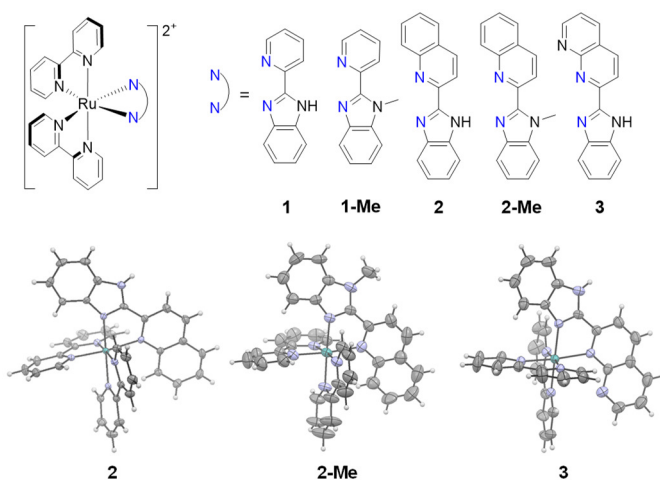
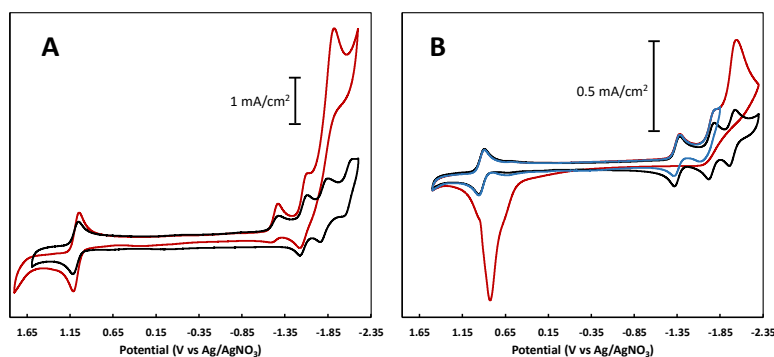


Several specific project aims have seen significant progress in the first year of work. Additionally, new opportunities and avenues of research have opened up through discoveries made in the pursuit of the synthesis and electrochemistry of NADH mimics. One of the main thrusts of the proposal was to utilize metal complexes as scaffolds for active organic moieties in the reduction of CO<sub>2</sub>. Two students have been working exclusively on this project and have been successful in the synthesis of five Ru complexes with crystal structures of three of these (**Figure 1**). Each complex consists of a Ru(bpy)<sub>2</sub> scaffold with a third bidentate ligand acting as a site for CO<sub>2</sub> reactivity. The third ligand in these cases involves a benzimidazole moiety with a 2° or 3° basic amine that can serve as a nucleophile in CO<sub>2</sub> activation. Cyclic voltammetry of these complexes under Ar reveals three ligand-centered reductions, two reductions for the two bipyridines and one for the benzimidazole ligand. In the case of **1** and **2**, the benzimidazole-centered reduction is irreversible under both Ar and CO<sub>2</sub> (**Figure 2, A**). The irreversible feature is likely due to the presence of the N–H on the backbone of the ligand that can achieve different protonation states. Further evidence that the irreversibility is due to the N–H comes from CVs of the methylated complex, **2-Me**, which shows three *reversible* reductions under Ar (**Figure 2, B**). Interestingly,



**Figure 1.** Structures of synthesized Ru complexes and crystal structures of **2**, **2-Me**, and **3**.

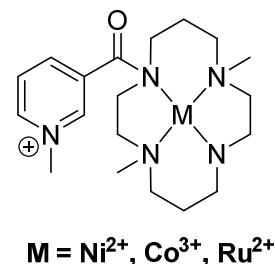


**Figure 2.** Electrochemistry of **2** (A) and **2-Me** (B) in CH<sub>3</sub>CN with 0.1 M TBAPF<sub>6</sub> using a GC working electrode, Pt counter electrode, and Ag/AgNO<sub>3</sub> reference electrode, taken at a scan rate of 50 mV/s. **Black** – Ar, **Red** – CO<sub>2</sub>, **Blue** – CO<sub>2</sub>.

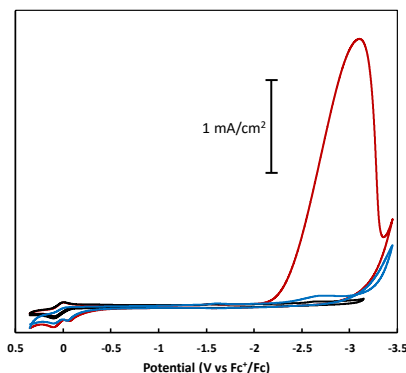
both the methylated and non-methylated complexes show activity for CO<sub>2</sub> reduction. Analysis under CO<sub>2</sub> atmosphere shows increased current in the CV consistent with catalytic activation of CO<sub>2</sub>, although the product of reduction with the methylated complex appears to adsorb to the electrode surface as evidenced by the sharp, oxidative desorption peak (**Figure 2, B**). This peak is only present if the atmosphere is CO<sub>2</sub> and the third reduction is reached. Only scanning through the second reduction (**Figure 2, B, Blue**) does not give rise to this new oxidative feature.

NMR experiments utilizing pinacol borane as a chemical reductant under <sup>13</sup>CO<sub>2</sub> were used to investigate product distributions of CO<sub>2</sub> reduction. Complexes **1**, **1-Me**, **2**, and **2-Me** all show the ability to reduce CO<sub>2</sub> to formate and methyl oxidation states as indicated through analysis of <sup>1</sup>H and <sup>13</sup>C NMR shifts of the borane products in comparison to literature. The mechanism does not appear to involve a formation of a dihydropyridine, as reactions with NaBH<sub>4</sub> or pinacol borane and the Ru complexes without the addition of CO<sub>2</sub> do not show any reaction via <sup>1</sup>H NMR. We currently hypothesize that the mechanism involves a nucleophilic attack of the secondary or tertiary amine on CO<sub>2</sub> after reduction of the ligand. This is consistent with the activity of the methylated ligand as the tertiary amine should be a better nucleophile. Studies are ongoing to better understand both the electrochemical and chemical mechanism as well as to design second-generation complexes. The two students who have worked on this project have both been able to present at the South Eastern Regional Meeting of the American Chemical Society and internal (University of Richmond) conferences. Currently, they are both working on writing a manuscript, which we hope to submit later this year.

Two other students have been working to synthesize cyclam ligands that have been derivatized with NADH-mimics as a way to utilize secondary coordination spheres of metal-cyclam complexes for CO<sub>2</sub> reduction. Typically, metal cyclam complexes bind CO<sub>2</sub> at a reduced metal center and facilitate the 2e<sup>-</sup> reduction to CO. Our hope was to make use of well-known chemistry to attach pyridinium NADH mimics via N-functionalization reactions. Initially we had some success with the synthesis of functionalized cyclams and the resulting Ni, Co, and Ru complexes (**Figure 3**). Unfortunately, these complexes are rather insoluble in most solvents making characterization and electrochemical experiments challenging. The Ru complex,



**Figure 3.** Structures of metal cyclam complexes.



**Figure 4.** Electrochemistry of **Ru-cyclam** in DMSO with 0.1 M TBAPF<sub>6</sub> using a GC working electrode, Pt counter electrode, and Ag/Ag<sup>+</sup> reference electrode, taken at a scan rate of 50 mV/s. Potentials have been adjusted using an internal Fc reference. **Black** – Ar, **Red** – CO<sub>2</sub> first scan, **Blue** – CO<sub>2</sub> second scan.

however, does show some promising electrochemical activity in DMSO under CO<sub>2</sub> although it appears that this catalyst may be rapidly poisoned as subsequent scans show significantly diminished current (**Figure 4**). Continued purging of the electrochemical solution with CO<sub>2</sub> does result in the return of activity, however. Also, addition of up to 5 % by volume H<sub>2</sub>O to the electrochemical sample prevents significant loss of activity after the first scan. Our current efforts in this area have moved on to functionalization of the carbon backbone of the cyclam to allow for a wider variety of NADH mimics to be incorporated as well as improved solubility. We hope to maintain the activity, but increase the solubility in order to perform more mechanistic studies and analyze products. The student who started this project did most of this work his senior year and was also able to present at SERMACS in the Fall of 2017. He is currently a graduate student in the chemistry department at the University of Virginia working towards his Ph.D.

This research has also positively affected my career. At an undergraduate institution it is essential to have students working during the 10-week summer period and I was able to fund three students during the summer

of 2017 with this grant. The research has also resulted in an invited presentation at the ACS National Meeting in New Orleans last spring where I was able to talk about the excellent progress with the Ru complexes. Additionally, the research has spawned several exciting new directions. One of these projects involves the immobilization of molecules in electrode films. Originally, the specific aim was to use organic catalysts for electrochemical CO<sub>2</sub> reduction; however, radical formation and rapid dimerization were persistent complications. In an attempt to limit or slow down these interactions, one of my students has been working on making thin films of silica using various silane precursors on glassy carbon electrodes to entrap molecules. Somewhat serendipitously, the strategy has been successful with known catalysts for water oxidation operating under aqueous conditions at near neutral pH (pH = 6.1). We have been able to gather rotating-ring disk electrochemistry to show O<sub>2</sub> formation and CVs that indicate stability over an extended number of scans. The simplicity of the strategy using a simple drop-casting approach to film formation should make it widely applicable to a variety of electrocatalytic applications. In an extension of immobilization of catalysts and controlling the secondary coordination sphere, another student has been working toward the synthesis of cross-linked micelles as hallow cages for catalytic molecules. Both of these new directions have come from our attempts to solve problems encountered during the course of research for this proposal and I believe that these avenues of research may lead to new and impactful chemistry.