

Synthesis, characterization, and electrocatalytic hydrogen evolution of transition metal Schiff-
base calixpyrrole complexes with pendant hydrogen bond donors

by

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Abstract

Three novel calixpyrrole complexes with pendant hydrogen bond donors were synthesized via the condensation of 5,5'-diformyl-2,2'-diphenyldipyrromethane and an aniline precursor. Single crystal X-ray diffraction revealed that these complexes displayed distorted square planar geometries, and significantly the pendant groups remained uncoordinated from the metal. Electrochemical studies, along with density functional theory (DFT) calculations, indicated that the ligand exhibited redox non-innocence as evidenced experimentally by similar irreversible oxidations in both the ligands and complexes. Electrochemical analysis in the presence of *p*-toluenesulfonic acid generated an irreversible reduction about 400-500 mV more positive than the background reduction by the glassy carbon electrode, indicative of electrocatalytic hydrogen evolution. All the complexes exhibited similar catalytic waves which persisted after rinse tests signifying the generation of an electrode-adsorbed catalyst which was stable under catalytic conditions.

A square planar Ni(II) complex, Ni(DPMDA) (DPMDA=2,2'-((diphenylmethylen)bis(1H-pyrrole-5,2-diyl))bis-(methaneylylidene))bis(azaneylylidene)dianiline), of the previously reported calixpyrrole ligand of was synthesized and analyzed for electrocatalytic hydrogen evolution in the presence of anilinium tetrafluoroborate. It was found that under catalytic conditions a heterogeneous species was formed on the electrode surface which was found to be stable and operate at turnover frequencies (TOF) of up to 25,900 s⁻¹ or 366,000 s⁻¹ cm⁻². Kinetic isotope effect (KIE) and Tafel analysis suggest rate-limiting proton coupled electron transfer (PCET) likely facilitated by the pendant amines which enabled high TOF despite evidence of redox-mediated outer-sphere electron transfer.

Ni(DPMDA) was evaluated for electrocatalytic hydrogen evolution in the presence of a weaker proton donor, triethylammonium tetrafluoroborate. Under catalytic conditions, a heterogeneous species was similarly formed. Experimental evidence suggested that the identity of this species differed from that formed in the presence of anilinium as evidenced the absence of redox features attributable to the heterogeneous species, peak potential dependence on bulk catalyst concentration, and lower overpotential despite the use of a weaker proton donor. The lack of features attributable to the heterogeneous species indicated inner-sphere electron transfer

and TOF of $5,700\text{ s}^{-1}$ or $80,000\text{ s}^{-1}\text{cm}^{-2}$ were observed. Similarly, KIE and Tafel analysis suggest rate-limiting PCET for which the pendant groups were implicated as hydrogen bond acceptors/donors during buffered solution studies.

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Table of Contents

List of Figures	xi
List of Tables	xxi
List of Schemes	xxii
Acknowledgements	xxiii
Chapter 1 – Introduction	1
1.1 Homogeneous Catalysts.....	2
1.1.1 Hydrogenase Mimics	2
1.1.2 Ni(II) bis(diphosphine) Complexes	5
1.1.3 Hangman Porphyrins	7
1.1.4 Schiff-base Ligands	9
1.2 Heterogeneous Catalysts.....	11
1.2.1 Covalent Attachment	12
1.2.2 Electrostatic and π - π Attachment.....	15
1.2.3 Electrodeposition	21
1.3 Pyrrolide Ligands.....	24
1.4 Sues Group Chemistry	25
1.5 Thesis Goals.....	25
1.6 References.....	28
Chapter 2 – Palladium Complexes Bearing Calixpyrrole Ligands with Pendant Hydrogen Bond Donors: Synthesis, Structural Characterization, Electrochemistry and Dihydrogen Evolution	47
2.1 Abstract.....	47
2.2 Introduction.....	47
2.3 Results and Discussion	51
2.3.1 Synthesis and Characterization of Compounds 1a-c.....	51
2.3.2 Synthesis and Characterization of Compounds 2a-c.....	57
2.3.3 Electrochemical Properties of 1-2.....	60
2.3.4 Theoretical Calculations	62
2.3.5 Preliminary Small Molecule Reactivity Studies	67

2.3.6 Electrocatalytic H ₂ Evolution.....	68
2.4 Conclusion	77
2.5 Experimental	79
2.5.1 General Considerations	79
2.5.2 Synthesis of 1a (C ₃₅ H ₃₀ N ₆)	80
2.5.3 Synthesis of 1b (C ₃₉ H ₃₄ N ₆ O ₂).....	81
2.5.4 Synthesis of 1c (C ₄₅ H ₄₆ N ₆ O ₄)	82
2.5.5 Synthesis of 2a (Pd(1a)).....	84
2.5.6 Synthesis of 2b (Pd(1b))	86
2.5.7 Synthesis of 2c (Pd(1c)).....	87
2.5.8 Computational Details	90
2.5.9 Preliminary Small Molecule Activation Studies.....	91
2.5.10 Electrocatalytic H ₂ Evolution	91
2.6 References.....	91
Chapter 3 – Electrocatalytic Hydrogen Evolution using a Nickel-based Calixpyrrole Complex:	
Controlling the Secondary Coordination Sphere.....	100
3.1 Abstract.....	100
3.2 Introduction.....	100
3.3 Results and Discussion	104
3.3.1 Synthesis and Characterization	104
3.3.2 Electrochemical Characterization	106
3.3.3 Electrocatalytic Hydrogen Production	110
3.3.4 Kinetic Investigations	117
3.3.5 Mechanistic Investigations.....	132
3.3.6 Implications for Catalyst Design	139
3.4 Conclusions.....	142
3.5 Experimental Section.....	143
3.5.1 General Considerations	143
3.5.2 Synthesis of Ni(DPMDA).....	145
3.5.3 Discussion of Ni(DPMDA) Structure	149
3.5.4 Synthesis of Anilinium Tetrafluoroborate- <i>d</i> ₃	150

3.5.5 Electrocatalytic H ₂ Evolution.....	151
3.5.6 Sample Overpotential Calculation ^{55,63}	152
3.5.7 Sample Turnover Frequency Calculation ⁶⁸⁻⁶⁹	152
3.5.8 Controlled Potential Electrolysis	152
3.5.9 Computational Details	153
3.6 References.....	155
Chapter 4 – Electrocatalytic Hydrogen Evolution with Ni(II) Calixpyrrole: Acid Strength	
Governs Catalyst Formation	161
4.1 Abstract	161
4.2 Introduction.....	161
4.3 Results and Discussion	164
4.3.1 Electrocatalytic Hydrogen Evolution.....	164
4.3.2 Kinetic Investigations	175
4.4 Conclusions.....	184
4.5 Experimental	186
4.5.1 General Considerations	186
4.5.2 Electrocatalytic Hydrogen Evolution.....	187
4.5.3 Controlled Potential Electrolysis	187
4.5.4 Synthesis of Triethylammonium Tetrafluoroborate- <i>d</i>	188
4.6 References.....	190
Chapter 5 – Conclusions and Future Directions	
5.1 Conclusions.....	197
5.2 Future Directions	199
5.2.1 Electronic Tuning of Calixpyrroles	199
5.2.2 Cation Inclusion	200
5.2.3 Pendant Group Basicity	201
5.3 References.....	203
Copyright Acknowledgements.....	206

List of Figures

Figure 1.1.1. Structure of [Fe-Fe] hydrogenase mimics bearing a pendent adt ligand (left) or propanedithiolate (right).	3
Figure 1.1.2. Structure of catalytically active <i>t</i> -H adt complex.	3
Figure 1.1.3. Structure of the pdt ligated [Ni-Fe] hydrogenase mimic.	4
Figure 1.1.4. Structure of a [Ni-Fe] hydrogenase mimic with an adt ligand.	5
Figure 1.1.5. General structure of the diphosphacyclooctane (left) and diphosphacycloheptane (right) Ni(II) bis(diphosphine) complexes.	6
Figure 1.1.6. Structure of protonated “pinched” exo-exo isomer of Ni(0) bis(diphosphine) complex (left), exo protonated isomer of Ni(I) bis(diphosphine) with diphosphacycloheptane rings (middle) and endo protonated isomer of Ni(I) bis(diphosphine) (right).	6
Figure 1.1.7. Structure of a Co “hangman” porphyrin with xanthene spacer.	8
Figure 1.1.8. Structure of Co hangman porphyrins with phenyl spacers between the metal and pendant group.	9
Figure 1.1.9. Structure of Jacobsen’s catalyst.	10
Figure 1.1.10. Structure of a bimetallic Co macrocyclic Schiff-base calixpyrrole complex.	11
Figure 1.2.1. Ni(II) diphosphacycloheptane complex covalently attached to a glassy carbon electrode surface.	13
Figure 1.2.2. Structure of Co(TPP) covalently linked to glassy carbon.	15
Figure 1.2.3. Structure of a Ni(II) bis(diphosphine) complex with attached pyrene functionalities.	16
Figure 1.2.4. Structure of a [Fe-Fe] hydrogenase mimic with attached pyrene functionalities.	17
Figure 1.2.5. Structure of a metallopolymer [Fe-Fe] hydrogenase mimic with attached pyrene functionalities.	18
Figure 1.2.6. Structure of a Ni(II) cyclam with appended pyrene moiety.	19
Figure 1.2.7. Structures of a naphthalene-terminated Fe(III) polypyridyl complex (left), a naphthalene-terminated Co(II) bis(terpyridine) complex (right), and a Co(III) bis(benzenedithiolate) complex (bottom).	20

Figure 1.2.8. General structure of a Co-salophen complex with <i>t</i> -butyl substituted phenol rings.	22
Figure 1.2.9. Structure of $[\text{Ni}(\text{N}-\text{N}-\text{SCH}_3)_2]^{2+}$ complex (left) and $[\text{Ni}(\text{pyridine-2-thiolate})_3]^-$ studied for electroadsorption.....	23
Figure 1.2.10. Structure of diacetyl-2-(4-methyl-3-thiosemicarbazone)-3-(2-pyridinehydrazone) complexes studied by Grapperhaus <i>et al</i>	24
Figure 1.3.1. Resonance structures of pyridine-pyrrole-pyridine ligands.	24
Figure 2.2.1. General structure of diiron azadithiolate-bridged complexes (left), nickel diphosphacycloheptane complexes (middle), and “hangman” porphyrin complexes (right).	48
Figure 2.2.2. Example of a binuclear macrocyclic Schiff-base calixpyrrole complex.	50
Figure 2.3.1. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: A single molecule of 1a, the solvent, most of the hydrogens, and three other molecules of 1a have been omitted for clarity (left); A single molecule of 1c, the solvent, most of the hydrogens, and the other molecule of 1c have been omitted for clarity (right).	53
Figure 2.3.2. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: A top view of the intertwined dimer of 1a, the solvent, most of the hydrogens, and the other dimer of 1a have been omitted for clarity (top left); A side view of the intertwined dimer of 1a, the solvent, most of the hydrogens, the phenyl substituents between the pyrrole groups, and the other dimer of 1a have been omitted for clarity (top right); The hydrogen bonding between two dimers of 1a, the solvent and most of the hydrogens have been omitted for clarity (bottom).	54
Figure 2.3.3. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: A top view of the intertwined dimer of 1c, the solvent and most of the hydrogens have been omitted for clarity (left); A side view of the intertwined dimer of 1c, the solvent, most of the hydrogens, and the phenyl substituents between the pyrrole groups have been omitted for clarity.	55
Figure 2.3.4. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for 1b where most of the hydrogens have been omitted for clarity.	56
Figure 2.3.5. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: 2a, most of the hydrogens have been omitted for clarity (top left); 2b, the solvent and	

most of the hydrogens have been omitted for clarity (top right); 2c, the solvent and most of the hydrogens have been omitted for clarity (bottom).	59
Figure 2.3.6. Cyclic voltammograms of 1a-c (top) and 2a-c (bottom) in acetonitrile. (0.25 mM ligand or complex, 0.1 M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 800 mV/s).	62
Figure 2.3.7. Visual representations and energies of the ligand-based HOMO, HOMO-1, HOMO-2 orbitals (labelled L ₁ , L ₂ , and L ₃ respectively) of 2a _H (top); ligand-based HOMO, HOMO-1, and HOMO-2 (SOMO) orbitals of 2a _H ⁺ (α and β manifolds, labelled L ₁ , L ₃ , and L ₂ , respectively, in reference to the orbitals with similar character in 2a _H (middle); HOMO (SOMO), HOMO-1 (SOMO), and HOMO-2 orbitals of 2a _H ²⁺ with S = 1 (α and β manifolds, labelled L ₁ , L ₂ , and L ₃ , respectively, in reference to the orbitals with similar character in 2a _H) (bottom).....	65
Figure 2.3.8. Visual representations of the a) LUMO; b) HOMO-4; c) HOMO-5; d) HOMO-6; e) HOMO-8; f) HOMO-9; g) HOMO-10 (showing some degree of backdonation from the metal into the imine bonds); h) HOMO-11 orbitals of 2a _H , which display significant d-orbital character.....	66
Figure 2.3.9. Cyclic voltammograms in acetonitrile (0.25 mM complex, 0.1 M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 100 mV/s) of 2a-c in the presence of 600 equivalents of <i>p</i> TSA (0.15 M).	69
Figure 2.3.10. Cyclic voltammograms of H ₂ evolution using 2a at various scan rates (0.25 mM complex, 0.1 M TBAP, 0.15 M <i>p</i> TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode) (top); Peak catalytic current versus square-root of scan rate (bottom).	70
Figure 2.3.11. Cyclic voltammograms of H ₂ evolution using 2b at various scan rates (0.25 mM complex, 0.1 M TBAP, 0.15 M <i>p</i> TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode) (top); Peak catalytic current versus square-root of scan rate (bottom).	71
Figure 2.3.12. Cyclic voltammograms of H ₂ evolution using 2c at various scan rates (0.25 mM complex, 0.1 M TBAP, 0.15 M <i>p</i> TSA, glassy carbon working electrode, platinum wire	

counter electrode, 0.01 M Ag/AgNO ₃ reference electrode) (top); Peak catalytic current versus square-root of scan rate (bottom).....	72
Figure 2.3.13. Cyclic voltammograms of H ₂ evolution using 2a (top), 2b (middle), and 2c (bottom) before (0.25 mM complex, 0.1 M TBAP, 0.15 M <i>p</i> TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 100 mV/s) and after ‘rinse’ test (no complex, 0.1 M TBAP, 0.15 M <i>p</i> TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 100 mV/s).	74
Figure 2.3.14. Representative example of a cyclic voltammogram using only ligand (1a) for H ₂ production (0.25 mM ligand, 0.1 M TBAP, 0.15 M <i>p</i> TSA), glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 100 mV/s).....	75
Figure 2.3.15. ¹ H NMR spectra (400 MHz, CD ₃ CN) of sealed CV reaction mixtures carried out in CD ₃ CN (0.25 mM 2a, 0.1 M TBAP, 0.015 M <i>p</i> TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 600 mV/s) showing H ₂ in solution after: 24 scans (top), 308 scans (middle), and 516 scans (bottom).....	75
Figure 2.3.16. Representative cyclic voltammogram of H ₂ evolution with 500 scans using 2a in CD ₃ CN (0.25 mM complex, 0.1 M TBAP, 0.015 M <i>p</i> TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 60 mV/s).....	76
Figure 2.5.1. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of 1a.....	81
Figure 2.5.2. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of 1b.....	82
Figure 2.5.3. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of 1c.....	84
Figure 2.5.4. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of 2a.....	85
Figure 2.5.5. ¹ H NMR spectrum (400 MHz, CDCl ₃) of 2b.	87
Figure 2.5.6. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of 2c.....	88
Figure 3.2.1. Structure of the [FeFe]-hydrogenase active site (left) with the azodithiolate ligand highlighted, and a nickel diphosphacycloheptane complex (right) with analogous pendant amine highlighted.....	101

Figure 3.2.2. General structure for the nickel diphosphacyclooctane catalyst covalently attached to a carbon nanotube reported by Artero and co-workers.....	102
Figure 3.2.3. General structure of the palladium-based Schiff-base calixpyrrole complexes with pendant hydrogen-bond donors.....	104
Figure 3.3.1. ORTEP3 representation (thermal ellipsoids at 50 % probability) and atom numbering for Ni(DPMDA), most of the hydrogens have been omitted for clarity. Selected bond lengths (Å): Ni(1)-N(1) = 1.839(4), Ni(1)-N(2) = 1.843(4), Ni(1)-N(3) = 1.955(4), Ni(1)-N(4) = 1.947(4). Selected bond angles (deg): N(1)-Ni(1)-N(2) = 87.3(2), N(1)-Ni(1)-N(3) = 83.8(2), N(2)-Ni(1)-N(4) = 83.7(2), N(3)-Ni(1)-N(4) = 105.0(2).	105
Figure 3.3.2. CV showing the irreversible redox features of Ni(DPMDA) at positive potentials (0.1 M TBAP, 0.25 mM Ni(DPMDA), glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 800 mV/s).....	106
Figure 3.3.3. CV showing the quasi-reversible redox couples of Ni(DPMDA) at negative potentials (0.1 M TBAP, 0.25 mM Ni(DPMDA), glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 800 mV/s). ..	107
Figure 3.3.4. CVs of the quasi-reversible redox couples of Ni(DPMDA) at various scan rates (0.1 M TBAP in acetonitrile, 0.25 mM Ni(DPMDA), glassy carbon working electrode, platinum wire counter electrode, 0.01 M AgNO ₃ reference electrode, scan rate = 100 to 800 mV/s) (top); plot of anodic and cathodic current vs the square-root of scan rate (bottom).	109
Figure 3.3.5. CVs of Ni(DPMDA) in the absence and presence of acid (0, 0.5, and 1.25 mM anilinium tetrafluoroborate, 0.25 mM Ni(DPMDA), 0.1 M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 800 mV/s).	111
Figure 3.3.6. CVs of Ni(DPMDA) in the presence of acid with different scanning windows (1.25 mM anilinium tetrafluoroborate, 0.25 mM Ni(DPMDA), 0.1 M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 800 mV/s).	111
Figure 3.3.7. Catalytic CVs at different scan rates (0.1 M TBAP in acetonitrile, 0.25 mM Ni(DPMDA), 25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M AgNO ₃ reference electrode, scan rate = 5—to 60 V/s) (top); plot of normalized catalytic current vs scan rate (bottom).	113

- Figure 3.3.8. CVs of rinse test results using acetonitrile as the rinsing solvent (0.1 M TBAP in acetonitrile, 0.25 to 0 mM Ni(DPMDA), 7.5 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode scan rate = 40 V/s) (top); rinse test results with a wider scan window (bottom)..... 114
- Figure 3.3.9. CVs of mercury pool test for hydrogen evolution using Ni(DPMDA) (0.1 M TBAP in acetonitrile, 0.25 or 0 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, mercury pool working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s)..... 115
- Figure 3.3.10. CVs of rinse test results using acetone as the rinsing solvent (0.1 M TBAP in acetonitrile, 0.25 to 0 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, graphite rod counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s)..... 115
- Figure 3.3.11. CV of the surface supported/adsorbed active catalytic species in the absence of acid (0.1 M TBAP in acetonitrile, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s)..... 117
- Figure 3.3.12. Catalytic CVs with increasing acid concentration (0.1 M TBAP in acetonitrile, 0.25 mM Ni(DPMDA), 7.5 to 87.5 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M AgNO₃ reference electrode, scan rate = 40 V/s) (top); plot of normalized catalytic current vs acid concentration (bottom). 119
- Figure 3.3.13. Catalytic CVs with increasing concentration of Ni(DPMDA) (0.1 M TBAP in acetonitrile, 0.0039 mM to 0.25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M AgNO₃ reference electrode, scan rate = 40 V/s) (top); plot of normalized catalytic current vs concentration of Ni(DPMDA) (bottom). 120
- Figure 3.3.14. CV of the supported Ni(DPMDA) catalyst under optimized conditions showing all of the scan cycles (0.1 M TBAP, 0.25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s)..... 121
- Figure 3.3.15. a); c); e); g); and i) Consecutive 300 scan CVs of hydrogen evolution (with stirring in between experiments) using the surface supported/adsorbed active catalytic species (0.1 M TBAP, 81.25 mM anilinium tetrafluoroborate, glassy carbon working

electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 40 V/s); b); d); f); h); and j) representative CV traces of the stabilized catalytic current for each 300 scan experiment.	126
Figure 3.3.16. CVs of hydrogen evolution in a non-buffered solution, as well as a buffered solution (0.1 M TBAP, 0.25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate or 8.25 mM anilinium tetrafluoroborate and 81.25 mM aniline, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 40 V/s).	129
Figure 3.3.17. A representative CV trace of the stabilized catalytic current along with a control experiment with no Ni(DPMDA) in solution (0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 40 V/s).....	130
Figure 3.3.18. A representative controlled potential electrolysis experiment in acetonitrile (0.1 M TBAP, 0.25 mM Ni(DPMDA), and 81.25 mM anilinium tetrafluoroborate with a 6 mm glassy carbon rod working electrode, 0.01 M Ag/AgNO ₃ reference electrode; 0.1 M TBAP, 81.25 mM ferrocene with a 6 mm graphite counter electrode; 1 C of charge passed, potential held at -2.02 V vs Fc/Fc ⁺) showing: current vs time (top); normalized charge transferred vs time (bottom).	131
Figure 3.3.19. CVs of air- and moisture-stability tests using acetonitrile as the rinsing solvent (0.1 M TBAP in acetonitrile, 0.25 to 0 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 40 V/s).	132
Figure 3.3.20. Tafel plot and slope from a linear sweep voltammogram (LSV) of hydrogen evolution at low current densities and high scan rate (0.1 M TBAP, .25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 40 V/s) (top); Tafel plot and slope from a LSV of hydrogen evolution at high current densities and high scan rate.....	134
Figure 3.3.21. Tafel plot and slope from a linear sweep voltammogram (LSV) of hydrogen evolution at low current densities and low scan rate (0.1 M TBAP, .25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire	

counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 5 mV/s (top); Tafel plot and slope from a LSV of hydrogen evolution at high current densities and low scan rate.....	135
Figure 3.3.22. CVs of H/D KIE experiments (0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 81.25 mM anilinium or anilinium- <i>d</i> ₃ tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 40 V/s).....	136
Figure 3.3.23. CVs of hydrogen evolution (0.1 M TBAP in acetonitrile, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, graphite rod counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 40 V/s) using pre-treated glassy carbon working electrodes (sanning to various negative potentials in 0.1 M TBAP, 0.25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, scan rate = 40 V/s, and then rinsing with acetonitrile with: narrow scanning window (top); a wider scanning window (bottom).	137
Figure 3.3.24. Visual representation of the ground state structure of the protonated analog of Ni(DPMDA).	138
Figure 3.3.25. Free energies of 1 (left) vs 2 (right).....	139
Figure 3.5.1. ¹ H NMR spectrum (600 Mhz, DMSO- <i>d</i> ₆) of Ni(DPMDA).	146
Figure 3.5.2. ¹³ C NMR spectrum (600 MHz, DMSO- <i>d</i> ₆) of Ni(DPMDA).	147
Figure 3.5.3. IR spectrum (solid pellet) of Ni(DPMDA).....	148
Figure 3.5.4. ² H NMR spectrum (61 MHz, DME- <i>h</i> ₁₀) of anilinium tetrafluoroborate- <i>d</i> ₃ with on equivalent of CD ₃ CN added as an internal standard.....	151
Figure 3.5.5. Image of the electrolysis cell utilized for controlled potential electrolysis after 1 C of charge had been passed.....	153
Figure 4.2.1. Examples of a Rauchfuss hydrogenase mimic (left), a Nocera “hangman porphyrin” (middle), and a Bullock Ni diphosphacycloheptane complex (right).	162
Figure 4.2.2. Structure of Ni(DPMDA).	164
Figure 4.3.1. CVs of Ni(DPMDA) with low concentrations of HNEt ₃ (top) and a representative CV trace of the stabilized catalytic current along with a control experiment with no Ni(DPMDA) in solution (bottom). (0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 0, 0.25, 2.5, or 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 1 V/s.	166

Figure 4.3.2. Rinse tests performed after scanning a solution of Ni(DPMDA) to various negative potentials vs reference (0.1 M TBAP, 0 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 1 V/s).....	167
Figure 4.3.3. Rinse test after catalysis with Ni(DPMDA) using acetonitrile as the rinsing solvent (top), repetitive scans of the rinsed electrode (middle), and rinse test with acetone as the rinsing solvent (bottom, 0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 1 V/s).....	169
Figure 4.3.4. Mercury pool test for Ni(DPMDA) (0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, mercury pool working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 1 V/s).....	169
Figure 4.3.5. CVs of Ni(DPMDA) and triethylammonium tetrafluoroborate in non-buffered and buffered solutions (top) and CV of a rinse test without buffer after running in buffered solution (bottom). (0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, 0 or 25 mM triethylamine, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 1 V/s).....	171
Figure 4.3.6. CVs of the Ni(DPMDA) modified electrode in electrolyte only solution or in the presence of 0.25 mM triethylammonium. (0.1 M TBAP, 0 or 0.25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 1 V/s).....	173
Figure 4.3.7. A representative controlled potential electrolysis experiment in acetonitrile showing charge passed over time (top) and current response over time (bottom) (0.1 M TBAP, 0.25 mM Ni(DPMDA), and 25 mM triethylammonium tetrafluoroborate with a 6 mm glassy carbon rod working electrode, 0.01 M Ag/AgNO ₃ reference electrode; 0.1 M TBAP, 5 mM ferrocene with a 6 mm graphite counter electrode; 1 C of charge passed, potential held at -1.87 V vs. Fc/Fc ⁺).	174
Figure 4.3.8. CVs of Ni(DPMDA) in the presence of increasing amounts of triethylammonium (top) and linear correlation of triethylammonium concentration with current response (0.1 M TBAP, 2.5 mM to 50 mM triethylammonium tetrafluoroborate, glassy carbon working	

electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate= 1 V/s).....	176
Figure 4.3.9. CVs of Ni(DPMDA) in the presence of triethylammonium at various scan rates (top) and graph of observed current vs scan rate (bottom) (0.1 M TBAP, 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate= 1 to 14 V/s).	177
Figure 4.3.10. CVs of Ni(DPMDA) in the presence of triethylammonium at different catalyst concentrations (top) and linear variation of catalytic peak potential with varying catalyst concentration (bottom, 0.1 M TBAP, 0.025 to 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 1 V/s).....	180
Figure 4.3.11. Tafel slope plot from LSV of Ni(DPMDA) at low current density region. (0.1 M TBAP, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 5 mV/s).....	181
Figure 4.3.12. CVs of Ni(DPMDA) in the presence of triethylammonium or triethylammonium- <i>d</i> (0.1 M TBAP, 0.25 mM Ni(DPMDA), 50 mM triethylammonium tetrafluoroborate or triethylammonium tetrafluoroborate- <i>d</i> , glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO ₃ reference electrode, scan rate = 8 V/s).....	182
Figure 4.5.1. ² H NMR spectrum (61 MHz, DME-h10) of triethylammonium tetrafluoroborate- <i>d</i> with one equivalent of CD ₃ CN added as an internal standard.	189
Figure 5.2.1. Structures of proposed substituted diketodipyrromethanes.....	200
Figure 5.2.2. Proposed structures of a crown ether calixpyrrole complex (left) and of doubly cationic trimethyl anilinium complex.	201
Figure 5.2.3. Proposed structure of calixpyrrole complex with substituted pendant amines. ...	202

List of Tables

Table 2.3.1. Selected Bond Lengths (Å) and Angles (deg) for 1a and 1c.	55
Table 2.3.2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a-c	60
Table 2.4.1. Comparison of Relevant Catalyst Parameters	78
Table 2.5.1. Selected Crystal Data, Data Collection, and Refinement Parameters for Compounds 1a-c.	89
Table 2.5.2. Selected Crystal Data, Data Collection, and Refinement Parameters for Compounds 2a-c.	89
Table 3.4.1. Comparison of Relevant Catalyst Parameters	143
Table 3.5.1. Selected Crystal Data, Data Collection, and Refinement Parameters for Ni(DPMDA).	148
Table 4.4.1. Comparison of Relevant Catalyst Parameters.	186

List of Schemes

Scheme 2.3.1. General Synthetic Procedure for Calixpyrrole Ligands 1a-c.	51
Scheme 2.3.2. General Synthetic Procedure for Palladium Complexes 2a-c.	58
Scheme 3.3.1. General Synthetic Procedure for Ni(DPMDA).	104

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Chapter 1 – Introduction

As global energy consumption continues to rise, the necessity of finding alternative fuel sources is of increasing importance. Between 2012 and 2022 world energy consumption increased more than 14%.¹ Furthermore, while utilization of renewable energy is increasing,¹ the intermittency of these energy sources remains a significant challenge in developing a sustainable future.² Additionally, as a consequence of increased fossil fuel consumption, humanity is experiencing increases in natural disasters, air quality deterioration, increased prevalence of droughts, and rising sea levels.³ In an effort to meet energy requirements, while also reducing environmental impacts, significant research contributions toward small molecule activation (i.e. CO₂, N₂, H⁺/H₂, etc.) have been investigated.⁴⁻⁸ A major challenge in activating these small molecules is the necessity of transfer ring multiple protons and electrons, such as with the reduction of dioxygen, where the buildup of charge on the substrate make subsequent reductions less favorable.⁹

To circumvent the problems that arise from the transfer of multiple protons and electrons to a substrate, nature provides inspiration for synthetic catalyst design. One of the most well-studied enzymes, the Fe-Fe hydrogenase, provides insight into the significance of proton relays. In 2020 Lampret *et al.* reported modifications to the Fe-Fe hydrogenase enzyme where glutamate was exchanged for aspartate in the amino acid side chain adjacent to the active site.¹⁰ This amino acid side chain was implicated in proton transfer to the catalytic active site and its utility as a proton shuttle was demonstrated by the marked decrease in catalytic activity upon modification.¹⁰ Furthermore, an important feature of the hydrogenase active site is the presence of a Brønsted basic moiety in the secondary coordination sphere in the form of a bridging azadithiolate ligand.^{10,11} Such moieties in the secondary coordination sphere have found utility as proton-shuttles, which lower activation barriers by positioning protons near metal centers.^{4,12} Additionally, H-bonding moieties in the secondary coordination sphere enable stabilization of catalytic intermediates and improve catalysis by the Sabatier Principle, which states that interactions between a catalyst and substrate should be neither too weak nor too strong.^{13,14} The advantages of these proton relays manifest themselves in catalysis by lowering overpotentials and increasing turnover frequencies. This is achieved by coupling the transfer of protons and

electrons, thereby avoiding higher energy charged intermediates. One study which highlights this effect was carried out by Rauchfuss and colleagues where a dramatic decrease in catalytic rate, in addition to a much larger overpotential, was observed upon exclusion of the proton relay in an Fe-Fe hydrogenase mimic.¹⁵ Despite multiple investigations into improving catalysis through control over the secondary coordination sphere, synthetic catalysts rivaling the hydrogenase enzyme, which is thought to operate at overpotentials <100 mV, have yet to be realized.¹⁶

1.1 Homogeneous Catalysts

When studying control over the secondary coordination sphere via proton shuttling, researchers often look to homogeneous catalysts where the catalyst is in the same phase as the substrate.^{4,5,11,16–18} One advantage of homogeneous catalysts is the greater degree of control over the catalyst structure compared to heterogeneous catalysts. On this note, it has been observed that heterogenized molecular catalysts suffer from their inability to isomerize due to increased structural rigidity¹⁹ and other heterogeneous catalysts, such as metal-alloys^{20–22}, lack the organic ligand structure necessary for structural modifications such as proton relays. Additionally, homogeneous catalysis is not limited to a catalytically active surface area. Likewise, the study of homogeneous catalysts allows easier examination of reaction kinetics because of the ability to more easily determine catalyst concentrations whereas heterogeneous catalysis often requires more complicated characterization techniques such as XPS to determine surface-bound catalyst concentrations.

1.1.1 Hydrogenase Mimics

Over the years a large amount of progress has been made in homogeneous electrocatalytic hydrogen evolution reactions (HER). As mentioned above, the hydrogenase enzyme found in nature is the best hydrogen evolving catalyst in terms of overpotential requirements and as such, a large amount of research has been dedicated to replicating its activity.^{23–53} A notable example of synthetic HER electrocatalysts is a model system investigated by Rauchfuss *et al.* where a diiron complex with a bridging amine dithiolate (adt) ligand was meant to mimic the Fe-Fe hydrogenase active site (**Figure 1.1.1**).^{15,54} This complex, which closely resembles the active site of the Fe-Fe hydrogenase except that it employs a 1,2-

bis(diphenylphosphino)ethene ligand, was shown to be active for HER using chloroacetic acid and trifluoroacetic acid (TFA).¹⁵ The authors

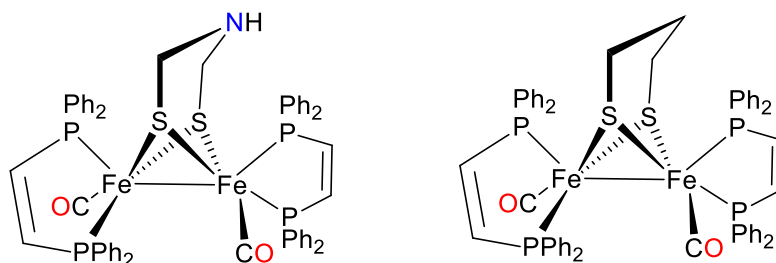


Figure 1.1.1. Structure of [Fe-Fe] hydrogenase mimics bearing a pendent adt ligand (left) or propane dithiolate (right).

of this study also drew a comparisons between two different variants of the catalyst where one contained the bridging adt ligand, while the other analogous complex had a propane dithiolate (pdt) ligand, omitting the pendant amine.¹⁵ The results showed that inclusion of the amine moiety in the secondary coordination sphere between the two Fe centers significantly improved catalysis, as evidenced by the ability of the terminal hydride (*t*-H) adt complex (**Figure 1.1.2**) to reduce weaker acids, as well as the *t*-H adt complex exhibiting lower overpotentials of 510 mV with TFA as compared to 1,032 mV using HBF₄ for the *t*-H pdt complex. Additionally, under those same conditions, the *t*-H adt complex exhibited turnover frequencies (TOFs) of 58,000 s⁻¹ while the *t*-H pdt complex was much slower showing TOFs of only 5 s⁻¹ even with a stronger acid.¹⁵ Similarly, in 2010, a Ni-Fe analogue was reported by Barton and Rauchfuss where the

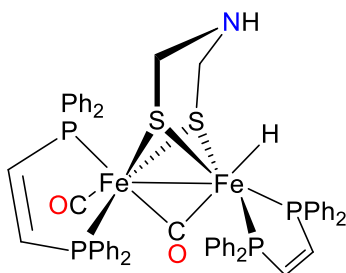


Figure 1.1.2. Structure of catalytically active *t*-H adt complex.

two metal centers were bridged by a propane dithiolate ligand (**Figure 1.2.3**).⁵³ The nickel center is further chelated by bis(diphenylphosphino) ethane while two CO molecules are coordinated to the iron center in addition to a sixth ligand being either CO, triphenyl phosphite,

triphenylphosphine, or diphenylphosphinopyridine. Electrocatalytic HER investigations revealed that the $E_{cat/2}$ values for the complexes ranged from -1.2 to -1.32 V vs Fc/Fc⁺ with the triply CO ligated complex having the lowest overpotential of 310 mV in agreement with its more anodic reduction potential. However, the overpotential of the protonated diphenylphosphino pyridinium ligated complex was shown to be significantly lower at only 260 mV showcasing the effects of a protonation site in the secondary coordination sphere.⁵³ Additionally, the CO ligated complex gave a TOF that was 60% lower than the other three complexes which may be attributed to the character of the metal-hydride intermediate. As discussed above, typically the *t*-H intermediate is invoked in [Fe-Fe] hydrogenase mimics. The authors noted that while these series of [Ni-Fe] complexes formed bridging hydrides, the hydride was significantly closer to the iron center, indicating that it may be considered more as a terminal hydride rather than a bridging hydride. Interestingly, comparison of the relative M-H bond lengths indicated that in the triply CO ligated complex, the hydride was closer to the nickel center than in the triphenylphosphine ligated complex, perhaps indicating that more *t*-H character is responsible for the increase in TOF.⁵³

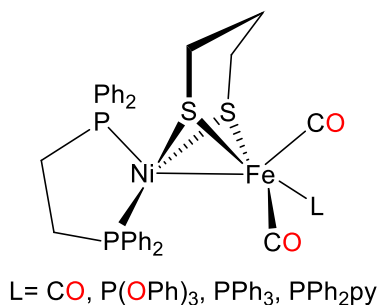


Figure 1.1.3. Structure of the pdt ligated [Ni-Fe] hydrogenase mimic.

More recently, Song *et al.* reported a [Ni-Fe] hydrogenase mimic in which the nickel center adopted a piano stool geometry with a cyclopentadienyl ligand, while the pseudooctahedral iron center was bound by CO and either bis(diphenylphosphino) ethane (dppe) or bis(diphenylphosphino) ethene (dppv) (**Figure 1.1.4**).⁴¹ Significantly, unlike the previously discussed [Ni-Fe] hydrogenase mimic, this paper reported the first [Ni-Fe] adt complex, providing a potential proton shuttle in the secondary coordination sphere. The authors found that the amine substituents affected catalysis observing that the Cbz (benzyloxycarbonyl) substituted amine, which is more electron-withdrawing, produced higher normalized catalytic currents (i_{cat}/i_p – where i_{cat} is the catalytic current in the presence of acid and i_p is the current response of the

catalyst in the absence of acid) than the more basic NH bridges.⁴¹ Interestingly, all of the variants with a bridging amine gave higher i_{cat}/i_p values than the pdt bridge [Ni-Fe] complexes discussed above (at 10 mM TFA concentrations). In contrast, the NH bridged complex with a presumably more basic amine, attained lower overpotentials than the Cbz substituted variant.⁴¹ This was likely due to more effective protonation of the more basic moiety which caused an anodic shift of 45 mV compared to 15 mV for the Cbz substituted complex. Even still, the pdt bridged [Ni-Fe] complex discussed in the previous paragraph gave lower overpotentials as a result of catalysis operating through a reduction potential which was ~50 mV more positive in the absence of acid, likely as a result of different ancillary ligands between the two metal centers, thus influencing redox properties.^{41,53}

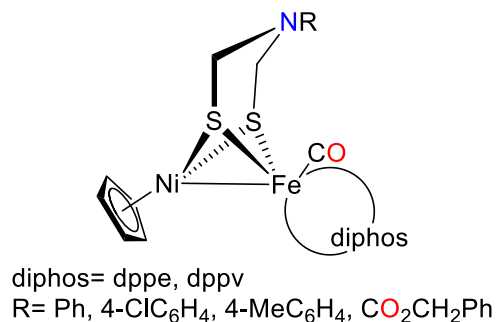


Figure 1.1.4. Structure of a [Ni-Fe] hydrogenase mimic with an adt ligand.

1.1.2 Ni(II) bis(diphosphine) Complexes

Another notable example of proton relays in electrocatalytic HER is that of the Ni(II) bis(diphosphine) complexes studied extensively by Bullock, Dubois, and colleagues (**Figure 1.1.5**).^{5,16,16,55–58} Throughout various studies, the authors observed differences in catalytic activity upon making changes to the pendant amine substituents. For example, early studies indicated that when the ligand with phenyl-substituted amines was used, TOFs of 350 s⁻¹ were observed.⁵⁷ However, when these substituents were exchanged for benzyl groups,⁵⁸ TOFs were much lower at only 5 s⁻¹, thus showing early indications that the pendant groups were mediating catalysis.⁵⁵

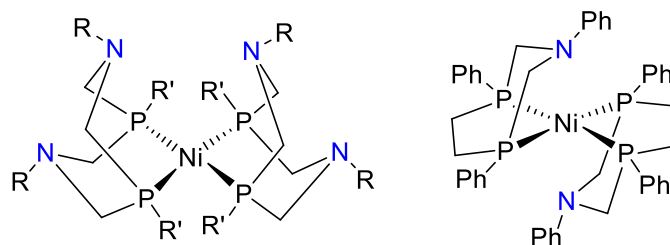


Figure 1.1.5. General structure of the diphosphacyclooctane (left) and diphosphacycloheptane (right) Ni(II) bis(diphosphine) complexes.

Interestingly, when the phosphine ligands were changed from an eight-membered ring containing two pendant amines each (as in the aforementioned complexes) to a seven-membered ring only containing one pendant amine each, the TOFs for electrocatalytic HER of up to $33,000 \text{ s}^{-1}$ were seen, which were shown to be enhanced to over $100,000 \text{ s}^{-1}$ in the presence of water.¹⁶ The large enhancement in the presence of water was attributed to water facilitating the conversion of an inactive exo-protonated isomer to a catalytically active endo-protonated isomer.¹⁶ Such high TOFs make this catalyst one of the fastest known molecular electrocatalysts; however the marked increase in catalytic turnover was accompanied by an increased overpotential compared to the phenyl-substituted eight-membered ligand variant. The inclusion of only one amine was hypothesized to avoid an inactive pinched isomer where the proton is bound between the two pendant hydrogen-bond donors (**Figure 1.1.6**). The authors also noted that the greater planarity of the seven-membered ring caused a more negative reduction potential for the $\text{Ni}^{\text{II/I}}$ couple and therefore a larger overpotential for HER. Likewise, the more reducing nature of this catalyst produced a more hydridic intermediate facilitating the final H_2 elimination step more than its eight-membered analogue.¹⁶

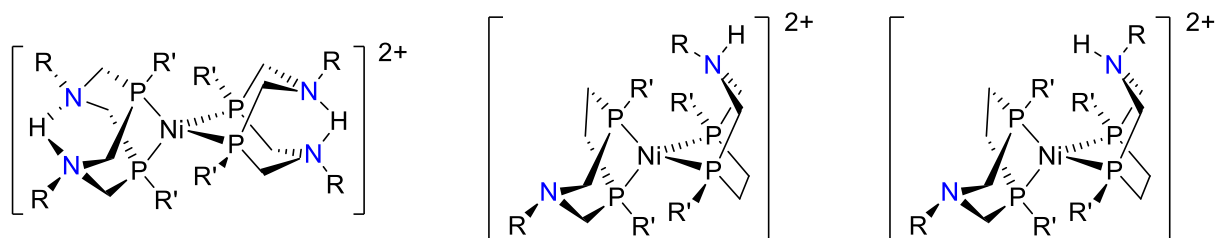


Figure 1.1.6. Structure of protonated “pinched” exo-exo isomer of Ni(0) bis(diphosphine) complex (left), exo protonated isomer of Ni(I) bis(diphosphine) with diphosphacycloheptane rings (middle) and endo protonated isomer of Ni(I) bis(diphosphine) (right).

Inspired by previous studies, Bullock and coworkers set out to investigate how the aforementioned exo-protonation of the pendant amine could be inhibited.¹⁸ Rather than install a tertiary amine to more accurately control pendant group pK_a , an analogous complex bearing secondary amines was developed with the aim of ensuring that an endo-proton would be available at all times to interact with the metal center after protonation.¹⁸ Studies with addition of water to the catalytic system showed no effect in contrast to the previously discussed variant with tertiary amine shuttles. Given the perceived role of water in the conversion of inactive exo-isomers into catalytically active endo-protonated intermediates, it was hypothesized that the lack of effect of water confirmed the availability of an endo-proton at all times as desired. Because of the different acids used in each study, Bullock and coworkers conducted a comparison experiment using a solution of anilinium buffer in the presence of the previously discussed phenyl substituted variant. The TOF was found to be over 1 order of magnitude less than that of the complex bearing secondary amines. Even in the presence of water the tertiary amine complex exhibited only a modest increase in TOF. This was in part due to: 1) the bulkiness of the acid and amine, encouraging exo-protonation; and 2) the less basic nature of the tertiary amine hindering protonation by a weaker acid.¹⁸ Together, these studies highlighted the importance of controlling the pK_a and steric parameters of the proton relay in the secondary coordination sphere.

1.1.3 Hangman Porphyrins

Another notable series of complexes that utilize pendant groups are “hangman” porphyrins, corroles, and chlorins investigated extensively by Nocera and coworkers.^{4,8,59–63} These catalysts feature a carboxylic acid moiety in the secondary coordination sphere which has been identified as a proton shuttle for reduction catalysis such as HER, oxygen reduction, and carbon dioxide reduction.^{4,64–67} Originally, the porphyrin system consisted of a xanthene backbone and a carboxylic acid group positioned over the catalytic center (**Figure 1.1.7**).⁶⁷ The cobalt complex of this ligand was shown to be active for HER in the presence of relatively weak acids such as benzoic acid. Significantly, the authors found that when they substituted the carboxylic acid moiety with a bromine group, the overpotential for hydrogen evolution from

benzoic acid increased by about 120 mV.⁶⁷ For weak acids, catalysis was shown to go through a $\text{Co}^{\text{I}/0}$ redox couple. Upon addition of benzoic acid, the authors found that while the bromo-substituted variant did exhibit an anodic shift at the $\text{Co}^{\text{I}/0}$ redox couple, the carboxylic acid-substituted complex, in contrast, did not show a shift in the $\text{Co}^{\text{I}/0}$ redox owing to facile (and therefore non-rate-determining) proton transfer from the carboxylic acid moiety.⁶⁷ Conversely, with stronger acids, both complexes exhibited catalytic waves at similar potentials, with catalytic onset beginning closer to the $\text{Co}^{\text{II/I}}$ couple. This indicated that a stronger acid was able to directly protonate Co^{I} and thus the “hangman” effect was not observed.⁶⁷ Similarly, analogous Ni^{II} complexes were synthesized and shown to be active for electrocatalytic HER using benzoic acid.⁴ Compared to the parent Co^{II} complex, the Ni^{II} complex operated with lower overpotential due to the ability of the benzoic acid to directly protonate the Ni^{I} intermediate following reduction. Contrary to the Co complex, initial cyclic voltammograms (CVs) of the Ni complex bearing a pendant carboxylic acid moiety showed an additional irreversible wave between two reversible redox couples (assigned as $\text{Ni}^{\text{II/I}}$ and $\text{Ni}^{\text{I}/0}$) whereas the bromo-substituted Ni complex showed only two reversible redox couples. The additional irreversible reduction wave was attributed to proton reduction, and these results solidified the role of the pendant carboxylic acid as a proton shuttle for HER. Additionally, as expected, the bromo-substituted complex showed a catalytic wave in the presence of benzoic acid at significantly more cathodic potentials.⁴

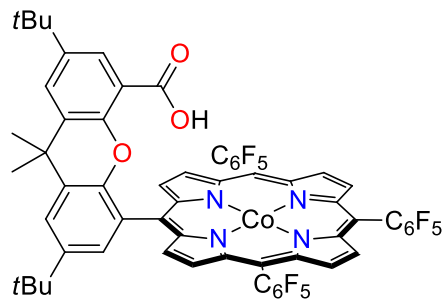


Figure 1.1.7. Structure of a Co “hangman” porphyrin with xanthene spacer.

More recently, Nocera and coworkers further investigated the role of pendant proton relays by altering the distance between the pendant carboxylic acid and the metal center in Co^{II} “hangman” porphyrins.⁶⁸ Specifically, two new complexes bearing pendant carboxylic acid groups were synthesized. Rather than the xanthene backbone, these complexes consisted of a phenyl ring at the *meso* position of the porphyrin substituted with a carboxylic acid in the *ortho*

or *para* position (**Figure 1.1.8**). The CVs of these complexes revealed a reversible $\text{Co}^{\text{II/I}}$ couple for at almost identical potentials to those seen for the complex bearing the xanthene backbone, which is in agreement with a catalytic pathway following protonation through a doubly reduced cobalt intermediate (Co^0).^{67,68} The second redox feature, corresponding to the $\text{Co}^{\text{I/0}}$ couple, differed for the two complexes with the *ortho*-substituted complex having an irreversible redox couple, while the *para*-substituted complex displayed a reversible redox event 290 mV more cathodic vs. the ferrocene/ferricium redox couple (Fc/Fc^+). Notably, the irreversible redox event in the *ortho*-substituted complex was ~ 170 mV more positive than that of the xanthene-substituted hangman porphyrin, further showcasing that placing a proton donor closer to the catalytically active metal center increases catalytic efficiency. In addition to the closer distance of the hanging carboxylic acid group, the authors noted that the use of a phenyl backbone compared to the xanthene backbone increased the acidity of the pendant group. This also resulted in stepwise proton transfer/electron transfer (PTET) and/or a simultaneous proton-coupled electron transfer (PCET) mechanism for HER rather than a stepwise electron transfer/proton transfer (ETPT) as was seen in the xanthene substituted complex.⁶⁸ This simultaneous transfer, likely facilitated by the closer proximity of the acidic moiety, importantly avoided energetically unfavorable charged intermediates.⁶⁹

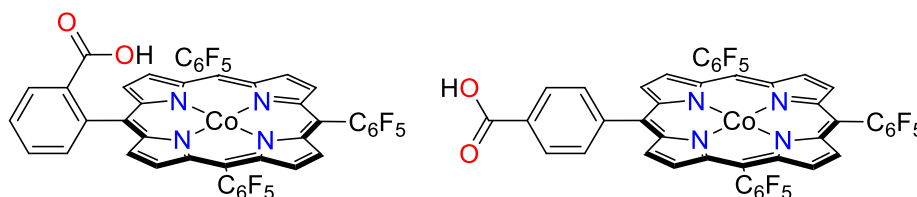


Figure 1.1.8. Structure of Co hangman porphyrins with phenyl spacers between the metal and pendant group.

1.1.4 Schiff-base Ligands

Aside from the porphyrin/porphyrinoid and phosphine containing complexes discussed above, Schiff-base ligands are another commonly employed chelate in transition metal catalysis. An advantage of Schiff-base ligands over porphyrin and phosphine systems is their ease of synthesis which allows simple modification using a variety of functionalized amines and aldehydes/ketones. One prominent class of Schiff-base ligands in homogeneous catalysis are

salens or salophens which are derived from the condensation of salicylaldehyde and a diamine.⁷⁰ Importantly, this class of Schiff-base ligands coordinates a variety of metal ions and demonstrates increased moisture tolerance due to increased stability of the imine upon metal coordination.⁷¹ One of the most notable homogeneous catalysts bearing salen ligands is Jacobsen's catalyst (**Figure 1.1.9**), which features a chiral ligand coordinated to Mn(III). This complex, as well as analogous systems, were found to be efficient catalysts for asymmetric epoxidation of cis-alkenes.^{70,72} Additionally, salens and salen-like complexes have been shown to catalyze a variety of transformations including, but not limited to: alkene aziridination,⁷³ epoxide ring opening,⁷⁴ epoxide kinetic resolution,⁷⁵ and sulfimination.⁷⁶ In contrast, examples of salen complexes as homogeneous electrocatalysts are less common owing to their propensity to adsorb to electrode surfaces.^{77–79}

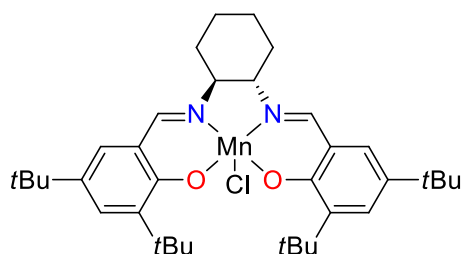


Figure 1.1.9. Structure of Jacobsen's catalyst.

Another relevant example of homogeneous Schiff-base catalysts are binuclear macrocyclic Co(II) Schiff-base calixpyrrole complexes (**Fig 1.1.10**).^{80–82} These ligands adopt wedged “pacman”-like shapes resembling similar cofacial diporphyrin complexes.^{17,83–85} Significantly, these ligand architectures, independently investigated by Love⁸⁶ and Sessler,⁸⁷ were obtained in much higher yields and with less expensive starting materials in contrast to the “pacman” porphyrins, while retaining a similar binuclear cleft.⁸¹ Interestingly, these complexes were found to affect the reduction of dioxygen using reductants with potentials similar to the potentials seen for cofacial diporphyrins.⁸¹ However, the authors also noted another similarity to cofacial porphyrins in that a desired superoxo intermediate was only formed as a minor species during catalysis giving low selectivity toward the four electron reduction of oxygen to water. This was ascribed to faster electron transfer (as compared to proton transfer) generating a peroxo intermediate. This, once again, emphasizes the need for proton shuttling to facilitate faster proton

transfer or PCET.⁸¹ Later studies by the Love group investigated the effect of altering the angle and distance between the two metal centers, and these investigations showed that substituting an anthracenyl backbone in favor of an *o*-phenylenediamine spacer favored reversible oxygen binding, which also favored the formation of the desired superoxo complex over a peroxo intermediate.⁸⁸ In contrast to the porphyrinic analogues, the authors found that the use of stronger acids inhibited catalysis, and they hypothesized that using too strong of an acid may protonate the pyrrolide donors causing metal dissociation.⁸⁸

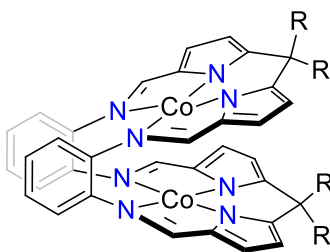


Figure 1.1.10. Structure of a bimetallic Co macrocyclic Schiff-base calixpyrrole complex.

1.2 Heterogeneous Catalysts

While homogeneous catalysts have been the subject of much research and advancement, heterogeneous catalysts offer their own set of advantages, which make them more industrially viable. For example, catalyst separation from the product is much easier, and both liquid and gas phase substrates can be used in continuous flow reactors.⁸⁹ Additionally, immobilization of catalysts on electrodes may avoid bimolecular decomposition pathways associated with homogeneous molecular species.^{90,91} Therefore, electrode materials have received a lot of attention in the field of heterogeneous electrocatalysis, and while platinum has been the most efficient HER catalysts,⁹² its high cost and relatively low abundancy hinder its practicality. This has led to wide interest in developing novel electrode materials such as metal-alloy,^{20–22} chalcogenide,^{93–95} carbide,^{96–98} nitride,^{99–101} boride,^{102–104} and phosphide catalysts.^{105–107} Disadvantages, however, of heterogeneous catalysts include that they may suffer from diminished reactivity and selectivity compared to their homogeneous counterparts, which have more well-defined active sites.¹⁰⁸

To this end, there has been a significant amount of research towards the immobilization of known molecular species on electrode surfaces to combine the favorable properties of homogeneous and heterogeneous electrocatalysts.^{19,65,109–126} This is advantageous in that greater control over the structures of the primary, secondary, and outer coordination spheres is more attainable using this strategy. Additionally, as mentioned above, immobilization of molecular catalysts may avoid bimolecular decomposition pathways. Confinement of catalysts to electrode surfaces is also inherently more atom economical since all the catalyst on the electrode is active as compared to homogeneous electrocatalytic systems where most of the catalyst is inactive in the bulk solution. Furthermore, attaching molecular species to electrode surfaces allows for easier comparison between different catalysts under the same conditions because the catalyst-modified electrode can be utilized in various solvents in which the original homogeneous complexes may not be soluble.¹²⁴

1.2.1 Covalent Attachment

A particular advantage to covalent attachment as opposed to other electrode immobilization methods is the stability of the covalent bond, which may help prevent leaching of the catalyst into solution.¹²⁶ Additionally, covalent attachment with functionalized complex ligands allows precise control over the surface concentration of the catalyst. One example of this is the covalent attachment of homogeneous Ni(II) diphosphacycloheptane complexes developed by Bullock and coworkers to an electrode surface.¹⁹ The attachment proceeded via coupling of 1,2,3-triazolyl lithium sites on the surface of a pre-treated glassy carbon electrode with activated ester linkages on the Ni(II) and Ni(0) complexes (**Figure 1.2.1**). The free homogeneous complex was shown to exhibit similar redox features to the previously studied Ni bis(diphosphine) complexes (discussed above), and similarly were shown to be active for catalytic hydrogen evolution with a TOF_{max} of 1900 s^{-1} and an overpotential of 700 mV. When the covalently attached complex was subjected to the same catalytic conditions, a catalytic wave with identical onset potential to the soluble parent complex was observed, however the TOF_{max} was found to be significantly lower at just 28 s^{-1} .¹⁹ It was noted that the marked decrease in TOF could be due to restrictions in boat/chair conformational changes that control the endo/exo position of the amines

to the metal center. Given that previous studies have indicated the substituents on the amine functionalities could slow the isomerization to the necessary boat conformation (pointing the amine endo to the metal center), it is feasible that the electrode anchor, attached through a pendant group, could slow this isomerization.¹²⁷ In addition, steric crowding may have limited the proximity of the metal center to the electrode surface slowing down electron transfer.¹⁹ Another example from Artero and coworkers looked at covalently attaching a Ni bis(diphosphine) complex to multi-walled carbon nanotubes.¹⁰⁹ While the catalyst showed an impressive overpotential of only 200 mV in aqueous media, it was likewise hindered by a TOF of only 5.5 s^{-1} . The authors similarly hypothesized that the bulky linkers utilized to immobilized the transition metal complexes on to the solid supports may have hindered necessary conformational changes for catalytic turnover.¹⁰⁹ These results highlighted the challenges faced when trying to control the secondary coordination sphere at an electrode surface, and perhaps suggested that more planar or rigid molecules would perform better on an electrode surface because they would not experience the same isomerization mechanisms that are likely to be restricted by covalent attachment methods.

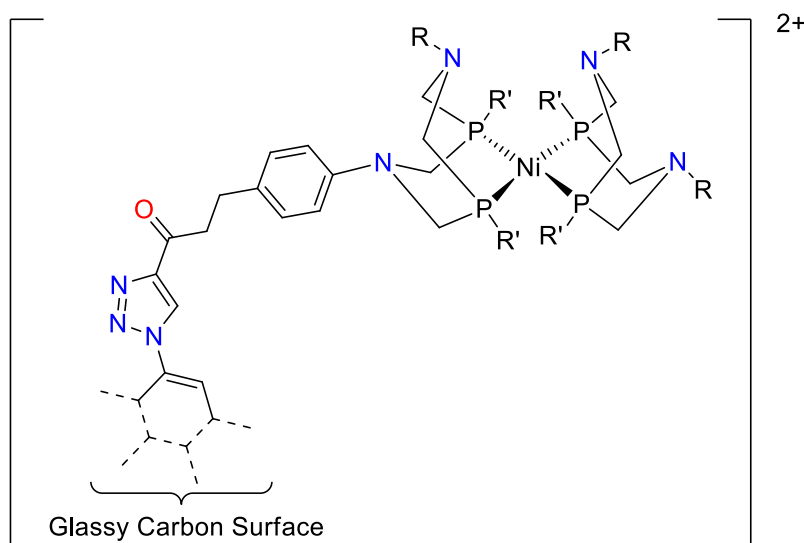


Figure 1.2.1. Ni(II) diphosphacycloheptane complex covalently attached to a glassy carbon electrode surface.

More recently, important progress in understanding the kinetics of adsorbed catalysts has been presented by Surendranath *et al.* where the authors studied HER using a Co(II) tetraphenyl

porphyrin (TPP) complex tethered to a glassy carbon electrode by aliphatic cyclohexyl linkers (**Figure 1.2.2**).¹¹⁰ CV measurements in an organic solvent, acetonitrile, revealed an outer sphere redox event attributed to the $\text{Co}^{\text{II/I}}$ couple. Moreover, HER was shown to be tied to this redox couple. When weaker acids were used, catalysis ceased, suggesting that HER was mediated by the $\text{Co}^{\text{II/I}}$ couple and initiated by outer sphere electron transfer to the metal.¹¹⁰ Remarkably, when water was used as the solvent, no outer sphere electron transfer was observed in the CV. Moreover, unlike the response in acetonitrile, the adsorbed Co tetraphenyl porphyrin catalyzed hydrogen evolution across a broad pH range with the onset of catalysis varying linearly with pH.¹¹⁰ This remarkable result was similar to that seen with Co(II) corroles covalently attached to carbon nanotubes where the modified electrode catalyzed HER and OER across an unusually broad pH range.^{111,128} Likewise, conjugated covalent attachment of a phenanthroline through imine bonds gave way to strong electronic coupling and accessible hydrogen evolution catalysis across the entire pH range by eliminating the possibility of a stepwise mechanism.¹²⁹ Tafel slope analysis of the Co(TPP) catalyst in aqueous media revealed rate limiting charge transfer step. Subsequent H/D kinetic isotope effect (KIE) studies revealed that rate determining proton transfer occurred, giving evidence for a PCET mechanism. This behavior was rationalized by hypothesizing that the Co(TPP) occupied different positions relative to the electrode surface in different solvents. Unlike acetonitrile, a solvent in which the complex was soluble, in water the Co(TPP) was directly adsorbed on the electrode surface (within the electric double layer), producing strong electronic coupling between the electrode and complex, and inducing inner sphere electron transfer.¹¹⁰ These qualities were potentially ascribed to π - π interactions with the electrode in water, which engendered a catalytic species that surprisingly behaved more like a metal surface rather than a molecular species. These results challenge the way other heterogenized catalysts are viewed.¹¹⁰ With this new perspective, that adsorbed molecular species may behave more like metal surfaces, it may be beneficial to develop heterogeneous catalysts directly adsorbed on the electrode surface, which also control the secondary coordination sphere within the electric double layer.

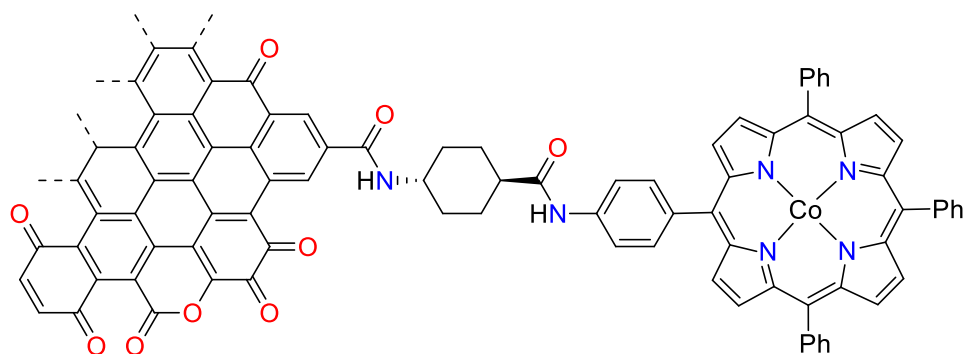


Figure 1.2.2. Structure of Co(TPP) covalently linked to glassy carbon.

1.2.2 Electrostatic and π - π Attachment

Non-covalent attachment of catalysts to electrode surfaces offers some advantages with respect to covalent attachment. One of the biggest advantages is that for noncovalent attachment, electrode preparation is often much simpler, making this approach more accessible for larger scale industrial reactions.¹¹² One noteworthy example, as it pertains to the previously mentioned catalysts, is an investigation carried out by Artero and coworkers where they utilized π - π interactions to attach a Ni bis(diphosphine) complex (similar to the homogeneous analogues used by Bullock and Dubois) onto multi-walled carbon nanotubes (MWCNT).¹¹² The complex, modified to include a pyrene moiety (**Figure 1.2.3**), was able to be adsorbed onto MWCNT and used with commercial proton exchange membranes. While catalytic rates were quite sluggish, with TOFs of only up to 3.9 s^{-1} achieved, the catalyst showed good durability, remaining stable for at least 6 hours under a constant applied potential. Furthermore, when compared to a previously studied electrodeposited analogue of the Ni bisdiphosphine system (discussed further below) the surface concentration of active sites increased by nearly one order of magnitude. Additionally, adsorption through π - π interactions allowed for precise control over catalyst loading.¹¹²

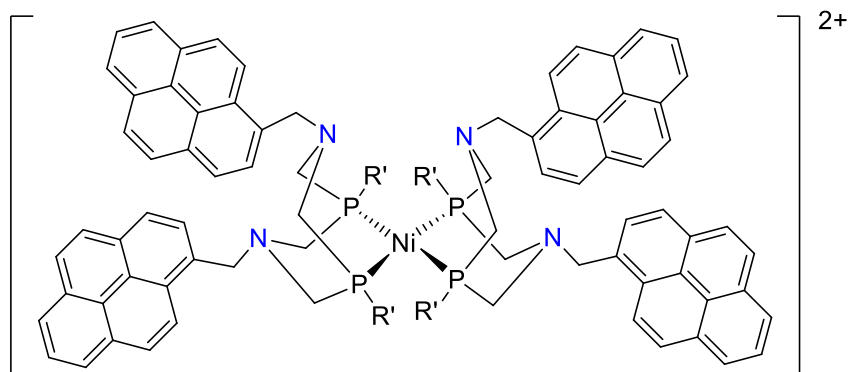


Figure 1.2.3. Structure of a Ni(II) bis(diphosphine) complex with attached pyrene functionalities.

Similarly, in parallel with the previously discussed hydrogenase mimics, Artero and coworkers recently established $\{(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6\}$ derivatives (simplified [Fe-Fe] hydrogenase mimics) adsorbed to CNT electrodes via π - π stacking through a pyrene moiety (**Figure 1.2.4**).¹¹³ Inspired by previous studies showing the utility of π - π adsorption toward improving catalyst loading, enhancing electronic communication with the electrode, and increasing stability under acidic conditions,^{114–117} the authors aimed to circumvent these issues, which have been shown to arise from $\{(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6\}$ adsorption techniques such as nonspecific physisorption and covalent linkages.^{113,118,119} The prepared catalyst featured two iron centers bridged by a 1,4-naphthaquinone-2,3-dithiolate ligand, from which two pyrene moieties were attached. The adsorbed complex was active for HER, however, as seen with the previously discussed adsorbed complexes, the modified MWCNT electrodes showed low TOFs of $<1 \text{ s}^{-1}$. This result was hypothesized to be a consequence of degradation of the Fe-S bond during catalysis (observed spectroscopically). Nonetheless, attachment of the two pyrene moieties to the electrode surface through π - π interactions proved to enhance surface coverage and give higher TOFs when compared with the parent heterogenized complex, which incorporated only the bridging naphthaquinone-dithiolate moiety.¹¹³

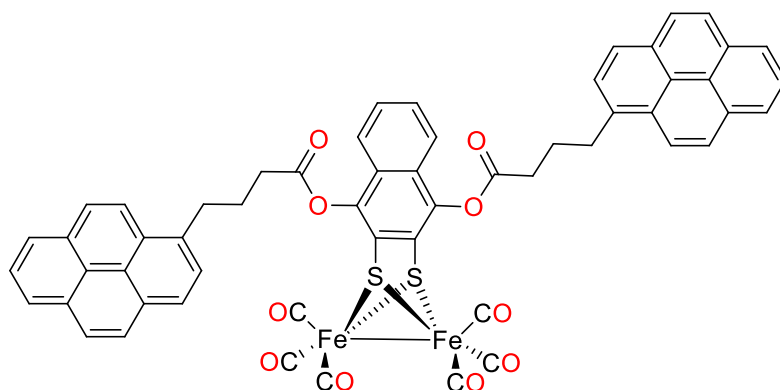


Figure 1.2.4. Structure of a [Fe-Fe] hydrogenase mimic with attached pyrene functionalities.

Building on these results, Artero *et al.* recently reported the π - π adsorption of a similar metallopolymer complex (**Figure 1.2.5**).¹²⁰ With this complex and its variants, the authors studied the effects of multiple pyrene anchor points, as well as dangling amine groups. Increasing the relative pyrene content of the polymer up to 8% showed increased catalytic activity, with decreases in activity above that point rationalized to be a result of increased hydrophobicity limiting H^+ diffusion to the catalyst. Remarkably, the metallopolymer outperformed the previously discussed pyrene anchored complex, attaining TOFs ~60 times higher despite achieving loadings of less than 25% of the aforementioned complex. These results illustrated how the tertiary amines in the secondary coordination sphere environment could increase catalytic efficiency in heterogeneous HER.¹²⁰

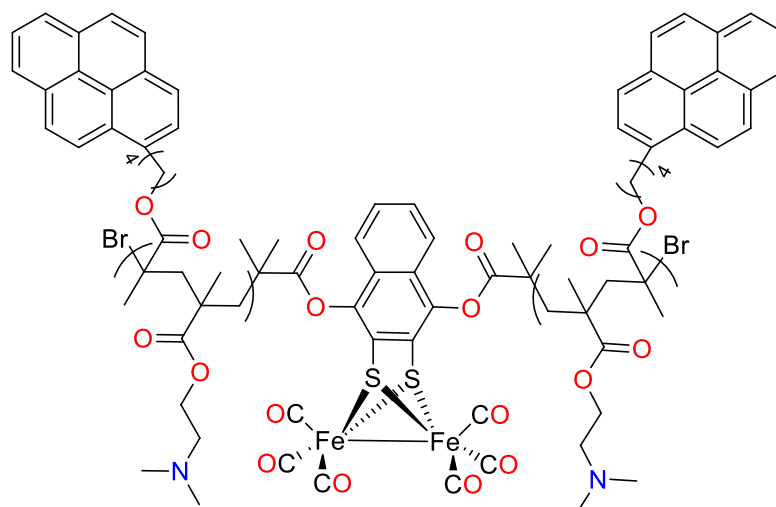


Figure 1.2.5. Structure of a metallopolymer [Fe-Fe] hydrogenase mimic with attached pyrene functionalities.

Another example of an eminent homogeneous catalyst that has been heterogenized using non-covalent attachments to an electrode surface is the Ni(II) cyclam complex. This catalyst, known for its activity toward CO₂ to CO reduction^{130–132} was appended to a pyrene moiety (**Figure 1.2.6**) through one of the four amine groups by Fontecave *et al.*¹¹⁵ The authors noted that the best electrode material for the parent unfunctionalized [Ni(cyclam)]²⁺ was a mercury electrode to which the complex adsorbs well,¹³⁰ and indeed the pyrene-adjointed complex performed relatively poorly as a homogeneous catalyst when used with carbon electrodes. While the pyrene-appended complex did not effectively adsorb to glassy carbon, as indicated by variable scan rate studies and rinse tests, the catalyst readily adsorbed onto MWCNT functionalized electrodes. The adsorbed complex retained high selectivity toward CO production and demonstrated an increased TOF compared to the homogeneous complex. This marked one of the few examples of catalytic improvement upon heterogenizing a molecular CO₂ reduction catalyst.¹¹⁵ Importantly, when compared with a previous study of a covalently attached [Ni(cyclam)]²⁺ catalyst to glassy carbon, the π - π adsorbed catalyst offered significantly improved CO selectivity and higher TOFs due to its ability to adsorb to MWCNT electrodes with high surface area.¹¹⁵

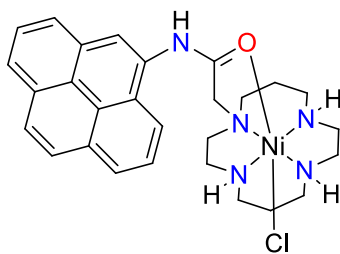


Figure 1.2.6. Structure of a Ni(II) cyclam with appended pyrene moiety.

It is worth noting that additional examples of π - π adsorption to electrode surfaces via other aromatic moieties exist. For example, heterogeneous iron(III) polypyridyl complexes have been reported, which were appended by a naphthalene-terminated moiety. The complex was found to be active for HER, although the authors noted that at higher concentrations of strong acids, such as tosic acid, the complex started to desorb.¹²¹ Likewise, the functionalization of carbon surfaces with a Co(II) bis(terpyridine) complex was previously studied.¹²² In this study the authors compared adsorption of a naphthalene terminated ligand with the adsorption of a pyrene terminated ligand. Importantly, the adsorption free energy of the naphthalene terminated complex was found to be much less favorable in comparison to the pyrene analog, which was rationalized by the smaller π -delocalization system relative to pyrene.¹²² In addition, simple phenyl groups have also been used to adsorb catalysts via π - π interactions, such as with Cobalt(II) benzenedithiolate complexes which were active for catalytic HER.¹²³ Importantly, the authors were able to tune the concentration of the adsorbed species through the addition of halogenated substituents on the phenyl rings with increasing substitution yielding higher surface coverage.¹²³ However, it was also found that an analogous naphthalenedithiolate complex adsorbed at surface concentrations twice that of the best halogen-substituted benzenedithiolate.¹²³ Together, these studies indicated that while smaller π -delocalization systems can generate electrode adsorbed species, larger polycyclic moieties, specifically pyrene, perform much better.

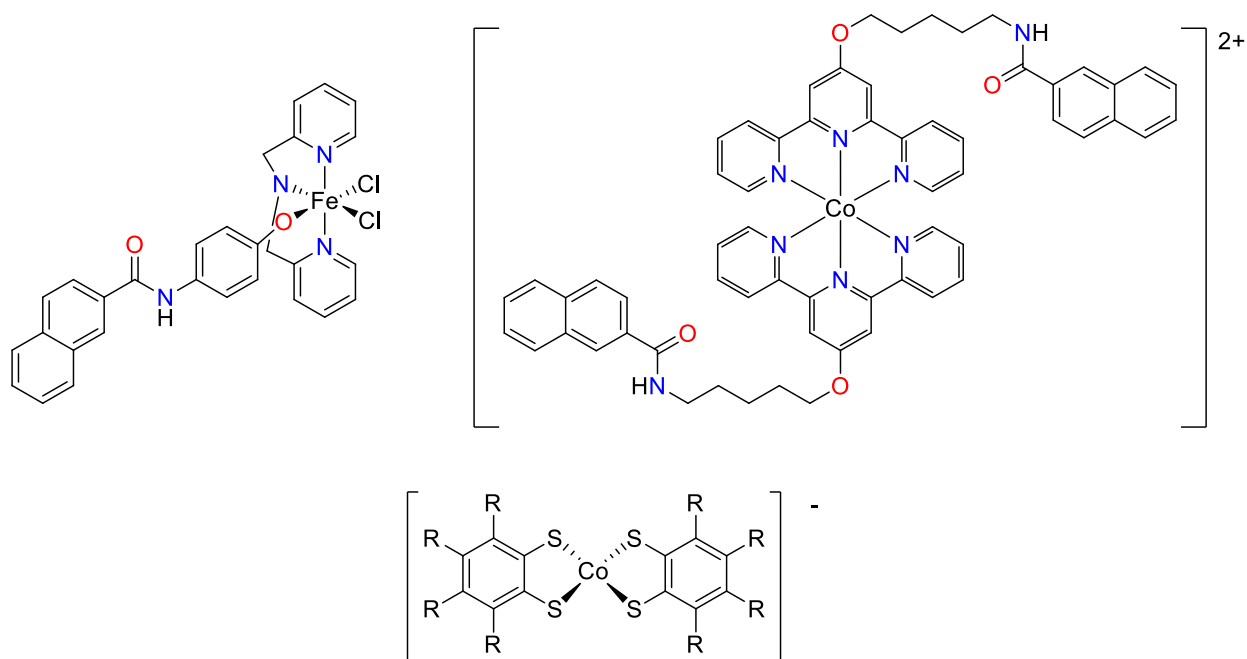


Figure 1.2.7. Structures of a naphthalene-terminated Fe(III) polypyridyl complex (left), a naphthalene-terminated Co(II) bis(terpyridine) complex (right), and a Co(III) bis(benzenedithiolate) complex (bottom).

Other aromatic systems, such as porphyrins, can also be adsorbed to electrodes such as graphene^{133–137} or MWCNTs.^{65,138–141} One such example is that of Co(II) “hangman” porphyrins studied by Nocera *et al.*⁶⁵ This study reported the adsorption of “hangman” porphyrins onto MWCNT electrodes and evaluated their activity toward selective oxygen reduction to water. The results of this study showed that the hangman porphyrin adsorbed onto MWCNT behaved similarly to the cofacial cobalt bisporphyrin system adsorbed to the same support in terms selective oxygen reduction to water.^{65,84} Specifically, the study found that the combination of the hanging carboxylic acid functionality and the electron-withdrawing groups at the *meso* positions of the porphyrin provided the highest selectivity for the four-electron reduction to water. Conversely, exclusion of the pendant group, even in the presence of electron-withdrawing *meso* substituents, produced a selectivity for water that was 23% lower than the analogous “hangman: porphyrin. Similarly, changing the *meso* substituents of the hangman porphyrin to groups that were less electron-withdrawing resulted in a marked decrease in selectivity. Altogether, the results of this study prove that redox cooperativity between two metal centers, such as that seen in the cofacial bisporphyrins, is not necessary for selective reduction of oxygen to water.

Furthermore, it established that the pendant carboxylic acid group aided in directing proton transfer to an oxygen-adduct intermediate. The importance of this principle was highlighted with DFT studies on homogeneous “pacman” complexes where the authors found that *meso* phenyl substituents *trans* to the pendant group interrupted proton transfer, and lowered selectivity towards the four-electron reduction of oxygen to water.^{17,65}

1.2.3 Electrodeposition

Electrodeposition or electropolymerization is another approach that can be utilized to heterogenize molecular catalysts onto an electrode surface. This method differs in that the heterogeneous films that form are often generated through decomposition pathways, as seen with nickel bis(glyoximate) complexes,¹⁴² and the formation of nanoparticles from molecular cobalt species.^{143–145} Given this route often involves complex degradation, electrodeposition may obscure the identity of the catalytically active species when compared with methods that involve more precise attachment methods.

A well-studied class of complexes that have been shown to form deposited films under electrocatalytic conditions are salens and salophens.^{146–148} These complexes are known to form metallopolymer films on the surface of electrodes through oxidative pathways, which are influenced by the substituents on the phenol rings. These groups affect the planarity of the systems and ultimately control the ability to form an electroactive polymer.^{149,150} This characteristic was illustrated with different cobalt salen complexes, where *t*-butyl substituents were added to the *ortho* and *para* position of the phenol moieties (**Figure 1.2.8**).¹⁵¹ The presence of the *t*-butyl functionalities resulted in poorer catalyst performance towards water oxidation, despite high surface coverage.¹⁵¹ These results highlighted the inherent limitations of improving catalytic efficiency in electrodeposited systems through modifications of the ligand architecture, without ultimately disturbing the ability to form a polymeric film.

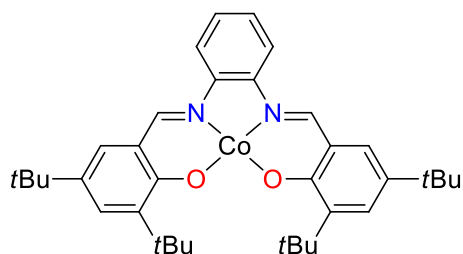


Figure 1.2.8. General structure of a Co-salophen complex with *t*-butyl substituted phenol rings.

Dempsey and coworkers also reported a $[\text{Ni}(\text{N}-\text{N}-\text{SCH}_3)_2][\text{BF}_4]_2$ complex (**Fig 1.2.9**) that was active toward electrocatalytic hydrogen evolution.¹⁵² Initial voltammograms of the complex indicated that the observed redox couples corresponded to a homogeneous species. Under catalytic conditions in the presence of acid, however, a pre-wave formed more cathodic in comparison to the catalytic wave. The authors found that this pre-wave corresponded to a 2-electron⁻ transfer that was thought to arise from the reduction of an imine bond in the ligand. Moreover, when compared with an analogous complex bearing secondary amines in place of imines (**Fig 1.2.9**), it was found that under catalytic conditions this complex catalyzed hydrogen evolution at similar potentials to the parent imine-ligated complex, but did not exhibit the pre-wave. Interestingly, rinse tests revealed that when the CV was scanned past the pre-wave potential, a catalytically active species was deposited on the electrode surface, which evolved hydrogen at similar potentials as the original system. For the comparative amine complex, electrodeposition was found to occur in the absence of acid, demonstrating that acid was required to first hydrogenate the imine bond prior to electrodeposition. X-ray photoelectron spectroscopy (XPS) results indicated the presence of Ni^0 , as well as a second unidentified nickel species on the surface. Further studies revealed that catalysis resulted from both species on the electrode surface. It was also noteworthy that the reduction of the ligand only took place at more negative potentials than the pre-wave, suggesting that the $\text{Ni}^{\text{II/I}}$ reduction assisted ligand reduction.¹⁵² Similar electrochemical hydrogenation of an imine ligand was also invoked by Dempsey *et al.* in their study of an analogous iron (II) complex.¹⁵³ Moreover, they found that electrochemical imine reduction, catalyzed by the metal center, was implicated in deposition of catalytically active cobalt nanoparticles using tris(glyoximate)Co complexes.¹⁵⁴ Other macrocyclic Schiff

base complexes have also been shown to decompose and form surface adsorbed nanoparticles under extended periods of electrolysis.¹⁵⁵

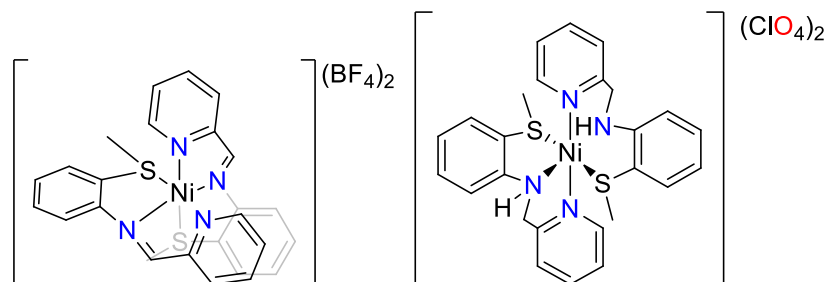


Figure 1.2.9. Structure of $[\text{Ni}(\text{N}-\text{N}-\text{SCH}_3)_2]^{2+}$ complex (left) and $[\text{Ni}(\text{pyridine-2-thiolate})_3]^-$ studied for electroadsorption.

More recently, Grapperhaus *et al.* have reported nickel and palladium complexes containing C=N bonds which were active for HER (**Figure 1.2.10**).¹⁵⁶ Under catalytic conditions, these complexes both exhibited pre-waves cathodic to the catalytic wave suggesting that a side reaction was occurring. Mechanistic studies revealed that catalysis proceeded through multiple ligand-centered reduction pathways; initiating through PCET to the ligand, then stepwise reduction and protonation to form a doubly protonated hydrogen evolving species. Rinse test studies revealed the deposition of a catalytically active film, and, interestingly, it was found that the film that was generated had a large contribution to the observed catalytic current. Furthermore, it retained high faradaic efficiencies.¹⁵⁶ Even more recently, Grapperhaus *et al.* reported similar results with an analogous Zn complex and its activity toward electrocatalytic CO_2 reduction.¹⁵⁷ Characterization of the resulting catalytically active film (generated from the reductive catalytic conditions utilized) revealed that elemental zinc was deposited on a carbonaceous film.¹⁵⁷ These results highlight how ligand design may influence decomposition pathways and lead to different heterogeneous materials with different morphologies.

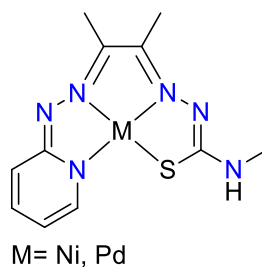


Figure 1.2.10. Structure of diacetyl-2-(4-methyl-3-thiosemicarbazone)-3-(2-pyridinehydrazone) complexes studied by Grapperhaus *et al.*

1.3 Pyrrolide Ligands

Pyrrolide ligands are anionic donor ligands when coordinated through the deprotonated nitrogen moieties. These ligands are known to be redox active and serve as possible electron reservoirs due to their high energy π -orbitals.^{158–160} Particularly, dipyrromethanes are prone to oxidation, forming a bond between the two α -carbons.^{158,161} Because of their high energy orbitals, pyrrolide donors can enhance the reducing power of metals allowing for activation of small molecules such as CO_2 ^{162,163} and N_2 .^{164–167} Other characteristics of these calixpyrrole ligands specifically include the effects of *meso*-substituents, which, while not conjugated to the rest of the ligand, have recently been shown to affect the bite angle and thus metal coordination in Ni(II) dipyrromethane-phosphine complexes.¹⁶⁸ The ability of pyrrolide ligands to act as electron reservoirs has also been exploited in ligand design by conjugating the π system with that of pyridine rings (**Figure 1.3.1**).^{162,163,169,170} This coupling of the aromatic rings has been hypothesized to create a “push-pull” effect as the pyridine π orbitals are lower lying in energy and are capable of being reduced.¹⁶⁹ Other studies, however, have indicated that the conjugation between pyridine and pyrrole rings instills amide-like character in the pyridine nitrogen, suggesting that reduction of a pyridine-pyrrole ligand would be more difficult than other pyridine derivatives.^{170–172} Additionally, this conjugation between rings has been shown to stabilize high oxidation state metals and increase the reducing power of lower oxidation state metals.¹⁷⁰

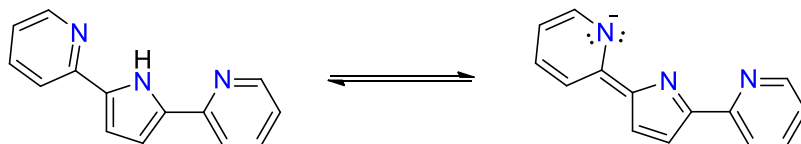


Figure 1.3.1. Resonance structures of pyridine-pyrrole-pyridine ligands.

1.4 Sues Group Chemistry

Following years of studies on cofacial “pacman” porphyrins,^{83,85,173–176} Love and Sessler both independently developed analogous macrocyclic Schiff base calixpyrroles.^{80,81,81,82,87,88,177,178,178,179} Importantly, Schiff base calixpyrroles offer a more facile synthetic route for accessing the ligand utilizing cheap materials, while still accessing macrocycles that adopt cofacial geometries. Furthermore, as discussed above, Nocera and coworkers took inspiration from the cofacial porphyrin systems for their “hangman” porphyrin complexes. Their modifications to these systems favored inclusion of a proton shuttling group in the secondary coordination sphere over a second metal center.^{4,8,59–63} Given the promising results generated by the Nocera group, the Sues group has applied a similar approach to the macrocyclic Schiff base calixpyrroles as seen with hangman porphyrins. That is, targeting “half” of the Love calixpyrrole macrocycles, and retaining unreacted amine groups on the backbone moieties to potentially act as proton shuttles in the secondary coordination sphere in place of a second metal center.

1.5 Thesis Goals

The goal of this thesis is the development and characterization of novel dipyrromethane Schiff base complexes bearing pendent hydrogen bonding moieties for use as small molecule activation electrocatalysts. Synthesis and characterization of both the ligands and metal complexes are discussed, as well as their electrochemical properties as they pertain to electrocatalysis, especially HER. Mechanisms are probed by electrochemical methods, as well as by computational studies using density functional theory (DFT).

Chapter 2 discusses the development of the novel calixpyrrole ligand architecture with pendant groups, the first reported coordination complexes using these ligands, and preliminary catalytic activity toward proton reduction in organic solvent. The results of this work were published in *Polyhedron*.¹⁸⁰ The synthesis of the calixpyrrole ligands is presented which allowed for the isolation of the “half pacman” tetradentate donor in good yield. Various pendent group modifications were also tolerated, and all the isolated ligand variants were coordinated to palladium. Electrocatalytic HER was also explored in the presence of *para*-toluenesulfonic acid, which revealed the generation of a stable catalytically active heterogeneous film. Computational

studies indicated that the highest occupied molecular orbitals of the metal complexes were mostly ligand-centered and that oxidations were likely ligand-centered.

Chapter 3 focuses on the corresponding Ni(II) complex of the calixpyrrole ligand bearing pendant amines. The characterization of this complex by spectroscopic, crystallographic, and electrochemical methods is discussed. The results of this study were published in *Chem. Eur. J.*¹⁸¹ and revealed electrodeposition of a catalytically species on the electrode surface in the presence of a sufficiently acidic proton donor. The generation of this film/monolayer was potential dependent, and the resulting system displayed remarkable stability, while attaining a TOF of up to $366,000\text{ s}^{-1}\cdot\text{cm}^{-2}$. DFT results supported possible active catalytic intermediates. KIE studies along with Tafel analysis supported a rate-limiting PCET step.

Chapter 4 builds on the results of Chapter 3 and explores proton reduction by the Ni(II) calixpyrrole complex utilizing a weaker proton source (triethylammonium). Importantly, experimental results indicated that a heterogeneous catalyst was formed, which was not dependent on nickel-centered redox couples, suggesting that a different electrode-adsorbed species was generated in the presence of a weaker acid. Additionally, the complex showed to exhibit TOF of $4,900 \pm 800\text{ s}^{-1}$ or $69,000 \pm 11,000\text{ s}^{-1}\text{cm}^{-2}$ and lower overpotentials ($745 \pm 5\text{ mV}$) despite the use of a weaker acid. Significantly, the lack of a redox response by the electrode adsorbed species was indicative of strong electronic coupling to the electrode which, along with the pendant groups, is believed to lead to PCET. Tafel analysis and KIE studies lend further support toward a rate limiting PCET step.

Chapter 5 postulates on future opportunities with these unique ligand architectures. Specifically, ways that metal-centered reductions may become more accessible by shifting to more positive potentials. This may be achieved by addition of electron withdrawing groups at imine carbons, or by inclusion of a charged species into the ligand framework. The latter may be carried out in multiple ways such as quaternary amine salt formation on the pendant groups, or by incorporation of a crown ether moiety which may coordinate +1 and +2 cations. Additionally, the basicity of the pendant groups may be tuned with varying alkyl substituents on the pendant nitrogen. Although this is likely to cause a cathodic shift in the metal reduction potentials (due to conjugation) this could be avoided by utilization of diamines with alkyl backbones instead of phenyl.

1.6 References

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Chapter 2 – Palladium Complexes Bearing Calixpyrrole Ligands with Pendant Hydrogen Bond Donors: Synthesis, Structural Characterization, Electrochemistry and Dihydrogen Evolution

2.1 Abstract

A series of three calixpyrrole ligands (1a-c) with pendant nitrogen-based hydrogen bond donors, R, were synthesized and coordinated to palladium to produce metal complexes (2a-c), where R = NH₂ (a); NHC(O)CH₃ (b); or NHC(O)OC(CH₃)₃ (c). The calixpyrrole compounds were generated using a Schiff-base reaction starting with 5,5'-diformyl-2,2'-diphenyldipyrromethane and an aniline precursor. The deprotonated calixpyrrole species were subsequently bound to palladium to generate distorted square planar complexes. The pendant groups were not coordinated to the metal with Pd-N distances of 3.36 to 4.79 Å. The electrochemical properties of the palladium complexes were also explored, and 2a-c displayed two irreversible oxidations above 0.0 V vs. ferrocene/ferrocenium (Fc/Fc⁺), as well as two irreversible reductions below -0.70 V vs. Fc/Fc⁺. Interestingly, the free ligands showed similar electrochemical features, suggesting redox non-innocence. Preliminary reactivity studies indicated the palladium complexes did not activate small molecules, but they did catalyze H₂ evolution in the presence of acid. The onset of catalysis for 2a-c was approximately 0.4-0.5 V more positive than a glassy carbon electrode, and the active species could undergo 500 scans without significant changes in activity. The catalysts were found to be heterogeneous in nature and adsorbed onto the working electrode.

2.2 Introduction

Despite efforts to curb global reliance on fossil fuels, the use of such non-renewable energy sources has been steadily growing. Through a 20 year span from 1998 to 2018, worldwide fossil fuel consumption has increased more than 50%, and future projections predict that these values will continue to rise.¹ In order to avoid the consequences of increased global

temperatures,^{2,3} a substantial shift towards renewable energy sources is needed. To this end, there has been a surge in interest toward the activation of small molecules (such as N₂, CO₂, CH₃OH, H₂, etc.), which will be an integral part of creating a sustainable energy economy.⁴⁻⁸ One of the current barriers to implementing these technologies, however, is the transfer of multiple electrons and protons that is required for the activation of these types of molecules. While enzymes, such as hydrogenase or nitrogenase enzymes, can efficiently affect these transformations, synthetic catalysts, which often lack the complexity of enzymes, are commonly much less effective than their biological counterparts.⁹⁻¹³

One approach for facilitating small molecule activation is the placement of a proton shuttle (an acidic or basic moiety) near the catalytic center to enable the simultaneous transfer of a proton and electron, or proton-coupled electron transfer (PCET).¹⁴⁻¹⁶ This is commonly seen in protein active sites where the secondary coordination sphere is used to enable catalysis. A well-studied example that illustrates the importance of PCET is the [Fe-Fe]-hydrogenase, which can generate H₂ very efficiently with turnover frequencies >10,000 s⁻¹.¹⁷⁻¹⁹ The active site of this enzyme has a cofactor with a crucial bridging azadithiolate ligand that acts as a proton shuttle.^{5,11,17}

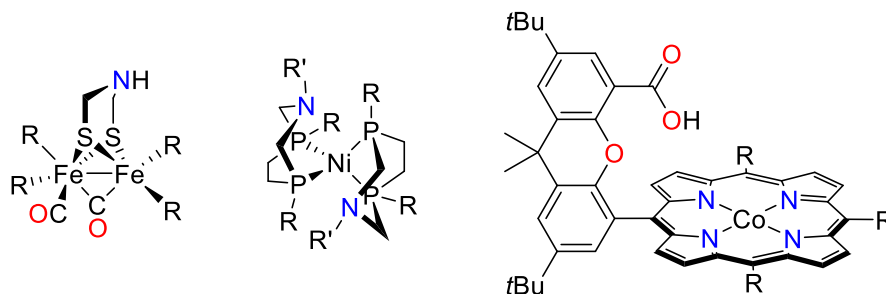


Figure 2.2.1. General structure of diiron azadithiolate-bridged complexes (left), nickel diphosphacycloheptane complexes (middle), and “hangman” porphyrin complexes (right).

In order to mimic enzyme active sites, a large amount of research on synthetic catalysts has focused on designing ligands that can place proton shuttles near the metal center.^{20,21} Rauchfuss *et al.*,²² have created diiron complexes bearing a pendant amine (via a bridging azadithiolate ligand) meant to mimic the active sites of [Fe-Fe]-hydrogenases (**Figure 2.2.1**). These complexes were able to participate in H₂ evolution, while operating at

overpotentials >700 mV.²² Similarly, Bullock *et al.* have developed a series of monometallic nickel diphosphacycloheptane complexes with pendant amines in an effort to mimic the proton shuttling capabilities of natural hydrogenases (**Figure 2.2.1**).^{5,23–25} These species are extremely active catalysts and were found to participate in both H₂ evolution and oxidation.^{5,23–25} While the turnover frequencies of some of these complexes have eclipsed 100,000 s⁻¹, the impressive catalytic rate is hindered by overpotentials of 625 mV (in comparison to some hydrogenases, which are thought to have overpotentials <100 mV).²³ Lastly, Nocera *et al.* have also demonstrated the utility of proton shuttles in electrocatalysis through the development of “hangman” porphyrins (**Figure 2.2.1**), chlorins, and corroles, which bear a carboxylic acid moiety overhanging the catalytic center.^{26–37} These species were found to be active for O₂ reduction, CO₂ reduction, and H₂ production. Unlike the previously mentioned catalysts, however, the hangman porphyrins could only facilitate the donation of a proton due to the less amphoteric nature of the carboxylic acid functionality. In addition, another drawback of the Nocera “hangman” systems is the difficult ligand synthesis, which hinders systematic modifications to the ligand architecture. A class of compounds related to porphyrins are macrocyclic Schiff-base calixpyrroles, which were researched independently by the Love group,^{38–46} as well as Sessler and co-workers.^{47,48} Shown in **Figure 2.2.2**, the co-facial complexes are analogous to the bimetallic “pacman” porphyrins developed by Collman, and many others.^{49–63} In contrast to porphyrins, calixpyrrole ligands are prepared in significantly higher yields utilizing a much more facile synthetic route (a Schiff-base reaction).⁴² Moreover, Love and co-workers have studied the use of cobalt “pacman” calixpyrrole complexes for the four-electron reduction of O₂.^{40–42} While they found that these systems do catalytically reduce oxygen, the active species (a bridged superoxo intermediate) is only generated in small amounts, leading to slow turnover.⁴² As noted by Love *et al.*, this issue was likely driven by ineffective protonation of the superoxo intermediate, generating a peroxo species which favoured the two-electron reduction of O₂ to H₂O₂.⁴² As such, incorporating proton shuttles into the secondary coordination sphere of the calixpyrrole ligand framework (in order to facilitate PCET) could help generate more effective catalysts for the activation of small molecules.

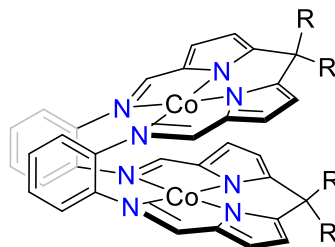


Figure 2.2.2. Example of a binuclear macrocyclic Schiff-base calixpyrrole complex.

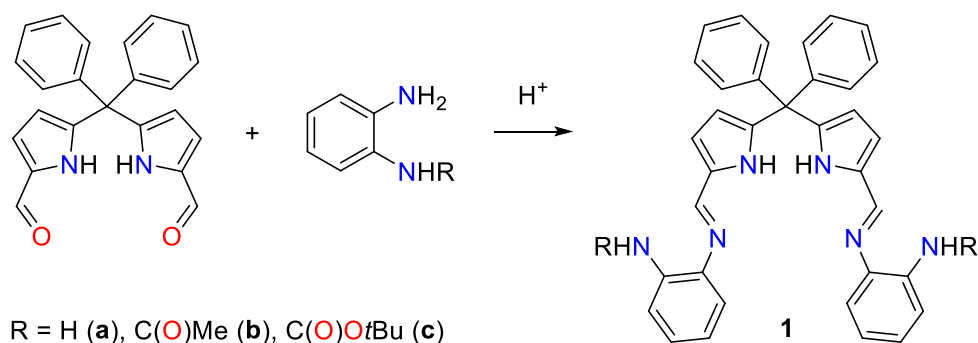
In this paper, we present the syntheses of Schiff-base calixpyrrole ligands with pendant functional groups, as well as their characterization. These species are similar to the “hangman” porphyrins developed by Nocera *et al.*^{26–37} in that the pendant functional groups provide an avenue for controlling the secondary coordination sphere, while also combining the ease of synthesis seen for the “pacman” calixpyrrole compounds.^{38–46} In addition, the first metal complexes bearing these ligands, palladium species, are discussed and the coordination geometry of the ligands is investigated with the aim of confirming that the pendant groups remain uncoordinated and discerning pendant group distance from the metal. Furthermore, it is expected that the lack of a macrocyclic structure (in contrast to the previously reported complexes) may improve flexibility of the ligand design, thus enabling accommodation of varying pendant group sizes while retaining the same mode of coordination to the metal center. Lastly, the electrochemical properties of the calixpyrrole systems are explored as well as electrocatalytic hydrogen evolution ability using *p*-TSA as the proton source. Given the electron-rich nature of pyrrolide donors, it is of interest to determine if metal-centered reductions are accessible in this system. Additionally, it is hypothesized that each complex, given their varying pendant group substituents, may exhibit varying catalytic activity. It is expected in this case that the complex bearing free amino pendant groups exhibits higher basicity in contrast to an acyl or boc substituted amine, which may aid in the proton-shuttling capability of the complex. With respect to nomenclature, throughout this paper the calixpyrrole ligands (**1**) will be named according to their pendant groups (**a** for amino; **b** for acyl; **c** for *tert*-butoxycarbonyl or Boc), while the palladium complexes will be named according to the bound calixpyrrole ligand (**2a-c** for **1a-c**, respectively).

2.3 Results and Discussion

2.3.1 Synthesis and Characterization of Compounds 1a-c.

Compounds **1a-c** were synthesized using an acid catalyzed Schiff-base reaction (**Scheme 2.3.1**). One equivalent of 5,5'-diformyl-2,2'-diphenyldipyrromethane was combined with an appropriate aniline precursor (*ortho*-phenylenediamine for **1a**, *N*-(2-aminophenyl)acetamide for **1b**, or *tert*-butyl (2-aminophenyl)carbamate for **1c**) in the presence of either trifluoroacetic acid (**1a**) or *para*-toluenesulfonic acid monohydrate (*p*TSA, **1b-c**). The synthesis of the dialdehyde precursor was previously reported by Love *et al.*,⁶⁴ using diphenyldipyrromethane as a starting material (the synthesis of which was described by Freckmann *et al.*).⁶⁵ In addition, the syntheses of *N*-(2-aminophenyl)acetamide⁶⁶ and *tert*-butyl (2-aminophenyl)carbamate⁶⁷ are known in the literature. The calixpyrrole ligands **1a** and **b** were obtained as orange or yellow solids, respectively, in moderate yields (60-62%), whereas **1c** gave much poorer yields overall (26%). We attributed this lower yield to the Boc protecting groups, which enhanced the solubility of the calixpyrrole ligand in organic solvents.

Scheme 2.3.1. General Synthetic Procedure for Calixpyrrole Ligands **1a-c**.



As mentioned above, **1b** and **1c** were prepared using *p*TSA, following a procedure very similar to the one used by Love and co-workers to generate calixpyrrole “pacman” ligands.³⁸ This synthetic route was extremely straightforward as the ligands precipitated cleanly from the methanol solvent. For **1a**, on the other hand, this approach also generated the desired product, but the ligand remained soluble in methanol and could not be separated from unwanted side-products (purification via silica gel chromatography was unsuccessful as the calixpyrrole ligand was sensitive to the acidic silica). Following a procedure similar to the one used by Trofimov *et al.*⁶⁸, however, **1a** could be synthesized and cleanly isolated. This

route utilized trifluoroacetic acid as the catalyst, as well as a concentrated dimethyl sulfoxide reaction mixture. By carefully limiting reaction times, the generation of unwanted side products could be avoided.

The ^1H NMR spectra of **1a-c** displayed several characteristic peaks that confirmed the proposed calixpyrrole species had been generated. For all three ligands a single imine peak was present in the expected region between 8 and 9 ppm. In addition, when utilizing DMSO- d_6 as the NMR solvent, the NH groups of the pyrrole moieties were visible between 11.36 and 11.46 ppm, as were the pyrrole methine protons between 5.79 and 6.80 ppm. The most characteristic peaks, however, arose from the hydrogens on the arene rings linking the pendant groups to the calixpyrrole ligand framework (between 6.5 and 8.2 ppm). All four of these protons had distinct chemical environments, unlike the symmetric calixpyrrole ligands developed by Love³⁸ and Sessler.⁶⁹ It should also be noted that compounds **1b** and **1c** displayed additional characteristics with the Boc- and acyl-NH peaks visible at 8.22 and 9.26 ppm, respectively, in conjunction with prominent singlets at 1.43 (methyl) and 1.98 ppm (*tert*-butyl), respectively. In contrast, for **1a** a broad singlet indicative of the pendant NH_2 was apparent at 5.28 ppm.

In addition to NMR experiments, compounds **1a-c** were characterized in the solid state utilizing single crystal X-ray diffraction. Crystals of both **1a** and **1c** (**Figure 2.3.1**) were grown under similar conditions (cold ether), and formed intertwined dimers in the solid state with intermolecular hydrogen bonding between the pyrrole hydrogens, the imine nitrogens, and the hydrogens from the pendant groups (NH_2 for **1a** and Boc-NH for **1c**; **Figure 2.3.2** and **Figure 2.3.3** respectively). On average, the dimer of **1a** was more tightly bound together than the dimer of **1c**, most likely due to the bulkier Boc groups in **1c**. There also appeared to be some degree of intermolecular π - π stacking between the arene backbone of one ligand and the phenyl substituent of another (centroid distances between 3.94 and 4.47 Å for **1a**, as well as 3.75 and 3.96 Å for **1c**), which could have provided some driving force for dimer formation (although this could also be due to crystal packing effects due to the relatively long centroid distances). For the unprotected ligand, **1a**, hydrogen bonding interactions between adjacent dimers was also seen: 2.97 and 3.04 Å for H5d--N5a and H5a--N5d (3.39 Å for N5a--N5d), respectively. The hydrogen bonding distances for the dimer of **1a** were: 2.35 Å for H5b--N4a (3.26 Å for N5b-

-N4a), 2.45 Å for H6a--N3b (3.28 Å for N6a--N3b), 2.30 Å for H1b--N4a (3.12 Å for N1b--N4a), 2.37 Å for H2a--N3b (3.20 Å for N2a--N3b), 2.11 Å for H1a--N4b (2.97 Å for N1a--N4b), 2.85 Å for H2b--N3a (3.50 Å for N2b--N3a), 2.43 Å for H5a--N4b (3.28 Å for N5a--N4b), and 2.12 Å for H6b--N3a (2.98 Å for N6b--N3a). For **1c**, on the other hand, hydrogen bonding distances were: 2.78 Å for H5b--N4a (3.57 Å for N5b--N4a), 2.90 Å for H6a--N3b (3.85 Å for N6a--N3b), 2.28 Å for H1b--N4a (3.14 Å for N1b--N4a), 2.24 Å for H2a--N3b (3.14 Å for N2a--N3b), 2.38 Å for H1a--N4b (3.20 Å for N1a--N4b), 2.21 Å for H2b--N3a (3.09 Å for N2b--N3a), 2.68 Å for H5a--N4b (3.45 Å for N5a--N4b), and 2.87 Å for H6b--N3a (3.65 Å for N6b--N3a).

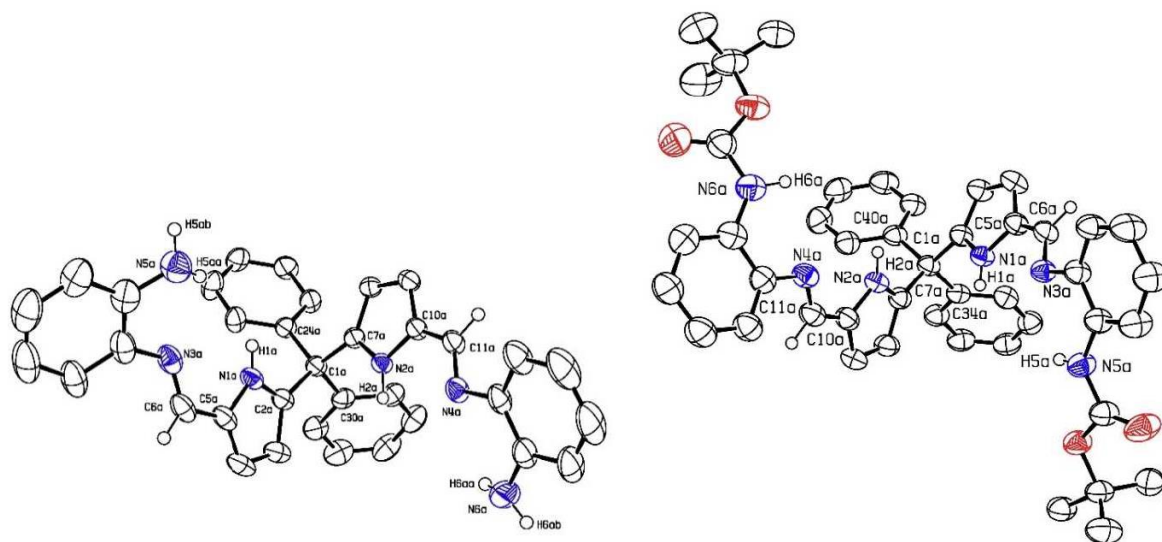


Figure 2.3.1. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: A single molecule of **1a**, the solvent, most of the hydrogens, and three other molecules of **1a** have been omitted for clarity (left); A single molecule of **1c**, the solvent, most of the hydrogens, and the other molecule of **1c** have been omitted for clarity (right).

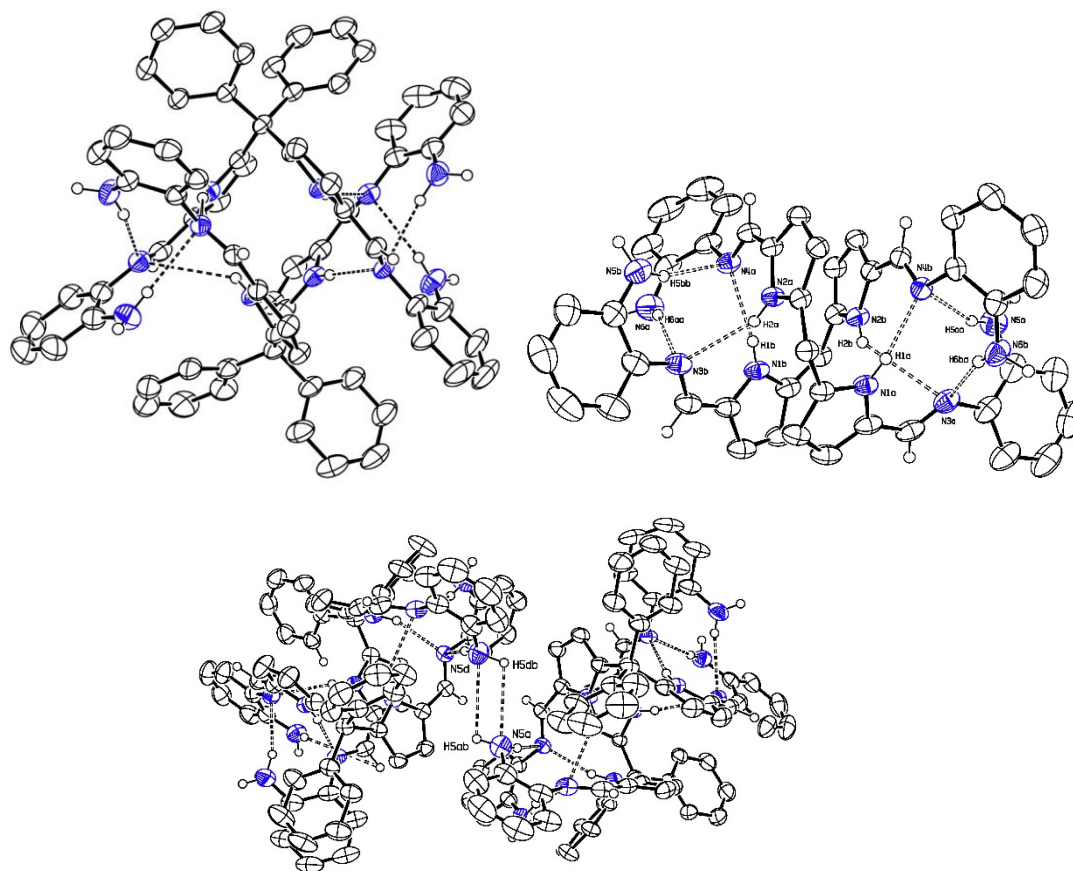


Figure 2.3.2. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: A top view of the intertwined dimer of **1a**, the solvent, most of the hydrogens, and the other dimer of **1a** have been omitted for clarity (top left); A side view of the intertwined dimer of **1a**, the solvent, most of the hydrogens, the phenyl substituents between the pyrrole groups, and the other dimer of **1a** have been omitted for clarity (top right); The hydrogen bonding between two dimers of **1a**, the solvent and most of the hydrogens have been omitted for clarity (bottom).

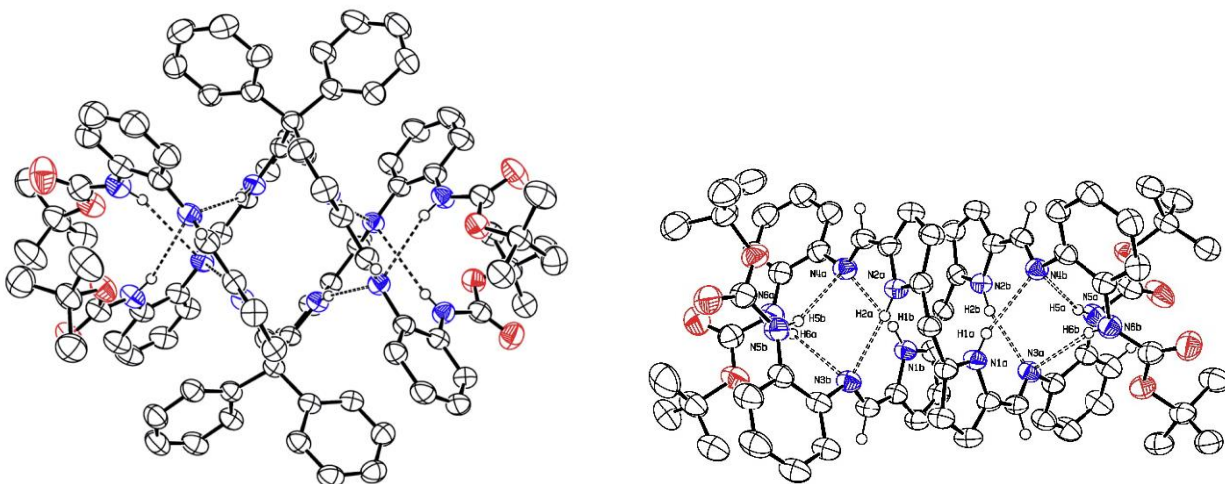


Figure 2.3.3. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: A top view of the intertwined dimer of **1c**, the solvent and most of the hydrogens have been omitted for clarity (left); A side view of the intertwined dimer of **1c**, the solvent, most of the hydrogens, and the phenyl substituents between the pyrrole groups have been omitted for clarity.

Crystals of **1b**, on the other hand, were not forthcoming using the same conditions as **1a** and **1c**. Instead, a different solvent system (THF layered with pentane) was needed to grow single crystals. As such, **1b** did not form dimers in the solid state (**Figure 2.3.4**); a single molecule of **1b** was present in the asymmetric unit, which displayed hydrogen bonding to a THF solvent molecule: 2.15 and 2.59 Å for H2--O1s and H6--O1s (3.02 and 3.33 Å for N2--O1s and N6--O1s), respectively. It is not entirely clear at this time why a dimeric species of **1b** did not form in the solid state, but steric factors can likely be ruled out as an acyl protecting group is less sterically demanding than a Boc protecting group. It is possible that hydrogen bonding to THF solvent molecules, which was apparent in the crystal structure of **1b**, disrupted dimer formation as the crystals grew. When comparing **1b** to **1a** and **1c**, many of the bond lengths and angles were very similar, although the N(3)-C(6)-C(5) and N(4)-C(11)-C(10) bond angles for **1b** were slightly closer to the ideal bond angle of 120° (for notable bond lengths and angles for **1a-c** see **Table 2.3.1**).

Table 2.3.1. Selected Bond Lengths (Å) and Angles (deg) for **1a** and **1c**.

1a	1c
Bond Lengths (Å)	

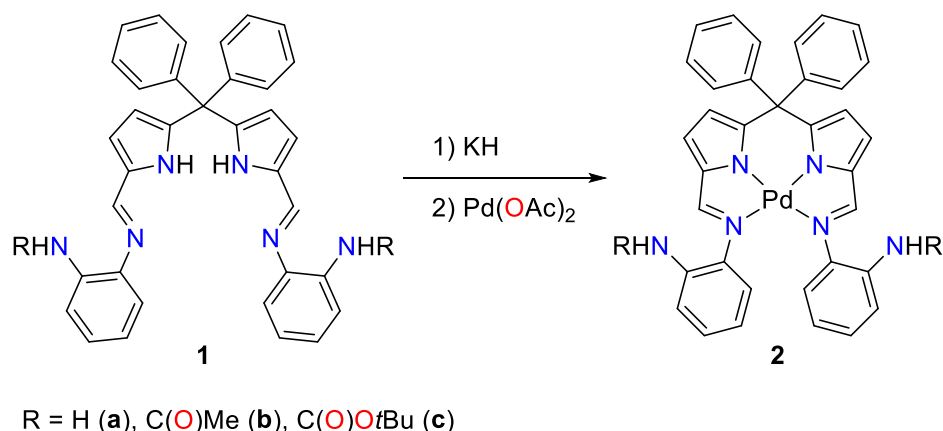
bond-formation to become sluggish. These types of modifications could be extremely useful in future studies for tuning the pK_a values of the pendant groups, as well as the electron donating ability of the imine moieties.

With respect to the 5,5'-diformyldipyrromethane starting material, it is likely that the general synthetic procedure outlined in Scheme 1 will tolerate a range of dialdehyde precursors. Several analogues of these species are known in the literature with alkyl and aryl substituents between the pyrrole donors.³⁸⁻⁴⁸ Substitutions in these positions would offer a useful site to adjust the steric encumbrance of the targeted systems.

2.3.2 Synthesis and Characterization of Compounds 2a-c.

In order to probe the binding modes of **1a-c** the calixpyrrole ligands were coordinated to palladium(II) and the resulting complexes were characterized. Palladium(II) was chosen in order to generate diamagnetic species, which would aid with spectroscopic characterization, and because palladium complexes with pendant nitrogen-based groups have been shown to electrocatalytically reduced oxygen.²⁰ The pyrrole species were first deprotonated with two equivalents of KH, followed by a salt metathesis reaction with one equivalent of $Pd(OAc)_2$ to give four coordinate square planar complexes, **2a-c** (**Scheme 2.3.2**). These compounds could be isolated as red (**2a**) or orange (**2b-c**) solids in moderate to good yields (35-57%). The ^1H NMR spectra of compounds **2a-c** all showed characteristic peaks that were shifted from the free ligand forms. In particular, a significant upfield shift of the imine C-H signals was seen, with peaks at 7.75, 7.55, and 7.60 ppm for **2a**, **2b**, and **2c**, respectively. Moreover, the absence of the pyrrole NH signals between 11 and 12 ppm indicated that the calixpyrrole ligands had been successfully deprotonated in the desired positions. This was in contrast to the pendant groups, which still displayed NH peaks at 4.45, 7.65, and 8.33 pm for **2a**, **2b**, and **2c**, respectively.

Scheme 2.3.2. General Synthetic Procedure for Palladium Complexes **2a-c**.



In addition to NMR spectroscopy complexes **2a-c** were all characterized in the solid state utilizing single crystal X-ray diffraction (Figure 5). In all three structures the palladium centers adopted distorted square planar coordination geometries with the metal bound slightly out of the plane of the four nitrogen donors (0.08, 0.06, and 0.02 Å for **2a**, **2b**, and **2c**, respectively). In addition, the metal center was found to sit closer to the pyrrolide nitrogens, consistent with the results reported by Love *et al.*³⁸ for bimetallic palladium “pacman” complexes. This distortion was reflected in the shorter Pd(1)-N(1) and Pd(1)-N(2) bond lengths (1.947(9) and 1.951(9) Å for **2a**; 1.945(4) and 1.938(4) Å for **2b**; 1.941(6) and 1.940(6) Å for **2c**) in comparison to longer Pd(1)-N(3) and Pd(1)-N(4) bond lengths (2.086(9) and 2.080(9) Å for **2a**; 2.080(4) and 2.0999(4) Å for **2b**; 2.075(6) and 2.065(6) Å for **2c**). The bond angles for the palladium species were also consistent with previous findings for palladium-based “pacman” complexes.³⁸ The N(1)-Pd(1)-N(2) bond angle between the pyrrolide donors was only slightly compressed below 90°, while the N(1)-Pd(1)-N(3) and N(2)-Pd(1)-N(4) bond angles were significantly smaller. This can be attributed to the five membered rings that formed between the imine, pyrrolide, and palladium center upon coordination (the N(3)-C(6)-C(5) and N(4)-C(11)-C(10) imine bond angles were also compressed in comparison to the free ligands). In order to compensate for all of the other metal-ligand bond angles, the N(3)-Pd(1)-N(4) bond angle was expanded above 90° (110.6(4), 112.2(2), and 110.6(2)° for **2a**, **2b**, and **2c**, respectively). Interestingly, the imine bond lengths (C(6)-N(3) and C(11)-N(4)) increased by 0.029 Å on average upon coordinating a metal center suggesting that some degree of back-bonding was occurring from

the palladium. This hypothesis was supported by density functional theory (DFT) calculations, which showed a molecular orbital (HOMO-1) with significant d-orbital character on the metal center and antibonding character on the imine donors (see Figure A.8 in Appendix A. Supplementary Data for a visualization of this orbital). For other notable bond lengths and angles see Table 2.

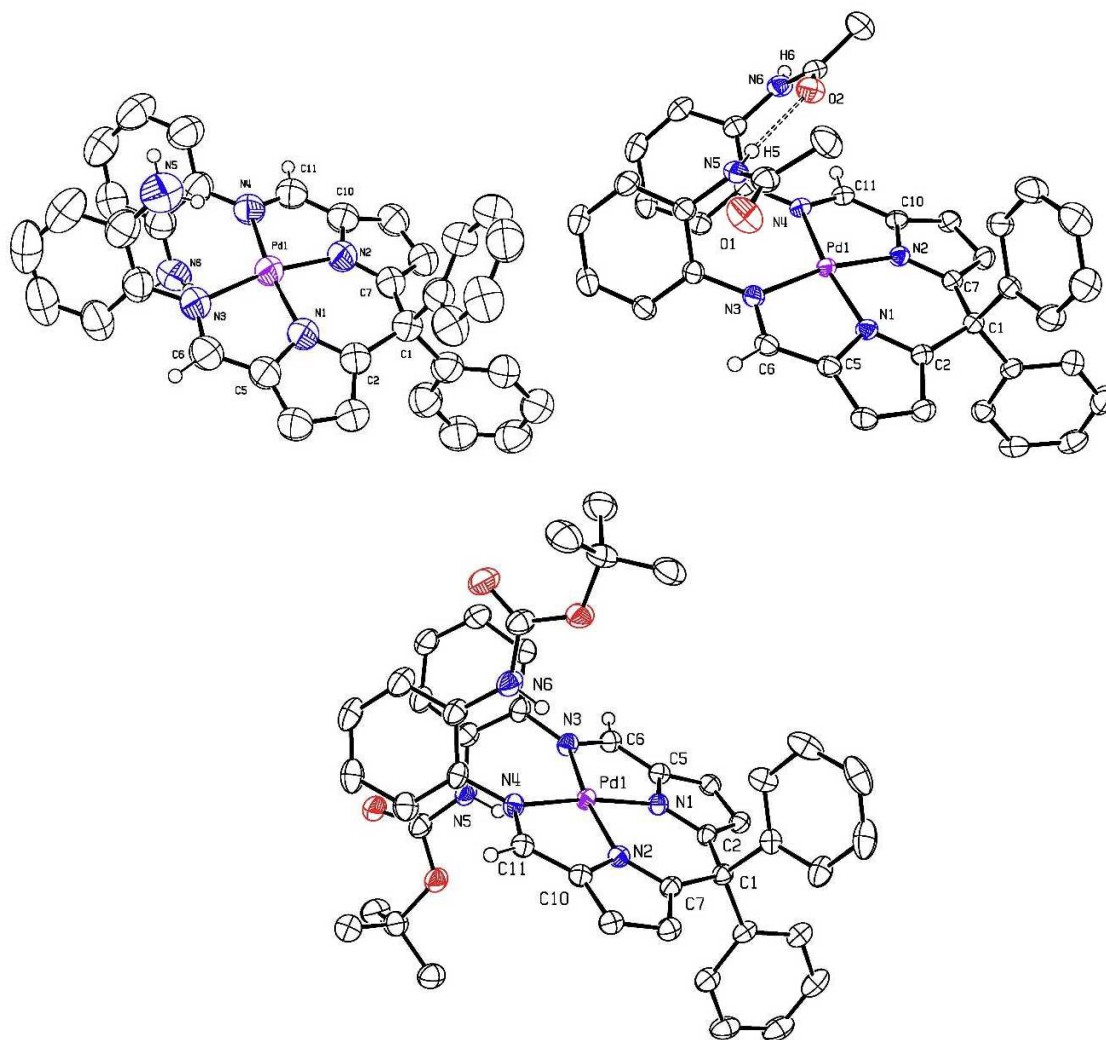


Figure 2.3.5. ORTEP3 representation (thermal ellipsoids at 50% probability) and atom number for: **2a**, most of the hydrogens have been omitted for clarity (top left); **2b**, the solvent and most of the hydrogens have been omitted for clarity (top right); **2c**, the solvent and most of the hydrogens have been omitted for clarity (bottom).

With respect to the pendant groups, no interaction with the metal center was apparent in the solid state, as indicated by the Pd(1)-N(5) and Pd(1)-N(6) distances of 3.49 and 3.52 Å for **2a**, 3.36 and 4.79 Å for **2b**, as well as 3.61 and 3.47 Å for **2c**. These moieties are likely

close enough, however, to interact with a ligand bound in an axial coordination site. The large asymmetry in values seen for the acyl-protected species was caused by hydrogen bonding (2.18 Å for H(5)–O(2) and 2.97 Å for N(5)–O(2)) between the adjacent amide moieties, which oriented N(6) further away from the metal center. Additionally, the intramolecular interaction caused both pendant groups to align on the same side of the palladium complex. In **2a** and **2c**, on the other hand, no hydrogen bonding was seen and the pendant groups were located on opposite sides of the calixpyrrole ligand. In solution, however, the pendant groups can freely rotate as determined by NMR spectroscopy.

Table 2.3.2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a-c

	2a	2b	2c
Bond Lengths (Å)			
Pd(1)-N(1)	1.947(9)	1.945(4)	1.941(6)
Pd(1)-N(2)	1.951(9)	1.938(4)	1.940(6)
Pd(1)-N(3)	2.086(9)	2.080(4)	2.075(6)
Pd(1)-N(4)	2.080(9)	2.099(4)	2.065(6)
N(3)-C(6)	1.31(2)	1.308(6)	1.313(9)
N(4)-C(11)	1.30(2)	1.314(6)	1.317(9)
Bond Angles (deg)			
N(1)-Pd(1)-N(2)	87.9(4)	88.0(2)	88.2(2)
N(1)-Pd(1)-N(3)	80.7(4)	79.8(2)	80.6(2)
N(2)-Pd(1)-N(4)	80.4(4)	79.8(2)	80.7(2)
N(3)-Pd(1)-N(4)	110.6(4)	112.2(2)	110.6(2)
N(3)-C(6)-C(5)	119(1)	117.5(4)	118.4(6)
N(4)-C(11)-C(10)	119(1)	118.3(4)	118.3(6)

2.3.3 Electrochemical Properties of 1-2

The electrochemical properties of compounds **1a-c** and **2a-c** in acetonitrile were evaluated using cyclic voltammetry (CV) with tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte (**Figure 2.3.6**). The acyl- and Boc-protected ligands showed similar features: an irreversible oxidation at higher potentials (around 1.22 and 1.27 V vs. ferrocene/ferrocenium, Fc/Fc⁺, for **1b** and **1c**, respectively) and two irreversible reductions at

lower potentials (-1.04 and -1.61 V for **1b**, as well as -1.04 and -1.71 V for **1c**). The Boc-protected system, however, exhibited an additional oxidation and reduction at 0.07 and -0.01 V, respectively. The unprotected ligand, **1a**, on the other hand, had two irreversible oxidations at 0.07 and 0.74 V vs. Fc/Fc⁺, as well as two irreversible reductions at -1.09 and -1.74 V. With respect to the palladium complexes, they all produced analogous features to one another: two irreversible oxidations seen at higher potentials and two irreversible reductions seen at lower potentials. For **2b** and **2c** the irreversible reductions and oxidations occurred at very similar potentials (-1.42, -0.8, 0.45, and 0.84 V for **2b**; -1.34, -0.99, 0.47, and 0.82 V for **2c**), but for **2a** they occurred at lower potentials (0.08 and 0.58 V for the oxidations and -1.10 and -1.64 V for the reductions). When comparing the CVs of **1a-c** and **2a-c** it is clear that the ligands are redox non-innocent, and that the locations of the irreversible oxidations and reductions were only shifted somewhat upon metal coordination.

From the CV experiments it is also apparent that the unprotected compounds **1a** and **2a** behaved somewhat differently than their corresponding Boc- and acyl-protected analogues. In particular their irreversible reduction and oxidations occurred at lower potentials in comparison to **1b**, **1c**, **2b**, and **2c**. Deprotonation of the pendant NH₂ groups upon oxidation can be ruled out, however, as the addition of triethylamine or pyridine did not shift these irreversible oxidations to more reducing potentials, and did not induce an increase in peak current. Instead, the more electron-rich nature of **1a** and **2a** can be rationalized by the increased electron-donating ability of the aniline moieties in comparison to acetamide and carbamate functionalities.

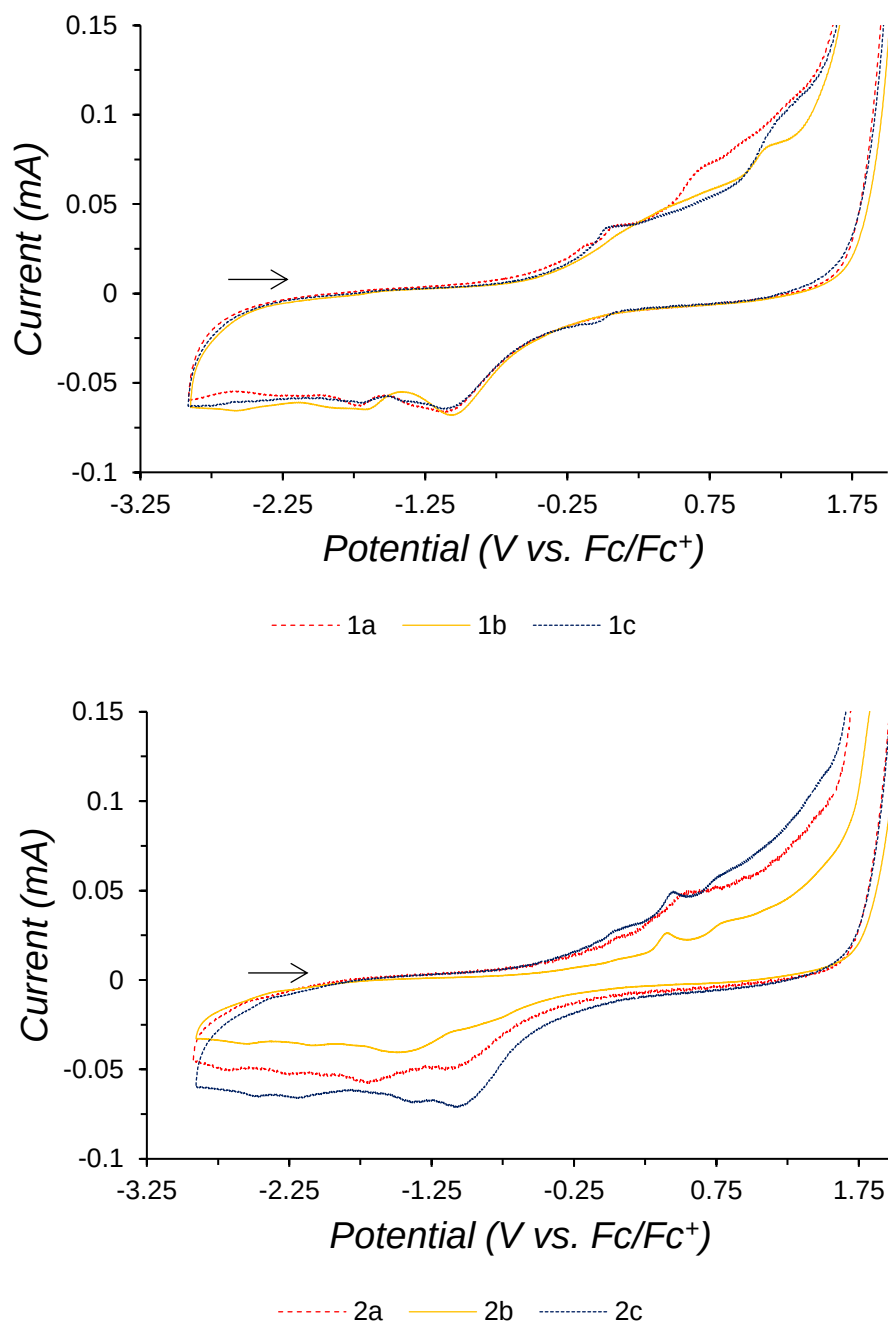


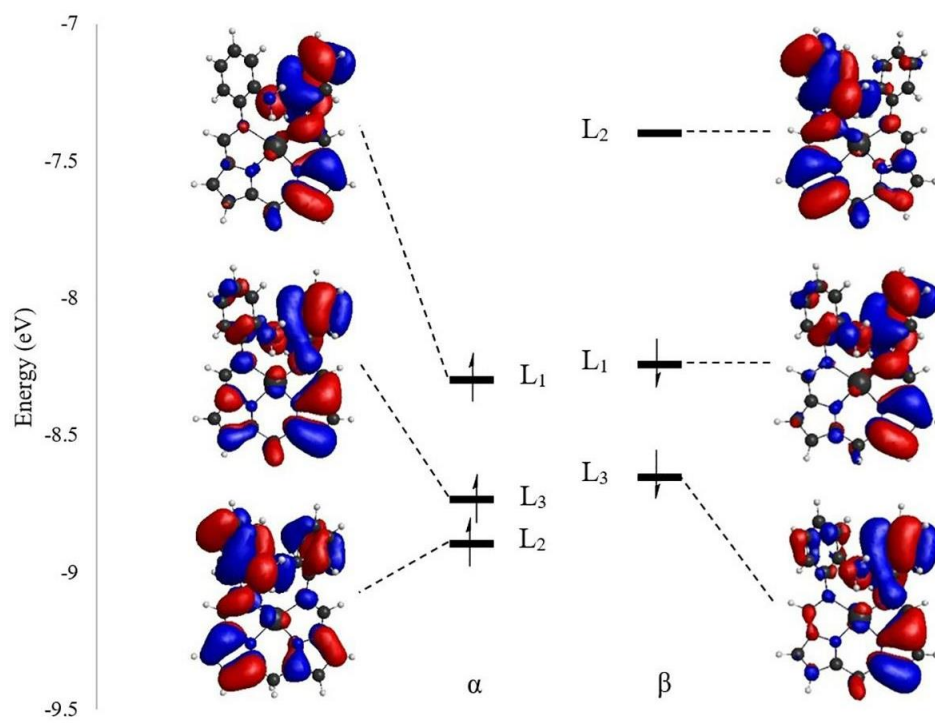
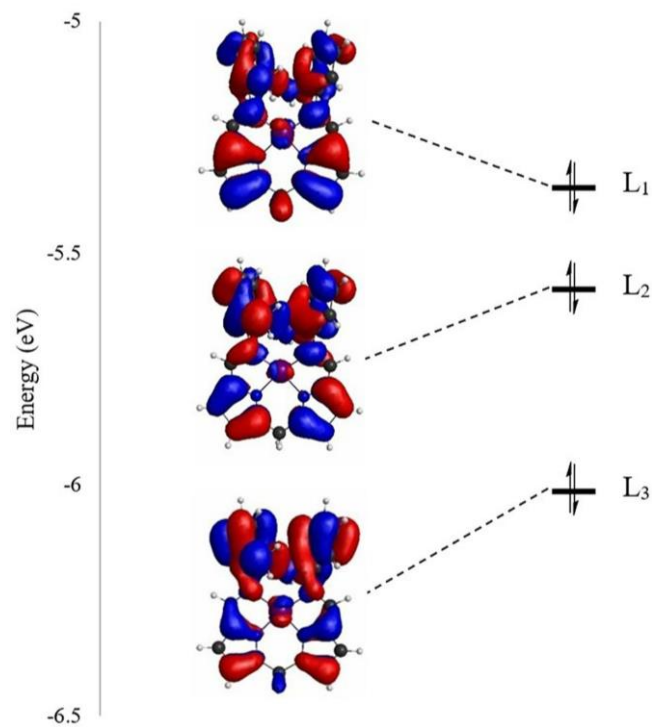
Figure 2.3.6. Cyclic voltammograms of **1a-c** (top) and **2a-c** (bottom) in acetonitrile. (0.25 mM ligand or complex, 0.1 M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 800 mV/s).

2.3.4 Theoretical Calculations

In order to assign the CVs of **2a-c**, DFT calculations utilizing the B3LYP functional and 6-311++G** (H, C, N) + Def2-TZVP + ECP (Pd) basis sets were performed. A model

system with pendant NH₂ groups on the aryl backbone and hydrogen atoms in place of the phenyl groups between the pyrrole moieties (to reduce computational cost) was used. Ground state optimizations and frequency calculations were carried out for neutral (**2a_H**) and cationic (**2a_H⁺** and **2a²⁺**) species. For **2a_H²⁺** both open- (S = 1) and closed-shell (S = 0) states were calculated, with the S = 1 state being lower in energy by 7.3 kcal/mol (further discussions below for **2a_H²⁺** will refer to the S = 1 state).

When examining the HOMO, HOMO-1, and HOMO-2 orbitals of **2a_H** they were mainly ligand-based with very little metal d-character (**Figure 2.3.7**). For the charged species shown in **Figure 2.3.7**: **2a_H⁺** the SOMO had significant ligand character (similar in character to the HOMO-1 in **2a_H⁺**) and in **2a_H²⁺** both SOMOs were mostly ligand-based (similar in character to the HOMO and HOMO-1 in **2a_H⁺**, respectively). These results suggested that in all of the complexes examined, the Pd center stayed in the +2 oxidation state, and that electrons were removed from mainly ligand-based orbitals upon oxidation. This was also reflected in the Mulliken charge on the metal in **2a_H**, **2a_H⁺**, and **2a_H²⁺**: 1.71, 1.54, and 1.46, respectively.



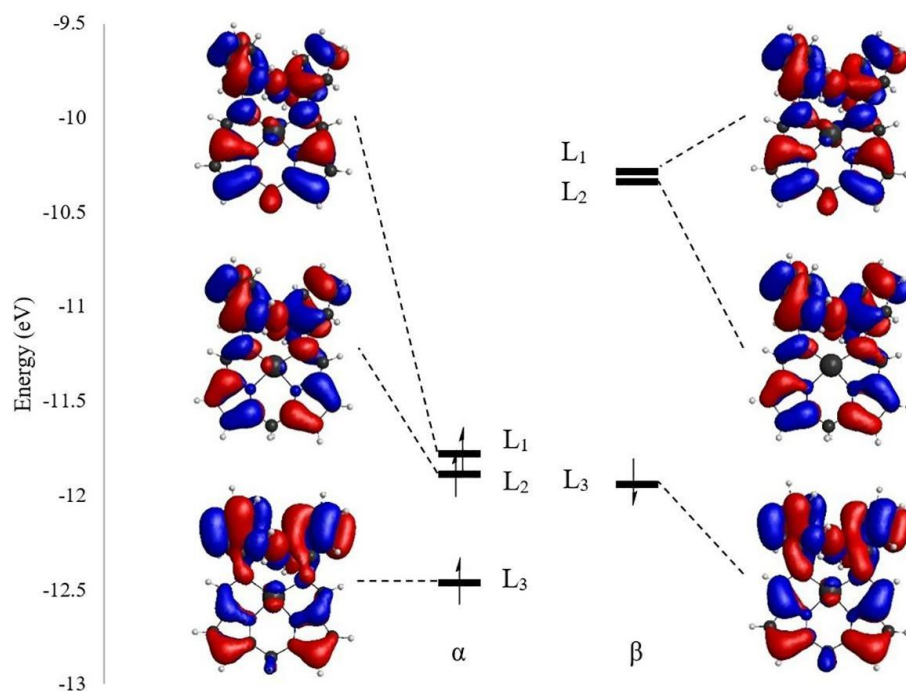


Figure 2.3.7. Visual representations and energies of the ligand-based HOMO, HOMO-1, HOMO-2 orbitals (labelled L₁, L₂, and L₃ respectively) of **2aH** (top); ligand-based HOMO, HOMO-1, and HOMO-2 (SOMO) orbitals of **2aH⁺** (α and β manifolds, labelled L₁, L₃, and L₂, respectively, in reference to the orbitals with similar character in **2aH** (middle); HOMO (SOMO), HOMO-1 (SOMO), and HOMO-2 orbitals of **2aH²⁺** with S = 1 (α and β manifolds, labelled L₁, L₂, and L₃, respectively, in reference to the orbitals with similar character in **2aH**) (bottom).

Therefore, the DFT calculations indicated that all of the oxidations seen in the CVs of **2a-c** were mainly ligand-based. This matched well with the experimental data, as the CVs of **1a-c** and their corresponding metal complexes were very similar. Additionally, pyrrole groups are known to be prone to oxidation, which would explain the redox non-innocence seen for the calixpyrrole ligands.⁷⁰ What is particularly striking about these results, however, is that they suggest a total of two electrons could be removed from the calixpyrrole ligand without greatly affecting the oxidation state of the metal center. Looking at the orbitals shown in Figure 7, this is likely facilitated by the extensive conjugation across the whole ligand, which would prevent the build-up of localized charge. As such, the calixpyrrole ligands **1a-c** displayed redox non-innocence somewhat similar to porphyrin ligands, except that the oxidized forms of **1a-c** were much less stable (leading to the mainly irreversible electrochemistry observed). This is encouraging when considering the calixpyrrole species for small molecule activation studies as the ligands themselves can act as an electron reservoir

and delocalize charge across the whole molecule. Lastly, with respect to the two irreversible reductions seen in the CVs of **2a-c**, it is believed that these were mainly metal-based reductions. This hypothesis was also supported by the theoretical calculations that were performed, in that the LUMO of **2a_H** displayed significant metal d-orbital character (**Figure 2.3.8**).

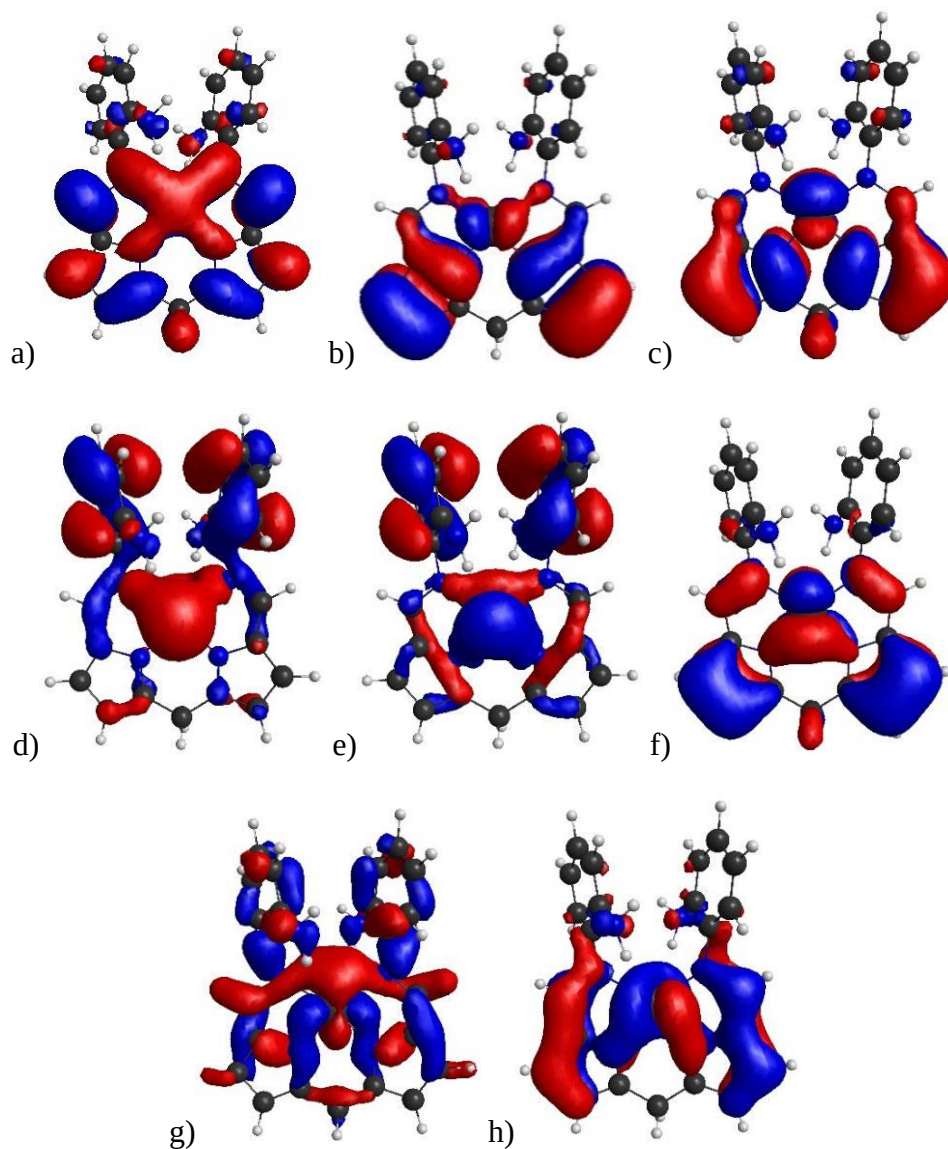


Figure 2.3.8. Visual representations of the a) LUMO; b) HOMO-4; c) HOMO-5; d) HOMO-6; e) HOMO-8; f) HOMO-9; g) HOMO-10 (showing some degree of backdonation from the metal into the imine bonds); h) HOMO-11 orbitals of **2a_H**, which display significant d-orbital character.

2.3.5 Preliminary Small Molecule Reactivity Studies

Preliminary binding studies utilizing **2a-c** and O₂, H₂O, N₂, NH₃, H₂, CO₂, and MeOH indicated that there was little to no interaction with the neutral palladium complexes at room temperature. This was perhaps to be expected given the square planar binding mode of palladium and the Jahn-Teller distortions that would disfavour ligand binding in the axial positions. The CVs of **2a-c** in the presence of various substrates were also carried out to examine the potential reactivity of the calixpyrrole complexes. No catalytic currents were observed under an N₂, O₂, or CO₂ atmosphere in the presence of various acids (lutidinium tetrafluoroborate or trifluoroacetic acid), nor were they observed under an H₂ or NH₃ atmosphere or with MeOH and/or H₂O in the presence of various bases (triethylamine, lutidine, or pyridine).

When examining the CV data and the electronic structure of **2a_H**, the reasons for the lack of reactivity displayed by **2a-c** under the reaction conditions that were explored become apparent. Based on the reduction potentials of the palladium species, they are more likely to engage in reduction reactions than oxidation reactions. The DFT calculations, however, showed that the HOMO to HOMO-3 orbitals were all mainly ligand-based, with the HOMO-4, HOMO-5, HOMO-6, HOMO-8, HOMO-9, HOMO-10, and HOMO-11 orbitals displaying more significant metal character (see Figure A.8 in Appendix A. Supplementary Data for visualizations of these orbitals). It is likely that the metal-based orbitals are too low in energy to facilitate electron transfer from Pd(II) to a substrate of interest. This hypothesis was supported by the results reported herein, where upon oxidation (as discussed above), the frontier orbitals remained mainly ligand-based and the electrochemistry of **2a-c** was mostly irreversible.

Although the palladium complexes were not able to activate the small molecules that were investigated, we still view the calixpyrrole species **1a-c** as promising ligand frameworks. The amount of control over the secondary coordination sphere enabled by these calixpyrrole architectures should provide an avenue for facilitating PCET, and the high degree conjugation across the ligand structure is anticipated facilitate electron transfer reactions. It is clear, however, that increased metal d-orbital character in the HOMO to HOMO-3 orbitals will be

crucial in order to get the metal center involved in redox processes and lead to more desirable electrochemical properties (reversible redox couples). More studies are needed to explore alternative metals and different coordination geometries using ligands **1a-c**.

2.3.6 Electrocatalytic H₂ Evolution

While the palladium complexes **2a-c** did not engage in small molecule activation under the conditions outlined above, they did exhibit electrocatalytic H₂ production in the presence of a strong acid: *p*TSA (**Figure 2.3.9**). The onset of catalysis for **2a-c** was approximately 0.4-0.5 V more positive than the glassy carbon electrode itself (between - 0.65 V to 0.71 V for **2a-c**, and - 1.08 V for the glassy carbon electrode) and the peak current varied linearly with the square root of the scan rate (**Figures 2.3.10, 2.3.11 and 2.3.12**). The catalytic peak did shift to more negative potentials at higher scan rates, however, and the nature of the ligand (**a-c**) did not seem to have a significant impact on catalysis under the conditions that were examined (using 600 equivalents of a strong acid *p*TSA). These results suggested that hydrogen evolution was limited by diffusion of protons to the electrode surface and that the active catalytic species was heterogeneous in nature. This was confirmed upon performing a “rinse” test:⁷¹ after carrying out electrocatalysis in a 0.25 mM solution of **2a-c** in acetonitrile (0.1 M TBAP and 0.15 M *p*TSA), the working electrode was gently rinsed in a 0.1 M TBAP solution in acetonitrile, and then submerged in a fresh acetonitrile solution without any palladium complex (0.1 M TBAP and 0.15 M *p*TSA). It was found that H₂ production still proceeded in the absence of palladium complex in the bulk solution (up to 100 cycles without significant changes in activity), indicating that the active catalyst was supported on the working electrode surface (**Figure 2.3.13**). Moreover, after electrocatalysis the working electrode was visually no longer “glassy” (suggesting the formation of a heterogeneous species).

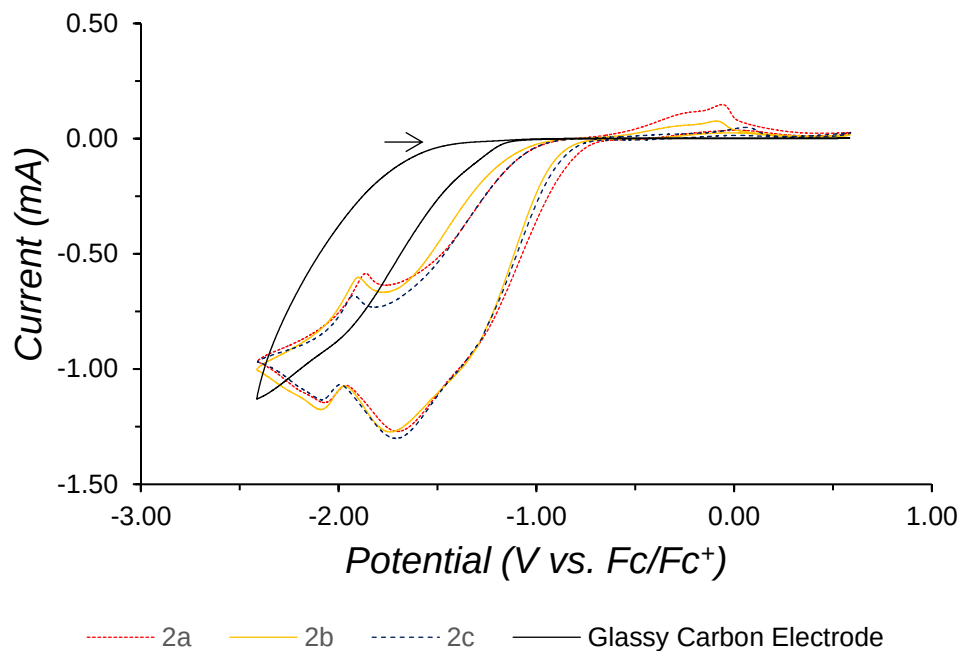
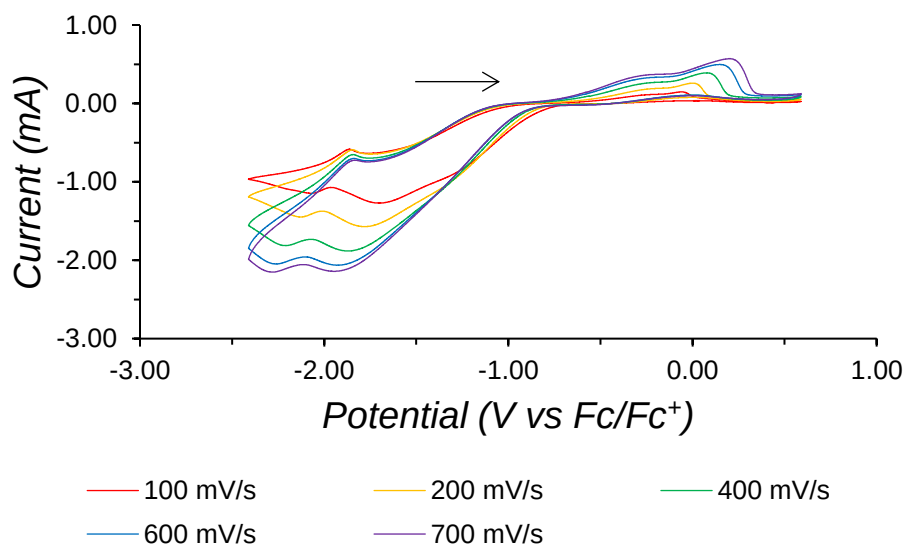


Figure 2.3.9. Cyclic voltammograms in acetonitrile (0.25 mM complex, 0.1 M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO_3 reference electrode, scan rate = 100 mV/s) of **2a-c** in the presence of 600 equivalents of *p*TSA (0.15 M).



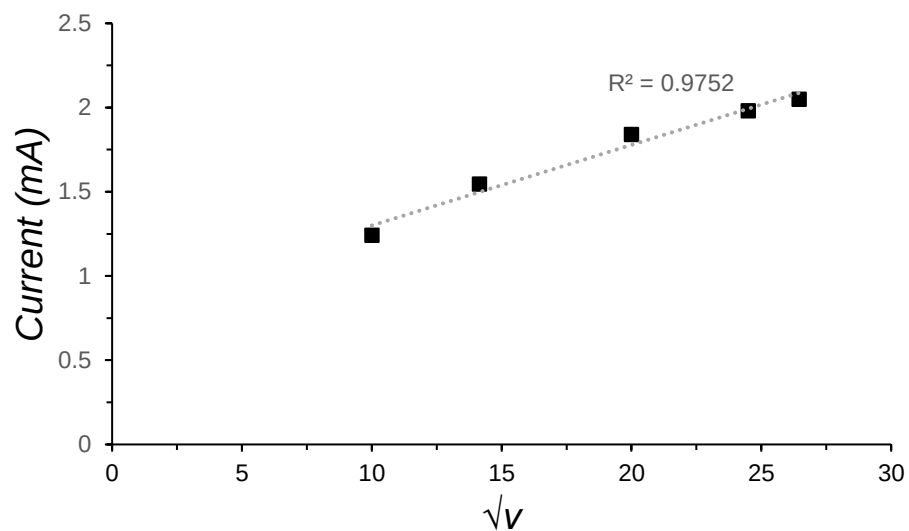


Figure 2.3.10. Cyclic voltammograms of H₂ evolution using **2a** at various scan rates (0.25 mM complex, 0.1 M TBAP, 0.15 M *p*TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode) (top); Peak catalytic current versus square-root of scan rate (bottom).

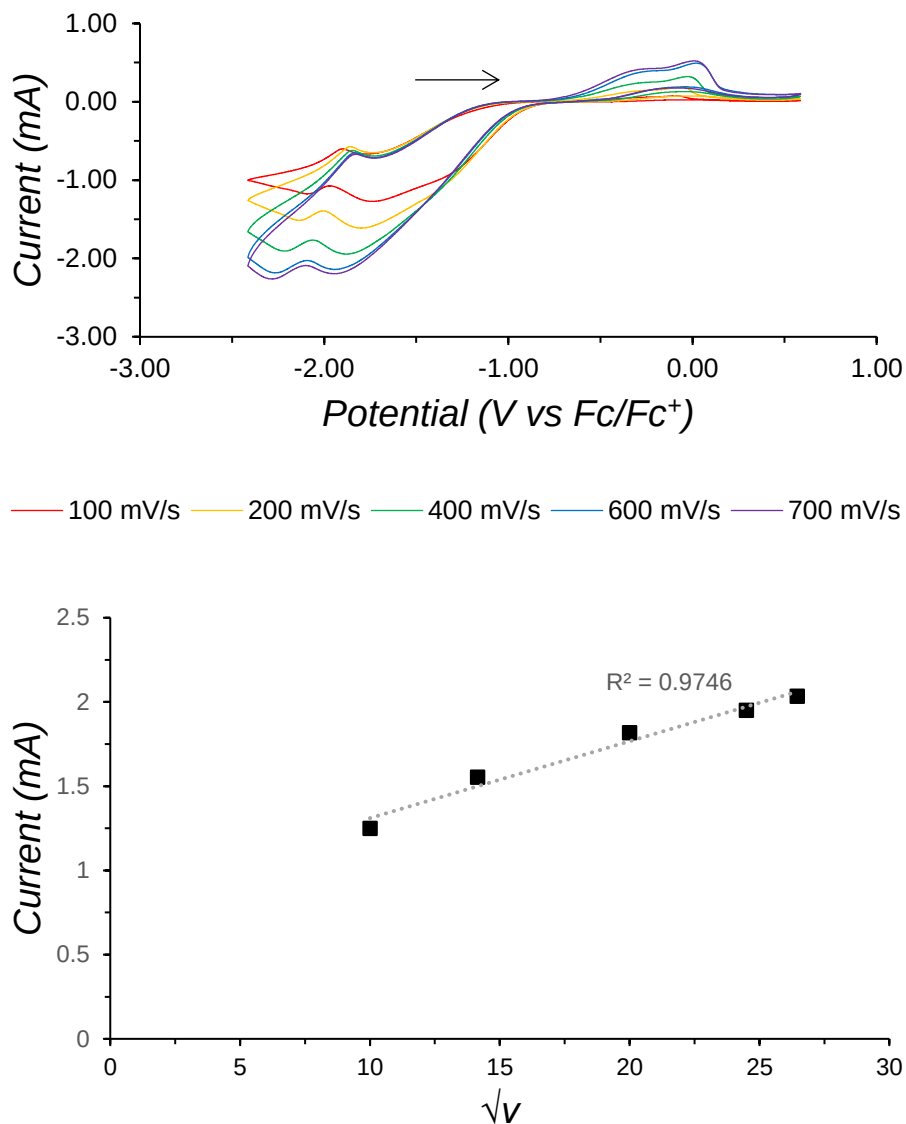


Figure 2.3.11. Cyclic voltammograms of H₂ evolution using **2b** at various scan rates (0.25 mM complex, 0.1 M TBAP, 0.15 M *p*TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode) (top); Peak catalytic current versus square-root of scan rate (bottom).

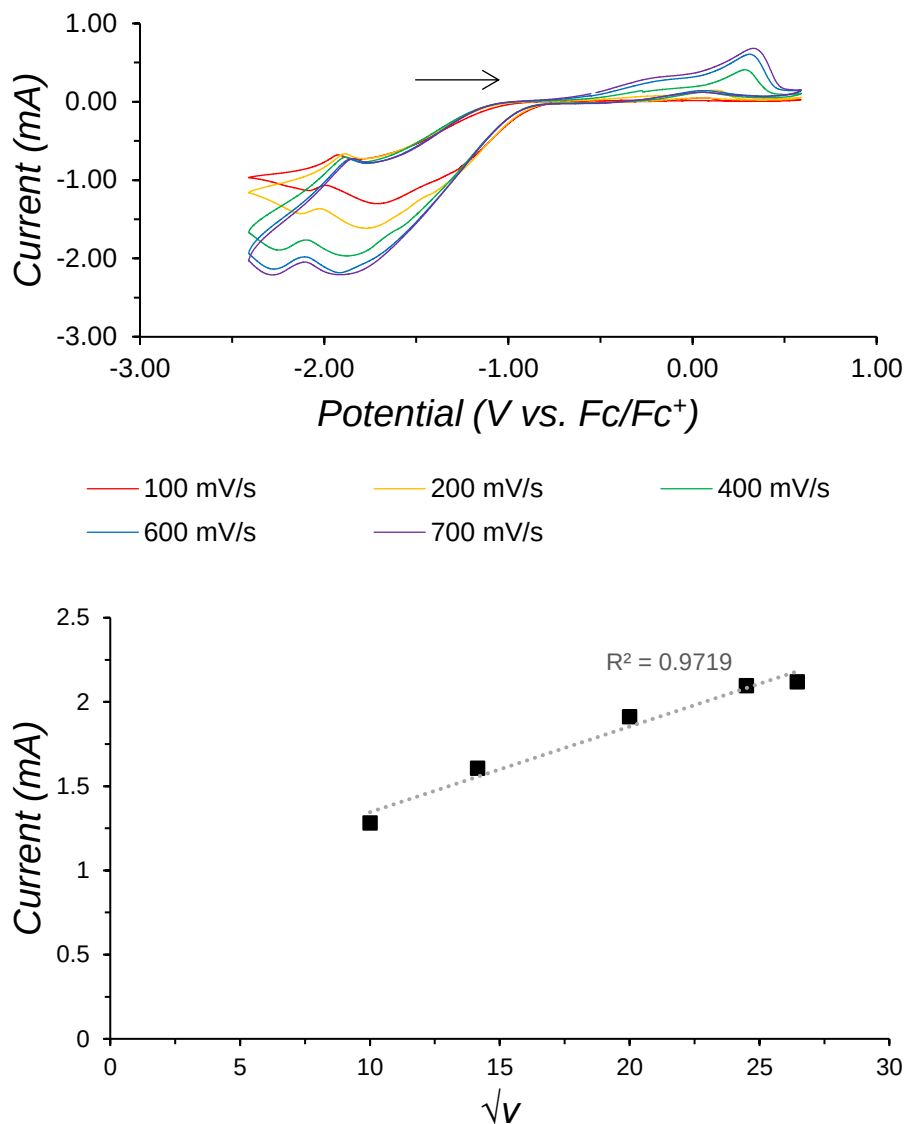
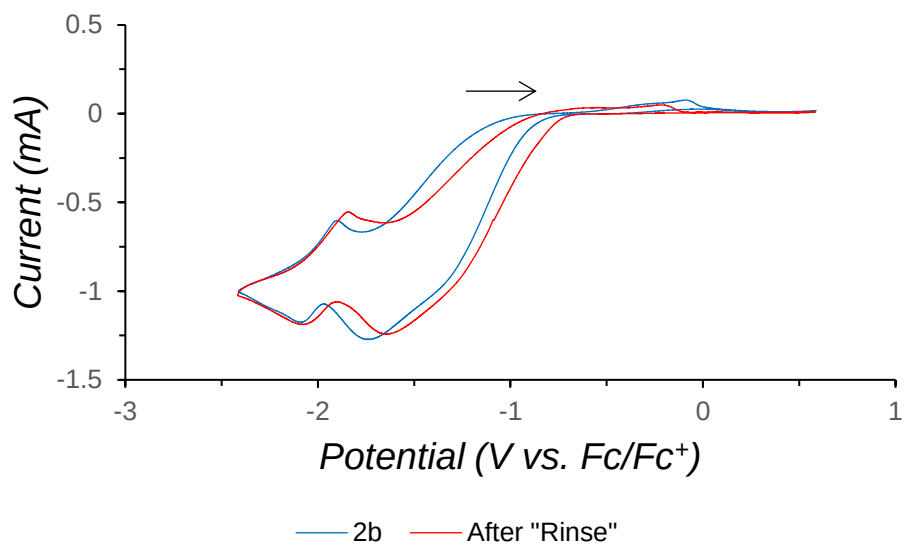
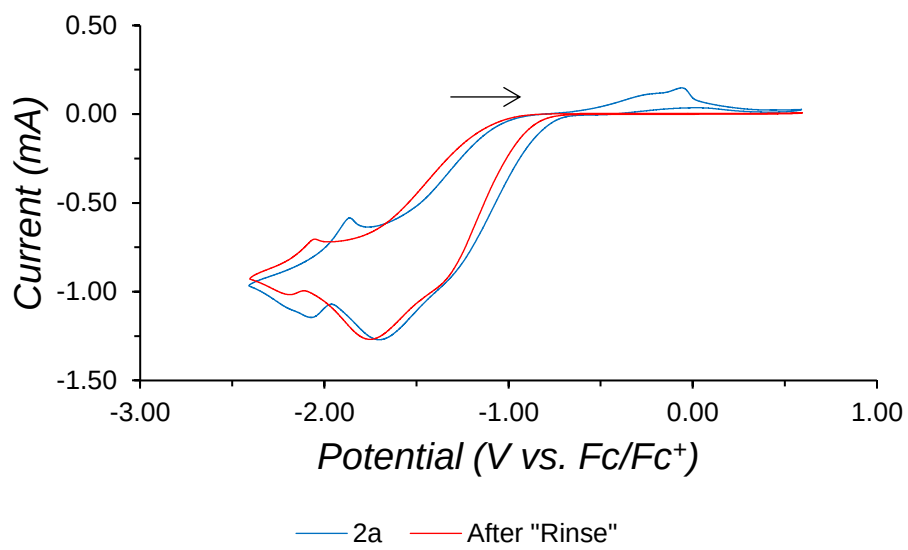


Figure 2.3.12. Cyclic voltammograms of H_2 evolution using **2c** at various scan rates (0.25 mM complex, 0.1 M TBAP, 0.15 M *p*TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode) (top); Peak catalytic current versus square-root of scan rate (bottom).



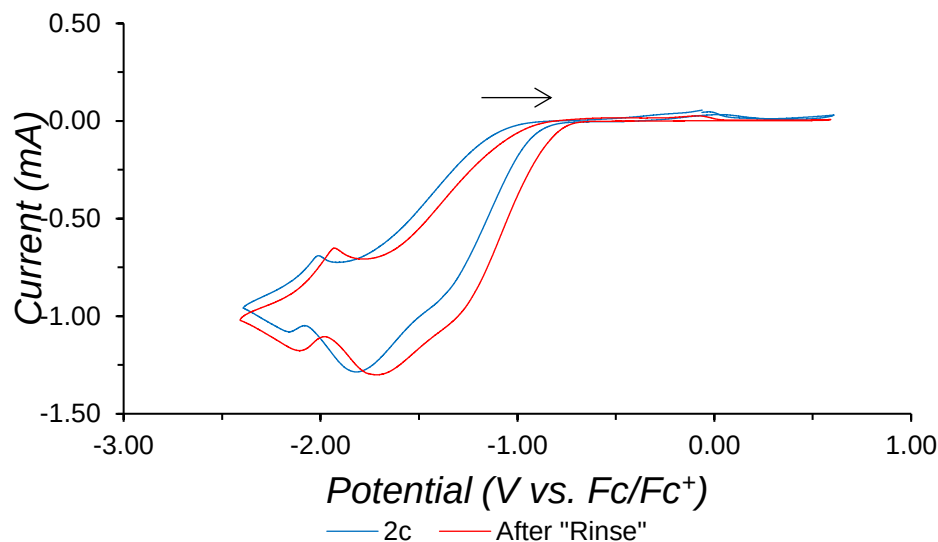


Figure 2.3.13. Cyclic voltammograms of H₂ evolution using **2a** (top), **2b** (middle), and **2c** (bottom) before (0.25 mM complex, 0.1 M TBAP, 0.15 M *p*TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 100 mV/s) and after ‘rinse’ test (no complex, 0.1 M TBAP, 0.15 M *p*TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 100 mV/s).

Due to the redox non-innocent nature of ligands **1a-c**, control experiments investigating the catalytic abilities of the free calixpyrrole species were carried out (**Figure 2.3.14**). The non-coordinated ligand species did not catalyze H₂ production, demonstrating that palladium was crucial for this transformation. Moreover, CV experiments were carried out in deuterated acetonitrile to verify that the effervescence seen at the working electrode was due to H₂ evolution. A characteristic H₂ peak around 4.56 ppm was observed (**Figure 2.3.15**) supporting that the catalytic currents displayed in the CVs of **2a-c** were due to H₂ production. Interestingly, the active species were fairly robust, undergoing over 500 scans without significant changes in the CV features (**Figure 2.3.16**).

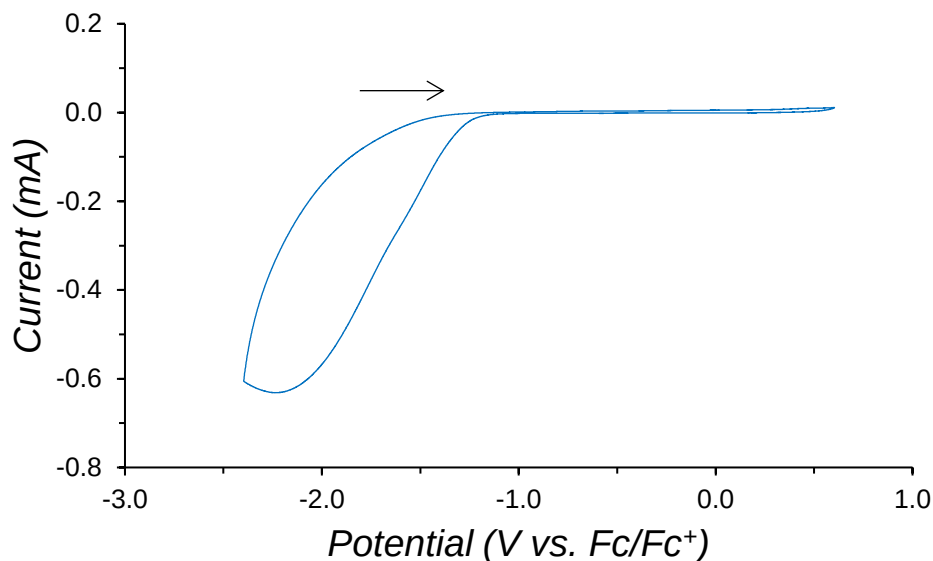


Figure 2.3.14. Representative example of a cyclic voltammogram using only ligand (**1a**) for H₂ production (0.25 mM ligand, 0.1 M TBAP, 0.15 M *p*TSA), glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 100 mM/s).

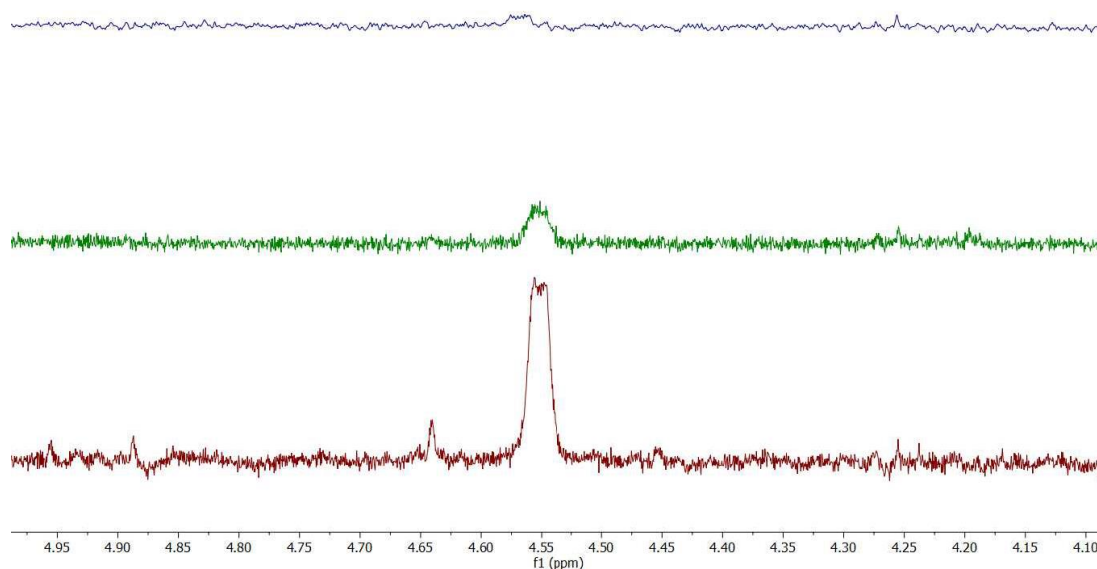


Figure 2.3.15. ¹H NMR spectra (400 MHz, CD₃CN) of sealed CV reaction mixtures carried out in CD₃CN (0.25 mM **2a**, 0.1 M TBAP, 0.015 M *p*TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 600 mMs) showing H₂ in solution after: 24 scans (top), 308 scans (middle), and 516 scans (bottom).

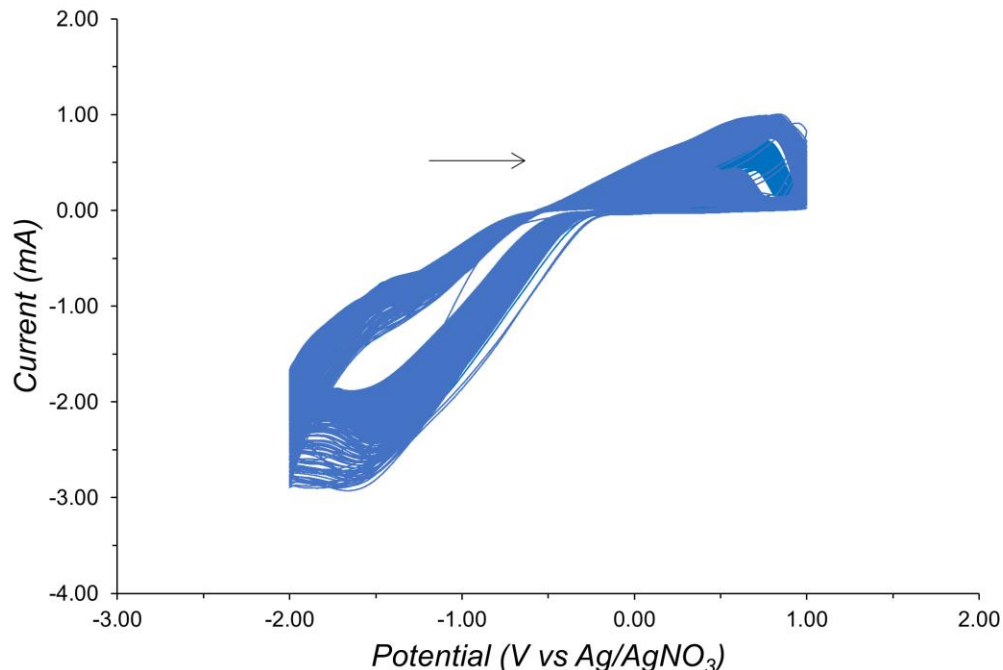


Figure 2.3.16. Representative cyclic voltammogram of H₂ evolution with 500 scans using **2a** in CD₃CN (0.25 mM complex, 0.1 M TBAP, 0.015 M *p*TSA, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 60 mV/s).

Based on all of the observations outlined above (both experimental and theoretical), it is believed that reduction of palladium in **2a-c** (corresponding to the first irreversible reduction seen around -0.8 to -1.10 V in Figure 6) under acidic conditions forms the active catalytic species, which is heterogeneous in nature. Once the active species initially forms on the electrode surface, it does not appear that further reactions with **2a-c** in solution are necessary for catalytic activity (as shown by the “rinse” test studies). Furthermore, the active catalyst does not seem to react further with **2a-c** in solution over the course of 500 scans under catalytic conditions (or if it does, this does not change the activity and electrochemical properties of the catalytic site significantly). It is hypothesized that the working electrode becomes innervated with respect to reaction with palladium species in solution after catalyst formation, potentially by a thin film (caused by electropolymerization of the porphyrin-like calixpyrrole ligand)⁷² that prevents further deposition of **2a-c**. If clusters or nanoparticles are formed, they are likely stabilized by the calixpyrrole ligand, or possibly one of its decomposition products. Additionally, if the catalyst is a nanoparticle species, the active catalytic surface area does not change

appreciably over 500 cycles of use. These results are particularly exciting because they suggest only a small amount of the palladium in solution is needed to generate a robust catalytic system for H₂ evolution.

Due to the heterogeneous nature of the active catalyst, however, very different methods are needed to characterize this species in comparison to those outlined for the homogeneous compounds **1a-c** and **2a-c**. As such, further studies are needed to identify the exact nature of the heterogeneous catalyst (i.e. whether thin films, small clusters, or larger nanoparticles are formed), before a proper kinetic analysis of these systems can be carried out (determining turnover frequencies, faradaic efficiencies, etc.). These investigations will be the subject of a future publication, and are currently underway.

2.4 Conclusion

In summary, a series of calixpyrrole ligands with pendant nitrogen-based functionalities, **1a-c**, were synthesized using a modular Schiff-base reaction starting with either commercially available or easily accessible starting materials. The hydrogen bond donors in the secondary coordination sphere could be readily varied, and the ligand architecture could accommodate varying pendant groups such as amino, amide, and *t*-butylcarbamate. This was particularly attractive as the pendant groups could be easily tuned, which could provide a high degree of control over the secondary coordination sphere in future studies. In order to investigate the binding modes of these tetradentate ligands, they were coordinated to palladium generating square planar complexes **2a-c**. No interaction was observed between the metal center and the pendant groups in the solid state, but structures with both hydrogen bond donors on the same side of the calixpyrrole ligand, as well as on opposite sides of the calixpyrrole ligand, were seen, highlighting the flexibility of the ligands. Interestingly, the nitrogen-based substituents in the secondary coordination sphere seemed well positioned to interact with ligands binding in the axial coordination sites (N-Pd = 3.5-4.08 Å), indicating that they could potentially activate substrates and facilitate PCET under the right conditions (**Table 2.4.1**). In addition, the electrochemical properties of **1-2** were explored. The calixpyrrole ligands were found to be redox non-innocent, and theoretical studies suggested that up to two electrons could be removed from the ligand system without affecting the oxidation state of the palladium center. This was likely facilitated by extensive conjugation across the calixpyrrole species; a property

which could potentially be leveraged for multi-electron transfer processes. In addition, irreversible reductions were seen at negative potentials. While DFT studies indicated that the LUMO had a large amount of d-orbital character, most of the observed reductions are thought to be tied to the irreversible oxidations. Given the electron-rich nature of pyrrolide donors, it is likely that metal-centered redox couples would be accessible only at very reducing potentials. Lastly, although oxidations were seen at potentials relevant for small molecule activation, **2a-c** were found to be unreactive towards a variety of small molecule substrates. Based on preliminary binding studies, it is believed that Jahn-Teller distortions disfavoured substrate binding to the square planar palladium complexes. Moreover, theoretical calculations suggested that the metal-based orbitals were too stabilized to properly engage in redox processes. Despite the initial lack of reactivity seen with **2a-c**, they were found to generate systems that could catalyze H₂ evolution in the presence of *p*TSA. The onset of electrocatalysis was around 0.4-0.5 V more positive than the glassy carbon working electrode, and the catalysts were stable for over 500 scans with no signs of deactivation. The catalytically active species were found to be heterogeneous in nature, and affected H₂ production in the absence of palladium complex in the bulk solution. Interestingly, all complexes displayed nearly identical catalytic waves despite varied pendant group substituents. This is believed to be due to the innate presence of water in *p*TSA which may act as a hydrogen acceptor/donor and exogenous proton shuttle. Further studies exploring these exciting ligand frameworks and heterogeneous H₂ evolution electrocatalysts are currently underway.

Table 2.4.1. Comparison of Relevant Catalyst Parameters

Complex	Avg. Pendant-Metal Distance (Å)	O.P. (mV)	Acid	Reference
2a	3.50	~620	<i>p</i> TSA	This Work
2b	4.08	~620	<i>p</i> TSA	This Work
2c	3.54	~620	<i>p</i> TSA	This Work
$[(term-H)Fe_2(adt^H)(CO)_2(dppv)_2]^+$	3.53	710	ClCH ₂ CO ₂ H	22
$[Ni(7P^{Ph}_2N^{C6H4OMe})_2][BF_4]_2$	3.18	640	$[(DMF)H]^+$	5
CoHPX-CO ₂ H	4.31	~800	C ₆ H ₅ COOH	29,32

2.5 Experimental

2.5.1 General Considerations

All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. Solvents were dried and deoxygenated under argon using a LC Technology Solutions Inc. SP-1 stand-alone solvent purification system. All alcohols were dried and distilled over activated magnesium (magnesium turnings and a crystal of iodine) under a nitrogen atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Sigma Aldrich, Acros Organics, or Alfa Aesar, degassed, and dried over activated molecular sieves prior to use. 5,5'-diformyl-2,2'-diphenyldipyrromethane,⁶⁴ *N*-(2-aminophenyl)acetamide,⁶⁶ and *tert*-butyl-(2-aminophenyl)carbamate⁶⁷ were synthesized according to literature procedures. All other reagents were purchased from commercial sources and utilized without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature and pressure using a Bruker 400 MHz spectrometer (400 MHz for ¹H, and 100 MHz for ¹³C). The ¹H and ¹³C NMR spectra were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane (TMS). Elemental analyses were performed at the University of Rochester, Department of Chemistry, on a PerkinElmer 2400 Series II Analyzer. Single crystal X-ray data were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source (Cu K α λ = 1.54184 Å). The data collection strategy was calculated using CrysAlisPro to ensure desired data redundancy and percent completeness. Unit cell determination, initial indexing, data collection, frame integration, Lorentz-polarization corrections and final cell parameter calculations were carried out using CrysAlisPro. An absorption correction was performed using the SCALE3 ABSPACK scaling algorithm embedded within CrysAlisPro. The structures were solved using the ShelXT structure solution program using Intrinsic Phasing and refined by Least Squares using the ShelXL program. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Olex2 was used for the preparation of the publication materials. All crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Cyclic voltametric measurements were recorded using a Bio-Logic model SP-50 potentiostat. The working

electrode was a glassy carbon electrode; the reference electrode was a Ag/AgNO₃ (0.01 M in CH₃CN); and a platinum wire was used as the counter electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte and was recrystallized prior to use by slow addition of pentane into a THF solution followed by cooling in a freezer (-30 °C). The glassy carbon electrode was polished with 0.05 µm alumina and washed with distilled water prior to each measurement. Electrochemical measurements were conducted at room temperature in a nitrogen glovebox, argon glovebox, on a Schlenk-line, or in air and processed using EC-Lab V11.21. Reported half-wave potentials were referenced to the Fc/Fc⁺ redox couple by adding high purity ferrocene to the sample solution.

2.5.2 Synthesis of **1a** (C₃₅H₃₀N₆)

A round bottom flask was charged with 1.00 g of 5,5'-diformyl- 2,2'-diphenyldipyrromethane (1 equiv., 0.0014 mol) and 0.910 g of *ortho*-phenylenediamine (3 equiv., 0.0042 mol). The solids were dissolved in 6 ml of DMSO and then 1% TFA (with respect to the combined weight of the reagents) was added. The flask was sealed and the solution stirred for 1 hour. The solution turned dark red in colour and was quenched with 16 ml of 1% aqueous Na₂CO₃. The aqueous layer was extracted with 10 x 5 mL ether and the combined organic layers were then washed with 5 x 100 mL of 1% aqueous Na₂CO₃ to remove excess diamine. The combined organic layers were then dried with sodium sulfate and the solvent removed under reduced pressure to give **1a** as an orange solid. Yield: 0.903 g (60.3 %). Crystals suitable for single crystal X-ray diffraction studies were grown from a diethyl ether solution cooled to -8 °C. **¹H NMR** (400 MHz, DMSO-d₆) δ: 11.36 (br s, 2H, pyrrole-NH), 8.41 (s, 2H, imine-CH), 7.43-7.28 (m, 6H, aromatic-CH), 7.10 (dd, 2H, aromatic-CH, *J* = 8.0, 1.4 Hz), 7.04 (d, 4H, aromatic-CH, *J* = 8 Hz), 6.89 (td, 2H, aromatic-CH, *J* = 8.1, 1.3 Hz), 6.66 (dd, 2H, aromatic-CH, *J* = 8.0, 1.4 Hz), 6.63 (dd, 2H, pyrrole-CH, *J* = 3.7, 2.1 Hz), 6.52 (td, 2H, aromatic-CH, *J* = 7.6, 1.4 Hz), 5.79 (d, 2H, pyrrole-CH, *J* = 2.8 Hz), and 5.28 (br s, 4H, amine-NH₂) ppm. **¹³C NMR** (100 MHz, DMSO-d₆) δ: 145.66 (imine-C), 144.67 (aromatic-C), 144.05 (aromatic-C), 140.23 (aromatic-C), 135.09 (aromatic-C), 132.59 (aromatic-C), 129.42 (aromatic-CH), 127.82 (aromatic-CH), 127.15 (aromatic-CH), 126.56 (aromatic-CH), 116.03 (aromatic-CH), 115.84 (aromatic-CH), 114.27 (aromatic-CH), 114.21 (pyrrole-CH), 112.87 (pyrrole-CH), and 56.28 (C-

Ph₂) ppm. Anal. Calcd for C₃₅H₃₀N₆·0.5((CH₃CH₂)₂O): C, 77.7; H, 6.2; N, 14.7%. Found: C, 77.8; H, 5.95; N, 14.6%.

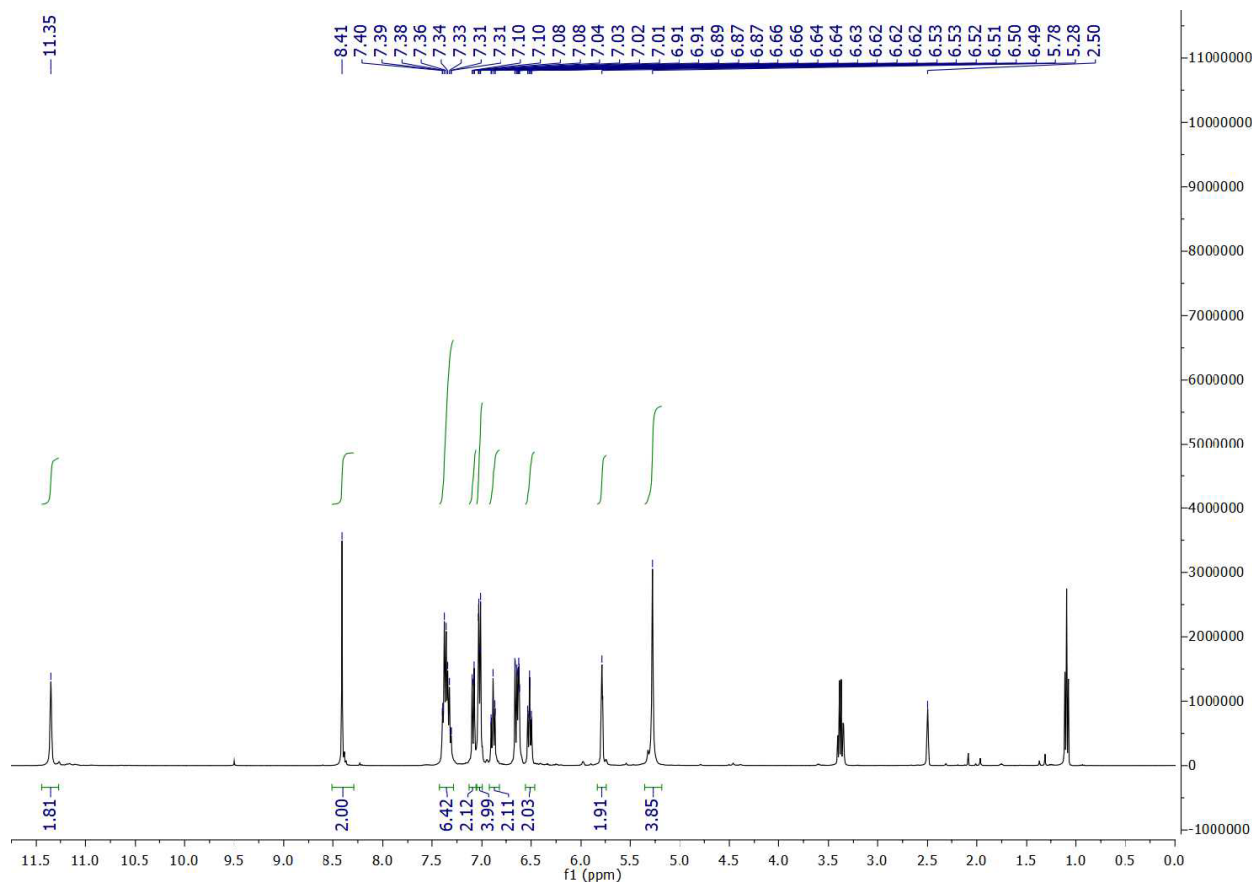


Figure 2.5.1. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **1a**.

2.5.3 Synthesis of **1b** (C₃₉H₃₄N₆O₂)

A round bottom flask was charged with 2.37g of N-(2-aminophenyl)acetamide (4 equiv., 0.0112 mol), 1.07g of *para*-toluenesulfonic acid (2 equiv., 0.0056 mol), and approx. 50 mL of methanol. To the solution was added 1.00 g of 5,5'-diformyl- 2,2'-diphenyldipyrromethane (1 equiv., 0.0028 mol). The mixture was stirred overnight, and the resulting precipitate was isolated by vacuum filtration and washed with cold methanol to give **1b** as a pale-yellow solid. Yield: 1.08 g (62.5%). Crystals suitable for single crystal X-ray diffraction studies were grown from a THF solution layered with pentane and cooled to -8 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ: 11.42 (br s, 2H, pyrrole-NH), 9.26 (s, 2H, amide-NH), 8.43 (s, 2H, imine-CH), 8.18 (d, 2H, aromatic-CH, *J* = 8.0 Hz), 7.43-7.28 (m, 6H, aromatic-CH), 7.25 (dd, 2H, aromatic-CH, *J* = 7.9, 1.6 Hz),

7.17-7.07 (m, 6H, aromatic-CH), 7.05 (td, 2H, aromatic CH, $J = 7.6, 1.5$ Hz), 6.80 (dd, 2H, pyrrole-CH, $J = 3.8, 1.8$ Hz), 5.91 (m, 2H, pyrrole-CH), and 1.98 (s, 6H, CH₃) ppm. ¹³C NMR (100 MHz, DMSO-d₆) δ : 168.48 (carbonyl-C), 149.53 (imine-C), 145.04 (aromatic-C), 141.56 (aromatic-C), 139.86 (aromatic-C), 133.65 (aromatic-C), 132.44 (aromatic-C), 129.85 (aromatic-CH), 128.37 (aromatic-CH), 127.60 (aromatic-CH), 126.18 (aromatic-CH), 124.03 (aromatic-CH), 120.20 (aromatic-CH), 116.91 (aromatic-CH), 115.72 (pyrrole-CH), 113.30 (pyrrole-CH), 56.76 (C-Ph₂), and 24.68 (CH₃) ppm. Anal. calcd for C₃₉H₃₄N₆O₂·0.25(CH₃CH₂OH): C, 75.3; H, 5.7; N, 13.3%. Found: C, 74.9; H, 5.6; N, 13.2%.

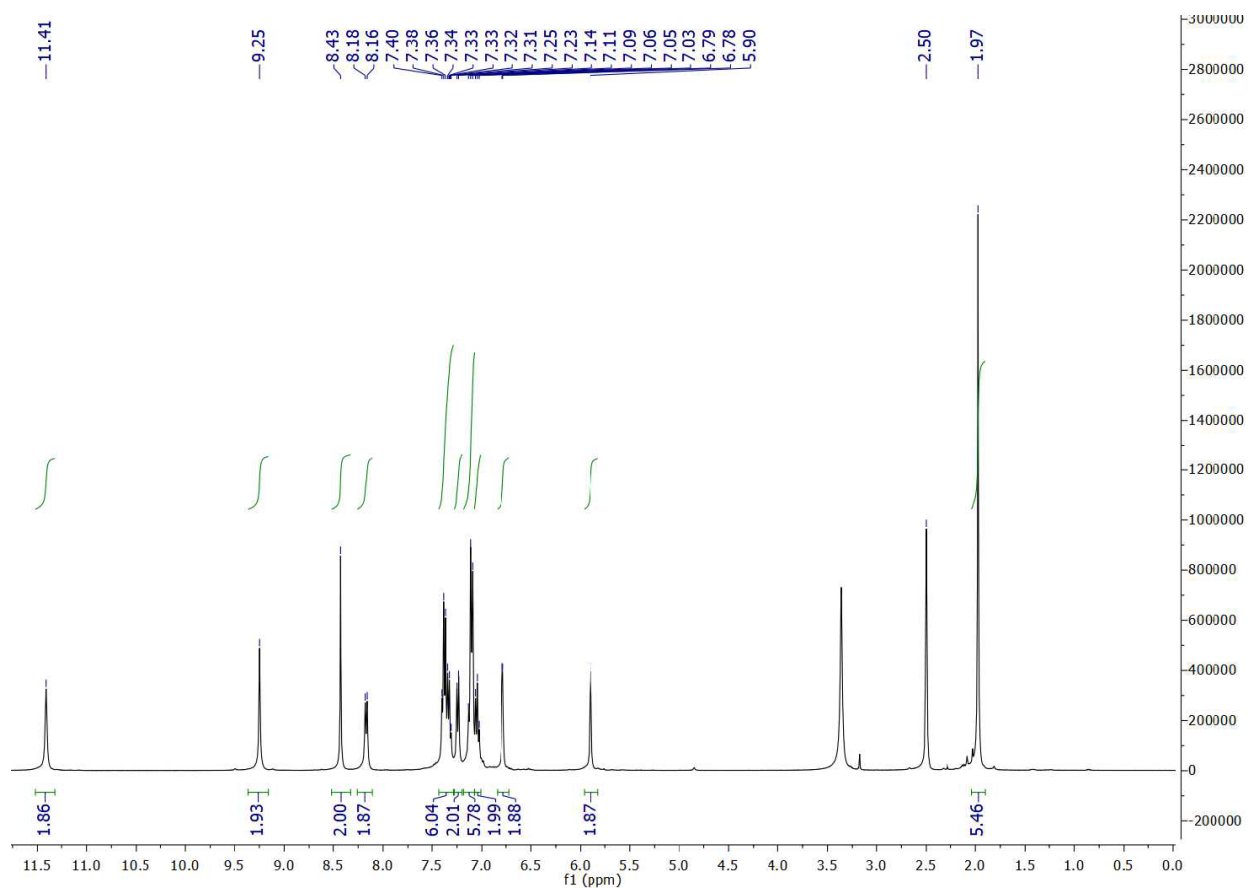


Figure 2.5.2. ¹H NMR spectrum (400 MHz, DMSO-d₆) of **1b**.

2.5.4 Synthesis of **1c** (C₄₅H₄₆N₆O₄)

A round bottom flask was charged with 0.500 g of 5,5'-diformyl-2,2'-diphenyldipyrromethane (1 equiv., 0.0014 mol), 0.600 g of *tert*-butyl-(2-aminophenyl)carbamate (2 equiv., 0.0028 mol), and 0.12 g of *para*-toluene sulfonic acid (0.5 equiv., 0.0007 mol). The

solids were dissolved in 30 mL of methanol and stirred overnight. The resulting precipitate was isolated by filtration and washed with cold methanol to give **1c** as a yellow solid. Yield: 0.264 g (25.7%). Crystals suitable for single crystal X-ray diffraction studies were grown from a diethyl ether solution cooled to -8 °C. **¹H NMR** (400 MHz, DMSO-*d*₆) δ: 11.46 (s, 2H, pyrrole-NH), 8.41 (s, 2H, imine-CH), 8.22 (s, 2H, Boc-NH), 7.94 (d, 2H, aromatic-CH, *J* = 8 Hz), 7.40-7.34 (m, 4H, aromatic-CH), 7.34-7.28 (m, 2H, aromatic-CH), 7.18 (dd, 2H, aromatic-CH, *J* = 8.0, 1.5 Hz), 7.14-7.07 (m, 6H, aromatic-CH), 7.00 (td, 2H, aromatic-CH, *J* = 7.6, 1.5 Hz), 6.78 (d, 2H, pyrrole-CH, *J* = 3.8 Hz), 5.91 (d, 2H, pyrrole-CH, *J* = 3.8 Hz), and 1.43 (s, 18H, C(CH₃)₃) ppm. **¹³C NMR** (100 MHz, DMSO-*d*₆) δ: 152.63 (carbonyl-C), 149.99 (imine-C), 145.09 (aromatic-C), 141.56 (aromatic-C), 139.86 (aromatic-C), 133.55 (aromatic-C), 132.28 (aromatic-C), 129.77 (aromatic-CH), 128.36 (aromatic-CH), 127.49 (aromatic-CH), 126.25 (aromatic-CH), 123.19 (aromatic-CH), 118.54 (aromatic-CH), 117.12 (aromatic-CH), 115.23 (pyrrole-CH), 113.24 (pyrrole-CH), 79.91 (C(CH₃)₃), 56.75 (C-Ph₂), and 28.44 (C(CH₃)₃) ppm. Anal. calcd for

C₄₅H₄₆N₆O₄: C, 73.55; H, 6.3; N, 11.4%. Found: C, 73.4; H, 6.2; N, 11.4%.

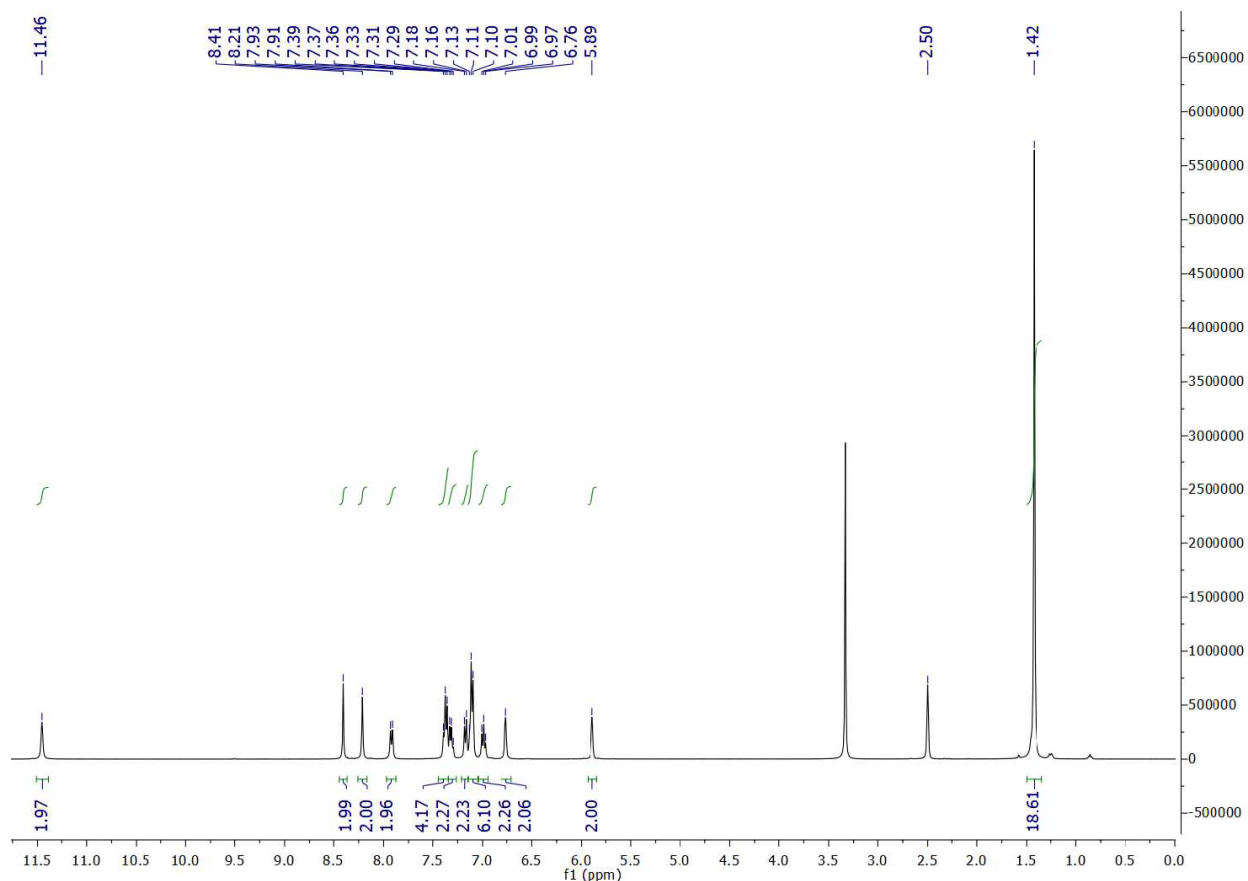


Figure 2.5.3. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **1c**.

2.5.5 Synthesis of **2a** (Pd(**1a**))

Under a nitrogen atmosphere, 0.266 g of **1a** (1 equiv., 0.498 mmol) in approx. 6 ml of THF was added to 0.040 g of KH (2 equiv., 0.997 mmol) in approx. 3 ml of THF. The reaction was stirred until gas evolution had ceased and a colour change was observed from orange to dark red. The mixture was then added to 0.112 g of Pd(OAc)₂ (1 equiv., 0.498 mmol) in approx. 3 ml of THF and stirred overnight. The solvent was then removed under reduced pressure and the resulting residue was dissolved in approx. 9 ml of DCM. The DCM solution was filtered through Celite to remove insoluble solids, and the solvent was once again removed under reduced pressure. The resulting solid was stirred in approx. 6 mL of methanol for about 30 min. and then cooled in a freezer (-30 °C) for approx. one hour. The mixture was removed from the freezer, the solid was collected by filtration, and then dried under vacuum to give **2a**

as a dark red solid. Yield: 0.183 g (57.4 %). Crystals suitable for single crystal X-ray diffraction studies were grown from the slow evaporation of an ethanol/dichloromethane solution. ^1H NMR (400 MHz, DMSO- d_6) δ 7.75 (s, 2H, imine-CH), 7.32-7.20 (m, 6H, aromatic-CH), 7.10 (dd, 4H, aromatic-CH, J = 8.7, 1.8 Hz), 6.75 (d, 2H, pyrrole-CH, J = 3.9 Hz), 6.69-6.60 (m, 4H, aromatic-CH), 6.29 (td, 2H, aromatic-CH, J = 7.5, 1.2 Hz), 6.16 (dd, 2H, aromatic-CH, J = 7.9, 1.3 Hz), 5.80 (d, 2H, pyrrole-CH, J = 3.9 Hz), and 4.45 (br s, 4H, NH_2) ppm. ^{13}C NMR (100 MHz, DMSO- d_6) δ : 161.80 (imine-CH), 148.86 (aromatic-C), 146.74 (aromatic-C), 140.60 (aromatic-C), 136.85 (aromatic-C), 133.82 (aromatic-C), 128.96 (aromatic-CH), 127.74 (aromatic-CH), 126.49 (aromatic-CH), 126.22 (aromatic-CH), 122.78 (aromatic-CH), 118.09 (pyrrole-CH), 116.28 (aromatic-CH), 114.93 (aromatic-CH), 111.73 (pyrrole-CH), and 61.54 (C- Ph_2) ppm. Anal. calcd for $\text{C}_{35}\text{H}_{28}\text{N}_6\text{Pd}\cdot 0.33(\text{CH}_2\text{Cl}_2)$: C, 63.6; H, 4.3; N, 12.6%. Found: C, 63.9; H, 4.25; N, 12.25%.

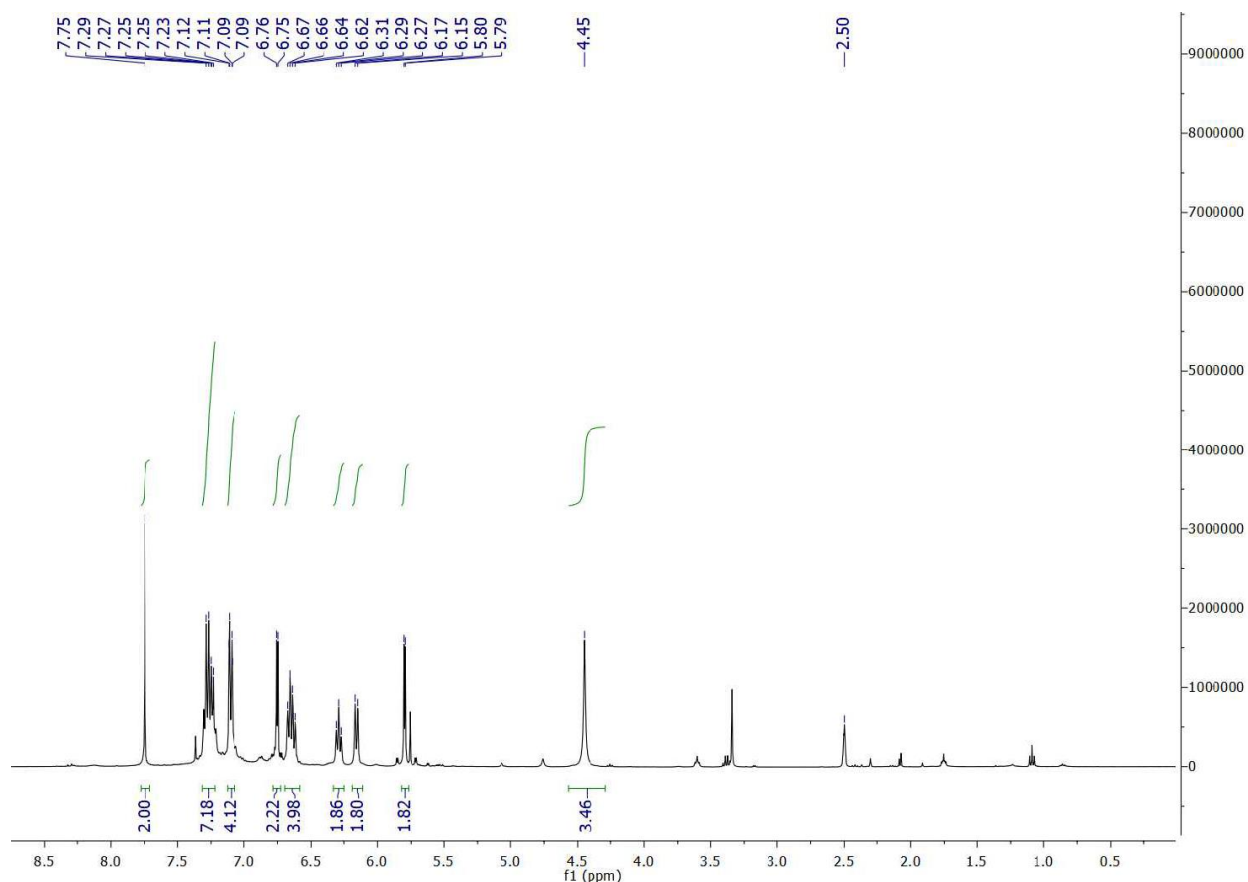


Figure 2.5.4. ^1H NMR spectrum (400 MHz, DMSO- d_6) of **2a**.

2.5.6 Synthesis of **2b** (Pd(**1b**))

Under a nitrogen atmosphere, 0.308 g of **1b** (1 equiv., 0.498 mmol) in approx. 6 ml of THF was added to 0.0400 g of KH (2 equiv., 0.997 mmol) in approx. 3 ml of THF. The reaction was stirred until gas evolution had ceased and a colour change was observed from orange to dark red. The mixture was then added to 0.112 g of Pd(OAc)₂ (1 equiv., 0.498 mmol) in 3 ml of THF and stirred overnight. The solvent was then removed under reduced pressure and the resulting residue was dissolved in approx. 9 ml of DCM. The DCM solution was filtered through Celite to remove insoluble solids, and the solvent was once again removed under reduced pressure. The resulting solid was stirred in approx. 6 ml of methanol for about 30 minutes and then cooled in a freezer (-30 °C) for one hour. The mixture was removed from the freezer, the solid was collected by filtration, and then dried under vacuum to give **2b** as an orange solid. Yield: 0.127 g (35.4%). Crystals suitable for single crystal X-ray diffraction studies were grown from an acetone solution cooled to -30 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (br s, 2H, NH), 7.55 (m, 4H, aromatic-CH and imine-CH), 7.29 (m, 6H, aromatic-CH), 7.24 (m, 4H, aromatic-CH), 7.01 (m, 4H, aromatic-CH), 6.89 (m, 4H, aromatic-CH and pyrrole-CH), 6.06 (d, 2H, pyrrole-CH, *J* = 4.1 Hz), and 2.13 (s, 6H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 161.24 (imine-CH), 151.65 (carbonyl-C), 145.99 (aromatic-C), 137.23 (aromatic-C), 129.38 (aromatic-CH), 128.10 (aromatic-CH), 127.39 (aromatic-CH), 127.03 (aromatic-CH), 124.80 (aromatic-CH), 122.18 (aromatic-CH), 120.27 (aromatic-CH and pyrrole-CH), 113.88 (pyrrole-CH), 77.36 (aromatic-C), 62.58 (C-Ph₂), and 25.25 (CH₃) ppm. Anal. calcd for C₃₉H₃₂N₆O₂Pd·0.66(CH₃OH): C, 64.0; H, 4.7; N, 11.3%. Found: C, 64.3; H, 4.6; N, 10.9%.

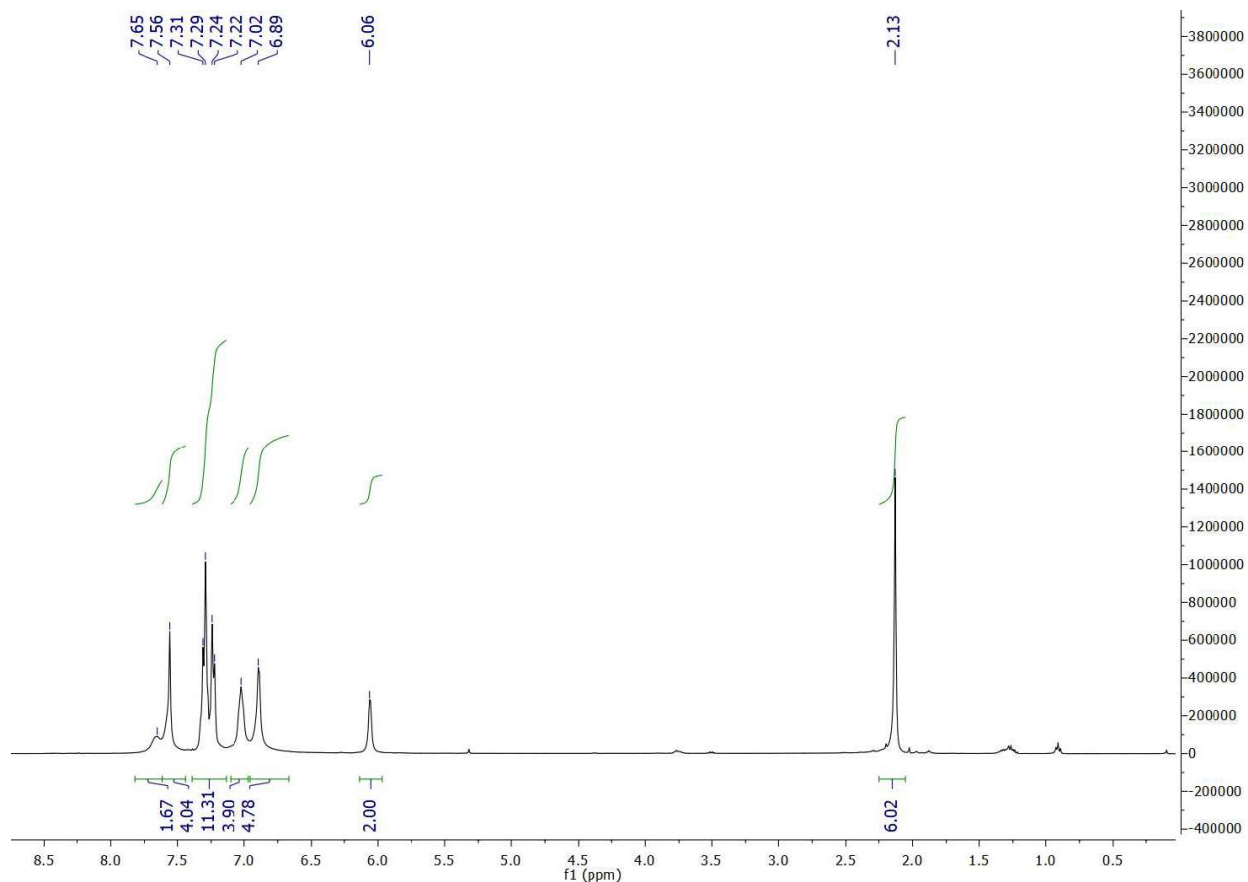


Figure 2.5.5. ^1H NMR spectrum (400 MHz, CDCl_3) of **2b**.

2.5.7 Synthesis of **2c** (**Pd(1c)**)

Under a nitrogen atmosphere, 0.366 g of **1c** (1 equiv., 0.498 mmol) in approx. 6 ml of THF was added to 0.0400 g of KH (2 equiv., 0.997 mmol) in approx. 3 ml of THF. The reaction was stirred until gas evolution had ceased and a colour change was observed from orange to dark red. The mixture was then added to 0.112 g of $\text{Pd}(\text{OAc})_2$ (1 equiv., 0.498 mmol) in 3 ml of THF and stirred overnight. The solvent was then removed under reduced pressure and the resulting residue was dissolved in approx. 9 ml of DCM. The DCM solution was filtered through Celite to remove insoluble solids, and the solvent was once again removed under reduced pressure. The resulting solid was stirred in approx. 6 ml of methanol for about 30 minutes and then cooled in a freezer ($-30\text{ }^\circ\text{C}$) for one hour. The mixture was removed from the freezer, the solid was collected by filtration, and then dried under vacuum to give **2c** as an orange solid. Yield: 0.152 g (36.4 %). Crystals suitable for single crystal X-ray diffraction

studies were grown from the slow diffusion of pentane into toluene solution. **¹H NMR** (400 MHz, DMSO-*d*₆) δ: 8.32 (s, 2H, Boc-NH), 7.60 (s, 2H, imine-CH), 7.31-7.23 (m, 6H, aromatic-CH), 7.08 (dd, 4H, aromatic-CH, *J* = 8.3, 1.8 Hz), 7.03-6.94 (m, 2H, aromatic-CH), 6.89 (td, 2H, aromatic-CH, *J* = 6.8, 1.6 Hz), 6.80 (d, 2H, aromatic-CH, *J* = 7.8 Hz), 6.77 (d, 2H, pyrrole-CH, *J* = 3.9 Hz), 6.66-6.53 (m, 2H, aromatic-CH), 5.79 (d, 2H, pyrrole-CH, *J* = 3.9 Hz), 1.31 (s, 18H, C(CH₃)₃). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ: 161.43 (imine-CH), 153.33 (carbonyl-C), 149.32 (aromatic-C), 146.51 (aromatic-C), 142.59 (aromatic-C), 137.00 (aromatic-C), 130.08 (aromatic-C), 128.90 (aromatic-CH), 127.70 (aromatic-CH), 126.49 (aromatic-CH), 125.53 (aromatic-CH), 125.40 (aromatic-CH), 125.23 (aromatic-CH), 124.05 (aromatic-CH), 118.51 (pyrrole-CH), 111.99 (pyrrole-CH), 78.94 (C(CH₃)₃), 61.55 (C-Ph₂), 27.98 (C(CH₃)₃). Anal. calcd for C₄₅H₄₄N₆O₄Pd·0.33(CH₂Cl₂): C, 62.8; H, 5.2; N, 9.7%. Found: C, 62.9; H, 5.1; N, 9.65%.

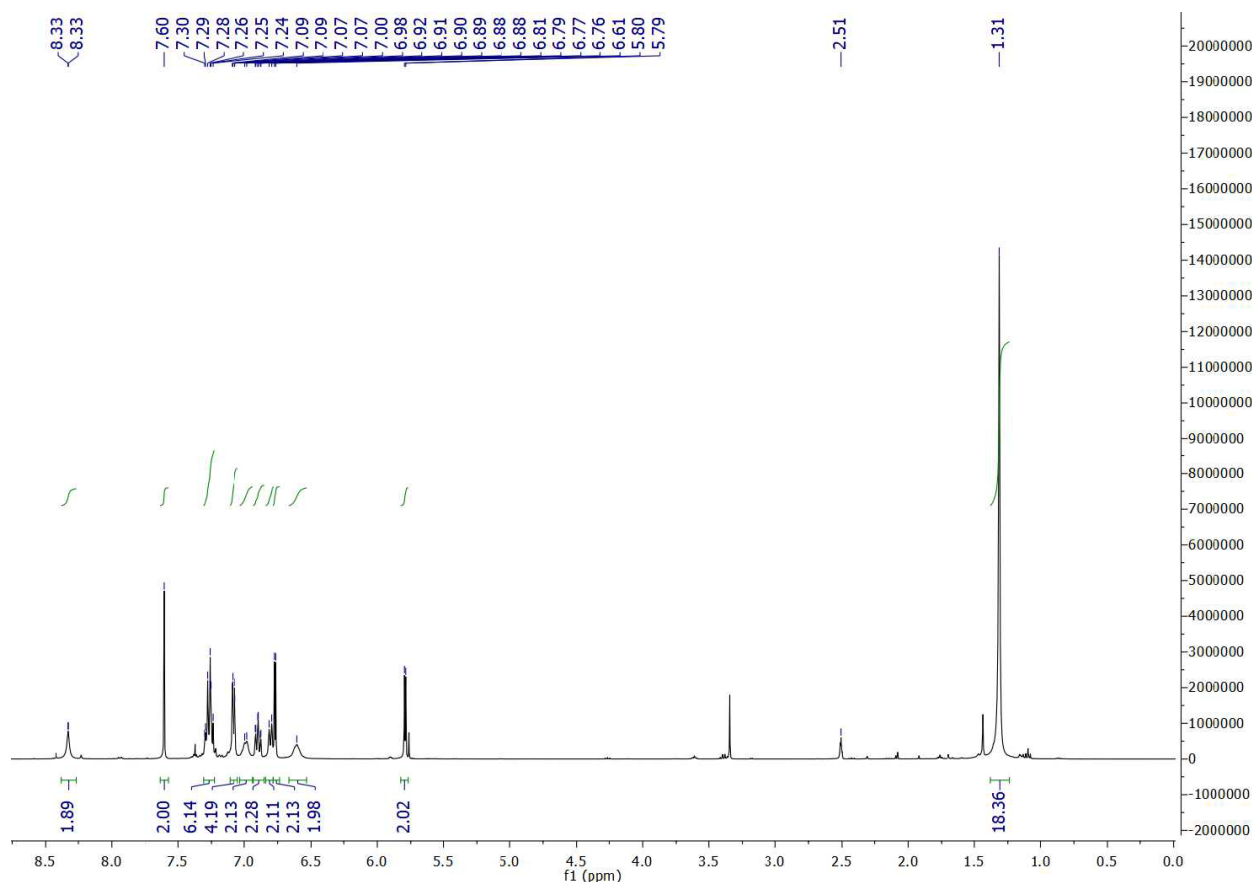


Figure 2.5.6. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of 2c.

Table 2.5.1. Selected Crystal Data, Data Collection, and Refinement Parameters for Compounds 1a-c.

	1a·0.75(C₄H₁₀O)	1b·(C₄H₈O)	1c·0.25(C₄H₁₀O)
empirical formula	C ₃₈ H _{37.5} N ₆ O _{0.75}	C ₄₃ H ₄₂ N ₆ O ₃	C ₄₆ H _{48.5} N ₆ O _{4.25}
FW	590.24	690.82	753.41
lattice type	triclinic	triclinic	orthorhombic
space group	P-1	P-1	Pbca
T, K	150.0(1)	139.6(6)	200.0(1)
a, Å	13.3432(2)	10.7275(3)	11.3057(3)
b, Å	16.3520(3)	13.5560(7)	34.223(2)
c, Å	30.8801(4)	13.7081(5)	42.076(2)
α, deg	76.296(1)	85.243(4)	90
β, deg	82.0335(9)	68.724(3)	90
γ, deg	83.097(1)	89.258(3)	90
V, Å ³	6455.9(2)	1850.88(13)	16279.7(9)
Z	8	2	16
ρ _{calc} /Mg m ⁻³	1.215	1.24	1.23
μ(Cu/Mo, Ka) mm ⁻¹	0.583 (Cu)	0.631 (Cu)	0.639 (Cu)
F(000)	2508	732	6408
cryst size, mm ³	0.25 x 0.173 x 0.057	0.08 x 0.06 x 0.02	0.173 x 0.036 x 0.018
range Θ collected, deg	2.7910 to 77.4720	3.4760 to 77.1060	2.6330 to 76.8150
reflns	116338/27162	27828/7604	21069/16754
collected/unique			
abs cor	Semi-empirical from equivalents		
Max and min transmn			
coeff.	0.967 and 0.886	0.987 and 0.951	0.989 and 0.973
goodness of fit	1.038	1.023	1.027
R ₁ (I>2σ(I)) ^a	0.0456	0.0451	0.0531
wR ₂ (all data) ^a	0.1287	0.1211	0.1591
peak and hole, e Å ⁻³	0.422 and -0.326	0.462 and -0.411	0.330 and -0.252

^a Definition of R indices: $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]]^{1/2} / [\Sigma[w(F_o^2)^2]]^{1/2}$

Table 2.5.2. Selected Crystal Data, Data Collection, and Refinement Parameters for Compounds 2a-c.

	2a	2b·2(C₃H₆O)	2c·(C₇H₈)
empirical formula	C ₃₅ H ₂₈ N ₆ Pd	C ₄₅ H ₄₄ N ₆ O ₄ Pd	C ₅₂ H ₅₂ N ₆ O ₄ Pd

FW	639.03	839.26	931.39
lattice type	monoclinic	triclinic	triclinic
space group	P121/n1	P-1	P-1
T, K	200.0(1)	200.0(1)	100.0(1)
a, Å	16.0704(9)	11.7246(2)	10.9860(9)
b, Å	9.4831(4)	13.1608(3)	12.5725(9)
c, Å	20.0343(9)	13.3391(3)	17.994(2)
α , deg	90	97.804(2)	69.906(6)
β , deg	113.379(6)	92.088(2)	88.064(6)
γ , deg	90	103.530(2)	75.157(6)
V, Å ³	2802.5(2)	2574.2(1)	2252.1(3)
Z	4	2	2
$\rho_{\text{calc}}/\text{Mg m}^{-3}$	1.515	1.409	1.373
$\mu(\text{Cu/Mo, Ka}) \text{ mm}^{-1}$	5.624 (Cu)	4.200 (Cu)	3.744 (Cu)
F(000)	1304	868	968
cryst size, mm ³	0.055 x 0.043 x 0.034	0.2 x 0.2 x 0.2	0.4 x 0.039 x 0.019
range Θ collected, deg	2.9430 to 76.6980	3.353 to 77.295	2.624 to 76.539
reflns collected/unique	51287/5844	87168/8335	41955/9436
abs cor	Semi-empirical from equivalents		
Max and min transmn coeff.	0.15630 and 0.05497	1.000 and 0.804	1.000 and 0.494
goodness of fit	1.066	1.068	1.1
R1(I>2s(I)) ^a	0.0569	0.0223	0.0363
wR ₂ (all data) ^a	0.1545	0.0605	0.0991
peak and hole, e Å ⁻³	1.229 and -0.0400	0.523 and -0.648	1.123 and -0.838

^a Definition of R indices: $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]]/[\Sigma[w(F_o^2)^2]]^{1/2}$

2.5.8 Computational Details

Density functional theory calculations were performed using the GAMESS(US) package (2016 R1)^{73,74} and the B3LYP hybrid functional.^{75,76} Palladium was treated with the Def2-TZVP relativistic effective core potential and associated basis set,⁷⁷ while all other atoms were treated with the 6-31++G(d,p) basis set.^{78,79} A tight integration grid where NRAD=99 and NLEB=1202 was used throughout for increased accuracy. Open-shell doublet state optimizations were performed for **2aH**⁺; closed-shell as well as open-shell triplet

state optimizations were performed for $2\mathbf{aH}^{2+}$. Stationary points were characterized by normal-mode analysis. Full vibrational and thermochemical analyses (1 atm, 298 K) were performed on optimized structures to obtain free energies (G°) and enthalpies (H°). Optimized ground states were found to have zero imaginary frequencies. Three dimensional visualizations of calculated structures and orbitals were generated using MacMolPlt.⁸⁰

2.5.9 Preliminary Small Molecule Activation Studies

Reactivity studies were carried out in the presence of acid or base where appropriate. The electrochemical conditions of the catalytic trials included 0.1 M TBAP electrolyte, 0.25 mM of complex ($2\mathbf{a-c}$), and 600 equivalents of acid or base. The three-electrode setup consisted of a glassy carbon working electrode, a platinum wire counter electrode, and a 0.01 M Ag/AgNO₃ reference electrode. All CVs were referenced versus the Fc/Fc⁺ redox couple. All CVs were recorded under a nitrogen atmosphere in dry acetonitrile with the exception of oxygen reduction. During methanol oxidation studies, 0.25 mL of methanol was used in addition to the 600 eq of base. Each of the reductions and oxidations were tested with three different acids (TFA, *para*-toluenesulfonic acid monohydrate, and 2,6-lutidinium tetrafluoroborate) and bases (triethylamine, pyridine, 2,6-lutidine) respectively.

2.5.10 Electrocatalytic H₂ Evolution

The electrochemical conditions of the catalytic trials included 0.1 M TBAP electrolyte, 0.25 mM of complex ($2\mathbf{a-c}$), and 600 equivalents of *para*-toluenesulfonic acid monohydrate (0.15 M). The three-electrode setup consisted of a glassy carbon working electrode, a platinum wire counter electrode, and a 0.01 M Ag/AgNO₃ reference electrode. All CVs were referenced versus the Fc/Fc⁺ redox couple except for those carried out in CD₃CN. All CVs were recorded under an argon or nitrogen atmosphere in dry acetonitrile.

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Chapter 3 – Electrocatalytic Hydrogen Evolution using a Nickel-based Calixpyrrole Complex: Controlling the Secondary Coordination Sphere on an Electrode Surface

3.1 Abstract

Incorporating design elements from homogeneous catalysts to construct well defined active sites on electrode surfaces is a promising approach for developing next generation electrocatalysts for energy conversion reactions. Furthermore, if functionalities that control the electrode microenvironment could be integrated into these active sites it would be particularly appealing. In this context, a square planar nickel calixpyrrole complex, **Ni(DPMDA)** (**DPMDA**=2,2'-((**diphenylmethylene**))bis(1H-pyrrole-5,2-diyl))bis(**methaneylylidene**))bis(**azaneylylidene**))**dianiline**) with pendant amine groups is reported that forms a heterogeneous hydrogen evolution catalyst using anilinium tetrafluoroborate as the proton source. The supported **Ni(DPMDA)** catalyst was surprisingly stable and displayed fast reaction kinetics with turnover frequencies (TOF) up to 25,900 s⁻¹ or 366,000 s⁻¹ cm⁻². Kinetic isotope effect (KIE) studies revealed a KIE of 5.7, and this data, combined with Tafel slope analysis, suggested that a proton-coupled electron transfer (PCET) process involving the pendant amine groups was rate-limiting. While evidence of an outer-sphere reduction of the **Ni(DPMDA)** catalyst was observed, it is hypothesized that the control over the secondary coordination sphere provided by the pendant amines facilitated such high TOFs and enabled the PCET mechanism. The results reported herein provide insight into heterogeneous catalyst design and approaches for controlling the secondary coordination sphere on electrode surfaces.

3.2 Introduction

Climate change caused by the large-scale emission of greenhouse gases is fast becoming the defining challenge of our time. This issue is inextricably linked to our reliance on fossil fuels

and associated CO₂ production.¹ Global energy consumption, however, continues to rise along with worldwide population growth, and as such the need for alternative, sustainable energy sources is increasingly paramount. While wind turbines and solar panels are promising candidates for renewable power generation, they are also notoriously intermittent. Technologies that can stockpile the energy harvested from these sources for later use will therefore be a crucial component of any sustainable energy economy.

Electrolytic cells that generate hydrogen gas from water are an attractive solution for the long-term storage of renewable power in the form of chemical bonds.^{2, 3} A major barrier to the widespread implementation of these cells is a reliance on rare and expensive platinum-based metal catalysts.⁴ Biological systems, in contrast, can evolve hydrogen efficiently using earth-abundant metals with enzymes such as [FeFe]- and [NiFe]-hydrogenases.⁵⁻⁷ In particular, the [FeFe]-hydrogenase active site has been a source of inspiration for many synthetic catalysts based on sustainable metals.⁸⁻¹⁰ One key design element from this metalloenzyme is a bridging azodithiolate ligand (**Figure 3.2.1**), which acts as a proton shuttle in the secondary coordination sphere and facilitates proton-coupled electron transfer (PCET).¹¹ Nickel diphosphacycloheptane complexes are notable examples of synthetic hydrogen evolution catalysts that incorporate proton relays in the secondary coordination sphere (**Figure 3.2.1**).^{12, 13} Bullock et al. showed that the pendant amines were critical in generating highly efficient hydrogen evolution catalysts with turnover frequencies (TOFs) greater than 100,000 s⁻¹.^{14,15} Moreover, these nickel systems demonstrated complementary reactivity for hydrogen oxidation with the correct ligand tuning.^{16,17}

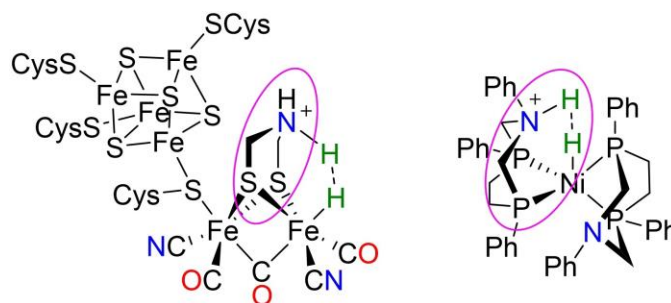


Figure 3.2.1. Structure of the [FeFe]-hydrogenase active site (left) with the azodithiolate ligand highlighted, and a nickel diphosphacycloheptane complex (right) with analogous pendant amine highlighted.

The image shows a chemical structure of a functionalized carbon nanotube (CNT) on the left, which is connected via a biphenyl linker to a chain containing an amine group (NH_2) and an amide group ($\text{NH}-\text{C}=\text{O}$). The amide is linked to a phenyl ring, which is part of a nickel complex. The nickel complex features a central Ni atom coordinated by two phosphorus atoms (P) and two nitrogen atoms (N), with various ligands including R, Ph, and H.

102

It should be noted that a recent study from Surendranath and co-workers on cobalt porphyrin complexes anchored to glassy carbon supports with aliphatic linkers has challenged the way molecular catalysts are viewed when tethered to electrode surfaces.²⁶ In acetonitrile, the cobalt species did not interact directly with the electrode material and mediated H₂ evolution through an outer-sphere stepwise mechanism, much like a homogeneous catalyst. In contrast, the cobalt porphyrin complexes were directly adsorbed onto the glassy carbon support when utilizing an aqueous medium, and H₂ evolution was mediated through a highly desirable concerted PCET process, more like a metal surface. Therefore, designing tightly adsorbed molecular species with strong electrode interactions could lead to major enhancements in electrocatalysis.

To this end, we examined a nickel complex bearing a porphyrin-like, Schiff-base calixpyrrole ligand with pendant amine groups. Modelled after the macrocycles developed by Love and Sessler,²⁸⁻³⁶ these ligand architectures also resemble the “hangman” porphyrins from the Nocera group.³⁷⁻⁴⁹ A major advantage of the calixpyrroles, however, is their ease of synthesis, which makes them attractive alternatives to porphyrin systems. Moreover, a series of palladium-coordinated calixpyrrole ligands bearing pendant hydrogen-bond donors in the secondary coordination sphere have been reported (**Figure 3.2.3**).⁵⁰ The palladium species were found to evolve H₂ electrocatalytically, but the active species were deposited on the electrode surface. Herein, we report the coordination geometry, electrochemical properties, and catalytic activity of an analogous nickel-coordinated Schiff-base calixpyrrole complex towards H₂ evolution.

Within this study, we aim to investigate redox couple accessibility of the **Ni(DPMDA)** complex with the intention of evaluating catalytic activity. Based off the previous report of the corresponding Pd complexes, it was initially believed the formation of a heterogeneous catalyst under catalytic conditions could be likely.⁵⁰ Additionally, unlike the previous study,⁵⁰ anilinium was chosen as the proton source to investigate catalytic activity to minimize water content while still retaining the ability to protonate the pendant groups. It is hypothesized that use of an acid strong enough to directly protonate the pendant groups may allow the amines to act as secondary coordination sphere proton-shuttles and facilitate PCET-aided catalysis. Furthermore, it is hypothesized that the imine may be susceptible to reduction which may be an intermediate in the heterogenization of the metal complex.

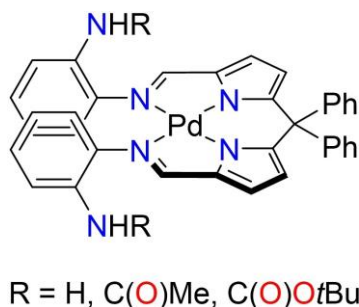


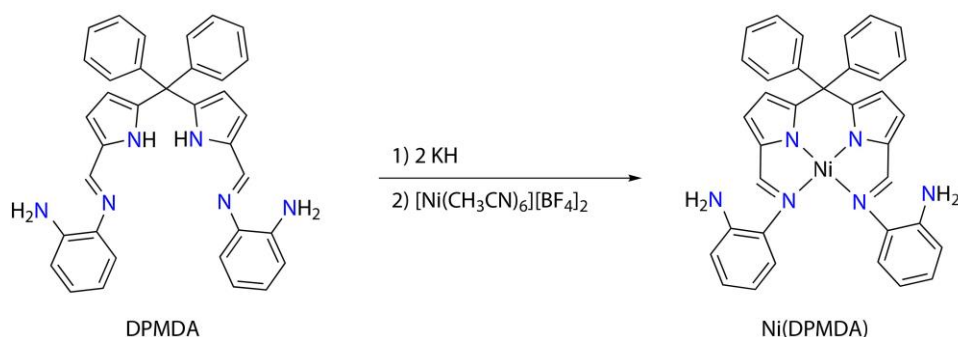
Figure 3.2.3. General structure of the palladium-based Schiff-base calixpyrrole complexes with pendant hydrogen-bond donors.

3.3 Results and Discussion

3.3.1 Synthesis and Characterization

The nickel calixpyrrole complex, **Ni(DPMDA)**, was synthesized as shown in **Scheme 3.3.1** in a similar manner reported for the corresponding palladium complexes.⁵⁰ The pyrroles of the 2,2'-((**diphenylmethylene**)bis(1H-pyrrole-5,2-diyl))bis(**methaneylylidene**))bis(**azaneylylidene**))**dianiline** ligand, **DPMDA**, were deprotonated with 2 equivalents of KH and then the corresponding salt was stirred with 1 equivalent of $[\text{Ni}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. The product conveniently precipitated from acetonitrile and the resulting square planar **Ni(DPMDA)** was isolated in good yields (60.9 %). The ^1H NMR spectrum of the complex gave characteristic peaks for metal coordination, with upfield shifts of the imine protons from 8.41 to 7.35 ppm. Additionally, the absence of the pyrrole NH signal was observed indicating successful deprotonation of the ligand.

Scheme 3.3.1. General Synthetic Procedure for **Ni(DPMDA)**.



In addition to NMR characterization, the **Ni(DPMDA)** complex was characterized by single crystal X-ray diffraction (**Figure 3.3.1**). The coordination geometry mirrored the

previously reported palladium calixpyrrole complexes,⁵⁰ with nickel adopting a distorted square planar geometry (for a brief discussion, see Experimental). What was particularly notable about the structure was that the distance between the nitrogen atoms of the pendant groups and the metal center was around 3.5 Å (Ni(1)-N(5), Ni(1)-H(5B), Ni(1)-N(6), and Ni(1)-H(6B) distances of 3.52, 2.83, 3.54, and 2.85 Å, respectively) indicating that they were not coordinated to nickel, but were almost within hydrogen-bonding distances seen for N–H–N (3.32 Å, sums of heavy atom van der Waals radii).⁵¹ Furthermore, the Ni–N distances seen for **Ni(DPMDA)** were similar to those reported for nickel diphosphacycloheptane catalysts (3.17–3.68 Å),¹⁵ which are known to utilize pendant amines in the secondary coordination sphere to facilitate nickel-hydride formation, as well as hydrogen gas formation. This data gives strong support that the pendant functionalities in **Ni(DPMA)** are properly positioned and within a reasonable distance to deliver protons to the nickel center to form a nickel-hydride intermediate, as well as to deliver protons to a nickel hydride intermediate to form hydrogen gas. Lastly, it should be noted that the pendant N(5) amine group was disordered across two positions: opposite N(6), as well as on the same side of the calixpyrrole plane as N(6), indicating rotational freedom about the C(12)–N(3) and C(18)–N(4) bonds. For selected bond lengths and angles see **Figure 3.3.1**.⁵²

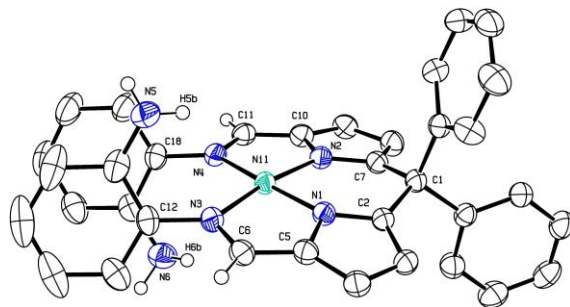


Figure 3.3.1. ORTEP3 representation (thermal ellipsoids at 50 % probability) and atom numbering for Ni(DPMDA), most of the hydrogens have been omitted for clarity. Selected bond lengths (Å): Ni(1)–N(1) = 1.839(4), Ni(1)–N(2) = 1.843(4), Ni(1)–N(3) = 1.955(4), Ni(1)–N(4) = 1.947(4). Selected bond angles (deg): N(1)–Ni(1)–N(2) = 87.3(2), N(1)–Ni(1)–N(3) = 83.8(2), N(2)–Ni(1)–N(4) = 83.7(2), N(3)–Ni(1)–N(4) = 105.0(2).

3.3.2 Electrochemical Characterization

The electrochemical properties of **Ni(DPMDA)** were probed via cyclic voltammetry (CV) in acetonitrile with tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte (**Figures 3.3.2 and 3.3.3**). A redox couple was evident around 0 V vs the ferrocene/ferricinium (Fc/Fc^+) couple, which corresponded to a similar feature seen in the CV of the free ligand.⁵⁰ Moreover, in the positive region of the voltammogram, the complex exhibited four irreversible oxidation peaks, several of which are anticipated to be ligand-based oxidation processes based on past results seen with analogous palladium calixpyrrole species.⁵⁰ The appearance of a variable weak reduction peak between 0.5 V and 0.65 V vs Fc/Fc^+ , however, suggested that the $\text{Ni}^{\text{III/II}}$ redox couple was also potentially accessible. Further theoretical studies are needed to examine the nature of these irreversible redox events more conclusively.

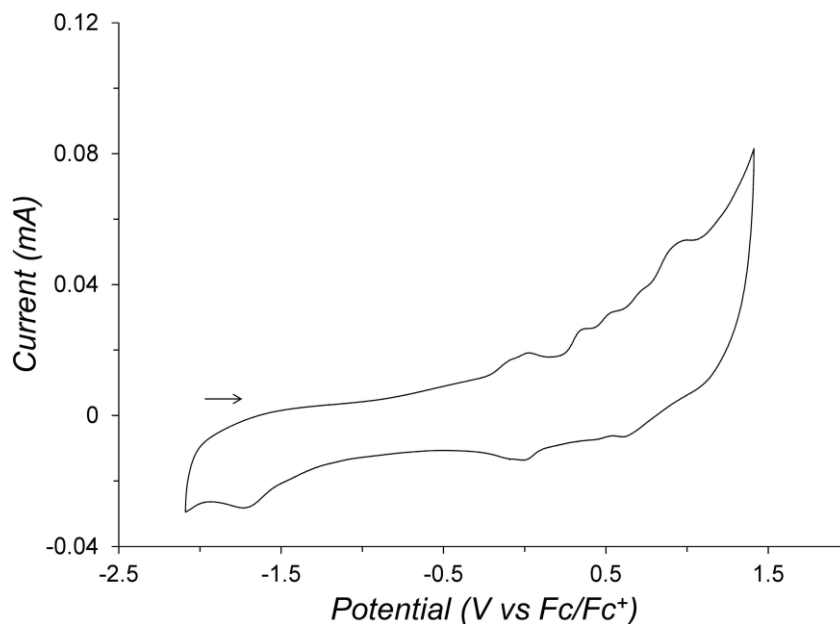


Figure 3.3.2. CV showing the irreversible redox features of **Ni(DPMDA)** at positive potentials (0.1 M TBAP, 0.25 mM **Ni(DPMDA)**), glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO_3 reference electrode, scan rate = 800 mV/s).

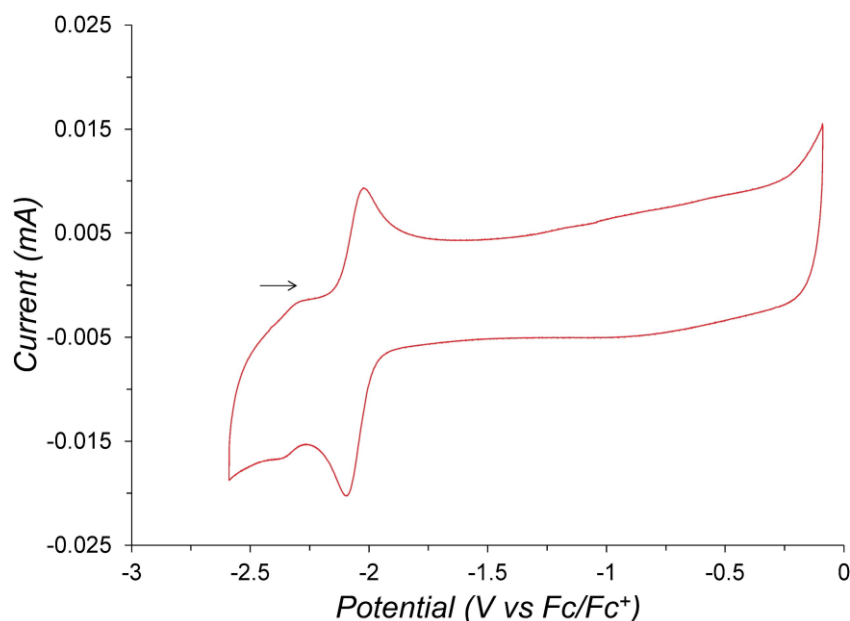


Figure 3.3.3. CV showing the quasi-reversible redox couples of **Ni(DPMDA)** at negative potentials (0.1 M TBAP, 0.25 mM **Ni(DPMDA)**, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 800 mV/s).

In contrast to the previously reported palladium calixpyrrole complexes, **Ni(DPMDA)** exhibited two redox couples at very negative potentials; one at $E_{1/2} = -2.03$ V vs Fc/Fc⁺ and a weaker couple at $E_{1/2} = -2.31$ V vs Fc/Fc⁺ (**Figure 3.3.3**). Such negative potentials are attributed to the electron-rich pyrrolide donors. The more positive and pronounced quasi-reversible redox couple has tentatively been assigned to Ni^{II/I}. This feature had a ΔE value in near unity with Fc/Fc⁺ suggesting a one-electron transfer, and the peak current varied linearly with the square-root of the scan rate indicating a diffusion-controlled process (**Figure 3.3.4**). For the more negative redox couple, on the other hand, the anodic and cathodic peak current ratios could not be accurately determined due to the proximity of the Ni^{II/I} feature.

It is believed, however, that this redox process is likely a Ni^{I/0} couple. These assignments are supported by the electrochemistry of analogous nickel porphyrin species reported by Nocera et al., which exhibited two narrowly separated reversible redox processes at negative potentials.⁴⁶ These were assigned as Ni^{II/I} and Ni^{I/0}. Moreover, Wilson et al. also saw two consecutive redox couples in a series of Ni complexes bearing diphosphine ligands with pendant nitrogen bases.⁵³ Similarly, these redox features were assigned as Ni^{II/I} and Ni^{I/0} couples.

Interestingly, the authors noted variable reversibility of the second reduction, which was attributed to precipitation of the corresponding Ni^0 species on the electrode surface. It should also be noted that upon narrowing the scanning window for **Ni(DPMDA)** and excluding positive potentials, the irreversible reduction near -1.7 V vs Fc/Fc^+ disappeared, suggesting that this feature was coupled with one of the oxidations in the positive region.

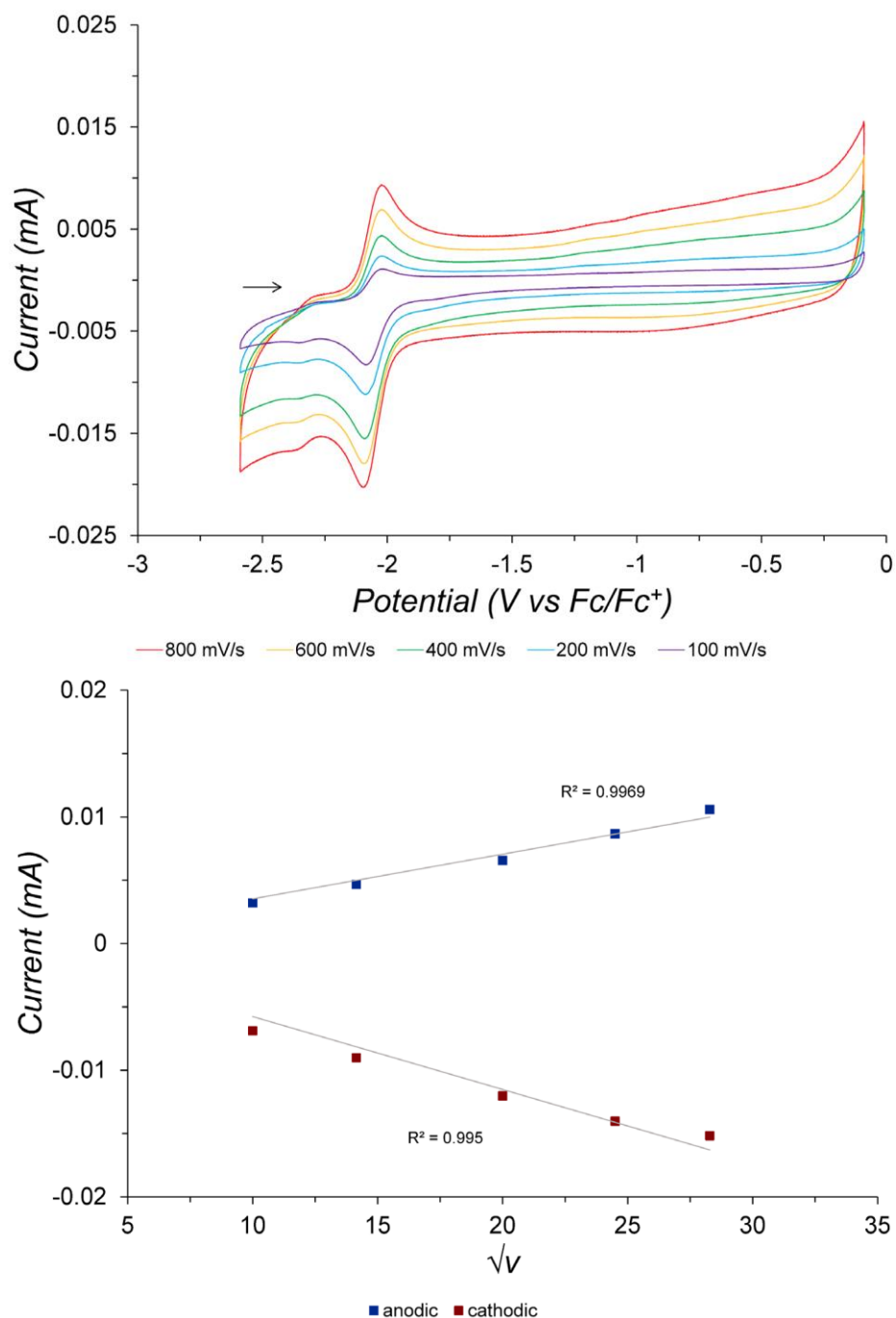


Figure 3.3.4. CVs of the quasi-reversible redox couples of **Ni(DPMDA)** at various scan rates (0.1 M TBAP in acetonitrile, 0.25 mM **Ni(DPMDA)**, glassy carbon working electrode, platinum wire counter electrode, 0.01 M AgNO₃ reference electrode, scan rate = 100 to 800 mV/s) (top); plot of anodic and cathodic current vs the square-root of scan rate (bottom).

3.3.3 Electrocatalytic Hydrogen Production

The electrochemical behaviour of **Ni(DPMDA)** was subsequently examined using a selection of proton sources. When 2 equivalents (0.5 mM) of acetic acid ($pK_a=23.5$)⁵⁴ or triethylammonium tetrafluoroborate ($pK_a=18.83$)⁵⁵ were utilized, no significant changes in the CVs were detected and no new electrochemical features were apparent. If, however, 2 equivalents of anilinium tetrafluoroborate ($pK_a=10.62$)⁵⁴ were used (anticipated to be a strong enough acid to protonate the pendant amine groups on **Ni(DPMDA)** based on their similar structures), a new irreversible reduction peak appeared about 450 mV more positive than the $Ni^{II/I}$ couple (**Figure 3..5**). These results gave strong indications that protonation of the **Ni(DPMDA)** complex was occurring in the presence anilinium tetrafluoroborate, and not in the presence of the weaker acids triethylammonium tetrafluoroborate and acetic acid. As such, anilinium tetrafluoroborate was used in all subsequent experiments. Upon increasing the concentration of anilinium tetrafluoroborate to 5 equivalents (1.25 mM), the new feature split into two distinct irreversible reductions: one near -1.80 V vs Fc/Fc^+ and the other near -1.37 V vs Fc/Fc^+ . Notably, when the scan window was narrowed to only include the reduction at -1.37 V, a larger current response was observed (**Figure 3.3.6**). Further increases in acid concentration were accompanied by greater peak currents for the two irreversible features, as well as a cathodic shift to -2.19 V and -1.80 V vs Fc/Fc^+ . It was hypothesized that the two irreversible reductions were indicative of two competing mechanisms for hydrogen production, much like Queyriaux et al. observed with cobalt polypyridyl complexes.⁵⁶ The authors reported a single homogeneous electrocatalyst that displayed two catalytic waves when the ligand was protonated (at -1.90 V and -1.65 V).⁵⁶ The more cathodic process was attributed to a pathway involving a ligand-based reduction, whereas the more anodic process was shown to proceed through a metal-centered reduction.⁵⁶ Queyriaux et al. were also able to isolate the more anodic process by using a weaker acid.⁵⁶ For the **Ni(DPMDA)** system, however, neither of the competing pathways for hydrogen production could be isolated by employing a weaker acid. Instead, they both appear to “turn on” when an acid strong enough to protonate the pendant proton shuttles is employed.

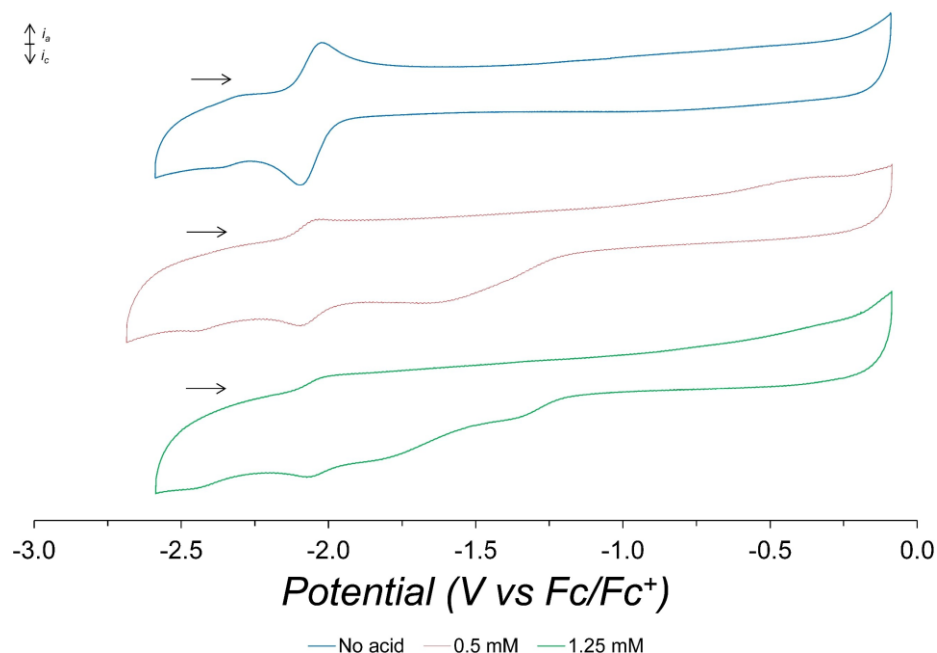


Figure 3.3.5. CVs of **Ni(DPMDA)** in the absence and presence of acid (0, 0.5, and 1.25 mM anilinium tetrafluoroborate, 0.25 mM **Ni(DPMDA)**, 0.1 M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 800 mV/s).

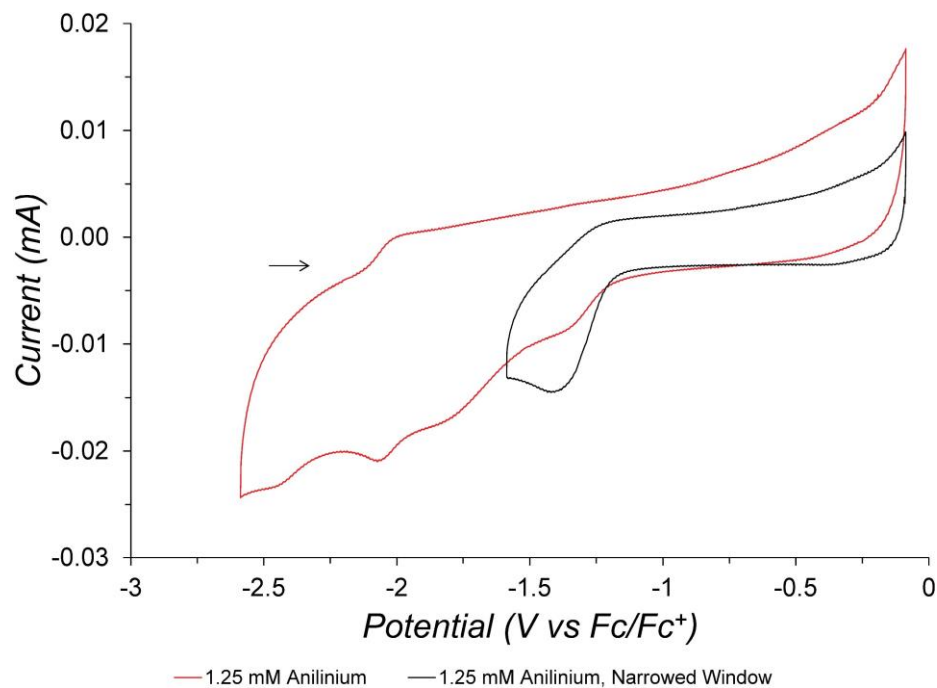


Figure 3.3.6. CVs of **Ni(DPMDA)** in the presence of acid with different scanning windows (1.25 mM anilinium tetrafluoroborate, 0.25 mM **Ni(DPMDA)**, 0.1 M TBAP, glassy carbon

working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 800 mV/s).

Next, the scan rate dependence of hydrogen evolution using **Ni(DPMDA)** was examined. It became immediately clear that the current response of the more anodic catalytic peak varied linearly with scan rate, suggesting a heterogeneous process (**Figure 3.3.7**). The peak current of the more cathodic feature, however, could not be accurately determined due to the proximity of the first catalytic wave. Several controls were then carried out to probe the heterogeneity of the catalytic processes.⁵⁷ A simple “rinse” test confirmed that the active catalytic species were adsorbed on the glassy carbon electrode surface (**Figure 3.3.8**). Moreover, a mercury pool test was also performed to rule out nanoparticle formation (**Figure 3.3.9**). The strong catalytic current that was observed supported that the adsorbed catalytic species were molecular in nature. It was initially hypothesized that, given the relatively low solubility of **Ni(DPMDA)** in acetonitrile, deposition of the protonated active catalytic species on the carbon support could be partially driven by poor solubility in acetonitrile. As such, a rinse test was performed with acetone as the washing solvent (a solvent in which **Ni(DPMDA)** is more soluble). The catalytic waves associated with hydrogen evolution were eliminated after rinsing with acetone, which also gave support that the active catalysts were molecular species (**Figure 3.3.10**). Therefore, it is believed that the deposited catalytic species are adsorbed on the working electrode, likely through non-covalent interactions. This is similar to several known porphyrin systems, such as the cobalt porphyrin investigated by Surendranath and co-workers,²⁶ the iron tetrakis(N-methyl-4-pyridyl)porphyrin reported by Constentin, Dridi, and Savéant,⁵⁸ or the manganese tetraphenylporphyrin reported by Marianov and Jiang.⁵⁹ Another possibility is that **Ni(DPMDA)** has been immobilized on the glassy carbon electrode through electropolymerization (less likely based on the ease with which the active catalyst was removed with small amounts of acetone).⁶⁰⁻

62

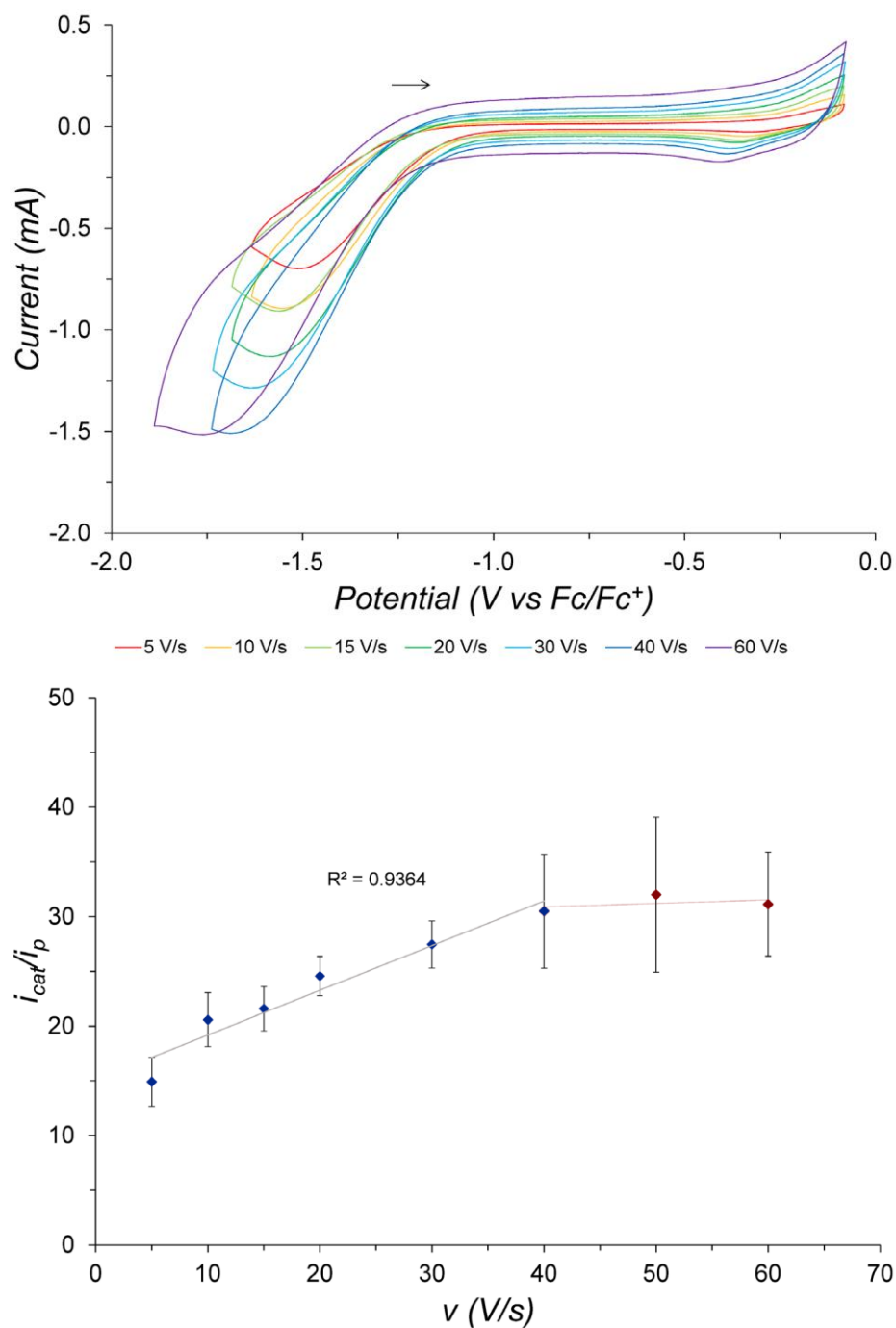


Figure 3.3.7. Catalytic CVs at different scan rates (0.1 M TBAP in acetonitrile, 0.25 mM Ni(DPMDA), 25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M AgNO₃ reference electrode, scan rate = 5—to 60 V/s) (top); plot of normalized catalytic current vs scan rate (bottom).

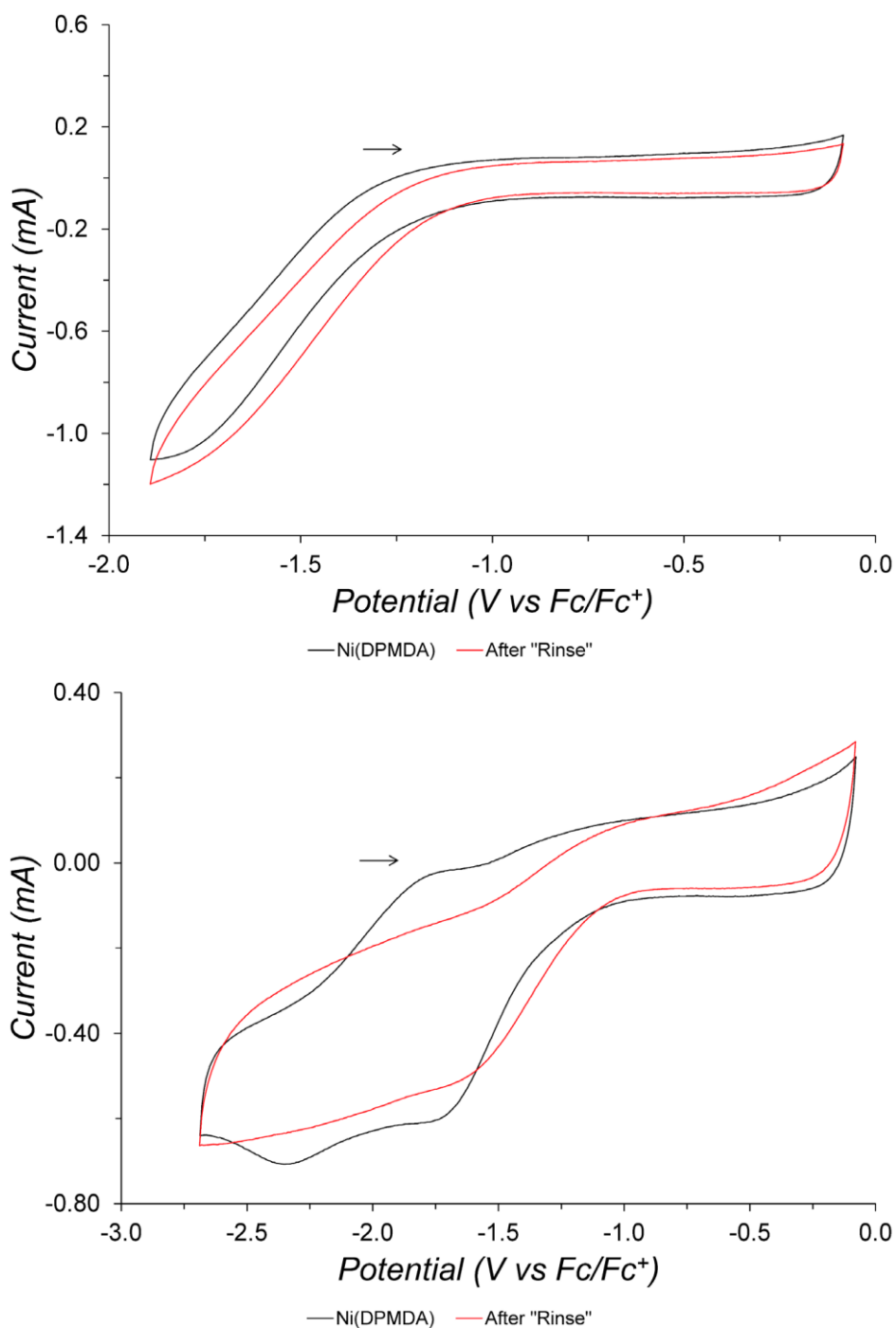


Figure 3.3.8. CVs of rinse test results using acetonitrile as the rinsing solvent (0.1 M TBAP in acetonitrile, 0.25 to 0 mM Ni(DPMDA), 7.5 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode scan rate = 40 V/s) (top); rinse test results with a wider scan window (bottom).

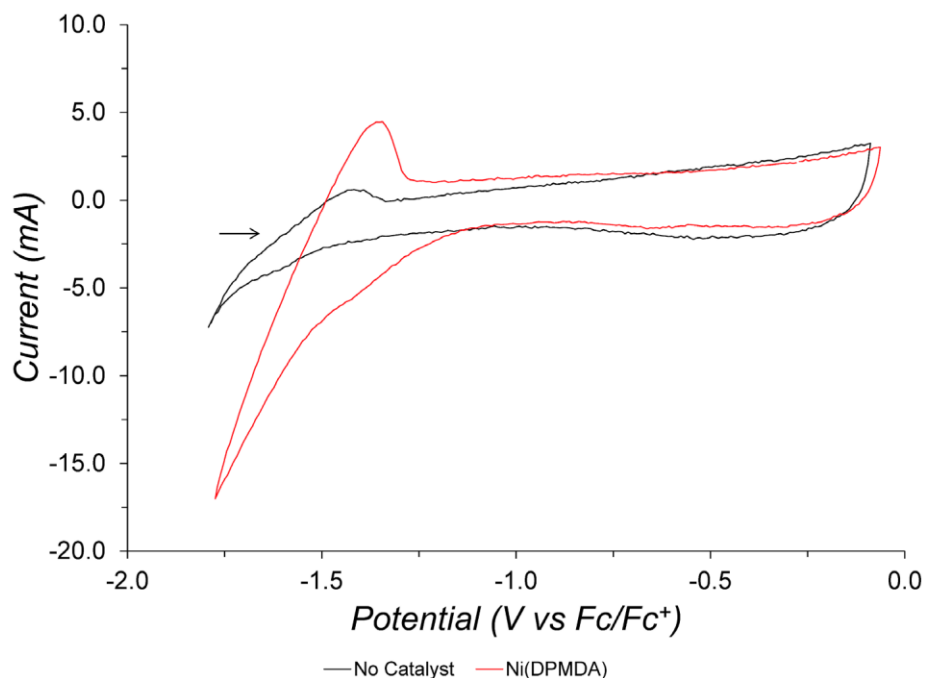


Figure 3.3.9. CVs of mercury pool test for hydrogen evolution using **Ni(DPMDA)** (0.1 M TBAP in acetonitrile, 0.25 or 0 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, mercury pool working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).

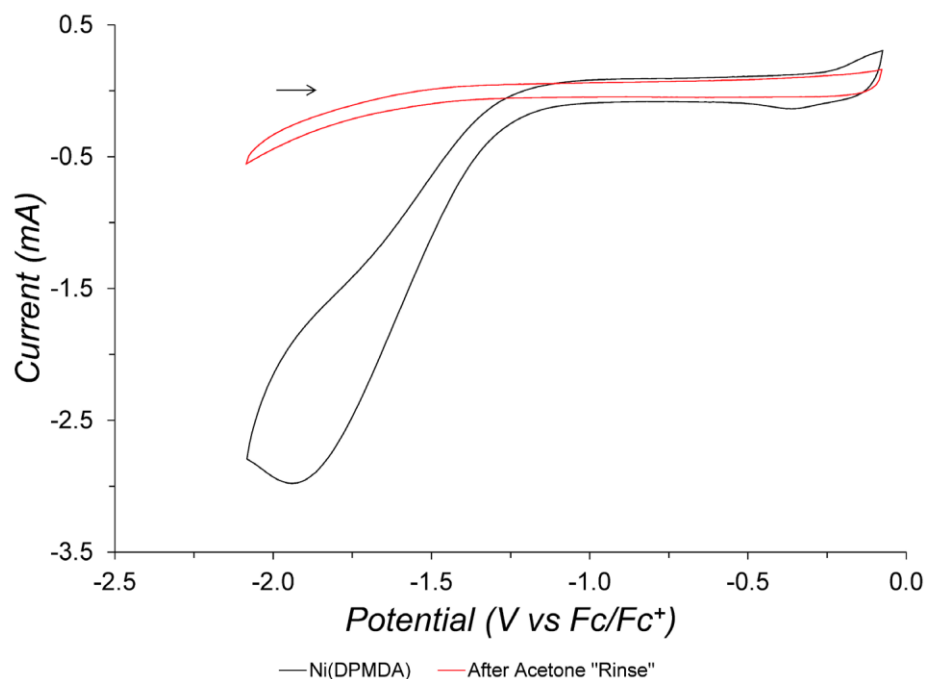


Figure 3.3.10. CVs of rinse test results using acetone as the rinsing solvent (0.1 M TBAP in acetonitrile, 0.25 to 0 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, glassy carbon

working electrode, graphite rod counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).

The electrochemical response of the adsorbed species were then investigated in the absence of acid. After performing CV with **Ni(DPMDA)** and anilinium tetrafluoroborate, the working electrode was rinsed with an acetonitrile/TBAP solution, and then used to record a CV in fresh electrolyte without acid. A single, stable redox couple at $E_{1/2} = -1.15$ V was observed, where the reduction peak corresponded with the onset of hydrogen evolution for the first catalytic wave (**Figure 3.3.11**). Notably, an additional redox feature that matched the more cathodic hydrogen evolution process was not evident. This result could potentially signal that a single heterogeneous species was catalyzing two different hydrogen evolution pathways depending on the electrochemical potential applied to the system. Based on literature precedent, this could occur through competing ligand- and metal-based reduction pathways.⁵⁶ Another possibility could be that two distinct heterogeneous electrocatalysts were being generated: one that displayed a redox couple at $E_{1/2} = -1.15$ V (corresponding to the more anodic process) and one where the redox features were not observed due to extremely strong electronic coupling, as described By Surendranath and co-workers,²⁶ between the active catalyst and the glassy carbon electrode (corresponding to the more cathodic catalytic wave). All of the results discussed above, however, suggested that supported nickel catalysts were being generated that could control the local environment at the electrode surface through the pendant amine groups (based on the clear pK_a dependence demonstrated by the systems which was linked to the pK_a of the aniline moieties in the secondary coordination sphere). In addition, because the current response of the second catalytic wave could not be accurately measured due to its proximity to the more anodic feature, further kinetic investigations focused solely on the catalytic process that occurred at more positive potentials, which could be rigorously measured.

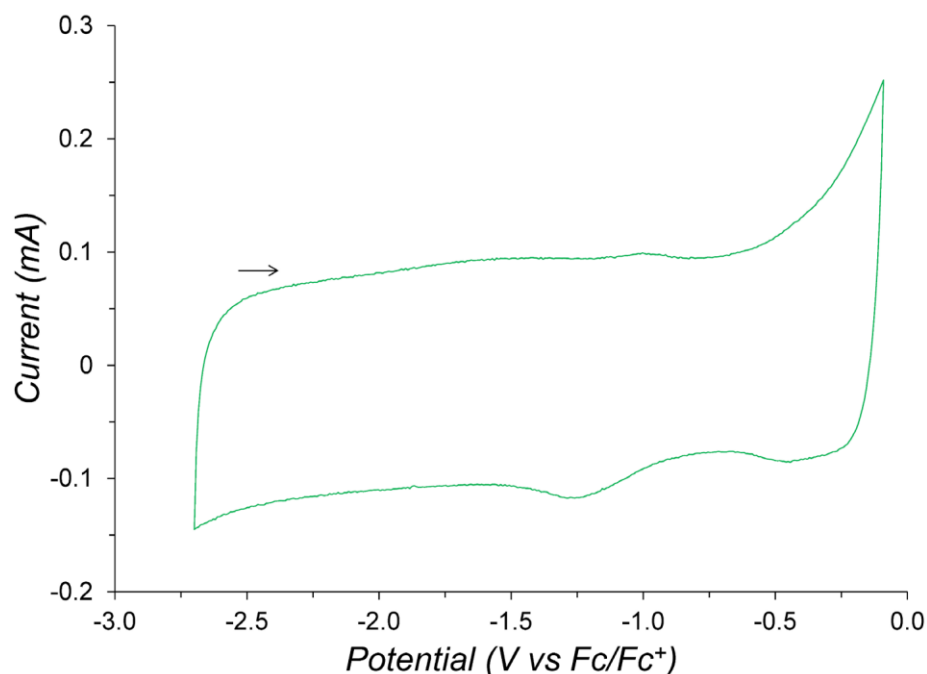


Figure 3.3.11. CV of the surface supported/adsorbed active catalytic species in the absence of acid (0.1 M TBAP in acetonitrile, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).

3.3.4 Kinetic Investigations

Initial studies examined the scan rate independence of the first catalytic wave, which was achieved at 40 V/s and above (**Figure 3.3.7**). Such high values needed for scan rate independence are often characteristic of fast reaction kinetics. The acid dependence of hydrogen evolution was also probed, and catalytic current was found to increase linearly with acid concentration (**Figure 3.3.12**). This continued until 325 equivalents of anilinium tetrafluoroborate were utilized (81.25 mM), after which a plateau was observed (**Figure 3.3.12**). At the acid independence point, the heterogeneous **Ni(DPMDA)** catalyst operated at an overpotential of 900 ± 30 mV (see Experimental for calculations).^{63, 64} Although somewhat high (especially when compared to Pt-based catalysts), this overpotential is similar to known nickel-based hydrogen production catalysts (around 0.70 V),^{12, 22} and was also achieved using much less acidic proton sources. The first order dependence on acid concentration also gave some insight into the mechanism of action. For heterogeneous hydrogen evolution catalysts, this is indicative of a rate-determining Volmer or Heyrovsky step.⁶⁵⁻⁶⁷ Lastly, the catalyst dependence of the supported species was probed, and at very low catalyst concentrations (3.91 μ M to 15.6 μ M

Ni(DPMDA)) a linear correlation was seen with respect to peak current (**Figure 3.3.13**). Upon increasing catalyst concentration to 31.25 μM , however, a plateau was observed, indicating a catalyst independence point (**Figure 3.3.13**). This result was completely consistent with a supported catalytic species affecting hydrogen evolution, as it would be expected that the electrode surface would become saturated at a certain point, after which, increasing catalyst concentration would not enhance hydrogen evolution.

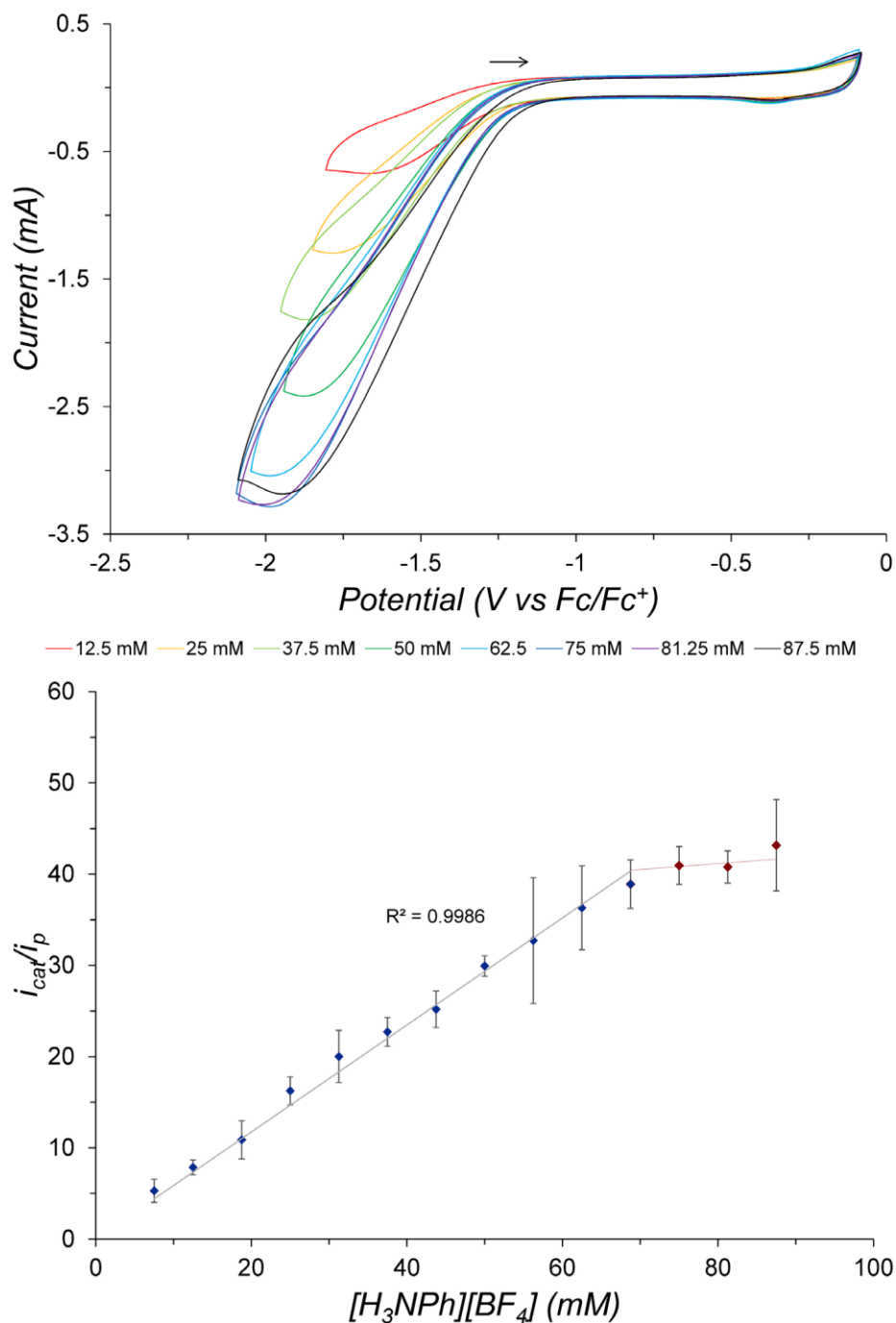


Figure 3.3.12. Catalytic CVs with increasing acid concentration (0.1 M TBAP in acetonitrile, 0.25 mM $Ni(DPMDA)$, 7.5 to 87.5 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M $AgNO_3$ reference electrode, scan rate = 40 V/s (top); plot of normalized catalytic current vs acid concentration (bottom).

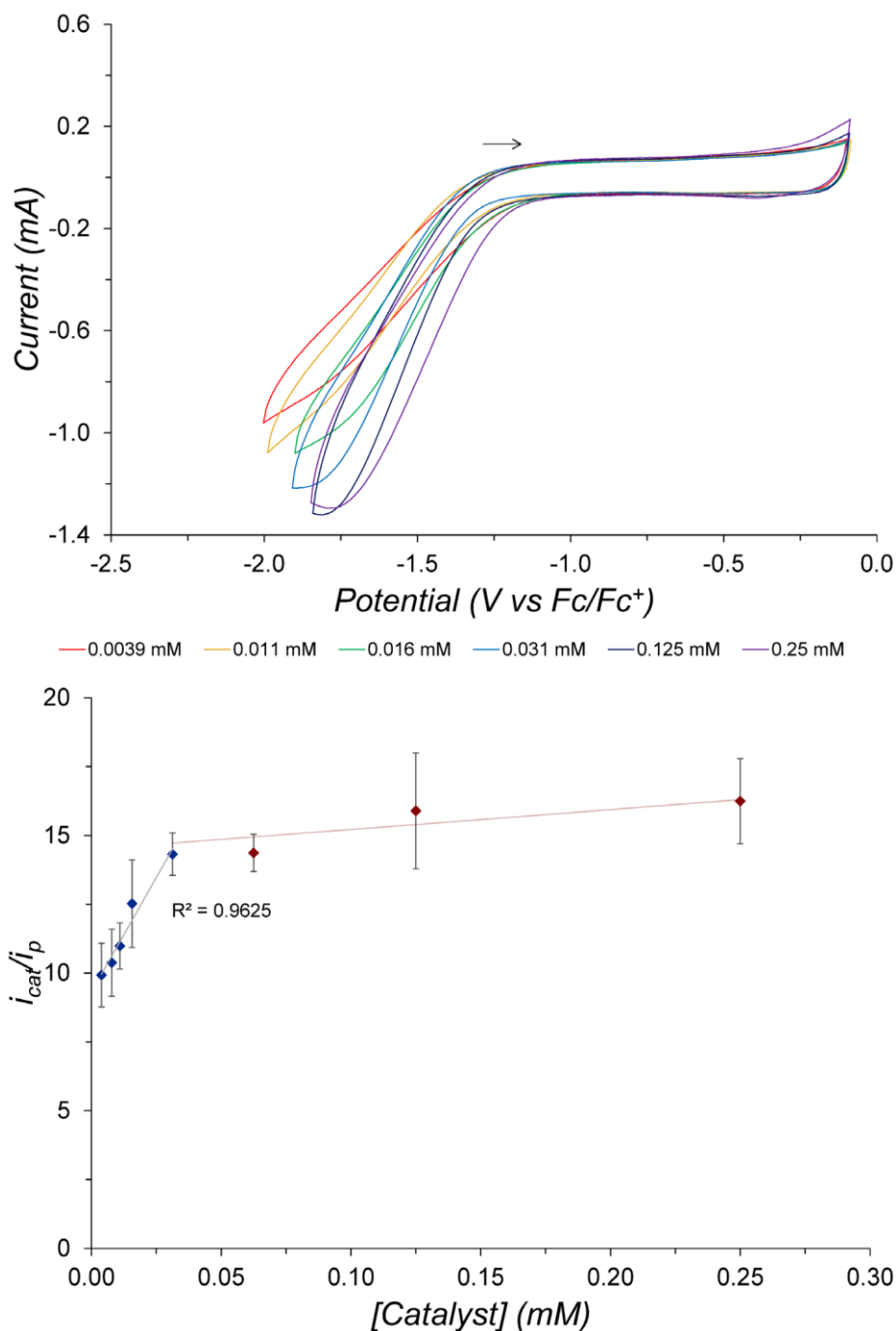


Figure 3.3.13. Catalytic CVs with increasing concentration of **Ni(DPMDA)** (0.1 M TBAP in acetonitrile, 0.0039 mM to 0.25 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M AgNO₃ reference electrode, scan rate = 40 V/s) (top); plot of normalized catalytic current vs concentration of **Ni(DPMDA)** (bottom).

It should be noted that during hydrogen evolution using the supported **Ni(DPMDA)** catalyst, initial CV scans showed very high current values, which steadily decreased with additional cycles (approximately 20–30) before finally stabilizing (**Figure 3.3.14**). Moreover, if the reaction mixture was stirred, this behaviour was recovered (**Figure 3.3.15**). This could suggest that the catalyst depleted the available acid at the electrode surface before becoming a diffusion controlled process (transport of anilinium tetrafluoroborate from bulk solution to the glassy carbon support). Another possibility could be that oversaturation with hydrogen gas inhibited mass transport and reduced effective surface area during catalysis (bubble formation on the electrode surface was observed). Therefore, for increased reproducibility, all of the kinetic results discussed above report values for the stabilized catalytic current. In addition, once conditions were fully optimized (Figure 12), turnover frequency (TOF) was determined using stabilized peak currents (unless stated otherwise).

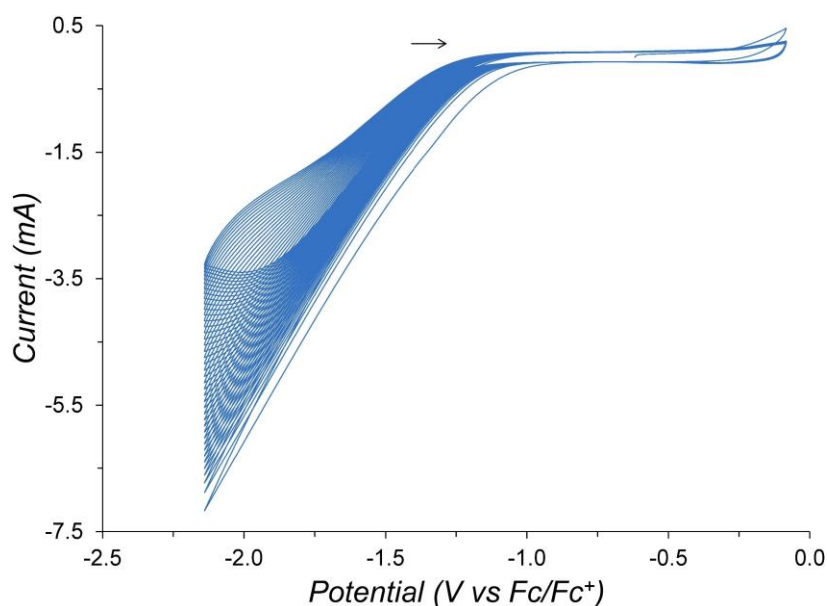
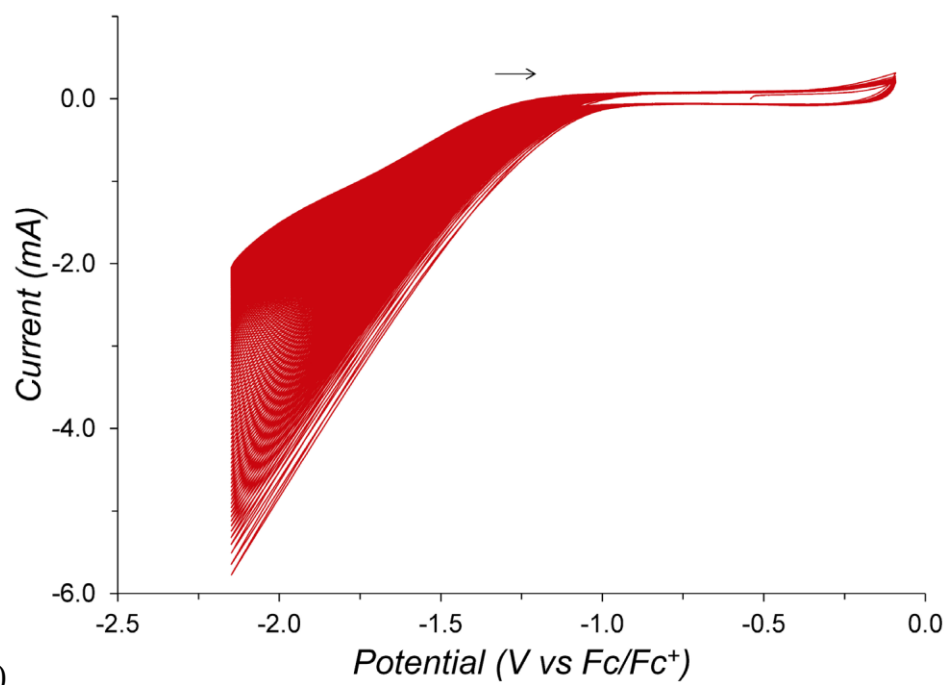
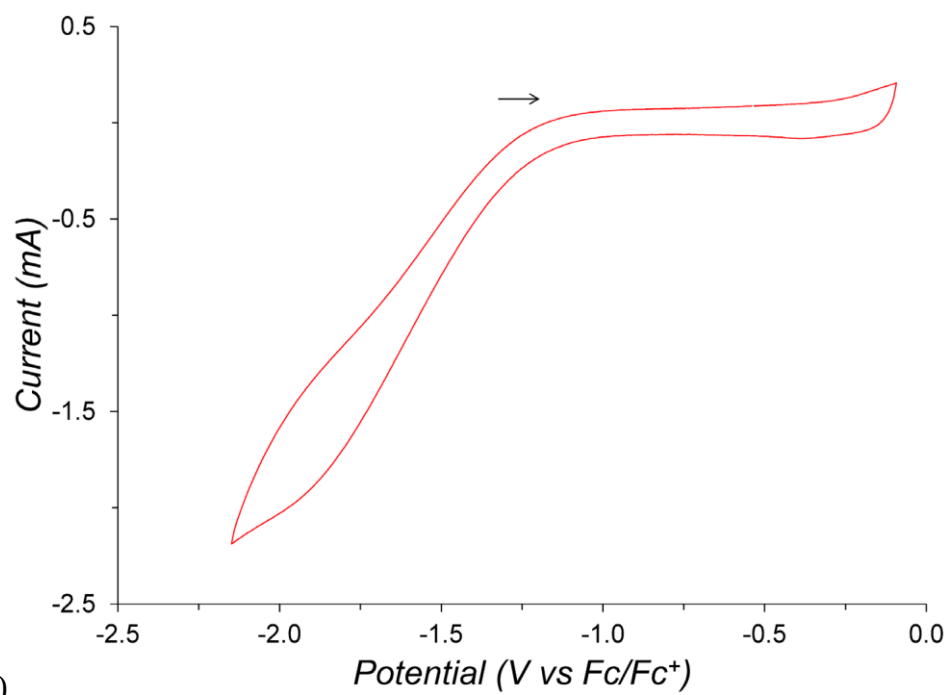


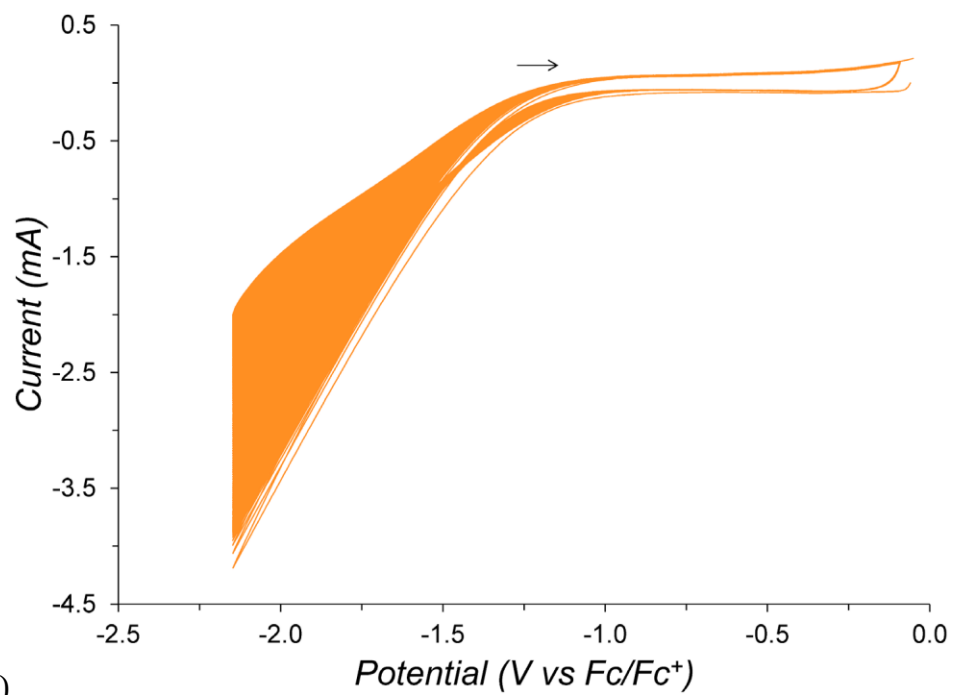
Figure 3.3.14. CV of the supported **Ni(DPMDA)** catalyst under optimized conditions showing all of the scan cycles (0.1 M TBAP, 0.25 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).



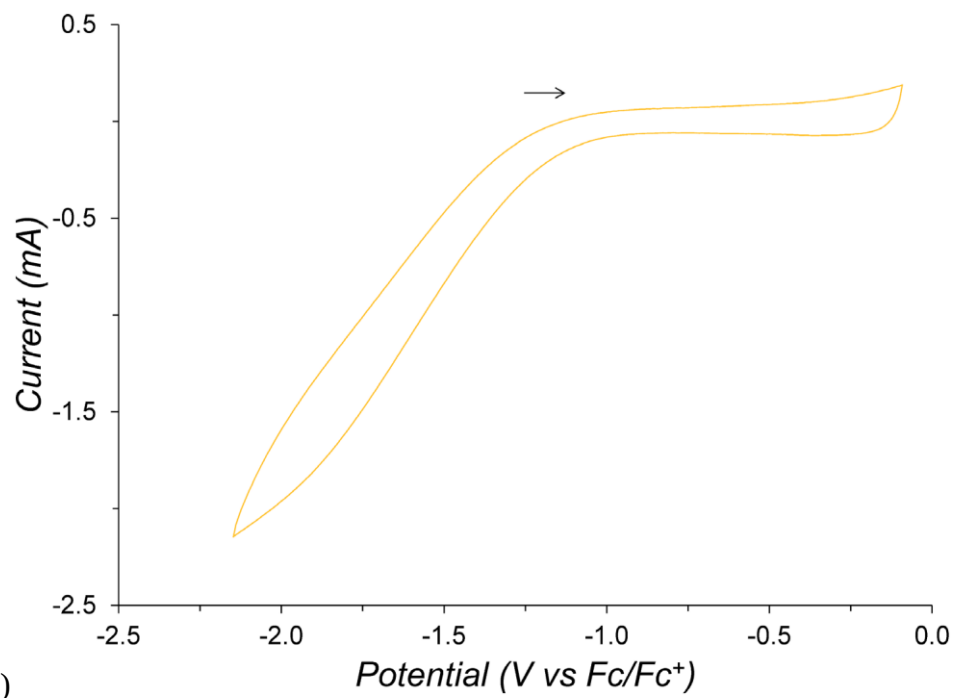
a)



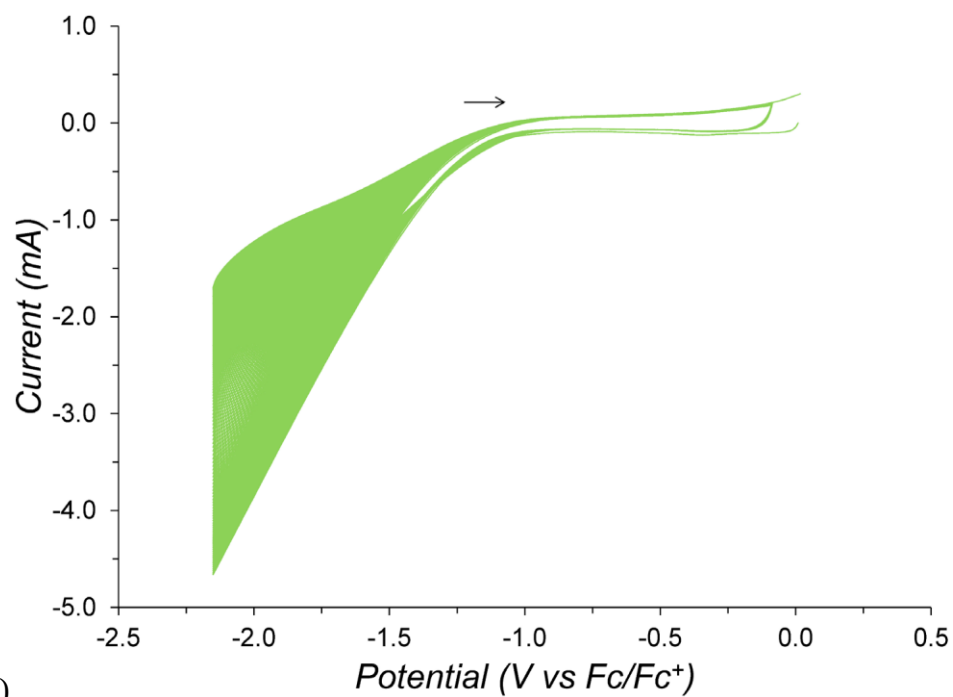
b)



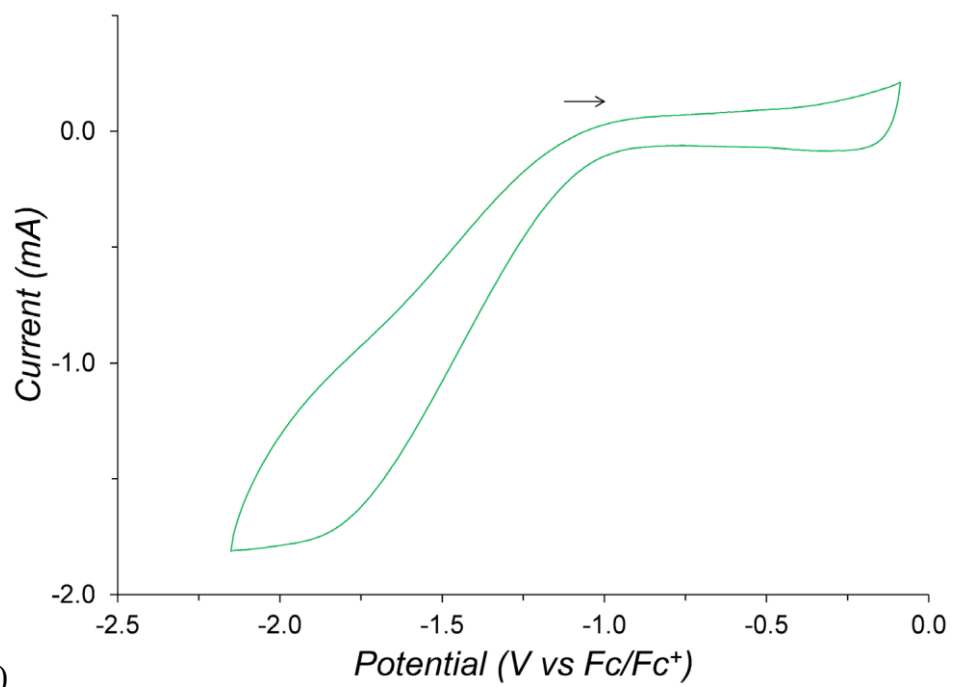
c)



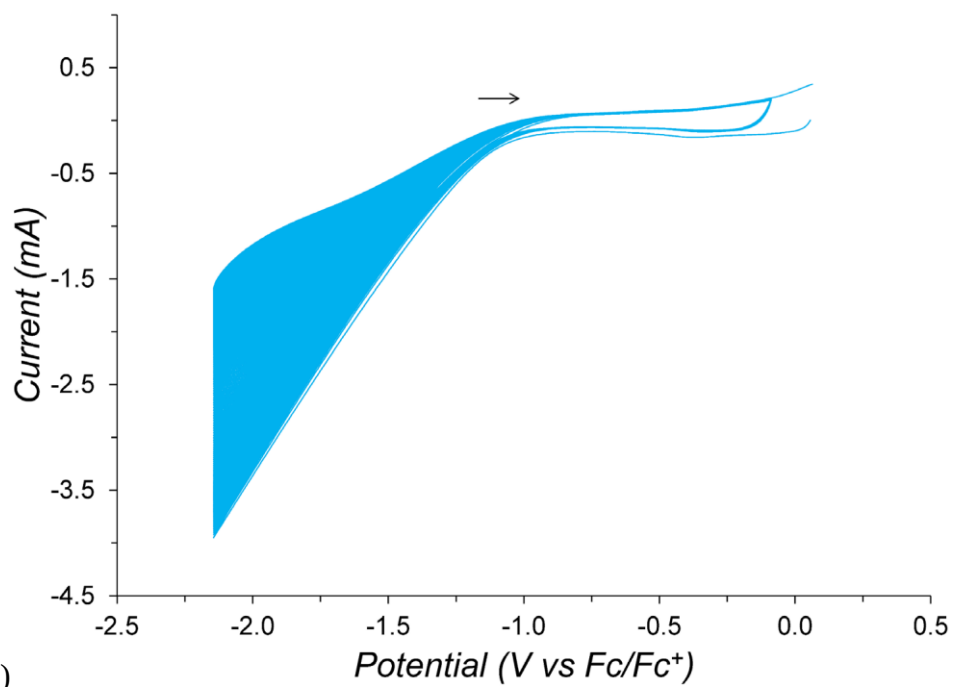
d)



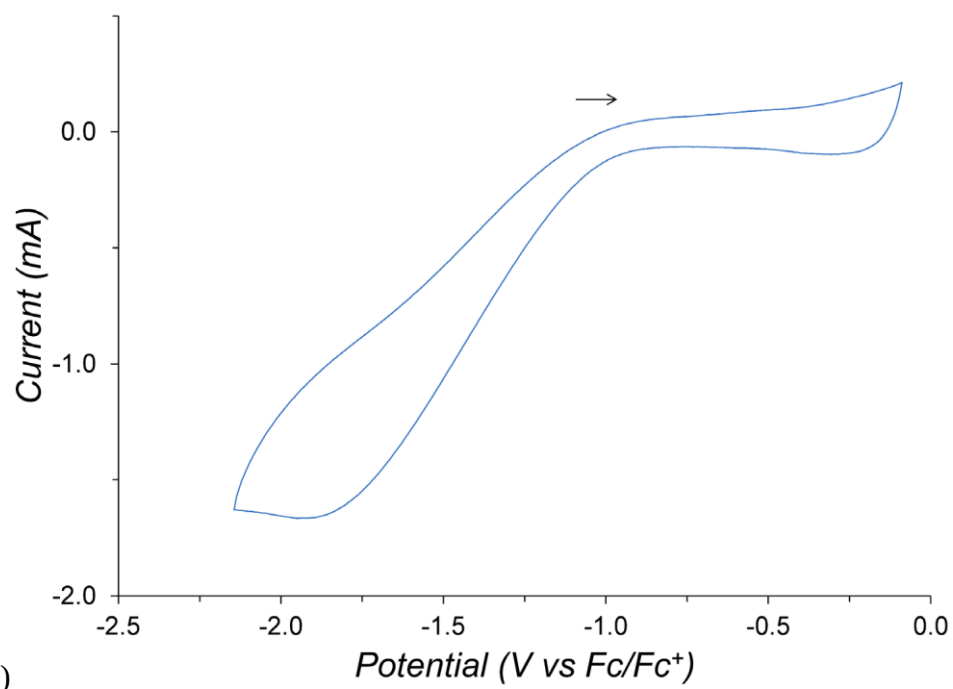
e)



f)



g)



h)

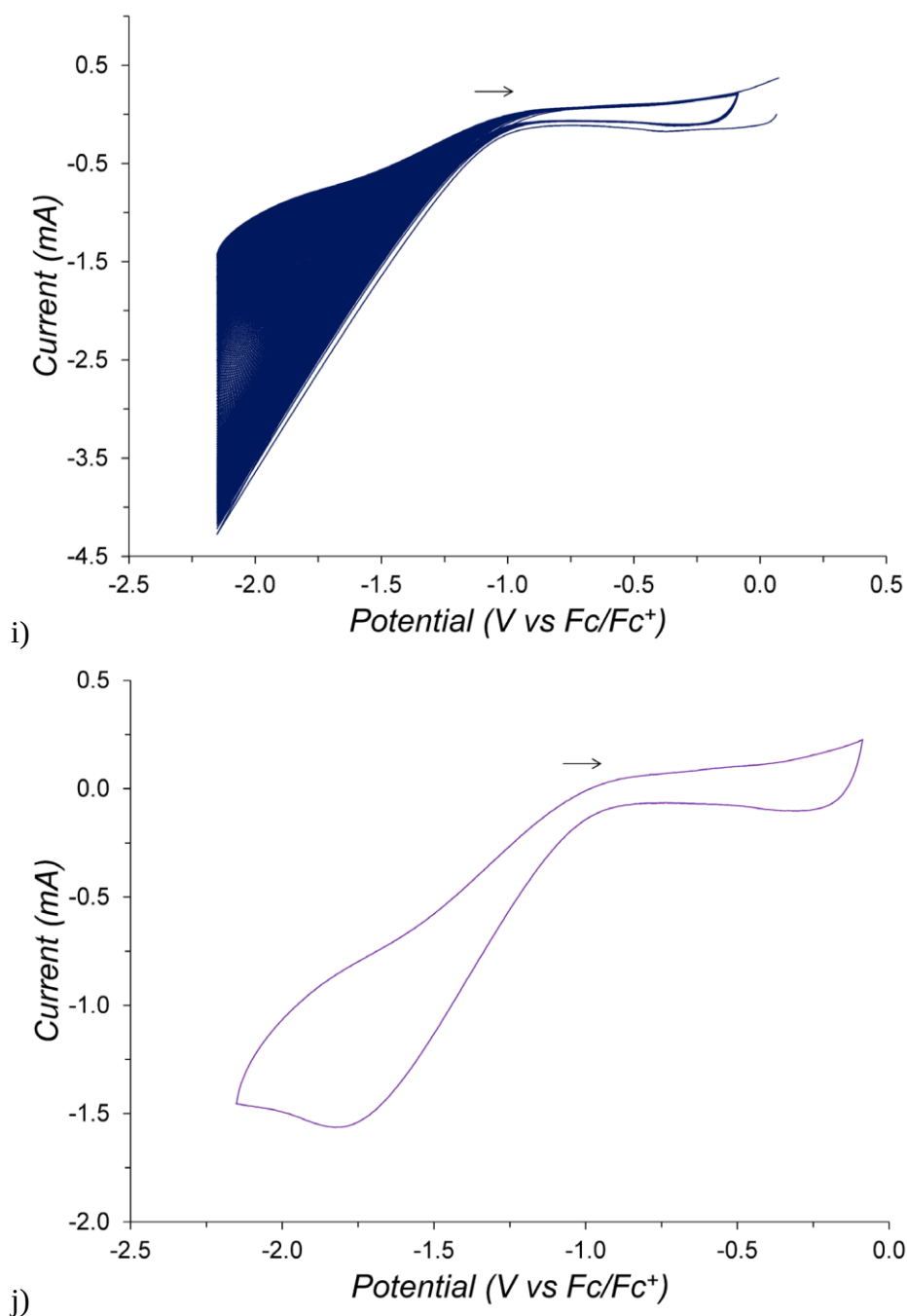


Figure 3.3.15. a); c); e); g); and i) Consecutive 300 scan CVs of hydrogen evolution (with stirring in between experiments) using the surface supported/adsorbed active catalytic species (0.1 M TBAP, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s); b); d); f); h); and j) representative CV traces of the stabilized catalytic current for each 300 scan experiment.

To calculate TOF,^{68, 69} the surface area coverage of the adsorbed species was first determined using the following equation:

$$i_p = \frac{n^2 F^2}{4RT} v \Gamma^*$$

where i_p , n , F , R , T , v , and Γ^* are the peak current of the adsorbed species in the absence of acid, the number of electrons transferred (estimated to be 1 for the observed redox couple, Figure S10), Faraday's constant, the ideal gas constant, the temperature, the scan rate, and surface area coverage of the electrode, respectively. This methodology for counting active centers assumes that the **Ni(DPMDA)** catalyst adsorbs in a monolayer and that the electrode surface is relatively homogeneous without any significant defects or cavities. In addition, this calculation assumes that the active catalytic species does not exhibit the extremely strong electronic coupling described Surendranath and co-workers,²⁶ and as such, that surface coverage can be measured through the peak current of the redox response in the absence of acid. Lastly, this methodology also assumes that all of the redox active sites are catalytically competent during the reaction, and are not inhibited by things like gas bubble formation. With this value in hand, the TOF was calculated using the following equation:

$$TOF = \frac{j}{nF\Gamma^*}$$

where j and n are the catalytic current density and the number of electrons transferred (2 for hydrogen evolution). A first-order dependence on **Ni(DPMDA)** surface coverage was anticipated based on the kinetic data discussed above, and it was also assumed that all of the surface confined species were catalytically active. Using this method,^{68, 69} the TOF was calculated to be $14,900 \pm 2700 \text{ s}^{-1}$ or $211,000 \pm 40,000 \text{ s}^{-1} \text{ cm}^{-2}$. These remarkably high reactions rates compared very favourably with known supported nickel diphosphacycloheptane catalysts, with values 3 to 4 orders of magnitude larger.¹⁸⁻²³ Furthermore, when the heterogeneous **Ni(DPMDA)** catalyst is compared with some of the fastest reported platinum nanoparticles (TOFs of 1500 to 9000 s^{-1}),⁷⁰ it remains more than competitive. Lastly, even higher TOFs can be calculated for the **Ni(DPMDA)** system if the stabilized peak current is not utilized ($25,900 \pm 5000 \text{ s}^{-1}$ or $366,000 \pm 71,000 \text{ s}^{-1} \text{ cm}^{-2}$ for the second cycle under optimized conditions, Figure 11). For sample calculations for Γ^* and TOF, see the Supporting Information.

Additional control experiments were performed to rule out homoconjugation effects and potential platinum leaching from the counter electrode.⁶³ No significant changes in peak current or location were seen when a large excess of 1 : 1 aniline:anilinium tetrafluoroborate buffer

solution was employed (**Figure 3.3.16**), nor were any changes detected when a graphite counter electrode was utilized in a clean glass vessel (**Figure 3.3.17**). The durability of the supported **Ni(DPMDA)** catalyst was also investigated. Initially, it was thought that these systems would be prone to leaching, especially considering that surface interactions were thought to be dominated by π - π interactions. Surprisingly, despite not being covalently linked to the electrode surface, the heterogeneous active species was much more durable than originally anticipated, remaining active for hydrogen evolution for a minimum of 1500 scans without any **Ni(DPMDA)** in solution (**Figure 3.3.15**). While a slight decrease in stabilized peak current was observed with consecutive experiments, it is believed that this can be attributed to consumption of acid, rather than dissociation/solvation of the adsorbed species over time. Moreover, given that the stabilized current response of the heterogeneous catalyst remained relatively steady over 1500 scans, this suggested that the catalyst structure was not changing/degrading on the electrode surface. The stability of the heterogeneous electrocatalyst was also supported by controlled potential electrolysis experiments. A faradaic efficiency of $96.8 \pm 0.9 \%$ was achieved for the nickel system, and a stable current response was seen (**Figure 3.3.18**) after an initial rapid decrease in current, which was consistent with the behaviour seen in the CV experiments (**Figure 3.3.14**). A linear increase in charge transferred versus time was also observed (**Figure 3.3.18**), which supported that the catalyst structure was not changing. Furthermore, another highly desirable characteristic exhibited by the supported **Ni(DPMDA)** catalyst was air- and moisture stability, with little decrease in stabilized peak current after exposure to ambient atmosphere for 15 min. (**Figure 3.3.19**). Notably, the calixpyrrole system showed much higher durability than the diphosphacycloheptane catalysts reported by Bullock et al.²² and Natali et al.,²³ which showed significant deactivation under acidic conditions. The durability of the **Ni(DPMDA)** catalyst is not unprecedented, however, as Artero and co-workers have also reported a robust molecular hydrogen evolution catalyst grafted onto carbon nanotubes using π - π stacking.²¹

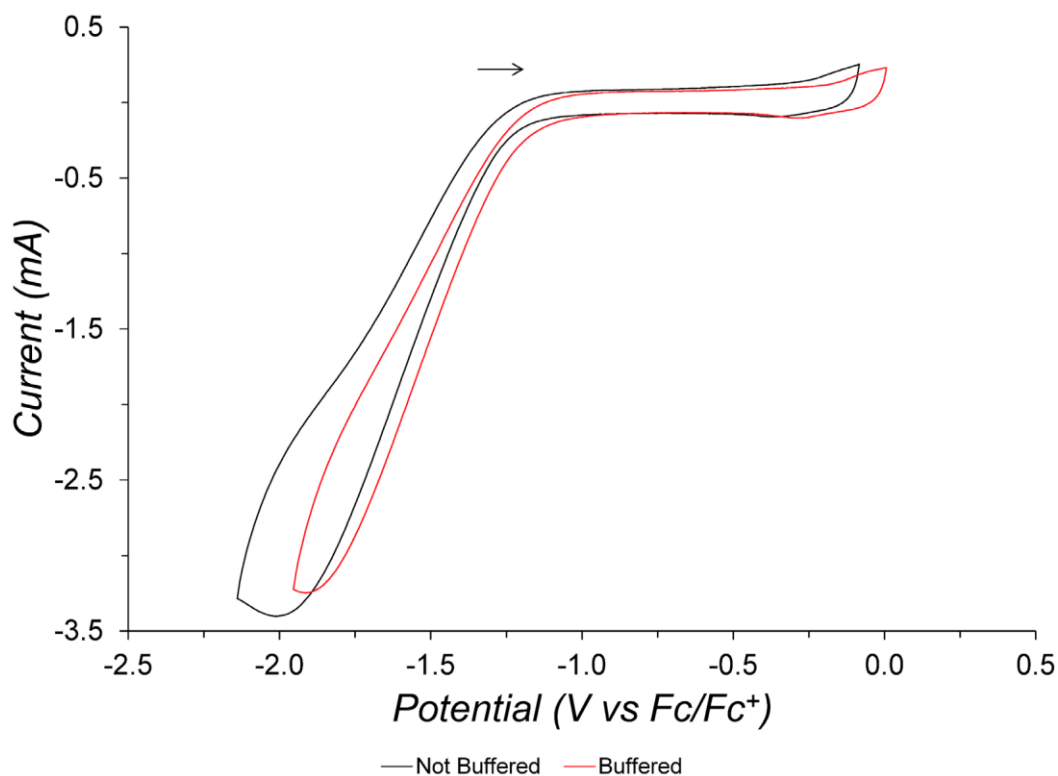


Figure 3.3.16. CVs of hydrogen evolution in a non-buffered solution, as well as a buffered solution (0.1 M TBAP, 0.25 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate or 8.25 mM anilinium tetrafluoroborate and 81.25 mM aniline, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).

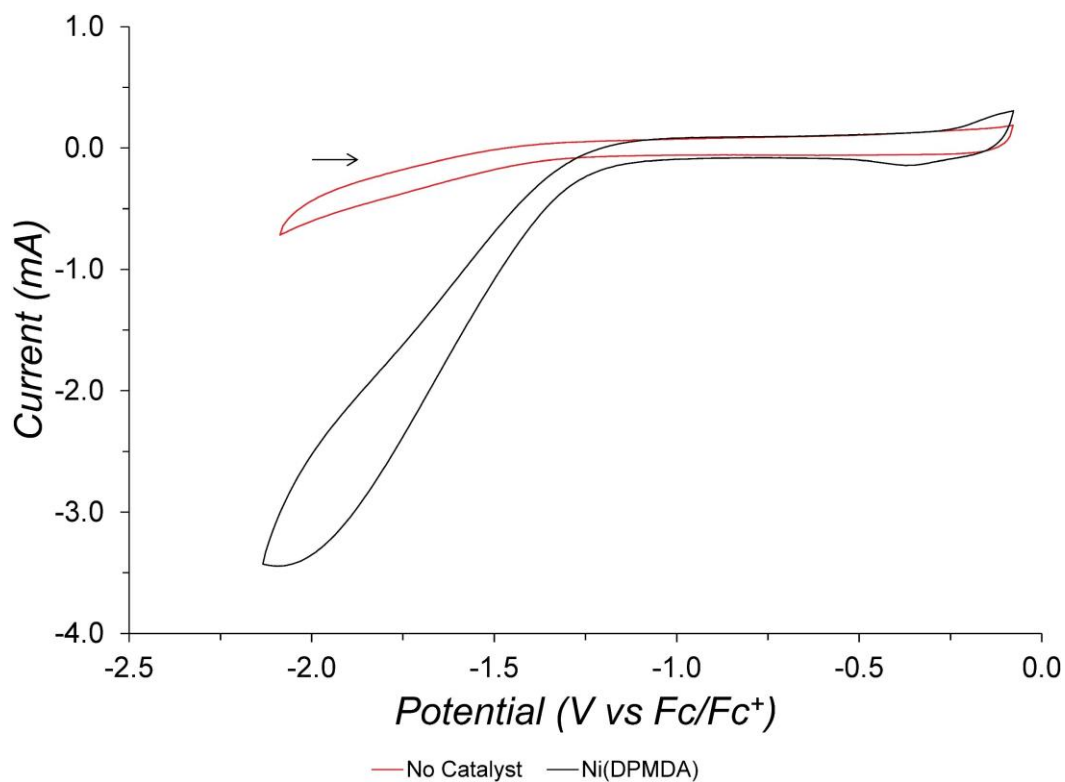


Figure 3.3.17. A representative CV trace of the stabilized catalytic current along with a control experiment with no **Ni(DPMDA)** in solution (0.1 M TBAP, 0 or 0.25 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).

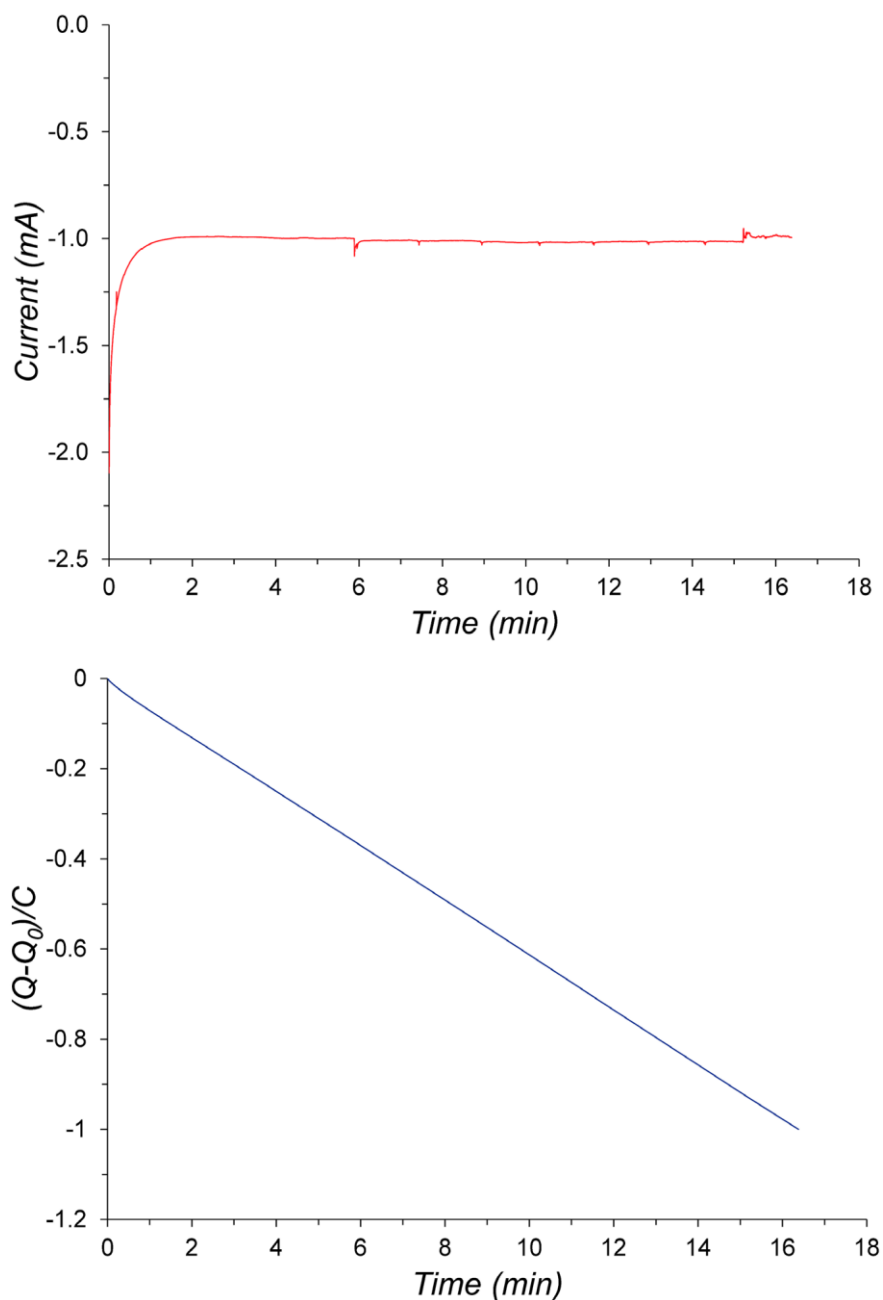


Figure 3.3.18. A representative controlled potential electrolysis experiment in acetonitrile (0.1 M TBAP, 0.25 mM **Ni(DPMDA)**, and 81.25 mM anilinium tetrafluoroborate with a 6 mm glassy carbon rod working electrode, 0.01 M Ag/AgNO₃ reference electrode; 0.1 M TBAP, 81.25 mM ferrocene with a 6 mm graphite counter electrode; 1 C of charge passed, potential held at -2.02 V vs Fc/Fc⁺) showing: current vs time (top); normalized charge transferred vs time (bottom).

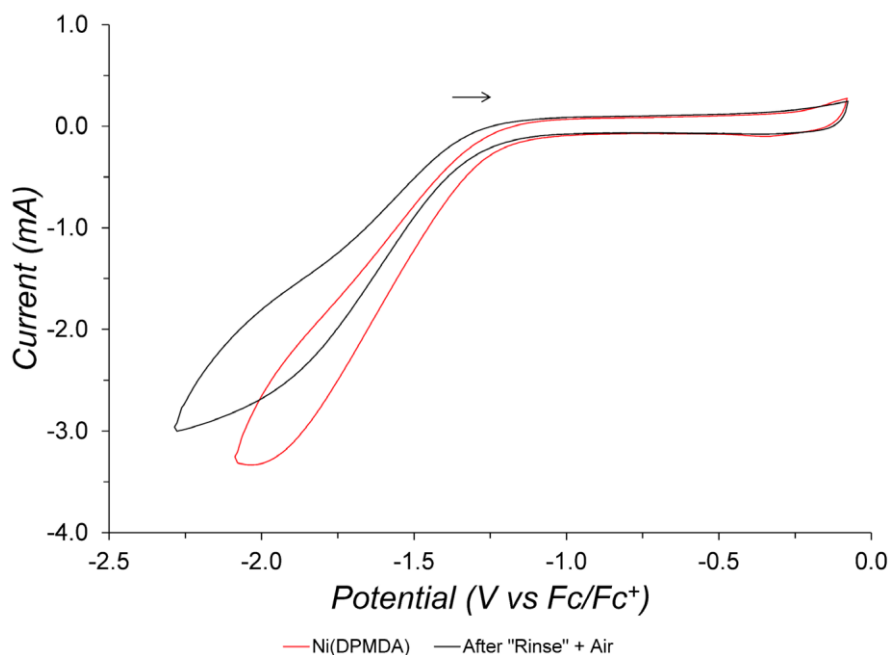


Figure 3.3.19. CVs of air- and moisture-stability tests using acetonitrile as the rinsing solvent (0.1 M TBAP in acetonitrile, 0.25 to 0 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).

3.3.5 Mechanistic Investigations

In order to elucidate more details about the mechanism of hydrogen production using **Ni(DPMDA)**, Tafel plots were constructed using linear sweep voltammetry (LSV). Initially, a scan rate of 40 V/s was utilized and the Tafel slopes were found to be very large; 333 mV dec⁻¹ and 569 mV dec⁻¹ at catalytic onset and high current densities, respectively (**Figure 3.3.20**). It has been reported, however, that using fast scan rates in LSV Tafel analysis can impart greater double-layer charging.⁷¹ Therefore, a scan rate of 5 mV/s was also explored, but the observed Tafel slopes were still quite large: 149 mV dec⁻¹ and 232 mV dec⁻¹ at catalytic onset and high current densities, respectively (**Figure 3.3.21**). Regardless of the scan rates utilized, the Tafel slopes did not conform to known values of 120 mV dec⁻¹, 40 mV dec⁻¹, or 30 mV dec⁻¹, which are characteristic of a rate limiting Volmer, Heyrovsky, or Tafel step, respectively.^{72, 73} While the observed Tafel slopes for the supported **Ni(DPMDA)** catalyst did not exactly align with the expected 120 mV dec⁻¹ value for a Volmer-like step, previous studies of

hydrogen evolution with a molecular heterogeneous electrocatalyst (where proton discharge was identified as being rate-determining) have also reported Tafel slopes in excess of 120 mV dec^{-1} , with values ranging from 160 mV dec^{-1} in acetonitrile to 220 mV dec^{-1} in water.^{67, 74} This, along with the kinetic measurements showing a first order dependence on acid concentration for the **Ni(DPMDA)** system suggested rate-determining nickel-hydride formation. To gain further insight into the catalytic mechanism, kinetic isotope effect (KIE) measurements were also carried out using anilinium- d_3 tetrafluoroborate (**Figure 3.3.22**). The H/D KIE value was found to be 5.7 ± 0.7 , which showed that hydrogen/deuterium was involved in bond formation during the rate-determining step. Furthermore, such large KIE values are consistent with a PCET mechanism.⁷⁵ Together, the kinetic data are consistent with rate-limiting PCET and nickel-hydride formation (a Volmer-like step).^{74, 76} It should be noted, though, that proton transfer to the ligand would also be consistent with these results, and cannot be ruled out at this time.

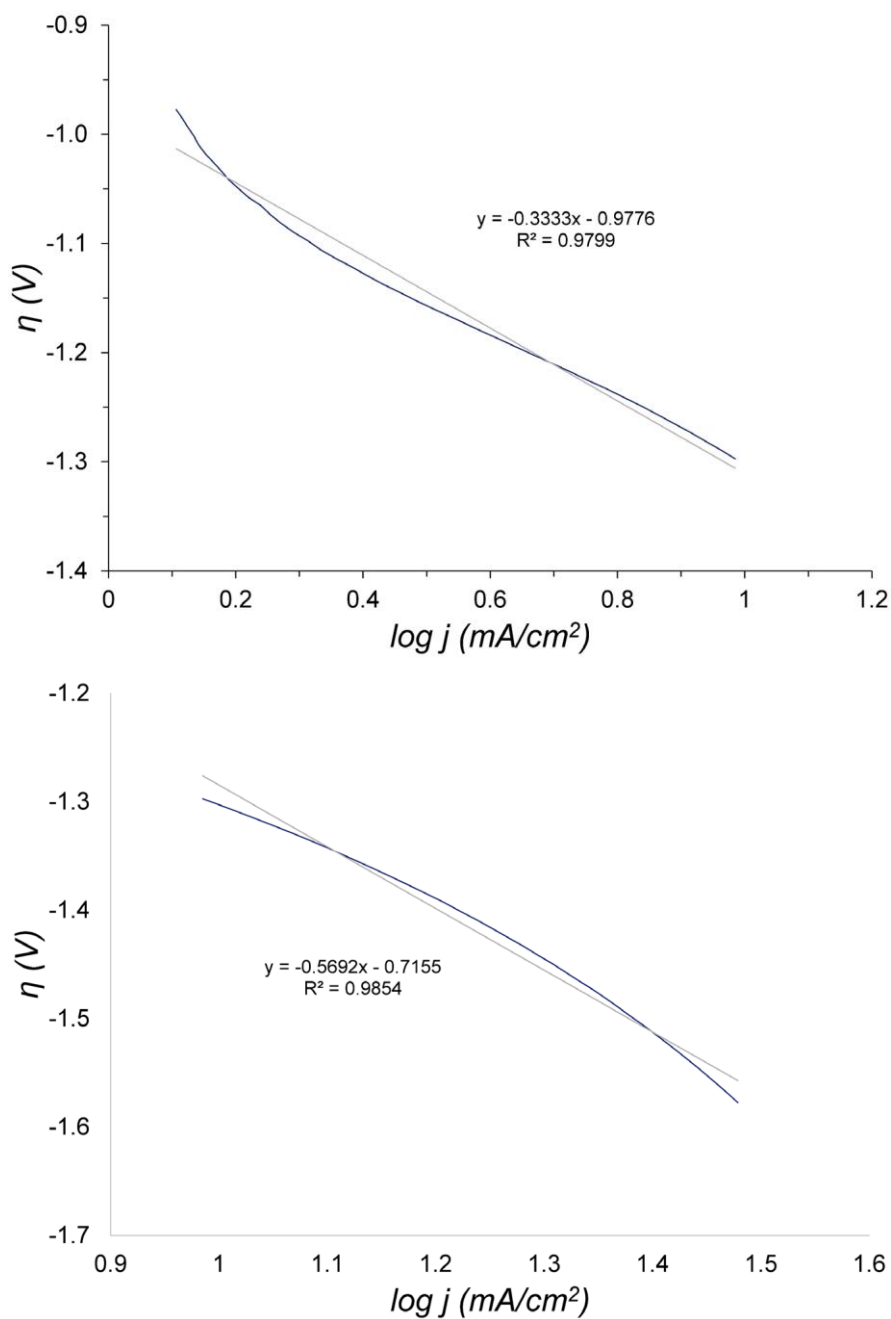


Figure 3.3.20. Tafel plot and slope from a linear sweep voltammogram (LSV) of hydrogen evolution at low current densities and high scan rate (0.1 M TBAP, .25 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s) (top); Tafel plot and slope from a LSV of hydrogen evolution at high current densities and high scan rate.

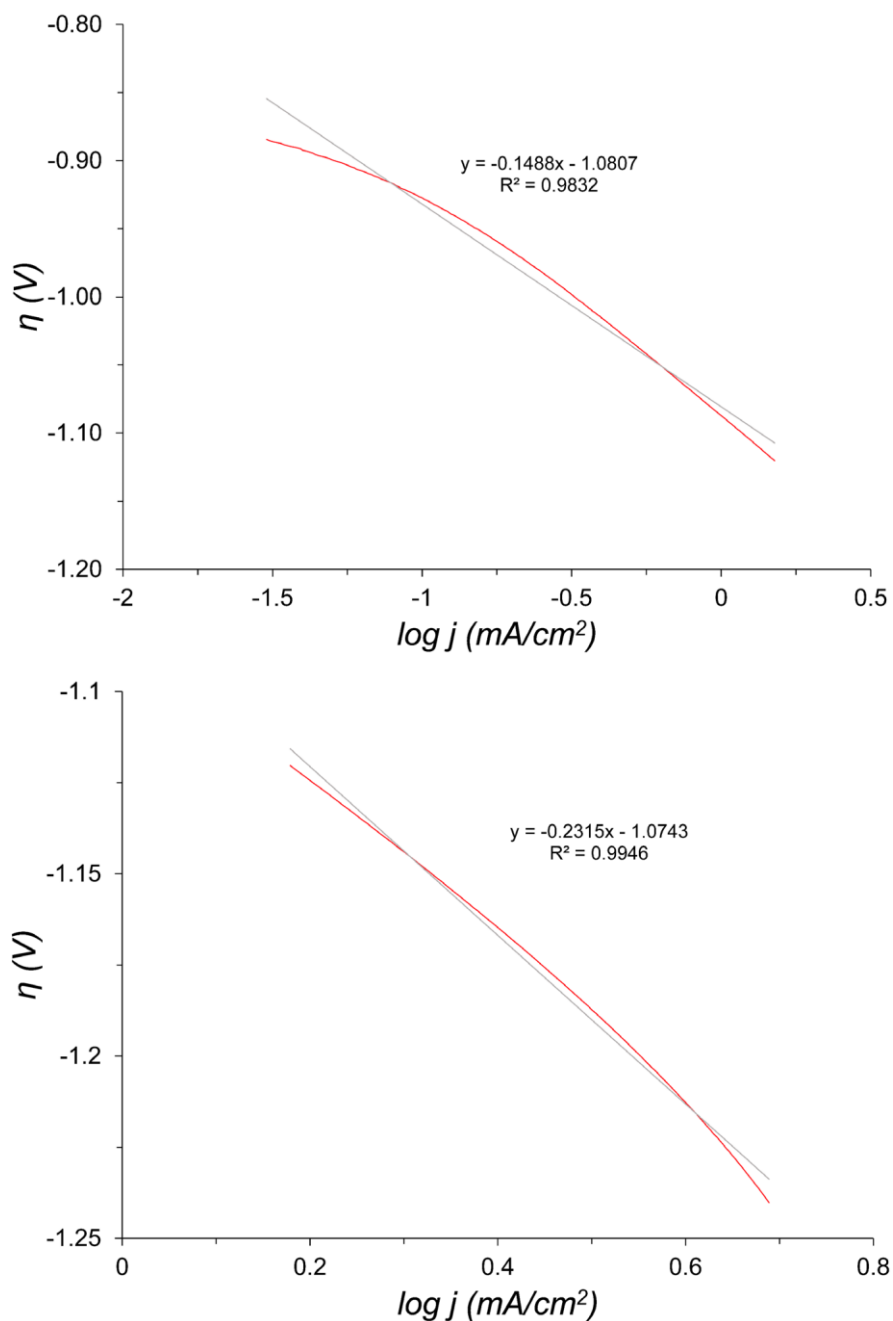


Figure 3.3.21. Tafel plot and slope from a linear sweep voltammogram (LSV) of hydrogen evolution at low current densities and low scan rate (0.1 M TBAP, .25 mM **Ni(DPMDA)**, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 5 mV/s) (top); Tafel plot and slope from a LSV of hydrogen evolution at high current densities and low scan rate.

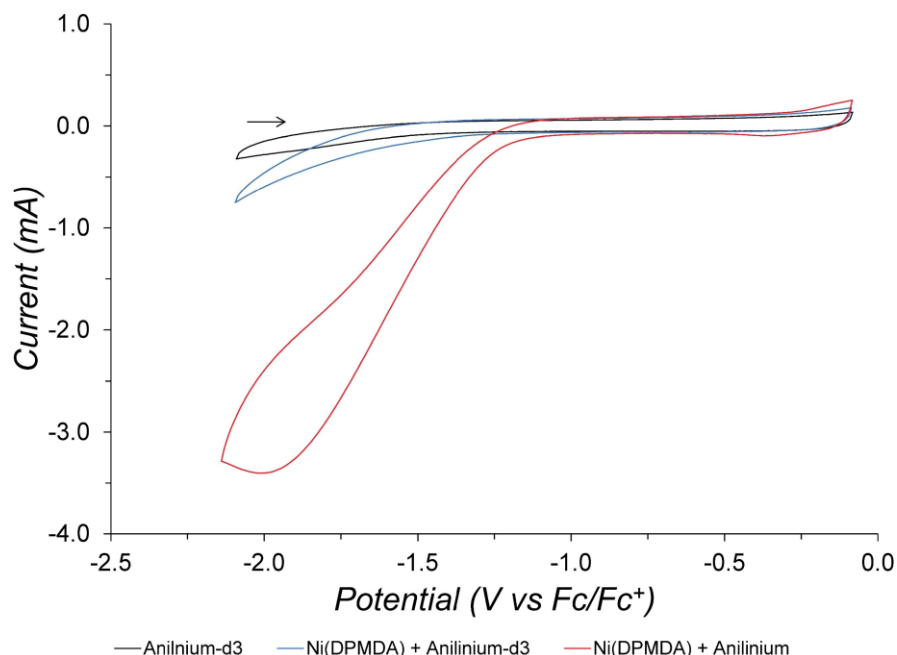


Figure 3.3.22. CVs of H/D KIE experiments (0.1 M TBAP, 0 or 0.25 mM **Ni(DPMDA)**, 81.25 mM anilinium or anilinium- d_3 tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s).

Additional CV studies were carried out to interrogate the nature of the active catalytic species. Glassy carbon working electrodes were submerged in acidic media in the presence of **Ni(DPMDA)**, and then scanned to various negative potentials. The electrodes were subsequently rinsed with acetonitrile, and hydrogen evolution was carried out in the absence of calixpyrrole complex in solution. It was found that a potential of around -2.6 V was needed to “turn on” hydrogen evolution and reproduce the stabilized catalytic current discussed above in the kinetic investigations (**Figure 3.3.23**). This negative potential corresponded to the second quasi-reversible redox couple for the parent **Ni(DPMDA)** complex, which was tentatively assigned to $\text{Ni}^{\text{I}}/\text{Ni}^0$, and suggests that the active species is a reduced form of the starting nickel calixpyrrole.

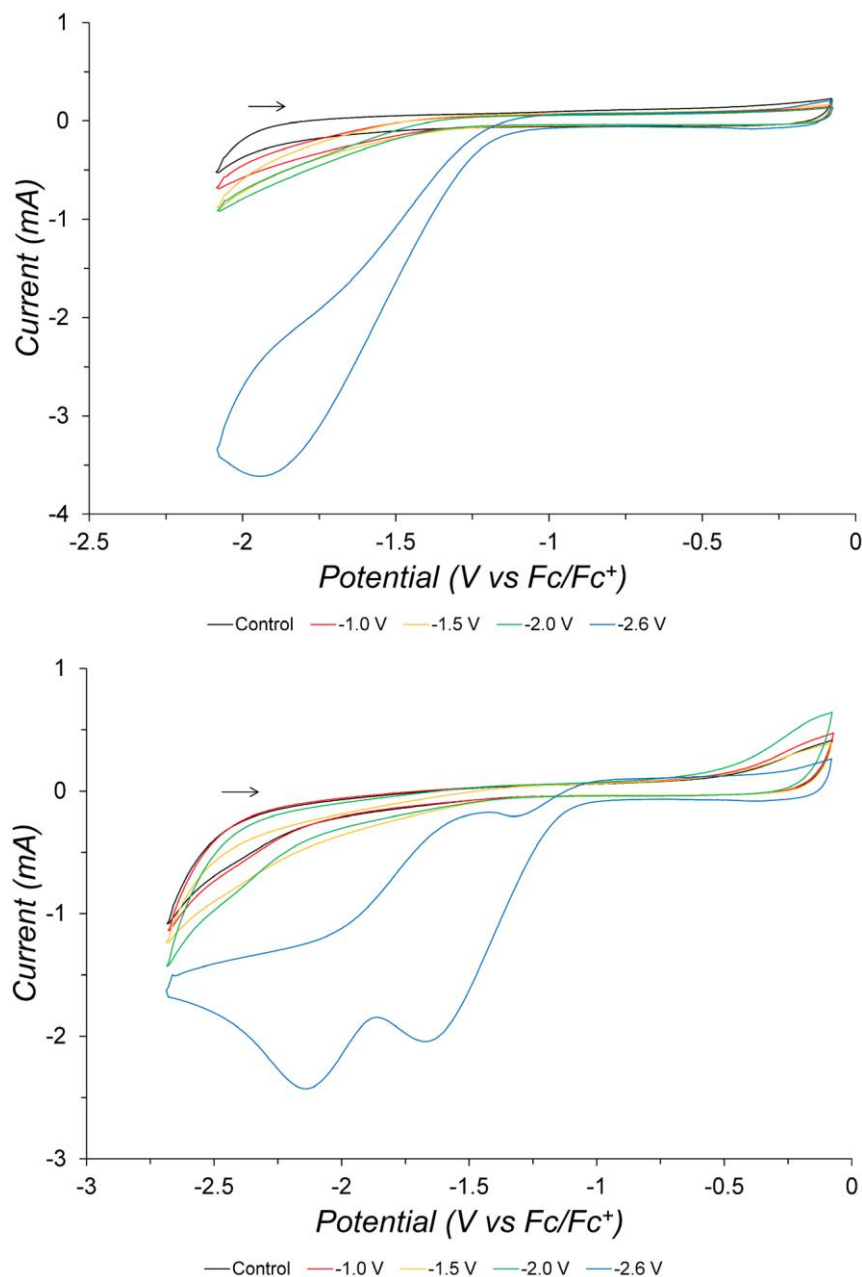


Figure 3.3.23. CVs of hydrogen evolution (0.1 M TBAP in acetonitrile, 81.25 mM anilinium tetrafluoroborate, glassy carbon working electrode, graphite rod counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 40 V/s) using pre-treated glassy carbon working electrodes (sanning to various negative potentials in 0.1 M TBAP, 0.25 mM Ni(DPMDA), 81.25 mM anilinium tetrafluoroborate, scan rate = 40 V/s, and then rinsing with acetonitrile with: narrow scanning window (top); a wider scanning window (bottom).

Preliminary density functional theory (DFT) calculations utilizing the B3LYP functional and 6-311++G** (H, C, N)+Def2-TZVP (Ni) basis sets were also performed to provide insight

into the possible active catalytic species.⁷⁷⁻⁸¹ A model system with hydrogen atoms in place of the phenyl groups between the pyrrole moieties (to reduce computational cost) was used. A ground state structure with a single protonated aniline moiety in the secondary coordination sphere was used as the starting geometry (**Figure 3.3.24**), and then two electrons were added to the system. Two ground state structures were subsequently found: a nickel(II) hydride species with a de-coordinated imine arm (Mulliken charge of 1.61 on Ni), **1**, and a complex with a partially reduced calixpyrrole ligand, **2** (**Figure 3.3.25**). Using **1** as the reference point ($\Delta G^\circ_1=0.0$ kcal/mol), the ground state energy of **2** was found to be significantly more stable ($\Delta G^\circ_2=-10.1$ kcal/mol). This could potentially mean that hydrogen evolution with **Ni(DPMDA)** is enabled by ligand reduction, similar to work described by Phipps et al.,⁸² Solis et al.,⁸³ and others.^{56, 84} Moreover, the two catalytic peaks that were observed with wider scanning windows (**Figure 3.3.11** and **3.3.23**) could correspond to two active species with structures similar to **1** and **2**. Efforts to isolate catalytic intermediates, as well as to independently synthesize partially reduced nickel calixpyrrole complexes are currently underway. Furthermore, it should be noted that hydrogen evolution pathways that invoke a Ni^{III} -hydride cannot be ruled out at this time.⁸⁵⁻⁸⁹

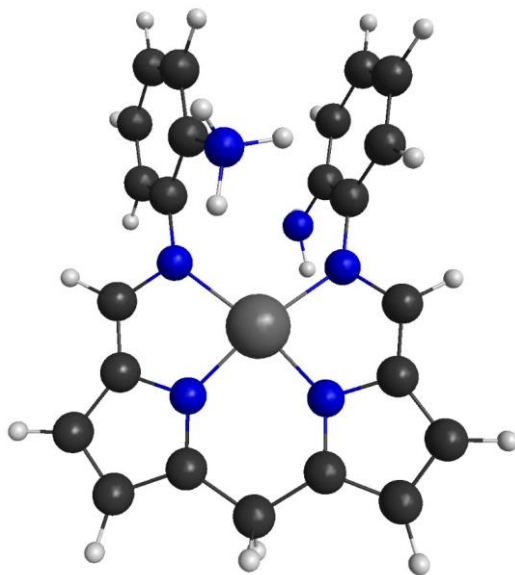


Figure 3.3.24. Visual representation of the ground state structure of the protonated analog of **Ni(DPMDA)**.

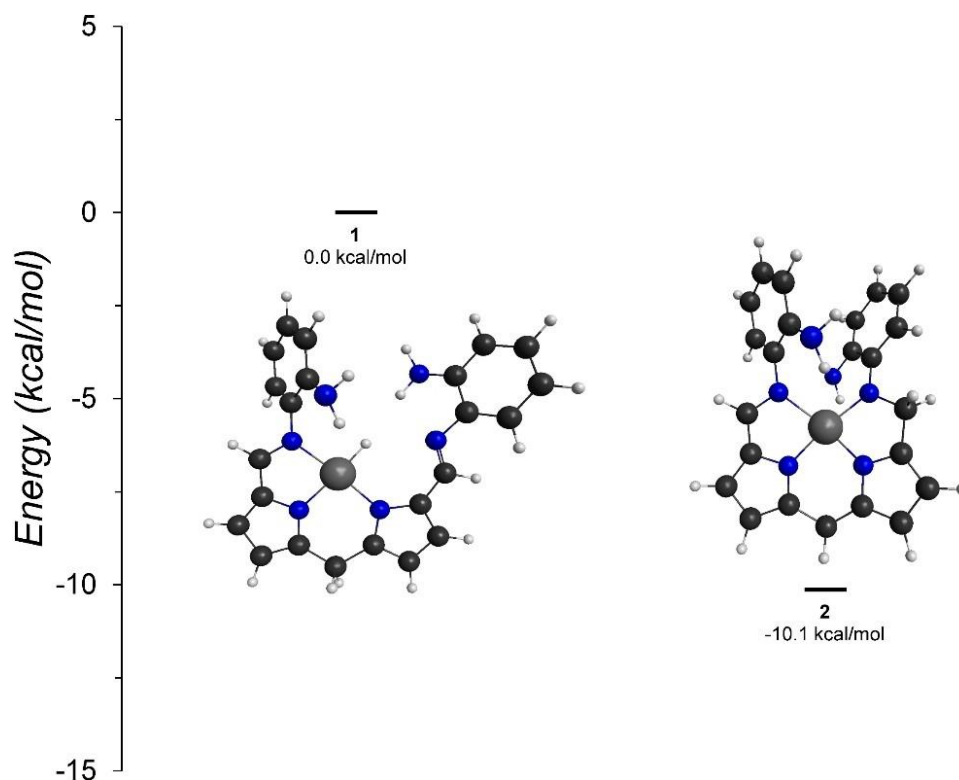


Figure 3.3.25. Free energies of **1** (left) vs **2** (right).

3.3.6 Implications for Catalyst Design

Accessing a PCET mechanism to form a metal hydride species (a Volmer-like step) is a highly desirable catalytic pathway for hydrogen evolution that is often seen with metal surfaces and nanoparticles, but is not commonly seen with molecular systems. Previously, the Surendranath group has reported a way of facilitating this type of mechanism with heterogeneous molecular electrocatalysts, but this required specially designed systems that had such strong electronic coupling between the metal complexes and the electrode supports that the molecular species integrated into the band structure of the electrode.^{26, 90-92} Moreover, due to this extremely strong electronic coupling, the redox features of the metal complexes were not observed and hydrogen evolution was seen across a wide pH range (negative potentials were not necessary to reduce the metal complexes, but were instead needed to drive protons across the electrical double layer, which is consistent with an inner-sphere reduction model).²⁶ What was particularly striking about the reactivity of the surface adsorbed **Ni(DPMDA)** system was that hydrogen evolution proceeded through a Volmer-like concerted proton-electron transfer step without the type of

strong electronic coupling described above. In contrast, for the **Ni(DPMDA)** system reported herein, the redox features of the metal complex were observed in the CV of the adsorbed complex, and the reduction wave was tied to the catalytic onset of hydrogen evolution (evidence for the electroactive surface sites mediating catalysis). This suggested outer-sphere reduction of the supported catalyst, even though the heterogeneous species likely resided within the electrical double layer. Another difference seen for the **Ni(DPMDA)** systems was a clear pK_a dependence for hydrogen evolution that was linked to the basicity of the pendant amine groups, as shown by the results with acetic acid and triethylammonium tetrafluoroborate in comparison to anilinium tetrafluoroborate (additional evidence that the electroactive surface sites were mediating catalysis, and not strongly coupled species operating through inner-sphere electron transfer). This suggested that the functionalities in the secondary coordination sphere influenced the microenvironment at the electrode surface and facilitated proton transfer from the bulk solution to the catalytic active site. Despite these differences, the surface supported **Ni(DPMDA)** complexes were still able to access a highly desirable concerted proton-electron transfer pathway in the rate-determining step (a Volmer-like mechanism) and generate catalytic systems with exceptionally fast reaction kinetics. Furthermore, a significant advantage of the **Ni(DPMDA)** system is that it is deposited onto a practical glassy carbon electrode surface without any pretreatment necessary. In contrast, the supported nickel diphosphacycloheptane catalysts that have been reported require more complicated preparations. In these cases, specialized nanotube electrodes were needed,^{20, 21} pretreatment with 1,2,3-triazolyl lithium and soaking for 18 h was required,²² or a mesoporous TiO_2 electrode and soaking for 16 h was necessary.²³ Additionally, all of the previous catalytic systems needed specialized linkers to graft onto the electrode supports, which positioned the catalytic active sites further away from the electrode surface. It is believed that the **Ni(DPMDA)** system directly adsorbs onto the glassy carbon surface through π - π stacking, similar to related porphyrin complexes, which may play a significant role in promoting the catalytic activity that was seen, which far surpassed the TOFs seen for other heterogeneous molecular catalysts with pendant proton shuttles. These results have important implications for catalyst design; if strong electronic coupling between a metal complex and electrode surface cannot be achieved, then incorporating proton shuttles in the secondary coordination sphere can impart similar benefits. Moreover, directly adsorbing onto the electrode

support, and not requiring tethering functionalities, may also be a key factor in facilitating high TOFs.

When considering the reaction kinetics of hydrogen evolution, however, recent papers by Zeradjanin and co-workers have questioned whether or not activation energy or the preexponential frequency factor are responsible for high catalytic activities.^{93, 94} The authors reported a linear relationship between the two variables for polycrystalline metal based electrodes, such that a decrease in activation energy corresponded to a decrease in the frequency factor and vice versa.^{93, 94} For the **Ni(DPMDA)** system, on the other hand, we believe that the high activity could be coming from a combination of both relatively low activation energy and high preexponential factor. Given the proton shuttles in the secondary coordination sphere, these groups are known to pre-organize proton positioning to optimally facilitate both hydride and hydrogen gas formation. In a sense, the design principles behind incorporating such groups are to increase the number of “effective collisions”, and thus increase the preexponential frequency factor (therefore breaking the linear scaling relationship reported by Zeradjanin and co-workers).^{93, 94} Based on the reported results with heterogeneous molecular nickel diphosphacycloheptane catalysts,²⁰⁻²³ however, which also have pendant amine groups to pre-organize proton positioning and effectively increase the preexponential factor, the **Ni(DPMDA)** catalysts displayed significantly faster reaction kinetics. We believe this could be linked to a lower activation barrier as well, which is commonly seen with PCET pathways.

Finally, while the overpotential of the **Ni(DPMDA)** catalyst was relatively large for hydrogen evolution, this is likely due to the electron rich nature of the calixpyrrole ligand that was utilized. One major advantage of using molecular catalysts that proceed through an outer-sphere reduction, however, is that catalytic onset is tied to the reduction potentials of the metal complexes themselves, which was seen for the **Ni(DPMDA)** system. The reason this is a major advantage is that the reduction potentials of molecular complexes can be readily tuned, and further catalyst optimization is currently underway. As such, we expect that the overpotential can be optimized, while still retaining the fast reaction kinetics imparted by the pendant proton shuttles.

3.4 Conclusions

In summary, a novel nickel complex, **Ni(DPMDA)**, bearing a previously reported Schiff-base calixpyrrole ligand with pendant amine functionalities was synthesized, fully characterized, and its electrochemical properties were studied. Based on the distances seen between metal center and the proton shuttles in the secondary coordination sphere, which were similar to those seen for reported nickel diphosphacycloheptane catalysts,¹⁵ the pendant functionalities were properly positioned to facilitate hydrogen evolution and PCET. The calixpyrrole ligand was found to be redox non-innocent and two consecutive metal-centered quasi-reversible redox couples were observed at particularly cathodic potentials (assigned to $\text{Ni}^{\text{II/I}}$ and $\text{Ni}^{\text{I/0}}$) likely due to the electron-rich nature of the pyrrolide donors. Upon protonation of one of the pendant groups, however, two new irreversible reductions appeared at more positive potentials (over 400 mV more anodic). A clear pK_a dependence tied to the basicity of the pendant amine groups was seen for this behaviour, with weaker acids such as triethylammonium tetrafluoroborate and acetic acid not causing the new features to appear, whereas the stronger acid anilinium tetrafluoroborate did. The **Ni(DPMDA)** system was shown to be active for hydrogen production, with two competing proton reduction mechanisms. The two processes were attributed to heterogeneous molecular species adsorbed to the electrode surface, likely through π - π interactions.

The supported catalysts were explored in more detail and catalytic onset was tied to the redox features of a surface bound metal complex. Moreover, the heterogeneous **Ni(DPMDA)** system was found to be first-order in acid concentration (indicative of a rate-limiting Volmer or Heyrovsky step), as well as first-order in catalyst (up to a point at which the electrode surface became saturated). While the overpotential of hydrogen evolution was 900 mV, the active catalyst exhibited exceptionally fast reaction kinetics with TOFs up to $25,900 \text{ s}^{-1}$ or $366,000 \text{ s}^{-1} \text{ cm}^{-2}$. These catalytic rates were 3 to 4 orders of magnitude larger than known supported nickel diphosphacycloheptane catalysts,¹⁸⁻²³ and were also faster than reported platinum nanoparticles (see **Table 3.4.1** for other relevant literature comparisons).⁷⁰ Additionally, the heterogeneous **Ni(DPMDA)** system displayed unanticipated durability, as well as air- and moisture tolerance.

What was perhaps the most exciting feature about these supported species was that Tafel slope analysis and KIE studies suggested a rate-limiting Volmer-like step. While previous studies by Surendranath and co-workers found that heterogeneous electrocatalysts with strong electronic coupling to electrode supports adopt this type of mechanism,^{26, 90-92} the **Ni(DPMDA)** systems clearly showed outer sphere reduction. Despite this, the heterogeneous **Ni(DPMDA)** complexes were still able to access concerted proton-electron transfer pathways for hydrogen evolution. It is believed that the pendant functionalities in the secondary coordination sphere influenced the electrode surface environment, facilitated proton transfer from the bulk solution, and enabled PCET. Moreover, these results have important implications for catalyst design in that incorporating proton shuttles in the secondary coordination sphere can impart similar benefits as strong electronic coupling between a metal complex and an electrode surface. Directly adsorbing onto the electrode surface and not requiring a tethering group may also be key in ensuring fast reaction kinetics. Additionally, DFT studies suggest that imine reduction may be a key intermediate step in the adsorption process. Further studies aimed at elucidating the exact role of the pendant groups and isolating catalytic intermediates are currently underway.

Table 3.4.1. Comparison of Relevant Catalyst Parameters

Complex	TOF (s ⁻¹)	O.P. (mV)	Acid	Reference
Ni(DPMDA)	14,900	900	[PhNH ₃][BF ₄]	This Work
[Ni(8P ^{Ph} ₂ N ^{Ar} ₂) ₂][BF ₄] ₂ @ MWCNT	5.6	200	[(DMF)H] ⁺	20
Ni(8P ^{Ph} ₂ N ^{ArNH₂} ₂) ₂ @ GC	28	700	[(DMF)H] ⁺	22
[Ni(P ^{Ph} ₂ N ^{Ph}) ₂][BF ₄] ₂	106,000	625	[(DMF)H] ⁺	14
[Ni(DO)(DOH)pn][ClO ₄]	N/A	320	[PhNH ₃][BF ₄]	95
[Co(DO)(DOH)pnBr ₂]	0.15	200	[PhNH ₃][BF ₄]	95

3.5 Experimental Section

3.5.1 General Considerations

All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. Solvents were dried and deoxygenated under argon using a LC Technology Solutions Inc. SP-1 stand-alone solvent purification system. All alcohols were dried and distilled over activated magnesium (magnesium turnings and a crystal of iodine) under a nitrogen atmosphere. Deuterated solvents

were purchased from Cambridge Isotope Laboratories, Sigma Aldrich, Acros Organics, or Alfa Aesar, degassed, and dried over activated molecular sieves prior to use. **DPMDA**⁵⁰ and $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ ⁹⁶ were synthesized according to literature procedures and spectroscopic characterization matched reported data. All other reagents were purchased from commercial sources and utilized without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature and pressure using a Bruker 400 MHz spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , and 61 MHz for ^2H) or a Bruker 600 MHz spectrometer (600 MHz for ^1H and 151 MHz for ^{13}C). The ^1H and ^{13}C NMR spectra were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane (TMS). FTIR characterization was performed using an Agilent Technologies Cary 630 FTIR spectrometer with an ATR sampling module. Data was collected using Microlab FTIR software. Elemental analyses were performed at the University of Rochester, Department of Chemistry, on a PerkinElmer 2400 Series II Analyzer. All crystals were mounted in inert oil and transferred to the cold gas stream of a diffractometer. Single crystal X-ray data were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source ($\text{Cu K}\alpha \lambda = 1.54184 \text{ \AA}$). The data collection strategy was calculated using CrysAlisPro to ensure desired data redundancy and percent completeness. Unit cell determination, initial indexing, data collection, frame integration, Lorentz-polarization corrections and final cell parameter calculations were carried out using CrysAlisPro. An absorption correction was performed using the SCALE3 ABSPACK scaling algorithm embedded within CrysAlisPro. The structures were solved using the ShelXT structure solution program using Intrinsic Phasing and refined by Least Squares using the ShelXL program. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Olex2 was used for the preparation of the publication materials. Cyclic voltametric measurements were recorded using a Bio-Logic model SP-50 potentiostat. Tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte and was recrystallized prior to use by slow addition of pentane into a THF solution followed by cooling in a freezer ($-30 \text{ }^\circ\text{C}$). The working electrode was a glassy carbon electrode or a mercury pool electrode; the reference electrode was a Ag/AgNO_3 non-aqueous electrode (0.01 M in CH_3CN with 0.1 M TBAP); and a platinum wire or graphite rod was used as

the counter electrode. The glassy carbon electrode was polished with 0.05 μm alumina and washed with distilled water prior to each measurement. Electrochemical measurements were conducted at room temperature under an argon or nitrogen atmosphere and processed using EC-Lab V11.21. Ohmic drop was accounted for using the current interrupt method available in EC-Lab V11.21. Reported half-wave potentials were referenced to the Fc/Fc^+ redox couple by adding high purity ferrocene to the sample solution. Controlled potential electrolysis experiments were also performed with a Biologic SP-50 model potentiostat and processed using EC-Lab V11.21. The working electrode was a 6 mm glassy carbon rod, the counter electrode was a 6 mm graphite rod, and the reference electrode was a 0.01 M Ag/AgNO_3 non-aqueous electrode (0.01 M in CH_3CN with 0.1 M TBAP). The amount of hydrogen produced was quantified using an ATO Inc. model ATO-SKY2000-H2 handheld gas detector (0 to 500 ppm) and a calibration curve derived from known volumes of ultra-high purity hydrogen gas (Airgas). High-resolution mass spectrometry (HRMS) was recorded on a Waters Xevo G2-XS QToF mass spectrometer that is equipped with a NanoLockSpray exact mass ionization source. All samples for HRMS were filtered using a 0.2 μm PTFE syringe to remove particles before injection.

3.5.2 Synthesis of Ni(DPMDA)

A solution of 0.133 g (0.249 mmol) of **DPMDA** in ~ 4.5 mL MeCN was added to a suspension of 0.020 g (0.499 mmol) of KH in ~ 3 mL MeCN. The solution was stirred until gas evolution had ceased and the solution was added to 0.119 g (0.249 mmol) of $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$. The reaction was stirred overnight and the precipitate was collected on a frit. After drying under reduced pressure for several hours, the solid was dissolved in ~ 4.5 mL of DCM, and then filtered through Celite. The filtrate was evaporated under reduced pressure to give **2** as an orange solid. Yield: 0.090 g (61 %). Crystals suitable for single crystal X-ray diffraction were grown from the slow diffusion of pentane into a toluene solution of **Ni(DPMDA)**. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ : 7.35 (2H, s, imine-CH), 7.27 (4H, d, aromatic-CH, $J=7.6$ Hz), 7.23 (2H, t, aromatic-CH, $J=7.3$ Hz), 7.13 (4H, d, aromatic-CH, $J=7.9$ Hz), 6.72–6.64 (4H, m, aromatic-CH and pyrrole-CH), 6.52 (2H, t, aromatic-CH, $J=7.9$ Hz), 6.22 (2H, t, aromatic-CH, $J=7.8$ Hz), 6.08 (2H, d, aromatic-CH, $J=8.2$ Hz), 5.78 (2H, d, pyrrole-CH, $J=4.0$ Hz), and 4.64 (4H, br s, amine NH_2). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 162.22

(imine-CH), 151.59 (aromatic-C), 146.57 (aromatic-C), 140.79 (aromatic-C), 137.27 (aromatic-C), 132.79 (aromatic-C), 128.58 (aromatic-CH), 127.35 (aromatic-CH), 126.04 (aromatic-CH), 125.98 (aromatic-CH), 123.41 (pyrrole-CH), 117.88 (aromatic-CH), 116.11 (aromatic CH), 114.56 (aromatic-CH), 112.41 (pyrrole-CH), and 58.08 (C-Ph₂). IR (solid pellet): ν =3423 (w, br, N-H), 3340 (w, br, N-H), and 1559 (s, C=N) cm⁻¹. HRMS (ESI) m/z calcd for C₃₅H₂₉N₆Ni⁺: 591.1807 [M+H]⁺; found: 591.1830; calcd for C₃₅H₂₈N₆Ni+Na⁺: 613.1627 [M+Na]⁺; found: 613.1661; calcd for C₃₅H₂₈N₆Ni+K⁺: 629.1366 [M+K]⁺; found: 629.1409. Elemental analysis calcd for C₃₅H₂₈N₆Ni · 0.5DCM: C, 67.3, H, 4.6, N, 13.3, found: C, 66.9, H, 4.4, N, 13.2.

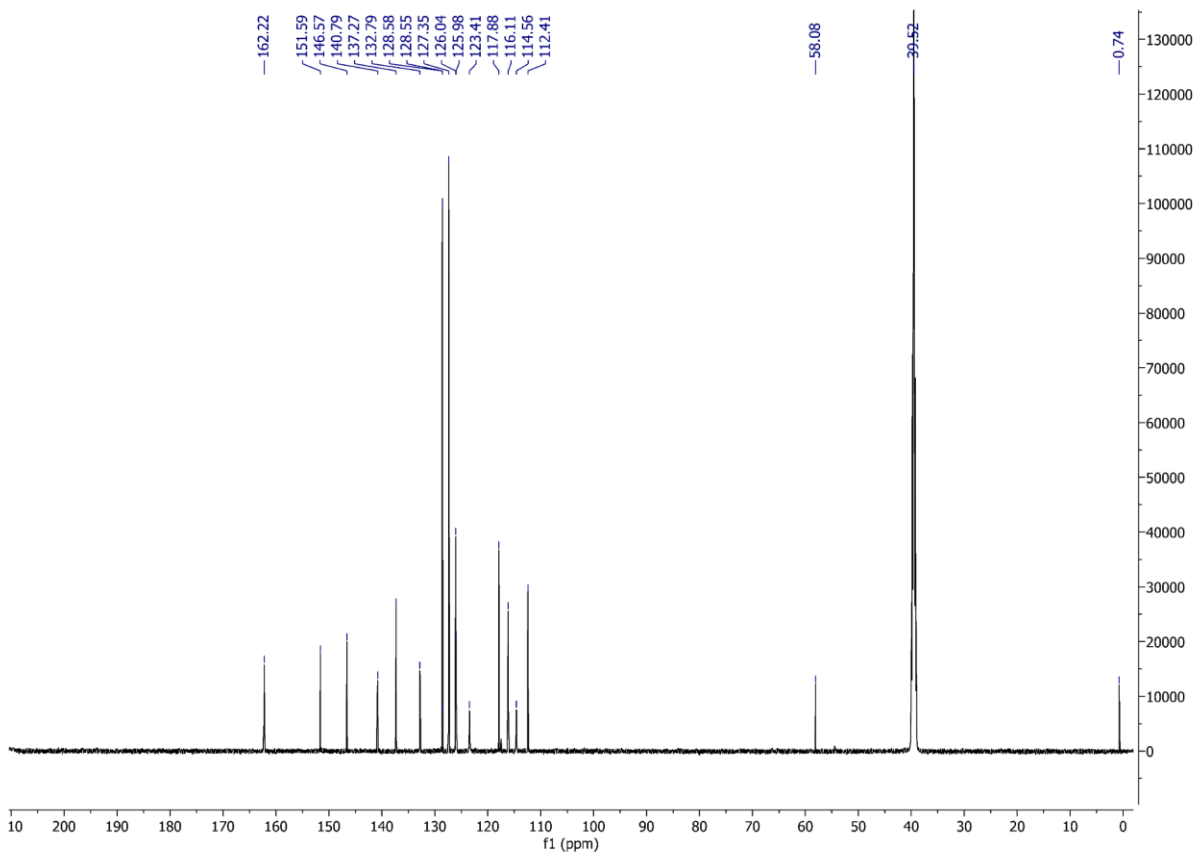


Figure 3.5.1. ¹³C NMR spectrum (600 Mhz, DMSO-*d*₆) of Ni(DPMDA).

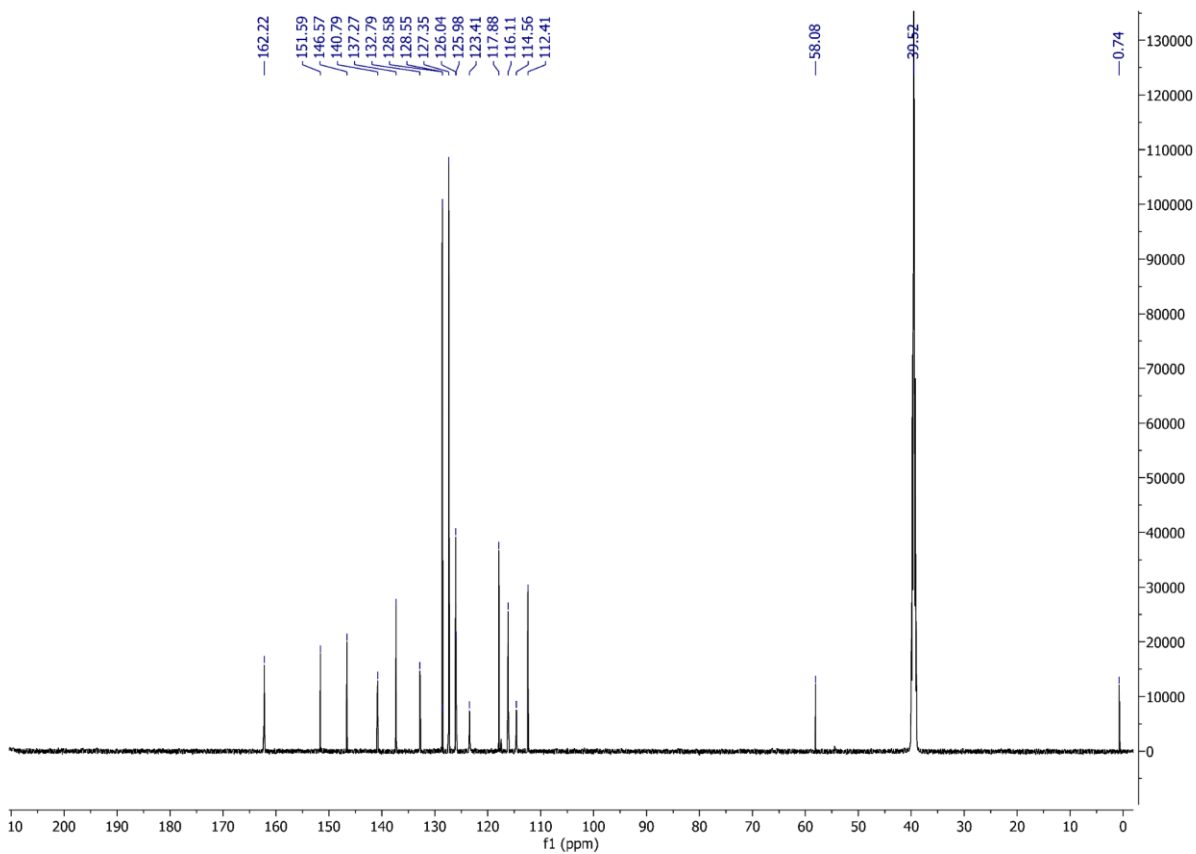


Figure 3.5.2. ^{13}C NMR spectrum (600 MHz, $\text{DMSO-}d_6$) of $\text{Ni}(\text{DPMDA})$.

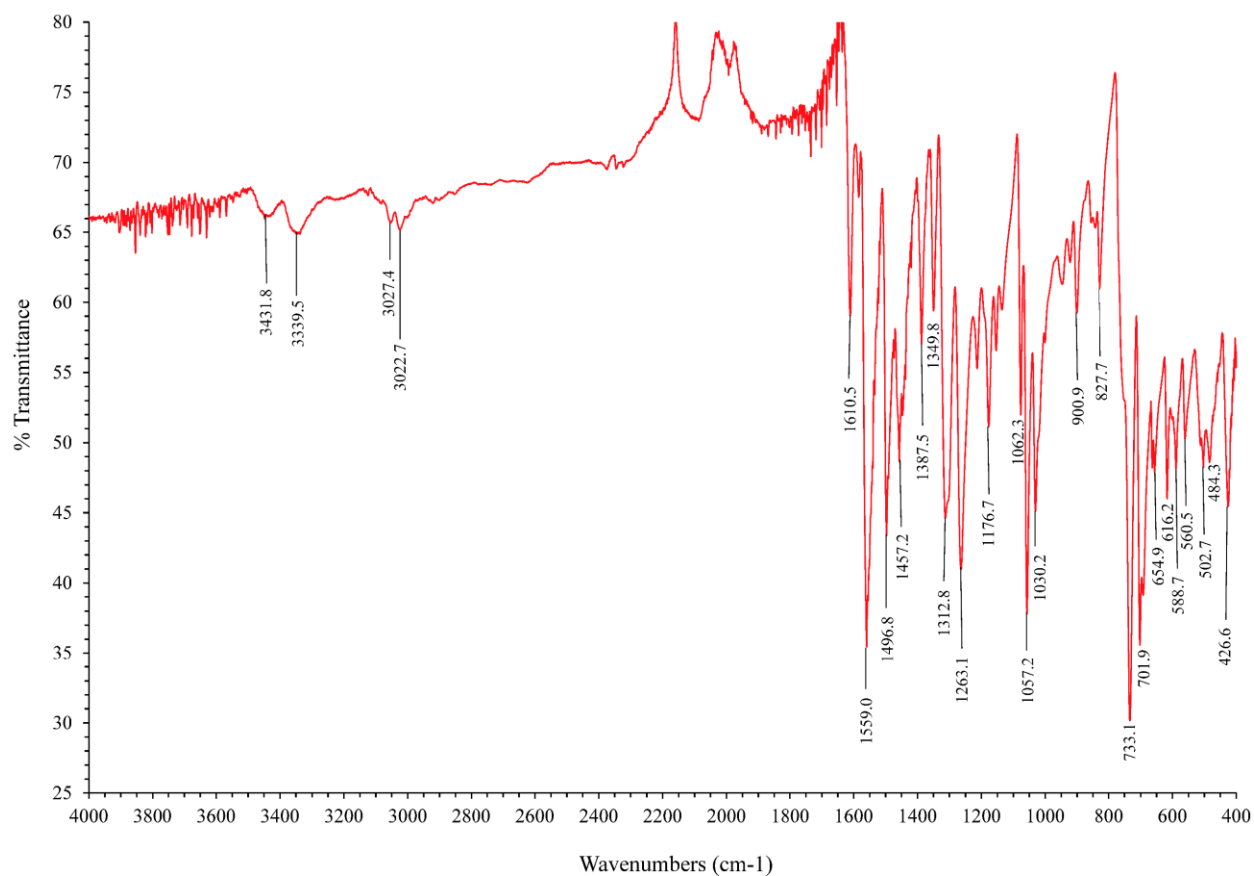


Figure 3.5.3. IR spectrum (solid pellet) of Ni(DPMDA).

Table 3.5.1. Selected Crystal Data, Data Collection, and Refinement Parameters for Ni(DPMDA).

Ni(DPMDA)	
empirical formula	C ₃₅ H ₂₈ N ₆ Ni
FW	591.34
lattice type	monoclinic
space group	P2 ₁ /n
T, K	170.0(1)
<i>a</i> , Å	15.9752(4)
<i>b</i> , Å	9.3388(2)
<i>c</i> , Å	20.0944(5)
<i>α</i> , deg	90
<i>β</i> , deg	112.961(3)
<i>γ</i> , deg	90
<i>V</i> , Å ³	2760.4(2)
<i>Z</i>	4

$\rho_{\text{calc}}/\text{Mg m}^{-3}$	1.423
$\mu(\text{Cu/Mo, Ka}) \text{ mm}^{-1}$	1.299 (Cu)
F(000)	1232
cryst size, mm^3	0.197 x 0.115 x 0.022
range Θ collected, deg	6.044 to 154.108
reflns	30235/5804
collected/unique abs cor	Semi-empirical from equivalents
Max and min transmn coeff.	1.000 and 0.720
goodness of fit	1.045
$R_1(I > 2\sigma(I))^a$	0.0347
wR_2 (all data) ^a	0.0963
peak and hole, $\text{e \AA}^{-3}$	0.41 and -0.31

^a Definition of R indices: $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / [\Sigma[w(F_o^2)^2]]^{1/2}$

3.5.3 Discussion of Ni(DPMDA) Structure

The coordination geometry of **Ni(DPMDA)** was very similar to the previously reported palladium calixpyrrole complexes,⁵⁰ where the Ni center adopted a square planar geometry with the metal bound slightly out of the plane of the calixpyrrole ligand (0.07 Å). Moreover, the nickel center was more tightly bound to the pyrrolide nitrogens (Ni(1)-N(1) and Ni(1)-N(2) bond lengths of 1.839 and 1.843 Å, respectively) in comparison to the imine donors (Ni(1)-N(3) and Ni(1)-N(4) bond lengths of 1.955 and 1.947 Å, respectively). The bond lengths for **Ni(DPMDA)**, however, were approximately 0.1 Å shorter than the corresponding palladium species,⁵⁰ likely due to the smaller size of the metal. It was also observed that the N(1)-Ni(1)-N(2) bond angle between the pyrrolide donors for **Ni(DPMDA)** was compressed slightly below 90° (87.32°), whereas the N(1)-Ni(1)-N(3) and N(2)-Ni(1)-N(4) bond angles for the five-membered ring systems were more significantly compressed (83.8 and 83.7°, respectively). In contrast, the N(3)-Ni(1)-N(4) bond angle between the imine donors was expanded beyond 90° (105.0°). Lastly, the C=N imine bond lengths for **Ni(DPMDA)** were slightly longer than those seen in the free ligand (N(3)-C(6) and N(4)-C(11) bond lengths of 1.32 and 1.31 Å, respectively, vs N(3)-C(6) and N(4)-C(11) bond lengths of 1.28 and 1.29 Å, respectively)² and were very similar

in length to those of the analogous palladium systems. It is believed that the weakening of the imine bond is due to π back-bonding from the nickel center.

3.5.4 Synthesis of Anilinium Tetrafluoroborate- d_3

N-benzylideneaniline was synthesized according to literature procedure and spectroscopic characterization matched reported data.¹⁰⁰ Deuterated anilinium tetrafluoroborate was synthesized by stirring 3.00 g (0.0166 mol) N-benzylideneaniline in a suspension of 30 mL dry ether and 12 mL of 20% DCl in D₂O diluted with additional 25 mL of D₂O (under a nitrogen atmosphere). The ether layer was removed via syringe and the D₂O layer was evaporated to dryness under reduced pressure. The resulting 1.322 g anilinium- d_3 chloride was suspended in 20 mL CD₃CN and stirred with 1.10 g (1 eq.) NaBF₄ in an argon glovebox overnight. The resulting suspension was filtered through a fritted glass funnel to remove the insoluble NaCl, and the filtrate was evaporated to dryness under reduced pressure to give anilinium tetrafluoroborate- d_3 as a white solid. Yield: 1.65 g (54%).

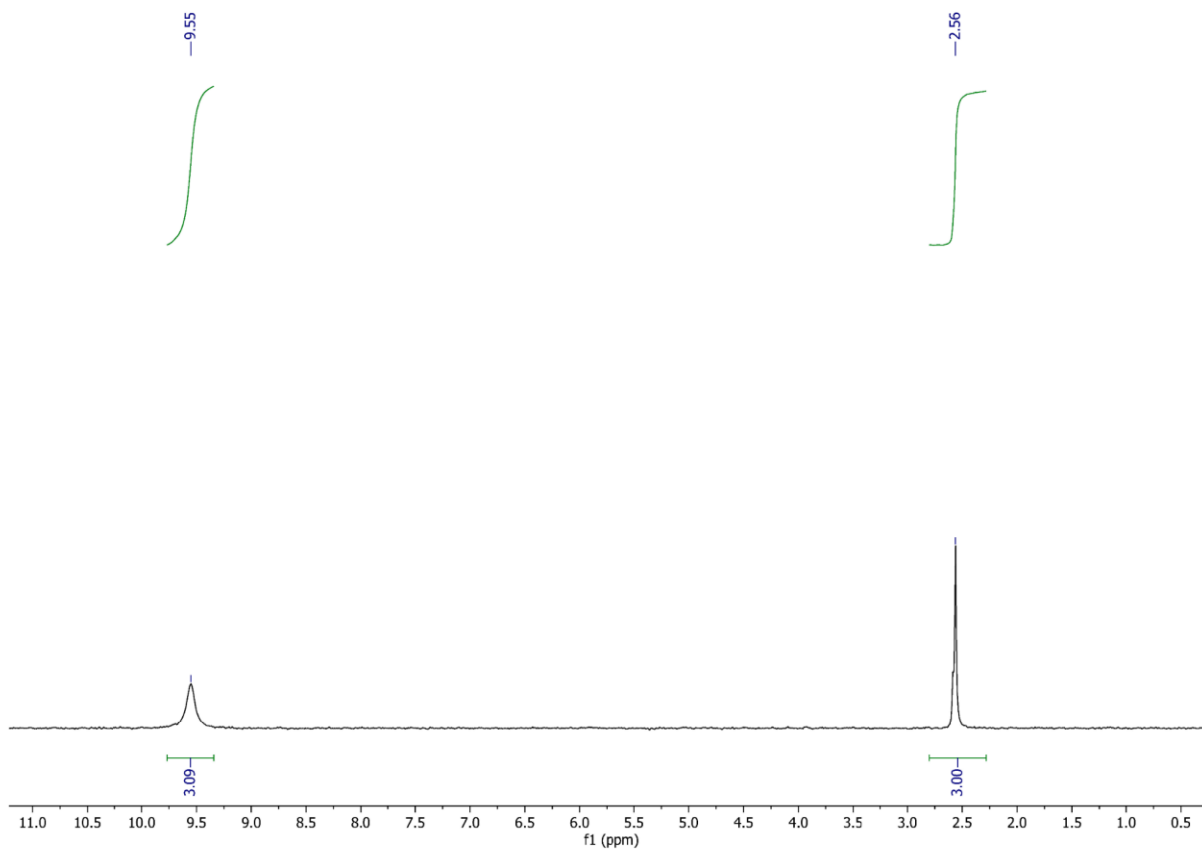


Figure 3.5.4. ^2H NMR spectrum (61 MHz, $\text{DME-}h_{10}$) of anilinium tetrafluoroborate- d_3 with one equivalent of CD_3CN added as an internal standard.

3.5.5 Electrocatalytic H_2 Evolution

The electrochemical conditions of the catalytic trials included 0.1 M TBAP electrolyte in acetonitrile, 0.039 mM to 0.25 mM of **Ni(DPMDA)**, 30 to 350 equivalents of anilinium tetrafluoroborate (7.5 to 87.5 mM), and scan rates between 5 to 60 V/s. The three-electrode setup consisted of a glassy carbon working electrode, a platinum wire or graphite rod counter electrode, and a 0.01 M Ag/AgNO_3 reference electrode. All CVs were referenced versus the Fc/Fc^+ redox couple. All CVs were recorded under an argon or nitrogen atmosphere in dry acetonitrile. For the “rinse” test results, the working electrode was removed from the cell following catalysis, rinsed with either acetonitrile or acetone solvent, and then placed in a fresh electrolyte solution without **Ni(DPMDA)** present (0.1 M TBAP). To determine the kinetic isotope effect (KIE), anilinium tetrafluoroborate- d_3 (81.25 mM) in acetonitrile- d_3 was utilized (0.1 M TBAP, 0.25 mM **Ni(DPMDA)**).

3.5.6 Sample Overpotential Calculation^{55,63}

$$E_{H^+} = E_{H^+}^{\circ} - 0.05916 V \times pK_a$$

$$E_{H^+} = -0.028 V - 0.05916 V \times 10.62 = -0.66 V$$

$$\eta = |E_{H^+} - E_{cat/2}|$$

$$\eta = |-0.66 V - (-1.568 \pm 18 V)| = 0.912 \pm 0.18 V$$

3.5.7 Sample Turnover Frequency Calculation⁶⁸⁻⁶⁹

$$i_p = \frac{n^2 F^2}{4RT} v \Gamma^*$$

$$0.0429 \pm 0.0076 mA = \frac{(1 \text{ mole } e^-)^2 (96485 C / (\text{mol}))^2}{4(8.314 J / \text{molK})(298 K)} (40 V / s) (0.070686 \text{ cm}^2) \Gamma^*$$

$$\Gamma^* = 1.62 \times 10^{-11} \pm 1.4 \times 10^{-12} \text{ mol/cm}^2$$

$$TOF = \frac{j}{nFm}$$

$$TOF = \frac{i_{cat}}{nFA\Gamma^*}$$

$$TOF = \frac{3.28 \pm 0.14 mA}{(2) \left(\frac{96485 C}{mol} \right) \left(1.62 \times 10^{-11} \pm \frac{1.4 \times 10^{-12} \text{ mol}}{\text{cm}^2} \right)}$$

$$TOF = 14,900 \pm 2700 \text{ s}^{-1} \text{ or } 211,000 \pm 39,000 \text{ s}^{-1} \cdot \text{cm}^{-2}$$

3.5.8 Controlled Potential Electrolysis

Prior to controlled potential electrolysis, CV experiments utilizing the glassy carbon working electrode (6 mm rod) were carried out in 0.1 M TBAP electrolyte in acetonitrile, 81.25 mM anilinium tetrafluoroborate, and 0.25 mM **Ni(DPMDA)** where the potential was scanned to sufficiently negative potentials (-2.6 V) to ensure catalyst deposition onto the electrode surface. The prepared glassy carbon working electrode was then placed into a sealed bulk electrolysis cell filled with a solution of 0.1 M TBAP in acetonitrile, 0.25 mM **Ni(DPMDA)**, and 81.25 mM

anilinium tetrafluoroborate, along with a 0.01 M Ag/AgNO₃ reference electrode reference electrode (Figure S5). The graphite counter electrode, separated by a porous frit, was submerged in a solution of 0.1 M TBAP in acetonitrile and 81.25 mM ferrocene. Bulk electrolysis experiments were carried out at a controlled potential of -2.02 V vs. Fc/Fc⁺ until 1 C of charge was passed. The solution in the cell was then stirred for 1 h to ensure equilibration between the solvent and headspace before sampling.



Figure 3.5.5. Image of the electrolysis cell utilized for controlled potential electrolysis after 1 C of charge had been passed.

3.5.9 Computational Details

Density functional theory calculations were performed using the GAMESS(US) package (2016 R1)^{97, 98} and the B3LYP hybrid functional.⁷⁶ Nickel was treated with the Def2-TZVP basis set,⁷⁶ while all other atoms were treated with the 6-311++G(d,p) basis set.^{78, 79} A tight integration grid where NRAD=99 and NLEB=1202 was used throughout for increased accuracy. Stationary points were characterized by normal-mode analysis. Full vibrational and thermochemical

analyses (1 atm, 298 K) were performed on optimized structures to obtain free energies (G°) and enthalpies (H°). Optimized ground states were found to have zero imaginary frequencies. Three dimensional visualizations of calculated structures and orbitals were generated using MacMolPlt.⁹⁹

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Chapter 4 – Electrocatalytic Hydrogen Evolution with Ni(II)

Calixpyrrole: Acid Strength Governs Catalyst Formation

4.1 Abstract

Integration of molecular species on electrode surfaces presents opportunities to combine the advantages of homogeneous and heterogeneous catalysts by enabling control over the secondary coordination sphere in interfacial environments. To this end, we report electrocatalytic hydrogen evolution by the previously reported Ni(DPMDA) complex (DPMDA=2,2'-((diphenylmethylene)bis(1H-pyrrole-5,2-diyl))bis-(methaneylylidene))bis(azaneylylidene)dianiline) in the presence of triethylammonium as the proton source. Similar to electrochemical studies in the presence of anilinium, this species forms a heterogeneous catalyst on the electrode surface reaching TOF of up to $5,700\text{ s}^{-1}$ or $80,000\text{ s}^{-1}\cdot\text{cm}^{-2}$. Furthermore, overpotentials of about 745 mV were observed. Rinse tests with acetone suggest that this species is molecular in nature and buffer studies suggest that the pendant amines may remain intact on the electrode surface and act as hydrogen bond acceptors/donors with solution phase acid. Moreover, kinetic isotope effect (KIE) studies found a H/D KIE value of about 4.2, and Tafel analysis yielded a Tafel slope of 125 mV/dec. Together, these results suggest rate-limiting PCET. Interestingly, evidence of strong electronic coupling with the electrode surface is observed, perhaps giving rise to the lower observed overpotentials compared to the previously reported species. The results presented herein not only give insight into how acid strength may govern catalyst formation, but also provide further understanding of molecular approaches for heterogeneous catalyst design.

4.2 Introduction

Increased demands for alternative energy sources¹ and the detrimental effects of fossil fuel consumption have generated additional research interest in catalysts capable of producing chemical fuel carriers.² One such fuel carrier is hydrogen which can be used to store and transport the energy obtained from renewable sources, such as wind and solar power, in chemical bonds.³⁻⁵ While fuel cell technology is progressing, the fact remains that the majority of

hydrogen is produced from the steam reforming process of fossil fuels, thus perpetuating reliance on nonrenewable sources.⁴ Additionally, current electrode materials are based on platinum and palladium, which is problematic due to the relative expense and rarity of these metals.⁶ Because of this, it is important to develop new, cheaper electrocatalysts for hydrogen production using more sustainable metal sources, and within that, to develop a greater fundamental understanding of the elementary steps needed to produce hydrogen.

Much research has been carried out to investigate molecular species for electrocatalytic hydrogen evolution, and often inspiration is taken from nature. Specifically, the hydrogenase enzyme is known to evolve hydrogen with low overpotentials, and this is aided by a bridging hydrogen-bonding moiety in the secondary coordination sphere.^{7–9} Prime examples of utilizing this concept of proton shuttling via a secondary coordination sphere moiety are given in reports by Rauchfuss,^{10–13} Nocera,^{14–18} and Bullock (**Figure 4.2.1**).^{19–24} In these reports the authors studied [Fe-Fe] hydrogenase mimics, Co(II)/Ni(II) “hangman” porphyrins, and Ni(II) diphosphacycloheptane complexes, respectively, for hydrogen evolution, with the latter system representing the fastest known molecular catalyst for hydrogen evolution, eclipsing turnover frequencies (TOFs) of over 100,000 s⁻¹.²⁰

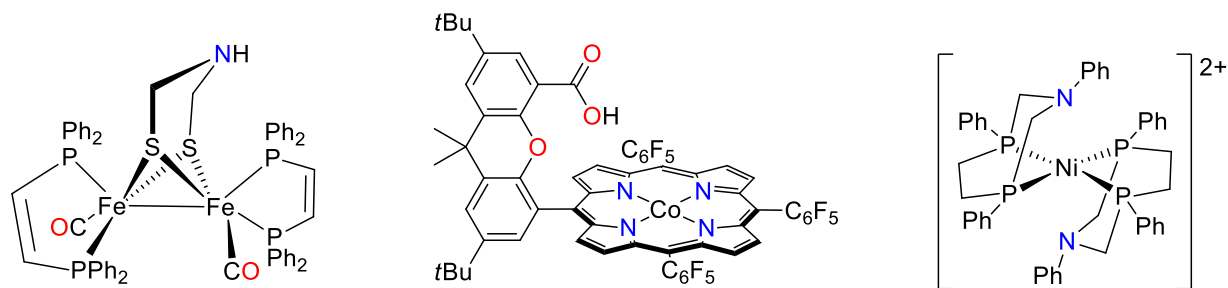


Figure 4.2.1. Examples of a Rauchfuss hydrogenase mimic (left), a Nocera “hangman porphyrin” (middle), and a Bullock Ni diphosphacycloheptane complex (right).

While high TOFs can be obtained with molecular catalysts, it is of industrial relevance to develop catalysts that can be immobilized on electrode surfaces, giving unique advantages over their homogeneous counterparts, such as easier catalyst separation, increased stability with respect to bimolecular decomposition pathways, and viability in continuous flow reactors.²⁵ With this in mind, successful molecular catalysts have been explored on electrode surfaces through various attachment methods, such as covalent attachment,^{26–30} electrostatic or π - π interactions on carbonaceous surfaces,^{31–37} or electrodeposition.^{38–42} One example of this includes the

attachment Ni diphosphacyclooctane complexes to carbonaceous electrodes via covalent linkers.³⁰ Interestingly, reports of attachment to glassy carbon or carbon nanotubes found that TOFs were significantly decreased, which was attributed to the inability of the pendent groups to effectively isomerize on the surface due to steric crowding.³⁰ Similar results were also seen (a marked reduction in turnover frequency) when the catalyst was appended with pyrene moieties and adsorbed through π - π interactions to a carbonaceous surface. These results highlight some of the challenges that come with heterogenizing molecular species.³⁶ Likewise, heterogenized [Fe-Fe] hydrogenase mimics have also been reported, albeit with lower TOFs than their homogeneous counterparts.^{35,37}

Another prominent example of a heterogenized molecular catalyst that has recently been reported is a cobalt porphyrin complex covalently linked to an electrode surface described by Surendranath *et al.*²⁸ This study has proved to be instrumental in changing the way heterogenized catalysts are viewed, in that the authors found different behaviors in acetonitrile and water. In acetonitrile the cobalt center did not interact directly with the electrode surface, and catalysis proceeded through an outer-sphere mechanism tied to the $\text{Co}^{\text{II/I}}$ redox couple. When the electrode was placed in water, however, the authors found evidence of strong electronic coupling of the catalyst with the electrode surface, and catalysis proceeded through a concerted inner-sphere mechanism as evidenced by the lack of redox features for the catalyst in water. Unlike most other heterogenized species, this electrode-adsorbed species behaved more like a metal surface when placed in water, illustrating the utility of a tightly adsorbed molecular species on an electrode surface.

Recently, we have reported a Ni(II) Schiff-base calixpyrrole complex (**Figure 4.2.2**) with pendant hydrogen bond donors (Ni(DPMDA)) and its hydrogen evolution activity in the presence of anilinium tetrafluoroborate in acetonitrile.⁴³ This species was shown to form an electrode-adsorbed catalyst at reducing potentials corresponding to the $\text{Ni}^{\text{II/I}}$ redox couple in the presence of the acid. While it was found to operate through an outer-sphere mechanism as evidenced by redox activity of the adsorbed catalyst in the absence of acid, kinetic studies revealed fast turnover frequencies as well as a rate-limiting Volmer-like metal-hydride forming step, as shown by Tafel slope analysis and kinetic isotope effect (KIE) studies. A major issue, however, was that overpotentials were quite large, around 900 mV. Here we report the

electrocatalytic hydrogen evolution activity of the aforementioned Ni(DPMDA) complex in the presence of a weaker proton donor, triethylammonium tetrafluoroborate. In this context, we aim to explore how utilization of a weaker acid, one that is not expected to be able to directly protonate the pendant groups, may change the catalytic activity. One hypothesis is that use of a weaker acid (with more negative background reduction potentials) may allow for an accessible homogeneous pathway. Additionally, it is of interest to study whether a PCET pathway is still accessible without direct protonation of the pendant groups.

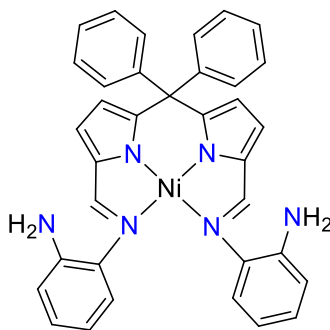


Figure 4.2.2. Structure of Ni(DPMDA).

4.3 Results and Discussion

4.3.1 Electrocatalytic Hydrogen Evolution

Ni(DPMDA) was synthesized as previously reported and its structure was confirmed by spectroscopic characterization. As noted previously, using only one equivalent of triethylammonium tetrafluoroborate ($pK_a=18.83$) produced no catalytic current other than that of the background reduction at the glassy carbon electrode using cyclic voltammetry (CV).⁴³ However, in the presence of a greater concentration of the proton source (at least 10 equivalents of triethylammonium tetrafluoroborate), it was found that a catalytic wave positioned anodic of both the $Ni^{II/I}$ redox couple ($E_{1/2} = -2.03$ V vs. ferrocene/ferricenium, Fc/Fc^+) and the background reduction at the electrode was observed (**Figure 4.3.1**). Similar results, as shown below, were seen with increased triethylammonium tetrafluoroborate concentrations of 25 mM (**Figure 4.3.1**). Interestingly, with consecutive CV scans, the catalytic wave continued to shift more positively until it stabilized near -1.87 V vs Fc/Fc^+ , possibly suggesting the generation of an increasing amount of a catalytically active species. Moreover, unlike the catalyst generated in the presence of anilinium tetrafluoroborate, only a single irreversible reduction wave was observed.

Additionally catalysis proceeded without scanning past the $\text{Ni}^{\text{II/I}}$ redox couple, suggesting that the observed activity was due to a catalytic species that was unique with respect to the system that was previously reported. This hypothesis was also supported by the much higher pK_a of triethylammonium tetrafluoroborate, and its presumed inability to protonate the pendant amine groups, in contrast to anilinium tetrafluoroborate. Furthermore, most other reports of hydrogen evolution electrocatalysts utilizing acids of two different strengths require more reducing potentials for weaker acids, and often operate through different mechanisms. This was seen with a polypyridyl cobalt complex reported by Queyriaux *et al.* where use of triethylammonium acids triggered hydrogen evolution through a more cathodic ligand based redox couple, while tetrafluoroboric acid triggered hydrogen evolution at more positive potentials through a metal-centered redox couple.⁴⁴ Similarly, Phipps *et al.* investigated Ni(II) and Pd(II) diacetyl-2-(4-methyl-3-thiosemicarbazone)-3-(2-pyridinehydrazone) complexes using three different acid sources: triethylammonium, acetic acid, and HDBU⁺ (1,8-diazabicyclo(5.4.0)undec-7-enium) with pK_a s of 18.63, 23.51, and 24.34, respectively. They found that electrocatalysis proceeded at more positive potentials with decreasing pK_a .³⁹ Given that the results presented here proceed at more positive potentials than those reported for Ni(DPMDA) in the presence of anilinium tetrafluoroborate (a stronger proton donor), it is believed that the catalytically active species is markedly different.⁴³

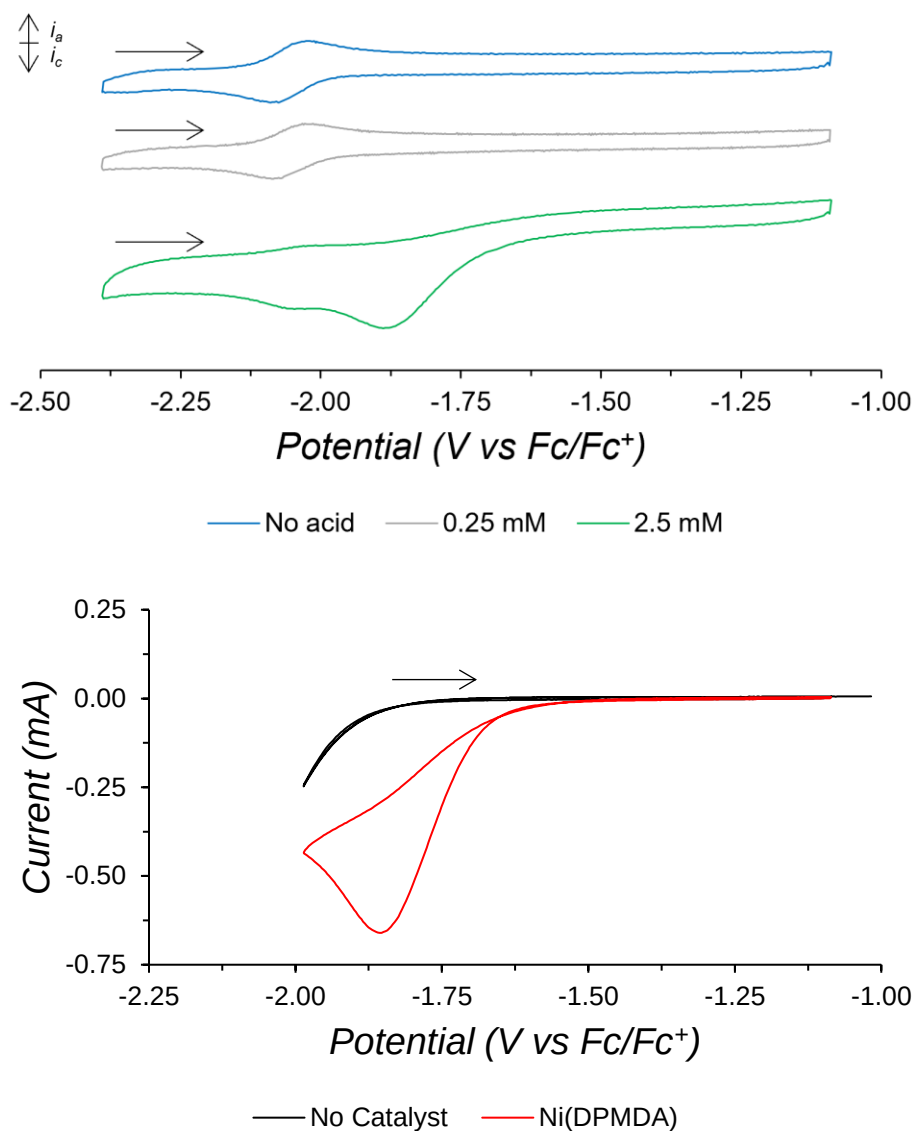


Figure 4.3.1. CVs of **Ni(DPMDA)** with low concentrations of HNEt_3 (top) and a representative CV trace of the stabilized catalytic current along with a control experiment with no **Ni(DPMDA)** in solution (bottom). (0.1 M TBAP, 0 or 0.25 mM **Ni(DPMDA)**, 0, 0.25, 2.5, or 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO_3 reference electrode, scan rate = 1 V/s).

With catalytic activity established, rinse tests were first carried out to confirm the presence of a heterogeneous species. It was found that after rinsing the electrode with acetonitrile and scanning in a solution of only electrolyte and 25 mM triethylammonium tetrafluoroborate, catalytic activity remained. Additionally, negative scanning/rinse tests revealed that a potential of no more than -1.9 V vs Ag/AgNO_3 was necessary to adsorb the catalytic species to the glassy

carbon electrode (**Figure 4.3.2**). However, this heterogeneous species seems to be less stable than the one formed in the presence of anilinium tetrafluoroborate, as the catalytic wave shifts further negative with consecutive scans (**Figure 4.3.3**). Similarly, rinse tests were carried out with acetone as the rinsing solvent, a solvent in which the Ni(DPMDA) is much more soluble (**Figure 4.3.3**). After this acetone rinse, catalytic activity was significantly diminished when compared to the acetonitrile rinse. The perceived ability of acetone to decrease catalytic activity, presumably by washing off some of the active catalyst, suggests that the adsorbed catalytically active species is molecular in nature and likely adsorbed through noncovalent interactions. Additionally, this adsorbed species is distinct from the one generated in the presence of anilinium tetrafluoroborate, as catalytic activity was completely lost for the latter system after rinsing with acetone. A mercury pool test was also conducted (**Figure 4.3.4**). In this case, we observed that catalytic activity was retained giving evidence against the formation of nickel nanoparticles.

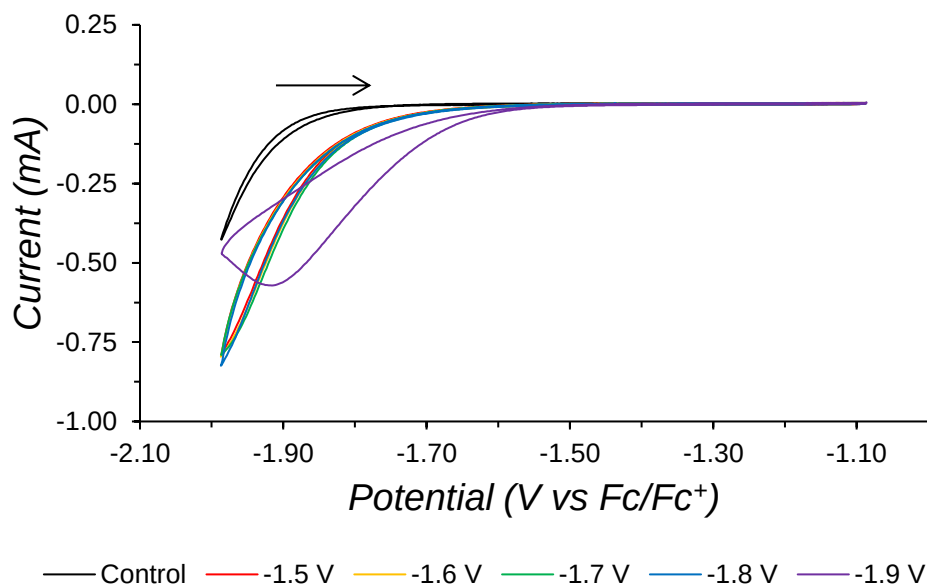
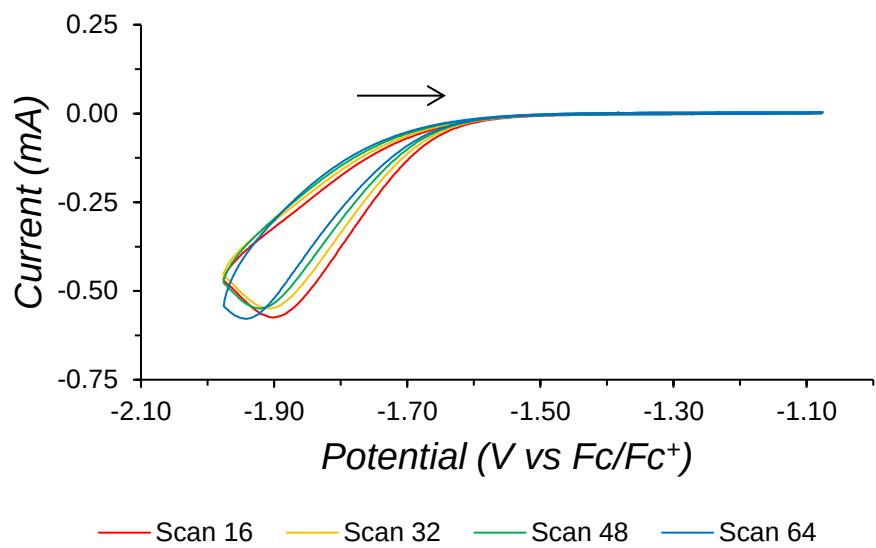
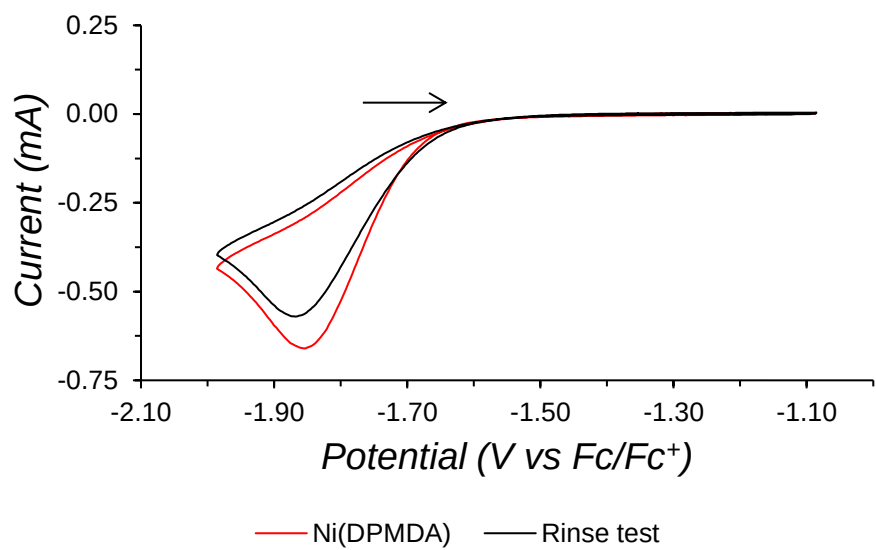


Figure 4.3.2. Rinse tests performed after scanning a solution of Ni(DPMDA) to various negative potentials vs reference (0.1 M TBAP, 0 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 1 V/s).



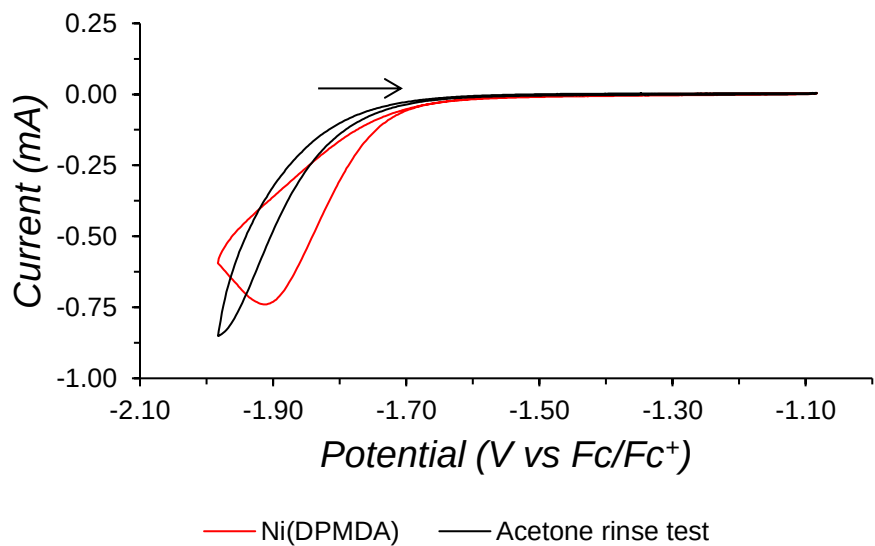


Figure 4.3.3. Rinse test after catalysis with Ni(DPMDA) using acetonitrile as the rinsing solvent (top), repetitive scans of the rinsed electrode (middle), and rinse test with acetone as the rinsing solvent (bottom, 0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 1 V/s).

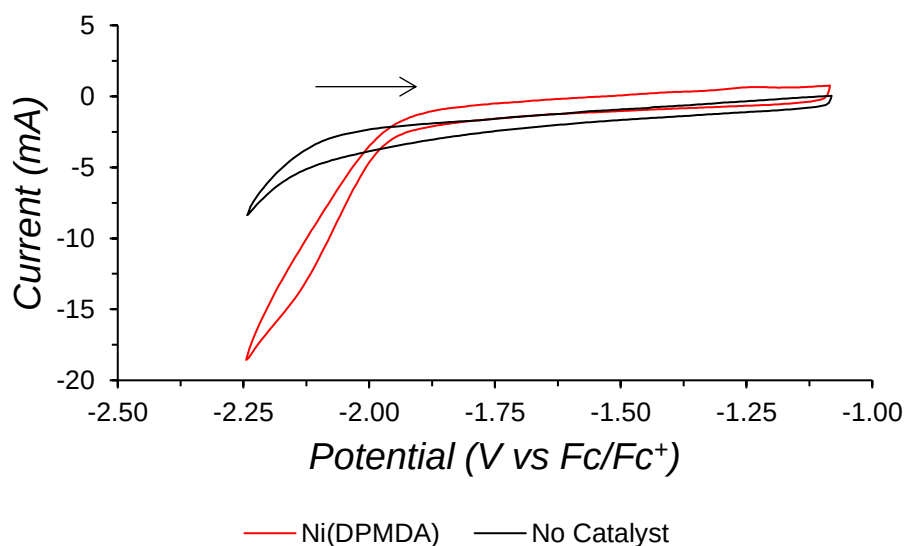


Figure 4.3.4. Mercury pool test for Ni(DPMDA) (0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, mercury pool working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 1 V/s).

In electrocatalytic proton reduction, buffered solutions can be used to negate the effects of homoconjugation, where hydrogen bonding between the conjugate base of an acid and a molecule of acid can increase the apparent acidity of the acid.⁴⁵ While triethylammonium has a

very low homoconjugation constant ($\log K_f \approx 0$),⁴⁵ we set out to examine the effects of a buffered solution on catalysis (**Figure 4.3.5**). To test this, catalysis was carried out in a non-buffered solution of 25 mM triethylammonium and 0.25 mM Ni(DPMDA) until maximum anodic shifting of the catalytic wave was observed. The same electrode was then rinsed with acetonitrile, and scanned in a 1:1 buffered solution with 0.25 mM Ni(DPMDA). It was observed that the catalytic wave began to shift to more negative reduction potentials with increasing scans. While triethylammonium is not expected to be able to protonate the pendant amine groups, it is anticipated that hydrogen bonding to the pendant groups on the electrode surface facilitates catalysis. Thus, the buffered solution may be disrupting catalytic activity by interrupting the necessary hydrogen bonding between the pendant groups on the surface and the acid in solution. This is further supported by recovery of the catalytic wave when the electrode was rinsed and placed in a non-buffered solution of only electrolyte and acid (**Figure 4.3.5**).

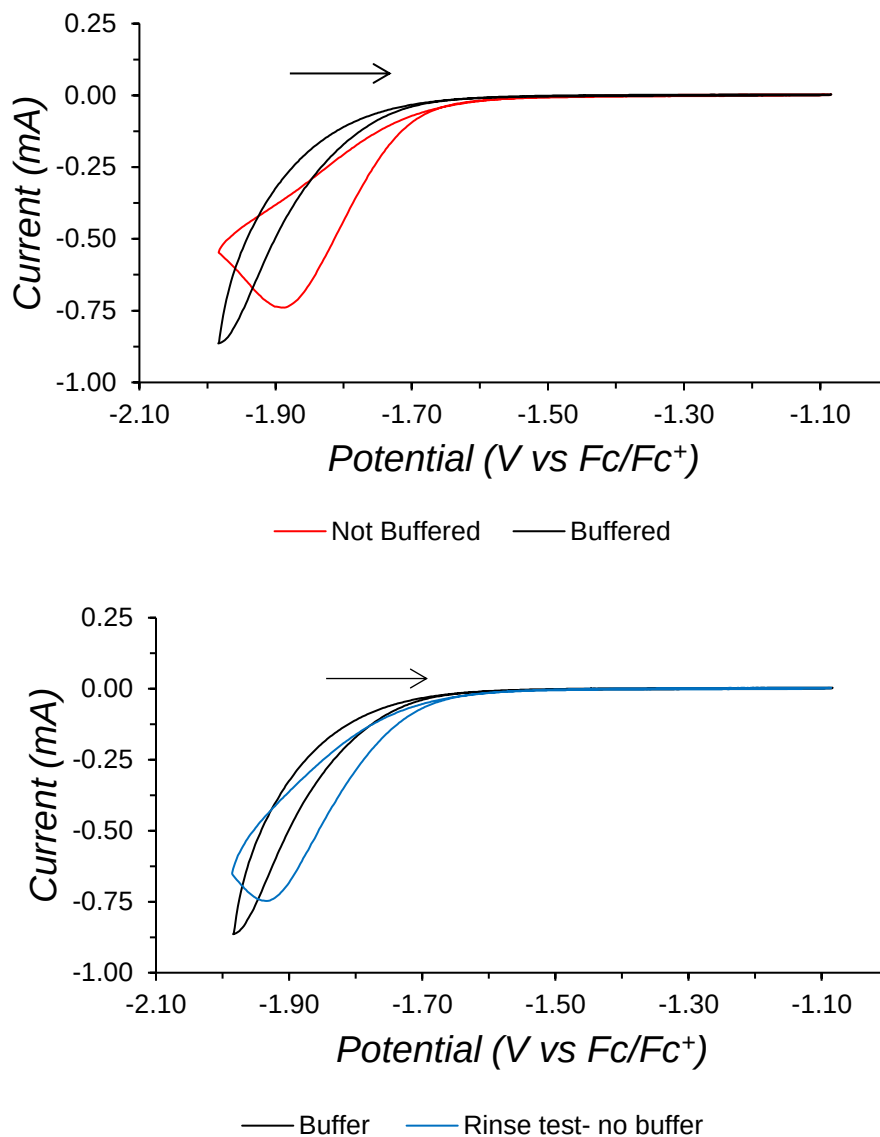


Figure 4.3.5. CVs of Ni(DPMDA) and triethylammonium tetrafluoroborate in non-buffered and buffered solutions (top) and CV of a rinse test without buffer after running in buffered solution (bottom). (0.1 M TBAP, 0 or 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, 0 or 25 mM triethylamine, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 1 V/s).

Next, we attempted to electrochemically characterize the adsorbed species. This was done by scanning the electrode under the conditions discussed above for catalyst adsorption, then rinsing with acetonitrile, and finally scanning in a fresh solution with TBAP electrolyte only (**Figure 4.3.6**). Surprisingly, no electrochemical response was observed, unlike the heterogeneous species formed in the presence of anilinium tetrafluoroborate. This lends further

support to the hypothesis that the two adsorbed species are significantly different in nature. This lack of an electrochemical response of the adsorbed catalyst is not unprecedented, as shown by Surendranath *et al.* with their covalently immobilized cobalt porphyrin system, which lacked redox features in water.²⁸ We can likewise hypothesize that the Ni(DPMDA) derived heterogeneous catalyst (in the presence of triethylammonium tetrafluoroborate) displays a similar strong electronic coupling with the electrode, as shown by the lack of redox features and its limited solubility in acetonitrile. Because of a lack of current response, estimation of surface area coverage became more complicated. To conservatively estimate the surface area coverage, a freshly polished electrode was subjected to the aforementioned adsorption conditions where it was repetitively scanned in 25 mM of triethylammonium tetrafluoroborate and 0.25 mM Ni(DPMDA) until anodic shifting of the catalytic wave had ceased. Then, the electrode was placed in a solution of only electrolyte and 0.25 mM triethylammonium (1 eq. of acid with respect to initial Ni(DPMDA) concentration, **Figure 4.3.6**). Under these conditions a current response anodic of the background reduction at glassy carbon was observed and a surface area coverage of $3.5 \times 10^{-11} \pm 4.0 \cdot 10^{-12} \text{ mol/cm}^2$ was calculated according to the following equation:

$$i_p = \frac{n^2 F^2}{4RT} v \Gamma^*$$

where i_p is the peak catalytic current in Figure 8, n is the number of electrons transferred, F is Faraday's constant, R is the ideal gas constant (in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the temperature in K, v is the scan rate in V/s, and Γ^* is the surface area coverage in $\text{mol} \cdot \text{cm}^{-2}$. In this case, because current response is derived from the addition of acid, and not the complex directly, we assume a two electron transfer process.

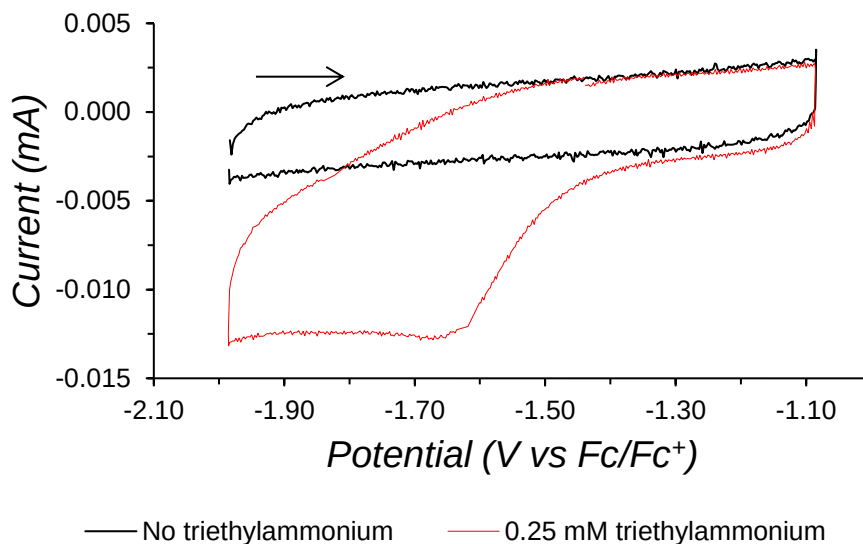


Figure 4.3.6. CVs of the Ni(DPMDA) modified electrode in electrolyte only solution or in the presence of 0.25 mM triethylammonium. (0.1 M TBAP, 0 or 0.25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 1 V/s).

To further probe the stability of the adsorbed species, as well as to confirm hydrogen evolution, controlled potential electrolysis experiments were carried out on the adsorbed species. First, Ni(DPMDA) was scanned in the presence of 100 eq of triethylammonium tetrafluoroborate until maximum anodic shifting of the catalytic wave was observed using a glassy carbon rod. The electrode was then placed in a fresh solution of 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, and electrolyte inside a bulk electrolysis cell. The potential was held at -1.87 V vs Fc/Fc⁺ (the average peak potential under adsorption conditions) until 1 coulomb of charge had been passed. Over a period of about 45 min, the observed current response slowly decreased indicating gradual decomposition of the active catalyst (**Figure 4.3.7**). Analysis of the graph of current vs time shows that initial current response (measured at $t = 2$ min to avoid capacitive charging currents) is 0.45 mA at which point 0.058 C of charge has passed. Halfway through the experiment, after about 20 min. when 0.5 C of charge had been passed, the current response dropped by about 16%. By the end of the 42 min. experiment, when 1 C of charge had passed, the current had dropped a bit more to a final reading of 0.36 mA (20% drop). Furthermore, given that the applied potential was not negative enough for catalyst formation, as evidenced by the aforementioned negative scanning experiments, it is feasible that

the decomposed surface catalyst was unable to be replenished by solvated Ni(DPMDA). Moreover, as shown in the buffered studies, another plausible explanation is that over the course of the bulk electrolysis experiment more conjugate base was generated, thus shifting the peak of the catalytic wave negative of the applied potential. Even so, headspace analysis after bulk electrolysis indicated a faradaic efficiency of $96.0 \pm 2.6 \%$.

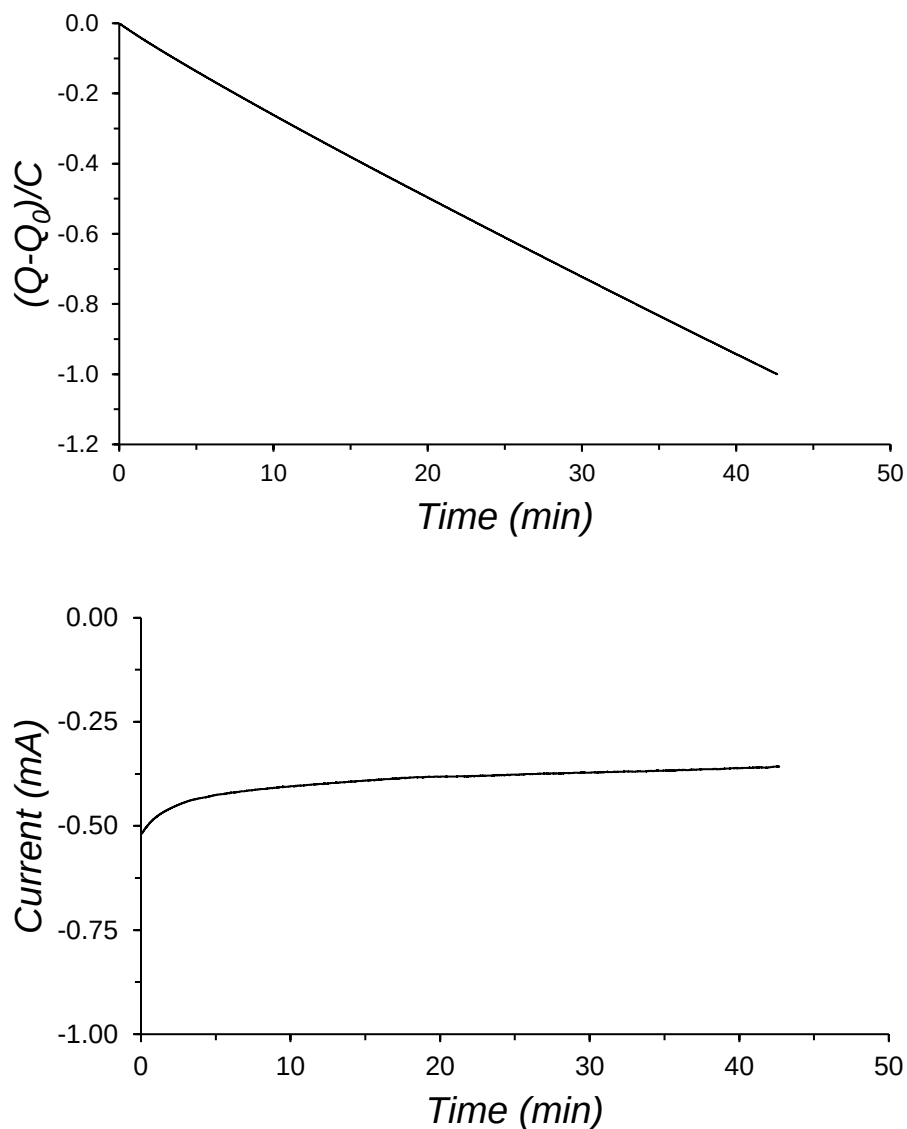


Figure 4.3.7. A representative controlled potential electrolysis experiment in acetonitrile showing charge passed over time (top) and current response over time (bottom) (0.1 M TBAP, 0.25 mM Ni(DPMDA), and 25 mM triethylammonium tetrafluoroborate with a 6 mm glassy carbon rod working electrode, 0.01 M Ag/AgNO₃ reference electrode; 0.1M TBAP, 5 mM

ferrocene with a 6 mm graphite counter electrode; 1 C of charge passed, potential held at -1.87 V vs. Fc/Fc⁺).

4.3.2 Kinetic Investigations

To optimize catalytic conditions, investigations examining the effects of acid concentration were carried out (**Figure 4.3.8**). Upon increasing acid concentration, an increase in current was observed. Interestingly, very little cathodic shift was observed in the catalytic peak potential, in contrast to the observations made in the presence of anilinium tetrafluoroborate. Additionally, a very slight anodic shift was observed at higher acid concentrations. Above 200 eq. (50 mM) triethylammonium tetrafluoroborate, the CV traces became very unstable with considerable current variation between scans. Since a stable CV was unable to be obtained above 200 eq. of acid, no plateau was observed. Nonetheless, current varied linearly with increasing acid concentration, which is suggestive of first order kinetics and a rate-limiting Volmer- or Heyrovsky-like step for a heterogeneous catalyst.^{46–48} Similarly, scan rate dependence tests were carried out (**Figure 4.3.9**). Upon varying scan rate, it was found that initially the catalytic current varied linearly with the scan rate, after which a plateau was observed at around 8,000 mV/s. Such high scan rate independence points are often associated with fast reaction kinetics. The linear variation with scan rate also agreed with the previously mentioned rinse tests, indicating the presence of a heterogeneous species.

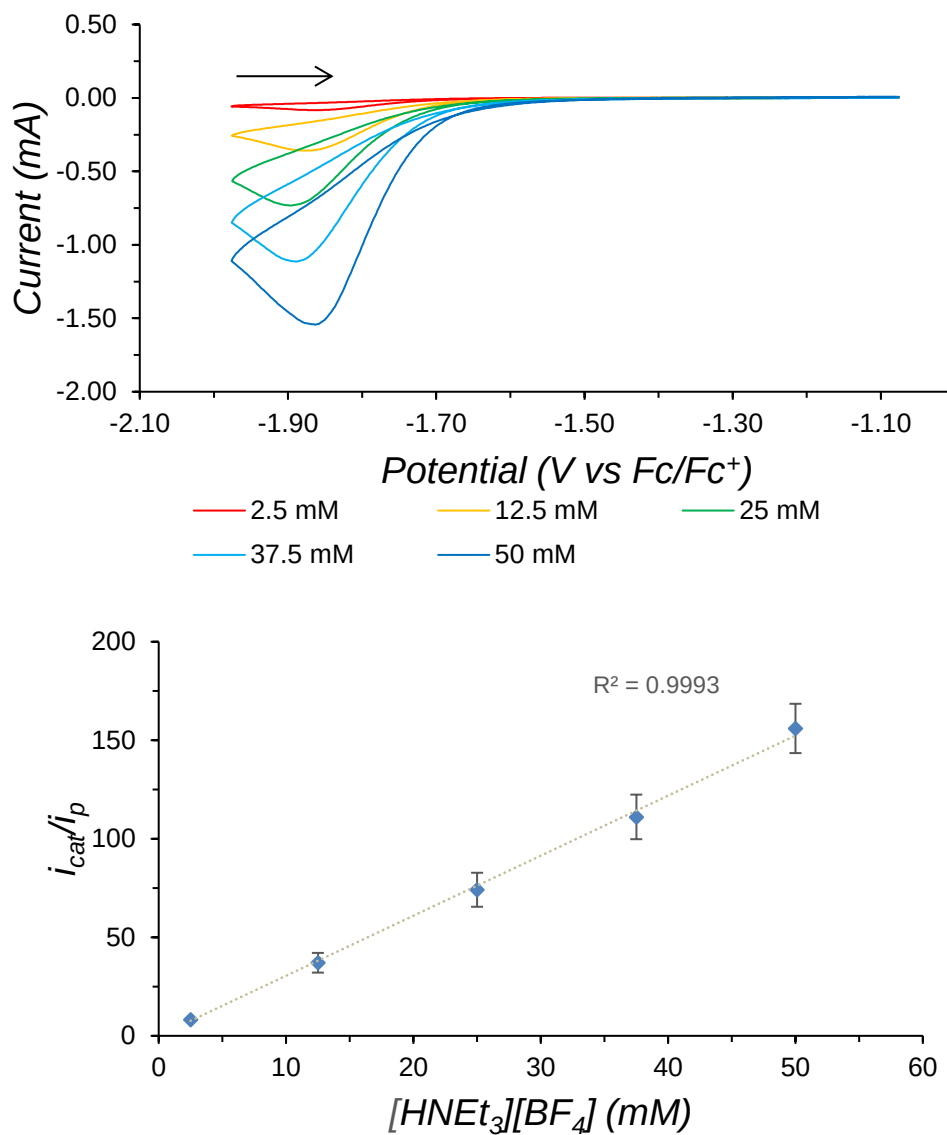


Figure 4.3.8. CVs of Ni(DPMDA) in the presence of increasing amounts of triethylammonium (top) and linear correlation of triethylammonium concentration with current response (0.1 M TBAP, 2.5 mM to 50 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate= 1 V/s).

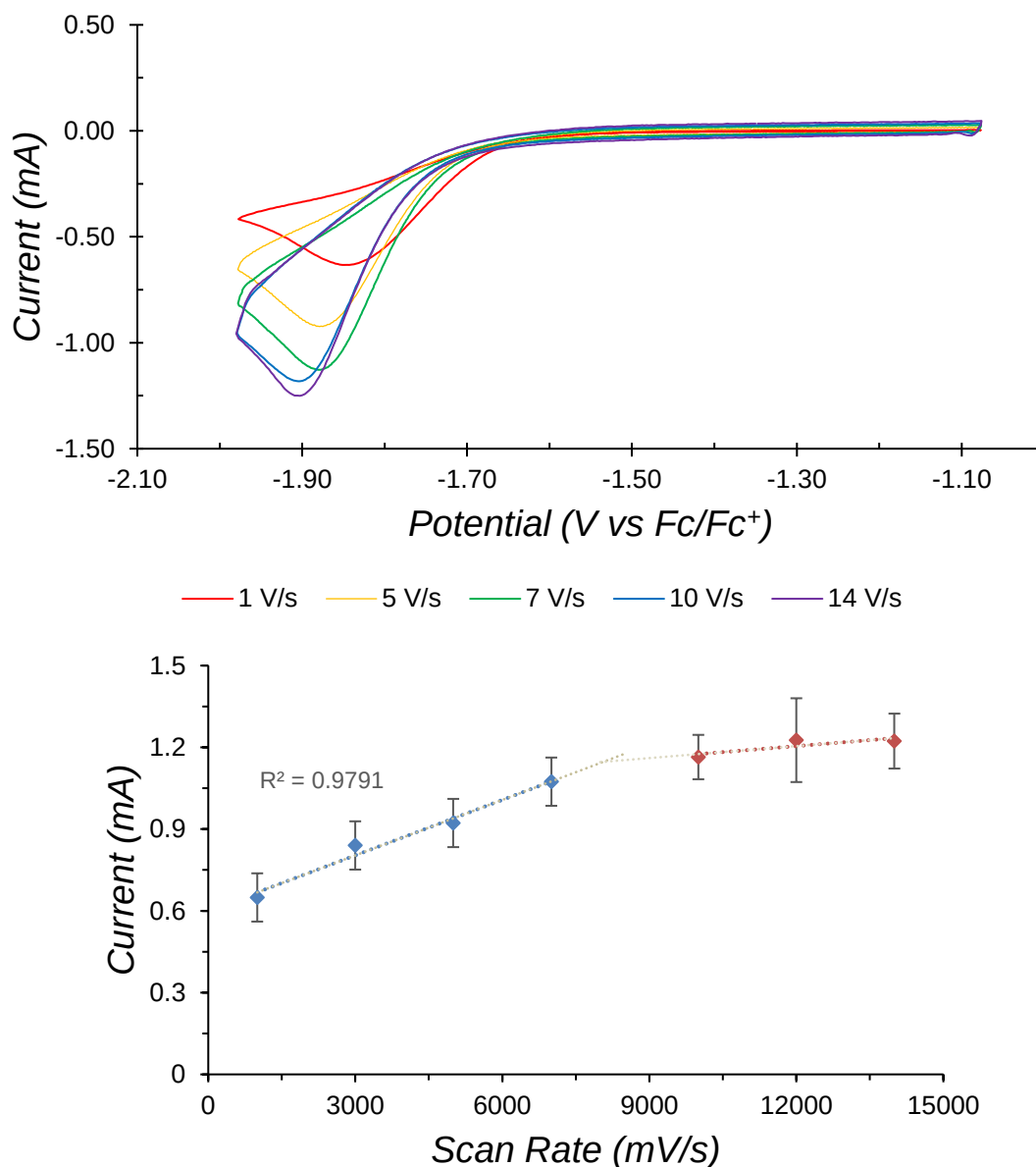


Figure 4.3.9. CVs of Ni(DPMDA) in the presence of triethylammonium at various scan rates (top) and graph of observed current vs scan rate (bottom) (0.1 M TBAP, 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate= 1 to 14 V/s).

Next, the effect of catalyst concentration was studied. Surprisingly, the peak current did not change significantly with varying catalyst concentration. Instead, a cathodic shift in the stabilized catalytic wave was observed with decreasing catalyst concentration (**Figure 4.3.10**). These observations are similar to results described by Dempsey *et al.* for their cobalt dithiolene

complex.⁴⁹ In this study, a catalytic wave appeared more anodic of the redox couple suggesting that substrate was completely consumed by a small amount of active catalyst prior to reduction of the remaining complex in solution. Furthermore, the authors observed that the peak position varied with the $\log([\text{catalyst}])$.⁴⁹ These results were also seen by Dempsey *et al.* in a homogeneous cobaloxime complex.⁵⁰ In these cases, a catalytic wave was observed which appeared more anodic of the redox couple. This response, referred to as total catalysis, derives from the small amount of active catalyst quickly consuming the substrate during the forward CV scan. Because of substrate consumption, a peak shaped response is seen.⁵¹ The relation between different wave responses and the parameters λ and γ is given by the kinetic zone diagram as derived by Savéant for a homogeneous one electron transfer.⁵² These parameters are related to experimental conditions by the following equations:

$$\lambda = \left(\frac{RT}{F}\right) \left(\frac{k_e C_p^\circ}{v}\right)$$

$$\gamma = \frac{C_A^\circ}{C_p^\circ}$$

where k_e is the homogeneous electron transfer rate constant, C_p° is the catalyst concentration, v is scan rate, and C_A° substrate concentration.⁵² For example, to transition from zone KT2 (peak shape described above) to zone KT1 (where the catalytic wave has shifted negative to obscure the redox couple, accompanied by substrate depletion) an increase in γ is necessary. Therefore, as shown in above, this can be achieved by increasing acid concentration or decreasing catalyst concentration. Likewise, zone KT2 stipulates a high λ value which may be achieved through higher catalyst concentration. Thus, these variables control both peak position and shape. Likewise, as derived by Savéant and Dempsey,^{50,53} peak position should be influenced by catalyst concentration for an EC(EC) (electrochemical step followed by a chemical step) mechanism for zones KT1 and KT2 according to the follow equation:

$$E_p = E^{\circ'} - \frac{RT}{F}(0.409) + \frac{RT}{2F} \ln \left(\frac{RT k_1 D_p (2C_p^\circ)^2}{F v D_A C_A^\circ} \right)$$

where E_p is the peak potential, $E^{\circ'}$ is the formal potential, k_1 is the rate constant of the first elementary chemical step, D_p is the diffusion coefficient of a homogeneous catalyst, and D_A is the diffusion coefficient of the analyte. In our case, while a plot of $\ln([\text{Ni}(\text{DPMDA})]^2)$ vs. peak

position or a plot of $\log([\text{Ni}(\text{DPMDA})])$ vs. peak position does yield a weak linear relationship, a stronger correlation is observed for the plot of $[\text{Ni}(\text{DPMDA})]$ vs. peak position. While these equations and zone diagrams are derived for homogeneous systems, some of the same principles have been invoked in heterogeneous systems.⁵⁴ Moreover, the schemes have also been extended to extract qualitative kinetic data from multi-electron/substrate reactions despite modeling a single electron/substrate reaction.^{49–51,55} Additionally, our observation that catalyst concentration controls peak position, which is similar to that seen in homogeneous systems in zone KT2, leads us to hypothesize that an initial EC step is occurring, possibly through proton-coupled electron transfer (PCET) aided by the pendant groups. However, because of the limitations for direct application of the above equation to our system, quantitative kinetic data cannot be extracted. Nevertheless, this leads us to ascertain that an increase in electrode adsorbed species is present with increasing solution concentrations of $\text{Ni}(\text{DPMDA})$.

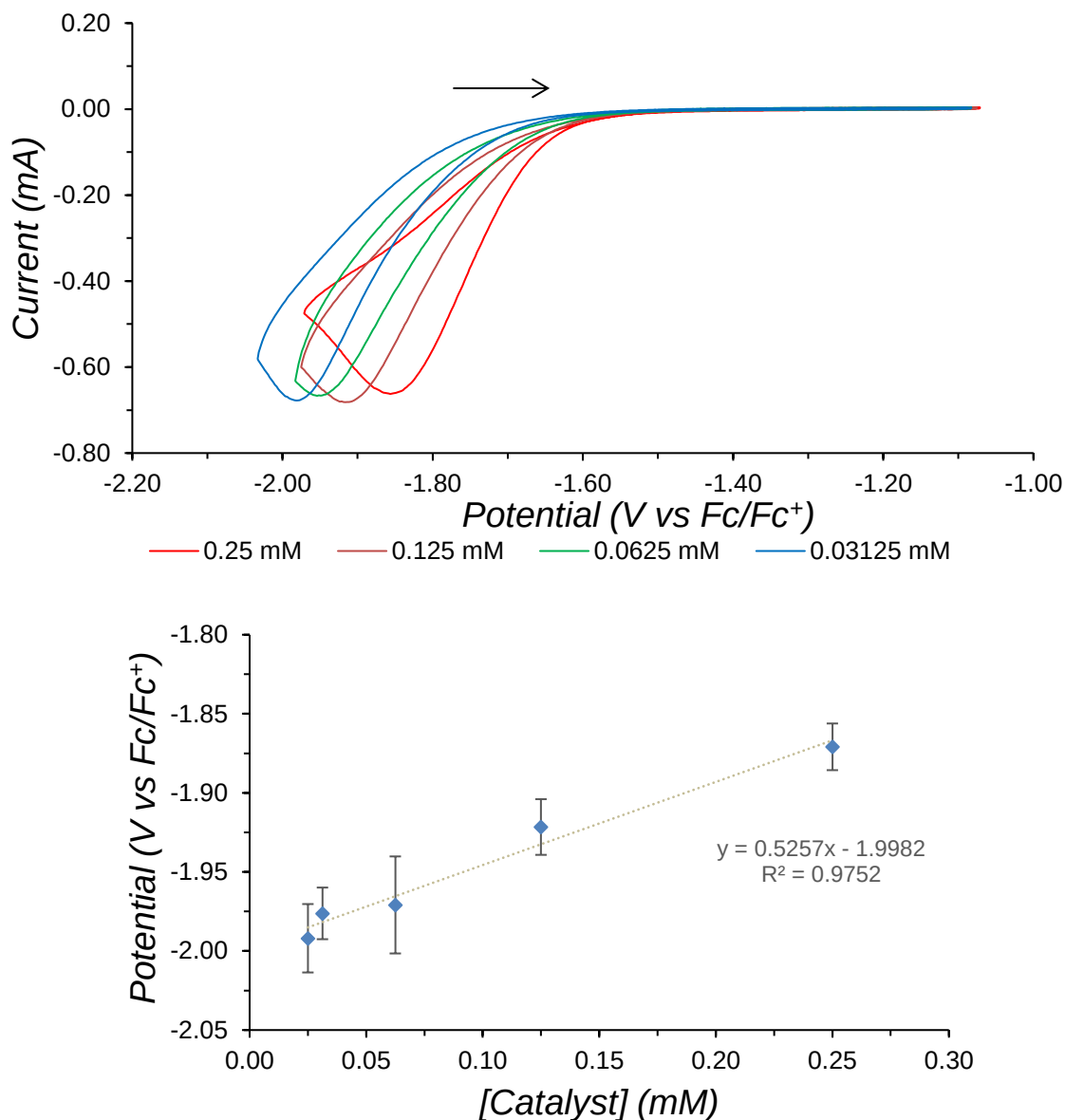


Figure 4.3.10. CVs of Ni(DPMDA) in the presence of triethylammonium at different catalyst concentrations (top) and linear variation of catalytic peak potential with varying catalyst concentration (bottom, 0.1 M TBAP, 0.025 to 0.25 mM Ni(DPMDA), 25 mM triethylammonium tetrafluoroborate, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 1 V/s).

The Ni(DPMDA) catalyst was also investigated by Tafel slope analysis (**Figure 4.3.11**). The Tafel slope was extracted from a linear sweep voltammogram (LSV) using a scan rate of 5 mV/s to minimize double layer charging effects.⁵⁶ A Tafel slope of 125 mV/dec was obtained, which is near the ideal slope of 120 mV/dec for a rate-limiting Volmer step. This suggested that

the rate-determining step could involve bond formation.⁵⁶ Further mechanistic investigation of the rate-limiting step was carried out through KIE studies (**Figure 4.3.12**), which revealed a primary H/D KIE value of 4.2 ± 0.7 . Such a large KIE value is often reflective of a PCET step,⁵⁷ and in conjunction with the Tafel analysis and a first-order dependence on acid concentration, these results suggest rate-limiting PCET and possible nickel hydride formation.⁵⁸

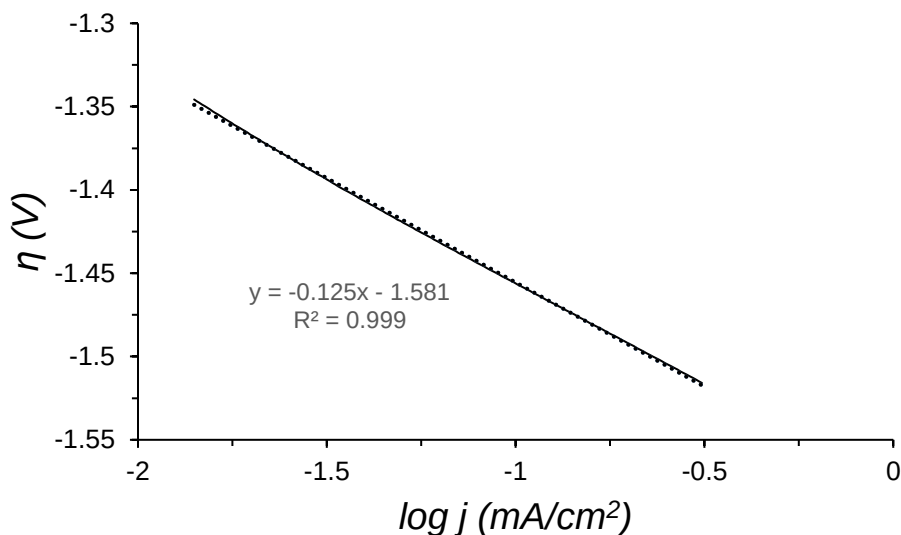


Figure 4.3.11. Tafel slope plot from LSV of Ni(DPMDA) at low current density region. (0.1 M TBAP, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 5 mV/s).

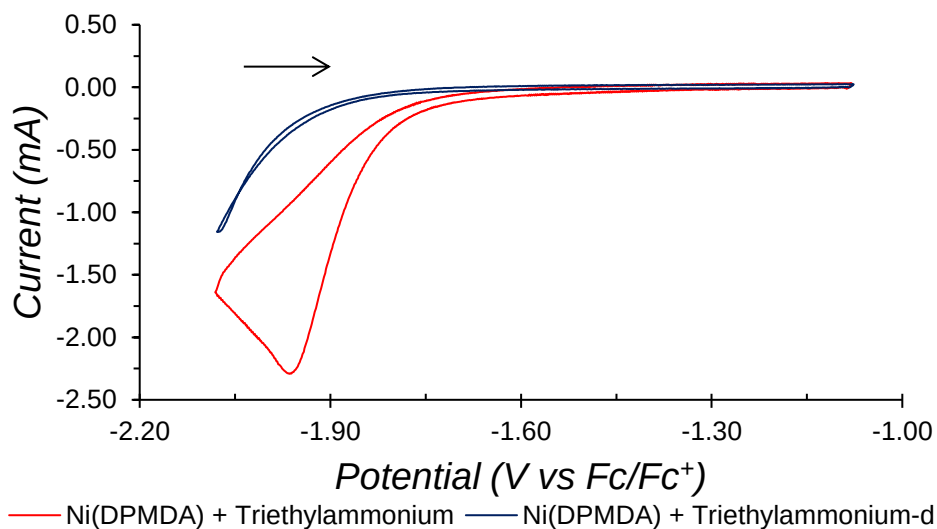


Figure 4.3.12. CVs of Ni(DPMDA) in the presence of triethylammonium or triethylammonium-*d* (0.1 M TBAP, 0.25 mM Ni(DPMDA), 50 mM triethylammonium tetrafluoroborate or triethylammonium tetrafluoroborate-*d*, glassy carbon working electrode, graphite counter electrode, 0.01 M Ag/AgNO₃ reference electrode, scan rate = 8 V/s).

Next, TOFs were estimated using CV with 50 mM (200 eq) of triethylammonium tetrafluoroborate and the scan rate independence point (8 V/s). Using the previously calculated surface area coverage, Γ^* , the TOF was estimated to be $4,900 \pm 800 \text{ s}^{-1}$ or $69,000 \pm 11,000 \text{ s}^{-1} \cdot \text{cm}^{-2}$ using the following equation:

$$TOF = \frac{j}{nF\Gamma^*}$$

where j is catalytic current density. Using this equation, we assume that all surface adsorbed species were catalytically active, and that catalysis exhibits a first-order dependence on surface catalyst concentration. This compares very favorably with heterogenized Ni bis(diphosphine) complexes, which achieved TOFs of 2-3 orders of magnitude less using much stronger acid sources.^{29,30,36,59-61} Moreover, this catalyst displayed higher TOFs than even the fastest platinum nanoparticles.⁶² In regards to overpotentials, for this system it was calculated using the following equations:

$$\eta = |E_{H^+} - E_{cat/2}|$$

$$E_{H^+} = E_{H^+}^\circ - 0.05916 \text{ V} \times pKa = -0.028 \text{ V} - 0.5916 \text{ V} \times 18.83 = -1.14 \text{ V vs. } Fc/Fc^+$$

where $E_{1/2}$ is the halfwave potential and E_{H^+} is the thermodynamic reduction potential for triethylammonium in acetonitrile, -1.14 V.⁶³ This analysis revealed an overpotential of 745 ± 5 mV. For comparison, Phipps *et al.* reported hydrogen evolution with a Ni(II) diacetyl-2-(4-methyl-3-thiosemicarbazone)-3-(2-pyridinehydrazone) complex in the presence of triethylammonium and observed an overpotential over 700 mV.³⁹ Likewise, a recent report of a Co(II) pyridinone complex, reported as the fastest cobalt hydrogen evolution complex in nonaqueous media, displayed an overpotential of 780 mV in the presence of triethylammonium.⁶⁴ Additionally, a Co(II) polypyridyl complex reported to mediate proton reduction from triethylammonium through a ligand-centered reduction, exhibited overpotential of 890 mV at the halfwave potential.⁴⁴

Molecular design of heterogeneous catalysts is advantageous in that it combines advantages of homogeneous catalysts such as greater control over the primary, secondary, and outer coordination spheres, with advantages of heterogeneous catalysts such as simple separation of catalyst from the product, and the ability to catalyze reactions in solvents where the parent complex is not soluble.⁶⁵ Conveniently, the catalyst reported here is easily adsorbed to the electrode surface in the presence of triethylammonium tetrafluoroborate at reducing potentials. This facile electrode preparation is advantageous in comparison to other methods of electrode attachment such as covalent linkage or π - π stacking via aromatic appendages as immobilization is easily achieved under catalytic conditions and does not require additional synthetic strategies for catalyst immobilization. Additionally, this adsorption was accompanied by strong electronic coupling which helps to facilitate concerted proton-electron transfer and lower overpotentials.^{28,66} In contrast, other molecular species anchored to electrode surfaces require specific electrode pretreatment/preparation and specially designed covalent linkers to establish strong electronic coupling with the electrode.^{26,28,66,67} Similar to the previously reported Ni(DPMDA) catalyst in the presence of anilinium tetrafluoroborate, the heterogeneous catalyst studied here exhibited a Volmer-like concerted proton-electron transfer step.⁴³ Thus, it is likely that the surface catalyst is either operating through a rate-limiting PCET ligand-centered pathway, or through a Ni-H intermediate generated by rate-limiting PCET. Importantly, the Tafel analysis revealed a smaller Tafel slope than that of the previously reported complex meaning less overpotential was needed to increase current density by a factor of ten. This can be rationalized

by the strong electronic coupling exhibited where, once the catalyst was adsorbed, negative potentials were not necessary to reduce a surface-bound redox active species, but only to drive protons across the electrode double layer. Thus, in this case lower overpotentials were achieved despite the use of a weaker acid.

Given that catalysis and adsorption precede the $\text{Ni}^{\text{III/I}}$ redox couple, as well as the evidence above, this suggests that the initial adsorption may occur through a ligand based PCET reduction. The appearance of a catalytic wave that shifts positively indicates that a small amount of surface catalyst relative to the amount of $\text{Ni}(\text{DPMDA})$ in solution is present. Once adsorbed, the catalyst exhibits strong electronic coupling with the electrode surface allowing proton reduction at increasingly positive potentials, as more catalyst slowly forms on the surface with increasing scans, until stabilization of the catalytic peak potential. While direct protonation of the ligand is not observed with triethylammonium, buffered studies indicated that the pendant groups may still be involved in hydrogen bonding even after the catalyst has already been immobilized. This suggests that they remain intact on the electrode adsorbed species. Although the fate of the electrode adsorbed species is not entirely clear at this point, the evidence seems to suggest that the pendant groups may help to increase the concentration of protons in the electrode double layer through hydrogen bonding interactions. Additionally, it is feasible that the lower TOF reported here in contrast to $\text{Ni}(\text{DPMDA})$ in the presence of anilinium is due to the inability of triethylammonium to protonate the ligand effectively.

4.4 Conclusions

In summary, electrocatalytic hydrogen evolution by the previously reported $\text{Ni}(\text{DPMDA})$ complex in the presence of a weaker proton donor (triethylammonium tetrafluoroborate) was explored. Interestingly, catalysis proceeded at lower overpotentials than with anilinium tetrafluoroborate as the proton donor. Through rinse tests it was found that rather than accessing a homogeneous pathway, instead a heterogeneous catalytic species was formed on the electrode surface. The activity of the adsorbed species was found to be less stable than a previously reported catalyst that formed from $\text{Ni}(\text{DPMDA})$ in the presence of anilinium tetrafluoroborate. Other features that distinguish this species are the more positive reduction potentials required to adsorb the catalyst and strong electronic coupling to the electrode surface.

The kinetic properties of this catalytic system were further explored by varying scan rates and concentrations of triethylammonium tetrafluoroborate. It was found that a scan rate independence point was observed near 8 V/s and that the catalyst exhibited first order kinetics with respect to acid concentration (indicative of a rate-limiting Volmer- or Heyrovsky-like step). Surprisingly, varying the concentration of Ni(DPMDA) in the bulk solution did not significantly change the current response observed for hydrogen evolution. However, a cathodic shift of the catalytic peak position was observed upon lowering catalyst concentration. Similar to the results seen by Dempsey and co-workers,^{49,50} the change in peak position could be indicative of less active catalyst being formed with decreasing Ni(DPMDA) concentrations. Moreover, no plateau was observed up to 0.25 mM Ni(DPMDA), suggesting that the active species was not saturating the electrode surface, unlike what was previously seen with Ni(DPMDA) and anilinium tetrafluoroborate despite reaching similar surface area concentrations.⁴³ Additionally, TOF was calculated using the estimated surface area coverage, and found to be around $4,900 \pm 800 \text{ s}^{-1}$. While these rates are much faster than supported nickel diphosphacyclooctane complexes,^{29,30,59–61} they are slightly lower than the TOFs seen for our previously reported Ni(DPMDA) electrocatalyst generated in the presence of anilinium tetrafluoroborate, although anilinium has a much lower pKa in acetonitrile.⁴³ Perhaps even more exciting is the lower overpotential exhibited by this system, of only $745 \pm 5 \text{ mV}$ at the halfwave potential. This value also compares favorably against other recently reported electrocatalysts that evolve hydrogen in the presence of triethylammonium as the proton source.^{39,44,64} For other relevant literature comparisons, see **Table 4.4.1**.

To further understand the electrocatalytic properties of our catalyst, additional kinetic experiments were carried out. KIE studies using triethylammonium-*d* tetrafluoroborate indicated a primary KIE of 4.2 ± 0.7 demonstrating that nickel hydride formation may be rate-limiting. In agreement with this hypothesis was Tafel analysis data, which revealed a Tafel slope characteristic of a rate-limiting Volmer-like step. Additionally, controls using a buffered solution suggested importance of hydrogen bonding between the proton source and the active catalyst as evidenced by catalytic disruption when triethylamine was added as a competitive hydrogen bond acceptor. These results suggested that the pendant groups remained intact on the electrode surface as hydrogen bond acceptors and facilitated PCET despite not expected lack of direct

protonation of the pendant groups. Moreover, strong electronic coupling with the electrode surface was observed (as shown by a lack of outer-sphere electron transfer to the heterogenized active species), which is believed to help lower overpotentials and increase TOFs in comparison to the previously reported heterogeneous system generated using Ni(DPMDA).

Table 4.4.1. Comparison of Relevant Catalyst Parameters.

Catalyst	TOF (s ⁻¹)	O.P. (mV)	Acid	Reference
Ni(DPMDA)	4,900	745	[HNEt ₃][BF ₄]	This Work
Ni(DPMDA)	14,900	900	[PhNH ₃][BF ₄]	43
[(<i>term</i> -H)Fe ₂ (adt ^H)(CO) ₂ (dppv) ₂] ²⁺	58,000	510	CF ₃ CO ₂ H	10
CoHPX-CO ₂ H	N/A	~800	C ₆ H ₅ COOH	14
[Ni(P ^R ₂ N ^{CH₂pyrene} ₂) ₂][BF ₄] ₂ @ MWCNT	3.9	~280	H ₂ SO ₄	36
Ni(8P ^{Ph} ₂ N ^{ArNHS} ₂) ₂ @ GC	28	700	[(DMF)H] ⁺	30
Ni(DMTH)	6,200	740	[HNEt ₃][BF ₄]	39
Co ^{-NHC} U	13,700	780	[HNEt ₃][BF ₄]	64

4.5 Experimental

4.5.1 General Considerations

All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. Solvents were dried and deoxygenated under argon using a LC Technology Solutions Inc. SP-1 stand-alone solvent purification system. All alcohols were dried and distilled over activated magnesium (magnesium turnings and a crystal of iodine) under a nitrogen atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Sigma Aldrich, Acros Organics, or Alfa Aesar, degassed, and dried over activated molecular sieves prior to use. Ni(DPMDA)⁴³ was synthesized according to literature procedures and spectroscopic characterization matched reported data. All other reagents were purchased from commercial sources and utilized without further purification unless stated otherwise. CV measurements were recorded using a Bio-Logic model SP-50 potentiostat. Tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte and was recrystallized prior to use by slow addition of pentane into a THF solution followed by cooling in a freezer (-30 °C). The working electrode was a glassy carbon electrode or a mercury pool electrode; the reference electrode was a Ag/AgNO₃ non-aqueous

electrode (0.01 M in CH₃CN with 0.1 M TBAP); and a graphite rod was used as the counter electrode. The glassy carbon electrode was polished with 0.05 μ m alumina and washed with distilled water prior to each measurement. Electrochemical measurements were conducted at room temperature under an argon or nitrogen atmosphere and processed using EC-Lab V11.46. Ohmic drop was accounted for using the current interrupt method available in EC-Lab V11.46. Reported half-wave potentials were referenced to the Fc/Fc⁺ redox couple by adding high purity ferrocene to the sample solution. Controlled potential electrolysis experiments were also performed with a Biologic SP-50 model potentiostat and processed using EC-Lab V11.46. The working electrode was a 6 mm glassy carbon rod, the counter electrode was a 6 mm graphite rod, and the reference electrode was a 0.01 M Ag/AgNO₃ non-aqueous electrode (0.01 M in CH₃CN with 0.1 M TBAP). The amount of hydrogen produced was quantified using an ATO Inc. model ATO-SKY2000-H2 handheld gas detector (0 to 500 ppm) and a calibration curve derived from known volumes of ultra-high purity hydrogen gas (Airgas).

4.5.2 Electrocatalytic Hydrogen Evolution

The electrochemical conditions of the catalytic trials included 0.1 M TBAP electrolyte in acetonitrile, 0.025 mM to 0.25 mM of Ni(DPMDA), 10 to 200 equivalents of triethylammonium tetrafluoroborate (2.5 to 50 mM), and scan rates between 1 to 14 V/s. The three-electrode setup consisted of a glassy carbon working electrode, a graphite rod counter electrode, and a 0.01 M Ag/AgNO₃ reference electrode. All CVs were referenced versus the Fc/Fc⁺ redox couple. All CVs were recorded under an argon or nitrogen atmosphere in dry acetonitrile. For the “rinse” test results, the working electrode was removed from the cell following catalysis, rinsed with either acetonitrile or acetone solvent, and then placed in a fresh electrolyte solution without Ni(DPMDA) present (0.1 M TBAP and 50 mM triethylammonium tetrafluoroborate). To determine the kinetic isotope effect (KIE), triethylammonium tetrafluoroborate-*d* (50 mM) in acetonitrile-*d*₃ was utilized (0.1 M TBAP, 0.25 mM Ni(DPMDA)).

4.5.3 Controlled Potential Electrolysis

Prior to controlled potential electrolysis, CV experiments utilizing the glassy carbon working electrode (6 mm rod) were carried out in 0.1 M TBAP electrolyte in acetonitrile, 25 mM anilinium tetrafluoroborate, and 0.25 mM Ni(DPMDA) where the potential was scanned to

sufficiently negative potentials (- 1.9 V) to ensure catalyst deposition onto the electrode surface. The prepared glassy carbon working electrode was then placed into a sealed bulk electrolysis cell filled with a solution of 0.1 M TBAP in acetonitrile, 0.25 mM Ni(DPMDA), and 25 mM anilinium tetrafluoroborate, along with a 0.01 M Ag/ AgNO₃ reference electrode reference electrode. The graphite counter electrode, separated by a porous frit, was submerged in a solution of 0.1 M TBAP in acetonitrile and 5 mM ferrocene. Bulk electrolysis experiments were carried out at a controlled potential of -1.87 V vs. Fc/Fc⁺ until 1 C of charge was passed. The solution in the cell was then stirred for 1 h to ensure equilibration between the solvent and headspace before sampling.

4.5.4 Synthesis of Triethylammonium Tetrafluoroborate-*d*

To a solution of 5 mL (0.0358 mol) of triethylamine in 10 mL D₂O was added 5.6 mL of 20 wt% DCl/D₂O (1 eq) under an inert atmosphere. The reaction was stirred overnight and evaporated under reduced pressure. The resulting solid was then suspended in 20 mL of CD₃CN and 1.8763 g of NaBF₄ (1 eq) was added. The solution was stirred overnight, and the insoluble salts were removed by filtration. The filtrate was evaporated to dryness under reduced pressure to yield triethylammonium tetrafluoroborate-*d* as a white solid. Yield: 2.72 g (40 %).

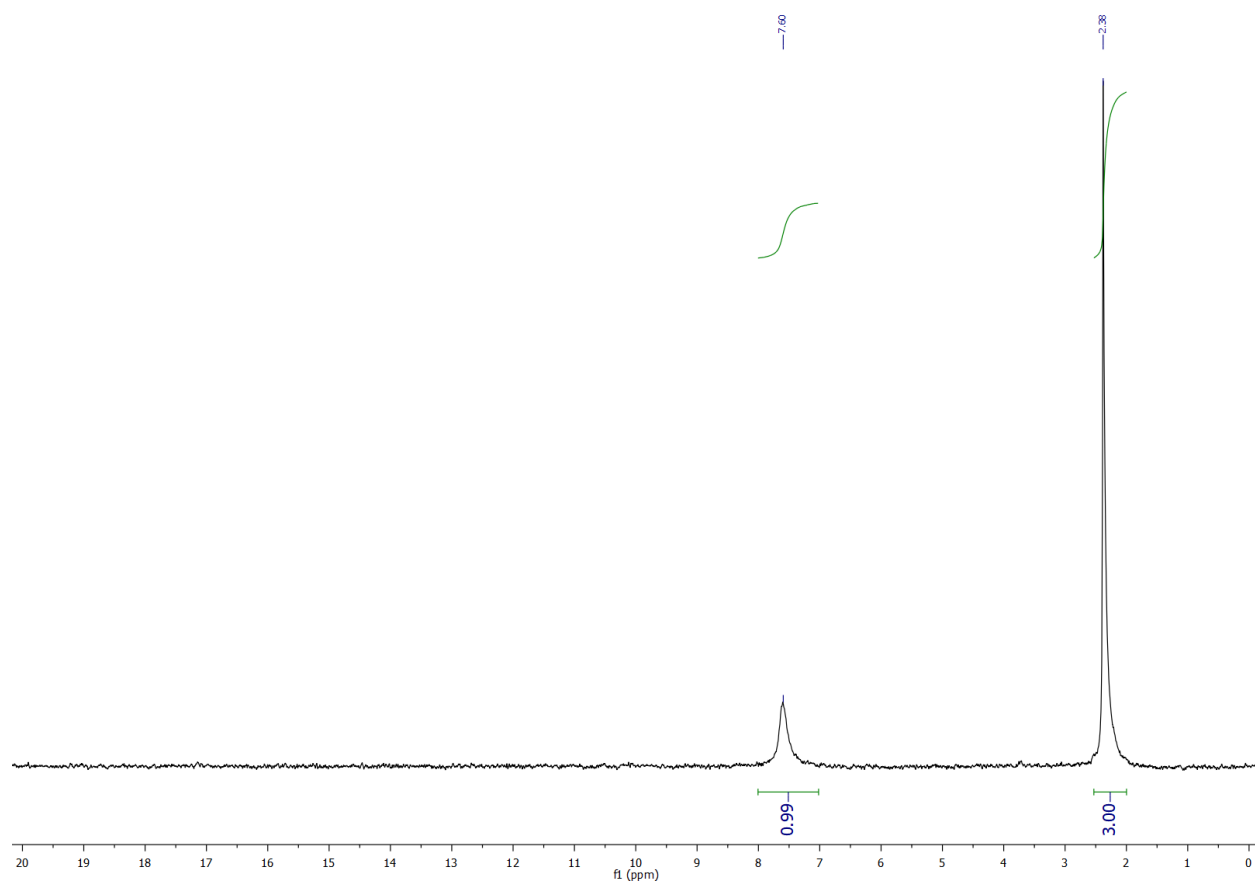


Figure 4.5.1. ^2H NMR spectrum (61 MHz, DME- h_{10}) of triethylammonium tetrafluoroborate- d with one equivalent of CD_3CN added as an internal standard.

4.6 References

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Chapter 5 – Conclusions and Future Directions

5.1 Conclusions

In Chapter 2, three novel calixpyrrole ligands with pendant nitrogen groups were reported. These ligands were successfully isolated after the condensation reaction of 5,5'-diformyl-2,2'-diphenyldipyrromethane and facilely sourced aniline precursors. The ligand architectures could accommodate substituents of various sizes, namely amino, acetamide, and *tert*-butylcarbamate, highlighting the flexibility of these ligands. This promising observation suggests that other substituents on the pendant groups may be utilized to tune the steric properties and basicity of the pendant nitrogen. Next, the three ligands were coordinated to palladium. Single crystal X-ray diffraction studies indicated a distorted square planar geometry. Significantly, the pendant nitrogens remained uncoordinated, yet were positioned near enough to the metal center to interact with potential axially bound substrates. Both the ligands and complexes were then characterized by cyclic voltammetry (CV) finding that the ligands exhibited redox non-innocent character. Similarly, density functional theory calculations found indicated that the oxidation state of the palladium center remained unchanged even after a two electron oxidation of the complex. Based off these results, it is likely that extensive conjugation throughout the complex is able to delocalize charge enabling ligand based-oxidations. Despite a lack of reactivity toward various substrates, the three complexes were found to generate heterogeneous hydrogen evolution catalysts on the glassy carbon electrode surface. With catalytic onset about 450 mV more positive than background reduction of *p*TSA, the catalyst was also surprisingly stable; for over 500 CV scans.

In chapter 3, the corresponding nickel complex, **Ni(DPMDA)**, bearing pendant amino functionalities was reported. Similar to the palladium complex, a distorted square planar geometry was reported, and electrochemical studies revealed similar ligand-based oxidations. In contrast, Ni(DPMDA) also exhibited two quasi-reversible features in the negative region attributable to $\text{Ni}^{\text{II/I}}$ and $\text{Ni}^{\text{I/0}}$ couples. In the presence of anilinium tetrafluoroborate, an irreversible reduction wave at a potential 400 mV positive of the $\text{Ni}^{\text{II/I}}$ couple. Upon increasing

the acid concentration, the single irreversible wave split into two irreversible waves and rinse tests of the electrode revealed the catalytic species was heterogeneous in nature. This deposition was found to require both acid and reducing potentials.

Further catalytic studies on the more anodic irreversible feature indicated a rate-limiting Volmer or Heyrovsky step due to first-order dependence on acid concentration. Interestingly, varying catalyst concentration yielded a linear correlation with peak current only at very low concentrations. Upon further increasing catalyst concentration, a plateau was observed indicating saturation of the electrode surface with the catalytic species. While this catalyst operates at large overpotentials of 900 mV, impressive TOFs up to $25,900\text{ s}^{-1}$ or $366,000\text{ s}^{-1}\cdot\text{cm}^{-2}$ were achieved while the catalyst also remained durable. These especially fast rates surpass that of previous reports of supported molecular catalysts.¹⁻⁶

Further analysis of Tafel slope and KIE suggested rate limiting proton discharge onto the electrode surface, or a Volmer-like step. Unlike previously reported catalysts that adopt this mechanism,⁷⁻¹⁰ this system showed to mediate hydrogen evolution through an outer-sphere electron transfer as evidence by the redox response of the adsorbed species in the absence of acid. It is reasoned that the pendant amines, intact on the electrode surface, influence the acid concentration in the double-layer thus providing access to a PCET mechanism despite weak electronic coupling.

In chapter 4, electrocatalytic hydrogen evolution with the previously reported Ni(DPMDA) with triethylammonium tetrafluoroborate. Similarly, a heterogeneous species was found to be responsible for the catalytic wave observed which shifted to more positive potentials with increasing cyclic scans in contrast to that reported in the presence of anilinium. Furthermore, rinse test results that found the catalytic species to be less stable initially distinguished this species from that discussed in Chapter 3.

Further kinetic studies with this complex similarly revealed first-order dependence on acid concentration suggesting rate-limiting Volmer or Heyrovsky steps. In contrast, variation of catalyst concentration did not significantly affect the current response, however a linear variation with peak potential was observed. While no plateau was observed in this case up to 0.25 mM **Ni(DPMDA)** potentially suggesting that higher surface coverages may be achieved with this species and that the two heterogeneous catalysts exhibit different morphologies on the surface.

Additionally, TOF values compared well to supported molecular nickel complexes^{1–3,5,6} however were about one order of magnitude smaller than reported in Chapter 3. However, overpotentials observed for this species were lower than reported in Chapter 3 despite the use of a weaker acid. In this case overpotentials of only 745 mV were observed which compares well to other recent reports of hydrogen evolution catalysts using triethylammonium.^{11–13}

The kinetics were further probed by KIE and Tafel studies which indicated a rate-limiting Volmer step and specifically rate-limiting PCET. Additionally, in contrast to the heterogeneous species reported in Chapter 3, electrochemical studies of adsorbed species revealed the absence of a current response with no acid suggesting strong electronic coupling with the electrode. Furthermore, buffered studies indicate that introduction of a hydrogen-bond acceptor into solution disrupts catalysis as evidenced by an immediate shift to negative potentials. Moreover, the catalytic response was able to be mostly recovered by placing the electrode back into a non-buffered solution. These observations implicate the pendant groups as proton acceptors/donors able to influence acid concentration in the electrode double layer. It is this principle which is expected to be able to facilitate lower overpotentials in the presence of a weaker acid, and along with the pendant amines, facilitate a concerted proton-electron transfer mechanism.

5.2 Future Directions

5.2.1 Electronic Tuning of Calixpyrroles

The presented calixpyrrole ligand architecture offers a modular synthetic route, which is amenable to various modifications. Currently, the presented ligand architectures produce metal complexes with particularly negative reduction potentials and accessing these reduction potentials possibly requires scanning past potentials cathodic enough to reduce the imine bond in the presence of acid. At this point, it is believed that this imine reduction may play a role in adsorption of a catalytically active heterogeneous species. Unfortunately, this complicates in depth catalytic studies aiming to elucidate structure-function relationships. Thus, modifications to the ligand architectures may allow access to homogeneous pathways. It is hypothesized that homogeneous systems can be accessed if more anodic reduction potentials can be accessed. Furthermore, if the reduction potentials of the metal can be shifted positive and homogeneous pathways can be accessed, overpotential could be diminished. One such way the electronic

parameters of the complexes may be tuned is through synthesis of various keto-substituted dipyrromethanes which can readily form imine ligands (**Figure 5.2.1**). These substitutions are proposed to have similar effects to the *meso* substituents on porphyrin rings, where electron withdrawing substituents produced complexes with more anodic reduction potentials.¹⁴ This is expected to be important in avoiding ligand reduction in the presence of acids. Furthermore, this could also be an avenue for reducing the overpotentials during HER.

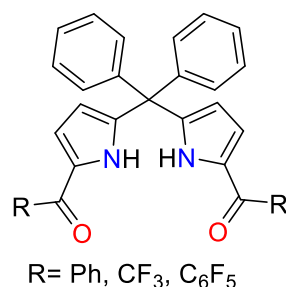


Figure 5.2.1. Structures of proposed substituted diketodipyrromethanes.

5.2.2 Cation Inclusion

Another way in which the reduction potential of the complexes may be tuned is through the inclusion of a cationic ion. One way in which this may be achieved is through that encapsulation of a metal cation within a crown ether moiety (**Figure 5.2.2**). Previous studies have shown that cation inclusion into the metal complexes can anodically shift redox potentials.^{15,16} Incorporation of a crown-ether would allow the complexation of 1⁺ and 2⁺ cations, which may facilitate the reduction of the complex.^{17,18} Cations may also be introduced to the ligand architecture is through quaternary amine salt formation (**Figure 5.2.2**). Previous studies have shown that inclusion of a positive charge in the secondary coordination sphere may help stabilize charged intermediates during catalysis, and other studies have found that remote positive charges cause an anodic shift in reduction potential of up to 600 mV.^{19–22}

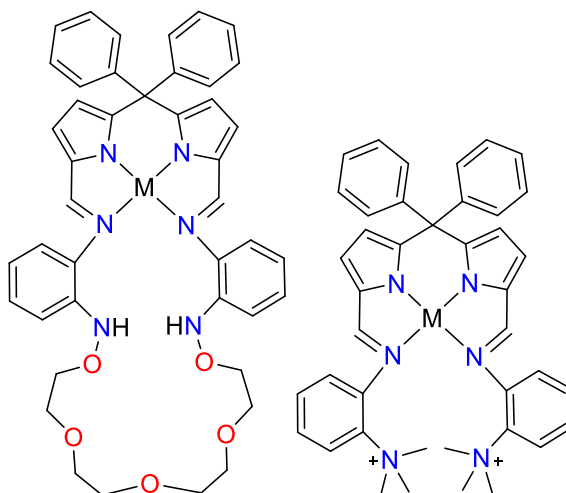
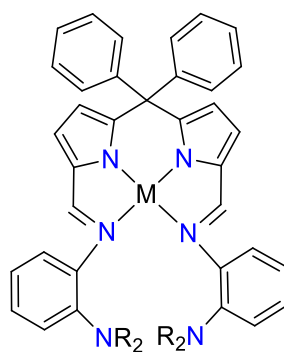


Figure 5.2.2. Proposed structures of a crown ether calixpyrrole complex (left) and of doubly cationic trimethyl anilinium complex.

5.2.3 Pendant Group Basicity

Lastly, these complexes can be modified through tuning the basicity of the pendant amines. As mentioned in Chapter 1, substituents on pendant amine groups have been shown to change catalytic properties.^{23–25} In these particular systems, increasing the alkyl substitution of the amine groups (**Figure 5.2.3**) could increase the basicity of the amines, and therefore electron donation through the conjugated ligand (perhaps making the imine moiety more difficult to reduce). Increasing the basicity of the pendant amines may also reduce the likelihood of protonation of the imine nitrogen. On this note, it is likely that increased amine basicity in these current systems would shift metal reductions to more negative potentials meaning there would likely be a tradeoff between amine basicity and reduction potential (due to extensive ligand conjugation). To this end, it would also be of interest to investigate various saturated alkyl amine pendant groups where the basicity could be tuned without greatly affecting redox activity of the metal center. It is hypothesized that if a homogeneous pathway can be accessed, while also being able to alter the basicity of the pendant amines, then the exact role and *pK_a* dependence of the pendant groups can be elucidated. With this in mind, it is clear that this novel ligand architecture offers a unique platform for which much more exciting research is possible.



R= Me, Et, iPr

Figure 5.2.3. Proposed structure of calixpyrrole complex with substituted pendant amines.

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