

Background

Thienyl-based chemistry is an alternative to typical semiconductive materials and has been largely unexplored despite thiophene's availability in crude oil as a waste product. Halogenated thienyl complexes (e.g., 5-bromo) can be polymerized via coupling reactions. The incorporation of a redox-active transition metal (Re, Mn) allows for a "tuning" of the electronic properties of the material by changing the oxidation state of the metal. The thienyl rhenium and the thienyl manganese complexes, $Re(CO)_3[1,2-C_5H_3(CO-(C_4H_3S))_2]$ and $Mn(CO)_3[1,2-C_5H_3(CO-(C_4H_3S))_2]$, respectively, has been synthesized in decent yields and characterized by nuclear magnetic resonance (NMR) and Infrared (IR) spectroscopy, along with melting point analysis and X-ray crystallography. NMR and X-ray crystallography was done at the University of Findlay, and the IR and melting point analysis was performed at Liberty University. The complexes were synthesized by an undergraduate research team at Liberty University, led by Dr. Chad Snyder, from a convenient route beginning with a disubstituted fulvene with the chemical formula $1,2-C_5H_3(CO(C_4H_3S))(CO(C_4H_3S))$, using the methods described herein. This disubstituted fulvene was synthesized at the University of Findlay by a team of researchers led by Dr. Tice. A strong, stable salt was formed to encourage a full negative charge on the fulvene through aromaticity, using a cation with an oxidation state of +1. The use of a cation that does not have partially filled δ -orbitals is considered less than ideal in terms of safety, as it does not have the proper stability to be used in an environment open to air. For example, potassium and sodium cyclopentadienyl salts (Cp salt) are pyrophoric, which is far too dangerous to be considered for simple synthesis. Thus, a thallium Cp salt was chosen for this synthesis as it has more stability in open environments.

Introduction

Curiosity is our God-given drive to wonder, which fuels our need to understand. This is a fundamental aspect of our humanity and is the force that subconsciously encourages us to explore the details of the world God has hidden. Psalms 111:2 says, "Great are the works of the Lord, studied by all who delight in him." The Bible tells us that it is a form of worship to wonder, and it is a form of worship to research. With that understanding, it has been the desire of inorganic chemists and physicists alike to have a deeper understanding of the nature of semiconductive materials, which are materials whose band gap between its valence and conducting bands are energetically insignificant. For this research, the synthesized products of interest, rhenium complexes, are an example of a semiconductive material. These complexes can exist in many forms. In this project, a new, never-before synthesized rhenium complex has been developed, and it has been spectroscopically confirmed that the synthesis of the proposed material was successful.

Methods

Synthesis of $[Tl^+][1,2-C_5H_3(CO-C_4H_3S)_2]^-$

- To a solution of $1,2-C_5H_3(CO-C_4H_3S)(COH-C_4H_3S)$ (0.33 g, 1.15 mmol) in THF (15 mL) was added TIOEt (0.09 mL, 1.1 mmol). The solution was stirred at room temperature for 3 hours, filtered, and allowed to dry to yield $[Ti-1,2-C_5H_3(CO-C_4H_3S)_2]^-$ (0.609 g, 1.24 mmol) and $[Tl-1,2-C_5H_3(CO-C_4H_3S)_2]^-$ (0.528 g, 1.08 mmol) as a yellow solid.

Synthesis of $M(CO)_3[1,2-C_5H_3(CO-C_4H_3S)_2]$

- To a refluxing solution of $[Ti-1,2-C_5H_3(CO-C_4H_3S)_2]^-$ (0.603 g, 1.24 mmol) in benzene (20 mL, 2.56 mmol) was added $[Re(CO)_5Br]$ (0.550 g, 1.35 mmol). The solution was refluxed for 4 hours to yield a dark red solution. After the solution was allowed to cool it was filtered (Celite) and the solvent removed *in vacuo* to yield a red semi-solid. The semi-solid was triturated with several aliquots of cold pentane (6 x 5 mL) to yield $[Re-\eta^5-1,2-C_5H_3(CO-C_4H_3S)_2(CO)_3]$ (0.264 g, 0.48 mmol), compound 2A, as a red powder. This was done again but with $[Mn(CO)_5Br]$ to yield $[Mn-\eta^5-1,2-C_5H_3(CO-C_4H_3S)_2(CO)_3]$ (0.088 g, 0.207 mmol).

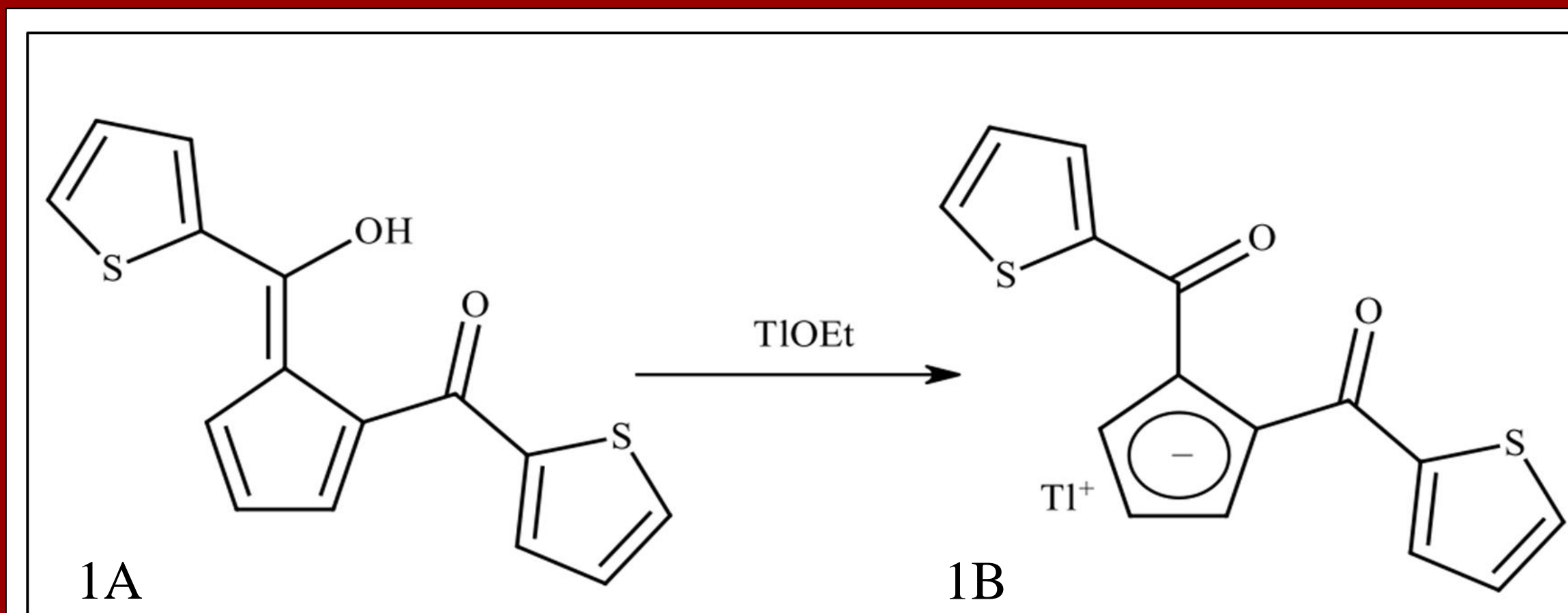


Figure 1. Synthetic route for intermediate disubstituted thallium Cp salt

(1A) 1,2-dithienyl fulvene (1B) thallium 1,2-dithienyl cyclopentadienyl salt

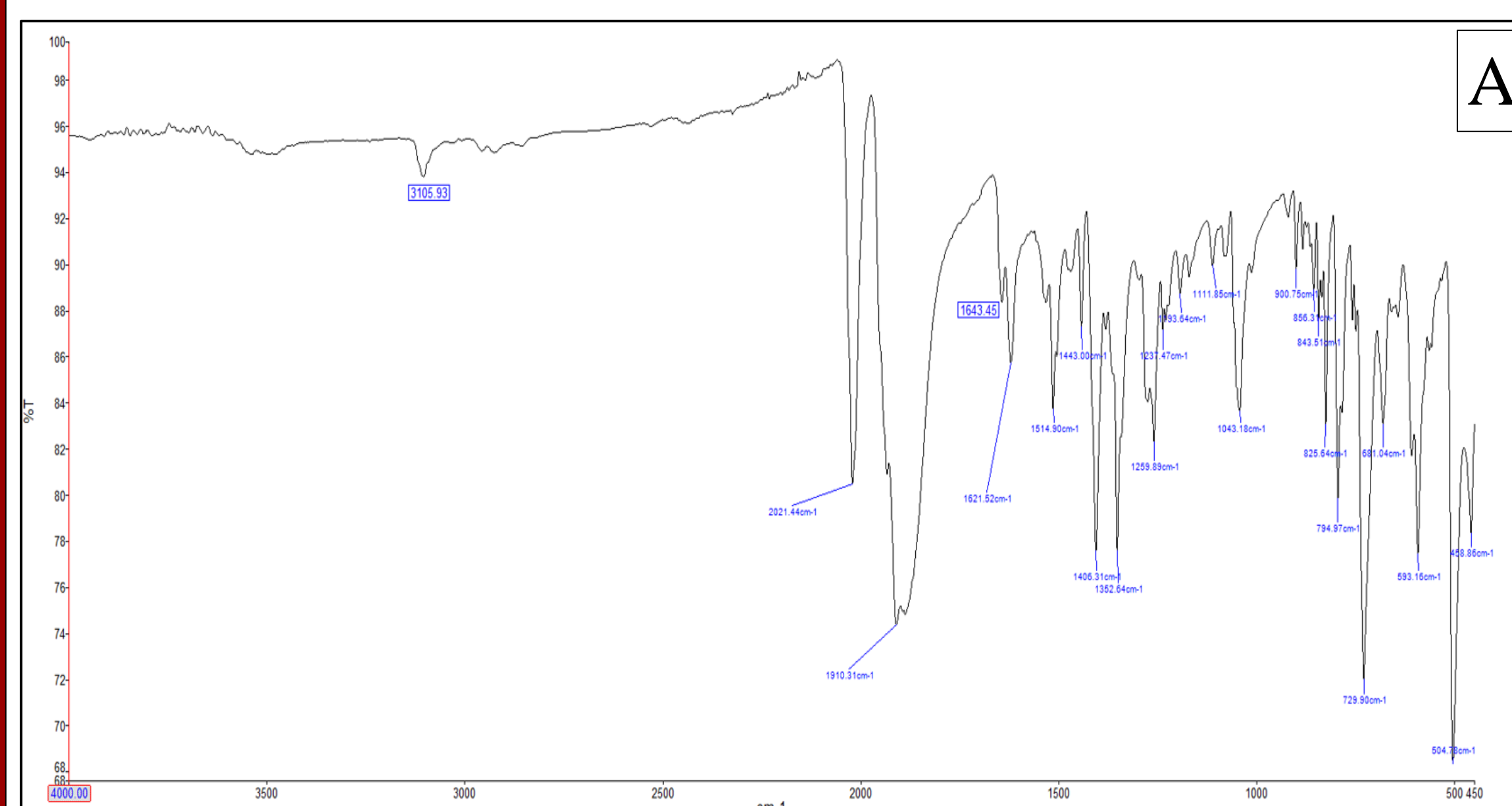


Figure 3. IR Spectra of the disubstituted thienyl cyclopentadienyl rhenium complex (A) and the disubstituted thienyl cyclopentadienyl manganese complex (B).

(A) The strong peaks present at 1910 cm^{-1} and 2021 cm^{-1} are indicators of bonds between the rhenium and bonded carbonyl groups. The peak at 1643 cm^{-1} corresponds to the carbon-carbon double bond and the peak at 1621 cm^{-1} was expected for the oxygen double bonded to the carbon.

(B) Similar to spectrum (A), two strong peaks seen at 1924 cm^{-1} and 2022 cm^{-1} indicate the presence of the manganese and carbonyl bonds seen in the structure. The carbon-oxygen double bonds are represented by the peak at 1619 cm^{-1} and the carbon-carbon double bonds are represented by the peak at 1642 cm^{-1} .

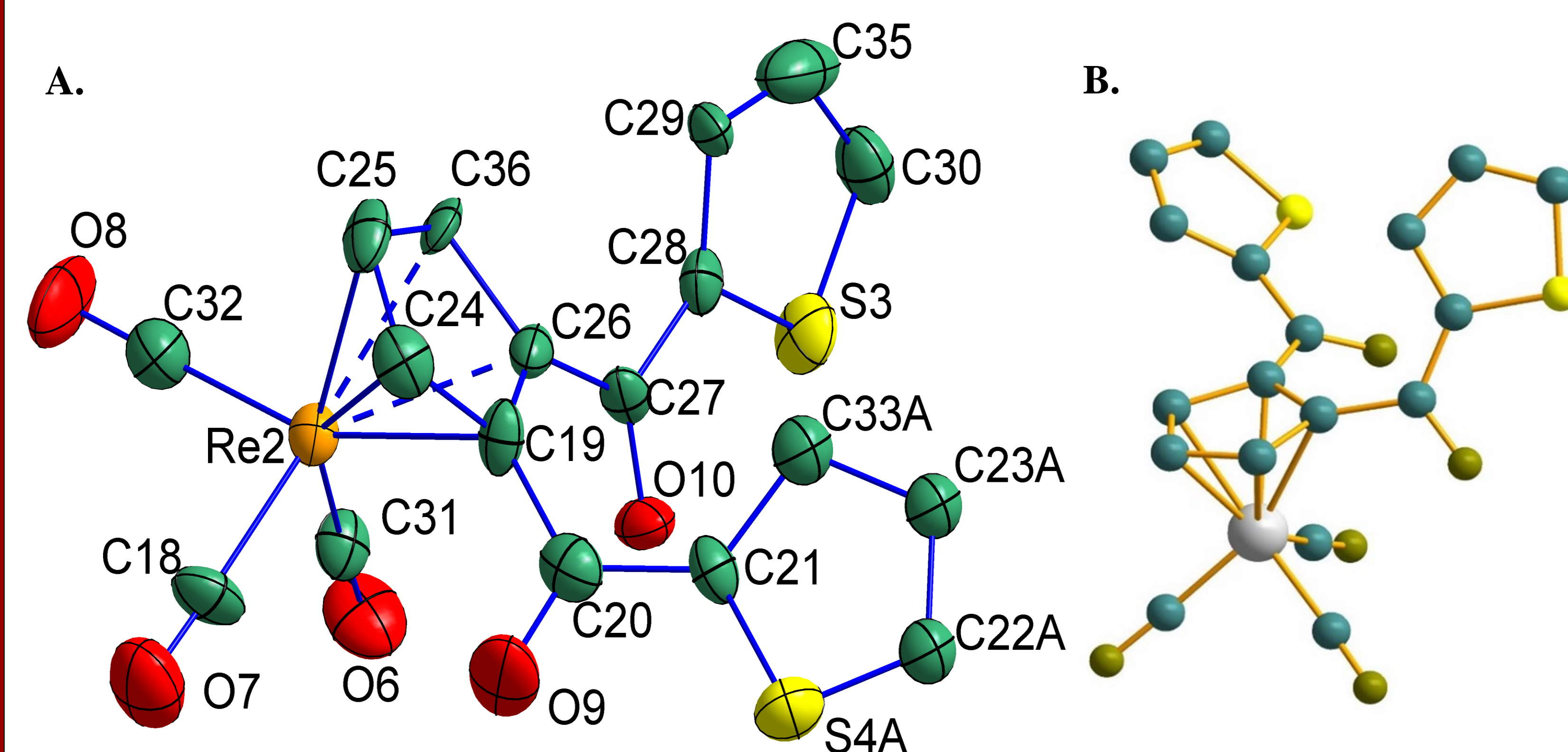


Figure 4. X-ray crystal structure of complex 2A with labeled atoms (A) and in ball-and-stick representation (B).

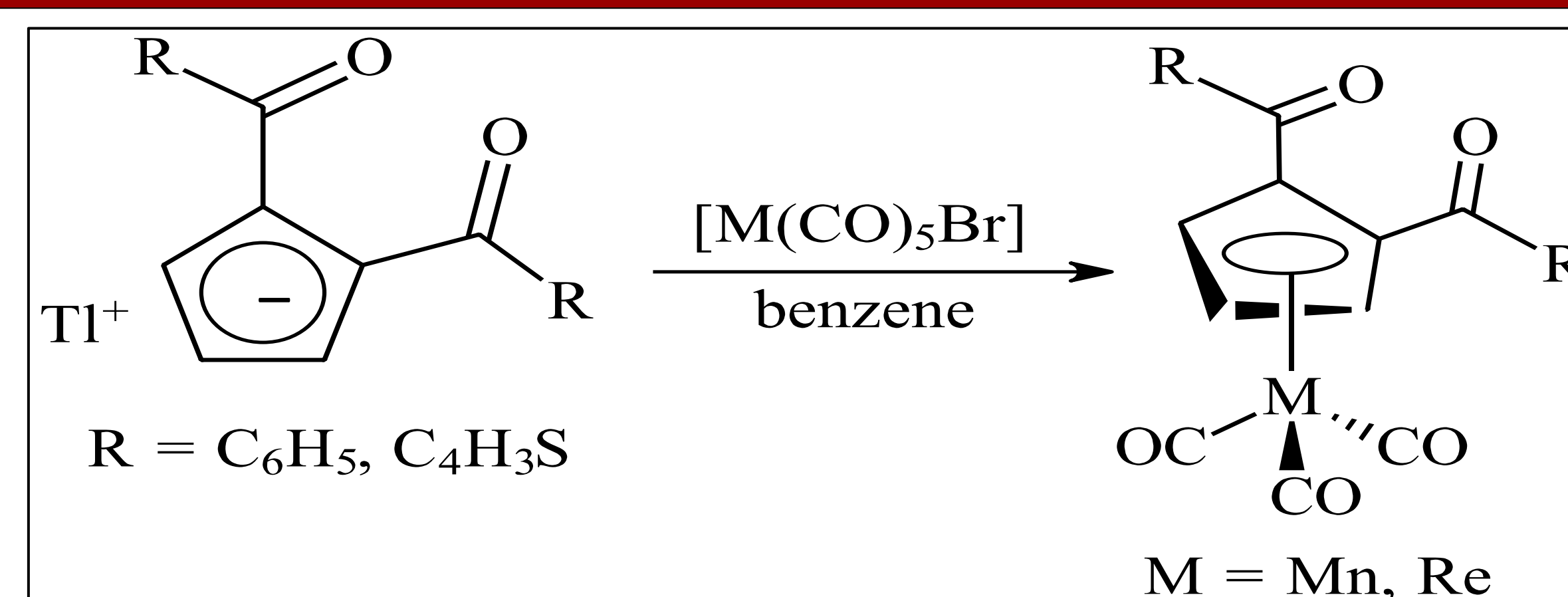
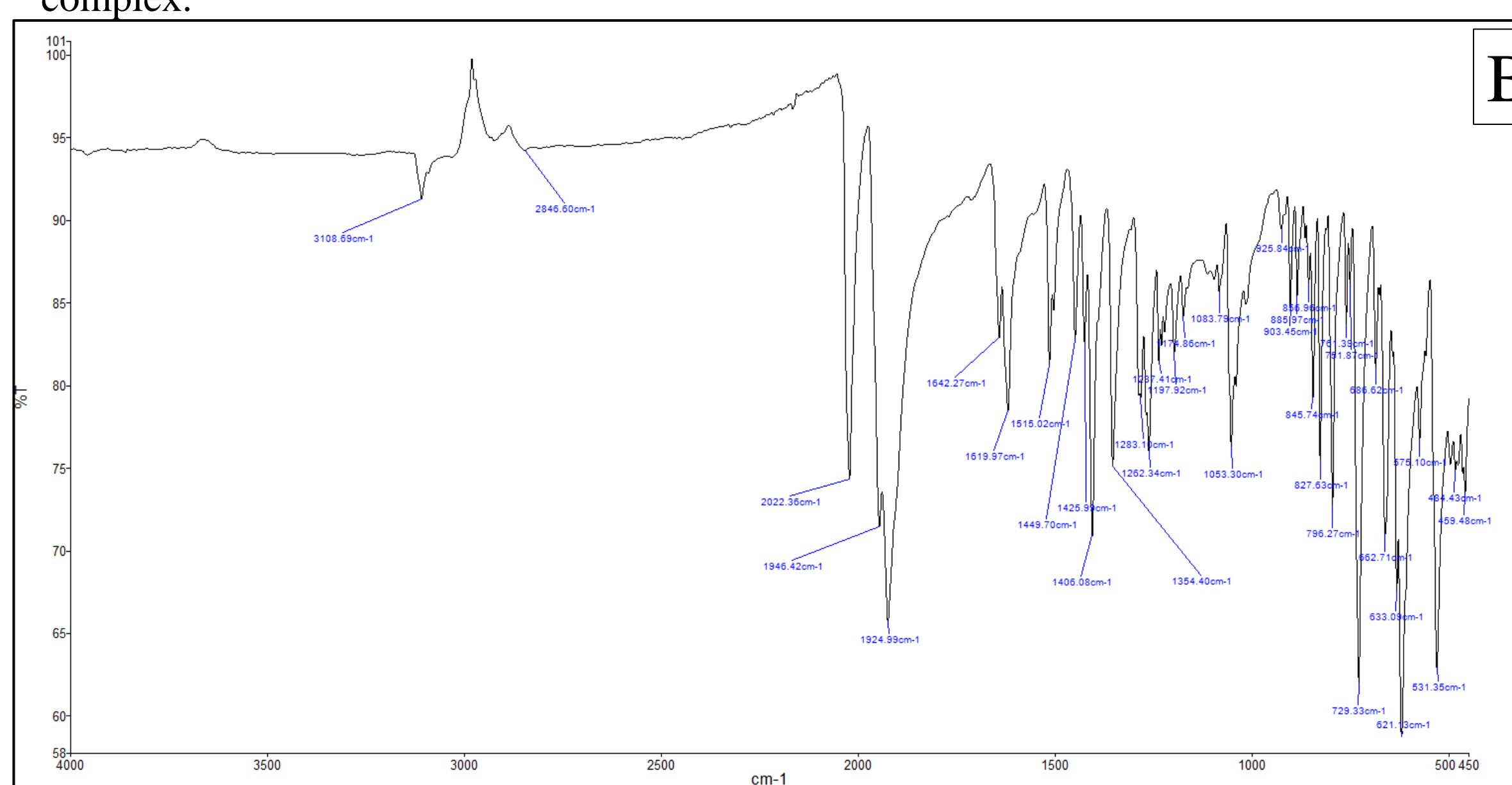


Figure 2. Synthetic route for final disubstituted thienyl

cyclopentadienyl rhenium complex (2A) disubstituted thienyl cyclopentadienyl rhenium complex, (2B) disubstituted thienyl cyclopentadienyl manganese complex.



Bond	Literature Frequency (cm ⁻¹)	Experimental Frequency (A) (cm ⁻¹)	Experimental Frequency (B) (cm ⁻¹)
C=O	1715	1621	1619
C=C	1600-1700	1643	1642
C-S	1200	1193	1197
C-H <i>sp</i> ²	3000-3100	3105	3108
C-H <i>sp</i> ³	2800-3000	2980	2846
C-M	2000, 1900	2021, 1910	2022, 1925

Table 1. Accepted frequency values from IR Spectroscopy bonds and the corresponding experimental values from each spectrum (Fig. 3)

Bond	Lit. Length (Å)	Exp. Length (Å)
C(29)-H(29)	1.09	0.9300
C(25)-C(36)	1.30	1.397
S(3)-C(28)	1.80	1.741
O(10)-C(27)	1.21	1.215
Re(2)-C(24)	N/a	2.268
Re(2)-C(18)	N/a	1.951
O(7)-C(18)	1.13	1.104

Table 2. Bond lengths (Å) of 2A (Fig. 4).

Angle	Exp. Angle (°)
C(31)-Re(2)-C(32)	89.7
O(7)-C(18)-Re(2)	176.6
C(25)-Re(2)-C(26)	59.1
C(24)-C(25)-C(36)	108.3
O(9)-C(20)-C(21)	120.0
C(30)-S(3)-C(28)	93.7
S(3)-C(30)-H(30)	126.4

Table 3. Bond angles (°) of 2A (Fig. 4).

Results

Compound	Amount Obtained (mg)	Percent Yield	Melting Point (°C)
2A	264	38.2%	162-164
2B	88	33.2%	153.2-153.9

Table 4. Percent Yield and Melting Point Range for Synthesized Compounds

The thallium cyclopentadienyl salts and the two disubstituted thienyl cyclopentadienyl complexes were successfully synthesized, indicated by Infrared Spectroscopy (Figure 3, Table 1). NMR, both ¹H and ¹³C, and X-ray crystallography (Figure 2, Tables 2 and 3) results confirm the identity of the disubstituted thienyl cyclopentadienyl rhenium complex (2A). X-ray crystallography results show the actual structure of the synthesized compound in its solid state and as of now, X-ray crystallography has not been done on Compound 2B but will be done in future work. NMR results confirm the structure of the compounds, in relation to their hydrogen and carbon atoms, and provide information on coupling constants. The low percent yields of both compounds can be attributed to losing product during the purification steps, filtering and triturating. The melting point ranges indicated high purity as both ranges are narrow, within 2 °C.

It has been previously shown that the precursor to the disubstituted thienyl cyclopentadienyl complexes, the thallium Cp salts, can be synthesized in high yields. The transition metal complexes could be synthesized in higher yields and work is being done to optimize these reactions.

Future Work

- As the rhenium complex has the potential to be used in semiconductive technology, an analysis of the toxicological effects of this product will be required.
- Synthesizing a small library of organometallic compounds with varying substituent groups capable of transmetalation reactions. One goal is to discover a link between the oxidative and reductive capabilities in transition metal substituents for semiconductive tunability.
- A comparative study of the general conductivity of the thienyl-rhenium complex to known semiconductors would also be beneficial.

References and Acknowledgements

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