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Authors: Elsa Quartapelle Procopio, Alessandro Boni, Lorenzo Veronese, Massimo Marcaccio, Pierluigi Mercandelli, Giovanni Valenti, Monica Panigati, and Francesco Paolucci

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Dinuclear Re(I) complexes as new electrocatalytic systems for CO₂ reduction.

Elsa Quartapelle Procopio,^[a] Alessandro Boni,^[b] Lorenzo Veronese,^[a] Massimo Marcaccio,^[b] Pierluigi Mercandelli,^[a] Giovanni Valenti,^[b] Monica Panigati,^{[a][c]*} Francesco Paolucci^{[b]*}

Dedication to *Jean-Michel Savéant* for his pioneering work on molecular electrochemistry and on CO₂ reduction.

[a] Dr. Quartapelle Procopio, Dr. Veronese, Dr. Mercandelli, Dr. Panigati
Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.
E-mail: monica.panigati@unimi.it

[b] Dr. Boni; Prof. Marcaccio; Prof. Valenti; Prof. Paolucci
Dipartimento di Chimica "Giacomo Ciamician", Alma Mater Studiorum Università di Bologna, via F. Selmi 2, 40126 Bologna, Italy.
E-mail: francesco.paolucci@unibo.it

[c] Dr. Panigati
Consorzio INSTM, via G. Giusti 9, 50121, Firenze, Italy.

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Abstract: A family of dinuclear tricarbonyl rhenium (I) complexes, containing bridging 1,2-diazine ligand and halide anions as ancillary ligands, able to catalyze CO₂ reduction is presented. Electrochemical studies show that the highest catalytic efficiency is obtained for the complex containing the 4,5-bipentyl-pyridazine and iodide as ancillary halogen ligands. This complex gives rise to TOF = 15 s⁻¹ that clearly outperform the values reported for the benchmark mononuclear Re(CO)₃Cl(bpy) (11.1 s⁻¹). The role of the substituents on the pyridazine ligand, together with the nature of the bridging halide ligands on the catalytic activity has been deeply investigated, through a systematic study on the structure-properties relationship, in order to understand the improved catalytic efficiencies of this class of complexes.

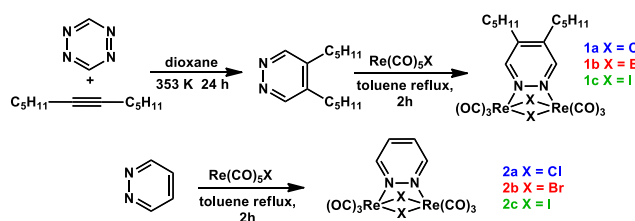
The dramatic increase in the amount of CO₂ in the atmosphere is regarded as the main responsible of the greenhouse effect and the related global warming.^{[1][2]} The complete replacement of fossil fuels by alternative energy sources is not rapidly viable and therefore there is an urgent need of developing new technologies for the catalytic conversion of CO₂ to higher energy products by the use of renewable energy sources.^[3] In this context, the photo- or electro-reduction of CO₂ is a very attracting prospect.^[4–8] Many organometallic catalysts have been explored for this purpose especially thanks to the contribution of *Jean-Michel Savéant* and co workers in the field of molecular electrocatalysis^[9–16] Among them, the rhenium complexes of general formula [*fac*-Re(bpy-R)(CO)₃Cl] (bpy-R = 4,4'-disubstituted-2,2'-bipyridine), introduced in the middle 80s by J. M. Lehn,^[17] are among the most robust and selective catalysts for the electrochemical reduction of CO₂ to CO, both in homogeneous^[18–23] as well as heterogeneous^[24–26] conditions.

From the mechanistic point of view, many studies have provided evidence for the formation of dinuclear intermediates as active species during the catalysis^[27–34] and in order to prove this hypothesis different bimetallic catalysts have been synthesized and tested.^[35–37]

However only few examples have been related to catalysts with a rigid bridging ligand that links two rhenium active sites in close proximity with a predictable intermetallic distance and orientation,

in order to clearly highlight the contribution of the dinuclear pathway.^[38]

Recently it was reported by some of us the new dinuclear rhenium complex [Re₂(μ-Cl)₂(CO)₆(μ-4,5-dipentylpyridazine)] (**1a** in Scheme 1). This is the first example in which the beneficial interaction of two "Re(CO)₃" active sites, connected by three bridging ligands and forming a dinuclear scaffold, has been experimentally evaluated suggesting that the use of binuclear complexes could be very promising in this field.^[39] This complex belongs to the recently reported family of dinuclear Re(I) complexes containing a bridging 1,2-diazine ligand and two anionic ancillary ligands, such as halides,^{[40][41]} hydrides,^[42] alcohoxides or chalcogenide,^{[43][44]} bridging between two Re(CO)₃ moieties. Members of this family have found applications as dopants of the emitting layer in OLED devices,^{[45][36][45][46]]} as probes for cell imaging in biological applications,^{[47][48]} and as sensitizers for Dye Sensitized Solar Cells (DSSCs).^[49] We present here the catalytic performances in the CO₂ electroreduction of new complexes of this family (see scheme 1), with higher catalytic activity than the previously reported one.^[39] Starting from the precursor complex **1a**, here we change both the halide and the diazine ligands providing a correlation between structure-activity for this new class of catalysts.



Scheme 1. Synthesis and structure of the 4,5-bipentylpyridazine ligand and of the six Re(I) complexes **1a-c** and **2a-c**.

The six complexes here considered, of general formula [Re₂(μ-X)₂(CO)₆(μ-diazine)], are shown in Scheme 1, with diazine = 4,5-bipentylpyridazine (**1**) or pyridazine (**2**), and X = Cl (**1a** or **2a**), Br (**1b** or **2b**) or I (**1c** or **2c**). All the complexes have been obtained

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in good yields (50-90 % after purification on silica gel) by refluxing 2 equivalents of $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with the proper diazine ligand in toluene solution (see Experimental Section in Supplementary Information), and have been completely characterized from the spectroscopic point of view (FT-IR, NMR, UV-vis spectra see Supporting Information). The three complexes **2** had been previously described as photoluminescent molecules,^[40] while complexes **1b** and **1c** are here reported for the first time. The most significant photophysical properties of all the six complexes are reported in Table 1 and in Figures S1 of the Supporting Information.

At room temperature, each complex displays, beside the intra-ligand $\pi\text{-}\pi^*$ absorptions at ca 250 nm, a broad absorption at lower-energy (maxima in the range 351-390, with tails up to 500 nm, see Figure S2). This band can be assigned to $^1\text{MLCT}$ transitions, or better to metal-ligand to ligand charge transfer ($^1\text{MLLCT}$) transitions, by the analogy with previous attributions in related complexes.^[41] As a consequence, the position of the absorption maxima is modulated both by the nature of the ancillary halide ligands (affecting mainly the HOMO levels) and by the diazine's substituents (which vary the LUMO level). Indeed, the absorption maxima of the **2a-c** complexes are bathochromically shifted by about 20 nm with respect to the analogous transition observed for **1a-c** complexes. Such a feature is due to the presence of the two electron-donating alkyl groups in the β positions of the diazine ligand, which destabilize the LUMO levels of the **2a-c** complexes. On the contrary, keeping constant the diazine ligand, a bathochromic shift of the maximum is observed on going from Cl to Br to I in both the **1** and **2** series, which follows the decrease in electronegativity of the ancillary ligand.

The charge transfer nature of the electronic transition is also confirmed by the modulation effect of the polarity of the solvent: namely a general hypochromic shift has been observed in the absorption spectra of all the complexes, on going from CH_2Cl_2 to the more polar solvent acetonitrile (see Figure S3 of the Supporting Information)

Table 1. Photophysical data for all the complexes at 298 K

Compound	$\lambda_{\text{abs MLCT}}$ [nm] ^a	$\epsilon \times 10^3$ [M ⁻¹ cm ⁻¹] ^a	λ_{em} [nm] ^b	Φ^b	τ [μs] ^b
1a	351	8.75	557	0.51	5.45
1b	366	8.63	572	0.064	0.340
1c	372	8.30	580	0.0017	0.008
2a	370	8.31	603 ^d	0.07 ^d	0.80 ^d
2b	382	6.82	630 ^d	0.0026 ^d	0.02 ^d
2c	390	6.90	- ^c	- ^c	- ^c

[a] Data measured in CH_2Cl_2 solution. [b] Data measured in de-aerated toluene solution. Samples were excited in the range 340-450 nm for the steady state measurements. Emission spectra were corrected for emission spectral response (detector and grating) by standard correction curves. [c] Emission of **2c** is too low to allow reliable measures of lifetime and quantum yields. [d] Data from ref^[40].

The pyridazine rhenium complexes have been studied by means of density functional and time dependent density functional (TD-

DFT) calculations (see SI for the details). The steric and electronic effects associated with the introduction of electron-donating substituents at the β positions of the pyridazine ring had previously been evaluated, together with the effect of changing the nature of the bridging halogen ligands.^[40]

The effect of the halide size can be recognized by comparing the geometry of the three unsubstituted pyridazine complexes **2a-c**. The increase in the covalent radius on going from Cl to Br to I leads to a noticeable change in geometrical parameters involving the $\mu\text{-X}$ ligand, in particular, the Re-X bond distance. As a consequence, the Re-Re distance increases as well, leading to lesser overlap between the metal atoms and the nitrogen lone pairs of the bridging pyridazine ligand (an optimal coordination geometry requires a Re-Re distance of 323 pm.^[40]) Therefore, the larger the halogen, the weaker is the interaction between the pyridazine and the metal dimer.

However, the strength of the diazine binding to the metal core is also affected by the donor capability of the aromatic ligand. In order to quantify the extent of such an interaction, we have calculated the interaction energy (ΔE_{int}),^[50] which corresponds to the difference between the energy of the complex $[\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\mu\text{-diazine})]$ and that of the metal and ligand fragments ($[\text{Re}_2(\mu\text{-X})_2(\text{CO})_6]$ and $\mu\text{-diazine}$, respectively), computed employing the frozen geometry of the complex. Computation of this parameter for complex **1a** and **2a** indicates a stronger metal-ligand interaction on going from pyridazine to 4,5-biphenylpyridazine ligand (-283 kJ mol^{-1} for **2a** and -293 kJ mol^{-1} for **1a**).

The electrochemical properties of the complexes have been investigated by cyclic voltammetry (CV), in ultra-dry Ar-saturated acetonitrile solutions. The CV trace of **1c** is reported in Figure 1, as representative of the whole series of complexes **1** and **2**. The main features are in line with what observed for related dinuclear Re complexes, whose behavior has been investigated in detail.^{[40],[41]} At positive potentials all the complexes displayed a typical bielectronic anodic peak, assigned to the oxidation of the two metal centers, as confirmed by the strong modulation of the half-wave potential by the nature of the bridging halide (see Table 2).

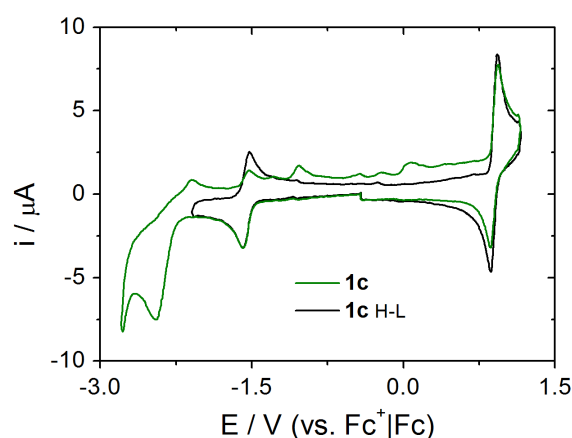


Figure 1. Cyclic voltammetry of **1c** in dry MeCN, $[\text{NBu}_4]\text{PF}_6$ 0.1 M, using a GC electrode of 1 mm in diameter. Scan rate 0.5 V s^{-1} . The black CV stops at the first reduction wave, whereas the green CV shows how the second irreversible reduction process leads to the appearance in the CV of several other features. Potentials are reported vs. the standard $\text{Fc}^+|\text{Fc}$ redox couple.

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At negative potentials, a first monoelectronic reversible reduction wave was observed, whose position was only slightly affected by the nature of the halide ligand, whereas it was significantly shifted to more negative values in the presence of the electron-donating alkyl substituents on the diazine (see Table 2). Therefore, such a reduction process was attributed to the diazine ligand, where in fact the LUMOs of this family of binuclear complexes are mainly localized.

In Figure 1, the first reduction was followed by a second irreversible wave, located at potentials that were more sensitive to the nature of the bridging halide than to the diazine substituents (see Table 2), although no clear trend along the series of compounds could be outlined.

Table 2. Electrochemical data for the complexes here discussed. Potential are referred to the Fc^+/Fc couple in the operating medium (MeCN, 0.1 M $[NBu_4]PF_6$). Working electrode GC. Scan rate 0.2 Vs^{-1}

Compound	$E_{1/2,a}$ [V]	1 st $E_{1/2,c}$ [V]	2 nd $E_{1/2,c}$ [V]
1a	1.31	-1.52	-2.38
1b	1.15	-1.53	-2.36
1c	0.93	-1.55	-2.21
2a	1.31 a	-1.34 a	-2.36
2b	1.16 a	-1.36 a	-2.31
2c	0.94 a	-1.38 a	-2.40

[a] Data from ref ^[40].

Such an irreversible reduction process does correspond, at relatively low scan rates (Figure 1), to the exchange of 2 electrons while, at faster scan rate ($\geq 10 V s^{-1}$, Figure S4), it becomes comparable to the first mono-electronic reduction peak. This suggest the occurrence of an ECE mechanism,^[40] in which two mono-electronic reductions are interconnected by a chemical step. The presence of the complex features observed in the backward CV scan (green curve in Figure 1) would in fact be in line with the occurrence of multiple follow-up chemical equilibria coupled to the reduction process, each of them producing different electroactive species.

Importantly, such an irreversible reduction process was found to be strongly affected in the presence of CO_2 as shown in Figure 2 (and in Figure S5 of the Supporting Information), where the voltammetry experiments were performed in a CO_2 -saturated solution: the sizeable enhancement of the cathodic current relative to such a second reduction process would indicate that at this potential catalytic CO_2 electroreduction takes place, likely involving the 2-electron reduced complex. For the sake of comparison, a blank experiment without the rhenium complex in solution reveals that CO_2 reduction is observed on a GC electrode only starting at $-2.6 V$, with a shift of ~ 400 - $500 mV$ towards more negative potential (see Figure S5).

The relative catalytic efficiencies toward the CO_2 reduction of the various complexes were estimated by comparing the corresponding current enhancement that was found to depend strongly on the nature of the halide ligand and to increase in the order chloride < bromide < iodide, in both the series 1 and 2. Moreover, for any halide, larger catalytic currents were observed for complexes 1, which bear alkyl substituents in the β positions of the diazine, with respect to the corresponding complexes 2.

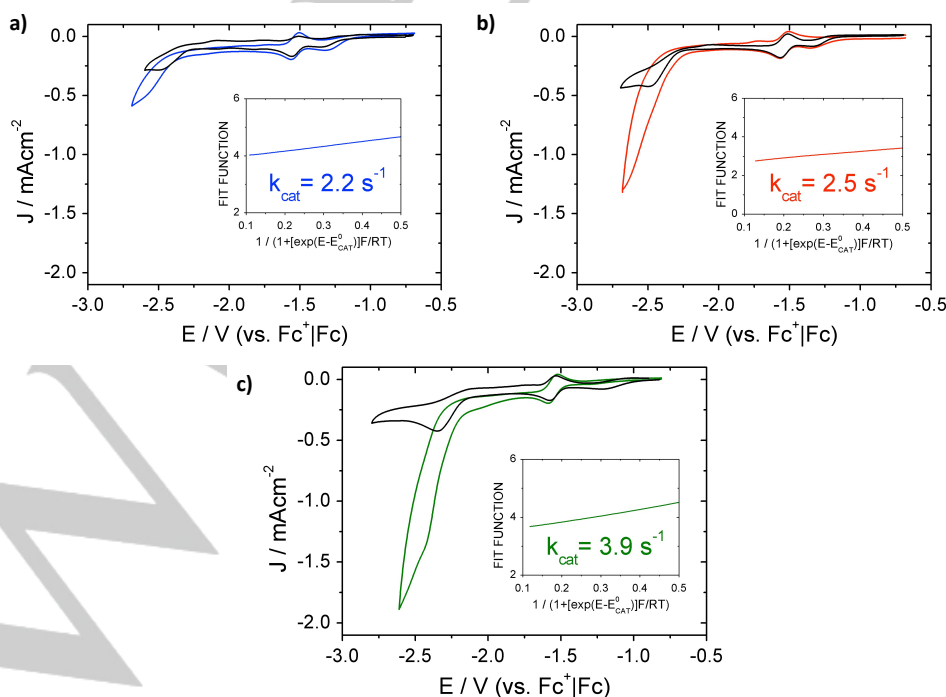


Figure 2. CVs of complexes 1a (a), 1b (b) and 1c (c) in CO_2 saturated CH_3CN , 0.1 M $[NBu_4]PF_6$. Black traces refer to the respective CVs recorded in Ar-saturated CH_3CN solutions, on GC electrode at 0.2 Vs^{-1} . The CVs of a bare GC electrode in a CO_2 saturated solution are also displayed.

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For those species displaying the best performances (complexes **1a-c**), the quantification of the electrocatalytic activity was obtained by evaluating the kinetic constants relative to the catalytic process of CO₂ reduction and the corresponding turnover frequencies, according to a method recently introduced by Savéant and coworkers.^[9] Analysis of the *foot-of-the-wave* displayed in Figure 2 revealed increasing rate constants for the catalytic process in the series **1a** < **1b** < **1c** (k_{cat} 2.2 < 2.5 < 3.9 s⁻¹, respectively). Alternatively, we analyze the $(i_{\text{cat}}/i_p)^2$ as useful benchmark of the electrocatalytic activity that is proportional to the turnover frequency (TOF).^{[51][52]} The catalytic TOF of 3, 8 and 15 s⁻¹ were identified for **1a**, **1b** and **1c** respectively. The maximum TOFs for the dinuclear Re catalyst is higher than that of the mononuclear Re(bpy)(CO)₃Cl benchmark (TOF 11 s⁻¹),^[38] thus confirming the involvement of a bimetallic core in CO₂ activation. In conclusion, we have described five dinuclear rhenium complexes whose catalytic activity was compared with the previously reported complex **1a**. All the complexes are active electrocatalysts and the nice increasing trends, quantified by using Savéant methods, confirm the strong correlation between molecular structure and catalytic activity in CO₂ reduction. The maximum TOFs was observed for complex **1c**, showing the effect of both the ancillary ligand and the substituents on the diazine on catalytic activity. In particular, the lower electronegativity of the iodide, together with the higher donor power of the diazine, increases the electronic density on the Re centers, thus increasing the catalytic activity. Although efficiencies are lower than those reported by Jurs and co-worker for similar dinuclear Re complexes, our work highlights a crucial role of catalyst structure, in terms of distance of the metal centers and capability to allow the CO₂ insertion step. Actually, the presence of the bridging halide ligands, more labile on going from Cl to I, and the short N-N distance of the pyridazine bridging ligand, could partially hamper the coordination of CO₂ thus reducing the efficiency. Further design and development of new dinuclear Re(I) tricarbonyl complexes for the homogeneous and heterogeneous CO₂ conversion are still under investigation in our laboratories.

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Keywords: molecular electrochemistry • CO₂ reduction • Re(I) tricarbonyl complexes

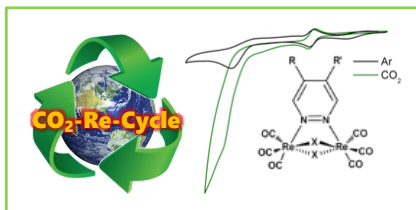
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Molecular electrochemistry: We reported here a new family of dinuclear tricarbonyl rhenium (I) complexes, containing bridging 1,2-diazine ligand and halide anions (I, Cl and Br) as ancillary ligands, able to catalyze CO₂ reduction. We elucidate the role of the substituents on the pyridazine ligand, together with the nature of the bridging halide ligands on the catalytic activity, through a systematic study on the structure-properties relationship.

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