2016

Synthesis and Studies of Cyclopentadienyl Molybdenum Complexes

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ABSTRACT   The synthesis and electrochemical responses of $[CpMo(CO)_3]_2$, $CpMo(CO)_3I$, $CpMo(CO)_3(OTf)$, and $[CpMo(bpy)(CO)_2]$ (Cp = cyclopentadienyl, bpy = 2,2'-bipyridine, OTf = trifluoromethansulfonate) in organic solvent are reported. Transition metal compounds such as $Re(bpy)(CO)_3Cl$ have been shown to be effective carbon dioxide reduction catalysts. The molybdenum metal complexes studied herein were examined under argon and carbon dioxide gas for the potential reduction of carbon dioxide. Proton Nuclear Magnetic Resonance (^1H NMR) spectroscopy, infrared (IR) spectroscopy and an electrochemical method know as cyclic voltammetry were used to gather data on the complexes. Electrochemical response peaks under carbon dioxide were analyzed for the relative efficiency and potentials of the molybdenum catalysts. The addition of the bpy ligand to the molybdenum resulted in an unstable compound in solution. The molybdenum compounds studied were not found to be competent catalysts for the reduction of carbon dioxide.

INTRODUCTION

Fossil fuel consumption has caused countless tons of carbon dioxide to be released into the atmosphere. The continuing population growth and dependence on fossil fuels has only increased the severity of this problem. Carbon dioxide is a well-known "greenhouse" gas responsible for increases in global temperatures and the acidification of the ocean [1]. The carbon dioxide in the atmosphere acts as an insulator for the sun's rays, causing a gradual increase in the overall temperature. The effect on the atmosphere is not the only negative impact; oceans have been gradually acidifying over time as well [2]. This is causing ocean life and ecosystems to suffer. One potential solution for these problems would be capturing and recycling carbon dioxide into a fuel. Work toward the reduction of carbon dioxide into a potential new fuel needs further development to make this solution a reality.

Research by the Kubiak group and others with $Re(bpy)(CO)_3Cl$ (bpy = 2,2'-bipyridine) has shown that this compound and related species have great potential for the electrochemical reduction of carbon dioxide [3]. Electrochemical

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reduction involves passing a charge through a solution and delivering electrons to a substrate. If the substrate is CO_2, this results in the reduction of CO_2 to a potentially valuable chemical, therefore reducing the carbon dioxide in the atmosphere while at the same time generating useful products. Previous studies in which just $Re_2(CO)_{10}$ was studied for the reduction of carbon dioxide showed no catalytic reduction of carbon dioxide [4]. Therefore, the inclusion of the 2,2'-bipyridine (bpy) in $Re(bpy)(CO)_3Cl$ seems to play an important role in its ability to catalytically reduce carbon dioxide at a low potential. The 2,2'-bipyridine ligand is known as a "non-innocent" ligand, which means that it can participate in the chemistry of the compound it is attached to [5]. On the other end of the spectrum, "innocent" ligands are bystanders that do not intervene with the chemistry but only act to support the metal, which is the active species shuttling electrons to CO_2.

Rhenium has been a well-studied central metal for various catalysts. Unfortunately rhenium is expensive and not very abundant compared to other transition metals. Due to this knowledge, other metals like molybdenum should be explored as the metal centers of catalysts. Molybdenum could be a potential replacement as the metal center since it is more abundant and less expensive than rhenium. With this in mind, we specifically attempted to attach a bpy ligand to $[CpMo(CO)_3]_2$ (Cp = cyclopentadienyl ligand) and then examined its ability to recycle carbon dioxide. The complexes were examined by cyclic voltammetry (CV) and various spectroscopic methods. Our results are described below.

EXPERIMENTAL SECTION

GENERAL CONSIDERATIONS

Acetonitrile, tetrahydrofuran (THF), and pentane were purified using an Innovative Technology PureSolv system under N_2 gas. Tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized from HPLC-grade (HPLC = High Pressure Liquid Chromatography) methanol and dried in a vacuum oven prior to use. Carbon dioxide ("bone dry") and argon were purchased from the American Gases Corporation. Infrared spectra were obtained with an ABB FTLA2000 spectrometer using a Buck Scientific demountable liquid cell equipped with KBr windows and a 0.1 mm spacer. Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra were acquired with a Bruker Avance 300 MHz NMR spectrometer at 298 K. NMR data were referenced to the residual solvent signal and reported as shifts (δ) in ppm downfield of tetramethylsilane (δ = 0 ppm). Peaks are reported as s = singlet, d = doublet, t = triplet, followed by the integration and the peak identity. For example, "(s, 5H, Cp)" refers to a singlet peak that integrates to five protons and is identified as the cyclopentadienyl (Cp) ring protons. The starting material $[CpMo(CO)_3]_2$ was obtained from Aldrich and all other chemicals, unless otherwise stated, were obtained from commercial sources.

ELECTROCHEMISTRY

The cyclic voltammetry experiments were performed using an eDaq ER466 potentiostat. The cell setup consisted of 2.5 mL of solution in a 5 mL cell with a 1 mm diameter glassy carbon working electrode, a Ag/AgCl pseudo-reference electrode, and a Pt/Ti alloy rod or Pt wire counter electrode. The working electrode was cleaned with diamond polish, rinsed, and dried prior to each use. All cyclic voltammograms were performed at a scan rate of 250 mV/s. Solutions were sparged with Ar or CO_2 for several minutes prior to analysis.

SYNTHESIS OF CpMo(CO)$_3$I

The synthesis of $CpMo(CO)_3I$ involved the reaction of $[CpMo(CO)_3]_2$ and I_2. A 100.3 mg (0.79 mmol) sample of I_2 was combined with 302.0 mg (0.60 mmol) of $[CpMo(CO)_3]_2$ in a 20 mL scintillation vial. Approximately 6 mL of THF was added to the scintillation vial along with a stir bar. The reaction was stirred at room temperature for two days. The reaction contents were transferred to a round bottom flask and the material was isolated using a rotary evaporator. The product was collected (336 mg, 0.97 mmol) and a 79.5% yield was obtained. The product

was characterized by proton Nuclear Magnetic Spectroscopy (^{1}H NMR) and infrared spectroscopy. The ^{1}H NMR data in CDCl$_3$ displayed a singlet for the 5 protons on the Cp ring at δ = 5.62 ppm. Infrared Spectroscopy (IR) data was collected in Tetrahydrofuran (THF) and notable peaks were: 1960, 2039 and 1645 cm^{-1}.

SYNTHESIS OF CpMo(CO)$_3$(OTf) AND [CpMo(bpy)(CO)$_2$](OTf)

The synthesis of [CpMo(bpy)(CO)$_2$](OTf) involved the reaction of CpMo(CO)$_3$I with AgOTF and then the addition of bpy to the reaction vessel. A sample of 336.0 mg of CpMo(CO)$_3$I (0.97 mmol) was added into a 20 mL scintillation vial with 230.1 mg (0.90 mmol) of AgOTF and 10 mL of THF. A stir bar was added, and the solution was allowed to stir for 1 hour. Then bpy (142.5 mg, 0.91 mmol) was added, and the reaction was allowed to proceed for approximately another hour. The solution was filtered, and the solution was isolated using a rotary evaporator. The product was then stored in a freezer and analyzed the next day before attempting purification. The ^{1}H NMR of the crude sample was obtained in CDCl$_3$ (^{1}H NMR (CDCl$_3$): δ = 5.62 (s, 5H, Cp), 7.67 (t, 2H, bpy), 8.15 (t, 2H, bpy), 8.32 (d, 2H, bpy), and 8.89 (d, 2H, bpy) ppm). Signals for the five protons in the cyclopentadienyl ring and the eight protons in the coordinated bipyridine ligands were observed at 5.62 ppm and 7.67–8.89 ppm, respectively. The cyclopentadienyl signal was a singlet, whereas the bipyridine protons were four separate doublets and triplets due to coupling between the separate proton signals. Two crystallizations were set up to purify the product. Both crystallizations resulted in decomposition of the desired product (see results and discussion).

RESULTS AND DISCUSSION

The overall scheme for the synthesis of the desired product is shown in Figure 1. The Cyclopentadienylmolybdenum tricarbonyl dimer was commercially obtained. A proton NMR spectrum, IR spectrum, and a CV were obtained of this starting material for comparison with the reaction products. The starting material's CV is shown in Figure 2. The CV was performed in a

N,N-Dimethylformamide (DMF) solution with 0.1 M of TBAH as the supporting electrolyte. Argon gas was used to obtain a base line current when conducting the cyclic voltammetry experiments and then compared to the current observed under carbon dioxide. Then a small amount of water was added to see if a proton source would help promote the reduction of carbon dioxide. From Figure 2, it can be seen that there were two reduction events at *ca.* -0.5 V and -1 V, but they did not change under CO$_2$, even with water. Some current enhancement was seen at *ca.* -3 V, but this could be due to direct reduction of CO$_2$ by the electrode. Therefore [CpMo(CO)$_3$]$_2$ was not determined to be a CO$_2$ reduction catalyst. If it were a catalyst, large current enhancements (such as 2-10 times the current height) would be observed at the reduction peaks under CO$_2$ as compared to under argon.
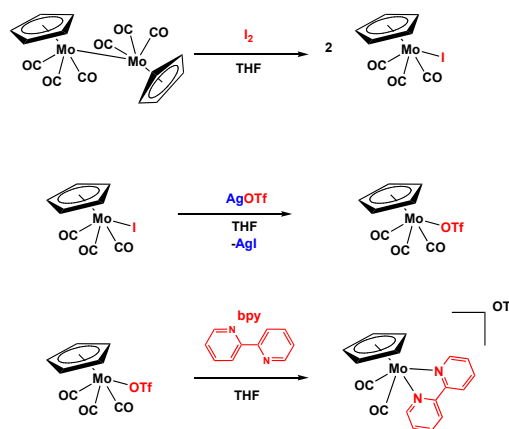

Figure 1: Synthesis scheme for the desired [CpMo(bpy)(CO)$_2$]OTf complex.

Then [CpMo(CO)$_3$]$_2$ was reacted with molecular iodine, I$_2$, in a scintillation vial with THF. The reaction proceeded at room temperature in the presence of air and the product was isolated using rotary evaporation. This process also removed any excess I$_2$ because it is a volatile compound. The product was identified as CpMo(CO)$_3$I based on ^{1}H NMR and IR spectra, showing a singlet in the ^{1}H NMR spectrum for the Cp ring and three carbonyl signals in the IR spectrum.
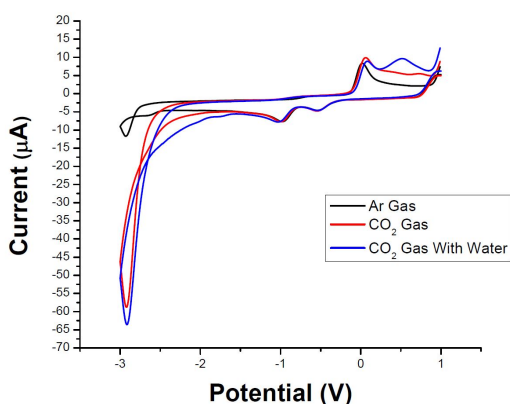
Figure 2: Cyclic Voltammetry of [CpMo(CO)$_3$]$_2$ in DMF, showing the lack of a significant catalytic response under CO_2.

Figure 3: Proton NMR of [CpMo(CO)$_2$bpy] in CDCl$_3$, showing the presence of the bpy ligand and the Cp ligand on the complex. Integrations are shown in red and peak locations (in ppm) are shown in green. The y-axis is in relative absorbance (rel).

We attempted to synthesize the desired bpy-containing product by using salt metathesis to remove the iodide ligand. The synthesized CpMo(CO)$_3$I was reacted with AgOTf in THF. A metallic layer formed on the inside of the scintillation vial, indicating that the reaction between the molybdenum and the silvent reagent had occurred. Then, the bpy ligand was added to the solution and it was allowed to react at room temperature. The reaction solution was then filtered through a glass frit. A blue solid believed to be AgI and impurities was collected on the frit. The filtrate was presumed to contain the product obtained from this reaction. A proton NMR was then obtained of the crude product (see Figure 3). From the NMR spectrum, it can be seen that the compound contains both a bipyridine ligand (peaks between 7.5 and 9 ppm) as well as a Cp ligand (at 5.7 ppm).

This crude product was then used for cyclic voltammetry (see Figure 4). The CV shows two major reduction events under Ar, at *ca.* -1 V and -2.5 V. Interestingly, a three-fold enhancement is seen under CO_2 at the -2.5 V peak (*ca.* -30 μA to -90 μA), suggesting CO_2 reduction catalysis. The product was isolated using a rotary evaporator and then stored in a freezer. Two separate crystallizations were set up to purify the crude product. Unfortunately, an IR spectrum that was obtained from the crystalized solid showed that there were no carbonyl stretches, and thus no Mo-CO groups. The proton NMR
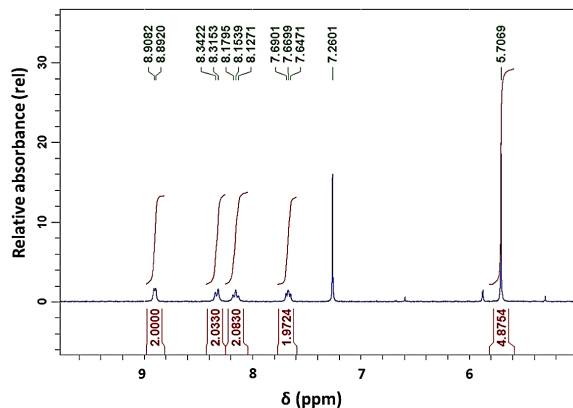
spectrum also showed that the Cp ligand resonance had disappeared. Both of these results indicate that the compound was unstable and decomposed during crystallization, losing both the CO ligands and the Cp ligand.
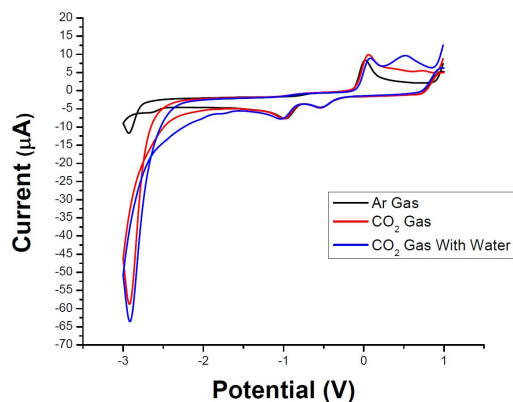

Figure 4: Cyclic Voltammetry of crude [CpMo(CO)$_2$bpy]OTf in DMF, showing catalytic enhancement under CO_2 at -2.5 V.

The fact that the original starting material [CpMo(CO)$_3$]$_2$ did not exhibit much catalytic behavior when cyclic voltammetry was preformed on it, but the bpy-containing species did show catalytic behavior supports the concept

that the "non-innocent" bpy ligand was a useful ligand in catalysis. Unfortunately, [CpMo(CO)$_2$bpy]OTf decomposed in solution to the point that it was no longer usable for cyclic voltammetry analysis. In addition, the reduction of carbon dioxide displayed in the CV occurred at potentials that were very negative. Therefore, the [CpMo(CO)$_2$bpy]OTf compound would not be a good catalyst.

CONCLUSIONS AND FUTURE DIRECTIONS

The syntheses of [CpMo(bpy)(CO)$_2$](OTf) ended up being somewhat successful in that the combination of [CpMo(CO)$_3$]$_2$ and I$_2$ reacted to form a stable compound. However, when AgOTf was reacted with the product and then bpy ligand was added to the reaction, the new product [CpMo(bpy)(CO)$_2$](OTf) was not very stable in solution. Electrochemistry of the partially stable bpy-containing compound showed that it did react with CO$_2$ but was not a great catalyst for carbon dioxide reduction.

Future work involves attaching different ligands to molybdenum-based compounds. Stabilizing the final products is important so that the compounds can be more reliably studied. Additionally, ligand modification could potentially improve the molybdenum complexes' abilities to reduce carbon dioxide.

AUTHOR CONTRIBUTIONS

All authors contributed extensively to this project. K. G. designed the experiments, helped analyze the data, and helped with manuscript revisions. C. S. performed the syntheses, collected and analyzed the data, and wrote the paper.

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