Off-Metal Synthesis of Some Aryl Substituted Rhenium n5-Cyclopenta [C] Pyridazyl Complexes

James Leif Neathery
Western Kentucky University, james.neathery181@wku.edu

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OFF-METAL SYNTHESIS OF SOME ARYL SUBSTITUTED RHENIUM $\eta^5$-CYCLOPENTA[C]PYRIDAZYL 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
James Leif Neathery

December 2009
OFF METAL SYNTHESIS OF SOME ARYL SUBSTITUTED RHENIUM η5-
CYCLOPENTA[C]PYRIDAZYL COMPLEXES

Date Recommended____11/20/09_______

Dr. Chad Snyder____________________________________
Director of Thesis

Dr. Cathleen Webb___________________________________

Dr. Kevin Williams____________________________________

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

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

Finally, I would like to thank my parents Tilford and Suzanne Neathery for their understanding and compassion during my time at Western Kentucky University.
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Heterocyclic organic and organometallic compounds (e.g. polypyrrole), and their derivatives, have been of great interest for conductive polymers due to their novel properties and environmental stability as compared to non-aromatic analogs (e.g. polyacetylene). Our current interests focus upon the potential role of pyridazines in next generation electronic devices that utilize organics as the semiconducting material. Pyridazines, 6-membered aromatic rings with two adjacent nitrogens, are promising candidates for a variety of materials and commercial applications. These molecular electronic materials possess several advantages over traditional inorganic semiconducting materials including lower cost of production, higher processibility, and the ability to function on flexible substrates (so called “plastic electronics”). These compounds offer new materials suitable for a variety of real world applications such as Organic Light Emitting Diodes (OLEDs) and Organic Photovoltaic Cell (OPVs). Our recent efforts has been focused on the synthesis of a variety of 5,6-fused ring pyridazines. These fused heterocycles will serve as synthetic models and building blocks for potential organic or organometallic conducting polymers.

Our work is focused on the synthesis of pyridazines and their organometallic rhenium complexes and polymer research. Several aryl-substituted 5,6-fused ring
pyridazines have been synthesized and characterized. A pyridazyl complexe of rhenium was synthesized in three steps beginning with a 5,6-fused pyridazine. Off-metal synthesis and characterization of \([\text{Re(CO)}_3\{1,2-\text{C}_5\text{H}_3(\text{CC}_6\text{H}_5\text{N})(\text{CC}_6\text{H}_5\text{N})\}]\) and some aryl-substituted pyridazines \((1,2-\text{C}_5\text{H}_3(\text{CRNH})(\text{CRN}); \text{R} = \text{C}_6\text{H}_5, \text{C}_4\text{H}_3\text{S}, \text{C}_8\text{H}_5\text{S})\) are reported herein.
I. Introduction

**Organic and Organometallic Semiconductors**

**Organic Semiconductors.** An organic semiconductor is any organic compound that possesses electrical conductivity between a conductor and an insulator. Through careful synthesis of donor-acceptor elements, the intramolecular charge transfer (ICT) between the elements can be manipulated to achieve certain optical and electrical properties in semiconductors. Charge transfer complexes often exhibit similar conduction mechanisms to inorganic semiconductors. In the solid phase, properties of materials can be explained using band theory. This theory states that atomic orbitals of each atom overlap with the same orbitals of their neighboring atoms in all directions to produce molecular orbitals similar to those in small molecules.\(^1\) When enough overlap occurs within a given range, it results in continuous energy band overlap. If the band gap is small enough, then these materials possess electrical properties that are similar to metals. The original atomic orbitals depend on the relative energies and number of electrons these bands possess (relative energy of highest occupied (valence band) and lowest unoccupied band (conduction band); Figure 1.1). Greater conductivity occurs from increased band overlap. If the band gap is too large, the valence band electrons fail to migrate to the conduction band that results in an insulator (Figure 1.1). An insulator, such as plastic, can be described by a band that is empty and does not permit conduction. The requirements for a conventional conductive material at room temperature is a band gap narrow enough to allow thermally excited electrons to move from the valence to conduction band.
Figure 1.1. A molecular orbital illustration of an insulator, semiconductor, and conductor.²
Once this occurs the material behaves as a semiconductor such as silicon (Si), Germanium (Ge), or gallium arsenide (GaAs). However highly conductive metals possess a zero band gap resulting in a full valence band and empty conduction band (metal) or partially full valence band and empty conduction band. Typical carriers in organic semiconductors are holes and electrons in \( \pi \)-electrons. Almost all organic solids are insulators. However when molecules have \( \pi \)-conjugated systems, electrons can move via \( \pi \)-electron cloud overlaps (Figure 1.2).³

**Polymer Conduction.** The mechanism for polymer conduction differs from conventional conductive materials. Polymer conduction does not need to have partially filled or partially empty bands. As a result, their electrical conductivity cannot be explained by simple band theory. The introduction of charge carriers (usually electrons or holes) promotes conduction. Charge carriers are formed by doping, i.e., oxidation (p-type) or reduction (n-type) reactions of the polymer chain. For p-type polymers charge carriers leave a vacancy that does not delocalize completely. This vacancy is a hole or a radical cation that only partially delocalizes over several monomeric units causing them to structurally deform. The newly deformed structure is higher in energy than the undoped polymer. Different charge carriers will be generated depending upon the ground state of the polymer (Figure 1.3).⁴ The radical cation has destabilized bonding orbitals that are higher in energy than the valence band. The difference between the destabilized bonding orbital and the valence band is the band gap. A value of 1.5eV has been arbitrarily decided as the cut-off for low-band gap conducting polymers.⁵
Figure 1.2. Illustration of a $\pi$-bond overlapping.
Undoped polymer = energy of conduction band = energy of valence band
Slightly doped polymer

Polaron energy levels

Bipolaron energy levels

Heavily doped polymer

$E$

Figure 1.3. Relative energies of polaron and bipolaron levels.
A polymer produces a soliton\textsuperscript{6} or polaron\textsuperscript{7} when a radical cation is generated depending upon the polymer’s ground-state configuration. If the compound has a degenerate ground state (Figure 1.4), such as polyacetylene, the resulting radical cation will generate a soliton (Figure 1.4a). Since there is no preferred sense of bond alternation, the positive charge and the unpaired electron can move independently along the polymer chain, which allows for conduction, forming domains between the two identical parts of the bond alternation. On the other hand, a radical cation known as a polaron (Figure 1.4b), is generated by oxidation of a polymer with a nondegenerate ground state, such as polythiophene. The quinoidal form results from oxidation and is higher in energy than the ground state. The quinoidal form confines the charge and spin density to the localized structural deformation that is mobile along the chain. There are then two things that happen upon further oxidation of the nondegenerate polymer. One, a second electron can be removed from another segment of the polymer chain, resulting in a new polaron, or the unpaired electron from the previously formed polaron is removed. The later produces a spinless state known as a bipolaron (Figure 1.4b). Conduction by bipolarons and polarons are generally considered to be the dominant mechanism of conductive polymers (Figure 1.5).
Figure 1.4. Representation of (a) soliton of polyacetylene and (b) polaron and bipolaron of polythiophene.²
A large variety of conjugated polymers has been synthesized and investigated in terms of their suitability to operate as active materials in devices such as organic light emitting diodes (OLEDs), organic thin-film diodes (OTFTs), organic photovoltaic diodes (OPVDs), or lasers. For example, an OLED has been realized with para-hexaphenyl, which exhibits remarkable optical properties. The polarization of its electroluminescence can be changed through the molecular alignment. OLEDs are already being used today in copy machines, laser printers, and flat screen televisions.

**Conductive Polymer Background.** Polymers or plastics are generally thought to behave opposite from metals. In an ideal situation, polymers should behave as insulators while metals conduct electricity, yet the work conducted by Shirakawa and coworkers challenged this view with their discovery of conductive polymers in 1977. These conductor polymers have been extensively studied, discovering that charge transfer oxidative doping of polyacetylene could increase its conductivity by an order of 12 magnitudes.

There have been other groups who have envisioned a new class of polymers since Shirakawa’s work. This new class would have either a zero energy band gap (a single continuous band consisting of valence and conduction bands) or a small band gap. Polymers that possess a single, continuous band of overlapping valence and conduction bands should conduct as well as metals without the need for doping polymers that have overlapping bands display high electrical conductivity. Polyacetylene will only be conductive if it is oxidized with chlorine, bromine, or iodine vapor. Polyacetylene, by itself, is not conductive \((10^{-15} - 10^{-14} \text{ S} \cdot \text{m}^{-1})\) with a band gap of \(1.50 - 1.7\text{eV}\). Upon
doping, polyacetylene possesses a conductivity of $105 \, \text{S} \cdot \text{m}^{-1}$. For comparison, silver and copper have a conductivity of $108 \, \text{S} \cdot \text{m}^{-1}$.\(^7\)

Even though polyacetylene shows promise as an organic conductor, it is highly air-sensitive and oxidizes when exposed to molecular oxygen, therefore making this an unattractive use for commercial products. Attention has been focused on heterocyclic aromatic polymers such as polythiophene and polypyrrole, in efforts to produce conductive polymers that are air-stable, tractable, and have a low band gap (Figure 1.5). The lone pair electrons of the sulfur and nitrogen atoms tend to stabilize the positive charges of the p-doped polymers through resonance.\(^9\)

One can envision the field of conductive organic polymers to have grown from simple polythiophene to alkyl-substituted thiophenes to fused 5,6-membered thiophene derivatives. Our work focuses on a rarely investigated approach to the construction of diazine (Figure 1.6a) derivatives; in particular aryl-substituted 5,6-fused ring pyridazines and their metal complexes (Figure 1.6b). These novel heterocycles are structurally important components of several biologically active compounds and have been explored as $\alpha$-helix mimetics. Pyridazines have also been found to be efficient water oxidation catalysts when compared to dinuclear ruthenium complexes and have shown high efficiencies in catalytic water oxidation having turnover numbers of up to 700. Additionally, pyridazines have been incorporated into iptycene frameworks, compounds researched for polymer sensors, gas absorption storage, and host-guest chemistry. Furthermore, they continue to serve as useful intermediates in the synthesis of several other classes of heterocycles. For example, Boger and coworkers reported pyrrole
synthesis when treating pyridazines to a solution of activated zinc in acetic acid. Our current interests focus upon the potential role of pyridazines in next generation electronic devices which utilize organics as the semiconducting polymer material (Figure 1.6c).
Figure 1.5.  A) Polythiophene derivatives.⁶ B) Polypyrrole⁸ and a derivative.
Figure 1.6. Structure of A. pyridazine (1,2-diazine), B. a 5,6-fused ring pyridazines complex, and C. an organometallic polypyridazine.
II. Experimental

Reactions were carried out by using standard organic synthetic techniques under air unless otherwise noted. CDCl$_3$ (Cambridge Isotopes) was used without further purification. 1,2-C$_5$H$_3$(COHPh)(COPh) (1a), 1,2-C$_5$H$_3$(COC$_4$H$_5$S)(COHC$_4$H$_5$S) (1b), and 1,2-C$_5$H$_3$(COC$_8$H$_5$S)(COHC$_8$H$_5$S) (1c) were prepared according to modified literature methods. Butyllithium, benzoylchloride, thienoyl chloride, benzo[b]thienyl chloride, and hydrazine hydrate (Aldrich) were used without further purification. Thallium ethoxide (I) and rhenium pentacarboynl bromide were used without further purification. Benzene was dried over sodium benzophenone ketyl.

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

Synthesis of 1,2-C$_5$H$_3$(CPhOH)(COPh) (1a). Preparation of 1,2-C$_5$H$_3$(CPhOH)(COPh) (1a) has been previously synthesized by Linn and Sharkey. The procedure has been slightly altered. Freshly cracked cyclopentadiene (5.04 g, 628 mL, 77.5 mmol) was added dropwise to a cooled solution (0°C) of butyllithium (32.0 mL of 2.50 M, 80.0 mmol) in dry ethyl ether (75 mL). A white precipitate of cyclopentadienyllithium was formed. The solution was stirred for 15 minutes and benzoyl chloride (7.05 g, 5.82 mL, 50.0 mmol) was added dropwise. A bright yellow color formed immediately. Solution stirred for 45 minutes at room temperature. The
reaction was then hydrolyzed with 3% acetic acid (20 mL). The ether layer was separated, and the aqueous layer was extracted twice more with ethyl ether (3 x 50 mL). The combined ether extracts were dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure leaving an orange product. Recrystallization from methanol yielded an orange solid (3.19 g, 0.0110 mol, 45.4%). M.P. = 94-96°C. $^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 6.50 (t, 1H, $^3J = 4.0$ Hz, CHCHCH), 7.28 (d, 2H, $^3J = 4.0$ Hz, CHCHCH), 7.50-7.81 (m, 10H, Ph), 18.52 (s, 1H, OH). $^{13}$C NMR (500 MHz, CDCl$_3$, ppm) δ 123.1 (CHCHCH), 124.5 (CCO), 137.7 (CHCHCH), 128.3, 129.8, 131.5, 137.8, 141.8 (Ph), 185.5 (CO). IR (KBr, cm$^{-1}$) 1538, 1403 (CO). Lit. $^10$ M.P. = 102-103°C. $^1$H NMR (200 MHz, CCl$_4$, ppm) δ 6.35 (t, 1H, CHCHCH), 7.15 (d, 2H, CHCHCH), 7.25-7.9 (m, 10H, Ph), 18.45 (s, 1H, OH). Lit$^10$ (KBr, cm$^{-1}$) 1537.9, 1401.

Synthesis of 1,2-C$_5$H$_3$(CC$_6$H$_5$NH)(CC$_6$H$_5$N) (2a). 1,2-C$_5$H$_3$(CPhOH)(COPh) (1a, 1.06 g, 3.87 mmol) was dissolved in 50 mL of methanol in a 200 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 48 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$_4$), and filtered. The volatiles were removed in vacuo and the crude product was triturated with cold hexane to give 1,2-C$_5$H$_3$(CPhNH)(CPhN) (2a, 0.753 g, 2.79 mmol, 71.7%) as a green powder. Mp: 218-222 °C. $^1$H NMR (500 MHz, CDCl$_3$, ppm): δ 7.08 (d, 1H, $^3J = 4.0$ Hz, CHCHCH), 7.48-7.49, 7.51-7.52 (m, 1H, Ph), 7.51 (d, 1H, $^3J = 4.0$ Hz, CHCHCH), 7.93 (d, 1H, $^3J = 8.1$ Hz, Ph), 11.1 (br s, 1H, NH). $^{13}$C NMR (125 MHz,
CDCl₃, ppm): δ 108.9 (CHCHCH), 120.5 (CHCHCH), 128.7, 129.0, 130.0 (Ph) 147.0
(CHCHCN). IR (KBr, cm⁻¹): 1543 (CN), 3001 (C-H), 3059 (N-H). Anal. Calcd. for
C₁₉H₁₂N₂Cl₂: C, 67.27; H, 3.57. Found: C, 67.56; H, 3.56.

Synthesis of 1,2-C₅H₃(CC₄H₅SNH)(CC₄H₅SN) (2b). 1,2-
C₅H₃(COC₄H₅S)(COHC₄H₅S) (1b, 164 mg, 0.573 mmol) was dissolved in 50 mL of
methanol in a 200 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 48 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 (MgSO₄), and filtered. The volatiles were removed in vacuo and the
 crude product was triturated with cold hexane to give 1,2-C₅H₃(CC₄H₅SNH)(CC₄H₅SN)
(2b, 124 mg, 0.439 mmol, 76.5%) as a red powder. Mp: 131-134 °C. ¹H NMR (500
MHz, CDCl₃, ppm): δ 7.21 (t, 1H, ³J = 4.0 Hz, CHCHCH), 7.29 (d, 1H, ³J₇₅ = 4.55 Hz,
CHCHCHS), 7.54 (d, 1H, ³J₈₇ = 4.55 Hz, CHCHCHS), 7.68 (dd, 1H, ³J₉₈ = 4.55 Hz,
³J₉₈ = 8.0 Hz CHCHCHS), 7.84 (br s, 1H, CHCHCH), 11.2 (br s, 1H, NH). ¹³C NMR
(125 MHz, CDCl₃, ppm): δ 109.5 (CHCHCH), 119.8 (CHCHCH), 123.2 (NCCCH),
127.9, 128.1, 128.6, 132.7, 133.1, 134.0 (Ar) 139.4 (CHCHCN). IR (KBr, cm⁻¹): 1592
(CN), 3064, 3095 (C-H), 3171 (N-H).

Synthesis of 1,2-C₅H₃(CC₈H₅SNH)(CC₈H₅SN) (2c). 1,2-
C₅H₃(COC₈H₅S)(COHC₈H₅S) (1c, 257 mg, 0.665 mmol) was dissolved in 50 mL of
methanol in a 200 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 48 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\textsubscript{4}), and filtered. The volatiles were removed in vacuo and the crude product was triturated with cold hexane to give 1,2-C\textsubscript{5}H\textsubscript{3}(CC\textsubscript{8}H\textsubscript{5}SNH)(CC\textsubscript{8}H\textsubscript{5}SN) (2c, 60.0 mg, 0.157 mmol, 26.4%) a purple powder. \textbf{Mp:} 168-172 °C. \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 6.66 (dd, 1H, \(\text{J}_{AB} = 3.5\) Hz, \(\text{J}_{AC} = 1.7\) Hz Fr), 7.25 (d, 1H, \(\text{J} = 4\) Hz, CHCHCH), 7.33 (d, 1H, \(\text{J} = 4\) Hz, CHCHCH), 7.53 (t, 1H, \(\text{J} = 4\) Hz, CHCHCH), 7.66 (m, 2H, Ar), 11.2 (br s, 1H, NH). \textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}, ppm): \(\delta\) 108.5 (CHCHCH), 112.4 (CHCHCH), 112.7 (NCCCH), 112.6, 118.0, 133.2 (Ar) 144.3 (CHCHCN). \textbf{IR} (KBr, cm\textsuperscript{-1}): 1578 (CN), 3006 (C-H), 3063 (N-H). Anal. Calcd. for C\textsubscript{25}H\textsubscript{14}N\textsubscript{2}S\textsubscript{2}: C, 72.22; H, 3.69. Found: C, 65.74; H, 4.72.

\textbf{Synthesis of [Tl{1,2-C\textsubscript{5}H\textsubscript{3}(CNPh)}\textsubscript{2}]} (3a). Thallium (I) ethoxide (0.0350 mL, 122 mg, 0.49 mmol) was added to a solution of 1,2-C\textsubscript{5}H\textsubscript{3}(CPhNH)(CNPh) (2a, 132 mg, 0.490 mmol) in THF (30 mL). A greenish gray solid precipitated immediately. The solution was stirred for 3 hours. The precipitate was filtered and washed with 20 mL of cold ethyl ether affording [Tl{1,2-C\textsubscript{5}H\textsubscript{3}(COPh)}\textsubscript{2}] (3a) as a dark green, air-stable powder (121 mg, 0.490 mmol, 100%). \textbf{M.P.} 160-170 °C. \textbf{IR} (KBr, cm\textsuperscript{-1}) 1556 (CN). NMR data could not be obtained due to thallium salt’s insolubility in available NMR solvents.

\textbf{Synthesis of [Re(CO)\textsubscript{3}-1,2-C\textsubscript{5}H\textsubscript{3}(CNPh)}\textsubscript{2}] (4a). Rhenium pentacarbonyl bromide (0.247mmol, 100mg) was added to a solution of [Tl(1,2-C\textsubscript{5}H\textsubscript{3}(CNPh)\textsubscript{2}] (0.247mmol, 0.117mg) in dry benzene (30 mL) and refluxed for 10 hours. The solution was filtered through celite and washed with hexane. The yellow organic solution was
dried (MgSO₄), filtered, and reduced via rotary evaporation to a green solid (4a, 133 mg, 0.247 mmol, 11.4 %). **Mp:** 130-155°C. **¹H NMR** (**200 MHz, CDCl₃, ppm**): δ 5.36 (m, 1H, CHCH), 5.56 (m, 2H, CHCHCH), 7.53-7.56 (m, 6H, Ar), 7.93-8.02 (m, 4H, Ar). **¹³C NMR** (**50 MHz, CDCl₃, ppm**): δ 74.2 (CHCH), 109.2 (CHCHCH), 120.6 (CC), 128.7, 129.2, 130.2, 147.2 (Ar), 157.6 (CN), 221.9 (CO). **IR (KBr, cm⁻¹):** 2023, 1898 (CO)
III. Results and Discussion

Pyridazines 2a-c were synthesized by addition of fulvenes 1a-c to a solution of excess hydrazine hydrate in methanol at room temperature (Scheme 3.1). These reactions were allowed to stir for 24-48 hours. Percent yields ranged from 26-77%. IR spectroscopy confirmed the N-H and C=N stretches ranging from 3059-3171 cm$^{-1}$ and 1543-1592 cm$^{-1}$, respectively. $^1$H NMR spectroscopy confirmed structures 2a-c. Cyclopentadiene (Cp) signals were seen ranging from $\delta$ 7.08-7.54 with coupling constants of $^3J = 4.0-4.55$ Hz. $^{13}$C NMR spectroscopy confirmed Cp carbon signals ranging from $\delta$ 112.4-120.5 (CHCHCH), $\delta$ 108.5-109.5 (CHCHCH), and $\delta$ 139.4-147.0 (CHCHCN) for pyridazines 2a-c.

Thallium salt 3a was synthesized by the addition of thallium ethoxide to pyridazine 2a in dry THF (Scheme 3.1). The percent yield was 100% for the thallium compound 3a. IR spectroscopy confirmed the C=N stretch at 1556 cm$^{-1}$ (CN). $^1$H and $^{13}$C NMR spectroscopy data could not be obtained due to the thallium salt being insoluble in all available NMR solvents.

Rhenium complex 4a was synthesized by the addition of rhenium pentacarbonyl bromide to thallium salt 3a in dry benzene (Scheme 3.1). The solution was allowed to reflux for 10 hours. The percent yield was 11.4%. The percent yield for the off-metal route of 4a was much lower than the on-metal route (Scheme 3.2, 36.0%) as observed by Scott and Snyder.$^{11}$ IR spectroscopy confirmed the ReCO carbonyl stretches at 1898 and 2023 cm$^{-1}$. $^1$H NMR spectroscopy showed the Cp signals at $\delta$ 5.36 (m, 1H, CHCHCH),
and δ 5.56 (m, 2H, CHCHCH) for the rhenium complex 4a. Selected NMR and IR spectra are observed in Figures 3.11-3.12 and Table 3.5.
Scheme 3.1  Off-metal synthetic route to [Re(CO)₃-1,2-C₅H₅(CNPh)₂] (4a).
Scheme 3.2  On-metal synthetic route to $[\text{Re(CO)}_3\text{-1,2-C}_5\text{H}_3(\text{CNR})_2]$ (4a-d).\textsuperscript{11}
### Table 3.1  Selected characterization data of fulvene 1a.

<table>
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<th>R = Ph</th>
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<td><strong>% Yield</strong></td>
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<td><strong>M.P.</strong></td>
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<tr>
<td><strong>IR</strong></td>
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<tr>
<td><strong>¹³C NMR</strong></td>
<td>δ 123.1 (CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>δ 124.5 (CCO)</td>
</tr>
<tr>
<td></td>
<td>δ 137.7 (Ph)</td>
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<tr>
<td></td>
<td>δ 185.5 (CO)</td>
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<tr>
<td><strong>¹H NMR</strong></td>
<td>δ 6.50 (t, 1H, ³J = 4.0Hz, CHCHCH)</td>
</tr>
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<td></td>
<td>δ 7.28 (d, 2H, ³J = 4.0Hz, CHCHCH)</td>
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<tr>
<td></td>
<td>δ 7.50-7.81 (m, 10H, Ph)</td>
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<tr>
<td></td>
<td>δ 18.52 (s, 1H, OH)</td>
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</table>
Figure 3.1. $^1$H NMR spectrum of fulvene 1a.
Figure 3.2. $^{13}$C NMR spectrum of fulvene 1a.
Table 3.2. Selected characterization data of pyridazine 2a.

<table>
<thead>
<tr>
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<th>2a</th>
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<td>% Yield</td>
<td>71.7%</td>
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<tr>
<td>M.P.</td>
<td>218-222°C</td>
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<tr>
<td>IR</td>
<td>1543 (CN), 3001 (C-H), 3059 (N-H) cm⁻¹</td>
</tr>
<tr>
<td>^{13}C NMR</td>
<td>δ 108.9 (CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>δ 120.5 (CHCHCH)</td>
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<tr>
<td></td>
<td>δ 130.0 (Ph)</td>
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<tr>
<td></td>
<td>δ 147.0 (CHCHCN)</td>
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<td>^{1}H NMR</td>
<td>δ 7.08 (d, 1H, ^{3}J = 4.0Hz, CHCHCH)</td>
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<td>δ 7.51 (t, 1H, ^{3}J = 4.0Hz, CHCHCH)</td>
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<td>δ 7.51-7.52 (m, 1H, Ph)</td>
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<td></td>
<td>δ 7.93 (d, 1H, ^{3}J = 8.1Hz, Ph)</td>
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<tr>
<td></td>
<td>δ 11.1 (br s, 1H, NH)</td>
</tr>
</tbody>
</table>
Figure 3.3. $^{13}$C NMR spectrum of pyridazine 2a.
Figure 3.4. $^1$H NMR of pyridazine 2a.
Table 3.3.  Selected characterization of pyridazines 2b and 2c.

<table>
<thead>
<tr>
<th></th>
<th>2b  R = Tp</th>
<th>2c  R = BzTp</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Yield</td>
<td>76.5%</td>
<td>26.4%</td>
</tr>
<tr>
<td>M.P.</td>
<td>131-134°C</td>
<td>168-172°C</td>
</tr>
<tr>
<td>IR</td>
<td>1592 (CN), 3064,3095 (C-H), 3171 (N-H) cm⁻¹</td>
<td>1511 (CN), 3006 (C-H), 3063 (N-H) cm⁻¹</td>
</tr>
<tr>
<td>¹³C NMR</td>
<td>δ 109.5 (CHCHCH)</td>
<td>δ 108.5 (CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>δ 119.8 (CHCHCH)</td>
<td>δ 112.4 (CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>δ 123.2 (NCCCH)</td>
<td>δ 112.7 (NCCCH)</td>
</tr>
<tr>
<td></td>
<td>δ 139.4 (CHCHCN)</td>
<td>δ 144.3 (CHCHCN)</td>
</tr>
<tr>
<td>¹H NMR</td>
<td>δ 7.21 (t, 1H, ³J = 4.0 Hz, CHCHCH)</td>
<td>δ 7.25 (d, 1H, ³J = 4 Hz, CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>δ 7.29 (d, 1H, ³J_BC = 4.55 Hz, CHCHCHS)</td>
<td>δ 7.33 (d, 1H, ³J = 4 Hz, CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>δ 7.54 (d, 1H, ³J_AB = 4.55 Hz, CHCHCHS)</td>
<td>δ 7.53 (t, 1H, ³J = 4 Hz, CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>δ 7.68 (dd, 1H, ³J_AB = 8.55 Hz, ³J_AC = 8.0 Hz, CHCHCHS)</td>
<td>δ 7.66 (m, 2H, Fr)</td>
</tr>
<tr>
<td></td>
<td>δ 7.84(br s, 1H, CCHCN)</td>
<td>δ 11.2(br s, 1H, NH)</td>
</tr>
<tr>
<td></td>
<td>δ 11.2(br s, 1H, NH)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.5. IR spectrum of pyridazine 2b.
**Figure 3.6.** $^1$H NMR of pyridazine 2b.
Figure 3.7. $^{13}$C NMR spectrum of pyridazine 2b.
Figure 3.8. IR spectrum of pyridazine 2c.
Table 3.4. Selected characterization table for thallium salt 3a.

<table>
<thead>
<tr>
<th></th>
<th>R = Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Yield</td>
<td>100%</td>
</tr>
<tr>
<td>M.P.</td>
<td>160-170°C (dec)</td>
</tr>
<tr>
<td>IR</td>
<td>1556 (CN) cm⁻¹</td>
</tr>
</tbody>
</table>
Table 3.5. Selected characterization data of rhenium complex 4a.

<table>
<thead>
<tr>
<th></th>
<th>R = Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Yield</td>
<td>11.4%</td>
</tr>
<tr>
<td>M.P.</td>
<td>130-150°C</td>
</tr>
<tr>
<td>IR</td>
<td>(ReCO) 2023, 1894 cm⁻¹</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>$\delta$ 1.19-1.28 (m, 1H, CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ 3.45-3.50 (m, 2H, CHCHCH)</td>
</tr>
<tr>
<td></td>
<td>$\delta$ 7.53-7.58 (m, 6H, Ph)</td>
</tr>
</tbody>
</table>
Figure 3.9. IR spectroscopy of rhenium complex 4a.
Figure 3.10. $^1$H NMR spectra of rhenium complex 4a
IV. Conclusions

A series of organic and organometallic reactions lead to the synthesis of pyridazyl rhenium complex \( \text{[Re(CO)}_3 \{\eta^5-1,2-\text{C}_5\text{H}_3(\text{CNPh})(\text{CNPh})\}\] ) \( \text{(4a)} \). The percent yield for fulvene \( \text{1a} \) was 63.4%. The pyridazine compound \( \text{2a} \) was 71.7%. Pyridazines \( \text{2b} \) and \( \text{2c} \) had a percent yield of 76.5 and 26.4, respectively. For the thallium complex \( \text{3} \) the percent yield was 69.1%. The rhenium complex \( \text{4a} \) had an 11.4% yield.

\(^1\text{H NMR confirmed the presence of the cyclopentadiene and its substituents on compounds 1a, 2a, 2b, 2c and 4a.} \) \(^{13}\text{C NMR confirmed the presence of the dicarbonyls and the rhenium tricarbonyls for compounds 1a, 2a, and 4a.} \)

IR spectroscopy confirmed the presence of the dicarbonyls ranging from 1403-1652 cm\(^{-1}\) for compounds \( \text{1-4} \). IR Spectroscopy also confirmed the presence of the rhenium tricarbonyls by having wavenumbers ranging from 1898-1930 cm\(^{-1}\) for compound \( \text{4a} \).
REFERENCES


VITA

The author was born in White Plains, Kentucky on December 21, 1983. He earned his Bachelor of Science degree from Brescia University in the spring of 2008. In the fall of 2008 he began his graduate school at Western Kentucky University where he will earn his Master of Science degree in Chemistry working under Dr. Chad A. Snyder. He is expected to defend his thesis on November 20, 2009.