[M(CO)4(2,2'-bipyridine)] (M = Cr, Mo, W) as efficient catalysts for electrochemical reduction of CO2 to CO at a gold electrode

[M(CO)$_4$(2,2′-bipyridine)] (M=Cr, Mo, W) Complexes as Efficient Catalysts for Electrochemical Reduction of CO$_2$ at a Gold Electrode

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Dedicated to Dr. Alain Deronzier (Université Joseph Fourier, Grenoble) to acknowledge his enormous contribution in the field of electro-catalytic reduction of carbon dioxide

Group 6 complexes of the type [M(CO)$_4$(bpy)] (M=Cr, Mo, W) are capable of behaving as electrochemical catalysts for the reduction of CO$_2$ at potentials less negative than those for the reduction of the radical anions [M(CO)$_4$(bpy)]$^{·-}$. Cyclic voltammetric, chronoamperometric and UV/Vis/IR spectro-electrochemical data reveal that five-coordinate [M(CO)$_3$(bpy)]$^{2-}$ are the active catalysts. The catalytic conversion is significantly more efficient in *N*-methyl-2-pyrrolidone (NMP) compared to tetrahydrofuran, which may reflect easier CO dissociation from 1e$^-$-reduced [M(CO)$_4$(bpy)]$^{·-}$ in the former solvent, followed by second electron transfer. The catalytic cycle may also involve [M(CO)$_4$(H-bpy)]$^-$ formed by protonation of [M(CO)$_3$(bpy)]$^{2-}$, especially in NMP. The strongly enhanced catalysis using an Au working electrode is remarkable, suggesting that surface interactions may play an important role, too.

Reduction of CO$_2$ to produce compounds that could be used as fuel sources or as chemical feedstock for organic synthesis has attracted growing interest since the late 20th century.[1] Photochemical and electrochemical catalysts have been explored to make the reduction energetically favorable, in particular transition-metal-based catalysts facilitating multi-electron transfer coupled to proton transfer.[2] Many of the most promising electrocatalysts that have been identified incorporate the heavier homologues of the Group 7, 8 and 9 metals, meaning that costs and availability preclude practical large-scale applications.[3] Among them, [Re(CO)$_3$(bpy)Cl] (bpy=2,2′-bipyridine)

and its derivatives are well-established as catalyst precursors for both photochemical and electrochemical CO$_2$ reduction.[4] It has recently been shown that the analogue containing the cheaper and more abundant manganese(I) metal centre, [Mn(CO)$_3$(bpy)Cl] (and its 4,4′-di-*t*Bu-bpy derivative), can also be used as precursor for both photo- and electrocatalytic CO$_2$ reduction in the presence of a Brønsted acid.[5] Efficient electrocatalytic conversion of CO$_2$ to CO is associated both with the 2e$^-$-reduced 5-coordinate anion [M(CO)$_3$(bpy)]$^-$ (M=Re,[4] Mn[5a,b, 6]) and the dimer [M(CO)$_3$(bpy)]$_2$ (M=Re,[4b] Mn[5d]).

The initial 1e$^-$ electrochemical reduction of the analogous Group 6 carbonyls, [M(CO)$_4$(bpy)] (M=Cr, Mo, W), generates stable six-coordinate radical anions;[6–8] their subsequent 1e$^-$ reduction has been suggested[9] to result in dissociation of CO to give [M(CO)$_3$(bpy)]$^{2-}$. Until very recently no reports have described the investigation of their potential as electrocatalysts for CO$_2$ reduction, despite the importance of Group 6 metals in analogous enzymatic reductive processes.[10] However, studies of the formally Mo(II) complex [Mo(NCS)(CO)$_2$(η^3-allyl)(bpy)] have shown evidence of the catalytic CO$_2$ conversion to CO and formate via 2e$^-$-reduced [Mo(CO)$_2$(η^3-allyl)(bpy)]$^-$.[11]

This work provides a more detailed study of the reduction pathway of the Group 6 [M(CO)$_4$(bpy)] triad, hereinafter with the emphasis on the Mo(0) complex and a gold cathode, and investigates its implementation as a potentially more economically viable catalyst for CO$_2$ reduction.

The spectro-electrochemical investigations were undertaken in non-aqueous organic solvents, namely tetrahydrofuran (THF) and less commonly used *N*-methyl-2-pyrrolidone (NMP), which provide fairly high CO$_2$ solubility and both feature large negative potential windows. NMP is much less volatile than THF and, importantly, has also been used as a commercial CO$_2$ scrubbing solvent (the Purisol process).[12]

The reduction of [Mo(CO)$_4$(bpy)] representing the triad was first studied with cyclic voltammetry at Au, Pt and GC disk

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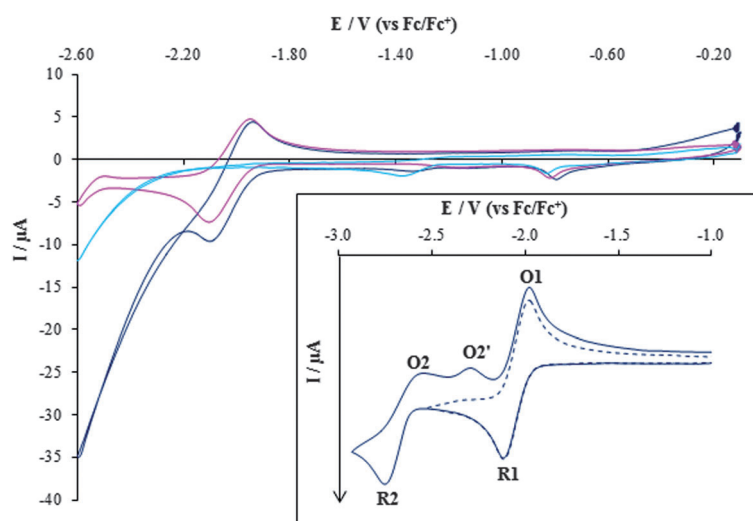 *E-mail: robert.dryfe@manchester.ac.uk*

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Table 1. Electrochemical potentials for [M(CO)$_4$(bpy)] (M=Cr, Mo, W) and their reduction products in THF/Bu$_4$NPF$_6$.

Redox step	E [V] vs Fc/Fc$^+$		
	Cr	Mo	W
$E_{1/2}$[M(CO)$_4$(bpy)]↔[M(CO)$_4$(bpy)]$^{·-}$	−2.16	−2.07	−1.99
$E_{p,c}$[M(CO)$_4$(bpy)]$^{·-}$→[M(CO)$_4$(bpy)]$^{2-}$	−2.78	−2.73	−2.65
$E_{p,a}$[M(CO)$_3$(bpy)]$^{2-}$→[M(CO)$_3$(bpy)]$^{·-}$	−2.34	−2.32	−2.17

Figure 1. Cyclic voltammograms (CVs) showing the 1e⁻ reduction of [Mo(CO)$_4$(bpy)] (0.5 mM) both with (blue) and without (pink) CO$_2$ dissolved in the electrolyte. Conditions: THF/Bu$_4$NBF$_4$ (0.1 M), $v = 200$ mV s^{-1}, Au disk ($d = 2$ mm), 293 K. The turquoise curve represents the background cathodic scan of the electrolyte saturated with CO$_2$. Inset: CV of [Mo(CO)$_4$(bpy)] (1 mM) showing the reversible first reduction and irreversible second reduction. The anodic wave O2′ belongs to oxidation of [Mo(CO)$_3$(bpy)]$^{2-}$. Conditions: THF/Bu$_4$NPF$_6$ (0.1 M), $v = 200$ mV s^{-1}, Pt microdisc ($d = 0.42$ mm), 293 K.
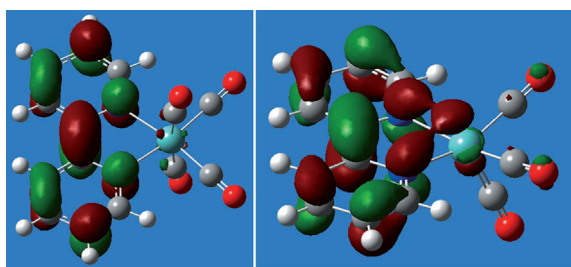
Figure 2. SOMO of [Mo(CO)$_4$(bpy)]$^{\cdot-}$ (left) and the HOMO of [Mo(CO)$_3$(bpy)]$^{2-}$ (right) calculated at the B3LYP/TZVP level of theory.

electrodes. Under nitrogen or argon the one-electron reduction of [Mo(CO)$_4$(bpy)] to [Mo(CO)$_4$(bpy)]$^{\cdot-}$ is reversible [see Table 1 (THF) and Table S1 (NMP), and also Figure 1 for the the R1/O1 couple, and Figures S1 and S2], with the added electron occupying the bpy-based SOMO (Figure 2, left). [Mo(CO)$_4$(bpy)] is thus reduced more negatively by ca. 0.5 V than the CO$_2$ catalyst precursor [Mn(CO)$_3$(bpy)Br] and by ca. 0.25 V than the dimer [Mn(CO)$_3$(bpy)]$_2$, forming [Mn(CO)$_3$(bpy)]$^-$.[5] The subsequent reduction of [Mo(CO)$_4$(bpy)]$^{\cdot-}$ to [Mo(CO)$_4$(bpy)]$^{2-}$ (Figure 1, cathodic wave R2, and Figures S1–S3) results in the appearance of a new anodic wave O2′ on the reverse scan (see Figure 1, inset and Figures S1 and S2) belonging to oxidation of the strongly π-delocalized five-coordinate dianion, [Mo(CO)$_3$(bpy)]$^{2-}$ (see the HOMO in Figure 2, right) resulting from the loss of a carbonyl ligand from [Mo(CO)$_4$(bpy)]$^{2-}$ (as supported by IR spectroelectrochemistry). At the potential of O2′ the five-coordinate radical anion, [Mo(CO)$_3$(bpy)]$^{\cdot-}$, rapidly recoordinates the carbonyl ligand and converts back to the tetracarbonyl radical [Mo(CO)$_4$(bpy)]$^{\cdot-}$.

The changes in the cyclic voltammogram of [Mo(CO)$_4$(bpy)] in THF at the gold disk cathode on the addition of CO$_2$ are shown in Figure 1. On the subsecond time scale the first reversible reduction producing [Mo(CO)$_4$(bpy)]$^{\cdot-}$ appears to be only mildly affected. However, strongly rising cathodic currents were measured in the potential range -2.1 V to -2.5 V, that is, beyond the cathodic wave R1 but significantly less negatively than the cathodic wave R2, pointing to electrocatalytic reduction of CO$_2$. Cyclic voltammograms of [Mo(CO)$_4$(bpy)] at a gold cathode measured in NMP/CO$_2$ (Figures S3 and S4) share the same general features as those in THF but the redox responses can be slightly more distorted, perhaps due to the viscosity of the NMP solutions. Importantly, using a platinum (or glassy carbon) cathode moves the catalytic reduction of CO$_2$ to the vicinity of the cathodic wave R2 both in THF and NMP (Figure S4).[13, 14]
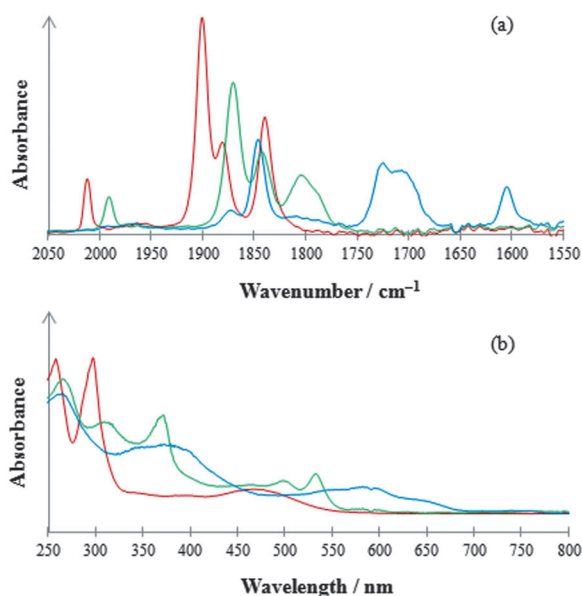
Similar redox responses as in Figure 1 and Figures S1–S4 were also observed in the cathodic cyclic voltammograms of [Cr(CO)$_4$(bpy)] (Figure S5) and [W(CO)$_4$(bpy)] (Figure S6) under comparable conditions. The detailed mechanistic study will be presented elsewhere.

The onset potential of the catalytic current in Figure 1 and Figure S3 coincides with the potential observed for the oxidation of [Mo(CO)$_3$(bpy)]$^{2-}$ to [Mo(CO)$_3$(bpy)]$^{\cdot-}$ (Tables 1 and S1). Thus, the catalytic reduction of CO$_2$ occurs close to a cathodic potential where the reduction of [M(CO)$_3$(bpy)]$^{\cdot-}$ to [M(CO)$_3$(bpy)]$^{2-}$ would be observed, pointing to the five-coordinate dianion as the catalyst. It is proposed that 1e⁻-reduced [M(CO)$_4$(bpy)]$^{\cdot-}$ exists in an equilibrium with a small (hardly observable) quantity of [M(CO)$_3$(bpy)]$^{\cdot-}$. Beyond -2.1 V the radical will be reduced to [M(CO)$_3$(bpy)]$^{2-}$, persisting in the vicinity of the cathodic surface. When CO$_2$ is dissolved in the solution it can be catalytically reduced by this small quantity of [M(CO)$_3$(bpy)]$^{2-}$. The alternative catalyst is a protonated 2e⁻-reduced species, [M(CO)$_4$(bpy-H)]$^-$, detected by IR spectro-electrochemistry. NMP may support the transient formation of [M(CO)$_3$(bpy)]$^{\cdot-}$, explaining the additional enhancement of the catalytic current observed in this solvent (Figure S3).

The cathodic current enhancement resulting from the catalysis can be readily observed in the chronoamperometric responses (Figure 3). The applied potential step (-2.2 V) corresponded to the onset of the catalytic current in Figure 1 and Figure S3. A very low current was observed for the CO$_2$-saturated NMP/Bu$_4$NBF$_4$ electrolyte. For the [Mo(CO)$_4$(bpy)] complex in the absence of CO$_2$ a moderate current was observed after the double-layer charging (≈ 20 μA, $t = 1$ s after the potential step); then upon returning to -1 V a re-oxidative current was seen. After CO$_2$ saturation of the [Mo(CO)$_4$(bpy)] solution in NMP the reductive step resulted in considerably higher currents than the combined current obtained for [Mo(CO)$_4$(bpy)] in the absence of CO$_2$ and the CO$_2$-saturated basis electrolyte, particularly in the later reductive steps. As seen from the lower re-oxidative currents observed for the catalyzed system when
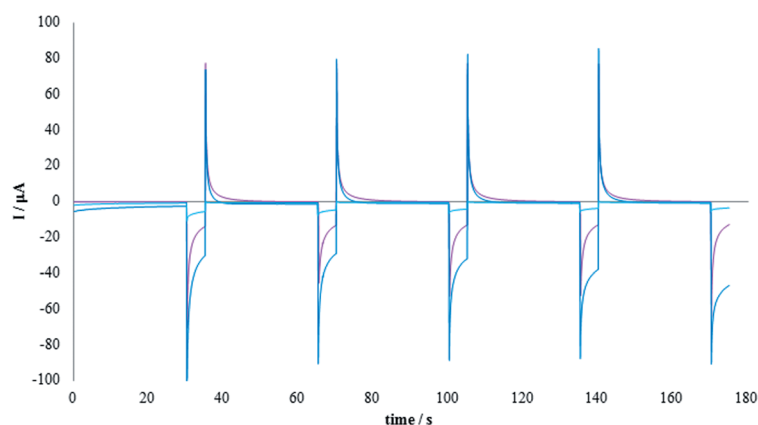
Figure 3. Multistep chronoamperograms showing direct CO_2 reduction (turquoise) and reduction of [Mo(CO)$_4$(bpy)] (0.5 mM) in the absence (pink) and presence (blue) of CO_2 in the electrolyte. Measurements were conducted in NMP/Bu$_4$NBF$_4$ (0.1 M) at a freshly polished Au disk ($d = 2$ mm) working electrode, Pt counter and Pt wire pseudo-reference electrode at room temperature and pressure. Potential stepped between -1.0 V vs Fc/Fc$^+$ where no redox reaction is observed for 30 s and -2.2 V for 5 s.

at 491 and 532 nm (Table 2) which signifies the presence of the reduced 2,2'-bipyridine ligand, [bpy]$^{•-}$.[15,16] These results confirm that the species produced is stable [Mo(CO)$_4$(bpy)]$^{•-}$. The reversible reduction to [Mo(CO)$_4$(bpy)]$^{•-}$ was also observed in NMP. Further reduction of [Mo(CO)$_4$(bpy)]$^{•-}$ in THF at R2 leads to the appearance of three intense ν(CO) bands characteristic for the formation of the five-coordinate dianion, [Mo(CO)$_3$(bpy)]$^{2-}$. Its electronic absorption spectrum shows a composed $\pi\pi^*$ absorption band in the visible spectral region (Table 2), similar to that observed for the analogous π-delocalized anion [Mn(CO)$_3$(bpy)]$^-$.[6] Reoxidation of [Mo(CO)$_3$(bpy)]$^{2-}$ at -2.32 V (O2') gave back [Mo(CO)$_4$(bpy)]$^{•-}$.

A second species with ν(CO) peaks at slightly larger wavenumbers than those of [Mo(CO)$_4$(bpy)]$^{•-}$ was also observed during the reduction of [Mo(CO)$_4$(bpy)]$^{•-}$ in THF. In NMP, this tetracarbonyl secondary species was the major product upon the reduction of

Figure 4. a) IR and b) UV/Vis spectroelectrochemistry in THF/Bu$_4$NPF$_6$ (0.3 M) within an OTTLE (optically transparent, thin-layer electrochemical) cell showing [Mo(CO)$_4$(bpy)] (red), [Mo(CO)$_4$(bpy)]$^{•-}$ (green), and [Mo(CO)$_3$(bpy)]$^{2-}$ (blue).

Table 2. IR and UV/Vis absorption of [M(CO)$_4$(bpy)] (M = Cr, Mo, W) and their reduction products in THF, unless stated otherwise.

Complex	ν(CO) [cm^{-1}]	λ_{max} [nm]
[Cr(CO)$_4$(bpy)]	2007, 1897, 1884, 1837	243, 297, 332, 503
[Mo(CO)$_4$(bpy)]	2012, 1900, 1882, 1840	258, 297, 393, 462
[W(CO)$_4$(bpy)]	2005, 1888, 1879, 1837	253, 298, 362, 473
[Cr(CO)$_4$(bpy)]$^{•-}$	1988, 1869, 1844, 1800	244, 340, 367, 473, 504, 536
[Mo(CO)$_4$(bpy)]$^{•-}$	1991, 1871, 1843, 1805	260, 306, 366, 463, 491, 532
[W(CO)$_4$(bpy)]$^{•-}$	1984, 1857, 1834, 1800	256, 302, 370, 461, 488, 523
[Cr(CO)$_4$(bpy-H)]$^{-}$[a]	1990, 1870, 1847, 1799	250, 351, 397, 518
[Mo(CO)$_4$(bpy-H)]$^{-}$[a]	1994, 1874, 1848, 1807	265, 304, 396, 509
[W(CO)$_4$(bpy-H)]$^{-}$[a]	1988, 1854, 1835, 1796	260, 297, 352, 393, 523
[Cr(CO)$_3$(bpy)]$^{2-}$	1829, 1710, 1695	259, 382, 583, 629
[Mo(CO)$_3$(bpy)]$^{2-}$	1846, 1725, 1706	258, 369, 580, 644
[W(CO)$_3$(bpy)]$^{2-}$	1838, 1713, 1701	259, 381, 538, 621

[a] The presented values were recorded in NMP where this species was a major product of the reduction of [M(CO)$_4$(bpy)]$^{•-}$.

compared to that seen for the pure [Mo(CO)$_4$(bpy)] response, the quantity of [Mo(CO)$_4$(bpy)] electrochemically regenerated from [Mo(CO)$_4$(bpy)]$^{•-}$ is lower. This is in keeping with an electro-catalytic mechanism.

IR and UV/Vis spectroelectrochemistry was used to confirm the assignments of the reduced species and to identify which of them may be involved in the catalytic reduction of CO_2. The reduction path of [Mo(CO)$_4$(bpy)] in THF/TBAPF$_6$ is presented in Figure 4. IR spectroelectrochemistry shows the ν(CO) bands shift to smaller wavenumbers upon 1e$^-$ reduction at R1 (see Table 2) while retaining the same band pattern. UV/Vis monitoring shows the appearance of a bifurcated absorption band

[Mo(CO)$_4$(bpy)]$^{•-}$ (Table 2, Figure S7). The ν(CO) band pattern and wavenumbers point to a tetracarbonyl anion. The thin-layer CV recorded in NMP reveals that this species is oxidized at a less negative potential than [Mo(CO)$_4$(bpy)]$^{•-}$. Its UV/Vis spectrum (Table 2, Figure S8) does not feature the bifurcated peak typical for the [bpy]$^{•-}$ ligand. However, it shows an intense absorption at $\lambda_{max} = 393$ nm indicative of a 2,2'-bipyridine anion. Based on these data, we assume that the species arises from the reaction of [M(CO)$_3$(bpy)]$^{2-}$ at the formally 2e$^-$-reduced 2,2'-bipyridine ligand with a proton source in the solution. The resulting anionic species then rapidly recoordinates the released carbonyl ligand to give [M(CO)$_4$(bpy-H)]$^-$. The difference in the behavior between THF and NMP most likely result from a higher moisture content in NMP, or from an interaction between the solvent and the reduced species.[16]

IR spectroelectrochemistry was also carried out in a solution saturated with CO_2. The smooth reduction of [Mo(CO)$_4$(bpy)] to [Mo(CO)$_4$(bpy)]$^{•-}$ was observed in both THF and NMP on both

Pt and Au minigrid working electrodes, with no significant evidence for catalytic reduction of CO_2. When the cathodic potential was set at just about 150 mV beyond the cathodic wave of the parent complex there was an apparent increase in the cathodic current accompanied by a decrease in the $^{13}CO_2$ satellite peak at 2272 cm^{-1}. The concurrent disappearance of the $[Mo(CO)_4(bpy)]^{\cdot-}$ $\nu(CO)$ bands was accompanied by the appearance of several new, presently yet unassigned $\nu(CO)$ bands (Figures S9–S11). No $\nu(CO)$ bands due to $[Mo(CO)_3(bpy)]^{2-}$ were observed. Remarkably, the catalysis appeared to be by far most effective (fastest) in the NMP solution when using a gold minigrid working electrode (Figure S11). CO bubbles were formed at the working electrode surface and absorption due to Au-adsorbed CO was seen to rise at 2130 cm^{-1}. IR spectroscopic evidence for other carbonyl species produced by the reduction of CO_2 could not be gained due to NMP absorption below 1700 cm^{-1}, but in THF peaks were observed around 1675 and 1640 cm^{-1}, corresponding to subordinate bicarbonate which often accompanies CO formation. A similar catalytic behavior was also observed for $[Cr(CO)_4(bpy)]$ and $[W(CO)_4(bpy)]$.

The catalytic process in NMP was also investigated using in situ EPR spectroscopy. The potential applied (-2.2 V) corresponded to the complete first reduction of $[Mo(CO)_4(bpy)]$, with the EPR signal of $[Mo(CO)_4(bpy)]^{\cdot-[8]}$ rising rapidly (Figure S12). Under CO_2, however, the radical anion was no longer detectable.

In summary, Group 6 complexes of the type $[M(CO)_4(bpy)]$ are capable of behaving as electrochemical catalysts for the reduction of CO_2 at potentials less negative than those of the reduction of $[M(CO)_4(bpy)]^{\cdot-}$. The appearance of the catalytic current already around the electrode potential where $[M(CO)_3(bpy)]^{2-}$ is oxidized strongly suggests that this five-coordinate dianion is the active catalyst, similar to $[Mn(CO)_3(bpy)]^-$.[5a,b,14] The catalytic conversion is significantly more efficient in NMP compared to THF, which may reflect easier CO dissociation from $[M(CO)_4(bpy)]^{\cdot-}$ in the former solvent. The role of $[M(CO)_4(bpy-H)]^-$ in the catalytic cycle remains to be unraveled. The enhanced catalysis using an Au working electrode is remarkable, suggesting that surface interactions may play an important role, too. Despite the relatively high cathodic potentials needed to trigger the catalytic process, this class of complexes would be of more than academic interest if they were also capable of being used as part of a photocatalytic system for CO_2 reduction. Optimization of electrode surface, coordination chemistry and solvent will be used to further improve the electrocatalytic properties of this class of compounds.

Experimental Section

All experimental and computational details are presented in the Supporting Information.

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[13] In the course of completing this manuscript, Kubiak and co-workers [14] published the first concise report on the electrocatalytic reduction of CO_2 with the complexes [M(CO)$_4$(R-bpy)] (M = Mo, W; R = H, *t*Bu) in THF at Pt and GC working electrodes. In full agreement with our results, only a moderate catalytic activity was observed under these conditions at the cathodic wave R2 (sensu Figure 1) where the catalyst [M(CO)$_3$(R-bpy)]$^{2-}$ is generated on the 1e$^-$ reduction of the stable tetracarbonyl radical anions formed at the cathodic wave R2. Our results obtained in this work at gold cathodes (in particular in NMP) show a strong catalyt-

ic activity already at the less negative hypothetical cathodic wave R2′, which corresponds to the reduction of partially stabilized tricarbonyl radical anions.

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