

Exploring the Chemistry of Re^I : Physical and Theoretical Investigations

by

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Abstract

The development of Rhenium I photocatalysts has been pursued since Lehn first showed the excellent performance of the Re^{I} bipyridine tricarbonyl catalyst. Since then, development has modified the organic ligand to demonstrate continued or improved activity with other α -diimine bidentate geometries. Geometry has been limited to κ_2 motifs, with *fac*-(CO)₃ and axial halide. This work will demonstrate the synthesis, characterization, and testing of a new $\kappa_3(\text{L}_3)\text{-Re}^{\text{I}}\text{-mer}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{CN}, \text{OTf}$) family of compounds for CO₂ reduction, as well as computational investigations into the mechanism of the reduction,

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I'd like to thank Dr. Ilia Korobkov for his work measuring and solving the x-ray crystal structures of the compounds discussed. He assisted with some paper writing as well.

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Chapter 1

Introduction

1.1 Inorganic Chemistry

Common distinctions split most chemical compounds into one of two categories: organic and inorganic. Organic molecules contain carbon and hydrogen, with or without additional nitrogen, oxygen, phosphorus, sulfur, and the halides. Inorganic chemistry is, therefore, considered to be the remainder of the molecules possible. While they may include some aspect of organic chemistry (especially in organometallic molecules), the main structural motif or reactive center is a non-organic feature. These inorganic compounds can range from compounds such as lithium or grignard reagents with significant organic influence, to metallic alloys or mineral compounds. With such a wide range of possibilities, inorganic chemistry has many facets. A widely active research area is the development and testing of transition metal complexes for catalytic, photo-physical, biochemical or manufacturing uses.

1.2 Photochemistry & Catalysis

A report of the first synthesized organometallic complex was published by Zeise in 1831.¹ To form what is now known as Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$, he mixed platinum chloride with ethanol, followed by a reaction with potassium chloride.² After some controversy to the composition of this, it was confirmed by Griess and Martius,³ and later expanded upon by Birnbaum.⁴

The field of organometallics was expanded greatly by Frankland,² and many of his complexes were catalytically active. Further development of this new type of chemistry quickly led to useful catalysts for the conversion of petroleum products or the production or destruction of other chemicals to be developed using nearly all of the transition metals. These catalysts take all forms, from simple olefin and halide compounds to multi-metallic complexes with large organic ligands.

Some of the most interesting organometallic catalysts since the late 1990s have been the development of earth metal pincer complexes to replace noble metal or early transition metal catalysts, which are often more toxic or expensive to produce. Brookhart and Gibson published a series of papers⁵⁻⁸ on the use of iron and cobalt with bis(imino)pyridine ligands to perform ethylene polymerization at rates exceeding those of similar noble metal complexes and metallocenes.⁹ The role of the ligand in the mechanism is still up for debate, but many modified systems have been synthesized and tested since the first work was published.¹⁰

Many of these types of pincer complexes are photochemically active. In transition metal complexes, the interaction between the metal atom(s) and the ligands can cause significant electron mobility upon the absorption of incident photons. The metal atom's d orbitals typically lie at or near the Highest Occupied Molecular Orbital (HOMO) energy, while the ligands often have low energy anti-bonding orbitals (π^*) at the Lowest Unoc-

cupied Molecular Orbital (LUMO) levels. When a photon is absorbed and is promoted from the ground state to the excited state, that state is geographically removed from the metal centre, this motion of the electron is labelled a Metal-Ligand Charge Transfer (MLCT). Formally, the metal atom is oxidized by the photons, this oxidation allows for redox reactivity at the metal centre for as long as the electron remains removed to the ligand. Relaxation (through photon emission via fluorescence or phosphorescence, or via vibrational or other motion processes) can return the electron to the metal to reform the ground electronic state.

1.3 Rhenium

Rewrite to
more verbose

Rhenium compounds display a broad scope of applications ranging from catalysis^{11–13} to radiopharmaceutical applications,^{14,15} as well as possessing interesting fundamental photophysical properties.¹⁶ Since the mid-1970's, complexes containing the α -diimine Re^{I} tricarbonyl core have attracted a great deal of attention due to their attractive photochemical properties with pseudo-octahedral *fac*- $[\text{L}_2\text{Re}(\text{CO})_3\text{X}]$ and *fac*- $[\text{L}_2(\text{L}')\text{Re}(\text{CO})_3]^+$ complexes being the dominant species.^{17–27} A large family of compounds with these formulations have been accessed by the addition of chelating diimine σ -donor ligands to $[\text{Re}(\text{CO})_5\text{X}]$ with the quantitative replacement of two *cis* carbonyls in the Re^{I} starting material.^{17,28–35} Significantly, these reactions form only bidentate coordinated ligands with *facial* tricarbonyl isomers as products even when a potentially tridentate σ -donor, such as bis(imino)pyridine or 2,2':6',2''-terpyridine are employed in the reaction (Figure 1.1).^{36–38} These robust species have been examined for potential applications in organic light-emitting diodes (OLEDs),³⁹ chemosensors and biotechnology probes,^{40–44} fluorescence microscopy imaging of cells,^{40,45,46} and the photochemical reduction of CO_2 to CO .^{47–51} Among the key photophysical features of these α -diimine Re^{I} compounds is the

electron transfer capability of this system and the interplay between the Re center and the well-known non-innocent redox-activity of the ligands.⁵²

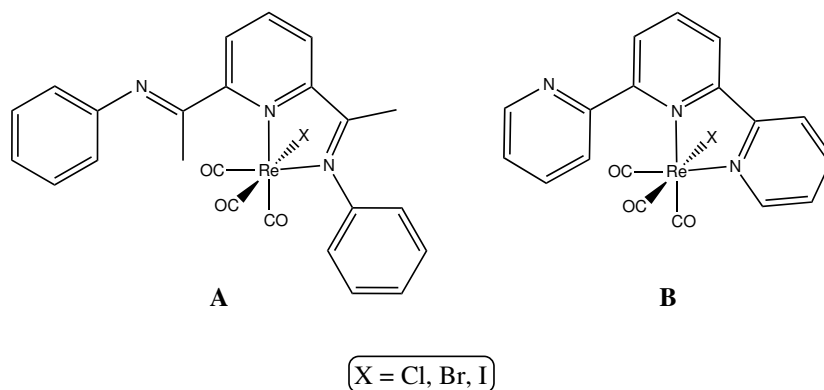


Figure 1.1 Two common *fac*-[L₂Re(CO)₃X] complexes with tridentate σ -donor ligands: L = bis(imino)pyridine (**A**) and 2,2':6',2''-terpyridine (**B**)

Further development of this chemistry has been restricted by the limited structural and electronic variability of the common pseudo-octahedral *fac*-[L₂ReX(CO)₃] (L₂ = α -diimine) products. While these systems continue to receive considerable attention, studies detailing the coordination chemistry of the meridionally-coordinated tridentate triimine Re^I dicarbonyl core are quite limited.⁵³ For example, while $\kappa^3(\text{terpy})\text{Re}(\text{CO})_2\text{Cl}$ was initially reported in 1988,⁵⁴ closer analysis of the reported analytical data (including ¹H NMR) indicate that this compound is more likely $\kappa^2\text{LRe}(\text{CO})_3\text{Cl}$. A more recent report for this compound provides spectroscopic details of this species as well as the preliminary report for the generation of [$\kappa^3(\text{terpy})\text{Re}(\text{CO})_2\text{L}$]⁺ cations (L = PPh₃, PEt₃, NC₅H₅, and NCCH₃).⁵⁵ Finally, the ¹H NMR data for $\kappa^3(\text{terpy})\text{Re}(\text{CO})_2\text{Br}$ has been reported.³⁸

In order to fully exploit the potential of this versatile family of compounds, the limits imposed by the bidentate coordination need to be addressed. Furthermore, it would appear that, on the basis of the tridentate ligands that have been investigated, the

concerted effort to produce the tridentate species has been unsuccessful. Attracted by this challenge we sought to synthesize, crystallographically authenticate, and investigate the photophysical properties of low-valent rhenium pincer complexes displaying an N,N',N''-chelated terpyridine array.

Take out
spoilers

We recently reported the conversion of bidentate bis(imino)pyridine complexes 2,6-{2,6-Me₂C₆H₃N=CPh}₂(NC₅H₃)Re(CO)₃X (X = Cl, Br) into tridentate pincer ligand compounds, 2,6-{2,6-Me₂C₆H₃N=CPh}₂(NC₅H₃)Re(CO)₂X (X = Cl, Br).⁵³ This transformation was performed in the solid-state by controlled heating of these bidentate species above 200°C in a tube furnace under a flow of nitrogen gas giving excellent yields ($\geq 95\%$). These compounds defined a new coordination environment for Re^I carbonyl chemistry where the metal center is supported by a planar, tridentate pincer coordinated bis(imino)pyridine ligand.

Complexes of 2,2':6',2''-terpyridine (terpy) are of interest due to the conceptual relationship to established bis(imino)pyridine compounds.^{56,57} Herein, we provide rational synthetic procedures to these novel species as well as their characterization and analysis of their visible electronic transitions. These results will broaden the accessibility of such compounds for investigation and application. This report for the unconventional but accessible synthesis of tridentate pincer complexes promises to enhance the versatile chemistry of Re^I and yield new venues for exploration.

This thesis will be a discussion of the development of chemistry of Re^I complexes, their characterization, and comparison of structural and photo-physical properties to computed values. Further exploration of the CO₂ reduction by photo-catalysis of these new complexes will be analyzed. This thesis will also take a more detailed look at specifics of the mechanisms proposed for current Re^I diimine catalysts, and propose new geometries for prior mechanistic steps based on experimental, computational, and

literature review work.

Chapter 2

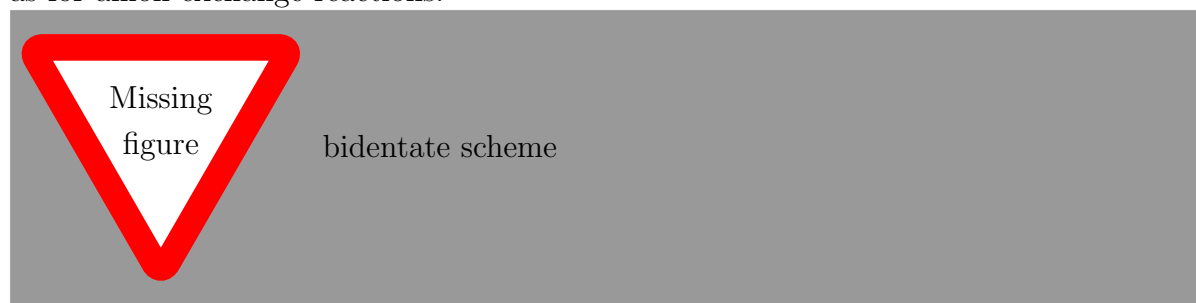
New Coordination Geometries for Re^{I}

2.1 Introduction

As mentioned previously in the thesis introduction, Re^{I} compounds have been typically bidentate (κ^2) compounds, even when using a potentially terdentate (κ^3) ligand such as bis(imino)pyridine or terpyridine (refer to Figure 1.1). The chemistry of this rhenium α -imino complex has been extensively investigated, with over 1700 references appearing in a structure search for that metal-ligand motif. The extraction of an additional carbonyl and the chelation of the pendant arm of the ligand was attempted to extend the pi system of the ligand and its interaction with the metal centre. This was first demonstrated by prior work in our group for the bis(imino)pyridine ligand.⁵³

2.2 Synthesis of Bidentate and Terdentate Re^{I} Complexes

Similar to the prior work, synthesis began with the production of the bidentate complex $\kappa^2(\text{terpy})\text{Re}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) by coordination of 2,2':6',2''-terpyridine (Sigma) with a $\text{Re}(\text{CO})_5\text{X}$ (Strem) starting material in dry toluene at reflux for 4 hours, as shown in Scheme 2.1. A bright yellow powder precipitated from solution and was collected by filtration, washed with cold hexanes, and dried *in vacuo* to a good yield of **1** and **2** respectively.ⁱ These bidentate compounds were characterized fully and used without further purification to produce $\kappa^3(\text{terpy})\text{Re}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) via thermolysis, as well as for anion exchange reactions.



Scheme 2.1 Synthesis of **1** and **2**

Thermolysis was completed via a method first described by Buckingham with an osmium complex.⁵⁸ In this method, a ceramic sample boat was placed in a tube furnace at elevated temperature, under a flowing atmosphere of N_2 . After some time, the sample is removed and collected at nearly quantitative yield. Determination of the appropriate thermolysis temperature was performed by Thermogravimetric Analysis (TGA) of the

ⁱExperimental details for all compounds can be seen in Appendix A Experimental Procedures

sample. A 6-8 % mass loss (dependant on sample) indicated the departure of one carbonyl group from the complex. Results of TGA on **1** and **2** is shown in Figure 2.1. For **1**, thermolysis was performed at 240°C, and for **2** thermolysis was performed at 260°C, yielding **3** and **4** respectively, at quantitative yields.

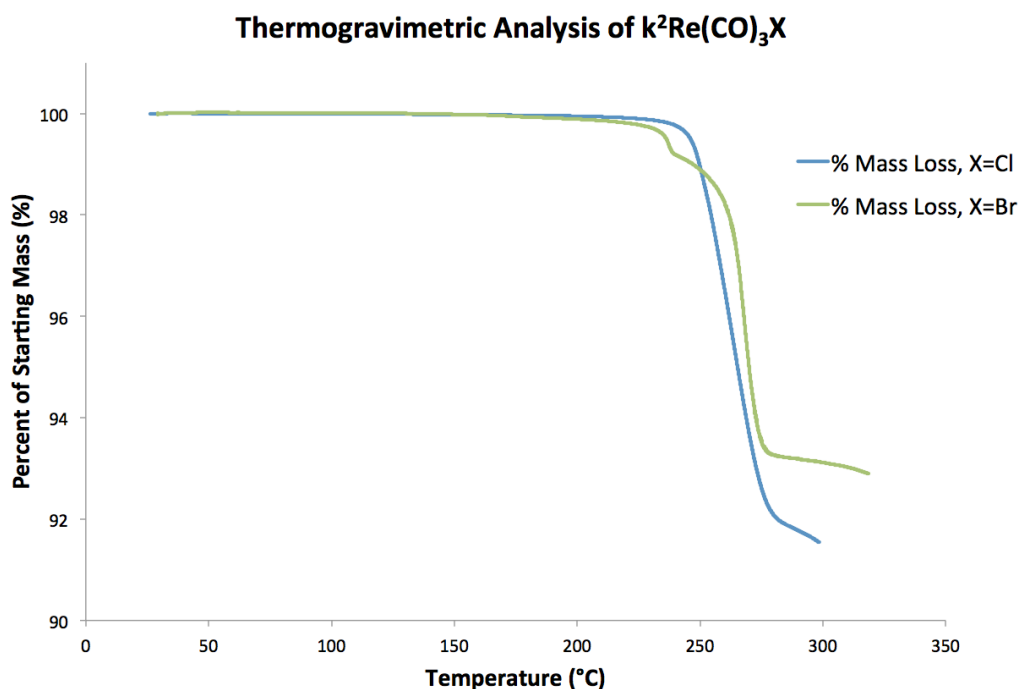
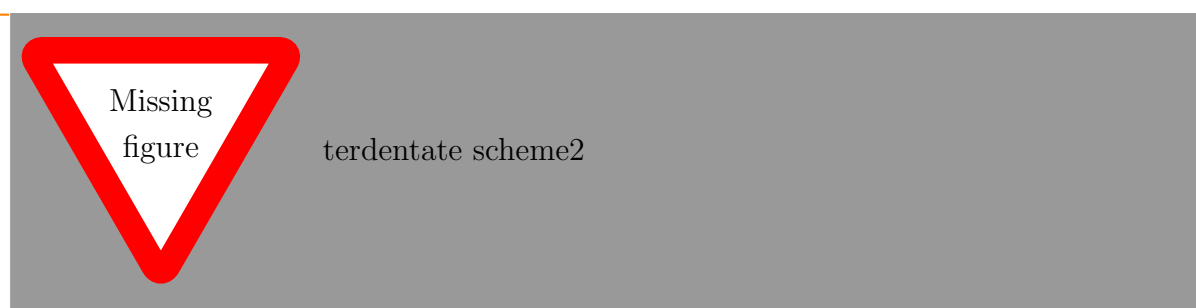


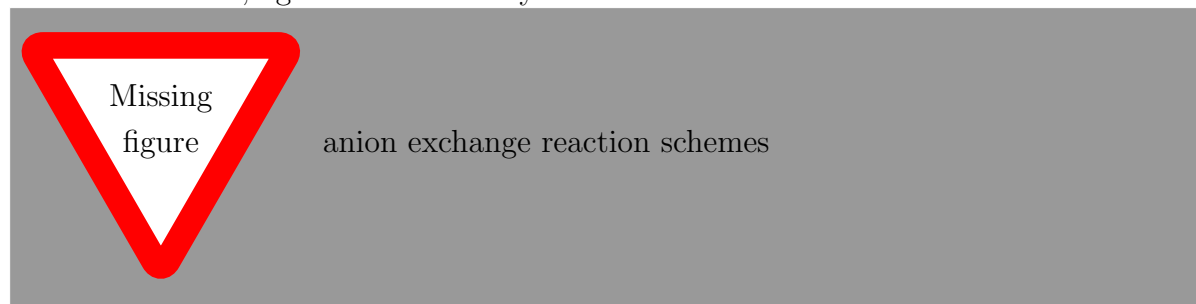
Figure 2.1 Results of TGA analysis on **1** and **2**

Further discuss TGA & terdentate rxn to build a space to put in scheme2



Further reactions were carried out on the above products to yield triflate and cyano

complexes of bidentate and terdentate geometries. These anion exchange reactions were performed by the addition of the silver salt to **1** or **3**, to precipitate AgCl, leaving $\kappa^2(\text{terpy})\text{Re}(\text{CO})_3\text{CN}$ (**5**), $\kappa^3(\text{terpy})\text{Re}(\text{CO})_2\text{CN}$ (**6**), $\kappa^2(\text{terpy})\text{Re}(\text{CO})_3\text{OTf}$ (**7a**) and $\kappa^3(\text{terpy})\text{Re}(\text{CO})_2\text{OTf}$ (**8a**). Resulting in only moderate yields, **7b** and **8b** were synthesized by the direct addition of neat triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) to **1** and **2** respectively. HCl was released, the solutions were quenched by addition of aqueous NaCO_3 , and product was collected, again at moderate yield.



2.3 Characterization

Characterization was performed on each of the products synthesized as discussed above. Nuclear Magnetic Resonance (NMR) analysis, x-ray crystallography, as well as UV-Vis and IR spectroscopy was performed. Computational Density Functional Theorem (DFT) methods were used to solve the geometries, and Time Dependant Density Functional Theorem (TD-DFT) was performed to predict UV-Vis spectra and identify electronic transitions.

2.3.1 NMR Analysis

Proton NMR was performed on each of the samples. Each sample was dissolved completely in deuteroacetonitrile (CD_3CN) and analysis was performed on a Bruker AVANCE

400 MHz spectrometer. Data was processed from the FID signal via the TopSpin program, and spectra were analyzed using ACD NMR Processor v12.0.

Detailed peak analysis comparing bidentate samples **1**, **3**, **5**, and **7** or terdentate **2**, **4**, **6**, and **8** show little difference between samples. This is due to the distance between the anion and any protons on the ligand. While anions with different σ donor strength marginally impact the metal-ligand interactions, these have only small effect on the location of peaks, shifting between samples by typically less than 0.1 ppm. As is shown in Figure 2.2, the characteristic shape of each spectra remains constant, only exact peak locations and some peak order varies with anion choice.

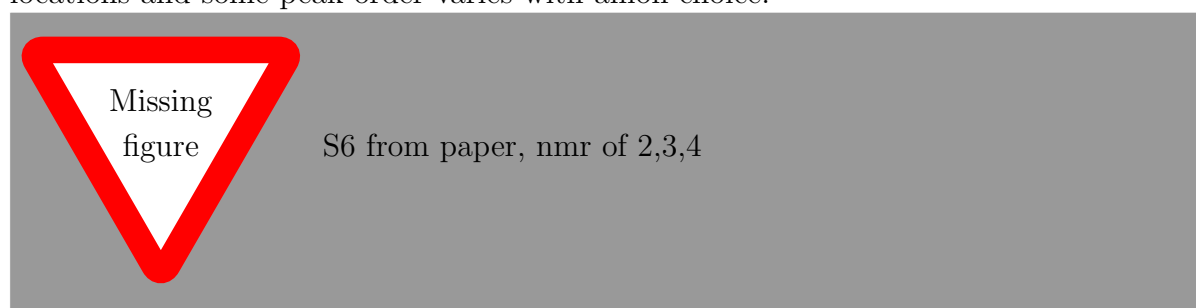


Figure 2.2 The aromatic region of the ^1H NMR spectra for compounds (red), (green), and (blue)

The characteristic feature in the NMR spectra after the transformation from bidentate to terdentate (e.g. sample **1** to **2**) is the simplification of the signals in the aromatic region (between 7 and 9 ppm). This simplification is due to the increased symmetrization of the ligand, while the κ^2 bidentate ligand has a freely rotating pendant group, the κ^3 terdentate ligand is in a more rigidly fixed geometry. Prior work in literature and in our group shows the temperature dependence of the rate of rotation of this pendant arm for various ligand species.

check compounds & spectra

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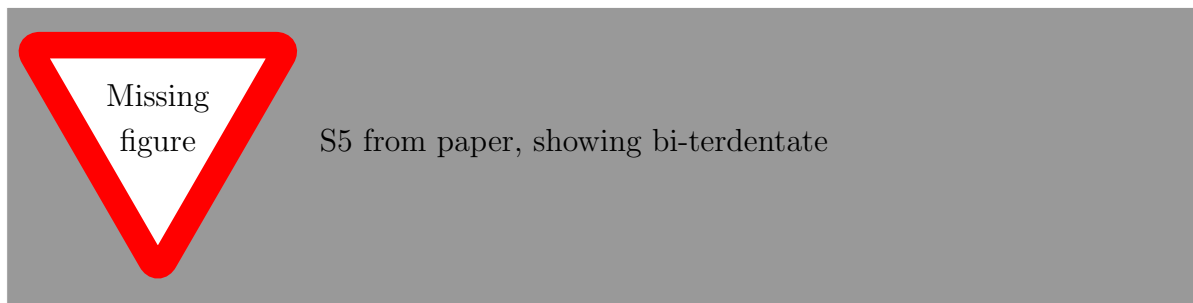


Figure 2.3 The aromatic region of the 1H NMR spectra for compounds (red) and (blue), showing the simplification of the spectra upon the conversion from bidentate to terdentate

check compounds & spectra

Put in nmr peak values

The simplification of peaks due to the symmetrization of the ligand results in the peaks from () and () aligning with their mirror peaks at () and (). ?? shows the proton expanded ligand, the peaks at () and () correspond with the protons () and ().

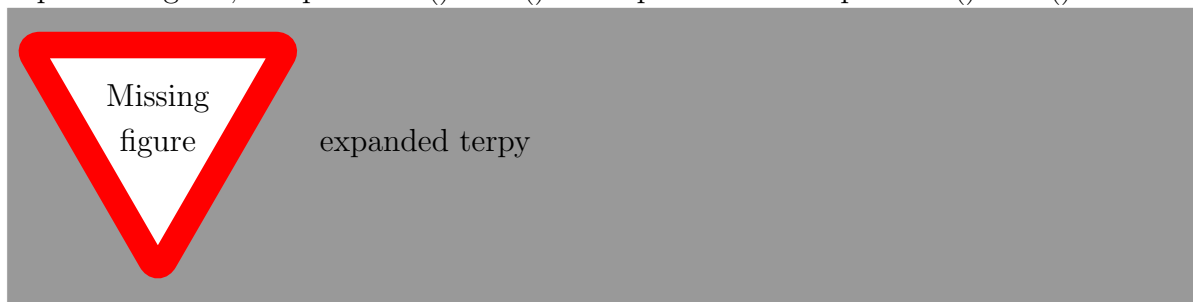


Figure 2.4 Proton-explicit skeletal drawing of 2,2':6',2''-terpyridine

Carbon NMR (^{13}C) was attempted on the complexes as well. Unfortunately, Re^I complexes perform poorly in ^{13}C NMR experiments, the signal to noise ratio is incredibly poor (if a signal is even visible). The effect of this is a lack of ^{13}C NMR analysis of these compounds in literature, with a very few exceptions.

why poor, show an ok result & discuss

2.3.2 X-Ray Crystallography

Rewrite section from paper on xray results

2.3.3 Spectroscopy

Base writing off of paper.

Infrared Spectroscopy

This can be short... discuss triplet to doublet

UV-Vis Spectroscopy

This will be longer. Should be lots of discussion about results differences. I need to
a) highlight the importance of anion exchange, and then b) highlight the importance of
bidentate vs. terdentate

2.3.4 Conclusions

Conclusion shows that manipulations can be done, this affects the photophysical
properties of the compounds and may affect the photochemical

Chapter 3

Photocatalysis of CO₂

3.1 Introduction

Only 6 years after Re^I complexes using 2,2'-bipyridine were characterized, Hawecker, Ziessel, and Lehn showed the effectiveness of the compound for CO₂ catalytic photoreduction.⁴⁷ Since then, many have shown the efficacy of a wide range of α -diimino complexes for the reaction, and expansion of the systems to dimetallic complexes with ruthenium and osmium has produced a wide range of results. The mechanism of reduction has been subject of some debate, while mechanisms have been proposed since Lehn et. al. soon after their original publication,⁴⁸ modifications have been submitted routinely over the past decades. Further discussion and a proposal of a new mechanism geometry based on computational and experimental data can be read in chapter 4.

3.2 Photocatalytic Reactions with New Compounds

The photocatalytic cycle is, simply, a photon-induced MLCT, followed by the extraction of an electron from a sacrificial reductant. This radical, negatively charged species sheds

the anion, opening up a reaction site. Reaction between a CO_2 , a proton (from the decomposition of the reductant or elsewhere), and the catalyst yields any number of CO , H_2O , formate (HCO_2^-), or carbonate (COOH^-).

3.2.1 Conditions

Reaction conditions in use in literature have remained typically unchanged since the original papers. A mixture of N,N-dimethylformamide (DMF) with Triethanolamine (TEOA) or Triethylamine (TEA) at a 5:1 ratio is used to make a 1.0 mM solution of catalyst, with 'excess' tetraethylammoniumchloride Et_4NCl salt added as a stabilizer. Solutions are degassed by bubbling of CO_2 and a consistent headspace is left to form over the solution. The reaction is monitored via GC analysis of the headspace, using a .

3.2.2 Experimental Results

SubSubSection

SubSubSection

SubSubSection

3.3 Section

3.4 Section

3.4.1 Subsection

Chapter 4

Mechanism of CO₂ Reduction

4.1 Literature Mechanisms

Literature has proposed three general mechanistic pathways for the photoreduction of CO₂. In general, as seen in Figure 4.1, these pathways result in the formation of CO and H₂O, formate (HCO₂⁻), or carbonate (COOH⁻). The formation of proceeds via the formation of a catalyst dimer over a molecule of CO₂, with the insertion of a second molecule of CO₂ to produce the and a molecule of CO. The formation of CO without carbonate or formate byproducts occurs via the insertion of CO₂ into a metal-hydride bond, followed by a proton addition and the release of a molecule of H₂O prior



Three mechanistic pathway quick

carbonate or
formate?

carbonate or
formate

Make mecha-
nism (or get
morris?)

Figure 4.1 An overview of the mechanistic pathways of photochemical CO₂ reduction

4.1.1 Subsection

4.1.2 Subsection

4.1.3 Subsection

SubSubSection

SubSubSection

SubSubSection

Chapter 5

Conclusions

5.1 Section

5.1.1 Subsection

5.1.2 Subsection

5.1.3 Subsection

SubSubSection

SubSubSection

SubSubSection

5.2 Section

5.3 Section

5.3.1 Subsection

Appendix A

Experimental Procedures

Experimental synthesis and characterization data for the compounds discussed in this thesis are shown below by compound number:

A.1 1

Compound

A.2 2

Compound

A.3 3

Compound

A.4 4

Compound

Glossary of Terms

DFT Density Functional Theorem.

DMF N,N-dimethylformamide.

HOMO Highest Occupied Molecular Orbital.

LUMO Lowest Unoccupied Molecular Orbital.

MLCT Metal-Ligand Charge Transfer.

NMR Nuclear Magnetic Resonance.

TD-DFT Time Dependant Density Functional Theorem.

TEA Triethylamine.

TEOA Triethanolamine.

TGA Thermogravimetric Analysis.

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