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FINAL REPORT

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**HOMOGENEOUS SOLUTION ELECTROCATALYSTS FOR CO₂
REDUCTION**

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HOMOGENEOUS SOLUTION ELECTROCATALYSIS FOR CO₂ REDUCTION

ONR Final Report

The goal of the research funded by this grant was to develop new electrocatalysts for CO₂ reduction, and to probe the fundamental mechanisms of the steps that lead to the reduction of CO₂. As the title suggests, this initially involved the synthesis of soluble transition metal complexes. More recently, the inability of the homogeneous catalysts to reduce CO₂ past the two-electron stage, and the results of mechanistic studies, led us to investigate heterogeneous systems that could access more than two electron equivalents.

Our initial investigations led to the preparation of polypyridyl complexes of ruthenium, osmium, rhenium, iridium, and rhodium. These complexes, of the general formula $[M(\text{bpy})_2\text{LL}]^{n+}$, were shown to be effective electrocatalysts for the reduction of CO₂ to CO and/or formate, and the results have been reported in technical reports 1, 2, 3, and 4. These homogeneous systems proved amenable to mechanistic studies, and considerable mechanistic insight was obtained. Technical reports 5 and 6 cover the development of new techniques that aided in the study of reactive intermediates and multimetallic complexes, both of which were necessary for the mechanistic work. Technical reports 2 and 9 discuss the reduction of CO₂ by $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}]^+$, in which the mechanism involves the electrochemically-induced insertion of CO₂ into the Ru-H bond and the electrochemically-induced reformation of the hydride. A subsequent study of $\text{cis-}[\text{Os}(\text{bpy})_2(\text{CO})\text{H}]^+$ showed that, unlike the ruthenium analog, the Os complex reduced CO₂ by a mechanism involving associative attack by CO₂ on the twice-reduced catalyst.

Our more recent investigations, such as that covered in technical report 8, have shown that Rh and Pd metal particles deposited in polymer films can electrochemically reduce CO₂ to C₁-C₄ products. Similarly, electrode surfaces modified with ruthenium polypyridyl clusters were also shown to reduce CO₂ to multielectron products such as methane and ethylene. These results signal the ability of multimetallic complexes to give CO₂ reduction product distributions similar to that seen for Fischer-Tropsch systems. This shows that these catalysts have the ability to carry out electrochemically-driven F-T type reactions where CO is replaced with the more soluble CO₂, and H₂ is replaced with proton/electron steps under ambient conditions.



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Technical Reports:

1. "Electrocatalytic Reduction of Carbon Dioxide using Metal Cluster Compounds" Bruce, M. R. M.; Pugh, J. R., Sullivan, B. P.; Meyer, T. J.
2. "Electrochemically-Induced CO₂ Insertion and Metal Hydride Formation" Bruce, M. R. M.; Pugh, J. R.; Sullivan, B. P.; Meyer, T. J.
3. "Electrocatalytic Reduction of Carbon Dioxide by 2,2'-Bipyridine Complexes of Rhodium and Iridium" Bolinger, C. M.; Story, N.; Sullivan, B. P.; Meyer, T. J.
4. "Synthesis of New Bipyridine Complexes of Re(I). CO₂ Reduction and Related Chemistry." Silliman, S.; Thorp, H. H.; Meyer, T. J.; Sullivan, B. P.
5. "Thermodynamics of Kinetically Irreversible Organometallic Processes. Metal-Metal Bonds." Pugh, J. R.; Meyer, T. J.
6. "1,2-Difluorobenzene. A Relatively Inert and Noncoordinating Solvent for Electrochemical Studies on Transition Metal Complexes." O'Toole, T. R.; Younathon, J. N.; Sullivan, B. P.; Meyer, T. J.
7. "Electrocatalytic Reduction of CO₂ by Thin Polymeric Films Containing Metallic Rhodium." O'Toole, T. R.; Sullivan, B. P.; Meyer, T. J.
8. "The Formation of a Metal Hydride Bond and the Insertion of CO₂. Key Steps in the Electrocatalytic Reduction of Carbon Dioxide to Formate." Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J.

Papers Submitted to Refereed Journals:

1. "Electrocatalytic Reduction of Carbon Dioxide by 2,2'-Bipyridine Complexes of Rhodium and Iridium" Bolinger, C. M.; Story, N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4582.
2. "Synthesis of New Bipyridine Complexes of Re(I). CO₂ Reduction and Related Chemistry." Silliman, S.; Thorp, H. H.; Meyer, T. J.; Sullivan, B. P. Submitted to *Inorg. Chem.*
3. "Thermodynamics of Kinetically Irreversible Organometallic Processes. Metal-Metal Bonds." Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 8245.
4. "1,2-Difluorobenzene. A Relatively Inert and Noncoordinating Solvent for Electrochemical Studies on Transition Metal Complexes." O'Toole, T. R.; Younathon, J. N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 3923.
5. "Reduction of Carbon Dioxide With Platinum Metal Electrocatalysts." Sullivan, B. P. *Platinum Metals Rev.* **1989**, *33*, 2.
6. "Electrocatalytic Reduction of CO₂ by Thin Polymeric Films Containing Metallic

Rhodium." O'Toole, T. R.; Sullivan, B. P.; Meyer, T. J. *Chem. of Materials*, **1989**, *1*, 574.

7. "The Formation of a Metal Hydride Bond and the Insertion of CO₂. Key Steps in the Electrocatalytic Reduction of Carbon Dioxide to Formate Anion." Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.*, **1991**, *30*, 86.

Papers in Preparation:

1. "Thermodynamics of Redox Couples Involving Metal-Metal Bonds. Mn₂(CO)₁₀, [Fe(η⁵-C₅H₅)(CO)₂]₂, and [Mo(η⁵-C₅H₅)(CO)₃]₂." Pugh, J. R.; Meyer, T. J., manuscript in preparation.
2. "Electrocatalytic Reduction of Carbon Dioxide Based on 2,2'-Bipyridyl Complexes of Osmium." Bruce, M. R.; Megehee, E.; Sullivan, B. P.; Thorp, H.; O'Toole, T. R.; Downard, A.; Meyer, T. J., manuscript in preparation.

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