π -acceptor properties, which lead to unique stability. However, several NHC-based molecular complexes show low efficiency in CO₂ reduction and low catalyst stability.^{51–55} Recently, in 2018, a highly active NHC Manganese (I) complex has been reported as selective electrocatalyst for CO₂ to CO reduction (Scheme 2.3a).⁵⁶ This electrocatalyst was tested in anhydrous acetonitrile solution and resulted to be electrocatalytically active towards CO₂ reaching a TOF_{max} of 2100 s⁻¹. It is worth noting that only few examples of molecular Mn(I) complexes capable of activating CO₂ without addition of external Brønsted acids are present in literature.^{42,57,58} Controlled potential electrolysis of this NHC-Mn complex in acetonitrile afforded a TON for CO of 56 with a FE of 92% in 4 hours of operation. The authors also investigated the reductive mechanism in presence of CO₂ and proposed a catalytic cycle which is depicted in Scheme 2.3a.



Scheme 2.3. a) Proposed mechanism for the reduction of CO₂ to CO mediated by a purely NHC-carbene, adapted from ref.⁵⁶ b) Schaefer NHC-pyridyl catalysts.

Similarly, Schaefer and coworkers investigated the electrochemical mechanisms of three NHC-pyridyl ligated complexes capable of converting CO₂ to CO (Scheme 2.3b).⁵⁹ The authors concluded that, since CO₂ binding is strongly preferred over H⁺ binding, even with the inclusion of a pendant phenol (**Mn3**), stronger acids could safely be used without significantly increasing H₂ production. Furthermore, the inclusion of a pendant phenol near the active site was shown

to dramatically decrease the barriers to the C–O bond cleavage step of the catalytic pathway and is predicted to yield an increased turnover frequency. Those results were generally consistent with previous experimental work on $\text{MnBr}(\text{N-C})(\text{CO})_3$ catalysts and expand on previous studies on CO_2 reduction with $\text{Mn}(\text{I})$ tricarbonyl compounds.

2.6. Selective molecular electrocatalysts for CO_2 to HCOOH (or HCOO^-)

The most important class of homogeneous molecular electrocatalyst for formate production is currently the one of $\text{Ir}(\text{III})$ PCP type pincer complexes (Chart 2.6), mainly developed by the Meyer's group.^{60–64}

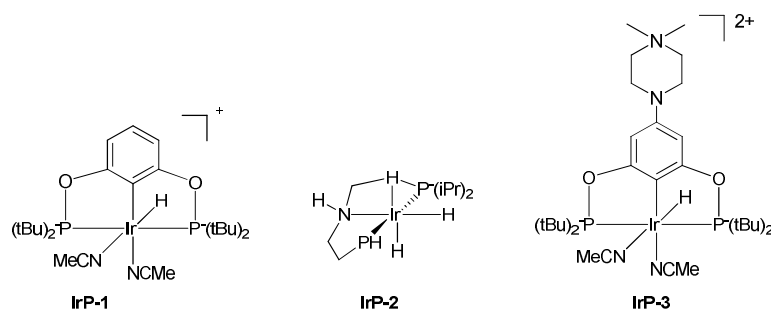
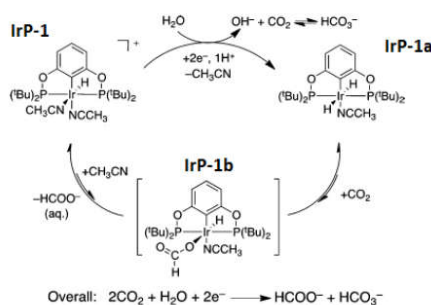


Chart 2.6. $\text{Ir}(\text{III})$ PCP pincer complexes for CO_2 electroreduction.

CO_2 has been successfully reduced employing **IrP-1** complex in a $\text{CH}_3\text{CN}/5\% \text{H}_2\text{O}$ mixture. Bulk electrolysis experiments performed at -1.45 V vs. NHE revealed a high selectivity toward HCOO^- production ($\text{FE} \sim 85\%$ and corresponding TON of 40 after 25 h), with a residual background H_2 amount (FE for $\text{H}_2 \sim 15\%$), deriving from direct water reduction. Notably, no CO was detected in the gaseous fraction of products.⁶¹ Accordingly with a proposed mechanism for the electrocatalytic cycle, **IrP-1** undergoes a two-electron one-proton process converting into the dihydride species **IrP-1b**, which rapidly binds CO_2 to form a η^1 -formate adduct (**IrP-1c**) via an insertion into the Ir-H bond. Formate is finally easily released by **IrP-1c**, regenerating the starting species (see Scheme 2.4).



Scheme 2.4. Proposed mechanism for CO_2 water-assisted reduction mediated by **IrP-1**. Reproduced from ref. ⁶⁴

Water molecule plays a non-negligible role in the catalytic process: it does not only act as proton donor, but it significantly stabilizes the formate anion by hydrogen bonding. The co-solvent effect was explored in detail either by DFT-based studies⁶¹ or experimentally by synthesizing **IrP-2**, whose pincer ligand bears a H-bond donor. This ligand modification allows the achievement of formate in higher efficiencies (97%) at lower overpotential (*ca* 300 mV less negative) with respect to **IrP-1**.⁶² Conversely, worse kinetics were observed by using **IrP-2**, essentially due to a major energy requirement for formate release from the adduct. This results as a direct consequence of an intramolecular H-bond between the bound formate and the local ligand N–H unit.

Additionally, water-soluble Ir(III) derivatives like **IrP-3**, bearing a quaternary amine functional group to the ligand, showed an almost quantitative electrochemical catalytic conversion of CO₂ into formate in pure water.⁶³ HCOO[−] was afforded at an applied potential of −1.41 V vs. NHE, with 93% FE accompanied by a small amount of H₂ (7%). Acetonitrile was used in small quantities in the aqueous reaction medium (1% v/v) in order to efficiently regenerate the starting complex, being the catalytic cycle very similar to that shown in the Scheme 2.4. The catalytic performances of this family of complexes has recently been further improved by immobilization of these molecular systems onto CNT-coated gas diffusion electrodes.⁶⁴ Selective CO₂ reduction to formic acid or formate has also been observed in the case of cobalt diphosphine complexes with amine group⁶⁵

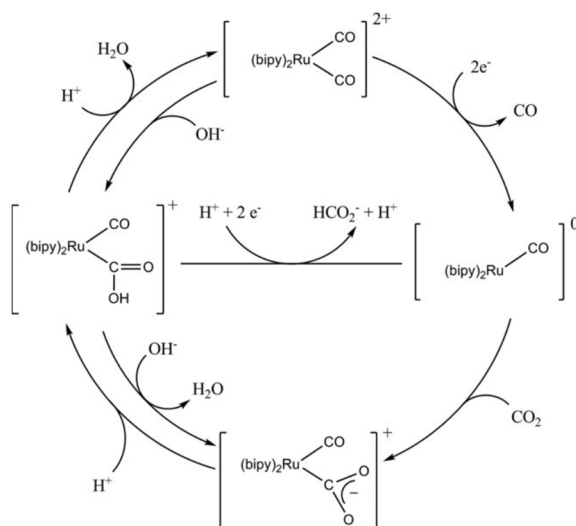
2.7 Tuning the selectivity of molecular catalysts towards HCOOH (or HCOO[−])

Molecular electrocatalysts for CO₂ reduction are not selective considering that most of them afford CO, HCOO[−] and H₂ in different yields. It should be mentioned that every catalyst able to reduce CO₂ is also able to reduce water to H₂, for thermodynamic reasons. Hence kinetics is fundamental for improving selectivity. The desirable increased selectivity towards formate can be reached through fruitful modifications of the experimental setup (applied potential, acidity of the reaction medium) as well as tuning the ligand and/or the metal center.

Ru(II) molecular electrocatalysts bearing polypyridyl ligands, are known to be affected by rather low efficiencies and/or selectivity under CO₂.^{66–76} A Ru(bpy) electrocatalyst precursor complex was reported by Bolinger et al. in 1985.⁶⁶ It was later reported by Tanaka and co-workers that bipyridine complexes of ruthenium could catalyze the reduction of CO₂.⁶⁷ Ru(bipy)(CO)₂²⁺ and Ru(bipy)(CO)Cl⁺ were found to electrocatalytically reduce CO₂ to CO, H₂, and HCOO[−]. Both complexes were shown to reduce CO₂ at −1.40 V vs. SCE. A reductive mechanism has been proposed and it is reported in Scheme 2.5. Following a two-electron

reduction CO is released to form a five-coordinate neutral complex. In the presence of CO₂ the complex forms a η^1 -CO₂ adduct of Ru(0). This species can also be formed by addition of two equivalents of OH⁻ to Ru(bipy)(CO)₂²⁺. Addition of a proton leads to the formation of LRu(CO)(COOH) species which gains another proton under acidic conditions (pH 6.0), loses water and regenerates the catalyst as shown in Scheme 2.5. Under basic conditions (pH 9.5) the catalyst may undergo a two-electron reduction with the involvement of a proton to afford HCOO⁻ and restore the five coordinate Ru(0) complex.

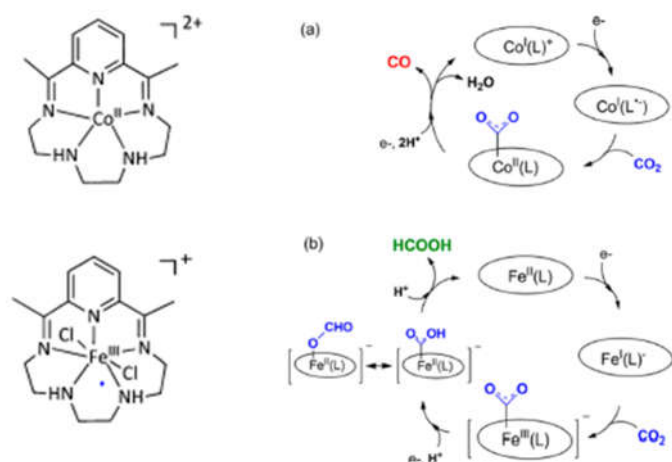
Moreover, Deronzier et al. discovered that those Ru catalysts can undergo a selective electrocatalytic conversion of CO₂ to CO in CH₃CN/5% H₂O or pure water, when a solid carbon electrode is used. This peculiarity is due to polymerization of a catalytically active film of a [Ru⁰(bpy)(CO)₂]_n polymer onto the surface during reduction.^{70–72} By introducing a sterically hindered diimine ligand in the [Ru(mesbpy)(CO)₂Cl₂] (mesbpy = 6,6-dimesityl-2,2-bipyridine), the polymer formation was inhibited and an alternative reduction pathway under CO₂ in CH₃CN with added PhOH was activated.⁷³ A strong dependence of the CO/HCOOH ratio on the applied potential was confirmed, as a consequence of speeding up the thermal dehydration process of HCOO⁻ (in presence of H⁺) to form CO and H₂O at negative potentials. Almost quantitative production of CO was reached at an applied potential of –2.20 V vs. Fc/Fc⁺, whereas formate started to be detected by applying more positive potentials at the expense of CO (η_{CO} =63% at E=–1.70 V vs. Fc/Fc⁺).



Scheme 2.5. Proposed mechanism for the Tanaka catalyst. Reproduced from ref.¹

On the other hand, the idea of switching the metal center for tuning the selectivity of a given molecular catalyst has been explored very recently. This idea has been applied coordinating the same pentadentate N5 ligand to Co and Fe metals (Scheme 2.6).⁷⁷ It was reported the Co complex showed a catalytic CO production during bulk electrolysis with high faradaic

efficiencies (82%) at a relatively low overpotential (566 mV); conversely, HCOO^- was detected in high yields (75-80%) by applying a potential of -1.25 V vs. SCE (a 310 mV overpotential) to a DMF solution of the Fe complex for ca. 3 hours. This is a remarkable example of the non-negligible role of different metals when coordinated to the same ligand.



Scheme 2.6. Chemical sketches of the investigated complexes and proposed mechanism for the reduction of CO_2 .

Additionally, some bipyridine complexes have also been demonstrated to be selective towards formate production⁴², but all the molecular bipyridine-based metal complexes will be discussed in detail in the following section (2.8), since this PhD thesis is entirely focused on homogeneous and heterogeneous CO_2 electro- and photoreduction mediated by Re(I) and Mn(I) tricarbonyl bipyridine complexes.

2.8 Metal complexes with bipyridine ligands

Lastly described, not because more recent or less important, polypyridine ligands have been extensively used in catalysis for the activation of small molecules, amongst other applications, and thus represent an extremely broad and diverse class of ligands. The term polypyridine is referred to ligands possessing a minimum of two conjugated pyridine moieties (see Chart 2.1), these include bpy, tpy, qtpy where 2, 3 or 4 pyridine groups are linked and conjugated, and also phenanthroline derivatives which offer a more rigid structure. These ligands and corresponding Re and Mn complexes will represent hereafter the focus of the dissertation.

In 1983, Lehn and co-workers published a paper reporting the ability of *fac*-Re(bpy)(CO)₃Cl as photo-catalyst for CO_2 reduction to CO.⁷⁸ The next year, the same authors followed the photochemical study with the first report of electrochemical CO_2 reduction to CO. This report was striking in that CO_2 was reduced to CO in 98% FE, even in the presence of a large

concentration of water, indicating a kinetic preference for CO₂ reduction over the reduction of protons to H₂.⁷⁹ Lehn's discovery of the catalytic activity of *fac*-Re(bpy)(CO)₃Cl garnered immediate attention from the group of Meyer. Meyer and co-workers had reported the reaction of *fac*-Re(bpy)(CO)₃H with CO₂ to form *fac*-Re(bpy)(CO)₃(O₂CH) in 1984⁸⁰, the same year that Lehn reported the electrocatalytic CO₂ reduction system. Although this stoichiometric CO₂ insertion reaction to produce formate was studied later by Meyer⁸¹, CO is the primary, and often exclusive, product from electrocatalysis with *fac*-Re(bpy)(CO)₃X species. In 1985 Meyer and coworkers studied the electrochemical reduction of CO₂ by *fac*-Re(bpy)(CO)₃Cl in further detail.⁸²

However, due to the importance of more sustainable methods and earth-abundant materials for CO₂ reduction, the focus has recently shifted from Re toward the bpy-Mn tricarbonyl congeners. In 2011, Chardon-Noblat and Deronzier⁸³ firstly described the activity of *fac*-Mn(bpy)CO₃Cl towards CO₂ reduction.⁸³ (Since all of the Mn and Re catalyst precursors discussed in this section have three facially coordinated CO ligands, the *fac* label is henceforth omitted). An extensive study has been conducted on [Ru(bpy)₂-(CO)_n(X)_m]^{(2m)+} family of compounds over the past decades (see Paragraph 2.7). Recently the [M(bpy)(CO)₃X] architecture was extended to Mo- and W-based catalysts.^{84–86} Other 4d, 5d (Os, Rh, Ir, Pd)⁸⁷ and 3d (Cr, Fe, Co, Ni, Cu)⁸⁷ metals have been tested as polypyridine based metal complexes for CO₂ reduction over the years.

2.9 Re(bpy)CO₃Cl and Mn(bpy)CO₃Br: electrochemical mechanisms

Re(bpy)CO₃Cl showed the selective reduction of CO₂ to CO at a potential of –1.49 V vs. SCE using a 9:1 DMF–H₂O solution. It was also noted that as the percentage of water was increased the selectivity for CO was diminished, and when the reduction was run under an atmosphere of argon, only molecular hydrogen was produced. While this system had high current efficiencies (98%), and excellent selectivity for carbon monoxide over hydrogen production, the limiting factor was the low TOF of 21.4 h^{–1}.⁷⁹

Mn(bpy)CO₃Br showed the selective reduction of CO₂ to CO at markedly less overpotential (a gain of 400 mV) with respect to the corresponding rhenium. This implies a substantial advantage in terms of the overpotential required for the formation of the catalytically active species under CO₂. Significant current enhancement was observed when water was included as proton source in the solution. Selectivity and FE are almost identical. For instance, prolonged exhaustive electrolysis experiments carried out in CH₃CN/5% H₂O at –1.40 V vs. SCE produced CO with high efficiencies (85%) and H₂ as a minor product (15%) after 22 h.⁸³

2.9.1 ELECTROCHEMICAL MECHANISM OF $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ UNDER Ar

CV of $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ is reported in Figure 2.2. Two successive $1e^-$ reduction waves are observed. The first reversible redox wave ($E_{1/2} = -1.34$ V vs. SCE in CH_3CN) is mainly localized over the bpy moiety and leads to the reduction of the π^* molecular orbital of the bpy, whereas the second irreversible reduction process ($E_p = -1.73$ V vs. SCE in CH_3CN) is accompanied by Cl^- loss, providing the five-coordinate $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ species.

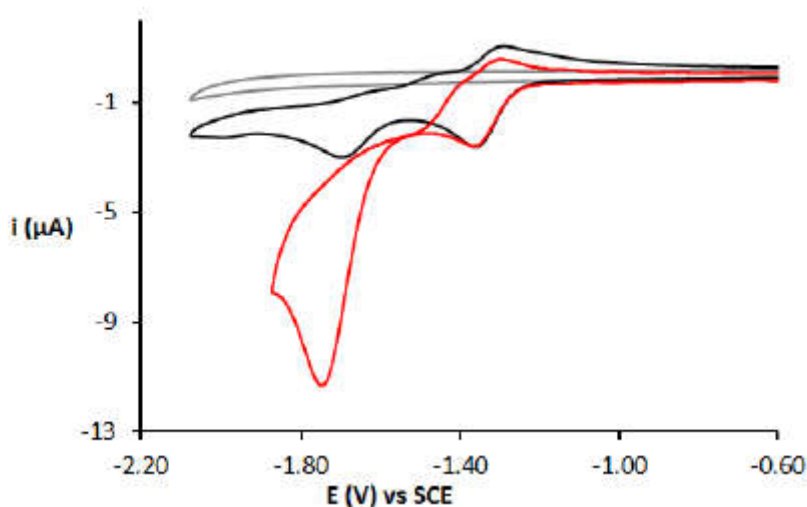
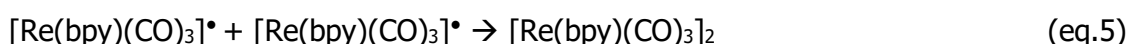
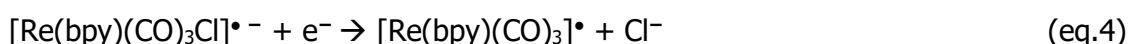
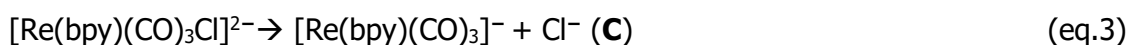
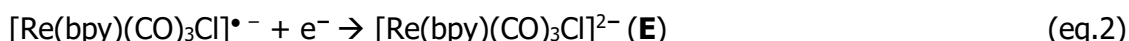
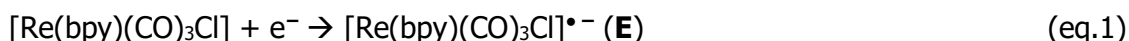
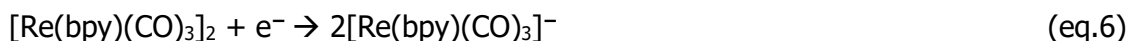


Figure 2.2. CVs of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ under Ar (black line) and CO_2 (red line) in $\text{CH}_3\text{CN}/0.1$ M Bu_4NPF_6 ($v = 200$ mV s^{-1}). The background under CO_2 is represented by grey line.

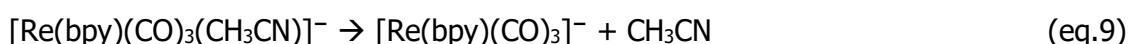
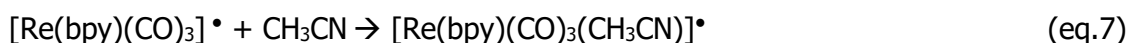
Reductive pathways are summarized in the following equations. The first reduction leads to the formation of the radical anion which is further reduced at the potential of the second peak observed in CV, bearing to the five-coordinate $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ (which is the active species towards CO_2) after Cl^- loss, via an EEC scheme. However, $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{\bullet-}$ is thermally unstable and is prone to lose Cl^- producing the five-coordinate $[\text{Re}(\text{bpy})(\text{CO})_3]^{\bullet}$ radical (eq.4), which can subsequently undergo, in absence of substrate, a dimerization process forming a $\text{Re}^0\text{-Re}^0$ dimer (eq. 5).





The reductive cleavage of the $\text{Re}^0\text{-Re}^0$ dimer species takes place at ca. -1.60 V vs. SCE, with subsequent formation of $[\text{Re}(\text{bpy})(\text{CO})_3]^-$. These two electrochemical pathways are competitive depending on the kinetics of Cl^- dissociation. Both $[\text{Re}(\text{bpy})(\text{CO})_3]_2$ (deep green-colored) and $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ (deep purple-colored) have been experimentally characterized by Infrared- Spectroelectrochemistry (IR-SEC) and chemical reduction.^{66,88–90} It has been demonstrated that Cl^- loss from $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{\bullet-}$ is a relatively slow process at room temperature, on the CV time scale the radical anion is stable enough to be directly reduced upon the second wave. This behavior explains the reversibility or quasi-reversibility of the first peak in CV. Conversely, the $\text{Re}^0\text{-Re}^0$ dimer is quantitatively produced by electrolysis at potentials ranging from -1.40 V to -1.50 V vs. SCE.⁸²

It must be also considered that, once $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ is dissolved in a coordinating solvent like CH_3CN , the formation of a solvento complex (eq. 7-8) is thermodynamically more favorable than the dimerization process. This pathway involves the rapid formation of a six-coordinate acetonitrile radical complex by interaction of $[\text{Re}(\text{bpy})(\text{CO})_3]^{\bullet}$ with a solvent molecule: an alternative route to produce the five-coordinate anion has been proposed.^{88,91,92}



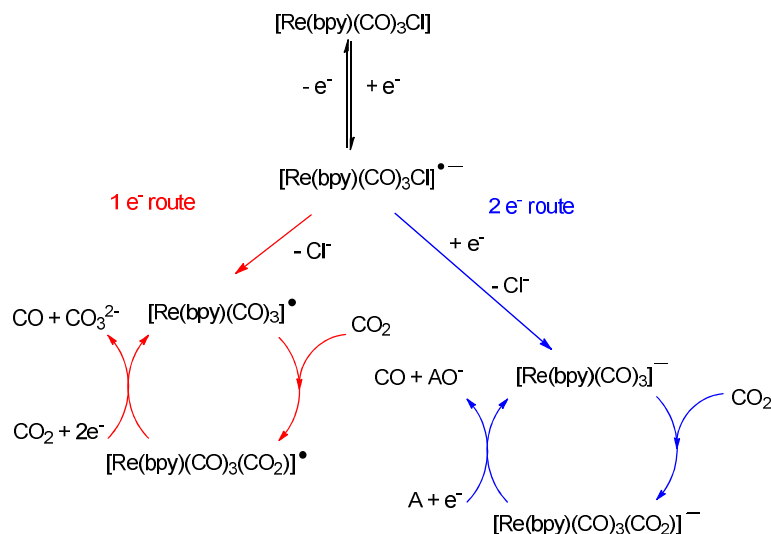
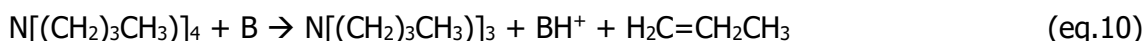
Equation 1 and 8 occur at very similar potential values (ca -1.42 V vs. SCE), therefore $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{\bullet-}$ and $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^-$ can be produced simultaneously in CH_3CN solutions. This hypothesis has been confirmed by experimental evidences by means of IR-SEC measurements carried out in a CH_3CN solution of the catalyst with an excess of Cl^- anions, which completely suppressed dimerization.⁹²

2.9.2 ELECTROCHEMICAL MECHANISM OF $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ UNDER CO_2

The catalytic pathway of $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ has been primarily investigated through CV and Controlled Potential Electrolysis (CPE). As it can be observed from Figure 2.2 (red CV), when the solution is saturated with CO_2 , the first peak remains almost unchanged, nevertheless a current enhancement is observed upon the second reduction, suggesting a 2e^- catalytic process. Originally, this catalyst has been tested in DMF solutions with excess of Cl^- anions and an initial CO loss from $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{\bullet-}$ was proposed. Further CO_2 binding to the metal

center, double protonation and successive regeneration of $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ by reducing a strongly oxidizing $[\text{Re}^{\text{II}}(\text{bpy})(\text{CO})_3\text{Cl}]^+$ species was hypothesized.⁷⁹ However, this proposed mechanism was not supported by experimental evidences.⁸⁸

Electrochemical studies suggested two alternative catalytic pathways for $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ in CH_3CN :⁸² a slower 1e^- and a more rapid 2e^- pathway (Scheme 2.7). The former proceeds after the first reduction and results in the reductive disproportionation of CO_2 to CO and CO_3^{2-} . In the latter, catalysis after the second reduction is faster and affords CO as the primary product in high FE. Meyer proposed an oxide acceptor (A) as being necessary for the 2e^- pathway and, additionally, absence of CO_3^{2-} suggested that the rhenium catalyst could scavenge protons from the electrolyte (tetrabutylammonium hexafluorophosphate, Bu_4NPF_6), based on the observation of NBu_3 in solution after CPE. Small amounts of NBu_3 are likely due to the Hoffman degradation process (eq.10, B is a generic base present in solution) taking place in some cases when the electrochemical CO_2 reduction is performed in a non-protic medium.^{82,93,94}

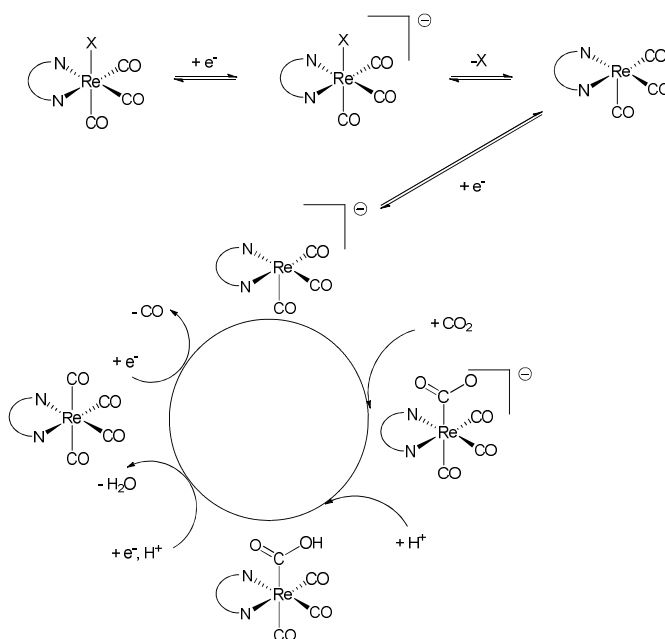


Scheme 2.7. The 1e^- (red arrows) and 2e^- (blue arrows) mechanisms for CO_2 reduction by $\text{Re}(\text{bpy})\text{CO}_3\text{Cl}$ proposed by Meyer et al.⁸²

The mechanisms reported in the Scheme 2.7 were studied by means of IR-SEC measurements, confirming the catalytic activity of either $[\text{Re}(\text{bpy})(\text{CO})_3]^{\bullet}$ and $[\text{Re}(\text{bpy})(\text{CO})_3]^{\bullet-}$ in an CH_3CN solution under CO_2 .⁸⁸ More specifically, using a supporting electrolyte bearing to an excess of Cl^- , both catalytic species are present in solution, providing an efficient catalytic response, with CO and CO_3^{2-} production. Conversely, when performing electrochemical measurements in THF, dimer formation became predominant under Ar, and a reduced formate complex was

spectroscopically characterized under CO₂ atmosphere. This last species is likely responsible for formate as byproduct.

The focus on the mechanistic insight of Re(bpy-R)CO₃X catalysts showed no signs of slowing down and in more recent years the stretching modes typical of a η^1 -Re(I)-COOH intermediate were found to increase during the reaction between [Re(bpy)(CO)₃]⁻ and CO₂.⁹⁵ This assignment was confirmed by DFT calculations, isotopic labeling studies with ¹³CO₂ as well as by comparison with the experimental IR spectrum of the synthesized carboxylic Re(I) complex. Stopped-flow IR spectroscopy was an essential tool in order to get the first experimental evidence of the Re-COOH key intermediate. The proposed mechanism (Scheme 2.8) involves two sequential 1e⁻ reductions leading to the catalytically active state [Re(bpy)(CO)₃]⁻, which can then interact with CO₂ to form a η^1 -bound CO₂ adduct at the rhenium center. Upon protonation (which is likely the rate determining step of the overall reaction) of this proposed CO₂-adduct, a Re-COOH species can form, followed by loss of H₂O and formation of a rhenium tetracarbonyl complex, albeit not yet experimentally detected.⁹⁵ Release of CO can occur upon further reduction, allowing regeneration of the catalytic species.



Scheme 2.8. Proposed electrocatalytic mechanism for Re(bpy-R)CO₃X. (X = halide or solvent molecule).⁹⁵

Additionally, in 1998 Re(bpy-Me)(CO)₃COOH was independently synthesized by Gibson and Yin.⁹⁶ The carboxylic acid complex was obtained via nucleophilic attack of hydroxide on the corresponding stable tetracarbonyl cation [Re(bpy-Me)(CO)₄]⁺.^{97,98}

2.9.3 *Re(bpy)CO₃Cl* AND BRØNSTED ACIDS: A SYNERGISTIC EFFECT FOR CO₂ REDUCTION

In 1998, an important finding in the field of CO₂ reduction by $\text{Re}(\text{bpy-R})(\text{CO})_3\text{X}$ appeared in the literature. This achievement was described by Wong and coworkers, who systemically tested the effects of various Brønsted acids on CO₂ reduction catalysis by $\{[\text{Re}(\text{bpy})(\text{CO})_3\text{py}](\text{OTf})\}$ (py = pyridine, OTf = trifluoromethanesulphonate) in acetonitrile.⁹⁹ Water, methanol, 2,2,2-trifluoroethanol and phenol were added in a different concentration range and were found to significantly enhance the current response of the second reduction under CO₂ (Figure 2.3). Noteworthy, it has been examined that the stronger the acid, the greater the catalytic current enhancement. As a general trend, it was observed that the efficiency of the synergist is strictly related to its acidity, so that the lower the pK_a of the acid, the higher the catalytic current.¹⁰⁰ This report found that 2e⁻ mechanism for CO₂ reduction is proton coupled and kinetic studies revealed that the reaction is first order for Re and CO₂ and second order for all Brønsted acids used. The kinetic parameters for this process, such as the catalytic rate constants, *k*, and TOFs were evaluated by CV analysis or by means of spectroscopic techniques for several Re complexes with polypyridyl ligands.^{95,99–101}

In agreement with the CV experiments, bulk-electrolysis data highlighted that added acids not only enhance the activity of Re catalysts for CO₂ conversion to CO with faradaic efficiencies close to 100%, but also improve their durability over time. This suggests that protons might play a key role in stabilizing the Re-CO₂ adduct in the catalytic mechanism.⁹⁹ A similar role is played by Brønsted acids via stabilization of the Fe-CO₂ adduct in the case of iron porphyrins (see Paragraph 2.3). The contribution of a proton transfer process in the rate-determining step of the catalytic reaction was further confirmed by the observation of a normal primary H/D kinetic isotope effect for analogous Re(I) complexes in presence of deuterated acids.¹⁰⁰

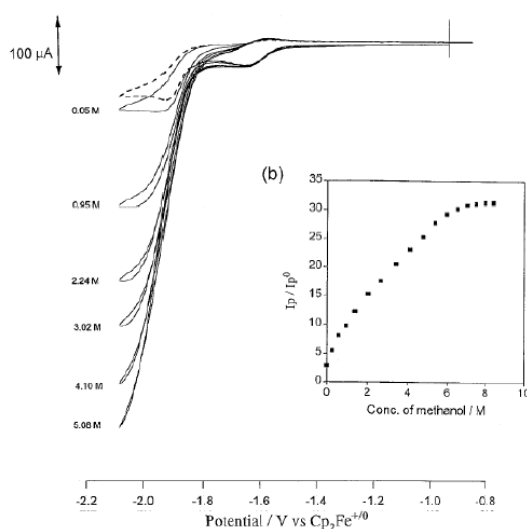


Figure 2.3. Cyclic voltammograms of 1 mM {[Re(bpy)(CO)₃py](OTf)} in CH₃CN-0.1 M TBAH under 1 atm of CO₂ and in the presence of different concentrations of methanol. Scan rate: 0.1 V s⁻¹. A plot of the change in catalytic plateau current as a function of methanol concentration is shown in the subsidiary figure (b). Reproduced from ref.⁹⁹

2.9.4 ELECTROCHEMICAL MECHANISM OF Mn(bpy)CO₃Br UNDER Ar

Manganese is ca. 1 million times more abundant than rhenium in the earth's crust¹⁰², therefore manganese was proposed as a more feasible and economic alternative to rhenium. Deronzier and coworkers found that the corresponding Mn(bpy-R)(CO)₃Br catalysts were able to reduce CO₂ to CO.⁸³

CVs of Mn(bpy)CO₃Br are reported in Figure 2.4. Preliminary differences in the electrochemical behavior when compared to the rhenium analogue can be listed: the Mn complex undergoes two successive irreversible reduction reactions ($E_{p1} = -1.26$ V, $E_{p2} = -1.50$ V vs. SCE) corresponding to the formation of the dimer [Mn(bpy)(CO)₃]₂ and the mononuclear anion [Mn(bpy)(CO)₃]⁻, respectively (equations 11-14).

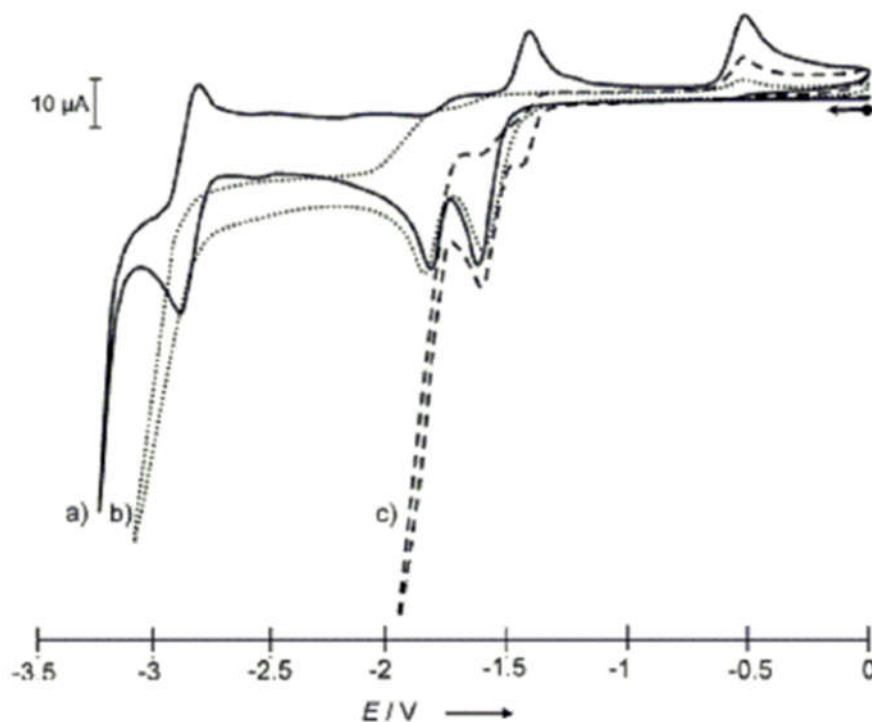
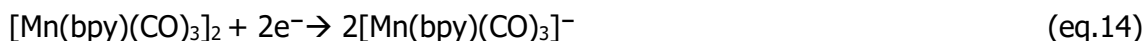
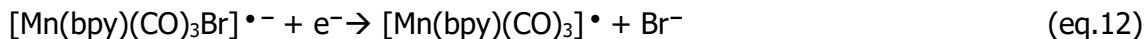
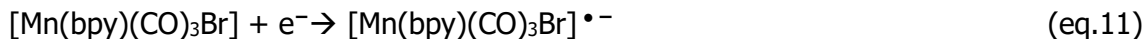


Figure 2.4. CVs of [Mn(bpy)(CO)₃Br] in CH₃CN/0.1 M Bu₄NPF₆ ($v = 100$ mV s⁻¹) under Ar (a, full lines) and CO₂ (b, dotted lines). The effect due to addition of 5% of H₂O under CO₂ atmosphere is described by the dashed lines (c). For the experiments, a glassy carbon electrode of 3 mm diameter and an Ag/AgNO₃ (10 mM) reference electrode were employed.

The corresponding potential values vs. SCE can be obtained by using +0.298 mV as a conversion factor.¹⁰³ Reproduced from ref.⁸³



The irreversibility of the first reduction wave is maintained also at high scan rates: this behavior is ascribed to the very fast kinetics for Br^- loss after a single-electron reduction to form a five-coordinate radical, which dimerizes quickly. Therefore, Mn^0 - Mn^0 dimer formation is extremely favored, whilst Re^0 - Re^0 dimer is considered a result of a side reaction pathway. The major difference between Re and Mn lies in the fact that $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]^{\bullet -}$ is highly unstable differently from $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{\bullet -}$ which is relatively stable at room temperature.

Equations 12 and 13 are expected to proceed quickly, hence $[\text{Mn}(\text{bpy})(\text{CO})_3]_2$ is the only product experimentally observed upon the first reduction. The short-lived intermediates $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]^{\bullet -}$ and $[\text{Mn}(\text{bpy})(\text{CO})_3]^{\bullet}$ were not observed in common IR-SEC experiments,^{90,104,105} but the latter was detected as a transient species by time-resolved IR spectroscopic techniques.¹⁰⁶ Another experimental evidence of the fast dimerization is provided by the presence of a large reoxidation peak at *ca.* -0.3 V vs. SCE (Figure 2.4) which is absent in the CVs of rhenium complexes. This oxidation peak is assigned to the dimer reoxidation to the starting material or to the positively charged solvento complex as reported in eq. 15.



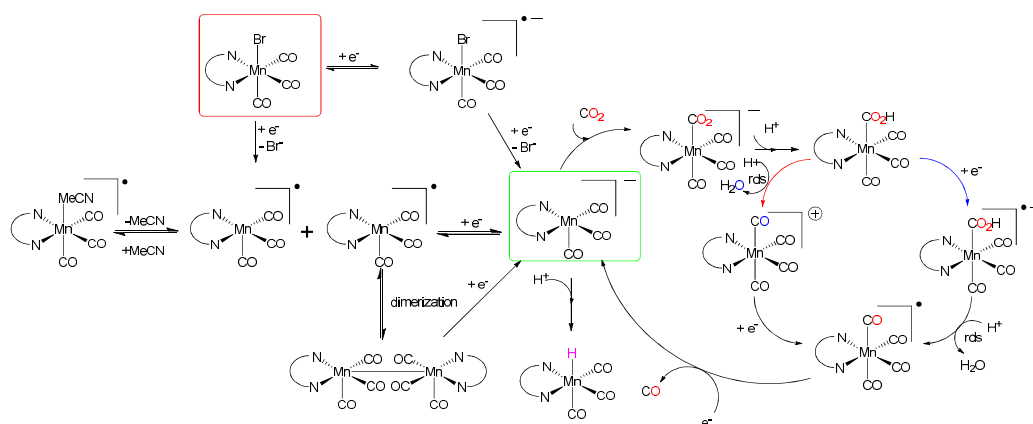
DFT calculations have been used as a complementary tool to better shed light on the different attitude toward the axial ligand (halide ion) shown by Re and Mn bipyridyl complexes. In the case of Re, the bpy-based π^* orbital is lower in energy than the Re $5d_{z^2}$ one, and the extra-electron is primarily stored over the bpy unit; conversely, in Mn complexes, the electron transfer is basically metal-centered, due to stabilization of the Mn $3d_{z^2}$ orbital relative to the bpy-based π^* orbital, leading to a weaker Mn-Br bond after the first electron uptake.¹⁰⁷

Equation 14 describes the reductive cleavage of the dimer to form the penta-coordinated anion, which is, similarly to rhenium, the main catalytic species.

The potential at which $[\text{Mn}(\text{bpy})(\text{CO})_3]^-$ is oxidized to the dimer occurs ~ 400 mV more positively than the potential required for eq. 14.⁸³ To some extent, the five-coordinated radical $[\text{Mn}(\text{bpy})(\text{CO})_3]^{\bullet}$ may be directly reduced to $[\text{Mn}(\text{bpy})(\text{CO})_3]^-$ with no production of the dimer,

2.9.5 ELECTROCHEMICAL MECHANISM OF $\text{Mn}(\text{bpy})\text{CO}_3\text{Br}$ UNDER CO_2 : PROTONATION-FIRST AND REDUCTION-FIRST

This feature suggests the involvement of a proton-assisted electrocatalytic pathway. The general $2e^-$ mechanism proposed for rhenium can reasonably be considered valid for Mn-bpy based catalysts. Once CO_2 binds the metal center of the five coordinate species $[Mn(bpy)(CO)_3]^-$, a sequence of protonation and reduction steps occurs (Scheme 2.9). Two possible catalytic pathways, focused on the different sequences of the reduction/protonation steps for evolution of the above mentioned metal carboxylic adduct have been recently proposed: in comparison with its Re counterpart, $[Mn(bpy)(CO)_3Br]$ was found to be more versatile, as it is able to undergo both catalytic pathways, depending on the applied potential.^{107,109,110}



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protons, resulting in the catalytic reduction of CO₂ to CO by two different pathways, reduction-first and protonation-first: blue and red arrows, respectively. (rds = rate-determining step). Adapted from ref.¹¹⁰

In the seminal mechanistic studies of Carter and co-workers,^{107,111} both Mn and Re based pre-catalysts in CH₃CN solutions were expected to start with a 1e⁻ ligand-based reduction resulting in the formation of the radical anion or the neutral penta-coordinated radical, depending on whether the halide anion stays bound or dissociates during the reduction event, i.e., an electrochemical-chemical (EC) pathway. Being the Mn radical anion not stable, as previously discussed, the penta-coordinated radical can then dimerize to form the Mn⁰ – Mn⁰ dimer complex; after the second reduction step, a reactive 2e⁻ reduced species (green box of Scheme 2.9) is formed and may react with CO₂ or, alternatively, with a proton donor to form a hydride species. Formation of CO and H₂O originates from the Mn- carboxylic adduct via the two possible mechanisms proposed by Carter and co-workers: *protonation-first* and *reduction-first*.

The protonation-first pathway starts with heterolytic C–OH bond cleavage of the [Mn(bpy)(COOH)] species facilitated by a proton donor leading to the formation of H₂O and [Mn(bpy)(CO)₄]⁺, which is further reduced to generate [Mn(bpy)(CO)₄][•]. In contrast, the reduction-first pathway proceeds with reduction of [Mn(bpy)(COOH)] followed by heterolytic C–OH bond cleavage yielding H₂O and the common [Mn(bpy)(CO)₄][•] intermediate. Stepwise or concerted one-electron reduction and CO evolution steps complete the catalytic cycle, regenerating the active catalyst.

The catalytic behavior in presence of different acids is similar to that described for the Re bipyridyl complexes, as an experimental CV study of [Mn(bpy-^tBu)(CO)₃Br] showed that the catalytic current under CO₂ increases as the acid strength is increased (CF₃CH₂OH > CH₃OH ~ H₂O).¹⁰⁴

Theoretical studies pinpoint a crucial role of the bpy ligand as an electron reservoir during the electrocatalytic process of both Re and Mn catalysts.

In the following paragraph (2.10), the role of the second coordination sphere in Re and Mn bipyridine for tuning the selectivity and the mechanistic behavior of the catalysts towards CO₂ will be analyzed.

2.10 The effect of substituted bipyridines and the role of second-coordination sphere

Many secondary sphere strategies for CO₂ reduction have been applied to molecular systems over the years.¹¹² Approaches which have been shown to increase catalytic activity and selectivity include:

- proton donors/shuttles in the form of Brønsted sites
- charged moieties
- sterically demanding functional groups
- bimetallic active species
- stoichiometric participation of alkali and alkaline earth metal cations

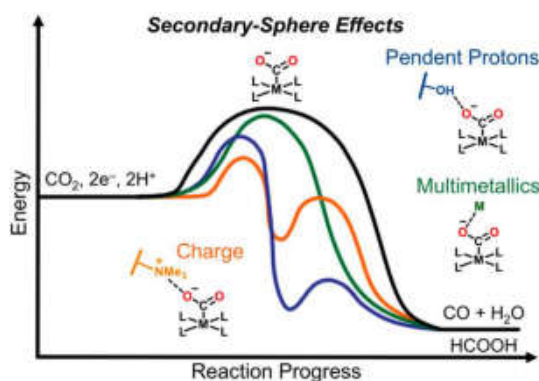


Figure 2.6. Secondary sphere effects. Reproduced from ref.¹¹²

After the pioneer work of Lehn^{78,79}, many efforts for improving the catalytic activity have been conducted. In the Re(bpy)(CO)₃X catalyst family, most work has focused on modulating the steric and electronic properties of the bipyridine ligand in attempts to modulate the reducing power and activity of Re. Alongside with mechanistic insights developments^{82,96,113,114}, the first substitution studied regarded the 4,4' positions of the bpy ring (Chart 2.7). In the case of Re-dmbpy (4,4'-dimethyl-2,2'-bipyridine) **Re1**, it has been demonstrated that the five-coordinate complex [Re(bpy)(CO)₃Cl]^{•-} can react with CO₂ directly, even in CH₃CN, via the one-electron pathway: the 2e⁻ path seemed to be absent. Faradaic efficiency for CO production in DMF with added water almost traced the unsubstituted Rebpy one.⁸⁸ More recently, in 2010, Kubiak and collaborators reported a systematic study of bipyridyl ligands variations for Rebpy complexes (**Re1**; **Re2**; **Re3**; **Re4**) in acetonitrile solutions.^{101,115} The best catalytic activity, as defined by TOF, was obtained with ^tBubpy. They outlined a general trend: the catalytic current increased for more electron-donating substituents. The better activity of **Re3**, albeit at larger overpotentials, as ascertained from bulk electrolysis experiments, can be ascribed to the inhibition of the inactive dimer.

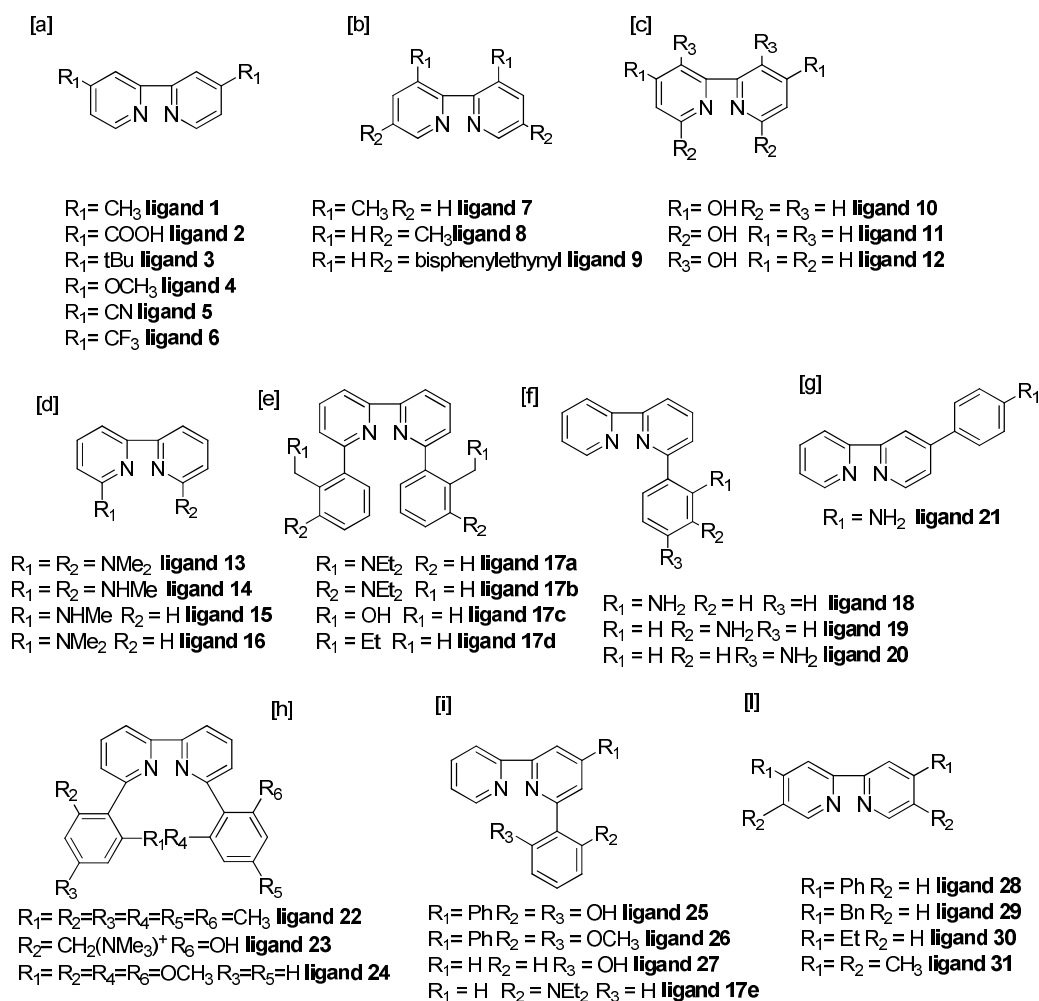


Chart 2.7. Various substituted bipyridines [a]^{101,115,121,128,132}, [b]^{116,117}, [c]^{119,120,128}, [d]¹²², [e]^{41,42}, [f]¹²³, [g]¹³³, [h]^{108,124,127}, [i]^{57,129,130}, [j]¹³².

The steric and electronic effects on the bpy ligand were further investigated always by Kubiak and coworkers in 2014.¹¹⁶ They positioned methyl groups at 3,3' (**Re7**) and 5,5' (**Re8**) positions of the bpy. They reported the 3,3' substitution in **Re7** to negatively affect the catalysis: despite both bpy derivatives display comparable σ Hammett values, the different electrocatalytic behavior of **Re7** and **Re8** could be explained by the larger steric hindrance created by the methyl groups on 3- and 3'-positions of the bpy. They demonstrated that steric considerations could supersede electronic effects in this class of catalysts. In 2012, the 5,5' positions were substituted by bisphenylethynyl groups (**Re9**).¹¹⁷ The original aim of the work was to introduce an extended conjugated π - electron system for increasing the optical absorption in the visible spectral range, thus favoring photocatalysis. Nevertheless, this complex, under electrochemical conditions, resulted in a 6.5-fold increase in current density with respect to simple Rebpy, under CO₂ saturated atmosphere.

Drawing inspiration from the pioneer work of Saveant¹¹⁸ regarding the positive effect of local proton sources on the porphyrin ring, the effect of secondary sphere modifications on the $\text{Re}(\text{bpy})\text{CO}_3\text{X}$ system was explored by Manbeck et al.¹¹⁹ through the incorporation of $-\text{OH}$ groups at the 4,4' - and 6,6' -positions of the bpy, with the goal of using them both as a pendant proton source and to contribute electron density to the bpy ligand. The authors reported atypical behavior during electrocatalysis: cleavage of the O–H bonds occurs upon stepwise electrochemical reduction, leading to dearomatization of the doubly reduced bpy ligand. Interestingly, only **Re10** is active as an electrocatalyst for CO_2 reduction, while **Re11** complex completes only ~ 1 TON for CO, despite having nearly identical electrochemical properties under Faradaic conditions by CV. This result suggests slow CO release and decomposition of intermediates at applied potentials limit activity for the 6,6' - dihydroxybpy derivative. Very recently, the 3,3'-dihydroxybpy complex (**Re12**) was tested by Hartl and collaborators.¹²⁰ In analogy with the earlier reported isomer also **Re12** undergoes facile reductive deprotonation generating $[\text{Re}(3,3'\text{-DHBPY-H}^+)(\text{CO})_3\text{Cl}]^-$. The stabilizing strong intra-ligand hydrogen bonding in 3,3'-DHBPY- H^+ is the most likely reason for the unusually large positive shift of the reduction potential, and the instantaneous deprotonation in basic DMF compared to the other two isomers. The modest catalytic performance places precursor **Re12** between more efficient **Re10** and poorly performing **Re11** congeners.¹¹⁹

In 2018, Kubiak and coworkers published their findings on a systematic study of kinetic and mechanistic effects of bipyridine substituents.¹²¹ With respect to their above-mentioned works, they confirmed how substituents with moderate electron-donating ability (tBu and CH_3) increased activity and overpotential for **Re1** and **Re3** in comparison to the unsubstituted complex $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$. In contrast, substituents resulting in too much electron density distributed over the bpy ligand, either from too-strong electron-donating ability (OCH_3) or from the requirement of a third reduction to activate the complex (CN and CF_3), destabilized **Re4**, **Re5** and **Re6**, respectively. In 2019, Marinescu and coworkers tested the effect of rhenium tricarbonyl bipyridine complexes modified with pendant secondary and tertiary amines in the 6- and 6'-positions.¹²² Under CO_2 , **Re13**, **Re14**, **Re15** and **Re16** display irreversible current enhancements at the second reduction feature. Titrations with TFE lead to greater current enhancements at the first reduction feature, attaining current densities up to 12 mA cm^{-2} for **Re16**.

During CPE experiments, mono-substituted complexes **Re15** and **Re16** performed analogously to $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ under identical conditions, producing similar volumes of CO, whereas bis-substituted complexes **Re13** and **Re14** produced only small amounts of CO.

Differently from **Re13**, **Re14**, **Re15** and **Re16**, in May 2020, Daasbjerg and coworkers studied the effect of pendant amines in the second coordination sphere. **Re17a** has been tested as CO₂ electrocatalyst. The major reduction product is CO, alongside with some formic acid and hydrogen. The effect on selectivity of the same benzylic amine ligand on Mn will be mentioned afterwards. In the same month, another recent paper of Jurss et. al.¹²³ has been published. They reported a series of Rebpy catalysts (**Re18**, **Re19** and **Re20**) decorated with -NH₂ moieties acting as second sphere hydrogen bond donors. These catalysts outperform the benchmark catalyst, Re(bpy)(CO)₃Cl, in CH₃CN with and without added trifluoroethanol (TFE), with turnover frequency (TOF) values increasing in the following order of position of the -NH₂ group on the phenyl ring, para < ortho < meta. The effect of -NH₂ group on the phenyl ring in the 6-position of the bpy, is more significative than the same group on the phenyl in the 4-position (**Re21**). **Re21** has been synthesized by our group with the further goal of functionalizing the complex on glassy carbon electrodes. Nevertheless, the less activity in homogeneous acetonitrile solutions of **Re21** with respect to the corresponding isomers (**Re18**, **Re19** and **Re20**) can be ascribed by the greater distance of -NH₂ to the metal center. Always very recently, Matsubara et al.¹²⁴ reported the first example of a bi-functional second-coordination sphere (**Re23**). In this case, the bpy ligand comprises a high local concentration of protons and local coulombic interactions provided by the quaternary ammonium group. This catalyst has been tested as CO₂ to CO electrocatalyst and compared with **Re22**, which only shows steric effects. With respect to catalysts possessing single functional groups in the spheres, they found that **Re23** exhibits a concerted improvement over the single functional groups in the efficiencies of catalysis, based on experimental standard electrode potentials for the reduction in aqueous *N,N*-dimethylformamide or acetonitrile solutions and the equilibrium potentials depending on the catalytic systems.

In analogy with Re, the effect of different substituted bipyridines has also been tested for Mn complexes. Before getting into specifics, it must be recalled that one of the most important mechanistic detail about the Mn(bpy)(CO)₃X system is that upon reduction by a single electron and subsequent loss of X, a Mn–Mn dimer [Mn(bpy)(CO)₃]₂ can rapidly form with rates approaching the diffusion limit.¹⁰⁶ Once this dimer is formed, it increases the electrochemical driving force to generate the catalytically active species and reduces the catalytic activity.^{104,125} **Mn1** (Chart 2.7) has been synthesized in 2011⁸³ concomitantly to unsubstituted Mnbp. **Mn1** was more effective at the same applied potential with a quantitative CO production over a longer time (TON_{CO}=34 after 18 h vs. TON_{CO} for Mnbp = 13 after 4h).^{110,126} Trying to fight the detrimental effects deriving from dimerization, a bulky bpy was designed (**Mn22**)^{108,127}. The modification on the 6,6'-position, the closest to the metallic center revealed that a single two-

electron reversible reduction process was occurring. This feature implied the suppression of the dimer, offering a more easily doubly reduced catalytically active species.

The functionalization of the bpy ligand with electron-donating or electron-withdrawing groups has shown to be a convenient way for tuning the electrochemical properties of the corresponding complexes. **Mn3** has been one of the most studied electrocatalyst¹⁰⁴ and behaves very similarly to Mnbpv. In addition to **Mn3**, Cowan and coworkers also investigated the effect of carboxy [(COOH)₂bpy] and hydroxy [(OH)₂-bpy].¹²⁸ **Mn2** and **Mn11** were studied in an aqueous environment using Nafion/MWCNTs electrodes. These two complexes showed less negative reduction potentials than Mnbpv and **Mn3**. It must be considered that ligand **11** is nominally an electron-withdrawing group, although it becomes a strong electron donor after the reductive deprotonation occurs, like for the previously studied **Re11**.¹¹⁹ Initial attempts to incorporate pendent proton functionalities involved the asymmetric attachment of phenolic moieties onto the bpy ligand. Our research group synthesized **Mn25**^{57,129} which was capable to afford both CO and formate as reduction products, differently from **Mn27** reported by Agarwal et al.¹³⁰ The presence of 2 OH groups is mandatory to direct the mechanism towards the formation of formate. Another experimental evidence showing how the phenolic protons were necessary for significant catalytic activity is proven by **Mn26** which did not show current enhancement if not with added Brønsted acids.¹²⁹ To extend these studies to symmetrically functionalized systems, Rochford and co-workers synthesized **Mn24**,¹³¹ a methoxy ether-containing analog of the bulky bpy ligand **26**. A combined experimental and theoretical analysis demonstrated that the introduction of sufficiently acidic exogeneous proton sources, may activate the slower "protonation-first" pathway seen in the original bulky bpy study at lower overpotentials in comparison to the "reduction-first" pathway at more negative potentials. Recently, Bocarsly and collaborators systematically analyzed a series of electronically and sterically differentiated newly and previously synthesized complexes¹³²: **Mn28**, **Mn29**, **Mn2**, **Mn4**, **Mn1**, **Mn30**, **Mn3** and **Mn31**. The UV–Vis, cyclic voltammetry, and calculation data showed that the bipyridine π^* level is controlled by the incorporation of different substituents on the bipyridine and through this interaction moderates the observed catalytic activity of the complex toward CO₂ reduction. Electronically deficient species were not able to act as catalysts for the conversion of CO₂ to CO, while species with unbiasing or electron-donating substituents on the bipyridine were effective electrocatalysts, with catalytic efficiency generally increasing as the steric bulk of the substituents was increased. Analogously to **Re17**, Daasbjerg and collaborators recently reported a series of Mn complexes with elaborated bipyridines (**Mn17a**, **Mn17b**, **Mn17c**, **Mn17d**, **Mn17e**)⁴² that can reduce CO₂ to either formic acid, if the ligand structure contains strategically positioned tertiary amines, or CO, if the amine groups are

absent in the ligand or are placed far from the metal center. These studies revealed that properly positioned amines in the secondary coordination sphere of the complexes could alter the product formation from CO to HCOOH. Mechanistically, the formation of a Mn–hydride species aided by in situ protonated amine groups was determined to be a key intermediate by cyclic voltammetry, ^1H -NMR, DFT calculations, and Infrared Spectroelectrochemistry.

The role of local proton sources on Re complexes and electronic effects on both Re and Mn of other substituents are object of further investigations (Chapter 3 and 4) that have been performed during this PhD project.

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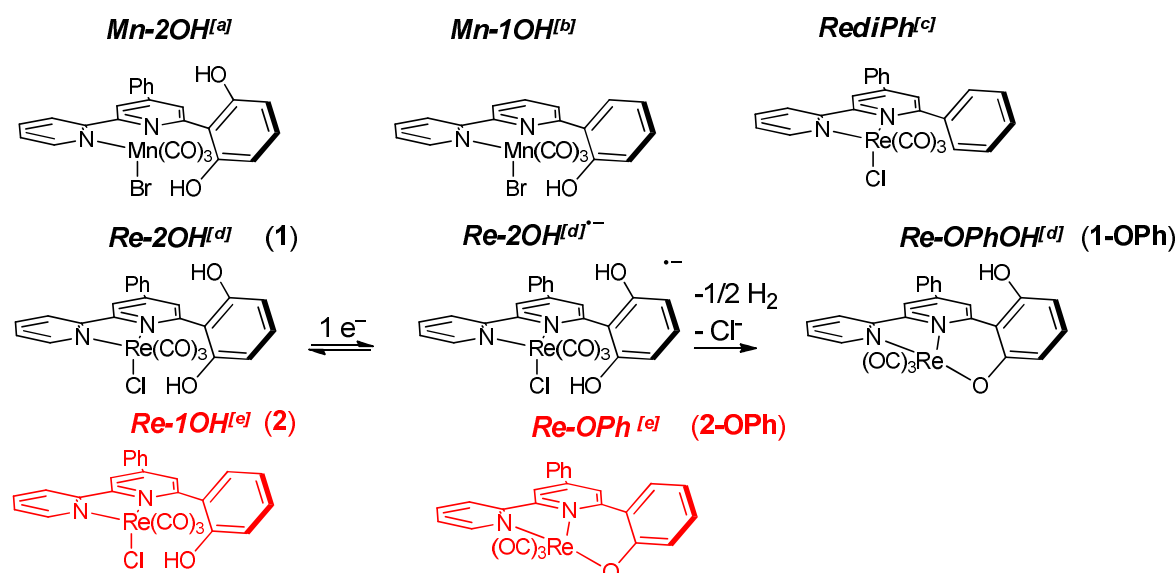
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CHAPTER 3. Local proton source effect on *fac*-Re(bpy-R)(CO)₃Cl

3.1 Introduction

Studies on electrocatalytic CO₂ reduction with homogeneous catalysts are often carried out in organic solvents under rigorous exclusion of water. Such conditions provide two advantages over aqueous electrolytes, namely, a broader potential window for the electrocatalytic experiment and a higher solubility of CO₂ and (often) the employed homogeneous catalyst. Although the solubility of CO₂ in aqueous electrolytes can be significantly improved by altering the pH, solvated CO₂ is always in equilibrium with carbonic acid, bicarbonate, and carbonate, whereby bicarbonate and carbonate are much harder to reduce than CO₂ and are not reduced under regular electrolysis conditions. In order to enable the electrocatalytic reaction, a suitable proton donor (e.g. water or alcohols) is typically added in small defined quantities. The concept of local proton source was firstly reported by Saveant et al.¹. Starting from the promising role of proton donors, they attached phenolic groups to the iron porphyrin ring: a significant increase of current was achieved. The positive effect is played by the large local concentration of acid present, which would be impossible to introduce in such amounts in solution in the context of a bimolecular reaction. The same concept applied to the electrochemical reduction of CO₂ has been extended to the Mn-bpy system,²⁻⁴ and we recently applied it to the Re-bpy complexes.⁵⁻⁷ Scheme 3.1 shows a set of Mn and Re catalysts bearing pendent phenolic groups near the metal center acting as intramolecular proton sources. We initially reported *fac*-Mn(pdbpy)(CO)₃Br^{2,3} (**Mn-2OH**) and we herein study the effect of the two OH functionalities on *fac*-Re(pdbpy)(CO)₃Cl⁸ (**Re-2OH**, **1**), (pdbpy = 4-phenyl-6-(phenyl-2,6-diol)-2,2'-bipyridine). A similar catalyst, Mn(6-(2-hydroxyphenol)-2,2'-bipyridine)(CO)₃Br (**Mn-1OH**) was previously described by Bocarsly and coworkers.⁹ The intermediate **Re-OPhOH** (**1-OPh**) (Scheme 3.1) is proposed to be produced after the first 1e⁻ reduction. **1-OPh** is characterized by the presence of the intramolecular Re-O bond and undergoes electrochemical reduction to generate the actual catalyst in the CO₂ conversion. IR-SEC measurements supported by DFT calculations suggested the formation of this intermediate following reductive deprotonation; however, its identity was not corroborated by other experimental techniques and its precise effect on catalysis remained unclear. We concluded that the local proton source effects of the pdbpy ligand altered the selectivity for CO₂ electroreduction depending on the metal involved. Indeed, while **Mn-2OH** gives the hydride form with subsequent production of formate, our newly synthesized **1** undergoes a different reduction pathway and no formate is afforded.⁸ To better shed light on the fundamental aspects of this electrochemical mechanism and to provide additional spectroscopic evidence for phenolate coordination to the metal, a novel complex bearing a single hydroxyl group instead of two, namely *fac*-Re(pmbpy)(CO)₃Cl (pmbpy

= 4-phenyl-6-(2-hydroxy-phenyl)-2,2'-bipyridine), **Re-1OH** (**2**), has been synthesized (Scheme 3.1)¹⁰. We hypothesized that a single pendent phenolic group could simplify the system by eliminating complications arising from the reductive or chemical deprotonation of the second phenolic group. Hydroxy-bipyridine-type ligands with the OH group close to the metal center are known to experience the electronic effects of the oxyanion formed by deprotonation to catalytic site.⁷ The complex **2** has been characterized by cyclic voltammetry (CV), infrared Spectro-Electrochemistry (IR-SEC), and chemical reduction with Na-Hg. Data have been analyzed through comparison to Re(4,6-diphenyl-2,2'-bipyridine)(CO)₃Cl (**RediPh**), which does not bear phenolic groups. The corresponding intermediate **Re-OPh** (**2-OPh**) has been isolated and characterized, and **2** has been tested as catalyst for CO₂ electroreduction with reactivity discussed in terms of the observed intermediates and performances compared to **1** and to literature data for related complexes.



Scheme 3.1. Chemical sketches of sample Mn and Re bipyridine electrocatalysts bearing local proton sources and proposed intermediates formed during electrochemical reduction. [a]^{3,2}, [b]⁹, [c]¹¹ [d]⁸, [e]¹⁰.

3.2 Synthesis and characterization

The pd bpy and pmbpy ligands were prepared by the Kröhnke reaction¹² by using appropriately modified chalcone and pyridinium salts as precursors to cyclization (all details are provided in the "Ligands synthesis" Appendix section). Complexes **1** and **2** were obtained as pure yellow solids from the reaction of Re(CO)₅Cl with the respective ligand in toluene. The infrared (IR) spectra confirm the *fac* geometry with three strong CO stretching frequencies at 2023, 1918, 1901 cm⁻¹ and 2022, 1919, and 1895 cm⁻¹ for **1** and **2**, respectively.

The 298 K ^1H NMR spectra of **1** and **2** are shown in Figure 3.1, and NMR correlation spectroscopy (COSY) with all signal assignments and the ^{13}C spectrum are provided in Appendix (Figures A1-A4). Notably, for complex **2** there are two sharp resonances of unequal intensity at 9.96 and 9.89 ppm assigned to the $-\text{OH}$ proton. The total integration of these two peaks is one, and they are present in the same ratio for each preparation of the complex. The $-\text{OH}$ resonances are shifted downfield relative to the two resonances of **1** at 9.60 and 9.56 ppm, but the similar separation suggests two environments differing by comparable electronic effects. Additional evidence for the proposed isomers is found in separate resonances of the H_5 singlets that appear in comparable ratios to the $-\text{OH}$ singlets (Figure A1). The carbonyl region of the ^{13}C NMR spectrum of **2** reveals six carbonyl resonances instead of three in agreement with the presence of two isomers, and two sets of resonances of several other carbon signals are also evident (Figure A3).

The two possible isomeric structures were investigated by DFT calculations (Figure 3.2). The form **2-cis** is the most stable, by 5.1 kJ mol^{-1} , due to the interaction between the $-\text{OH}$ group and the Cl atom.

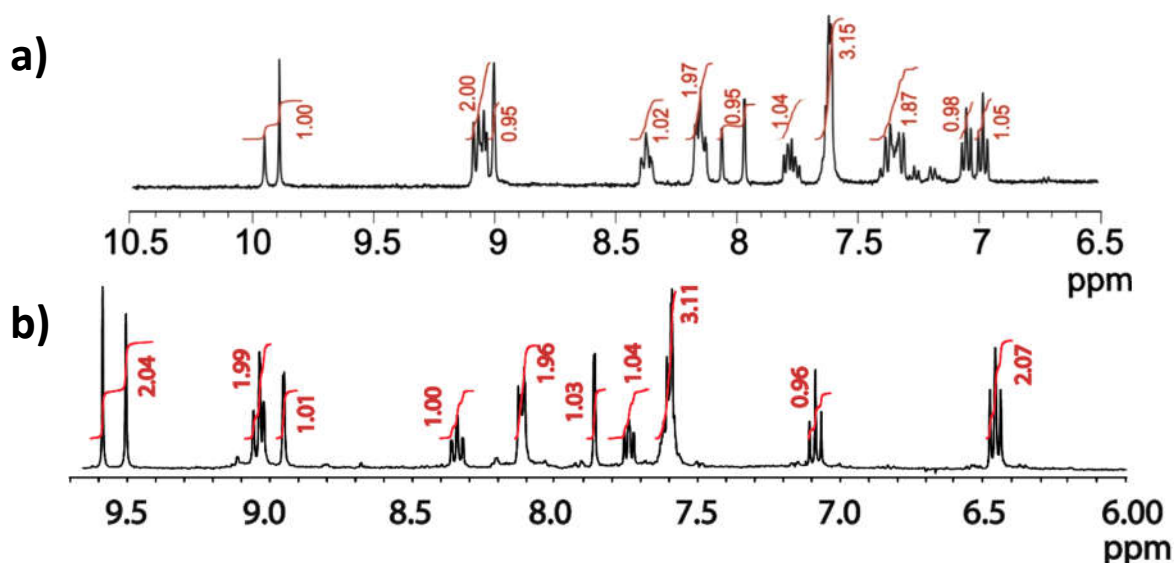


Figure 3.1. ^1H NMR spectra of **1** (a) and **2** (b) in $\text{d}_6\text{-DMSO}$.

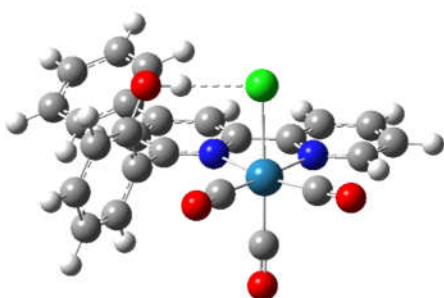
2-*cis***2-*trans***

Figure 3.2. Representation of the two isomers **2-*cis*** and **2-*trans*** computed by DFT calculations.

Intrigued by the NMR that evidenced a non-negligible rotational barrier of the phenolic group, we searched for two transition states connecting the two isomers. The first, **TS2'**, may be thought to be obtained by the counterclockwise rotation of the **2-*cis*** phenolic group (i.e. the OH group is on the opposite side of the $\text{Re}(\text{CO})_3$ moiety), while the second, **TS2''**, may be thought to be reached by the clockwise rotation of the **2-*cis*** phenolic group (i.e. the OH group is on the same side of the $\text{Re}(\text{CO})_3$ moiety). As expected, the energy barrier of **TS2'** (75.5 kJ mol^{-1} , single negative frequency at -28.8 cm^{-1}) is lower than that of **TS2''** (95.0 kJ mol^{-1} , single negative frequency at -35.0 cm^{-1}), because the rotation of the phenolic group occurs when the OH moiety is far from $\text{Re}(\text{CO})_3$. The relatively high rotational barrier accounts for the presence of the two isomers and hence the splitting of NMR signals observed experimentally.

3.3 X-Ray crystallography

Single-crystal X-Ray diffraction data of **Re-2OH**, namely **1**, has been obtained from a yellow prismatic crystal, grown by slow evaporation under dark conditions from a toluene/dichloromethane 1:1 solution. **1** (Figure 3.3) crystallizes in a triclinic centrosymmetric $P\bar{1}$ space group. The metallic center has a slightly distorted octahedral geometry. The phenyl group in the 4' position of the ligand is almost coplanar with the aromatic bpy system (torsional angle of 32°), but the ellipsoids show a weak barrier to rotation. The diphenolic ring in the 6' position is instead nearly perpendicular to the α, α' -diimine plane (dihedral angle of 72.5°). This part of the structure is more ordered because of the presence of intramolecular hydrogen bond interaction with the chlorine bonded to the central metallic atom ($d \text{ O5-H5}\cdots\text{Cl1} = 3.102(10) \text{ \AA}$, see Table A1). The overall packing of the molecular complex shows a multiplicity of weak hydrogens bonds and is stabilized by the presence of channels running along an axis filled by disordered toluene molecules that show $\text{C-H}\cdots\pi$ interactions (Figure 3.3b).

Re-10H, namely **2**, crystallizes from slow evaporation of CH₃CN as subtle yellow platelets, often twinned along the basal plane. Therefore, a judicious choice of the crystal has been necessary to obtain sufficient quality X-ray diffraction data. This compound shows a monoclinic P2₁/c space group, with one molecule in the asymmetric unit. Rhenium shows a distorted octahedral environment typical of this class of phenyl substituted complexes, with the distortions due to steric hindrance ($d(\text{Re1-N2}) = 2.120(8) \text{ \AA}$ respect to $d(\text{Re1-N1}) = 2.068(8) \text{ \AA}$, see Figure 3.4a). The aromatic structure is inclined at 15.15° with respect to the axial carbonyls-rhenium plane (see Figure 3.4b), probably because of the position and steric hindrance of the lateral phenyl group on the C1O1 carbonyl ligand. This last group is rotated by 36.2° with respect to the plane perpendicular to that of the aromatic structure due to an intramolecular hydrogen bond starting from the OH substituent to the chloride ligand of the nearest neighbour molecule ($d(\text{O1} \cdots \text{Cl1}') = 3.139(10) \text{ \AA}$, $\text{ang}(\text{O1-H1} \cdots \text{Cl1}') = 118.06(20)^\circ$, $'' = -x, -1/2+y, 3/2-z$). This interaction forms a chain of hydrogen-bonded molecules along the b axis (see Figure 3.4c). The tendency of **2** to interact through a hydrogen bond with other molecules, forming a 1D supramolecular architecture in the solid state (Figure 3.4c) is in contrast with the crystal structure of the similar dihydroxy molecule **1** which shows an intramolecular hydrogen bond to the internal chloride ligand. The chains interact with each other through π - π stacking interactions along the whole aromatic skeleton between the inverted molecules of nearest neighbors (see Figure 3.4b).

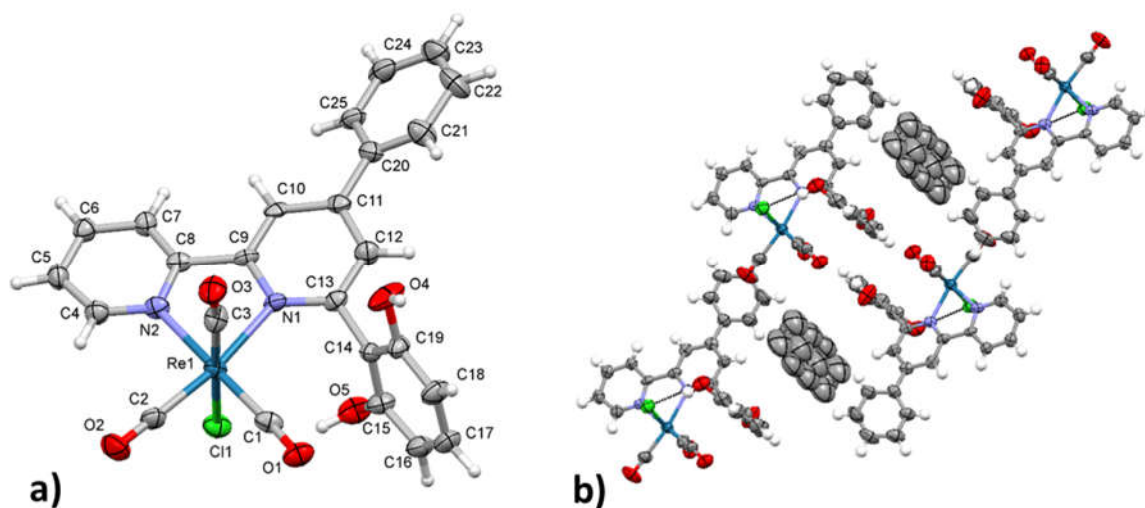


Figure 3.3. Molecular structure of **1** from X-Ray single crystal diffraction (a) and representation of axial structural channels (b).

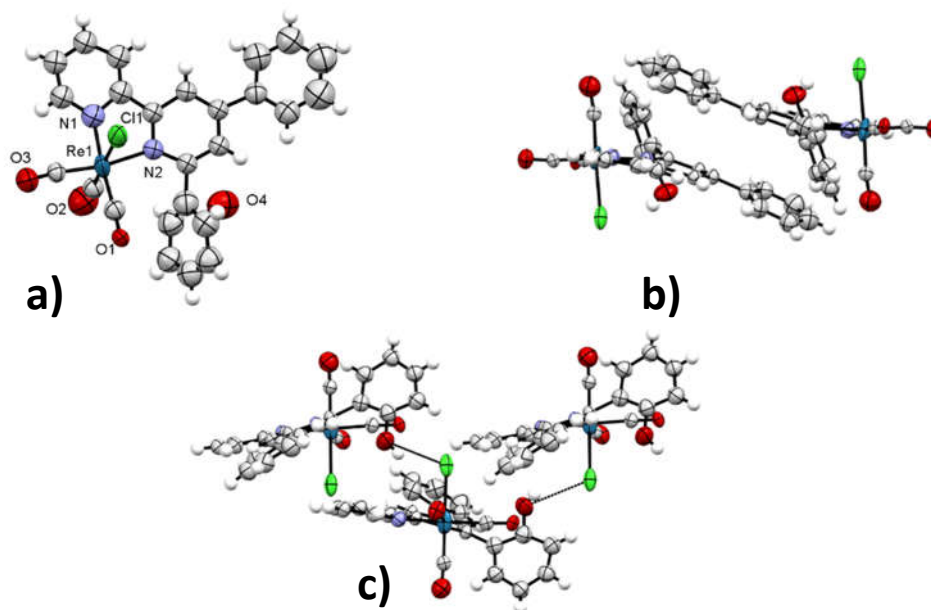


Figure 3.4. (a) Asymmetric unit of **2**, (b) π - π stacking interactions between nearest neighbor molecules, and (c) hydrogen bonded chains of complexes along the b axis.

3.4 Electrochemistry of **1**

3.4.1 CYCLIC VOLTAMMETRY OF **1** UNDER Ar AND CO₂

The electrochemical behaviour of **1** in anhydrous CH₃CN under Ar atmosphere (Figure 3.5) resembles that of a common Re(bpy)(CO)₃Cl system.^{13,14} The 0/1⁻ reduction of **1** ($E^\circ = -1.30$ V vs. Ag/AgCl) is chemically and electrochemically reversible, localized on the organic ligand with a non-negligible contribution of the Re metal.¹⁵ The radical anion is usually stable in CV time scale, but in certain conditions and solvents Re(bpy-type)(CO)₃Cl radical anions may release Cl⁻.¹⁴ The 1⁻/2⁻ reduction of **1** is chemically irreversible ($E_p = -1.59$ V vs. Ag/AgCl) and forms, after Cl⁻ dissociation, the intermediate penta-coordinated anion, [Re(pdbpy)(CO)₃]⁻ acting as a precursor for CO₂ binding and subsequent reduction. The third process at more negative potentials is commonly assigned to a ligand-centred reduction. The broad reoxidation process observed after the second reduction and located between -0.5 and -0.8 V is due to adsorbed species on the electrode surface, since the current peak is proportional to the scan rate.^{16,17}

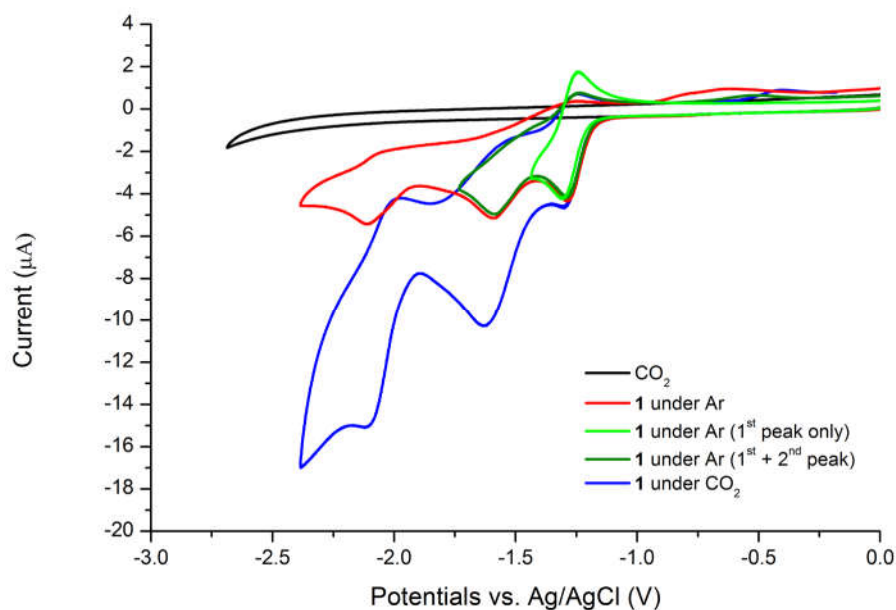


Figure 3.5. Cyclic voltammograms of 1 mM solution of **1** in CH₃CN / 0.1 M Bu₄NPF₆ at glassy carbon electrode, scan rate 200 mV/s. The black line is the electrolyte saturated with CO₂.

The reversibility of the 0/1⁻ reduction of **1** (see also Figure A5) suggests that the release of Cl⁻ only occurs after the second electron transfer. This is nicely highlighted by relaxed geometry scan of the Re–Cl bond performed by DFT calculations on the radical anion **1**⁻ and the dianion **1**²⁻. Re–Cl bonds in the optimized structures of **1**⁻, **1**²⁻, [Re(bpy)(CO)₃Cl]⁻ and [Re(bpy)(CO)₃Cl]²⁻ are 2.779, 2.913, 2.776 and 4.609 Å, respectively, showing clearly the weakening of the Re–Cl bond after 2e⁻ reduction. The dissociation of Cl⁻ in CH₃CN as solvent requires 32.0 and only 1.7 kJ/mol for **1**⁻ and **1**²⁻, respectively (Figure A6). The energetic barrier for the dissociation of the monoanion [Re(bpy)(CO)₃Cl]⁻ is 40.1 kJ/mol, while it is barrierless in the dianion [Re(bpy)(CO)₃Cl]²⁻ (leading to an optimized geometry in which the Re–Cl bond, 4.609 Å, is already broken). Thus, the calculations suggest that pd bpy in **1**⁻ slightly facilitates the release of Cl⁻ from the complex, when compared to [Re(bpy)(CO)₃Cl]⁻ in the same conditions. Equally important is the fact that release occurs from the doubly reduced species with very small barrier.

The CV of complex **1** in anhydrous CH₃CN under CO₂ atmosphere exhibits a small catalytic activity (increased current) already at the first reduction peak ($E_p = -1.30$ V, Figure 3.5). This is a notable difference from the other bipyridine-based rhenium catalysts, where the catalytic activity is observed in CV only at the second reduction peak.^{13,18}

The catalytic performance of **1** has been also investigated with the addition of two different external Brønsted acids: H₂O and MeOH. CVs in Figure A7 show that the addition of 5% of the

two acids enhances the reactivity of **1** with CO₂ on the first and particularly on the second peak.

3.4.2 CONTROLLED POTENTIAL ELECTROLYSIS OF **1**

Bulk electrolysis with **1** under CO₂ were performed upon setting the potential at values slightly negative to the first and second reductions, with and without added Brønsted acids (water and methanol, 5%). Table 3.1 summarizes the results obtained during these CPE experiments. A CO₂ flow of 30 mL min⁻¹ was kept constant during the experiments, CO and H₂ were identified by gas chromatography, and formate, if present, was assessed by NMR spectroscopy at the end of the experiments. In CH₃CN/H₂O at the first reduction (−1.5 V vs. Ag/AgCl) the TON_{CO} for **1** (7.5) is lower than the TON_{CO} of the corresponding **Mn-2OH** (28).³

Table 3.1. TON and faradic efficiencies (η) upon CPE (applied potential E in V vs. Ag/AgCl) of solutions containing **1** (0.5 mM) in 0.1M Bu₄NPF₆/CH₃CN in the presence of Brønsted acids (5%v).

Complex	E [V]	T [min]	Acid [5%]	TON _{CO}	η_{CO} [%]
1	−1.5	120	-	2.2	60
		270	H ₂ O	7.5	76
		270	MeOH	4.0	52
1	−1.7	150	-	2.9	49
		300	H ₂ O	14.1	88
		240	MeOH	4.4	64

3.5 Spectroelectrochemistry in optically transparent thin-layer electrode (OTTLE) cell and DFT calculations of spectral bands of **1**

3.5.1 IR-SEC OF **1** IN CH₃CN UNDER Ar

IR-SEC of **1** in acetonitrile under Ar was performed to monitor the spectral changes of the CO stretching bands (ν_{CO}). For all IR-SEC figures the arrows indicate the growing and decreasing of the corresponding bands. DFT calculations have been used as complementary tool for the assignment of the products and intermediate species observed during IR-SEC bulk electrolysis

under Ar. Figure 3.6a shows spectral changes during the potential scan up of -1.4 V vs. Ag/AgCl, i.e. just after the first reduction peak. As a main feature a progressive loss of the ν_{CO} stretches of the starting complex (2023 , 1918 and 1901 cm^{-1}) was observed along with the simultaneous growth of a new species (**1-OPh**, in Table 3.2 and Scheme 3.2) characterized by IR absorptions at 2010 , 1901 and 1879 cm^{-1} . The reduction in the OTTLE cell is irreversible (the reversed potential scan does not lead to the original spectrum), however this is not in contradiction with the CV reversibility, because of the quite different time scales of CV and IR-SEC.³ The longer time scale in IR-SEC experiments allows ligand exchange between Cl^- and a solvent molecule and the subsequent rearrangement to **1-OPh** (Scheme 3.2). The decrease in intensity of the OH stretches at 3318 cm^{-1} (inset in Figure 3.6a) suggests that **1-OPh** is a species originated from a reductive single deprotonation of the starting complex **1**, i.e. **1-OPh** is formulated as $([\text{Re}(\text{CO})_3(\text{pdbpy}-\text{H}^+)])$. A similar reductive deprotonation has already been observed for the analogous Mn complex.³

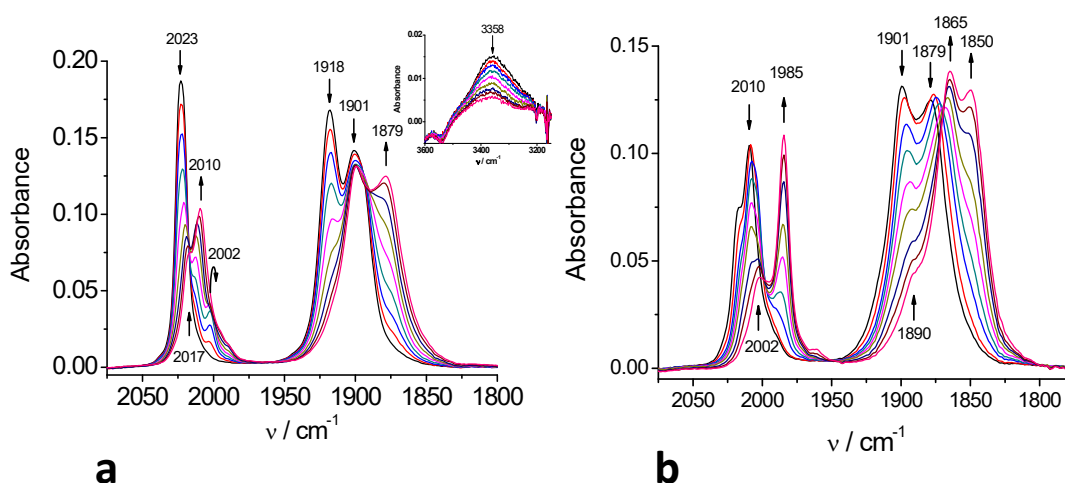


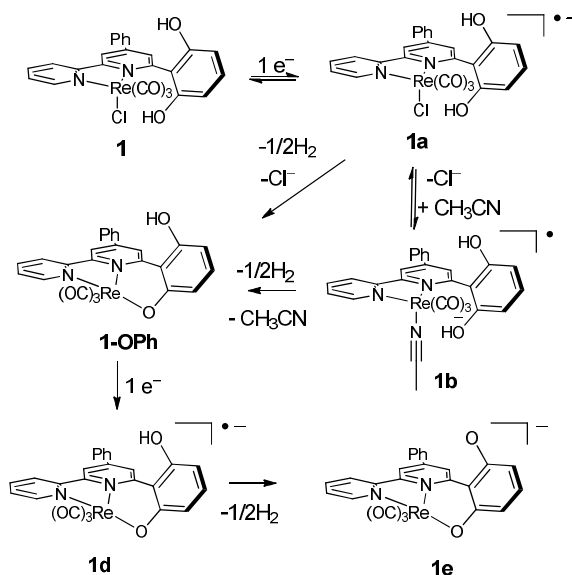
Figure 3.6. IR-Spectroelectrochemical reduction of a 2.9 mM solution of **1** in CH_3CN / 0.1 M Bu_4NPF_6 under Ar: **(a)** at the first reduction wave (final potential -1.4 V vs. Ag/AgCl). The inset shows the decrease of ν_{OH} , **(b)** at the second reduction (final potential -1.7 V vs. Ag/AgCl).

The transition from **1** to **1-OPh** (bands at 2010 , 1901 and 1879 cm^{-1} , see Figure 3.6a and Scheme 3.2) proceeds via the formation of other intermediate species, as revealed by the presence of ν_{CO} at 2017 and 2002 cm^{-1} , which finally converge into the peak at 2010 cm^{-1} . Two possible intermediates could be involved in the transformation.^{18,19} The band at 2002 cm^{-1} is attributed to the radical anion **1a** (1998 cm^{-1} observed for the analogous complex with unsubstituted bipyridine),¹⁹ and the band at 2017 cm^{-1} could be due to the corresponding radical **1b** obtained by substitution of Cl^- by CH_3CN (2011 cm^{-1} observed for bpy analogue).¹⁹

In conclusion, **1-OPh** is the predominant species at the end of the first reduction in IR-SEC time scale experiments.

Table 3.2. Selected experimental (IR-SEC) and calculated ν_{CO} frequencies of **1** and other related complexes from IR spectroelectrochemistry in CH_3CN and DFT computed data. ^a from ref.¹⁹

Complex	Experimental ν_{CO} (cm^{-1})	DFT (cm^{-1})
$[\text{Re}(\text{pdbpy})(\text{CO})_3\text{Cl}]$ (1)	2023, 1918, 1901	2021, 1921, 1902
$[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$	2021, 1914, 1897a	2017, 1911, 1901
$[\text{Re}(\text{pdbpy})(\text{CO})_3\text{Cl}]^{\bullet-}$ (1a)	2002, 1891, 1871sh	1999, 1892, 1875
$[\text{Re}(\text{pdbpy})(\text{CO})_3\text{CH}_3\text{CN}]^{\bullet}$ (1b)	2017	2017, 1917, 1899
$[\text{Re}(\text{bpy})(\text{CO})_3\text{CH}_3\text{CN}]^{\bullet}$	2011, 1895(br) ^a	2007, 1898, 1892
$[\text{Re}(\text{pdbpy})(\text{CO})_3\text{CH}_3\text{CN}]^-$ (1c)	1993	1989, 1890, 1869
$[\text{Re}(\text{pdbpy}-\text{H})(\text{CO})_3]$ (1-OPh)	2010, 1901, 1879	2008, 1901, 1888
$[\text{Re}(\text{pdbpy}-\text{H})(\text{CO})_3]^{\bullet-}$ (1d)	1985, 1865, 1850	1986, 1870, 1861
$[\text{Re}(\text{pdbpy}-2\text{H})(\text{CO})_3]^-$ (1e)	2002, 1890	1997, 1888, 1871



Scheme 3.2. Electrochemical reductive mechanism for **1** under Ar.

IR-SEC of **1** in anhydrous acetonitrile under Ar at the second reduction wave (Figure 3.6b) shows that the bands at 2010, 1901 and 1879 cm^{-1} are replaced by 2002, 1985, 1890, 1865 and 1850 cm^{-1} . The species (**1-OPh**), formed after the first reduction, undergoes further reduction (Scheme 3.2) leading to species (**1d**) ($1985, 1868$ and 1850 cm^{-1}) which could

subsequently generate (**1e**) (2002 and 1890 cm^{-1}) after loss of $\frac{1}{2} \text{H}_2$ (where the charge may now formally be localized on the oxygen atom).

3.5.2 IR-SEC OF **1** IN CH_3CN UNDER CO_2

IR-SEC spectra of **1** in CH_3CN under CO_2 -saturated solutions at the first reduction peak are quite similar to those obtained under Ar atmosphere, with a small exception of the growth of a peak at 1684 cm^{-1} (Figure A8a), assigned to the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ species.¹⁹ During the reduction at the second peak under CO_2 , IR-SEC at early stage (Figure A8b) rapidly reach a steady-state situation (Figure 3.7): the bands at 2010, 1901 and 1875 cm^{-1} , close to those found for (**1-OPh**) (2010, 1901, 1879 cm^{-1}) (Figure 3.5.1a, Table 3.2), remain almost unchanged, while new strong ν_{CO} bands at 1684, 1645 ($\text{HCO}_3^-/\text{CO}_3^{2-}$ system¹⁹) increase continuously. Under these conditions stationary concentration of (**1d**) is too small to be detected: only a weak shoulder of its strong absorption is present at 1985 cm^{-1} (Figure A8a and 3.7).

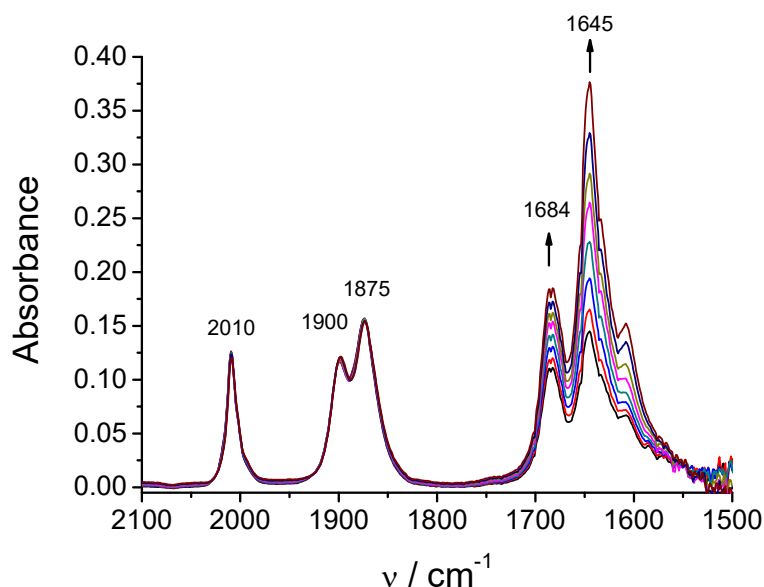


Figure 3.7. IR spectroelectrochemistry of **1** in $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$ under CO_2 : steady state established at continuing electrolysis at the second reduction wave (final potential -1.7 V vs Ag/AgCl).

It is interesting to underline that passing from **Mn-2OH** to **1 (Re-2OH)**, the same ligand has an important effect on the electrochemical properties: the hydride formation in Re is apparently suppressed. No formate production has been observed during exhaustive electrolysis (see below).

The active catalytic species are supposed to be the radical anion (**1d**) and/or the anion (**1e**), obtained by loss of $\frac{1}{2}$ H₂ from (**1d**). By analogy with the Muckerman and Schaefer mechanism,²⁰ CO production may involve a carbonate-bridged complex. In that paper the authors highlighted the affinity of Re with O atom, allowing the CO₂ insertion into the carbonate-bridged complex. O atom in **1** is close to Re, resulting in the formation of a Re-O bond of the entropically favoured intermediate (**1-OPh**), which is reduced to **1d**. Preliminary DFT calculations suggest that an alternative mechanistic pathway, not involving carbonate-bridged intermediate, may also be possible for **1**. A CO₂ insertion into the Re-O bond of the reduced species **1d** (or **1e**) is feasible, and results into carbonate species (Figure A9) that may further react with a second CO₂ molecule leading to CO and CO₃²⁻ as products.

3.6 Electrochemistry of **2**

Since the original goal was to better shed light on the role of the -OH groups in electrocatalysis and adding experimental evidence for **1-OPh** formation, complex **2** has been synthesized. Elimination of one phenolic group could allow a deeper mechanistic insight avoiding complications derived from reductive or chemical deprotonation of the second phenolic group. The cyclic voltammogram (CV) of **2** in anhydrous acetonitrile exhibits three reduction processes labeled I-III at intermediate sweep rates, ν (0.05 to 2 V s⁻¹) (Figure 3.8). Reduction I is reversible with an associated reoxidation wave IV and $E_{1/2} = -1.70$ vs. Fc^{+/0}. At a scan rate of 0.25 V s⁻¹ wave II is irreversible and wave III is quasireversible, with peak potentials at -2.06 and -2.26 V, respectively.

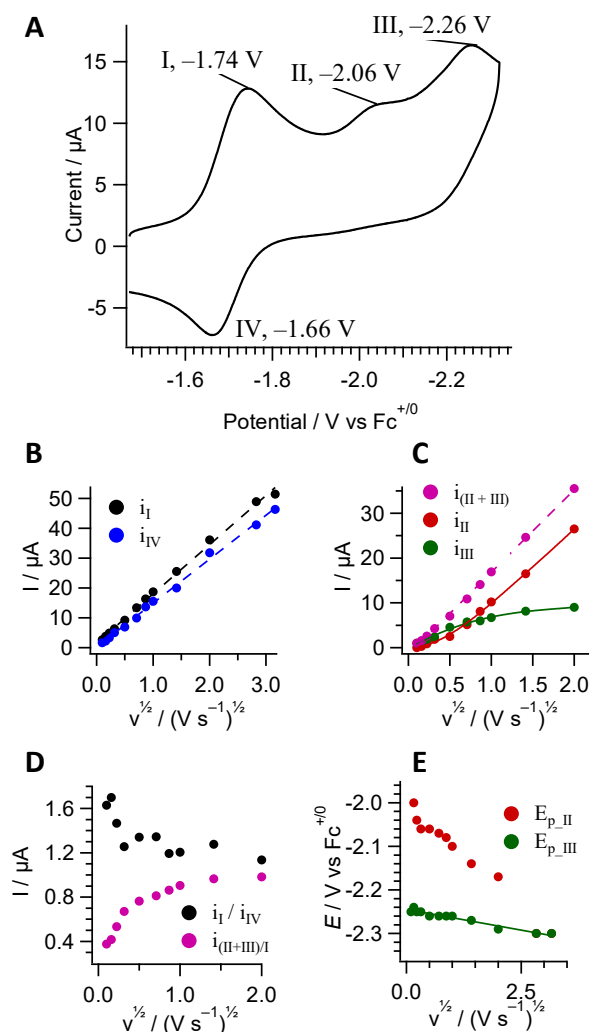


Figure 3.8. (A) Cyclic voltammogram of 0.4 mM **2** in Ar-saturated CH₃CN with 0.1 M Bu₄NPF₆ at a glassy carbon electrode, scan rate = 0.25 V s⁻¹. (B) Current at peaks I and IV. (C) Current at peaks II and III. (D) Ratios of currents at peaks I/IV and the sum of (II+III)/I. (E) Peak potentials of reductions II and III.

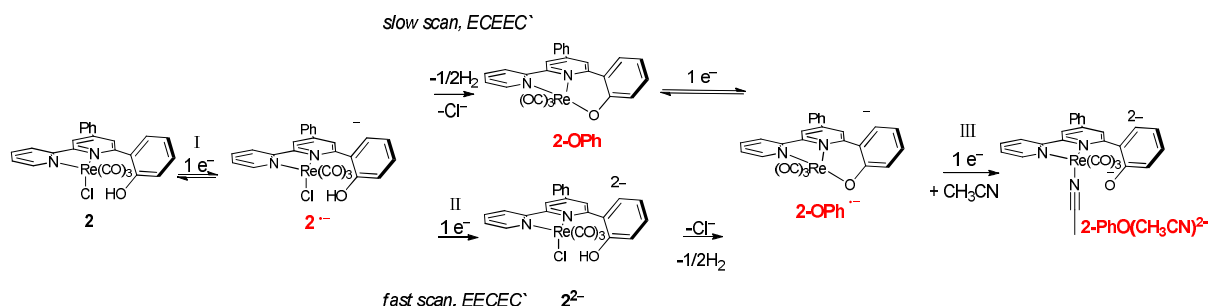
Peak currents at waves I and IV are linearly dependent upon $v^{1/2}$ consistent with diffusional processes (Figure 3.8B), but the ratio of i_I / i_{IV} decreases from a maximum of ~ 1.6 at slow scan rates to ~ 1 as the sweep rate is increased (Figure 3.8D). The decreasing current ratio i_I / i_{IV} could be a simple effect of different diffusion coefficients of the oxidized and reduced species of the I/IV couple; however, further observations below suggest the participation of a chemical step and an additional reduction near wave I.

Peak currents at waves II and III are shown in Figure 3.8C, and sample CV's with variable scan rates are shown in Figure A10. At the lowest limit of 0.01 V s⁻¹, wave II is absent. As the scan rate is increased, current at wave II increases at the expense of current at wave III, and wave II shifts in potential from about -2 V to -2.15 V after which it begins to overlap with wave III. The sum of peak currents at waves II and III remains proportional to $v^{1/2}$ throughout

the entire range of sweep rates. The ratio of currents at (peaks II + III) / peak I is ~ 0.5 at 0.05 mV s^{-1} and increases to ~ 1 at 4 V s^{-1} . Above 4 V s^{-1} it is difficult to differentiate currents from overlapping processes II and III.

Multisweep voltammograms (Figure A11) show decreasing current for reduction I and complete loss of reduction II without accumulation of any distinct redox processes. For comparison, the multisweep CV of $[\text{Re}(\text{4,6-diphenyl-2,2'-bpy})(\text{CO})_3\text{Cl}]^{11}$ is also shown. This complex differs only by the absence of the $-\text{OH}$ group and represents the electrochemical behavior expected of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ -type complexes. The dominant reductive pathway follows an EEC mechanism with a reversible $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{0/-}$ couple and an irreversible $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{-/2-}$ couple followed by chloride dissociation to produce $[\text{Re}(\text{bpy})(\text{CO})_3]^-$,²¹ although a competing ECE pathway with a relatively slow dissociation of the chloride from the singly reduced radical is possible as well.²² Dimerization of the singly reduced species is possible,^{14,22} but we did not observe characteristic features of dimerization during reduction or re-oxidation, especially at 0.4 mM analyte concentration. Multiple scans of the $[\text{Re}(\text{4,6-diphenyl-2,2'-bpy})(\text{CO})_3\text{Cl}]^{0/-}$ couple (Figure A11B) verified its reversibility while multiple scans through the second reduction showed the accumulation of the solvento complex indicated by the appearance of the reversible $[\text{Re}(\text{4,6-diphenyl-2,2'-bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^{+/0}$ couple, which typically appears at less cathodic potentials than the reduction of the chloro complex.^{8,23} CVs of **1** measured at 195 K showed only the typical EEC mechanism (Figure A12).

Collectively, these observations indicate reductive mechanisms differing from the usual EEC pathway. Scan rate-dependent currents at waves I, II, and III suggest the involvement of one or more chemical steps proposed in Scheme 3.3, and evidence for the assignments are provided by CV (Figures 3.8-3.9, A10-A12), IR-SEC (Figures 3.10-3.11), chemical reduction with sodium amalgam (Figure 3.12), and chemical deprotonation of **2** (Figure A13). The potential of the first reduction and its reversible nature are similar to related complexes,^{11,23,24} allowing assignment of the I/IV couple as $[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]^{0/-}$ (or **2**^{0/-}). Subsequent competing mechanisms can be isolated at the fast and slow scan rate extremes and assignments made by comparison to $[\text{Re}(\text{4,6-diphenyl-2,2'-bpy})(\text{CO})_3\text{Cl}]$ (**RediPh**). At 1 V s^{-1} , peak II is well-resolved from peak III, and the current ratio $i_{\text{II}} / i_{\text{I}}$ of ~ 0.5 is similar to the ratio observed for the irreversible **RediPh**^{-/2-} reduction at -2.1 V vs $\text{Fc}^{+/0}$. This process in the reference compound also shifts positive by $\sim 100 \text{ mV}$ as the scan rate is decreased 100 mV s^{-1} due to its irreversible nature. Peak III is over 150 mV more negative than the **RediPh**^{-/2-} reduction ruling out an analogous assignment to peak III. Therefore, the irreversible peak II is assigned to the reduction of $[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]^-$ followed by fast chloride dissociation to produce **[2-Cl]⁻** (Scheme 3.3) by the standard EEC mechanism through wave II.



Scheme 3.3. Proposed electrochemical mechanisms for reduction of **1**. Species observed by IR-SEC are labeled in red.

The diminished CV current of peak II as the scan rate is slowed suggests that a chemical reaction of modest rate consumes the singly reduced complex, **2**^{•-}, on the timescale of the CV experiment (Figure A10). At 10 mV s⁻¹, peak II is absent showing complete consumption of **2**^{•-} by the alternate pathway. The nature of this pathway is proposed as an ECE mechanism in which the chemical step is a composite net H atom loss (reductive deprotonation) and chloride dissociation to produce the phenolate-ligated **2-OPh**, and characterization of this species will be presented below. As a neutral Re(I) complex with an anionic ligand, **2-OPh**, will have similar electronic structure and reduction potential to **2**, therefore the high *i*_i / *i*_{iv} current ratio (Figure 3.8D) at slow scan rate is attributed to further reduction to **2-OPh**^{•-} after the chemical step.

At fast or slow scan rates, peak III is present without significant changes in potential or current. Its assignment is proposed as the **2-OPh**^{-1/2-} couple, which is a shared final electron transfer step on both pathways, namely EEEEC' and ECEEC'. The shared chemical step indicates that both mechanisms provide **2-OPh**^{•-} prior to the final step with the difference being whether the Cl⁻ dissociation and H atom loss occur after one or two initial reductions of the complex. The **2-OPh**^{-1/2-} couple is most accurately described as an EC process itself because dissociation of the phenolate is proposed (see below).

The proposed reductive mechanism was simulated using Digisim²⁵ software and parameters were adjusted until reasonable models of the data collected at 100 and 1000 mV s⁻¹ were produced (Figure 3.8 and A14). A perfect simulation was not expected for several reasons. The initial state of **2** exists as two isomers (see Paragraph 3.2) with potentially different rates of chemical steps. The low solubility of **2** may cause a more pronounced effect of a slightly sloped baseline since the software models capacitance has a constant value. Finally, the chemical steps of chloride dissociation, net H atom loss (1/2 H₂), and phenolate coordination are modeled as single step with equilibrium *K*_{eq} and a rate determining "*K*", while in reality heterogeneous or homogeneous electron transfers of any putative intermediates are possible

and may contribute to wave distortions. Nevertheless, the model shown in Figure 3.8 captures the experimental properties well, and the EEC portion of the fast scan pathway in Scheme 3.3 ($k_{Ca} = 920 \text{ s}^{-1}$) was simulated in good agreement with the reference compound [(4,6-diphenyl-2,2'-bipyridine)Re(CO)₃Cl] (Figure A15) for which $k_{f_{\text{Cl loss}}} = 900 \text{ s}^{-1}$.

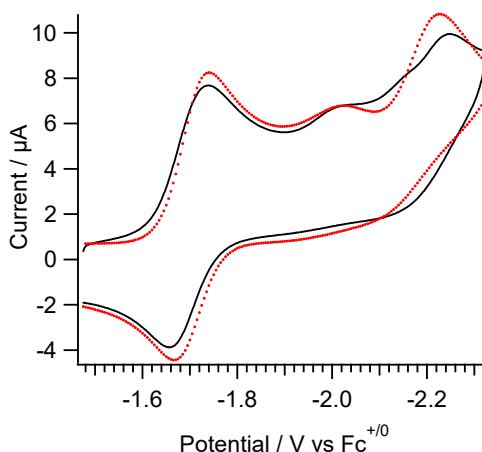


Figure 3.9. Experimental (black) and simulated (red) reductive voltammograms of **1** according to the mechanism in Scheme 2 with $k_{Ca} = 920 \text{ s}^{-1}$ for the $EECaEC'$ pathway, and $k_{Cb} = 0.43 \text{ s}^{-1}$ for the $ECCbEEC'$ pathway. See Figure A14 for additional details.

The simulated mechanism reproduces the scan rate dependent potential and current of peak II. The potential shifts due to the irreversible reaction that drives the equilibrium toward product, and the current is low at slow scan rates due to the competing $ECCbEEC'$ pathway, with $k_{Cb} = 0.43 \text{ s}^{-1}$. Both chemical steps represent the same processes occurring at species differing by an additional reduction, and the extra charge accelerates the reaction rate by over 2000-fold. The simulated mechanism shows that $E_{1/2}$ for the reduction of **2-OPh** along the $ECCbEEC'$ pathway is only 30 mV more negative than that of **2**. The implications of these comparable potentials will be discussed in the context of spectroelectrochemistry and preparative electrolysis.

3.7 Spectroelectrochemistry in a reflective infrared cell, DFT calculations of spectral bands of **2** and Na-Hg reduction

3.7.1 IR-SEC OF **2** IN CD₃CN UNDER Ar

The reductive electrochemical mechanism was investigated by IR-SEC in N₂-saturated CD₃CN where the improved solvent window relative to CH₃CN allows observation of the changes in carbonyl stretching frequencies as well as low energy bands associated with aromatic vibrational modes.

Electrolysis at the onset of the first reduction (-1.5 V vs Fc^{+/0}) resulted in an immediate bleach of the vibrational bands of **2** and the simultaneous appearance of a small band at 2002 cm⁻¹ and a pronounced set of peaks at 2013, 1907, and 1884 cm⁻¹ (Figure 3.10 and Table 3.3). These peaks are convoluted with the bleach of **2**; however, the clean spectrum was obtained by other means discussed below. With reference to **1**, the band at 2002 cm⁻¹ is tentatively assigned to the radical anion, **2**^{•-} which should have additional bands near 1890 and 1970 cm⁻¹.²⁶⁻²⁸ The species with $\nu_{\text{CO}} = 2013, 1907, \text{ and } 1884$ cm⁻¹ is assigned as **2-OPh** along the proposed ECEEC' pathway. The complex is a neutral Re(I) species, and these data are in good agreement with the singly reduced form of **1** which underwent the same proposed reaction. The frequencies of this species are similar to reference data²⁷ of neutral radical solvento complexes, [Re(bpy)(CO)₃(CH₃CN)][•], but this possibility was ruled out by an acid/base reaction of **2** with (iPr)₂NH which cleanly produced **2-OPh** (Figure A13). Moreover, solvento radicals often exhibit two broad IR bands experimentally, and the computed IR frequencies of the corresponding neutral radical solvento complex [Re(pmbpy)(CO)₃(CH₃CN)][•] (2014, 1918, 1899 cm⁻¹) do not fit. The IR spectrum of **2-OPh** in the low energy IR region matches well the DFT computed spectrum of this species (Figure 3.11). Vibrations around 1600 cm⁻¹ can be assigned to C-C stretches of the bpy ligand, the band at 1532 cm⁻¹ is mainly due to C-C stretching modes of the bpy-Ph ligand, two peaks at 1479 cm⁻¹ and 1469 cm⁻¹ are in-plane C-H bending modes of bpy-Ph, and the 1400 cm⁻¹ peak is due to strongly coupled C-C and C-O stretching modes of the phenolate ligand. While overall charge and the oxidation state of the metal center in **2** and **2-OPh** are the same, observed shifts of ligand vibrational modes are consistent with significant distortion of phenyl-bpy ligand due to the binding of the phenolate to the Re metal center. This observation is also consistent with significant shifts of ¹H NMR signals of bpy ligand upon the formation of **2-OPh** (see below).

Stepping the electrolysis potential by only -100 mV to -1.6 V immediately produced a mixture of **2**^{•-}, **2-OPh**, and a new species with $\nu_{\text{CO}} = 1990, 1872, \text{ and } 1858$. The new species, assigned as **2-OPh**^{•-}, is the sole product of electrolysis at -1.7 V, which is very close to $E_{1/2}$ of the **2**^{0/-}

couple in agreement with simulations. Here the parallel between **2-OPh**, **2-OPh^{•-}** and the reductively deprotonated imidazolate complex and its subsequent radical in the literature is noteworthy (Table 3.3).²⁹ The reductive chemistry was further probed by briefly electrolyzing the sample, stopping electrolysis, and continuing IR data collection. These experiments show that **2^{•-}** dissociates chloride and converts to **2-OPh**, without electrolysis verifying the chemical nature of this step.

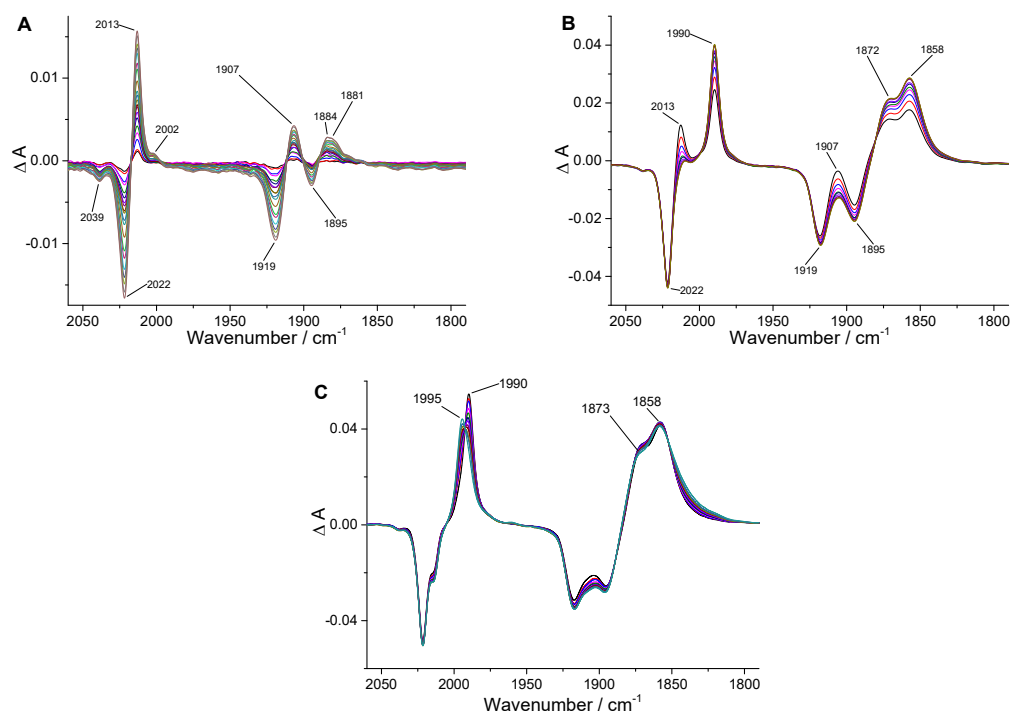


Figure 3.10. Difference IR spectra (expanded metal carbonyl region) measured during controlled potential electrolysis of **2** in CD₃CN containing 0.1 M Bu₄NPF₆ under N₂ atmosphere. Applied potentials: **(A)** −1.5 V vs Fc^{+/0}; **(B)** −1.7 V vs Fc^{+/0} and **(C)** −2.3 V vs Fc^{+/0}.

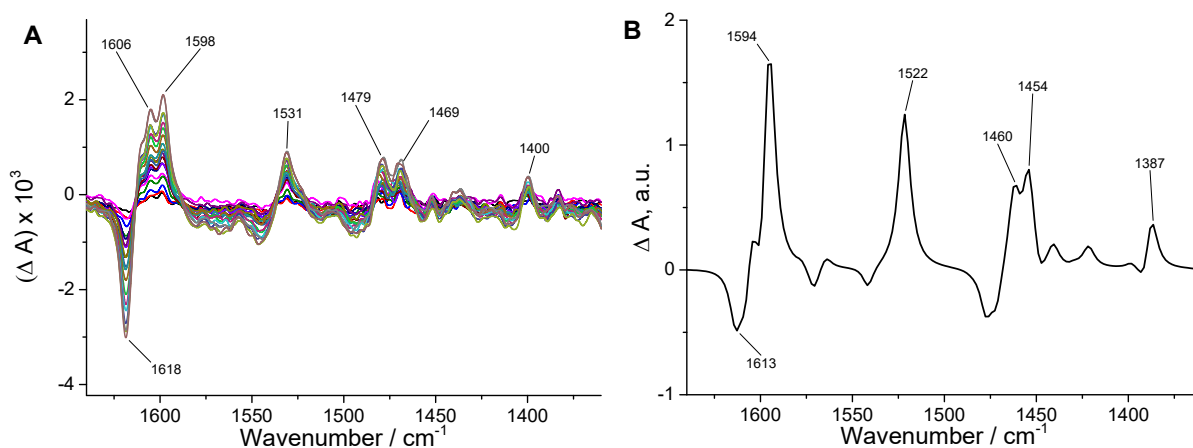


Figure 3.11. (A) Difference IR spectra (expanded ligand region) measured during controlled potential electrolysis of **2** at -1.5 V vs $\text{Fc}^{+/0}$ in CD_3CN containing 0.1 M Bu_4NPF_6 under N_2 atmosphere. **(B)** Difference IR spectrum obtained from subtraction of DFT calculated spectrum of **2-OPh** from calculated spectrum of **2**. Wavenumber axis is scaled by a factor of 0.965 .

Table 3.3. Selected experimental and calculated ν_{CO} vibrational frequencies of **2**, its reduced forms, and related complexes in acetonitrile. All assignments are also made in analogy with species already reported in literature.^{3,8,19}

Complex	$\nu_{\text{CO}} / \text{cm}^{-1}$		
	Experimental	Calculated	
$[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]$ (2)	2022, 1919, 1895	2022, 1921, 1904 2018, 1917, 1895	<i>cis</i> <i>trans</i>
$[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]^{\bullet-}$ (2^{•-})	2002	2001, 1893, 1877 1997, 1889, 1868	<i>cis</i> <i>trans</i>
2-OPh	2013, 1907, 1884	2011, 1903, 1891	
2-OPh^{•-}	1990, 1872, 1858	1989, 1873, 1864	
2-PhO(CH₃CN)²⁻	1995, 1873, 1858	1970, 1874, 1843	<i>cis</i>
2-PhO²⁻		1935, 1844, 1823	<i>cis</i>
$[\text{Re}(\text{bpy})(\text{CO})_3(\text{imidazolate})]$	2018, 1908 ^a		
$[\text{Re}(\text{bpy})(\text{CO})_3(\text{imidazolate})]^{\bullet-}$	1995, 1878 ^a		
2-CH₃CN⁺	2039, 1942, 1926	2036, 1946, 1929	<i>cis</i>
2-CH₃CN[•]	2022, 1912, 1893	2014, 1918, 1899	<i>cis</i>
2-PhO(CH₃CN)^{•-}	2000, 1909, 1876	2005, 1909, 1881	<i>cis</i>

According to CV data, **2-OPh^{•-}** is reduced at -2.26 V (peak III). IR-SEC at this potential, induced small blue shifts in ν_{CO} to 1995, 1873, and 1858 cm^{-1} inconsistent with calculated values of $1960, 1839, 1830 \text{ cm}^{-1}$ for **2-OPh²⁻** with retention of the chelate or of $1935, 1844$, and 1826 cm^{-1} for the 5-coordinate complex **2-PhO²⁻** with a dissociated Re-O bond. Instead, we propose that the product of peak II is the solvento complex **2-PhO(CH₃CN)²⁻** with a dangling phenolate group. While dissociation of the anionic ligand is expected, the affinity for solvent in this highly reduced state is unexpected and has implications regarding catalysis as will be discussed below.

3.7.2 Na-Hg REDUCTION OF **2** IN CH_3CN

Reduction of **2** to **2-OPh**, **2-OPh⁻**, and **2-PhO(CH₃CN)²⁻** was also investigated using sodium amalgam with UV-vis detection (Figure 3.12). The first reaction cleanly produced **2-OPh** as a pale-yellow solution after reaction of the phenol with sodium and substitution of chloride for phenoxide. Reduction to **2-OPh⁻** was indicated by intense structured bands at 500 nm and a broad band at 650 nm (the complex is dark purple). A final change indicated by a shift in isosbestic points and characterized by growth of radical absorptions was observed for the reduction to **2-PhO(CH₃CN)²⁻**. Both **2-OPh⁻** and **2-PhO(CH₃CN)²⁻** are expected to have

ligand radical character, and similar transitions are observed for both species. Identities of each step were confirmed by stopping the experiment at appropriate stages and transferring the sample to a sealed IR cell under an inert atmosphere. The ν_{CO} were identical to those obtained during electrolysis. **2-PhO(CH₃CN)²⁻** is strongly reducing and slowly oxidized back to **2-OPh⁻**. Separately, **2-OPh⁻** was oxidized to **2-OPh** by exposure to air.

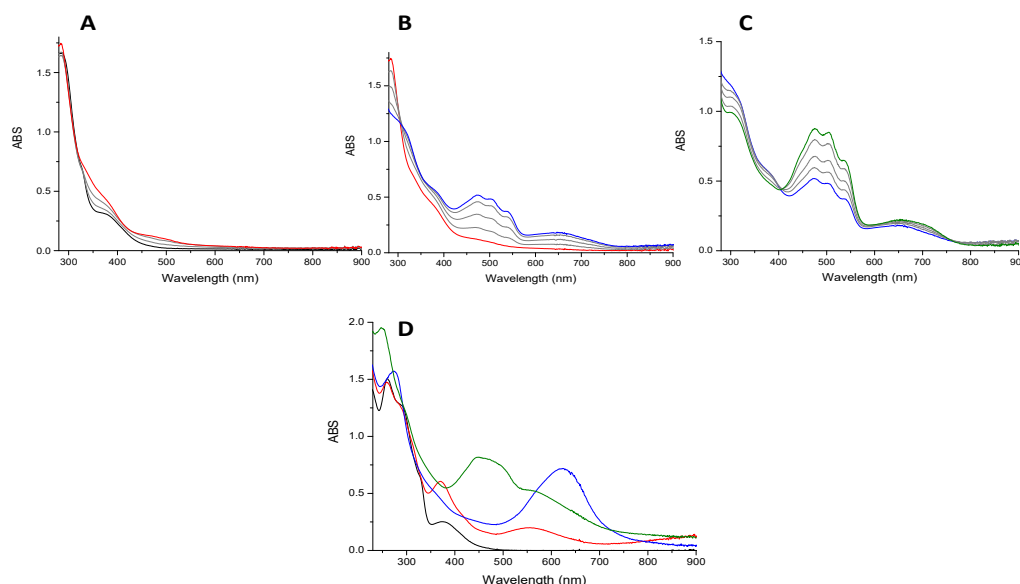


Figure 3.12. Sodium amalgam reduction of **2** (A-C) and [Re(4,6-diphenyl-2,2'-bpy)(CO)₃Cl] (D). The stepwise reduction of **2** produces **2-OPh** (A, red), **2-OPh^{•-}** (B, blue), and **2-PhO(CH₃CN)²⁻** (C, green). The species is a ligand radical with a dissociated phenolate. In (D), the starting complex is sequentially reduced to [Re(4,6-diphenyl-2,2'-bpy)(CO)₃Cl]⁻ (red), [Re(4,6-diphenyl-2,2'-bpy)(CO)₃]⁻ (blue), and [Re(4,6-diphenyl-2,2'-bpy)(CO)₃]²⁻ (green).

The IR and amalgam data support the proposed “slow scan” EECEC’ pathway of Scheme 3.3 in which **2^{•-}** undergoes reductive deprotonation and dissociation of Cl⁻ to produce **2-OPh**. The mechanism of reductive deprotonation is unclear, and is counterintuitive because a reduced complex should be more basic, not more acidic, but there are now several precedents of this reaction in the literature.^{8,3,30,31} A theoretical approach to understanding the mechanism in Ru and Re complexes proposed a pathway involving protonation of the bpy ligand at carbon followed by disproportionation with net loss of ½ H₂.^{7,32} In agreement with loss of H₂ and not H⁺, electrolysis of **2** under Ar produced ~0.45 equiv. of H₂.

To investigate the mechanism and any role of Cl⁻ in the reductive deprotonation, CV’s and IR-SEC of the solvento complex, **2-CH₃CN⁺** were measured. The CV (Figure A16) shows a reversible **2-CH₃CN^{+/0}** couple at -1.48 V, and the **2-OPh^{0/-}** couple expected at -1.65 V

confirming formation of the chelate in the absence of chloride. The IR-SEC (Figure A17) confirmed the existence of the neutral solvent radical **2-CH₃CN**, and interestingly showed that this species is present at a much higher concentration than **2-Cl^{•-}** upon initial reduction, although **2-OPh** is also present immediately. This observation suggests that the rate of reductive deprotonation is attenuated by the less cathodic standard potential for the solvento complex, and may support the previously proposed pathway involving ligand-based protonations. Stepping the potential resulted in the presence of a minor species with red-shifted ν_{CO} consistent with deprotonation prior to coordination, i.e. **2-PhO(CH₃CN)⁻** (2000, 1909, 1876 cm⁻¹) although this species was observed as a mixture and no clear CV wave was isolated. Changes during further reduction were identical to the experiment starting with **2**. During reduction of **2**, the immediate deprotonated species with a dangling phenolate was not observed by IR. Therefore, we cannot determine whether formation of the phenolate or chloride dissociation is rate limiting; however, it is clear that a combination of H₂ loss and the chelate effect of **2-OPh** destabilize the singly reduced **2^{•-}**, which is observed only in small concentrations by IR-SEC. The IR data also confirm that **2-OPh** is reduced at a very similar potential to **2**, which is logical considering their identities as neutral Re(I) complexes. The final reduction observed by CV (III) produces **2-PhO(CH₃CN)²⁻**. This couple is observed at fast and slow rates confirming that the chemical step of the fast scan EECEC' is a composite Cl⁻ dissociation, CH₃CN binding, and reductive deprotonation.

In summary, the electrochemical mechanisms as observed by CV and characterized by IR-SEC and sodium reduction occurs by competing EECEC' (waves I, II, C, III, C'; isolated at fast scans) and ECEEC' (I, C, I', III, C'; isolated at slow scans) pathways with the chemical steps in the slow limit being a composite of reductive deprotonation, chloride dissociation, and oxygen coordination to the metal center. Importantly, the I/IV couple of **2^{0/-}** includes the **2-OPh^{0/-}** couple at slow scan rates and after a full three-electron sweep, peak IV is the reoxidation of the **2-OPh^{•-}**, not **2^{•-}**.

3.8 Isolation of complex **2-OPh**

As discussed in the Introduction, one hypothesis of this work was that a simplified system with a single pendent -OH group could confirm the validity of the mechanism shown in Scheme 3.1 by obtaining additional characterization of the species assigned as **2-OPh**. The IR-SEC data, supported by DFT calculations, suggest the presence of this intermediate after reduction of **2** similarly to the reduction of **1**. As a neutral Re(I) complex, **2-OPh** should be sufficiently stable for preparation by electrolysis and analysis by NMR.

In order to accomplish this goal, we took advantage of the clean formation of **2-OPh** as ascertained by IR-SEC and increased the reaction volume to the preparative scale. Upon bulk electrolysis in CH₃CN at the first reduction potential in an N₂-filled glovebox, the solution changed color from yellow to dark green and the flow of current ceased. It is known from the amalgam experiment that the dark green solution is an indication of slight over reduction. Once the electrolysis was completed, an IR spectrum showed the majority presence of **2-OPh** with a small amount of **2-OPh^{•-}** (Figure A18). The CV recorded after bulk electrolysis also confirmed completion of the reaction (Figure 3.13A). The second reduction peak, assigned as the irreversible reduction of [Re(pmbpy)(CO)₃Cl]⁻ is absent, and the **1-OPh^{0/-}** couple is observed nearly identical to the **1^{0/-}**-couple. The solvent was removed under reduced pressure to afford a solid, which was poorly soluble in CH₃CN, but sufficiently soluble in d₆-DMSO for NMR characterization.

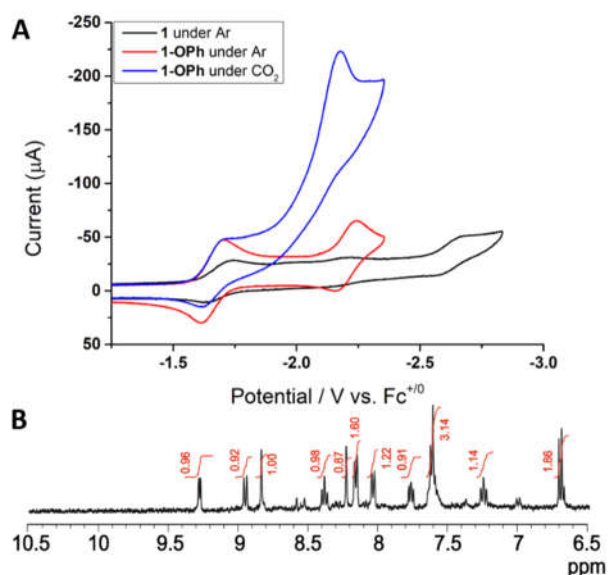


Figure 3.13. (A) CVs of **2** in acetonitrile/Bu₄NPF₆ before and after controlled potential electrolysis (CPE at -1.8 V vs. $\text{Fc}^{+/0}$) at 100 mV s^{-1} . The working electrode was a 5 mm glassy carbon electrode. (B) ¹H-NMR spectra of **2-OPh** in d₆-DMSO.

The ¹H NMR spectrum of the resultant product **2-OPh** (Figure 3.13B) reveals the absence of the -OH resonances and distinct changes in the chemical shifts of the protons of the phenolate ring (see Appendix for additional data, Figures A19-A22). Chemical shifts of the protons of the bipyridine rings also shift significantly, presumably due to the strained puckered conformation of the tridentate chelate relative to the planar orientation in **2**. The carbonyl region of the ¹³C spectrum (Figure A21) shows three CO resonances unique relative to those of **2**. A new and

distinct resonance is observed at 170 ppm in a frequency region where ^{13}C spectrum of **2** has no signals. This new resonance is tentatively assigned to the quaternary carbon atom connected to the phenolate oxygen which now coordinates the rhenium metal. Its appearance at 170 ppm is consistent with $\text{C}=\text{O}$ character of the phenolate resonance structure. Another significant difference from compound **2** is the absence of signals below 118.50 ppm due to the different chemical environment experienced by CH groups in the phenolate ring of **2-OPh**.

3.9 Reactivity of **2** toward CO_2

Complex **2** was evaluated as homogeneous electrocatalyst for CO_2 reduction in CH_3CN by CV and bulk electrolysis. In the presence of CO_2 , the CVs show a catalytic current beginning at wave II and an increase in slope at wave III (Figure 3.14). The solution of **2-OPh** prepared *in-situ* shows similar behavior in Figure 3.14. The nature of this current enhancement was investigated at various scan rates. Equation 1 is derived for the condition of kinetic control with no substrate consumption (i.e. the rate of consumption is countered by the rate of diffusion), where the catalytic current is "S-shaped" and i_c is read as the plateau current.³³ According to equation 1, where $n = 2$, F is Faraday's constant, A is the electrode area, D is the diffusion coefficient, k is the rate constant, and a is the reaction order with respect to CO_2 , an electrocatalytic current should be scan-rate independent provided the necessary conditions are met.

$$i_c = nFA[\text{cat}]\sqrt{D(k)[\text{CO}_2]^a} \quad (1)$$

Data in Figure 3.15, panel B show that the additional current observed under CO_2 is proportional to $v^{1/2}$ over the entire range of data collection, suggesting that the electrochemical currents here are controlled by electron transfers (equation 2), and that catalysis is slow on the CV timescale. For comparison, the same experiment was performed on the reference compound, [(4,6-diphenyl-2,2'-bipyridine) $\text{Re}(\text{CO})_3\text{Cl}$], which shows a catalytic current that becomes scan rate-independent above 2 V s^{-1} (Figure A23). The total current at II_{CO_2} and III_{CO_2} relative to peak I is a maximum of 4 at slow scan rates but converges to 3 as the sweep rate exceeds 250 mV s^{-1} suggesting that CO_2 may bind to the metal in a reduced state, but a competing reaction is limiting the turnover frequency.

$$i_p = 0.4463FA[\text{cat}]\sqrt{\frac{FvD}{RT}} \quad (2)$$

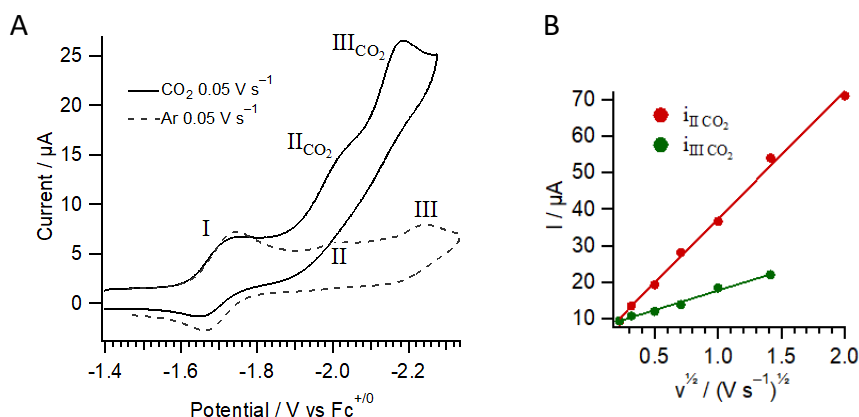
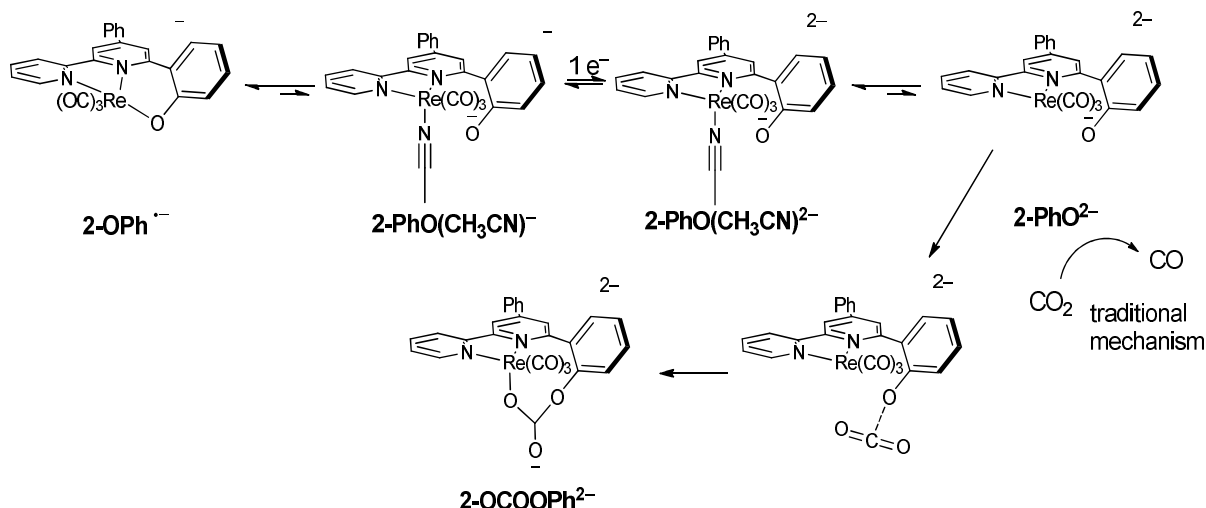


Figure 3.14. (A) CV's of 0.4 mM **2** in Ar or CO₂-saturated CH₃CN with 0.1 M Bu₄NPF₆ at a glassy carbon electrode, scan rate = 50 mV s⁻¹. (B) Current at peaks II_{CO₂} and III_{CO₂}.

Bulk electrolysis in CO₂-saturated CH₃CN was performed to examine the products of catalysis. The potential was cathodic of peak II or at peak III, and experiments were performed in dry solvent or with 5% Brønsted acids (water, methanol and phenol). Table 3.4 summarizes results obtained by these CPE experiments. Fewer than 3 turnovers were obtained in dry solvent or in the presence of water or methanol. An experiment in the presence of phenol performed slightly better, yet turnovers were underwhelming. Electrolysis at wave III (−2.3 V vs Fc⁺⁰) yielded 9 turnovers; however, the catalyst ceased activity faster at this strongly reducing potential.

The catalytic reactivity is interpreted according to Scheme 3.4. When **2-OPh** is reduced to **2-OPh^{•−}**, a small amount of the solvento complex, **2-PhO(CH₃CN)^{•−}** may exist in equilibrium. At the potential of the **2-OPh^{0/−}** couple, the solvento complex will be reduced immediately to the dianion, **2-PhO(CH₃CN)^{2−}**. Evidence for this reaction was found during chemical reduction in which samples partially reduced from **2-OPh** to **2-OPh^{•−}** showed small shoulders assignable to **2-PhO(CH₃CN)^{2−}**. This equilibrium is uphill by 51.7 kJ mol⁻¹ and inhibits catalysis at peak II. Direct reduction of **2-OPh^{•−}** at peak III produces **2-PhO(CH₃CN)^{2−}**, which explains the increased catalytic current at peak III; however, overall catalysis is inefficient for two reasons: (1) the strong affinity of the dianion for solvent, and (2) reactivity of CO₂ at the oxyanion. The latter is predicted by the Mulliken and Hirshfeld atomic charges of **2-PhO^{2−}** which predict that the phenolate is the most nucleophilic site. The reaction with CO₂ is mildly endergonic, but the rearrangement to the chelating carbonate **2-OCOOPh^{2−}** is exergonic by 21.2 kJ mol⁻¹. Identification of the precise pathway for CO production is computationally uncertain; however, we propose that CO₂ which interacts with the Re center of **2-PhO^{2−}** may convert to CO via standard pathways.³⁴ The **2-OCOOPh^{2−}** may release CO; however, this species is likely stable and may reduce catalytic rates. The “slow one-electron

pathway³⁴ is also characterized by a intermolecular Re-O bond (which is stronger than Re-C bond), but **2-OCOOPh**²⁻ displays an entropically stabilized intramolecular Re-O bond. The IR-SEC of **2** under CO₂ atmosphere produces spectra very similar to those observed under N₂, indicating that the steady state concentration of any CO₂ adduct intermediate is below the detection limit of the experiment.



Scheme 3.4. Proposed electrochemical mechanisms for reduction of **1** in the presence of CO₂.

Catalytic performances of **1** with respect to **2** are only marginally better, yielding a TON_{CO} of 14 (Table 3.1), whereas the presence of three OH groups in meta and para phenolic positions decrease the catalytic activity towards CO₂ reduction,⁸ thus confirming that despite the close proximity of the OH group to the metal center in which chelation of a carbonate can be inhibitive, the close metal-OH proximity also has beneficial effects. Similar proximity conclusions were drawn by Bocarsly on **Mn-10H**, which showed enhanced reactivity attributed to better hydrogen bonding compared to related congeners with distal OH groups.⁴ Mn(bpy)(CO)₃Br reported by Deronzier³⁵ displayed TON_{CO} of 13, while **Mn-10H** showed a reduced TON_{CO} value of 2.7.⁹ Conversely, our **Mn-20H**³ yielded higher TON_{CO} (28) together with formate production (TON_{HCOO}⁻ 12). Interestingly their predicted catalytic mechanism involves the formation of a hydrogen bonding between the phenolic proton and the Mn-bound CO₂ molecule, followed by facile proton-assisted C-O bond cleavage of the CO₂ to form CO.^{4,9} Contrary, our investigations on **Mn-20H** show that the reductive deprotonation of phenolic OH takes place before CO₂ binding to the Mn center, similar to complexes **1** and **2** in the present study. Meanwhile the effect of second coordination sphere³⁶ has been investigated for a Mn complex, Mn^I([(MeO)₂Ph]₂bpy)(CO)₃(CH₃CN)}(OTf), reported by Rochford et al.,³⁷ where

$[(\text{MeO})_2\text{Ph}]_2\text{bpy}$ = 6,6'-bis(2,6-dimethoxyphenyl)-2,2'-bipyridine. Together with the steric influence preventing dimerization,³⁸ the four pendent methoxy groups exhibit weak hydrogen bonding interaction, playing a significant role during CO₂ reduction. Complexes **1**, **2** and **Mn-2OH** prevent the dimerization too, by forming the intramolecular chelating M-O (M = Re, Mn) bond, but the resulting Re-O bond appears to be strong enough to limit the catalytic activity towards CO₂ reduction or formation of a carbonate may also limit catalysis. On the other hand, Mn-based catalysts provide better TON values than their precious metal congeners, probably because greater strain in the Mn-O bond leads to less stability of the intermediate.

Table 3.4. Bulk electrolysis data of 0.5 mM solution of **1** in acetonitrile.

E / V^a	Time / min ^b	Acid ^c	TON _{CO}	FE _{CO} %
-2.0	75	–	1.4	100
-2.0	160	H ₂ O	3	98
-2.0	60	CH ₃ OH	1.2	100
-2.0	150	phenol	4	104
-2.3	100	phenol	9	102

^a V vs Fc^{+/0}. ^b Time before activity ceased. ^c 5% by volume.

3.10 Concluding remarks

This study provides an intimate understanding of the role of the local proton source on Re-bpy type electrocatalysts. The electrochemical behavior of *fac*-Re(pmbpy)(CO)₃Cl (**2**) has been deeply investigated. NMR data suggest the existence of two different isomers, **2-cis** characterized by the proximity of Cl and OH moieties, and **2-trans**, where Cl and OH are oriented *trans* to each other. DFT calculations confirmed that a non-negligible energy barrier separates the two isomers, and reveal two transition states, **TS2'** and **TS2''**, with activation energy of 75.5 and 95.0 kJ mol⁻¹, respectively. By experimental evidence we confirmed the tendency, in analogy with the proposed mechanism for **1**, toward the formation of **2-OPh** bearing a Re-O intramolecular bond. **2-OPh** has been synthesized by controlled potential electrolysis and characterized by ¹H NMR spectroscopy which revealed the absence of the OH resonances and distinct changes in the chemical shifts of the protons of the phenolate and bpy rings when compared to **2** due to coordination of the phenolate and a puckered distortion of the bpy backbone. The IR spectrum of isolated **2-OPh** exhibits three new CO stretching bands

(2013, 1907, 1884 cm^{-1}) which exactly overlap with the bands obtained after the first 1e^- reduction during IR-SEC, in agreement with DFT calculations. The CV recorded after bulk electrolysis added further evidence of the formation of **1-OPh**, and confirmed competition between EECEC' and ECEEC' pathways for the reduction of **2**. After electrolysis, the peak assigned to the irreversible reduction of **2** $^{\bullet-}$, is absent, and the **2-OPh** $^{0/-}$ couple is observed at a potential nearly identical to the **2** $^{0/-}$ redox couple. Similar intermediates, as depicted in Scheme 3.1 in the Introduction were already proposed to be formed during electrochemical reductions of the closely related **1** and **Mn-2OH**. The electrocatalytic properties of these two complexes were deeply investigated in current and previous works. As we previously concluded, the effect of the local proton source is more beneficial in terms of electrocatalytic turnovers by Mn compared to Re, and also changes the selectivity for CO and formate. Previous conclusions are consistent with the low CO turnover numbers of **2** and the absence of formate as reduction product. We can conclude that a reductive deprotonation of **2** affords **2-OPh**, evidencing the capability of the pendent OH group to behave as a chelating ligand. Two subsequent reductions are needed to provide the active catalyst; however, a small equilibrium dissociation of the Re-O bond after the first reduction provides a minor pathway for catalysis at a lower overpotential. The active catalyst is a dianion with a dangling phenolate that strongly favors solvent coordination over a five-coordinate intermediate. This equilibrium disfavors catalysis, and calculations suggest that the oxyanion is more nucleophilic toward CO_2 than the Re(0) center. Formation of a stable carbonate and metal chelation lead to diminished CO_2 interaction with the reduced complexes consistent with small CV catalytic currents and low TON_{CO} under CO_2 . The mechanistic characterization and comparison to related complexes highlight the importance of considering deleterious reactivity by coordination or ligand-based reactivity of CO_2 when designing catalysts with pendent acid/base functionality in the second coordination sphere; however, the greater reactivity of the same ligand set on Mn is a promising observation considering that the $(\text{L})\text{M}(\text{CO})_3\text{X}$ motif is one of few examples where first and third row metal congeners with the same ligand set undergo similar reactions.

3.11 Experimental section

General. All reagents for synthesis were purchased from Sigma Aldrich or Alfa Aesar and used without further purification. Anhydrous toluene for synthesis was stored over activated molecular sieves under Ar. Acetonitrile for electrochemical experiments was dried on a solvent drying tower by passage through activated alumina then stored in a glovebox or transferred directly to electrochemical cells using standard Schlenk techniques. Alternatively, acetonitrile was freshly distilled over calcium hydride. NMR spectra were recorded on a 400 MHz Bruker

Avance spectrometer (^1H operating frequency 400 MHz) at 25°C or, alternatively on a JEOL ECP 400 FT-NMR spectrometer (^1H operating frequency 400 MHz) at 25°C. ^{13}C spectra of **2** and **2-OPh** have been recorded on a JEOL ECZ 600 R. ^1H and ^{13}C chemical shifts are reported in ppm relative to TMS ($\delta = 0$) and referenced against solvent residual peaks. UV-vis spectra were measured on an Agilent 8453 spectrophotometer. Electrospray mass spectra (ESI-MS) were measured using a Thermo Scientific Q Exactive high resolution mass spectrometer. Samples **2** and **2-CH₃CN⁺** for microanalysis were dried in vacuum to constant weight (20°C, ca. 0.1 Torr). Elemental analysis (C, H, N) was performed in-house with a Fisons instrument 1108 CHNS-O Elemental Analyzer.

Synthesis of *fac*-Re(pdbpy)(CO)₃Cl (1**).** [Re(CO)₅Cl] (0.500 mmol, 1 equiv) and pdbpy (0.501 mmol, 1.01 eq) were refluxed for 3 hours in anhydrous toluene (20 mL) while stirring. Alternatively, reaction proceeded in a sealed flask for microwave reactor and evolved at 130 °C for an hour. After cooling of the reaction mixture to room temperature, petroleum ether was added to precipitate the yellow product, which was then centrifuged, filtered and washed once with cold diethyl ether (yield 75 %).

^1H -NMR: [400 MHz, (CD₃)₂SO]: δ /ppm 9.60 (s, 1H), 9.56 (s, 1H), 9.05 (t, J = 8.8 Hz, 2H), 9.01 (s, 1H), 8.35 (t, J = 7.4 Hz, 1H), 8.11 (d, J = 7.8 Hz, 2H), 7.85 (s, 1H), 7.73 (t, J = 6.3 Hz, 1H), 7.60 (m, 3H), 7.15 (t, J = 7.5 Hz, 1H), 6.45 (t, J = 7.5 Hz, 2H).

^{13}C -NMR: [400 MHz, (CD₃)₂SO]: δ /ppm = 198.87, 194.61, 191.23, 160.25, 157.47, 156.99, 156.70, 156.58, 153.00, 150.25, 140.24, 135.61, 131.10, 129.89, 129.46, 128.77, 128.19, 126.73, 125.46, 120.09, 118.03, 107.35, 106.64.

IR (CH₃CN, $\tilde{\nu}_{\text{CO}}$ / cm⁻¹): 2023, 1918, 1901.

Anal. Calcd. (%) for C₂₅H₁₆ClN₂O₅Re: C (38.85) H (2.09) N (3.62). Found: C (39.09) H (2.16) N (3.50)

Synthesis of *fac*-Re(pmbpy)(CO)₃Cl (2**).** Complex **2** was prepared according to the typical literature procedure. [Re(CO)₅Cl] (0.500 mmol, 1 equiv) and the pmbpy ligand (0.501 mmol, 1.01 equiv) were dissolved in anhydrous toluene (20 mL) in a sealed flask and heated in a Biotage microwave reactor at a constant temperature of 130°C for one hour. After cooling of the reaction mixture to room temperature, petroleum ether was added to precipitate the yellow product, which was then centrifuged, filtered, and washed once with cold diethyl ether (yield: 92%).

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): 9.96 s– 9.89 s (1H), 9.03–9.08 (m, 2H), 9.00 (s, 1H), 8.37 (t, J = 8 Hz, 1H), 8.12 – 8.17 (m, 2H), 8.05 d – 7.96 d (J = 1.8 Hz, 1H), 7.59 – 7.62 (m, 3H), 7.76 – 7.98 (m, 1H), 7.30 – 7.37 (m, 2H), 7.04 (t, J = 7.0 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H).

^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$), carbonyl signals: 198.67, 198.50, 194.67, 193.85, 192.11, 190.78; 162.18 (Cq), 161.55 (Cq), 157.43 (Cq), 157.03 (Cq), 156.65 (Cq), 155.34 (Cq), 155.21 (Cq), 153.13 (-CH), 150.72 (Cq), 149.84 (Cq), 140.36 (-CH), 140.31 (-CH), 135.56 (Cq), 135.41 (Cq), 131.81 (-CH), 131.79 (-CH), 131.68(-CH), 131.33 (-CH), 131.25 (-CH), 131.19 (-CH), 129.91 (-CH), 129.84 (-CH), 129.43 (-CH), 129.13, 128.75 (-CH), 128.35 (-CH), 128.23 (-CH), 128.14 (-CH), 127.66 (-CH), 126.25 (-CH), 125.96 (-CH), 125.85 (-CH), 125.74 (-CH), 125.69 (-CH), 120.49 (-CH), 120.42 (-CH), 119.58 (-CH), 118.96 (-CH), 117.06 (-CH), 116.22 (-CH).

UV-vis (CH_3CN λ_{max}): 379 nm. IR (CH_3CN , $\tilde{\nu}_{\text{CO}}$ / cm^{-1}): 2022, 1919, 1895 cm^{-1} . HRMS (ESI+): m/z calcd for $[\text{M}-\text{Cl}+\text{Na}]^+$ 653.0254, found 653.0223; $[\text{M}-\text{Cl}+\text{CH}_3\text{CN}]^+$ 636.0933, found 636.0910; $[\text{M}-\text{OH}]^+$ 614.0407, found 614.0620. Anal. calcd. (%) for $\text{C}_{25}\text{H}_{16}\text{ClN}_2\text{O}_4\text{Re}$: C (47.66), H (2.56), N (4.45). Found: C (47.02), H (3.2), N (4.45).

Synthesis of *fac*-[Re(pmbpy)(CO)₃(CH₃CN)](PF₆). The acetonitrile complex was prepared by heating complex **2** (7 mmol, 1 equiv) and AgPF₆ (7 mmol, 1 equiv) in anhydrous acetonitrile (25 mL) at reflux overnight. After cooling of the mixture, it was filtered through celite to remove AgCl and the solution was then evaporated to dryness (yield: 60%).

^1H NMR (400 MHz, CD_3CN): 9.08 d (J = 5.1 Hz, 1H), 8.70–8.72 m (2H), 8.32 t (J = 7.8 Hz, 1H), 8.03 d (J = 2.0 Hz, 1H), 7.97–7.99 m (2H), 7.73 td (^1J = 5.4 Hz, ^2J = 2.5 Hz, 1H), 7.60–7.63 m (2H), 7.54 d (J = 3.2 Hz, 1H), 7.45 t (J = 7.3 Hz, 1H), 7.35 d (J = 7.6 Hz, 1H), 7.05–7.12 m (2H).

^{13}C NMR (100 MHz, CD_3CN) carbonyl signals: 194.09, 189.85, 184.17; 157.34 (Cq), 156.84 (Cq), 154.36 (Cq), 153.92 (-CH), 152.07 (Cq), 151.71 (Cq), 140.63 (-CH), 135.28 (Cq), 132.03 (-CH), 131.13 (-CH), 130.32 (-CH), 129.59 (-CH), 127.84 (-CH), 126.85 (-CH), 125.14 (-CH), 122.46 (Cq), 120.81 (-CH), 120.36 (-CH), 120.13 (-CH), 117.45 (-CH), 116.68 (-CH), 116.27 (-CH). (Figures S9–10). Anal. calcd. (%) for $\text{C}_{27}\text{H}_{19}\text{F}_6\text{N}_3\text{O}_4\text{PRe}$: C (41.54), H (2.45), N (5.38). Found: C (40.86), H (3.16) N (5.22).

IR (CH_3CN , ν_{CO} / cm^{-1}): 2039, 1942, 1927 cm^{-1}

Synthesis of 2-O^{Ph}. In two-compartment electrochemical cell inside an N₂-filled glovebox, a 0.5 mM solution of **2** in CH_3CN containing 0.035 mM Bu₄NPF₆ was subject to controlled

potential electrolysis at -1.7 V vs $\text{Fc}^{+/0}$ using a Pt mesh electrode. After complete consumption of **1** as judged by CV, the solution was evaporated to dryness. The resultant solid was dissolved in d_6 -DMSO and analyzed by NMR in a J-Young tube. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): 9.28 d ($J = 5.1$ Hz, 1H), 8.96 d ($J = 8.6$ Hz, 1H), 8.84 s (1H), 8.39 t ($J = 8.2$ Hz, 1H), 8.24 s (1H), 8.17 d ($J = 8.1$ Hz, 2H), 8.05 d ($J = 8.1$ Hz, 1H), 7.77 t ($J = 6.7$ Hz, 1H), 7.57-7.64 m (3H), 7.26 t ($J = 7.5$ Hz, 1H), 6.71 d, ($J = 7.5$ Hz, 2H). ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$): 199.50, 197.80, 193.68, 171.64 (Cq), 157.87 (Cq), 157.70 (Cq), 155.41 (Cq), 153.64 (Cq), 151.53 (-CH), 140.44 (-CH), 136.05 (Cq), 133.56 (-CH), 131.05 (-CH), 130.34 (-CH), 129.72 (-CH), 129.44 (-CH), 126.75 (-CH), 124.83 (-CH), 120.87 (-CH), 120.27 (Cq), 119.55 (-CH), 119.45 (-CH), 118.50 (-CH). IR (CH_3CN , ν_{CO} / cm^{-1}): 2013, 1907, 1884 cm^{-1} .

Electrochemistry. Cyclic voltammetry (CV) and controlled potential electrolysis (CPE) experiments were performed using a BASi Epsilon potentiostat. Data were collected in dry acetonitrile with tetrabutylammonium hexafluorophosphate Bu_4NPF_6 (0.1 M) as the supporting electrolyte. CVs were collected in a single-compartment cell with a three-electrode configuration using a glassy carbon (GC) working electrode ($d=3$ mm), a Pt counter electrode, and a solid-state Ag/AgCl reference electrode (eDAQ) or a silver wire pseudo reference. CVs at 195 K were collected in a sealed cell submerged in a dry ice/acetone bath. All potentials are reported relative to the ferrocenium/ferrocene couple ($\text{Fc}^{+/0}$). Solutions were saturated with Ar or CO_2 that were passed through an acetonitrile pre-bubbler to maintain a constant concentration of analyte. CPE experiments under N_2 or CO_2 were performed in two-compartment cells where anodic and cathodic compartments were separated by a glass frit. Preparative electrolysis experiments were carried out in an N_2 -filled glovebox, and Pt mesh was used as the working electrode or counter electrode. CPE under CO_2 was performed in a 30 ml cell using a glassy carbon rod working electrode and an aqueous SCE reference electrode in the cathodic compartment and a Pt wire counter electrode in the second compartment. Some experiments under CO_2 were performed in the presence of water or methanol (5% by volume). A controlled flow of CO_2 (50 mL min^{-1}), measured just before arrival into the cell, was maintained during the CPE measurements by means of a Smart Trak 100 (Sierra) flow controller. The cell was airtight and equipped with a bubbler that maintained the inner atmosphere but avoided gas overpressure.

Quantitative analysis of CO_2 reduction products. CO was detected and quantified using an Agilent 490 Micro GC gas chromatograph equipped with a CP-Molsieve 5 Å columns, which was kept at 85°C and at a pressure of 21 psi, with a thermal conductivity detector. The carrier gas was He. The backflush vent option time was set to 4.5 s. A second module equipped with a CP-Molsieve 5 Å column using Ar as carrier gas was used for H_2 analysis. The gas inside the

measurement cell was sampled for 30 s every three minutes to fill the Micro GC 10 μ L sample loop, and eventually 500 nL were injected into the column for the analyses. We used Ar, He, CO₂ pure gases (>99.9995%) from Sapio for the operation, and two different certified standard concentrations of CO and H₂ in Ar matrix (Rivoira) for calibration. Detection limits for CO and H₂ were 1 ppmv and 0.5 ppmv, respectively. Formate production was quantitatively evaluated using NMR spectroscopy.

Spectroelectrochemistry. A custom reflective infrared spectroelectrochemical (IR-SEC) cell equipped with boron-doped diamond working, platinum counter, and solid-state leakless miniature Ag/AgCl reference (EDAQ) electrodes was attached to a Fourier transform infrared (FTIR) spectrometer (Bruker, IFS 66/S) using a VeeMAX III Variable Angle Specular Reflectance Accessory (Pike Technologies), and the IR absorption changes were monitored following application of fixed potentials. IR-SEC of **1** has been performed in a OTTLE cell,³⁹ analogously as previously reported.³

Na-Hg reduction. Sodium amalgam reduction was performed in a homemade vessel equipped with a quartz spectrophotometric cell separated by a glass frit from a second compartment containing 0.5 % Na in Hg. Samples were prepared under high vacuum with vacuum distilled CH₃CN and were reduced gradually by introducing small portions to the amalgam chamber under vacuum.

DFT calculations. Gaussian 16 Rev. B.01 and Gaussian 09 Rev. D.01 packages⁴⁰ were adopted for all DFT calculations. Solvent effects were taken in account by the conductor-like polarizable continuum model (CPCM)^{41,42} with acetonitrile as solvent. No constraints were imposed during geometry optimizations. The B3LYP functional,^{43,44} with the optimized def2-TZVP basis set for Re and Cl and the def2-SVP basis set^{45,46} for all other atoms was employed. The D3 version of Grimme's dispersion method was applied adopting the Becke–Johnson damping scheme.⁴⁷ Gibbs free energies were determined using thermal corrections for entropy and enthalpy at 298 K to the electronic energies. In these calculations, the computed harmonic frequencies were scaled by 0.965 to account for anharmonicity. For radical anions, unrestricted Kohn–Sham formalism was adopted. The nature of all stationary points was confirmed by normal-mode analysis.

Single-Crystal X-ray diffraction. Data for compound **1** have been collected on a Gemini R Ultra diffractometer using graphite-monochromated Mo K α radiation ($k = 0.71073$ Å) with the ω -scan method. Cell parameters were retrieved using CrysAlisPro⁴⁸ software, and the same program has been used for performing data reduction, with corrections for Lorentz and

polarizing effects. Scaling and absorption corrections were applied by the CrysAlisPro multi-scan technique. The structure was solved by Patterson Function using Sir2014⁴⁹ and refined with full-matrix least-squares on F^2 using SHELXL⁵⁰. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were calculated and riding on the corresponding atom. Structural illustrations have been drawn with Mercury.⁵¹ The crystallographic data for **1** have been deposited within the Cambridge Crystallographic Data Centre as supplementary publications under the CCDC number 1857181. This information can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cifcode CCDC. The crystallographic data for **2** have been deposited within the Cambridge Crystallographic Data Centre (CCDC) as supplementary publications. This information can be obtained free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

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CHAPTER 4. Electronic effects of substituents on *fac*-M(bpy-R)(CO)₃ (M = Mn, Re) complexes for homogeneous CO₂ electroreduction

4.1 Introduction

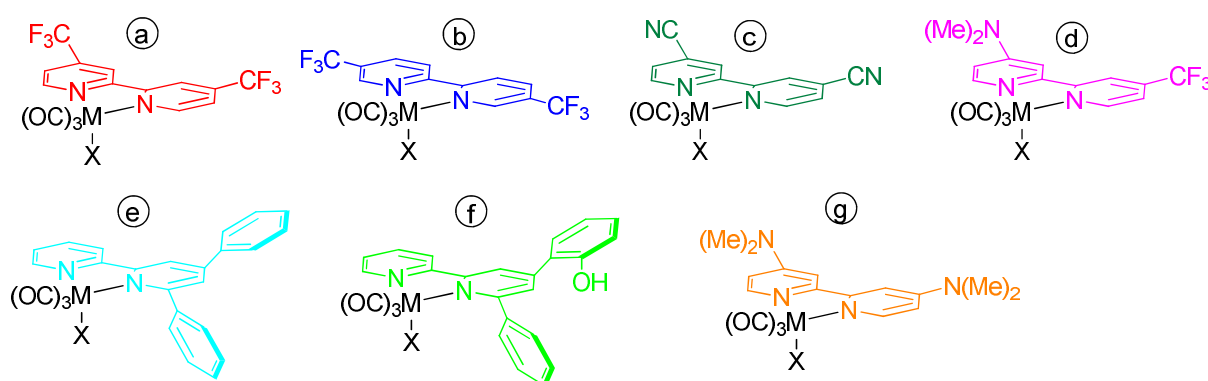
As a natural extension of the concept of the local proton source on Re and Mn bipyridine complexes, which has been extensively investigated in Chapter 3, herein we study the electrochemical behavior of fourteen 2,2'-bipyridine metal complexes *fac*-M(bpy-R)(CO)₃X (where M = Mn, X = Br or M = Re, X = Cl and R = -CF₃, -CN, -Ph, -PhOH, -NMe₂).

The electrochemical behavior of the two well-known Re and Mn-bpy complexes (Chapter 2, Paragraph 2.8) could be reasonably altered by varying the bipyridine moiety, i.e. introducing electron-withdrawing and electron-donating groups¹⁻³. Kubiak and his group investigated the effect of 4,4'-di-tertbutyl-2,2'-bipyridine (^tBu₂-bpy) firstly on rhenium carbonyl complexes, secondarily on manganese^{4,5}. In other works they studied the role of the modification in the 6,6' position of the bipyridine^{6,7}. A similar approach has already been applied to Mo and W-bpy complexes^{8,9}, to both Mn and Re-bpy complexes by some of us^{8,10} and in the current work. Recently, Daasbjerg and coworkers reported a series of manganese carbonyl complexes with elaborated bipyridine or phenanthroline ligands that can reduce CO₂ both to formic acid, if the ligand structure contains strategically positioned tertiary amines, or CO, if the amine groups are absent in the ligand or are placed far from the metal center.¹¹ Additionally, they also evaluated the effect of (dEAbpy) (N,N'-([2,2'-bipyridine]-6,6'-diylbis(2,1-phenylene))bis(methylene))bis(N-ethylethanamine) on the electrocatalytic reduction of carbon dioxide by Re^I and Ru^{II} bipyridine.¹² In both cases, the major reduction product is CO alongside with some formic acid, although the yield of the latter never reaches the predominant level known from the corresponding Mn(dEAbpy)-(CO)₃Br complex.

This provides evidence for the intimate effect of the identity of the metal center, in addition to the ligand, for the product distribution, in agreement with our previous conclusions on the role of the local proton source on Mn and Re-bpy type complexes.^{8,10,13}

The target of the modification is the reduction potential of the catalyst, namely E_{cat}^0 : usually a less negative E_{cat}^0 corresponds to a decreased rate of CO₂ conversion¹⁴. Electronic properties of organic groups are commonly described by the inductive ($\pm I$) and mesomeric ($\pm M$) effects. Substituents with electron withdrawing groups like -CF₃ (strong $-I$ effect) and -CN (weaker $-I$ effect) and with electron donating groups, like -N(Me)₂ (strong $+M$ effect), -Ph and -PhOH (weaker $+M$ effect), were placed in the 4,4', 4,6 and 5,5' positions of the bipyridine ligand coordinated to the metals. Combining both push and pull effects in the so called "push-pull"

system, an electronic gradient is forced through the bipyridine. In this paper we explore the electrocatalytic properties of novel Mn and Re bpy-type complexes, bearing 7 differently substituted ligands (Scheme 4.1). More generally electron-donating groups are expected to convey greater nucleophilicity to the metal-center, although catalysis should require higher overpotentials. DFT calculations have been used as complementary tool to better correlate experimental electrochemical data, whereas Controlled Potential Electrolysis (CPE) experiments are useful to elucidate the stability and durability of the catalysts in acetonitrile solutions.



Scheme 4.1. Chemical sketches of the investigated complexes, where M = Mn, X = Br or M = Re, X = Cl.

4.2 Synthesis of the complexes

Fourteen new 2,2'-bipyridine metal complexes *fac*-M(bpy-R)(CO)₃X where M = Mn, X = Br or M = Re, X = Cl are reported, namely Mn(bpy-4,4'-CF₃)(CO)₃Br (**1a**), Mn(bpy-5,5'-CF₃)(CO)₃Br (**1b**), Mn(bpy-4,4'-CN)(CO)₃Br (**1c**), Mn(bpy-4,4'-CF₃-NMe₂)(CO)₃Br (**1d**), Mn(dpbbpy)(CO)₃Br (**1e**), Mn(hpbpy)(CO)₃Br (**1f**), Mn(bpy-4,4'-NMe₂)(CO)₃Br (**1g**), Re(bpy-4,4'-CF₃)(CO)₃Cl (**2a**), Re(bpy-5,5'-CF₃)(CO)₃Cl (**2b**), Re(bpy-4,4'-CN)(CO)₃Cl (**2c**), Re(bpy-4,4'-CF₃-NMe₂)(CO)₃Cl (**2d**), Re(dpbbpy)(CO)₃Cl (**2e**), Re(hpbpy)(CO)₃Cl (**2f**), Re(bpy-4,4'-NMe₂)(CO)₃Cl (**2g**).

The synthetic procedure for the ligands is reported in the "Ligands synthesis" Appendix section. Mn complexes have been prepared starting from [Mn(CO)₅Br] (0.100 mmol, 1 equiv) and the corresponding bipyridyl ligand (0.101mmol, 1.01 equiv) dissolved in sealed flasks containing 5mL of diethyl ether (anhydrous for complex **1f**), and heated in a Biotage Initiator+ microwave reactor. When the microwave vial has been inserted into the microwave cavity and the cavity lid has been closed, high-frequency microwaves (2.45 GHz), generated by the magnetron, heat the reaction mixture at a constant temperature of 75°C for 15min. The reaction mixtures were cooled to room temperature and the products centrifuged and washed once with diethyl

ether. Yields of reactions: (**1a**: 75%, **1b**: 84%, **1c**: 70%, **1d**: 81%, **1e**: 68%, **1f**: 65%, **1g**: 78%).

Similarly, the corresponding Re complexes have been synthesized from a toluene solution of $[\text{Re}(\text{CO})_5\text{Cl}]$ (0.100 mmol, 1 equiv) and the corresponding bipyridyl ligand (0.101 mmol, 1.01 equiv) sealed flasks containing 5 mL of solvent (anhydrous for complex **2f**) and heated in the Biotage microwave reactor at a constant temperature of 130°C for an hour. After cooling of the reaction mixtures to room temperature, petroleum ether was added to precipitate the products, which were then centrifuged, filtered, and washed once with cold diethyl ether. Yields of reactions: (**2a**: 70%, **2b**: 82%, **2c**: 67%, **2d**: 85%, **2e**: 65%, **2f**: 65%, **2g**: 75%). The complexes have been characterized by NMR, IR spectroscopy and elemental analysis.

4.3 X-Ray crystallography

Single crystal X-Ray diffraction structures have been solved for **2e** and **2f**. The complex $\text{Re}(\text{dpbpy})(\text{CO})_3\text{Cl}$ (**2e**) crystallized from both acetonitrile and benzene solutions by slow evaporation, forming prismatic orange platelets of a phase of the pure molecular product (Figure B1, structure A) and a solvate with two benzene molecules (Figure B1 structure B). The first presents the monoclinic centrosymmetric $P2_1/a$ space group (Figure B1c) while the second the monoclinic centrosymmetric $P2_1/n$ space group (Figure B1d). The complex $\text{Re}(\text{hpbpy})(\text{CO})_3\text{Cl}$ (**2f**) crystallized in dark by slow evaporation of solutions of toluene and benzene as yellow platelets and from ethyl acetate as orange prisms, both stable to air. The crystal structure has been obtained from a platelet obtained from toluene solution and has monoclinic $P2_1/n$ space group type (Figure B2b). The structures of both **2e** and **2f** present a quite distorted octahedral geometry around the rhenium center, as can be seen by the values in Table 4.1. The coordination bond of N1 is 0.1 Å longer than that of N2 (see Figure 4.1 for numeration) and a similar asymmetry can be observed in the coordination of CO in trans position to the nitrogens. This asymmetric coordination, also present in other terpyridine derivatives^{15–18} is completely different from the very symmetrically bonded bpy derivatives (with N-Re average distances equal in the two coordinating pyridyl rings and long 2.17 Å). At the same time, while most of the 2,2'-bipyridine derivatives of *fac*- $\text{Re}(\text{CO})_3\text{Cl}$ complex unit are almost planar respect to the basal OC-Re-CO plane^{1,5,19–21}, in the case of **2e** and **2f**, the ligand is distorted outside this plane (see Table 4.1). This behavior can be detected in all the terpyridines, in which the third pyridine ring is not coordinated to the metal center and is equivalent to a phenyl ring, and in 6-phenyl substituted 2,2'-bipyridine derivatives. The reason of such distortion is clarified by considering the steric hindrance of the vicinal phenyl ring (the

distance between the nearest CO group and the centroid of the phenyl ring in ortho to N1 is about 3.2 Å) that pushes up all the framework of the organic ligand, modifying the Re environment. This phenyl group is rotated to follow the shape of carbonyls with a torsion angle respect to the central pyridine ring of about 130°.

The distortion effects observed in the solid state are predicted also by molecular DFT calculations. Indeed, the optimized geometries of **2e** and **2f** perfectly overlap with the experimentally determined structures (Figure 4.1d and Figure B3), confirming that these anomalies originate from the coordination of 6-phenyl substituted 2,2'-bipyridine ligands to carbonyl complexes and are not induced by crystal packing contributions.

The crystal packing of **2e** (both structure A and structure B) and **2f** is dominated by weak C–H···Cl, C–H···O and $\pi\cdots\pi$ stacking interactions. In the case of **2f**, the presence of -OH group on the organic ligand interacting with the chloride induces the formation of hydrogen-bonded molecular chains (see Figure 4.1c).

Table 4.1. Selected X-ray bond lengths [Å] and angles [°] for **2e** and **2f**.

	2e (structure A)	2e (structure B)	2f
Re–C1	1.906(5)	1.919(5)	1.919(5)
Re–C2	1.936(5)	1.952(5)	1.935(5)
Re–C3	1.890(5)	1.933(5)	1.898(5)
Re–N1	2.160(5)	2.177(5)	2.164(5)
Re–N2	2.220(5)	2.233(5)	2.214(5)
N2–C13–C14–C15	132.85(5)	125.66(4)	125.47(4)
C2O2–ph	3.110(5)	3.239(3)	3.233(5)
Re1–N2–C11	165.28(6)	162.38(6)	159.09(6)

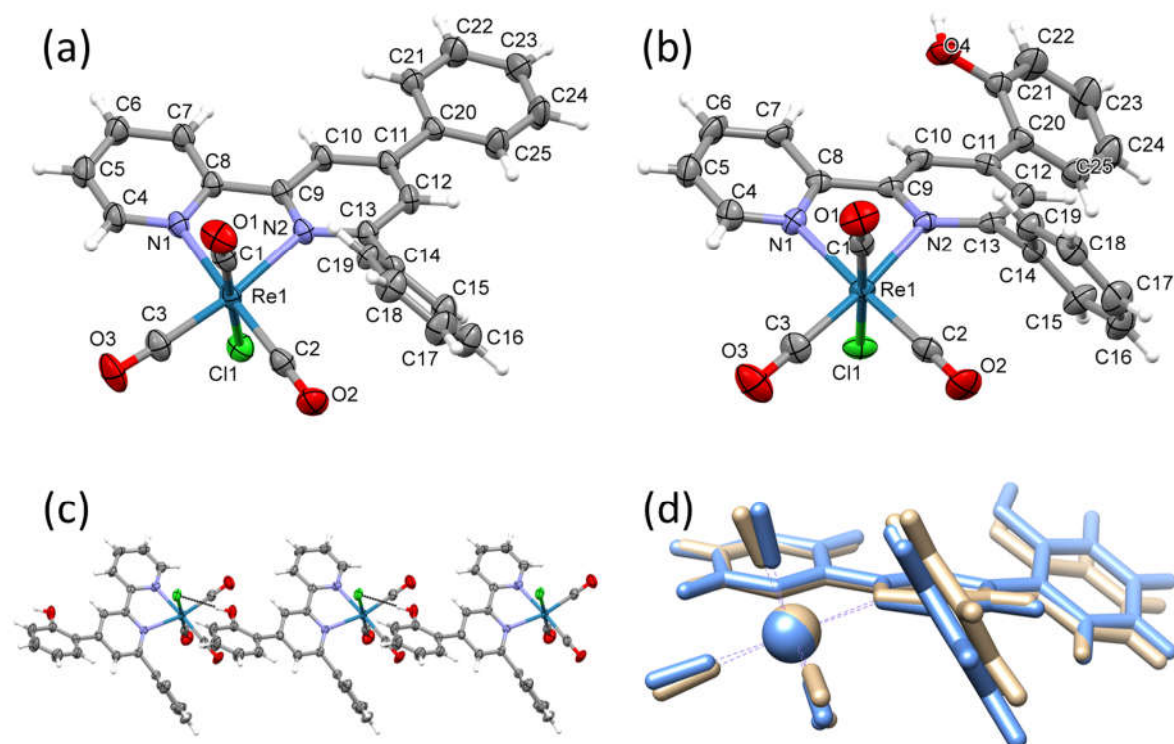


Figure 4.1. (a) molecular structure of $\text{Re}(\text{dpbpy})(\text{CO})_3\text{Cl}$ (**2e**, structure A), (b) molecular structure of $\text{Re}(\text{hpbpy})(\text{CO})_3\text{Cl}$ (**2f**), (c) chain formed by $\text{O}-\text{H}\cdots\text{Cl}$ intermolecular contacts in the crystal structure of **2f** and (d) comparison of DFT optimized (light blue) and X-ray (brown) structures of **2f**.

4.4 Electrochemical behavior under Ar

4.4.1 CV OF Mn COMPLEXES

Cyclic Voltammetries (CVs) of all manganese complexes are reported in Figure 4.2. The CV of the $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$ under our experimental conditions (in black) is included for comparison. This complex undergoes two successive irreversible reduction reactions and two reoxidation peaks²². The first ($E_{p1} = -1.29$ V vs Ag/AgCl) and the second ($E_{p2} = -1.51$ V vs Ag/AgCl) reduction processes lead to the formation of the dimer and the mononuclear penta-coordinated anion species, respectively. Reoxidations of the penta-coordinated anion and of the dimer are located at -1.09 and -0.21 V vs Ag/AgCl, respectively. The new synthesized complexes are supposed to display similar electrochemical behavior. Table 4.2 reports the peak potentials of the first and second reductions. As expected, the presence of $-\text{CF}_3$ (**1a** and **1b**) and $-\text{CN}$ (**1c**) shifts first and second potentials towards more positive values, when compared to $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$. In a recent paper²³ DFT calculations suggested that electron-withdrawing

substituents like $-\text{CF}_3$ stabilize the radical anion. Furthermore, the formation of all Mn-Mn dimers was indicated as unfavorable. However, the electrochemical mechanism outlined above is commonly accepted, and the Mn dimer is strongly favored. We experimentally found that all complexes undergo a first and second chemically irreversible reductions. For example, **1a** shows two chemical irreversible processes followed by the reoxidations of the penta-coordinated radical anion and that of the dimer (Figure B4), even at high scan rates (1 V/s, Figure B5), thus confirming the general mechanism. CV of **1g** confirms that the strong electron-donating properties of dimethyl amino group result in more negative reduction potentials with respect to $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$. The push-pull system **1d**, **1e** and **1f** display similar potential values to the unsubstituted bpy-complex. In some complexes decomposition processes occurring after reduction generate small peaks (i.e. for **1e** and **1f** $E_p = -1.65$ and -1.63 V vs. Ag/AgCl are observed, respectively). The very negative peak around -3 V vs Ag/AgCl, is commonly assigned to a ligand-centered reduction.

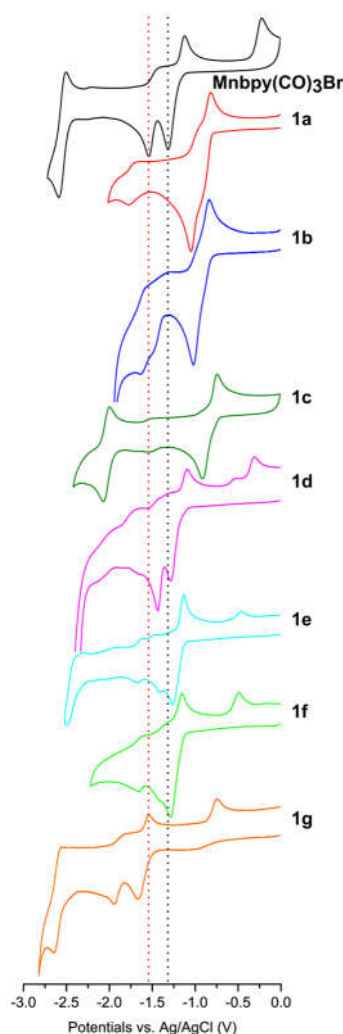


Figure 4.2. CVs of 1 mM solutions of **1a-1g** Mn complexes in $\text{CH}_3\text{CN}/0.1$ M Bu_4NPF_6 at GCE, scan rate 200 mVs^{-1} under Ar. CV of the reference $\text{fac-Mn}(\text{bpy})(\text{CO})_3\text{Br}$ is in black.

4.4.2 CV OF Re COMPLEXES

CVs of all rhenium complexes are reported in Figure 4.3. CV of the reference $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ under our experimental conditions is included for comparison. This complex exhibits a first reversible reduction, due to the formation of the radical anion, which is more stable than the analogous with manganese, thus resulting in electrochemical reversibility and no presence of the reoxidation peak of the dimer ²⁴. The second reduction leads to the penta-coordinated anion. Intrinsically, rhenium complexes require slightly higher overpotentials with respect to the corresponding manganese ones. The first reversible reduction of $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ is located at $E_{1/2} = -1.35$ V vs. Ag/AgCl, whereas the second chemically irreversible reduction is at $E_{p2} = -1.80$ V vs. Ag/AgCl. Some of the new synthesized rhenium complexes show no significant difference in the electrochemical pathway under Ar when compared to the reference $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ (Table 4.2). Electron withdrawing groups (**2a**, **2b** and **2c**) shift the reduction processes toward less negative values; electron donating groups like in **2g** essentially merge the first and second reductions into a single peak. The push-pull system **2d**, in analogy with the case of **1d**, do not significantly alter the positioning of the reduction potentials. However, its $2e^-$ wave is partially reversible. The third peak, around -2.5 V, also for these complexes, is generally attributed to a bpy-centered reduction.

The reduction potentials estimated by DFT calculation are in excellent agreement with the experimental values obtained for the first reduction potential of all rhenium complexes (Figure 4.4). This confirms the reversible nature of the first reduction process, leading to stable radical anions characterized by a very small increase (about $0.05 \text{ \AA}$) in the Re–Cl bond length (Figure B6). Conversely, in the case of manganese complexes, DFT calculations, which compute thermodynamic reduction potentials, are not suitable to estimate the irreversible electrochemical behavior of the compounds (Figure B8). Indeed, the high instability of the radical anion leads to the weakening of the Mn–Br bond, as clearly evidenced by the significant increase of the Mn–Br bond length in the anion structures (Figure B7). Our DFT calculations that include weak interactions, agree well with the chemical irreversibility of the first reduction and dimer production, even in the case of electron-withdrawing substituents. For example, the formation of the dimer $[\text{Mn}(\text{bpy})(\text{CO})_3]_2$ from its radical anion is favored by 143.5 kJ/mol, and in the case of **1a** is favored by 102.6 kJ/mol.

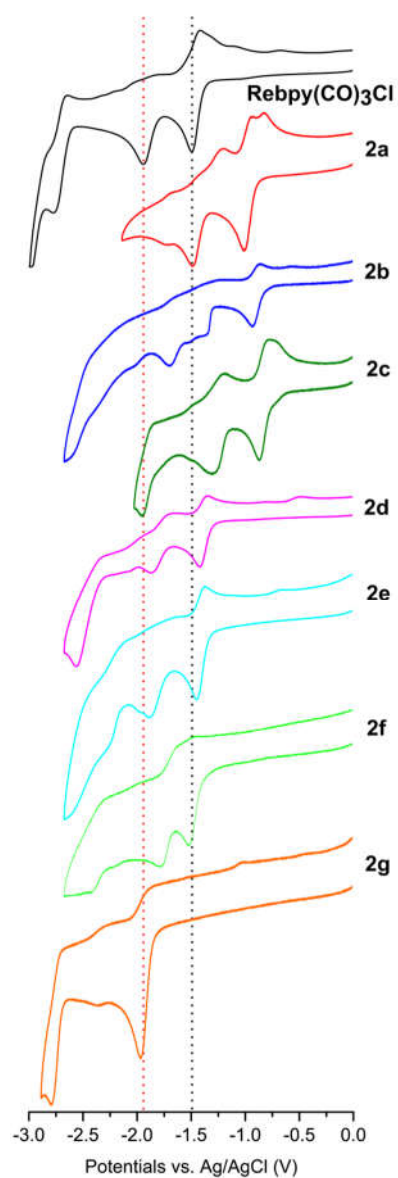
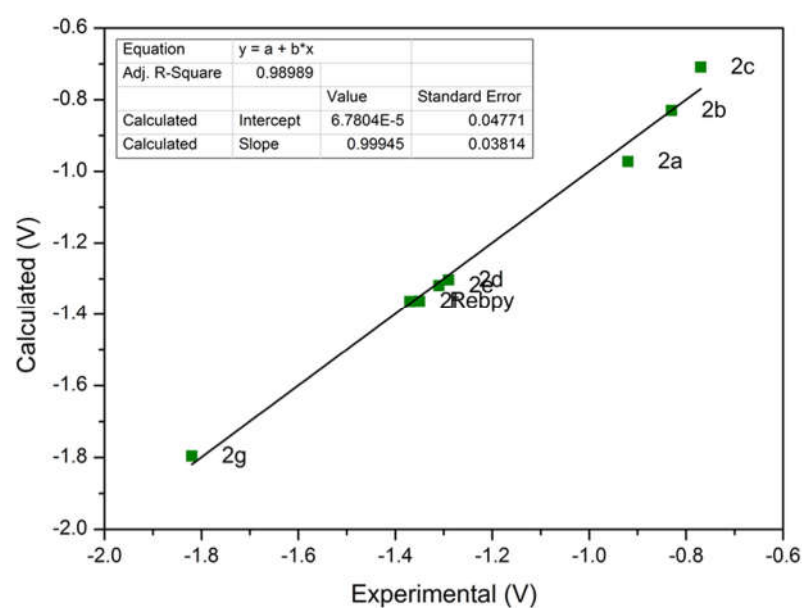


Figure 4.3. CVs of 1 mM solutions of **2a-2g** Re complexes in CH₃CN/0.1 M Bu₄NPF₆ at GCE, scan rate 200 mVs⁻¹ under Ar. CV of the reference *fac*-Re(bpy)(CO)₃Cl is in black.

Table 4.2. Reduction peak potentials [V] from the CV of Mn and Re complexes.

Mn complexes	E _{p1}	E _{p2}
Mn(bpy)(CO) ₃ Br	-1.29	-1.51
1a	-0.92	-1.07
1b	-0.88	-0.99
1c	-0.89	-0.89
1d	-1.31	-1.42
1e	-1.26	-1.4
1f	-1.24	-1.39
1g	-1.64	-1.91
Re complexes	E _{1/2} (or E _{p1})	E _{p2}
Re(bpy)(CO) ₃ Cl	-1.35	-1.80
2a	-0.92	-1.45
2b	-0.83	-1.57
2c	-0.77	-1.85
2d	-1.29	-1.77
2e	-1.31	-1.68
2f	-1.37	-1.66
2g	-1.82 (1 st + 2 nd peak)	

**Figure 4.4.** Plot of the calculated vs. experimental standard reduction potentials for **2a-2g**.

4.5 Electrochemical behavior under CO₂

4.5.1 CATALYTIC ACTIVITY OF Mn COMPLEXES

The electrochemical behavior of manganese complexes under CO₂ and with H₂O (5%v) is reported in Figure 4.5 for **1d** to **1g**. Conversely, **1a**, **1b** and **1c** are catalytically inactive

towards CO₂ reduction. CVs of **1a-1g** under CO₂ with 5%v MeOH are included for comparison in Appendix B (Figure B9). All complexes do not show significant current increases switching from Ar to CO₂ atmosphere. While this is expected for manganese complexes, **1g** shows a current increase, though limited, even in absence of Brønsted acid addition.

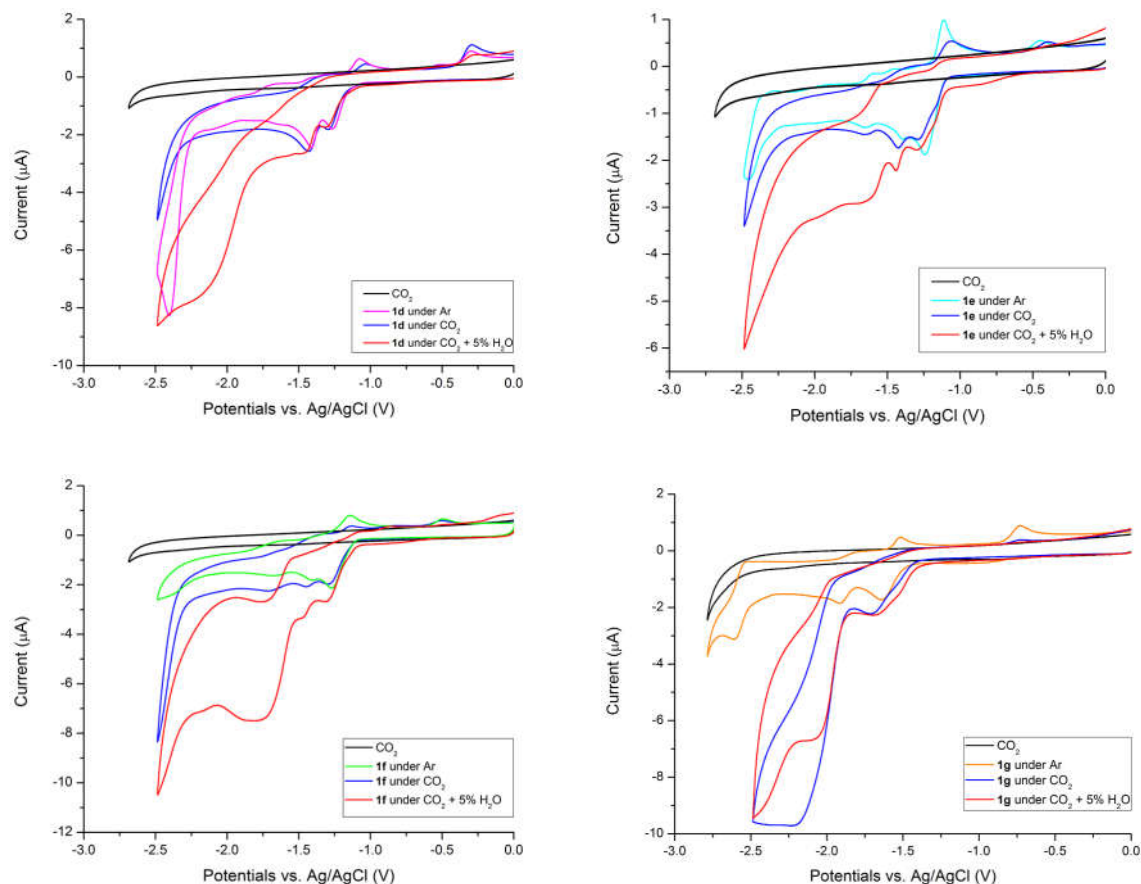


Figure 4.5. CVs of 0.5 mM solutions of **1d-1g** Mn complexes in CH₃CN/0.1 M Bu₄NPF₆ at GCE, scan rate 200 mVs⁻¹ under Ar, under CO₂ and with H₂O (5%v). CV in black is the electrolyte saturated with CO₂.

4.5.2 CATALYTIC ACTIVITY OF Re COMPLEXES

The electrochemical behavior of rhenium complexes under CO₂ and with 5%v MeOH is reported in Figure 4.6 for **2d** to **2g** and in Figure B10 for **2a**, **2b** and **2c**. CVs of **2a-2g** under CO₂ with 5%v H₂O are included for comparison in Appendix B (Figure B10). All complexes exhibit catalytic current switching from Ar to CO₂ atmosphere, even in absence of Brønsted acid, as expected for rhenium complexes.

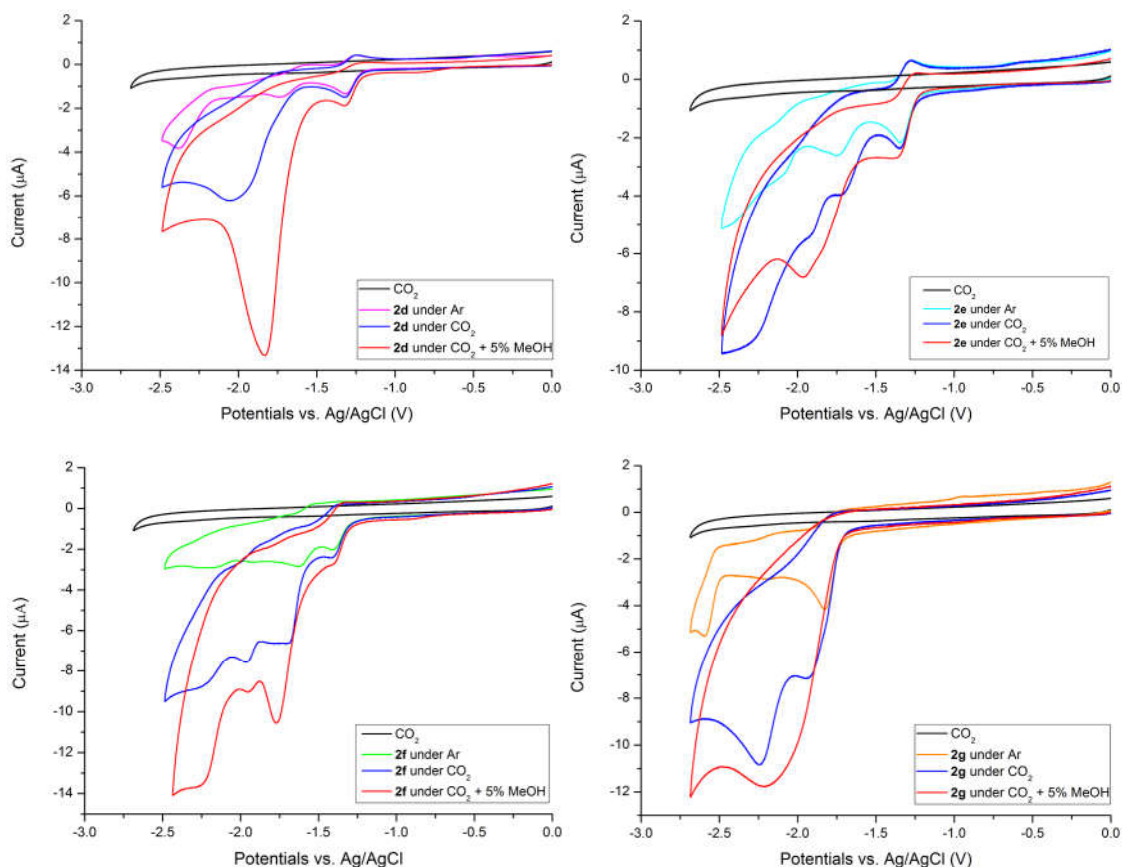


Figure 4.6. CVs of 0.5 mM solutions of 2d-2g Re complexes in $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$ at GCE, scan rate 200 mVs^{-1} under Ar, under CO_2 and with 5%v MeOH. CV in black is the electrolyte saturated with CO_2 .

4.5.3 CONTROLLED POTENTIAL ELECTROLYSIS OF Mn AND Re COMPLEXES

Bulk electrolysis experiments of all manganese and rhenium complexes series under CO_2 were performed upon setting the potential at values slightly negative to the second reductions, with and without external added Brønsted acids (water and methanol, 5%v). A CO_2 flow of 50 mL min^{-1} was kept constant during the experiments, gaseous products were determined by gas chromatography, and formate, if present, was assessed by NMR spectroscopy at the end of the experiments. Table 4.2 summarizes the results obtained during these CPE experiments. A general trend can be outlined: addition of water results in increased TONs for Mn complexes (Table 4.3 and Figure B9), differently from methanol, which drops them to lower values (Table A14). On the other hand, for the case of Re complexes, addition of methanol (Table 4.2 and Figure B10) seems to enhance the catalytic activity with respect to water, except for complex **2d**, which is catalytically inactive, despite the promising current increase in presence of MeOH under CO_2 . This behavior can be ascribed by the fact that being the 2e^- wave partially reversible, the complex could stay as six-coordinate, not displaying a vacant site for CO_2 .

coordination. Wong et al. (see Chapter 2, Paragraph 2.9.3) already concluded that the efficiency of the catalyst increases with the acidity of the Brønsted acid used.²⁵ Bourrez et al.²² showed that $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ electrocatalyzes CO_2 if H_2O is present but not noticeably without. Carter and Riplinger used density functional theory together with continuum solvation and microkinetics simulations to understand these differences. They found that some of the commonly experimentally used acids are too weak to protonate CO_2 or to stabilize CO_2 binding. The different effect of Brønsted acids with Mn and Re can be explained by the fact that catalysis with these acids requires more negative applied potentials or higher acid concentrations compared to catalysis with stronger acids. This trend is more pronounced for the Mn catalysts than for the Re ones.²⁶ Our findings are in agreement with data previously published by Smieja et al.^{4,27}. They investigated the influence of different Brønsted acids on CO_2 electrocatalytic reduction by $[\text{Mn}(\text{bpy}-t\text{Bu})(\text{CO})_3\text{Br}]$ and compared their results with previous ones for the Re catalyst. They concluded that with H_2O as the Brønsted acid, the Mn catalyst is faster than the Re catalyst. With all other acids, both catalysts exhibit similar TOFs.

Table 4.3. TON and faradic efficiencies (η) upon CPE (applied potential E in V vs. Ag/AgCl) of solutions of manganese and rhenium complexes (0.5 mM) in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ in the presence of Brønsted acids (5%v).

Complex	E [V]	T [min]	acid [5%]	TON _{CO}	η_{CO} [%]	TON _{H₂}	η_{H_2} [%]
Mnbpy(CO) ₃ Br	-1.6	240	H ₂ O	13	100	-	-
1d	-1.5	420	H ₂ O	24	90	3	14
1e	-1.5	300	H ₂ O	12	72	2.3	5
1f	-1.5	300	H ₂ O	13	64	3	10
1g	-1.95	120	-	3.5	85	-	-
1g	-1.95	300	H ₂ O	13	90	-	-
Rebpy(CO) ₃ Cl	-1.85	180	MeOH	15	80	-	-
2d	-1.8	180	MeOH	-	-	-	-
2e	-1.7	300	MeOH	5	56	-	-
2f	-1.7	240	-	5	64	-	-
2f	-1.7	300	MeOH	15	86	-	-
2g	-2	420	-	17.6	100	-	-
2g	-2	600	MeOH	31.5	100	-	-

4.6 Concluding remarks

In summary, a systematic study of the effect of the electronic properties of the substituents on 2,2'-bipyridine Mn and Re complexes was conducted. Electron-withdrawing substituents shift the reduction potentials to more positive values, and eventually inhibit the catalytic activities of the corresponding Mn and Re complexes toward CO₂ reduction. In the case of electron-donating substituents the opposite trend is observed. These observations are in agreement with the induced electron density localized on the metal, strongly influencing the change in the reactivity with the weak electrophile CO₂. Increasing or decreasing the electron density on the metal should facilitate or prevent the formation of intermediate in which the CO₂ is coordinated to the metal. Another interesting effect in varying the electron properties of the substituents is the merging of the first and second reduction processes, observed in some Re and Mn complexes. A judicious selection of bpy substituents provide an alternative way to the use of bulky substituents to prevent dimer formation⁶, with the aim of transforming two 1e⁻ reduction into a single 2e⁻ reduction process (CO₂ to CO reduction requires 2e⁻).

It is interesting to note that in spite of the presence of a -OH group in **1f**, no formic acid is detected, probably because in contrast with Mn carrying local proton sources^{8,13} the hydroxyl group is located far from the metal center, thus the generation of the metal-hydride, commonly considered catalyst for formate production, is no longer entropically favored. It is interesting to note how CVs under CO₂ of the push-pull systems **1d** and **2d** show enhanced catalytic currents; during CPE the Mn derivative **1d** displays the higher TON value, while the corresponding Re derivative **2d**, albeit from CV appears to be a potentially highly active catalyst, undergoes decomposition. While Mn catalysts suffer from the presence of MeOH, they appear to work well in water, which seems to react promptly with reduced Mn. In fact, although the reduction potential of **1g** is rather negative (Table 4.2), no hydrogen is produced. This is in line with the high TON values observed for the CO₂ electrochemical reduction in pure water by Mn electrocatalysts supported on electrode surface^{3,10,28}. DFT calculations performed with dispersion correction agree with the experimental data for both Mn and Re complexes. The Mn-Br bonds computed for the Mn radical anions undergo a significant elongation, around 0.2 Å, which indicate non-negligible weakening of the Mn-Br bonds. The release of halogen is also very probably favored by the polar and coordinating solvent CH₃CN; indeed Br substitution by CH₃CN has been experimentally observed not only in the radical anion, but also in neutral Mn species⁸. We demonstrated here how the appropriate choice of the electron properties of the ligands is of critical importance in the design of more effective bipyridine Mn and Re electrocatalysts for CO₂ reduction.

4.7 Experimental section

General

CV and CPE experiments were performed using a Metrohm Autolab 302n potentiostat. CO and H₂ as CO₂ reduction products were detected and quantified by an Agilent 490 Micro GC. NMR spectra were recorded on a JEOL ECP 400 FT-NMR spectrometer (¹H operating frequency 400 MHz) or on a JEOL ECZR 600 FT-NMR spectrometer (¹H operating frequency 600 MHz) at 298 K. ¹H and ¹³C chemical shifts are reported relative to TMS ($\delta = 0$) and referenced against solvent residual peaks. IR-ATR spectra were collected on a Fourier transform Equinox 55 (Bruker) spectrophotometer equipped with an ATR device; resolution was set at 2 cm⁻¹ for all spectra. A spectral range of 400–4000 cm⁻¹ was scanned, using KBr as a beam splitter. GC-MS spectra were obtained on a mass selective detector Agilent 5970 B operating at an ionizing voltage of 70 eV connected to a HP 5890 GC equipped with a HP-1 MS capillary column (25 m length, 0.25 mm I.D., 0.33 μ m film thickness. Elemental analyses (C, H, N) were performed on a Fisons Instruments 1108 CHNS-O Elemental Analyzer.

Mn and Re complexes NMR assignments

Mn^I(bpy-4,4'-CF₃)(CO)₃Br (**1a**). ¹H-NMR: [400 MHz, (CD₃)₂CO]: δ /ppm = 9.63 (d, J = 5.13 Hz, 2H), 9.22 (s, 2H), 8.12 (d, J = 4.83 Hz, 2H). ¹³C-NMR: [100 MHz, (CD₃)₂CO]: δ /ppm = 156.59, 155.37, 140.14 (q, CF₃), 123.96, 122.69, 121.23, 120.26. IR-ATR (CO selected bands): ν /cm⁻¹ = 2026, 1945, 1918.

Mn^I(bpy-5,5'-CF₃)(CO)₃Br (**1b**). ¹H-NMR: [400 MHz, (CD₃)₂CO]: δ /ppm = 9.64 (s, 2H), 9.00 (d, J = 6.15 Hz, 2H), 8.70 (d, J = 4.83 Hz, 2H). ¹³C-NMR: [100 MHz, (CD₃)₂CO]: δ /ppm = 158.12, 150.35, 137.00, 128.72 (q, CF₃), 125.04, 124.08, 121.37. IR-ATR (CO selected bands): ν /cm⁻¹ = 2024, 1941, 1915.

Mn^I(bpy-4,4'-CN)(CO)₃Br (**1c**). ¹H-NMR: [400 MHz, (CD₃)₂CO]: δ /ppm = 9.60 (d, J = 4.83 Hz, 2H), 9.15 (s, 2H), 8.17 (d, J = 5.05 Hz). ¹³C-NMR: [100 MHz, (CD₃)₂CO]: δ /ppm = 155.95, 155.02, 128.43, 126.10, 122.75, 115.45. IR-ATR (CO selected bands): ν /cm⁻¹ = 2030, 1926.

Mn^I(bpy-4,4'-CF₃-NMe₂)(CO)₃Br (**1d**). ¹H-NMR: [400 MHz, (CD₃)₂CO]: δ /ppm = 9.52 (d, J = 5.56 Hz, 1H), 8.86 (s, 1H), 8.65 (d, J = 6.44 Hz, 1H), 7.97 (d, J = 4.98 Hz, 2H), 6.95 (d, J = 6.15 Hz, 1H), 3.24 (s, 6H). ¹³C-NMR: [100 MHz, (CD₃)₂CO]: δ /ppm = 159.64, 158.75, 154.94, 153.95, 152.17, 139.64 (q, CF₃), 121.35, 118.32, 109.64, 106.82, 39.00. IR-ATR (CO selected bands): ν /cm⁻¹ = 2022, 1931, 1904.

Mn^I(dpbpy)(CO)₃Br (**1e**). ¹H-NMR: [400 MHz, (CD₃)₂CO]: δ/ppm = 9.32 (d, *J* = 5.27 Hz, 1H), 8.87 (d, *J* = 7.03 Hz, 2H), 8.25 (t, 1H), 8.11 (d, *J* = 7.61 Hz, 2H), 7.97 (s, 1H), 7.72–7.74 (m, 3H), 7.59–7.61 (m, 6H). ¹³C-NMR: [100 MHz, (CD₃)₂CO]: δ/ppm = 165.65, 157.69, 157.32, 153.26, 150.43, 142.77, 138.83, 135.96, 130.48, 129.87, 129.44, 127.69, 126.11, 124.69, 124.06, 119.15. IR-ATR (CO selected bands): ν/cm⁻¹ = 2022, 1954, 1925.

Mn^I(hpbpy)(CO)₃Br (**1f**). ¹H-NMR: [400 MHz, (CD₃)₂CO]: δ/ppm = 9.31 (d, *J* = 5.27 Hz, 1H), 9.21 (s, OH), 8.81 (s, 1H), 8.70 (d, *J* = 8.20 Hz, 1H), 8.23 (t, 1H), 7.97 (s, 1H), 7.70–7.73 (m, 4H), 7.58–7.61 (m, 3H), 7.37 (t, 1H), 7.03–7.11 (m, 2H). ¹³C-NMR: [100 MHz, (CD₃)₂CO]: δ/ppm = 164.82, 157.74, 156.34, 153.23, 149.05, 142.97, 138.85, 131.49, 130.69, 129.73, 129.44, 127.32, 125.96, 123.68, 121.54, 120.53, 116.79. IR-ATR (CO and OH selected bands): ν/cm⁻¹ = 3267, 2022, 1934, 1917.

Mn^I(bpy-4,4'-NMe₂)(CO)₃Br (**1g**). ¹H-NMR: [400 MHz, (CD₃)₂CO]: δ/ppm = 8.59 (d, *J* = 6.44 Hz, 2H), 7.57 (s, 2H), 6.83 (d, *J* = 6.74 Hz, 2H), 3.19 (s, 12H). ¹³C-NMR: [100 MHz, (CD₃)₂CO]: δ/ppm = 156.16, 155.44, 151.98, 108.68, 104.61, 38.85. IR-ATR (CO selected bands): ν/cm⁻¹ = 2008, 1914, 1891.

Re^I(bpy-4,4'-CF₃)(CO)₃Cl (**2a**). ¹H-NMR: [400 MHz, (CD₃)₂SO]: δ/ppm = 9.48 (s, 2H), 9.34 (d, *J* = 5.86 Hz, 2H), 8.17 (d, *J* = 5.13 Hz, 2H). ¹³C-NMR: [100 MHz, (CD₃)₂SO]: δ/ppm = 197.73, 189.41, 156.79, 155.24, 140.14 (q, CF₃), 124.79, 124.08, 122.47, 121.39. IR-ATR (CO selected bands): ν/cm⁻¹ = 2019, 1909, 1872.

Re^I(bpy-5,5'-CF₃)(CO)₃Cl (**2b**). ¹H-NMR: [400 MHz, (CD₃)₂SO]: δ/ppm = 9.32 (s, 2H), 9.18 (d, *J* = 8.64 Hz, 2H), 8.93 (d, *J* = 8.49 Hz, 2H). ¹³C-NMR: [100 MHz, (CD₃)₂SO]: δ/ppm = 197.61, 189.48, 158.21, 150.14, 138.81, 129.19 (q, CF₃), 126.82, 124.03, 121.31. IR-ATR (CO selected bands): ν/cm⁻¹ = 2023, 1923, 1895.

Re^I(bpy-4,4'-CN)(CO)₃Cl (**2c**). ¹H-NMR: [400 MHz, (CD₃)₂SO]: δ/ppm = 9.38 (s, 2H), 9.29 (d, *J* = 5.56 Hz, 2H), 8.22 (d, *J* = 4.10 Hz, 2H). ¹³C-NMR: [100 MHz, (CD₃)₂SO]: δ/ppm = 197.45, 189.16, 155.89, 154.78, 130.61, 128.07, 123.38, 116.19. IR-ATR (CO selected bands): ν/cm⁻¹ = 2019, 1920, 1893.

Re^I(bpy-4,4'-CF₃-NMe₂)(CO)₃Cl (**2d**). ¹H-NMR: [400 MHz, (CD₃)₂SO]: δ/ppm = 9.21 (d, *J* = 5.27 Hz, 2H), 8.37 (d, *J* = 6.74 Hz, 1H), 8.03 (d, *J* = 7.03 Hz, 1H), 7.93 (s, 1H), 6.89 (d, *J* = 4.10 Hz, 1H), 3.21 (s, 6H). ¹³C-NMR: [100 MHz, (CD₃)₂SO]: δ/ppm = 198.86, 198.30, 191.21, 158.93, 155.65, 154.87, 154.01, 152.06, 123.34, 120.60, 110.05, 107.95. IR-ATR (CO selected bands): ν/cm⁻¹ = 2013, 1902, 1880.

Re^I(dpbpy)(CO)₃Cl (**2e**). ¹H-NMR: [400 MHz, (CD₃)₂SO]: δ/ppm = 9.13 (d, *J* = 7.32 Hz, 1H), 9.12 (s, 1H), 9.08 (d, *J* = 5.27 Hz, 1H), 8.81 (d, *J* = 4.83 Hz, 1H), 8.40 (t, *J* = 7.91 Hz, 1H),

8.21 (m, 3H), 8.06 (t, $J = 8.49$ Hz, 1H), 7.92 (d, $J = 7.61$ Hz, 1H), 7.79 (t, $J = 6.44$ Hz, 1H), 7.62-7.66 (m, 5H). ^{13}C -NMR: [100 MHz, $(\text{CD}_3)_2\text{SO}$]: $\delta/\text{ppm} = 162.14, 156.85, 153.29, 151.24, 149.81, 140.54, 137.49, 131.51, 129.94, 128.48, 128.06, 126.10, 125.76, 125.52, 124.99, 121.29, 110.84$. IR-ATR (CO selected bands): $\nu/\text{cm}^{-1} = 2013, 1903, 1871$.

$\text{Re}^{\text{I}}(\text{hpbpy})(\text{CO})_3\text{Cl}$ (**2f**). ^1H -NMR: [400 MHz, $(\text{CD}_3)_2\text{SO}$]: $\delta/\text{ppm} = 10.35$ (s, 1H), 9.05 (d, $J = 5.72$ Hz, 1H), 8.92 (d, $J = 1.73$ Hz, 1H), 8.90 (s, 1H), 8.35 (td, $^1J = 7.84$ Hz, $^2J = 1.57$ Hz, 1H), 8.03 (d, $J = 1.73$ Hz, 1H), 7.77 (m, 2H), 7.61 (m, 5H), 7.38 (td, $^1J = 8.63$, $^2J = 1.65$, 1H), 7.04 (m, 2H). ^{13}C -NMR: [100 MHz, $(\text{CD}_3)_2\text{SO}$]: $\delta/\text{ppm} = 162.90, 157.25, 156.53, 156.08, 153.28, 150.17, 142.57, 140.53, 132.37, 131.40, 130.38, 129.67, 129.47, 128.77, 127.95, 127.78, 125.70, 123.00, 120.47, 117.23$. IR-ATR (CO and OH selected bands): $\nu/\text{cm}^{-1} = 3309, 2020, 1912, 1883$.

$\text{Re}^{\text{I}}(\text{bpy-4,4'-NMe}_2)(\text{CO})_3\text{Cl}$ (**2g**). ^1H -NMR: [400 MHz, $(\text{CD}_3)_2\text{SO}$]: $\delta/\text{ppm} = 8.30$ (d, $J = 6.74$ Hz, 2H), 7.59 (s, 2H), 6.80 (d, $J = 4.03$ Hz, 2H), 3.35 (s, 12 H). ^{13}C -NMR: [100 MHz, $(\text{CD}_3)_2\text{SO}$]: $\delta/\text{ppm} = 199.73, 192.84, 156.28, 155.53, 151.83, 109.30, 105.74$. IR-ATR (CO selected bands): $\nu/\text{cm}^{-1} = 2006, 1895, 1865$.

Single-Crystal X-ray diffraction

The single-crystal data were collected with a Gemini R Ultra diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$) by the ω -scan method. The cell parameters were retrieved with the CrysAlisPro²⁹ software, and the same program was used to perform data reduction with corrections for Lorentz and polarizing effects. Scaling and absorption corrections were applied through the CrysAlisPro. **Errore. Il segnalibro non è definito.** multiscan technique. The structures of complex **2e** (both structure A and B) were solved with direct methods, while in the case of **2f** a meaningful initial guess for electron density was obtained only with Patterson Function by using SHELXS-14^{30,31}. All the structures were refined with full-matrix least-squares techniques on F² with SHELXL-14³² using the program Olex2³³. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated and riding on the corresponding bonded atoms. The graphic of the crystal structures was generated using Mercury 3.9³². CCDC codes 1891407-1891409 contain the supplementary crystallographic data for **2e** (structure A), **2e** (structure B) and **2f**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

CV and CPE experiments

Acetonitrile used for the experiments was freshly distilled over calcium hydride and purged with Ar before use. 0.5-1 mM solutions of the complexes were prepared with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , Sigma-Aldrich, 98%) as supporting electrolyte (0.1 M). A single-compartment cell was employed for CV measurements, equipped with working a glassy carbon electrode (GCE, $\varnothing = 1$ mm), alongside a Pt counter electrode and a Ag/AgCl (KCl 3 M) reference electrode. The Ar- and CO_2 -saturated conditions were achieved by purging gases for 5 min before each potential sweep. A double-compartment H-type cell was used for CPE measurements, thus allowing to separate through a glass frit the anodic compartment from the cathodic one (a Pt wire is placed as counter electrode). A glassy carbon rod is employed as working electrode jointly with the Ag/AgCl reference electrode. A controlled and constant flow of CO_2 (50 mL min^{-1}) was maintained during the CPE measurements by means of a Smart Trak 100 (Sierra) flow controller. Under these experimental conditions, the redox couple ($\text{Fc}^{+/0}$) is located at $E_{1/2} = 0.35 \text{ V}$.

Quantitative analysis of CO_2 reduction products

μGC measurements were used to detect CO and H_2 . Two modules equipped with CP-Molsieve 5 Å columns were kept at 105°C and at a pressure of 30 and 28 psi, with a thermal conductivity detector. The carrier gases were Ar for H_2 and He for CO detection, respectively. The backflush vent option time was set to 7 s. The gas inside the measurement cell was sampled for 30 s every three minutes to fill the Micro GC 10 μL sample loop, and eventually 500 nL was injected into the column for the analyses. Instrument calibration was carried out measuring two different certified standards of CO and H_2 in Ar matrix (Rivoira). Formate production was assessed by NMR spectroscopy.

Computational details

All the calculations were performed by the Gaussian 16 Revision B.01 (G16) program package³⁴, employing density functional theory (DFT). Calculations were run using the Becke three-parameter hybrid functional³⁵, and the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP)³⁶. Dispersion effects were added as semiempirical corrections with Becke–Johnson damping approach (GD3BJ)^{37,38}. The solvent effect was included using the conductor-like polarizable continuum model (CPCM) with acetonitrile as solvent³⁹. The def2TZVP basis set and effective core potential were used for the Mn, Br and Cl atoms and the def2-SVP basis set was used for all the other atoms⁴⁰. Unrestricted open-shell calculations were performed on the radical anions. Geometry optimizations were carried out without any

symmetry constraints. The nature of the stationary points in the potential energy hypersurface was characterized by using harmonic vibrational frequency calculations. No imaginary frequencies were found, thus indicating we had located the minima on the potential-energy surfaces. Molecular-graphic images were produced by using the UCSF Chimera package from the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco ⁴¹.

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CHAPTER 5. Towards heterogenization of a *fac*-Mn(apbpy)(CO)₃Br electrocatalyst

5.1 Introduction

While most research efforts have been primarily focused on homogeneous CO₂ electroreduction, the heterogenization of molecular catalysts by attachment to the electrode surface has been far less explored, although some works in the field have been published in recent years.^{1–14}

Nevertheless, the transition from the homogeneous to the heterogeneous approach, which in some cases displays superior stability and durability, can find considerable support whenever the intimate molecular mechanism responsible for the catalysis is initially deeply investigated in the homogeneous phase. This is the experimental approach adopted herein.

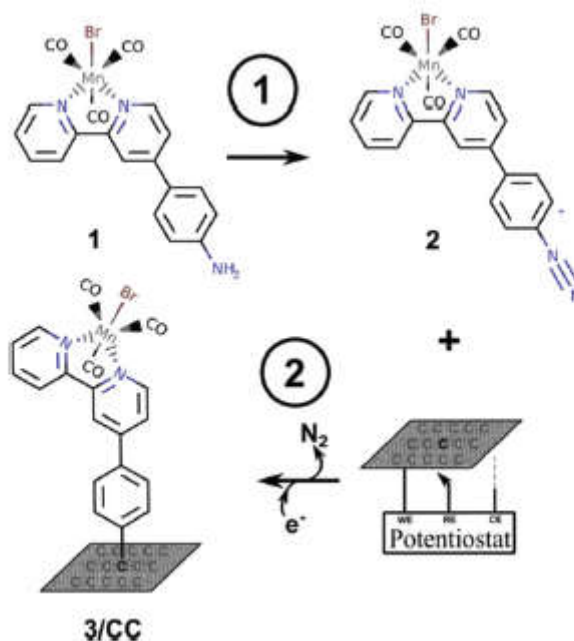
A new Mn complex, namely *fac*-Mn(apbpy)(CO)₃Br (**1**) [apbpy=4-(4-aminophenyl)-2,2'-bipyridine]] has been synthesized and firstly tested as homogeneous electrocatalysts for CO₂ reduction in acetonitrile. The further step consisted in attaching this catalyst as an intact organometallic fragment via a stable C-C bond onto the glassy carbon electrode surface.

Most of the heterogenized molecular electrocatalysts are supported on a conductive material via van der Waals interactions^{8,11–13,15} or by the hybrid homogeneous–heterogeneous approach, which involves covalent bond⁴ formation between the electrode surface and intact organometallic catalysts. This is an appealing method that usually leads to increased durability, efficiency, TON values and recyclability. In particular, Mn-bpy type catalysts have been adsorbed on carbon nanotubes by Reisner, showing promising properties in water.¹¹ A similar approach has been adopted in another very recent work,¹² in which low-energy electrocatalytic CO₂ reduction was driven in water over a Mn-complex catalyst electrode aided by a nanocarbon support and K⁺ cations.

Amongst others, one approach of functionalizing carbonaceous electrodes has drawn our attention: the reduction of diazonium salts. Therefore, the bipyridine has been modified to apbpy, which bears an amine moiety available for diazonium salt formation. Once the electrode has been decorated with **1**, it has been tested towards CO₂ electroreduction in acetonitrile: an increase of the TON_{CO} was observed.

Finally, we anchored **1** in a similar fashion to Carbon Cloth (CC) electrodes (Scheme 5.1). CC is a material with low electrical resistance, relatively low cost, large surface area, and widely used for the preparation of electrodes for low temperature fuel cells. Herein, **1** was chemically bonded to CC, via a direct in situ^{16,17} generation of the corresponding diazonium salt (employing amyl nitrite) and immediate electrochemical reduction. The modified CC electrode

was tested for CO₂ electroreduction in a three-electrode cell with two gastight compartments in CO₂-saturated aqueous KHCO₃. The functionalized CC has been also used as Gas Diffusion Layer (GDL) in a gas-fed complete electrolysis cell which overcomes the mass transport limitations of using dissolved CO₂ leading to higher TONs. Another substantial difference of this experimental setup with respect to the previous, is the production of formate alongside with CO. The same electrocatalyst has been shown to be largely affected by different experimental conditions for CO₂ electroreduction: a change in selectivity occurred.



Scheme 5.1. Preparation of the *fac*-Mn(apbpy)(CO)₃Br/CC (**3/CC**) electrode via diazonium salt reduction; (1) in situ preparation of the diazonium salt and (2) direct electrochemical reduction on carbon cloth.

5.2 Synthesis and characterization

The apbpy ligand synthesis is reported in the “Ligands synthesis” Appendix section.

Complex **1** has been prepared reacting apbpy and Mn(CO)₅Br in in sealed flasks containing 5mL of diethyl ether and heated in a Biotage Initiator+ microwave reactor. When the microwave vial has been inserted into the microwave cavity and the cavity lid has been closed, high-frequency microwaves (2.45 GHz), generated by the magnetron, heat the reaction mixture at a constant temperature of 75 °C for 15min. The reaction mixtures were cooled to room temperature and the products centrifuged and washed once with diethyl ether. Yields of reaction: 90%.

¹H NMR (400 MHz, CD₃CO): δ=9.31 (d, 1H, J=4.0 Hz), 9.11 (d, 1H, J=6.0 Hz), 8.73-8.79 (m, 2 H), 8.22 (t, 1H, J=8.0 Hz), 7.91-7.70 (m, 4 H), 6.85 (d, 2H, J=10.0 Hz), 5.31 ppm (s, 2H).

IR-ATR ($\tilde{\nu}_{\text{CO}}$ / cm^{-1}): = 2016 , 1914, 1895.

The corresponding diazonium salt chloride of **1** was synthesized by an ordinary procedure. The complex was solubilized into a 37% HCl solution, cooled at $-58\text{ }^{\circ}\text{C}$ by salt ice bath, and an aqueous solution of NaNO_2 (1.01 molar ratio) was added over 40 min to the mixture, with a continuous vigorous stirring for further 5 h. The starting yellow color changed to brown and the resulting solid was washed twice with 37% HCl, then with ethanol and diethyl ether, and finally dried under vacuum.

Diazonium salt of complex IR-ATR ($\tilde{\nu}_{\text{CO}}$ / cm^{-1}): 2264, 2024, 1907.

5.3 Complex 1 as homogeneous electrocatalyst

5.3.1 CYCLIC VOLTAMMETRY OF **1** UNDER Ar AND CO_2 AND CPE EXPERIMENTS

Figure 5.1 shows the CVs of complex **1** in acetonitrile solution under Ar. The electrochemical behavior is similar to that of the parent compound $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$. After the first irreversible reduction ($E_p = -1.52\text{ V}$) the Br^- is quickly released. Consequent dimerization occurs, forming the neutral Mn-Mn dimer that is reduced at -1.76 V vs. $\text{Fc}^{+/0}$. The reoxidation of the radical anion and the dimer can be observed at -1.42 V and -0.61 V , respectively.

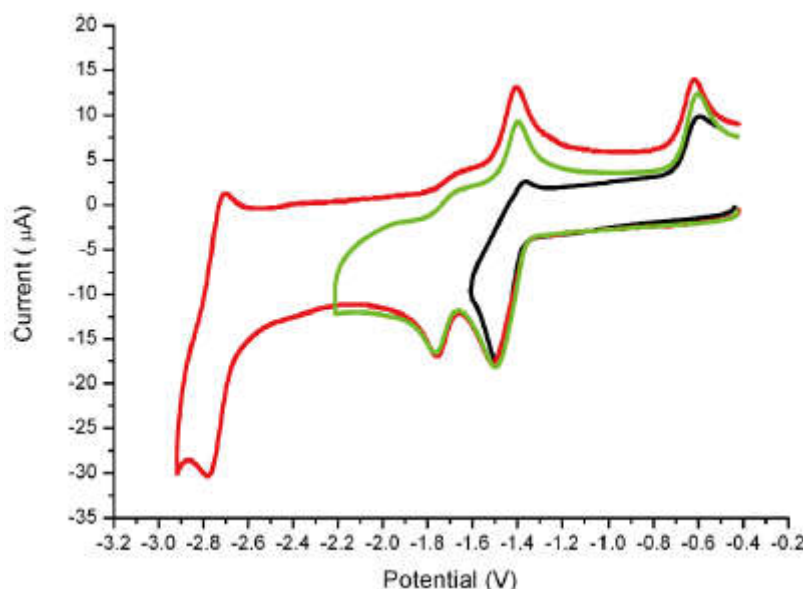


Figure 5.1. CVs of a 1 mm solution of **1** in Ar-saturated CH_3CN with 0.1 M Bu_4NPF_6 at a glassy carbon electrode (3 mm diameter), scan rate = 200 mV s^{-1} .

The Randles-Sevcik analysis (plot of peak currents vs. square root of the scan rate) is linear, indicating that the electrochemical behavior of **1** is diffusion-controlled.

Since **1** does not have local proton sources, under CO₂-saturated conditions (Figure 5.2a) it does not show any catalytic activity. The progressive addition of a Brønsted acid (water or methanol) results in a dramatic increase of current after the second reduction. The maximum peak current was obtained with the addition of 8% (v/v) water or 4% (v/v) methanol (Figure 5.2b and 5.2c and Table 5.1). Higher quantities had limited effects on the observed catalytic current peak. The TOFs can be roughly estimated by Equation (1)^{18,19} at catalyst peak potential from a single CV, as proposed by Saveant and co-workers:²⁰ where i_c and i_p are the catalytic and peak current in the presence and absence of catalysis, respectively; n_c (=2) and n_p (=1) are the number of electrons involved in the catalytic and catalyst reduction, respectively, F is the Faraday constant and v is the applied scan rate.

$$\frac{i_c}{i_p} = \frac{1}{0.4463} \frac{n_c}{\sqrt{n_p^3}} \sqrt{\frac{RT}{F}} \sqrt{\frac{(TOF)}{v}} \quad (\text{equation 1})$$

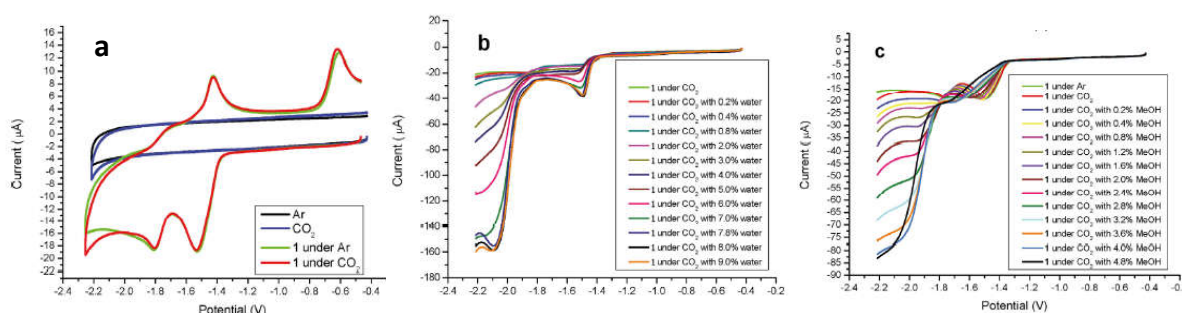


Figure 5.2. (a) CVs of a 1 mm solution of **1** in CO₂-saturated CH₃CN with 0.1 M Bu₄NPF₆ at a glassy carbon electrode (3 mm diameter), (b) with added water, (c) with added methanol. Scan rate = 200 mV s⁻¹.

Table 5.1. Catalysis properties of **1** with and without added Brønsted acids.

	i_c/i_p	[Acid] %v	TOF [s ⁻¹]	E_p [V]
1	1.0	75	–	–1.76
1 + MeOH	6.0	4	99	–1.76
1 + H₂O	16	8	14	–1.76

While the CV is suitable for getting a rough estimation of the catalytic process at the very beginning of the cycle, a better overall picture can be guessed from the longer time controlled potential electrolysis (CPE) experiments.

Results of CPE experiments performed with **1** as electrocatalyst are reported in Table 5.2. This complex exhibits much better selectivity with MeOH than water and it is more stable under lower potential. The catalyst has a comparable activity with the unsubstituted Mn-bpy parent complex,²¹ although at a less negative potential. It can be also pointed out how, analogously to the findings of results reported in Chapter 4, addition of MeOH as external Brønsted acid for Mn-bpy type complexes provides lower TONs for CO than added water.^{22–26}

Table 5.2. Results of CPE experiments of **1**.

Acid	Time [min]	FE _{CO} [%]	TON _{CO}	E _p [V] vs. Fc ^{+/0}
–	–	–	–	–1.85
H ₂ O (4%)	90	93	12	–1.73
H ₂ O (4%)	120	56.5	10.9	–1.85
MeOH (8%)	120	3.6	96.0	–1.85

5.4 Reductive functionalization to form C-C bonds

This method, which employs the diazonium chloride of complex **1**, leads to the formation of strong C-C bonds between the surface and the catalysts. Figure 5.3 displays the electrode functionalization by CV scans at reduction potentials. During the first cycle there is no evident current peak, but instead a broad plateau. In the following cycles, a more marked peak appears, the shift of peak position indicates multi-layer formation.

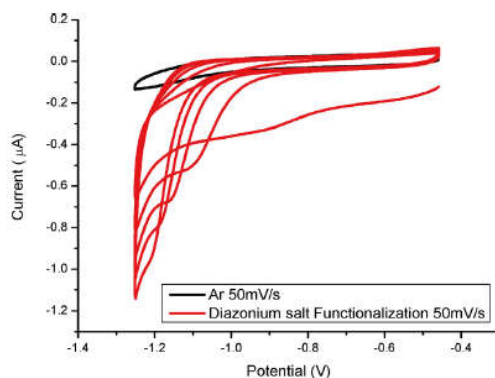


Figure 5.3. Electrode functionalization with diazonium salts of **1**. Scan rate: 50 mVs⁻¹.

The resulting functionalized electrode exhibits an evident and sharp reduction peak in the first CV, which vanishes in the following cycles (Figure 5.4). From the analysis and comparison of CVs of **1** in homogeneous solution, the peaks around -1.36 V can be directly assigned to the release of Br^- . The surface shows a non-diffusive controlled electrochemical behavior (Figure 5.5) and is stable. If only one or two CV cycles are applied, a very thin and stable film of **1** can be obtained after the release of bromine (Figure 5.5). CV shows three cathodic (-1.78 , -1.45 , -1.35 V) and three anodic (-1.66 , -1.44 , -0.58 V) peaks in a single CV. The peak at -1.35 V can be assigned to the reduction of **1** in which Br^- has been substituted by a single acetonitrile molecule. The peak at -1.45 V is assigned to the one electron reduction of the dimer, which is formed by adjacent monomers. The peak at -1.78 V is the reduction of the dimer to get one electron charged monomer, in a similar fashion as reported in homogeneous solutions.²⁷

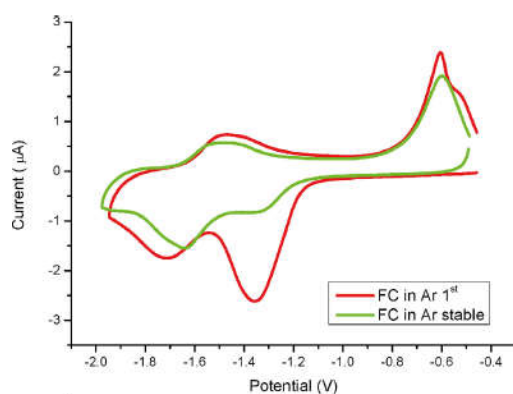


Figure 5.4. First and steady-state CVs of electrodes modified with diazonium salts of **1**.

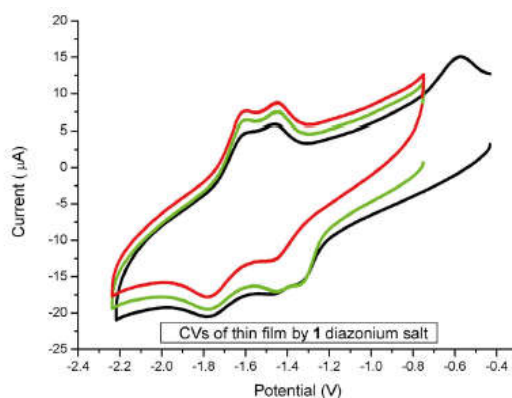


Figure 5.5. CVs of an electrode functionalized by a diazonium salt of **1** (black: origin stable CV by full scan; green: first CV by scan start from -0.75 V; red: stable CV by scan start from -0.75 V continuously).

5.5 Surface coverage evaluation

The surface coverage (Γ) has been assessed by means of Equation 2^{28,29}:

$$\Gamma = \frac{Q}{FA} \quad (\text{equation 2})$$

where Q is the charge oxidizing (or reducing) the organometallic complex on the electrode surface evaluated by integration of the background-corrected CVs, F is the Faraday constant and A is the area of the electrode.

Continuous CVs scan from -0.75 to -2.25 V, avoiding the oxidation of the dimer at -0.58 V, show that the peak at -1.35 V vanishes (Figure 5.5). When the CV scan is performed starting again from -0.4 V (i.e. the dimer is oxidized), the peak at -1.35 V reappears, restoring the original stable CV. All these data suggest that this peak is associated to the reduction of the solvated complex. According to the stable CVs, the coverage calculated by the charge method (equation 2) is $5.7 \times 10^{-10} \text{ mol cm}^{-2}$. Plotting the peak current versus scan rate, the surface coverage is calculated to be $4.1 \times 10^{-10} \text{ mol cm}^{-2}$ (Figure 5.6).

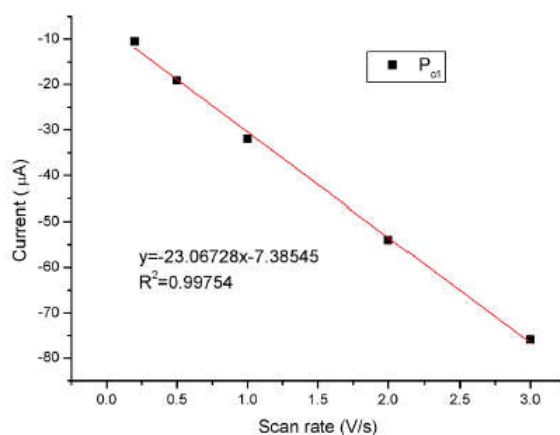


Figure 5.6. Plot of the current peak of the first reduction versus the scan rate for a surface functionalized with diazonium salt of **1**.

5.6 Complex 1 as heterogenized electrocatalyst in an acetonitrile solution

The freshly functionalized Glassy Carbon Electrode (GCE) has been tested in an acetonitrile solution saturated with CO_2 . No significant difference is observed in the first two reduction peaks, while the addition of methanol induces a dramatic change at the second reduction peak. When the volume of methanol reaches 20%, the current reaches the maximum value (Figure 5.7).

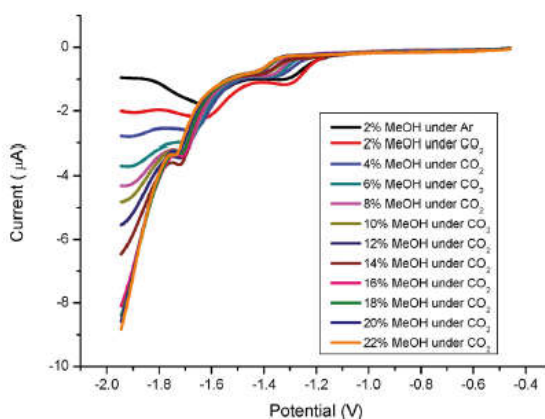


Figure 5.7. CO₂ reduction CVs of an electrode functionalized with diazonium salt of **1** in acetonitrile with added methanol at a scan rate of 0.2 Vs⁻¹.

Applying a voltage of -1.9 V the activity is retained for 100 cycles. To roughly estimate the catalytic activity, TON' were calculated for three different electrodes to be 209, 218 and 201 for coverages of $14.3 \cdot 10^{-10}$, $10.1 \cdot 10^{-10}$, and $6.4 \cdot 10^{-10}$ molcm⁻² and applied potentials of -2.15, -2.00 and -1.90 V, respectively. These data suggest that there is no effect of the potential applied in the adopted range, and a mean TON' of 209 can be assumed for **1** with methanol.

5.7 Complex 1 functionalized on Carbon Cloth

5.7.1 CATHODE PREPARATION ON CC

Considering the much higher roughness of CC with respect to GCE, the real electrochemical surface area (ECSA) of a CC with a geometric area of 3.4 cm² was estimated by performing cyclic voltammetry on a 1.0 mM solution of ferrocene (Fc) at different scan rates (the diffusion coefficient of Fc is $2.24 \cdot 10^{-5}$ cm²/s)³⁰. The peak current was then plotted against the square of the scan rate (Figure 5.8) and the slope is used to determine the real surface area according to the Randles-Sevcik law (equation 3).

$$i_p = 2.686 \cdot 10^5 n^{3/2} A D^{1/2} C \nu^{1/2} \quad (\text{equation 3})$$

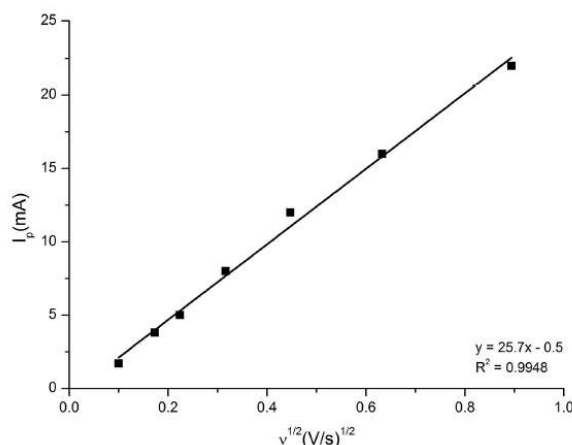


Figure 5.8. Plot of the i_p vs square root of the scan rate for carbon cloth sample of geometric surface area of 3.4 cm².

The 3.4 cm² geometric surface area of a carbon cloth electrode accounted for 19.95 cm² of ECSA (corresponding to a roughness factor of 5.87). Differently from the previous part of the work, the corresponding diazonium salt was synthesized *in situ* directly in the electrochemical cell under Ar atmosphere from a solution of the corresponding complex (5 mM) and trichloroacetic acid (30 μ l) in acetonitrile (10 ml). The starting pale-yellow solution was initially cooled in an ice water bath, and isoamyl nitrite (10 μ l) was added; the solution became orange. Bu₄NPF₆ (0.1M) was added as supporting electrolyte. The carbon cloth functionalization was driven by CVs scans at reduction potential. In the first CV the peak at -0.3 V vs Ag/AgCl (KCl 3M) is attributed to the diazonium salt of **1**. The peak vanishes after following cycles indicating the grafting of covalently bounded layer. (Figure 5.9). This deposition in situ method has the advantage of avoiding isolation and purification of the diazonium salt.¹⁶ To estimate the amount of electrocatalyst covalently bonded on ECSA, the electrochemical methods of charge integration of CV scan, like for functionalized GCE^{3,28}, could be adopted. However, the electrochemical reduction of **1** functionalized onto CC, is chemically irreversible (as that of **1**) and overlaps with the reduction of water.

An indirect method for evaluating the surface coverage Γ (mol/cm²) is via charge integration of CV data of CC bonded nitroaniline. This approach has the advantage of using an electrochemically reversible system in CH₃CN solutions, and it has Γ values about 10 times higher than those of bpy-type metal complexes, as previously reported.^{3,31} The surface coverage of nitroaniline on CC (Figure 5.10) has been experimentally evaluated to be 1.4×10^{-8} mol cm_{ECSA}⁻². This value is comparable with that previously found for glassy carbon electrode (about 10^{-9} mol cm⁻²), considering the much higher roughness of CC. Hence, we estimate that Γ of **1/CC** is about 1.4×10^{-9} mol cm_{ECSA}⁻².

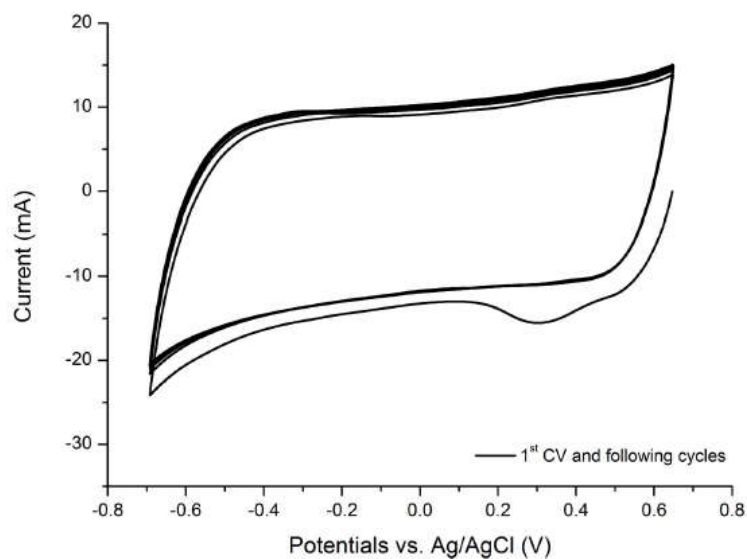


Figure 5.9. First and steady state CVs of carbon cloth modified with in situ reduction of diazonium salt of **1**. Scan rate of 50 mV/s.

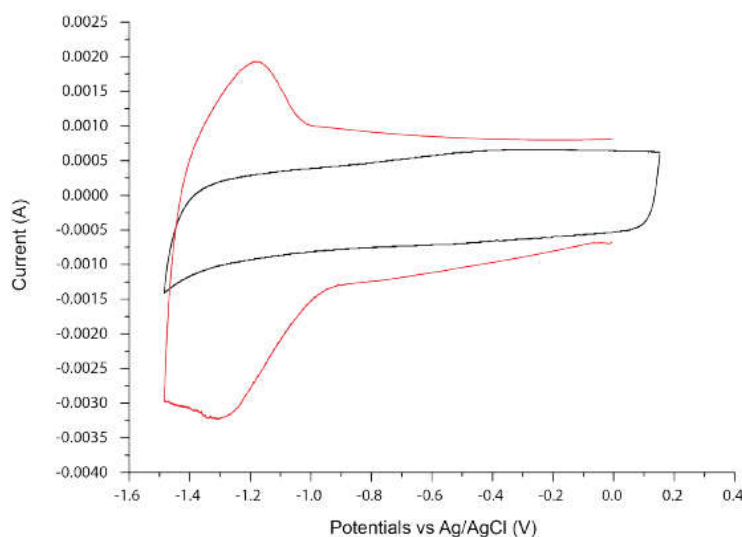


Figure 5.10. CV (red line) of nitroaniline/CC in CH_3CN solution used for the evaluation of surface coverage. Scan rate 10 mV/s. The black line is the background in CH_3CN under Ar of the pristine CC.

The functionalized carbon cloth was characterized by ATR spectroscopy (Figure 5.11). After 5 min of continuous washing and sonication in CH_3CN , the carbonyl signals are still present and evident on the support surface, although broadened, in agreement with the IR signals of the free complex (2016 , 1914 and 1895 cm^{-1}). This clearly indicates that **1** is present in an intact form on the CC surface.

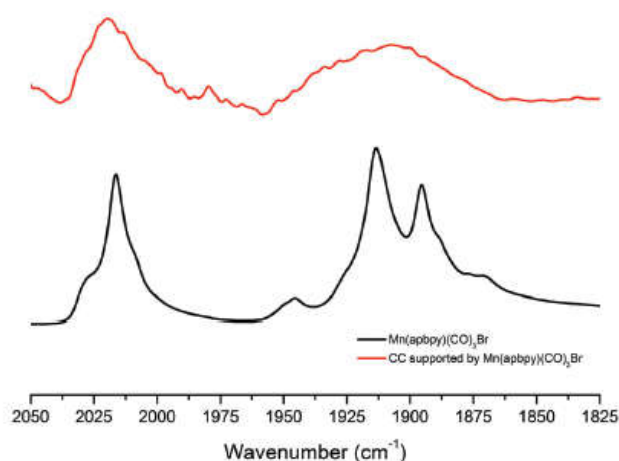


Figure 5.11. Attenuated total reflection (ATR) spectra of **1** (black line) and **1** supported on CC (red line).

5.7.2 COMPLEX **1** SUPPORTED ON CC AS ELECTROCATALYST IN A KHCO_3 AQUEOUS SOLUTION

The modified CC electrode was tested for CO_2 electroreduction in a three-electrode cell with two gastight compartments in CO_2 -saturated aqueous KHCO_3 (Appendix C for Chapter 5, Figure C1). Fig. 5.12A and B show faradaic efficiency (FE) and the current density as a function of cathode potential during the electrolysis. The faradaic efficiency for CO production (Fig. 5.12A) is higher than 60% for potentials up to -1.4 V (vs. $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat})$); at more negative potentials, the hydrogen evolution reaction (HER) is favored. No other products were detected, either in solution or in the gas phase. Both the CO-partial current and the TOF (turnover frequency) (Fig. 5.12B and C) reach a plateau at potentials more cathodic than -1.35 V, while the total current increases exponentially following a Tafel-like curve, due to increasing HER. The presence of this plateau for CO_2 electroreduction activity can have several origins: saturation of the electrocatalytic active sites due to the extremely low loading of the catalyst and low CO_2 concentration. Phenomena like CO_2 mass transport limitations seem not to be crucial under these conditions.

We have estimated that the CO_2 diffusion limiting current density is more than one order of magnitude higher than the CO-partial current measured (14 mA cm^{-2} @ 25°C for CO_2 -saturated 0.1 M KHCO_3). At more cathodic potentials (< -1.5 V) the FE_{CO} drops.

This is associated with a large increase in the HER that may cover the electrode surface with H_2 bubbles. The electrocatalyst stability experiments show that the **1/CC** faradaic efficiency for the production of CO at -1.35 V (Fig. 5.13A) increases slightly, indicating good electrocatalyst performance stability over 10 h operation. The cumulative TON for CO production (Fig. 5.13B) reaches more than 33 000 after 10 h, with an average faradaic efficiency of 53%. It is worth noting how **1/CC** reaches a TON which is two orders of

magnitude higher than that of the same complex tested under homogeneous conditions in acetonitrile solutions. (Table 5.2).

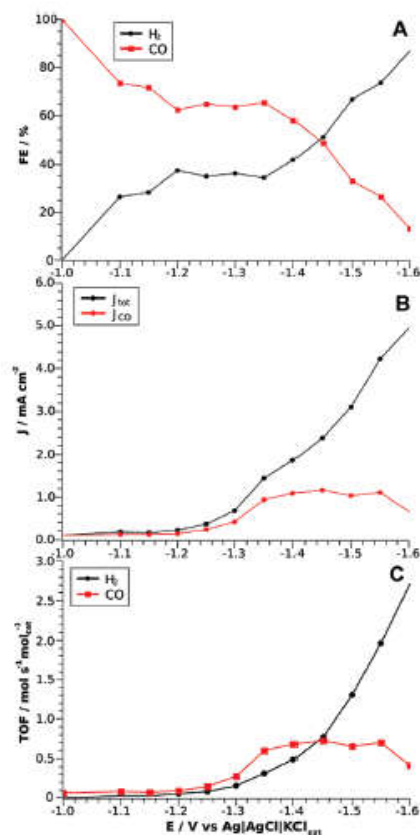


Figure 5.12. (A) Faradaic efficiency; (B) electrolysis current; and (C) turnover frequency profiles for the **1/CC** electrocatalyst.

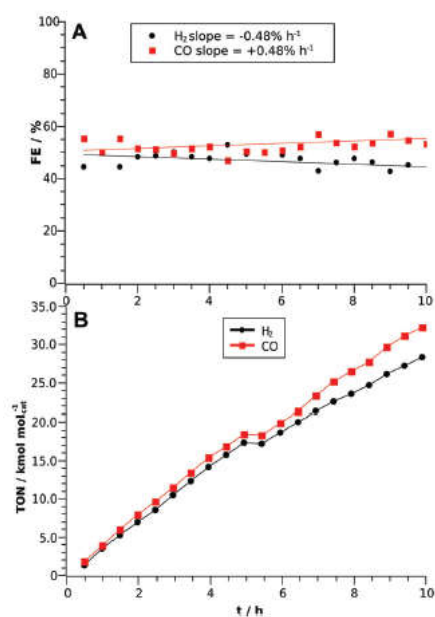


Figure 5.13. (A) Faradaic efficiency and (B) turnover number time profiles for the **1/CC** electrocatalyst.

5.7.3 COMPLEX 1 SUPPORTED ON CC AS GAS DIFFUSION LAYER FOR CO₂ ELECTROREDUCTION

The same electrocatalyst is used in a gas-fed complete electrolysis cell (Figure 5.14).

In order to effectively establish an optimized three-phase boundary between water (necessary as proton source), electrocatalyst and CO₂ gas, a buffer layer configuration (shown in Figure C2) was chosen to ensure sufficient hydration of the electrocatalytic layer.^{32–36} Furthermore, hydration also controls the local pH at the electrocatalyst interface, that also influences the selectivity between different CO₂RR products.^{37,38} To benchmark the performance, the same configuration was tested with a state of the art carbon-supported Au nanoparticle CO-selective electrocatalyst (Au/C, gold 10 wt% on Vulcan XC-72).³⁹ The modified carbon cloth electrodes (**1/CC**) and carbon supported gold nanoparticles (Au-C/CC) were first tested at different cathodic potentials. Each potentiostatic experiment was performed for an appropriate operation time (from 2 hours at -0.37 V to 30' at -0.82 V vs RHE) depending on the cell current.

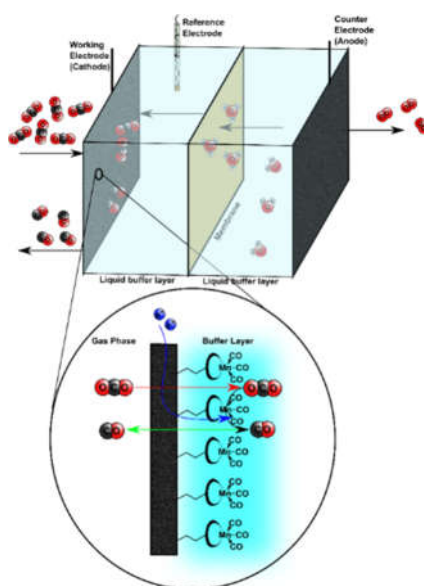


Figure 5.14. Gas diffusion layer-supported **1** electrocatalyst at the interface between gas and buffer layer phase in the flow electrochemical cell.

The faradaic efficiency and partial current profiles at different potentials of both **1/CC** and Au-C/CC are reported in Figures C3 and C4, respectively. The best operating cathode potential was chosen that maximizes the CO-partial current density, to trade-off between faradaic efficiency and CO-productivity. The optimal cathode potentials for **1/CC** and Au-C/CC were -0.67 and -0.57 V (RHE), respectively. Once the best operating point was determined, an extended electrolysis experiment was performed at each potential. Both electrocatalysts began with a CO-faradaic efficiency (FE_{CO}) close to 100% (95% Mn, 90% Au-C/CC) (Figure 5.15). The instantaneous cell current and whole cell potential profiles are reported in the Appendix

(Figures C5-C8). During the electrolysis, the faradaic efficiency for both electrocatalysts dropped by 25% and 10% for **1/CC** and Au-C/CC respectively (Figure 5.15). The total average current (between each sampling event) for **1/CC** remained almost the same from the beginning to the end, while the CO-partial current shows a decrease accompanied by a steady increase in the H₂-partial current (Figure C9), possibly indicating partial electrocatalyst degradation to species promoting HER. The total average current of benchmark Au-C/CC instead showed a drastic decrease of the total current in the first hour, almost totally driven by the CO-partial current, then a steady decrease at a much slower rate during the rest of the experiment. The H₂-partial current increased only slightly during the experiment, remaining almost constant. Such a performance drop can be ascribed to nanoparticle surface modification during electro-catalysis since no aggregation for this particular Au/C-based material was reported in a comparable time window.³⁹

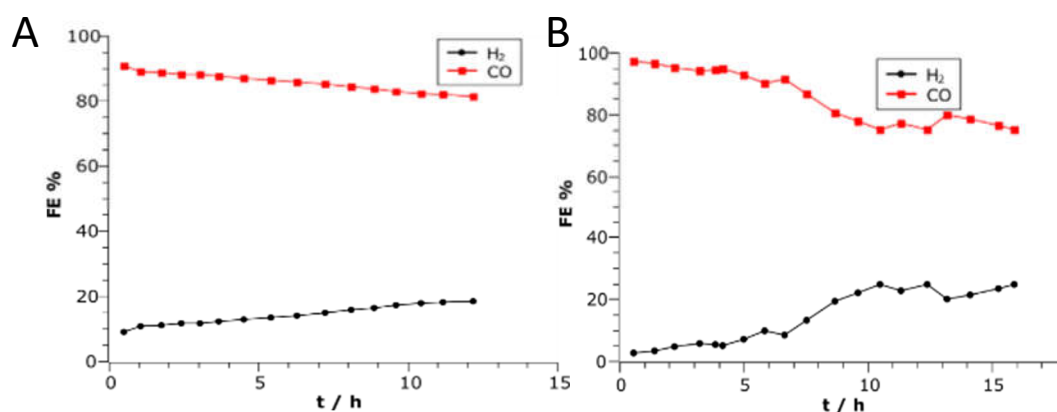


Figure 5.15. Faradaic efficiency time profile for gaseous products of (A) **1/CC** ($1.4 \cdot 10^{-9}$ mol $\text{cm}_{\text{ECSA}}^{-2}$, $4.51 \cdot 10^{-7}$ g_{Mn} $\text{cm}_{\text{geom}}^{-2}$) and (B) Au/C NPs (0.081 mg_{Au} $\text{cm}_{\text{geom}}^{-2}$) operating in buffer layer configuration, CO₂ flow rate 0.2 mL min^{-1} , buffer flow rate 0.4 mL min^{-1} .

Table 5.3 summarizes the relevant electrocatalytic parameters of the constant potential experiments for **1/CC** and Au-C/CC. Interestingly, the TON value for the former electrocatalyst operating in the buffer layer cell was almost four times that reported for a half cell (CO₂-saturated electrolyte) study, suggesting that the enhanced mass transport due to CO₂ gas-feeding plays an important role in the overall electrocatalytic performance. Furthermore, the CO average productivity observed for **1/CC** was 70 normal-liters of CO min⁻¹ per gram of Mn, more than four times than the half-cell study ($14.5 \text{ Nl}_{\text{CO}} \text{ min}^{-1} \text{ gMn}^{-1}$). The metal mass-weight productivity for Au-C/CC electrocatalyst was instead almost three orders of magnitude less, about $0.32 \text{ normal-liters of CO min}^{-1} \text{ per gram of Au}$ (Figure C10). It is noteworthy that the

metal loading for **1/CC** (corresponding to a monolayer of anchored complex) is more than two orders of magnitude less than Au/C, with similar CO-partial current performance. Hence, a different electrocatalyst activity picture is given by the CO-mass specific currents, 8930 A gMn⁻¹ for the anchored Mn-complex electrocatalyst and 41.6 A gAu⁻¹ for Au-C electrocatalyst after 16h and 12h of operation respectively. The CO₂RR turnover number of **1/CC** electrocatalyst over 16h of operation is more than 1.6·10⁵ (1.2·10⁵ in 12h) compared to Au-C/CC electrocatalyst (calculated on the total gold mass present) that is almost two orders of magnitude less (2·10³).

Table 5.3. Relevant electrochemical parameters for electrolysis experiments with **1/CC** and Au/CC NPs. [a] TON for nanoparticles are considered with respect to the total metal mass present.

	1/CC (E = -0.67 V)	Au/C NPs (E = -0.57 V)
FE _{H₂}	13.7%	15.7%
FE _{CO}	76.2%	82.4%
FE _{HCOOH}	10.1%	1.9%
FE _{totalCO₂}	86.3%	89.0%
Prod _{CO} (NI min ⁻¹ gMet ⁻¹)	69.2	0.318
HCOOH (g min ⁻¹ gMet ⁻¹)	16.9	0.0152
TON _{CO}	145286	1999 ^[a]
TON _{HCOOH}	19252	47.4 ^[a]
TON _{totalCO₂}	164539	2045.97 ^[a]

It is worth noting the difference in HCOOH-selectivity in the gas-fed cell when compared to the half-cell study for the **1/CC**. In particular, no formate was detected after 10h of operation at the same cathodic potential in the half-cell study, while a FE_{HCOOH} of 10% was observed in the gas-fed system, with a productivity of 16.9 g min⁻¹ gMn⁻¹ (1.01 kg h⁻¹ gMn⁻¹). Such a selectivity difference was also observed by Reisner et al. at different electrocatalyst loadings for [MnBr(2,2'-bipyridine)(CO)₃].¹¹ In particular, at high electrocatalyst loading, the CO-producing pathway is preferred. These observations have been explained considering that at high loading the Mn centers can interact (and dimerize), leading to the production of CO, while at low loading the formation of Mn hydride become feasible, which enhances the formate production. In the case of the gas-fed full cell experiments compared to the half-cell experiments the difference cannot be ascribed to a different loading of the electrocatalyst as

the preparation is identical. Also, a decrease in the electrocatalyst loading during the experiment can be ruled out, as no significant degradation of the electrocatalyst is observed. The difference in selectivity can be hypothesized to be related to a lower interfacial pH due to the presence of pure CO₂ in the GDL, buffering the pH by consuming OH⁻ formed both by CO₂RR and HER to produce HCO₃⁻. It is known that more acidic conditions in homogeneous Mn-bpy solutions increase the production of the hydride and hence formate.²⁷ The higher proton activity (compared to half-cell, buffered only with HCO₃⁻) can slightly shift the kinetics to the monomer pathway with the formation of a hydride that reacts with CO₂ to form HCOOH. This can explain the side production of HCOOH in the gas-fed case. Despite this lower CO-selectivity, the two products (CO and HCOOH, as formate) are in different phases (gas and buffer layer respectively), hence their separation is not challenging. In order to investigate the stability of **1/CC** electrocatalyst, the pristine and used electrode was scrutinized with SEM microscopy with an EDS dispersive detector to map the distribution of the elements on the electrode surface. The pristine and used electrode micrographs are shown in Figure 5.16. The microanalysis of the pristine electrode (Figure 5.16 and Figures C10-C16) shows a uniform distribution of Mn on the electrode surface, with no aggregates present.

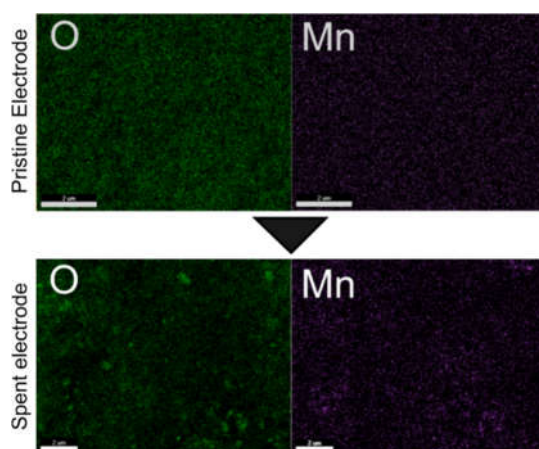


Figure 5.16. SEM EDAX element mapping of both pristine and used **1/CC** electrode.

The used electrode (Figure 5.16) does not show significant Mn loss phenomena as the Mn surface distribution and density are almost unchanged (Table C1 and C2). Some areas show a higher oxygen density with no apparent correlation with the manganese distribution. This can be related to residual potassium carbonate crystals covering the electrocatalyst surface as a result of contact with the electrolyte: Table C2 shows a dramatic increase in the element fraction of both oxygen and potassium compared to the pristine electrode (Table C1). Conversely, the formation of manganese hydroxides or carbonates deriving from the decomposition of *fac*-Mn(apbpy)(CO)₃Br can be ruled out. Furthermore, it should be noted that

the limited drop of FE and J_{CO} occurs after $1.6 \cdot 10^5$ CO_2 turnovers in 16 hours: during this time frame the electrocatalyst can be considered stable.

5.8 Concluding remarks

Electrocatalytic structures based on metal nanoparticles are known to convert CO_2 to CO: gold, silver, palladium and, to a certain extent, copper are able to produce CO under a variety of conditions, including in aqueous media.^{40–42} The use of metal based catalysts usually requires high metal loadings and careful nanoparticle morphology control in order to guarantee selectivity and faradaic efficiencies and avoid performance degradation due to nanoparticle coalescence phenomena. The use of organometallic molecular complexes as electrocatalysts for CO_2 electroreduction is a viable strategy to overcome such limitations affording more efficient metal utilization (as it is intrinsically single site) and allowing the possibility to control the selectivity and the activity of the electrocatalyst by adjusting the coordination of the metal center to tune both electronic properties and steric hindrance.^[18–25]

Furthermore, the immobilization of organometallic complexes on a conductive support has been proven to be an extremely powerful tool to further improve the advantages of the use of organometallic complexes,^{3,4,11–13,15,43–52} when covalently bound. We herein demonstrated that the use of a *fac*-Mn(apbpy)(CO)₃Br complex grafted electrochemically onto a carbon cloth support via electrochemical diazonium salt reduction with subsequent formation of a C-C covalent bond is much more efficient than the corresponding homogeneous solution. The cumulative TON for CO production for **1/CC** reaches in a half-cell experiment more than 33 000 after 10 h, with an average faradaic efficiency of 53%. It is worth noting how **1/CC** reaches a TON which is two orders of magnitude higher than that of the same complex tested under homogeneous conditions in acetonitrile solutions ($\text{TON}_{\text{CO}} = 12$). Furthermore, covalently bound electrocatalysts result in faster electron transfer kinetics, higher TOFs and TONs, and significant improved stability when compared to the same catalysts dissolved in solution.^{3,4,12,52} A further improvement is provided by the same *fac*-Mn(apbpy)(CO)₃Br complex anchored on CC and used in a gas-fed complete electrolysis cell that overcomes the mass transport limitations of using dissolved CO_2 .⁵³

The performance was almost four times greater in terms of TON, 50% higher in terms of FE, and more than an order of magnitude in terms of volumetric productivity compared to the same material in a half-cell study. In addition, the electrode outperforms a benchmark state-of-the-art gold metal nanoparticle on carbon electrocatalyst, despite a metal loading more than two orders of magnitude less. The *fac*-Mn(apbpy)(CO)₃Br electrocatalyst was able to reach

more than $1.6 \cdot 10^5$ turnovers in 16 hours of operation, producing up to 70 NI min^{-1} of CO and 17 g min^{-1} of HCOOH per gram of Mn with limited H_2 evolution and stable performance in aqueous media. To the best of our knowledge this is the first example of a covalently bound organometallic complex employed in a complete gas-fed CO_2RR electrolyzer, opening the possibility of scaling up the process employing a cost-effective Mn-based electrocatalyst. Increasing the electrochemical surface area (by replacing the support material) of the electrode can allow larger metal loadings on a geometric area basis, allowing much longer and higher performance, opening the possibility of scaling up the process to an industrial scale.

5.9 Experimental section

Electrochemistry

Cyclic voltammetry experiments and diazonium salt reduction were performed using a Metrohm Autolab 302n potentiostat. 0.5–1.0 mM solutions of the compounds were used in dry CH_3CN , with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte (0.1M). A single-compartment cell, with a carbon cloth (CC) as working electrode was employed, alongside a Pt counter electrode and an Ag/AgCl (KCl 3M) as reference electrode. Under our experimental conditions, the reference ferrocene/ferrocinium ($\text{Fc}^{+/0}$) redox is at $E_{1/2}=0.40 \text{ V}$ ($\Delta E_p=65 \text{ mV}$) *vs.* Ag/AgCl.

Half-cell assembly and experimental conditions

The experiments were conducted in a base-resistant 3d-printed ABS cell (Figure C1) designed with a gas collector cone housed on the top of the cell. The cell, oriented vertically, was assembled in two halves, one housing the cathodic compartment and the other the anodic one, separated by a Nafion 117 membrane in the middle, hold by a Teflon gasket. The cathode composed connected to the outside of the cell with enamelled copper wire; the reference was of an Ag|AgCl|KCl_{sat} electrode placed in close proximity with the working electrode. The counter electrode, a platinum wire, was housed into the anodic compartment. Both compartments were filled with 0.1M KHCO_3 and sealed with rubber gaslock® plugs. Prior to each electrolysis experiment, the cathodic compartment electrolyte was saturated by bubbling 99.99% purity CO_2 and the collector cone gas headspace was completely evacuated and filled with electrolyte.

The electrolysis experiments were conducted at different potentials, ranging from -1.0V to -1.6V *vs* Ag|AgCl|KCl_{sat} for an appropriate electrolysis time, in order to collect enough gas for GC analysis, ranging from 15 minutes (high currents) to 1 hour (low currents). After the

electrolysis time is elapsed, the current is integrated to obtain the charge and the gas is collected by a syringe, measured and injected (100 μ l) into a gas chromatograph (Carboxen Column, designed to separate hydrogen, O₂, N₂, CO, CO₂ and C1-C3 gases) with a 140°C 9 minute isotherm, followed by a 30 °C/min ramp to 225°C and a holding time of 25 minutes. The cell was saturated again with CO₂ prior each experiment. The liquid catholyte sample was collected in order to detect any trace soluble product present at the end of the experiment cycle. The stability experiments were conducted by subsequent electrolysis cycles at fixed potential, -1.3V in this case, each elapsing 1 hour time; the products were analysed following the same protocol of the potential variation test. The potential was chosen accordingly to the activity test, as a tradeoff between electrolysis current and faradaic efficiency.

Gas-fed complete electrolysis cell and experimental conditions

Anode preparation on carbon cloth: 10mg of IrO₂ and 20mg of Vulcan XC-72 were dispersed ultrasonically for 60 minutes in mixture of 1.5 mg 2-propanol and 0.5g of water, together with 85mg of a 5 wt% nafion oligomer solution in lower aliphatic alcohols. The uniform ink obtained was brush-painted by subsequent 7-9 depositions-drying cycles on a 37x30mm carbon cloth previously cleaned ultrasonically and tape-masked to expose an area of 4.3 cm² (Figure C2b). The IrO₂ loading (approx. 1.8 mg cm⁻²) was estimated by weight difference.

Au-C cathode preparation on carbon cloth: 45.2 mg of Au/C 10% electrocatalyst was dispersed ultrasonically for 60 minutes in mixture of 2.0 mg 2-propanol and 1.0 g of water, together with 96 mg of a 5 wt% nafion oligomer solution in lower aliphatic alcohols. The uniform ink obtained was brush-painted by subsequent 5-6 depositions-drying cycles on a 37x30mm carbon cloth previously cleaned ultrasonically and tape-masked to expose an area of 4.3 cm² (see scheme S2a) until the maximum possible loading on the surface was achieved. The Au/C loading (approx. 0.81 mg_{cat} cm_{geom}⁻², 0.081 mg_{Au} cm_{geom}⁻²) was estimated by weight difference.

Electrochemical reactor experiments: experiments were conducted in a 3d-printed ABS gas diffusion flow reactor (Figure C2) equipped with two flow buffer layers (cathode and anode) with a circulating 0.2M KHCO₃ (Sigma Pure PA) solution on both compartments. Both the liquid and the gases were fed by using a Gilson peristaltic pump equipped with Tygon tubes. The cell, vertically oriented, housed in a CO₂-filled drybox, has four compartments: starting from cathode side, i) a gas compartment where pure CO₂ (99.995% purity) was fed; the gas diffusion electrode modified with *fac*-Mn(apbpy)(CO)₃Br complex was housed at the interface between the gas compartment and the cathode buffer layer; the gas tightness was ensured by two silicon rubber rectangular gaskets with the additional purpose of masking the active

area (23 x 18 mm, 4.3 cm² exposed surface, (Figure A2b); ii) and iii) cathodic and anodic buffer layers that were separated by a Nafion 117 membrane; and iv) the anode gas compartment, continuously purged with nitrogen. The anode buffer layer and the anode gas compartment were separated by the carbon cloth GDL modified with IrO₂ water oxidation reaction electrocatalyst. The cathode buffer layer houses also the reference electrode (Ag|AgCl|KCl_{sat}) which is closely placed to the cathode electrocatalyst in order to minimize the uncompensated resistance. The buffer layers were filled with circulating 0.2M Bioultra™ KHCO₃, (pre-saturated with CO₂ for 30 minutes to remove dissolved oxygen) and high purity (99.995%) CO₂ was fed instead to the cathode gas compartment. The anode gas compartment was continuously evacuated with nitrogen to minimize detrimental oxygen contaminations. The cathode exhaust was fed to the cathode buffer layer tank for gas-liquid separation and pressure equilibration to avoid gas bubbling through the gas diffusion layer. The buffer layer solutions were continuously recycled; the cathode exhaust was sent to and hydraulic guard and vented. Gas was sampled directly in the cathodic cell compartment with a 200ul Hamilton™ gastight syringe through a GC-grade silicon rubber port. The flow rate was 0.2 and 0.4 mL min⁻¹ for buffer layers and CO₂ cathode fed respectively. The gas flow rate was traded off to ensure an excess of CO₂ at the cathode without excessively diluting the gas sample. The cathode potential was controlled by setting it to values referenced to the internal reference electrode, while the total cell potential was measured by an external voltmeter. The current collectors were made of stainless steel in a control-sense double connector configuration (Figure C2a) to minimize the contact IR_{drop}. The solution was not allowed to come in contact with the steel to avoid Fe ions contamination inside the cell. The potential was constantly held (between -1.0V to -1.6V vs Ag|AgCl|KCl_{sat}) during every experiment and the gas was sampled at regular time intervals after reaching a steady state and analysed via gas chromatography; the current was integrated to obtain the charge elapsed. Each electrocatalyst assembly was first tested at different potential to determine the optimal (in terms of FE and productivity) operating point, then constant cathode potential electrolysis experiments up to 16 hours of duration were performed.

Product analysis: the gas sampled from the cathodic compartment (100ul) was injected into a Shimadzu gas chromatograph using high purity He (99.995%) as carrier and equipped with a Carboxen WCOT Column, designed to separate hydrogen, O₂, N₂, CO, CO₂ and C1-C3 gases; the temperature program was a 140°C 9 minute isotherm, followed by a 30 °C/min ramp to 225°C and an additional holding time of 25 minute. Gas calibration was performed prior to the experiments. The liquid products were analysed with a Shimadzu high performance liquid chromatograph (HPLC) equipped with a 100ul loop, a column specific for light carboxylic acids

and alcohols and a refractive index detector; prior to the injection of the sample the 0.2M KHCO_3 buffer was suppressed by passing it in a cationic exchange resin to replace K^+ with H^+ , decomposing the HCO_3^- as CO_2 . The standard calibration curve was made in the same conditions (HCOO^- in 0.2M KHCO_3) to minimize the matrix effect. The detection limit was below 50uM for HCOO^- in those conditions.

Pre- and post-experiments microscopy analysis: the pristine and spent electrode morphological and compositional characterization on the electrode surface was carried out using a Tescan GAIA 3 FIB/SEM microscope equipped with an Edax EDS Octane detector. Both Images and EDS compositional characterization were acquired using an impinging beam energy of 15 keV. Element distribution maps were acquired with a collection time of 600s. The spots analyzed are shown in Figure C10.

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CHAPTER 6. Photochemical CO₂ reduction using Re(I) tricarbonyl complexes with bipyridyl-type ligands with and without 2nd coordination sphere effects

6.1 Introduction

Photocatalytic CO₂ reduction with Re(I) tricarbonyl diimine complexes, e.g., *fac*-ReCl(bpy)(CO)₃ (bpy = 2,2'-bipyridine), was first reported by Lehn and co-workers in 1983.¹ Since then, many related complexes have been extensively studied both as electro- and photocatalysts for selective CO₂ reduction to CO.²⁻¹⁰ While the Re(I) complexes do not exhibit the greatest catalytic ability amongst CO₂ reduction catalysts, they offer the advantage of being self-sensitized, i.e., in addition to being a catalyst, they can simultaneously act as a photosensitizer (PS) due to their long-lived excited states, which triggers their reaction with a sacrificial reductant (D) to initiate catalysis.¹¹⁻¹³ The photophysical properties of Re(I) complexes have been investigated by many researchers due to their strongly emissive and long-lived excited states.^{9, 14-21} The photochemical properties of rhenium bipyridyl tricarbonyl complexes are influenced by metal-centered ligand field excited states, π - π^* excited states localized on the bipyridyl ligand, and the metal-to-ligand charge transfer (MLCT) excited state. In many cases, the MLCT state is the lowest lying excited state, because the π^* orbital energy is lower than that of the lowest energy empty d orbital of Re(I). This is a direct consequence of the large conjugated π^* system of the bpy ligand. The emissive ³MLCT state can be tuned by chemical modification of the bpy ligand and by an appropriate choice of the axial monodentate ligand.

In 1985, Meyer and co-workers reported one- and two-electron pathways in the electrocatalytic reduction of CO₂ to CO using *fac*-ReCl(bpy)(CO)₃ (**Rebpy**) in an acetonitrile (CH₃CN) solution containing ⁿBu₄N⁺PF₆⁻ as an electrolyte. The electrochemically produced one-electron-reduced species (OERS), which is a bpy ligand-based radical, dissociates Cl⁻ to yield [Re(bpy^{*})(CO)₃] that reacts with CO₂ during bulk electrolysis via a slow one-electron pathway.²² They also proposed a faster reaction mechanism via the two-electron-reduced species, [Re(bpy)(CO)₃]⁻. Interestingly, they observed the formation of CO₃²⁻ as a side product in the one-electron pathway. However, in the two-electron pathway, instead of CO₃²⁻, Bu₃N was observed, presumably via Hofmann degradation of the quaternary ammonium salt. Metalcarboxylic acids (M-COOH) have been proposed as intermediates in the production of CO. Gibson et al. isolated a key compound, Re(dmb)(CO)₃(COOH), (dmb = 4,4'-dimethyl-2,2'-bipyridine) by the reaction of Re(dmb)(CO)₄(OTf) (OTf = trifluoromethanesulfonate) with aqueous KOH.²³ They observed conversion of Re(dmb)(CO)₃(COOH) to

$(\text{CO})_3(\text{dmb})\text{Re}-\text{CO}(\text{O})-\text{Re}(\text{dmb})(\text{CO})_3$ as a major species in acetone upon irradiation with UV light. They suggested that the pathway involves loss of CO_2 from $\text{Re}(\text{dmb})(\text{CO})_3(\text{COOH})$ to form the hydride species, followed by its reaction with another $\text{Re}(\text{dmb})(\text{CO})_3(\text{COOH})$ molecule to form the CO_2 -bridged dimer together with liberation of H_2 . Interestingly, the formate complex that can potentially be formed by the interaction of CO_2 with the Re-hydride species was not the major product. They also reported the conversion of $\text{Re}(\text{dmb})(\text{CO})_3(\text{COOH})$ with CO_2 to the bicarbonate complex, $\text{Re}(\text{dmb})(\text{CO})_3(\text{OCO}_2\text{H})$, in DMSO.^{24, 25} While Gibson did not specifically discuss the conversion of CO_2 to CO with Re-COOH, Muckerman et al. explored CO_2 reduction pathways involving $\text{Re}(\text{bpy})(\text{CO})_3(\text{COOH})$ with CO_2 to form $\text{Re}(\text{bpy})(\text{CO})_3(\text{OCO}_2\text{H})$ and CO by DFT calculations.²⁶ The predicted pathway involves two transition states: the interaction of the bound COOH with a CO_2 molecule, followed by a heptacoordinate transition state.²⁶ One of us tried to determine the binding rate of CO_2 to the photoproduct $\text{Re}(\text{dmb})(\text{CO})_3$ by photolysis of $[\text{Re}(\text{dmb})(\text{CO})_3]_2$ in CO_2 -saturated tetrahydrofuran (THF) using time-resolved step-scan FTIR spectroscopy, but it was too slow to be accurately measured. The estimated reaction rate was $\sim 0.003 \text{ s}^{-1}$.²⁷ However, the stoichiometric reaction in dry *N,N*-dimethylformamide (DMF) produces CO with a 25-50% yield based on $[\text{Re}]$ without any proton or sacrificial electron donor. A CO_2 -bridged dimer, $(\text{CO})_3(\text{dmb})\text{Re}-\text{CO}(\text{O})-\text{Re}(\text{dmb})(\text{CO})_3$ is identified as an intermediate with a trace amount of $\text{Re}(\text{dmb})(\text{CO})_3(\text{COOH})$. Both $[\text{Re}(\text{dmb})(\text{CO})_3]_2(\text{OCO}_2)$ and $\text{Re}(\text{dmb})(\text{CO})_3(\text{OCO}_2\text{H})$ are detected as oxidation products. However, the previously reported formato-rhenium species was not detected, probably due to the absence of a proton source. The proposed pathway involving the Re dimer has been investigated by DFT calculations.²⁸ A decade later, Kubiak and Sharp reported the faster CO_2 addition ($k_{\text{CO}_2} = 120 \text{ M}^{-1} \text{ s}^{-1}$ and $12 \text{ M}^{-1} \text{ s}^{-1}$, respectively) to the doubly reduced $\text{Re}(\text{dmb})(\text{CO})_3^-$ and $\text{Re}(\text{bpy})(\text{CO})_3^-$ complexes, to form the corresponding Re-COOH species using stopped-flow IR experiments in THF containing 18-crown-6.²⁹

Ishitani's group has extensively studied homogeneous photochemical CO_2 reduction with Re complexes, including self-sensitized systems, bimolecular systems (i.e., a $\text{Ru}(\text{bpy})_3$ -type PS and a Re catalyst), and supramolecular systems where a PS is covalently attached to a Re catalyst via a linker.^{3, 4, 7, 13, 17, 30-35} The most interesting discoveries are: (1) $\text{Re}(\text{bpy})(\text{CO})_3(\text{DMF})^+$ can capture CO_2 in DMF in the presence of triethanolamine (TEOA) to produce $\text{Re}(\text{bpy})(\text{CO})_3(\text{OC}(\text{O})-\text{OCH}_2\text{CH}_2\text{NR}_2)$, where $\text{R} = \text{CH}_2\text{CH}_2\text{OH}$, via $\text{Re}(\text{bpy})(\text{CO})_3(\text{OCH}_2\text{CH}_2\text{NR}_2)$; (2) observation of $\text{Re}(\text{bpy})(\text{CO})_3(\text{OC}(\text{O})-\text{OCH}_2\text{CH}_2\text{NR}_2)$ during photocatalytic CO_2 reduction; (3) supramolecular systems are typically more efficient than the corresponding bimolecular systems, although the catalytic activity depends on the nature of the linkers; and (4) contrary to a commonly held conception that a p-conjugated linker is

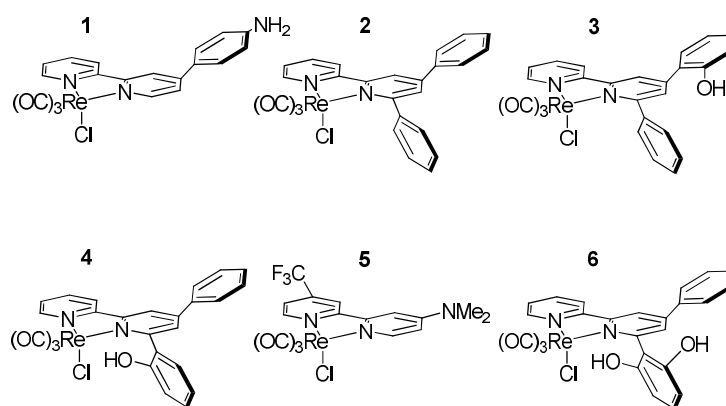
required for fast electron transfer between the PS and the catalyst units in a supramolecular photocatalyst, systems with saturated ethylene linkers adequately transfer photoproduced electrons to the catalyst unit ($k_{\text{ET}} = 10^9 \text{ s}^{-1}$) in the photocatalytic reduction of CO_2 . Ishitani et al. have also proposed that the $\text{Re-CO}_2\text{-TEOA}$ adduct acts as a catalyst, receiving an electron twice from the photo-produced one-electron-reduced species, i.e., $[\text{ReX}(\text{bpy})(\text{CO})_3]^-$ ($\text{X} = \text{Br}^-$, formate), which is itself generated upon reductive quenching by TEOA.^{8, 10, 33}

Kubiak and his collaborators have conducted extensive studies on: kinetics/mechanisms of CO_2 reduction to CO using $\text{Re}(\text{CO})_3$ complexes with peripheral 4,4'-substituents on the bipyridyl ligand and added Brønsted acids; highly active bio-inspired hydrogen-bonded dimer catalysts; catalysis with immobilized Re complexes on electrode/semiconductor surfaces, and mechanisms predicted by DFT calculations.^{29, 36-46} Manbeck et al. investigated electrochemical CO_2 reduction using $\text{Re}(\text{CO})_3$ complexes with proton-responsive ligands such as 6,6'- (or 4,4'-) dihydroxy-2,2'-bipyridine (6DHBP and 4DHBP), assuming that these ligands offer control of the reaction through pH-dependent properties, second coordination sphere effects, and possibly by providing a local proton for catalytic reactions.⁴⁷ These complexes show stepwise electrochemical reductive deprotonation of the OH group, yielding the equivalent chemically deprotonated species. While the 4DHBP complex is an effective catalyst similar to that which contains the $^t\text{Bu-bpy}$ ligand, the 6DHBP complex surprisingly exhibits a turnover number (TON) of < 1 . Jurss recently reported enhanced electrocatalytic activity by a series of $\text{Re}(\text{bpy}')(\text{CO})_3$ complexes with second coordination sphere hydrogen-bonded NH_2 donors ($\text{bpy}' = 6\text{-ortho-}$, *meta*-, and *para*-aminophenyl-2,2'-bipyridine).⁴⁸ These catalysts outperform the benchmark catalyst, $\text{ReCl}(\text{bpy})(\text{CO})_3$, in CH_3CN with and without added trifluoroethanol (TFE), with turnover frequency (TOF) values increasing in the following order of position of the NH_2 group on the phenyl ring, *para* $<$ *ortho* $<$ *meta*. The Faradaic efficiency for CO production of the complex with the *ortho*- NH_2 group was reported to be quite low ($\sim 40\%$) compared to the other catalysts in dry CH_3CN . This was explained by the relatively short distance between the NH_2 group and the Re center resulting in coordination during catalysis and deactivation of the catalyst.

We previously investigated the electrochemical CO_2 reduction performance of six Re complexes (**1** – **6**) shown in Scheme 1.⁴⁹⁻⁵³ Complexes **4** and **6** have an OH group in the second coordination sphere of the Re center. Detailed investigations revealed that the OERS of both **4** and **6** dissociates a coordinated Cl^- anion with net loss of $\frac{1}{2}$ of H_2 to form a neutral six-coordinate species with an internal Re-O (phenoxy) bond. The neutral Re-O species derived from **4** has been recently characterized by electrochemistry, UV-Vis, IR, NMR and DFT

calculations.^[53] The complex, **4**, exhibits a first reversible reduction potential at -1.70 V vs Fc^+/Fc , followed by an irreversible process (with a peak potential at -2.06 V), at which electrochemical CO_2 reduction catalytically takes place. Bulk electrolysis in CO_2 -saturated CH_3CN with phenol as a proton source produced CO at -2.3 V vs Fc^+/Fc with 100 % Faradaic efficiency and a TON of 9. While the mechanism for CO production is uncertain, the catalytic activity was interpreted by the Re–O bond being ruptured and the reduced Re species reacting with CO_2 to form CO by a traditional mechanism. However, the phenoxy group may also contribute to the CO production via Re-OC(O)OPh^{2-} according to DFT calculations.⁵³ Recently, Matsubara et al. reported the synthesis and electrochemical properties of bi-functional $[\text{ReBr(L)(CO)}_3]\text{PF}_6$, where L is 6-(2-hydroxyphenyl)-6'-(2-(trimethylaminomethyl)phenyl)-2,2'-bipyridine.⁵⁴ The complex not only has an OH group like in compound **4**, but also an NMe_3^+ group that provides a local coulombic interaction in the second coordination sphere. The compound exhibits a catalytic reduction wave that starts from -1.84 V with a small current enhancement under CO_2 in DMF containing 5% water ($i_c/i_p \sim 3.1$, where i_c and i_p are the catalytic current and the corresponding peak current in the presence and absence of CO_2 , respectively). Bulk electrolysis at -1.89 V proved the gaseous product is only CO with 88% Faradaic efficiency. However, the possible formation of a Re–O species by reductive deprotonation was not discussed.

While there are a number of reports of electrochemical CO_2 reduction with Re(CO)_3 complexes containing ligands that have OH group(s) in the second coordination sphere or with ligands bearing an amine group, they have received limited application in photochemical CO_2 reduction. In this work, the effect of different substituents on the 2,2'-bipyridine backbone, including OH and NH_2 groups, during photochemical CO_2 reduction has been explored in order to understand the structure-function relationship. We report the photocatalytic activities of all the complexes compared to the parent **Rebpy** under the same conditions in *N,N*-dimethylacetamide (DMA) as the reaction solvent. There is precedent in the literature for using this solvent instead of the more commonly employed DMF,^{10, 55, 56} since DMF undergoes hydrolysis to produce formate during ion chromatographic analysis of reaction product mixtures, which complicates the quantitative analysis of formate as a CO_2 reduction product.⁵⁵ We therefore report here photocatalytic CO_2 reduction systems consisting of a rhenium complex (**1** – **6**) acting as a Cat and a PS, and triethanolamine (TEOA) with/without 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]-imidazole (BIH) as a sacrificial reductant in DMA.



Scheme 6.1. Structures of the Re(I) bipyridine complexes that we have investigated as photocatalysts for CO₂ reduction.

6.2 Photophysical properties

The UV-Vis absorption spectra of complexes **1–6** in DMA are shown in Figure 6.1, while the λ_{max} of the MLCT absorption bands together with their molar absorption coefficients (ϵ) are summarized in Table 6.1. Emission spectra are shown in Appendix D for chapter 6 (Figure D1).

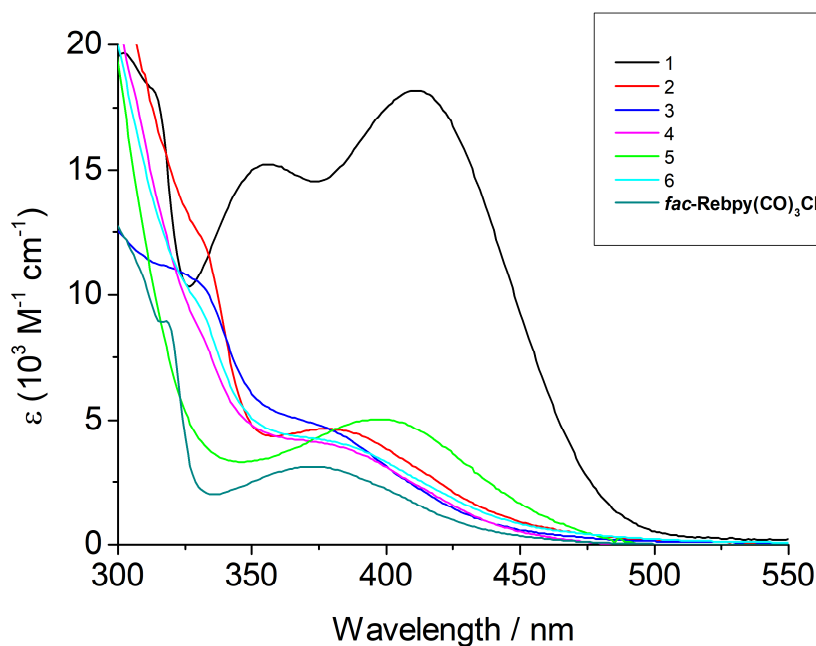


Figure 6.1. UV-Vis absorption spectra of **1–6** and **Rebpy** in DMA solution.

The UV-vis absorption spectrum of parent **Rebpy** in DMA exhibits a broad MLCT band at $\lambda_{\text{abs}} = 371$ nm and a more intense π - π^* band at 292 nm.¹³ Complexes **2–6** share similar characteristics to **Rebpy**, with the MLCT band shifted slightly to lower energy (by up to +27 nm), and being slightly more intense (by a factor of up to 1.61 in the case of **5**). In contrast,

complex **1** exhibits two bands in the MLCT region at 354 and 411 nm that are much more intense than the MLCT band of **Rebpy** and **2–6**, together with another strong shoulder band at 314 nm.

The placement of aryl substituents on the bpy ligand results in the observed bathochromic shift of the MLCT band in **1–6**, due to the extension of the π system which lowers the $^1\pi-\pi^*$ energy level. The significant difference between complex **1** and the others is the much larger molar absorption coefficient of its MLCT band ($\epsilon_{411\text{nm}} = 18,200 \text{ M}^{-1} \text{ cm}^{-1}$), which is almost four times larger than typical ϵ_{MLCT} values reported in the literature for this class of Re bpy complex (typically around $3000 \text{ M}^{-1} \text{ cm}^{-1}$).^{13, 57, 58} A non-negligible role must be played by the amino moiety placed in the para position of the phenyl in the 4-position. The $-\text{NH}_2$ group exerts both an inductive ($-I$) and mesomeric effect ($+M$) influence on the metal centre. To better understand the electronic structure of complex **1**, DFT calculations will be performed.

Table 6.1 Photophysical properties of $\text{ReCl}(\text{L})(\text{CO})_3$ complexes in argon-saturated DMA.

^a λ_{ex} was at the λ_{max} of the MLCT band. ^bFor reductive quenching of the MLCT excited state by BIH. ^cQuenching fraction with 0.1 M BIH (Figure D2); $\eta_{\text{q}} = K_{\text{SV}}[\text{BIH}]/(1 + K_{\text{SV}}[\text{BIH}])$.

Complex	MLCT λ_{max} (nm)	ϵ_{MLCT} (M^{-1} cm^{-1})	Emission λ_{max} (nm) ^a	Emission lifetime (ns) ^a	K_{SV}^{b} (M^{-1})	k_{q}^{b} ($\text{M}^{-1} \text{ s}^{-1}$)	h_{q}^{c}
Rebpy	371	3111	605	24	117	4.9×10^9	0.92
1	411	18200	608	6	d	$>>10^{10}$	1.00
2	379	4640	612	21	29	1.4×10^9	0.84
3	377	4640	605	25	741	2.9×10^{10}	0.99
4	383sh	3920	608	23	376	1.6×10^{10}	0.97
5	398	5020	623	40	461	1.2×10^{10}	0.98
6	383sh	~ 4500		21	-		

^aThe λ_{max} of the MLCT band was used as the excitation wavelength for emission measurements of each complex. ^bFor reductive quenching of the MLCT excited state by BIH. ^cQuenching fraction with 0.1 M BIH; $h_{\text{q}} = K_{\text{SV}}[\text{BIH}]/(1 + K_{\text{SV}}[\text{BIH}])$. ^dAccurate determination of K_{SV} and thus k_{q} was not possible due to the very short excited state lifetime.

The emission spectra of **Rebpy** and **1–6** consist of a single, broad band which is a direct consequence of a transition from the lowest $^3\text{MLCT}$ excited state to the ground state (Figure

D1). The lifetime of the ³MLCT state reported for the parent **Rebpy** in the literature is relatively short (25 ns in CH₃CN),⁵⁸ as also confirmed by our measurements in DMA (24 ns) listed in Table 1. Complexes **2**, **3**, **4**, and **6** have comparable emission lifetimes of 21, 25, 23, and 21 ns, respectively. However, complex **1** has a very short MLCT lifetime (6 ns) that is close to the limit of detection of our instrument. While a few BIH oxidation potentials are reported ($E_{\text{ox}} = -0.075$ V⁵⁹ or -0.068 V²⁴ (using CV) and -0.103 V²⁴ (using SQWV) vs Fc⁺/Fc), BIH is a powerful reagent for reductive quenching reactions of the excited states of complexes **2–6**, resulting in highly efficient formation of the OERS ($k > 10^9$ M⁻¹ s⁻¹), which initiates catalytic CO₂ reduction .

Table 6.2. Electrochemical (in CH₃CN) and photochemical (in DMA) properties of ReCl(L)(CO)₃ complexes when used as catalysts in the electrocatalytic and photocatalytic reduction of CO₂, respectively^a

Complex	Electrocatalytic CO ₂ Reduction				Photocatalytic CO ₂ Reduction				
	$E_{1/2}$ and E_p (V vs. Fc ⁺ /Fc)	$E_{\text{cat}/2}$ (V vs. Fc ⁺ /Fc)	i_c/i_p	Ref	LED used (nm)	TON without BIH (min) ^b	TON with BIH (min) ^c	TOF _{max} without BIH ($\times 10^{-3}$ s ⁻¹) ^d	TOF _{max} with BIH ($\times 10^{-3}$ s ⁻¹) ^d
Rebpy	-1.75, -2.09	-2.07	3.8	^g	365	40 (1200)	144 (3000)	1.9	2.0
Rebpy ^h	-1.73, -2.15	-2.12	4.4	[48]					
1	-1.70, -2.12	-2.04	5.3	[49]	415	32 (1200)	120 (1200)	0.5	3.0
2	-1.71, -2.14	-2.08	1.7	[50]	375	12 (660)	31 (1200)	1.0	1.3
3	-1.77, -2.02	-2.00	2.5	[50]	375	9 (660)	75 (660)	1.2	3.2
4	-1.70, -2.06	$\sim -2.0^e$	~ 2	[53]	375	7 (1050)	49 (780)	0.6	1.8
5	-1.68, -2.12	-2.20 ^f	4.4 ^f	[50]	405	1.0 (660)	23 (910)	0.6	4.7
6	-1.70, -1.99	-1.98	2.1	[52]	375	13 (2310)	72 (1590)	0.3	1.6

^aCathodic peak potential (E_p) for an irreversible process, catalytic half-wave potential ($E_{\text{cat}/2}$), catalytic peak current (i_c), and corresponding peak current in the absence of CO₂ (i_p), were measured by CV with a scan rate of 200 mV s⁻¹ except for complex **4** (50 mV s⁻¹) in CH₃CN containing 0.1 M ⁿBu₄N⁺PF₆⁻ electrolyte. All these values are vs Fc^{+/0}. ^b0.5 mM Re complexes, 1.25 M TEOA in DMA, 4.3 mW LED power. The value in parentheses is the total irradiation time. ^c0.5 mM Re complexes, 1.25 M TEOA and 0.1 M BIH in DMA, 4.3 mW LED power. The value in parentheses is the total irradiation time. ^dValues of TOF_{max} without BIH are typically determined at ~ 30 min irradiation, but that with BIH is at ~ 300 min. ^eDue to no peak catalytic

current, this is a rough estimate. ^fThe λ_c is unusually shifted 0.08 V more negative from the potential of E_p of this species.⁵⁰ ^gThis work, ^hAt a scan rate of 200 mV s⁻¹.

6.3 Photocatalytic CO₂ reduction in DMA

Photocatalytic CO₂ reduction has been carried out by irradiation of CO₂-saturated DMA solutions containing a rhenium complex (0.5 mM), TEOA (1.25 M), and either 0.1 M BIH or no BIH with low-powered LEDs (4.3 mW). Table 6.2 summarizes the results of the self-sensitized photolysis experiments that have been performed using 4.3 mW irradiation with and without BIH. All processes proceed via an initial reductive quenching mechanism, in which the ³MLCT excited state of the Re complex is efficiently quenched by a reductant (TEOA or BIH). Because BIH ($E_{ox}(BIH) \leq -0.068$ V vs Fc⁺/Fc)^{34, 59, 60} has a much greater reducing power than TEOA ($E_{ox}(TEOA) = +0.21$ V vs. Fc⁺/Fc)⁶¹, when BIH is present, it acts as the exclusive quencher, with TEOA taking on the role of a simple Brønsted base, deprotonating the one-electron oxidized BIH^{•+} species in order to suppress rapid back electron transfer, which generates the strongly reducing BI[•] radical ($E_{ox} = -2.06$ V vs Fc⁺/Fc).^{34, 60} This enables BIH to work as a two-electron donor in the presence of TEOA, with the latter being a proton acceptor.³⁴ No significant H₂ production (TON_{H₂} < 1) or formate production (TON_{HCOO⁻} < 1) have been observed in our experiments, except that a slightly higher TON_{HCOO⁻} (8) was obtained with complex **1**. While complex **6** has been reported to produce formate as a major product with Ir(ppy)₃ as a photosensitizer and triethylamine as an electron donor in CO₂-saturated CH₃CN under >420 nm irradiation,⁵² only a negligible amount of formate was produced under the current conditions. The parent **Rebpy** complex has been tested as a reference catalyst under the same conditions applied to other complexes, and our experimental TON_{CO} value (TON_{CO} = 16) when a 9.6 mW LED (365 nm) was used is in agreement with previously published data.^{8, 62} However, photocatalytic TON and TOF are strongly dependent on experimental conditions (such as solvent, irradiation wavelength, irradiation power, concentrations of catalysts/photosensitizers, choice of electron/proton donor, etc.) in photocatalytic reactions. Thus, when the irradiation power was reduced to 4.3 mW, the TON_{CO} for **Rebpy** increased to 40 (Figure D4).

Complex **1** is the best performing complex among the newly tested Re complexes in terms of TON_{CO} (32 and 120 without and with BIH, respectively, Figure 6.2 and Table 6.2), with only slightly smaller TON_{CO} values than **Rebpy**. In electrocatalytic CO₂ reduction without any added water, complex **1** was reported to outperform **Rebpy** (TON_{CO} 7.4 vs. 2.8).⁴⁹ It is interesting to note that the electrochemical efficiency of a related Re complex, ReCl(L)(CO)₃ (L = 4-([2,2'-bipyridin]-6-yl)aniline), is better than that of **Rebpy** with 4% TFE as a proton source in CH₃CN,

but worse in the absence of TFE. While the presence of an added proton source increases TON_{CO} of complex **1** in electrochemical CO_2 reduction, in photochemical CO_2 reduction, added water actually decreased the final TON_{CO} , both in the absence (Figure D5) and presence (Figure D6) of BIH, although the initial rate was slightly higher in the presence of BIH. This indicates that water may cause stability problems for this catalyst or the reactive intermediates involved in the catalytic reaction, or that water may be a poorer proton source than TEOA in DMA. Also, for complex **1**, as its concentration is decreased, the TON_{CO} decreases (Figure D5).

As has been discussed earlier, initial photoexcitation of all Re complexes in the absence of BIH results in the formation of singly reduced species. Despite proposed mechanisms published for the photochemical CO_2 reduction which involve the interaction of the singly reduced species with CO_2 , no clear evidence of the Re-CO_2 adduct has been reported.^{3, 10, 13} The substantial separation of the first and second reduction potentials (> 300 mV) would prevent the formation of doubly reduced complexes by a disproportionation reaction. As a result, the completion of the two-electron catalytic cycle is only possible by the reaction of two one-electron reduced species through the intermediacy of a CO_2 -bridged bimetallic complex, which has been demonstrated for a Re(dmb)(CO)_3 -based catalyst (where dmb is 4,4'-dimethyl-2,2'-bipyridine).²⁷ Interestingly, **Rebpy** shows the highest photochemical activity without BIH donor, which implies that the formation of the CO_2 -bridged intermediate is inhibited in the other complexes except for complex **1**. Complexes **2**, **3**, **4** and **6** possess two bulky phenyl substituents on the bpy ligand, which may create steric hindrance for the dimer formation. In addition, the presence of phenyl groups in complexes **3**, **4** and **6** triggers reductive deprotonation after the first reduction to produce 6-coordinate Re-OPh species.^{52, 53} Not only does this render the metal center more electron deficient, but it also requires structural rearrangement for CO_2 binding. The low catalytic activity of complex **5** cannot be explained by steric reasons, and possibly stems from the destabilizing electronic effect of electron donating and electron withdrawing groups on the bpy ligand. The photochemical performance of complex **1** is similar to that of **Rebpy** in terms of catalyst stability (TON) due to little variation in steric and electronic structure of the bpy ligand by the substitution at the 4- position with *p*-aniline.

Photocatalysis in the presence of BIH most likely proceeds through a completely different mechanism due to generation of the $\text{BI}^{\bullet}$ radical, which provides access to the doubly reduced form of the catalyst.⁶⁰ As was established earlier,^{22, 63} catalysis initiated by the two-electron reduction of **Rebpy** is more efficient compared to the one-electron reduction and dimerization pathway. This is clearly reflected in significant improvements in TON for all catalysts shown in Table 6.2. It should be noted that while TON does not directly report on the rate of a catalytic

reaction, the access to a faster catalytic regime would generally allow the catalyst to engage in catalysis-related reactions to a larger extent as compared to detrimental side reactions, which render the catalyst non-reactive. While the increase in TON with **Rebpy** and catalysts **1** and **2** is about 3-4 times in the presence of BIH, the improvement in stability is more dramatic (6-8 times) for catalysts **3**, **4** and **6** containing phenyl groups. The increase in TON for complex **5** is even more significant by a factor of 23. The previous electrochemical data of complex **5** showed that the potential of $E_{\text{cat}/2}$ is 0.08 V more negative than E_p of the second reduction,⁵⁰ which is quite different compared to the other catalysts. The large difference between the first reduction potential at -1.68 V and $E_{\text{cat}/2}$ clearly shows the benefit of BIH to produce the doubly-reduced species that is highly active for CO_2 reduction.

Some insights into such improvements can be obtained from analyzing TOF, which directly reports on overall catalytic rates. The presence of BIH does not alter TOF values for **Rebpy** and complex **2**, while the rest of the compounds exhibit a moderate to significant increase in catalytic rates. Interestingly, only the rates of compounds containing an internal base are affected. We hypothesize that the presence of proton-accepting amino substituents, such as $-\text{NH}_2$ and $-\text{NMe}_2$ in compounds **1** and **5**, respectively, or $-\text{OH}$ (or $-\text{O}^-$ after reductive deprotonation) in compounds **3**, **4** and **6**, facilitates the deprotonation of BIH^{*+} while it is still in close proximity to the metal complex after the first electron transfer. In this case, the formation of the doubly reduced state of the catalyst can be achieved faster, as compared to the situation when BIH^{*+} needs to encounter a TEOA molecule and the resulting $\text{BI}^\bullet$ radical has to react with a singly reduced complex again.

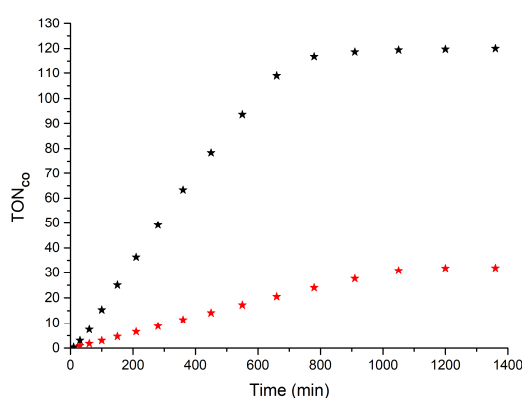


Figure 6.2. Trend of TON_{CO} over time for complex **1** (red stars without BIH, black stars with BIH).

For all photocatalytic experiments, there are two major factors that contribute to catalytic efficiency: “the electron relay cycle” and “the catalytic cycle”. The results of quenching experiments combined with the emission lifetimes of all the complexes under study indicate that the rate-determining step for all the reactions comes from the slow catalytic cycle under our experimental conditions. Except for complex **2**, the reductive quenching of the newly-investigated Re complexes with BIH is faster than that of unsubstituted **Rebpy**, with the latter being more durable under our photocatalytic conditions. However, complex **1** is somewhat comparable to **Rebpy** in terms of stability (TON_{CO}) and the rate of photocatalysis (TOF_{max}). Does the NH_2 group capture CO_2 or reductively deprotonate? Would modification of the NH_2 group to NMe_3^+ (or NMe_2) be beneficial as found for $\text{ReBr}(\text{bpy})(\text{CO})_3$ and FeTPP derivatives?^{54, 64} Our research will continue along these lines to design better catalysts.

6.4 Concluding remarks

We investigated the effect of different substituents on the 2,2'-bipyridine backbone, including PhOH and PhNH_2 groups, during photochemical CO_2 reduction of tricarbonyl Re complexes in order to understand the structure-function relationship and to compare the catalytic activity with the previously published electrochemical results. The Re complex with a PhNH_2 group at the peripheral position in the 2,2'-bipyridine, **1**, is the best performing complex among the newly tested Re complexes. While the Re complex with an OH group in the second coordination sphere, **4**, generates a 6-coordinate species, **4-OPh**, that has a Re–O bond derived from reductive deprotonation at the beginning stage of reduction, the complex is still active for photochemical CO_2 reduction with lower TON and TOF compared to those of **2** when BIH is absent. However, an OH group in the peripheral position provides more electron donation to the Re center and helps to increase the TON and TOF as found in the cases of **3** and **6**. Also, these deprotonated groups might effectively pull out a proton from BIH^{*+} to yield a potent $\text{BI}^\bullet$ radical for the generation of the doubly-reduced Re catalysts. The emission lifetimes of these complexes are similar to that of **Rebpy** within a range of 6 to 40 ns in DMA. The addition of BIH to the Re self-sensitized systems accelerates the rate of formation of the reduced Re catalysts and allows higher TOF and TON for CO formation with negligible formation of H_2 and formate.

6.5 Experimental section

General

All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification. All rhenium compounds were prepared as previously reported.⁴⁹⁻⁵³ Bipyridine ligands were dissolved with $[\text{ReCl}(\text{CO})_5]$ in anhydrous toluene. The reaction mixtures were then refluxed for 4 hours at 110 °C. After cooling to room temperature, fine yellow solids started to precipitate, after which petroleum ether was added, and the mixtures were then centrifuged, filtered and the pure compounds washed with cold diethyl ether. DMA (Sigma-Aldrich, ReagentPlus®, ≥99%) for photochemical experiments was used as received and purged with argon before manipulation. TEOA (Sigma-Aldrich, puriss. p.a., ≥99%) and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]-imidazole (BIH) were employed as reductants (D). BIH was synthesized according to a literature procedure.⁶⁵

NMR spectra were recorded on a JEOL ECP 400 FT-NMR and a Bruker Avance 400 spectrometer (¹H operating frequency 400 MHz) at 25 °C. NMR characterization of complexes is in agreement with our previously published data.^{49, 52, 53} UV-Vis spectra were measured on an Agilent 8453 spectrophotometer. Reduction potentials in this paper are reported vs Fc^+/Fc .

Quenching experiments.

In the case of reductive quenching, the efficiency for the electron transfer, i.e., the quenching efficiency of PS^* by the quencher (BIH), is expressed by the Stern-Volmer relationship, which uses a plot of the relative emission intensity versus the concentration of the quencher:

$$\frac{I_f^0}{I_f} = 1 + k_q \tau_0 [\text{BIH}]$$

Where I_f^0 and I_f represent the intensity of fluorescence without and with the quencher, respectively. 2 mL of previously degassed solutions of Re complexes in DMA having an absorbance less than 0.2 were used for I_f^0 measurements. Aliquots of a concentrated BIH solution containing the same concentration of the analyte as used for I_f^0 measurements were titrated into the original septum-sealed quartz cuvette of analyte. Steady-state emission spectra were measured using a QuantaMaster fluorometer (Photon Technology International, Inc.).

Emission lifetimes.

Transient absorption and emission were measured at 25 °C using a home-built flash photolysis system, with excitation by ~2 ns pulses from a tunable OPO (VersaScan/240/ULD) pumped by the 354.7 nm output of Nd/YAG laser (SpectraPhysics Lab 170). The excitation energy was maintained in the 2-3 mJ/pulse range. Emission was detected by a PMT (Hamamatsu, R928) at a fixed wavelength.

Photocatalytic CO₂ reduction and quantitative analysis of gaseous products.

Photocatalytic systems have been evaluated with Re complexes acting both as catalyst (Cat) and photosensitizer (PS). The complex (0.5 mM) and TEOA (1.25 M) were dissolved in DMA to a final volume of 10 mL. Each complex has also been tested by adding 0.1 M BIH. The solutions were prepared in a 25 mL Pyrex[®] glass bottle with a homemade GL-25 threaded screw cap containing embedded ¼-28 flat bottom HPLC fitting ports, allowing for the airtight connection of 1/16" OD gas tubes (CO₂ gas inlet, exhaust outlet, and a tube to the gas chromatograph (GC) sampling loop) via actuated solenoid valves (Bio-Chem Fluidics). The solutions were continuously mixed by an orbital shaker. Various LEDs (365, 375, 405, 415 nm) that have been calibrated for the input power using a power meter (ThorLabs S120VC and have been used to irradiate the solutions through the bottom of the bottle at wavelengths near to the MLCT absorption maxima of the Re complexes. All photons were absorbed by complexes under reaction conditions. An automated, homemade LabVIEW program controlling the LED, the opening and closing of all actuated valves, and the GC data collection has been used for the experiments. CO₂ was first purged through the solution via the CO₂ inlet port, exiting through the exhaust port. The purging time was set to 20 minutes prior to photolysis and then 10 minutes between every injection to the GC, which removed all the gaseous products previously produced. During injection and purging, the LED was switched off. The irradiation time was set to 10 minutes and then it was increased through an arithmetic progression. Three minute intervals were used as an equilibration time between switching off the LED and injection into the GC, allowing the gaseous products to evolve from the solution into the headspace. Between injections, the GC loop was evacuated for 3 minutes. Gaseous products were quantitatively analyzed using an Agilent 6890N GC equipped with an HP-PLOT Molesieve column (30 m × 0.32 mm × 1.5 µm). Any O₂, N₂, or H₂ present were detected using a TCD detector, and CO was converted to methane on a methanizer and detected using an FID detector.

Formate determination.

Formate analysis was carried out using a Dionex ICS/1600 ion Chromatograph (Thermo Scientific) equipped with a Dionex Ion Pac ICE column. The eluent phase was 1 mM aqueous HFBA (heptafluorobutyric acid). Formate, if present, is all converted to formic acid. The chemical regeneration was afforded by a 5 mM TBAOH (tetrabutylammonium hydroxide) solution. Small volume aliquots (25 μ L) were withdrawn in order to fill the 5 μ L sample loop.

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Conclusions and future perspectives

Global warming coupled to a severe climate change is threatening our ecosystem: amongst greenhouse gas emissions, CO₂ levels must be kept under control and Carbon Capture, Storage and Utilization must be widely implemented. Exploiting CO₂ emissions for producing biofuel or valuable chemicals is not a simple task. The shift from a linear C-economy to a circular C-economy would be highly desirable. It has been delineated how CO₂ is a highly stable molecule, thus a large energy input is required for its transformation. Scientists should handle this complex issue.

This PhD thesis has been directed towards electroreduction of CO₂ both in homogeneous and heterogeneous conditions mediated by Re and Mn bipyridine complexes. In particular, focusing on the pivotal role of the second coordination sphere, the effect of the local proton source on Re bipyridine complexes has been clarified: the presence of pendent phenolic groups in **Re(pdbpy)(CO)₃Cl** and **Re(pmbpy)(CO)₃Cl** is crucial and the stable intermediate bearing a Re-O bond has been isolated (Chapter 3). We evidenced through an in-depth electrochemical investigation the capability of pendent OH group to behave as a chelating ligand, thus limiting catalysis. The mechanistic characterization and comparison to related complexes highlight the importance of considering deleterious reactivity by coordination or ligand-based reactivity of CO₂ when designing catalysts with pendent acid/base functionality in the second coordination sphere; also, the same ligand with Mn displayed better catalytic activities and changed the selectivity for CO and formate. This behavior provides evidence for the intimate effect of the identity of the metal center, in addition to the ligand, for the product distribution: this is a promising observation considering that the (L)M(CO)₃X motif is one of few examples where first and third row metal congeners with the same ligand set undergo similar reactions (Chapter 2).

In Chapter 4, the effect of different substituted bipyridines have been tested; electron-withdrawing substituents (e.g. -CF₃) shift the reduction potentials to more positive values, and eventually inhibit the catalytic activities of the corresponding Mn and Re complexes toward CO₂ reduction. In the case of electron-donating substituents (i.e. -NMe₂) the opposite trend is observed. More generally electron-donating groups are expected to convey greater nucleophilicity to the metal-center, although catalysis should require higher overpotentials. This is in agreement with the highest TON_{CO} (31) for [Re(4,4'-NMe₂)(CO)₃Cl], complex **2g**, although its occurrence at -2V vs. Ag/AgCl.

The transition from the homogeneous to the heterogeneous approach, which in some cases displays superior stability and durability, can find considerable support whenever the intimate molecular mechanism responsible for the catalysis is initially deeply investigated in the homogeneous phase. This is the approach followed in Chapter 5, where the bpy ligand has been previously modified to apbpy in order to allow further heterogenization of $\text{Mn}(\text{apbpy})(\text{CO})_3\text{Br}$ catalyst onto the electrode surface. The $-\text{NH}_2$ moiety was indispensable for the preparation of a diazonium salt which can be subsequently electrochemically reduced forming a stable C-C bond with the carbonaceous electrode surface. Firstly, the complex has been grafted on glassy carbon electrodes and tested in acetonitrile solutions, afterwards it has been anchored on carbon cloth (CC). The functionalized CC has been tested in a three-electrode cell with two gastight compartments in CO_2 -saturated aqueous KHCO_3 . The cumulative TON for CO production reaches more than 33 000 after 10 h, with an average faradaic efficiency of 53%. It is worth noting this TON value is two orders of magnitude higher than that of $\text{Mn}(\text{apbpy})(\text{CO})_3\text{Br}$ tested under homogeneous conditions in acetonitrile solutions ($\text{TON}_{\text{CO}}=12$). A significant improvement is provided by using the same modified CC in a gas-fed complete electrolysis cell that overcomes the mass transport limitations of using dissolved CO_2 . TONs for CO production reached more than $1.6 \cdot 10^5$ turnovers in 16 hours of operation, and, additionally, 17 g min^{-1} of HCOOH per gram of Mn were afforded. The same electrocatalyst has been shown to be largely affected by different experimental conditions for CO_2 electroreduction: a change in selectivity occurred.

Since most of the electrocatalysts can also be employed as photocatalysts, some Re bipyridine complexes have been tested for photocatalytic CO_2 reduction in dimethylacetamide solutions in presence of TEOA and BIH as sacrificial electron donor (Chapter 6). This is part of a work which is still in progress, but preliminary results showed that the Re complex with a NH_2 group at the peripheral position in the 2,2'-bipyridine, **1**, is the best performing complex among the newly tested Re complexes. Once again, the effects of the second coordination sphere amongst the complexes under study has been revealed to be crucial also in photocatalytic conditions, although simple Rebpy allows better TON_{CO} under these experimental conditions. Nevertheless, we can conclude that the rate determining step for all the experiments comes from the slow catalytic cycle in our experimental conditions since the reductive quenching with BIH for all the new Re complexes is faster than that of simple Rebpy , which displays higher durability.

The results reported in this thesis should stimulate further investigations in understanding homogeneous molecular catalysis and structure-property relationships in order to optimize

catalysts performances. TONs for CO₂ reduction products in homogeneous conditions are not sufficiently high, mostly due to scarce durability of the catalysts over time. Research efforts should be directed towards highly stable, durable and cost-effective catalysts: the heterogenization of molecular catalysts can represent a valid alternative. One of the major advantages of this approach is the elimination of solubility problem, hence the CO₂ reduction can be performed in aqueous solutions.

Taken together, the studies reported herein suggest that a close connection between homogeneous and heterogeneous CO₂RR electrocatalysis would be beneficial for both fields. The knowledge of traditional coordination chemistry and molecular catalysis may be extremely useful to overcome the limiting factors of the state-of-the-art heterogeneous catalysts, especially in terms of selectivity. On the contrary, approaches used in materials science and heterogeneous catalysis applied to molecular systems would contribute to extend their applicability. Hybrid materials in which molecular catalysts are connected to bulk electrodes or semi-conductive particles represent a field that can take advantage of such synergistic integration of homogenous and heterogeneous catalysis. Development of such processes using earth-abundant metal complexes will provide for a significative step forward in the CO₂ reduction chemistry.

Appendix "Ligands synthesis"

The majority of the ligands have been synthesized by the Kröhnke reaction between the pyridinium salt and the corresponding α,β -unsaturated chalcone.

pdbpy ligand

[(E)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one] (a). An emulsion of benzaldehyde (19 mmol) in cold distilled water (100 ml) was prepared in a flask and then an equimolar amount of 2-acetylpyridine was added under vigorous stirring. A solution of 10% KOH in water (10 ml) was then added dropwise and the mixture became pale yellow. The emulsion was stirred for 24 hours at 4°C and the yellow product was filtered and washed with water and methanol (yield 98%).

$^1\text{H-NMR}$ [400 MHz, $(\text{CD}_3)_2\text{CO}$]: δ/ppm = 8.79 (d, J = 4.7 Hz, 1H), 8.38 (d, J = 16.1 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 8.04 (td, $1J$ = 7.6 Hz, $2J$ = 1.5 Hz, 1H), 7.89 (d, J = 16.1 Hz, 1H), 7.82 (m, 2H), 7.66 (ddd, $1J$ = 7.6 Hz, $2J$ = 5.0 Hz, $3J$ = 1.5 Hz, 1H), 7.49 (m, 3H).

[1-(2-(2,6-dimethoxyphenyl)-2-oxoethyl)pyridinium iodide] (b). 20 mmol of (2',6'-dimethoxy)-acetophenone and 24 mmol of iodine were refluxed for 3 hours in 50 ml of pyridine. The reaction mixture was cooled to 0° C and the yellow product was precipitated, filtered and washed with cold pyridine (yield 88%).

$^1\text{H-NMR}$ [400 MHz, $(\text{CD}_3)_2\text{CO}$]: δ/ppm = 9.19 (d, J = 6.6 Hz, 2H), 8.88 (t, J = 7.6 Hz, 1H), 8.40 (t, J = 6.8 Hz, 2H), 7.50 (t, J = 8.5 Hz, 1H), 6.81 (d, J = 8.5 Hz, 2H), 6.30 (s, 2H), 3.92 (s, 6H).

[4-phenyl-6-(2,6-dimethoxy-phenyl)-2,2'-bipyridine] (dmobpy). A suspension of 11 mmol of **b**, 11 mmol of **a** and 0.110 mol of ammonium acetate was refluxed in methanol (30 ml) for 6 hours. The mixture was then cooled to room temperature and the yellow product was filtered and washed with cold methanol (yield 83%).

$^1\text{H-NMR}$ [400 MHz, $(\text{CD}_3)_2\text{CO}$]: δ/ppm = 8.71 (m, 2H), 8.47 (d, J = 8.2 Hz, 1H), 7.89 (m, 3H), 7.57 (m, 3H), 7.50 (t, J = 8.5 Hz, 1H), 7.40 (m, 2H), 6.81 (d, J = 8.2 Hz, 2H), 3.74 (s, 6H).

$^{13}\text{C-NMR}$ [100 MHz, $(\text{CD}_3)_2\text{CO}$]: δ/ppm = 159.31, 157.27, 157.07, 156.08, 150.07, 149.42, 139.50, 137.95, 137.65, 130.63, 130.11, 129.87, 127.90, 124.80, 124.67, 121.83, 117.11, 105.41, 56.38.

[4-phenyl-6-(2,6-dihydroxy-phenyl)-2,2'-bipyridine] (pdbpy). In a three-necked flask pyridinium chloride was prepared by heating a mixture of concentrated HCl (17.6 ml) and pyridine (16 ml) for 2 hours at 195° C under a flow of Ar. Then, dmobpy (0.3 mmol) was added and the reaction mixture was heated at 195° C under Ar for 3 hours. Once cooled to room temperature, the solid was dissolved in 20 ml of H₂O and neutralized with an aqueous solution of KOH. The solid product was then filtered and washed with H₂O and CH₂Cl₂ (Yield 71%).

¹H-NMR [400 MHz, (CD₃)₂SO]: δ/ppm = 8.79 (m, 2H), 8.52 (s, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.06 (t, J = 7.6 Hz, 1H), 7.88 (d, J = 7.3 Hz, 2H), 7.60 (m, 2H), 7.55 (m, 2H), 7.12 (t, J = 8.2 Hz, 1H), 6.49 (d, J = 7.9 Hz, 2H).

¹³C-NMR [100 MHz, (CD₃)₂SO]: δ/ppm = 158.64, 156.13, 154.02, 152.84, 149.87, 149.79, 137.81, 130.88, 129.56, 129.43, 127.08, 124.67, 123.00, 120.60, 116.37, 108.80, 107.61.

pmbpy ligand

[N-((2-pyridylacetyl) pyridinium iodide)] (c). The reaction was carried out under inert atmosphere (N₂). 9.25 mL of 2-acetylpyridine (82.50 mmol) were dissolved in 100 mL of pyridine, then, while stirring, 90.05 mmol of iodine were added to the solution, which is heated at reflux for 3 h. The precipitated black solid was filtered on a Büchner funnel, washed with 20 mL of ethyl ether and dried: shiny black crystals were obtained (yield 54%). Part of the product was crystallized from ethanol and used for the following steps (golden thin crystals).

¹H-NMR [400 MHz, (CD₃)₂SO]: δ/ppm = 9.00 (dd, 2H, J = 6.7 Hz, J = 1.1 Hz), 8.87 (ddd, 1H, J = 4.4 Hz), 8.73 (tt, 1H, J = 7.8 Hz, J = 1.0 Hz), 8.27 (dd, 2H, J = 7.8 Hz, J = 6.7 Hz), 8.14 (td, 1H, J = 7.8 Hz, J = 2.2 Hz), 8.08 (dt, 1H, J = 6.9 Hz), 7.84 (ddd, 1H, J = 6.9 Hz, J = 4.4 Hz), 6.51 (s, 2H).

[3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one] (d). 2'-Methoxyacetophenone (1.09 g, 6.60 mmol) and 10% potassium hydroxide aqueous solution (80 mL, 142mmol) were dissolved in ethanol (15mL), and stirred at 0°C for 30 min. Benzaldehyde (0.800 mL, 7.92mmol) was added dropwise, and the mixture was stirred overnight at room temperature. Ethanol was evaporated, and the remaining mixture was extracted 4 times with ethyl acetate (30mL), dried with magnesium sulfate, and the filtered solution was concentrated. The residue was purified using silica gel column chromatography (silica gel 60, eluant: ethyl acetate/hexane=1:7 (v/v)) to obtain the subject compound (1.52 mg, 6.36 mmol, yield: 96%) as a yellow oil-like substance.

^1H NMR [400 MHz, CDCl_3] δ/ppm = 7.64 (d, J = 4.8 Hz, 1H), 7.61-7.57 (m, 3H), 7.48 (ddd, J = 15.2, 15.2, 2.0 Hz, 1H), 7.41-7.35 (m, 4H), 7.05 (dd, J = 6.4, 6.4 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 3.91 (s, 3H).

[4-phenyl-6-(methoxyphenyl)-2,2'-bipyridine] (mobpy). **c** (6.13 mmol), **d** (6.13 mmol), ammonium acetate (61.3 mmol) and methanol (40 ml) were combined in a three-neck flask. The solution was purged with Ar and heated at reflux for 4 hours. The progress of the reaction was monitored via TLC. After complete consumption of the reagents, the solvent was removed *in vacuo* to afford a brown oil. The crude product was dissolved in ethyl acetate and washed three times with aqueous 10% NaHCO_3 . The oil collected after evaporation of ethyl acetate was purified on a silica gel column eluting with petroleum ether: ethyl acetate (7:1) to provide the title complex as a yellow oil in 56% yield. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ 8.75 (d, J = 4.7 Hz, 1H), 8.59 (d, J = 1.8 Hz, 1H), 8.53 (d, J = 7.9 Hz, 1H), 8.18 (d, J = 1.5 Hz, 1H), 7.95-8.02 (m, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.59 (t, J = 7.0 Hz, 2H), 7.46-7.55 (m, 2H), 7.22-7.29 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 3.9 (s, 3H).

[4-phenyl-6-(2-hydroxyphenyl)-2,2'-bipyridine] (pmbpy). mobpy (3 mmol) was dissolved in 30 ml of HBr (48% aqueous solution) and heated at reflux for 24 hours. The mixture was then cooled to room temperature and the pH adjusted to pH 7 using a NaHCO_3 aqueous solution. When the solution became neutral, pmbpy precipitated as a white solid, which was filtered and then washed with water and CH_2Cl_2 . No further purification was needed (yield 89%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ 8.82 (d, J = 4.4 Hz, 1H), 8.59 (s, 1H), 8.53 (s, 1H), 8.31 (t, J = 10.0 Hz, 2H), 8.1 (td, ^1J = 6.2 Hz, ^2J = 1.2 Hz, 1H), 8.05 (d, J = 7.0 Hz, 2H), 7.60 (m, 5H), 7.38 (td, ^1J = 7.9 Hz, ^2J = 1.16 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H).

hpbpy ligand

[(E)-3-(2-hydroxyphenyl)-1-phenyl-2-propen-1-one] (e): is synthesized by Claisen-Schmidt condensation of salicylaldehyde (50 mmol) with acetophenone (40 mmol) dissolved in 50 mL of ethanol. The solution is vigorously stirred and 10 mL of KOH 40% (w/w) is dropwise added. The mixture is then heated to 60 °C for 2-4 hours until the disappearance of the starting reagents, monitored by TLC (EtAc: hexane 1:4). Once the reaction is completed, the suspension is poured into cold distilled water and acidified with HCl 2 M (final pH 2-3). The resulting precipitate is collected and washed once with water and then with cyclohexane. (yield: 70%).

$^1\text{H-NMR}$: [400 MHz, CDCl_3]: δ/ppm = 8.13 (d, J = 15,92 Hz, 1H), 8.03 (d, J = 7,1, 1H), 7.70 (d, J = 15,85, 1H), 7.58 (t, J = 8,82, 2H), 7.50 (t, J = 7,54, 2H), 7.27 (t, J = 7,95, 1H), 6.97 (t, J = 7,58, 1H), 6.88 (d, J = 8,09, 1H).

[4-(2-hydroxy-phenyl)-6-phenyl-2,2'-bipyridine] (hpbpy). Precursors **c** (4.8 mmol) and **e** (4.8 mmol) are added to a three-necked flask with an excess of ammonium acetate (48 mmol) and glacial acetic acid (4 mL). The solution is refluxed for 3h. The glacial acetic acid is removed, and the residue dissolved in methanol. The yellowish product crystallizes on cooling (yield: 63%).

$^1\text{H-NMR}$: [400 MHz, $(\text{CD}_3)_2\text{SO}$]: δ/ppm = 8.73 (d, J = 4,81 Hz, 1H), 8.64 (s, 1H), 8.62 (d, J = 3,11 Hz, 1H), 8.27 (d, 7,24 Hz, 2H), 8.16 (s, 1H), 8.01 (td, ^1J = 8,63 Hz, ^2J = 1,8 Hz, 1H), 7.53 (m, 5H), 7.30 (t, J = 8,59 Hz, 1H), 7.06 (d, J = 9,29 Hz, 1H), 6.98 (t, J = 7,45 Hz, 1H).

$^{13}\text{C-NMR}$: [100 MHz, $(\text{CD}_3)_2\text{SO}$]: 172.97, 156.20, 156.10, 155.58, 155.37, 149.85, 148.96, 139.41, 137.93, 130.82, 129.71, 129.39, 127.38, 125.72, 124.79, 121.36, 121.06, 120.20, 119.99, 117.04.

dpbpy ligand

[(E)-3-phenyl-1-(pyridine-2-yl)prop-2-en-1-one] (f). 19 mmol of 1-(pyridin-2-yl)ethanone were added to an emulsion of benzaldehyde (19 mmol) and 100 mL of cold distilled water under vigorous stirring. A 10% solution of NaOH in water (10 mL) was then slowly added and the mixture became pale yellow. The emulsion was stirred for 24 h at 4 °C and the resulting yellow solid was filtered and washed with water and methanol (yield 98%).

$^1\text{H NMR}$ [400 MHz, $(\text{CD}_3)_2\text{CO}$]: δ/ppm = 8.79 (d, J = 4.7 Hz, 1H), 8.38 (d, J = 16.1 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 8.04 (td, 1 J = 7.6 Hz, 2 J = 1.5 Hz, 1H), 7.89 (d, J = 16.1 Hz, 1H), 7.82 (m, 2H), 7.66 (ddd, 1 J = 7.6 Hz, 2 J = 5.0 Hz, 3 J = 1.5 Hz, 1H), 7.49 ppm (m, 3H).

[4,6-diphenyl-2,2'-bipyridine] (dpbpy). Precursors **c** (4.8 mmol) and **f** (4.8 mmol) are added to a three-necked flask with an excess of ammonium acetate (48 mmol) and glacial acetic acid (4 mL). The solution is refluxed for 3h. The glacial acetic acid is removed, and the residue dissolved in methanol. The yellowish product crystallizes on cooling. (yield: 87%).

$^1\text{H-NMR}$: [400 MHz, $(\text{CD}_3)_2\text{SO}$]: δ/ppm = 8.77(d, 4.69 Hz, 1H), 8.65 (d, 7.61 Hz, 1H), 8.63 (s, 1H), 8.34 (d, 7.32 Hz, 2H), 8.32 (s, 1H), 8.05 (d, 7.91 Hz, 1H), 8.00 (d, 7.32 Hz, 2H), 7.5-7.65 (m, 7H).

¹³C-NMR: [100 MHz, (CD₃)₂SO]: δ/ppm = 157.11, 156.27, 155.78, 150.19, 149.89, 139.10, 138.22, 138.10, 130.11, 130.00, 129.85, 129.38, 127.74, 127.60, 125.17, 125.05, 121.51, 118.69, 117.13.

apbpy ligand

[(E)-4-(4-nitrophenyl)-2-oxo-3-butenic acid] (g). A mixture of 27.40 mmol of 4-nitrobenzaldehyde in 50 mL of ethanol was heated to 70 °C, until a clear dark yellow solution is formed. Sodium pyruvate (28.00 mmol) was dissolved in 15 mL of water and added to the solution, which is then cooled into an ice bath and a precipitate is formed. 15 mmol of NaOH dissolved in 25 mL of water are then added to the cold mixture: the color turns to a dark orange and an other precipitate can be seen. The mixture is left at 0 °C for 2.5 h, then it is transferred into a beaker and neutralized with a few mL of HCl 2 M: the color turns back to yellow. The precipitate is recovered by filtration and washed with ethanol 96% (yield 28%).

¹H-NMR: [400 MHz, (CD₃)₂SO]: δ/ppm = 8.23 (d, 2H, J = 9.2 Hz), 7.95 (d, 2H, J = 8.4 Hz), 7.56 (d, 1H, J = 16.4 Hz), 7.07 (d, 1H, J = 16.0 Hz).

[Ammonium 4-(4-nitrophenyl)-2,2'-bipyridine-6-carboxylate]. 3.10 mmol of **g**, 3.1 mmol of **c**, 24.6 mmol of ammonium acetate and 25 mL of water were put together in a flask. The mixture was refluxed under stirring for 5 h and then filtered on a Büchner funnel. The grey solid was washed with water and then acetone (yield 82%).

¹H-NMR: [400 MHz, (CD₃)₂SO]: δ/ppm = 8.73 (dm, 1H, J = 3.2 Hz), 8.67 (d, 1H, J = 1.7 Hz), 8.53 (d, 1H, J = 7.8 Hz), 8.38 (d, 2H, J = 8.6 Hz), 8.24 (d, 1H, J = 1.7 Hz), 8.15 (d, 2H, J = 8.6 Hz), 8.00 (td, 1H, J = 7.5 Hz, J = 1.7 Hz), 7.50 (ddd, 1H, J = 7.8 Hz, J = 4.6 Hz, J = 1.4 Hz).

[4-(4-nitrophenyl)-2,2'-bipyridine]. 4.80 mmol of 4-(4-nitrophenyl)-2,2'-bipyridine-6-carboxylate were placed into a flask connected to a water pump. The compound is gradually heated to 350 °C: between 50 and 100 °C a white condensation is formed on the flask walls, probably due to the water contained in the reagent, while around 350 °C the solid, initially grey, became black and produced bubbles. Then the product was cooled down under vacuum. Subsequently, the black compound was suspended in ethyl acetate and refluxed for 15 minutes with active carbon to eliminate the carbonaceous residual. The mixture was filtered on celite and the solvent removed using the rotary evaporator. The obtained solid was purified through flash chromatography on silica gel (ethyl acetate: petroleum ether 9:1 as eluent), affording a light brown product (yield 64%).

$^1\text{H-NMR}$: [400 MHz, $(\text{CD}_3)_2\text{CO}$]: δ/ppm = 8.83 (s, 1H), 8.82 (d, 1H, J = 5.6 Hz), 8.73 (d, 1H, J = 4.4 Hz), 8.54 (d, 1H, J = 8.8 Hz), 8.43 (d, 2H, J = 8.8 Hz), 8.17 (d, 2H, J = 8.5 Hz), 7.98 (td, 1H, J = 7.6 Hz, J = 1.6 Hz), 7.83 (dd, 1H, J = 4.8 Hz, J = 2.0 Hz), 7.47 (ddd, 1H, J = 7.8 Hz, J = 4.4 Hz, J = 1.2 Hz).

[4-(4-aminophenyl)-2,2'-bipyridine] (apbpy). 1.60 mmol of 4-(4-nitrophenyl)-2,2'-bipyridine and 0.16 g of Pd/C 10% were put in 25 mL of ethanol and the mixture was heated at reflux for 1 h. Afterwards, 1.5 mL of hydrazine (30.90 mmol) were added and the mixture was refluxed for another hour, then it was filtered on celite to remove the Pd/C. The solid was washed twice with 10 mL of CH_2Cl_2 . The solution was then transferred into a separatory funnel and washed with water (2 x 15 mL). The organic phase was dried with Na_2SO_4 and the solvent was removed at the rotary evaporator: a white solid was obtained (yield 71%).

$^1\text{H-NMR}$ [400 MHz, $(\text{CD}_3)_2\text{SO}$]: δ/ppm = 8.71 (s, 1H), 8.70 (dm, J = 5.0 Hz, 1H), 8.60 (d, J = 7.9 Hz, 1H), 7.92 (td, J = 7.8 Hz, J = 1.8 Hz, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.60 (dd, J = 5.3 Hz, J = 2.0 Hz, 1H), 7.41 (ddd, J = 7.9 Hz, J = 5.0 Hz, J = 1.2 Hz, 1H), 6.83 (d, 8.8 Hz, 2H), 5.07 (s, 2H).

$^{13}\text{C-NMR}$ [400 MHz, CDCl_3]: δ/ppm = 156.50, 150.29, 149.85, 149.37, 149.18, 136.94, 127.89, 125.78, 124.02, 120.88, 120.26, 116.75, 114.85.

MS: (ESI+) 248 (100%, $\text{M} + \text{H}^+$) 517 (97%, $2\text{M} + \text{Na}^+$).

IR: 3350 cm^{-1} (w), 3197 cm^{-1} (b, N-H), 3030 cm^{-1} (w, C-H), 1582 cm^{-1} (s), 1525 cm^{-1} (m), 1460 cm^{-1} (m), 830 cm^{-1} (m), 792 cm^{-1} (m).

[4,4'-bis(trifluoromethyl)-2,2'-bipyridine]. The method of O'Donnell was slightly modified to synthesize 4,4'-bis(trifluoromethyl)-2,2'-bipyridine first reported by Furue. In a degassed 20 mL screw cap vial a solution of 2-bromo-4-(trifluoromethyl)pyridine (500 mg, 2.2 mmol) in 7.5 mL of anhydrous DMF was poured and degassed for 5 min. $\text{Pd}(\text{OAc})_2$ (25 mg, 0.11 mmol) was added later and the mixture degassed for additional 5 min. TBAI (815 mg 2.2 mmol), anhydrous K_2CO_3 (460 mg, 3.3 mmol), and *i*-PrOH (0.35 mL, 4.4 mmol) were then added to the mixture, subsequently heated at $100\text{ }^\circ\text{C}$ for 20 h. The heating was suspended, and the reaction mixture was filtered through a pad of celite. The filtrate was diluted in 25 mL of DCM and was washed with deionized water (3x25 mL). The organic phase was collected, and the water layer further extracted with 10 mL of DCM. The collected organic phase was dried with anhydrous MgSO_4 , filtered, and the solvent removed under reduced pressure to

afford the crude solid that was purified by column chromatography on silica gel (eluent PE/AcOEt 10/1) to afford 220 mg of white solid as product. (Yield = 80%).

^1H NMR [600 MHz, CDCl_3]: δ/ppm = 8.88 (d, J = 4.0 Hz, 2H), 8.73 (s, 2H), 7.59 (d, J = 4.0 Hz, 2H).

^{13}C NMR [150 MHz, CDCl_3]: δ/ppm = 156.2 (2 $\times$ Cq), 150.4 (2 $\times$ CH), 139.9 (2 $\times$ Cq (CF_3), $J_{\text{C-F}}$ = 34.2 Hz), 122.9 (2 $\times$ Cq (CF_3), $J_{\text{C-F}}$ = 273.2 Hz), 120.0 (2 $\times$ CH (CF_3), $J_{\text{C-F}}$ = 3.6 Hz), 117.2 (2 $\times$ CH (CF_3), $J_{\text{C-F}}$ = 3.7 Hz).

[2,2'-bipyridine]-4,4'-dicarbonitrile. The procedure reported by Losse was followed with slight modifications. 4-Cyanopyridine (700 mg, 6.7 mmol) and 10% Pd/C (50 mg) were added into a 25 mL round-bottomed flask and five vacuum/nitrogen cycle were operated to minimize the amount of oxygen, then the flask was connected to a reflux condenser under nitrogen atmosphere. The mixture was heated to 230°C in a sand bath in order to reflux the 4-Cyanopyridine. After 24 h the mixture was cooled to room temperature, CHCl_3 (15 mL) was added and the black suspension filtered through a frit. Solvent was removed under reduced pressure from the pale-yellow solution obtained until the product started to crystallize. Pentane (15 mL) was then added, and the concentrated solution cooled at 4-6 °C for 16 h. The precipitated solid was filtered on Buchner funnel and washed with cold EtOH and dried to yield 100 mg of the product as a yellow-orange solid. (Yield 15%).

^1H NMR [600 MHz, CDCl_3]: δ/ppm = 8.85 (d, J = 5.2 Hz, 2H), 8.69 (s, 2H), 7.58 (d, J = 4.8 Hz, 2H).

^{13}C NMR [150 MHz, CDCl_3]: δ/ppm = 155.4 (2 $\times$ Cq), 150.3 (2 $\times$ CH), 125.8 (2 $\times$ CH), 123.1 (2 $\times$ Cq), 121.82 (2 $\times$ CH), 116.32 (2 $\times$ Cq).

General procedures for synthesis of 2-substitued N,N-dimethylpyridin-4-amine derivatives.

The previously reported procedure of Cuperly was adapted according to the used electrophile. 2-(dimethylamino)-ethanol (0.8 mL, 8.0 mmol) was added to a three-necked round bottomed flask and dissolved in hexane (10 mL) under a N_2 atmosphere. The solution was cooled at -5 °C, BuLi (2.5 M, 6.4 mL, 16.0 mmol) was added dropwise for 10 min and the resulting mixture stirred for 40 min at -5°C. 4-DMAP (488 mg, 4.0 mmol) was then added and stirring continued for additional 60 min at 0°C, then the reaction medium was cooled at -78°C and the solution of the appropriate electrophile (10.0 mmol) was added dropwise by mean of a dropping funnel with pressure balance. Once the addition of the electrophile was completed the temperature

was allowed to raise to 0 °C (1.5 h) and the reaction quenched with deionized water at this temperature.

[*N,N*-dimethyl-2-(tributylstannyl)pyridin-4-amine]. 2-(dimethylamino)ethanol (0.8 mL, 8.0 mmol) in hexane (10 mL), BuLi (2.5 M, 6.4 mL, 16.0 mmol) and 4-DMAP (0.488 g, 4.0 mmol) were reacted as previously described then a solution of Bu₃SnCl (3.255 g, 10.0 mmol) in 15 mL of hexane was added dropwise for 20 min. The reaction was quenched with deionized water (15 mL) then the aqueous phase was extracted with DCM (2×20 mL) and AcOEt (2×20 mL). The collected organic phase was dried with anhydrous Na₂SO₄, filtered, and the solvent removed under reduced pressure to afford a crude orange oil, that was used without further purification in the cross-coupling reactions. (NMR-calculated yield = 69%) .

¹H NMR [600 MHz, CDCl₃]: δ/ppm = 8.38 (d, *J* = 5.9 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 6.36 (dd, *J* = 5.9, 3.0 Hz, 1H), 2.99 (s, 6H), 1.55 (m, 6H), 1.28 (m, 6H), 1.15 (t, *J* = 8.0 Hz, 6H), 0.85 (t, *J* = 8.0 Hz, 9H).

¹³C NMR [150 MHz, CDCl₃]: δ/ppm = 172.0 (Cq), 152.8 (Cq), 149.9 (Cq), 115.5 (CH), 105.2 (CH), 38.6 (CH₃), 29.4 (CH₂), 27.0 (CH₂), 13.8 (CH₂), 9.2 (2×CH₃).

[2-iodo-*N,N*-dimethylpyridin-4-amine]. 2-(dimethylamino)ethanol (1.6 mL, 16.0 mmol) in hexane (25 mL), BuLi (2.5 M, 12.8 mL, 32.0 mmol) and 4-DMAP (0.980 g, 8.0 mmol) were reacted as previously described, then a solution of risublimed I₂ (5.080 g, 20.0 mmol) in 50 mL of freshly distilled Et₂O was added dropwise for 35 min. The reaction was quenched with a saturated solution of Na₂S₂O₃ (25 mL) and stirred for additional 20 min at 0°C. The organic phase was separated and washed again with Na₂S₂O₃ solution (2×15 mL) and brine (2×15 mL). The collected organic phase was dried with anhydrous Na₂SO₄, filtered, and the solvent removed under reduced pressure to afford a crude brown solid that was purified by column chromatography on silica gel (eluent: PE/AcOEt 5/5) to afford 1.683 g of white solid as product. (Yield = 86%).

¹H NMR [600 MHz, CDCl₃]: δ/ppm = 7.91 (d, *J* = 5.9 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.47 (dd, *J* = 5.9, 2.5 Hz, 1H), 2.98 (s, 6H).

¹³C NMR [150 MHz, CDCl₃]: δ/ppm = 154.2 (Cq), 149.7 (CH), 119.3 (CH), 115.8 (Cq), 106.5 (CH), 39.0 (2×CH₃).

General Procedure for Stille cross-coupling of *N,N*-dimethyl-2-(tributylstannyl)pyridin-4-amine with 2-halopyridine.

In a degassed 50 ml screw cap vial freshly distilled toluene (25 mL) was added and degassed for 10 min then Pd(OAc)₂ (22 mg, 0.1 mmol) and PPh₃ (52 mg, 0.2 mmol) were added in one portion. The resulting mixture was stirred and degassed until toning of the solution to red. Subsequently, *N,N*-dimethyl-2-(tributylstannyl)pyridin-4-amine (370 mg, 0.9 mmol), LiI (40 mg, 0.3 mmol) and CuI (57 mg, 0.3 mmol) were added to the mixture, then degassed for additional 5 min. Finally, the appropriate 2-halopyridine (1.1 mmol) was poured in the reaction medium that was kept under N₂ atmosphere and heated to reflux for 16 h. After being cooled at room temperature, the resulting mixture was diluted with EtOAc (30 mL) and washed with a NH₄OH solution (10 M) until the water layer did not turn blue any more, indicating that all the copper had been extracted. The collected organic phase was filtered on a pad of celite, diluted with DCM (30 mL) and dried with anhydrous Na₂SO₄. Then the solvents were removed under reduced pressure to afford the crude solid subsequently purified to yield the desired product.

[*N,N,N',N'*-tetramethyl-[2,2'-bipyridine]-4,4'-diamine]. Following the general procedure, *N,N*-dimethyl-2-(tributylstannyl)pyridin-4-amine (370 mg, 0.9 mmol) and 2-iodo-*N,N*-dimethylpyridin-4-amine (270 mg, 1.1 mmol) in 25 mL of freshly distilled toluene were reacted to afford a crude yellowish solid that was suspended in 25 mL of Et₂O and vigorously stirred for 30 min. The desired product was separated by filtration to yield 115 mg of a brown powder (Yield = 53 %).

¹H NMR [600 MHz, CDCl₃]: δ/ppm = 8.30 (d, *J* = 5.9 Hz, 2H), 7.68 (d, *J* = 2.7 Hz, 2H), 6.50 (dd, *J* = 5.9 Hz, 2.7 Hz, 1H), 3.1 (s, 12H).

¹³C NMR [150 MHz, CDCl₃]: δ/ppm = 157.1 (2×Cq), 155.4 (2×Cq), 149.1 (2×CH), 107.0 (2×CH), 103.6 (2×CH), 39.2 (4×CH₃).

[*N,N*-dimethyl-4'-(trifluoromethyl)-[2,2'-bipyridin]-4-amine]. Following the general procedure, *N,N*-dimethyl-2-(tributylstannyl)pyridin-4-amine (370 mg, 0.9 mmol) and commercially available 2-bromo-4-(trifluoromethyl)pyridine (250 mg, 1.1 mmol) in 25 mL of freshly distilled toluene were reacted to afford a crude brown solid that was purified by column chromatography on silica gel (eluent: MeOH/DCM 5/95) to yield 169 mg of the desired product as a brown powder (Yield = 70%).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 8.80 (d, J = 5.0 Hz, 1H), 8.66 (s, 1H), 8.33 (d, J = 5.9 Hz, 1H), 7.72 (d, J = 2.7 Hz, 1H), 7.48 (d, J = 5.0 Hz, 1H), 6.56 (dd, J = 5.9, 2.7 Hz, 1H), 3.10 (s, 6H).

^{13}C NMR [100 MHz, CDCl_3]: δ/ppm = 158.4 (Cq), 155.4 (Cq), 154.7 (Cq), 149.8 (CH), 149.5 (CH), 139.2 (Cq, (CF_3) , $J_{\text{C-F}}$ = 33.7 Hz), 123.1 (Cq (CF_3) , $J_{\text{C-F}}$ = 273.5 Hz), 118.8 (CH, (CF_3) , J = 3.1 Hz), 117.1 (CH, (CF_3) , J = 3.1 Hz), 107.3 (CH), 104.2 (CH), 39.4 ($2\times\text{CH}_3$).

^{19}F (564 MHz, CDCl_3): -64.60 (m, 3F). GC-MS: 267 (molecular ion), 252 (base peak), 224.

IR (FT-ATR, cm^{-1}): 2954, 2925, 2854, 1595, 1478, 1427, 1333, 1161, 990.

Appendix A "Chapter 3"

NMR Characterization

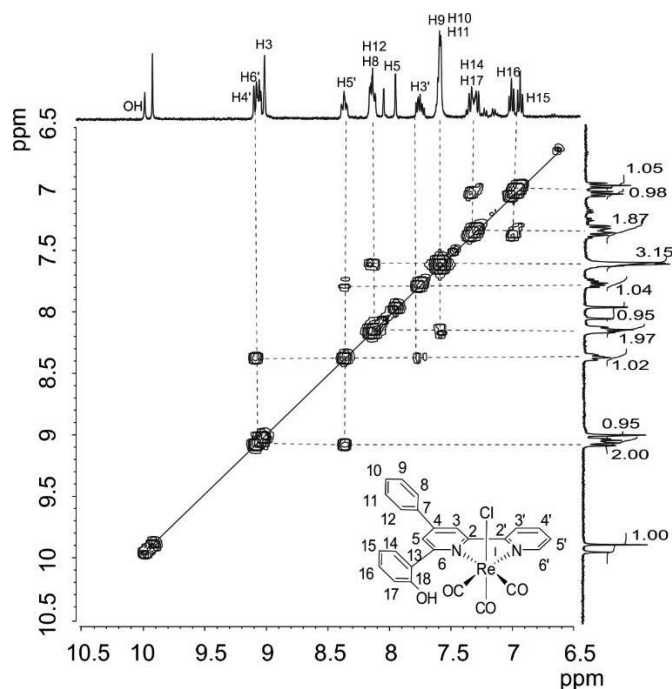


Figure A1. 2d-COSY spectrum of $[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]$ (**1**) in d_6 -DMSO. Numeration in the chemical structure reported in the figure is referred to the carbon skeleton for 2,2' bipyridines. Each $-\text{CH}$ proton has been named with the respective number of the carbon.

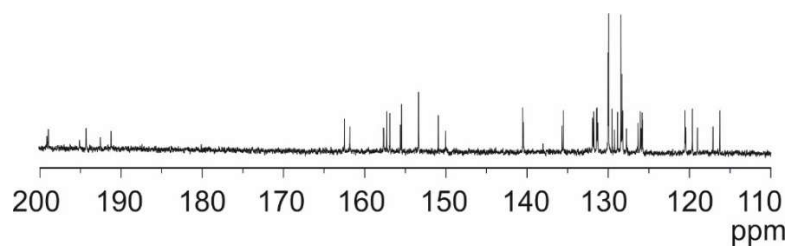


Figure A2. ^{13}C NMR spectrum of $[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]$ (**1**) in d_6 -DMSO.

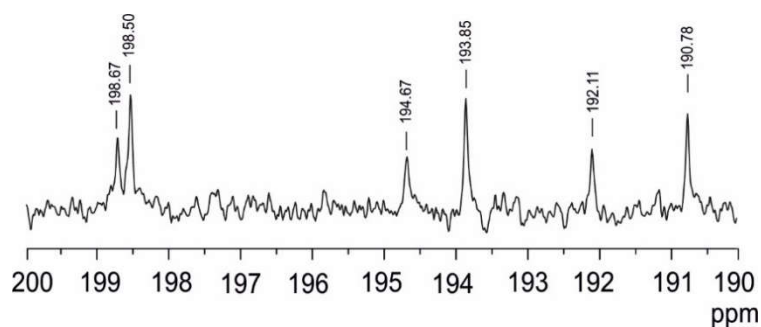


Figure A3. Expansion of the carbonyl region of ^{13}C NMR spectrum of $[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]$ (**1**) in d_6 -DMSO.

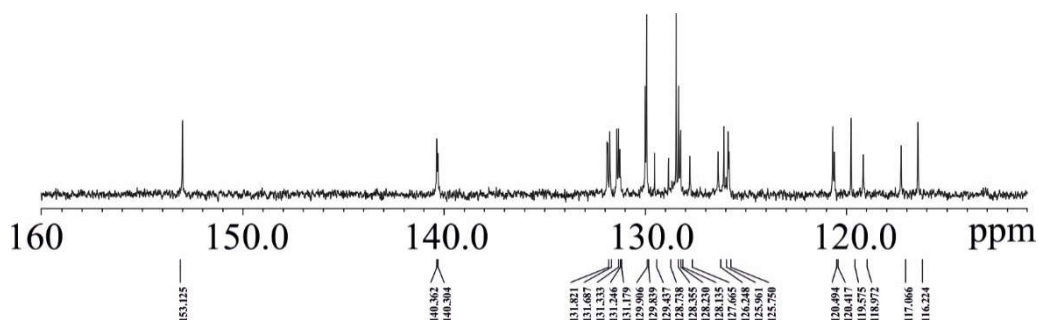


Figure A4. DEPT-135 spectrum of $[\text{Re}(\text{pmbpy})(\text{CO})_3\text{Cl}]$ (**1**) in d_6 -DMSO.

Table A1. Summary of the crystallographic data for **1**.

Chemical formula	$2(\text{C}_{25}\text{H}_{16}\text{ClN}_2\text{O}_5\text{Re}) \cdot \text{C}_7$
M_r	1376.19
Crystal system, space group	Triclinic, $P-1$
Temperature (K)	293
a, b, c (Å)	7.1460 (8), 11.8648 (17), 15.668 (2)
α, β, γ (°)	104.276 (13), 93.09 (1), 93.142 (10)
V (Å ³)	1282.3 (3)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	4.89
Crystal size (mm)	0.45 × 0.15 × 0.14
Diffractometer	Xcalibur, Ruby, Gemini ultra
$T_{\min}, T_{\max}$	0.906, 1.000
No. of measured, independent and	8651, 4451, 2874

observed reflections	$[I > 2\sigma(I)]$
R_{int}	0.086
$(\sin \theta/\lambda)_{\text{max}}$ ($\text{\AA}^{-1}$)	0.595
$R[\text{\AA}^2 > 2\sigma(\text{\AA}^2)], wR(\text{\AA}^2), S$	0.068, 0.134, 0.96
No. of reflections	4451
No. of parameters	372
No. of restraints	664
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($\text{e \AA}^{-3}$)	1.42, -1.06

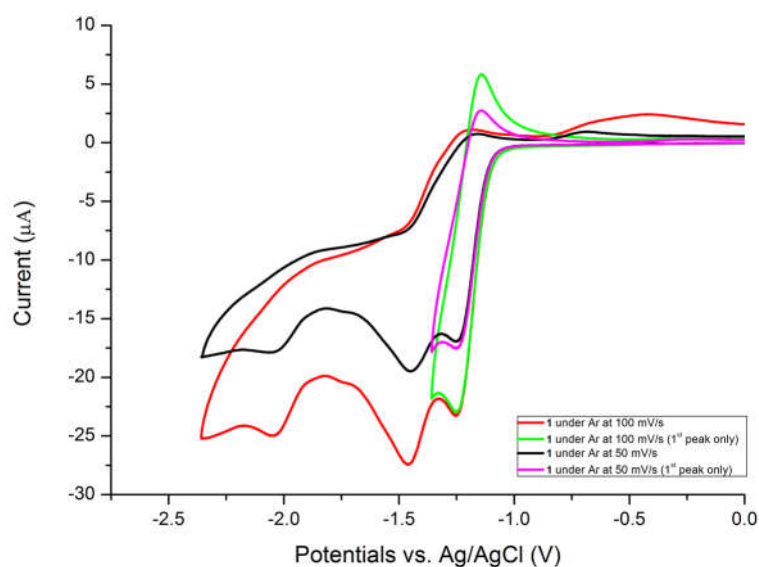


Figure A5. CVs at low scan rate (50 and 100 mV/s) of a 1mM solution of **1** in $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$ under Ar, at a glassy carbon electrode

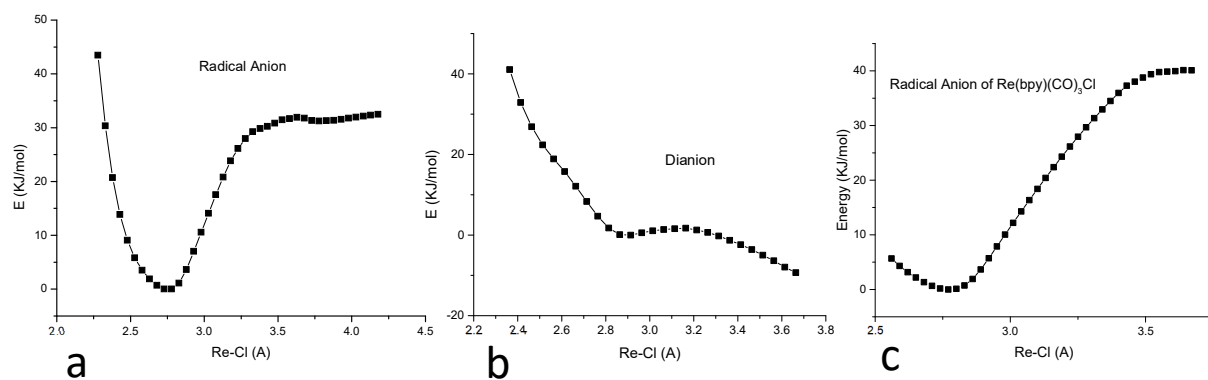


Figure A6. Relaxed geometry scan of the Re-Cl bonds in the optimized structures of the radical anion (**1**⁻, a) and the dianion (**1**²⁻, b), and the radical anion of $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ (c).

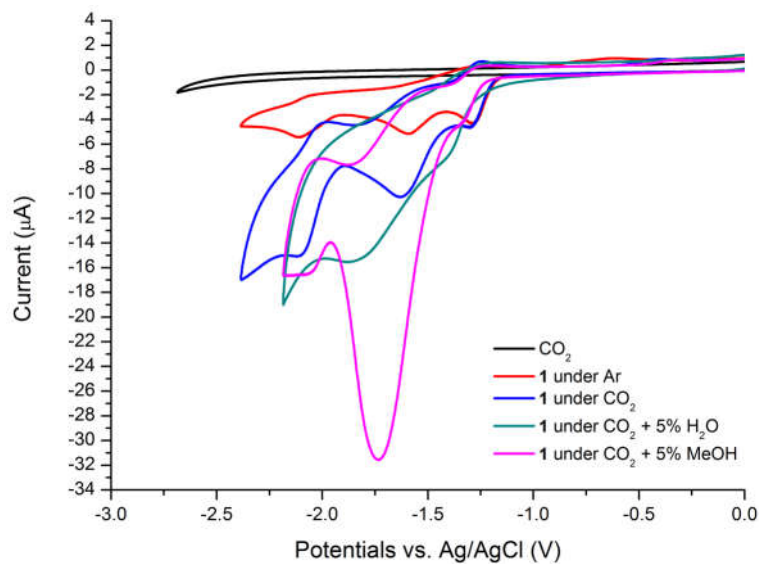


Figure A7. Cyclic voltammograms of 1 mM solutions of **1** in CH_3CN / 0.1 M Bu_4NPF_6 at 200 mV/s; black line is the background under CO_2 .

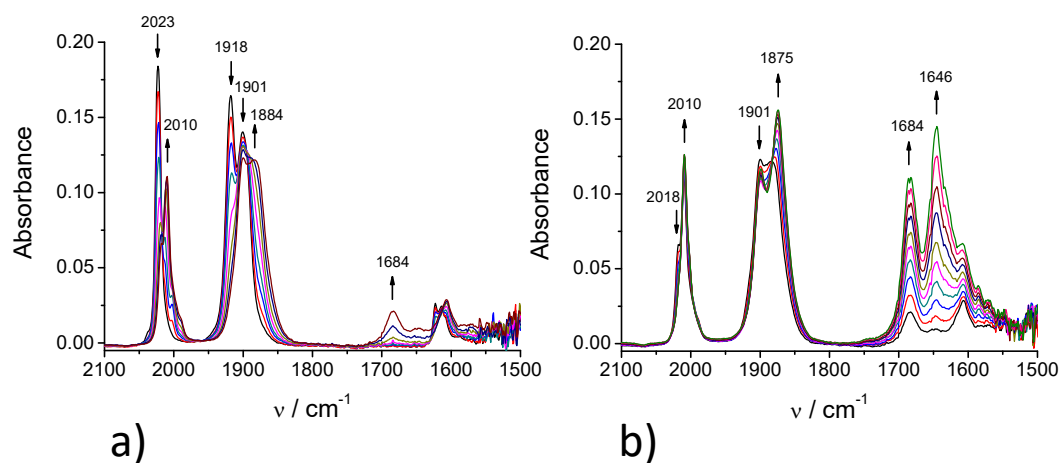


Figure A8. IR-Spectroelectrochemistry of **1** in CH₃CN/0.1 M Bu₄NPF₆ under CO₂: a) at the first reduction wave (−1.4 V vs Ag/AgCl); b) early stage of the electrolysis at the second reduction peak (−1.7 V vs Ag/AgCl).

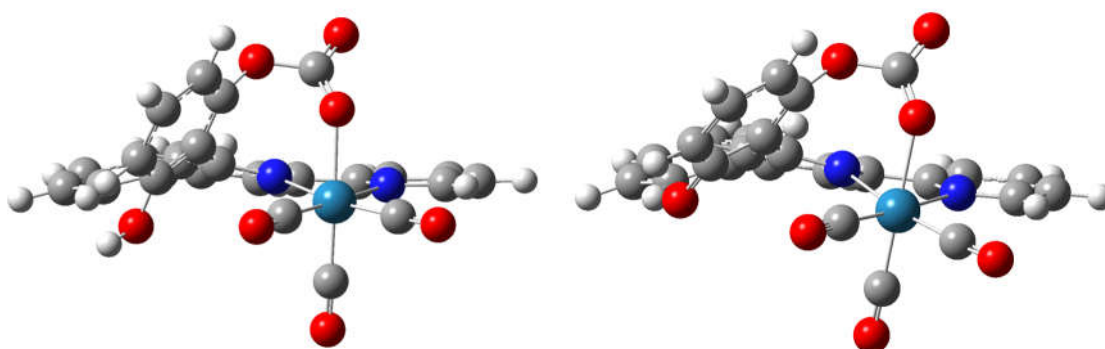


Figure A9. Optimized structures (carbonates) obtained for CO₂ insertion into the Re-O bond of (**1d**) and (**1e**). These carbonates are stabilized by 40.0 and 34.8 kJ/mol (electronic energies corrected with the zero-point energies) with respect the starting reactants **1d** + CO₂ and **1e** + CO₂, respectively.

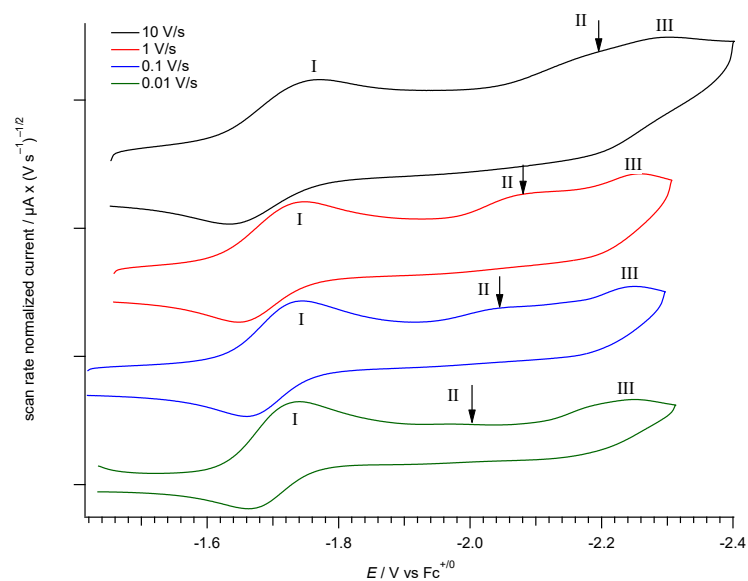


Figure A10. Current normalized cyclic voltammograms of 0.4 mM **2** in Ar-saturated CH₃CN with 0.1 M Bu₄NPF₆ at a glassy carbon electrode with varied scan rates.

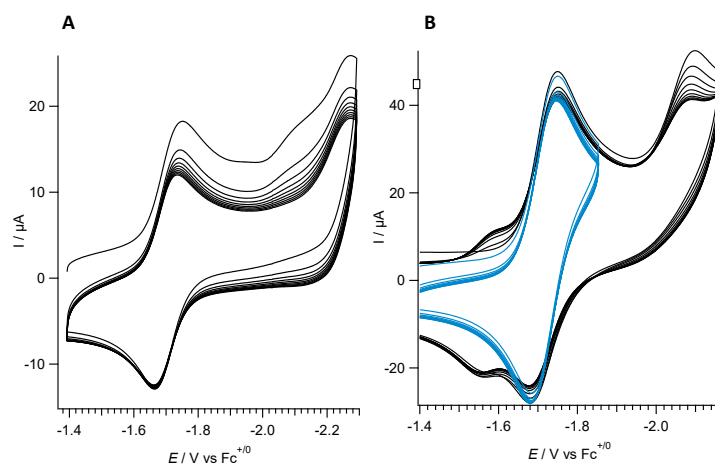


Figure A11. (A) Multisweep cyclic voltammograms of 0.4 mM **2** (A) and 1 mM [Re(4,6-diphenyl-2,2'-bpy)(CO)₃Cl] (B) in Ar-saturated CH₃CN with 0.1 M Bu₄NPF₆ at a glassy carbon electrode at 500 mV s⁻¹.

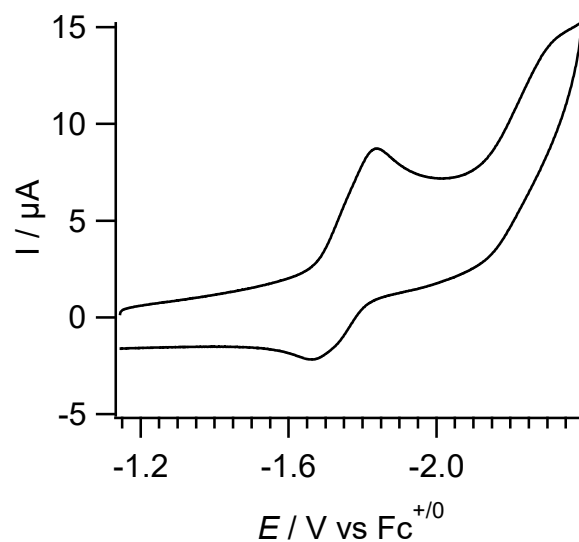


Figure A12. CV of 0.4 mM **2** in Ar-saturated butyronitrile with 0.1 M Bu₄NPF₆ at 195 K. Scan rate = 500 mV s⁻¹.

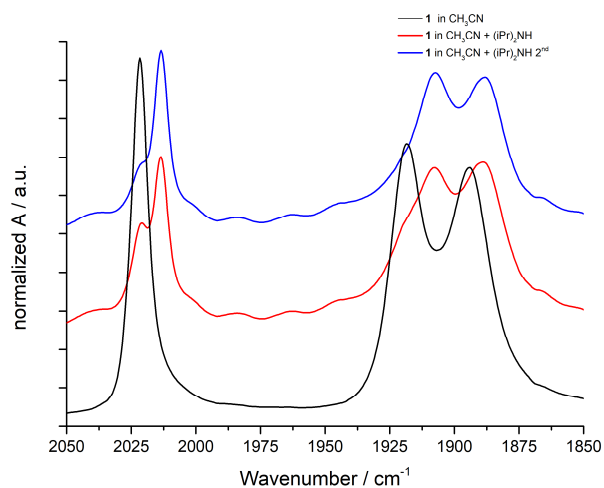


Figure A13. IR spectra before (black) and after (red and blue) addition of 0.5 mM (iPr)₂NH to a 0.5 mM solution of **2** in CH₃CN. Red spectrum: equimolar addition of base; blue spectrum: excess of base was added.

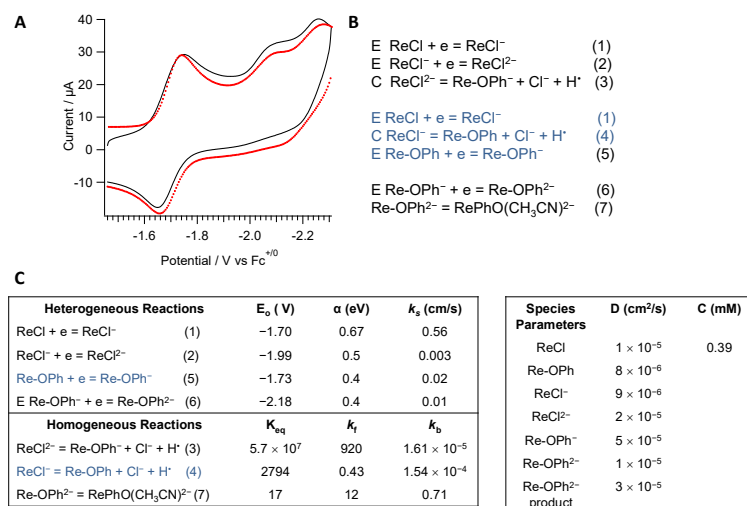


Figure A14. (A) Experimental CV (black) and simulated CV (red) of 0.39 mM **2** at 1 V s^{-1} in Ar-saturated CH_3CN . (B) Mechanism from Scheme 3.3 in Paragraph 3.6. (C) Simulation parameters.

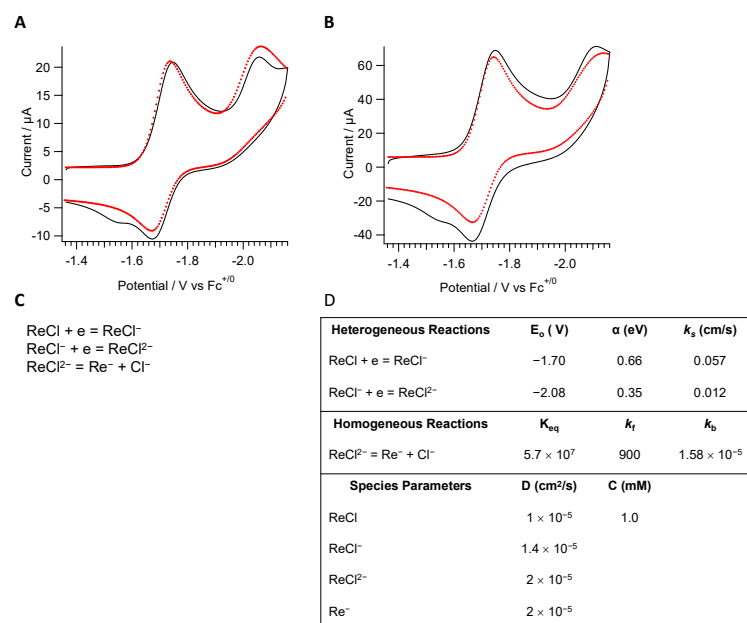


Figure A15. (A) Experimental CV (black) and simulated CV (red) according to an EEC reductive mechanism of 1 mM $[\text{Re}(\text{4,6-diphenyl-2,2'-bpy})(\text{CO})_3\text{Cl}]$ in Ar-saturated CH_3CN at 100 mV s^{-1} and (B) 1000 mV s^{-1} . (C) Mechanism. (D) Simulation parameters.

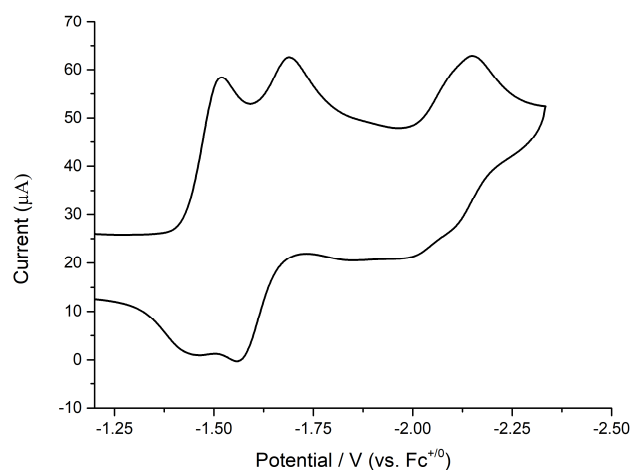


Figure A16. CV of $[\text{Re}(\text{pmbpy})(\text{CO})_3(\text{CH}_3\text{CN})]$ (**2- CH_3CN^+**) in Ar-saturated CH_3CN at 100 mV s^{-1} .

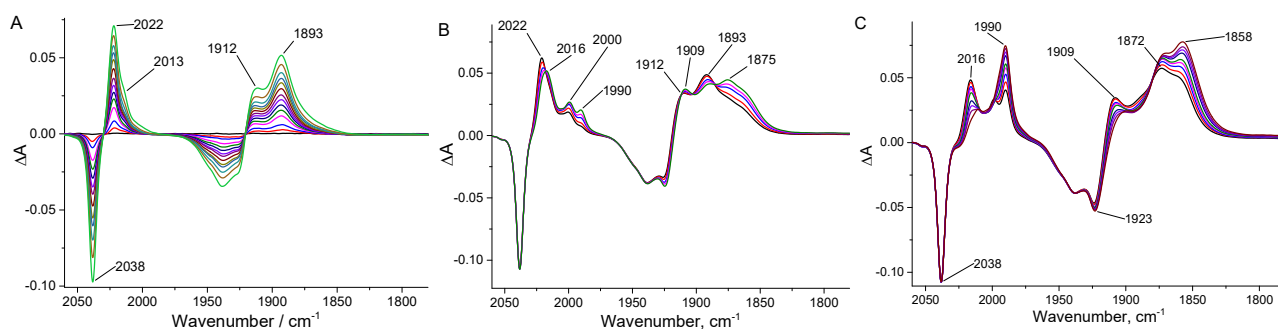


Figure A17. Difference IR spectra (expanded metal carbonyl region) measured during controlled potential electrolysis of **2- CH_3CN^+** in CD_3CN containing $0.1 \text{ M Bu}_4\text{NPF}_6$ under an N_2 atmosphere. Applied potentials: (A) $-1.4 \text{ V vs Fc}^{+/0}$; (B) $-1.6 \text{ V vs Fc}^{+/0}$ and (C) $-1.7 \text{ V vs Fc}^{+/0}$

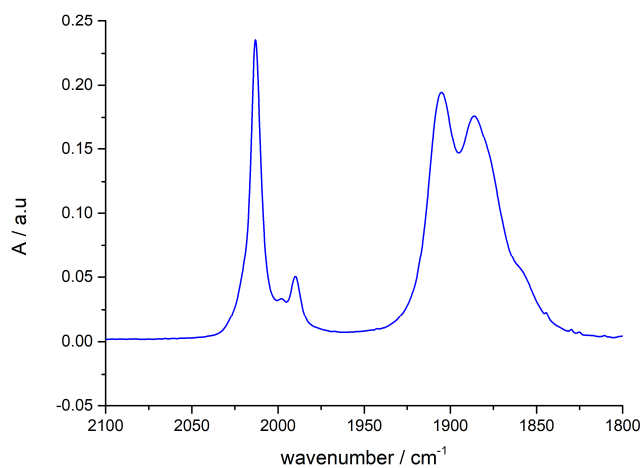


Figure A18. IR-spectrum in acetonitrile of isolated **2-OPh** species after bulk electrolysis experiment.

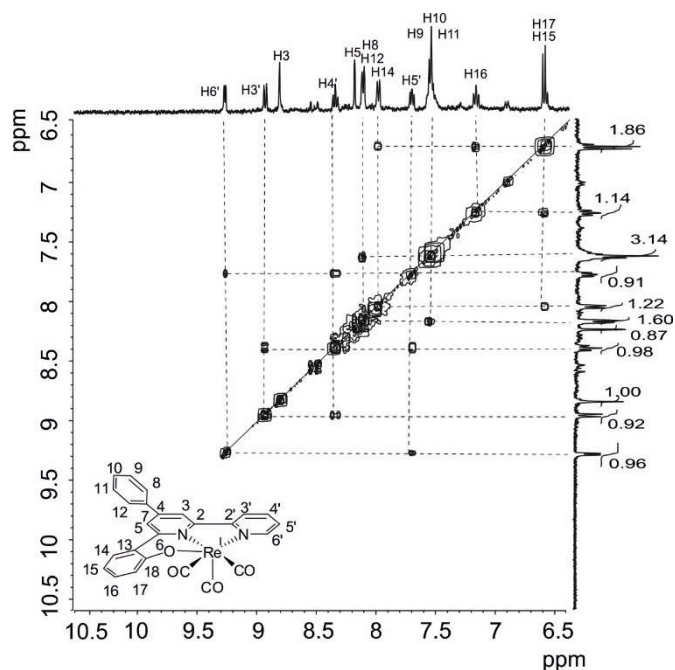


Figure A19. 2d-COSY spectrum of **2-OPh** in d_6 -DMSO. Numeration in the chemical structure reported in the figure is referred to the carbon skeleton for 2,2' bipyridines. Each $-CH$ proton has been named with the respective number of the carbon.

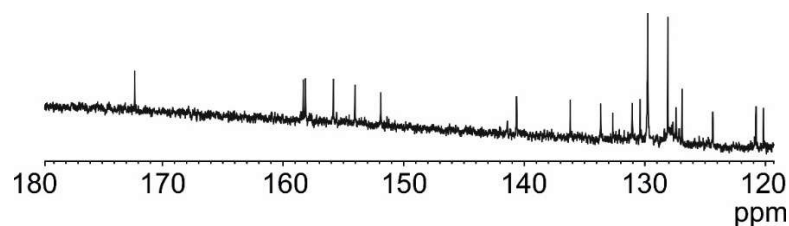


Figure A20. ^{13}C NMR spectrum of **2-OPh** in d_6 -DMSO.

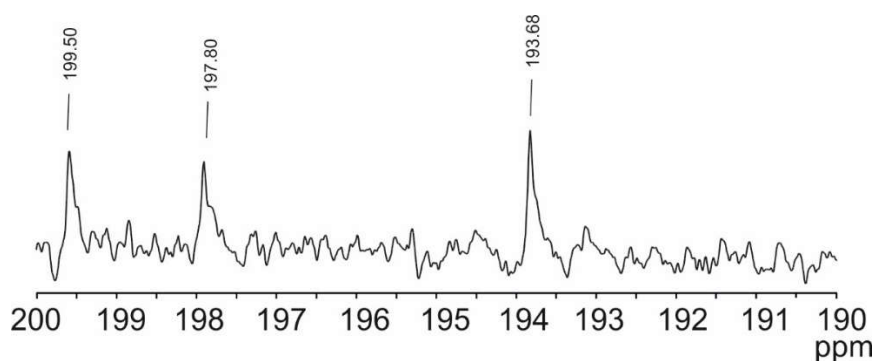


Figure A21. Expansion of the carbonyl region of ^{13}C NMR spectrum of **2-OPh** in d_6 -DMSO.

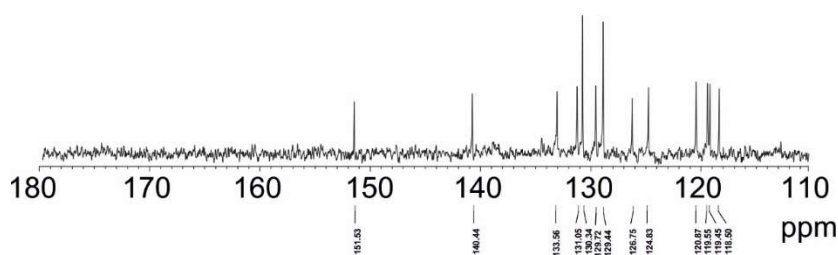


Figure A22. DEPT-135 spectrum of **2-OPh** in d_6 -DMSO.

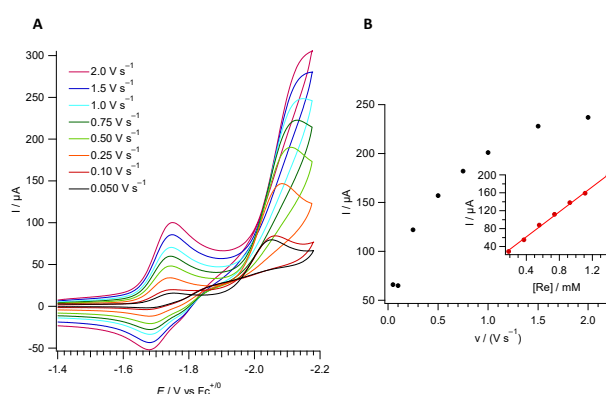
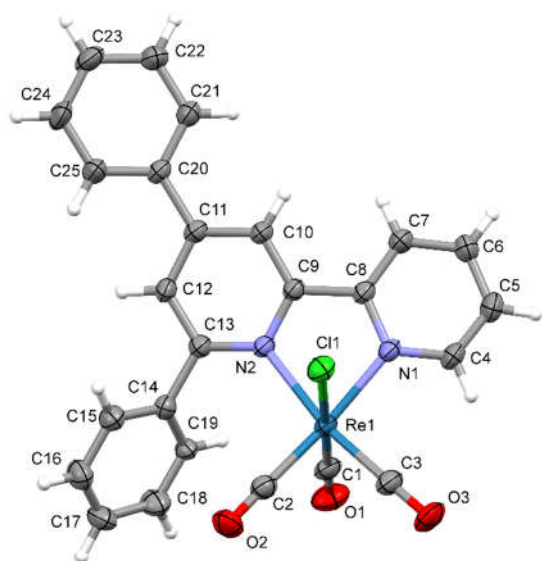


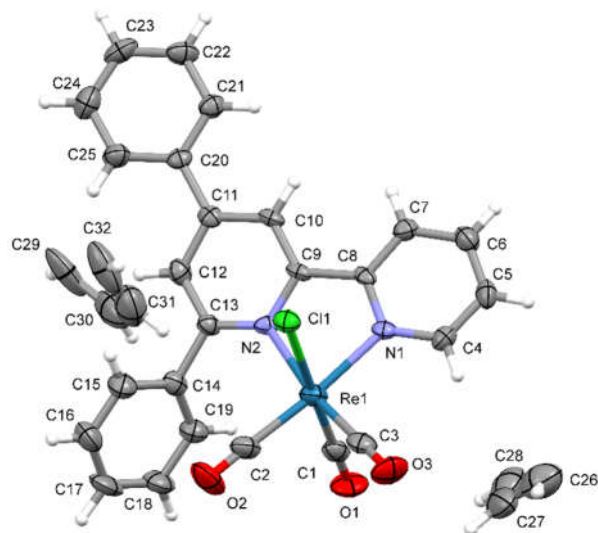
Figure A23. (A) Variable scan rate cyclic voltammograms of 1 mM [(4,6-diphenyl-2,2'-bipyridine) $\text{Re}(\text{CO})_3\text{Cl}$] in CO_2 -saturated CH_3CN with 0.1 M Bu_4NPF_6 at a glassy carbon electrode. (B) Catalytic current vs scan rate; inset: current dependence on catalyst concentration at 2 V s^{-1} .

Appendix B "Chapter 4"

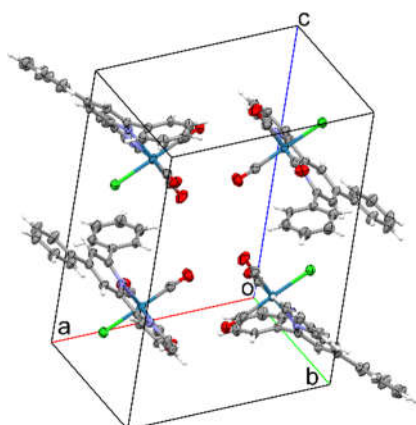
(a)



(b)



(c)



(d)

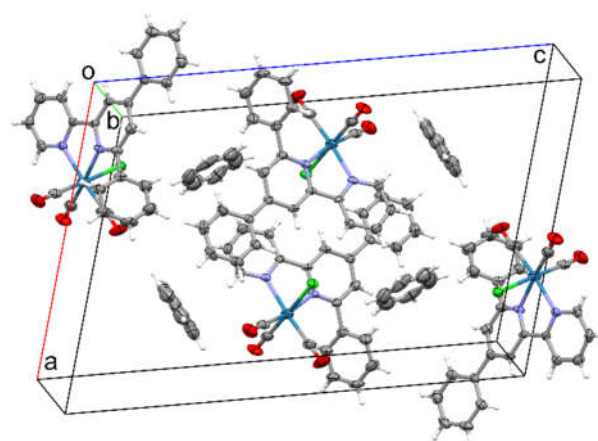


Figure B1. (a) asymmetric unit of **2e** (structure A), (b) asymmetric unit of **2e** (structure B), (c) unit cell of **2e** (structure A) and (d) unit cell of **2e** (structure B).

Table B1. Crystal data for structure A and B of complex **2e**.

	structure A	structure B
Chemical formula	C ₂₅ H ₁₆ ClN ₂ O ₃ Re	C ₃₁ H ₂₂ ClN ₂ O ₃ Re
M_r	614.06	692.17
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2/n$
Temperature (K)	293	293
a, b, c (Å)	11.6691 (3), 11.6098 (3), 16.0455 (4)	15.3042 (3), 7.7657 (1), 23.2383 (5)
β (°)	102.600 (2)	103.231 (2)
V (Å ³)	2121.43 (9)	2688.51 (9)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	5.89	4.66
Crystal size (mm)	0.35 × 0.15 × 0.11	0.84 × 0.15 × 0.10
$T_{\min}, T_{\max}$	0.705, 1.000	0.437, 0.628
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12425, 5063, 4444	11348, 4720, 3508
R_{int}	0.026	0.036
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.059, 1.03	0.026, 0.066, 1.04

No. of reflections	5063	3508
No. of parameters	289	344
No. of restraints	0	1
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e $\text{\AA}^{-3}$)	0.74, -0.85	0.42, -0.37

Table B2. Bond distances ($\text{\AA}$) and angles (degree) for **2e** (structure A).

Atom1	Atom2	Length ($\text{\AA}$)	Atom1	Atom2	Atom3	Angle ($^{\circ}$)
Re1	Cl1	2.483(1)	Cl1	Re1	N2	83.03(6)
Re1	N2	2.220(2)	Cl1	Re1	N1	84.14(6)
Re1	N1	2.160(2)	Cl1	Re1	C1	179.0(1)
Re1	C1	1.906(4)	Cl1	Re1	C2	91.3(1)
Re1	C2	1.936(5)	Cl1	Re1	C3	93.8(1)
Re1	C3	1.890(3)	N2	Re1	N1	74.33(9)
N2	C9	1.356(4)	N2	Re1	C1	96.0(1)
N2	C13	1.355(4)	N2	Re1	C2	101.9(1)
N1	C8	1.354(3)	N2	Re1	C3	169.9(1)
N1	C4	1.349(4)	N1	Re1	C1	95.8(1)
O2	C2	1.138(5)	N1	Re1	C2	174.4(1)
O1	C1	1.138(5)	N1	Re1	C3	95.9(1)
O3	C3	1.154(4)	C1	Re1	C2	88.7(2)
C8	C9	1.479(4)	C1	Re1	C3	87.2(1)
C8	C7	1.374(5)	C2	Re1	C3	87.7(2)
C9	C10	1.382(3)	Re1	N2	C9	114.4(2)

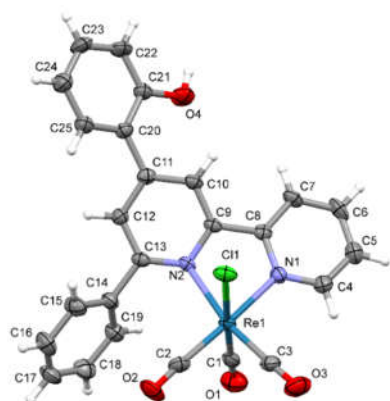
	Re1	N2	C13	127.7(2)
	C9	N2	C13	117.0(2)
	Re1	N1	C8	117.5(2)
	Re1	N1	C4	124.8(2)
	C8	N1	C4	117.7(3)
	Re1	C1	O1	176.1(3)
	Re1	C2	O2	179.4(3)
	N1	C8	C9	115.2(2)
	N1	C8	C7	121.5(3)
	C9	C8	C7	123.1(3)
	N2	C9	C8	115.5(2)
	N2	C9	C10	122.8(3)
	C8	C9	C10	121.6(3)
	Re1	C3	O3	176.7(3)

Table B3. Bond distances (Å) and angles (degree) for **2e** (structure B).

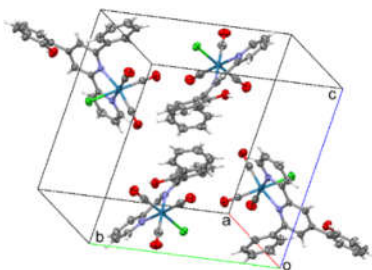
Atom1	Atom2	Length	Atom1	Atom2	Atom3	Angle
Re1	Cl1	2.486(2)	Cl1	Re1	N1	85.3(1)
Re1	N1	2.177(4)	Cl1	Re1	N2	81.6(1)
Re1	N2	2.233(5)	Cl1	Re1	C2	90.8(2)
Re1	C2	1.952(7)	Cl1	Re1	C3	91.1(2)
Re1	C3	1.933(7)	Cl1	Re1	C1	178.5(2)
Re1	C1	1.919(7)	N1	Re1	N2	74.6(2)
N1	C8	1.352(8)	N1	Re1	C2	174.9(3)
N1	C4	1.338(8)	N1	Re1	C3	97.2(2)
N2	C13	1.338(8)	N1	Re1	C1	93.2(2)

N2	C9	1.364(7)	N2	Re1	C2	101.6(3)
O2	C2	1.116(9)	N2	Re1	C3	169.3(2)
			N2	Re1	C1	98.0(2)
			C2	Re1	C3	86.1(3)
			C2	Re1	C1	90.7(3)
			C3	Re1	C1	89.1(3)
			Re1	N1	C8	116.3(4)
			Re1	N1	C4	124.7(4)
			C8	N1	C4	118.8(5)
			Re1	N2	C13	127.5(4)
			Re1	N2	C9	113.2(4)
			C13	N2	C9	117.7(5)
			Re1	C2	O2	177.2(7)
			N2	C13	C12	121.9(6)
			N2	C13	C14	119.7(6)

(a)



(b)



(c)

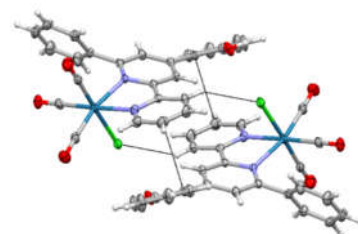


Figure B2. (a) asymmetric unit, (b) unit cell and (c) C-H $\cdots$ Cl and $\pi\cdots\pi$ stacking contacts in the crystal structure of **2f**.

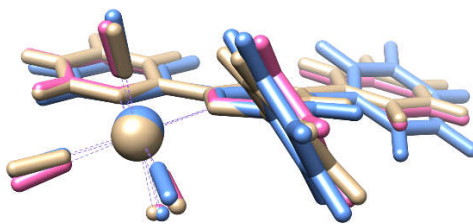


Figure B3. Comparison of DFT optimized (light blue) and X-ray structure A (brown) and B (pink) of **2e**.

Table B4. Data for **2f**.

Chemical formula	C ₂₅ H ₁₆ ClN ₂ O ₄ Re
M_r	630.06
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å), β (°)	9.6474 (6), 15.8756 (10), 14.8432 (8), 93.292 (5)
V (Å ³)	2269.6 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	5.51
Crystal size (mm)	0.53 × 0.37 × 0.22
No. of measured, independent and observed reflections	10670, 3786, 3073
R_{int}	0.047
$R[\mathcal{F}^2 > 2\sigma(\mathcal{F}^2)]$, $wR(\mathcal{F}^2)$, S	0.031, 0.073, 1.02
No. of reflections and parameters	3786, 299
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.96, -1.01

Table B5. Bond distances (Å) and angles (degree) for **2f**.

Atom1	Atom2	Length (Å)	Atom1	Atom2	Atom3	Angle (degree)
Re1	Cl1	2.490(2)	Cl1	Re1	N2	80.2(1)
Re1	N2	2.214(4)	Cl1	Re1	N1	85.1(1)
Re1	N1	2.164(5)	Cl1	Re1	C1	177.1(2)
Re1	C1	1.921(6)	Cl1	Re1	C2	94.9(2)
Re1	C2	1.935(6)	Cl1	Re1	C3	91.0(2)
Re1	C3	1.898(6)	N2	Re1	N1	74.9(2)
O1	C1	1.106(8)	N2	Re1	C1	99.0(2)
O2	C2	1.137(8)	N2	Re1	C2	102.1(2)
O3	C3	1.158(8)	N2	Re1	C3	167.3(2)
N1	C4	1.338(8)	N1	Re1	C1	92.0(2)
C7	C6	1.378(9)	N1	Re1	C2	177.0(2)
C20	C11	1.482(7)	N1	Re1	C3	95.3(2)
C20	C21	1.398(8)	C1	Re1	C2	88.0(3)
C20	C25	1.383(8)	C1	Re1	C3	89.4(3)
C11	C12	1.397(8)	C2	Re1	C3	87.6(3)
C11	C10	1.378(7)	Re1	C1	O1	177.3(5)
C13	C12	1.382(8)	Re1	C2	O2	176.7(5)
O4	C21	1.357(8)	Re1	C3	O3	177.5(6)
			Re1	N1	C8	116.5(3)
			Re1	N1	C4	124.9(4)

Table B6. Contact table for **2f**.

Atom1	Atom2	Length	Length-VdW	Symm. op. 1	Symm. op. 2
O4	Cl1	3.117	-0.153	x,y,z	$-1+x,y,z$
O4	C2	3.142	-0.078	x,y,z	$-1+x,y,z$
H23	N2	2.750	-0.000	x,y,z	$-1/2-x,-1/2+y,1/2-z$
Cl1	H7	2.864	-0.086	x,y,z	$-x,-y,1-z$
C20	C5	3.395	-0.005	x,y,z	$-x,-y,1-z$
H6	O1	2.515	-0.205	x,y,z	$-1/2+x,1/2-y,1/2+z$

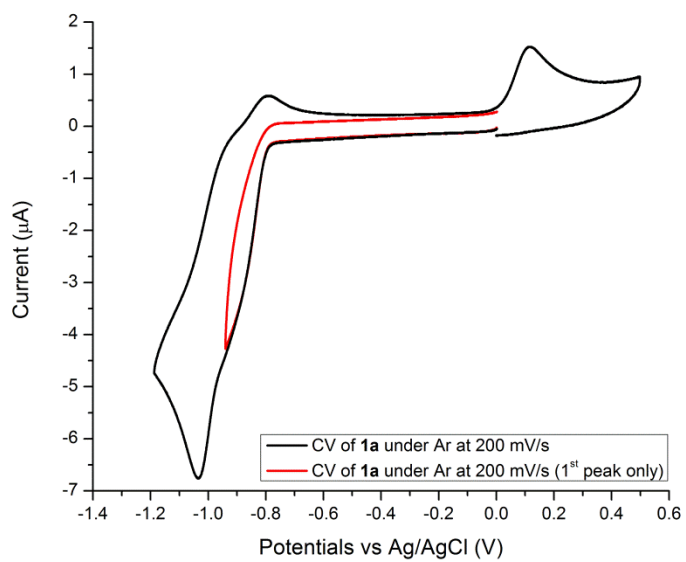


Figure B4. CVs of 1mM solution of **1a** in $\text{CH}_3\text{CN}/0.1\text{M Bu}_4\text{NPF}_6$ at GCE, scan rate 200 mVs^{-1} under Ar.

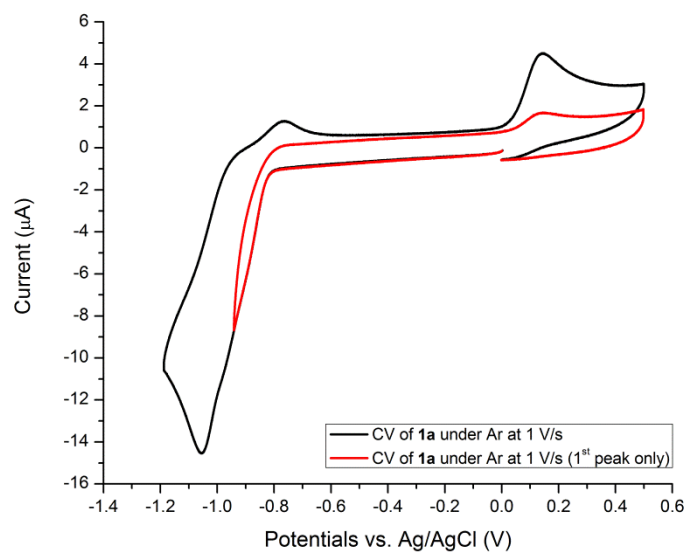


Figure B5. CVs of 1mM solution of **1a** in CH₃CN/0.1M Bu₄NPF₆ at GCE, scan rate 1Vs⁻¹ under Ar.

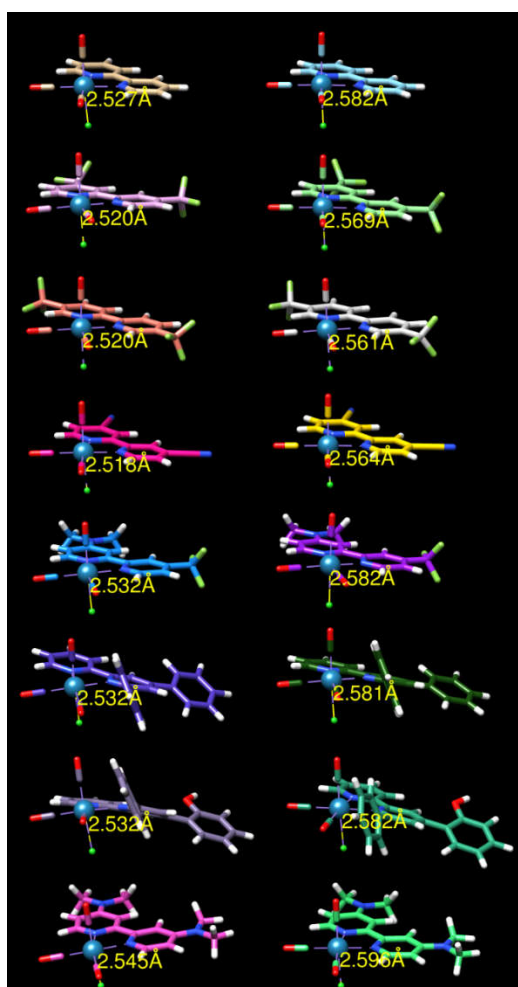


Figure B6. DFT optimized structures of the investigated Re complexes in their ground state (left) and reduced (right) form.

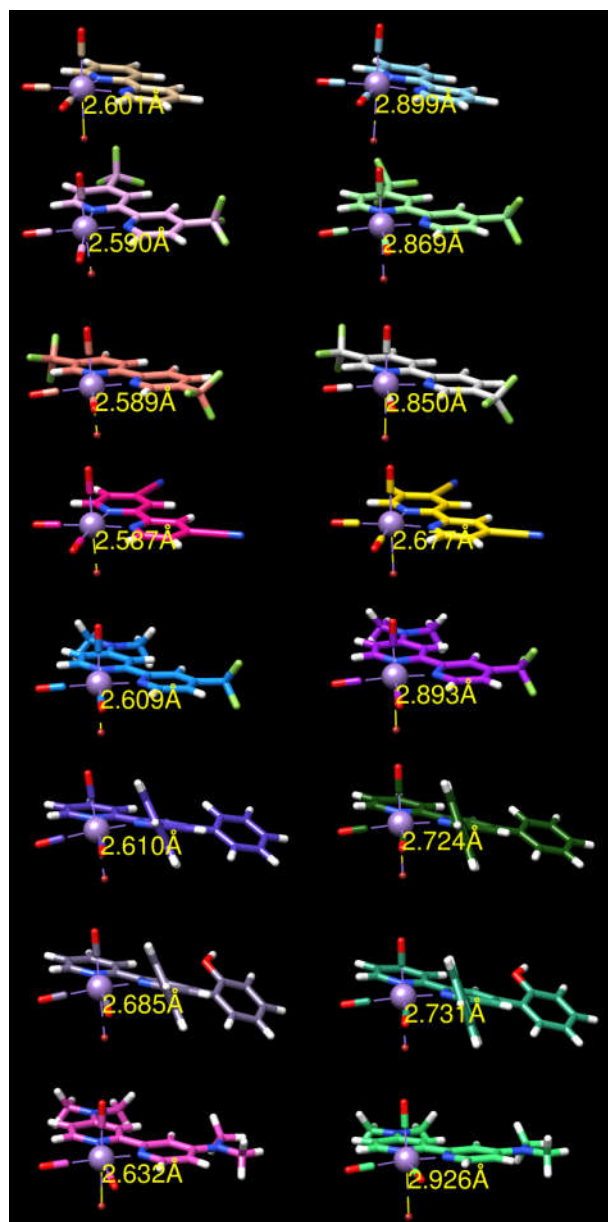


Figure B7. DFT optimized structures of the investigated Mn complexes in their ground state (left) and reduced (right) form.

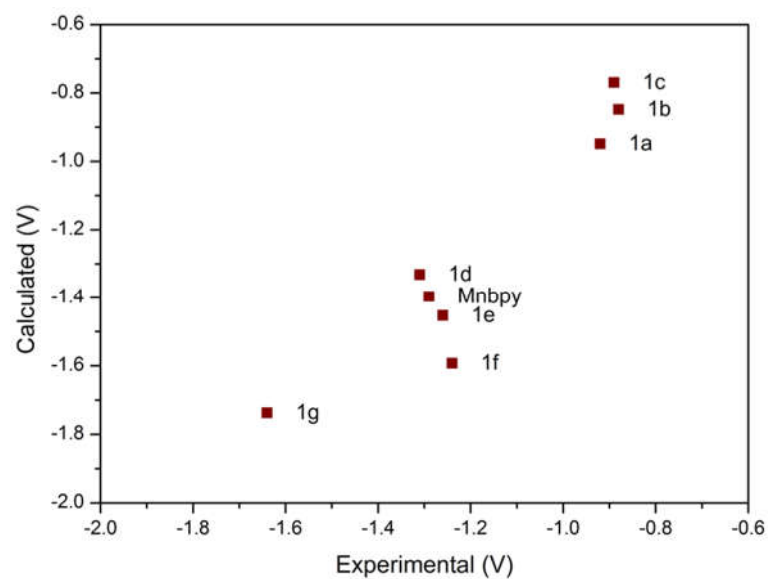


Figure B8. Plot of the calculated *vs.* experimental standard reduction potentials for **1a-1g**.

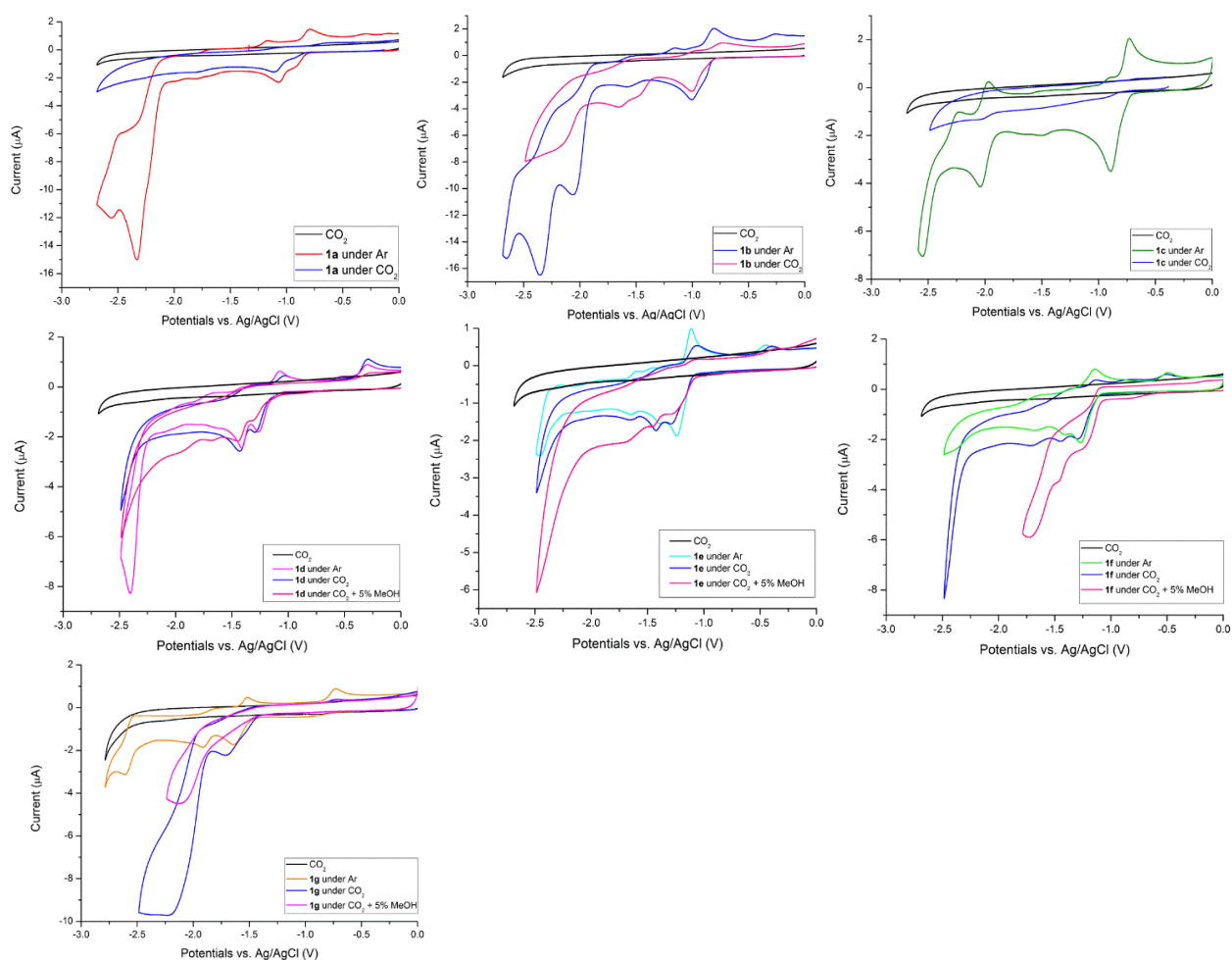


Figure B9. CVs of 0.5 mM solutions of **1a-1g** Mn complexes in $\text{CH}_3\text{CN}/0.1\text{M Bu}_4\text{NPF}_6$ at GCE,

scan rate 200 mVs^{-1} under Ar, under CO_2 and for **1d-1g** + 5%v MeOH. CV in black is the electrolyte saturated with CO_2 .

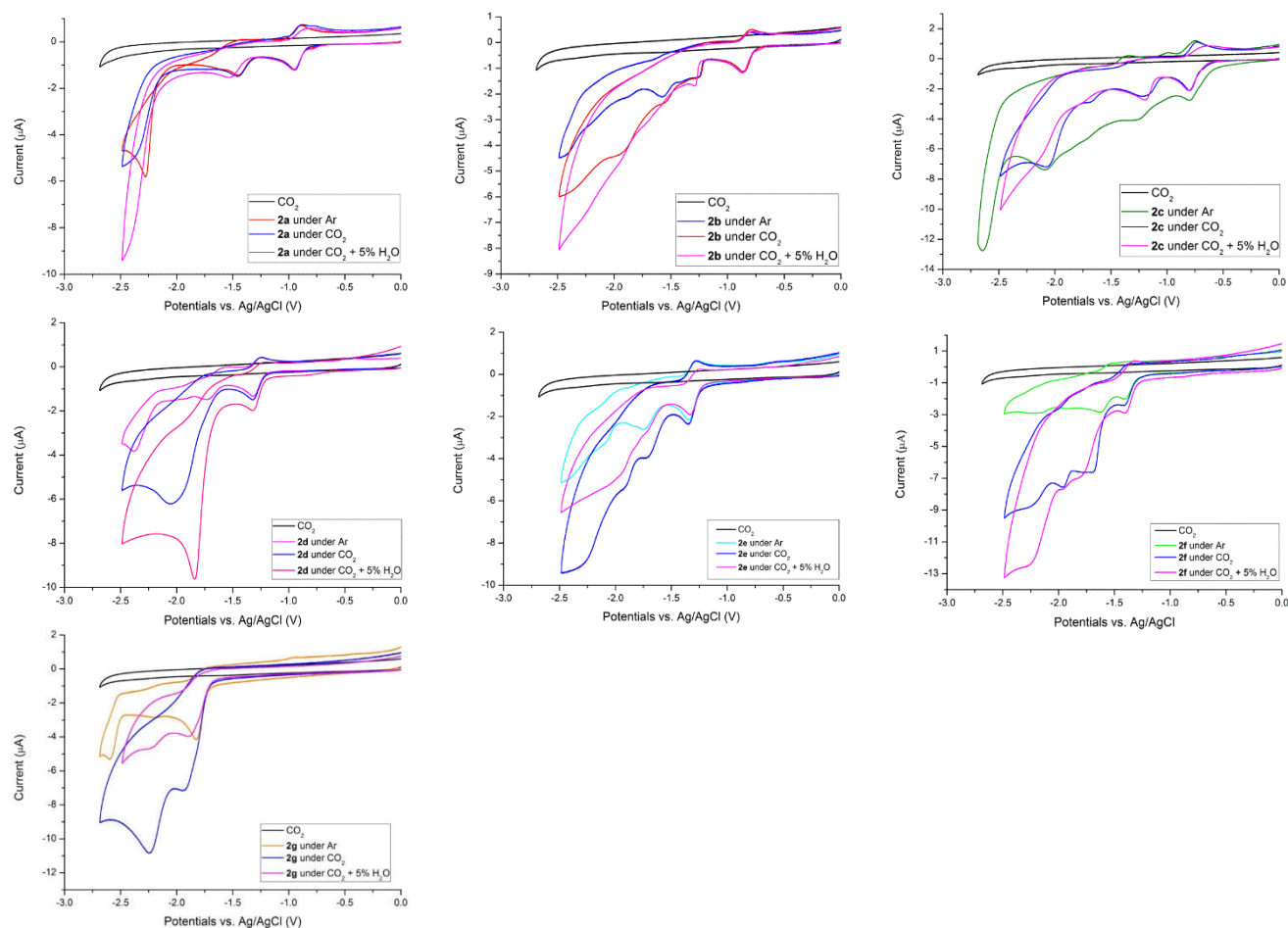


Figure B10. CVs of 0.5 mM solutions of **2a-2g** Re complexes in $\text{CH}_3\text{CN}/0.1\text{M Bu}_4\text{NPF}_6$ at GCE, scan rate 200 mVs^{-1} under Ar, under CO_2 and + 5%v H_2O . CV in black is the electrolyte saturated with CO_2 .

Table B7. TON and faradic efficiencies (η) upon CPE (applied potential E in V vs. Ag/AgCl) of solutions of manganese and rhenium complexes (0.5 mM) in 0.1 M Bu₄NPF₆/CH₃CN in the presence of Brønsted acids (5%v).

Complex	E [V]	T [min]	acid [5%]	TON _{CO}	η_{CO} [%]	TON _{H₂}	η_{H_2} [%]
1d	-1.5	90	MeOH	0.5	-	-	-
1e	-1.5	60	MeOH	0.7	-	-	-
1f	-1.5	300	MeOH	1.5	-	-	-
1g	-1.95	60	MeOH	2.6	85	-	-
2d	-1.8	60	-	0.5	-	-	-
2d	-1.8	300	H ₂ O	2	-	-	-
2e	-1.7	120	-	1	-	-	-
2e	-1.7	120	H ₂ O	1.5	-	-	-
2f	-1.7	360	H ₂ O	14	85	-	-
2g	-2	300	H ₂ O	23	100	-	-

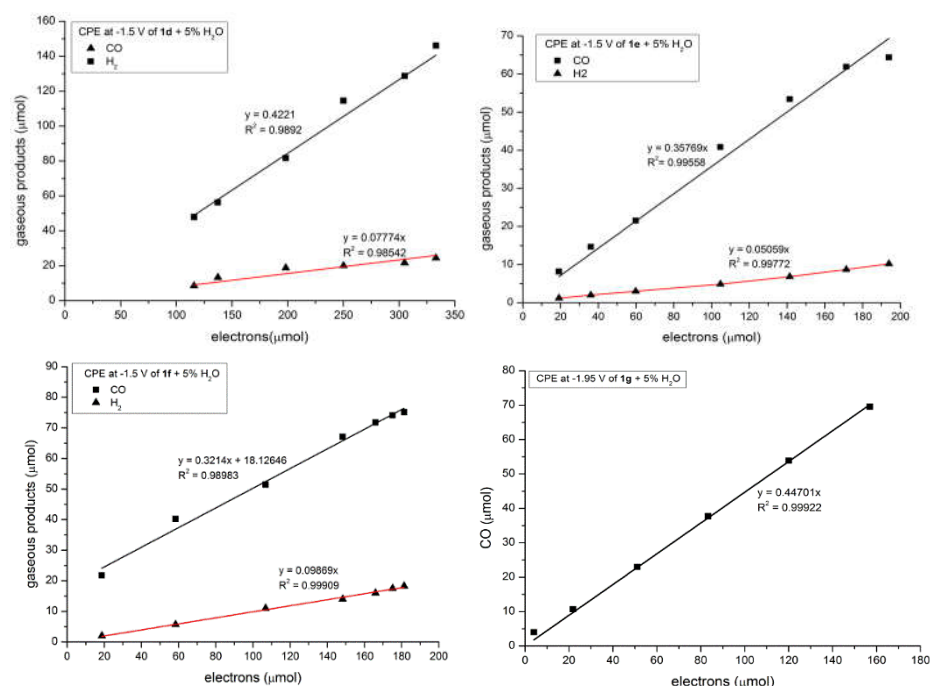


Figure B11. Catalytic CO and H₂ production from CO₂ as a function of the charge during CPE carried out in CH₃CN solutions of **1d-1g** (0.5 mM) with 5%v H₂O.

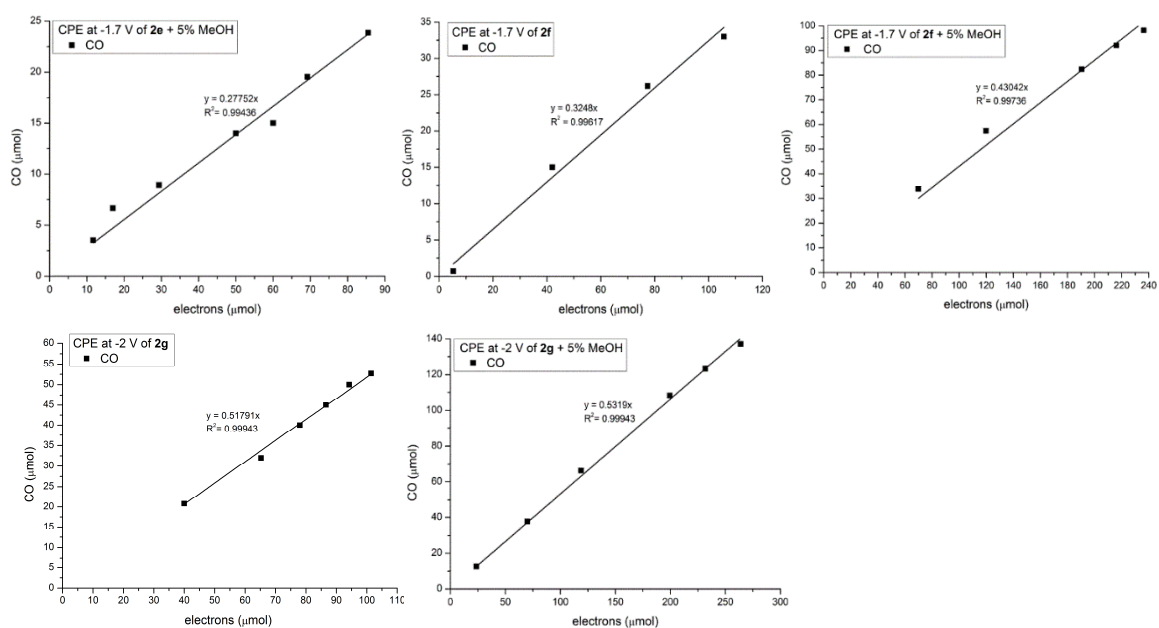


Figure B12. Catalytic CO production from CO_2 as a function of the charge during CPE carried out in CH_3CN solutions of **2e-2g** (0.5 mM) both in absence and presence of 5%v MeOH.

Appendix C “Chapter 5”

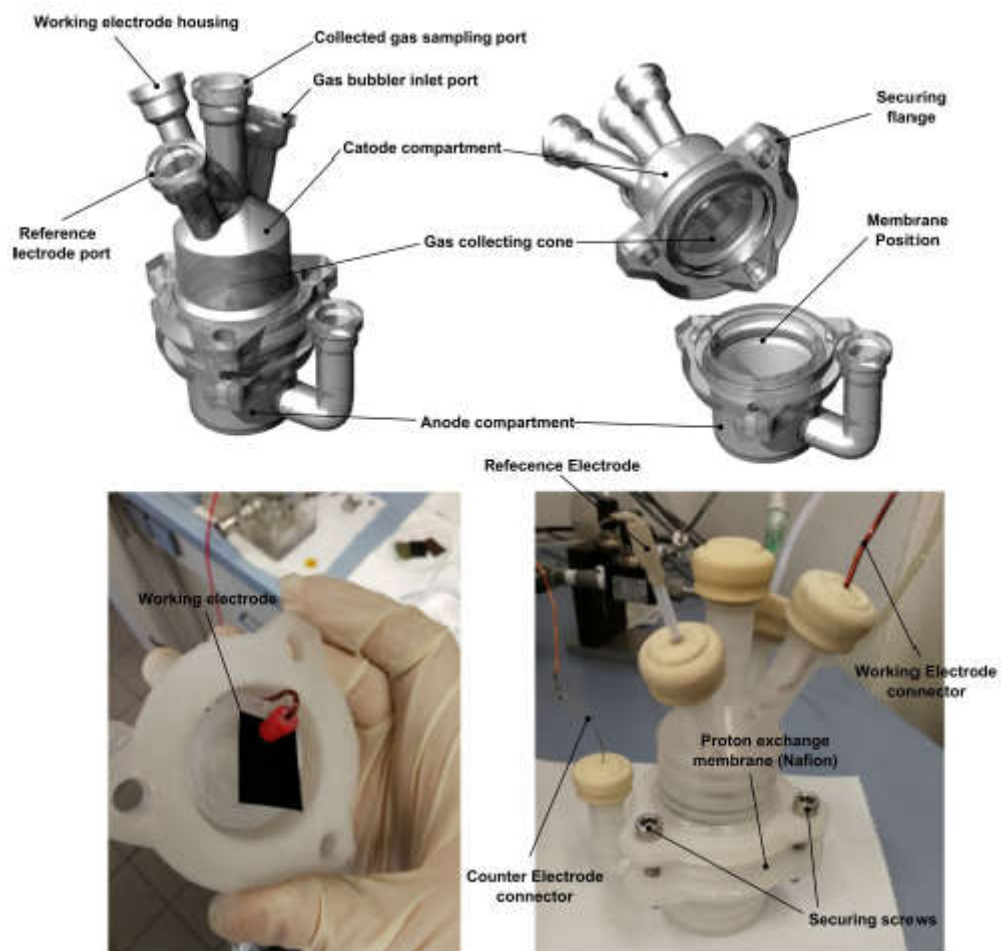


Figure C1. 3D-printed ABS electrochemical cell used for CO₂RR experiments.

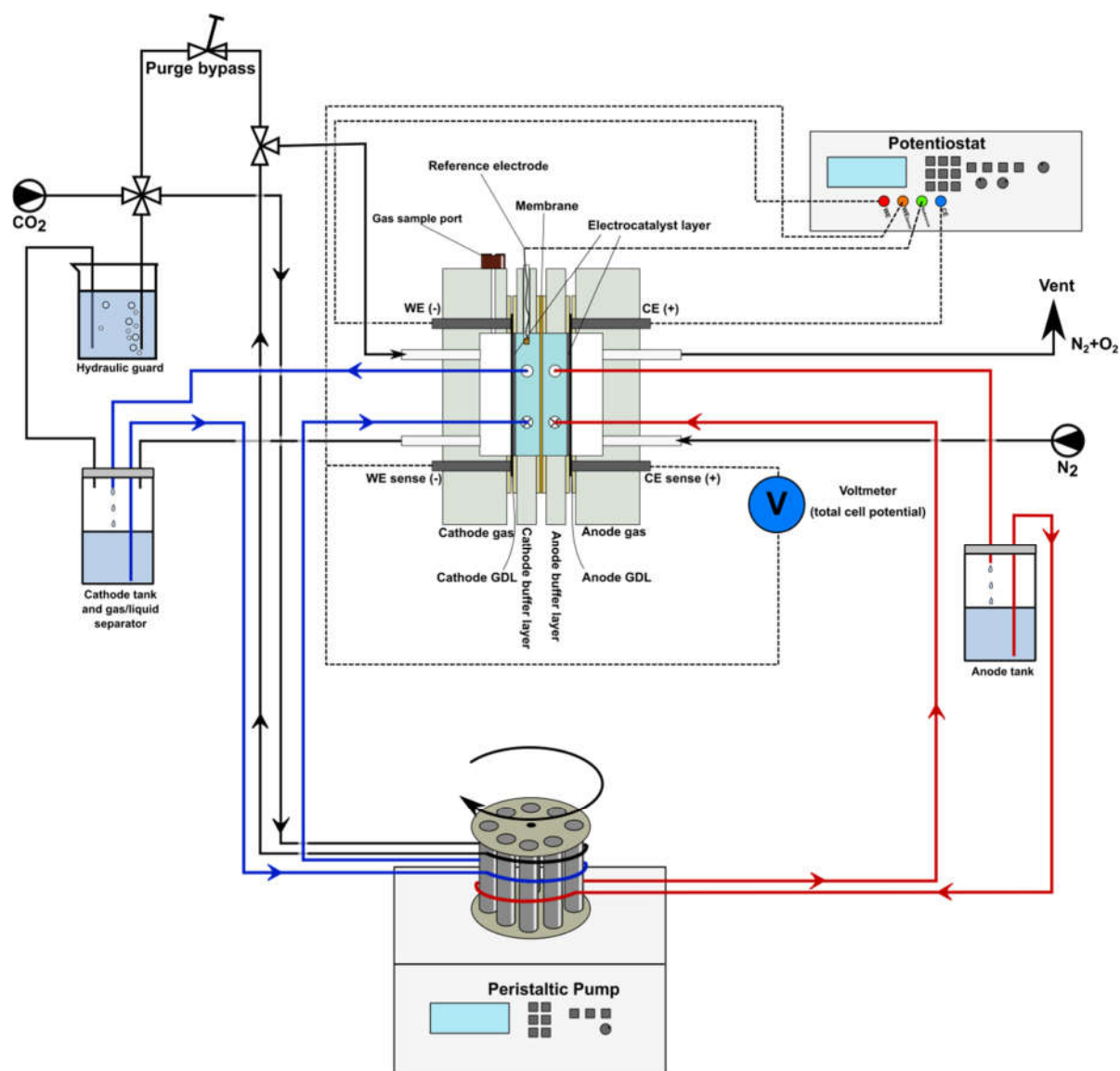


Figure C2a. Flow reactor experimental setup scheme

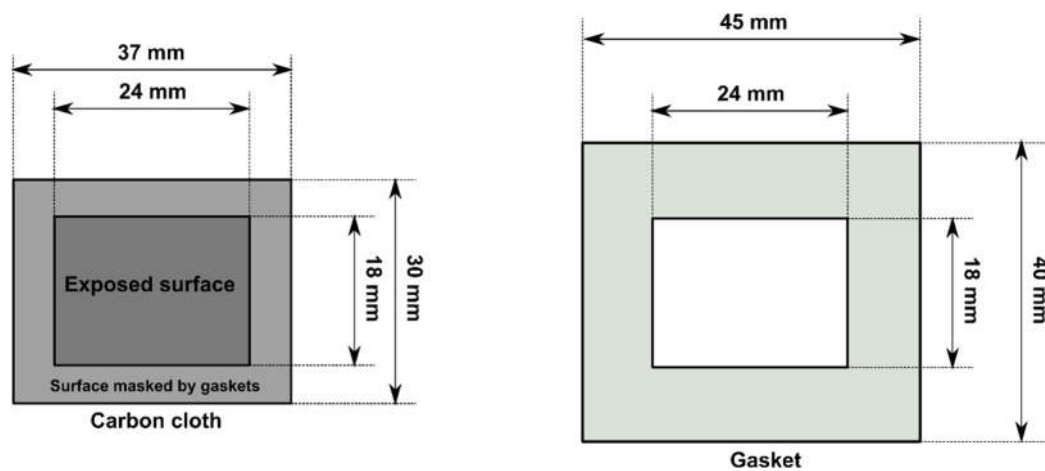


Figure C2b. Electrode masking and gasket configuration

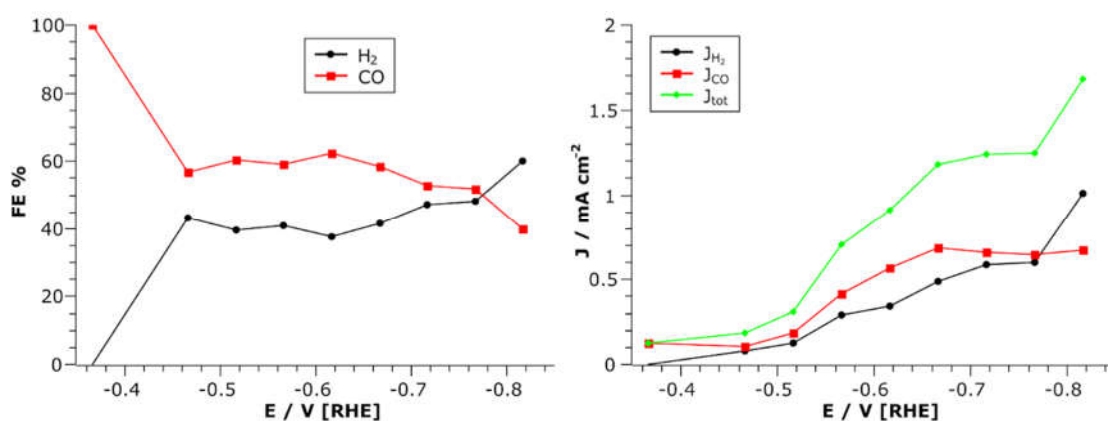


Figure C3. (left) Faradaic efficiency and (right) partial and total current density profiles for gaseous products of carbon cloth-supported *fac*-Mn(apbpy)(CO)₃Br ($1.4 \cdot 10^{-9}$ mol cm_{ECSA}⁻², $4.51 \cdot 10^{-7}$ g_{Mn} cm_{geom}⁻²) operating in buffer layer configuration, CO₂ flow rate 0.2 mL min⁻¹, buffer flow rate 0.4 mL min⁻¹

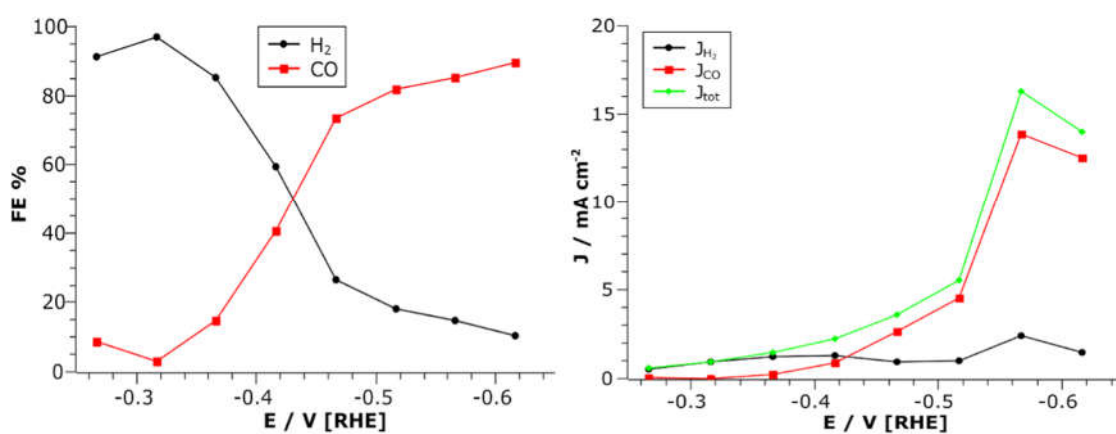


Figure C4. (left) Faradaic efficiency and (right) partial and total current density profiles for gaseous products of Au/C NPs (0.081 mgAu cm⁻²) operating in buffer layer configuration, CO₂ flow rate 0.2 mL min⁻¹, buffer flow rate 0.4 mL min⁻¹.

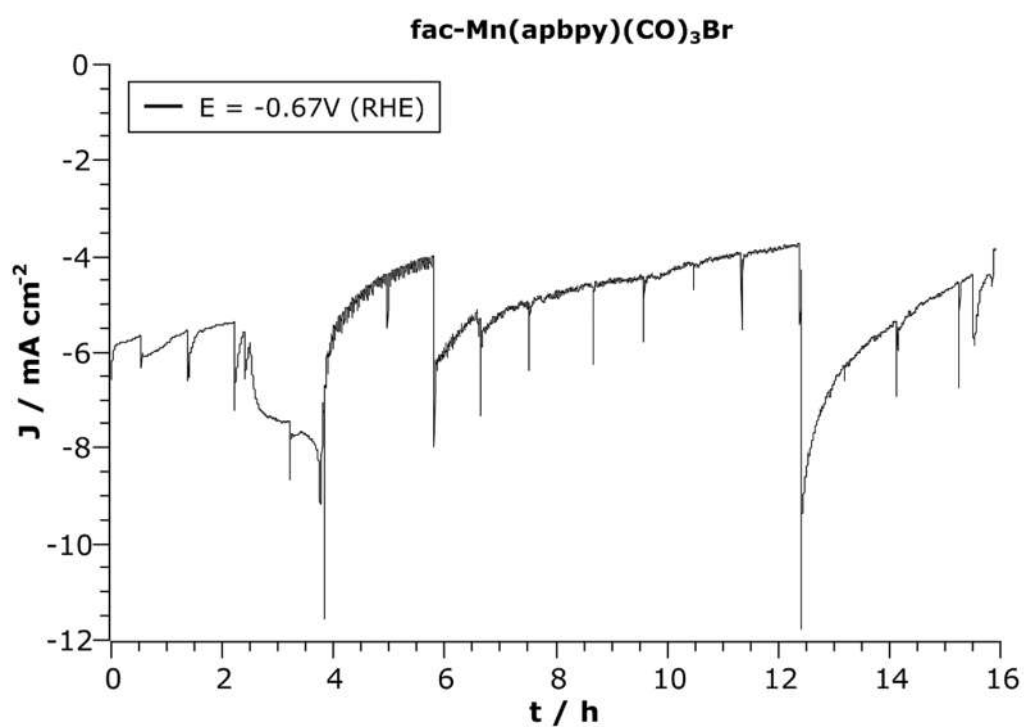


Figure C5. Electrolysis current profile for **1/CC** ($1.4 \cdot 10^{-9}$ mol cm_{ECSA}⁻², $4.51 \cdot 10^{-7}$ g_{Mn} cm_{geom}⁻²) cathode.

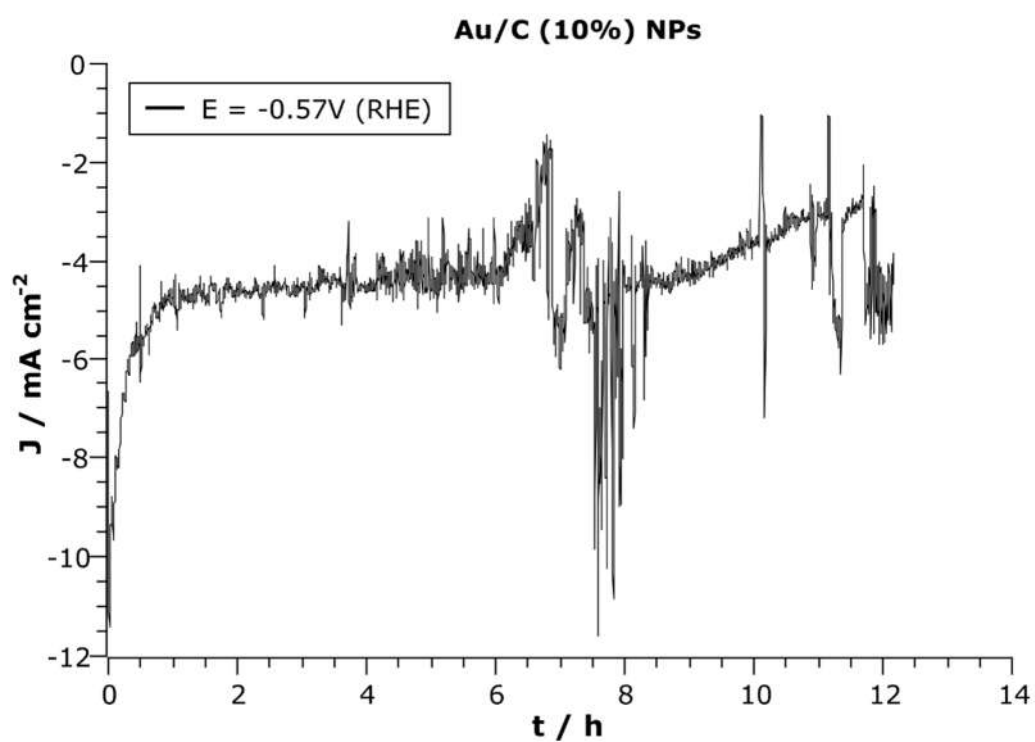


Figure C6. Electrolysis current profile for Au/C (10%) NPs (0.081 mgAu cm_{geom}⁻²) cathode.

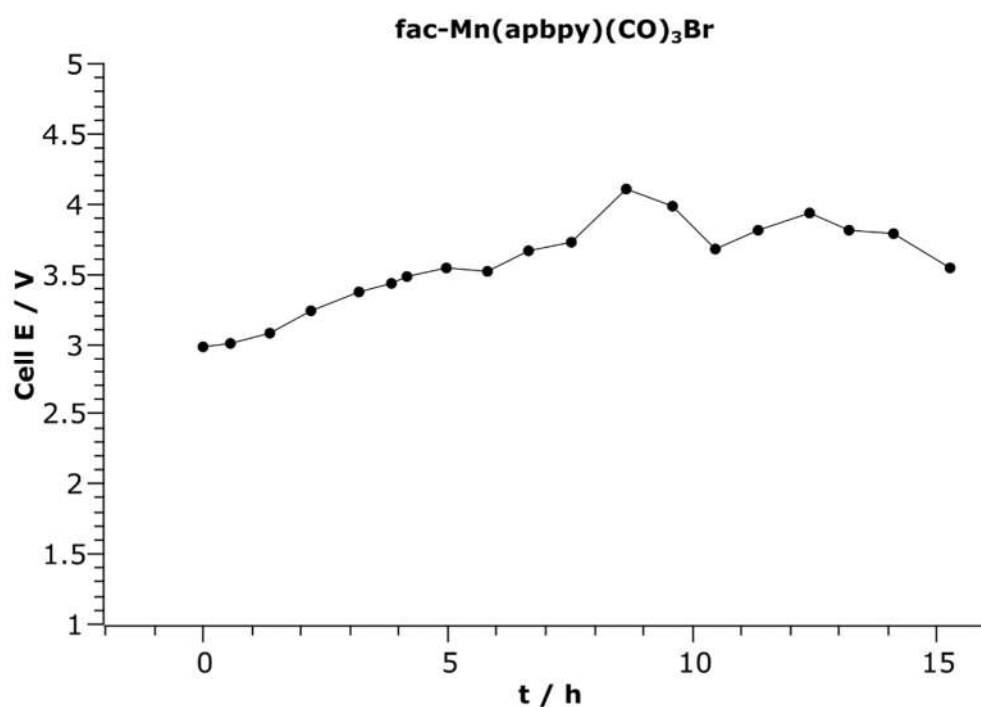


Figure C7. Cell potential profile for **1/CC** ($1.4 \cdot 10^{-9}$ mol $\text{cm}_{\text{ECSA}}^{-2}$, $4.51 \cdot 10^{-7}$ g_{Mn} $\text{cm}_{\text{geom}}^{-2}$) cathode, IrO₂/CC anode (1.8 mg $\text{cm}_{\text{geom}}^{-2}$).

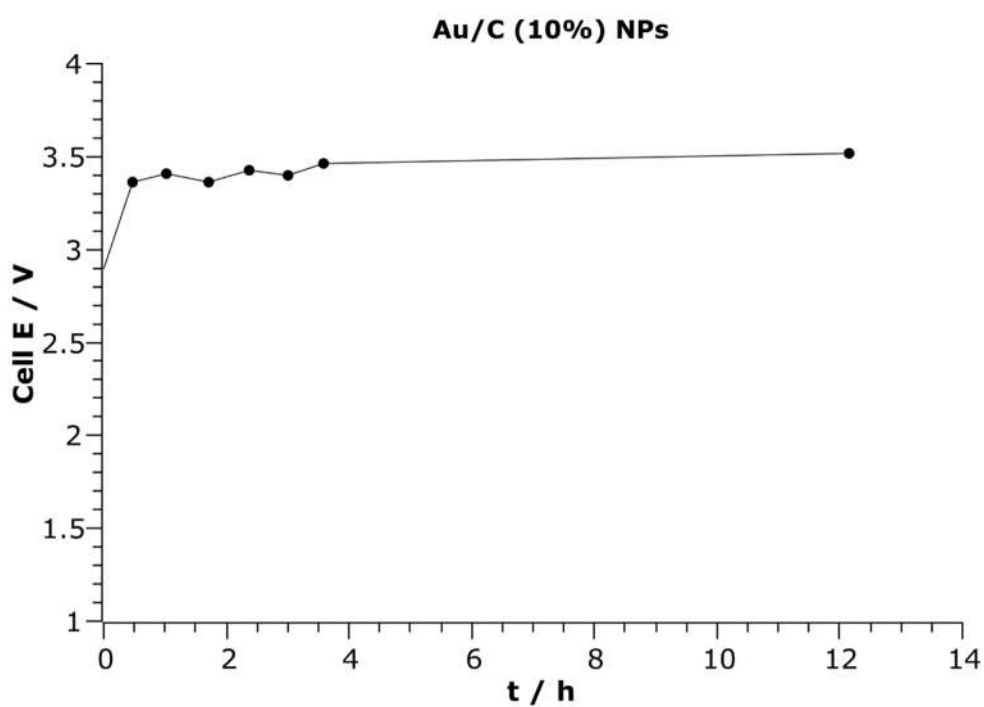


Figure C8. Cell potential profile for Au/C (10%) NPs (0.081 mgAu $\text{cm}_{\text{geom}}^{-2}$) cathode, IrO₂/CC anode (1.8 mg $\text{cm}_{\text{geom}}^{-2}$).

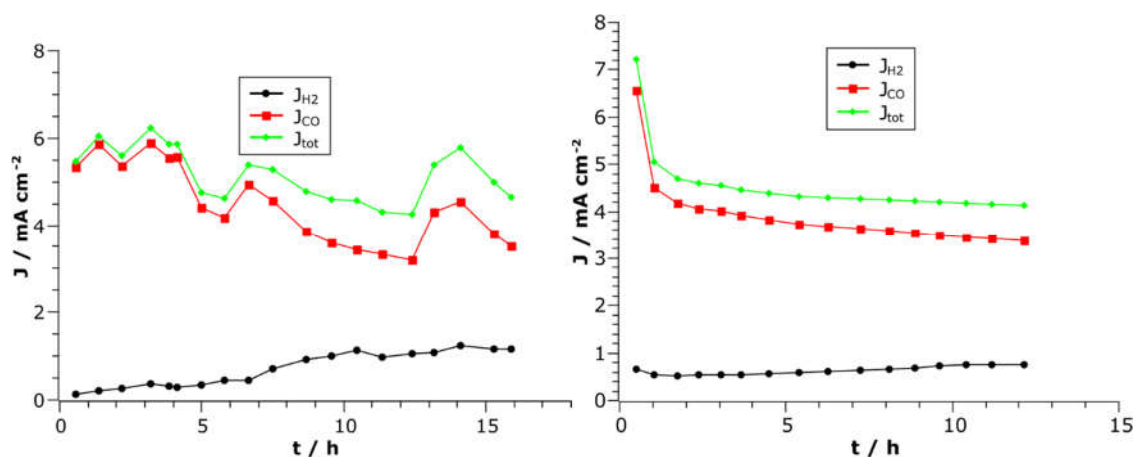


Figure C9. Partial and total current density time profiles for gaseous products of (left) **1/CC** ($1.4 \cdot 10^{-9} \text{ mol cm}_{\text{ECSA}}^{-2}$, $4.51 \cdot 10^{-7} \text{ g}_{\text{Mn}} \text{ cm}_{\text{geom}}^{-2}$) and (right) Au/C NPs ($0.081 \text{ mgAu cm}_{\text{geom}}^{-2}$) operating in buffer layer configuration, CO_2 flow rate 0.2 mL min^{-1} , buffer flow rate 0.4 mL min^{-1} .

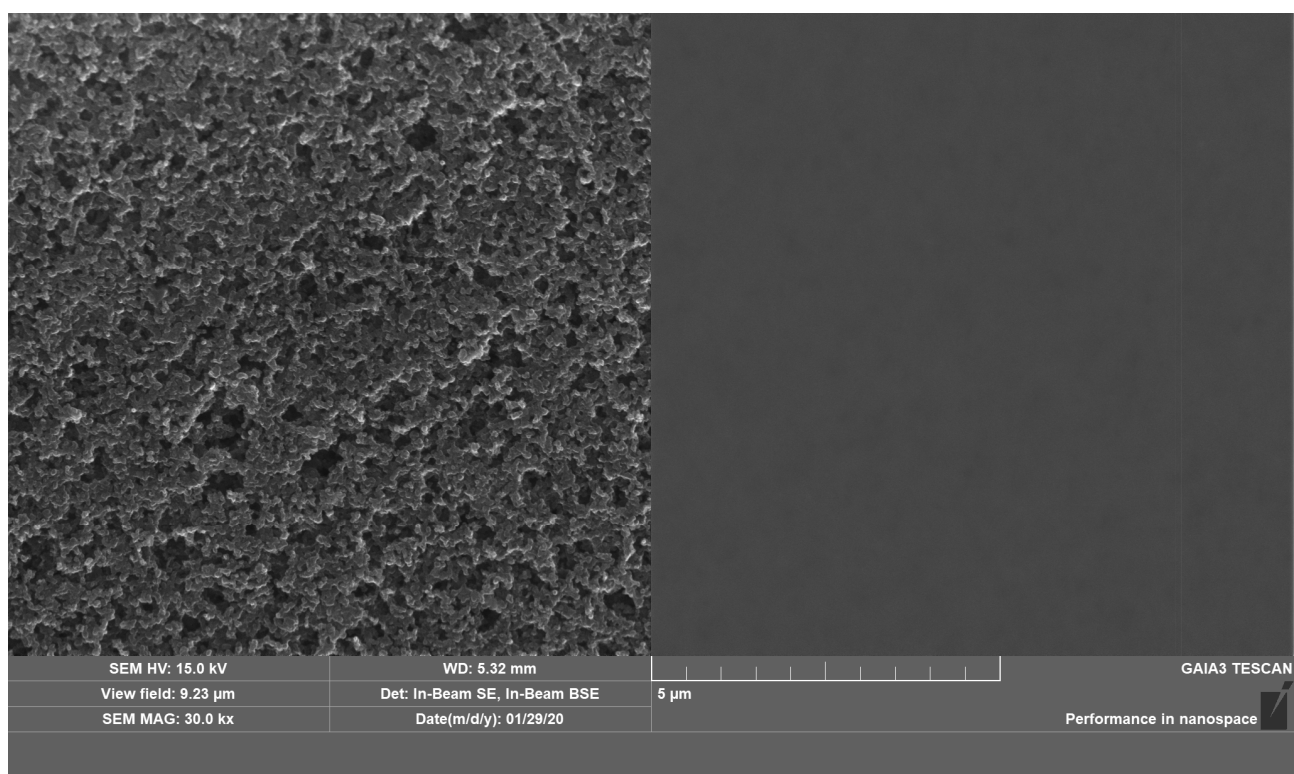
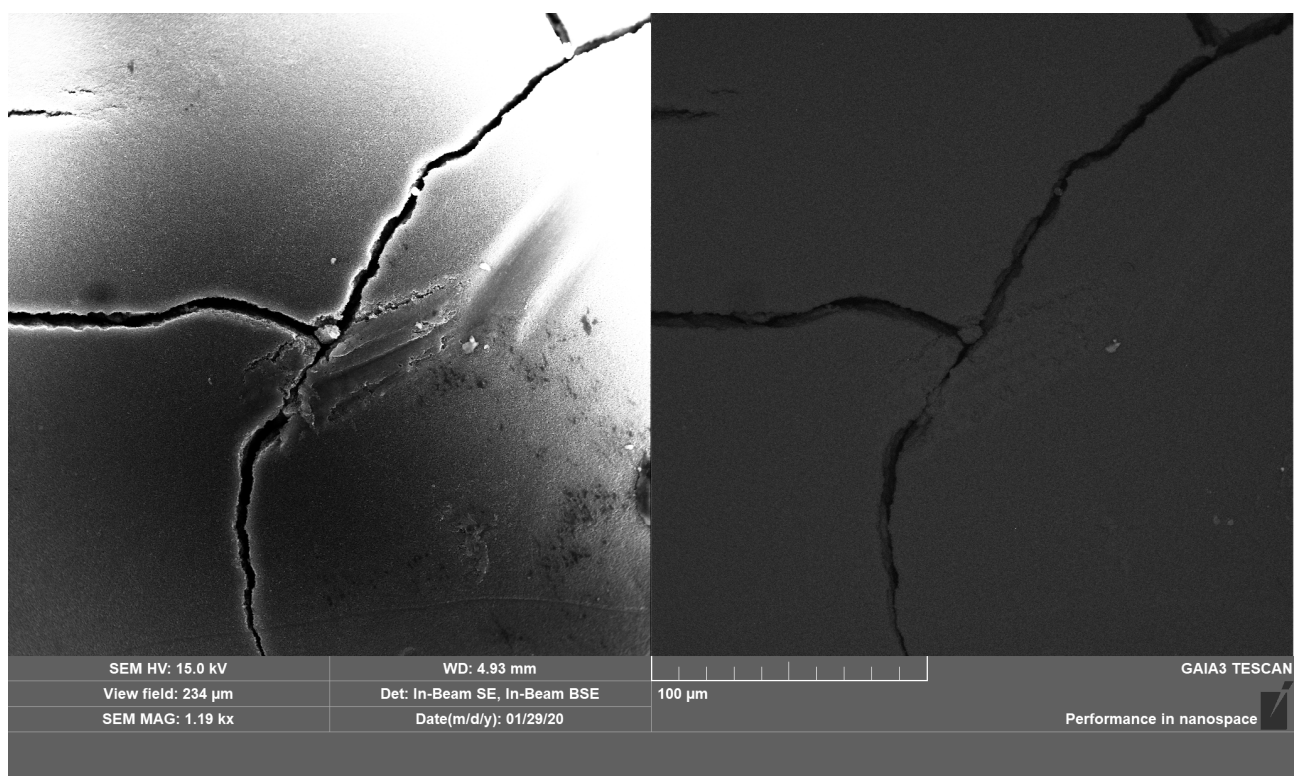


Figure C10. Spot 3 (pristine) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface SEM micrograph.

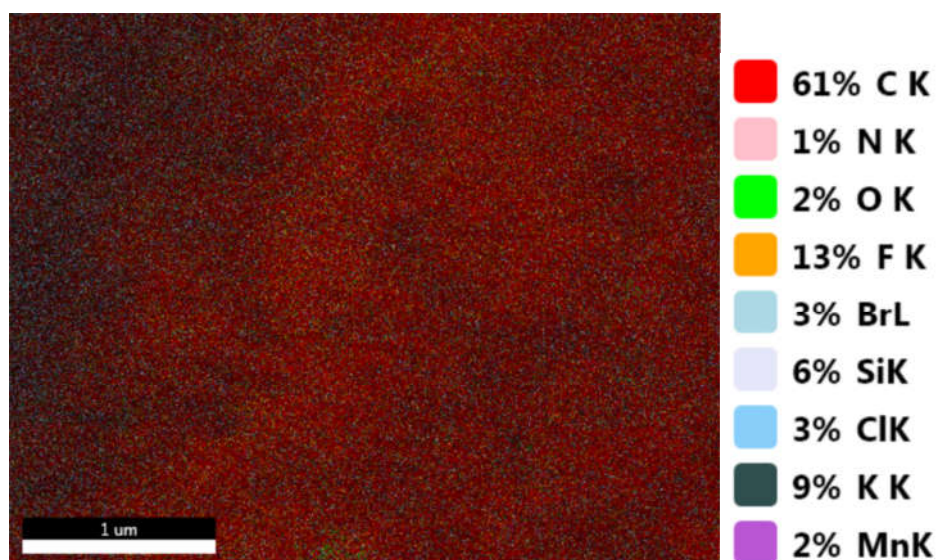


Figure C11: Spot 3 (pristine) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface EDAX element mapping.

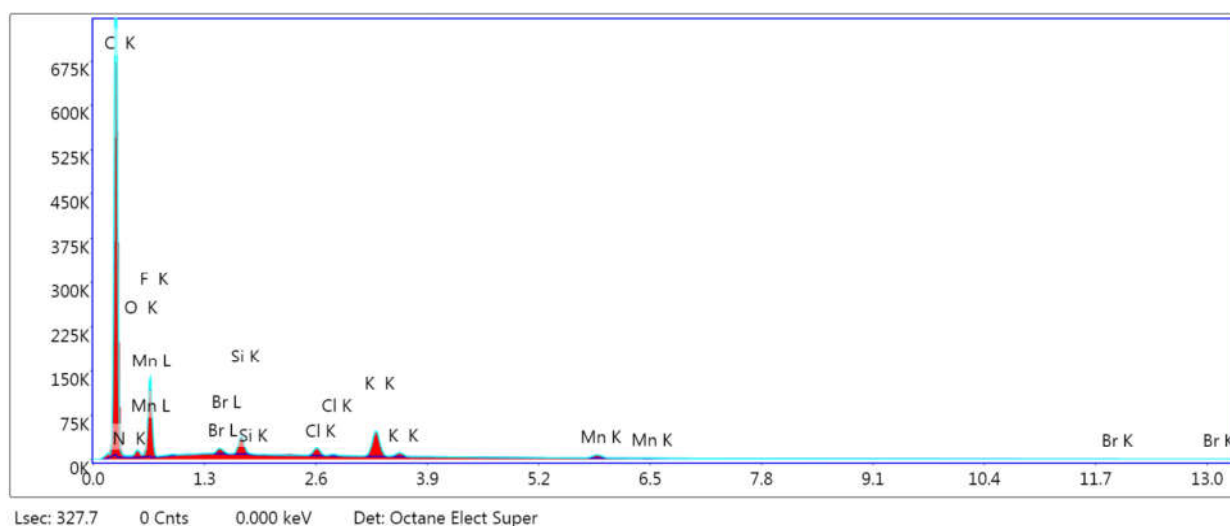


Figure C12. Spot 3 (pristine) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface sum spectrum.

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	77.80	86.51	11870.60	5.31	0.4531	1.0280	0.5665	1.0000
N K	0.00	0.00	0.00	99.99	0.0000	1.0036	0.0664	1.0000
O K	1.48	1.24	112.30	22.08	0.0017	0.9824	0.1189	1.0000
F K	14.34	10.08	2334.50	9.05	0.0275	0.9127	0.2100	1.0000
BrL	0.51	0.09	172.80	2.45	0.0037	0.6978	1.0477	1.0003
SiK	1.13	0.54	784.40	2.86	0.0087	0.8912	0.8590	1.0063
ClK	0.69	0.26	378.80	1.73	0.0059	0.8298	1.0015	1.0227
K K	3.14	1.07	1446.60	1.72	0.0272	0.8255	1.0253	1.0231
MnK	0.90	0.22	222.40	3.34	0.0076	0.7374	1.0236	1.1099

Table S1. Spot 3 (pristine) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface element analysis.

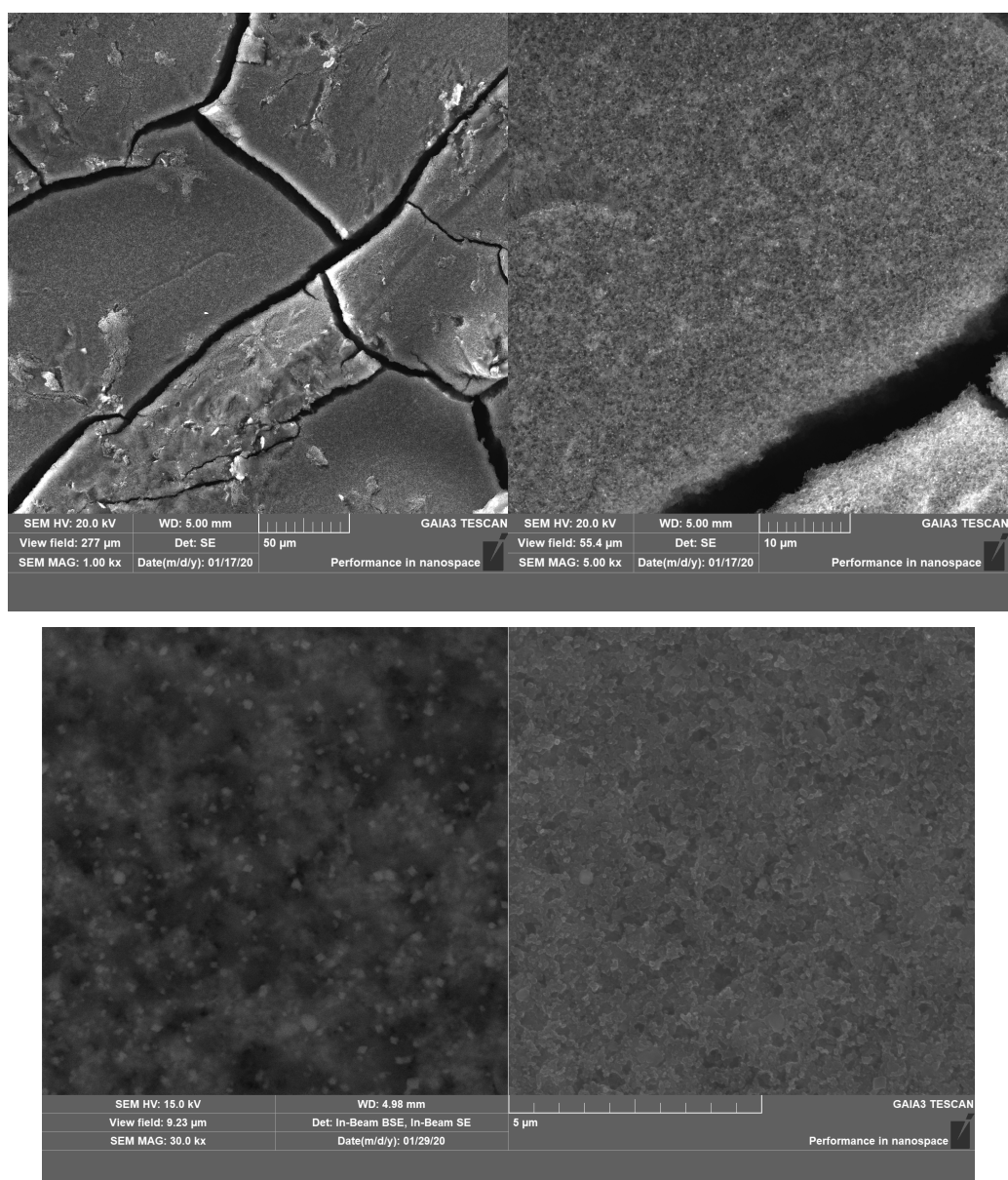


Figure C13. Spot 2 (spent) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface SEM micrograph.

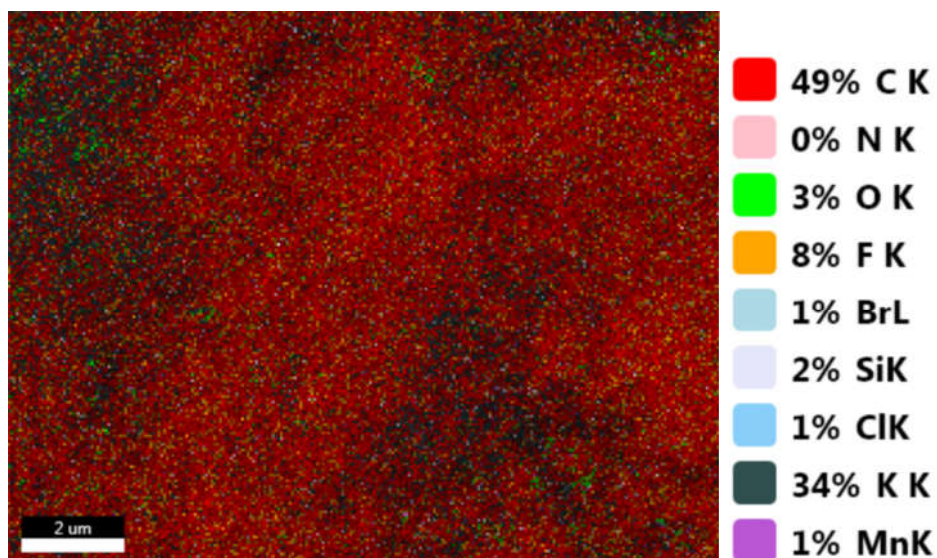


Figure C14. Spot 2 (spent) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface EDAX element mapping.

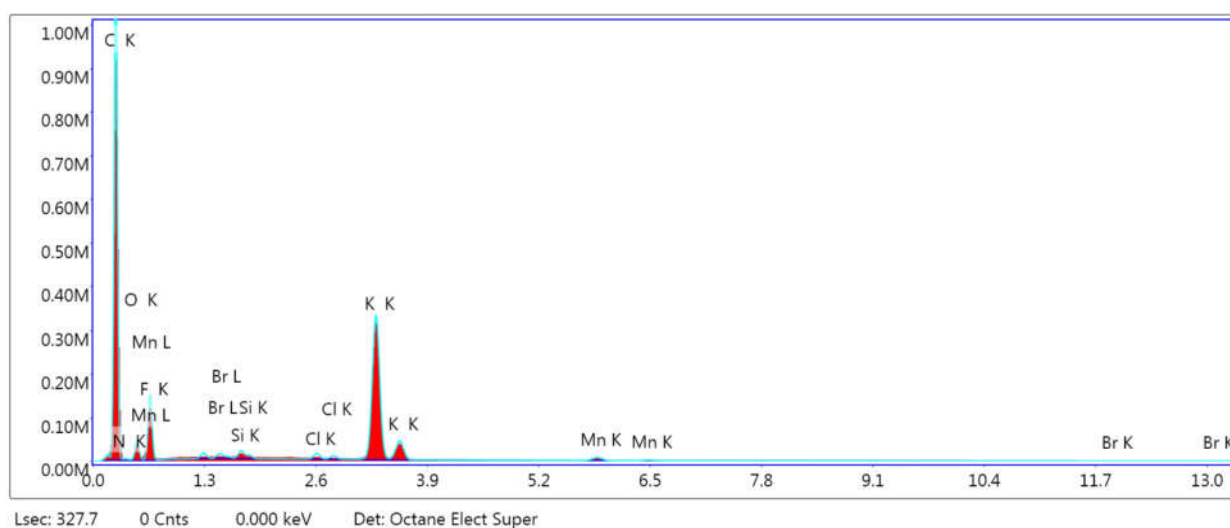


Figure C15. Spot 2 (spent) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface sum spectrum.

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	64.06	78.27	15695.20	5.10	0.3935	1.0481	0.5861	1.0000
N K	0.00	0.00	0.00	99.99	0.0000	1.0238	0.0646	1.0000
O K	6.47	5.94	726.30	11.33	0.0074	1.0027	0.1136	1.0000
F K	12.14	9.38	2626.80	9.33	0.0203	0.9318	0.1796	1.0000
BrL	0.41	0.08	208.40	1.32	0.0030	0.7131	1.0010	1.0008
SiK	0.42	0.22	437.20	3.03	0.0032	0.9110	0.8320	1.0080
ClK	0.44	0.18	379.30	1.58	0.0038	0.8486	0.9942	1.0321
K K	15.29	5.74	10775.50	1.42	0.1332	0.8444	1.0223	1.0091
MnK	0.77	0.21	276.40	2.60	0.0062	0.7547	1.0068	1.0564

Table S2. Spot 2 (spent) *fac*-Mn(apbpy)(CO)₃Br-modified carbon cloth electrode surface element analysis.

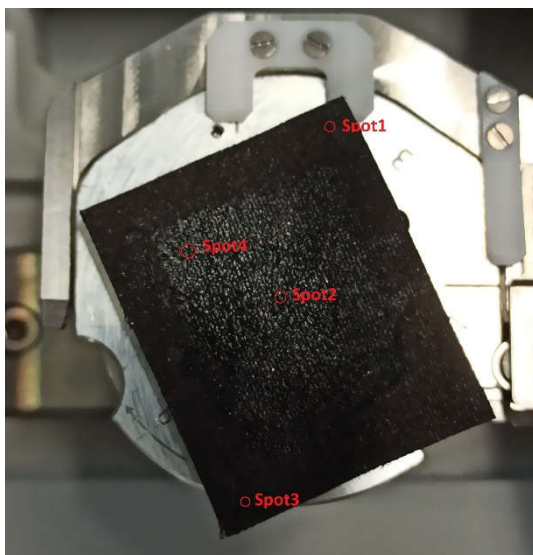


Figure C16. Areas of the electrode scrutinized with the GAIA 3 FIB/SEM microscope. The two outer areas (the odd spots) are masked with the gasket cell sealing; the inner areas (even) have undergone the electro-catalysis CO₂RR experiment.

Appendix D "Chapter 6"

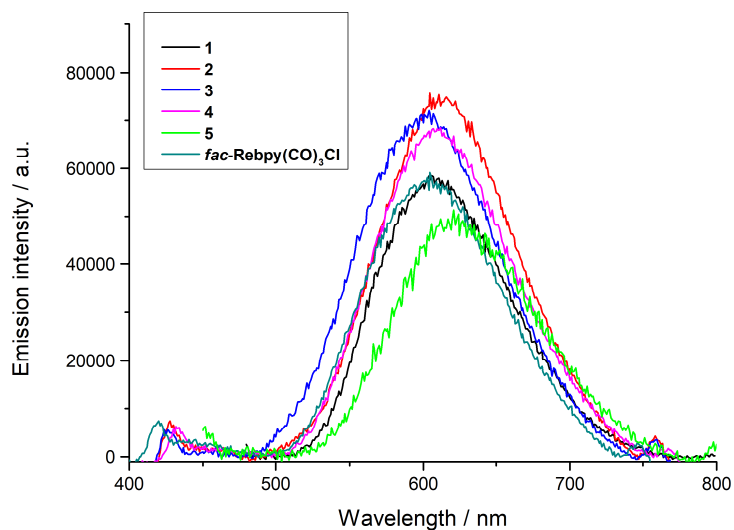


Figure D1. Emission spectra of the investigated complexes.

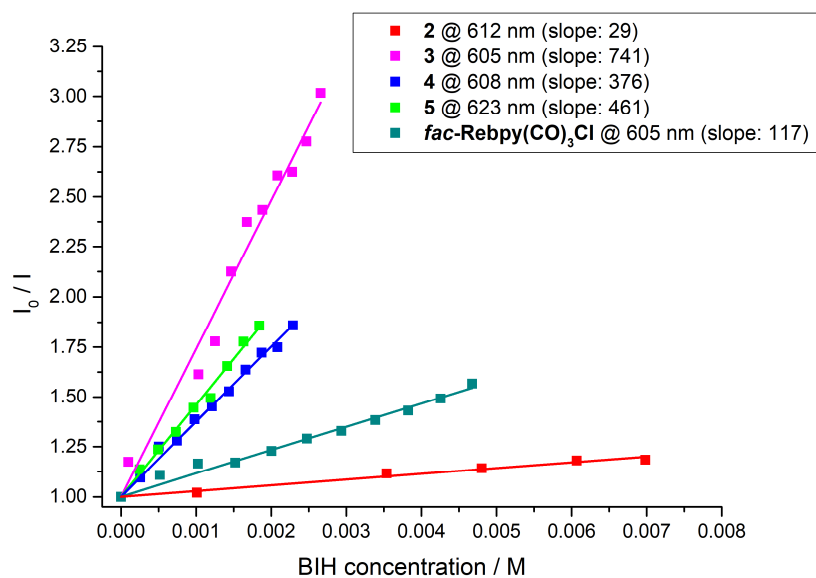


Figure D2. Quenching experiments of complexes **2-5** and *fac*-Rebpy(CO)₃Cl for comparison in DMA solutions. The employed quencher is BIH.

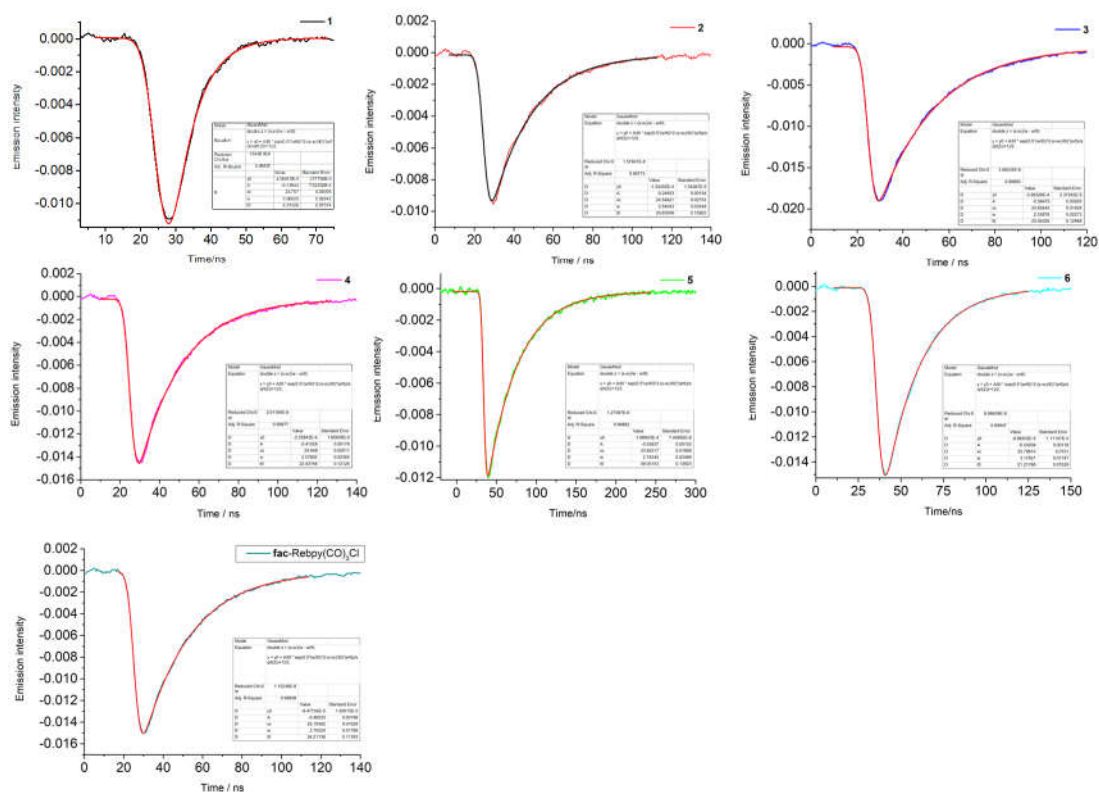


Figure D3. Emission lifetime measurements for complexes **1-6** and *fac*-Rebpy(CO)₃Cl for comparison in DMA solutions. The fit function is the convolution of a single exponential and Gaussian functions as defined in Origin software. The t_0 value is the lifetime in ns.

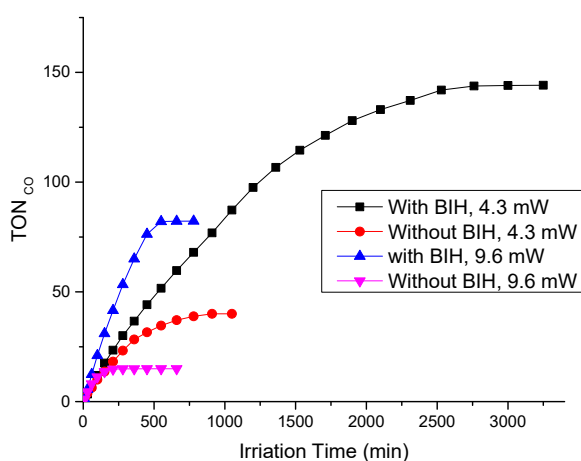


Figure D4. Effect of irradiation power with Rebpy: 4.32 mW with BIH (black) and without BIH (red); 9.6 mW with BIH (blue) and without BIH (pink).

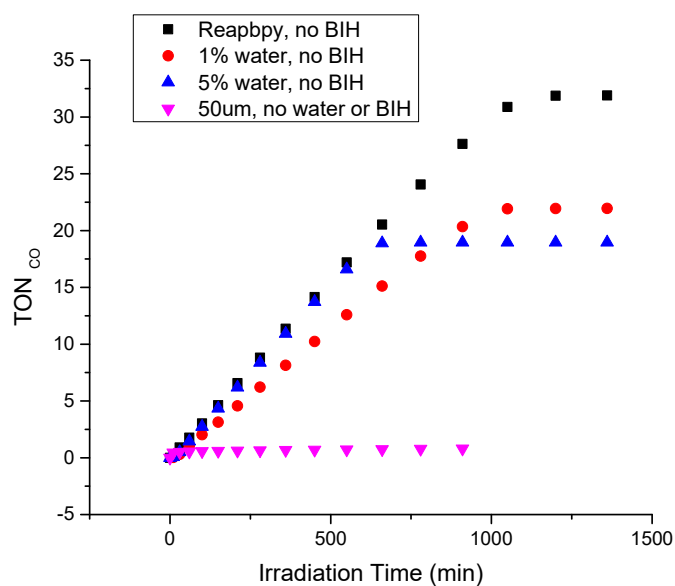


Figure D5. Photocatalytic reaction with $\text{Re}(\text{apbpy})(\text{CO})_3\text{Cl}$ and 1.25 M TEOA in DMA: black, 0.5 mM Re in dry DMA; red, 0.5 mM Re in DMA containing 1% water; blue, 0.5 mM Re in DMA containing 5% of water same as in DMA containing 5% water; and pink, 0.05 mM Re in dry DMA.

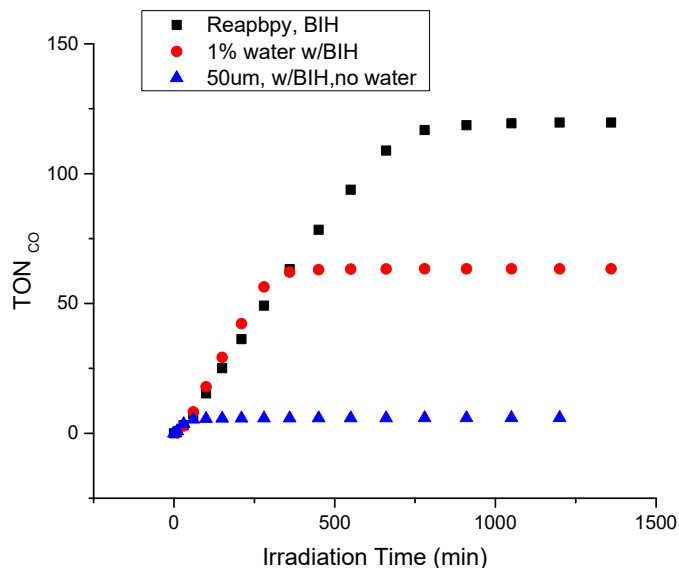


Figure D6. Photocatalytic reaction with complex **1**, $\text{Re}(\text{apbpy})(\text{CO})_3\text{Cl}$, 1.25 M TEOA and 0.1 M BIH in DMA: black, 0.5 mM Re in dry DMA; red, 0.5 mM Re in DMA containing 1% water; blue, 0.05 mM Re in dry DMA.

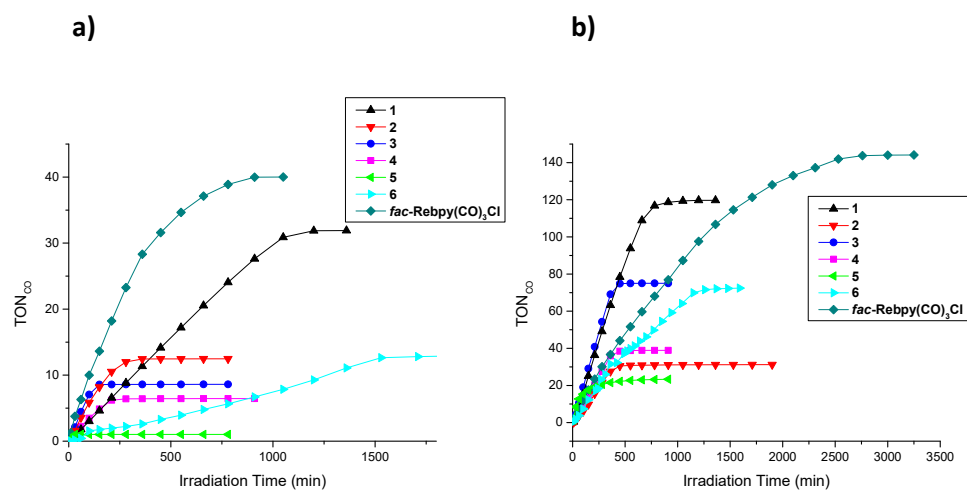


Figure D7. Photocatalytic reactions without (a) and with BIH (b), respectively.

Appendix E “Scientific publications”

Published papers:

- Rotundo, L.; Polyansky, D. E.; Gobetto, R.; Grills, D. C.; Fujita, E.; Nervi, C.; Manbeck, G. F. Molecular Catalysts with Intramolecular Re–O Bond for Electrochemical Reduction of Carbon Dioxide. *Inorg. Chem.* **2020**, *59* (17), 12187–12199.
- Rotundo, L.; Filippi, J.; Gobetto, R.; Miller, H. A.; Rocca, R.; Nervi, C.; Vizza, F. Electrochemical CO₂ Reduction in Water at Carbon Cloth Electrodes Functionalized with a *fac*-Mn(apbpy)(CO)₃Br Complex. *Chem. Commun.* **2019**, *55* (6), 775–777.
- Rotundo, L.; Garino, C.; Priola, E.; Sassone, D.; Rao, H.; Ma, B.; Robert, M.; Fiedler, J.; Gobetto, R.; Nervi, C. Electrochemical and Photochemical Reduction of CO₂ Catalyzed by Re(I) Complexes Carrying Local Proton Sources. *Organometallics* **2019**.
- Rotundo, L.; Azzi, E.; Deagostino, A.; Garino, C.; Nencini, L.; Priola, E.; Quagliotto, P.; Rocca, R.; Gobetto, R.; Nervi, C. Electronic Effects of Substituents on *fac*-M(bpy-R)(CO)₃ (M = Mn, Re) Complexes for Homogeneous CO₂ Electroreduction. *Front. Chem.* **2019**, *7*, 417.
- Rotundo, L.; Garino, C.; Gobetto, R.; Nervi, C. Computational Study of the Electrochemical Reduction of W(CO)₄(2,2'-Dipyridylamine). *Inorg. Chim. Acta.* **2018**, *470*, 373–378.
- Sun, C.; Rotundo, L.; Garino, C.; Nencini, L.; Yoon, S. S.; Gobetto, R.; Nervi, C. Electrochemical CO₂ Reduction at Glassy Carbon Electrodes Functionalized by Mn^I and Re^I Organometallic Complexes. *ChemPhysChem* **2017**, *18* (22), 3219–3229.

Submitted Papers:

- Filippi, J.; Rotundo, L.; Gobetto, R.; Miller, H.A.; Nervi, C.; Lavacchi, A.; Vizza, F. Turning Manganese into Gold: efficient electrochemical CO₂ reduction to CO and HCOOH by a *fac*-Mn(apbpy)(CO)₃Br complex in a gas-liquid interface flow cell.

In preparation papers:

- Rotundo, L.; Polyansky, D. E.; Gobetto, R.; Priola, E.; Grills, D. C.; Fujita, E.; Nervi, C. Photochemical CO₂ reduction using Re(I) tricarbonyl complexes with bipyridyl-type ligands with and without 2nd coordination sphere effects.