Inorganic Chemistry Communications 61 (2015) 221–224

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

Redox properties of a bis-pyridine rhenium carbonyl derived from an anthracene scaffold

Taylor A. Manes, Michael J. Rose *

The University of Texas at Austin, Austin, TX 78712, United States

ARTICLE INFO

Article history:
Received 21 September 2015
Accepted 8 October 2015
Available online 13 October 2015

Keywords:
Rhenium
Electrochemistry
Redox
Scaffold
X-ray
NMR

ABSTRACT

We report the synthesis of a novel bis-pyridine chelate derived from an anthracene scaffold. Complexation of the N2 ligand with rhenium carbonyl affords the Re tricarbonyl bromide complex [(Anth-N2)Re$(CO)_3$Br]. In THF solution, the title complex exhibits two quasi-reversible reductions located near −2.1 and −2.5 V vs Fc/Fc^+, which are similar to those observed in the free Anth-N2 ligand, suggesting the non-innocent behavior of the complexed anthracene scaffold. Under CO_2 atmosphere, the title complex exhibits an electrocatalytic response consistent with $CO_2 \rightarrow CO$ reduction, and the presence of electrocatalytically generated CO was confirmed by bulk electrolysis. These results suggest that alternate locations of redox activity (other than at the Re metal center, pyr donors, or bpy framework) can lead to interesting electrochemical behavior.

Communication

In an ideal energy utilization paradigm, the carbon dioxide (CO_2) produced by biological and industrial processes would be balanced with the CO_2 consumed by biological processes and industrial needs [1–5]. With industrial processes increasing in size and output, and global population continually growing, the amount of CO_2 in the atmosphere continues to increase and climate change continues to be a pressing issue in science and society. To be a viable contributor to a 'greener' energy landscape, a renewable energy source must be able to produce large quantities of electricity or fuel and have long term storage capabilities [6]. Wind power and solar power produce large amounts of electricity but only intermittently and do not have sustainable long term storage options and since grid storage is not available there is a trade-off between batteries and supercapacitors. Batteries have a high energy density but limited lifetimes, and supercapacitors have low energy density [7]. A solution to this problem would be chemical storage. The combination of processes such as water oxidation, hydrogen generation, solar power, and CO_2 reduction could produce an artificial photosynthetic device to generate a carbon neutral fuel source [8]. Such a CO_2 to CO process could be beneficial for production of syngas, but direct reduction to methanol is preferable to generate liquid fuels [9–12]. Current challenges to the electrochemical reduction of CO_2 include large overpotentials [13] and poor selectivity [14]. Thus on the molecular catalyst front, the focus of much recent work has been to address both the efficiency and selectivity of the catalytic process for $CO_2 \rightarrow CO$ conversion by employing new modifications to the catalytic system by means of ionic liquids [15,16], as well as employing novel ligand designs to support rhenium and other metal centers for electrocatalysis.

Rhenium bis-pyridine carbonyl complexes (see Fig. 1) have become the 'gold standard' for the CO_2 reduction catalysts due to their high turnover rates, turnover numbers and faradaic efficiencies [1,8,20]. Lehn et al. [17] studied the reduction of CO_2 to CO using the [*fac*-(bpy)Re$(CO)_3$Cl] catalyst that has since been the focus of many studies regarding the mechanism elucidation and selectivity optimization during the catalytic process. More recently Kubiak et al. [21] reported several common degradation pathways in the catalytic process, one of which is the formation of the Re_2 dimer, which occurs slowly once the halide is reductively eliminated from the metal center. To solve this problem, more recent work from the same group has successfully employed the use of bulky substituents at the 2 and 2′ positions on the bipyridine framework [12]. Substitution studies have been performed related to Re-bpy complexes to determine if similar catalysis occurs upon modulating the strength of the ligand field [9]. However, there are presently no reports that investigate the effect of orientation of the pyridine donors (with respect to the equatorial plane of the Re center), nor are there reports regarding alternate modes of displaying the bidentate array of pyridine donors. In this Communication, we report an isoelectronic bis-pyridine Re carbonyl complex with interesting, non-innocent redox features that may participate in the $CO_2 \rightarrow CO$ conversion process.

The synthesis of the bis-pyridine ligand was performed in three steps (see Scheme 1). Starting from 1,8-dichloroanthraquinone, successive reductions using $NaBH_4$ afforded 1,8-dichloroanthracene in good yields [22,23]. Suzuki coupling catalyzed by XPhos/[Pd$(dba)_2$] with

---

* Corresponding author.
E-mail address: mrose@cm.utexas.edu (M.J. Rose).

http://dx.doi.org/10.1016/j.inoche.2015.10.012
1387-7003/

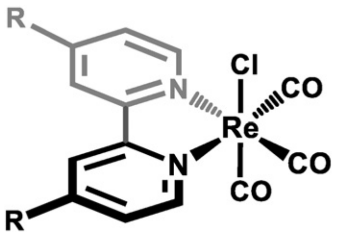


Fig. 1. The original Lehn catalyst [17] [Re(bpy)(CO)$_3$Cl] with 4,4′ **R** group substitutions related to recent reports [18,19].

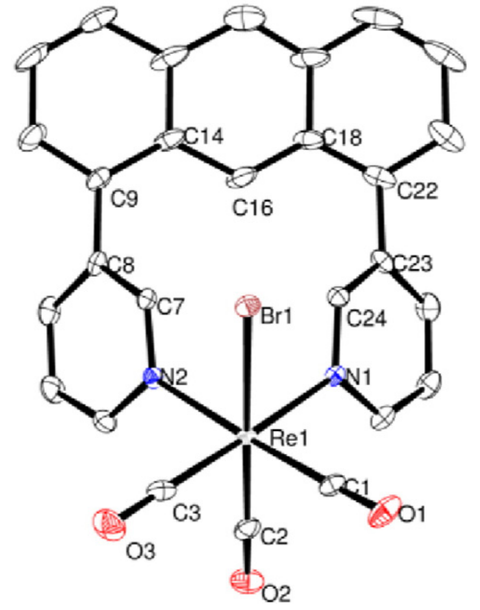


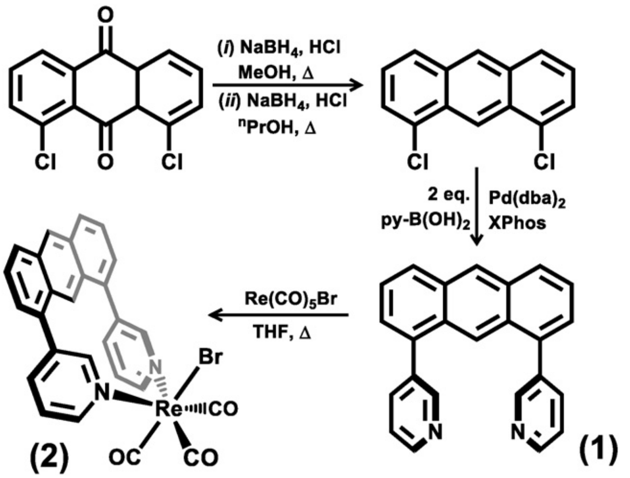
Fig. 2. ORTEP diagram (30% ellipsoids) of the molecular structure of [Re(Anth-N2)(CO)$_3$Br] (**2**); H atoms have been omitted for clarity. Selected bond distances (Å): $Re_1–N_1 = 2.247(3)$, $Re_1–N_2 = 2.242(3)$, $Re_1–C_1 = 1.931(4)$, $Re_1–C_2 = 1.922(5)$, $Re_1–C_3 = 1.923(5)$, $C_1–O_1 = 1.138(5)$, $C_2–O_2 = 1.115(5)$, $C_3–O_3 = 1.135(5)$. Selected angles (deg): $N_1–Re_1–N_2 = 87.23(12)$, $N_1–Re_1–C_1 = 92.52(15)$, $N_2–Re_1–C_3 = 89.91(15)$, $C_1–Re_1–C_3 = 90.32(18)$. Selected torsion angles (deg): $C_7–C_8–C_9–C_{14} = 48.2(6)$, $C_{18}–C_{22}–C_{23}–C_{24} = 48.0(6)$.

two equivalents of 3-pyridinyl boronic acid in THF/H_2O generated the final product, Anth-N2 (**1**), in 80% yield as a yellow powder.

Under inert atmosphere, a 1:1 mixture of Anth-N2 and [Re(CO)$_5$Br] was heated in THF (Scheme 1) to afford pure product as a bright yellow powder in good yield (48%). The infrared spectrum of the product confirmed formation of the $\{Re(CO)_3\}^+$ moiety, evidenced by bound CO features at 2025, 1886, and 1872 cm^{-1}. The CO stretches observed in **2** coincide reasonably with the stretches seen at 2019 and 1907 cm^{-1} in the Re(bpy) congeners.

Yellow needles of [(Anth-N2)Re(CO)$_3$Br] (**2**) were grown using vapor effusion of a DCM solution of the complex into *n*-hexane, and the resulting crystal structure is depicted in Fig. 2. The binding of the Re tricarbonyl fragment to the Anth-N2 is analogous to that of the Re-bpy family of complexes. A key difference in the present complex is the torsion angles exhibited by the pyridine donors. The anthracene-appended pyridine donors are displaced from the plane of the anthracene backbone and when complexed with the Re carbonyl fragment the torsion ranges from 45.0–48.1°. The close positioning of the donor atoms promotes the *cis* binding motif rather than a *trans* orientation, and this facilitates sufficient rotation of the pyridine moiety for monometallic binding. The bite angle of the Anth-N2 ligand is 86.9° compared to the more acute ~75° reported in Re(bpy) complexes. The Re–N distances of 2.247(3) and 2.242(3) Å are similar to the ~2.20 Å distances seen in the Re(bpy) system [24].

Electrochemical studies were performed on **1** (N2 ligand) and **2** (Re complex) to determine their redox activities. The cyclic voltammogram of the free ligand **1** (Fig. 3, black line) exhibits two quasi-reversible features −2.20 and −2.64 V vs Fc/Fc$^+$. The cyclic voltammogram of **2** (Fig. 3, red line) exhibits similar reversible features at −2.10 and −2.58 V vs Fc/Fc$^+$ that are quite similar to those of the free ligand. The peak currents in the CV follow a scan rate dependence that is linear with $\sqrt{\nu}$ (insets, Figs. 3 and 4). The more positive features in the CVs of both the free ligand and the rhenium complex show redox events similar to that reported for anthracene [25]. For comparison, a cyclic voltammogram of 1,8-dichloroanthracene was obtained (Fig. 3, gray line; and Fig. S3, supporting information). A single redox event at −2.23 V vs Fc/Fc$^+$ occurs, suggesting that the more positive peaks observed for free ligand and metal complex emanate from an anthracene-based redox event. The more negative peak that occurs in the free ligand and metal complex is not observed for 1,8-dichloroanthracene, suggesting that the feature is due to a pyridine-based redox event. Rhenium-based redox events were not observed. The more negative wave observed in the CV of free ligand **1** exhibits greater irreversibility ($i_{pa}/i_{pc} = 0.39$),



Scheme 1. Synthesis of the ligand Anth-N2 (**1**) and the corresponding complex [(Anth-N2)Re(CO)$_3$Br] (**2**).

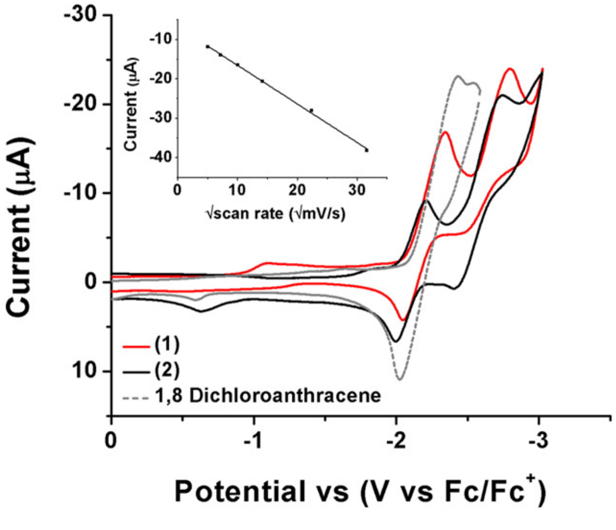


Fig. 3. Cyclic voltammograms of 1 mM 1,8-dichloroanthracene (line), (Anth-N2) (**1**, black line) and [(Anth-N2)Re(CO)$_3$Br] (**2**, red line) in THF with 0.1 M TBAPF$_6$ as supporting electrolyte under N_2 atmosphere. *Inset*: scan rate dependence of the reversible reduction wave of (**1**) at −2.34 V. *Experiment conditions*: scan rate, 100 mV/s; WE, glassy carbon (3 mm); CE, Pt wire; Re, Ag wire pseudo-reference; all potentials were converted to Fc/Fc$^+$ by inclusion of Fc in the final scan (not shown).

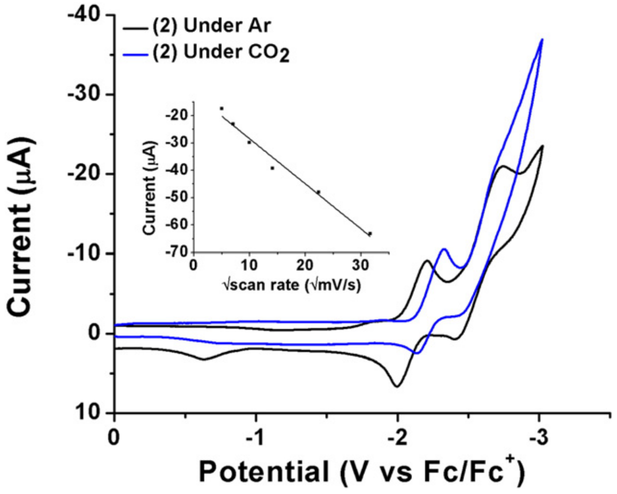


Fig. 4. Cyclic voltammograms of 1 mM [(Anth-N2)Re(CO)$_3$Br] (**2**) under argon (black line) or CO_2 (blue line) in THF with 0.1 M TBAPF$_6$ as supporting electrolyte. *Inset*: scan rate dependence of the reversible reduction wave of (**2**) at −2.74 V. *Experiment conditions*: scan rate, 100 mV/s; WE, glassy carbon (3 mm); CE, Pt wire; RE, Ag wire pseudo-reference; all potentials were converted to Fc/Fc$^+$ by inclusion of Fc in the final scan (not shown).

compared to the analogous redox process in the Re complex **2** ($i_{pa}/i_{pc} = 0.72$). This change in reversibility may indicate enhanced electronic communication between two pendant pyridine moieties due to the conjoining Re metal center.

Given the novel redox properties of **2** compared with Re-bpy complexes, CV experiments were performed under CO_2 atmosphere (Fig. 4). First, a shift of the peak near −2.12 V to a more negative potential of −2.24 V vs Fc/Fc$^+$ is observed. Second, a marked increase in current is observed at −2.62 V vs Fc/Fc$^+$, along with a complete loss of reversibility. Both of these features are hallmarks of electrocatalytic CO_2 reduction by a molecular catalyst of this type [8,26]. This phenomenon provided a sound basis to continue the investigation by controlled potential electrolysis (CPE).

Bulk electrolysis experiments under CO_2 (1 atm) were carried out in a two compartment H-cell cell with a glassy carbon rod working electrode, platinum mesh counter electrode, and Ag wire reference electrode. The silver electrode was further separated with a vycor tip. For comparison, the widely accepted [Re(bpy)(CO)$_3$Br] complex (FY ≈ 95%) [16–18,26] was standardized in the above apparatus (−2.1 V vs Ag for 1.5 h) in a CO_2 saturated MeCN solution with GC headspace analysis directly after the electrolysis. As reported previously, the presence or absence of MeOH did not greatly affect the $CO_2 \rightarrow CO$ conversion efficiency for the Re(bpy) system [26].

In contrast, the title Re complex **2** was strongly affected by the presence of MeOH. The production of CO by **2** by CPE (−2.5 V vs Ag, 1.5 h) in a CO_2 saturated THF solution (~0.5 M TBAPF$_6$), was first analyzed in the absence of a proton source yielding *no production of CO*. In contrast, addition of 10 M MeOH (40% *v*/*v*), complex **2** produced 0.57 μmol of CO, corresponding to 20% Faradaic efficiency. The sub-optimal efficiency (compared to the Re-bpy system) may be due to a lack of facile electronic communication between the two pyridine moieties (not co-planar, and no direct C–C bond) compared with the standard Re-bpy complexes. The bpy system is known to be a highly efficient electron sink for multiple electron processes [8,27]. The conjugated π system of the co-planar bpy allows for greater delocalization of the electron (compared to more angled pyridines on the anthracene scaffold), and the alignment with the Re d_π orbitals may allow for facile movement back to the metal center. Lastly, the anthracene electron reservoir may be too geometrically far from the metal center to act as an efficient electron transfer agent during catalysis.

In conclusion, we have constructed a novel anthracene scaffold that displays a *meta*-linked, *cis*-coordinating bis-pyridine motif in alternate fashion compared to the standard bpy ligand. The Anth-N2 ligand supports a stable Re tricarbonyl complex, which exhibits redox behavior not unlike the free ligand. The observed potentials suggest that the anthracene moiety is redox active, but not directly involved in the electrocatalysis. Compared to the 'gold standard' Re(bpy) system, the present system exhibits an inefficiency that may be due to the distance from the metal center to the scaffold, and/or a break in conjugation between the ligating pyridine moieties. Future work will endeavor to better align the redox features of the supporting scaffold and the catalytically active event, with the aim of elaborating the scope and efficiency of available multi-electron transformations. Enhancing the rotational flexibility of the pyridine moieties may also lead to better orbital overlap with the metal center.

Acknowledgments

The authors gratefully acknowledge funding from the Robert A. Welch Foundation (F-1822), the ACS Petroleum Research Fund (53542-DN13) and the US Office of Naval Research (N00014-13-10530). We also thank Prof Allen Oliver (Notre Dame Univ) and Prof Jeanette Krause (Univ of Cincinnati) for the X-ray data collection at the Advanced Light Source, and we acknowledge Dr. Vince Lynch for the assistance with analysis of single crystal X-ray diffraction data. Crystallographic data for **2** were collected through the SCrALS (Service Crystallography at the Advanced Light Source) program at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.10.012.

References

[1] J. Qiao, Y. Liu, F. Hong, J. Zhang, A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels, Chem. Soc. Rev. 43 (2014) 631–675, http://dx.doi.org/10.1039/c3cs60323g.

[2] J.S. Sawyer, Man-made carbon dioxide and the "Greenhouse" effect, Nature 239 (1972) 23–26, http://dx.doi.org/10.1038/239023a0.

[3] T. Volk, The World's Greatest Environmental Challenge, The MIT Press, Cambridge, Massachusetts, 2008.

[4] G.A. Olah, A. Goeppert, G.K.S. Prakash, Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons, J. Org. Chem. 74 (2009) 487–498, http://dx.doi.org/10.1021/jo801260f.

[5] N.S. Spinner, J.A. Vega, W.E. Mustain, Recent progress in the electrochemical conversion and utilization of CO2, Catal, Sci. Technol. 2 (2012) 19, http://dx.doi.org/10.1039/c1cy00314c.

[6] C. Riplinger, M.D. Sampson, A.M. Ritzmann, P. Kubiak, E.A. Carter, Mechanistic contrasts between manganese and rhenium bipyridine electrocatalysts for the reduction of carbon dioxide, J. Am. Chem. Soc. 136 (2014)http://dx.doi.org/10.1021/ja508192y (16285–16298).

[7] P. Simon, Y. Gogotsi, B. Dunn, Where do batteries end and supercapacitors begin? Sci. Mag. 343 (2014) 1210–1211, http://dx.doi.org/10.1126/science.1249625.

[8] J.A. Keith, K.A. Grice, C.P. Kubiak, E.A. Carter, Elucidation of the selectivity of proton-dependent electrocatalytic CO_2 reduction by fac-Re(bpy)(CO)3Cl, J. Am. Chem. Soc. 135 (2013) 15823–15829, http://dx.doi.org/10.1021/ja406456g.

[9] M.V. Vollmer, C.W. Machan, M.L. Clark, W.E. Antholine, J. Agarwal, H.F.S. Iii, et al., Synthesis, spectroscopy, and electrochemistry of (α-Diimine)M(CO) 3 Br, M=Mn, Re, complexes: ligands isoelectronic to bipyridyl show differences in CO_2 reduction, Organometallics 34 (2015) 3–12, http://dx.doi.org/10.1021/om500838z.

[10] A.Y. Khodakov, W. Chu, P. Fongarland, Advances in the development of novel cobalt Fischer–Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels, Chem. Rev. 107 (2007) 1692–1744, http://dx.doi.org/10.1021/cr050972v.

[11] Y. Tamaki, T. Morimoto, K. Koike, O. Ishitani, Photocatalytic CO_2 reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes, Proc. Natl. Acad. Sci. 109 (2012) 15673–15678, http://dx.doi.org/10.1073/pnas.1118336109.

[12] M.D. Sampson, A.D. Nguyen, K.A. Grice, C.E. Moore, A.A.L. Rheingold, C.P. Kubiak, Manganese catalysts with bulky bipyridine ligands for the electrocatalytic reduction of carbon dioxide: eliminating dimerization and altering catalysis, J. Am. Chem. Soc. 136 (2014) 5460–5471, http://dx.doi.org/10.1021/ja501252f.

[13] R.J. Haines, R.E. Wittrig, C.P. Kubiak, Electrocatalytic reduction of carbon dioxide by the binuclear copper complex [Cu2(6-(diphenylphosphino)-2,2′-bipyridyl)2(MeCN)2][PF6]2, Inorg. Chem. 33 (1994) 4723–4728, http://dx.doi.org/10.1021/ic00099a024.

[14] M. Bourrez, F. Molton, S. Chardon-Noblat, A. Deronzier, [Mn(bipyridyl)(CO)3Br]: an abundant metal carbonyl complex as efficient electrocatalyst for CO_2 reduction, Angew. Chem. Int. Ed. 50 (2011) 9903–9906, http://dx.doi.org/10.1002/anie.201103616.

[15] D.C. Grills, Y. Matsubara, Y. Kuwahara, S.R. Golisz, D.A. Kurtz, B.A. Mello, Electrocatalytic CO_2 reduction with a homogeneous catalyst in ionic liquid: high catalytic activity at low overpotential, J. Phys. Chem. Lett. 5 (2014) 2033–2038, http://dx.doi.org/10.1021/jz500759x.

[16] M. Alvarez-Guerra, J. Albo, E. Alvarez-Guerra, A. Irabien, Ionic liquids in the electrochemical valorisation of CO_2, Energy Environ. Sci. 8 (2015) 2574–2599, http://dx.doi.org/10.1039/C5EE01486G.

[17] J. Hawecker, J.-M. Lehn, R. Ziessel, Electrocatalytic reduction of carbon dioxide mediated by Re(bipy)(CO)3Cl (bipy=2,2?-bipyridine), J. Chem. Soc. Chem. Commun. 984 (1984) 328, http://dx.doi.org/10.1039/c39840000328.

[18] J.M. Smieja, C.P. Kubiak, Re(bipy-tBu)(CO)3Cl-improved catalytic activity for reduction of carbon dioxide: IR-spectroelectrochemical and mechanistic studies, Inorg. Chem. 49 (2010) 9283–9289, http://dx.doi.org/10.1021/ic1008363.

[19] C.W. Machan, M.D. Sampson, S.A. Chabolla, T. Dang, P. Kubiak, Developing a mechanistic understanding of molecular electrocatalysts for CO_2 reduction using infrared spectroelectrochemistry, Organometallics 33 (2014) 4550–4559, http://dx.doi.org/10.1021/om500044a.

[20] C.W. Machan, C.J. Stanton, J.E. Vandezande, G.F. Majetich, H.F. Schaefer, C.P. Kubiak, et al., Electrocatalytic reduction of carbon dioxide by Mn(CN)(2,2′-bipyridine)(CO) 3 : CN coordination alters mechanism, Inorg. Chem. 2 (2015)http://dx.doi.org/10.1021/acs.inorgchem.5b01715.

[21] E.E. Benson, C.P. Kubiak, Structural investigations into the deactivation pathway of the CO_2 reduction electrocatalyst Re(bpy)(CO)3Cl, Chem. Commun. 48 (2012) 7374, http://dx.doi.org/10.1039/c2cc32617e.

[22] M. Goichi, K. Segawa, S. Suzuki, S. Toyota, Improved synthesis of 1,8-diiodoanthracene and its application to the synthesis of multiple phenylethynyl-substituted anthracenes, Synthesis-Stuttgart (2005) 2116–2118, http://dx.doi.org/10.1055/s-2005-869999.

[23] M. Pérez-Trujillo, I. Maestre, C. Jaime, A. Alvarez-Larena, J.F. Piniella, A. Virgili, Enantioselective preparation and structural and conformational analysis of the chiral solvating agent α,α′-bis(trifluoromethyl)-1,8-anthracenedimethanol, Tetrahedron Asymmetry 16 (2005) 3084–3093, http://dx.doi.org/10.1016/j.tetasy.2005.08.005.

[24] B.J. Liddle, S.V. Lindeman, D.L. Reger, J.R. Gardinier, A thallium mediated route to σ-arylalkynyl complexes of bipyridyltricarbonylrhenium(I), Inorg. Chem. 46 (2007) 8484–8486, http://dx.doi.org/10.1021/ic701406y.

[25] A.J. Bard, L.A. Faulkner, Wiley: Electrochemical Methods: Fundamentals and Applications, 2nd Edition Wiley, 2001.

[26] J.M. Smieja, E.E. Benson, B. Kumar, K.A. Grice, C.S. Seu, A.J.M. Miller, et al., Kinetic and structural studies, origins of selectivity, and interfacial charge transfer in the artificial photosynthesis of CO, Proc. Natl. Acad. Sci. 109 (2012) 15646–15650, http://dx.doi.org/10.1073/pnas.1119863109/-/DCSupplemental.www.pnas.org/cgi/doi/10.1073/pnas.1119863109.

[27] G. Sahara, O. Ishitani, Efficient photocatalysts for CO_2 reduction, Inorg. Chem. 54 (2015) 5096–5104, http://dx.doi.org/10.1021/ic502675a.