8-2009

Synthesis and Characterization of Some Rhenium Complexes

Joseph Brian Scott
Western Kentucky University, joseph.scott@wku.edu

Follow this and additional works at: http://digitalcommons.wku.edu/theses
Part of the Materials Chemistry Commons, Polymer Chemistry Commons, and the Polymer Science Commons

Recommended Citation
http://digitalcommons.wku.edu/theses/114

This Thesis is brought to you for free and open access by TopSCHOLAR®. It has been accepted for inclusion in Masters Theses & Specialist Projects by an authorized administrator of TopSCHOLAR®. For more information, please contact topscholar@wku.edu.
SYNTHESIS AND CHARACTERIZATION OF SOME RHENIUM COMPLEXES

A Thesis
Presented to
The Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

By
Joseph Brian Scott

August 2009
SYNTHESIS AND CHARACTERIZATION OF SOME RHENIUM COMPLEXES

Date Recommended_____8/13/2009__________

______Dr. Chad Snyder________________________
(Director of Thesis)

______Dr. Eric Conte____________________________________

______Dr. Kevin Williams____________________________

________________________________________
Dean, Graduate Studies and Research              Date
ACKNOWLEDGEMENTS

I would first like to thank my research advisor Dr. Chad A. Snyder for his constant support, guidance and knowledge throughout my graduate school experience at Western Kentucky University. He has been constant source of inspiration and his exquisite and innovative teaching methodology always stirred the realm of chemistry in myself. I would like to express my deep sense of gratitude to Dr. Cathleen J. Webb, Department of Chemistry, and also my committee members, Dr. Eric Conte and Dr. Kevin Williams. They have been constantly helpful and I sincerely appreciate it.

I wish to thank the faculty and staff of the Department of Chemistry for their support in my graduate career at Western Kentucky University.

Finally, I would like to thank my parents Pete and Brenda Scott for their understanding and compassion during my residence at Western Kentucky University.
TABLE OF CONTENTS

Acknowledgements.................................................................i

List of Tables.................................................................................iii

List of Schemes.............................................................................iv

List of Figures...............................................................................v

Abstract......................................................................................vi

Chapter One: Introduction.........................................................3

Chapter Two: Experimental.......................................................17

Chapter Three: Results and Discussion.....................................22

Chapter Four: Conclusions.........................................................49

References..................................................................................50

Vita.............................................................................................52
LIST OF TABLES

Table 3.1 Selected characterization data for fulvene compounds 1 and 5………………...26
Table 3.2 Selected characterization data for thallium salts 2 and 6……………………34
Table 3.3 Selected characterization data for rhenium complexes 3 and 7……………….38
Table 3.4 Selected characterization data of pyridazine complexes 4 and 8………………46
LIST OF SCHEMES

Scheme 1.1 Building of a thiophene star polymer .........................................................11

Scheme 3.1 Synthesis route for [Re(CO)₃{η⁵-1,2-C₅H₃(CRN)(CRN)}] ........................24

Scheme 3.2 Retro Diels-Alder reaction followed by deprotonation via n-butyl lithium B.
1,2-addition using acid chlorides ..............................................................................25

Scheme 3.3 A. Keto-Enol Tautomerism Mechanism B. Addition of thallium ethoxide
mechanism ......................................................................................................................33

Scheme 3.4 Synthesis route rhenium complexes 3 and 7 ............................................37

Scheme 3.5 Synthesis route of pyridazine complex 4 and 8 .........................................45
LIST OF FIGURES

Figure 1.1 Oligomeric structures of A. pentacene, B. anthracene, and C. rubrene...........5
Figure 1.2 Polymeric structures of A. bis-5'-hexylthiophen-2'-yl-2,6-anthracene, B. tetrabromopentacene, C. polythiophene, D. polypyrrole, E. poly(p-phenylene vinylene), F. poly(3-hexylthiophene), and G. polyaectylene..........................................................6
Figure 1.3 Organic Semiconductors A. polycyclic aromatic hydrocarbons B. phtalocyanine salt crystals............................................................7
Figure 1.4 A. Mixture of phenylene and thiaophenes B. pentacene nitriles...........12
Figure 1.5 A. Synthesis of CpMn(CO)₂-XR B. Synthesis of a fused iridapyrroles.....16
Figure 3.1 IR spectroscopy of fulvene 1............................................................75
Figure 3.2 IR spectroscopy of fulvene 5..........................................................28
Figure 3.3 ¹H NMR spectroscopy of fulvene 1................................................29
Figure 3.4 ¹H NMR spectroscopy of fulvene 5................................................30
Figure 3.5 ¹³C NMR Spectroscopy of fulvene 1..................................................31
Figure 3.6 ¹³C NMR spectroscopy of fulvene 5................................................32
Figure 3.7 IR spectroscopy for thallium salt 2....................................................35
Figure 3.8 IR spectroscopy of thallium salt 6....................................................36
Figure 3.9 IR spectra for rhenium complex 3....................................................38
Figure 3.10 IR spectra for rhenium complex 7..................................................40
Figure 3.11 ¹³C NMR spectroscopy of rhenium complex 3.................................41
Figure 3.12 ¹³C NMR spectroscopy of rhenium complex 7.................................42
Figure 3.13 ¹H NMR spectroscopy of rhenium complex 3.................................43
Figure 3.14 ¹H NMR spectroscopy of rhenium complex 7.................................44
Figure 3.15 IR spectroscopy of pyridazine complex 4.......................................47
Figure 3.16 ¹H NMR spectra of pyridazine complex 4.......................................48
Plastics or polymers are thought to behave oppositely from metals. Ideally, polymers behave as insulators while metals conduct electricity. Shirakawa and coworkers discovered conductive polymers in 1977.1 These conductor polymers have been extensively studied, discovering that charge transfer oxidative doping of polyacetylene could increase its conductivity by 12 orders of magnitude. Polyacetylene, although showing promise as an organic conductor, because it is highly air-sensitive and oxidizes when exposed to molecular oxygen, therefore making this an unattractive use for commercial products. Attention has been focused on heterocyclic aromatic polymers such as polythiophene and polypyrrole, in efforts to produce conductive polymers that are air-stable, tractable, and have a low band gap. The lone-pair electrons of the sulfur and nitrogen atoms tend to stabilize the positive charges of the p-doped polymers through resonance.2

By using Shirakawas’ idea of using polypyrrole as the focus point of our research and expanding upon that by the addition of a rhenium metal to an organic compound, (1,2-C₅H₃(CNR)₂) and this should offer some new and interesting chemical properties. These new properties are; new optical properties, new electronic properties, improved physical properties, and a reversible electrochemical shift. This research will help in the
field of organometallic semiconductors in applications such as OLED’s, and electrochromic windows. 3-6
CHAPTER ONE
INTRODUCTION

Organic Semiconductors.

Organic semiconductors are organic materials which have semiconductor properties, which have electrical conductivity that lies between typical metals and insulating compounds (0.1 eV - 4.0 eV). There are two types of organic semiconductors which include short chain (oligomers) and long chain (polymers) compounds. Examples of organic semiconductor oligomers include anthracene (Figure 1.1A), pentacene (Figure 1.1B), and rubrene (Figure 1.1C) as part of their basic structures. These compounds are entirely made up of aromatic carbon-based rings. A derivative of anthracene, bis-5’-hexylthiophen-2’-yl-2,6-anthracene (Figure 1.2A), has been shown to behave as an organic thin-film transistor (OTFT). Tetrabromopentacene (Figure 1.2B), a derivative of pentacene, has been shown to have electron-deficient properties therefore making it a suitable compound for OTFT studies. Examples of other OTFT polymers include polythiophene (Figure 1.2C), polypyrrole (Figure 1.2D), poly(p-phenylene vinylene) (Figure 1.2E), poly(3-hexylthiophene) (Figure 1.2F), and polyacetylene (Figure 1.2G). These compounds have interesting electrical properties as a result of being aromatic heterocycles that can also undergo charge transfers easily.7-9

Two classes of organic semiconductors are organic charge-transfer complexes and various “linear backbone” polymers. These polymers are typically derived from polypyrrole, polyaniline, and polyacetylene. Charge-transfer complexes will exhibit similar conduction mechanisms to inorganic semiconductors. Tunneling, localized states, mobility gaps, and photo-assisted hopping also contribute to conduction, particularly in
polyacetylenes. Highly doped organic semiconductors, such as polyaniline (Ormecon) is also known as an organic metal.

Different types of carriers help mediate conductivity in organic semiconductors, which include \( \pi \)-electrons or unpaired electrons. Generally organic solids are insulators, but when they are \( \pi \)-conjugate systems the electrons can move via \( \pi \)-electron cloud overlaps in three dimensions. Examples include polycyclic aromatic hydrocarbons (Figure 1.3A) and phatalocyanine salt crystals (Figure 1.3B).
Figure 1.1 Oligomeric structures of A. pentacene, B. anthracene, and C. rubrene.
Figure 1.2 Polymeric structures of A. bis-5’-hexylthiophen-2’-yl-2,6-anthracene, B. tetrabromopentacene, C. polythiophene, D. polypyrolle, E. poly(p-phenylene vinylene), F. poly(3-hexylthiophene), and G. polyaectylene.
Figure 1.3 Organic Semiconductors A. polycyclic aromatic hydrocarbons B. phthalocyanine salt crystals.
Advances in Organic Semiconductors.

Polythiophenes are the result of chemical or electrochemical polymerization of thiophene. This polymer’s conductivity increases when electrons are added or removed from the conjugated $\pi$-orbitals (known as doping). The most significant property of polyheterocycles is the delocalization of electrons along the polymer backbone that results in electrical conductivity, once doped. These polymers also have optical properties, which result from electron delocalization. Optical properties respond to environmental stimuli which can be seen with dramatic color shifts in response of changes in temperature, solvent, applied potential, and binding to other molecules. Conductivity and color change are affected by the twisting polymer backbone twisting, which disrupts conjugation. This effect provides a range of optical and electronic responses for sensors.

During the last two decades conjugated aromatic rings have been extensively investigated with focuses on applications including electronic and optical devices. Thiophene oligomers have attracted much of the attention due to their potential for organic light-emitting diodes (OLEDs) and OTFT. Mixing of two aromatic rings (phenylenes and thiophenes)\(^1\) produces structural motifs characterized by a diversity of molecular shapes and physical properties, which dramatically changes the physical properties. The disadvantage to oligothiophene derivatives is stability loss. Several groups have improved the stability by the choice of conjugated units and side chains, but a consequence of the improved stability is the cost of lower field-effect mobilities and higher substrate deposition temperature. Compared to pentacene-based devices,
anthracene OTFTs have significantly improved. Furan rings are also making advances in organic semiconductors because they behave similarly to thiophene.\(^7\)

Another type of thiophene that has been extensively investigated is star shaped thiophene polymer (Scheme 1.1). These star shaped molecules have been studied due to their strong potential applications OFETs and organic photovoltaic devices. Other advantages of these star shaped molecules include the ability to demonstrate multifunctionality in one molecule. Furthermore, the synthesis of $\pi$-conjugated star-shaped molecules allows for greater synthetic variability. This polymer exhibits high carrier mobilities $6.0 \pm 0.5 \times 10^{-3} \text{ cm}^2/\text{Vs}$. Ponomarenko and coworkers linked oligothiophenes through flexible aliphatic branches to a carbosilane core. The highest performance exhibited by a spin-coated sample of SiO$_2$ treated with octyldimethylchlorosilane was a linear mobility of $1.2 \times 10^{-2} \text{ cm}^2/\text{Vs}$ with an on/off ratio of $1 \times 10^5$. This was the best to device performance compared to any other thiophene polymer.\(^8\)

Another type of organic semiconductor are pentacenes (Figure 1.4A). One of the main reasons pentacenes are under research is the oxidation/reduction potentials. This may lead to improved charge injection in electronic devices. Dr. John Anthony and coworkers have worked with silylethynyl-functionalized pentacenes and have found the addition of cyclic ether groups to the ends of the pentacene fragment lowered the oxidation potential, while maintaining the high stability typically associated with these organic molecules.\(^7\) Derivatives of halogenated silylethynylated pentacenes have very interesting capabilities, such as halogenated-containing pentacenes, that will provide the ability to alter $\pi$-stacking by exploiting aryl-(halide)aryl interactions. Halogen
pentacenes will allow the further fictionalization of the pentacene backbone using palladium-based coupling reactions. Furthermore, the research is primarily interested in two types of halogens; bromide and fluoride. One of the reactions with the fluoride netted an impressive 75% yield. The last part of Anthonys’ research was to convert these newly formed halide pentacenes into pentacene nitriles (Figure 1.4B). In the case of the bromide conversion to a nitrile it was shown in all the cases that the substituted pentacenes had significantly higher oxidation potentials than the parent functionalized acene, 6,13-bis(trisopropylsilyl)ethynyl)pentacene.
Scheme 1.1  Building of a thiophene star polymer.7
Figure 1.4  Mixture of A. phenylenes and thiophenes  B. pentacene nitriles.
Organometallic Semiconductors.

Electronic engineering has been revolutionized in the past 15 years by the introduction of a host of new devices based on semiconductors. The major problem with organometallics is the limited number of suitable materials. Currently, the materials that are in current use are metalloids (e.g., germanium), alloys (e.g., indium antimonide), or simple inorganic compounds (e.g., cadmium oxide); the number of possible combinations of this kind are very limited. Organic compounds form molecular crystals, the forces between adjacent molecules being relatively weak. Therefore the little electronic coupling between adjacent molecules and electrons have low mobility and to overcome the low mobility by using very large molecules to reduce the number of gaps between one molecule and another. Conjugated organic polymers are not easy to prepare, and their physical properties are very unsatisfactory. These organic polymers are infusible, insoluble, amorphous powders, which makes it impossible to fabricate them into suitable shapes, but also reduces their carrier mobilities. If the ligands are aromatic and each can bind two metal atoms, then through conjugation becomes possible. An advantage to this is that the metal-ligand bonds are formed reversibly making it possible to crystallize polymers of this kind by heating them with a suitable solvent. In organic polymers this feat would be impossible but is possible with in the case of a suitable coordination polymer. When conjugated aromatic heterocycles get the addition of a metal then these organometallic complexes show increased conductive properties (increased tuneability, increased pi-stacking, and increased tunneling properties. Additionally, transition metal organometallic complexes are used as catalysts to carry out a variety of organic transformations. In many instances, the catalytically active species in condensed
phase is a coordinatively unsaturated metal complex in which the solvent weakly binds to the vacant site on the metal. Fast kinetic techniques have clearly demonstrated that photolytically generated unsaturated metal complexes are extremely reactive and rapidly bind to most solvents. Noble gases and haloalkanes are not usually thought of as donor ligands but can be a coordinatively unsaturated metal center.\textsuperscript{16}

Fan and coworkers studied the reactivity of the $\text{CpMn(CO)}_2\text{XR}$ by kinetics using rapid-scan FTIR spectroscopy. Fan reported in their results that the synthesis route (Figure 1.5A) that the Mn-haloalkane adducts were formed upon photolysis of $\text{CpMn(CO)}_3$ in the presence of the appropriate alkyl halide solvent. Theoretical calculations indicate that the Mn-XR bond is mostly broken in the transition state. The activation enthalpies of 16-17 kcal/mol for the Mn-CIR a18-19 kcal/mol for the Mn-BrR complexes are only slightly lower than the previous thermodynamic measurements of the Mn-haloalkane bond dissociation enthalpies. The rate of displacement of bromoalkanes was found to be \textasciitilde 10 times slower than for the analogous chloroalkanes. The differences of calculations suggest that the difference is primarily due to a more stable interaction between the Mn center and bromoalkanes.\textsuperscript{17}

Another type of organometallic that has been synthesized and characterized are fused-ring iridapyrroles. Iridium has been shown to be a cancer irradiation and be useful in helicopter spark plugs so the potential for human diseases and semiconductors is high. Bleeke and coworkers have synthesized and characterized a family of iridium-containing aromatic ring systems, which currently includes iridazbenzene, iridapyrylium, iridathiabenzene, iridafuran, and iridathiophene. Bleeke and coworkers have not been able use azapentadienide reagents to construct these desired nitrogen-containing
iridacycles, but do mention a new approach to the synthesis of fused five-membered iridaazacycles and their conversion to fused iridapyrroles. (Figure 1.5B). In their research they were able to synthesize a family of these iridium complexes at a high yield.¹⁸
**Figure 1.5** A. Synthesis of CpMn(CO)$_2$-XR  B. Synthesis of a fused iridapyrroles
II. EXPERIMENTAL

Reactions were carried out by using standard organic synthetic techniques under air unless otherwise noted. CDCl₃ (Cambridge Isotopes) were used without further purification. 1,2-C₅H₃(COHPh)(COPh) (1), 1,2-C₅H₃(COHTp)(COTp) (2), [Tl 1,2-C₅H₃(COHPh)(COPh)] (3), [Tl 1,2-C₅H₃(COHTp)(COTp)] (4) were prepared according to literature methods. Butyl lithium, methanol, ethyl ether, THF, benzoyl chloride, thionyl chloride, hydrazine hydrate (Sigma Aldrich), thallium ethoxide (I), rhenium pentacarboynl bromide (STREM), dicyclopentadiene (Fluka) were used without further purification. Benzene was dried over sodium benzophenone ketyl.

¹H and ¹³C NMR spectra were recorded on a JOEL-500MHz spectrometer at ca. 22°C and were referenced to residual solvent peaks. All ¹³C NMR spectra listed were decoupled. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR Spectrometer. Electron ionization (EI) mass spectra were recorded at 70 eV on a Varian Saturn GC/MS. Melting points were taken on a standard MEL-TEMP II apparatus.

Synthesis of 1,2-C₅H₃(COHPh)(COPh) (1).

Preparation of 1,2-C₅H₃(CPhOH)(COPh) has been previously synthesized by Linn and Sharkey. The procedure has been slightly altered. Freshly cracked cyclopentadiene (5.04 g, 628 mL, 77.5 mmol) was added dropwise to a cooled solution (0°C) of butyllithium (32.0 mL of 2.50 M, 80.0 mmol) in dry ethyl ether (75 mL). A white precipitate of cyclopentadienyllithium was formed. The solution was stirred for 15 minutes and benzoyl chloride (7.05 g, 5.82 mL, 50.0 mmol) was added dropwise. A bright yellow color formed immediately. Solution stirred for 45 minutes at room temperature. The reaction was then hydrolyzed with 3% acetic acid (20 mL). The ether
layer was separated, and the aqueous layer was extracted with ethyl ether (3 x 50 mL). The combined ether extracts were dried (Na$_2$SO$_4$) and the solvent was removed under reduced pressure leaving an yellow product. Recrystallization from methanol yielded a yellow solid (3.19 g, 0.0120 mol, 63.4%). M.P. = 94-96°C. $^1$H NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 66.50 (t, 1H, $^3$J = 4.0 Hz, CHCHCH), 7.28 (d, 2H, $^3$J = 4.0 Hz, CHCHCH), 7.50-7.81 (m, 10H, Ph), 18.52 (s, 1H, OH). $^{13}$C NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 123.1 (CHCHCH), 124.5 (CCO), 137.7 (CHCHCH), 128.3, 129.8, 131.5, 137.8, 141.8 (Ph), 185.5 (CO). IR (KBr, cm$^{-1}$) 1538, 1403 (CO). Lit.$^{13}$ M.P. = 102-103°C. $^1$H NMR (200 MHz, CCl$_4$, ppm): $\delta$ 66.35 (t, 1H, CHCHCH), 7.15 (d, 2H, CHCHCH), 7.25-7.9 (m, 10H, Ph), 18.45 (s, 1H, OH). Lit.$^{XX}$ (KBr, cm$^{-1}$) 1537.9, 1401.

**Preparation of [TI{1,2-C$_5$H$_3$(COPh)$_2$}] (2).**

Thallium (I) ethoxide (0.160 mL, 570 mg, 2.30 mmol) was added to a solution of 1,2-C$_5$H$_3$(COHPh)(COPh) (481 mg, 2.06 mmol) in THF (30 mL). A bright yellow solid precipitated immediately. The solution was stirred for 3 hours. The precipitate was filtered and washed with cold ethyl ether (5 mL) affording [TI{1,2-C$_5$H$_3$(COPh)$_2$}] (2) as a bright yellow, air-stable powder (0.749 mg, 1.57 mmol, 89.1%). M.P. 140-160°C (dec.) IR (KBr, cm$^{-1}$) 1497 (CO), 1351 (vs).

**Synthesis of [Re(CO)$_3$[$\eta^5$-1,2-C$_5$H$_3$(COPh)$_2$]] (3).**

To a 100 mL round bottom flask, [ReBr(CO)$_5$] (201 mg, 0.495 mmol) was added to a stirred solution of [TI{1,2-C$_5$H$_3$(COPh)$_2$}] (2) (236 mg, 0.495 mmol) in dry benzene (40 mL). The solution was allowed to reflux for 6 hours and changed from a yellow solution to an orange. The reaction was cooled and eluted through a thin pad of Celite and the volatiles were removed in vacuo. The product was triturated with hot hexanes
and filtered to give \( [\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{COPh})_2}\}] \) (3) (0.172 mg, 0.316 mmol, 74.8%) as an orange powder. **Mp**: 116-118°C. \(^1\)H NMR (500 MHz, \( \text{C}_6\text{D}_6 \), ppm): \( \delta \) 4.13 (t, 1H, \(^3\)J = 2.85 Hz, CHC\( \text{HCH} \)), 4.85 (d, 2H, \(^3\)J = 2.85 Hz, CHCHCH), 6.82-7.56 (m, 10H, Ph). \(^{13}\)C NMR (500 MHz, \( \text{C}_6\text{D}_6 \), ppm): \( \delta \) 81.5 (CHC\( \text{HCH} \)), 88.3 (CHCHCH), 103.1 (CC), 127.5, 128.3, 132.8, 136.4 (Ar), 187.2 (PhCO) 191.5 (ReCO). **IR** (KBr, cm\(^{-1}\)): 1652 (C=O), 2030, 1930, (ReCO).

**Synthesis of \([\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{CPhN})(\text{CPhN})]\}] \) (4).**

To a 100 mL round bottom flask, \([\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{COPh})_2]\}] \) (160 mg, 0.294 mmol) was added to a solution of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) in methanol (30 mL). The solution stirred overnight. The solution changed from a light orange to deep orange within an hour. After 24 hrs water (15 mL) was added to the reaction mixture, and a cloudy orange solution precipitated. The aqueous suspension was filtered, then washed with ethyl ether (3 x 30 mL) and the ether layers were collected and dried (MgSO\(_4\)). The volatiles were removed *in vacuo* and the crude product was trititated with cold pentane to give \([\text{Re(CO)}_3\ 1,2-\text{C}_5\text{H}_3(\text{CPhN})(\text{CPhN})]\] (58.0 mg, 0.101 mmol 36.0%) as a light brown powder. **Mp**: 130-155°C. \(^1\)H NMR (200 MHz, \( \text{CDCl}_3 \), ppm): \( \delta \) 5.36 (m, 1H, CHCHCH), 5.56 (m, 2H, CHCHCH), 7.53-7.56 (m, 6H, Ar), 7.93-8.02 (m, 4H, Ar). \(^{13}\)C NMR (50 MHz, \( \text{CDCl}_3 \), ppm): \( \delta \) 74.2 (CHCHCH), 109.2 (CHCHCH), 120.6 (CC), 128.7, 129.2, 130.2, 147.2 (Ar), 157.6 (CN), 221.9 (CO). **IR** (KBr, cm\(^{-1}\)): 2023, 1898 (CO).
**Synthesis of 1,2-C₅H₃(CTpOH)(COTp) (5).**

Freshly cracked cyclopentadiene (5.04g, 6.28 mL, 77.5 mmol) was added dropwise to a cooled solution (0 °C) of n-butyllithium (34.0 mL of 2.50 M, 80.0 mmol) in ethyl ether (150 mL). A white precipitate of cyclopentadienyllithium was formed immediately. The solution stirred for 15 minutes and 2-thiophenecarbonyl chloride (5.34 g, 5.34 mL, 50.0 mmol) was added dropwise. The solution turned orange immediately. The solution stirred for one hour at room temperature. The reaction was hydrolyzed with 3% acetic acid (70 mL). The organic layer was separated, and the aqueous layer was extracted twice more with ethyl ether (3 x 40 mL). The combined diethyl ether extracts were dried (Na₂SO₄) and removed via rotary evaporation to yield a brown solid (1.22 g, 4.25 mmol, 16.6%). **M.P.** 97-102 °C. **¹H NMR (500 MHz, CDCl₃, ppm):** δ 6.55 (brs, 1H, CHC₅H₃CH), 7.42 (brs, 2H, CHCH₃CH), 7.68-7.84 (m, 3H, Tp). **¹³C NMR (500 MHz, CDCl₃, ppm):** δ 123.2 (CHCH₃), 124.0 (CCO), 133.9 (CHCH₃), 127.9, 132.6, 139.3, 140.9 (Tp), 176.4 (CO) **IR (KBr, cm⁻¹):** 1696 (CO), 2956 (CH).

**Synthesis of [Tl{1,2-C₅H₃(COTp)₂}] (6).**

To a 100 mL round bottom flask thallium (I) ethoxide (1.05g, 0.300 mL, 4.20 mmol) was added via syringe to a stirred solution of 1,2-C₅H₃(COTp)₂ (5) (1.00 g, 3.50 mmol) in THF (30 mL). A yellow precipitate formed immediately. The suspension was allowed to stir for 2 hours at room temperature. The precipitate was filtered and the crude product was washed with cold ethyl ether to give [Tl{1,2-C₅H₃(COTp)₂}] (6), then washed with hexane, filtrated and yielded a yellow solid (0.998 mg, 2.03 mmol, 99.7%). **M.P.** 180-200 °C (dec). **IR (KBr, cm⁻¹):** 1575 (CO).
Synthesis of \([\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{COTp})_2\}](7)\).

To a 100 mL round bottom flask, \([\text{ReBr(CO)}_5]\) (200 mg, 0.495 mmol) was added to a stirred solution of \([\text{Tl}\{1,2-\text{C}_5\text{H}_3(\text{COTp})_2\}](6)\) (236 mg, 0.495 mmol) in benzene (40 mL). The solution was allowed to reflux for 6 hours and changed from a yellow solution to an orange. The reaction was cooled and eluted through a thin pad of Celite and the volatiles were removed in vacuo. The product was triturated with cold hexanes and filtered to give \([\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{COTp})_2\}](7)\) (0.160 mg, 0.287 mmol, 80.0%) as an orange powder. Mp. 142-158°C. \(^1\)H NMR (500 MHz, \(\text{C}_6\text{D}_6\), ppm): \(\delta\) 5.40 (brs, 1H, CHCHCH), 6.00 (brs, 2H, CHCHCH), 7.11-7.81 (m, 6H, Tp). \(^{13}\)C NMR (500 MHz, \(\text{C}_6\text{D}_6\), ppm): \(\delta\) 81.2 (CHCHCH), 89.1 (CHCHCH), 105.1 (CC), 128.4, 130.2, 134.1, 135.0 (Tp), 179.6 (TpCO), 191.1 (ReCO). IR (KBr, cm\(^{-1}\)): 2029, 1930, (CO).

Attempted Synthesis of \([\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{CTpN})(\text{CTpN})\}](8)\).

To a 100 mL round bottom flask, \([\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{COTp})_2\}](7)\) (160 mg, 0.288 mmol) was added to a solution of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) in methanol (30 mL). The solution stirred overnight. The solution changed from a light orange to deep orange within an hour. After 24 hrs water (15 mL) was added to the reaction mixture, and a cloudy orange solution precipitated. The aqueous suspension was filtered, then washed with ethyl ether (3 x 30 mL) and the ether layers were collected and dried (MgSO\(_4\)). The volatiles were removed in vacuo and the crude product was triturated with cold pentane to give \([\text{Re(CO)}_3\{\eta^5-1,2-\text{C}_5\text{H}_3(\text{CTpN})(\text{CTpN})\}](8)\) as a light brown powder. \(^1\)H and \(^{13}\)C NMR spectroscopy did not confirm the structure of 8.
III. RESULTS AND DISCUSSION

Fulvenes 1 and 5 were synthesized by the addition of freshly cracked cyclopentadiene to a solution of cold butyl lithium in diethyl ether. Acid chlorides, benzoyl chloride and 2-thiophene, were added to provide fulvene 1 and 5 respectively. The percent yields were 63.4% and 16.6% for fulvenes 1 and 5, respectively. IR spectroscopy showed a wavenumbers at 1403 and 1538 cm$^{-1}$ (CO) for the fulvene 1 and a 1696 cm$^{-1}$ (CO) for the fulvene 5. $^{13}$C NMR spectroscopy shows a carbonyl at $\delta$ 185.5 (CO) and $\delta$ 176.4 (CO) for fulvene 1 and 5, respectively. $^1$H NMR spectroscopy for both fulvenes confirmed the fulvene structure for 1 and (5). Cyclopentadiene signals were seen at $\delta$ 6.50 (t, 1H, $^3J$ = 4.0 Hz, CHCHCH), and $\delta$ 7.28 (d, 2H, $^3J$ = 4.0 Hz, CHCHCH), for the fulvene 1. Fulvene 5’s cyclopentadiene signals were observed at $\delta$ 6.55 (t, 1H, CHCHCH), and $\delta$ 7.42 (d, 2H, CHCHCH).

Thallium salts 2 and 6 were synthesized by the addition of thallium ethoxide to the fulvenes 1 and 5 in dry THF. The percent yields were 89.1% and 96.9% for the thallium compounds 2 and 6, respectively. IR spectroscopy of both compounds show a wave numbers at 1497 cm$^{-1}$ (CO) for the thallium compound 2 and 1574 cm$^{-1}$ (CO) for the thallium compound 6. $^1$H and $^{13}$C NMR spectroscopy data could not be obtained due to the thallium salt being insoluble in all NMR solvents.

Rhenium complexes 3 and 7 were synthesized by the addition of rhenium pentacarbonyl bromide to thallium salts 2 and 6 in dry benzene. The solution was allowed to reflux for six hours. The percent yields were 74.9% and 80.0% for rhenium complexes 3 and 7, respectively. IR spectroscopy showed wavenumbers at 2030, 1930 cm$^{-1}$ (ReCO) for rhenium complex 3 and 2029, 1930 cm$^{-1}$ (ReCO) for rhenium complex 7.
$^{13}$C NMR spectroscopy showed signals at $\delta$ 187.2 (PhCO), $\delta$ 191.5 (ReCO) for rhenium complex 3 and $\delta$ 179.6 (TpCO), $\delta$ 191.1 (ReCO) for the rhenium complex 7. $^1$H NMR spectroscopy showed cyclopentadiene signals at $\delta$ 4.13 (t, 1H, $^3J = 2.85$ Hz, CHCHCH), and $\delta$ 4.85 (d, 2H, $^3J = 2.85$ Hz, CHCHCH) for rhenium complex 3. Cyclopentadiene signals were seen at $\delta$ 5.40 (t, 1H, CHCHCH), and $\delta$ 6.00 (d, 2H, CHCHCH) for rhenium complex 7.

Pyridazine complex 4 was synthesized by adding hydrazine hydrate to rhenium complex 3 in methanol at room temp. The percent yield was 42.2% for complex 4. IR spectroscopy showed wave numbers at 2030, 1898 cm$^{-1}$ (ReCO) for pyridazine complex 4. $^1$H NMR spectroscopy showed the cyclopentadiene signals at $\delta$ 5.36 (m, 1H, CHCHCH), and $\delta$ 5.56 (m, 2H, CHCHCH) for the pyridazines complex 4.
\[ \text{BuLi} \text{ diethyl ether, } O^\circ C 15 \text{ minutes} \]
\[ \text{HOAc} \text{ diethyl ether, } rt 45 \text{ minutes} \]
\[ \text{TlOEt} \text{ THF rt, 3 hours} \]
\[ \text{N}_2\text{H}_4 \text{ MeOH rt, 24 hr} \]
Scheme 3.1. Synthesis route for $[\text{Re(CO)}_3 \{\eta^5-1,2-C_5\text{H}_3\text{(CRN)}(\text{CRN})\}]$. 
Scheme 3.2 A. Retro Diels-Alder reaction followed by deprotonation via n-butyl lithium
B. 1,2-addition using acid chlorides.
<table>
<thead>
<tr>
<th></th>
<th>R – Ph</th>
<th>R – Tp</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Yield</td>
<td>63.4%</td>
<td>16.6%</td>
</tr>
<tr>
<td>M.P.</td>
<td>94-96°C</td>
<td>97-102°C</td>
</tr>
<tr>
<td>IR</td>
<td>(C O) 1538, 1403 cm⁻¹</td>
<td>(C O) 1596 cm⁻¹</td>
</tr>
<tr>
<td>□ H NMR</td>
<td>δ 6.50 (s, 1H, CH\text{CHCH})</td>
<td>δ 6.55 (t, 1H, CH\text{CHCH})</td>
</tr>
<tr>
<td></td>
<td>δ 7.28 (d, 2H, J = 4.0 Hz, CH\text{CHCH})</td>
<td>δ 7.42 (d, 2H, Cl/Cl/Cl/I)</td>
</tr>
<tr>
<td></td>
<td>δ 7.50-7.81 (m, 10H, Ph)</td>
<td>δ 7.68-7.84 (m, 3H, Tp)</td>
</tr>
<tr>
<td></td>
<td>δ 18.52 (s, 1H, OH)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 Selected characterization data of fulvene compounds 1 and 5.
Figure 3.1 IR spectroscopy of fulvene 1.
Figure 3.2 IR spectroscopy of fulvene 5.
Figure 3.3 $^1$H NMR spectroscopy of fulvene 1.
Figure 3.4 $^1$H NMR spectroscopy of fulvene 5.
Figure 3.5 $^{13}$C NMR Spectroscopy of fulvene 1.
Figure 3.6 $^{13}$C NMR spectroscopy of fulvene 5.
Scheme 3.3 A. Keto-Enol Tautomerism Mechanism B. Addition of thallium ethoxide mechanism.
Table 3.2 Selected characterization table for thallium salts 2 and 6.
Figure 3.7 IR spectroscopy for thallium salt 2.
Figure 3.8 IR spectroscopy of thallium salt 6.
Scheme 3.4 Synthesis route rhenium complexes 3 and 7.
Table 3.3 Selected characterization data for rhenium complexes 3 and 7.

<table>
<thead>
<tr>
<th></th>
<th>R = Ph</th>
<th>R = Tp</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Yield</td>
<td>74.9%</td>
<td>80.0%</td>
</tr>
<tr>
<td>M.P.</td>
<td>116-118°C</td>
<td>142-158°C</td>
</tr>
<tr>
<td>IR</td>
<td>(ReCO) 2030, 1930 cm⁻¹</td>
<td>(ReCO) 2029, 1930 cm⁻¹</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>δ 81.5 (CiCtICtI)</td>
<td>δ 81.2 (CiCtICtI)</td>
</tr>
<tr>
<td></td>
<td>δ 88.3 (CiCtICtI)</td>
<td>δ 89.1 (CiCtICtI)</td>
</tr>
<tr>
<td></td>
<td>δ 187.2 (PhCO)</td>
<td>δ 179.6 (TpCO)</td>
</tr>
<tr>
<td></td>
<td>δ 191.5 (ReCO)</td>
<td>δ 191.1 (ReCO)</td>
</tr>
<tr>
<td>$^{1}$H NMR</td>
<td>δ 4.13 (t, 1H, $^3J = 2.85$ Hz, CHCl/CH)</td>
<td>δ 5.40 (l, 1H, CHCl/CH)</td>
</tr>
<tr>
<td></td>
<td>δ 4.85 (d, 2H, $^3J = 2.85$ Hz, Cl/CHCl)</td>
<td>δ 6.00 (d, 2H, Cl/CHCl)</td>
</tr>
<tr>
<td></td>
<td>δ 6.82-7.56 (m, 10H, Ph)</td>
<td>δ 7.49-7.81 (m, 6H, Tp)</td>
</tr>
</tbody>
</table>

![Chemical structures](image)
Figure 3.9 IR spectra for rhenium complex 3.
Figure 3.10 IR spectroscopy of rhenium complex 7.
Figure 3.11 $^{13}$C NMR spectroscopy of rhenium complex 3.
Figure 3.12 $^{13}$C NMR Spectroscopy of rhenium complex 7.
Figure 3.13 $^1$H NMR spectroscopy of rhenium complex 3.
Figure 3.14 $^1$H NMR spectroscopy of rhenium complex 7.
Scheme 3.5 Synthesis route of pyridazine complex 4 and 8.
<table>
<thead>
<tr>
<th></th>
<th>$R = \text{Ph}$</th>
<th>$R = \text{Tp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>% Yield</strong></td>
<td>42.2%</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>M.P.</strong></td>
<td>130-150$^\circ$C</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>IR</strong></td>
<td>(ReCO) 2030, 1898 cm$^{-1}$</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>$^{13}$C NMR</strong></td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>$^1$H NMR</strong></td>
<td>$\delta$ 1.19-1.28 (m, 1H, CHCHCH)</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>$\delta$ 3.45-3.50 (m, 2H, CHCHCH)</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>$\delta$ 7.53-7.58 (m, 6H, Ph)</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Table 3.4** Selected characterization data of pyridazine complexes 4 and 8.
Figure 3.15 IR spectroscopy of pyridazine complex 4.
Figure 3.16 $^1$H NMR spectra of pyridazine complex 4.
IV. CONCLUSIONS

A series of organic and organometallic reactions lead to the synthesis of pyridizayl rhenium complex $\text{[Re(CO)}_3\{\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{(CNPh)}\text{(CNPh)}\}]$, (4). The attempts to make the thionyl substituted product lead to the diacyl complex $\text{[Re(CO)}_3\{\eta^5\text{-}1,2\text{-C}_5\text{H}_3\text{(COTp)}_2\}]$, (7).

The yields for the fulvenes 1 and 5 were 63.4% and 16.6%, respectively. The thallium compounds 2 and 6 were 89.1% and 96.6%, respectively. Rhenium complexes 3 and 7 percent yields were 74.9% and 80.0%, respectively. The pyridizayl complex (4) percent yield was 42.2%.

$^1\text{H NMR}$ confirmed the presence of the cyclopentadiene and its substituents on compounds 1-7. $^{13}\text{C NMR}$ confirmed the presence of the dicarboxyls and the rhenium tricarboxyls for compounds 1-7.

IR spectroscopy confirmed the presence of the dicarboxyls ranging from 1403-1652 cm$^{-1}$ for compounds 1-4 and 1574-1696 cm$^{-1}$ for compounds 5-7. IR spectroscopy also confirmed the presence of the rhenium tricarboxyls by having wavenumbers ranging from 1898-1930 cm$^{-1}$, and 2030 cm$^{-1}$ for both compounds 3 and 4. IR spectroscopy also confirmed the presence of the rhenium tricarboxyls with a wavenumber at 1930 cm$^{-1}$ and 2029 cm$^{-1}$ for compound 7.

Attempts to make pyrdizayl complex 8 were unsuccessful.
V. REFERENCES


VITA

The author was born in Owensboro, Kentucky on October 20, 1980. He earned his Associate’s of Science degree from Owensboro Community College in 2005. In the spring of 2006 he enrolled at Western Kentucky University and received his Bachelor of Science from Western Kentucky University in the winter of 2007. In January 2008, he began his graduate school at Western Kentucky University where he will earn his Master of Science degree in Chemistry working under Dr. Chad A. Snyder. He is expected to defend his thesis in the summer of 2009.

___________Joseph Brian Scott_______

(Author)

___________8/15/2009______________

(Date)