

Synthesis and Characterization of Some Disubstituted Cyclopentadienyl Rhenium Complexes as
Potential Candidates in Semiconductive Materials

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Acceptance of Senior Honors Thesis

This Senior Honors Thesis is accepted in partial fulfillment of the requirements for graduation from the Honors Program of Liberty University.

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Abstract

Since 2000, when the Nobel Prize in Chemistry was awarded for conductive polymer research, few studies have been performed concerning the conductive capabilities of discrete organometallic compounds. For this project, organometallic compounds were formed specifically with a transition metal included in the structure. Through oxidation and reduction reactions, the variation in the electrical conductivity could allow for an analysis of whether this unique structure would allow for tunability. The goal of this research was to begin with aromatic substituted fulvenes and perform various multistep synthesis processes, utilizing thallium salt intermediates, to produce several disubstituted cyclopentadienyl rhenium complexes. In this project, different rhenium complexes were synthesized accurately and with high yield utilizing methods that were straightforward and generated replicable results. Through melting range analysis, IR spectroscopy, ^{13}C NMR, and ^1H -NMR, the identity and purity of these compounds were confirmed.

**Synthesis and Characterization of some Disubstituted Cyclopentadienyl Rhenium
Complexes as Potential Candidates in Semiconductive Materials**

Modern Advances in Conductive Polymerization

It is common knowledge to many that metals are excellent conductors. Although this characteristic is seemingly simple, the development of modern society has largely been enabled by this principle of metals. Electrical wiring, microprocessors, and even automobile engines rely on the application of a metals' conductivity to function. In the present age, metals are not the exclusive conductive chemical. In 2000, Dr. Hideki Shirakawa, Dr. Alan J. Heeger, and Dr. Alan J. MacDiarmid won the Nobel Prize in Chemistry for the discovery of the first conductive polymer (Moore, 2001). Historically, polymers have been the fundamental components of industrial products such as plastics, rubbers, adhesives, and even synthetic fibers for applications such as commonly used polyesters to even degradable sutures for medical procedures (Feldman, 2008). However, the crystalline form of polyacetylene film introduced a new application for polymers as the molecule, when oxidized through treatment with iodine, was determined to have conductive capabilities with a newly enabled charge transfer in the structure (Royal Swedish Academy of Sciences, 2000). From this initial discovery, the synthesis of polymers to investigate the behavior of these molecules as conductors and semiconductors became a popular focus of research. Through extensive research, a sophisticated class of intrinsically conductive polymers (ICPs) was created including molecules such as polyacetylene and polyaniline (Nambiar & Yeow, 2010). The research performed on ICPs expanded the application of polymers with these conductive capabilities now understood sufficiently to be applied in biosensors and bioelectronics. Despite the quick advancement research since the 2000 Nobel Prize in Chemistry sparked studies in this conductive polymers, very little research has been performed on the

potential conductive capabilities of discrete organometallic compounds. Therefore, the research presented in this paper focuses on this topic.

Discrete Organometallic Compounds with Transition Metal Constituents

Organometallic Chemistry: An Introduction

Organometallic chemistry looks to address how organic molecules interact with inorganic elements from the periodic table (Crabtree, 2014). Within this study, transition metals have a prominent role and their unique characteristics become accessible to organic based compounds. Unlike many elements commonly used in organic chemistry, transition metals enable additional interactions to be enabled through the presence of electrons found in their *d* and *f* orbitals (King, 1969). The presence of a metal within the compound causes electronic delocalization that effects the distance between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the molecule. This allows for electrons to be transferred more easily upon excitation or absorption of light. By using a metal moiety within the structure to increase conductivity, interesting electronic and redox properties are possible.

Mechanism of Conductivity for Organometallic Compounds

For organometallic complexes, semiconductive capabilities are correlated with the oxidative and reductive changes to the metal complex. There are two fundamental transitions strong charge-transfer absorption where “electrons are excited from ligands to the central metal atom” and crystal-field transitions where “the excited electrons remain on the metal ion” (Van der Put, 1998, p. 88). Common to both organic and inorganic chemistry, the excitation of electrons is often prompted by the absorption of light, specifically the discrete, quantized energy comes with the light’s frequency. Regardless of the source of the energy, when the electron is excited to the central metal atom, the ligand is oxidized while the metal ion is reduced by the

photoelectric nature of the transition (Van der Put, 1998). The opposite state is also possible if the electron transitions from the metal ion to the ligand. This fluidity in charge transfer that comes with an electron excitation enables conductive chemistry and molecular electronics (Van der Put, 1998).

The incorporation of a metal moiety into the structure of a particular compound is a novel approach as the addition of the transition metal center enables tunability of the electronic properties of the compound (Snyder, 2013). This can be accomplished through manipulating the fundamental redox principles of the metal component within the material. Through introducing transition metals as the attachment in compounds, variability in the tunability is maximized as transition metals have multiple transition states associated with them. For this specific study, rhenium was determined to be the metal of interest as, being a Group VII metal, is stable through many varying oxidation states (Snyder, 2013).

Applications of Semiconductive Organometallic Complexes

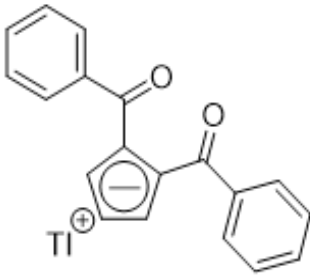
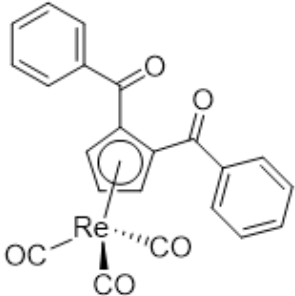
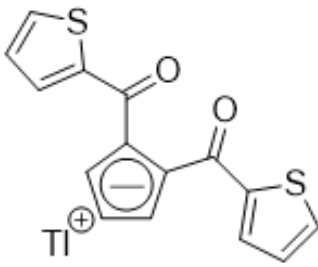
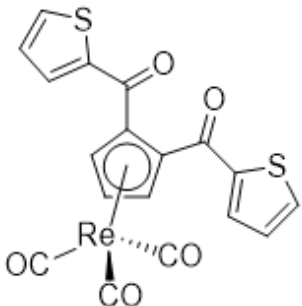
Semiconductors are an essential component of the modern development of electronics. With applications in integrated circuits, transistors, microchips, and even films for lighting electronic displays, semiconductive materials are required frequently in the technology of the modern age (*Britannica*, 2022). Through having characteristic behavior between that of conductors and insulators, semiconductors allow for flexibility in the functionality of a device. Through synthesizing a diacyl heterocyclic complex with a transition metallic constituent, tunability of its semiconductive capabilities is hypothesized to exist. Based upon the stability of rhenium, an organometallic complex with this metal as the moiety is hypothesized to allow for tunability of the semiconductive capability through the manipulation of oxidative states. Through allowing the conductivity of a complex to be adjusted, the material could be optimized in serving

different functions within an electrical function. To this point, control over conductivity in a material has yet to be accomplished. Although the electrochemical applications of these compounds would require an additional study performed within chemical engineering, the development of a small catalogue of possible complexes will enable this future work.

Summary of Organometallic Synthetic Targets

With the intention of building a small library of organometallic complexes with possible semiconductive capabilities, two diacyl rhenium complexes were synthesized with similar sigma bond connections within their structures differing only in their substituent groups. In order to effectively accomplish the synthesis, a thallium intermediate salt was synthesized from the original fulvene to allow for a successful transmetalation reaction yielding the desired rhenium complex. Thallium cyclopentadienide (Cp) salts are stable, relatively safe, and allow for a full negative charge on the fulvene to be enabled through aromaticity. This is accomplished with cation that holds an oxidation state of +1 being coordinated with a five-membered aromatic anion through strong electrostatic attraction. Thallium is an extremely toxic metal and could be replaced in this synthesis with potassium or sodium. However, despite both alternatives being safer starting materials, the sodium or potassium cyclopentadienyl salts (Cp salts) are extremely pyrophoric and unstable to air and moisture (Akhbari & Morsali, 2010). When forming a Cp salt with thallium, a product, stable to both air and moisture, is made due to the existence of *d* orbitals and the element having a larger ionic radius than either sodium or potassium. From the intermediate thallium Cp salts, the final diacyl rhenium complex can be obtained through a transmetalation reaction. The structures of the intermediate thallium salts and the final rhenium complexes for both the benzoyl and thienoyl case are shown in Table 1.

Table 1*Structures of target synthetic compounds*

Thallium 1,2-dibenzoylcyclopentadienide salt (1A)	1,2-Dibenzoyl rhenium complex (1B)
	
Thallium 1,2-dithienoylcyclopentadienide salt (2A)	1,2-Dithienoyl rhenium complex (2B)
	

Experimental Design

For the experiments conducted, the reagents and solvents outlined in this paper were used without additional purification beyond the commercially listed standards. The initial starting 1,2-diacylcyclopentadiene (fulvene derivative) compounds were synthesized at the University of Findlay by Dr. Nathan Tice, an Associate Professor of Chemistry and Chair of the Physical Sciences Department. The fulvenes provided with the benzoyl and thienoyl substituent groups were utilized for the synthetic efforts at Liberty University. These compounds acted as the starting materials for the syntheses completed as an effort to develop a collection of organometallic compounds with varying substituent groups capable of transmetalation reactions

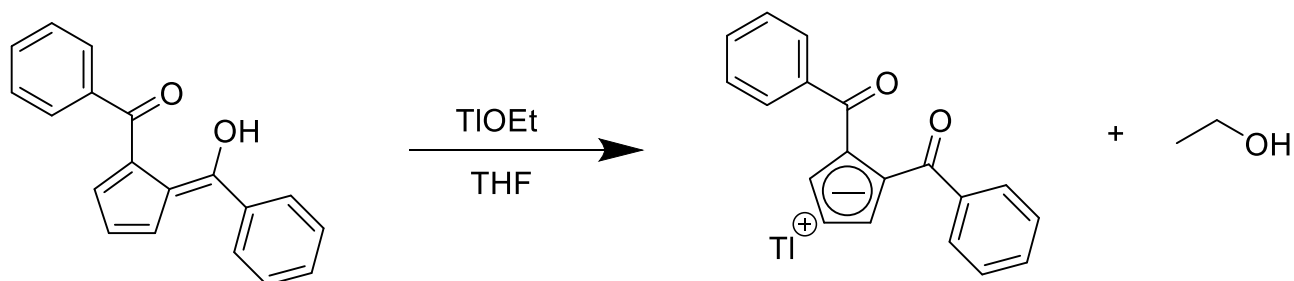
to ultimately discover a link between the oxidative and reductive capabilities in transition metal substituents for semiconductive tunability.

Synthesis of $[Tl\{1,2-C_5H_3(CO-C_6H_5)_2\}]$ (**1A**)

To a 100-mL round bottom flask was added 1,2- $C_5H_3(CO-C_6H_5)(COH-C_6H_5)$ (**1A**) (0.303 grams, 1.10 mmol), followed by the addition of 15-mL dry THF. The solution was allowed to stir for 1-4 minutes until all the fulvene dissolved. Next, thallium ethoxide (0.09 mL, 1.10 mmol) was slowly added via needle and syringe to the solution. The solution was stirred for 3 hours at 21°C. A mustard yellow precipitate formed immediately up TIOEt addition. The precipitate was filtered and dried to yield solid, yellow product $[Tl\{1,2-C_5H_3(CO-C_6H_5)_2\}]$ (**1A**) (0.514 g, 1.08 mmol, 97.4%). The synthetic route for this reaction was outlined in Figure 1.

Figure 1

*Synthetic route to develop $[Tl\{1,2-C_5H_3(CO-C_6H_5)_2\}]$ (**1A**).*



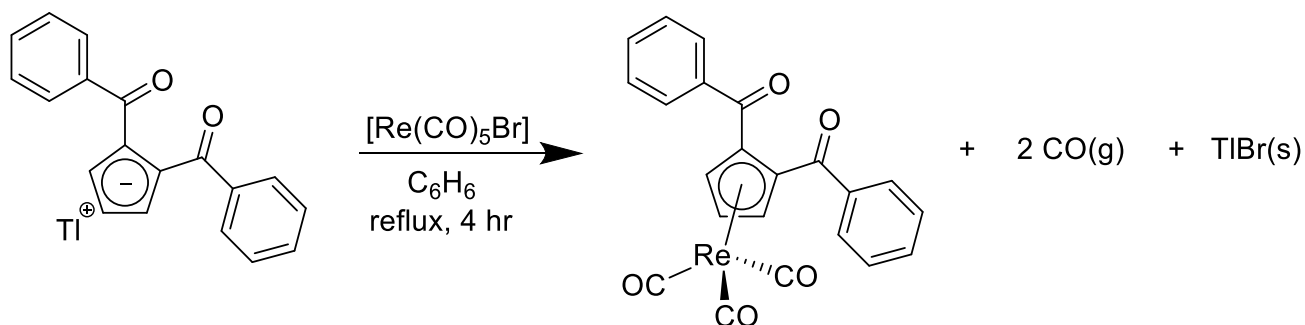
Synthesis of $[Re(CO)_3\{1,2-C_5H_3(CO-C_6H_5)_2\}]$ (**1B**)

To a refluxing solution of $[Tl\{1,2-C_5H_3(CO-C_6H_5)_2\}]$ (**1A**) (0.514 g, 1.08 mmol) in dry benzene (20 mL, 2.56 mmol) was added $[Re(CO)_5Br]$ (0.497 g, 1.22 mmol). The solution was refluxed for 6 hours. Through the reflux, the solution gradually changed from an initial bright, yellow to a final red. The solution was allowed to cool and then filtered using Celite. The solvent was removed in vacuo to yield a red semi-solid oil. The semi-solid was triturated with several

aliquots of cold hexane (6 x 5 mL) to yield the product, $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_6\text{H}_5)_2\}]$ (**1B**) (0.360 g, 0.562 mmol, 61.5% yield) as a dark red power. The route of the synthesis is shown in Figure 2.

Figure 2

*Synthetic route to develop $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_6\text{H}_5)_2\}]$ (**1B**).*

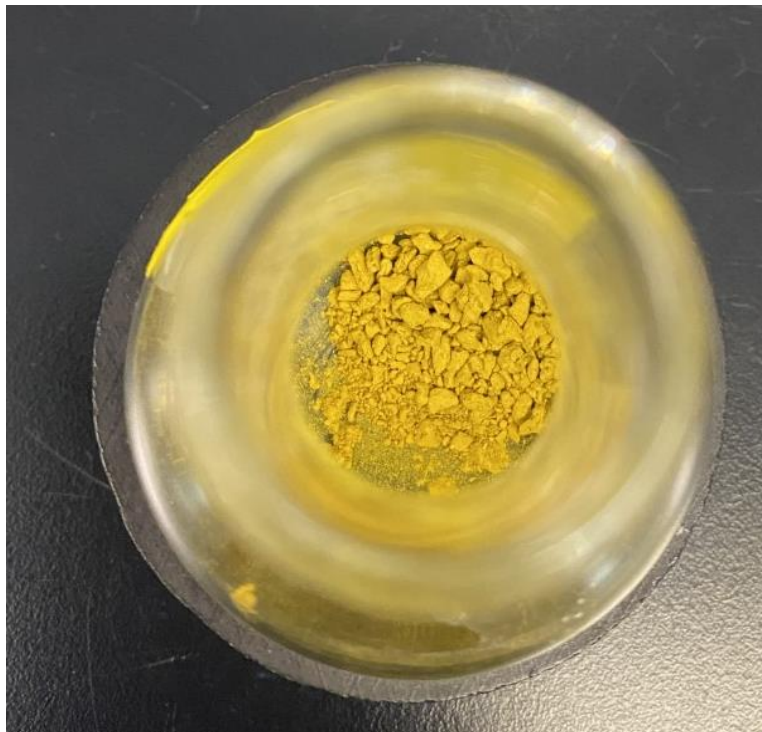


Synthesis of $[\text{Tl}\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (**2A**)

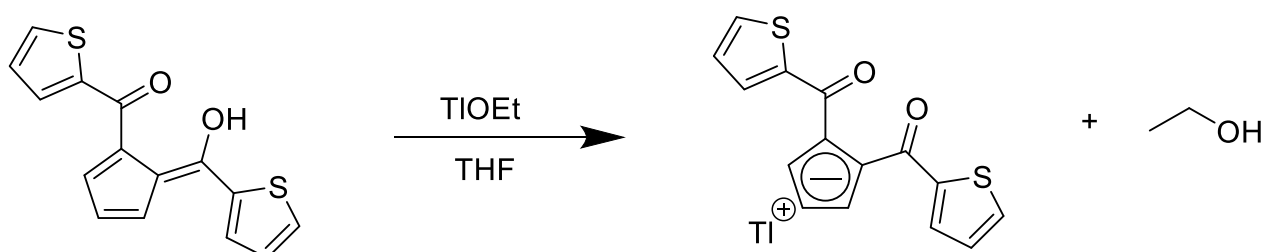
To a 100-mL round bottom flask was added $1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})(\text{COH-C}_4\text{H}_3\text{S})$ (**2A**) (0.330 grams, 1.15 mmol), followed by the addition of 15-mL dry THF. The solution was allowed to stir for 1-4 minutes until all the fulvene dissolved. Next, thallium ethoxide (0.09 mL, 1.10 mmol) was slowly added via needle and syringe to the solution. The solution was stirred for 3 hours at 21°C . A mustard yellow precipitate formed immediately upon TlOEt addition. The precipitate was filtered and dried to yield solid, yellow product $[\text{Tl}\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (**2A**) (0.603 g, 1.24 mmol, 108%). The final product was displayed in Figure 3 and the synthetic route for this reaction was outlined in Figure 4.

Figure 3

Image of final $[Ti-1,2-C_5H_3(CO-C_4H_3S)_2]$ (**2A**).

**Figure 4**

Synthetic route to develop $[Ti-1,2-C_5H_3(CO-C_4H_3S)_2]$ (**2A**).



Synthesis of $[Re(CO)_3\{1,2-C_5H_3(CO-C_4H_3S)_2\}]$ (**2B**)

To a refluxing solution of $[Ti\{1,2-C_5H_3(CO-C_4H_3S)_2\}]$ (**2A**) ((0.603 g, 1.24 mmol) in dry benzene (20 mL, 2.56 mmol) was added $[Re(CO)_5Br]$ (0.550 g, 1.35 mmol). The solution was refluxed for 4 hours. Through the reflux, the solution gradually changed from an initial bright,

yellow to a final dark red color. The solution was allowed to cool and then filtered using Celite. The solvent was removed in vacuo to yield a red semi-solid oil. The semi-solid was triturated with several aliquots of cold pentane (6 x 5 mL) to yield the product, $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (**2B**) (0.264 g, 0.480 mmol, 38.2% yield) as a orange-red power. The synthetic product was shown in Figure 5 and the route of the reaction was highlighted in Figure 6.

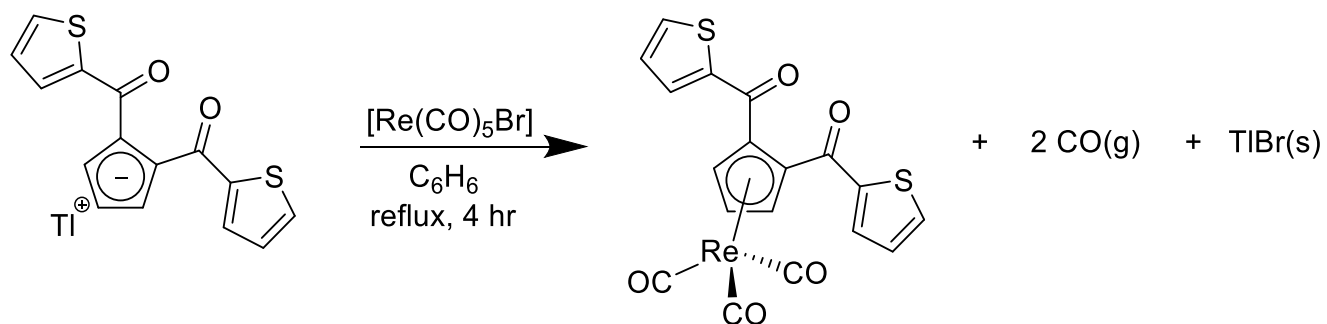
Figure 5

*Image of final $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (**2B**).*



Figure 6

*Synthetic route to develop $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (**2B**).*



Results and Discussion of Characterization

Characterization of [Tl{1,2-C₅H₃(CO-C₆H₅)₂}] (1A)

The identity of the synthesized intermediate thallium dibenzoyl salt (**1A**) was confirmed through melting point and IR spectroscopy. These values matched the previously published data for **2A**, so no further characterization was required. The percent yield was determined to be 97.4% for **1A**.

Characterization of [Re(CO)₃{1,2-C₅H₃(CO-C₆H₅)₂}] (1B)

Mass and Melting Point Analysis of [Re(CO)₃{1,2-C₅H₃(CO-C₆H₅)₂}] (1B)

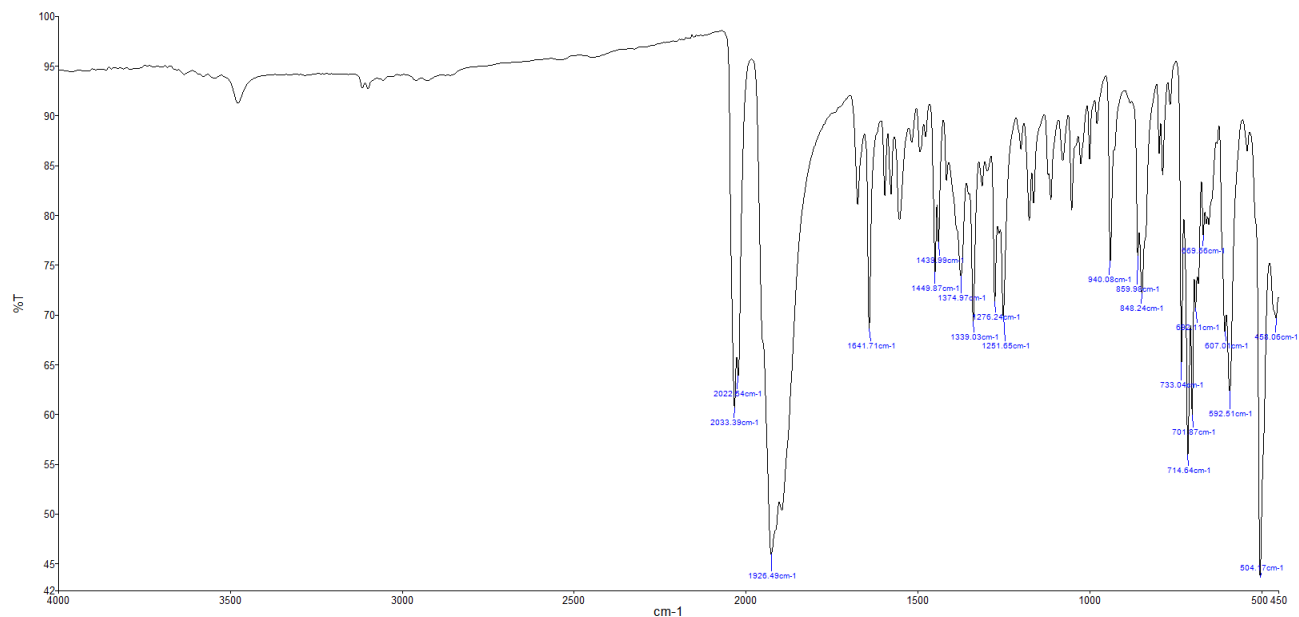
A percent yield of 61.5% was calculated for the synthesis of **1B**. This yield was appropriate for the first synthetic attempt and could be optimized for future studies. Complex **1B** was further characterized by its melting point. Using a digital melting point apparatus, the melting range was observed to be 115.4–120.8°C.

Infrared Spectroscopy Analysis of [Re(CO)₃{1,2-C₅H₃(CO-C₆H₅)₂}] (1B)

Infrared (IR) spectroscopy for **1B** was performed to determine whether the desired structure was present. From the IR spectrum shown in Figure 7, the strong peaks present at 2033 cm⁻¹ and 1926 cm⁻¹ were indicators of the bonds between the rhenium and bonded carbonyl groups. Additionally, these two stretches match the number of expected carbonyl stretches due to its C_{2v} point group. With the presence of the metal carbon bond, the signals corresponding to the carbon double bond at 1660 cm⁻¹ and the double bonded carbon to oxygen at 1641 cm⁻¹ were weaker than expected. The final bonds highlighted on the spectrum were the hybridized carbons at 2950 cm⁻¹ and 3100 cm⁻¹. From the infrared data, it was concluded that the correct complex had been synthesized.

Figure 7

*IR spectrum of synthesized $[Re(CO)_3\{1,2-C_5H_3(CO-C_6H_5)_2\}]$ (**1B**).*

**Table 2**

*Accepted frequency values from IR Spectroscopy bonds and the corresponding experimental values from the spectrum of $[Re(CO)_3\{1,2-C_5H_3(CO-C_6H_5)_2\}]$ (**1B**).*

Bond	Literature Frequency (cm⁻¹)	Experimental Frequency (cm⁻¹)
C=O	1715	1641
C=C	1600-1700	1660
C-H <i>sp</i> ²	3000-3100	3100
C-H <i>sp</i> ³	2800-3000	2950
C-Re	2000, 1900	2033, 1926

Characterization of [Tl-1,2-C₅H₃(CO-C₄H₃S)₂] (2A)***Mass and Melting Point Analysis of [Tl-1,2-C₅H₃(CO-C₄H₃S)₂] (2A)***

The synthesized intermediate thallium dithienoyl salt was calculated as having a 108% percent yield. This high yield was likely due to residual solvent being present in the product at the time of weighing or it could have also been indicative of impurities (e.g., unreacted reagents) present in the product. After the compound had dried completely, a melting point analysis was conducted for characterization. A unique characteristic of a thallium salt is that it decomposes at high temperatures as opposed to melting. The decomposition was observed as the original red powder turned to a black solid in the bottom of the capillary tube. The observed range of this was 226.7–228.4°C. Based upon this observation, the supported the assumption that the correct intermediate thallium dithienoyl salt (2A) had been synthesized.

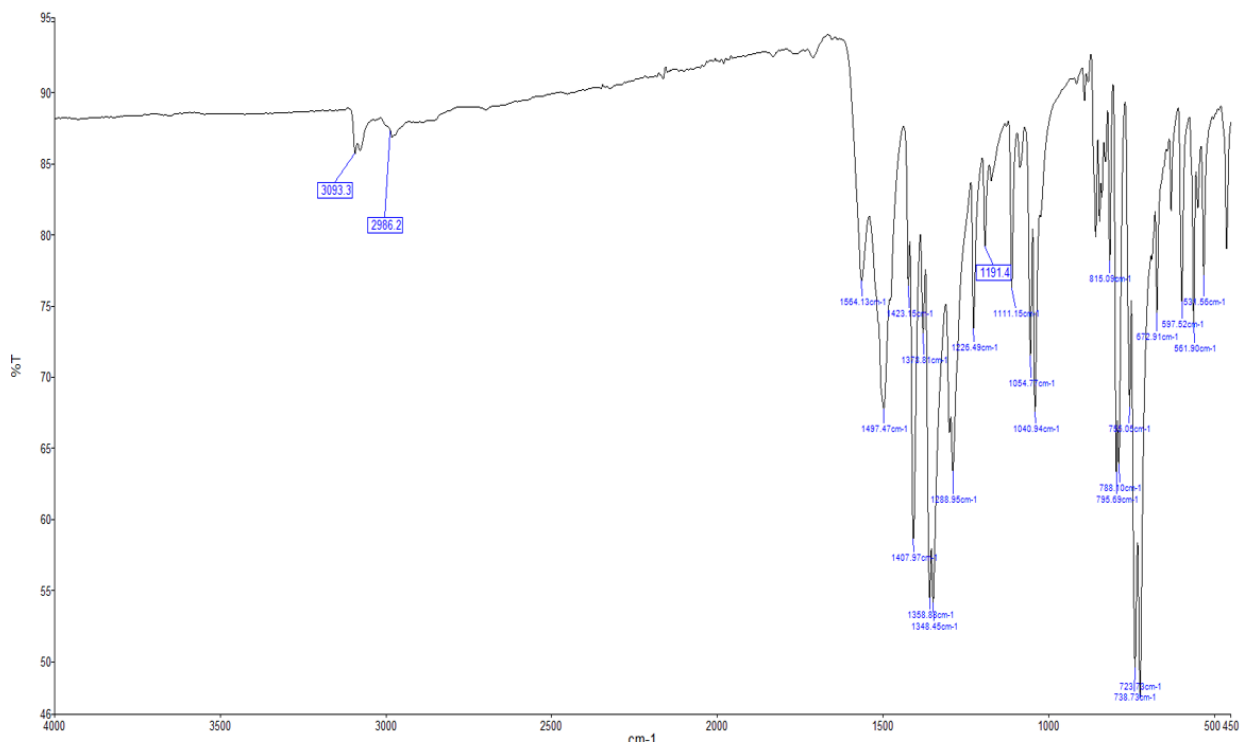
Infrared Spectroscopy Analysis of [Tl-1,2-C₅H₃(CO-C₄H₃S)₂] (2A)

Using an infrared spectrometer, it was concluded that the intended complex had been synthesized. Based upon the spectrum shown in Figure 8, the peaks corresponding to the expected structure were determined. The thienoyl substituent groups were observed at 1191 cm⁻¹ in the spectrum of the final synthetic product. The peak at 1497 cm⁻¹ corresponded to the double bonded carbon to oxygen while the signal at 1554 cm⁻¹ indicated the presence of the carbon double bond. The frequencies of the carbonyl and the carbon-carbon double bond were both lower than what would normally be observed for these bonds in simple organic compounds. This phenomenon may be explained by the presence of the heavy metal within the organometallic complex. Stable complexes have a very low electrical charge. In a complex with a heavy metal, this is enabled through the metal having a partial positive charge while the connected ligands exhibit a partial negative charge (Miessler, 2013). To further stabilize the carbonyl, the ligand

delocalizes the partial negative charge present over the bond between the carbon and oxygen atoms (Miessler,2013). This delocalization would force a shift to lower wavenumbers for the signal of the peak shown. Both the sp^2 and sp^3 hybridized carbons were also observed in the spectrum at 3093 cm^{-1} and 2986 cm^{-1} respectively.

Figure 8

IR spectrum of synthesized $[Tl-1,2-C_5H_3(CO-C_4H_3S)_2]$ (**2A**).

**Table 3**

Accepted frequency values from IR Spectroscopy bonds and the corresponding experimental values from the spectrum of $[Tl-1,2-C_5H_3(CO-C_4H_3S)_2]$ (**2A**).

Bond	Literature Frequency (cm ⁻¹)	Experimental Frequency (cm ⁻¹)
C=O	1462	1497
C=C	1450-1600	1554
C-S	1200	1191
C-H <i>sp</i> ²	3000-3100	3093
C-H <i>sp</i> ³	2800-3000	2986

Characterization of $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (2B)***Mass and Melting Point Analysis of $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (2B)***

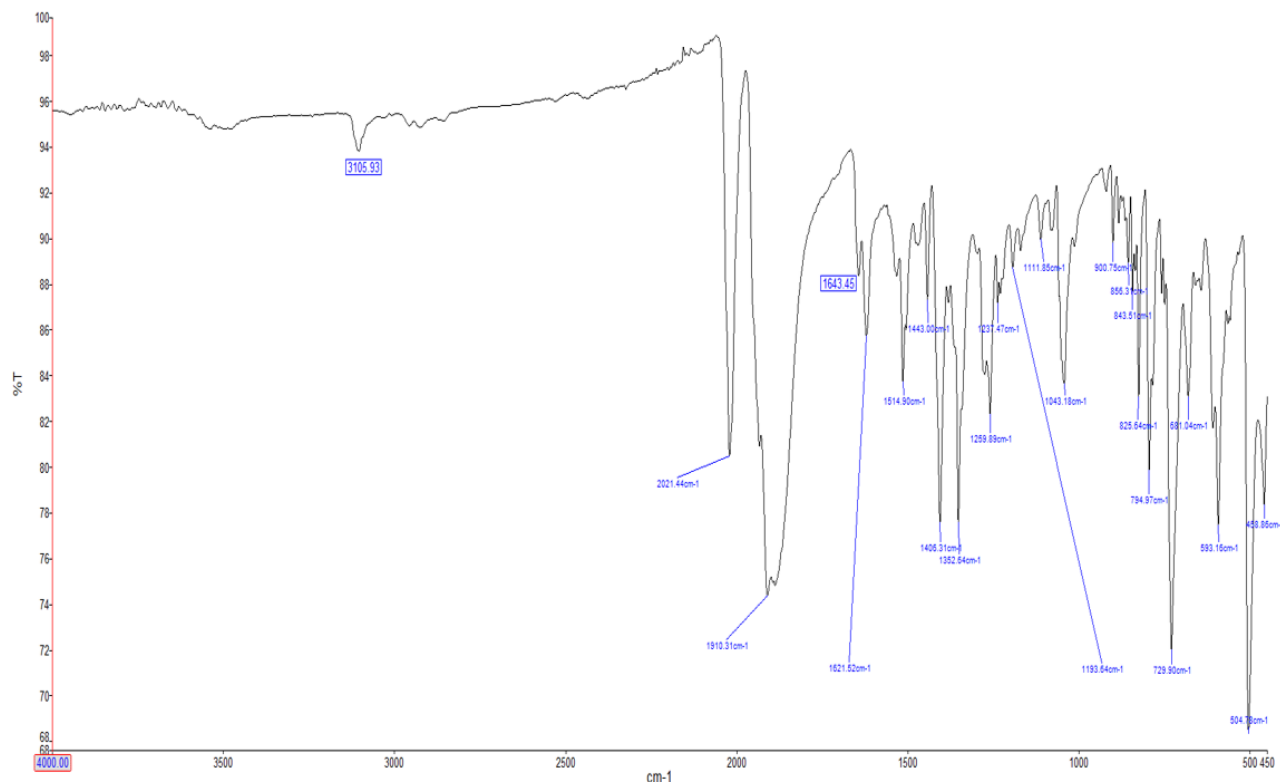
Complex **2B** was calculated to have been generated with a 38.2% percent yield. The low percent yield was attributed to laboratory error as the round bottom flask was inadvertently broken during the trituration. The next method of characterization performed was a melting point analysis of the complex. The experimentally determined melting point range was observed to be 143.2 –170.1°C. The nature of the complex melting was considered supporting evidence of the correct product having been synthesized as the intermediate compound used as a starting material would have decomposed rather than melting.

Infrared Spectroscopy Analysis of $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (2B)

From the IR spectrum shown in Figure 9, the strong peaks present at 1910 cm^{-1} and 2021 cm^{-1} were indicators of the bonds between the rhenium and bonded carbonyl groups. The peak shown at 1643 cm^{-1} corresponded to the carbon double bond and the peak at 1621 cm^{-1} was expected for the double bonded carbon to oxygen within the structure. Both signals were weakened by the metal carbon bond. The sulfur bond present in the thienoyl substituent remained visible in the final product spectrum at 1193 cm^{-1} along with the hybridized carbons at 3105 cm^{-1} . Therefore, from the data presented in the infrared spectrum, it was concluded that the desired complex had been synthesized.

Figure 9

IR spectrum of synthesized $[Re(CO)_3\{1,2-C_5H_3(CO-C_4H_3S)_2\}]$ (**2B**).

**Table 4**

Accepted frequency values from IR Spectroscopy bonds and the corresponding experimental values from the spectrum of $[Re(CO)_3\{1,2-C_5H_3(CO-C_4H_3S)_2\}]$ (**2B**).

Bond	Literature Frequency (cm ⁻¹)	Experimental Frequency (cm ⁻¹)
C=O	1715	1621
C=C	1600-1700	1643
C-S	1200	1193
C-H <i>sp</i> ²	3000-3100	3105
C-H <i>sp</i> ³	2800-3000	2980
C-Re	2000, 1900	2021, 1910

¹H-NMR and ¹³C-NMR Analysis of [Re(CO)₃{1,2-C₅H₃(CO-C₄H₃S)₂}] (2B)

As this project was conducted in collaboration with Dr. Tice, components of the characterization were conducted at the University of Findlay. To summarize the Nuclear Magnetic Resonance spectroscopy data, he stated:

¹H NMR spectroscopy confirms the structure for the diacyl complex **X**, showing both the expected symmetric Cp and thienoyl resonances. The Cp signals are observed shifted up field (5.81 and 6.52 ppm respectively) as compared to the free fulvene ligand, which is typical for the metallated cases. These Cp resonances also display the characteristic triplet and doublet splitting pattern. The thienoyl signals are observed in the expected, aromatic region ranging from 7.23 to 8.00 ppm. To further demonstrate complete conversion to the on-metal product, there is no presence of the enolic signal, observed in the 18-20 ppm range, typical for the fulvene starting material. The ¹³C NMR spectroscopy further confirms the formation of rhenium complex, with both the diacyl (180.02 ppm) and rhenium (192.63 ppm) carbonyl signals present. (Snyder & Tice, 2023)

The data obtained from the analysis was as listed: **¹H NMR (400 MHz, acetone-*d*, ppm):** 5.81 (t, 1H, J₃ = 2.8 Hz, Cp), 6.52 (d, J₃ = 2.8, 2H, Cp), 7.23 (d, 2H, J₃ = 4.0 Hz, Tp), 7.88 (d, 2H, J₃ = 4.0 Hz, Tp), 7.99 (d, 2H, J₃ = 5.2 Hz, Tp). **¹³C NMR (100 MHz, acetone-*d*, ppm):** 82.89, 90.79, 106.19, 129.01, 134.76, 135.78, 142.99, 180.02, 192.63.

X-ray Crystallographic Analysis of [Re(CO)₃{1,2-C₅H₃(CO-C₄H₃S)₂}] (2B)

The structure of [Re{η⁵-1,2-C₅H₃(CO-C₄H₃S)₂}(CO₃)] (2B) was determined by X-ray crystallographic methods and the plot of the molecular structure is shown in Figure 10 and 11.

The crystal for which data was collected was typical of others in the batch, which had been grown by slow evaporation from hexane at room temperature. The crystal was mounted on glass fibers with polyisobutene oil. Data was collected at 90 K on a Bruker 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. Hydrogen atoms were placed in geometrically calculated positions. Crystal data and a summary of experimental details are given in Table 5.

Recrystallization of **2B** affords the diacyl complex as orange block crystals. The diacyl complex **2B** crystallizes in an orthorhombic $Pca2(1)$ group, with four molecules within the unit cell. The Re–C bond lengths are highly uniform for **2B**, with the deviations from the average length of 2.306 (32) Å no more than 0.05 Å difference. X-ray analysis shows the two sets of carbonyls, the organic acyl C=O and the Re–CO, having average bond lengths of 1.214 (14) Å and 1.8924 (67) Å. In the solid state, **2B** thienoyl rings are highly asymmetric with respect to each other. The acyl portions for **2B** involving S1, C4–C7, are not planar with respect to the central Cp ring, with the C1–C2–C3–C4 torsion angles at 34.3(18)°. Likewise, the acyl moieties involving S2A, C12–C14, C34B (**2B**) are twisted out of the plane with the Cp ring, with the C12–C11–C8–C9 torsion angle at -118.7 (13)°.

Figure 10

*X-ray crystallography image of $[\text{Re}(\text{CO})_3\{1,2\text{-C}_5\text{H}_3(\text{CO-C}_4\text{H}_3\text{S})_2\}]$ (**2B**).*

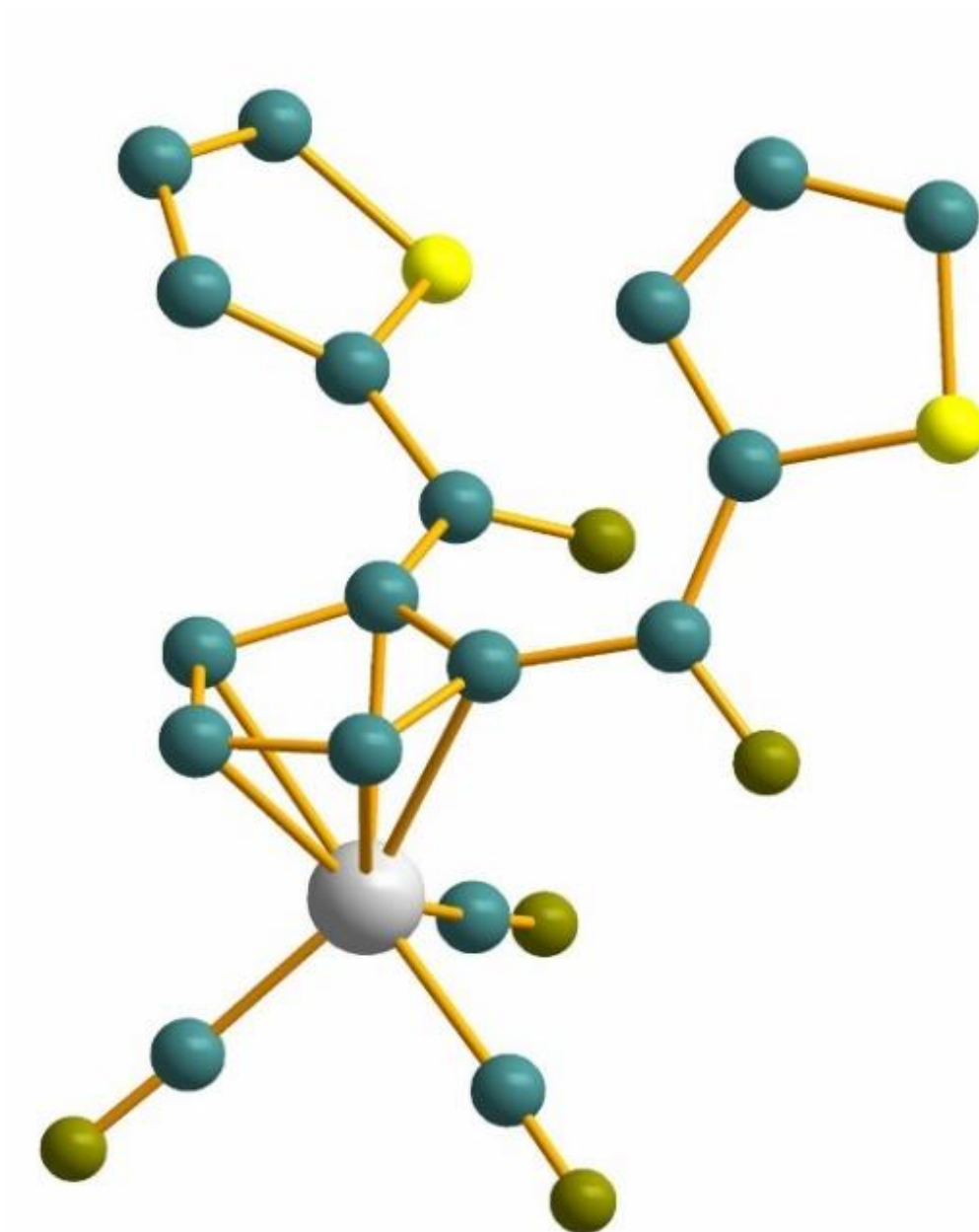


Figure 11

*X-ray crystallography image of $[Re(CO)_3\{1,2-C_5H_3(CO-C_4H_3S)_2\}]$ (**2B**).*

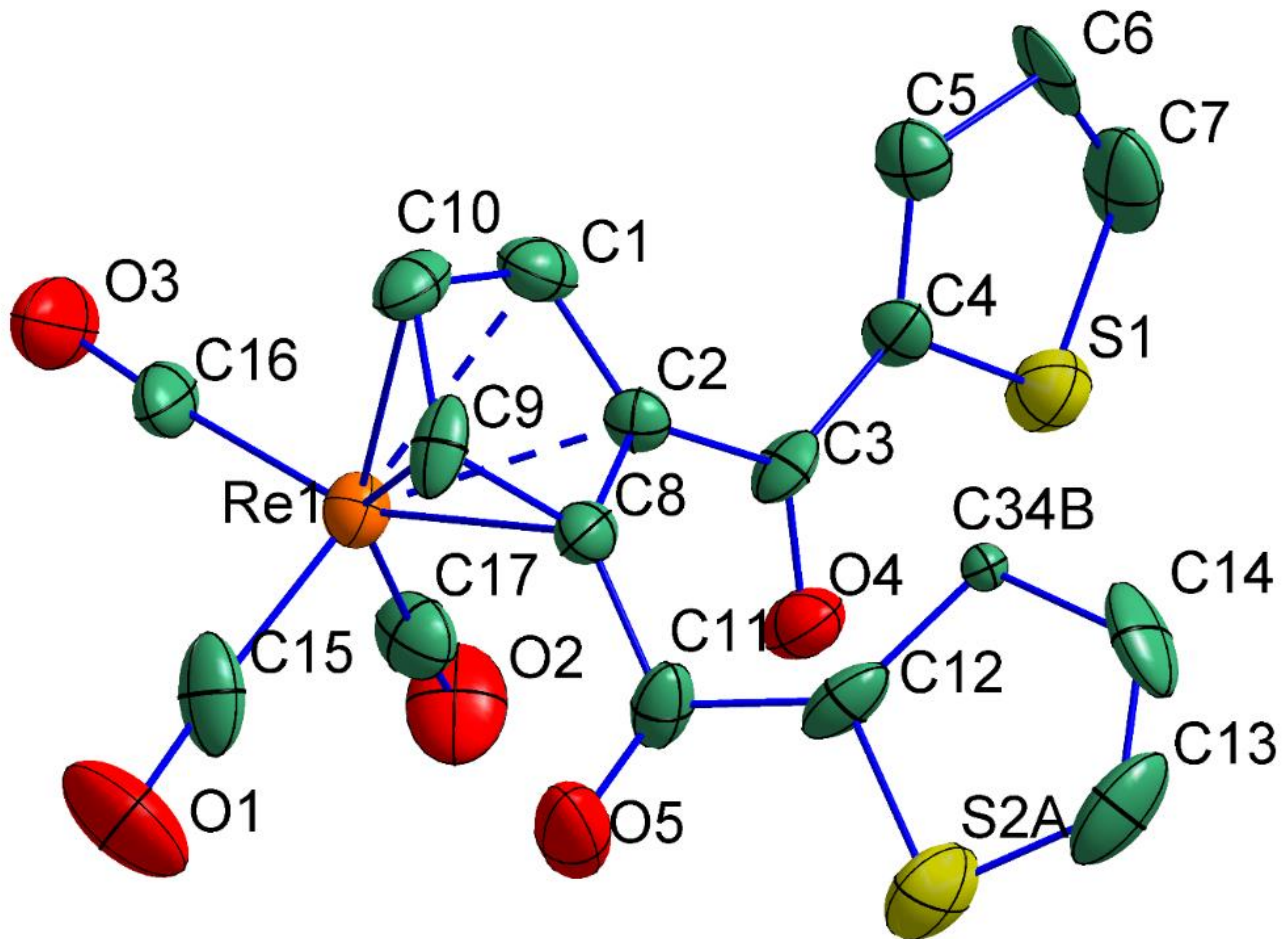


Table 5

Crystal data and structure refinement for [Re(CO)₃{1,2-C₅H₃(CO-C₄H₃S)₂}] (2B).

Structure	1
Empirical Formula	C ₁₈ H ₉ O ₅ S ₂ Re
Formula Weight	555.60
Temperature	296(2)
Wavelength	0.71073
Crystal system	Orthorhombic
Crystal system, Space group	Pca2(1)
Unit cell dimensions	a = 15.1124(2) b = 11.8824(2) c = 19.2429(3) α = 90.00 β = 90.00 γ = 90.00
Volume	3455.48(9)
Z	4
Calculated density	2.136
Absorption Coefficient	7.302
F(000)	2112
Crystal Size	0.2 x 0.1 x 0.1
Radiation	Mo K (λ = 0.7107 Å)
Monochromator	Graphite
Θ range for data collection	2.42 to 30.9
Limiting indices	$-19 \leq h \leq 19$
Reflections collected/unique	57936
Absorption correction	Multi-scan
Refinement method	Full-matrix
Data/restraints/parameters	7924/17/490
Goodness-of-fit on F ²	0.921
Final R indices [I > 2 σ (I)]	R1 = 0.0230, wR2 = 0.0514

Conclusion

This study introduced mechanisms and methods to develop various disubstituted cyclopentadienyl rhenium complexes, because, with the transition metal substituent in the structure, there are potential semiconductive capabilities associated with these complexes. Compounds **1A** and **1B** were synthesized correctly with yields of 97.4% and 61.5% respectively. Compound **1B** was characterized via melting point and infrared spectroscopy to identify the synthesized product. The IR spectrum indicated the rhenium and carbonyl bonds were present with strong peaks shown at 2033 cm^{-1} and 1926 cm^{-1} and confirmed that a successful transmetalation had been performed.

The synthesis of **2A** and **2B**, having the thienoyl substituent groups, were also considered successful with yields corresponding to 108% and 38.2%. Both synthetic products were characterized by melting range analysis and infrared spectroscopy. IR confirmed the structure of compound **2A** through the peaks at 3093 cm^{-1} and 2986 cm^{-1} that corresponded to hybridized hydrogen atoms along with the peak at 1191 cm^{-1} indicating the expected sulfur bonds in the thienyl substituent group. The characteristic two strong peaks indicating the presence of the bond between the rhenium and carbonyl groups was observed in the IR spectrum of **2B** at 1910 cm^{-1} and 2021 cm^{-1} . Compound **2B** was further analyzed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and x-ray crystallography. The expected Cp signals were observed for the $^1\text{H-NMR}$ at 5.81 ppm and 6.52 ppm in addition to the thienoyl signal found in range of aromatic molecules between 7.23 to 8.00 ppm. The $^{13}\text{C-NMR}$ signal also corresponded to the expected structure with the rhenium carbonyl signal present at 192.63 ppm and the diacyl signal at 180.02 ppm. The x-ray crystallography image, calculated bond lengths, and bond angles, all aligned with the intended structure of **2B** further confirming the correct complex had been formed.

Through these advanced methods of identification, the structure was confirmed. Based upon the characterization efforts, the four desired compounds were concluded to have been correctly synthesized and were considered successful candidates for tunable semiconductive complexes.

Future Work

Beyond the organometallic complexes synthesized herein, further work could be conducted to expand the library of possible semiconductive materials through performing an additional reaction on the rhenium complex to form an organometallic pyridazine. Another route for future research could be synthesizing a similar rhenium complex to those outlined in this paper with triphenylphosphine groups in replacement for the carbonyl groups. Through additional electrochemical research, the possibility of adjusting the conductivity of the complex using oxidative and reductive reactions could be further explored with industrial applications in mind. Ultimately, the complexes introduced and characterized within this paper serve as valuable material to advance research within chemical engineering for testing specific applications.

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