Inner and Outer Sphere Ligand Effects on Palladium Pincer Complexes as Electrocatalysts for CO₂ Reduction

by

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**Inner and Outer Sphere Ligand Effects on Palladium Pincer Complexes as Electrocatalysts for CO$_2$ Reduction**

submitted by Emile DeLuca in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

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Abstract

A series of novel palladium pincer complexes have been investigated for activity towards the electrochemical conversion of CO$_2$ to CO. Controlled variation of the inner and outer ligand sphere has provided mechanistic insight and valuable information towards rational ligand design for this variety of catalyst.

Stabilizing interactions between charged electrocatalytic intermediates and a host of cationic residues were explored through the synthesis and characterization of six isoelectronic palladium bis(N-heterocyclic carbene) (NHC) complexes bearing unique onium functionalities. The presence of a positively charged, pendant substituent was found to mediate electrode kinetics and facilitate CO$_2$ coordination to the catalytic center in a systematic fashion. Ultimately, the introduction of cationic moieties onto this system was shown to enhance catalytic selectivity for the conversion of CO$_2$ to CO by as much as 5 times that of an alkyl-bearing analog. A combination of electrochemical experiments and computational analysis demonstrate that catalyst performance is most benefited by a bulky onium unit tethered to the catalyst through a flexible linker. This behavior was interpreted as the preference for a wide, hydrophobic reaction pocket that allows for the unhindered formation of catalytic intermediates and mediated interaction with the solution.

With the aim of gaining better insight towards the influence of inner-sphere ligands on selectivity in palladium bis(N-heterocyclic carbene) CO$_2$ reduction catalysts, a novel, mixed phosphine-NHC complex was synthesized with variation in the fourth coordinate ligand and screened for activity towards the transformation of CO$_2$ to CO. The newly created structures were demonstrated to catalyze the reduction of CO$_2$ to CO in the presence of acetic acid with no
deactivation detected after several hours of electrolysis. In addition to exhibiting versatility in the palladium bis-(NHC) pincer motif, this marks the first report of a palladium pincer catalyst capable of sustained turnover of CO$_2$ to CO with the assistance of a weak acid.
Lay Summary

The global transition to a fossil fuel free energy network is imperative to limiting the influence of human-caused climate change and sustaining a livable planet. Existing technologies are capable of harnessing a host of alternative energy sources including wind, solar, tidal and geothermal to generate electricity that can be used to power homes, businesses and industry. However, finding methods for storing this power in a form that is useful for transportation has been challenging. One of the most promising approaches to this problem uses renewably generated electricity to convert atmospheric carbon dioxide into liquid fuels that may be used in the cars, planes and boats we pilot today. With the goal of realizing this technology on an industrial scale, the work presented in this thesis takes a chemical approach to optimizing the process of using electricity to transform carbon dioxide into usable fuels.
Preface

In all chapters I am the principle author of the work with Professor Michael O. Wolf acting in a supervisory role. I performed all experiments discussed in Chapters 2 and 3 with additional help from the collaborators listed below.

A version of the contents contained Chapter 2 are included in a manuscript in preparation. The work is authored by myself with contribution from Professor Michael O. Wolf. DFT calculations were performed by Zhen (Allen) Xu.

All of the experiments discussed in Chapter 3 were performed by myself with the exception of the crystallographic data which was collected by Dr. Brian Patrick and refined by Duane Hean.
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List of Symbols

\[ \Delta \] difference; heat
\[ \alpha \] charge transfer coefficient
\[ \text{Å} \] angstrom
Anal. Analysis
bpy 2,2'-bipyridine
BIP 2,6-bis((1H-imidazol-1-yl)methyl)pyridine
Bu butyl
\[ \text{\textsuperscript{n}Bu} \] linear butyl
\[ [\text{n-Bu}_4\text{N}]\text{PF}_6 \] tetra-\text{N}-butylammonium hexafluorophosphate
t-BuOK Potassium tert-butoxide
BE Bulk electrolysis
CAT catalytic conditions
C\[1\] single carbon molecule
Calcd calculated
CIF crystallographic information file
cod 1,5-cyclooctadiene
CNT carbon nanotube
CPCM conductor-like polarizable continuum model
CPE controlled potential electrolysis
CV cyclic voltammetry
Cy cyclohexyl
\textbf{C}^\text{N}\text{C} \quad \text{carbene-pyridyl-carbene pincer ligand motif} \\
\textbf{C}^\text{P}\text{C} \quad \text{carbene-phosphine-carbene pincer ligand motif} \\
d \quad \text{doublet} \\
\delta \quad \text{error; difference} \\
\text{DFT} \quad \text{Density Functional Theory} \\
\text{DMF} \quad N,N\text{-dimethylformamide} \\
\text{DMSO} \quad \text{dimethyl sulfoxide} \\
dt \quad \text{doublet of triplets} \\
E^{\circ} \quad \text{standard redox potential} \\
E_{\text{pcn}} \quad \text{cathodic peak potential of } n^\text{th}; \text{ counting increases falling in potential} \\
E_{p/2} \quad \text{half peak potential} \\
\text{Et} \quad \text{ethyl} \\
\text{Et}_2\text{O} \quad \text{Diethyl ether} \\
eq \text{molar equivalents} \\
\text{ESI-MS} \quad \text{electrospray ionization mass spectrometry} \\
\text{Fc} \quad \text{ferrocene} \\
\text{Fc}^{0/+} \quad \text{Ferrocene } 0/+ \text{ redox couple} \\
\text{FE} \quad \text{Faradaic efficiency} \\
\text{FID} \quad \text{flame ionization detector} \\
\text{GAA} \quad \text{glacial acetic acid} \\
\text{GC} \quad \text{gas chromatography} \\
\text{GJ} \quad \text{gigajoule} \\
\text{HBF}_4 \quad \text{tetrafluoroboric acid}
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR</td>
<td>high resolution</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>$i_p$</td>
<td>peak current</td>
</tr>
<tr>
<td>$i-V$</td>
<td>Current-potential scan</td>
</tr>
<tr>
<td>log</td>
<td>base 10 logarithm</td>
</tr>
<tr>
<td>LR</td>
<td>low resolution</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>$k$</td>
<td>rate constant</td>
</tr>
<tr>
<td>K</td>
<td>equilibrium constant</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>M</td>
<td>parent ion; molarity; metal</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Mes</td>
<td>mesityl</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>MS</td>
<td>molecular sieves; mass spectrometry</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NHE</td>
<td>normal hydrogen electrode</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>$\eta, \eta'$</td>
<td>overpotential; binding mode</td>
</tr>
<tr>
<td>OTf</td>
<td>trifluoromethanesulfonate</td>
</tr>
<tr>
<td>P$^+$</td>
<td>phosphonium center</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>Pc</td>
<td>phthalocyanine</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Redox</td>
<td>reduction/oxidation</td>
</tr>
<tr>
<td>ref</td>
<td>reference</td>
</tr>
<tr>
<td>rev</td>
<td>reversible</td>
</tr>
<tr>
<td>s</td>
<td>second(s)</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SOMO</td>
<td>singly occupied molecular orbital</td>
</tr>
<tr>
<td>sxt</td>
<td>sextet</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
<tr>
<td>TFA</td>
<td>2,2,2-trifluoroacetic acid</td>
</tr>
<tr>
<td>TFE</td>
<td>2,2,2-trifluoroethanol</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency</td>
</tr>
<tr>
<td>TON</td>
<td>turnover number</td>
</tr>
<tr>
<td>TPP</td>
<td>tetraphenylporphyrin</td>
</tr>
<tr>
<td>triflate</td>
<td>trifluoromethanesulfonate</td>
</tr>
<tr>
<td>triphos</td>
<td>triphosphine; bis(diphenylphosphinoethyl)phenylphosphine</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift (ppm)</td>
</tr>
<tr>
<td>v</td>
<td>scan rate</td>
</tr>
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</table>
Acknowledgements

I’d like to begin by thanking Professor Michael O. Wolf for his continued support as an accommodating, encouraging and genuinely engaged advisor. The pedagogy that is applied to our group provides a special environment for students to explore, understand and perform chemical research.

Each member of the lab has been a friend and wonderful to work with over the past two years. In particular, I want to acknowledge Chris Brown for acting as an excellent mentor in research and a great buddy outside of school. Additionally, I’d like to thank Duane Hean for his outstanding demeanor and ability to instigate stimulating conversation, Zhen (Allen) Xu for helping with DFT and teaching me about Confucius, Janet Ochola for her warm and jovial presence and Elise Caron for being an ambitious ski partner. I also want to mention Jasper Lam and the diligent work he performed under my supervision on a 449 project as well as the great sense humor he brought with him to lab.

Outside of the group, I’d like to thank Dan Bizzotto for his thorough and fundamental approach to teaching electrochemistry and Miguel Soto for helping with synthetic strategies and coaching a clean pick and roll on the basketball court. Also, thanks to David Wilkinson and the Wilkinson group for allowing us to use their GC and Maria Ezhova in the NMR lab for her help with designing experiments and assigning spectra.

Most importantly, I’d like to say that my mom, dad, two brothers and grandmother have and continue to be an enormous inspiration in my life. From nightly discussions at mandatory family dinner and Sunday forest marches to moving overseas on two occasions, being a son,
grandson and sibling to all of you has been a wonderful adventure and made me everything that I am.

Finally, I’d like to mention Leah. Growing up next to this beautiful, contemplative, patient and loving individual has been a gift and having you as a best friend is the biggest accomplishment of my life.
To Mom, Dad, Vince, Henry, Grammy and Andy
Chapter 1: Introduction

1.1 Background

For the past four and half billion years, Earth has been bathed in a persistent wash of radiant energy provided by the sun.\textsuperscript{1} The outer atmosphere currently comes in contact with an average of 340 Wm\(^{-2}\) of energy, having grown by \(\sim 30\%\) since the first signs of life.\textsuperscript{1,2} During this time, autotrophic microbial organisms slowly generated an oxygen-rich atmosphere that has dramatically altered the intensity and form of radiation that reaches the Earth’s surface. This process has been crucial to the evolution of terrestrial life and continues to provide a habitable environment for living organisms.\textsuperscript{1} Atmospheric composition also imposes a profound influence on the intensity of light that is reflected, scattered and reemitted to space. Collectively, the difference between incoming and outgoing fluxes of radiation accounts for the residual energy maintained within the planet’s system and governs the global energy budget. This sum is responsible for climate cycles and enables the chemical processes that constitute the Earth’s biogeochemical system.\textsuperscript{2,3}

Some of the solar radiation that reaches earth’s surface is absorbed and used by photo-autotrophic organisms in photosynthesis to drive the uphill conversion of water and carbon dioxide into energy-dense, organic molecules; a process that was greatly accelerated by the evolution of higher plants.\textsuperscript{1,4} The reduced carbon that is formed during photosynthesis is, for the most part, oxidized through numerous processes and cycled back to the atmosphere within a relatively short timeframe. Some of the energy, however, is stored in biomass (both living and dead). Under the right geological conditions, a portion of the reduced carbon becomes trapped below Earth’s surface, effectively removing it from physical and biological availability.\textsuperscript{5} This activity continued for hundreds of millions of years causing deposits to slowly accumulate until
they were discovered as an outstanding source of power during the industrial revolution.\textsuperscript{4,6} These reserves are commonly known as fossil fuels and have been mined and combusted for energy since the 1700s, thereby releasing the ancient, reduced C back into the atmosphere as CO\textsubscript{2} and H\textsubscript{2}O (Figure 1-1).\textsuperscript{7} The combustion of fossil fuels currently represents the vast majority of worldwide energy consumption and supplies the power for a global energy infrastructure that has developed around this cheap and highly available resource.\textsuperscript{8}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Average atmospheric CO\textsubscript{2} concentrations (black trace) and corresponding change in surface temperature (blue trace) dating back 800,000 years to 1950 determined from ice core samples. Values displayed after 1950 come from direct measurements. Adapted with permission from reference.\textsuperscript{9} Copyright (2010) American Chemical Society.}
\end{figure}

As a part of the atmosphere, H\textsubscript{2}O vapor and CO\textsubscript{2} absorb infrared radiation emitted by the earth’s surface and confine energy within the biosphere that would otherwise be reflected back to space.\textsuperscript{2} Although the exploitation of this high density fuel source has been beneficial to society in the short run, rapid and largescale combustion of geologically stored biomass is altering a
once stable carbon cycle and is beginning to fundamentally depress the flux of energy leaving earth.\textsuperscript{2,10} As a result, the mean global temperature has risen by an average of 0.8 °C over the past century, causing a growing concern about the future of the global climate.\textsuperscript{7,10,11} Since the 1970s this has been recognized as serious problem by the scientific community and efforts have grown to facilitate a transition to an energy economy that does not depend on the emission of CO\textsubscript{2} into the atmosphere.

![Figure 1-2](image)

**Figure 1-2.** Volumetric and Gravimetric energy density of several industrially available power sources. Plot was constructed from values provided in references.\textsuperscript{8,12,13}

### 1.2 Progress towards greener fuels

Perhaps the largest challenge of replacing fossil fuels has been their economic competitiveness. A diverse and high-volume demand for energy requires the fuel to be cheap and easily transported.\textsuperscript{8} In this respect, an ideal fuel is compact, possessing a high energy to
volume and weight ratio. Figure 1-2 displays the energy value of several industrially available fuels. The data displayed in this plot clearly demonstrate the high volumetric and gravimetric energy density possessed by the hydrocarbons: gasoline, biodiesel and natural gas relative to that which can be stored in a battery. Although the energy density of H₂ is large in terms of mass, H₂ retains a low per volume energy density as a liquid, making the large volumes associated with this fuel difficult to process and transport. In addition to possessing superior energy value, the cost to render and convert fossil fuels into a usable form is considerably cheaper than manufacturing either biodiesel, ethanol or hydrogen.

Table 1-1. Price in US dollars (USD) per Gigajoule of several commercially available fuels adapted from reference.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>USD/GJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>17.6</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>27.4</td>
</tr>
<tr>
<td>Electricity</td>
<td>16.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>22.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Electricity, on the other hand is often less expensive than gasoline and can be transported over long distances through powerlines. Electrical power is most often generated in coal and gas burning plants; however, recent gains in wind, solar and other non-CO₂ evolving power technologies have allowed the price of renewable electricity to become competitive with coal,
though storage and adaptation of renewable electricity for transportation systems remain a challenge.\textsuperscript{8,16}

The use of closed electrochemical cells to store electricity became commonplace during the mid-nineteenth century with the advent of the Daniel cell, a device that is now widely recognized as a battery.\textsuperscript{17} Despite undergoing vast technological advances since that time, the energy density of these devices remains rather limited due to the intrinsic weight associated with electrode materials (Figure 1-2, y-axis).\textsuperscript{12} For this reason, the application of batteries to store and transport renewable electricity on a large scale has been hindered while other strategies have evolved.\textsuperscript{18}

1.3 Electrochemical reduction of molecular substrates

Concomitant with the discovery of batteries was the realization that current could be used to drive homogenous chemical reactions, most notably the electrolysis of water to form hydrogen and oxygen first reported in 1800 by Nicholson and Carlisle.\textsuperscript{19} Electrolysis allows for the energy invested in chemical products by an external current to be separated, stored and used independently from the electrochemical cell, thus avoiding the issue of carrying the added weight of electrodes. However, the issue of handling hydrogen fuel persists in the case of water electrolysis.

The electrochemical reduction of CO\textsubscript{2} was first reported in 1870 when Royer was able to convert CO\textsubscript{2} into HCOOH at a bare Zn electrode with NaHCO\textsubscript{3} as a supporting electrolyte.\textsuperscript{20} Since that time, reduction of CO\textsubscript{2} into energy-added products has received significant attention and a diverse array of single carbon (C\textsubscript{1}) molecules have been generated electrochemically under a variety of conditions (Table 1-2).\textsuperscript{21,22} Perhaps the most significant and well-studied of these
transformations is the reduction of CO\(_2\) to CO. This reaction is of particular relevance to the energy sector for its use in the famous and industrially proven Fischer-Tropsch process (Equation 1-1).\(^{21,24}\) In this system, CO is combined with H\(_2\) to create the mixture syngas that is readily condensed over a catalyst to create long chain hydrocarbons, such as octane.

**Equation 1-1.** Condensation of hydrogen and CO into long chain hydrocarbons following the Fisher-Tropsch reaction.\(^{24}\)

\[
(2n+1)\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O}
\]

The net result of coupling a renewable electricity stream with the electrolytic generation of CO and H\(_2\), followed by Fischer-Tropsch catalysis, is the generation of a carbon-neutral fuel possessing an energy density equivalent to that of gasoline. Additionally, the fuel produced is fully compatible with the existing energy supply infrastructure. This process may prove to revolutionize the storage of renewable energy; however, considerable improvements in the efficiency of electrochemical CO\(_2\) activation are necessary for the technology to become economically competitive with fossil fuels.
1.4 Electrolysis of CO₂

The efficiency of an electrolytic reaction may be defined by the following parameters: overpotential (η) or the amount of additional voltage beyond the equilibrium potential that is required to drive a reaction of interest at an appreciable rate, Faradic efficiency (FE), defined as the stoichiometric ratio of product formed to the amount of charge passed from the electrode to solution and the overall reaction rate which is determined by the sum of rates for each elementary step.25,26,27 Complete electrolysis proceeds with 100% Faradaic efficiency at a high rate and small overpotential such that the minimum amount of energy is lost in the conversion of electrical to chemical energy.25

Table 1-2. Standard half-cell potentials of several H⁺ and CO₂ reduction reactions in water reported at pH 7 versus the normal hydrogen electrode (NHE).23 Corresponding standard potentials are estimated for non-aqueous conditions (CH₃CN) referenced to Fe⁰⁺ according to reference.28

<table>
<thead>
<tr>
<th>Half Reaction</th>
<th>Potential vs. NHE (V)</th>
<th>Potential vs. Fe⁰⁺ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ + 2e⁻ + 2H⁺ → CO + H₂O</td>
<td>-0.53</td>
<td>-1.16</td>
</tr>
<tr>
<td>CO₂ + 2e⁻ + 2H⁺ → HCO₃⁻</td>
<td>-0.61</td>
<td>-1.24</td>
</tr>
<tr>
<td>CO₂ + 4e⁻ + 4H⁺ → HCHO + H₂O</td>
<td>-0.48</td>
<td>-1.11</td>
</tr>
<tr>
<td>CO₂ + 6e⁻ + 6H⁺ → CH₃OH + H₂O</td>
<td>-0.38</td>
<td>-1.01</td>
</tr>
<tr>
<td>CO₂ + 8e⁻ + 8H⁺ → CH₄ + 2 H₂O</td>
<td>-0.24</td>
<td>-0.87</td>
</tr>
<tr>
<td>CO₂ + e⁻ → CO₂⁻</td>
<td>-1.90</td>
<td>-2.53</td>
</tr>
<tr>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>-0.41</td>
<td>-1.04</td>
</tr>
</tbody>
</table>

Table 1-2 lists several reduction reactions converting CO₂ to C₁ molecules that have relevance to energy storage. Two things should be noted when considering these data: 1) one-
electron reduction of CO₂ forms a radical anion and occurs at a considerably more negative potential than any of the two-electron reductions; 2) every higher order reduction is proton coupled, involving an equivalent number of proton and electron transfers. At a non-interacting (outer-sphere) electrode, formation of the one electron reduced species necessarily precedes any following step. Thus, regardless of the products formed, the reduction will require a very high overpotential. Additionally, the half-reaction for direct H⁺ reduction occurs at much less negative potentials and the requirement of protons in each reaction causes H₂ evolution to be a competitive process, potentially lowering Faradaic efficiency.

Due to the high energy associated with the one electron reduction of CO₂, an electrocatalyst is necessary to mediate the initial, electron-transfer step. Ideally, a catalyst will provide greater selectivity for electron transfer to CO₂ and improve the Faradaic efficiency towards the desired reaction (Scheme 1-1). Development of heterogeneous and molecular catalysts are currently active fields of chemical research. The discussion of catalysts in the following section will only focus on a survey of the molecular approach for its relevance to research presented in the thesis.
1.5 Electrocatalytic reduction of CO$_2$

**Scheme 1-1.** A generalized mechanism for homogeneously catalyzed CO$_2$ reduction. The black box on the left represents the working electrode and white to blue gradient signifies the interfacial diffusion zone transitioning to the solution bulk. Numbers indicate catalytic steps are referred to in the text. The schematic is adapted from descriptions provided in references.$^{26,31,32}$

Homogeneous electrocatalysts operate by mediating electron transfer (ET) between the electrode and CO$_2$ (Scheme 1-1). Generally, a cycle begins with an inert metal complex in its oxidized state (*step 1*). This species will then undergoes $n$ electron reductions at the electrode interface once the applied voltage is set to the appropriate potential (*step 2*).$^{26}$ The complex is now in the reduced form and is capable of performing electron transfer to CO$_2$ (*step 3*). In most cases, this proceeds through an inner-sphere mechanism wherein the CO$_2$ molecule becomes chemically bound to the catalyst.$^{29,32,33}$ The resulting adduct will undergo several homogeneous
steps (step 4), potentially accompanied by additional heterogeneous reductions until the reduced product is liberated and the catalyst is regenerated to its initial state (step 5). In this way, the potential at which the reaction proceeds is dependent on the redox properties of the catalytic system rather than that of CO₂.²⁹,³²,³³

An ideal catalyst for a specific transformation will exhibit fast electron transfer kinetics and possesses a formal redox potential that is near the E° of the reaction of interest. This way, a minimum amount of energy is consumed in electron transfer.³¹ Two terms for electrolytic performance are important when discussing electrocatalysis, namely, turnover frequency (TOF), the number of transformations achieved per catalyst per unit time, and turnover number (TON). TON is generally used as a metric for stability, describing the average number of cycles performed per catalyst molecule before deactivation; however, when TON is given for a specific duration of time, it can be considered as an approximation of TOF.²⁵

1.6 Complexes bearing macrocyclic ligands

A large number of metal complexes have been demonstrated as active electrocatalysts for CO₂ reduction over the past thirty years. The identity of the reaction product is determined by solution conditions and catalytic properties.³³,³² Due to the diversity of metal and ligand combinations that are capable of this transformation, it is useful to divide the discussion into classes based on a generic ligand type. Although more exotic and structurally complex catalytic systems have been reported, the majority of catalysts can be categorized as a metal center bearing one of the three following motifs: a macrocyclic ligand, a diimine ligand or a pincer ligand.³²
1.6.1 Metal phthalocyanines

The first account of CO$_2$ electrocatalysis by a metal complex came in the form of a short communication published in 1974 that discussed the current-potential (i-V) response to CO$_2$ of a graphite electrode dip coated with a metallophthalocyanine (MePc) (Figure 1-3). Although this system does not truly classify as homogeneous catalysis, several aspects of this study have had lasting importance in the field and are therefore worth mentioning.

![Figure 1-3. Linear sweeps of a cobalt phthalocyanine coated graphite electrode in solutions sparged with CO$_2$ (solid line) and N$_2$ (dashed line). Reproduced from reference 34 with permission from The Royal Society of Chemistry via Copyright Clearance Center.](image)

The authors demonstrated that the current measured in linear sweep voltammetry (LSV) through specific electrodes was significantly higher in the presence of dissolved CO$_2$. This was thought to indicate some form redox activity towards the substrate (Figure 1-3). The positive response in current to CO$_2$ was found to be unique to electrodes coated with cobalt and nickel phthalocyanines (Figure 1-4, 1 & 2) and the use of a quaternary ammonium supporting electrolyte was also found to benefit the observed catalysis. A discussion of reduction products
rendered here is brief and no attempt was made at quantification in this report. Nevertheless an occupied $d_{x^2}$ orbital was speculated to be critical to the activity of the MePcs, a notion that continues to be relevant to macrocyclic complexes.$^{33,35}$

Research on the electrocatalytic activity of MePcs for CO$_2$ conversion has been consistent since the first report in 1974 and remains an area of interest today.$^{35}$ However, a majority of studies have focused on complexes confined to an electrode surface by either physical or covalent attachment, likely due to the low electrochemical stability of MePcs in solution.$^{35}$ The most recent and scientifically advanced report of a MePc system demonstrated high stability, TOF and selectivity for CO$_2$ to CO reduction by a carbon paper electrode drop-coated in carbon nanotubes decorated with two immobilized variants of Co-phthalocyanine.$^{36}$ The authors attributed the unprecedented catalytic performance to an improved availability of the catalytic center and separation from direct contact with the electrode surface provided by the carbon nanotubes.

![Figure 1-4](image)

**Figure 1-4.** Left: generic structures of a substituted metal phthalocyanine. Specific complexes are numbered with associated R groups and metal indicated.
1.6.2 Metal porphyrins

Another class of complexes that received significant attention early on in CO\textsubscript{2} electrocatalysis research are closely related to MePc’s: metal porphyrins (Figure 1-5).\textsuperscript{33} Between 1977 and 1986 a number of studies examined the electrocatalytic performance of transition metals coordinated by substituted porphyrins.\textsuperscript{37,38,39} Although Ag and Pd porphyrins were demonstrated to possess some activity for this transformation (4, 5), Co-bearing porphyrins were found to be the most stable and active of the metal centers explored (6).\textsuperscript{35,37} Product distributions varied from HCOOH and oxalic acid, to CO, due to several factors including solvent, electrode material, ligand modification and metal center. Although these seminal investigations laid the groundwork for further research, mechanistic interpretation and speculation towards product selectivity were limited.\textsuperscript{33,35}

![Diagram of metal porphyrins]

**Figure 1-5.** Top: general structure of a metal porphyrin with R substituent groups and associated metal centers listed below with assigned complex number.
In 1988, Savéant, Hammouche, Lexa and Momenteau proposed a catalytic reaction scheme for the conversion of CO$_2$ to CO based on data collected from iron (II) tetraphenylporphyrin (TPP) (7) and ortho-substituted Fe(II)TPP basket-handle complexes (8) in an aprotic medium (Scheme 1-2). Their analysis suggested that the catalyst becomes active as an electrogenerated Fe(0) species (step 1). Once reduced, Fe(0)TPP undergoes an oxidative addition with CO$_2$ to form a carboxylate moiety with formal negative charges on the oxygen atoms (step 2). One of the oxygen atoms is then capable of nucleophilic addition into a second CO$_2$ molecule. The addition reaction forms a CO$_3^{2-}$ group that disassociates as carbonate to leave the complex as Fe(II)-CO (step 3). Elimination of CO in this pathway was found to be limiting due to the stability of the Fe(II)-CO intermediate and catalyst regeneration required two reductions or a reduction followed by a chemical step (steps 4, 5).

**Scheme 1-2.** Mechanism for the electrocatalytic reduction of CO$_2$ by iron tetraphenylporphyrin and related catalysts in an aprotic medium proposed by Hammouche, Savéant, Lexa and Momenteau in 1988. Steps are described by sequence in the text.
Although the overall rate and FE for CO were arrested by limited stability of 7 and 8, continued research by the same group would discover that addition of both weak Brønsted and alkaline Lewis acids dramatically improves catalytic performance.\textsuperscript{41,42} In both cases, the acid additive was thought to enhance catalysis by stabilizing the divalent carbenoid intermediate through H-bonding or ion-pairing, respectively.\textsuperscript{43,44} However, the presence of 2,2,2-trifluoroethanol was predicted to alter the reaction mechanism by favoring the dissociation of water rather than CO\textsubscript{3}\textsuperscript{2−}. As a result, catalyst lifetime improved by limiting Fe(II)TPP from precipitating with carbonate. This effect was less pronounced for Lewis acid additives. Faradaic efficiency for CO production in either system was determined to be 94 and 70\%, respectively, where the lower FE for a Lewis acid additive alone was caused by limited stability. It should be noted that this catalyst requires the use of a Hg electrode which does raise environmental concerns for potential use beyond a research setting.

Recently, the Savéant and coworkers reported unprecedented catalytic rates and low overpotential by substituting the phenyl groups in 7 for 1,3 benzenediol (10) and o-trimethylanilinium (9).\textsuperscript{45,46} Mechanistically, the effect of these substituents is analogous to that of the dissolved acid additives but with enhanced kinetic availability. A more in-depth explanation toward the importance of this research will be provided in Chapter 2.
1.6.3  Tetraazamacrocyclic ligands

![Diagram of tetraazamacrocyclic ligands and metal complexes]

**Figure 1-6. 11-15:** Metal complexes of the five tetraazamacrocyclic ligands examined in reference. Nickel cyclam is pictured on the far right as complex 16.

Shortly after the first reports of CO$_2$ electrocatalysis by metallophthalocyanines, a series of five tetraazamacrocyclic complexes of Co and Ni were surveyed for activity towards the electrocatalytic conversion of CO$_2$ (Figure 1-6, 11–15). Each complex was believed to operate homogeneously and demonstrated the capacity to generate a mixture of H$_2$ to CO. The ratio of H$_2$:CO produced was found to vary between 1:1 and 1:2 where complex 14 exhibited the highest selectivity for CO. In contrast to previous reports of molecular CO$_2$ electrocatalysis, several of the complexes explored in this study were remarkably stable and exhibited a trivial decrease in activity after 24 h of continual electrolysis in the presence of CO$_2$ and H$_2$O. Catalysis with these complexes was slow, however, and the observed rates were limited to 2–8 cycles per hour. Derivations of the motifs presented in this study continue to be the focus of scientific investigation. Perhaps the most encouraging result following this research came from a study in 1984 that investigated Ni$^{II}$ cyclam (1,4,8,11-tetraazacyclotetradecane) (Figure 1-6, 16). The first communication on this system reported the behavior of Ni$^{II}$ cyclam through long periods of electrolysis at a mercury electrode in CO$_2$ saturated, neutral aqueous solutions.
Quantitative yields for CO were measured and no catalyst degradation detected after 8000 cycles.\textsuperscript{51} In addition to demonstrating superior stability and selectivity, complex 16 expressed a TON of 1000 h\textsuperscript{−1} at a low overpotential (~0.5 V).\textsuperscript{52} This rate is two orders of magnitude larger than the previously reported tetraazamacroyclic complexes.

\begin{center}
\includegraphics[width=0.3\textwidth]{figure1-7.png}
\end{center}

\textbf{Figure 1-7.} Hydrogen bonding between cyclam ligand N-H group and a carboxylate intermediate in the proposed mechanism for the electrocatalytic reduction of CO\textsubscript{2} by Ni(II) cyclam.\textsuperscript{52}

In a second study, the mechanism of catalysis by 16 was predicted to be relatively similar to that described for 7 and 8, where a carbenoid intermediate is formed in the initial chemical step.\textsuperscript{52} However, complex 16 proceeds through two reduction events separated by chemical steps rather than the concerted mechanism described above. Nonetheless, cyclic voltammograms under CO\textsubscript{2} measured at increasing catalyst concentration uncovered that the peak catalytic current was only partially dependent on catalyst concentration and indicates that the active catalyst was adsorbed to the electrode surface.

Despite the apparent simplicity suggested by a two-dimensional representation, 16 exists in five isomeric forms. The particular conformation that exists as the surface adsorbed species was speculated by the authors as a critical aspect to performance.\textsuperscript{53} To further investigate structural contributions to catalytic behavior, the peripheral N atoms of the chelating cyclam
ligand were mono-methylated. The nickel complex produced by this modification was found to possess a considerably limited capacity for catalysis.

Based on this information, the mercury electrode was thought to promote a specific conformation of 16 that allowed for accessibility to the metal center and hydrogen bonding between carboxylate intermediates and the cyclam N-H protons (Figure 1-7). Further investigations into the electrocatalytic activity of Ni(II) cyclam would later confirm the hydrogen bonding hypothesis. However, the importance of a mercury electrode for this catalyst would also be supported which complicates the use of 16 in an industrial setting.53,54,55

Complex 16 and its structural analogs remain the most intensively studied tetraazamacrocyclic complexes for CO2 reduction owing to the outstanding catalytic performance by a coinage metal coordinated by a relatively simple ligand.29,32 Indeed, in many ways, macrocyclic complexes as CO2 reduction catalysts exhibit the best performance of any ligand class that has been investigated. In general, the catalysts operate at high rates, comparatively low overpotential and can be adapted to function in an aqueous medium with water acting solely as the proton source. Unfortunately, despite promising catalytic yields and compatibility with inexpensive solvents, many of these systems still require the use of mercury or an exotic electrode surface which presents an additional hurdle for their integration into power storage systems.36,53,56
1.6.4 Complexes with bipyridine ligands

Investigation of metal complexes bearing bipyridine ligands as catalysts for CO$_2$ reduction began in the mid-1980s with ruthenium and rhenium centered complexes (Figure 1-8).$^{57}$ Both Re and Ru analogs have been shown to operate as either electro or photocatalysts and their capacity to perform in both settings has been studied in parallel since this time.$^{58}$ Although photocatalytic conversion offers direct coupling of light energy to a C$_1$ fuel precursor, the chemistry and adaptation of this process differs somewhat from electrocatalysis$^{59}$ and will not be discussed directly here.

The general coordination environment employed in these systems has been quite consistent over the past three decades.$^{32}$ Unlike the macrocyclic themes discussed above, the diimine motifs are octahedral, containing one or two bipyridine ligands accompanied by an electro-labile donor (usually a halide) and 1–3 carbonyl groups.$^{32}$

The first report of CO$_2$ electrocatalysis by a bipyridine complex investigated the behavior of 17 in N,N-dimethylformamide (DMF) at a glassy carbon electrode with water as a proton
source. The catalyst was found to be quite stable over long periods of electrolysis (14 h), operating at −1.25 V vs NHE with a 98% current efficiency for CO formation. This communication was shortly followed by a more in depth study which sought to detail the mechanism of catalysis by a related complex, 18.

The product distribution generated by 18 is slightly different from the Ru system and primarily evolves CO in addition to small amounts of HCOOH and H₂. However, the mechanism proposed for CO formation serves as a benchmark for related catalysts and is described here (Scheme 1-3). In a wet DMF solution, 18 is believed to initially undergo a 2 e⁻ reduction that causes chloride to dissociate and opens up a coordination site for the oxidative addition of CO₂ (step 1). Following the binding step, the carboxylate intermediate undergoes two successive protonation steps to liberate H₂O, leaving the complex as the dicarbonyl species (steps 2, 3, 4). Finally, a two-electron reduction liberates CO and activates the catalyst for another cycle (step 5).
Despite the early success of 17 as a catalyst, it took more than 20 years before attempts at a less expensive metal center were published. In 2011, Deronzier’s group reported the electrocatalytic behavior of 19 towards CO$_2$ reduction and found the complex to be active at somewhat lower potentials than the Re(I) analogue. Through controlled potential electrolysis (CPE), the catalyst was determined to selectively reduce CO$_2$ to CO at a Faradaic efficiency of 85% and no side products were detected. However, the catalytic rate measured here was less competitive than 17. Significant deactivation through dimerization was also discovered in 17 and caused a 15% discrepancy in current efficiency observed in controlled potential electrolysis.

To address the issue deactivation through dimerization, Kubiak and coworkers modified the 2,2’-positions on the bipyridine ligand of 19 with mesityl groups in to form complex 20. The added steric bulk offered by the mesityl moieties was effective in curtailing dimerization; however, the large functionalities were found to simultaneously raise the overpotential of the
catalyst. Through careful examination of spectroelectrochemical data, the anodic shift in activity was demonstrated to be the result a Mn(I)–CO$_2$H intermediate that possessed a particularly negative reduction potential.$^{62}$ Ensuing research conducted by the same group would soon thereafter show that addition of Mg$^{2+}$ to the catholyte lowers the catalytic overpotential below that of unmodified 19 by acting as a Lewis acid co-catalyst (Figure 1-9).$^{63}$ However, catalytic rates were not fully restored at the lower overpotential.$^{62,63}$

**Figure 1-9.** CVs of 20 under CO$_2$ and 2,2,2-trifluoroethanol (TFE) (red) and N$_2$/TFE (blue). Expanded section: magnified 1 e$^-$ initiation wave and the influence of [Mg$^{2+}$] on the catalytic rate as evidenced by plateau current. Adapted with permission from reference $^{63}$ Copyright (2016) American Chemical Society.

In addition to the impressive catalytic performance of 17 and 20, the lack of a required Hg electrode makes these systems promising candidates for industrial scale up. Nevertheless, the interplay between stability, cost and catalytic rates afforded by variation in metal center and ligand design will require further optimization.
1.6.5 Palladium complexes of triphosphine pincer ligands

![Figure 1-10. Representations of basic palladium triphosphine pincer catalysts investigated by the Dubois group.][13]

Development of pincer ligand complexes as electrocatalysts for reduction of CO\(_2\) was largely pioneered by the Dubois group, beginning in the late 1980s. The first in-depth report of this chemistry surveyed three tridentate phosphine ligands coordinated to Ni, Pt and Pd to form a series of isoelectronic complexes (Metal[triphos]). The geometry of each complex varied from square planar to pseudo-tetrahedral and the fourth coordination site was systematically substituted with a variety of donors including CH\(_3\)CN, PEt\(_3\), PPh\(_3\) and P(OMe)\(_3\). The primary finding from this study was the discovery that only palladium centered complexes demonstrate activity towards CO\(_2\) reduction (21). Additionally, it was established that dissociation of the fourth coordinating ligand was essential to rapid catalysis. Palladium complexes of the appropriate design (structurally equivalent to 21) catalyzed the reduction of CO\(_2\) to CO with a Faradaic efficiency of ~75% (ensuing optimizations would later adjust this value to 98%). This species was also found to operate at very positive potentials, −0.75 V vs NHE. Unlike the
complexes discussed above, each Pd(II) triphosphine pincer complex explored required a strong acid (HBF₄) in a non-aqueous solvent in order to form CO catalytically.

Several years later, two investigations focusing on the behavior of Pd(II) triphosphine pincer complexes would further distinguish several important factors in catalyst design and action.⁶⁵,⁶⁷ In a 1994 publication, the pincer donor character was demonstrated to hold a strong influence on the electrochemical reactivity of the catalyst. Exchanging any single phosphine donor in the ligand scaffolding for N, As, O, S or C centers was found to deactivate CO turnover. In some cases, the complexes instead became catalysts for H₂ evolution. Another important aspect of this work found that the lability of the fourth coordinate ligand was critical to catalytic performance where stronger donors favored H₂ over CO generation.⁶⁵,⁶⁷

Scheme 1-4. Putative mechanism of CO₂ electrocatalysis by a generic palladium triphosphine complex. “Solv” represents a coordinated solvent ligand. Mechanism was adapted from Figures in reference. Steps are indicated by number in the text.⁶⁵
Applying a host of concentration dependent electrochemical experiments as well as spectroscopic measurements, the same research group was able to construct a putative mechanism for catalysis (Scheme 1-4).\textsuperscript{65} In similarity to 16, complex 21 becomes active after one electron reduction (\textit{step 1}), and binds CO\textsubscript{2} to form a carboxylate intermediate that is subsequently protonated (\textit{steps 2,3}). The protonated intermediate is then reduced, which causes the fourth coordinate ligand to disassociate (\textit{step 4}). After a second protonation step (\textit{step 5}), CO leaves and the complex is coordinated by a H\textsubscript{2}O molecule (\textit{step 6}). Finally, a solvent molecule is substituted for the aqua ligand and the catalyst is restored to its initial state (\textit{step 7}). The overall rate was found to have second-order dependence on H\textsuperscript{+} at low acid concentration and a first-order dependance in both catalyst & CO\textsubscript{2} at high HBF\textsubscript{4} concentration, a feature that is unique to this system. From these data, a second order rate constant was calculated (70 M\textsuperscript{-1} s\textsuperscript{-1}) which is equivalent to a turnover frequency of 280 h\textsuperscript{-1}.\textsuperscript{45,65}

Although 21 operates under very mild potentials at a reasonable rate, every structural variant of this catalyst was found to deactivate through the formation of a Pd(I)--Pd(I) dimer causing limited catalytic lifetimes.\textsuperscript{65} Several attempts were made to address deactivation, including variations on chelate bite angle, addition of bulky aryl groups (23) and substitution of ethyl-linked phosphonium residues (24) onto the ligand back bone.\textsuperscript{66,68} In each case, 21 was found to be the best catalyst; changes in bite angle caused for deleterious ring strain, the presence of a bulky aryl group crowded the catalytic center, and attachment of phosphonium groups had no effect on measured activity.
Dubois et al. also explored the possibility of cooperative catalysis between Pd[triphos] units by covalently attaching a number of Pd[triphos] centers through an assortment of linkers (Figure 1-11).\textsuperscript{69,70} Kinetically, profound enhancement in turnover frequency was observed for a binuclear complex of two Pd[triphos] constituents methylene linked through the central P of each pincer ligand (24).\textsuperscript{69} Through concentration–rate dependent studies the two metal centers were determined to operate synergistically, wherein one palladium center acts a nucleophile, binding through the carbon on CO\textsubscript{2} while the other metal center behaves as an electrophile, accepting an oxygen from the carboxylate-like intermediate.\textsuperscript{70} The observed rate constant for CO production in this bimetallic system was two orders of magnitude larger than that of the monomeric species.\textsuperscript{69} However, the rate of Pd(I)–Pd(I) deactivation was also enhanced by the close vicinity of a second catalytic unit which substantially diminished turnover number. A second binuclear permutation linked two bulkier Pd[triphos] units through the 1 and 3 positions of a benzene ring (25). This modification did improve turnover number beyond any of the previously reported catalysts, however, the added ligand bulk and fixed Pd–Pd separation did not allow for
cooperative catalysis and the observed rate of reaction in this case was similar to the monometallic complex.\textsuperscript{70}

The systematic investigation of Pd(triphos) carried out by Dubois and coworkers illustrates an encouraging potential for Pd pincer catalysts. In general, Pd triphosphine pincer complexes are extremely active and well-suited electrocatalysts for CO\textsubscript{2} activation under the appropriate conditions. However, after thorough examination, these catalysts appear to be temperamental, requiring an anhydrous environment and strong acid for efficient catalysis as well as an exotic structural solution for curbing deactivation. Nevertheless, this research is foundational in the pursuit of CO\textsubscript{2} electrocatalysts of Pd or any metal bearing a pincer motif.

1.6.6 Palladium bis(N-heterocyclic carbene) pincer catalysts

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pincer_catalysts.png}
\caption{26–28 were screened in an initial investigation of palladium bis(N-heterocyclic carbene) pincers for activity towards CO\textsubscript{2} reduction.\textsuperscript{71}}
\end{figure}

Since 2014, the Wolf group has studied a series of Pd(II)bis-N-heterocyclic carbene pincer complexes for their activity towards electrocatalytic CO\textsubscript{2} reduction. The ligand system consists of two NHC units bound to the 2- and 6- positions of a pyridine ring, creating a tridentate scaffolding with three neutral donors.
An initial investigation of this ligand system considered four quasi-square planar Pd(II) complexes bearing pincer ligands composed of imidazolilydene and benzimidazolilydene NHC units attached directly and methylene linked to pyridine with a chloride as the fourth coordinate ligand (Figure 1-12, 26–29). Each complex was found to undergo two sequential one-electron reductions at slightly more negative potentials than that of 21, wherein the halide ligand becomes labile after Pd(I) formation. Current enhancement was consistently observed in the presence of CO₂ which indicates electrocatalytic activity towards this substrate. However, the complexes that contained a methylene linked imidazolilydene-pyridyl backbone were the only species to demonstrate enhancement at the first reduction wave (Figure 1-12, 26–28). Addition of a strong acid to the CO₂ saturated solutions was found to generate a catalytic response in CV beginning at the first reduction event each complex. This behavior is consistent with that of related catalysts.⁶５,⁷¹ Controlled potential electrolysis experiments were carried out to determine FE and catalyst stability. While complexes 26 and 27 generated a ratio of H₂ and CO at both potentials and exhibited no degradation over a long period of electrolysis, 3 and 4 decomposed quickly with only trace amounts of CO produced.

Complexes 26 and 27 were exhaustively reduced electrochemically to the corresponding Pd(I) complexes to further investigate catalyst stability. Diffusion measurements carried out on the electrogenerated Pd(I) species determined the complexes to possess similar diffusion rates to the non-reduced species. This indicates the exclusive presence of a monomeric species and evidences that Pd(I)–Pd(I) formation, the major deactivation pathway in the previously reported palladium pincer catalysts, does not occur readily in this system.

Although the use of NHC donors appears to address the issue of deactivation observed in 21 and derived systems, complexes 26 and 27 were found to have considerably lower FE CO,
yielding ~10% CO at the first reduction event and ~30% CO at the second reduction event. The remainder of the current passed went to generate to H₂. Addition of Mg²⁺ to electrolysis solutions, however, improved selectively for CO by as much as 20% at the second reduction event. In similarity to previous work, the cation additive was believed to act as a Lewis acid and enhance performance by stabilizing anionic catalytic intermediates.⁷¹

In conclusion, the outstanding electrolytic stability of 26 and 27 is a step forward in the development of pincer complexes as CO₂ electrocatalysts, despite a comparatively low FE CO. Furthermore, harkening back to the development of iron tetraphenylporphyrin catalysts, it can be speculated that the positive response of these catalysts to a Lewis acid additive is a good indicator that considerable improvements can be made through systematic manipulation of the ligand system.

1.6.7 Summary of existing work and scope of thesis

The process of ranking electrocatalysts based on performance is difficult due to the number of factors in consideration. For every system there appears to be an interplay between overpotential, stability, rate and selectivity. Moreover, the nominal efficiency of a catalyst is often dependent on a non-scalable condition such as the requirement of a mercury electrode for many macrocyclic complexes and the use of HBF₄ in the case of 21.⁵²,⁶⁵,⁷² Nevertheless, Table 1-3 lists several catalytic parameters for a system belonging to each of the ligand families discussed in Chapter 1.
Table 1-3. Operating potential, turnover frequency, FE CO and electrolysis conditions tabulated for several well-studied and stable CO$_2$ electrocatalysts. \textit{a}: converted from a Fe$^{0/+}$ reference to NHE according to reference.$^{28}$

<table>
<thead>
<tr>
<th>Complex (#)</th>
<th>$E_{\text{CAT}}$ (V vs. NHE)</th>
<th>log (TOF s$^{-1}$)</th>
<th>FE CO (%)</th>
<th>Proton source/Solvent</th>
<th>Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoPc-CN/CNT (3) $^{36}$</td>
<td>$-0.6$</td>
<td>$0.61$</td>
<td>98</td>
<td>KHCO$_3$ / H$_2$O</td>
<td>Carbon/CNT</td>
</tr>
<tr>
<td>FeTPP-$\sigma$-TMA$^+$ (9) $^{72}$</td>
<td>$-1.3$</td>
<td>$6.0$</td>
<td>$&gt;99$</td>
<td>DMF / Phenol</td>
<td>Mercury</td>
</tr>
<tr>
<td>Ni$^{II}$ Cyclam (16) $^{52}$</td>
<td>$-1.0$</td>
<td>$1.2$</td>
<td>99</td>
<td>H$_2$O / H$_2$O</td>
<td>Mercury</td>
</tr>
<tr>
<td>Mn(mesbpy)(CO)$_3$Br (20) $^{62}$</td>
<td>$-1.4^a$</td>
<td>$3.7$</td>
<td>$98$</td>
<td>TFA/ ACN</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>Pd(triphos) (21) $^{63,45}$</td>
<td>$-0.7^a$</td>
<td>$0.7$</td>
<td>97</td>
<td>HBF$_4$ / DMF</td>
<td>Glassy carbon</td>
</tr>
</tbody>
</table>

The advances in knowledge and development of CO$_2$ electrocatalysts achieved over the past four decades have been substantial. Beginning from an observation that the presence of CO$_2$ increased current drawn from an electrode coated with a metal phthalocyanine, the stability and turnover rate expressed by several CO$_2$ electrocatalysts now surpass those of many industrial systems. The molecular of optimization of catalytic systems is well underway and progress towards large scale production will now require continued effort with an increasing focus on cost and environmental factors.$^{73}$

The work presented in this thesis takes two approaches in improving the catalytic performance of a palladium pincer complex that has been developed in our lab over the past six years. To better understand and address the intrinsically limited Faradaic efficiency observed in 26 and related catalysts, a combination of synthetic, electrochemical and computational methods are employed in Chapter 2 to model the influence of pendant onium functionalities on the stability and outcome of catalytic intermediates. The aim here is to simultaneously identify successful strategies for optimizing outer-sphere ligands while gaining an understanding of the underlying mechanisms that promote better catalysis by 26.
In Chapter 3, optimization of the redox behavior and catalysis using 26 are described by applying aspects of ligand design learned from palladium triphosphine structures to this system. Two new palladium pincer complexes were synthesized and screened for activity towards CO$_2$ reduction. The novel reactivity discovered in these catalysts was explored electrochemically with an emphasis on correlating redox behavior, electrolytic conditions and product output.
Chapter 2: Electrocatalytic Reduction of CO₂ Enhanced by Pendant Onium Arms with Palladium bis-(N-heterocyclic carbene) Pincer Complexes

2.1 Introduction

2.1.1 Secondary coordinate ligands in CO₂ reduction

Chapter 1 described a diverse collection of metal complexes that are known to electrochemically transform CO₂ into higher energy molecules. Although each system proceeds through a distinct catalytic cycle composed of a unique sequence of reaction steps, a partially charged and bent CO₂ adduct is believed to be formed during activation in most cases.¹¹,¹¹,¹¹ This often corresponds to an energy maximum and stabilization of the complexed CO₂ moiety through second coordinate sphere interactions is becoming increasingly recognized as a generalized strategy to improved activity.⁹,⁶,⁶ Addition of Mg²⁺ as a discrete Lewis acid has also been shown to enhance catalysis in diimine and porphyrin motifs through positive interaction with carboxylate adduct intermediates. However, the reaction isn’t strictly catalytic as MgCO₃ is formed as a byproduct.⁴,⁶³

Savéant et al. recently demonstrated a large electrocatalytic enhancement by tethering four o,o-phenol residues to iron porphyrin where the improved rate was attributed to a high local concentration of phenolic protons (8).⁶ The same group reported three years later the most efficient homogeneous CO₂ electrocatalyst to date by substituting the phenol functionalities with
positively charged $o-N,N,N$-trimethylanilinium groups (9). The gains were attributed to $\text{NMe}_3^+$-$\text{Fe-CO}_2$ ‘through space charge interactions’.\(^{46}\) Shortly thereafter, substitution of a methylene linked $N$-methyl-imidazolium onto a bipyridine ligand was demonstrated to lower overpotential and increase current density in an octahedral $\text{Re(bpy)(CO)}_3\text{Cl}$ system (Figure 2-1, 31).\(^{38}\) From the examples provided, it is evident that cooperativity with Lewis acids is not unique to a single class of $\text{CO}_2$ electrocatalysts. Despite the number of systems that have been reported to benefit from the presence of electropositive substituents, a systematic investigation probing structural and electronic variations of a tethered cationic unit has yet to be published.

![Figure 2-1](image)

**Figure 2-1.** Two examples of cationic outer-sphere ligands in $\text{CO}_2$ electrocatalysis.

The electrocatalytic behavior of 26 and related complexes has been studied thoroughly by the Wolf group since 2014.\(^{71,76,77,78}\) The redox properties of these complexes can be precisely controlled by ligand design, however, the presence of a cationic additive was found to be crucial to catalytic selectivity for CO that remained below 30% without an appending Lewis acid. In conjunction with the base of knowledge surrounding this catalyst family, the sensitivity of CO selectivity towards an external cation provides an excellent handle for quantifying the influence of secondary cationic ligands with FE CO as the independent variable.
2.1.2 Onium functionalized Pd[C^N^C] catalysts

Here we seek to understand how geometric and electronic factors influence the contribution of cationic, $N$-substituted outer sphere ligands on the performance of a palladium bis($N$-heterocyclic carbene) catalyst. A series of trimethylammonium, $N$-methyl pyridinium and triphenyl and triethylphosphonium functionalized catalysts were synthesized in order to complete a broad survey of cation type. Structural variations about the formal charge were also investigated to distinguish steric and electronic influences.

The four onium centers studied here were selected to span a range of ion hardness. Most alkylammonium ionic liquids are cathodically inert, however, aryl-phosphonium and methyl-pyridinium residues are reduced at reasonably positive potentials, where phenylphosphonium ions are reversibly reduced to form ylids.\textsuperscript{79,80} Accessibility to low-lying d orbitals differentiates P containing ions from their $N$-centered analogs and may allow for Lewis pairing with catalytic intermediates.\textsuperscript{80} This unique property of phosphonium and methyl pyridinium compounds may allow hard and soft ion stabilization to be distinguished, wherein, the electrochemically inert alkylammonium units are expected to interact through simple Coulombic attraction while interactions through phosphonium and $N$-methylpyridinium groups may possess molecular character. Nevertheless, when tethered to an identical and well-studied catalyst, controlled manipulation of ion character in this manner is expected to yield valuable information on the nature of this type of cooperative catalysis.
2.2 Results and Discussion

2.2.1 Synthesis of Complexes 32-36

Starting from the most basic analog of the palladium bis(N-heterocyclic carbene) pincer complex family, six new catalysts were synthesized by substituting the N-alkyl group for one of the charge bearing moieties described above (Figure 2-2). The synthesis of each ligand framework begins with heteroatom quarternization to form a cationic salt decorated with a side-group accessible for further reaction (see experimental section for further information). Quarternization early in the synthesis was found to limit unwanted product formation in later steps. In the case of the benzyl and alkyl linked groups, nucleophilic substitution of triaryl or alkyl pnictogens with a bis-bromo precursor afforded the desired salt in high purity and yield with an additional site available for bridging.

A nickel bromide catalyzed reaction was utilized to prepare ortho- and meta- substituted tetraphenylphosphonium bromide salts from triphenylphosphine and the corresponding bromobenzyl alcohol. The pendant alcohol was then halogenated through a modified Appel reaction yielding a mixture of chloro and bromo products, both of which were found to possess sufficient reactivity for the following reaction. The halogenated moieties were either condensed with imidazole under basic conditions and subsequently reacted with 2,6-bisbromomethyl pyridine or two equivalents were added to 2,6-bis((1H-imidazol-1-yl)methyl)pyridine, to form the C^N^C pincer ligand. Salt metathesis with KPF$_6$ was carried out at different stages in every synthetic pathway to aid with solubility in organic solvents.
Figure 2-2. Abbreviated synthetic route to each onium N-functionalized catalyst. Intermediates are labelled by the according complex number a subgroup designating to the step. Synthesis of 26 has been reported previously.\textsuperscript{71} Complexes 32-37 are listed below with corresponding \#. 
Finally, all ligands were metalated by Ag₂O–PdCl₂(cod) transmetalation with varying yields. All new compounds were characterized by \(^1\)H NMR, \(^{13}\)C \{\(^1\)H\}, \(^{31}\)P (where applicable) spectroscopies and high resolution ESI-MS; pro-ligands and metal complexes were characterized further by a combination of HSQC, HMBC, COSY NMR experiments.

2.2.2 Electrochemistry of 26 and 32-37 under N₂

The electrochemistry of each catalyst was initially evaluated by cyclic voltammetry (CV) in an anaerobic environment. All electrochemical measurements were performed at a glassy carbon electrode in DMF at a concentration of 2 mM with 0.1 M [n-Bu₄N]PF₆ as the supporting electrolyte. Potentials were measured with a Ag/AgNO₃ quasi-reference electrode and referenced internally to the Fc⁰/⁺ couple.

Complexes 32-37 all display two major reductions under nitrogen centered at ca. −1.8 and −2.1 V and a smaller anodic feature at 0.5 V that is associated with the first reduction event. CVs performed at scan rates up to 1.0 V/s failed to uncover reversibility in either reduction wave. Location of the two reductive peaks varied by as much as 150 mV depending on N-substitution (Table 2-1, Figure 2-2), where the onium bearing complexes were found to be reduced at appreciably lower potentials. Earlier work on 26 proposed the first and second cathodic features to be one and two electron reductions, respectively, while the anodic wave was assigned to freely diffusing chloride, liberated from the complex following the first reduction (Scheme 2-1).
Figure 2.3. Cyclic voltammograms of complexes 26, 32-37 [0.2 mM] in DMF collected at 100 mVs⁻¹ with 0.1 M [n-Bu₄N]PF₆ as the supporting electrolyte.
Scheme 2-1. Mechanism for the 1 e\textsuperscript{-} reduction of 26 followed by chloride elimination with associated rate constants.

These complexes are thought to dissociate chloride in the +1 oxidation state so it is tempting to attribute irreversibility to the ligand dissociation.\textsuperscript{77} However, close examination of the CVs in Figure 2-3 discloses fairly broad features. Half peak (E\textsubscript{p/2}) to peak separation (E\textsubscript{p1}) of the first waves are between 85–100 mV, depending on the modifying arm (Table 2-1). A large E\textsubscript{p}–E\textsubscript{p/2} value often indicates irreversibility of the redox couple, although an irreversible following chemical reaction can result in the same effect.\textsuperscript{31,82} In order to investigate this further, sweeps across the first reduction event were performed at increasing scan rate. Plots are displayed as the black traces in the insets of Figure 2-4.

E\textsubscript{p1} was found to shift negatively by \textgreater 45 mV with the log of scan rate, while a reversible electron transfer followed by an irreversible chemical reaction (EC mechanism) is expected to result in a shift of approximately 30 mV per decade change in scan rate.\textsuperscript{26} The strong influence of scan rate on peak potential distinguishes the CV response of this catalyst family as an irreversible electron transfer with a high kinetic barrier followed by a chemical reaction rather than the EC mechanism which assumes fast redox kinetics.\textsuperscript{82} The electron transfer coefficient, α, of an irreversible reduction may be estimated from the slope of ΔE\textsubscript{p} vs log (v) according to Equation 2-1.\textsuperscript{82} Values for α were calculated for each complex and are included in Table 2-1.
**Equation 2-1.** Calculation of charge transfer coefficient for an irreversible electrode process.\(^{82}\)

\[
\Delta E_p = \log \left( \frac{v}{\alpha} \right) \frac{30}{\alpha} \text{ mV}
\]

Half peak to peak separation of the second wave was found to be slightly smaller for complexes 26, 34, 35 & 36, while 32 and 33 show a larger half peak to peak separation. A control experiment was performed wherein CVs of each substituted pro-ligand were recorded under analogous conditions. Each proligand demonstrated an onset potential of ~ –2.3 V with a peak at –2.45 (Table 2-1) with the exception of 37. Therefore, it is possible that reduction of the cationic modifier is overlapping to a small extent with the second wave causing broadening. However, this effect will be small as the separation is >100 mV in every case.\(^{26}\)

**Table 2-1.** Peak potentials from CV measured at 100 mVs-1 of complexes 26, 32-37 with corresponding ligand peak potentials. Charge transfer coefficients, \(\alpha\), were calculated according to equation 2-1 and are tabulated with respective error.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{pc1} ) (V)</th>
<th>(\alpha \pm \delta \alpha)</th>
<th>(E_{pc2} ) (V)</th>
<th>Ligand (E_{pc} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>–1.84</td>
<td>0.40 ± 0.01</td>
<td>–2.40</td>
<td>vide Infra</td>
</tr>
<tr>
<td>32</td>
<td>–1.67</td>
<td>0.45 ± 0.03</td>
<td>–2.31</td>
<td>–2.43</td>
</tr>
<tr>
<td>33</td>
<td>–1.73</td>
<td>0.63 ± 0.04</td>
<td>–2.35</td>
<td>–2.43</td>
</tr>
<tr>
<td>34</td>
<td>–1.85</td>
<td>0.39 ± 0.01</td>
<td>–2.35</td>
<td>–2.50</td>
</tr>
<tr>
<td>35</td>
<td>–1.74</td>
<td>0.66 ± 0.03</td>
<td>–2.21</td>
<td>–2.46</td>
</tr>
<tr>
<td>36</td>
<td>–1.75</td>
<td>0.45 ± 0.03</td>
<td>–2.35</td>
<td>–1.59</td>
</tr>
<tr>
<td>37</td>
<td>–1.68</td>
<td>–</td>
<td>–2.41</td>
<td>–1.59</td>
</tr>
</tbody>
</table>

Scanning past the second reduction potential of each complex imposed a negligible influence on the intensity of the anodic wave corresponding to chloride oxidation. This indicates Cl\(^-\) disassociation is facile after Pd(I) formation, regardless of the N-modification.\(^{83}\)
Interestingly, $E_{p2}$ remains lower for complexes 32-36 relative to that of 26. It is unlikely that a Coulombic interaction between the positively charged pendant arms and a coordinated chloride is facilitating early reduction, given that Cl$^-$ elimination is expected to be complete before the second reduction. This is in contrast to a recent investigation that found linking an imidazolium residue to 17 altered reversibility by labilization of the halide ligand.$^{38}$ Here, it is likely the pendant onium groups are interacting with the electrode thus influencing the observed redox properties. Indeed, such an interaction would explain the broadened features at $E_{p2}$ of 32 and 33 where the smaller onium units may become absorbed to the electrode at higher potential causing lower electron transfer rates by forming a blocking layer.$^{26}$
2.2.3 Electrochemistry under CO₂

The CV response through the first wave of complexes 26 and 32-36 in 0.23 M CO₂ solutions are displayed in Figure 2-4 (dashed teal lines). Complex 37 is not included for reasons that will be discussed later. Peak currents measured under CO₂ ($I_{p1}$ CO₂) at $E_{p1}$ were considerably higher than $I_{p1}$ N₂ for every complex except for 35 and 37 (Table 2-2). Additionally, the anodic wave at 0.5 V was found to diminish in most cases and a new oxidative peak grows in between −0.5 and −1.0 V.

Scheme 2-2. Proposed reduction and binding mechanism of catalysts with solvated CO₂.

Irreversibility in the one electron reduction of complexes 26 and 32-36 is expected to cause the forward CV scan under CO₂ to appear unaltered from the response under N₂ unless the catalyst reacts with CO₂ to form a species that is electroactive near $E_{p1}$.

Therefore, any current increase brought on by the presence of CO₂ is most likely the result of an irreversibly generated Pd(I) complex reacting with CO₂ to form an adduct ($\text{PdCOO}^-$) that is active for a second reduction. In this situation, the observed peak will appear as a composite of both reductions, causing $I_{p1}$ CO₂ to increase with respect to $I_{p1}$ N₂. The current enhancement will be, in part, determined by the rate ($k_j$) and equilibrium constant (K) of the binding reaction where a fast and spontaneous homogenous step will allow the current to approach twice its original value i.e. $I_{p1}$ CO₂ / $I_{p1}$ N₂ = 2. 31,82
Table 2-2. Peak potential and change in peak potential from N₂ of complexes 1–7 in a CO₂ saturated solution generated from CVs recorded at 0.1 Vs⁻¹. The current increase in the presence of CO₂ is designated by i/iₚ₀.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Eₚc₁ (V)</th>
<th>ΔEₚc₁ (mV)</th>
<th>i/iₚ₀</th>
<th>Eₚc₂ (V)</th>
<th>ΔEₚc₂ (mV)</th>
<th>i/iₚ₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>−1.88</td>
<td>−42</td>
<td>1.89</td>
<td>−2.37</td>
<td>32</td>
<td>2.33</td>
</tr>
<tr>
<td>32</td>
<td>−1.66</td>
<td>15</td>
<td>1.36</td>
<td>−2.33</td>
<td>−17</td>
<td>1.14</td>
</tr>
<tr>
<td>33</td>
<td>−1.73</td>
<td>0</td>
<td>1.57</td>
<td>−2.54</td>
<td>−188</td>
<td>1.78</td>
</tr>
<tr>
<td>34</td>
<td>−1.83</td>
<td>12</td>
<td>1.78</td>
<td>−2.44</td>
<td>−96</td>
<td>1.11</td>
</tr>
<tr>
<td>35</td>
<td>−1.75</td>
<td>−10</td>
<td>1.06</td>
<td>−2.25</td>
<td>−46</td>
<td>1.41</td>
</tr>
<tr>
<td>36</td>
<td>−1.76</td>
<td>−10</td>
<td>1.61</td>
<td>−2.34</td>
<td>−66</td>
<td>2.11</td>
</tr>
<tr>
<td>37</td>
<td>−1.69</td>
<td>−7</td>
<td>1.08</td>
<td>−2.44</td>
<td>−37</td>
<td>0.77</td>
</tr>
</tbody>
</table>

A higher rate constant and lower standard potential of the second reduction will contribute to raise the observed current in an equivalent manner. Scheme 2-2 provides a proposed mechanism. Complexes 26, 33, 34, and 36 are assumed accept a second electron near Ep₁ after binding CO₂ based on the large Ip₁ CO₂ / Ip₁ N₂ ratios (1.6–1.9) exhibited by these complexes, where again, the magnitude of increased current is dictated by the parameters mentioned above. On the other hand, the current of 32 was enhanced by ~30% while the current of 35 was largely unchanged in the presence of CO₂. The marginal current enhancement observed in 32 and 35 may signify less favorable binding or limited electrochemical inactivity of the complexed species.

The peak potential of reduction under CO₂ (Eₚc₁ CO₂) is also influenced by the homogeneous reaction parameters. However, when CV sweeps are performed at higher scan rates, the response is uncomplicated by the binding step and Ep₁ CO₂ is predominately controlled by the reduction kinetics of the Pd-CO₂ adduct. Variation in peak position with scan rate at this limit is expected to follow the response of a simple irreversible charge transfer reaction and shift anodically with a lower Eo₂ and larger kr₂.
Figure 2-4. Cyclic voltammograms recorded at 100 mVs⁻¹ of the first cathodic wave under nitrogen (black dots) and CO₂ (teal dashes) for complexes 1-6. The inset plots represent the change in peak potential with respect to the log of scan rate under nitrogen (blue dots) and CO₂ with the current from the first reduction subtracted (red stars).
Interestingly, complexes 32–36 were found to shift between −24 and +48 mV of E_{p1} N\textsubscript{2} while complex 26 shifted negatively by 54 mV. The relative change in E_{p1} CO\textsubscript{2} here is solely influenced by a lower E\textsubscript{0} or larger k_{r2} of PdCOO\textsuperscript{−} and the less negative shift in E_{pc1} CO\textsubscript{2} for 32–36 can be taken as an indication that electron transfer to the Pd-CO\textsubscript{2} adduct occurs readily at higher potentials for these species relative to 26.

To gain more insight on the relative rate of reduction and complexation expressed by each species, the current measured under N\textsubscript{2} for Pd(I) formation was subtracted from the CO\textsubscript{2} scans recorded at a series of sweep rates (Figure 2-4, insets). In the subtracted scan of 26, change in E_{p1} CO\textsubscript{2} was found to be negative and linear with respect to log(ν) (from 0.05 to 1.0 Vs\textsuperscript{−1}) demonstrating rate dependence on the following reduction.\textsuperscript{82} The corresponding curves for complexes 32–36 show a changing response to log(ν) where the relationships generally approach linearity at higher scan rates (Figure 2-4, insets). The variation in peak position as a function of log(ν) demonstrated by 32-36 suggests mixed kinetic control.\textsuperscript{26,82} However, the linear response observed in the series 32-36 at large log(ν) is dominated by the heterogeneous kinetics of the second reduction step as described for 21.

The higher scan rate required for an unperturbed reduction in 32–36 can be interpreted as the result of a slower binding reaction.\textsuperscript{82} However, the slope of the linear section of these curves was found to be less steep than those measured for Pd(I/II) couple (Figure 2-4, insets). Considering the rate of charge transfer in the same manner as above, the shallower slopes of E_{p1} CO\textsubscript{2} vs log(ν) obtained at higher scan rate for complexes 32–36 indicates that CO\textsubscript{2} complexed from of these species experience faster electrode kinetics.\textsuperscript{82}

It appears from this experiment that the reduction of PdCOO\textsuperscript{−} may occur at a higher rate than the preceding reduction for 32–36 which is in contrast to the results for the previously
studied $N$-butyl analog. Installation of positively charged, pendant units onto this catalytic system manifests a change in electrocatalytic behavior at $E_{\text{p1}}$, whereby, the rate determining step is transitioned from reduction of the CO$_2$ adduct to one of the preceding steps. Based on the electrochemical data presented here, this is allowed by the comparatively facile reduction of PdCOO' at higher potentials. Furthermore, the geometry and charge distribution of the modifying arms hold a substantial influence on this behavior as well as the binding reaction as evidenced by the $I_p$ CO$_2$ / $I_p$ N$_2$ current ratios.

Quantitative analysis of $E_{\text{p2}}$ CO$_2$ is more difficult due to the complexity of possible diffusion profiles generated by reduction at lower potentials. Nevertheless, some trends may be noted from Table 2-2 and the representative full scan CV traces depicted by the teal dashed lines of Figure 2-5.

$E_{\text{pc2}}$ CO$_2$ was found to shift positive of $E_{\text{pc2}}$ N$_2$ for 26 while all other catalysts displayed a negative change in peak potential. The ratio of $I_p$ CO$_2$ / $I_p$ N$_2$ became larger at the second potential for all except catalysts 32 and 34. In the case of 26 and 36 the current enhancement at both events was found to be $\sim$2, representing a total of 4 electrons taken up into the system. This is sufficient to form a Pd(0) species as well as fully reduce CO$_2$ to CO, potentially indicating some degree of turnover in the absence of an acid source.
2.2.4 Electrochemistry under catalytic conditions

Figure 2-5. Full scan CVs recorded at 100mVs$^{-1}$ of complexes 26 and 32-36 under CO$_2$ (blue dashes) and with the addition of 10 mM TFA (orange trace).
Of several proton sources that were tested, trifluoroacetic acid (TFA) was discovered to be the most effective. While H₃PO₄ and glacial acetic acid did not allow for appreciable turnover, HBF₄ caused for high background currents, indicating a fairly narrow window for optimizing pKₐ. Addition of 10 mM TFA to CO₂ saturated solutions caused peak currents at both potentials to increase by a factor of 1.5 to 4 with respect to Iₚc CO₂, where the second wave was consistently enhanced to a greater extent. The presence of acid also elicited a positive change in Eₚc₁ and Eₚc₂ with respect to Eₚc₁ and Eₚc₂ CO₂ except in the case of 26 where the first reduction event shifted negatively by 20 mV. Figure 2-5 depicts the change in CV response accompanied by the addition of TFA to the CO₂ saturated solutions (Figure 2-5, orange traces). Unlike N-alkyl Pd [C^N^C] catalysts, the cation bearing complexes maintain two, well defined cathodic features in TFA. Sharp peaks in the CVs indicate a rate-limited process rather than the expected large plateau current defined by the turnover frequency of the catalyst. 25 26 and similar complexes are known to turnover a mixture of CO and H₂ at both potentials under these conditions which suggests that non-catalytic CV behavior of 32-37 is caused by the presence of an N-substituted onium unit which slows down one or more steps in the standard cycle. 71,74

Table 2-3  Peak potentials and current ratios to Iₚc N₂ of complexes 26 and 32-37 under catalytic conditions: 10 mM TFA + 0.2 M CO₂.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Eₚc₁ (V)</th>
<th>Eₚc₂ (V)</th>
<th>I CAT/ Iₚc₁ N₂</th>
<th>I CAT/ Iₚc₂ N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>−1.87</td>
<td>−2.31</td>
<td>2.61</td>
<td>2.27</td>
</tr>
<tr>
<td>32</td>
<td>−1.64</td>
<td>−2.29</td>
<td>2.32</td>
<td>3.93</td>
</tr>
<tr>
<td>33</td>
<td>−1.73</td>
<td>−2.34</td>
<td>1.98</td>
<td>2.83</td>
</tr>
<tr>
<td>34</td>
<td>−1.79</td>
<td>−2.36</td>
<td>2.64</td>
<td>1.53</td>
</tr>
<tr>
<td>35</td>
<td>−1.75</td>
<td>−2.24</td>
<td>1.21</td>
<td>1.87</td>
</tr>
<tr>
<td>36</td>
<td>−1.82</td>
<td>−2.32</td>
<td>1.75</td>
<td>1.68</td>
</tr>
<tr>
<td>37</td>
<td>−1.70</td>
<td>−</td>
<td>1.33</td>
<td>−</td>
</tr>
</tbody>
</table>
2.2.5 Bulk electrolysis

To determine the electrocatalytic selectivity of 32–37, Faradaic efficiency for gaseous products was measured at both reduction potentials by passing several Coulombs of charge through acidified (10 mM TFA), CO₂ saturated solutions containing 2 mM catalyst. The headspace was then sampled and analyzed with the use of a gas chromatograph equipped to quantify any gases produced. Each complex was found to generate a ratio of H₂:CO at both reduction potentials with a small degree of unaccounted charge consumed in several cases (Table 2-3). Post electrolysis CVs revealed relatively unchanged features in each complex, suggesting limited catalyst degradation and potentially the production of reduction products other than CO and H₂.

Table 2-3. Faradaic efficiency for H₂ and CO of 26 and 33–37 at E_{pc1} and E_{pc2} with the associated charge passed.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Potential</th>
<th>Charge passed (C)</th>
<th>FE CO (%)</th>
<th>FE H₂ (%)</th>
<th>FE total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>E_{pc1}</td>
<td>13</td>
<td>9</td>
<td>93</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>E_{pc2}</td>
<td>12</td>
<td>23</td>
<td>79</td>
<td>102</td>
</tr>
<tr>
<td>32</td>
<td>E_{pc1}</td>
<td>3.2</td>
<td>21</td>
<td>86</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>E_{pc2}</td>
<td>6.1</td>
<td>17</td>
<td>72</td>
<td>89</td>
</tr>
<tr>
<td>33</td>
<td>E_{pc1}</td>
<td>4</td>
<td>31</td>
<td>57</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>E_{pc2}</td>
<td>5.5</td>
<td>17</td>
<td>67</td>
<td>85</td>
</tr>
<tr>
<td>34</td>
<td>E_{pc1}</td>
<td>2.7</td>
<td>46</td>
<td>56</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>E_{pc2}</td>
<td>3.5</td>
<td>37</td>
<td>59</td>
<td>97</td>
</tr>
<tr>
<td>35</td>
<td>E_{pc1}</td>
<td>3.2</td>
<td>17</td>
<td>86</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>E_{pc2}</td>
<td>5.3</td>
<td>24</td>
<td>77</td>
<td>101</td>
</tr>
<tr>
<td>36</td>
<td>E_{pc1}</td>
<td>2.1</td>
<td>25</td>
<td>57</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>E_{pc2}</td>
<td>3.2</td>
<td>49</td>
<td>56</td>
<td>105</td>
</tr>
<tr>
<td>37</td>
<td>E_{pc1}</td>
<td>2.1</td>
<td>1.5</td>
<td>79</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>E_{pc2}</td>
<td>1.9</td>
<td>1.3</td>
<td>69</td>
<td>71</td>
</tr>
</tbody>
</table>
With the exception of 37, bulk electrolysis carried out at $E_{p1}$ uncovered a 2–5 fold improvement in CO selectivity for all onium functionalized complexes relative to 26, where 34 was the most selective. Controlled potential electrolysis at the second wave, however, afforded slightly different results. While 26, 35, and 36 demonstrated improved selectivity at $E_{p2}$, 35 in particular increasing to 49% FE, efficiencies decreased for all catalysts bearing a charged center attached with propyl linker. The diminished FE CO in the case 32, 33 and 34 at $E_{pc2}$ may be explained by adsorption to the electrode surface at higher potentials which could limit the homogeneous steps required for catalysis.

The behavior of complex 37 through electrolysis was unusual. Extremely low current densities were measured immediately after stepping the potential more than 200 mV beyond the peak value determined by CV. After passing less than two Coulombs of charge (~0.02 mmol e$^-$), the overall Faradaic efficiency measured for gaseous products was less than 85%. Additionally, prolonged periods of electrolysis resulted in a considerable buildup graphitic deposits on the electrode surface which is often caused by catalyst deactivation. This result was anticipated after discovering that the first reduction potential of the proligand was positive of the metalated species (Table 2-1).

As discussed in the Introduction, pyridinium moieties are reduced at relatively positive potentials and the early reduction of 37,3 (Figure 2-2) is most likely centered on the appending pyridinium units. Reduction of these moieties generally produces neutral dearomatized dimers.$^{80}$ Competition of this reaction with reduction of the catalytic center simultaneously accounts for low FE yield and FE for CO. In the latter case, the diminished catalytic activity may be caused by an unfavorable steric arrangement brought on by dimerization of the pyridinium units.$^{80}$
2.2.6 Trends in the electrochemical behavior and Faradaic efficiency

Figure 2-6. a) FE CO per complex vs. peak current under catalytic conditions / peak current under N₂ b) FE CO per complex vs. current ratio under CO₂ c) FE CO per complex vs. δEpc1 CO₂.

Faradic efficiency for CO determined at Epc1 was found to correlate with the peak current measured under catalytic conditions (Ipc CAT) in two trends (Figure 2-6 (a)). For complexes 33–36, FE CO increases with respect to Ipc CAT. The relationship across this series is positive and approximately linear but appears to reverse for 26 and 32.

The appearance of two trends in Figure 2-6 (a) may be understood by considering the CV response of 26 relative to the other species under investigation. The CVs of 26 in CO₂ + TFA become broad and ill-defined which is expected for a catalytic response, whereas 32–36 exhibit relatively unchanged features expressed at larger currents. In the latter case, this is consistent with inhibition of fast catalysis rendering a diffusion-limited response. The comparatively
large $I_{pc}$ CAT exhibited by 26 is consistent with faster catalysis, however, this complex was found to be the least selective, generating only 9% CO. This indicates that over 90% of the observed catalytic current is funneled through a pathway that ultimately produces H$_2$. Thus, the inverted relationship between FE CO and peak catalytic current witnessed across 26–33 and 33–35 is interpreted as a transition from a mechanism that generates H$_2$ to another that results in CO formation. The mechanisms producing H$_2$ and CO will entail distinct intermediates and rate phenomena. Herein, a higher FE for CO can be caused by inhibition of the H$_2$ forming pathway, causing $I_{pc}$ CAT to decrease, as well as acceleration of the CO generating route, rendering a larger $I_{pc}$ CAT.

Comparison of the results from bulk electrolysis with the CO$_2$ binding kinetics established in section 2.2.3 provides more insight on understanding the differences observed in FE for CO (Figure 2-6 (b) and (c)). As discussed above, the ratio $I_{pc1}$ CO$_2$/ $I_{pc1}$ N$_2$ is related to $k_f$ and K for CO$_2$ binding; ratios approaching 2 indicate a fast and complete reaction. With the exception of 26, it can be seen from Figure 2-6 (b) that improved Faradaic efficiency for CO is accompanied by a larger $I_{pc1}$ CO$_2$/ $I_{pc1}$ N$_2$ ratio, suggesting that within the series 32–36, FE CO grows with increasing binding efficiency for CO$_2$. This parallels the correlation expressed in Figure 2-6 (a) excluding the behavior complex 32.

Considering the behavior of 26 as a benchmark for poor CO selectivity, it appears that H$_2$ production is signified by the observation of a large overall rate when the complex is in the presence of CO$_2$ + H$^+$ (Figure 2-6 (a)) relative to that witnessed in the presence of CO$_2$ alone (Figure 2-6 (b)). Therefore, it is plausible that the pathway generating CO consists of an efficient CO$_2$ binding step accompanied by slower protonation equilibria.
Figure 2-6 (c) also displays a relationship between the shift in $E_{pc1} \text{CO}_2$ vs $E_{pc1} \text{N}_2$ ($\delta E_{pc1}$ CO$_2$) and Faradaic efficiency for CO, wherein, FE CO rises with respect to $\delta E_{pc1}$ CO$_2$ in two series: complexes demonstrating a low $k_f$ and $K$, 2 and 5 (lower trace), and complexes demonstrating a higher $k_f$ and $K$, 26, 36, 33 and 34 (upper trace). As discussed above, $\delta E_{pc1}$ CO$_2$ varies with the standard potential and rate of reduction following CO$_2$ complexation; faster electrode kinetics for the second reduction will cause the wave to shift to progressively less negative potentials. A smaller $\delta E_{pc1}$ CO$_2$ likely represents an accumulation Pd-COO$^-$ in solution due to unequal 1 and 2 e$^-$ reduction rates. For a complex exhibiting fast binding kinetics and a sluggish reduction rate, this effect will be the most pronounced. Considering the plots in Figure 2-6 (b) and Figure 2-6 (c) together, it can be seen that 26 should demonstrate this feature to the greatest extent.

**Scheme 2-3.** Proposed competing pathways for CO and H$_2$ formation under the one electron (left) two electron pathways (right).
Following a mechanistic study of 21 presented in earlier work, formation of the Pd-COO’ complex is followed by protonation to form a hydroxyl carbonyl group when a sufficiently strong acid is present.\textsuperscript{65} Although this reaction was proposed as a step in a catalytic cycle that generates CO, the observation made here that larger concentrations of Pd-COO’ may be associated with a lower selectivity for CO suggests that this reaction does not contribute CO production in this case but instead initiates a cycle that ultimately forms H\textsubscript{2} (Scheme 2-3). It seems likely that protonation of Pd-COO’ followed by a second reduction causes CO\textsubscript{2} to eliminate, rendering a hydride complex for the catalyst series under investigation. This behavior has been documented in isoelectronic platinum complexes and can result in the evolution of H\textsubscript{2} when a proton donor is available.\textsuperscript{84} Conversely, the reduction of Pd-COO’ to form a 2 e\textsuperscript{−} carboxylate moiety prior to protonation appears to be the appropriate sequence of events to initiate CO evolution.

The improvement of F\textsubscript{E} CO at E\textsubscript{pc2} for 26, 35, & 36 supports the hypothesis that that formation of the 2e\textsuperscript{−} reduced PdCOO species initiates a cycle that evolves CO. With the smallest \( \Delta E\textsubscript{pc1} \) CO\textsubscript{2} values of the series, these complexes are most likely to form the 1e\textsuperscript{−} reduced, protonated Pd-COO’ intermediate. At E\textsubscript{pc2}, a Pd(0) complex is available to react directly with CO\textsubscript{2}, forming a carboxylate group prior to protonation, thus avoiding the presence of Pd-COOH’. Unfortunately, H\textsubscript{2} remains the major reduction product under the 2e\textsuperscript{−} regime for 26 and 32-36, which may be explained by direct reaction of the Pd(0) species and solvated protons as previously described.\textsuperscript{65} Scheme 2-3 displays a description of the competing pathways proposed for H\textsubscript{2} and CO formation based on the data assembled in section 2.2.3 and the relationships established in Figure 2-6.
In summary, this work presents a reasonable argument that palladium bis-\(N\)-heterocyclic carbene complexes operate best as electrocatalysts for CO formation when CO\(_2\) complexation is followed by a reduction step that is rapid relative to the protonation equilibria. Fundamentally, the modest Faradaic efficiency of Pd[\(C^{\text{N}}\text{C}\)] for CO compared to other CO\(_2\) electrocatalysts may be caused by the sluggish redox kinetics discussed in Sections 2.2.2 and 2.2.3 that allow for the prevalence of long lived radical intermediates. Based on the electrochemical experiments performed here, the presence of an appending onium unit promotes CO selectivity by allowing the reduction of CO\(_2\) complexed intermediates to proceed at a greater rate. Additionally, the hydrophobic environment provided by the aryl and alkyl onium substituents may help mediate proton transfer to the catalyst and mitigate hydride forming reactions.

2.2.7 Structural and electronic contribution from pendant groups

So far, we have been able to distinguish several aspects of electrochemical behavior that are accompanied by an improved selectivity for CO\(_2\). Here, we seek to provide a systematic explanation of how architecture of the modifying arm contributes to the observed changes in catalytic performance. In order to construct a semi-quantitative model for secondary ligand interaction, DFT calculations were performed on each complex in the ground and one electron reduced state. The geometries were optimized to stationary points in a conductor-like polarizable continuum model (CPCM) of acetonitrile. See to the experimental section for more details.
Calculations performed on the unreduced complexes 33-36 demonstrate that the lowest unoccupied molecular orbital (LUMO) distribution is primarily located on the pyridyl ring with a small degree of Pd and NHC character while the highest occupied molecular orbital (HOMO) is largely centered on the Pd center and NHC units. One electron reduction of complexes 26, 32–36 causes the partial charge on palladium to decrease slightly and the singly occupied molecular orbital (SOMO) is distributed across the pyridyl ring and Pd atom. These results are consistent with previous calculations carried out on 26 and indicate that the pendant arms manifest a negligible impact on the electronic properties of the root catalyst. Complex 37 is an exception due to the positive reduction potential of the pyridinium groups which causes the LUMO of
complex 37 to be centered on the pendant arms. Figure 2-7 displays the optimized, one electron reduced geometry of 33–37. Computation analysis of complex 32 is undergoing.

In first considering the phosphonium modified catalysts, differences in reactivity from complex 26 can be explained by the geometry and flexibility of the pendant arms. For each species, optimizations performed on the 1 e\textsuperscript{−} reduced complex show one phosphonium group protruding ‘under’ the Pd atom (P\textsubscript{1}), while the other phosphonium arm extends out of the square planar surface and curves back towards the catalytic center (P\textsubscript{2}). This causes the relative Pd–P\textsubscript{1} and Pd–P\textsubscript{2} distances to differ where the positive charge of one arm remains closer to the reactive center than the other. Under electrocatalytic conditions, it may be speculated that the onium unit that is positioned near the catalyst body functions to mediate the formation of reaction intermediates while the other primarily negotiates interactions with the electrode surface.

Previous calculations carried out on 26 in Pd(I) oxidation state demonstrated that, during catalysis, CO\textsubscript{2} approaches and binds η\textsuperscript{1} through carbon to the Pd dz\textsuperscript{2} orbital, resulting in a bent carboxyl moiety.\textsuperscript{71,78} The optimized Pd-CO\textsubscript{2} bond length was calculated to be 2.0 Å with partial a partial charge symmetrically distributed across the oxygens and an OCO angle of 137º.\textsuperscript{71} The energy minima determined here corresponds to a total distance of approximately 2.5 Å from palladium to the origin of a plane containing both of the oxygen atoms. Treating this coordinate as the center of partial charge contained within the OCO adduct, distances to the nearest phosphonium center (P\textsuperscript{+}) were calculated for complexes 33–36 in order to gain insight on the dimensions of the Pd-CO\textsubscript{2}-P\textsuperscript{+} binding site (Table 2-4).
Table 2-4. DFT calculated Pd–CO₂ distances for complexes 33-36 in the +1 oxidation state. Position of bound carboxyl substituent relative to the Pd center was estimated based on existing work.⁷¹

<table>
<thead>
<tr>
<th>Complex</th>
<th>Pendant structure</th>
<th>Pd-CO₂—P⁺ Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td><img src="image" alt="Pendant structure 33" /></td>
<td>5.33</td>
</tr>
<tr>
<td>34</td>
<td><img src="image" alt="Pendant structure 34" /></td>
<td>5.54</td>
</tr>
<tr>
<td>35</td>
<td><img src="image" alt="Pendant structure 35" /></td>
<td>5.12</td>
</tr>
<tr>
<td>36</td>
<td><img src="image" alt="Pendant structure 36" /></td>
<td>5.26</td>
</tr>
</tbody>
</table>

Based on this model, the equilibrium position of P⁺ relative to the OCO center appears to be controlled by the steric and flexibility of the linking unit in addition to the coordination sphere of the P⁺ center. This distance was found to the smallest for 35 and closely followed by 36, where the point of charge contained within the pendant arm is confined over the Pd center by the ortho and meta-substituted benzylic linkers, respectively. Owing to a higher degree of rotational freedom, this value is larger for 33 and 34 wherein the smaller ethyl substituents surrounding P⁺ in 33 allow for a closer approach relative to phenyl bearing analog, 34.

With the aim of discerning a correlation between kinetic availability of a pendant charge and the behavior observed in electrochemical experiments, the values contained in Table 2-4 were contrasted with each of the catalytic parameters discussed in Section 2.2.6 (Figure 2-8). Considering each parameter expressed in Figure 2-8 with the same significance as discussed above, the optimized distance from the nearest phosphonium center to the point of interaction...
with CO$_2$ appears influence the homogeneous reactivity as well as the redox kinetics possessed by each catalyst.

Beginning first by comparing the electrochemical response of 33–36 to CO$_2$ in the absence of a proton donor, Figure 2-8 subplots (a) and (b) suggest that the initial, CO$_2$ binding and ensuing reduction steps benefit from a larger spatial gap between P$^+$ and the anchoring position of CO$_2$. An analogous trend is apparent from Figure 2-6 subplots (c) and (d), for the electrochemical results collected under catalytic conditions (TFA present). Here, peak catalytic current and Faradaic efficiency for CO also increases along with a larger Pd-CO$_2$--P$^+$ binding site. However, the correlations are remarkably linear in this case, indicating that the influence of P$^+$ orientation imposes a more consistent influence on the overall cycle compared to the initial steps alone.
Figure 2-8. Comparison of calculated P$^+$-CO$_2$ distances to, a) $\delta E_{pc1}$ CO$_2$ (defined above), b) current enhancement in the presence of CO$_2$, c) catalytic current and d) Faradaic efficiency for CO. Each data point is labelled with corresponding complex #.

The apparent requirement of a wide reaction pocket for efficient catalysis indicated by this model suggests that the stabilizing effect provided by the onium arms occurs through space. Although molecular interactions cannot be completely ruled out by this preliminary analysis, the decrease in selectivity accompanied by a P$^+$-CO$_2$ gap narrower than 5.5 Å indicates that the interaction is optimized for a distance much larger than what can be expected for dative bonding.$^{85}$

The behavior witnessed here is most consistent with P$^+$ stabilization of the carboxyl group through a cation–\(\pi\) interaction. This type of bonding is observed over longer length scales
and is less influenced by screening from solvent molecules than a classical Coulombic attraction.\textsuperscript{86}

The relative efficacy of each substituent at providing this stabilizing effect may be explained by the steric environment established by the R groups surround P\(^+\). The difference in degree of P\(^+\)–CO\(_2\) separation calculated for the two propyl linked analogs is most likely the result of the added steric bulk carried by the phenyl groups on 34. Although this causes the distance between the attracted charges to be larger, the sterically dense triphenylphosphonium appendage may also function to exclude electrolyte and solvent molecules from the intermittent space, allowing stronger stabilizing interaction. Moreover, the hydrophobic environment provided by the phenyl rings may limit accessibility for protonation of the PdCOO\(^-\) intermediate, thus limiting the departure down a pathway we propose ultimately produces H\(_2\). Although this effect was expected to be greater for the benzyl linked units, it seems likely from the results provided in Figure 2-8 that efficient catalysis of CO\(_2\) requires a larger degree of freedom about the palladium center and the immobility of these substituents may crowd the reactive center.
2.3 Conclusions

In summary, this chapter provides a preliminary description of the contribution of pendant onium units on electrocatalytic CO₂ conversion. A combination of electrochemical and computational experiments has allowed for the elucidation of steric and electronic factors of pendant cationic functionalities that contribute to enhanced catalysis with palladium bis-\(N\)-heterocyclic carbene pincer complexes. From these results, the interaction between the functional groups and catalytic intermediates appears to occur in a through space mechanism. Bulky phosphonium centers attached through a propyl linker allowed for the highest CO selectivity, potentially owing to the flexibility and hydrophobicity provided by this moiety. Calculations are ongoing on the 32 so that a direct comparison can be made between the behavior N and P centered onium arms.

2.4 Experimental

2.4.1 General

Unless otherwise stated, all reactions were performed according to standard Schlenk techniques. CH₃CN, and DMF were purchased as HPLC grades. DMSO was purchased as the ACS solvent grade. All three solvents solvent were dried and stored over 25% v/v activated 4 Å molecular sieves. All other solvents were purchased from a commercial source and used without further purification, unless stated otherwise.

NMR spectra were collected on a Bruker AV400 spectrometer. \(^1\)H and \(^{13}\)C chemical shifts were referenced to residual solvent and \(^{31}\)P shifts are reported relative to an 85% H₃PO₄ reference signal. Where possible, full structural assignments were deduced using a combination of COSY, HMBC and HSQC NMR techniques. High resolution mass spectrometry data were
obtained from Bruker Esquire LC ion trap mass spectrometer equipped with an electrospray ion source. Low-resolution mass measurements were determined with the use of a Waters LC-ESI-MS. Elemental compositions as determined by ESI-MS are reported as the \([n]^{+}\) charged molecular structure with accompanying counter ions indicated.

All electrochemical measurements were performed using either a Metrohm Autolab PGSTAT12 or a Pine AFCBP1 potentiostat with the use of an Ag/AgNO\(_3\) pseudo-reference electrode. Bulk electrolysis and simple CV experiments and were carried out in an air-tight three compartment cell while studies involving scan rate dependence were performed in a two-compartment cell to limit charging effects. Solutions were sparged with either N\(_2\) or analytical grade CO\(_2\) for 30 minutes before performing measurements. A 7 mm\(^2\) glassy carbon disk and a platinum mesh were used as the working and counter electrodes, respectively. Measurements were referenced to an internal Fc\(^{0/+}\) couple and carried out in DMF with analytically pure 0.1 M [n-Bu\(_4\)N]PF\(_6\) as the supporting electrolyte. The working electrode was regenerated and cleaned between measurements by polishing with alumina paste and sonicating in water and acetone, successively. The concentration of analyte was held to 2 mM unless discussed otherwise.

The gaseous compositions of headspace samples aliquoted through electrolysis were analyzed with the use of an SRI Model 8610C gas chromatograph equipped with a zeolite column, a methanizer and dual TCD and FID detectors.

### 2.4.2 Synthesis

Relevant \(^1\text{H}, \, ^{13}\text{C}\) and \(^{31}\text{P}\) spectra are also reported here following the synthetic procedure with the structure of the compound synthesized displayed at the top.
**General procedure for metalation C\(^{N}\)C ligands**

Metalation of each C\(^{N}\)C proligand was carried out according to the general procedure described here. The mass of starting material varied *per* complex, however, concentration and molar equivalent each reagent was held constant. Any additional workup required for a given complex is elaborated on in the appropriate subsection.

The pincer ligand (0.40 mmol) was weighed into an oven dry round bottom flask and dissolved in 10 mL of dry DMSO. The flask was covered in foil and powdered Ag\(_{2}\)O (0.40 mmol) was added along with ~1/4 solution volume of activated 4Å molecular sieves. The reaction was heated to 55 °C for 24 h under a blanket of N\(_2\) and then cooled to RT. Silver trifluoromethanesulfonate (0.44 mmol) was then weighed into the flask followed by (0.40 mmol) of palladium(II)dichloro(1,5-cyclooctadiene) (cod). The light grey-yellow suspension was stirred under N\(_2\) for 48 h at 30 ºC. The reaction mixture was transferred to a 50 mL centrifuge tube and the precipitates formed during the reaction as well as the molecular sieves were separated by centrifugation to expose a pale-yellow solution. The DMSO layer was transferred to a flame dried round bottomed flask and the solvent volume was reduced to ~0.5 mL by vacuum distillation at 55 ºC with the use of a short neck condenser. The bottom liquid was then diluted with 5 mL of DCM, filtered through Celite and dropped into 20 mL of anhydrous Et\(_2\)O to form an oily precipitate that was collected by centrifuging. After pouring off the Et\(_2\)O layer, the viscous oil was triturated under successive washes of dry Et\(_2\)O until a light solid was obtained.
Compound 32.1 ([3-bromo-N,N,N-trimethylpropan-1-aminium][PF$_6$]) was prepared according to literature procedure. The $^1$H NMR of the synthesized compound closely matched previously reported data.$^8$7

**Proligand 32.2**, [3,3'-(pyridine-2,6-diylbis(methylene))bis(1-(3-(trimethylammonio)propyl)-1H-imidazol-3-ium)][PF$_6$]$_2$[Br]$_2$

[Diagram of compound 32.1]

Compound 32.1 (Figure 2-2) [3-bromo-N,N,N-trimethylpropan-1-aminium][PF$_6$] (0.29 g, 0.87 mmol) was combined with 2,6-bis((1H-imidazol-1-yl)methyl)pyridine (BIP) (0.10 g, 0.42 mmol) in a round bottomed flask and 3 mL of dry CH$_3$CN was added to the container. The solution was brought to reflux overnight to yield a small amount of precipitated solid. The solvent was evaporated, and the crude mixture was recrystallized from a boiling 1:1 mixture of methanol and acetone to isolate a white crystalline solid. Isolated yield: 0.23g (0.2581 mmol, 62%). $^1$H NMR (400 MHz, DMSO-$_d$$_6$) $\delta$ 9.43 (s, 2H), 7.98 (t, $J$ = 7.8 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.82 (s, 2H), 7.49 (d, $J$ = 7.7 Hz, 2H), 5.59 (s, 4H), 4.32 (q, $J$ = 12.2, 9.7 Hz, 4H), 3.49 – 3.36 (m, 4H), 3.11 (s, 18H), 2.35 (t, $J$ = 8.2 Hz, 4H). $^{13}$C {$^1$H} NMR (101 MHz, DMSO-$_d$$_6$) $\delta$ 154.1, 139.5, 137.5, 123.9, 123.1, 122.8, 122.7, 62.4, 53.4, 53.0, 52.9, 52.9, 46.6, 23.7, 23.5. HR ESI-MS: Calcd for [M+3PF$_6$]$^+$$^*$, C$_{25}$H$_{43}$N$_7$P$_3$F$_{18}$: 876.2505; Found: 876.2497 [M+3PF$_6$]$^+$

$^*$ Calculated molecular formulae for [M+3PF$_6$]$^+$

$^+$ Experimental values for HR ESI-MS
Complex 32

Metalation of proligand 32.2 was carried out according to the general metalation route with 0.41 g (0.46 mmol) of pincer ligand. All other reagents were added according to the molar ratios provided in the general method and the volume of DMSO was scaled to keep molarities consistent. Following the general workup, the isolated crude product was dissolved in CH$_3$CN and recrystallized by slow diffusion of Et$_2$O into the complex containing solution. Isolated yield: 0.19 g (0.19 mmol, 41%) $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.25 (t, $J = 7.7$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 2H), 7.67 (d, $J = 1.9$ Hz, 2H), 7.51 (d, $J = 1.9$ Hz, 2H), 5.70 (s, 4H), 4.71 – 4.49 (m, 2H), 4.29 (dt, $J = 13.7$, 7.3 Hz, 2H), 3.32 – 3.24 (m, 5H), 3.05 (s, 18H), 2.39 – 2.23 (m, 4H). $^{13}$C {$^1$H} NMR (101 MHz, DMSO-$d_6$) $\delta$ 164.6, 155.8, 142.5, 126.2, 122.8, 122.6, 62.9, 55.1, 52.8, 46.7, 25.2, 1.6. HR ESI-MS: Calcd for [M+2PF$_6$]$^+$, C$_{25}$H$_{41}$ClN$_7$PdP$_2$F$_{12}$: 868.1436; Found: 868.1438 [M+2PF$_6$]$^+$

Compound 33.1 ((3-bromopropyl)triethylphosphonium bromide) was synthesized according to established methods. The $^1$H NMR of the product was found to agree with that reported in literature.$^{88}$
**Proligand 33.2,** [1,1′-(pyridine-2,6-diylbis(methylene))bis(3-(triethylphosphonio)propyl)-1H-imidazol-3-ium)] [PF$_6$]$_2$[Br]$_2$

Compound 33.1 ((3-bromopropyl)triethylphosphonium bromide) (Figure 2-2) (0.60 g, 1.88 mmol) of was dissolved in 3 mL of dry CH$_3$CN in a flame dried round bottomed flask and 0.21 g (0.89 mmol) of BIP was weighed into the solution. The solution was brought to reflux overnight to produce a translucent oil. After pouring off the reaction solution, the viscous bottom liquid was dissolved in a minimal volume of methanol and dropped into a saturated of KPF$_6$ to produce white precipitate. The solids were isolated by filtration, washed with water and dried in air. The isolated crude was dissolved in a small amount of acetone and dropped into Et$_2$O. This was repeated several times to produce a light yellow solid. Isolated yield: 0.93 g (0.92 mmol, 49%). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.26 (s, 2H), 8.00 (t, J = 7.8 Hz, 1H), 7.86 (d, J = 2.1 Hz, 2H), 7.81 (d, J = 1.8 Hz, 2H), 5.56 (s, 4H), 4.31 (t, J = 7.1 Hz, 4H), 2.25 (dp, J = 16.0, 8.6, 8.1 Hz, 16H), 2.09 (hept, J = 7.5, 7.1 Hz, 4H), 1.16 (dt, J = 18.0, 7.6 Hz, 18H). $^{13}$C {$^1$H} NMR (101 MHz, DMSO-$d_6$) δ 154.30, 139.62, 137.42, 123.81, 122.99, 122.54, 53.47, 49.53 (d, J = 18.6 Hz), 21.90 (d, J = 2.9 Hz), 14.18 (d, J = 49.6 Hz), 10.97 (d, J = 48.8 Hz), 5.62 (d, J = 5.4 Hz). $^{31}$P {$^1$H} NMR (162 MHz, DMSO-$d_6$) δ 39.91, (m) -144.20. HR ESI-MS: Calcd for [M+3PF$_6$]$^+$, C$_{31}$H$_{55}$N$_5$F$_{18}$P$_5$: 994.2858; Found: 994.2856 [M+3PF$_6$]$^+$. 

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Complex 33

Metalation of proligand 33.2 was carried out according to the general metalation procedure with 0.38 g (0.38 mmol) of pincer ligand. All other reagents were added according to the molar ratios described above and the volume of DMSO added was scaled to keep molarities consistent.

Following the workup discussed in the general procedure, the crude product was columned over neutral alumina with a 9:1 mixture of DCM and methanol to render a light yellow solid. Isolated yield: 0.11g (0.09 mmol, 25%) $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.26 (t, $J = 7.7$ Hz, 1H), 7.90 (d, $J = 7.8$ Hz, 2H), 7.66 (d, $J = 1.8$ Hz, 2H), 7.51 (d, $J = 1.8$ Hz, 2H), 4.58 (dt, $J = 13.0$, 6.4 Hz, 1H), 4.35 (dt, $J = 13.7$, 6.9 Hz, 2H), 2.23 (dq, $J = 13.1$, 7.6 Hz, 13H), 2.17 – 1.99 (m, 4H), 1.08 (dt, $J = 18.2$, 7.6 Hz, 19H). $^{13}$C $\{^1$H$\}$ NMR (101 MHz, DMSO-$d_6$) $\delta$ 164.6, 155.8, 142.5, 126.2, 123.0, 122.5, 55.1, 23.6, 10.9 (d, $J = 48.8$ Hz), 14.4, 5.5 (d, $J = 5.2$ Hz). $^{31}$P $\{^1$H$\}$ NMR (162 MHz, DMSO-$d_6$) $\delta$ 39.75, -144.20 (m). HR ESI-MS: Calcd for [M+2PF$_6$]$^+$,C$_{31}$H$_{53}$ClN$_5$PdP$_4$F$_{12}$: 986.1789; Found: 986.1794 [M+2PF$_6$]$^+$

Compound 34.1 ((3-bromopropyl)triphenylphosphonium bromide) was synthesized according to a literature procedure. $^1$H NMR of the prepared compound was in close agreement with reported data.$^{89}$
Proligand 34.2, [3,3’-(pyridine-2,6-diylbis(methylene))bis(1-(3-(triphenylphosphonio)propyl)-1H-imidazol-3-ium)][PF$_6$]$_2$[Br]$_2$

Compound 34.1 (Figure 2-2) ((3-bromopropyl)triphenylphosphonium bromide) (0.41 g, 0.89 mmol) was added to a flame dried flask round bottomed flask containing one equivalent of (0.1 g, 0.42 mmol) BIP dissolved in 3 mL of dry CH$_3$CN. The solution was brought to reflux under N$_2$ for 12 h to yield a white precipitate. The headspace then poured off and the isolated oil was washed with Et$_2$O before being dissolved in ~5 mL of water. This solution was then dropped into beaker of stirred sat. KPF$_6$ (aq), to form a white precipitate. The mixture was stirred for an additional 40 minutes and the solids were collected, washed with water, dried in air and recrystallized from a minimal volume of DCM at –12 °C to isolate a white solid. Degree of exchange of Br$^-$ for PF$_6^-$ was estimated by integrating resonances in $^{31}$P {$^1$H} NMR Isolated yield: 0.31g (0.23 mmol, 55%) 

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 9.24 (s, 2H), 8.02 – 7.88 (m, 7H), 7.86 – 7.76 (m, 26H), 7.75 (d, $J = 1.8$ Hz, 2H), 7.41 (d, $J = 7.7$ Hz, 2H), 5.52 (s, 4H), 4.36 (t, $J = 6.9$ Hz, 4H), 3.69 – 3.56 (m, 4H), 2.23 – 2.08 (m, 4H). $^{13}$C {$^1$H} NMR (101 MHz, DMSO-d$_6$) $\delta$ 154.3, 139.6, 137.6, 135.7 (d, $J = 3.1$ Hz), 134.1 (d, $J = 10.2$ Hz), 130.9 (d, $J = 12.5$ Hz), 123.8, 123.0, 122.5, 118.9, 118.0, 53.4, 49.3 (d, $J = 21.2$ Hz), 23.1, 18.6. $^{31}$P {$^1$H} NMR (162 MHz, DMSO-d$_6$) $\delta$ 23.93, –144.20 (m). HR ESI-MS: Calcd for [M+3PF$_6$]$^+$,C$_{55}$H$_{55}$N$_5$F$_{18}$P$_5$: 1282.2858; Found: 1282.2869 [M+3PF$_6$]$^+$
Complex 34

Synthesis of complex 34 was carried out according to the general metalation procedure with 0.27 g (0.21 mmol) of 34. All other reagents were added according to the molar ratios provided in the general method and the volume of DMSO was scaled to keep molarities consistent. Following the general workup, the crude product was dissolved in 2 mL of DCM and washed 2× with water, 2× with brine and dried over MgSO₄. Evaporation of the solvent afforded 0.16 g of a light yellow solid (0.11 mmol, 55% yield). ¹H NMR (400 MHz, CD₃CN) δ 8.06 (td, J = 7.8, 1.5 Hz, 1H), 7.81 (ddd, J = 9.1, 5.2, 1.8 Hz, 6H), 7.75 – 7.59 (m, 28H), 7.34 (t, J = 1.7 Hz, 2H), 7.13 (d, J = 1.7 Hz, 2H), 5.22 (dd, J = 15.3, 1.5 Hz, 2H), 4.89 (dd, J = 14.8, 9.7 Hz, 4H), 4.34 (ddt, J = 16.8, 12.3, 6.2 Hz, 2H), 3.24 (qd, J = 16.1, 14.4, 7.1 Hz, 4H), 2.70 – 2.45 (m, 3H), 2.17 (d, J = 1.5 Hz, 9H). ¹³C ¹H NMR (101 MHz, CD₃CN) δ 164.5, 155.1, 135.2, 135.2, 133.8, 133.7, 130.3, 130.2, 125.6, 122.6, 121.5, 118.1, 55.5, 24.9. ³¹P ¹H NMR (162 MHz, DMSO-d₆) δ 23.92, -144.19 (m). HR ESI-MS: Calcd for C₅₅H₅₃ClN₅PdP₄F₁₂ [M+2PF₆]⁺: 1274.1789; Found: 1274.1792 [M+2PF₆]⁺

Compound 35.1 ((2-(hydroxymethyl)phenyl)triphenylphosphonium)[PF₆]) was prepared according to a published method. ¹H NMR of the isolated compound closely matched reported data.⁹⁰

Compound 35.2

The following preparation was modified from a published procedure.⁹¹ Compound 35.1 (Figure 2-2) (3.00 g, 6.68 mmol) was dissolved in 20 mL
of DCM along with one equivalents of PPh₃ (1.75 g, 6.68 mmol). The solution was cooled to –15 °C in an ethylene glycol/dry ice slurry before and 1.19 g of N-bromosuccinimide (6.68 mmol) was added over the course of five minutes as a concentrated CH₃CN solution. This bath temperature maintained for 4 h; subsequent solvent removal produced a light-yellow oil. A white solid was afforded by vigorously stirring the isolated oil under a large volume of ethyl acetate. The ethyl acetate wash was poured off and the solid produced by washing was taken up into a minimal volume of methanol and dropped into a 200 mL saturated solution of KPF₆ (aq.). This immediately formed a white precipitate. The precipitated solids were collected by vacuum filtration, washed with water and then Et₂O and dried under high vacuum. Finally, the dried material was columned over silica in a (DCM:CH₃CN) (90:10) solution containing 0.1% formic acid yielding three bands; the first two were collected to produce a white solid. This procedure was found to produce chlorinated and brominated benzylic products; both were found to be adequately reactive for the next conversion and were used as a mixture. Yield: Overall: 2.04 g, 55%; bromo: 1.2 mmol (18%), chloro: 2.49 mmol (37%) (ratios from NMR). The resulting product was carried on to the next without further characterization. ¹H NMR (400 MHz, DMSO- d₆) δ 8.00 (m, 4H), 7.92 – 7.80 (m, 12H), 7.75 (tdd, J = 7.7, 2.6, 1.2 Hz, 1H), 7.34 (ddd, J = 15.6, 7.9, 1.3 Hz, 1H), 7.28 (s, 1H), 7.25 (ddd, J = 7.9, 5.5, 1.1 Hz, 1H), 6.87 (t, J = 1.1 Hz, 1H), 6.63 (t, J = 1.3 Hz, 1H), 4.87 (d, J = 1.4 Hz, 2H).

**Compound 35.3**, [(2-((1H-imidazol-1-yl)methyl)phenyl)triphenylphosphonium] [PF₆]₆

The following procedure was modified from published work. One equivalent of 35.2 (1.50 g, 2.79 mmol) was combined with ~5 eq. of
imidazole (0.93 g, 14.67 mmol) in a 50 mL glass bomb. THF (15 mL) was added to the bomb and the reaction vessel was sealed with a Teflon cap. The reaction mixture was brought to a reflux at 95 °C for 12 h. After being cooled to room temperature, the biphasic reaction mixture was transferred to a round bottom flask. Solvent removal exposed a light-yellow oil that was washed with ethyl acetate to solidify the oil. The off-white solid produced during the wash was isolated by vacuum filtration, dissolved in DCM and washed with 0.5 M NaOH until all solids had partitioned into the DCM layer. The organic layer was dried over MgSO₄. Evaporation of the solvent rendering a white solid. Yield: 1.24 g, 2.19 mmol, 78%. ¹H NMR (400 MHz, DMSO-d₆) δ 8.00 (ddddd, J = 9.5, 6.3, 3.7, 1.9 Hz, 4H), 7.92 – 7.80 (m, 12H), 7.75 (tdd, J = 7.7, 2.6, 1.2 Hz, 1H), 7.34 (dddd, J = 15.6, 7.9, 1.3 Hz, 1H), 7.28 (s, 0H), 7.25 (ddd, J = 7.9, 5.5, 1.1 Hz, 1H), 6.87 (t, J = 1.1 Hz, 1H), 6.63 (t, J = 1.3 Hz, 1H), 4.87 (d, J = 1.4 Hz, 2H). ¹³C ¹H NMR (101 MHz, DMSO-d₆) δ 142.7 (d, J = 7.8 Hz), 138.3, 136.9 (d, J = 11.6 Hz), 136.7 (d, J = 2.8 Hz), 136.0 (d, J = 3.0 Hz), 134.9 (d, J = 10.6 Hz), 130.3 (d, J = 12.7 Hz), 129.6, 129.2 (d, J = 11.9 Hz), 119.8, 118.5, 117.6, 116.4, 115.5, 48.7 (d, J = 5.5 Hz). ³¹P NMR (162 MHz, DMSO-d₆) δ 21.24, (m) -144.19. HR ESI-MS: Calcd for C₂₆H₂₅N₂P₂F₆ [M+HPF₆]⁺: 565.1397; Found: 565.1386 [M+HPF₆]⁺

**Proligand 35.4.** [2,2′-(pyridine-2,6-diylbis(methylene))bis(1-(3-(triphenylphosphonio)benzyl)-1H-imidazol-3-ium)] [PF₆]₂[Br]₂

![Diagram of Proligand 35.4](image)

This procedure was modified from the literature. Compound 35.3 (1.00 g, 1.77 mmol) was dissolved in 3 mL of CH₃CN along with 0.19 g (0.71 mmol) of 2,6-bisbromomethylpyridine in a round
bottomed flask. The solution was brought to reflux under N₂ for 12 h to yield off white precipitates. The solids were separated from the reaction mixture by centrifugation and ground 3× under Et₂O to remove most of the starting material. The crude product was then taken up into a minimal volume of CH₃CN and dropped into Et₂O to precipitate a white solid that was isolated by centrifuging. This process was repeated four times to obtain the bis-substituted proligand in acceptable purity. Yield: 0.94 g (0.68 mmol, 95%). ¹H NMR (400 MHz, DMSO-d₆) δ 8.12 (tt, J = 7.7, 1.6 Hz, 2H), 8.00 (d, J = 7.8 Hz, 1H), 7.97 – 7.92 (m, 4H), 7.89 (tdd, J = 7.7, 2.5, 1.2 Hz, 3H), 7.85 – 7.75 (m, 25H), 7.69 (t, J = 1.8 Hz, 2H), 7.44 – 7.35 (m, 4H), 7.21 (t, J = 1.9 Hz, 2H), 5.49 (s, 4H), 5.19 (s, 4H).¹³C {¹H} NMR (101 MHz, DMSO-d₆) δ 154.1, 139.6, 137.9 (d, J = 7.4 Hz), 137.7, 137.6, 137.0, 136.1 (d, J = 3.2 Hz), 135.0 (d, J = 10.7 Hz), 133.8 (d, J = 9.5 Hz), 131.7 (d, J = 12.4 Hz), 131.2 (d, J = 12.8 Hz), 123.8, 122.8, 122.7, 118.1, 117.8, 117.21, 116.9, 53.4, 51.3. ³¹P {¹H} NMR (162 MHz, DMSO-d₆) δ 21.35, (m) -144.21. HR ESI-MS: Calcd for C₆₃H₅₅N₅P₅F₁₈ [M+3PF₆]⁺: 1378.2858; Found: 1378.2871 [M+3PF₆]⁺

**Complex 35**

Metalation of 35.4 was carried out according to the general metalation procedure with 0.64 g (0.46 mmol) of 35.4. All other reagents were added according to the molar ratios provided in the general method and the volume of DMSO was scaled to keep molarities consistent. Following the workup described in the general procedure, the isolated solids was taken up into DCM, washed 2x with water, 2x with brine and dried over MgSO₄. The product was then purified further by recrystallizing from a minimum amount of DCM at -12 °C to render a white crystalline powder. Isolated yield: 0.29g (0.19 mmol, 42%). ¹H NMR (400
MHz, DMSO-\textit{d}_6) \delta 8.22 (t, J = 7.7 Hz, 1H), 8.03 (t, J = 7.8 Hz, 2H), 7.95 – 7.88 (m, 7H), 7.87 – 7.72 (m, 27H), 7.61 (d, J = 1.9 Hz, 2H), 7.39 – 7.29 (m, 2H), 7.24 (dd, J = 7.7, 5.8 Hz, 2H), 6.86 – 6.79 (m, 2H), 5.63 (d, J = 15.2 Hz, 2H), 5.42 (d, J = 15.1 Hz, 2H), 5.26 (d, J = 16.0 Hz, 2H), 5.03 (s, 2H). 13C \{^1\text{H}\} NMR (101 MHz, DMSO-\textit{d}_6) \delta 166.2, 155.3, 142.4, 142.0 (d, J = 7.5 Hz), 137.0 (d, J = 11.5 Hz), 136.5, 135.9 (d, J = 3.0 Hz), 134.9 (d, J = 10.6 Hz), 131.3 (d, J = 12.8 Hz), 131.0 (d, J = 9.9 Hz), 130.3 (d, J = 12.7 Hz), 126.3, 123.6, 122.0, 118.3, 117.4, 116.3, 115.5, 55.0, 52.0. 31P \{^1\text{H}\} NMR (162 MHz, DMSO-\textit{d}_6) \delta 21.09, -144.20. HR ESI-MS: Calcd for C_{63}H_{53}ClN_{5}PdP_{4}F_{12} [M+2PF_{6}]^+: 1370.1789; Found: 1370.1763 [M+2PF_{6}]^+

**Compound 36.1**, [(3-(hydroxymethyl)phenyl)triphenylphosphonium] [PF$_6$]

The synthesis and purification of was 36.1 performed following a literature procedure.\textsuperscript{90} \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \delta 8.01 – 7.94 (m, 3H), 7.91 – 7.86 (m, 1H), 7.86 – 7.70 (m, 14H), 7.67 (d, J = 13.5 Hz, 1H), 5.52 (t, J = 5.6 Hz, 1H), 4.60 (d, J = 5.4 Hz, 2H). 13C \{^1\text{H}\} NMR (101 MHz, DMSO-\textit{d}_6) \delta 145.71 (d, J = 12.1 Hz), 135.83 (d, J = 3.2 Hz), 135.03 (d, J = 10.4 Hz), 133.65 (d, J = 3.1 Hz), 133.38 (d, J = 10.7 Hz), 132.32 (d, J = 10.6 Hz), 132.00 (d, J = 11.0 Hz), 130.95 (d, J = 12.8 Hz), 118.69 (d, J = 2.1 Hz), 118.29, 117.81 (d, J = 1.9 Hz), 117.41, 62.25. 31P \{^1\text{H}\} NMR (162 MHz, DMSO-\textit{d}_6) \delta 22.46. HR ESI-MS: Calcd for C$_{25}$H$_{22}$N$_{2}$OP [M]$^+$: 369.1408; Found: 369.1415 [M]$^+$
**Compound 36.2**

The preparation of **36.2** was carried out according to the procedure reported for ortho analog (**35.2**) with the exception of the column conditions and mass of precursor, **36.1**, used (1.00 g 2.23 mmol). The crude in this case was separated over silica with a EtOAc/DCM/formic acid solution (20:80:0.01 v/v) eluting phase. A 4:1 mixture of the chlorinated and brominated benzylic products was isolated with a combined yield of 3.28 g (1.06 mmol Br: 16%), (4.28 mmol Cl: 64%). A small amount of impurity is carried over the column along with the halogenated products causing integration in the aromatic region to be slightly higher than expected. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.04 (dt, $J = 7.9$, 1.5 Hz, 1H), 7.98 (tdd, $J = 7.2$, 5.3, 2.7 Hz, 4H), 7.89 – 7.69 (m, 16H), 4.90 (s, 1.25H), 4.83 (s, 0.36H). $^{31}$P NMR (162 MHz, DMSO-$d_6$) δ 22.34, 22.29, 144.18.

**Compound 36.3, [(3-((1H-imidazol-1-yl)methyl)phenyl)triphenylphosphonium] [PF$_6$]**

Beginning with 2.5 g (4.70 mmol) of **36.2**, $N$-substitution of imidazole onto this compound was carried out according to the procedure reported for the ortho analog (**35.2**). Following the steps listed above, crude **36.2** was dissolved in 1 M HCl. Any insoluble material was removed from the suspension by vacuum filtration. The solution was then made basic with 10 M NaOH and caused a white solid to precipitate. The solids were isolated by filtration, washed with water and air dried. The purified product dissolved in DCM and dried with Na$_2$SO$_4$. Solvent removal produced a white solid. Isolated yield: 1.29 g (2.28 mmol, 49%) $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.98 (td, $J = 7.3$, 1.7 Hz, 3H), 7.82 (dt, $J = 7.4$, 3.9 Hz, 9H), 7.76 – 7.69 (m, 7H), 7.65 – 7.57.
(m, 2H), 7.18 (s, 1H), 6.91 (s, 1H), 5.35 (s, 2H). $^{13}$C $\{^1$H\} NMR (101 MHz, DMSO-$d_6$) $\delta$ 140.9 (d, $J = 12.7$ Hz), 138.0, 135.9 (d, $J = 3.0$ Hz), 135.0 (d, $J = 10.4$ Hz), 134.6 (d, $J = 3.1$ Hz), 134.4 (d, $J = 10.5$ Hz), 133.4 (d, $J = 11.0$ Hz), 131.3 (d, $J = 13.3$ Hz), 130.9 (d, $J = 12.9$ Hz), 129.5, 119.9, 119.2, 118.4, 118.3, 117.5, 49.1. $^{31}$P $\{^1$H\} NMR (162 MHz, DMSO-$d_6$) $\delta$ 22.27, –144.20 (m). HR ESI-MS: Calcd for C$_{28}$H$_{24}$N$_{2}$P $[M]^+$: 419.1679; Found: 419.1674 $[M]^+$

**Proligand 36.4.** [3,3’-(pyridine-2,6-diylbis(methylene))bis(1-(3-(triphenylphosphonio)benzyl)-1H-imidazol-3-ium)] [PF$_6$][Br]$_2$

This procedure was modified from an in-house method. Compound 36.3 (0.43g, 0.76 mmol) was weighed into a flame dried round bottom flask along with 0.09 g (0.34 mmol) of 2,6-bis(bromomethylpyridine). CH$_3$CN (3 mL) was added to the flask and the solution was brought to reflux under N$_2$ for 12 hrs. After cooling to RT, half of the solvent was removed *in vacuo* and the solution volume was doubled with dry Et$_2$O to form a light white precipitate. The precipitate was collected by centrifuging, re-dissolved in CH$_3$CN and precipitated a second time with Et$_2$O. The solids were isolated by centrifuging and dried to isolate 0.47 g (0.33 mmol, 97%) of a white solid. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.55 (d, $J = 1.9$ Hz, 2H), 8.03 – 7.96 (m, 9H), 7.92 – 7.80 (m, 20H), 7.80 – 7.72 (m, 14H), 7.49 (d, $J = 7.8$ Hz, 2H), 5.72 (s, 4H), 5.60 (s, 4H). $^{13}$C $\{^1$H\} NMR (101 MHz, DMSO-$d_6$) $\delta$ 154.1, 139.5, 136.0 (d, $J = 10.6$ Hz), 134.4 (d, $J = 11.0$ Hz), 131.7 (d, $J = 13.2$ Hz), 131.0 (d, $J = 12.8$ Hz), 124.2, 123.0, 122.7, 119.6, 118.7, 118.3, 117.4, 53.4, 51.6. $^{31}$P $\{^1$H\} NMR (162 MHz, DMSO-$d_6$) $\delta$ 22.30, (m) -144.20. HR ESI-MS: Calcd for C$_{63}$H$_{55}$N$_{5}$P$_5$F$_{18}$ $[M+3PF_6]^+$: 1378.2858; Found: 1378.2861 $[M+3PF_6]^+$
Complex 36

Synthesis of complex 36 carried out following the general metalation procedure with 0.43 g (0.31 mmol) of 36. All other reagents were added according to the molar ratios provided in the general method and the volume of DMSO was scaled to keep concentrations consistent. Following the general workup, the crude was purified by column chromatography over basic alumina with DCM:MeOH (90:10) as the eluting phase. The first fraction was found to contain the product. Subsequent solvent removal exposed the product as an off white solid. Isolated yield: 0.20 g (0.13 mmol, 42%).

1H NMR (400 MHz, DMSO-d6) δ 8.26 – 8.18 (m, 1H), 7.94 (t, J = 7.2 Hz, 10H), 7.89 – 7.61 (m, 32H), 7.59 (d, J = 2.1 Hz, 2H), 7.44 (d, J = 13.4 Hz, 2H), 7.36 (d, J = 2.2 Hz, 2H), 5.83 (d, J = 15.3 Hz, 2H), 5.68 (d, J = 15.4 Hz, 2H), 5.61 (d, J = 15.1 Hz, 2H), 5.42 (d, J = 15.0 Hz, 2H).

13C {1H} NMR (101 MHz, DMSO-d6) δ 165.2, 155.5, 142.51, 140.4 (d, J = 12.7 Hz), 135.9, 134.9 (d, J = 10.5 Hz), 134.42, 133.6 130.9 (d, J = 12.8 Hz), 126.2, 123.1, 118.8, 118.3, 117.9, 117.5, 54.9, 51.9.

31P {1H} NMR (162 MHz, DMSO-d6) δ 22.32, (m) -144.21. HR ESI-MS: Calcd for C63H53ClN5PdP4F12 [M+2PF6]+: 1370.1789; Found: 1370.1789 [M+2PF6]+

Compound 37.1, [3-(chloromethyl)-1-methylpyridin-1-ium][I]

Commercially available 3-chloromethylpyridine hydrogen chloride (2.00 g, 12.19 mmol) was weighed into a flame dried, 250 mL round bottomed flask charged with nitrogen. Degassed toluene (100 mL) was added to the flask along with K2CO3 (5 g, 36.23 mmol). The mixture was stirred vigorously for 1h. The reaction temperature was then brought to 80 °C for 1 h. The reaction was cooled to RT and the
residual solids were removed by vacuum filtration. The toluene solution was transferred to a dry 250 mL flask and the reaction vessel was flushed with N₂. While stirring, methyl iodide (6.80 mL, 0.11 mol) was added via syringe to the flask. This immediately produced a light white precipitate. The reaction was allowed to stir for three days at RT before the light green-yellow precipitate was collected by centrifuging. The solids were washed several times with DCM, Et₂O and dried under vacuum to isolate a light green solid (1.93 g, 7.19 mmol, 59%). ¹H NMR (400 MHz, DMSO-d₆) δ 9.15 (s, 1H), 8.97 (d, J = 6.1 Hz, 1H), 8.65 (d, J = 8.1 Hz, 1H), 8.20 – 8.13 (m, 1H), 4.99 (s, 2H), 4.36 (s, 3H).

**Proligand 37.2,** [3,3'-'-(((pyridine-2,6-diylbis(methylene))bis(1H-imidazole-3-ium-1,3-diyl))bis(methylene))bis(1-methylpyridin-1-ium)] [PF₆⁻]₂[Br⁻]₂

Compound 37.1 (0.54 g, 1.99 mmol) of was combined with 0.22 g (0.91 mmol) of BIP in a round bottomed flask and 25 mL of dry CH₃CN was added. The insoluble mixture was stirred vigorously and heated to a reflux. At reflux, complete dissolution of the solids was observed. The reaction was allowed to reflux overnight to produce a pale blue-green precipitate. The reaction was cooled to RT and the produced solids were isolated by filtration, taken up into a small amount of methanol and dropped into a saturated aqueous solution of KPF₆ to generate a precipitate that was collected and washed with water. The crude product was purified by recrystallizing from a mixture of boiling acetone and MeOH to yield a white crystalline powder. Isolated yield: 0.36 g (0.35 mmol, 38%). ¹H NMR (400 MHz, DMSO-d₆) δ 9.37 (t, J = 1.6 Hz, 2H), 9.09 (d, J = 1.5 Hz, 2H), 9.06 (dd, J = 6.1, 1.3 Hz, 2H), 8.60 (dt, J = 8.2, 1.5 Hz, 2H), 8.24 (dd, J = 8.1, 6.1 Hz, 2H), 8.01 (t, J = 7.8 Hz, 1H), 7.84 (d, J = 1.6 Hz, 4H), 7.47 (d, J = 7.8 Hz,
2H), 5.70 (s, 4H), 5.58 (s, 4H), 4.38 (s, 6H). $^{13}$C $\{^{1}$H$\}$ NMR (101 MHz, DMSO-$d_6$) δ 154.1, 146.8, 146.0, 145.4, 139.6, 138.2, 135.1, 128.3, 124.2, 123.2, 122.7, 53.6, 49.0, 48.7. HR ESI-MS: Calcd for C$_{27}$H$_{31}$N$_7$P$_3$F$_{18}$ [M+3PF$_6$]$^+$: 888.1566; Found: 888.1556 [M+3PF$_6$]$^+$

**Complex 37**

Metalation of proligand 37.2 was carried out according to the general metalation procedure with the following mass of pincer ligand: 0.35 g (0.34 mmol). All other reagents were added according to the molar ratios provided in the general method and the volume of DMSO was scaled to keep concentrations consistent. Following the general workup, the crude solid was columned over neutral alumina with 1% sat KNO$_3$ (aq.) in CH$_3$CN as the eluting phase. A white solid was isolated after the solvent was removed from the column fractions. This was then taken up into CH$_3$CN and dropped into sat KPF$_6$ (aq.) to produce a white precipitate that was washed with water, air dried, ground under Et$_2$O and dried thoroughly under high vacuum. Isolated yield: 0.11 g (0.09 mmol, 25%) $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.00 (s, 2H), 8.96 (d, $J$ = 6.1 Hz, 2H), 8.50 (d, $J$ = 8.1 Hz, 2H), 8.26 (t, $J$ = 7.7 Hz, 1H), 8.14 (dd, $J$ = 8.1, 6.0 Hz, 2H), 7.89 (d, $J$ = 7.8 Hz, 2H), 7.72 (d, $J$ = 1.8 Hz, 2H), 7.44 (d, $J$ = 1.9 Hz, 2H), 5.95 – 5.79 (m, 4H), 5.75 (s, 4H), 4.34 (s, 6H). $^{13}$C $\{^{1}$H$\}$ NMR (101 MHz, DMSO-$d_6$) δ 165.4, 155.7, 145.5, 145.2, 144.4, 142.4, 137.8, 128.1, 126.3, 123.5, 122.9, 55.2, 49.3, 48.6. HR ESI-MS Calcd for C$_{27}$H$_{29}$ClN$_7$Pd$_2$F$_{12}$ [M+2PF$_6$]$^+$: 880.0497; Found: 880.0494 [M+2PF$_6$]$^+$
2.4.3 Computational methods

DFT calculations were performed using Gaussian 16 (Revision A.03)\textsuperscript{93} using the long-range and dispersion corrected ωB97xD hybrid functional.\textsuperscript{94} The D95(d) basis set was used for all atoms except palladium, which employed the Stuttgart-DresdenBonn quasi-relativistic effective-core potential and corresponding correlation-consistent triple-ζ basis set.\textsuperscript{95,96} Frequency calculations were performed on all geometry-optimized structures to ensure that energy minima were achieved.
Chapter 3: Hybrid Phosphine-NHC Palladium Pincer Complexes as Electrocatalysts for CO₂ Reduction

3.1 Introduction

Since 1990, the market share of renewably sourced power has grown at an annual rate of 2.2%.⁹⁷ A combination of cost-effective production and improved technologies have allowed the price of electricity generated by wind and solar farms to become competitive with coal and natural gas.⁹⁸ However, the transient availability of most renewable energy sources requires the generated power to be stored for on-demand use. Existing mechanisms of storage struggle to provide an energy medium that is well suited for a diverse global demand, and more adaptable fuel technologies are needed.⁸,¹⁸ Electrochemical conversion of CO₂ into energy-rich molecules provides a route for transforming renewably generated electricity into liquid fuels that can be used to power internal combustion engines.⁷⁵ The potential of this solution has been realized for decades and a growing scientific effort has focused on improving the efficiency of systems that transform CO₂.³²

Electrochemical conversion of CO₂ to energy relevant substrates requires the use of a catalyst in order to mediate the high kinetic barrier associated with its initial activation.²⁹ Of several classes of organometallic catalysts, palladium(II) triphosphine pincer complexes (Figure 3-1, 21 and related structures) are capable of operating at low overpotential.⁶⁹ However, the limited catalytic lifetime (TON: ~200) of this motif has prompted an investigation into a related palladium(II) pincer system bearing stronger σ-donating NHC ligands and a pyridyl group as the third chelating center (Figure 3-1, complex 26).⁷¹ Although 26 and structurally analogous
complexes demonstrate improved stability and activity towards CO₂ conversion, selectivity for this transformation was significantly limited relative to the triphosphine pincer analogues.⁷⁴

![Structures of catalysts](image)

**Figure 3-1.** Structures of a palladium triphosphine pincer catalysts, 21 and 21p, and two palladium bis-NHC pyridyl pincer catalysts 26 and 26s.⁶⁵,⁶⁸,⁷¹

Early work on 21 outlined the importance of phosphine centers in the ligand scaffolding. Selectivity for CO was essentially lost by exchanging P for any of the five heteroatoms explored.⁶⁷ As the donor/acceptor behavior of NHC and phosphine ligands is believed to be similar, it seems possible that the diminished selectivity of 26 is caused by the altered binding mode provided by the pyridyl group.⁹⁹,¹⁰⁰ Indeed, a recent study demonstrated that functionalization of electron donating and withdrawing groups into the para-pyridyl position of 26 systematically varied redox properties, indicating a strong electrocatalytic dependence on this ligand center.⁷⁷

Pincer complexes of mixed phosphine and NHC units have been explored as catalysts for several transformations,¹⁰¹,¹⁰²,¹⁰³, most notably in a recent report, for the reduction of N₂ by H₂ to form NH₃.¹⁰³ The dinuclear molybdenum, hybrid NHC phosphine complex evaluated in this study demonstrated unprecedented performance for this conversion. According to the authors,
the enhanced catalysis was promoted by the strong $\sigma$-donating and $\pi$-accepting character of the hybrid ligand.\textsuperscript{103}

A mixed NHC-phosphine donor set has yet to be investigated as a scaffolding for CO\textsubscript{2} electrocatalysis. Herein, a carbene-phosphorus-carbene \([\text{C}^\text{P}^\text{C}]\) pincer complex that combines structural aspects of \textbf{21} and \textbf{26} is proposed. The novel Pd(II) catalyst will feature trans-NHC donors ethyl linked to a cis-phenyl phosphine unit. The stronger metal-ligand bonding of NHC donors,\textsuperscript{99} combined with the improved selectivity for CO\textsubscript{2} accompanying a phosphine center, could yield a complex with good stability and improved selectivity for CO\textsubscript{2} relative to Pd[triphos] and Pd[C\textsuperscript{N}C], respectively.

### 3.2 Results and discussion

Two new palladium C\textsuperscript{P}C pincer complexes have been synthesized and characterized using $\textsuperscript{1}H$, $\textsuperscript{13}C$, COSY, HSCQ, HMBC and $\textsuperscript{31}P$ NMR experiments, in addition to mass spectrometry and X-ray crystallography. Screening for catalytic activity towards CO\textsubscript{2} reduction was carried out via cyclic voltammetry. Following initial measurements, the stability and selectivity of each catalyst were determined through controlled potential electrolysis coupled with GC headspace analysis.
3.2.1 Synthesis

Scheme 3-1. Synthetic route to complexes 38 & 38S.

Synthesis of the pincer ligand (Scheme 3-1) begins with the N-alkylation of vinyl imidazole using iodobutane to afford the imidazolium iodide compound (38.1) in high yield. Performing salt metathesis at this stage to exchange the iodide for a hexafluorophosphate ion was found to greatly improve tractability and yields in later steps. Following ion exchange, compound 38.1 was condensed with phenyl phosphine in a single step utilizing a base catalyzed, anti-Markovnikov addition to form a secondary phosphine symmetrically substituted with two 1-N-butyl-3-ethyl-imidazolium groups (38.2).\textsuperscript{104,105} Palladation of the tridentate proligand was achieved through a silver transmetalation reaction involving Ag\textsubscript{2}O and PdCl\textsubscript{2}(cod). Workup of the reaction mixture yielded the chloride complex (38) in a 42% yield which could be further reacted with silver trifluoromethanesulfonate in CH\textsubscript{3}CN to produce a solvent species (38S). Compound 38 was fully characterized by \textsuperscript{1}H, \textsuperscript{13}C, COSY, HSCQ, HMBC and \textsuperscript{31}P NMR experiments as well as mass spectrometry. Single crystals of 38S were grown via vapor
diffusion of Et₂O into CH₃CN at -12° C and analyzed by X-ray crystallography for more insight on structural details.

3.2.2 Palladium C^P^C pincer complex structure

![Diagram of palladium complex structure]

**Figure 3-2.** Asymmetric unit of 38S with thermal ellipsoids drawn are at 50 % probability level. Structural refinements were made using ShelXL via the OLEX2 interface. ORTEP diagrams were generated using PLATON.

The pincer ligand was found to coordinate to Pd(II) forming a scorpion-like, quasi-square planar structure with the phosphine donor positioned *trans* to the CH₃CN ligand and the two NHC units binding *cis* to the CH₃CN-Pd-P axis (Figure 3-2). In contrast to 26S where the NHC
rings paddle in opposite directions at a 45° angle out of the plane of the molecule, the NHC units of 38S adopt an approximately coplanar orientation, both twisting at an 38° angle relative to the P1-Pd-CH3CN axis. The phosphine center assumes a tetrahedral geometry causing the P-bound phenyl ring to preside at a 115° angle above the plane of the molecule. This also forces the ethylene linker to exist above the square planar surface and adopt a syn-periplanar conformation. This orientation is similar to that expressed by Pd[triphos] complexes of a wider chelate angle (Figure 3-1, 21p).

The palladium-carbene bond lengths of 38S are essentially unchanged from 26S and coordinate more closely than the phosphine donors in 21p. However, both the Pd-P and Pd-CH3CN distances of 38S are elongated relative to the C^N^C analog and exhibit an equivalent bonding to 21p. Taken together, the bonding and structural orientation adopted by 38S appears to be intermediate to that of the two parent complexes. While the geometry about the CH3CN-Pd axis of 38S most closely resembles 21p, the palladium carbene bond lengths measured here suggest the NHC bonding character is retained from 26S.

3.2.3 Cyclic voltammetry of 38 and 38S under non-catalytic conditions

All electrochemical measurements were performed under the same conditions described in Chapter 2. The potentials were determined with an Ag/AgNO3 reference electrode and referenced to an internal Fe0/+ standard.
Figure 3-3. Cyclic voltammograms of complex 38S [2 mM] recorded at 0.1Vs⁻¹ in a 0.1M nBu4NPF6 DMF solution. The blue and red traces represent CVs recorded in N₂ and CO₂ saturated solutions, respectively.

Cyclic voltammograms of complex 38S recorded under N₂ demonstrate an irreversible reduction at –1.76 V and a smaller and a quasi-reversible feature at –2.1 V (Figure 3-3a). Scan rates up to 1000 mVs⁻¹ did not uncover reversibility in the first event. In the reverse scan, a small anodic event is observed around –0.4 V which was has been reported for similar complexes and is associated with the oxidation of an absorbed species. Analogous to the behavior of 26 and related structures discussed in Chapter 2, the first wave of this complex is broad with an $E_p$ to $E_{1/2}$ separation of 95 mV, potentially indicating slow reduction kinetics. Despite similarity in wave shape to 21S, 38S is reduced at considerably more negative potentials which may be explained by the greater basicity of a phosphine ligand relative to a pyridyl donor.

Saturation of the catholyte with CO₂ causes the first wave to shift positively by 70 mV and shrink in current intensity (Figure 3-3 (a)). Additionally, a second irreversible feature grows in at –2.2V with approximately twice the intensity of the first reduction. This behavior is nearly
identical to that of complex 21 and is consistent with the observation of two closely spaced, single electron reductions which appear as a concerted event under N₂. Addition of CO₂ to the solution causes this wave to split into two distinguishable reductions. This observation was attributed to the reaction of an electrogenerated Pd(I) species with CO₂ to form an adduct that is reduced a second time at higher potentials. Interestingly, this response is in sharp contrast to the results presented in Chapter 2 for complexes 32–36 where it was speculated that, under N₂, the Pd[C^N^C] catalysts undergo a single, one electron reduction at E_p{sub}c{sub}1. Addition of CO₂ to the solution caused the peak currents measured at E_p{sub}c{sub}1 to grow in height, due to the generation of a Pd-CO₂ adduct that is capable of being reduced a second time at this potential.

**Figure 3-4.** Cyclic voltammograms of complex 38 [2 mM] recorded at 0.1Vs⁻¹ in a 0.1M n-[Bu₄N]PF₆ DMF solution. The blue and red traces represent CVs recorded in N₂ and CO₂ saturated solutions, respectively.

Complex 38 displays two, fully irreversible reductions of equivalent magnitude under N₂ centered at –2.14 and –2.56 V (Figure 3-4 and Table 3-1). The negative shift in peak potential of 38 relative to the solvento species has been unambiguously observed in Pd[triphos] and
Pd[C^N^C] pincer complexes and results from the stronger coordinating ability of a halide ligand the divalent metal center.\textsuperscript{71,78,66} The wave shape and peak separation demonstrated by 38 is essentially unchanged from that of 26, however, the onset of reduction is shifted negatively by \(\sim 300\) mV relative to the pyridyl-bearing analog. Moreover, the reverse scans in CV of 38 are completely devoid of the signal at 0.5 V that is assigned to oxidation of chloride. This indicates that the fourth coordinate ligand is not electro-labile in this case, and Cl\(^-\) remains bound, even after scanning through the second reduction. This is a substantial change from the behavior of 26 and related complexes where chloride becomes labile after 1 e\(^-\) reduction.

CV of complex 38 under CO\(_2\) is unusual in that saturation of the electrode solution causes the voltammogram to collapse into a single wave centered at \(E_{\text{pc}1}\) N\(_2\) with 1.6 times the peak intensity measured under N\(_2\) (Figure 3-4 (b)). This transition from two events to a single observable reduction in the presence of CO\(_2\) is quite distinct from the response of 38S and indeed, is unique in palladium pincer complexes. The logic laid out in Section 2.2.3 that describes the \(i-V\) response of an irreversible reduction coupled to a homogeneous reaction was applied here. It is likely that 38 is operating analogously to 26, whereby, 1 e\(^-\) occurs before the complex binds CO\(_2\) and undergoes a second reduction as the CO\(_2\) adduct. This speculation is corroborated by the half peak to peak separation at \(E_{\text{pc}1}\) for 38 which was found to narrow by 30 mV in the presence of CO\(_2\). This behavior is typical for the observation of a chemical step followed by an electrode reduction. However, under these conditions, it appears that the 38 is not capable undergoing further reduction after accepting a second electron as the CO\(_2\) adduct. Divergence of the behavior expressed 38 from that of 26, in this regard, may be due to the particularly electron rich ligand field provided by the C\(^-\)P\(^-\)C ligand.\textsuperscript{106}
Table 3-1. Peak potential, peak width and relative current intensities extracted from cyclic voltammograms performed on complexes 38 and 38S in the presence of N2 and CO2. Dashes indicate that a peak was not observed.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conditions</th>
<th>$E_{p1}$ (V)</th>
<th>$\Delta E_{p1/2}$ (mV)</th>
<th>$\Delta I_{p1}$ CO2</th>
<th>$E_{p2}$ (V)</th>
<th>$\Delta I_{p2}$ CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>38S</td>
<td>N2</td>
<td>-1.76</td>
<td>98</td>
<td>-2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO2</td>
<td>-1.69</td>
<td>93</td>
<td>0.85</td>
<td>-2.18</td>
<td>2.13</td>
</tr>
<tr>
<td>38</td>
<td>N2</td>
<td>-2.15</td>
<td>93</td>
<td>-2.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO2</td>
<td>-2.17</td>
<td>63</td>
<td>1.57</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2.4 Cyclic voltammetry of electrocatalysts in the presence of an acid

Previous studies examining Pd(II) pincer complexes as electrocatalysts for CO2 reduction have consistently demonstrated that a strong acid required for sustained turnover of CO2 to CO. However, the comparatively negative reduction potentials of 38 & 38S suggest that these complexes may be more electron-donating towards CO2 in the reduced state. Theoretically, the greater nucleophilicity of 38 and 38S will generate an electron rich carboxylate moiety possessing a higher pKa and allow for the use of a weaker proton donor.

To probe this effect, three proton sources of decreasing acidity were explored, tetrafluoroboric acid (HBF4) (pKaCH3CN: 0.1) trifluoroacetic acid (TFA) (pKaCH3CN: 12.65) and glacial acetic acid (GAA) (pKaCH3CN: 23.51).

Comparison of CVs measured under CO2 and N2 in the presence of an identical acid concentration is often discussed as an indication of catalyst selectivity, wherein, selective turnover for CO is expected to accompany a larger current response with both CO2 and H+ available. Figure 3-5 conveys the $i$-V trace of complex 38S under N2 (solid green) and CO2
(yellow dash) with the addition of 10 mM HBF$_4$ (Figure 3-5 (a)) and 100 mM GAA (Figure 3-5 (b)).

### 3.2.5  Electrochemistry of 38S under catalytic conditions

The observation can be made from the CV traces in Figure 3-5 (a) that the onset of reductive current occurs at considerably more positive potentials with the presence of a strong acid relative to the unadulterated response of complex 38S. CVs measured with the addition of HBF$_4$ + N$_2$ and HBF$_4$ + CO$_2$ adopt the same wave shape up to approximately 2/3 of the peak potential, at which point, a slight gain in peak intensity is noticed with CO$_2$ available to the catalyst.

![Cyclic voltammograms of complex 38S in the presence (a) HBF$_4$ + N$_2$ (green trace) and HBF$_4$ and CO$_2$ (dotted orange line) as well as in a solution of (b) GAA + N$_2$ (green trace) and GAA + CO$_2$ (dotted orange line).](image)

**Figure 3-5.** Cyclic voltammograms of complex 38S in the presence (a) HBF$_4$ + N$_2$ (green trace) and HBF$_4$ and CO$_2$ (dotted orange line) as well as in a solution of (b) GAA + N$_2$ (green trace) and GAA + CO$_2$ (dotted orange line).

A nearly opposite situation occurs with the addition of a much weaker acid, GAA. Current enhancement is trivial across the first reduction event and the peak current of the N$_2$ + GAA CV approaches twice that measured under CO$_2$ + GAA at the most negative potentials.
Furthermore, the i-V curve measured here plateau beyond –2.5 V. This peak shape is expected for a pure catalytic response where the rate of reduction is defined by the TOF of the catalyst and current becomes independent of applied potential.\textsuperscript{25}

Analysis of the data presented in Figure 3-3 indicated that complex 33S is capable of binding CO\textsubscript{2} in Pd(I) oxidation state. However, more negative potentials were required to add a second electron to the resulting adduct. In the presence of a proton donor, protonation of the adduct may precede or follow an ensuing reduction depending on the relative pKa of the adduct and acid. The early onset of reduction in the presence of HBF\textsubscript{4} (Figure 3-5 (a)) suggests that this acid is of sufficient strength to protonate the 1 e\textsuperscript{-} reduced species, allowing catalysis to occur in a one electron reduction regime. This behavior closely matches the catalytic cycles proposed for 21.\textsuperscript{65} The similar response to HBF\textsubscript{4} in the absence of CO\textsubscript{2} however, suggests that protonation directly at the metal center may occur at a similar rate and signifies strong competition with catalysis for the hydrogen evolution reaction.\textsuperscript{67}

Conversely, catalytic currents are not observed until the second reduction event is traversed with GAA present as a proton source. This indicates that the Pd-CO\textsubscript{2} adduct is protonated after being reduced a second time with a weaker acid. Despite the standard interpretation that correlates a larger limiting current with product selectivity, the lower plateau current observed with 38S in the presence of CO\textsubscript{2} and GAA relative to N\textsubscript{2} and GAA demonstrates CO\textsubscript{2} modulation of the catalytic response. The most likely explanation here is that Pd(I)-CO\textsubscript{2} complexation is fast and protonation of the 2 e\textsuperscript{-} adduct is rate limiting. Without CO\textsubscript{2} present, the catalyst reverts back to undergoing two closely spaced single reductions (Figure 3-3). At this point, the Pd(0) species available for direct protonation which may cause a palladium hydride to form. However, considering the late onset of catalytic current here (Figure
3-5b green trace) it appears that a third reduction step may be necessary to turnover H₂ with a weaker acid.

3.2.6 Electrochemical behavior 38 under catalytic conditions.

![Cyclic voltammograms of complex 38](image)

**Figure 3-6.** Cyclic voltammograms of complex 38 in the presence (a) TFA + N₂ (green trace) and TFA and CO₂ (dotted orange line) as well as in a solution of (b) GAA + N₂ (green trace) and GAA + CO₂ (dotted orange line).

In complex 38, a similar situation is observed to 38S, whereby, larger currents are recorded in the absence of CO₂ with the addition of GAA ((Figure 3-6) (b)). This is contrasted by CV performed in the presence of a stronger proton donor (TFA), wherein, the currents recorded with CO₂ + H⁺ are modestly larger than that of N₂ + H⁺ (Figure 3-6 (a)). Unlike the solveto species, however, both acids, TFA and GAA, were discovered to be of adequate strength to induce a catalytic reaction in 38, beginning at the first reduction event.

Complex 33 is reduced in two separate 1e⁻ steps which merge into a single observable event when CO₂ is added to the solution (Section 3.2.3). The fact that the onset of catalysis begins before the first wave, under both N₂ + H⁺ and CO₂ + H⁺, suggests that the complex is
capable of interacting with either H\(^+\) or CO\(_2\) in the Pd(I) oxidation state. This feature may be accounted for by the particularly cathodic reduction potentials expressed by this complex in addition to the unusual stability of the Pd-Cl bond. It is expected that both aspects will function to produce a relatively electron dense Pd center.\(^{77}\) Nevertheless, the attenuated current of CO\(_2\) + GAA compared to N\(_2\) + GAA here, is most likely a consequence of the same rate determining factors discussed for \textbf{38S} and may be indicative of selectivity for CO\(_2\).

### 3.2.7 Bulk electrolysis of CO\(_2\) with 38 and 38S

In order to establish the stability and electrolytic selectivity of complexes \textbf{38} and \textbf{38S}, controlled potential electrolysis was performed in an air tight, three compartment cell containing 2 mM of catalyst and a proton source dissolved in a DMF solution saturated with CO\(_2\). The headspace was sampled during several hours of electrolysis and analyzed by gas chromatography to identify quantify any gaseous products produced.

The electrolytic stability of both complexes was determined to be a function applied potential and the acid present. Low overall Faradaic yield for gaseous products were measured when bulk electrolysis was carried out at potentials negative of \(\sim 2.4\) V (Table 3-2). In every case, the current was found to decay over time due the formation of a black insulating precipitate that coated the working electrode surface. In this case, post electrolysis CVs recorded on a clean electrode revealed diminished features that had been assigned to the catalyst, indicating that the precipitate resulted from degradation of the metal complex. This behavior was also noted when the potential was set positive of the catalytic onset which is, as discussed above, dependent upon the pKa of the acid.
Within the appropriate potential range, complexes 38 & 38S were found to produce a ratio of CO and H₂ in high yield with the assistance of GAA, TFA and HBF₄ proton donors (Table 3-2). Generally speaking, higher Faradaic efficiency for CO was observed with the application of a weaker acid and more cathodic potentials.

Complex 38S exhibited the highest Faradaic efficiency for CO at a potential of –2.2 V with GAA as the sole proton source (Table 3-2). No precipitation was detected in this case and a steady state current was maintained over the course of electrolysis. Additionally, the overall gaseous yield (98%) and CVs performed post electrolysis indicate limited catalyst deactivation under these conditions. However, long term stability experiments are needed to verify this result. Nevertheless, the selectivity for CO determined here is an improvement over the analogous C^N^C complex (26S). Moreover, this is the first report of a palladium pincer complex capable of sustained CO turnover with the use of a weak acid. Previous CPE
experiments with 26 and GAA required potassium as a supporting co-catalyst and substantial deactivation occurred during the run.

Complex 38 was found to possess somewhat lower selectivity for CO under the conditions listed in Table 3-2. In particular, electrolysis carried out at \( E_{pc1} \) with TFA yielded less than 2% FE CO. This result is not surprising considering the first reduction potential of 38 is 300 mV negative of the corresponding pyridyl complex. At potentials more negative than \(-1.6\) V, direct electrode reduction of protons becomes an increasingly large percentage of the current drawn from the electrode surface, causing FE for \( \text{H}_2 \) evolution to grow at the expense of a catalytically mediated reduction.\(^{71,107}\)

A much larger percentage of current goes to CO production when bulk electrolysis with 38 is carried out at the same potential with GAA as the proton source, possibly due to the lower concentration of \( \text{H}^+ \) under this condition. Interestingly, although the overall Faradaic yield for gaseous products accounted for less than 50% of the charge passed, post electrolysis CVs were identical to those measured before the experiment, indicating an intact catalyst.\(^71\) Moreover, the current measured during this electrolysis was steady over the course of 1 h with no precipitation detected. The discrepancy in coulombs of charge passed to moles of gas produced in combination with the appearance of a stable catalyst suggests catalytic evolution of an undetected product.

To investigate this further, the post-electrolysis solution was analyzed with \(^{31}\)P and \(^1\)H NMR spectroscopies. Two resonances were detected in the \(^{31}\)P \( \{^1\)H\} NMR after diluting the sample in CD\(_3\)CN, a multiplet centered at \(-144.20\) ppm corresponding to the [n-Bu\(_4\)N]PF\(_6\) electrolyte and a singlet observed at 26.60 ppm. The signal at 26.60 ppm is consistent with the palladium bound phosphorous center contained in the \( C^P^C \) ligand. The chemical shift
determined post-electrolysis is essentially unchanged from the value measured directly after purification (26.8 ppm), indicating that coordination environment of the phosphorous ligand remains intact through electrolysis.

$^1$H NMR spectra of the post electrolysis solution and a control containing the catalyst, electrolyte and GAA at identical concentration were collected to probe for any soluble reaction products. In addition to the expected resonances for [$n$-Bu$_4$N]PF$_6$ electrolyte, acetic acid and catalyst, a broad signal was detected at 4.15 ppm which was not observed in the control post CPE solutions analyzed for other in-house catalysts. Moreover, although H$_2$O generation is concomitant with CO$_2$ reduction catalysis, the location of this peak downfield by ~2 ppm from the expected position of H$_2$O in CD$_3$CN, suggesting that the presence of water in this sample is an unlikely explanation for the observation of a broad signal at 4.15 ppm.

With the intention of identifying this resonance as constituent to a C$_n$ molecule, a COSY NMR experiment was carried out on the electrolysis solution to identify correlations to any other protons in the $^1$H spectrum (Figure A-9). Unfortunately, coupling of the signal at 4.15 ppm was not detected, which indicates that this resonance does not originate from a hydrocarbon.

Nevertheless, the lack of degradation supported by $^{31}$P $^1$H NMR in combination with the low FE for gaseous products observed in this case is a good indication that an undetected reduction product was formed. A combination of better suited analytical techniques for product identification along with careful examination of the electrolysis conditions may allow insight into the products generated during electrocatalysis with 38.
3.3 Conclusion

In summary, two new palladium (II) pincer complexes of a hybrid C^P^C ligand system were synthesized and screened for activity towards the electrocatalytic reduction of CO₂. Both complexes exhibited a capacity for this transformation with acceptable stability through electrolysis when performed under suitable conditions. In addition to expressing an improvement in selectivity for CO₂ conversion over Pd[C^N^C], this is the first report of a palladium pincer complex that is capable of sustained CO turnover with the use of a weak proton donor. This unusual behavior may be the explained by a particularly electron rich palladium center afforded by the hybrid ligand. Further research will be required to optimize and understand catalysis with 38 and 38S as well as accurately identify the product distribution yielded by these species.
3.4 Experimental

3.4.1 General

Unless otherwise stated, all reactions were performed according to standard Schlenk techniques. DMSO, CH$_3$CN, and DMF were purchased as ACS reagent and HPLC grades, respectively. Each solvent was dried and stored over 25% v/v activated 4 Å molecular sieves. All other solvents discussed were purchased from a commercial source and used without further purification unless stated otherwise.

NMR spectra were collected on a Bruker AV400 spectrometer. $^1$H and $^{13}$C chemical shifts were referenced to residual solvent and $^{31}$P shifts are reported relative to an 85% H$_3$PO$_4$ reference signal. Full structural assignments were deduced using a combination of COSY, HMBC and HSQC NMR techniques. High resolution mass spectrometry data were obtained from Bruker Esquire LC ion trap mass spectrometer equipped with an electrospray ion source. Low-resolution mass measurements were determined with the use of a Waters LC-ESI-MS. Elemental compositions as determined by ESI-MS are reported as the [n]$^+$ charged molecular structure with counter ions indicated.

All electrochemical measurements were performed using a Pine AFCBP1 potentiostat with the use of an Ag/AgNO$_3$ pseudo-reference electrode. Bulk electrolysis and CV experiments were carried out in an air tight three compartment cell. Solutions were sparged with either N$_2$ or analytical grade CO$_2$ for at least 30 minutes before performing measurements. A 7 mm$^2$ glassy carbon disk and a platinum mesh were used as the working and counter electrodes, respectively. Measurements were referenced to an internal Fe$^{0/+}$ couple and carried out in (DMF) with quadrouply recrystallized n-[Bu$_4$N]PF$_6$ (0.1 M) as the supporting electrolyte. The working electrode was regenerated and cleaned between measurements by polishing with alumina paste
and sonicating in water and acetone, successively. Concentration of analyte was held to 2 mM unless discussed otherwise.

The gaseous composition of headspace samples aliquoted during electrolysis were analyzed with the use of an SRI Model 8610C gas chromatograph equipped with a zeolite column, a methanizer and dual TCD and FID detectors.

3.4.2 Synthesis

**Compound 38.1, [3-butyl-1-vinyl-1H-imidazol-3-iium][PF$_6$]**

1-vinyl imidazole (1.00 g, 10.62 mmol) was added to a flame dried, round bottomed flask containing 1.21 mL (10.62 mmol) of 1-iodobutane dissolved in 5.0 mL of THF. The solution was blanketet with N$_2$, brought to a reflux and allowed to react overnight. The mixture was then cooled to produce a light-yellow oil that was isolated after cooling to room temperature. The oil was washed with Et$_2$O, taken up into a minimal volume of methanol and dropped into a saturated solution of KPF$_6$ to render a white precipitate. The solids were collected by filtration and recrystallized with heat from isopropanol. Isolated yield: 1.76 g (5.95 mmol, 56%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.47 (t, $J = 1.6$ Hz, 1H), 8.19 (t, $J = 1.9$ Hz, 1H), 7.92 (t, $J = 1.8$ Hz, 1H), 7.28 (dd, $J = 15.6$, 8.7 Hz, 1H), 5.95 (dd, $J = 15.6$, 2.4 Hz, 1H), 5.43 (dd, $J = 8.7$, 2.4 Hz, 1H), 4.20 (t, $J = 7.2$ Hz, 2H), 1.90 – 1.74 (m, 2H), 1.30 (h, $J = 7.4$ Hz, 2H), 0.92 (t, $J = 7.4$ Hz, 3H). LR ESI-MS calcd. C$_{24}$H$_{37}$N$_4$P$_2$F$_6$ [M]$^+$: 151.124, Found 151.300 [M]$^+$
Oxygen was carefully excluded from this reaction. Phosphonation of 1,3 butyl-vinylimidazolium hexafluorophosphate was performed according to an adaptation of several literature procedures.\textsuperscript{104,105} Compound 38.1 (0.49 g, 1.65 mmol) was dissolved in 3.0 mL of degassed DMSO and kept under a blanket of nitrogen. In the glovebox, 1.45 mL of 10\% wt. phenyl phosphine in hexanes (0.91 mmol) were measured into a pear-shaped flask equipped with a side arm and the container was sealed with a rubber septum and a stopcock. Separately, 0.010 g of t-BuOK (0.09 mmol) was weighed into a scintillation vial and dissolved in 1 mL of DMSO. The solution of phenyl phosphine was then removed from the glovebox and diluted with 2.0 mL of degassed DMSO. The t-BuOK solution was added dropwise to the phenylphosphine solution and the resulting mixture as allowed to stir for 30 minutes before adding the entirety of the 38.1 solution via cannula. The reaction was brought to 35 °C and monitored with \textsuperscript{31}P NMR. After three days, the DMSO was removed by vacuum distillation at 55 °C leaving a light-yellow oil. This was taken up into ~10 mL of degassed DCM and precipitated with an equivalent volume of degassed Et\textsubscript{2}O. This process was repeated three times to render a sticky solid which was purified further by precipitation from isopropyl alcohol at −84 °C. Isolated yield: 0.34 g (0.49 mmol, 54\%). \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}CN) δ 9.08 (t, J = 1.7 Hz, 2H), 7.59 (td, J = 7.7, 2.0 Hz, 2H), 7.51 (t, J = 1.9 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.32 (t, J = 1.8 Hz, 2H), 4.31 (dddd, J = 18.1, 15.9, 7.5, 5.8 Hz, 4H), 4.11 (t, J = 7.3 Hz, 4H), 2.63 – 2.41 (m, 4H), 1.86 – 1.74 (m, 4H), 1.31 (h, J =
7.4 Hz, 4H), 0.93 (t, \(J = 7.4\) Hz, 6H). \(^{31}\text{P}\) \{\(^{1}\text{H}\}\) NMR (162 MHz, DMSO-\(d_6\)) \(\delta\) -34.92, (m) -144.20. LR ESI-MS calcd. \(C_{24}H_{37}N_4P_2F_6\) [\(M+PF_6^+\)]: 557.240, Found 557.150 [\(M+PF_6^+\)]

**Complex 38**

Proligand 38.2, (0.35 g, 0.50 mmol) was dissolved in 9 mL of dry DMSO in an oven-dry round bottom flask. The flask was covered in foil and \(Ag_2O\) (0.12 g, 0.50 mmol) was added along with ~1/4 solution volume of activated 4Å molecular sieves. Under a continuous flow of \(N_2\), the reaction was heated to 55 °C for 24 h. The mixture was then cooled to RT and 0.14 g of palladium(II)dichloro(1,5-cyclooctadiene) (cod) (0.50 mmol) to the mixture. The light grey-yellow suspension was stirred for 48 h at 30 °C under \(N_2\). The reaction mixture was then transferred to a centrifuge tube and the precipitated solids and molecular sieves were separated by centrifugation to expose a pale-yellow solution. Next, the solvent volume was reduced down to ~0.5 mL by vacuum distillation at 55 °C with a short neck condenser. The bottom liquid was diluted 3 mL of \(CH_3CN\) and \(Et_2O\) was added to the solution until precipitation ceased. The precipitate solids were collected by centrifuging and washed with DCM to remove an orange impurity. Finally, the washed product was dissolved in 3 mL of \(CH_3CN\), passed over Celite and recrystallized at −12° C from a 30:60 \(CH_3CN/MeOH\) solution. Isolated yield: 0.17 g (0.24 mmol, 49%). \(^{1}\text{H}\) NMR (400 MHz, \(CD_3CN\)) \(\delta\) 7.50 – 7.43 (m, 1H), 7.38 (ddd, \(J = 8.6, 6.9, 2.9\) Hz, 2H), 7.23 (d, \(J = 1.9\) Hz, 2H), 7.22 – 7.15 (m, 1H), 7.14 (d, \(J = 1.9\) Hz, 2H), 5.00 (ddd, \(J = 13.3, 8.3, 6.3\) Hz, 2H), 4.64 – 4.46 (m, 4H), 4.06 (ddd, \(J = 13.3, 8.2, 6.5\) Hz, 2H), 2.80 (ddt, \(J = 15.0, 12.1, 2.8\) Hz, 2H), 2.52 – 2.35 (m, 2H), 1.82 – 1.57 (m, 4H), 1.29 – 1.11 (m, 4H), 0.81 (t, \(J = 102\)
\[ \text{Complex 38S} \]

Complex 38 (99 mg, 0.14 mmol) was weighed into a scintillation vial and dissolved in 2 mL of CH\textsubscript{3}CN. Silver (I) hexafluorophosphate (54 mg, 0.21 mmol) was added and the vial was capped with a rubber septum. The reaction chamber was wrapped in tinfoil to exclude light and the mixture was stirred under a blanket of nitrogen at 35 °C for 24 h. This produced a light grey precipitate that was removed from suspension by centrifugation. The CH\textsubscript{3}CN solution was then passed over Celite and crystallized over the course of two weeks by slow diffusion of Et\textsubscript{2}O at -12 °C. The recrystallization procedure rendered clear, high quality single crystals that were analyzed by X-ray crystallography. Yield: 80 mg (0.094 mmol, 66%). $^1$H NMR (400 MHz, CD\textsubscript{3}CN) δ 7.55 – 7.46 (m, 1H), 7.44 – 7.37 (m, 2H), 7.35 (dd, J = 1.9, 0.7 Hz, 2H), 7.23 (d, J = 1.9 Hz, 2H), 7.13 (ddt, J = 13.2, 7.4, 1.2 Hz, 2H), 4.72 – 4.48 (m, 4H), 4.32 (dt, J = 13.8, 7.4 Hz, 2H), 4.10 (ddd, J = 13.9, 7.5, 6.6 Hz, 2H), 2.91 – 2.79 (m, 2H), 2.69 – 2.55 (m, 2H), 2.51 (s, 3H), 1.62 (ddddd, J = 13.8, 6.5, 2.3, 1.0 Hz, 4H), 1.23 – 1.09 (m, 4H), 0.80 (t, J = 7.3 Hz, 6H). $^{31}$P $^1$H NMR (162 MHz, CD\textsubscript{3}CN) δ 29.48, (m) -144.20. LR ESI MS calcd. C\textsubscript{26}H\textsubscript{38}N\textsubscript{5}PPd $[M]^+$: 550.124, Found 550.120 $[M]^+$.
3.4.3 Crystallography

Crystal structures of 38S were extracted from a colourless rod shaped crystal of C$_{26}$H$_{37.38}$F$_{12}$N$_5$P$_3$Pd, having approximate dimensions of 0.22 × 0.08 × 0.03 mm was mounted on a nylon loop. The data were collected at a temperature of -183.0 ± 0.1°C to a maximum 2Θ value of 59.0°. Data were collected in a series of φ and ω scans in 0.5° oscillations using 10.0-second exposures. Of the 21588 reflections that were collected, 15131 were unique (Rint = 0.027); equivalent reflections were merged. The material crystallized with two molecules in the asymmetric unit. The phenyl ring of molecule A is disordered and was modeled in two orientations as well as a PF$_6$ anion which was modelled in two positions. Additionally, the one of the butyl chains of molecule A is disordered and modelled over two positions however due to unresolvable electron density around the Pd atoms complete resolution of the butyl chain disorder is not possible hence the visibility of a large methyl thermal ellipsoid. A series of SADI, RIGU and SIMU commands were used to ensure reasonable geometries and displacement parameters. A list of the constraints and restraints used in this refinement can be found within the CIF. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement on F$^2$ was based on 21588 reflections and 946 variable parameters and converged. All refinements were performed using the ShelXL$^{109}$ via the OLEX2$^{110}$ interface. ORTEP diagrams were generated using PLATON$^{111}$. 
Chapter 4: Conclusions

The work presented in this thesis seeks to understand how inner and outer sphere ligands influence the behavior of palladium pincer complexes as electrocatalysts for CO₂ reduction. In Chapter 2, a set of six novel Pd[C^N^C] pincer complexes bearing positively charged pendant functional groups were synthesized and evaluated for activity towards the electrochemical conversion of CO₂ to CO. Concise, structural and electronic variation applied to the pendant functionality produced a series of isoelectronic complexes defined by a unique outer-sphere charge distribution.

Through iterated electrochemical experiments performed on each species under non-catalytic conditions, it was discovered that the pendant groups mediate electrode kinetics and facilitate coordination of CO₂ to the palladium center in a systematic fashion. Sustained chronocoulometric measurements also demonstrated a strong influence from the modifying arm on product selectivity, wherein a N-propyl-linked triphenylphosphonium substituent exhibited the best enhancement in Faradaic efficiency for CO.

Relationships identified from electrochemical experiments were contrasted against molecular models built for each structure using Density Functional Theory (DFT), resulting in several preliminary conclusions. Faradaic efficiency for CO was found to vary linearly with respect to increasing distance from the closest approaching cationic center to the binding site of CO₂. This result suggests that the mechanism of stabilization involving an onium moiety occurs through-space in this system. The interaction is optimized by allowing flexibility in the ionic linker and the presence of bulky substituents surrounding the charge. The larger substituents were speculated to enhance catalysis by precluding solvent from the reaction pocket while linker flexibility allows a spacious environment for the formation of intermediates. In addition to
providing insight on mechanistic features of Pd[C^N^C] electrocatalysis, the results from this study may aid in guiding the design of cationic outer-sphere functionalities in other catalytic systems.

The work presented in Chapter 3 transitions to a focus on optimizing the inner-sphere coordination environment of CO₂ reduction palladium pincer catalysts. Two novel, isostructural palladium carbene-phosphine-carbene [C^P^C] complexes bearing separate fourth coordinate ligands were synthesized and characterized structurally by NMR and X-ray crystallography. The new Pd[C^P^C] complexes were determined to possess structural features of both Pd[C^N^C] and Pd triphosphine analogs.

Electrochemical measurements performed under aerobic conditions and in the presence of CO₂ demonstrated the capacity of either complex to bind CO₂ in a reduced state, albeit under unique reduction schemes. Cyclic voltammetry and sustained bulk electrolysis were carried out in the presence of three proton donors of increasing strength. Catalytic activity for the electrochemical conversion of CO₂ to CO was detected in each case. However, the best results were obtained with the application of a weak proton donor and cathodic potentials. Both catalysts exhibited good electrolytic stability under suitable conditions and an improvement in Faradaic efficiency for CO over Pd[C^N^C] was achieved. Most importantly, in contrast to previously reported Pd pincer systems, the catalysts investigated in this study were shown to be capable of turning over CO with the use of a weak proton donor. The ability for Pd[C^P^C] complexes to operate in the presence of a weak acid may provide a strategy for optimizing ligand design in CO₂ electrocatalysts and marks a step towards industrial scale-up for Pd pincer complexes.
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Appendices

Appendix A

A.1 \(^1\)H NMR spectra for complexes discussed in Chapter 1 and Chapter 2

All \(^1\)HNMR spectra were collected on a Bruker AV400 spectrometer at room temperature and chemical shifts are referenced to residual solvent.

![Figure A-1. \(^1\)H NMR spectrum of 32 in DMSO-d\(_6\). Residual solvent a and water b indicated (25 °C, 400 MHz).](image)
Figure A-2. NMR spectrum of 33 in DMSO-$d_3$. Residual solvent a and water b indicated (25 °C, 400 MHz).

Figure A-3. $^1$H NMR spectrum of 34 in DMSO-$d_3$. Residual solvent a and water b indicated (25 °C, 400 MHz).
Figure A-4. $^1$H NMR spectrum of 35 in DMSO-$_d_3$. Residual solvent a and water b indicated (25 °C, 400 MHz).

Figure A-5. $^1$H NMR spectrum of 36 in DMSO-$_d_3$. Residual solvent a and water b indicated (25 °C, 400 MHz).
Figure A-6. $^1$H NMR spectrum of 37 in DMSO-$d_3$. Residual solvent a and water b indicated (25 °C, 400 MHz).

Figure A-7. $^1$H NMR spectrum of 38 in CD$_3$CN. Residual solvent a and water b indicated (25 °C, 400 MHz).
Figure A-8. $^1$H NMR spectrum of 38S in CD$_3$CN. Residual solvent a and water b indicated (25 °C, 400 MHz).

Figure A-9. COSY NMR spectrum of post electrolysis solution (DMF) with 38 in CD$_3$CN. Major peaks are from solvent and electrolyte. Unidentified resonance at 4.15 ppm indicated by grey bar. No correlations apparent from experiment (25 °C, 400 MHz).
Appendix B

B.1 Crystallographic information

Table B1: Crystal data and structure refinement for 38S

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<th>Property</th>
<th>Value</th>
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<td>Empirical formula</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
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<td>a/Å</td>
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</tr>
<tr>
<td>b/Å</td>
<td>17.197(3)</td>
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<tr>
<td>c/Å</td>
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<tr>
<td>β/°</td>
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<tr>
<td>γ/°</td>
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</tr>
<tr>
<td>ρ_{calc}/cm³</td>
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<tr>
<td>μ/mm⁻¹</td>
<td>0.779</td>
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<tr>
<td>F(000)</td>
<td>1710.0</td>
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Crystal size/mm$^3$ 0.22 × 0.08 × 0.03
Radiation MoKα ($\lambda = 0.71073$)
2Θ range for data collection/$^\circ$ 2.382 to 55.994
Index ranges $-15 \leq h \leq 15$, $-22 \leq k \leq 18$, $-15 \leq l \leq 24$
Reflections collected 21588
Independent reflections 15131 [$R_{\text{int}} = 0.0267$, $R_{\text{sigma}} = 0.0576$]
Data/restraints/parameters 15131/154/946
Goodness-of-fit on $F^2$ 1.041
Final R indexes [$I \geq 2\sigma (I)$] $R_1 = 0.0689$, $wR_2 = 0.1788$
Final R indexes [all data] $R_1 = 0.0885$, $wR_2 = 0.1964$
Largest diff. peak/hole / e Å$^{-3}$ 5.88/-1.18

Table B2. Selected Bond Lengths (Å) for Crystal Structure 38S.

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<td>Pd1A-C16A</td>
<td>2.045(5)</td>
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<td>2.2119(12)</td>
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<tr>
<td>Pd1B-C1B</td>
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Table B3. Selected Bond angles (º) for Crystal Structure 38S.

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