

5-2013

# Novel Materials for Use in Homeland Security Research

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NOVEL MATERIALS FOR USE IN HOMELAND SECURITY RESEARCH

A Thesis  
Presented to  
The Faculty of the Department of Physics and Astronomy  
Western Kentucky University  
Bowling Green, Kentucky

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

By  
Jason Osgood Ewen Young

December 2012

NOVEL MATERIALS FOR USE IN HOMELAND SECURITY RESEARCH

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## ACKNOWLEDGEMENTS

I would like to thank my research advisor, Dr. Chad A. Snyder, for his guiding hands, kind words, and all of the knowledge he has bestowed upon me throughout my graduate experience at Western Kentucky University. Dr. Snyder has been constant in his inspiration. I would like to display my sincerest gratitude to Dr. Cathleen J. Webb, Head of the Department of Chemistry, as well as committee member. Additionally, I would like to thank Dr. Alexander Barzilov, for his help in guiding me through the first year of the HSS program. Doctor Vladimir Dobrokhotov has placed a unique perspective on things, and has been an encouraging committee member.

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

The Homeland Security STEM fellowship I have received has been one of the greatest opportunities I have been able to enjoy. The funding provided by the fellowship has allowed me to focus on my research, rather than having to worry about working first and putting research second.

I wish to thank Graduate Studies, for supporting my research by allocating funding to my research project.

I wish to thank the Western Kentucky University Advanced Materials Institute, and in particular Mrs. Pauline Norris for her herculean efforts in aiding my research.

Finally, I would like to thank my parents, Faith and Roger Young, for their encouragement, support, and inspiration during my education at Western

Kentucky University. Without their support, I would not have been able to reach and achieve all that I have. Thank you.

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## NOVEL MATERIALS FOR USE IN HOMELAND SECURITY RESEARCH

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May 2012

55 Pages

Directed by: Dr. C. Snyder, Dr. C. Webb, and Dr. V. Dobrokhotov

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Organometallic pyridazines and compounds derived from them have been of interest in polymer research due to their atypical environmental stability (as compared to other non-aromatic organic semiconductors) as well as their conductivity. The off-metal synthesis and characterization of several pyridazyl thallium, manganese, and rhenium complexes, beginning with fulvenes 1,2- $C_5H_3(COHR)(COR)$ , are reported here. The diacyl fulvenes were treated with hydrazine hydrate to ring close to pyridazines. Next, the pyridazines were converted to their respective thallium salts through treatment with thallium (I) ethoxide. Lastly, the salts were transmetallated into the respective rhenium or manganese complexes through treatment with the respective metal bound to five carbonyl groups and one bromide ( $MnCO_5Br$ ,  $ReCO_5Br$ ). Our research focused on the synthesis of a variety of 5,6-fused ring pyridazines that will act as a model for homeland security research in polymer studies and medicinal research.

Synthesis and characterization of several aryl-substituted 5,6-fused ring pyridazines have been completed. The fulvenes, pyridazines, and thallium salts are important compounds for research due to their reactivity and stability in moisture and air. The complexes synthesized were confirmed using mass spectrometry, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and elemental analysis. Single crystal X-ray diffraction confirmed the structure of

compound **1A**. As evidenced by related previous papers published by the research group, the synthesized complexes displayed stability to air, moisture, and temperature.<sup>18, 19, 23, 25</sup>

## CHAPTER ONE

### INTRODUCTION

The novel materials described have a broad spectrum of applicable categories. The organic compounds synthesized could have a variety of biological applications in medicine, while the organometallic complexes have foreseeable use in semiconductor research. Organic transistors, resistors, and solar cells are not new ideas – renewable materials are highly enticing due to the nature of not worrying about not having enough of the resource – though as of yet there has not been a more cost effective means of their creation. This research aims to generate organic-based semiconductors that are on par or better with current inorganic ones. Similarly, “green” chemistry has come a long way in the past several decades – chemists are focusing on methods that reduce use of hazardous materials, as well as hazardous byproducts. This research continues in that trend, generating very little waste, and very little hazardous waste. The Department of Homeland Security’s Science and Technology Directorate publishes a “Long Range Broad Agency Announcement” containing solicitations for ideas and products to fill critical gaps in safety, security, and necessities. This research seeks to aid in filling two of these challenges, as based on previous studies regarding similar synthesized compounds.

**“IDD.02 – Advanced Materials:** Renew the infrastructure of the present and construct the infrastructure of the future to be resistant to many hazards and have sustainable properties. Hazards include blast, projectiles, fire, earthquakes, wind, flooding, deterioration and aging, corrosion, and especially combinations of these design challenges. Sustainable properties include self-healing, self-

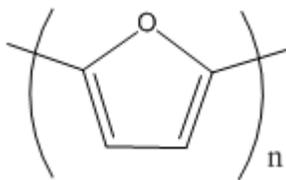
diagnosing, self-reporting, generating or conserving energy, minimal drain on nonrenewable resources, conserving water, long life, and affordability.”

“**IDD.04** – Resilient and Sustainable Infrastructure: Enhancing security, resilience, and recovery of the 18 critical infrastructure sectors for new and retrofit applications. Develop key critical infrastructure components that are affordable, highly transportable, and provide robust solutions during manmade and natural disruptions. Integrate infrastructure protection design with sustainable technologies and methodologies to reduce the consumption of energy, promote clean water, decrease pollutant emissions, and aim at resource conservation over the life of the project. It should use high-performance green materials that are self-monitoring, are self-healing, and stand the test of time. It should resist blast, earthquake, floods, and wind. Developing infrastructure that is sustainable means thinking differently about how we build, what we build, and whether we build at all. It means designing and maintaining infrastructures that are both highly efficient and all-hazard-resistant.”

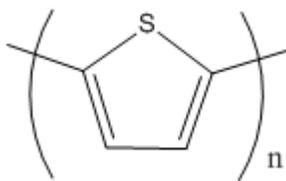
The particular qualities that we are likely to encounter are sustainable properties, such as those mentioned in IDD.02, as well as the resiliency mentioned in IDD.04. The compounds synthesized and described herein display stability to air, temperature, aging and corrosion, are affordable, and place a minimal drain on nonrenewable resources.<sup>1</sup>

Cyclic organic molecules containing atoms other than carbon - heterocycles - and their fused-ring derivatives have long been of interest for use in electronics due to their simple synthesis, variety of applications, and overall

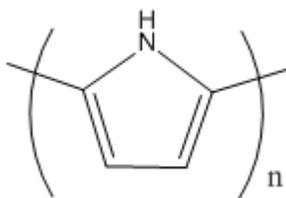
inexpensive nature.<sup>2</sup> Introducing electronegative atoms into a cyclic molecule, particularly a conjugated molecule, can have a variety of effects on the molecular chemistry - particularly stability. Poly-heterocycles, or polymerized heterocycles, are well documented with regards to furan (**1.1A**), thiophene (**1.1B**), and pyrrole (**1.1C**). Poly-pyridazine (**1.1D**) is yet to be studied extensively, and thus is one of the foundations for our research – novel synthesis of organometallic pyridazyl complexes.



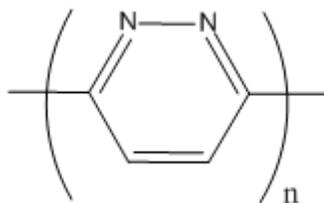
**A**



**B**



**C**



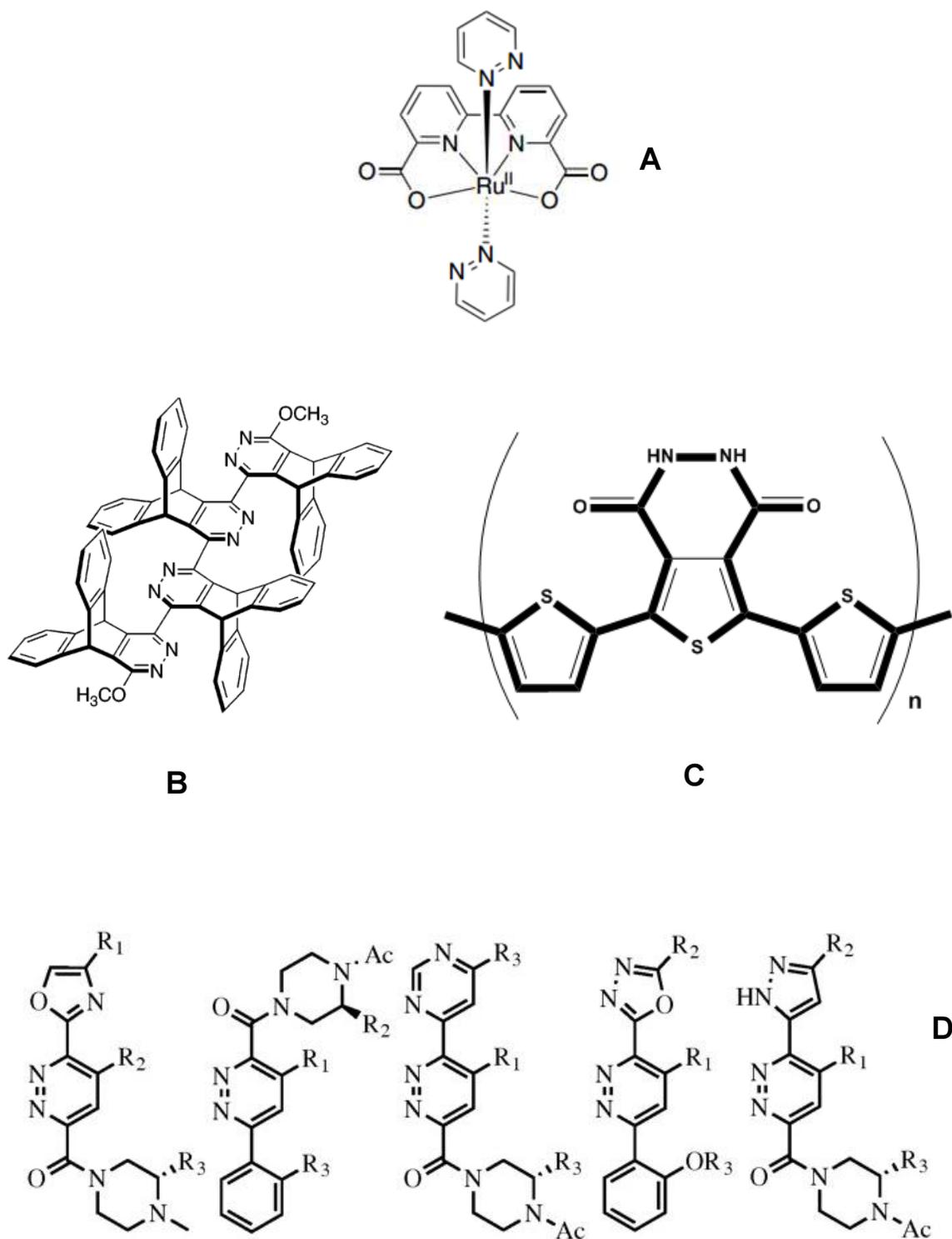
**D**

**Figure 1.1** Structures of **A.** poly-furan, **B.** poly-thiophene, **C.** poly-pyrrole and, **D.** poly-pyridazine.

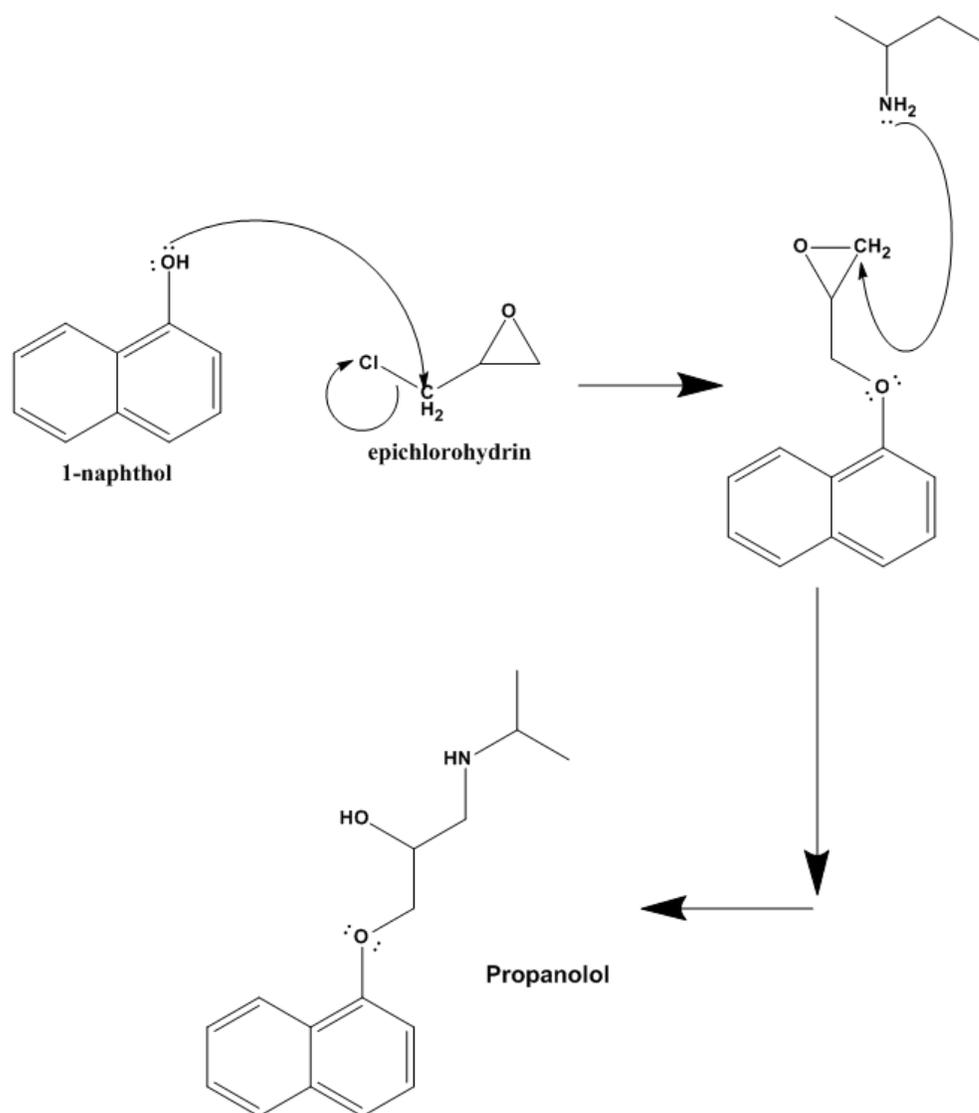
Polymerizing heterocycles, as with any polymerization, has an immense effect on their stability, conductivity, and optical properties.<sup>3</sup>

Pyridazine is an organic molecule, existing as a six-member ring containing two adjacent nitrogen atoms, with a conjugated  $\pi$  electron system. Pyridazine, and its derivative compounds, tend to be highly air and temperature stable – this being owed to aromaticity. This inherent stability of pyridazines is another primary reason they have been chosen as the backbone of our research. Pyridazine compounds have found use in a variety of arenas, such as: catalysts<sup>4</sup> (**1.2A**), storage of gases<sup>5</sup> (**1.2B**), polymer-based sensors<sup>6</sup> (**1.2C**), and biological mimetics<sup>7</sup> (**1.2D**). Pyridazine complexes have been shown to be effective water oxidizers as part of ruthenium complexes (286 oxidations/second).<sup>4</sup> Other catalytic uses of pyridazines include alkene hydration<sup>8</sup> as well as synthesis of epoxides<sup>9</sup>. Alkene oxidation is textbook chemistry in that it is a very common reaction, and performed often in industry in the preparation of compounds from their alkene precursors – for example, ethylene is oxidized into ethanol for an industry grade product. Also, synthesis of ethylene glycol is an oxidation reaction of ethylene. Epoxide chemistry is important both as reactions in the body and commercially in the synthesis of medicines. The synthesis of the blood pressure medication, Propanolol™, is an example of epoxide chemistry (**1.3**).<sup>9</sup> In the storage of gases, hydrogen storage has been of particular interest due to its capacity for use as a fuel.<sup>10</sup> Bulky steel containers of hydrogen gas are not desirable. Research has been carried out using friendlier methodologies, such as porous media. Pyridazyl complexes have shown they can stabilize hydrogen gas

in and around their ring, allowing for a greater storage capacity, with less risk involved.<sup>10</sup> Organic polymer-based sensors are unique in that as opposed to most current inorganic sensor technologies (silicone, printed circuits, metals) organic-based polymers were shown to be capable of detecting TNT as well as DNT<sup>6</sup> at the low vapor pressures of each ( $2 \times 10^{-4}$  torr at 25°C, and  $5.1 \times 10^{-2}$  torr, respectively).



**Figure 1.2** Examples of pyridazines as: **A.** water catalyst, **B.** gas storage, **C.** polymer-based sensor and, **D.**  $\alpha$ -helix mimetics for Bak/Bcl-X<sub>L</sub> complex.



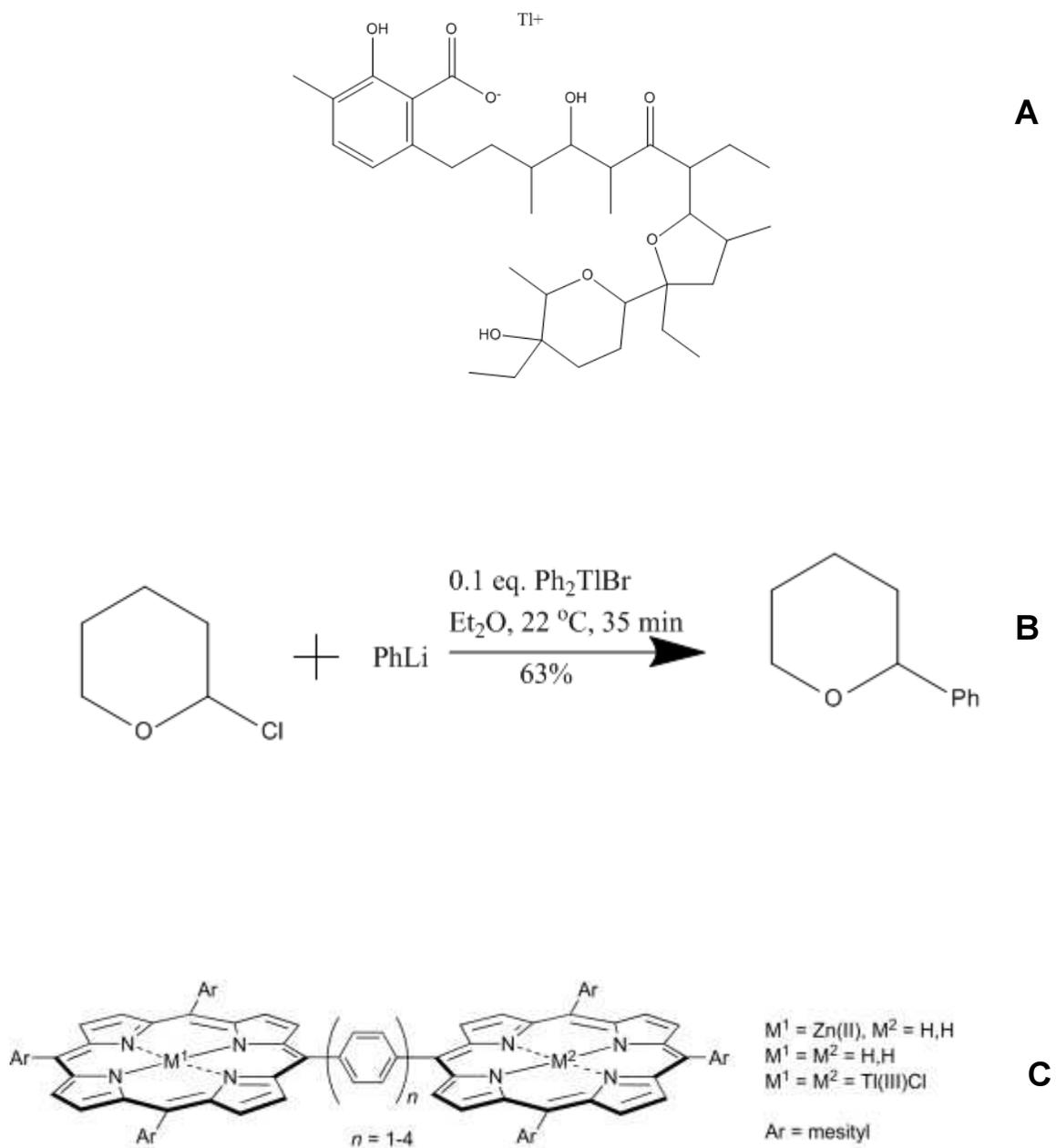
**Figure 1.3** Synthesis of Propanolol™ via an epoxide intermediate.

These sensors can be made into thin-films, so as to cover a wider area, which is of great benefit when attempting to detect a hazardous material with a low vapor pressure. Biological mimesis, or the imitation of biologically relevant compounds, is incredibly relevant and has served as a component in antibiotics, antifungals, and antivirals.<sup>13</sup> In particular, pyridazines have been found to serve as convenient  $\alpha$ -helix mimetics, which are capable of altering protein-protein interactions.<sup>11</sup> If the activity of a protein can be hindered, this can aid in the treatment of a variety of diseases where too much activity of a protein is observed. If the activity of the protein is enhanced, then these compounds could treat a disease where the activity of a protein is too low.

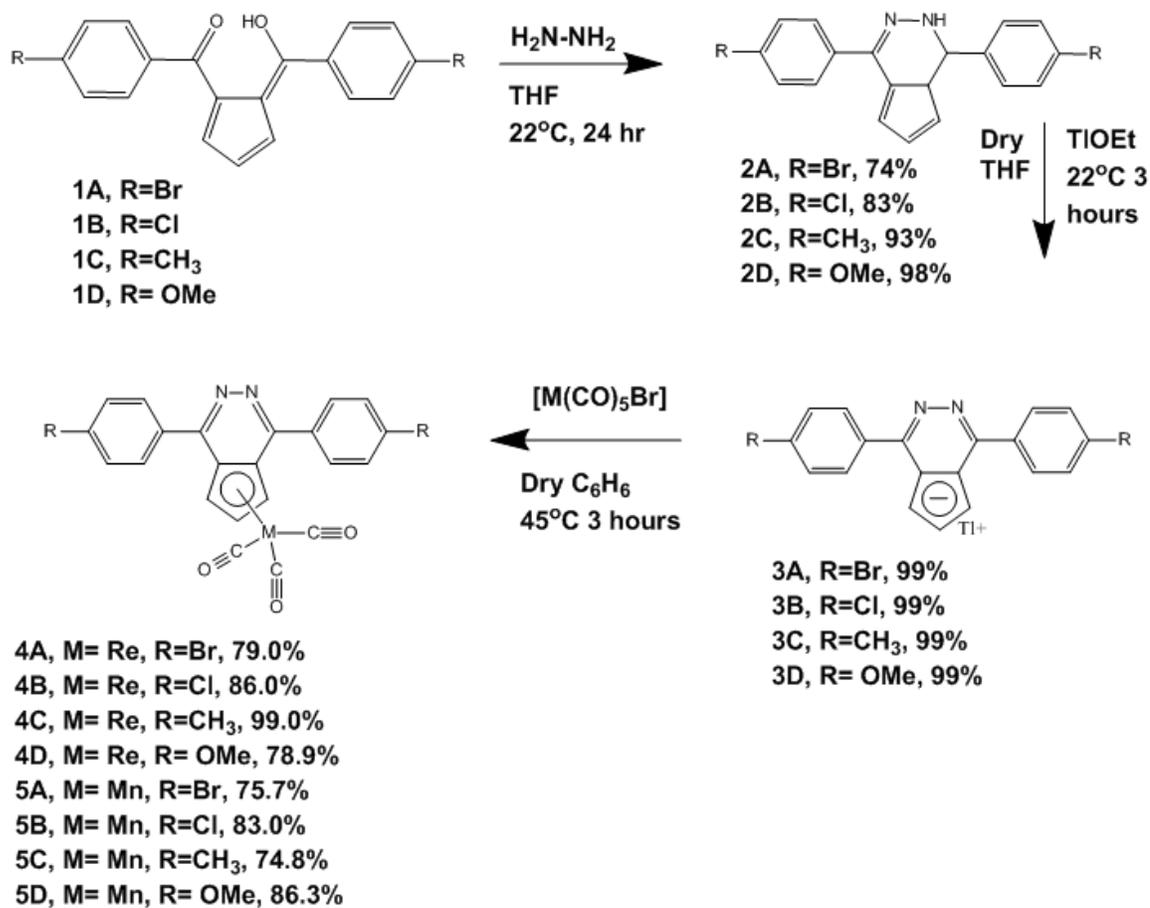
As previously mentioned, our eventual research goal involves organometallic pyridazyl complexes. Synthesis of our final products requires generation of an intermediate, which will create the proper reaction site. Thallium cyclopentadienide (Cp) salts have long been shown to be convenient transmetallating compounds in and of themselves.<sup>13-14</sup> Compared to their sodium or potassium analogs, thallium salts tend to display greater environmental stability due to thallium's slightly larger ionic radius, as well as it possessing *d* orbitals.<sup>13</sup> These *d* orbitals allow thallium the necessary capacity for a substantial stability gain by losing its *p*-1 electron, stabilizing it to the *d*-10 state – this can be contrasted to the same sodium or potassium compounds, where the stability gain is far less due to the loss of *s*-1 electrons.<sup>14</sup> In addition to the air, moisture, and temperature stability, thallium salts are well known for their ability to be replaced by transition metals, such as manganese and rhenium.<sup>17-18</sup> While thallium salts

are often used as intermediates, they are also often easy to synthesize and isolate, due to their stability and insolubility in non-polar organic solvents. In addition, thallium salts have been successfully utilized in a variety of applications, such as in antibiotics (**1.4A**),<sup>15</sup> catalysis (**1.4B**),<sup>16</sup> and synthetic photosynthesis (**1.4C**).<sup>16</sup>

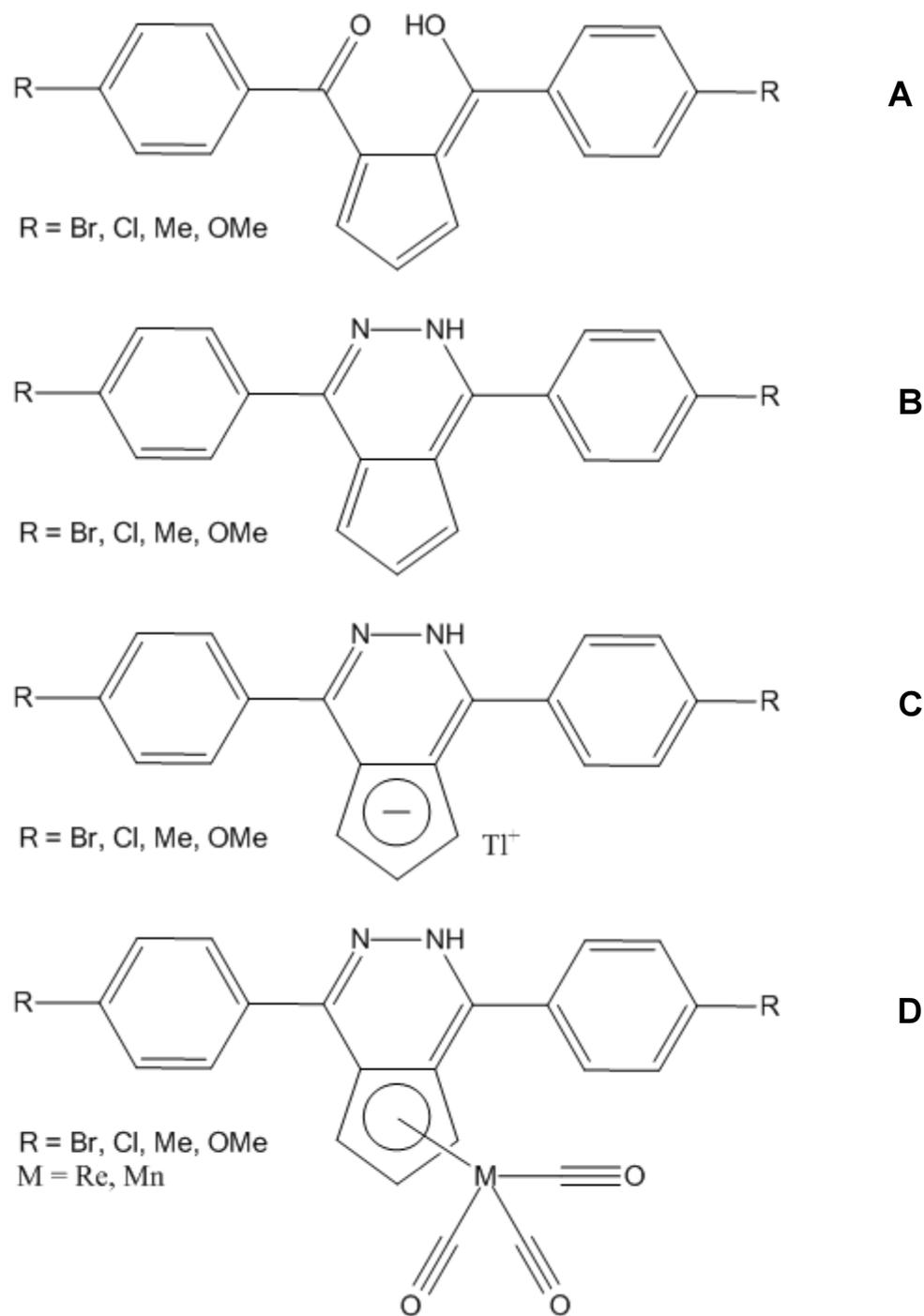
Our target pyridazine-based complexes can be easily synthesized through a three step process (see **Scheme 1**) – beginning with our fulvene (**1.5A**) of interest, ring-closing to the pyridazine (**1.5B**), synthesizing the pyridazyl thallium Cp salt (**1.5C**), and finally transmetallating to the target rhenium or manganese complex (**1.5D**).<sup>17</sup> Organometallics are a highly cost-effective option for semiconductor materials, due to their typical ease of production<sup>18</sup> and low cost compared to traditional inorganic semiconductors.<sup>18</sup> Additionally, organometallic semiconducting polymers have the ability to be tuned as needed. Increasing the number of organic components, and decreasing the number of the highly-conductive organometallic components, or vice versa, will allow for an increase or decrease in overall conductivity, thus achieving the desired properties of the target polymer. If a sensor requires a certain resistance, then a traditional inorganic semiconductor may or may not have the necessary resistance. However, with these highly tunable organometallic semiconductors, the synthesis of a product with the exact resistance needed would be possible – instead of having to incorporate resistors to bypass the inorganic material's natural limitations. Figure **1.6** portrays a noble metal organometallic semiconducting polymer.<sup>19</sup>



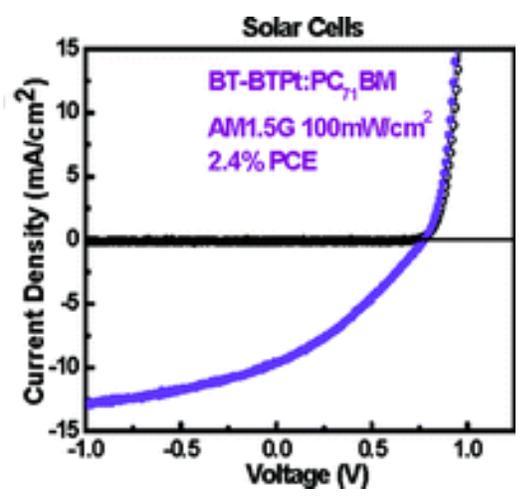
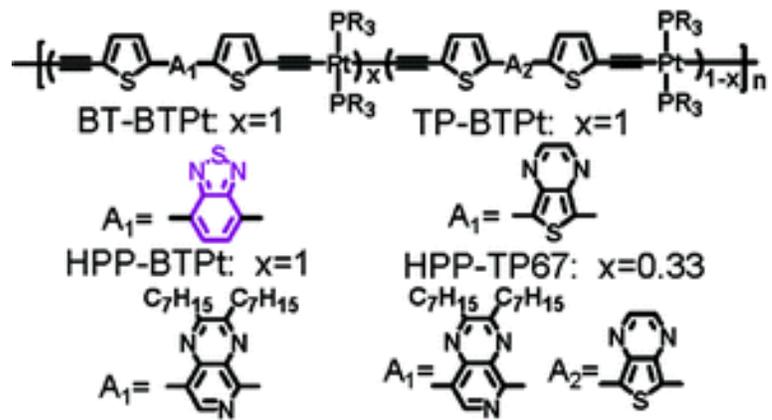
**Figure 1.4** Structures of **A.** Lasalocid (thallium), **B.** Catalysis of 2-phenyltetrahydro-2H-pyran, and **C.** Thallium (III) porphyrin used in artificial photosynthesis.



**Scheme 1** Off-metal synthesis of target organometallic complexes.



**Figure 1.5** Structures of **A.** fulvene, **B.** pyridazine, **C.** thallium salt, and **D.** organometallic complex.



**Figure 1.6** Structure of a noble metal organometallic semiconducting polymer.<sup>19</sup>

These new pyridazyl complexes will serve as the monomers for envisioned organometallic conducting polymers. Furthermore, these pyridazines can serve as useful intermediates in the synthesis of several other classes of heterocycles.<sup>20</sup> For example, Boger and coworkers reported pyrrole synthesis when treating pyridazines to a solution of activated zinc in acetic acid.<sup>21</sup> Our current interests focus upon the potential role of pyridazines in next generation electronic devices which utilize organics as the semiconducting material as well as potential use in medicinal chemistry for the newly synthesized organic compounds. All of these compounds offer new materials suitable for a variety of real world applications such as those targeted in IDD.02 and IDD.04.

## CHAPTER TWO

### EXPERIMENTAL

All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere unless otherwise noted. NMR solvents  $\text{CDCl}_3$ , acetone- $d_6$ , and  $\text{DMSO}-d_6$  (Aldrich) were used without further purification. Tetrahydrofuran (THF), hydrazine hydrate, ethyl ether, benzene (Aldrich), and thallium (I) ethoxide (Strem) were used without further purification. The fulvenes were prepared ahead of time according to the literature methods.<sup>22</sup> Ethyl ether and THF were dried over sodium benzophenone ketyl.<sup>24</sup>

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL-500 MHz NMR spectrometer at approximately 22 °C and were referenced to residual solvent peaks. All  $^{13}\text{C}$  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 70 eV on a Varian 500-MS Series LC/MS ion trap at Western Kentucky University's Advanced Materials Institute as well as on a DART SVP MS Thermo Scientific LTQ-XL at Eastern Kentucky University's Department of Chemistry. Melting points were taken on a standard Mel-Temp apparatus. X-ray diffraction data were collected at 90 K on a Nonius KappaCCD diffractometer at the University of Kentucky. Elemental analyses were performed at Western Kentucky University's Advanced Materials Institute and Atlantic Microlabs, Inc in Norcross, GA. Elemental analysis of the thallium salts afforded carbon and hydrogen values outside the acceptable range rather than those theoretically calculated. However, we attribute this observation due to the presence of thallium impurities commonly present in these types of thallium

cyclopentadienide (Cp) salts.<sup>23</sup> These trace inorganic byproducts did not affect the reactivity of the thallium salts and further purification was not attempted.<sup>24</sup>

### Synthesis of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN) (1A)

1,2-C<sub>5</sub>H<sub>3</sub>(COC<sub>6</sub>H<sub>4</sub>Br)(COHC<sub>6</sub>H<sub>4</sub>Br) (421 mg, 0.970 mmol) was dissolved in methanol (20 mL) in a 25 mL round-bottom flask. An excess of hydrazine hydrate (2.00 mL, 2.06 g, 41.2 mmol) was added to the solution. The solution was stirred 24 hours. To the reaction, water (10 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with dichloromethane (3 x 5 mL) and the organic layers were collected, dried (MgSO<sub>4</sub>), and filtered. The volatiles were removed *in vacuo* and the crude product was triturated with cold hexane to give 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN) (**2b**, 326 mg, 0.762 mmol, 78.6%) as an orange powder. **Mp:** 182–187 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):** δ 7.04 (d, 2H, <sup>3</sup>J = 3.5 Hz, CHCHCH), 7.54 (t, 1H, <sup>3</sup>J = 3.5 Hz, CHCHCH), 7.67 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCBr), 7.79 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCBr). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):** δ 109.3 (CHCHCH), 120.3 (CHCHCH), 124.8 (CCHCH), 130.1, 132.4 (Ph), 133.5 (CN). **IR (KBr, cm<sup>-1</sup>):** 1591 (CN), 3075 (C–H), 3200 (N–H). **MS:** *m/z* 428 (M<sup>+</sup>), 349 (M<sup>+</sup> – Br). **HRMS:** (M<sup>+</sup>) calcd 427.9348, obsd 427.9348. Anal. Calcd. for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>Br<sub>2</sub>: C, 53.3; H, 2.83; N, 6.54. Found: C, 53.1; H, 2.88.; N, 6.71

### Synthesis of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CINH)(CC<sub>6</sub>H<sub>4</sub>CIN) (1B)

1,2-C<sub>5</sub>H<sub>3</sub>(COC<sub>6</sub>H<sub>4</sub>Cl)(COHC<sub>6</sub>H<sub>4</sub>Cl) (**1f**, 256 mg, 0.766 mmol) was dissolved in 50 mL of THF in a 100 mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 24 hours. To the reaction, water (20 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3 x 10 mL) and the organic layers were collected, dried (MgSO<sub>4</sub>), and filtered. The volatiles were removed *in vacuo* and the crude product was triturated with cold hexane to give 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CINH)(CC<sub>6</sub>H<sub>4</sub>CIN) (**2f**, 186 mg, 0.548 mmol, 83.0%) as a yellow-orange powder. **Mp**: 218–222 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)**: δ 7.05 (d, 1H, <sup>3</sup>J = 3.45 Hz, CHCHCH), 7.46 (d, 1H, <sup>3</sup>J = 8.55 Hz, CHCHCCI), 7.54 (t, 1H, <sup>3</sup>J = 3.45 Hz, CHCHCH), 7.81 (d, 1H, <sup>3</sup>J = 8.55 Hz, CHCHCCI), 11.8 (br s, 1H, NH). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm)**: δ 109.2 (CHCHCH), 120.3 (CHCHCH), 129.4, 128.9, 133.4 (Ph) 136.5 (CHCHCN). **IR (KBr, cm<sup>-1</sup>)**: 1598 (CN), 3047 (C–H), 2931, 2965 (CH<sub>3</sub>), 3192 (N–H). **MS**: *m/z* 338 (M<sup>+</sup>), 302 (M<sup>+</sup> – Cl). Anal. Calcd. for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 67.27; H, 3.57. Found: C, 67.56; H, 3.56.

### Synthesis of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>N) (1C)

1,2-C<sub>5</sub>H<sub>3</sub>(COC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)(COHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) (**1h**, 369 mg, 1.22 mmol) was dissolved in 50 mL of THF in a 100 mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 24 hours. To the reaction, water (20 mL) was added and an orange precipitate

formed immediately. The aqueous suspension was washed with ethyl ether (3 x 10 mL) and the organic layers were collected, dried (MgSO<sub>4</sub>), and filtered. The volatiles were removed *in vacuo* and the crude product was triturated with cold hexane to give 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>N) (**2h**, 250 mg, 0.838 mmol, 93.0%) as a red powder. **Mp:** 182-186 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):** δ 2.46 (s, 3H, CH<sub>3</sub>), 7.07 (d, 1H, <sup>3</sup>J = 4.0 Hz, CHCHCH), 7.29 (d, 1H, <sup>3</sup>J = 8.0 Hz, CH<sub>3</sub>CHCH), 7.49 (t, 1H, <sup>3</sup>J = 4.0 Hz, CHCHCH), 7.81 (d, 1H, <sup>3</sup>J = 8.0 Hz, CH<sub>3</sub>CHCH), 11.5 (br s, 1H, NH). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):** δ 108.9 (CHCHCH), 120.4 (CHCHCH), 128.5, 129.0, 129.7, 130.0, 132.2 (Ph) 141.2 (CHCHCN). **IR (KBr, cm<sup>-1</sup>):** 1595 (CN), 3031 (C-H), 2918 (CH<sub>3</sub>), 3092 (N-H). **MS:** *m/z* 298 (M<sup>+</sup>), 283 (M<sup>+</sup> - CH<sub>3</sub>), 207 (M<sup>+</sup> - C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). **MS:** *m/z* 298 (M<sup>+</sup>). Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>: C, 84.53; H, 6.08. Found: C, 81.62; H, 6.55.

### Synthesis of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>N) (**1D**)

1,2-C<sub>5</sub>H<sub>3</sub>(COC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)(COHC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>) (**1g**, 383 mg, 1.15 mmol) was dissolved in 50 mL of THF in a 100 mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 24 hours. To the reaction, water (20 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3 x 10 mL) and the organic layers were collected, dried (MgSO<sub>4</sub>), and filtered. The volatiles were removed *in vacuo* and the crude product was triturated with cold hexane to give 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>N) (**2g**, 262 mg, 0.793 mmol, 98%) as a

yellow solid. **Mp:** 180-184 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):** δ 3.90 (s, 3H, CH<sub>3</sub>), 6.96 (d, 1H, <sup>3</sup>J = 8.6 Hz, OCHCH), 7.07 (d, 1H, <sup>3</sup>J = 3.4 Hz, CHCHCH), 7.54 (t, 1H, <sup>3</sup>J = 3.4 Hz, CHCHCH), 7.85 (d, 1H, <sup>3</sup>J = 8.6 Hz, OCCHCH), 12.1 (br s, 1H, NH). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):** δ 55.4 (OCH<sub>3</sub>), 108.8 (CHCHCH), 114.3 (CHCHCH), 120.2 (CCN), 130.0, 131.9 (Ph) 161.0 (CHCHCN). **IR (KBr, cm<sup>-1</sup>):** 1573 (CN), 2934, 2963 (CH<sub>3</sub>), 3057 (N-H). **MS:** *m/z* 298 (M<sup>+</sup> – HOCH<sub>3</sub>), 239 (M<sup>+</sup> – C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.34; H, 5.49. Found: C, 74.32; H, 6.30.

### Synthesis of [TI{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN)}] (2A)

Thallium (I) ethoxide was added to a solution of 1,2-C<sub>5</sub>H<sub>3</sub>(CNC<sub>6</sub>H<sub>4</sub>Br)(CNHC<sub>6</sub>H<sub>4</sub>Br) (**1A**, 269 mg, 0.628 mmol) in dry 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 10 mL) providing [TI{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN)}] (**2A**, Quantitative yield, 399 mg, 0.627 mmol) as a yellow solid. **Mp:** 178–195 °C (dec). **<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm):** δ 6.44 (d, 1H, <sup>3</sup>J = 3.4 Hz, CHCHCH), 6.79 (t, 1H, <sup>3</sup>J = 3.4 Hz, CHCHCH), 7.66 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCBr), 7.99 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCBr). **<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, ppm):** δ 110.0 (CHCHCH), 116.5 (CHCHCH), 127.0 (CCHCH), 131.0, 131.6 (Ph), 155.0 (CN). **IR (KBr, cm<sup>-1</sup>):** 1591 (CN), 3100 (CH). **MS(EI-pos):** *m/z* 632 (M<sup>+</sup>), 428 (M<sup>+</sup> – TI). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>Br<sub>2</sub>Tl: C, 36.0; H, 2.07; N, 4.42. Found: C, 29.6; H, 1.74.; N, 2.96

### Synthesis of [TI{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CINH)(CC<sub>6</sub>H<sub>4</sub>CIN)}] (2B)

Thallium (I) ethoxide was added to a solution of 1,2-C<sub>5</sub>H<sub>3</sub>(COC<sub>6</sub>H<sub>4</sub>CIN)(COHC<sub>6</sub>H<sub>4</sub>CIN) (**1B**, 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 10 mL) providing [TI{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CINH)(CC<sub>6</sub>H<sub>4</sub>CIN)}] (**2B**, quantitative yield, 869.1 mg, 1.60 mmol) as a yellow solid. **dec.** 160-165 °C. **<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, ppm):** δ 6.37 (br s, 1H, CHCHCH), 6.84 (br s, 2H, CHCHCH), 7.50 (d, 1H, <sup>3</sup>J = 8.0 Hz, CHCHCBr), 8.08 (d, 1H, <sup>3</sup>J = 8.0 Hz, CHCHCBr). **<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, ppm):** δ 92.0 (CHCHCH), 98.3 (CHCHCH), 121.5 (CCHCH), 128.5, 130.5, 132.1, 140.4 (Ph), 148.2 (CN). **IR (KBr, cm<sup>-1</sup>):** 1516 (CN), 3059 (CH). **MS(EI-pos):** m/z 339 (M<sup>+</sup> – TI). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>Cl<sub>2</sub>Tl: C, 41.9; H, 2.41; N, 5.14. Found: C, 33.7; H, 1.98.; N, 4.21.

### Synthesis of [TI{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>N)}] (2C)

Thallium (I) ethoxide was added to a solution of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>N) (**1C**, 202 mg, 0.676 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 10 mL) providing [TI{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>N)}] (**2C**, quantitative yield, 304 mg, 0.606 mmol) as a yellow solid. **Mp:** 115–120 °C (dec). **<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, ppm):** δ 2.36 (s, 1H, CHCHCCH<sub>3</sub>), 6.41 (d, 2H, <sup>3</sup>J = 2.9 Hz, CHCHCH), 6.84 (t, 1H, <sup>3</sup>J = 2.9 Hz, CHCHCH), 7.26 (d, 2H, <sup>3</sup>J = 7.5 Hz,

CHCHCOCH<sub>3</sub>), 7.95 (d, 2H, <sup>3</sup>J = 7.5 Hz, CHCHCOCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, ppm): δ 21.5 (CH<sub>3</sub>), 99.2 (CHCHCH), 121.6 (CHCHCH), 125.3 (CCHCH), 128.9, 129.2 (Ph), 149.3 (CN). IR (KBr, cm<sup>-1</sup>): 1526 (CN), 3013 (CH). MS(EI-pos): m/z 501.2 (M<sup>+</sup>). Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>Tl: C, 50.1; H, 3.80; N, 5.56. Found: C, 56.6; H, 3.37.; N, 5.09.

### Synthesis of [Tl{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>N)}] (2D)

Thallium (I) ethoxide was added to a solution of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>N) (1D, 321.8 mg, 0.993 mmol) in THF (30 mL). A yellow 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 10 mL) providing [Tl{1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>NH)(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>N)}] (2D, Quantitative yield, 530 mg, 0.993 mmol) as a yellow solid. Mp: 178–195 °C (dec). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, ppm): δ 3.80 (s, 1H, OCH<sub>3</sub>), 6.30 (d, 1H, <sup>3</sup>J = 3.4 Hz, CHCHCH), 6.73 (t, 1H, <sup>3</sup>J = 3.4 Hz, CHCHCH), 7.0 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCOCH<sub>3</sub>), 7.99 (d, 1H, <sup>3</sup>J = 8.6 Hz, CHCHCOCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, ppm): δ 99.5 (CHCHCH), 113.8 (CHCHCH), 129.9 (CCHCH), 125.0, 127.0 (Ph), 150.5 (CN). IR (KBr, cm<sup>-1</sup>): 1587 (CN), 3025 (CH). MS(EI-pos): m/z 632 (M<sup>+</sup>), 428 (M<sup>+</sup> – Tl). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>OCH<sub>3</sub>Tl: C, 47.3; H, 3.21; N, 5.25. Found: C, 50.6; H, 4.47.; N, 3.96.

### Synthesis of $[\text{Re}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{CC}_6\text{H}_4\text{BrN})(\text{CC}_6\text{H}_4\text{BrN})\}]$ (**3A**)

In a 100-mL Schlenk flask,  $[\text{Re}(\text{CO})_5\text{Br}]$  (313.7 mg, 0.772 mmol) was added to a stirred suspension of  $[\text{Ti}\{1,2\text{-C}_5\text{H}_3(1,4\text{-(4-Br)C}_6\text{H}_4)_2\text{N}_2\text{C}_2\}]$  (**2A**) (446.7 mg, 0.702 mmol) in 40 mL of dry benzene. The solution was then allowed to reflux gently for three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane or cold hexane afforded **3A** (388.4 mg, 0.554 mmol, 79%) as a yellow powder. **Mp**: 157-162 °C.  **$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , ppm)**:  $\delta$  6.95 (d, 1H,  $^3J = 3.4$  Hz, CHCHCH), 7.41 (t, 1H,  $^3J = 3.4$  Hz, CHCHCH), 7.80 (d, 1H,  $^3J = 8.0$  Hz, CHCHCBr), 7.99 (d, 1H,  $^3J = 8.0$  Hz, CHCHCBr).  **$^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO-}d_6$ , ppm)**:  $\delta$  107.7 (CHCHCH), 120.5 (CHCHCH), 130.7 (CCHCH), 132.0, 132.5 (Ph), 154.0 (CN). **IR (KBr,  $\text{cm}^{-1}$ )**: 1589 (CN), 3095 (CH), 2003, 2065 (ReCO). **MS(EI-pos)**:  $m/z$  698 ( $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{22}\text{H}_{11}\text{N}_2\text{Br}_2\text{O}_3\text{Re}$ : C, 37.9; H, 1.59; N, 4.02. Found: C, 38.3; H, 1.74.; N, 3.96.

### Synthesis of $[\text{Re}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{CC}_6\text{H}_4\text{ClN})(\text{CC}_6\text{H}_4\text{ClN})\}]$ (**3B**)

In a 100-mL Schlenk flask,  $[\text{Re}(\text{CO})_5\text{Br}]$  (186 mg, 0.458 mmol) was added to a stirred suspension of  $[\text{Ti}\{1,2\text{-C}_5\text{H}_3(1,4\text{-(4-Br)C}_6\text{H}_4)_2\text{N}_2\text{C}_2\}]$  (**2B**) (199.5 mg, 0.313 mmol) in 40 mL of dry benzene. The solution was then allowed to reflux gently for three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane or cold hexane afforded **3B** (157 mg, 79%) as a yellow powder. **Mp**: 162-167 °C (dec).  **$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , ppm)**:  $\delta$  7.05 (d, 2H,  $^3J = 4.0$  Hz,

CHCHCH), 7.48 (d, 4H,  $^3J = 8.0$  Hz, CHCHCl), 7.54 (t, 1H,  $^3J = 4.0$  Hz, CHCHCH), 7.83 (d, 4H,  $^3J = 8.0$  Hz, CHCHCl).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):**  $\delta$  109.3 (CHCHCH), 120.4 (CHCHCH), 129.4, 129.9, 133.4 (Ar), 176.2 (CN), 178.3 (ReCO). **IR (KBr,  $\text{cm}^{-1}$ ):** 1633 (C=N), 1904, 2028 (ReCO). **MS(EI):**  $m/z$  338 ( $\text{M}^+ - \text{Re}(\text{CO})_3$ ). Anal. Calcd. for  $\text{C}_{22}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}_2\text{Re}$ : C, 43.4; H, 1.8. Found: C, 43.2; H, 2.1.

### Synthesis of $[\text{Re}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{C}_6\text{H}_4\text{CH}_3\text{N})(\text{C}_6\text{H}_4\text{CH}_3\text{N})\}]$ (**3C**)

In a 100-mL Schlenk flask,  $[\text{Re}(\text{CO})_5\text{Br}]$  (186 mg, 0.458 mmol) was added to a stirred suspension of  $[\text{Ti}\{1,2\text{-C}_5\text{H}_3(1,4\text{-(4-Br)C}_6\text{H}_4)_2\text{N}_2\text{C}_2\}]$  (**2C**) (199.5 mg, 0.313 mmol) in 40 mL of dry benzene. The solution was then allowed to reflux gently for three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane afforded **3C** (157 mg, 79%) as a yellow powder. Mp: 182-187 °C.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):**  $\delta$  2.42 (s, 1H, CHCHCCH<sub>3</sub>), 5.97 (d, 2H,  $^3J = 2.9$  Hz, CHCHCH), 6.25 (t, 1H,  $^3J = 2.9$  Hz, CHCHCH), 6.63 (d, 2H,  $^3J = 7.5$  Hz, CHCHCCH<sub>3</sub>), 7.25 (d, 2H,  $^3J = 7.5$  Hz, CHCHCCH<sub>3</sub>).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ , ppm):**  $\delta$  23.7 (CH<sub>3</sub>), 100.2 (CHCHCH), 118.0 (CHCHCH), 122.7 (CCHCH), 129.7, 131.6 (Ph), 150.0 (CN), 183.4, 189.9 (ReCO). **IR (Nujol,  $\text{cm}^{-1}$ ):** 1644 (C=N), 1972, 2052 (ReCO). **MS(EI):**  $m/z$  568 ( $\text{M}^+$ ). Analysis Calcd. for  $\text{C}_{24}\text{H}_{17}\text{O}_3\text{N}_2\text{Re}$ : C, 50.8; H, 3.02. Found: C, 52.7; H, 4.3.

### Synthesis of $[\text{Re}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{CC}_6\text{H}_4\text{OCH}_3\text{N})(\text{CC}_6\text{H}_4\text{OCH}_3\text{N})\}]$ (**3D**)

In a 100-mL Schlenk flask,  $[\text{Re}(\text{CO})_5\text{Br}]$  (186 mg, 0.458 mmol) was added to a stirred suspension of  $[\text{Ti}\{1,2\text{-C}_5\text{H}_3(1,4\text{-(4-Br)C}_6\text{H}_4)_2\text{N}_2\text{C}_2\}]$  (**2D**) (199.5 mg, 0.313 mmol) in 40 mL of dry benzene. The solution was then allowed to reflux gently for three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane afforded **3D** (157 mg, 79%) as a yellow powder. **Mp**: 212-221 °C.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)**:  $\delta$  3.90 (s, 6H,  $\text{OCH}_3$ ), 7.00 (d, 4H,  $^3J = 8.6$  Hz,  $\text{NCCCH}$ ), 7.06 (d, 2H,  $^3J = 4.0$  Hz,  $\text{CHCHCH}$ ), 7.48 (t, 1H,  $^3J = 4.0$  Hz,  $\text{CHCHCH}$ ), 7.83 (d, 4H,  $^3J = 8.6$  Hz,  $\text{CHCHCO}$ ), 7.92 (d, 4H,  $^3J = 8.6$  Hz,  $\text{CHCHCO}$ ).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm)**:  $\delta$  55.4 ( $\text{OCH}_3$ ), 108.9 ( $\text{CHCHCH}$ ), 114.4 ( $\text{CHCHCH}$ ), 120.3, 130.0, 132.0 (Ar), 161.1 (CN), 186.4 ( $\text{ReCO}$ ). **IR (KBr,  $\text{cm}^{-1}$ )**: 1607 (C=N), 1900, 2014 ( $\text{ReCO}$ ). **MS(EI)**:  $m/z$  602 ( $\text{M}^+$ ), 330 ( $\text{M}^+ - \text{Re}(\text{CO})_3$ ). Anal. Calcd. for  $\text{C}_{24}\text{H}_{17}\text{O}_5\text{N}_2\text{Re}$ : C, 48.1; H, 2.9. Found: C, 58.6; H, 4.3.

### Synthesis of $[\text{Mn}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{CC}_6\text{H}_4\text{BrN})(\text{CC}_6\text{H}_4\text{BrN})\}]$ (**4A**)

In a 100-mL Schlenk flask,  $[\text{Re}(\text{CO})_5\text{Br}]$  (186 mg, 0.458 mmol) was added to a stirred suspension of  $[\text{Ti}\{1,2\text{-C}_5\text{H}_3(1,4\text{-(4-Br)C}_6\text{H}_4)_2\text{N}_2\text{C}_2\}]$  (**2A**) (199.5 mg, 0.313 mmol) in 40 mL of dry benzene. The solution was then allowed to reflux gently for three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane afforded **4A** (157 mg, 79%) as a yellow powder. **Mp**: 135-157 °C.  **$^{13}\text{C}$**

**NMR (125 MHz, CDCl<sub>3</sub>, ppm):** δ 107.7 (CHCHCH), 120.4 (CHCHCH), 128.3, 130.8, 132.0, 132.5 (Ar), 154.7 (CN), 202.5 (MnCO). **IR (KBr, cm<sup>-1</sup>):** 1522 (C=N), 1934, 2027 (MnCO). **MS(EI-pos):** m/z 566 (M<sup>+</sup>). Anal. Calcd. for C<sub>22</sub>H<sub>11</sub>N<sub>2</sub>Br<sub>2</sub>O<sub>3</sub>Mn: C, 46.7; H, 1.96; N, 4.95. Found: C, 45.2; H, 1.77; N, 4.2.

#### **Synthesis of [Mn(CO)<sub>3</sub>{η<sup>5</sup>-1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CIN)(CC<sub>6</sub>H<sub>4</sub>CIN)}] (4B)**

In a 100-mL Schlenk flask, [Mn(CO)<sub>5</sub>Br] (186 mg, 0.458 mmol) was added to a stirred suspension of [Ti{1,2-C<sub>5</sub>H<sub>3</sub>(1,4-(4-Br)C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>N<sub>2</sub>C<sub>2</sub>}] (**2B**) (199.5 mg, 0.313 mmol) in 40 mL of dry benzene. The solution was then allowed to reflux gently for three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane afforded **3A** (157 mg, 79%) as a yellow powder. **Mp:** 189-194 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):** δ 5.29-5.39 (m, 3H, Cp), 7.54 (d, 4H, <sup>3</sup>J = 6.4 Hz, Ar), 7.90 (d, 4H, <sup>3</sup>J = 6.4 Hz, Ar). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):** δ 92.4 (CHCHCH), 109.2 (CHCHCH), 121.0 (CC), 129.5, 129.9, 133.3, 137.4 (Ar), 156.5 (CN), 221.8 (MnCO). **IR (KBr, cm<sup>-1</sup>):** 1597 (C=N), 1949, 2032 (MnCO). **MS(EI):** m/z 477 (M<sup>+</sup>). Anal. Calcd. for C<sub>22</sub>H<sub>11</sub>O<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub>Mn: C, 55.3; H, 2.3. Found: C, 57.6; H, 3.9.

#### **Synthesis of [Mn(CO)<sub>3</sub>{η<sup>5</sup>-1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>N)(CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>N)}] (4C)**

In a 100-mL Schlenk flask, [Mn(CO)<sub>5</sub>Br] (186 mg, 0.458 mmol) was added to a stirred suspension of [Ti{1,2-C<sub>5</sub>H<sub>3</sub>(1,4-(4-Br)C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>N<sub>2</sub>C<sub>2</sub>}] (**2C**) (199.5 mg, 0.313 mmol) in 40 mL of dry benzene. The solution was then allowed to reflux gently for

three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane afforded **4C** (157 mg, 79%) as a yellow powder. **Mp**: 192-207 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)**: δ 2.57 (s, 1H, CHCHCCH<sub>3</sub>), 6.02 (d, 2H, <sup>3</sup>J = 2.9 Hz, CHCHCH), 6.36 (t, 1H, <sup>3</sup>J = 2.9 Hz, CHCHCH), 6.55 (d, 2H, <sup>3</sup>J = 7.5 Hz, CHCHCCH<sub>3</sub>), 7.45 (d, 2H, <sup>3</sup>J = 7.5 Hz, CHCHCCH<sub>3</sub>). **<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, ppm)**: δ 24.5 (CH<sub>3</sub>), 101.5 (CHCHCH), 120.0 (CHCHCH), 121.3 (CCHCH), 130.3, 132.6 (Ph), 153.1 (CN), 179.4 (C=O), 218.0 (MnCO). **IR** (Nujol, cm<sup>-1</sup>): 1601 (C=N), 1929, 2063 (MnCO). **MS(EI):m/z** 436 (M<sup>+</sup>). Analysis Calc. for C<sub>24</sub>H<sub>17</sub>O<sub>3</sub>N<sub>2</sub>Mn: C, 66.1; H, 3.93. Found: C, 65.9; H, 4.18.

#### **Synthesis of [Mn(CO)<sub>3</sub>{η<sup>5</sup>-1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>N)(CC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>N)}] (**4D**)**

In a 100-mL Schlenk flask, [Mn(CO)<sub>5</sub>Br] (382.3 mg, 1.39 mmol) was added to a stirred suspension of [Ti{1,2-C<sub>5</sub>H<sub>3</sub>(1,4-(4-OCH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>N<sub>2</sub>C<sub>2</sub>}] (**2D**) (978 mg, 1.95 mmol) in 60 mL of dry benzene. The solution was then allowed to reflux gently for three hours. The reaction mixture was cooled and passed through a thin pad (1 cm) of Celite, and the volatiles were removed *in vacuo*. Trituration with cold hexane afforded **3D** (567 mg, 86.3%) as a red powder. **Mp**: 160-170 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)**: δ 5.29-5.39 (m, 3H, Cp), 5.52 (s, 6H, OCH<sub>3</sub>), 7.53 (d, 4H, <sup>3</sup>J = 7.3 Hz, Ar), 7.89 (d, 4H, <sup>3</sup>J = 7.30 Hz, Ar).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):** δ 73.7 (OCH<sub>3</sub>), 92.5 (CHCHCH), 109.1 (CHCHCH), 120.0 (CC), 129.5, 129.9, 133.4, 137.5 (Ar), 157.6 (CN), 220.1 (MnCO). **IR (KBr, cm<sup>-1</sup>):** 1608 (C=N), 1932, 2027 (MnCO). **MS(EI):** m/z 468 (M<sup>+</sup>). Anal. Calcd. for C<sub>24</sub>H<sub>17</sub>O<sub>5</sub>N<sub>2</sub>Mn: C, 61.5; H, 3.6. Found: C, 64.7; H, 4.9.

## CHAPTER THREE

### RESULTS AND DISCUSSION

The target organometallic complexes presented herein were synthesized with the following in mind: the nitrogen atoms in pyridazines have been shown to act as excellent *p*-types semiconductors. This nature of the pyridazyl systems, with the added benefit of multiple oxidation states available with the rhenium and manganese metal centers, serves as the model for which this research was carried out. Synthesis is achieved in a three step process beginning with 1,2-diacylcyclopentadienes (fulvenes). Fulvenes, 1,2-C<sub>5</sub>H<sub>3</sub>(COR)(COHR) **A-D** (**1.5A**), were used to synthesize the 5,6-fused ring pyridazines **A-D** (**1.5 B**) using a procedure published by Snyder and Tice.<sup>25</sup> Treating fulvenes 1,2-C<sub>5</sub>H<sub>3</sub>(COR)(COHR) to a solution of excess hydrazine hydrate in methanol or THF at room temperature allotted the corresponding pyridazines **A-D** (Scheme 1). Reaction time was 24 hours, followed by quenching of the reaction with water, followed by extraction using methylene chloride. Pyridazines were purified from the extraction via hexane trituration. Percent yields for the pyridazines ranged from 74% to 98%.

The structures for pyridazines **1A-D** were confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectroscopy. Selected NMR data is presented in **Table 1** which displays the typical Cp and Ph protons as doublets and triplets in the expected ranges (7.05 to 7.54 ppm) for those either close to an electronegative atom or not. The amine protons tend to be delocalized and are observed downfield (10–12 ppm), closely matching previously reported pyridazine N-H chemical shifts.<sup>21</sup> For instance, the **1B** amine proton was seen at 11.8 ppm. Demonstrated from our previously

reported pyridazines, the NMR spectrum for all pyridazyl and thallium complexes showed the disappearance of the carbonyl group, which is observed in the fulvene precursors. Instead, the pyridazines show the characteristic C=N signals. IR spectroscopy for the pyridazines confirms the loss of the carbonyl stretches and the appearance of C=N, and can be found in **Table 5**. MS analysis confirmed the structure for the pyridazines, showing the expected masses,  $M^+$ .

The synthesis of the thallium cyclopentadienide salts **2A–D** was successfully performed using a modified procedure of Snyder and Tice.<sup>20</sup> Treating pyridazines 1,2- $C_5H_3(COR)(COHR)$  to a solution of thallium (I) ethoxide in THF at room temperature yielded the corresponding thallium cyclopentadienide salts **2A–D**. The thallium compounds reacted for 24 hours, were collected via filtration, and washed with cold hexane. The thallium cyclopentadienide salts were dried and characterized with no further purification. Percent yields for compounds **2A–D** were qualitative.

Synthesis of the thallium Cp salts were confirmed by  $^1H$ ,  $^{13}C$  NMR, and IR spectroscopy (**Table 2** and **Table 5**). The cyclopentadiene (Cp) ring protons are observed as a doublet ( $CHCHCH$ ) and triplet ( $CHCHCH$ ), having chemical shifts of 6.30–6.44 ppm and 6.73–6.84 ppm, respectively. The coupling constants for the Cp  $CHCHCH$  and  $CHCHCH$  chemical shifts ranged from 2.9–3.4 Hz for the Cp protons. The Cp ring carbons for thallium Cp salts **2A–D** fall in the range of 92.0–110.3 ppm and 92.0–121.6 ppm, for  $CHCHCH$ , and  $CHCHCH$ , which corresponds well with previously reported thallium Cp salts.<sup>20</sup> Like those previously reported thallium Cp salts, the aspect of these particular thallium salts,

that they can be characterized themselves is impressive. There are few papers in the literature that have characterized thallium Cp salts. Typically, these salts are simply understood to have been synthesized by their use in an intermediate step. As a result, if the target product can be characterized, then the intermediate step must have been made as well. IR spectroscopy corroborates the presence of the C=N bond, with a distinct stretching frequency range found between 1516–1600  $\text{cm}^{-1}$ . Analysis of the thallium Cp salts by MS also confirmed the structures for each of the salts, with either the  $\text{M}^+$  and/or  $\text{M}^+ - \text{Tl}$  observed for each case.

The synthesis of the rhenium and manganese complexes, **3A–D**, and **4A–D**, respectively, were successfully performed using a modified procedure of Snyder and Tice.<sup>21</sup> Treating thallium salts  $[\text{Tl}\{1,2\text{-C}_5\text{H}_3(\text{COR})(\text{COHR})\}]$  to a solution of the corresponding metal carbonyl bromide  $[(\text{M}(\text{CO})_5\text{Br})]$  in dry benzene at room temperature yielded the corresponding organometallic complex **3A–D**, and **4A–D**. The rhenium and manganese complexes refluxed gently for 3 hours, were filtered through a celite plug (1cm), the solvent was removed *in vacuo*, and the crude product triturated with cold hexane three times, resulting in our target organometallic complexes. Percent yields for compounds **3A–D**, and **4A–D** ranged from 79-99, and 75-86 percent, respectively.

Confirmation of rhenium complexes was carried out by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and IR spectroscopy (**Table 3** and **Table 5**). The cyclopentadiene (Cp) ring protons are observed as a doublet (*CHCHCH*) and triplet (*CHCHCH*), having chemical shifts of 5.97–7.06 ppm and 6.25–7.48 ppm, respectively. The coupling constants for the Cp *CHCHCH* and *CHCHCH* chemical shifts ranged from 2.5–

4.0 Hz for the Cp protons. The Cp ring carbons for rhenium Cp complexes **3A–D** fall in the range of 100.2–109.3 ppm and 114.4–120.5 ppm, for CHCHCH, and CHCHCH, which corresponds well with previously reported rhenium Cp products.<sup>27</sup> IR spectroscopy corroborates the presence of the C=N bond, with a distinct stretching frequency range found between 1589–1644 cm<sup>-1</sup>. Analysis of the rhenium Cp salts by MS also confirmed the structures for each of the organometallic complexes.

Confirmation of manganese complexes was carried out by <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectroscopy (**Table 4** and **Table 5**). The cyclopentadiene (Cp) ring protons are observed as a broad singlet or doublet (CHCHCH) and triplet (CHCHCH), having chemical shifts of 5.29–6.02 ppm and 5.39–6.36 ppm, respectively. The coupling constants for the Cp CHCHCH and CHCHCH chemical shifts were 2.9 Hz for those that could be calculated. The Cp ring carbons for manganese Cp complexes **4A–D** fall in the range of 92.4–107.5 ppm and 129.9–133.4 ppm, for CHCHCH, and CHCHCH, which corresponds well with previously reported rhenium Cp products.<sup>18</sup> IR spectroscopy corroborates the presence of the C=N bond, with a distinct stretching frequency range found between 1522–1608 cm<sup>-1</sup>. Analysis of the manganese Cp salts by MS also confirmed the structures for each of the organometallic complexes.

The structure of 1,2-C<sub>5</sub>H<sub>3</sub>(CC<sub>6</sub>H<sub>4</sub>BrNH)(CC<sub>6</sub>H<sub>4</sub>BrN) (**1A**) was determined by X-ray crystallographic methods. The crystals for which data were collected had been grown by slow evaporation from a 50:50 mixture of acetone and hexane at room temperature. These crystals were mounted on glass fibers with

Paratone N oil. Data were collected at 90 K on a Nonius KappaCCD diffractometer. The main programs used were DENZO-SMN to obtain cell parameters and for data reduction, SCALEPACK for absorption correction, SHELXS-86 for structure solution, and SHELXL-93 for refinement.<sup>20</sup> Hydrogen atoms were placed in geometrically calculated positions. Crystal data and experimental details are given in **Table 3**. **Figure 3.1** displays the solved crystal structure for **1A**, and its inherent  $\pi$ -stacking of electrons.

The average Cp carbon-carbon bond length for molecule **1A** is 1.4157(3) Å, the N1–N2 bond length is 1.359(2) Å, and the average aromatic ring carbon-carbon bond length is 1.389(6) Å. The carbon-bromine bond lengths for the para-bromo substituents are 1.9003(19) Å and 1.9023(19) Å. This can be compared to the typical Cp carbon-carbon bond length of 1.34 Å, a typical nitrogen-nitrogen bond length of 1.47 Å, and an average aromatic ring system having a length of 1.4 Å. The differences in Cp bond lengths can be attributed to the delocalization of electrons in the fused-ring pyridazine. Since nitrogen is an electronegative atom, it will have a tendency to draw the electrons away from the Cp ring. As a result, the Cp carbons will be less tightly bound, resulting in longer bond lengths. A typical carbon-bromine bond is 1.93 Å; there is little discrepancy between the XRD value, and the average length – the slight decrease in the XRD can be attributed to the delocalized nature of the electrons in the phenyl ring. The difference in the average and that derived from the XRD between the nitrogen-nitrogen bond lengths can also be attributed to the delocalized nature of the pyridazyl system. Additionally, the geometry of the nitrogens in the pyridazine is

different than that of diatomic nitrogen ( $sp^2$  hybridization vs. simply  $s$ ). The difference in an average aromatic ring system (such as benzene) and those found in our pyridazine occurs due to the inclusion of two nitrogen atoms in our six-membered ring. By increasing the number of electronegative atoms, the bond lengths will be shorter, as observed in our crystal structure.

**Table 1** Selected NMR data for pyridazines.

Pyridazine	<sup>1</sup> H Cp (ppm)	<sup>1</sup> H Ph (ppm)	<sup>1</sup> H Cp J (Hz)	<sup>1</sup> H Ph J (Hz)	<sup>13</sup> C Cp (ppm)	<sup>13</sup> C Ph (ppm)	<sup>13</sup> C C=N (ppm)
1A	7.40(d), 7.50(t)	7.67(d), 7.79(d)	3.5, 3.5	8.6, 8.6	109.3, 120.3	130.1, 132.4	133.5
1B	7.05(d), 7.54(t)	7.46(d), 7.81(d)	3.5, 3.5	8.6, 8.6	109.2, 120.3	129.4, 133.4	136.5
1C	7.07(d), 7.49(t)	7.29(d), 7.81(d)	4.0, 4.0	8.0, 8.0	108.9, 120.4	130.0, 132.2	141.2
1D	7.07(d), 7.54(t)	6.96(d), 7.85(d)	3.4, 3.4	8.6, 8.6	108.8, 113.3	130.0, 131.9	120.2

**Table 2** Selected NMR data for Cp thallium salts.

Thallium Salt	<sup>1</sup> H Cp (ppm)	<sup>1</sup> H Ph (ppm)	<sup>1</sup> H Cp J (Hz)	<sup>1</sup> H Ph J (Hz)	<sup>13</sup> C Cp (ppm)	<sup>13</sup> C Ph (ppm)	<sup>13</sup> C C=N (ppm)
2A	6.44(d), 6.79(t)	7.66(d), 7.99(d)	3.4, 3.4	8.6, 8.6	110.0, 116.5	131.0, 131.6	155.0
2B	6.37(bs), 6.84(bs)	7.50(d), 8.08(d)	----- ----	8.0, 8.0	92.0, 98.3	130.5, 132.1	148.2
2C	6.41(d), 6.84(t)	7.26(d), 7.95(d)	2.9, 2.9	7.5, 7.5	99.2, 121.6	138.9, 139.2	149.3
2D	6.30(d), 6.73(t)	7.00(d), 7.99(d)	3.4, 3.4	8.6, 8.6	99.5, 113.8	125.0, 127.0	150.5

**Table 3** Selected NMR data for organometallic rhenium complexes.

Rhenium Complex	<sup>1</sup> H Cp (ppm)	<sup>1</sup> H Ph (ppm)	<sup>1</sup> H Cp J (Hz)	<sup>1</sup> H Ph J (Hz)	<sup>13</sup> C Cp (ppm)	<sup>13</sup> C Ph (ppm)	<sup>13</sup> C C=N (ppm)
3A	6.95(d), 7.41(t)	7.80(d), 7.99(d)	3.4, 3.4	8.0, 8.0	107.7, 120.5	132.0, 132.5	154.0
3B	7.05(d), 7.48(t)	7.54(d), 7.83(d)	2.5, 2.5	8.0, 8.0	109.3, 120.4	129.9, 133.4	176.2
3C	5.97(d), 6.25(t)	6.63(d), 7.25(d)	2.9, 2.9	7.5, 7.5	100.2, 118.0	129.7, 131.6	150.0
3D	7.06(d), 7.48(t)	7.83(d), 7.92(d)	4.0, 4.0	8.6, 8.6	108.9, 114.4	130.0, 132.0	161.1

**Table 4** Selected NMR data for organometallic manganese complexes.

Manganese Complex	<sup>1</sup> H Cp (ppm)	<sup>1</sup> H Ph (ppm)	<sup>1</sup> H Ph J (Hz)	<sup>13</sup> C Cp (ppm)	<sup>13</sup> C Ph (ppm)	<sup>13</sup> C C=N (ppm)
4A	-----	-----	-----	107.7, 120.4	130.8, 132.0	154.7
4B	5.29- 5.39 (bs)	7.54(d) , 7.90(d)	6.4, 6.4	92.4, 109.2	129.9, 133.3	156.5
4C	6.02(d), 6.36(t)	6.55(d) , 7.45(d)	7.5, 7.5	101.5, 120.0	130.3, 132.6	153.1
4D	5.29- 5.39 (bs)	7.53(d) , 7.89(d)	7.3, 7.3	92.5, 109.1	129.9, 133.4	157.6

**Table 5** Selected IR data for compounds **1-4**.

Compound	CN (cm <sup>-1</sup> )	CH (cm <sup>-1</sup> )	CH <sub>3</sub> (cm <sup>-1</sup> )	NH (cm <sup>-1</sup> )	M(CO) (cm <sup>-1</sup> )
1A	1591	3075	-----	3200	-----
1B	1598	3047	2932, 2965	3192	-----
1C	1595	3031	2918	3092	-----
1D	1573	-----	2934, 2963	3057	-----
2A	1591	3100	-----	-----	-----
2B	1516	3059	-----	-----	-----
2C	1526	3013	-----	-----	-----
2D	1587	3025	-----	-----	-----
3A	1589	3095	-----	-----	2003, 2065
3B	1633	-----	-----	-----	1904, 2028
3C	1644	-----	-----	-----	1972, 2052
3D	1607	-----	-----	-----	1900, 2014
4A	1522	-----	-----	-----	1934, 2027
4B	1597	-----	-----	-----	1949, 2032
4C	1601	-----	-----	-----	1929, 2063
4D	1608	-----	-----	-----	1932, 2027

**Table 6** Crystal data and structure refinement for **1A**.

Identification code	Bromophenyl Pyridazine
Empirical formula	C <sub>19</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub>
Formula weight	428.13 grams per mole
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.4507(1) Å
	α = 112.7426(5)°
	b = 13.8248(1) Å
	β = 97.6426(5)°
	c = 15.1280(1) Å
	γ = 91.8075(5)°
Volume	1608.83(2) Å <sup>3</sup>
Z	4
Calculated density	1.768 Mg/m <sup>3</sup>
Absorption coefficient	5.038 mm <sup>-1</sup>
F(000)	840
Crystal size	0.18 x 0.14 x 0.12 mm
Theta range for data collection	1.48 to 27.46°
Limiting indices	-10<=h<=10
	-17<=k<=17
	-19<=l<=19

Reflections collected / unique	40102 / 7337 [R(int) = 0.0380]
Completeness to theta = 27.46	100.0 %
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.583 and 0.514
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	7337 / 0 / 415
Goodness-of-fit on F <sup>2</sup>	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0255
	wR2 = 0.0534
R indices (all data)	R1 = 0.0375
	wR2 = 0.0567
Largest difference between peak and hole	0.483 and -0.451 e.A <sup>-3</sup>

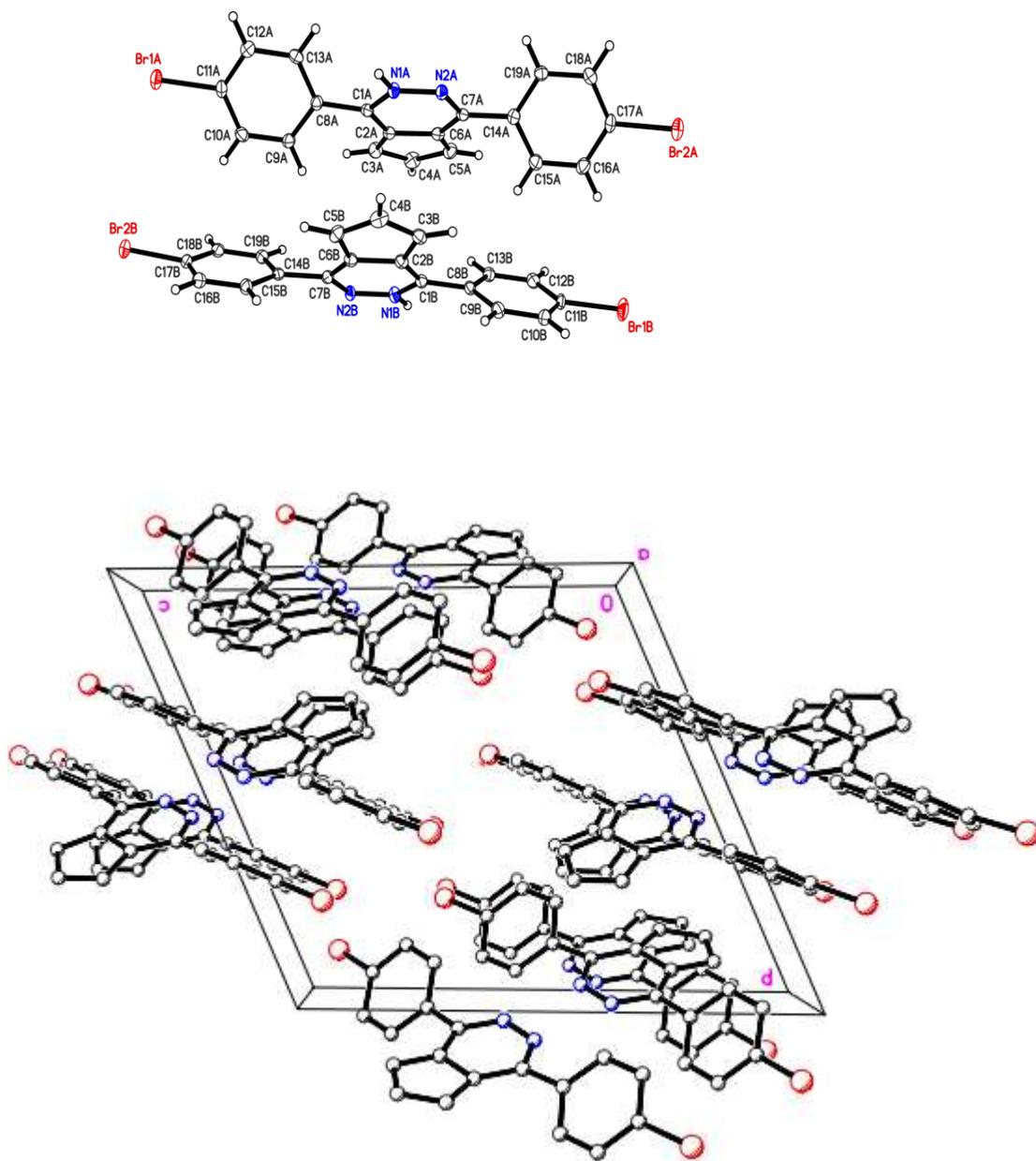
**Table 7** Atomic coordinates and equivalent isotropic displacement parameters for**1A.**

	X	Y	Z	U(eq)
N(1A)	8324(2)	9455(1)	4326(1)	14(1)
N(2A)	9386(2)	9826(1)	3906(1)	14(1)
Br(1A)	2606(1)	7639(1)	6326(1)	20(1)
Br(2A)	14042(1)	11201(1)	1140(1)	22(1)
C(1A)	6889(2)	8912(2)	3899(1)	14(1)
C(2A)	6393(2)	8720(2)	2929(1)	15(1)
C(3A)	4949(2)	8299(2)	2271(1)	19(1)
C(4A)	5131(2)	8460(2)	1435(2)	21(1)
C(5A)	6651(2)	8974(2)	1532(1)	19(1)
C(6A)	7464(2)	9141(2)	2453(1)	14(1)
C(7A)	8956(2)	9663(2)	2977(1)	13(1)
C(8A)	5922(2)	8608(2)	4511(1)	14(1)
C(9A)	4936(2)	7664(2)	4099(1)	16(1)
C(10A)	3973(2)	7370(2)	4639(2)	17(1)
C(11A)	3985(2)	8031(2)	5602(1)	16(1)
C(12A)	4957(2)	8968(2)	6037(1)	16(1)
C(13A)	5928(2)	9252(2)	5489(1)	15(1)
C(14A)	10142(2)	10064(2)	2534(1)	14(1)
C(15A)	10437(2)	9438(2)	1605(1)	19(1)
C(16A)	11565(2)	9776(2)	1176(2)	20(1)

C(17A)	12406(2)	10759(2)	1689(1)	16(1)
C(18A)	12117(2)	11405(2)	2598(1)	17(1)
C(19A)	10988(2)	11054(2)	3021(1)	15(1)

**Table 8** Bond lengths [Å] and angles [°] for heteroatoms in **1A**.

N(1A)-C(1A)	1.346(2)
N(1A)-N(2A)	1.359(2)
N(1A)-H(1A)	0.8800
N(2A)-C(7A)	1.331(2)
Br(1A)-C(11A)	1.9003(19)
Br(2A)-C(17A)	1.9023(19)
C(1A)-N(1A)-N(2A)	127.12(16)
C(1A)-N(1A)-H(1A)	116.4
N(2A)-N(1A)-H(1A)	116.4
C(7A)-N(2A)-N(1A)	117.09(16)
N(1A)-C(1A)-C(2A)	117.75(18)
N(1A)-C(1A)-C(8A)	117.44(17)
N(2A)-C(7A)-C(6A)	121.74(18)
N(2A)-C(7A)-C(14A)	116.01(17)



**Figure 3.1** Solved crystal structure for compound **1A**.

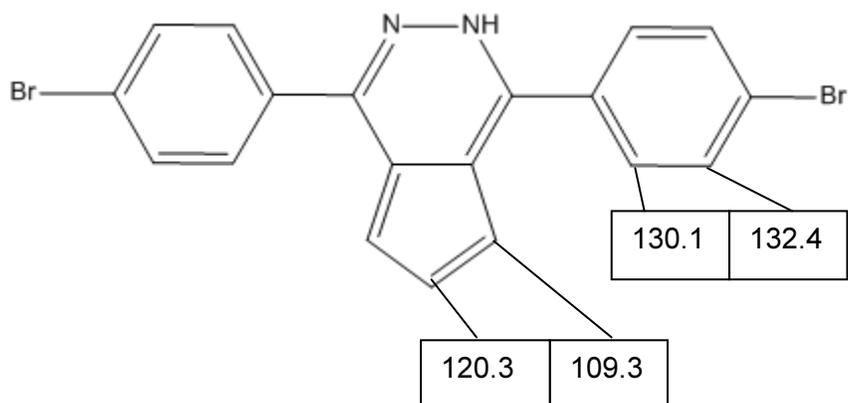
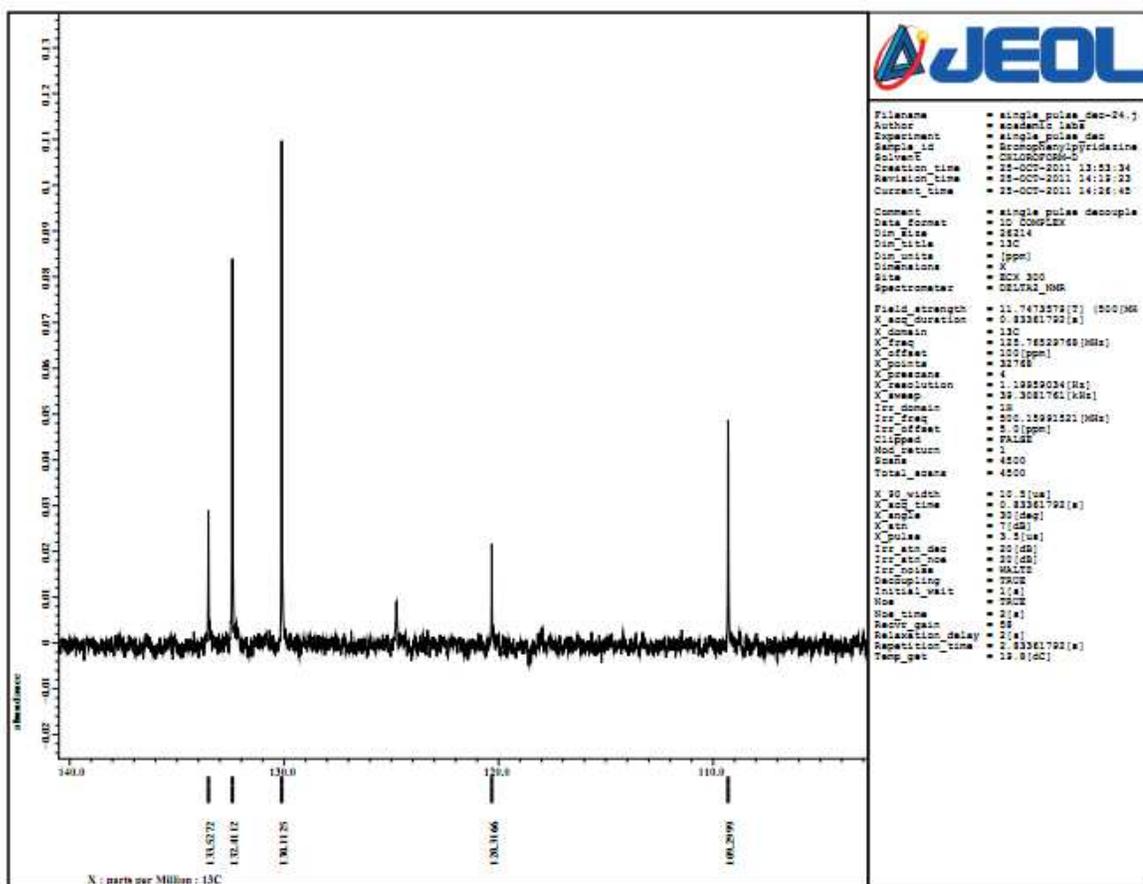


Figure 3.2  $^{13}\text{C}$  NMR for 1A.

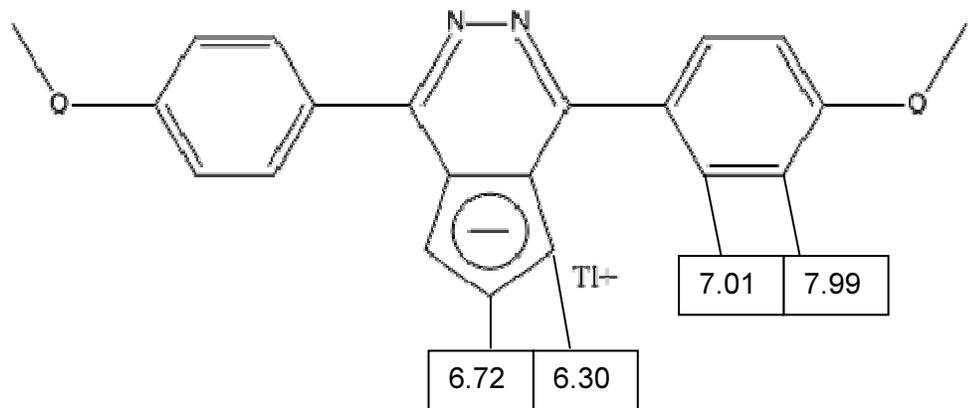
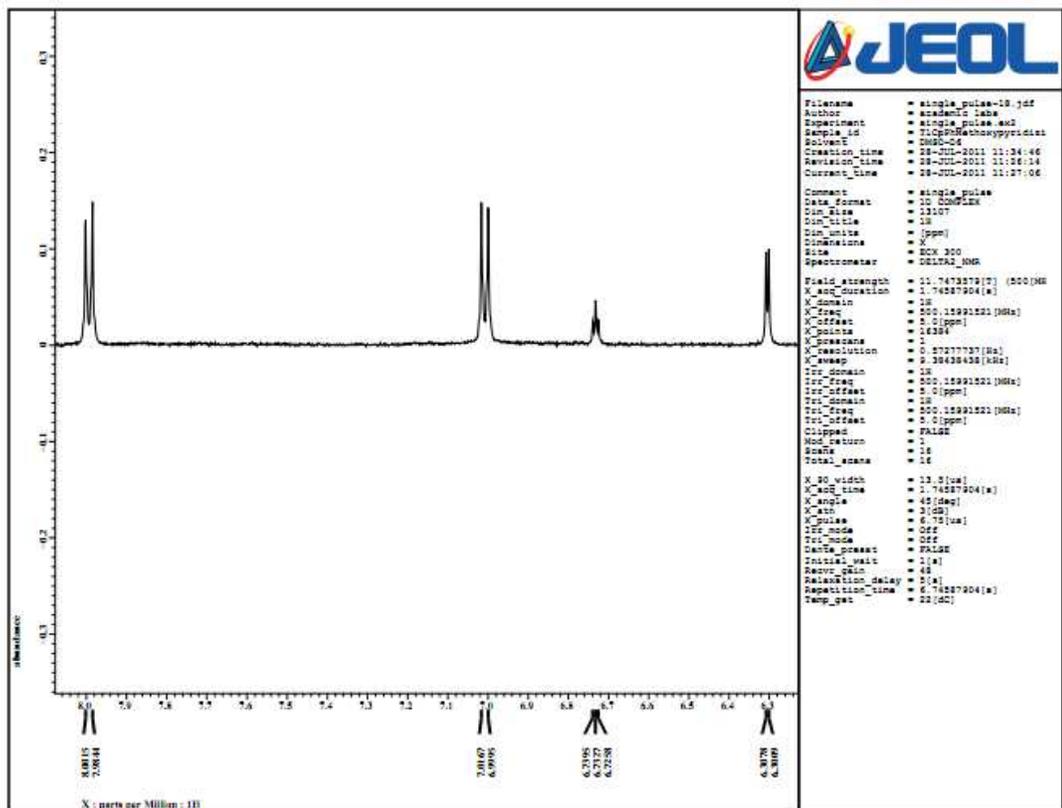


Figure 3.3  $^1\text{H}$  NMR for 2D.

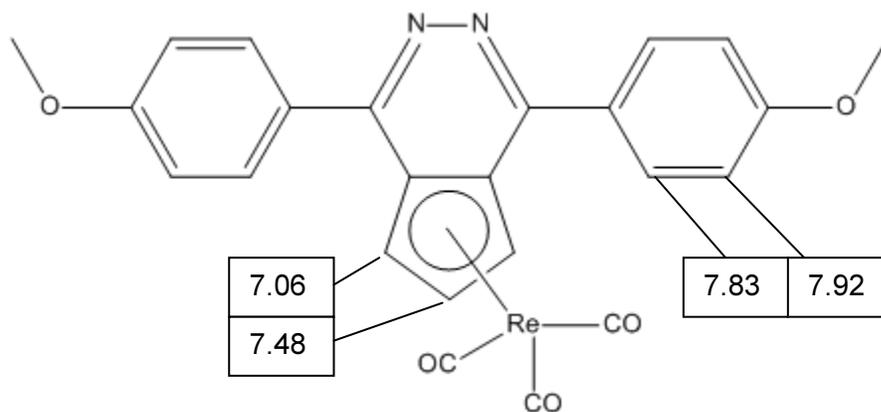
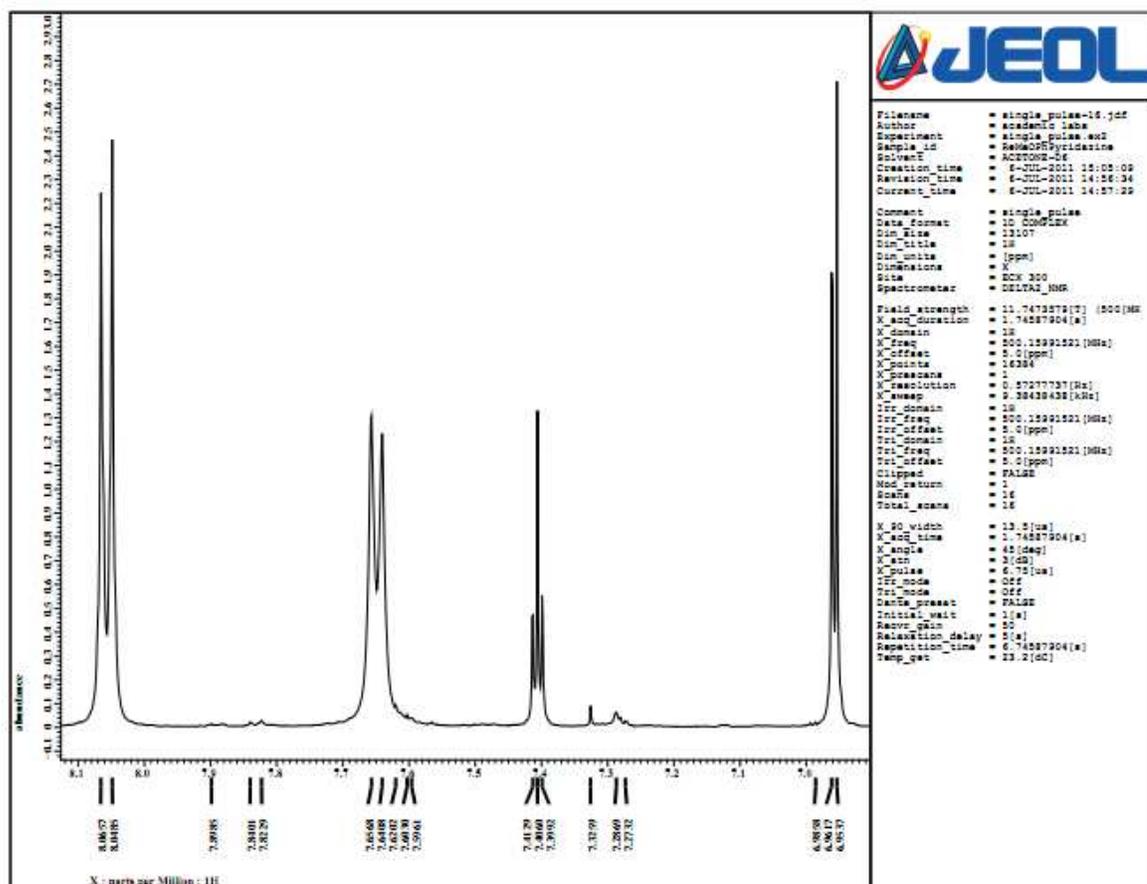


Figure 3.4  $^1\text{H}$  NMR for 3D.



## CHAPTER FOUR

### CONCLUSIONS

Novel materials for use in Homeland Security research have been described herein. The newly synthesized compounds have potential for use as monomers of highly enticing organometallic origin, potential water oxidation catalysts, compounds for synthetic photosynthesis, and potential medicinal chemicals. The yields of 74-99% over the span of the three reactions are encouraging with respect to the solicitation of the DHS Science and Technology Directorate's request for new materials. Materials synthesized from these pyridazyl, thallium salt, or organometallic complexes will: "place a minimal drain on nonrenewable resources, (have) long life, and affordability." The materials used to synthesize these novel complexes meet all of these solicitations found in IDD.02, and those found in IDD.04 as "(they can be made into) components that are affordable, highly transportable, and provide robust solutions during manmade and natural disruptions."

Confirmation of each compound's synthesis by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and mass spectrometry has been described. The C=N bond wave numbers reported match those of previous works.<sup>17</sup> Additionally, the Cp protons and carbons remain constant through the reaction scheme from start to finish. The consistency of the proton coupling constant, J, for both the Cp and phenyl protons suggests that, in each of the cases, we have successfully synthesized our desired products. Mass spectrometry confirmed the presence of our target products as ( $\text{M}^+$ ), in the case of the pyridazines, and the organometallic complexes, or as ( $\text{M}^+ - \text{Tl}^+$ ) in the case of the thallium Cp salts. The rhenium and

manganese exhibit a highly desirable innate stability by not losing the  $[\text{M}(\text{CO})_3]$  group during ionization.

## CHAPTER FIVE

### PERSPECTIVE

New organic-based materials have been made in this research project. The new compounds have potential for use as building blocks for electronics and potential medicinal chemicals. Ideally, chemical reactions would yield 100% product; the results of this research span 74-98% product. The materials synthesized respond to the Department of Homeland Security's (DHS) solicitation for new materials that use non-renewable resources sparingly, that last, and that are affordable. The raw materials used to create these new materials meet all of the solicitations of the DHS as the materials can be easily moved, and with further research will provide useful qualities during manmade and natural disruptions.

Each compound was confirmed by examining its unique positioning of the atomic constituents, its hydrogen and carbon fingerprints, and its mass. Additionally, the hydrogen and carbon fingerprints remain constant through the reactions from start to finish. Measuring each compounds mass confirmed the presence of our target products. The metal compounds used exhibit a highly desirable stability, displayed during the mass determination.

The future of this research lies in its potential for new solar cells, electronic device screens, and renewable lighting sources. These uses and others will encourage further study into these new materials and their unique properties.

## REFERENCES

1. Katritzky, A.R.; Rees, C.W. *Comprehensive heterocyclic chemistry: structure, reactions, synthesis, and uses of heterocyclic compounds*. Pergamon Press, Oxford. **1984**.
2. Roncali, J. *Journal of Chemical Reviews* **1997**, 97, 1, 173-206.
3. Boger, D. L.; Coleman, R. S.; Panek, J. S.; Yohannes, D. *Journal of Organic Chemistry* **1984**, 49, 23, 4405–4409.
4. Xu, Y.; Akermark, T.; Gyollai, V.; Zou, D.; Eriksson, L.; Duan, L.; Zhang, R.; Akermark, B.; Sun, L.A. *Inorganic Chemistry* **2009**, 48, 7, 2717-2719.
5. Ghanem B.S.; Msayib, K.J.; McKeown, N.B.; Harris, K.D.M.; Pan, Z.; Budd, P.M.; Butler, A.; Selbie, J.; Book, D.; Walton, A. *Chemical Communications* **2007**, 1, 1, 67-69.
6. Yang, J.S.; Swager, T.M. *Journal of the American Chemical Society* **1998**, 120, 21, 5321-5322.
7. Volonterio A.; Moisan L.; Rebek J. *Organic Letters* **2007**, 9, 19, 3733.
8. Kosaric, N.; Duvnjak, Z.; Farkas, A.; Sahm, H.; Bringer-Meyer, S.; Goebel, O.; Mayer, D. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH, Weinheim. **2011**.
9. Hornback, J.M. *Journal of Organic Chemistry*. Thomson Learning, Belmont. **2006**.
10. Bouffard, J.; Eaton, R. F.; Muller, P.; Swager, T. M. *Journal of Organic Chemistry* **2007**, 72, 26, 10166–10180.
11. Biroš, M.S.; Moisan, L.; Mann, E.; Carella, A.; Zhai, D.; Reed, J.C.; Rebek Jr., J. *Bioorganic and Medicinal Chemistry Letters* **2007**, 17, 16, 4641-4645.
12. Lin, S.; Liu, Z.; Hu, Y. *Journal of Combined Chemistry* **2007**, 9, 5, 742–744.
13. Akhbar, K.; Morsali, A. *Coordination Chemistry Reviews*. **2010**, 254, 17, 1977-2006.
14. Duhenk, G.A.; Mikhail, I.E.; Reck, G.; Chulz, B.; Chunke, A.Z.; Minkin, V.I. *Organometallic Chemistry* **2001**, 50, 5, 852-856.
15. Bumber, A.A.; Profatilova, I.A.; Dushenko, G.A.; Mikahilov, I.E. *Short Communications* **2003**, 39, 24, 699-702.

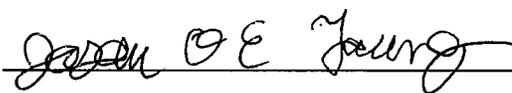
16. Taniguchi, M.; Lindsey, J.S. *Tetrahedron* **2010**, 66, 30, 5549-5565.
17. Tice, N.C.; Snyder, C.A.; Preston, A.Z.; Wieliczko, M.B.; Young, J.O.E.; Hinson, D.F. *Journal of Transition Metal Chemistry* **2011**, 37, 2, 141-147.
18. Snyder, C.A.; Tice, N.C.; Sriramula, P.G.; Neathery, J.L.; Mobley, J.K.; Phillips, C.L.; Preston, A.Z.; Strain, J.M.; Vanover, E.S.; Starling, M.P.; Sahi, N.V.; Bunnell, K.R. *Synthetic Communications* **2011**, 41, 9, 1357-1369.
19. Wu, P.; Bull, T.; Kim, F.S.; Luscombe, C.K.; Jenekhe, S.A. *Macromolecules* **2009**, 42, 3, 671-681.
20. Wisian-Neilson, P.; Allcock, H.R.; Wynne, K.J. *ACS Symposium Series 572*, Division of Polymer Chemistry, Denver, CO. **1994**.
21. Wright, M.E.; Sigman, M.S. *Macromolecules* **1992**, 25, 22, 6050-6054.
22. Snyder, C.A.; Seleque, J.P.; Tice, N.C.; Wallace, C.E.; Blankenbuehler, M.T.; Parkin, S.; Allen, K.D.E.; Beck, R.T. *Journal of the American Chemical Society* **2005**, 127, 43, 15010-15011.
23. Blankenbuehler, M.T., Selegue J.P. *Journal of Organometallic Chemistry* **2002**, 642, 92, 268-274.
24. Young, J.O.E.; Snyder, C.A.; Tice, N.C. *Synthetic Communications* **2012**, manuscript accepted, in press.

## VITA

The author was born in Livonia, Michigan on January 19, 1989. He earned his Bachelor of Science degree from Western Kentucky University in the spring of 2011. In summer of 2011, he entered graduate school at Western Kentucky University as a DHS-STEM fellow; he will earn his Master of Science degree in Homeland Security Sciences working under Dr. Chad A. Snyder, and is expected to defend his thesis in the fall of 2012. During the author's Master of Science research, he published three papers with one as first author. Two other manuscripts were in preparation at his time of completion. The author plans to enter into the University of Louisville Chemistry PhD program in the fall of 2013.

### Published Manuscripts

1. Young, J.O.E.; Snyder, C.A.; Tice, N.C. *Synthetic Communications* **2012**, manuscript accepted, in press.
2. Tice, N.C.; Snyder, C.A.; Preston, A.Z.; Wieliczko, M.B.; Young, J.O.E.; Hinson, D.F. *Journal of Transition Metal Chemistry* **2011**, 37, 141-147.
3. Tice, N.C.; Armstrong, J.R.; Maddox, J.B.; Ward, S.A.; Snyder, C.A.; Young, J.O.E. *Heterocycles* **2012**, 85, 4.

  
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