Synthesis and Characterization of some Thallium Salt Complexes

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SYNTHESIS AND CHARACTERIZATION
OF SOME THALLIUM SALT 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
Levi Dopierala

May 2014
SYNTHESIS AND CHARACTERIZATION
OF SOME THALLIUM SALT COMPLEXES

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ACKNOWLEDGEMENTS

I would like to thank my research advisor Dr. Chad Snyder for his support throughout my collegiate career at Western Kentucky University. His willingness to accept me into his lab as an undergraduate is an act that I cannot thank him enough for. Working in his lab has been one of the major highlights of my time at Western.

I would also like express my sincerest gratitude to Dr. Cathleen Webb, Head of the Department of Chemistry, and Dr. Matthew Nee for their acceptance and guidance within the 5-year BS/MS program. It has been a great honor to be a part of it.

I wish to thank my committee members, Dr. Hemali Rathnayake and Dr. Bangbo Yan, for their willingness to aid me with my thesis.

To remaining faculty and staff, as well as the members of Dr. Snyder’s research group, I would like to express my deepest thanks for their support.

To my parents David and Pamela Dopierala… I will never be able to thank them enough for all that they have done for me. If not for their constant encouragement and support I can honestly say I would not be where I am at today.

Thank you.
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SYNTHESIS AND CHARACTERIZATION OF SOME THALLIUM SALT COMPLEXES

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Research into conductive organic and organometallic polymers began in 1977 when Heeger, Macdiarmid, and Shirakawa first doped polyacteylene with Iodine. They found that this doping granted the polymer metallic properties increasing conductivity by 11 orders of magnitude.\textsuperscript{[1]} Unfortunately, polyacteylene is highly air-sensitive making it difficult to work with and limiting its applications. Therefore, current research is focused on synthesizing new organic and organometallic conductive polymers. The drive to discover these new polymers stems from their application flexibility and their low production cost.

Reported here is the synthesis of novel organometallic polymer precursors. Lead by Dr. Chad Snyder a library of chloro-phenyl based fulvenes, 5,6 fused ring pyridazines, and thallium Cp salts have successfully been synthesized. Research is currently underway to synthesize rhenium and manganese pyridazines through transmetalation of the thallium salts. The off-metal route of synthesis was followed as opposed to the previously reported on-metal route. Characterization was performed by $^1\text{H}$-NMR, $^{13}\text{C}$-NMR, and IR.

Additionally, research has begun on bromo-thiophene complexes. So far, bromothiophene fulvenes, pyridazines, and thallium Cp salts have been synthesized and work is currently underway to produced rhenium and manganese pyridazines as well. Characterization was performed by $^1\text{H}$-NMR and $^{13}\text{C}$-NMR.
CHAPTER ONE
INTRODUCTION

Organic Semiconductors:

Following the successful synthesis of polyacteylene by Shirakawa, et. al.[1], organic semiconductors have been looked to as a replacement of their metallic counterparts in electronics. For a material to be a semiconductor there should be an electrical conductivity between 0.1eV – 4.0eV. A large part of current research into organic semiconductors is focused around aromatic chains. Aromaticity promotes electron transfer due to a series of conjugated π-bonds which allow for overlapping π-orbitals. Within organic semiconductors there exist two types of compounds: oligomers (short chain with repeating units less than 10) and polymers (long chain with repeating units greater than 10). Common oligomers include pentacene (Figure 1.1A) and anthracene (Figure 1.1B). Both pentacene and anthracene, as well as their derivatives, can be used as organic thin film transistors (OTFTs) or organic field-effect transistors (OFETs). Synthesized by Swartz and co-workers (6, 13) bis-(triisopropylsilylethynyl)tetrabromo-pentacene (Figure 1.2A), a derivative of pentacene is an example of a suitable compound for these organic transistors.[2] Additionally this derivative should have increased structure control with the large TIPS (triisopropylsilylethynyl) preventing edge to face interactions.[3] An anthracene derivative reported by Meng and co-workers, 2,6-bis[2-(4-pentylphenyl)vinyl]anthracene (Figure 1.2B), also shows promise as an OTFT.[4] Both the pentacene and anthracene derivatives show larger charge mobility than their parent compound due to increased π-stacking.
Figure 1.1 Structures of (A) pentacene and (B) anthracene
Figure 1.2 Structures of (A) pentacene derivative and (B) 2,6-bis[2-(4-pentylphenyl)vinyl]anthracene
Extending these oligomer chains with repeating units creates polymers. In 2007, Lehnherr and Tykwinski synthesized a pentacene polymer using a silicon based modification similar to the TIPS method reported by Sheraw and co-workers. Instead of a three isopropyls on the silicon, Lehnherr only attached two followed by a primary alcohol ‘functional arm.’ The two isopropyl groups enhance solubility and stability while the primary alcohol acted as a polymerization site. The resulting synthesis successfully provided pentacene based dimers, trimers, and polymers (Figure 1.3A, B and Figure 1.4). Polymers being bulkier than their oligomeric analogs tend to degrade at a faster rate, however, Lehnherr’s synthesized polymer showed stability akin to that of its oligomers. Like pentacene, anthracene can be polymerized as well. In many organic polymers halogens are used as polymerization sites due to their ability to act as a leaving group for coupling reactions. Uemura and co-workers successfully synthesized an anthracene based polymer from 2,6-dibromoanthracene (Figure 1.5A) using a Diels-Alder precursor reaction. By reacting 2,6-dibromoanthracene and selected leaving groups through a Diels-Alder reaction and then after synthesizing the precursor polymer (Figure 1.5B and C) via a Stille copolymerization two conductive polymers (Figure 1.5D and E) can be synthesized with the just the application of heat ranging from 198°C to 295°C. The Diels-Alder reaction creates an insoluble polymer which allows for easier postprocessing applications like encapsulation.
Figure 1.3 Structures of 6,13-bis(diisopropylsilyl)ethynyl)pentacene (A) dimer and (B) trimer.
Figure 1.4 Structures of 6,13-bis(diisopropylethynyl)pentacene polymer
Figure 1.5 Structures of (A) 2,6-dibromoathracene, its precursor polymers (B) and (C) where the leaving groups (LG) are N-phenylmaleimide, N-n-hexyimaleimide, and diethyl axodicarboxylate, and the finished semiconducting polymers (D) and (E)
Organometallic Semiconductors:

As the name implies organometallic compounds are made of an organic and a metallic component. These compounds began to receive attention in the 1800’s when Edward Frankland tried preparing ethyl by reacting ethyl iodide with zinc. He found that when reacting metals with organic iodides an organometallic compound was formed.\[7\] By introducing a metal into an organic compound the interaction between the two cause electronic delocalization between the entire molecule effectively narrowing the HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) allowing for easier electron transfer. When a metal is added to an aromatic compound, which already exhibits electron delocalization, the conductive properties are increased.\[8\] These increases allow for more effective use as semiconductors by increasing tunability as well as π-stacking. If the attached metals are transition metals it can allow for better ON/OFF ratios due to multiple transition states.

Zhong and co-workers developed five ruthenium based organometallic compounds using a novel bridging ligand 2,3-di-2-pyridyl-5-6-diphenylpyrazine (Figure 1.6) By analyzing their synthesized compounds (Figures 1.7 A-C and 1.8 A-B) with cyclic voltammetry (CV) they found that the HOMO-LUMO gap had energies ranging from 1.63eV – 2.35eV.\[9\] These gap energies are on par with those of common inorganic semiconductors. The lower the HOMO-LUMO gap the easier it is for electron transfer to occur.
Figure 1.6 Structure of novel bridging ligand 2,3-di-2-pyridyl-5-6-diphenylpyrazine
Figure 1.7 Structures of Rhenium based organometallic complexes. (A) 
([(tpy)Ru(dpdpz)](PF_6)), (B) [(bpy)_2Ru(dpdpz)](PF_6)_2, and (C) 
([(tpy)Ru(dpdpz)Ru(tpy)])(PF_6)_2
Figure 1.8 Structure of Rhenium based organometallic complexes. (A) [(bpy)$_2$Ru(dpdpz)Ru(bpy)$_2$](PF$_6$)$_4$ and (B) [(bpy)$_2$Ru(dpdpz)Ru(tpy)](PF$_6$)$_3$
An interesting technique to control the conductivity of these organic semiconductors is referred to as doping. By doping, it is possible to make a semiconductor behave like an actual conductor by bring the HOMO-LUMO gap so close together that the orbitals overlap or further separate the HOMO-LUMO gap to create an insulator. Doping works by introducing impurities into a material to adjust material properties. Two types of doping exist: n-type and p-type. In n-type doping excess electrons are added to the semiconductor while in p-type the semiconductor is made electron deficient by introducing holes. Examples of a few p-type dopants are those derived from tetracyanoquinodimethane as synthesized by Mendez and co-workers in which they used 2,7-didecyl[1]benzothieno-[3,2-b][1]benzothiophene (Figure 1.9) as the organic semiconductor (Figure 1.10A-D).\textsuperscript{[10]} They found that the dopants increased conductivity by two orders of magnitude. Not all dopants have to be large bulky compounds however, as is the case in a study done by Some and co-workers.\textsuperscript{[11]} They show that a phosphorus atom can increase the electron mobility of graphene field effect transistors (FET) by roughly five times that of standard graphene FET devices. This is also greater than nitrogen n-doped graphene FET devices.

The research reported here is focused on the formation of Thallium Cp salts utilizing an off-metal route of synthesis. Thallium Cp salts are known to be used as transmetallating compounds. Within previously published works we have shown that these thallium Cp salts can be replaced with rhenium and manganese.\textsuperscript{[11-13]} Unlike there alkali or alkaline earth counterparts, thallium salts are more environmentally stable leading to easier synthesis of transmetalations.
Figure 1.9 Structure of 2,7-didecyl[1]benzothieno-[3,2-b][1]benzothiophene
Figure 1.10 Structures of (A) tetracanoquinodimethane and (B-D) its fluorinated derivatives.
CHAPTER 2
EXPERIMENTAL

All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere unless otherwise noted. NMR solvents CDCl$_3$ (Aldrich) and DMSO-d$_6$ (Aldrich) were used without further purification. N-butyllithium, dicyclopentadiene, tetrahydrofuran (THF), hydrazine hydrate, 4-chlorobenzoyl chloride (Aldrich), 2-thiophene carbonyl chloride (Aldrich) were used without further purification. Ethyl ether was dried over sodium benzophenone ketyl.

$^1$H and $^{13}$C NMR spectra were recorded on a JEOL-500 MHz NMR spectrometer at approximately 22°C and were referenced to residual solvent peaks. All $^{13}$C NMR spectra were listed as decoupled. Infrared spectra were recorded on a Spectrum One FT-IR Spectrometer. Electron ionization (EI) mass spectra were recorded at 70eV on a Varian Saturn GC/MS. Melting points were taken on a standard Mel-Temp apparatus.

**Synthesis of 1,2-C$_5$H$_3$(COC$_6$H$_4$Cl)(COC$_6$H$_4$Cl) (1)**

Freshly cracked cyclopentadiene (2.40 mL, 1.88 g, 28.4 mmol) diluted in diethyl ether (10mL) was added dropwise to cooled (0°C) diethyl ether (50mL) and n-butyllithium (13 mL of 2.50 M, 9.0 g, 140.4 mmol). A white precipitate formed immediately and was allowed to stir for 15 minutes upon which 4-chlorobenzoyl chloride (3.80 mL, 1.37 g, 7.82 mmol) dissolved in diethyl ether (10mL) was added dropwise. A yellow color formed and was stirred for 1 hour at room temperature. The reaction was hydrolyzed with dilute (5%) acetic acid (100mL). The organic layer was separated and extracted three times with methylene chloride (3 x 10mL). The organic layers were dried (MgSO$_4$) and filtered. Volatiles were removed *in vacuo* providing 1,2-
C₅H₅(COC₆H₄Cl)(COC₆H₄Cl) as a yellow powder (1, 81.1% yield). **Mp:** 158-160 °C  
**¹H NMR (200 MHz, CDCl₃, ppm):** 6.50 (t, 1H, ³J = 3.6 Hz, CHCH₂H), 7.32 (d, 2H, ³J = 3.6 Hz, CHCH₂H), 7.47 (d, 4H, ³J = 8.6 Hz, Ar), 7.73 (d, 4H, ³J = 8.6 Hz, Ar, 18.39 (s, 1H, OH).  
**¹³C NMR (50 MHz, CDCl₃, ppm):** 123.7 (CHCH₂CH), 124.6 (CH₂), 128.8 (CHCH₂CH), 131.4, 136.2, 138.2, 141.9 (Ar), 184.3 (CO) **IR (KBr, cm⁻¹):** 3448 (vb, OH), 1682 (CO) **HRMS:** (M⁺) calcd. 342.0209 (³⁵Cl), obsd. 342.0200 (³⁵Cl) **Analysis** Calc. for C₁₉H₁₂O₂Cl₂: C, 66.49; H, 3.52. Found: C, 65.89; H, 3.66

**Synthesis of 1,2- C₅H₅(CC₆H₄ClNH)(CC₆H₄ClN) (2)***

1,2-C₅H₅(COC₆H₄Cl)(COC₆H₄Cl)(1) (250 mg, 0.731 mmol) was dissolved in THF (50 mL). An excess of hydrazine hydrate (1 mL, 1.03 g, 20.6 mmol) was added and the solution was allowed to stir for 24 hours. Water (20 mL) was added to the solution and a orange precipitate formed immediately. The organic layer was separated and extracted three times with methylene chloride (3 x 10 mL). The organic layers were dried (MgSO₄) and filtered. Volatiles were removed *in vacuo* and then triturated with cold hexane providing 1,2- C₅H₅(CC₆H₄ClNH)(CC₆H₄ClN) as a yellow-orange powder (2, 74.0% yield). **Mp:** 218-222°C.  
**¹H NMR (500 MHz, CDCl₃, ppm):** δ 7.05 (d, 1H, ³J = 3.45Hz, CHCH₂H), 7.46 (d, 1H, ³J = 8.55Hz, CHCH₂Cl), 7.54 (t, 1H, ³J = 3.45 Hz, CHCH₂H), 7.81 (d, 1H, ³J = 8.55Hz, CHCH₂Cl), 11.8 (br s, 1H, NH).  
**¹³C NMR (125 MHz, CDCl₃, ppm):** δ 109.2 (CHCH₂H), 120.3 (CHCH₂H), 129.4 128.9, 133.4 (Ph) 136.5 (CHCH₂H), 118.8 (br s, 1H, NH). **IR (KBr, cm⁻¹):** 1598 (CN), 3047 (CH), 2931, 2965 (CH₃), 3192 (NH). **MS:** m/z 338 (M⁺), 302 (M⁺ - Cl). Anal. Calcd. for C₁₉H₁₂N₂Cl₂: C, 67.27; H, 3.57. Found: C, 67.56; H, 3.56.
Synthesis of [Tl{1,2-C₅H₃(CC₆H₄ClNH)(CC₆H₄ClN)}] (3)

Thallium (I) ethoxide was added to a solution of 1,2-C₅H₃(C₆H₄ClN)(C₆H₄ClN) (2, 490 mg, 1.44 mmol) in THF (30 mL). An orange precipitate formed after 5 minutes. The solution was stirred for 24 hours at 22 °C. The precipitate was filtered and washed with cold hexane (3 x 10mL) providing [Tl{1,2-C₅H₃(CC₆H₄ClNH)(CC₆H₄ClN)}] (3, quantitative yield, 869.1 mg, 1.60 mmol) as a yellow solid. Mp: 160-165 °C. ¹H NMR (500 MHz, DMSO-d₆, ppm): δ 6.37 (br s, 1H, CHCH), 6.84 (br s, 2H, CHCHCH), 7.50 (d, 1H, ³J = 8.0 Hz, CHCHCl), 8.08 (d, 1H, ³J = 8.0 Hz, CHCHCl). ¹³C NMR (125 MHz, DMSO-d₆, ppm): δ 92.0 (CHCH), 98.3 (CHCHCH), 121.5 (CCHCH), 128.5, 130.5, 132.1, 140.4 (Ph), 148.2 (CN). IR (KBr, cm⁻¹): 1516 (CN), 3059 (CH).


Synthesis of 1,2-C₅H₃(COC₄H₂SBr)(COC₄H₂SBr) (4)

Freshly cracked cyclopentadiene (3.14 ml, 2.51 g, 38.1mmol) was added dropwise to a solution of cooled (0°C) diethyl ether (120 mL) and n-butyllithium (16.2 mL of 2.50 M, 11.4 g, 178.5 mmol). A white precipitate formed immediately and was allowed to stir for 15 minutes upon which 2-thiophene carbonyl chloride (2.48 mL, 3.29g, 25.2 mmol) was added dropwise. A bright orange color formed immediately and was allowed to stir at room temperature for 45 minutes. The reaction was hydrolyzed with dilute (5%) acetic acid (100 mL). The organic layer was separated and extracted three times (3 x 10 mL). Volatiles were removed in vacuo to provide 1,2-C₅H₃(COC₄H₂S)(COC₄H₂S) (4, 75% yield) as a red powder. ¹H NMR (500 MHz,
DMSO-d$_6$, ppm): δ 6.58 (t, 1H, $^3J = 4.0$ Hz, CHCHCH), 7.32 (br s, 2H, CHCHCH), 7.76 (d, 1H, $^3J = 9.8$, CHCHCBr), 7.78 (d, 1H, $^3J = 9.8$, CHCHCBr).

Synthesis of 1,2-C$_5$H$_3$(CC$_4$H$_2$SBrNH)(CC$_4$H$_2$SBrN) (5)

1,2-C$_5$H$_3$(COC$_4$H$_3$S)(COC$_4$H$_3$S) (250 mg, 0.577 mmol) was dissolved in methanol (50 mL). An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added and the solution was allowed to stir for 24 hours. Water (20 mL) was added to the solution and an orange precipitate formed immediately. The organic layer was separated and extracted three times with ethyl ether (3 x 10 mL). The organic layers were dried (MgSO$_4$) and filtered. Volatiles were removed in vacuo and triturated with cold hexane to provide 1,2-C$_5$H$_3$(CC$_4$H$_2$SBrNH)(CC$_4$H$_2$SBrN) (5, 64% yield). $^1$H NMR (500MHz, DMSO-d$_6$, ppm): δ 6.56 (d, 2H, $^3J = 4$ Hz, CHCHC), 7.32 (t, 1H, $^3J = 4$ Hz, CHCHC).

$^{13}$C NMR (125MHz, DMSO-d$_6$, ppm): δ 107.7 (C=HCHCH), 120.4 (CHC=HCH), 132.5 (C=N).

Synthesis of [Tl{1,2-C$_5$H$_3$(CC$_4$H$_3$SBrCH$_3$NH)(CC$_4$H$_3$SBrCH$_3$N)}] (6)

Thallium (I) ethoxide was added to a solution of C$_5$H$_3$(CC$_4$H$_2$SBrNH)(CC$_4$H$_2$SBrN) (5, 250 mg, 0.469 mmol) in THF (25 mL). A brown precipitate formed after 5 minutes. The solution was allowed to stir for 3 hours are 22°C. The precipitate was filtered and washed with cold hexane (3 x 10 mL) providing [Tl{1,2-C$_5$H$_3$(CC$_4$H$_2$SBrCH$_3$NH)(CC$_4$H$_2$SBrCH$_3$N)}] as a gold solid (6, 65% yield). $^1$H NMR (500MHz, DMSO-d$_6$, ppm): δ 6.35 (d, 1H, $^3J = 3.4$ Hz, CHCHCH), 6.82 (t, 1H, $^3J = 3.4$ Hz, CHCHCH), 7.64 (d, 1H, $^3J = 8$ Hz, CHCHBr), 8.02 (d, 1H, $^3J = 8$ Hz, CHCHBr).

$^{13}$C NMR (125MHz, DMSO-d$_6$, ppm): δ 130.86 (CHCHCH), 131.32 (C=N)
CHAPTER 3

RESULTS AND DISCUSSION

Research Purpose

The short-term goal of this research project was to synthesize key thallium Cp salt complexes for utilization in future transmetallation research. However, the long term goals for this project are the synthesis of discrete organometallic Group VII metal complexes that have the potential as semiconductors (Figure 3.1). The complexes possess transition metals that have the ability to access different oxidation states. This gives the complex some degree of tunability. It is in this aspect we can make a unique, and hopefully significant, contribution to the field of organic and organometallic semiconductors. However, in order to synthesize these organometallic complexes, appropriate thallium (I) Cp salts have to be generated. The two novel thallium Cp salts synthesized were chlorophenyl thallium pyridazine (Figure 3.2A) and bromothiophene thallium pyridazine (Figure 3.2B). These Cp salts were synthesized by the routes proposed by Snyder, et. al. (Scheme 3.1). The proposed mechanism for which the thallium metal is attached to form the thallium Cp salt is shown in Scheme 3.3.
Figure 3.1 Shows previously published organometallic compound (A) methoxyphenyl M pyridazine as well as target organometallic complexes (B) bromothiophene M pyridazine and (C) chlorophenyl M pyridazine. (M = Mn, Re)
Figure 3.2 Shows the proposed thallium Cp salts: (A) chlorophenyl thallium pyridazine and (B) bromothiophene thallium pyridazine
Scheme 3.1 Synthetic route for proposed thallium Cp salts. (R = C₆H₄Cl, C₄H₂SBr)
Scheme 3.2 Mechanism for the formation of the proposed thallium Cp salts.

(R = C₆H₄Cl, C₄H₂SBr)
Synthesis Discussion

Fulvenes

Fulvene 1 was synthesized by the addition of freshly cracked cyclopentadiene diluted in diethyl ether to a solution of cold n-butyllithium in diethyl ether. After a white precipitate occurred, indicating the formation of cyclopentadienyllithium, the solution was allowed to stir. The acid chloride, 4-chlorobenzoyl chloride, was dissolved in diethyl ether and added. The solution immediately turned yellow and was allowed to stir at room temperature. After hydrolyzing with dilute acetic acid, the organic layers were separated and extracted. Once dried and filtered, volatiles were removed under reduced pressure via a Schlenk line to provide a yellow powder.

Fulvene 4 was synthesized the same way as fulvene 1 but with the addition of the acid chloride 2-thiophene carbonyl chloride instead of 4-chlorobenzoyl chloride. The solution immediately turned bright orange and was allowed to stir upon which it was hydrolyzed with dilute acetic acid. The organic layer was extracted and volatiles were removed *in vacuo* via a Schlenk line to give a red powder.

Fulvene 1 and 4 were similar in their $^1$H NMR (Table 3.1). The Cp protons showed a triplet for the CHCHCH at 6.50 ppm and 6.58 ppm, respectively. The coupling constant for the triplet in fulvene 1’s Cp proton was $^3J = 3.6$ Hz compared to fulvene 4’s $^3J = 4.0$ Hz. However, CHCHCH showed a doublet for fulvene 1 while a broad singlet was observe for this proton in fulvene 2. Both aromatic protons for fulvene 1 and 4 resolved as doublets at 7.47 / 7.73 ppm and 7.76 / 7.78 ppm, respectively. The calculated mass for fulvene 1 agrees with the observed mass within 0.0009 g/mol.
Table 3.1 Selected $^1$H and $^{13}$C NMR data for fulvene 1 and 4

<table>
<thead>
<tr>
<th></th>
<th>1H NMR (ppm)</th>
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<tr>
<td></td>
<td>CHCHCH</td>
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<td>Fulvene 1</td>
<td>t, 6.50</td>
<td>d, 7.32</td>
<td>d, 7.47</td>
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<td>J (Hz)</td>
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<td>Fulvene 4</td>
<td>t, 6.58</td>
<td>br s, 7.32</td>
<td>d, 7.76</td>
</tr>
<tr>
<td>J (Hz)</td>
<td>4</td>
<td>9.8</td>
<td>9.8</td>
</tr>
</tbody>
</table>

$R = C_6H_4Cl, C_4H_2SBr$
Pyridazines

Pyridazine 2 was synthesized by the addition of excess hydrazine hydrate to a solution of fulvene 1 dissolved in tetrahydrofuran. The solution was allowed to stir overnight throughout which the hydrazine hydrate reacted to ‘close’ the ring to form the desired pyridazine. Upon addition of water and orange precipitate formed and organic layer was separated and extracted with methylene chloride. Once dried and filtered, volatiles were removed under reduced pressure via a Schlenk line which was then triturated with cold hexane to provide a yellow-orange powder with a 74.0% yield.

Pyridazine 5 was synthesized in a similar manner. Fulvene 3 was dissolved in methanol to which excess hydrazine hydrate was added in order to close the ring. This solution was stirred overnight upon which an orange precipitate formed. The organic layer extracted with ethyl ether, dried, and volatiles were removed via Schlenk line. The resulting product was triturated with cold hexane resulting in a 64% yield.

The $^1$H NMR, for both pyridazine 2 and 5, show agreement within their respective Cp protons (Table 3.2). A triplet for CHCHCH proton exists at 7.54 ppm and 7.32 ppm for pyridazine 2 and 5 respectively. Doublets occur at 7.05 ppm and 6.56 ppm, respectively, for the CHCHCH Cp protons. The addition of nitrogen involved in the hydrazine hydrate ring closure is supported by the $^{13}$C NMR. Pyridazine 1 shows a peak at 136.5 ppm for the CN while pyridazine 2 has a CN peak resolved near 132.5 ppm. The Cp carbons also resolve similarly with CHCHCH peaks at 109.2 ppm and 107.7 ppm.
Table 3.2 Selected $^1$H and $^{13}$C NMR data for pyridazine 2 and 5

<table>
<thead>
<tr>
<th></th>
<th>1H NMR (ppm)</th>
<th>13C NMR (ppm)</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>Pyridazine 2</td>
<td></td>
<td></td>
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<tr>
<td>J (Hz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>t, 7.54</td>
<td>d, 7.05</td>
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<td>3.45</td>
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<td></td>
<td>d, 7.46</td>
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<tr>
<td></td>
<td>8.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d, 7.81</td>
<td>br s, 11.8</td>
</tr>
<tr>
<td></td>
<td>109.2</td>
<td>136.5</td>
</tr>
<tr>
<td></td>
<td>120.3</td>
<td>133.4</td>
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<tr>
<td>Pyridazine 5</td>
<td></td>
<td></td>
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<tr>
<td>J (Hz)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>t, 7.32</td>
<td>d, 6.56</td>
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<tr>
<td></td>
<td>107.7</td>
<td>132.5</td>
</tr>
<tr>
<td></td>
<td>120.4</td>
<td></td>
</tr>
</tbody>
</table>

$R = C_6H_4Cl, C_4H_2SBr$
Thallium Cp salts

Thallium Cp salt 3 was synthesized by the addition of thallium (I) ethoxide to a solution of pyridazine 2 in tetrahydrofuran. Within 5 minutes an orange precipitate formed and the solution was allowed to stir overnight at room temperature. After which the precipitate was filtered and washed with cold hexane to provide a yellow solid with quantitative yield.

For the synthesis of thallium Cp salt 6, thallium (I) ethoxide was added to a solution of THF and pyridazine 5. A brown precipitate formed after 5 minutes. The solution was stirred for 3 hours at room temperature upon which the precipitate was filtered and washed with cold hexane yielding a gold solid with a 65% yield.

The $^1$H NMR for the thallium Cp salt 3 did not resolve the Cp protons clearly (Table 3.3). At 6.37 ppm, a broad singlet for CHCHCH occurred where a triplet should have been. Likewise, at 6.84 ppm, another broad singlet for the outer Cp protons (CHCHCH) resolved instead of a doublet. Comparing to the thallium Cp salt 6, the Cp protons had much clearer peaks. A triplet for CHCHCH peaked at 6.82 ppm while the doublet for CHCHCH occurred at 6.35 ppm. For both thallium salts 3 and 6, the aromatic protons are in agreement. Doublets occur at 7.50 ppm (CHCHCCI) and 8.08 ppm (CHCHCCI) for thallium salt 3 and 7.64 ppm (CHCHCBr) and 8.02 ppm (CHCHCBr) for thallium salt 6. The $^{13}$C NMR for both thallium salts indicates a CN, however the peak for thallium salt 3 resolves further downfield at 148.2 ppm than the thallium salt 6 at 131.32 ppm.
Table 3.3 Selected $^1$H and $^{13}$C NMR data for thallium Cp salt 3 and 6

<table>
<thead>
<tr>
<th></th>
<th>$^1$H NMR (ppm)</th>
<th>$^{13}$C NMR (ppm)</th>
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<tbody>
<tr>
<td></td>
<td>CHCHCH</td>
<td>CHCHCH</td>
</tr>
<tr>
<td>Thallium Cp Salt 3</td>
<td>br s, 6.37</td>
<td>br s, 6.84</td>
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<tr>
<td>J (Hz)</td>
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<td>8.0</td>
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<tr>
<td>Thallium Cp Salt 6</td>
<td>t, 6.82</td>
<td>d, 6.35</td>
</tr>
<tr>
<td>J (Hz)</td>
<td>3.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

$R = C_6H_4Cl, C_4H_2SBr$
CHAPTER 4

CONCLUSION

Fulvenes 1 and 4 were synthesized with a percent yield of 81.1% and 75% respectively. The $^1$H NMR signals for both fulvene 1 and 4 supported the formation of the Cp and their respective aromatic groups. Although the outer Cp protons for fulvene 4 resolved as a broad singlet instead of a triplet at the same location as the outer Cp protons for fulvene 1. Fulvene 1 also revealed a peak at 18.39 ppm which supports the presence of an $–\text{OH}$ group. IR supports the presence of the $–\text{OH}$ group with a broad peak at 3448 cm$^{-1}$.

Pyridazines 2 and 5 were synthesized with a percent yield of 74.0% and 64%, respectively. For pyridazine 2 showed proper $^1$H NMR signals for all proton locations along with a signal at 11.8 ppm indicating a $–\text{NH}$ group. The $^{13}$C NMR indicated a $–\text{CN}$ group with a peak at 136.5 ppm. IR indicated both a CN and a NH bond at 1598 cm$^{-1}$ and 3192 cm$^{-1}$, respectively, supporting the successful ring close to pyridazine formation. Pyridazine 5 indicated the presence of a ring closing formation with a $^{13}$C NMR peak and 132.5 ppm corresponding to a CN signal.

Thallium Cp salts 3 and 6 were synthesized with a quantitative yield and a 65% yield, respectively. Thallium Cp salt 3 revealed weakly resolved peaks of broad singlets for the Cp protons. However, thallium salt 6 revealed a proper triplet and doublet peaks for the inner and outer Cp protons, respectively. Both compounds had indications of proper aromatic protons. The $^{13}$C NMR for both compounds revealed peaks supporting $–\text{CN}$ bonds. IR for thallium salt 3 supports the presence of the $–\text{CN}$ group with a peak at 1516 cm$^{-1}$.
FUTURE WORK

From the thallium Cp salts synthesized here, further work should be undertaken to attempt transmetallation with rhenium and manganese. Characterization by IR, $^1$H NMR, $^{13}$C NMR, Elemental Analysis should be attempted as well as further characterizing the bromothiophene compounds. Furthermore, crystal structures of the compounds reported here and any future work from these compounds should also be attempted and characterized via X-Ray Crystallography.
REFERENCES


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8) Scott, J. B. Synthesis and characterization of some rhenium complexes. Master Thesis, Western Kentucky University, Bowling Green, KY, **2009**


