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# Importance of Ligand Exchange in the Modulation of Molecular Catalysis. Mechanism of the Electrochemical Reduction of Nitrous Oxide with Rhenium Bipyridyl Carbonyl Complexes.

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Supporting Information

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**ABSTRACT:** Molecular catalysis of electrochemical reactions involving transition metal complexes as catalysts requires getting a free metal coordination site to bind the substrate. It implies that the generation of a strong coordinating ligand as product or co-product of the reaction might be detrimental for an efficient catalysis because it can bind the metal center and block or slow down the catalytic process. This self-modulation phenomenon is revealed and illustrated via a thorough spectro-electrochemical investigation of the mechanism of the electrochemical reduction of nitrous oxide with rhenium bipyridyl tricarbonyl complexes  $[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]^{n+}$  ( $\text{X} = \text{CH}_3\text{CN}, \text{Cl}^-$ ,  $n = 0$  or  $1$ ) as catalyst. We show that the bi-reduced  $[\text{Re}^0(\text{bpy}^*)(\text{CO})_3]^-$ , electrogenerated from  $[\text{Re}^0(\text{bpy})(\text{CO})_3\text{X}]^{n+}$ , readily reacts with  $\text{N}_2\text{O}$  and produces the hydroxo complex  $[\text{Re}^I(\text{bpy})(\text{CO})_3(\text{OH})]$ . Because hydroxide, a product of the reaction, is a stronger coordinating ligand than acetonitrile or chloride, catalysis does not occur significantly at a potential where  $[\text{Re}^0(\text{bpy}^*)(\text{CO})_3]^-$  is generated from  $[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]^{n+}$ . Substantial catalysis is only triggered at a potential corresponding to the second reduction of  $[\text{Re}^I(\text{bpy})(\text{CO})_3(\text{OH})]$ . Nonetheless, we show that a slower innersphere reduction of  $\text{N}_2\text{O}$  by the monoreduced  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3\text{X}]^{(n-1)+}$  ( $\text{X} = \text{CH}_3\text{CN}, \text{Cl}^-$ ) occurs due to the lability of acetonitrile and chloride in these species. Because hydroxide is less labile and cannot be displaced to create an open coordination position for  $\text{N}_2\text{O}$ , only an even slower outersphere reduction of  $\text{N}_2\text{O}$  by the monoreduced  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  takes place. However, we finally show that an excess of free chloride is able to displace hydroxide and then open the way for a faster innersphere process. This remarkable example emphasizes the critical role of ligand exchange in modulating molecular catalysis of electrochemical reactions with transition metal complexes as catalysts, a likely general phenomenon.

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Keywords: Molecular Catalysis, Nitrous Oxide, Electrochemistry, Mechanism, Self-modulation

## Introduction

Molecular catalysis of electrochemical reactions often involves transition metal complexes as catalysts due to their ability to bind and activate the substrate to be transformed. The current intense activity in the field of small molecules activation, in particular reduction of protons,<sup>1</sup>  $\text{O}_2$ ,<sup>2</sup>  $\text{CO}_2$ ,<sup>3</sup> or more recently  $\text{N}_2$ ,<sup>4</sup> offers a myriad of examples. A common feature of such processes is the necessity to get a free metal coordination site allowing the substrate to bind. The corollary is thus that among the various steps of such a catalytic process, ligand exchanges at the metal center are involved, often triggered by variation of the metal oxidation state. One consequence is that the formation of a reaction product or co-product being a strong coordinating ligand might bind the metal and then block the regeneration of a free coordination site required to sustain catalysis. The homogeneous electrochemical reduction of  $\text{CO}_2$  to  $\text{CO}$  by the molecular catalyst  $[\text{Ni}(\text{cyclam})]^{2+}$  provides a typical example in which the rate-limiting step during catalysis is  $\text{CO}$  decoordination from the deactivated intermediate  $[\text{Ni}(\text{cyclam})(\text{CO})]^+$  as shown by Kubiak and coworkers.<sup>5</sup> Even more drastic is the case  $\text{N}_2$  splitting by electrogenerated reduced rhenium or molybdenum complexes leading to stable nitride complexes, **which then would require additional**

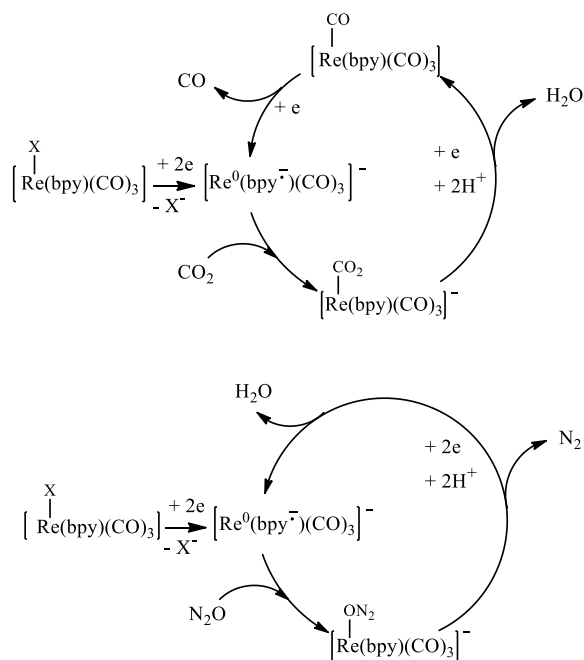
**overpotential to release  $\text{NH}_3$  via three proton-coupled electron transfers**.<sup>6,7,8,9,10,11</sup> In other cases, catalysis is not inhibited but only self-modulated as shown for the reductive cleavage of chloroacetonitrile catalyzed  $\text{Co}(\text{I})$  cobalamins and cobinamides where the production of free chloride, as catalysis goes on, shifts the generation of the  $\text{Co}(\text{I})$  active species toward more negative potentials thus slowing down catalysis.<sup>12</sup> Due to their ubiquity, it is of prime importance to identify and analyze these phenomena in order to fully understand catalytic processes and, more importantly, provide strategies to avoid or delay catalyst deactivation<sup>5</sup> or even design new reactions.<sup>13</sup>

In that context, we recently reported that rhenium carbonyl complexes catalyze nitrous oxide ( $\text{N}_2\text{O}$ ) electroreduction.<sup>14</sup>  $\text{N}_2\text{O}$  is a greenhouse gas responsible for 4% of the additional greenhouse effect observed since the start of the industrial era.<sup>15</sup> Its reduction to dinitrogen is thus of interest to minimize its release in the atmosphere. Additionally, deoxygenation of  $\text{N-O}$  bonds is currently relying on thermochemical methods and sacrificial reducing agents.<sup>16</sup> It is thus timely to elaborate selective, clean, and energy thrifty processes for deoxygenation reactions targeting  $\text{N-oxides}$ . Interestingly, rhenium bi-

pyridyl tri-carbonyl complexes able to catalyze the electrochemical reduction of  $\text{N}_2\text{O}$  have also proved to be efficient photocatalysts for pyridine N-oxide deoxygenation.<sup>17</sup> This suggests that an inner-sphere mechanism via metal-oxygen binding might be at work as opposed to an activation through a nucleophilic attack of the reduced metal to the electrophilic central nitrogen of  $\text{N}_2\text{O}$  proposed from the electronic analogy between  $\text{N}_2\text{O}$  and  $\text{CO}_2$ .<sup>18</sup>

We have thus investigated in detail the mechanism of  $\text{N}_2\text{O}$  electroreduction catalyzed by  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{X})]^{n+}$  complexes (bpy= bipyridine; X = chloride, hydroxide or acetonitrile, n depends on the X ligand). These complexes are indeed known for a long time to be efficient catalysts for  $\text{CO}_2$  to CO conversion and mechanistic studies have shown that the formation of the bi-reduced species  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  is required for  $\text{CO}_2$  to bind the rhenium center and trigger catalysis.<sup>19</sup> This involves via loss of the X ligand to generate a free coordinated site (scheme 1). As opposed to the case of nickel cyclam complexes, after the C-O bond breaking, CO is easily released allowing regenerating the vacant site.

**Scheme 1.** Proposed principle for  $\text{CO}_2$  and  $\text{N}_2\text{O}$  activation with rhenium bipyridyl carbonyl complexes.<sup>18,19</sup>

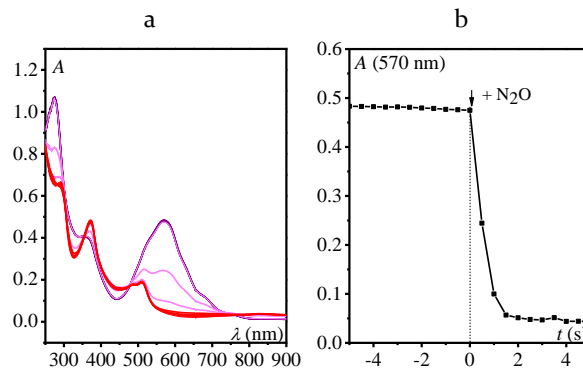


Activation of  $\text{N}_2\text{O}$  has also been proposed to be initiated by its reaction with  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  but, on the timescale of cyclic voltammetry, no substantial catalysis occurs at a potential where  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  is electrogenerated.<sup>14,18</sup> This is the first result of the present work which reveals that formation of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  is responsible for this lack of catalysis. This prompted us to investigate the role of the labile ligand in the catalytic process and uncover unexpected slower catalytic pathways but operating at a lower overpotential without requiring the generation of the bi-reduced species  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ . Kinetic analysis will show that ligand exchanges on the rhenium center will prove to be crucial in directing the reaction toward inner-sphere or slower outer-sphere pathways and hence modulate the catalysis.

## Results

*Chemical reduction of  $\text{N}_2\text{O}$  by electrogenerated  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ .*

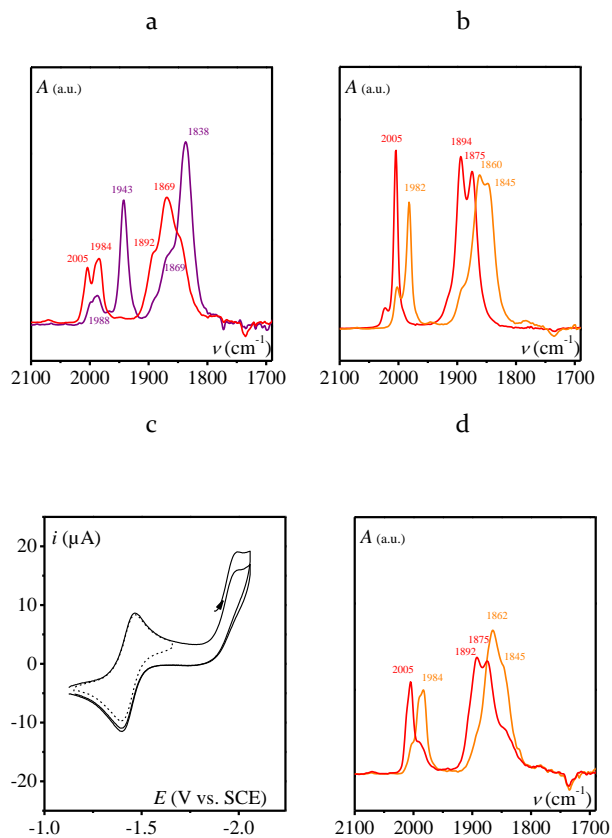
Starting from  $[\text{Re}^I(\text{bpy})(\text{CO})_3\text{Cl}]$ , a solution of the bi-reduced species  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  in acetonitrile is obtained by a two-step electrolysis (see Supporting Information (SI) for details). The first electrolysis is performed at  $-1.36$  V (all potentials are given vs. SCE) and leads to the formation of a metal-bonded Re-Re dimer,  $[\text{Re}^0(\text{bpy})(\text{CO})_3]_2$ , as attested by the dark green color of the solution (see Figure S1). Further reduction of the dimer at  $-1.82$  V gives the bi-reduced species  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  as a major product (see Figure S1). Under inert atmosphere, the electrogenerated solution of bi-reduced species (0.6 mM) is stable.  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  exhibits a large absorption band at 570 nm. A  $\text{N}_2\text{O}$  saturated solution of acetonitrile is then added so as to get 1.5 mM of  $\text{N}_2\text{O}$  and the evolution of the bi-reduced species is monitored in situ by UV-vis. Rapid decay is observed: half of the absorbance at 570 nm is lost after 0.5 s (Figure 1). This indicates a fast reaction between  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  and  $\text{N}_2\text{O}$ . **The reaction can be controlled by mass transport, i.e. mixing of  $\text{N}_2\text{O}$ , but the rapid decay indicates that a lower limit of the pseudo-first order rate constant can be evaluated as  $k_{ap} \approx 1.4$  s<sup>-1</sup>. Therefore, for a saturated  $\text{N}_2\text{O}$  solution (i.e.  $[\text{N}_2\text{O}] = 280$  mM, see SI for determination of the concentration), a lower limit of the pseudo-first order corresponding rate constant is ca.  $k_{ap}^{bi} = 250$  s<sup>-1</sup>.**



**Figure 1.** (a) Time evolution of UV-vis spectra (scans were taken every 0.5 s,  $l = 1$  mm) of a 0.6 mM solution of electrogenerated  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  in  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{NBu}_4\text{PF}_6$  with addition of 1.5 mM of  $\text{N}_2\text{O}$ . Spectra in light magenta: from  $t = 0$  (addition) to 2.5 s. Spectra for  $t < 0$  are in purple and  $t > 2.5$  s are in red. (b) Time evolution of the absorbance at 570 nm characteristic of  $[\text{Re}^0(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  absorption.

An IR spectrum was collected few minutes after the addition of  $\text{N}_2\text{O}$  to the bi-reduced species (Figure 2a) and reveals that a mixture of  $[\text{Re}^I(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  and  $[\text{Re}^I(\text{bpy})(\text{CO})_3(\text{OH})]$  is obtained. This conclusion was obtained from comparison of the IR spectra of authentic samples of  $[\text{Re}^I(\text{bpy})(\text{CO})_3(\text{OH})]$  and  $[\text{Re}^I(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  gathered from a synthesized  $[\text{Re}^I(\text{bpy})(\text{CO})_3(\text{OH})]$  complex (Figure 2b and Figure S3). Cyclic voltammograms (CV) recorded after the addition of  $\text{N}_2\text{O}$  shows a reversible system

with a standard potential of  $-1.43$  V as well as a new irreversible wave at ca.  $-2$  V (Figure 2c). The reversible wave matches the redox behavior of the synthesized  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  complex (Figure S3).<sup>20</sup> Successive application of an oxidative potential at  $-1.22$  V and then a reductive potential at  $-1.52$  V to the final solution with UV-vis and IR characterization after each step shows identical features (Figure 2d) of authentic samples of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  and  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  respectively (Figure 2b) further confirming the formation of both species upon addition of  $\text{N}_2\text{O}$  to  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$ .



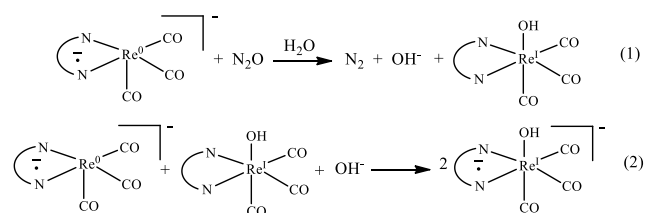
**Figure 2.** (a) Ex-situ IR spectrum of  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$   $0.6$  mM in  $\text{CH}_3\text{CN} + 0.1$  M  $\text{NBu}_4\text{PF}_6$  before (purple) and after (red) addition of  $1.5$  mM of  $\text{N}_2\text{O}$ . (b) IR spectrum of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  (red) and  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  (orange) in  $\text{CH}_3\text{CN} + 0.1$  M  $\text{NBu}_4\text{PF}_6$ . (c) CV of a solution of  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$   $0.6$  mM after addition of  $1.5$  mM of  $\text{N}_2\text{O}$  in  $\text{CH}_3\text{CN} + 0.1$  M  $\text{NBu}_4\text{PF}_6$  at  $0.1$  V/s on a  $3$  mm-diameter GCE (d) Ex-situ IR spectrum of a  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$   $0.6$  mM +  $1.5$  mM  $\text{N}_2\text{O}$  solution after exhaustive oxidative electrolysis at  $-1.22$  V (red) and then exhaustive reductive electrolysis at  $-1.52$  V (orange).

We thus propose the reaction scheme depicted in scheme 2a with consideration that the second step might not be completed. Moreover, the source of water is assumed being the residual water contained in acetonitrile. The key conclusion at this stage is that the bi-reduced species is indeed able to quickly react with  $\text{N}_2\text{O}$ . However, as observed on the cyclic voltammogram of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  under  $\text{N}_2\text{O}$  (Figure 3), at a potential where  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  is generated (second wave), there is no substantial catalysis, the wave

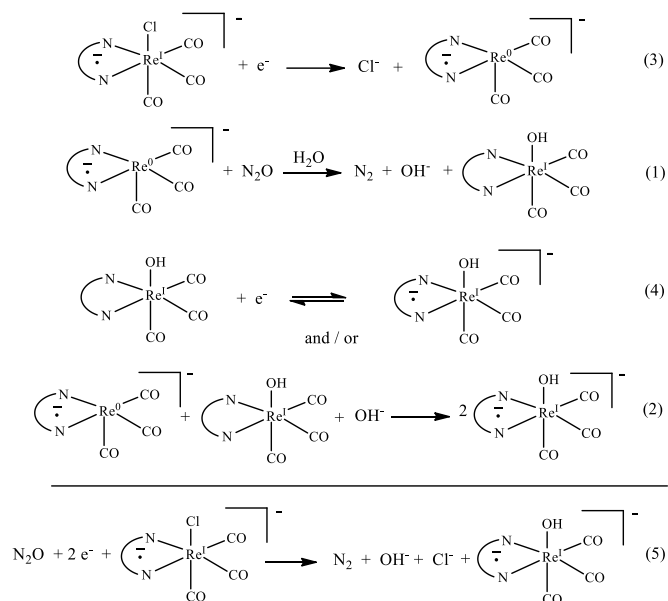
corresponding to a maximum of  $1.5$  electron per rhenium center as attested by linear scan voltammetry on a rotating disk electrode (Figure 3c). Our results reveal that the reason for lack of efficient catalysis is that the labile position is coordinated by hydroxide after the first turnover (equation (1) in scheme 2). Although  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  is reduced at this potential, either at the electrode or in solution by  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  (equation (4) and (2) respectively in scheme 2b), hydroxide is partially de-coordinated and released in solution on the timescale of CV.

### Scheme 2.

a) Reaction between  $\text{N}_2\text{O}$  and  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  in solution



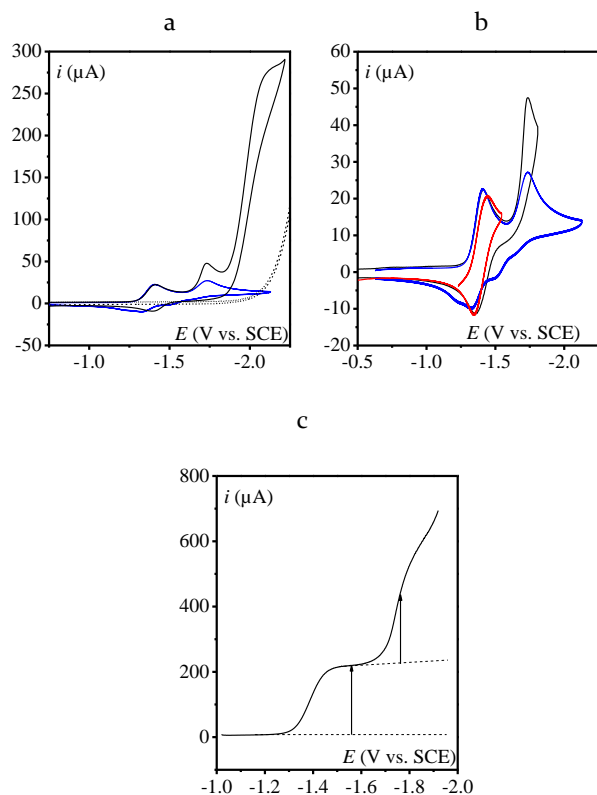
b) Electrochemical reduction of  $\text{N}_2\text{O}$  in the presence of  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$



The overall reaction at the level of the second CV wave thus corresponds to a net reduction of  $0.5$   $\text{N}_2\text{O}$  per rhenium complex and a ligand exchange on the rhenium center (equation (5) in scheme 2b). Fast release of hydroxide requires a further reduction at more negative potential (third wave in figure 3a). This additional reduction regenerates the bi-reduced species  $[\text{Re}^{\text{0}}(\text{bpy}^{\bullet-})(\text{CO})_3]^-$  via a “Proton-Coupled Electron transfer”-type reaction (“PCET”, *vide infra* in the discussion section) and catalysis can be sustained as summarized on scheme 3. **This process parallels the required PCETs to release  $\text{NH}_3$  from metal nitride complexes in nitrogen reduction reaction catalyzed by molecular catalysts.**<sup>6-11</sup>

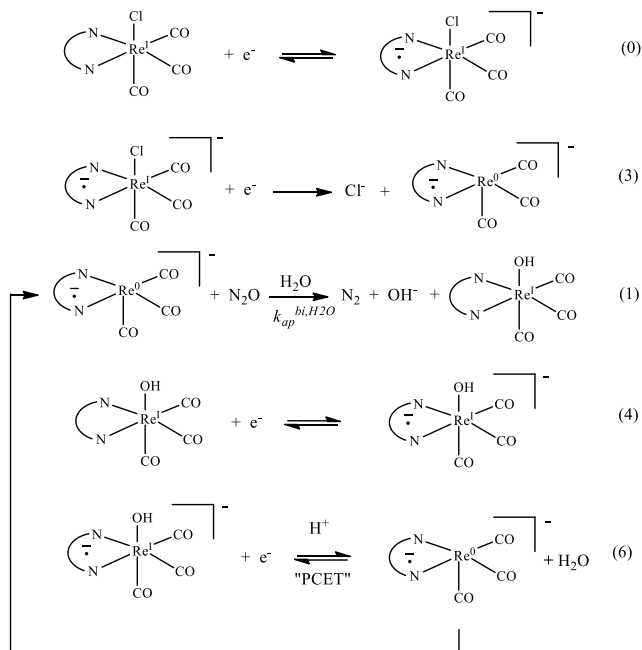
The established mechanism is at variance with the previously

suggested mechanism that was proposed on the sole basis of CV.<sup>14</sup> Our results show that formation of hydroxide as a by-product of N<sub>2</sub>O reduction is detrimental to catalysis because it is a strong coordinating ligand. Displacement of hydroxide is thus a requirement to get catalysis at lower overpotential. Moreover, the potential at which the initial reductive active species [Re<sup>0</sup>(bpy<sup>•-</sup>)(CO)<sub>3</sub>]<sup>-</sup> is formed is related to the labile ligand X present on the initial complex [Re(bpy)(CO)<sub>3</sub>X]. Therefore, we will now investigate the role of the labile ligand in the catalytic process.



**Figure 3** [Re(bpy)(CO)<sub>3</sub>Cl] 1 mM in CH<sub>3</sub>CN + 0.1 M NBu<sub>4</sub>PF<sub>6</sub> (a) CV at 0.1 V/s on a 3 mm-diameter GCE. under N<sub>2</sub>O (black) and under argon (blue). **Dashed line: direct reduction of N<sub>2</sub>O in the absence of [Re(bpy)(CO)<sub>3</sub>Cl]** (b) Same as (a); the red CV is the second part of the black curve obtained by reversing the reverse scan at -1.25 V. (c) Linear scan voltammetry at 10 mV/s on a 5-mm diameter GC rotating disk electrode at 1000 rpm under N<sub>2</sub>O. Vertical black arrows correspond to a stoichiometry of one electron per rhenium center.

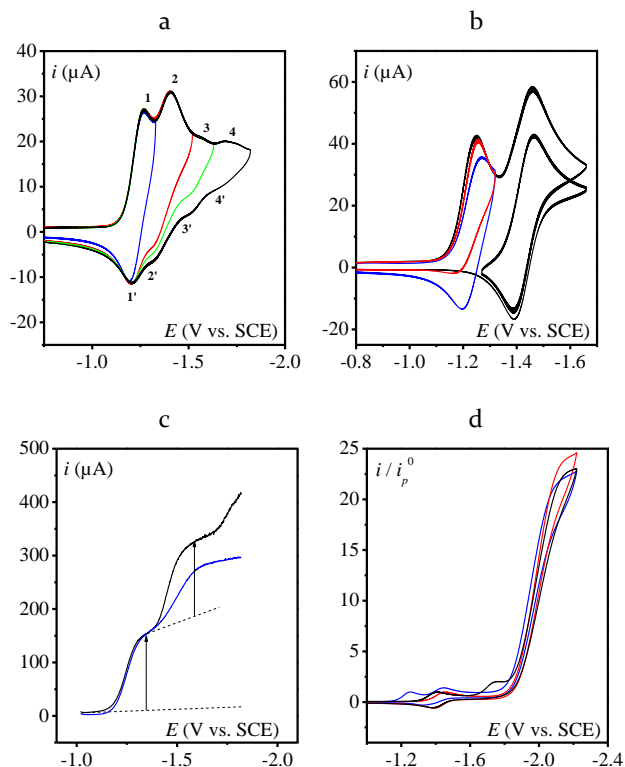
**Scheme 3.** Catalytic reduction of N<sub>2</sub>O via [Re<sup>0</sup>(bpy<sup>•-</sup>)(CO)<sub>3</sub>]<sup>-</sup>



#### Behavior of [Re(bpy)(CO)<sub>3</sub>(CH<sub>3</sub>CN)](PF<sub>6</sub>) under N<sub>2</sub>O

The reduction of [Re<sup>I</sup>(bpy)(CO)<sub>3</sub>(CH<sub>3</sub>CN)]<sup>+</sup> under argon shows an initial partially reversible one electron wave (standard potential -1.23 V) corresponding to the formation of [Re<sup>I</sup>(bpy<sup>•-</sup>)(CO)<sub>3</sub>(CH<sub>3</sub>CN)] (wave 1/1' in figure 4a). Rapid loss of the labile acetonitrile ligand leads to partial formation of the [Re<sup>0</sup>(bpy)(CO)<sub>3</sub>]<sub>2</sub> dimer. A second wave corresponding to the formation of the bi-reduced species [Re<sup>0</sup>(bpy<sup>•-</sup>)(CO)<sub>3</sub>]<sup>-</sup> is observed with a standard potential of -1.36 V (wave 2/2' in figure 4a) **similar to what was previously reported for [Re(bpy)(CO)<sub>3</sub>(Otf)]<sup>+</sup> in THF 0.1 M NBu<sub>4</sub>PF<sub>6</sub> THF electrolyte.**<sup>21</sup> The first and second reductions of the dimer occur at -1.52 V and -1.68 V respectively (waves 3/3' and 4/4' in figure 4a). Generation of the bi-reduced species [Re<sup>0</sup>(bpy<sup>•-</sup>)(CO)<sub>3</sub>]<sup>-</sup> occurs at less negative potential than with [Re(bpy)(CO)<sub>3</sub>Cl] (shift by ca. 300 mV) because decoordination of acetonitrile is easier than decoordination of chloride **and also because the overall charge is neutral for the singly reduced solvato complex and anionic for the singly reduced chloro complex.** When the solution is saturated with N<sub>2</sub>O, important changes are observed on CV (Figure 4b). The first wave becomes almost irreversible and slightly increases in intensity. However it remains mono-electronic (Figure 4c) thus excluding a pathway via the bi-reduced species which formation requires an additional 100 mV overpotential. It is then followed by a reversible one-electron wave (Figure 4b) with a standard potential equal to -1.43 V. Finally a catalytic wave is obtained at the same position than the one obtained when starting from either [Re<sup>I</sup>(bpy)(CO)<sub>3</sub>Cl] or [Re<sup>I</sup>(bpy)(CO)<sub>3</sub>(OH)] (Figure 4d). These observations strongly suggest that N<sub>2</sub>O reacts with the mono-reduced species [Re<sup>I</sup>(bpy<sup>•-</sup>)(CO)<sub>3</sub>(CH<sub>3</sub>CN)] (or presumably [Re<sup>I</sup>(bpy<sup>•-</sup>)(CO)<sub>3</sub>]) on the timescale of CV. An exhaustive electrolysis of [Re(bpy)(CO)<sub>3</sub>(CH<sub>3</sub>CN)](PF<sub>6</sub>) was thus performed at -1.22 V in the presence of a large excess of N<sub>2</sub>O (see SI). The solution product was characterized by UV-vis, IR and CV (Figure S4). It unambiguously shows that the

obtained product is  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  which reduction corresponds to the reversible second wave observed on CV (Figure 4b). We also note that no dimer was formed during electrolysis (UV-vis) indicating that the reaction of  $\text{N}_2\text{O}$  with  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3]$  is faster than dimerization.



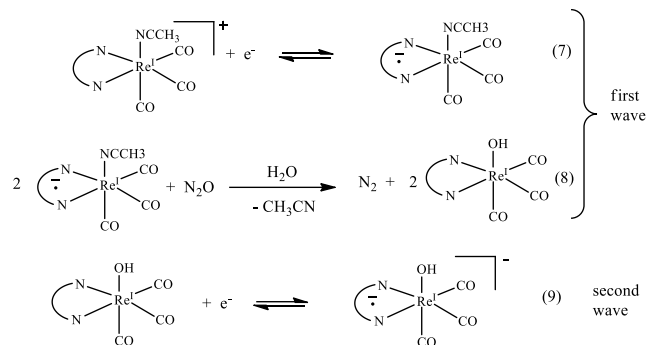
**Figure 4.** CV in  $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$  at  $0.1 \text{ V/s}$  on a  $3 \text{ mm}$ -diameter GCE at  $0.1 \text{ V/s}$ . (a)  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$   $1 \text{ mM}$  under argon (b)  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$   $1.6 \text{ mM}$  under argon (blue) and under  $\text{N}_2\text{O}$  (red and black). (c) Linear scan voltammogram at  $10 \text{ mV/s}$  on a  $5 \text{ mm}$ -diameter GC rotating disk electrode at  $1000 \text{ rpm}$  of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$   $1 \text{ mM}$  in  $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{PF}_6$  under  $\text{N}_2\text{O}$  (black) and under argon (blue). Vertical black arrows correspond to a stoichiometry of one electron per rhenium center. (d) Normalized CV of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$   $1 \text{ mM}$  under  $\text{N}_2\text{O}$  (blue),  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$   $1 \text{ mM}$  under  $\text{N}_2\text{O}$  (black),  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$   $1 \text{ mM}$  under  $\text{N}_2\text{O}$  (red).  $i_p^0$  is the peak current corresponding of a first one-electron wave of each catalyst under  $\text{N}_2\text{O}$ .

We have thus shown that reaction of  $\text{N}_2\text{O}$  with  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3]$  takes place on the timescale of CV at  $0.1 \text{ V/s}$ . Increasing the scan rate partially restores reversibility of the first CV wave (Figure S5) indicating that the pseudo first order rate constant is of the order of  $k_{\text{ap}}^{\text{mono,ACN}} \approx 10 \text{ s}^{-1}$  (see SI).

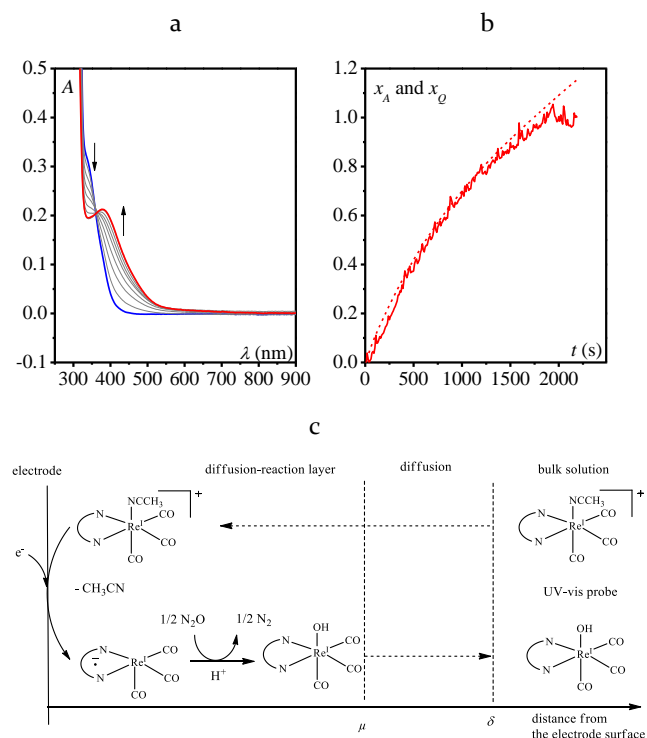
It is smaller than the corresponding value for the reaction of  $[\text{Re}^{\text{O}}(\text{bpy}^*)(\text{CO})_3]^-$  with  $\text{N}_2\text{O}$  (ca.  $250 \text{ s}^{-1}$ , *vide supra*). Importantly, the stoichiometry of the first wave remains one electron per rhenium center. This implies that the transformation of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  to  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  is associated with the net reduction of  $0.5$  equivalent of  $\text{N}_2\text{O}$  and substitution of acetonitrile by hydroxide on the rhenium

center (scheme 4).

**Scheme 4.** Reduction of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  under  $\text{N}_2\text{O}$ .



Constant potential electrolysis was performed with continuous bubbling of  $\text{N}_2\text{O}$  at  $-1.22 \text{ V}$ . UV-vis monitoring in the bulk shows the quantitative transformation of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  to  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  (Figure 5a). The absorption at  $450 \text{ nm}$ , where only  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  absorbs, i.e. not at  $\lambda_{\text{max}}$  (see figures S6 for characteristics UV-vis spectrum of each species), varies at the same pace as the charge transferred at the electrode surface (Figure 5b). This confirms that the chemical transformation (equation 8 in scheme 4) following the electrochemical reduction of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  (equation 7 in scheme 4) is fast. As sketched in figure 5c, it occurs in a diffusion reaction layer which thickness ( $\mu \approx \sqrt{D/k_{\text{ap}}^{\text{mono,ACN}}} \approx 7 \mu\text{m}$  with  $D \approx 5 \cdot 10^{-6} \text{ cm}^2/\text{s}$  the rhenium complex diffusion coefficient and  $k_{\text{ap}}^{\text{mono,ACN}} \approx 10 \text{ s}^{-1}$  the pseudo-first order rate constant) is smaller than the diffusion layer ( $\delta$ ) set by the stirring of the solution probably in the order of tens of  $\mu\text{m}$ .<sup>22</sup>



**Figure 5.** (a) Time evolution of UV-vis spectrum (1 scan / 250 s,  $l = 1$  mm) of the bulk solution upon electrolysis at  $-1.22$  V of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$  1 mM in  $\text{CH}_3\text{CN} + 0.1$  M  $\text{NBu}_4\text{PF}_6$  under  $\text{N}_2\text{O}$ . Blue: initial spectrum, red: final spectrum. (b) Full line: normalized absorption at 450 nm  $x_A = A/A(t > 2000 \text{ s})$ ; dashed line: normalized charge consumed  $x_Q = Q/nF$  where  $Q$  is the transferred charge and  $n$  is the initial quantity of moles of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)$ . (c) Sketch of the spatial localization of the (electro)-chemical transformations during electrolysis.

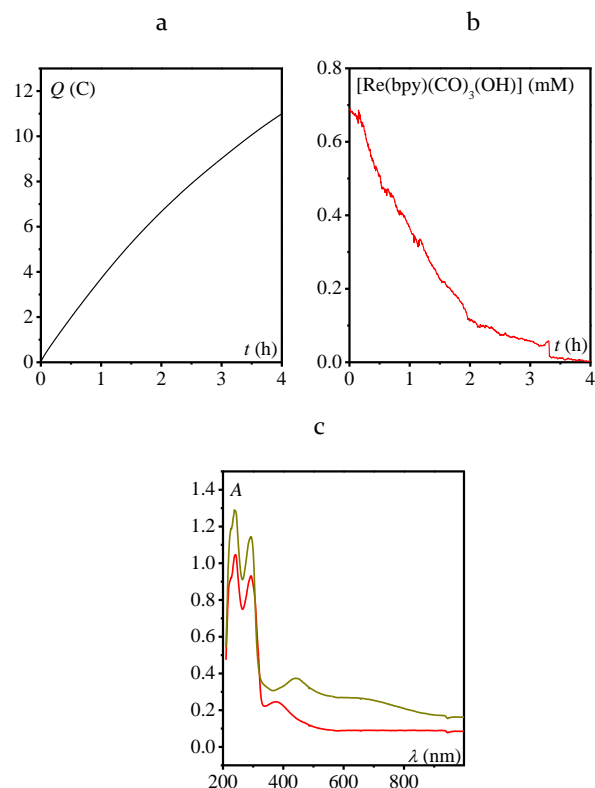
Importantly, the oxidation state of the rhenium complex ( $\text{Re}(\text{I})$ ) is not modified at the end of the experiment. It means that the reaction can be potentially catalytic if the hydroxide ligand could be displaced. Since it is not possible when starting with  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  because acetonitrile cannot displace hydroxide, we will now explore this possibility of a catalytic process when starting from  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  and  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{Cl})]$ .

*Behavior of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  and  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  under  $\text{N}_2\text{O}$  upon mono-electronic reduction*

On the timescale of CV (at  $0.1$  V/s), the mono-reduced complexes  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  and  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$  are stable both under argon and  $\text{N}_2\text{O}$  atmospheres as shown by the corresponding mono-electronic reversible waves (Figure S7). Under constant potential electrolysis conditions and stirring of the solution, the situation is different. At  $-1.52$  V under argon,  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  is converted to  $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  with a characteristic cell time constant  $t_{\text{cell}} = \frac{V\delta}{SD} \approx 250$  s, where  $V$  is the cell volume,  $S$  the electrode surface area,  $D$  the diffusion coefficient and  $\delta$  the size of the diffusion layer set by the stirring of the solution (Figure S8).

Under  $\text{N}_2\text{O}$ , a prolonged current is observed leading to the passage of 12 C after 4 h of electrolysis (Figure 6a), corresponding to 9.2 moles of electron per mole of rhenium complex in solution. UV-vis monitoring of the solution shows that  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  is slowly converted in the bulk (Figure 6b and SI). This indicates that, once formed at the electrode surface,  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  reacts with  $\text{N}_2\text{O}$  on its way to the bulk and  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  is regenerated. However, after ca 15 min (see figure S10),  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  starts to be converted in the bulk into a new compound with a broad absorption band in the visible (dark yellow spectrum in figure 6c). Such a band may suggest a decarbonylation of the rhenium complex<sup>23</sup> but we cannot exclude formation of other “degraded” catalysts. The reactivity of  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  with  $\text{N}_2\text{O}$  was further confirmed via the electrogeneration of  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  under inert atmosphere by constant potential electrolysis of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  at  $-1.52$  V and then addition of a small excess of  $\text{N}_2\text{O}$ . As shown in figure S9, the time evolution of the UV-vis spectrum after addition of  $\text{N}_2\text{O}$  shows at 508 nm an initial fast decay that we attribute to the reaction of some bi-reduced species resulting from a slight overoxidation of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{OH})]$  (see SI). Then a slow decay is observed corresponding to the reaction of  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  with  $\text{N}_2\text{O}$ . From this decay a rough evaluation of the pseudo first

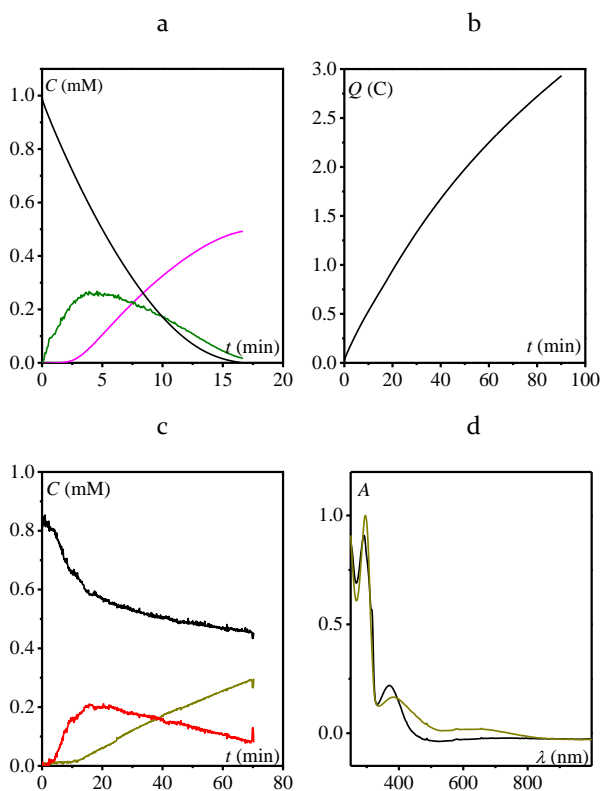
order rate constant for the reaction of  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$  with a saturated solution of  $\text{N}_2\text{O}$  is  $k_{\text{ap}}^{\text{mono,OH}} = 0.04 \text{ s}^{-1}$ . We thus conclude from these results that the electrochemical reduction of  $\text{N}_2\text{O}$  is catalyzed by  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  at a potential corresponding to the formation of the mono-reduced species but it is a slow process, probably limited by the unfavorable displacement of hydroxide by  $\text{N}_2\text{O}$  in  $[\text{Re}^{\text{I}}(\text{bpy}^{\bullet-})(\text{CO})_3(\text{OH})]^-$ . A concurrent decarbonylation of the catalyst may occur that is eventually detrimental to catalysis.



**Figure 6.** (a) Charge consumed upon electrolysis at  $-1.52$  V of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  0.69 mM in 18 mL  $\text{CH}_3\text{CN} + 0.1$  M  $\text{NBu}_4\text{PF}_6$  under  $\text{N}_2\text{O}$ . (b) Time evolution of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  concentration in the bulk solution calculated from the absorbance at 380 nm and 700 nm (see SI for details). (c) UV-vis of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  0.69 mM under  $\text{N}_2\text{O}$  before electrolysis (red) and after 4h electrolysis at  $-1.52$  V (dark yellow),  $l = 1$  mm.

Starting from  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ , the process is more complex. Constant potential electrolysis at  $-1.42$  V under argon shows the formation of  $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$  together with the dimer  $[\text{Re}^{\text{0}}(\text{bpy})(\text{CO})_3]_2$ . Analysis of the time evolution of UV-vis spectra of the solution (see SI for details) indicates that  $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$  initially builds up in the bulk of the solution and then decays at the expense of the dimer (Figure 7a). It is in line with a slow loss of chloride by  $[\text{Re}(\text{bpy}^{\bullet-})(\text{CO})_3\text{Cl}]^-$  and the observation of a reversible mono-electronic CV wave for the reduction of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  at  $0.1$  V/s (Figure S7). The transformation of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  to the dimer  $[\text{Re}(\text{bpy})(\text{CO})_3]_2$  is completed after 20 min and the consumption of 1.05 C corresponding to one electron per rhenium center. Under  $\text{N}_2\text{O}$ , application of a constant potential at  $-1.37$  V

leads to a prolonged current and the consumption of 3 C in 1.5 h (Figure 7b). The analysis of the time evolution of UV-vis spectra of the solution (see SI) shows that  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  concentration only slowly decreases over time and that no dimer is formed as well as no intermediate  $[\text{Re}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  (Figure 7c). This again indicates that  $[\text{Re}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  formed at the electrode surface at -1.37 V does not accumulate in the solution bulk but it reacts with  $\text{N}_2\text{O}$  with regeneration of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ . This reaction prevents evolution toward formation of the dimer seen under argon. The reaction is however slow enough for not taking place on the timescale of CV. Interestingly, we observe that, in the first 15 min, the decrease of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  concentration in solution is concomitant with the formation of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  (red trace in figure 7c) and then the appearance of a new compound with a broad absorption band in the visible attributed to the non-identified “degraded” catalyst (Figure 7d) previously observed (figure 6c). Finally, electrolysis at -1.37 V performed in a tight cell under  $\text{N}_2\text{O}$  atmosphere in the presence of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  as catalyst allows analysis of the gas in the headspace and reveals that after passing a charge of 10 C the faradaic yield for  $\text{N}_2\text{O}$  to  $\text{N}_2$  conversion is 90% (see SI). These results support the homogeneous reduction of  $\text{N}_2\text{O}$  by the electrogenerated  $[\text{Re}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  leading to hydroxide as co-product which accumulates in the solution and then progressively binds preferentially the rhenium center, slowing down catalysis and leading eventually to the degradation of the catalyst.

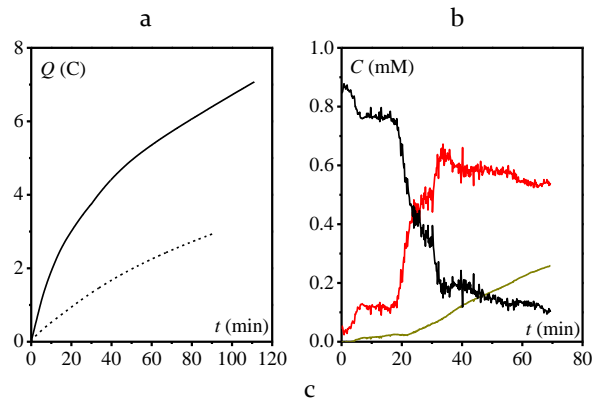


**Figure 7.** (a) Time evolution of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  (black) and  $[\text{Re}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  (green) and  $[\text{Re}(\text{bpy})(\text{CO})_3]_2$  (magenta) concentrations in the bulk solution calculated from UV-vis absorbance (see SI for details) during electrolysis at -1.42 V of

$[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  1 mM in 11 mL  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{NBu}_4\text{PF}_6$  under argon. (b) Charge consumed upon electrolysis at -1.37 V of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  0.83 mM in 18 mL  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{NBu}_4\text{PF}_6$  under  $\text{N}_2\text{O}$ . (c) Time evolution of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  (black) and  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  (red) concentrations in the bulk solution calculated from UV-vis absorbance (see SI for details) at -1.37 V of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  0.83 mM in 18 mL  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{NBu}_4\text{PF}_6$  under  $\text{N}_2\text{O}$ . Dark yellow: “degraded” catalyst (d) UV-vis spectrum of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  before electrolysis (black) and after 70 min electrolysis at -1.37 V under  $\text{N}_2\text{O}$  (dark yellow).

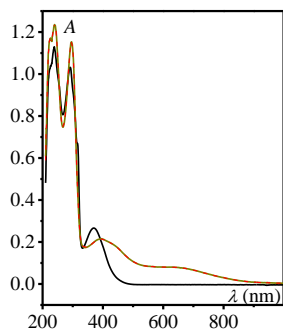
Direct evaluation of the pseudo-first order rate constant  $k_{ap}^{\text{mono,Cl}}$  for reaction of  $[\text{Re}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  with  $\text{N}_2\text{O}$  is not possible because the reaction is too slow to take place on the CV timescale and the lifetime of  $[\text{Re}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  is too small to prepare it as a bulk solution by electrolysis and then add  $\text{N}_2\text{O}$ . However a lower limit of  $k_{ap}^{\text{mono,Cl}}$  can be estimated from the absence of observation of  $[\text{Re}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  in the bulk under  $\text{N}_2\text{O}$  (Figure 7c). We obtain  $k_{ap}^{\text{mono,Cl}} > 0.5 \text{ s}^{-1}$  (see SI for details).

From the observation that catalytic reduction of  $\text{N}_2\text{O}$  by the monoelectronic reduction of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  fades due to the chloride decoordination (equation (3)) and hydroxide coordination (equation (1)), we surmise that addition of an excess of free chlorides in the solution might allow sustaining catalysis by preventing hydroxide coordination to the rhenium center and/or displace hydroxide. Constant potential electrolysis at -1.37 V of a  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  under  $\text{N}_2\text{O}$  atmosphere in the presence of 100 mM  $\text{NEt}_4\text{Cl}$  gives similar results as in the absence of  $\text{NEt}_4\text{Cl}$  but with higher current (Figure 8a). Unfortunately, after a while  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  accumulates in the solution, presumably because the concentration of hydroxide built from  $\text{N}_2\text{O}$  to  $\text{N}_2$  conversion is high enough to prevent regeneration of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  (Figure 8b). At the same time, we again observe apparition of a new compound with a broad absorption band in the visible, the “degraded” catalyst, tentatively attributed to a decarbonylation product (Figure 8c).<sup>23</sup> Nonetheless, it appears that the presence of free chloride in large concentration in the solution boosts the initial reduction of  $\text{N}_2\text{O}$ .



c



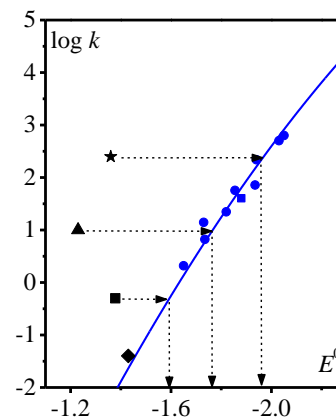


**Figure 8.** (a) Charge consumed upon electrolysis at  $-1.37$  V of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$   $0.88$  mM in  $18$  mL  $\text{CH}_3\text{CN}$  +  $0.1$  M  $\text{NBu}_4\text{PF}_6$  under  $\text{N}_2\text{O}$  with  $100$  mM  $\text{NEt}_4\text{Cl}$ . (b) Time evolution of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  (black) and  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  (red) concentrations in the bulk solution calculated from UV-vis absorbance (see SI for details) at  $-1.37$  V of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$   $0.88$  mM in  $18$  mL  $\text{CH}_3\text{CN}$  +  $0.1$  M  $\text{NBu}_4\text{PF}_6$  under  $\text{N}_2\text{O}$  with  $100$  mM  $\text{NEt}_4\text{Cl}$ . Dark yellow: degradation product. (c) UV-vis spectrum of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  before electrolysis (black) and after  $120$  min electrolysis at  $-1.37$  V under  $\text{N}_2\text{O}$  (dashed red/dark yellow) with  $100$  mM  $\text{NEt}_4\text{Cl}$ .

## Discussion

We have first shown that fast catalysis of  $\text{N}_2\text{O}$  electroreduction by  $[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]^{n+}$  complexes involves the formation of a bi-reduced species  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  as homogeneous reductant. A lower limit of the evaluated pseudo-first order rate constant in the presence of excess of  $\text{N}_2\text{O}$  (saturated in acetonitrile) and no specific addition of a proton donor, is  $k_{ap}^{bi} = 250$   $\text{s}^{-1}$  (step (i) in scheme 2). The corresponding expected catalytic plateau current in cyclic voltammetry considering pure kinetics conditions and scheme 3 as a mechanism is given by  $i_{pl} = FS\sqrt{2Dk_{ap}^{bi}} = 337$   $\mu\text{A}$  that is of the order of magnitude of the catalytic current observed experimentally (Figure 3a). This indicates that the homogeneous reduction of  $\text{N}_2\text{O}$  by electrogenerated  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  is rate determining. However, as previously shown and recalled in figure S13, addition of water has two effects on the catalytic wave: (i) cathodic shift of the onset of the catalytic current noting that the shallow increase of the current is indicative of partial limitation by an electron transfer process and (ii) increase of the plateau current. In the framework of the established mechanism corresponding to scheme 3, these experimental features confirm that: (i) the reduction of  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  to generate the homogeneous reductive species  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  involves water and thus corresponds to a “PCET”-type process (scheme 3) and (ii) the chemical step of the fastest catalytic process involves a proton donor such as water. Hence, this excludes that the chemical reduction of  $\text{N}_2\text{O}$  by  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  is a simple outersphere electron transfer process. Moreover, if it were a simple outersphere electron transfer process the dimer  $[\text{Re}^\circ(\text{bpy})(\text{CO})_3]_2$  would be formed from  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3]$ . That it is not the case is attested by the final UV-vis spectrum showing no absorption at  $590$  and  $780$  nm (Figure 1a). Finally, based on the activa-

tion-driving force relationship previously uncovered for homogeneous outersphere reduction of  $\text{N}_2\text{O}$ ,<sup>18</sup> the evaluated rate constant  $k_{ap}^{bi} = 250$   $\text{s}^{-1}$  would correspond to an electron donor with a standard potential of ca.  $-1.97$  V (Figure 9), i.e. much more negative than the oxidation potential of  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  evaluated above to be ca.  $-1.36$  V (Figure 4a).



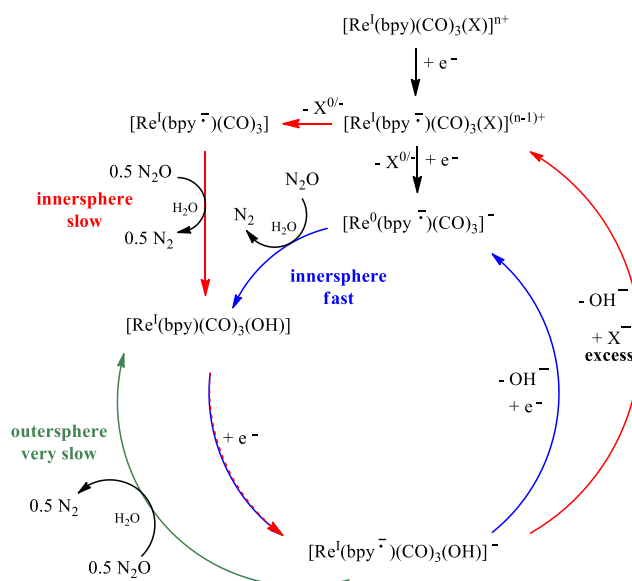
**Figure 9.** Rate constants (in  $\text{s}^{-1}$ ) as function of the standard potential of the reductant  $E^\circ$  (in V vs. SCE) for the homogeneous catalysis of reduction of  $\text{N}_2\text{O}$ . Blue data: reduction by electrogenerated anion radicals or dianions (from reference 18). The blue line corresponds to the prediction for outersphere electron transfers (see reference 18). Reduction by:  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  (black star),  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3]$  (black triangle),  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  (black diamond),  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  (black square). Partially adapted with permission from reference 18. Copyright 2021 RSC.

Our results confirm the innersphere character of the activation of  $\text{N}_2\text{O}$  by  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  in line with the requirement for the displacement of hydroxide from the pre-catalyst to trigger catalysis. It appears that water plays a crucial role in both the displacement of hydroxide (via the “PCET”-type step, equation (6)) and in the innersphere activation of the N-O bond (equation (1)). That the product formed from innersphere activation of  $\text{N}_2\text{O}$  by  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  is the hydroxide complex confirms the suggestion that  $\text{N}_2\text{O}$  binds the rhenium center via the oxygen atom and not the central electrophilic nitrogen.<sup>24</sup> It is in line with the report that rhenium bipyridyl tri-carbonyl complexes are efficient photocatalysts for pyridine N-oxide deoxygenation.<sup>17</sup>

We have then revealed that reaching the bi-reduced species  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  is not mandatory to activate and reduce  $\text{N}_2\text{O}$ . We have indeed shown that  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3]$  reduces  $\text{N}_2\text{O}$  albeit with a slower rate than  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$ ,  $k_{ap}^{mono,ACN} \approx 10$   $\text{s}^{-1}$  (pseudo-first order rate constant in  $\text{N}_2\text{O}$  saturated acetonitrile). Given the reductive power of  $[\text{Re}^I(\text{bpy}^*)(\text{CO})_3]$ , corresponding to a standard potential of  $-1.23$  V (Figure 4a), we can conclude that the reduction of  $\text{N}_2\text{O}$  by  $[\text{Re}^\circ(\text{bpy}^*)(\text{CO})_3]^-$  is an innersphere process because it is much faster than predicted for an outersphere electron transfer (Figure 9). Using  $[\text{Re}^I(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$  as a pre-catalyst was crucial as acetonitrile is a labile ligand allowing to

generate a vacant site on the rhenium center after a mono-reduction of the complex. This contention is confirmed by our results showing that  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  is able to reduce  $\text{N}_2\text{O}$  (Figure 6) but with a small rate constant  $k_{\text{ap}}^{\text{mono,OH}} = 0.04 \text{ s}^{-1}$  (pseudo-first order rate constant in  $\text{N}_2\text{O}$  saturated acetonitrile). Taking into account the standard potential of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]^{0/-}$ ,  $-1.43 \text{ V}$ , it appears that the rate constant  $k_{\text{ap}}^{\text{mono,OH}}$  aligns on the activation-driving force correlation predicted for an outersphere electron transfer (Figure 9). Therefore, the strong ligand hydroxide, not able to be displaced by  $\text{N}_2\text{O}$  in  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$ , prevents an inner-sphere activation of  $\text{N}_2\text{O}$ . This confirms that an inner-sphere catalytic activation of  $\text{N}_2\text{O}$  requires the regeneration of a free coordination site on the rhenium and the formation of the strong ligand hydroxide as a co-product of  $\text{N}_2\text{O}$  reduction induces a self-inhibition of the catalysis. We have also shown that electrogeneration of  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  allows reducing  $\text{N}_2\text{O}$  (Figure 7b) with a pseudo-first order rate constant  $k_{\text{ap}}^{\text{mono,Cl}} > 0.5 \text{ s}^{-1}$ . This rate constant does not correspond to a single event because it involves loss of chloride and reaction with  $\text{N}_2\text{O}$ . Knowing that the standard potential of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{0/-}$  is  $-1.38 \text{ V}$ , this lower limit of the rate constant indicates that the reaction is an inner-sphere process and not an outersphere electron transfer from  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  to  $\text{N}_2\text{O}$  (Figure 9). This indicates that chloride can be displaced by  $\text{N}_2\text{O}$  once the complex is mono-reduced whereas hydroxide cannot be displaced by  $\text{N}_2\text{O}$ . It is in line with chloride being more labile than hydroxide as  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  is stable in solution (Figure S8) whereas  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  evolves toward formation of a dimer  $[\text{Re}(\text{bpy})(\text{CO})_3]_2$  (Figure 7a). Interestingly, we have finally shown that, in the presence of large quantity of free chloride in solution,  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  can be converted back to  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  via displacement of hydroxide by the free chloride, provided that the concentration of free hydroxide produced by the reduction of  $\text{N}_2\text{O}$  is not too large (Figure 8).<sup>25</sup> **The exchange  $\text{OH}^-/\text{Cl}^-$   $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  is confirmed by addition of excess of chlorides to an electrogenerated solution of  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  showing first formation of  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3\text{Cl}]^-$  and then evolution toward formation of the dimer  $[\text{Re}(\text{bpy})(\text{CO})_3]_2$  (figure S15).** Therefore the catalysis of  $\text{N}_2\text{O}$  reduction via an inner-sphere process induced by the mono-reduction of  $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(\text{Cl})]$  can be prolonged before switching to a slower outersphere process due to the formation of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ . It is revealed by the time evolution of the charge which is initially fast (inner-sphere process) and then keeps increasing at a slower pace (outersphere process) when  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$  is dominant in the bulk after 30 min electrolysis as seen in Figure 8. This illustrates the role of ligand exchange on the catalysts in the modulation of the rate of catalysis.

**Scheme 5.** General mechanism for the reduction of  $\text{N}_2\text{O}$  by  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{X})]^{n+}$  complexes.



Based on all the results gathered in the present study, the general mechanism for  $\text{N}_2\text{O}$  electroreduction catalyzed by  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{X})]^{n+}$  complexes ( $\text{X} = \text{CH}_3\text{CN}, \text{Cl}^-$ ,  $n = 0$  or  $1$ ) can be summarized in scheme 5.

## Conclusion

The electrochemical reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  is catalyzed by rhenium bipyridyl tricarbonyl complexes  $[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]^{n+}$  ( $\text{X} = \text{CH}_3\text{CN}, \text{Cl}^-$ ). A requirement for efficient catalysis is that the bi-reduced  $[\text{Re}^0(\text{bpy}^*)(\text{CO})_3]^-$  species is electrogenerated. However, the reaction generates hydroxide, a strong ligand making the potential needed to regenerate  $[\text{Re}^0(\text{bpy}^*)(\text{CO})_3]^-$  more negative as the reaction progresses, amounting to a self-inhibition process. If the requirement is not fulfilled, a less efficient reduction is nonetheless taking place when mono-reduced species  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3(\text{X})]^{(n-1)+}$  are electrogenerated. An inner-sphere reduction of  $\text{N}_2\text{O}$  is triggered due to the lability of both acetonitrile and chloride allowing creating a free coordination site for  $\text{N}_2\text{O}$  binding. However, as in the case of the bi-reduced species pathway, generation of hydroxide as a co-product induces formation of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{OH})]$ . Its reduction leads to  $[\text{Re}^{\text{I}}(\text{bpy}^*)(\text{CO})_3(\text{OH})]^-$  which is only competent for a slower outersphere reduction of  $\text{N}_2\text{O}$  due to the lack of lability of hydroxide. This can be overcome if a large concentration of free chloride is present enabling to displace hydroxide. These results emphasize the critical role of ligand exchange in the modulation of the rate of catalysis. Self-modulation of catalysis by ligand exchange is a phenomenon likely to take place in many electrochemical reactions catalyzed by transition metal complexes, in particular in the context of small molecules activation. We think that this study will be an incentive to bring more attention to this phenomenon in the endeavor to understand efficiency of molecular catalysis.

## SUPPORTING INFORMATION

Experimental details. Determination of  $\text{N}_2\text{O}$  solubility in acetonitrile. Synthesis and characterization of

[Re(bpy)(CO)<sub>3</sub>(OH)]. UV-vis spectrum of the various species. Additional UV-vis and IR spectro-electrochemical data. Analysis of time evolution of UV-vis during electrolysis. Additional CVs. Evaluation of rate constants. UV-vis of [Re(bpy)(CO)<sub>3</sub>(OH)] in the presence of free chloride. This information is available free of charge on the ACS Publications website.

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### Notes

The author declares no competing financial interest.

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- (25) Note that hydroxide can be displaced by excess of free chloride in [Re<sup>I</sup>(bpy)(CO)<sub>3</sub>(OH)] as shown in figure S14.

TOC

