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On-Metal Synthesis of Some Aryl Substituted Rhenium η^5 Cyclopenta[C] Pyridazyl Complexes

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ON-METAL SYNTHESIS OF SOME ARYL SUBSTITUTED RHENIUM η^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
Phenahas Gandu Sriramulu

August 2010

ON-METAL SYNTHESIS OF SOME ARYL SUBSTITUTED RHENIUM η^5 -
CYCLOPENTA[C] PYRIDAZYL COMPLEXES

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TABLE OF CONTENTS

Acknowledgements.....	i
Abstract.....	iii
Chapter One: Introduction.....	3
Chapter Two: Experimental.....	14
Chapter Three: Results and Discussion.....	20
Chapter Four: Conclusions.....	48
References.....	49
Vita.....	50

ON-METAL SYNTHESIS OF SOME ARYL SUBSTITUTED RHENIUM η^5 -CYCLOPENTA[C] PYRIDAZYL COMPLEXES

Phenahas Gandu Sriramulu

August 2010

50 Pages

Directed by: Chad Snyder, Hemali Rathnayake, Rajalingam Dakshinamurthy

Department of Chemistry

Western Kentucky University

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). We are interested in synthesizing organometallic pyridazines and rhenium pyridazyl complexes for polymer research. Several 5,6-fused ring pyridazines (1,2-C₅H₃(CRNH)(CRN)) have been synthesized and characterized. Additionally, pyridazyl complexes of rhenium were synthesized in three steps beginning from fulvenes 1,2-C₅H₃(COHR)(COR). On-Metal synthesis and characterization of [Re(CO)₃{1,2-C₅H₃(CRN)(CRN)}] (R=C₆H₄OMe, C₆H₄Cl, C₄H₃O) and some off-metal pyridazines are reported here. Our research is focused on synthesis of a variety of 5,6- fused ring pyridazines which will serve as synthetic models and building blocks for organic and organometallic conducting polymers.

Our research focused on synthesis of 5 membered pyridazines and their organometallic rhenium complexes for polymer studies. Several aryl-substituted 5,6-fused ring pyridazines have been synthesized and characterized.

I.INTRODUCTION

Conductive Polymer Background

A conductive polymer is an organic material that has the properties of conducting electricity. Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa discovered these conducting polymers in the late 1960's.¹ The well known conductive polymers include polyacetylene, polyaniline, polypyrrole and polythiophene. These conductive polymers possess properties such as good resistivity at room temperature, low density and can be stretched to form thin films. Additionally, these conductive polymers can be incorporated into nanoparticles. Fibrillar morphology of these nanoparticles demonstrates that particles have pearl-chain-like oriented arrangement. These plastics have been extensively used by the electronic industry because of this very property and also have been utilized as inactive packing and insulating materials. This class has either a zero band gap or a small band gap.

Polyacetylene was first synthesized by Natta et al. as a black powder which behaves as semiconductor having conductivity between 7×10^{-11} to $7 \times 10^{-3} \text{ Sm}^{-1}$.² Exposing polyacetylene to halogens increased its conductivity a billion fold. In the undoped state polyacetylene has a silver color and it's insoluble and intractable. Some disadvantages of polyacetylene include air-sensitivity; it's easily oxidized and therefore is unattractive for commercial purposes. On the other hand, polyheterocycles behave very differently. Polythiophene and polypyrrole are much more air stable than polyacetylene although their conductivity is not as high (10^3 Sm^{-1}).

Organic semiconductors are an emerging class of new materials which have applications mostly in medicine and technology. The well known organic semiconductors

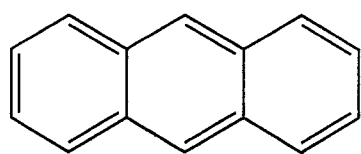
include single molecules, short chain oligomers such as pentacene, oligothiophene, and long chain polymers (Figure 1). The π -electrons and unpaired electrons are carriers which conduct electricity in organic semiconductors. Organic semiconductor applications include electronic and opto-electronic devices such as light emitting diodes (LEDs), thin film transistors, organic photovoltaics (OPVs),³ organic field effect transistors (OFETs), organic solar cells, sensor materials and radio-frequency identification (RF-ID) tags.

Organic semiconductors promise full flexibility for large-area displays, solid-state lighting and radio frequency identification tags. Additionally, these organic materials offer physical advantages such as easy fabrication, mechanical flexibility, low-cost, large surface area and low temperature device based on solution processes. Such processes offer the possibility of depositing materials from solution, enabling patterning.³ In OFETs, semiconducting materials play an important role in solubilizing, uniformity and large-area films.

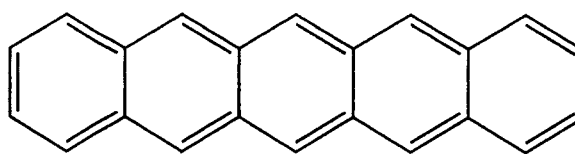
These have p-type (electron donor, hole transport) and n-type (electron acceptor, electron transport) properties.³ These n-type organic and polymer semiconductors are more efficient for high performance light emitting diodes (LEDs), photovoltaic cells and other building blocks of plastic electronics.⁴ Electron transport has been observed in organic and polymer LEDs using electron-transport materials to varied degree of success in improving performance.⁴

Pentacene (Figure 1B) is a p-type organic transistor which has π -stacked organic layer structure useful for multi-channel layer for application in organic field effect transistor because of high mobility associated with both the π - stacking and crystal like morphology.⁵ This crystalline material, which forms charge transfer complexes, enables

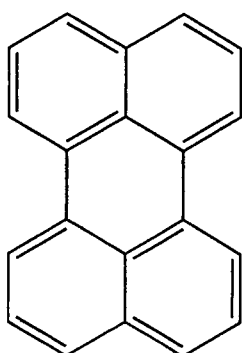
the study of charge transfer and effects on geometry and electronic structure of molecules. Substituted pentacene, such as asymmetric linear acenes, is an ideal candidate for solution processing using octadecyltrichlorosilane (OTS) treated SiO₂/Si and spin coated polyvinylphenol which is stable in ambient conditions.⁶



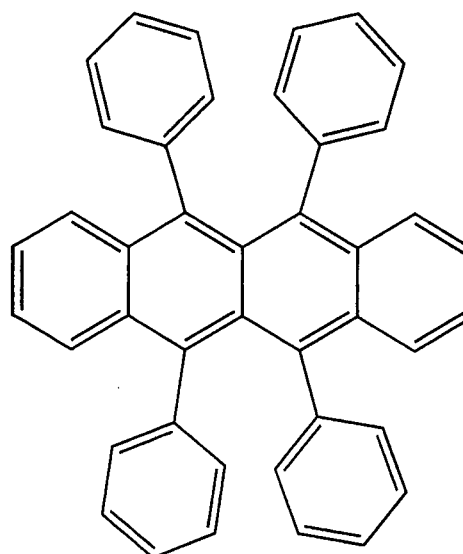
A. Anthracene



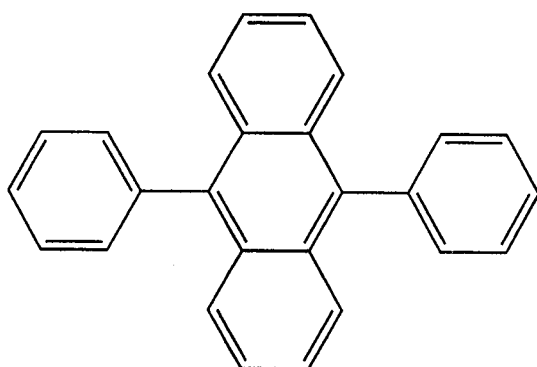
B. Pentacene



C. Perylene



D. Rubrene



E. DPA

Figure 1. Examples of some oligomeric organic semiconductors.

The OFET helps us to determine parameters such as charge-carrier field effect mobility (μ), threshold voltage (V_{th}), sub-threshold voltage (S), and on/of current ratio (I_{ON}/I_{OFF}). Molecular order of active thin film is controlled by processes such as Annealing, surface treatment of dielectric layer and variation of deposition rate.

Polymers form amorphous thin film which have a microcrystalline morphology that increase the carrier mobility in OFETs because of it strong π - π interaction. Face-to-face arrangement of unsubstituted arenes showed improved carrier mobilities. Small molecules showed reliable and efficient in OFET.⁷

These organic semiconductors can be doped by introducing electron accepting molecules such as polyaniline which is highly doped. The conduction mechanism is presence of hole and electron conduction layer separated by Band Gap (the energy difference between top of valence band and bottom of the conduction band). Electrons must move in a state between valence band and conduction band to conduct electric current which requires a specific amount of energy for transition. The electron gains enough energy to jump to the conduction band by absorbing a photon.

In the solid state, the energy gap also called as Band gap (Figure 2) which explains the movement of electrons which acts as carriers between the valence band and conduction band.

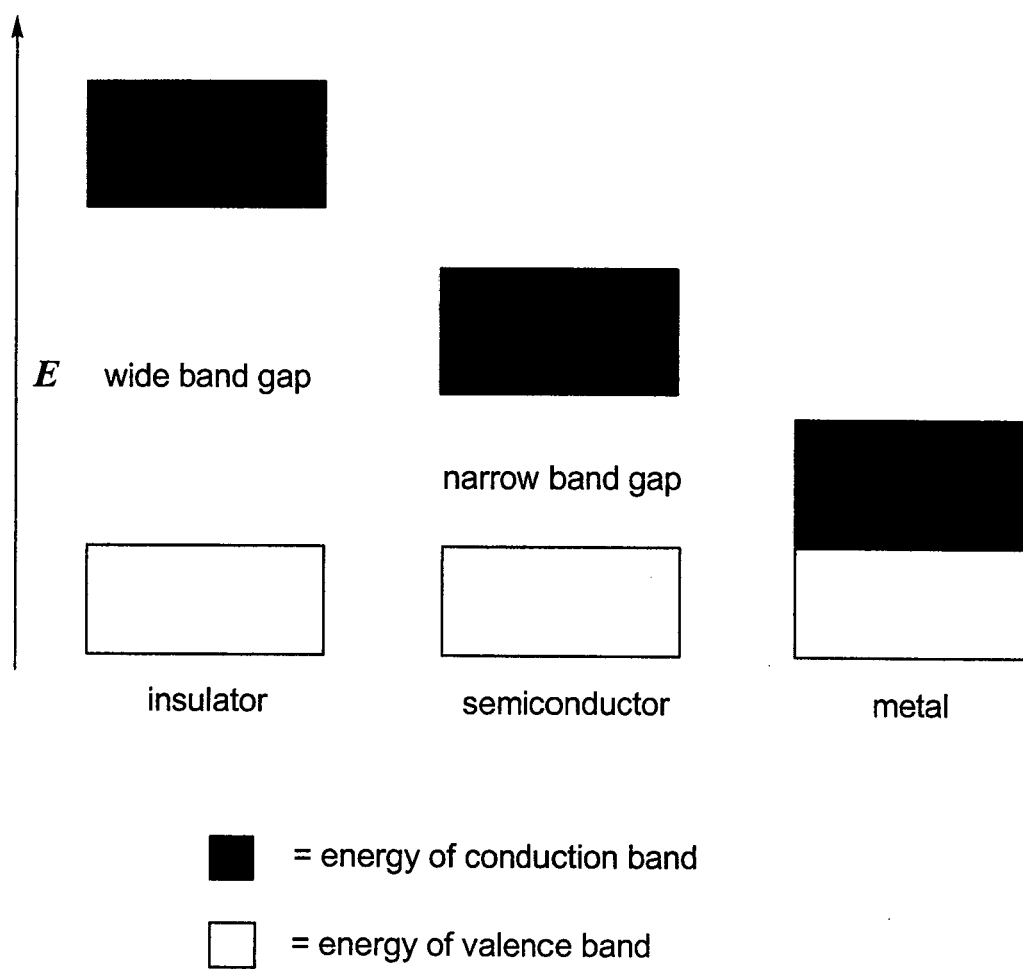


Figure 2. A molecular orbital illustration of an insulator, semiconductor, and conductor.

If the band gap between valence band and conduction band is too large then valence band electrons fail to migrate to the conduction band resulting in an insulator. An insulator has only a few electrons and possess lower electrical conductivity. In the semiconductor there is a narrow band gap and it has an electric conductivity between conductor and insulator. The greater conductivity occurs from increased band overlap. In metals the band gap is very small, partially filled and partially empty and possess high electrical conductivity.

Conduction Mechanism

Conductive polymers use Band theory as a mechanism of conduction. The ideal condition for polymers to conduct electricity is half filled valence band formed from continuous delocalized π -system. The polymers have a band width of 1.5 eV which is a high energy gap semiconductor. The polymers can be transformed into a conductor by doping with an electron donor or an electron acceptor. Polymers store charge in two ways, by oxidation and reduction. In the oxidation process it loses an electron from one of the bands which localizes the charge, decreases ionization energy and increases its electron affinity which eventually increases the energy of the polymer. Oxidizing dopants that cause this change include iodine, arsenic pentachloride, iron (III) chloride and NOPF_6 .

In oxidative doping of polypyrrole, when an electron is removed it forms a free radical and spinless positive charge at ground state configuration. The number of quinoid-like rings is formed by high distortion of energy, the positive charge and the unpaired electron can move independently along the polymer chain, which allows for conduction. This combination of charge site and radical is called 'polaron' it's an

energetically favourable process (Figure 3). This polaron state of polypyrrole has 0.5eV energy which creates new localized electronic states in the gap.

The 'bipolarons' are a pair of like charges which consist of two electrons coupled through lattice vibration also called 'phonon' are produced upon further oxidation have lower energy than polarons (Figure 4). These bipolarons are formed at higher doping level where two polarons combine which has a band gap of 0.75eV, which upon further oxidation forms continuous bipolaron bands.

Bipolarons are thermodynamically much more stable than polarons and are spinless. Conjugated polymers have different mechanism due to degenerate ground state configuration. Polypyrrole uses oxidation to produce polarons and bipolarons. In the case of conjugated polymers, such as polyacetylene, they have a two-fold degenerate ground state configuration that would be a Bipolaron and the two formed charges are not bound to each other due high energy bonding configuration and are readily separated. This process is favourable.⁸ Such a charge associated with boundary or domain wall is called a 'Soliton' (Figure 5). The charge delocalizes over several carbons where double bonds become longer and single bonds become shorter. The solitons may be neutral, positively or negatively charged. The presence of soliton leads to the creation of new localized electronic states at mid-gap. Neutral soliton is half occupied and $\frac{1}{2}$ spin whereas charged soliton is empty and spinless.¹¹ At high doping level the charged soliton interacts with each other and forms soliton bands which eventually merge with the band edges to create true metallic conductivity.

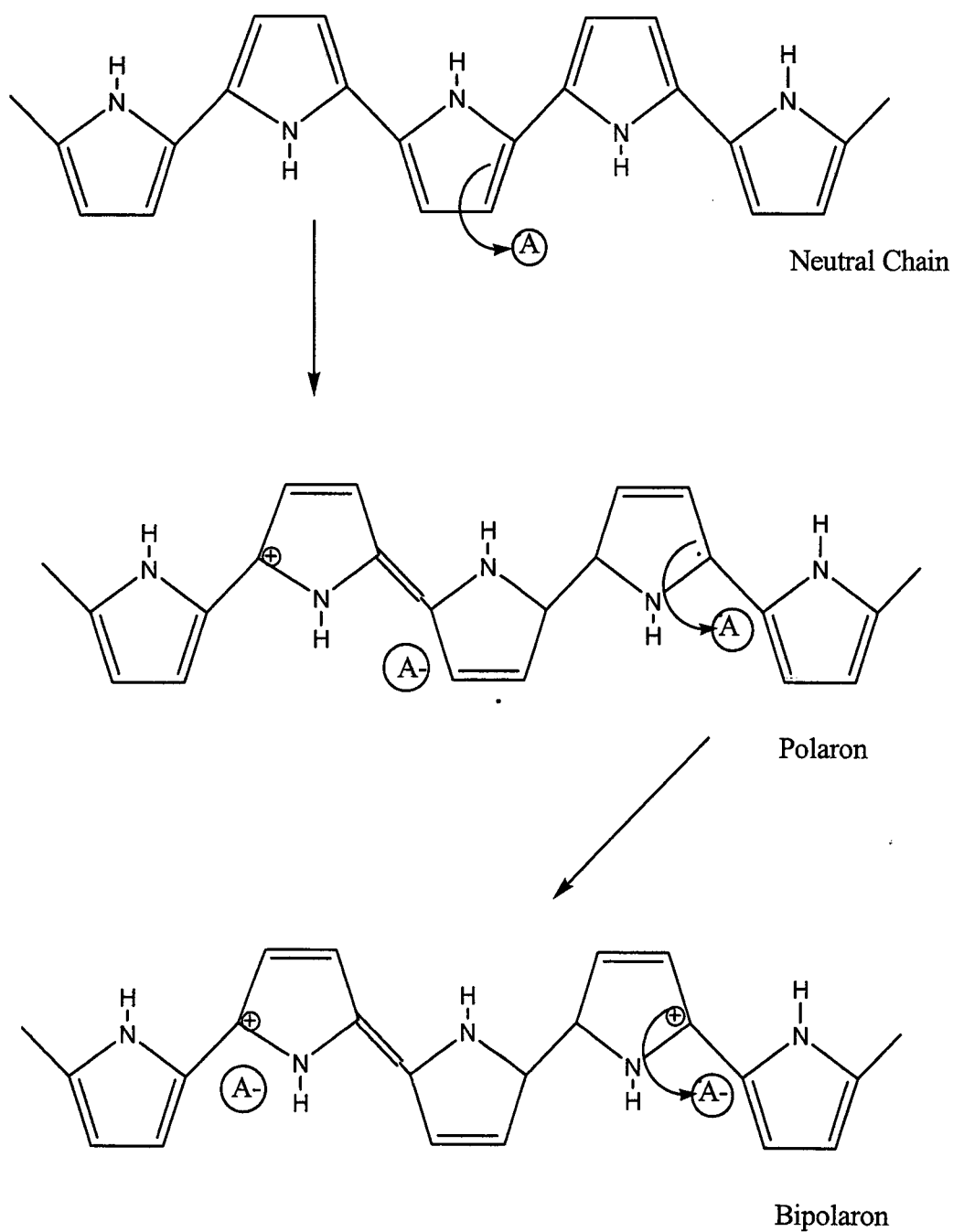


Figure 3. Representation of (a) neutral chain (b) polaron (c) bipolaron of polypyrrole.

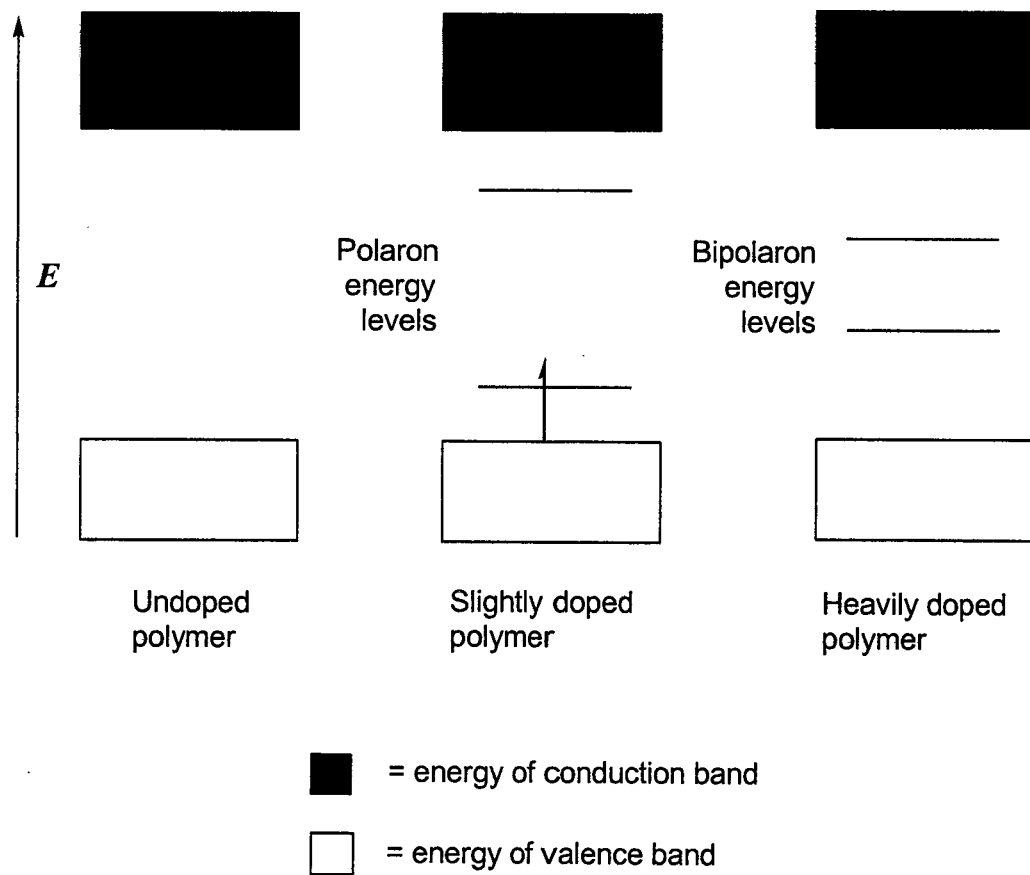


Figure 4. Relative energies of polaron and bipolaron levels.

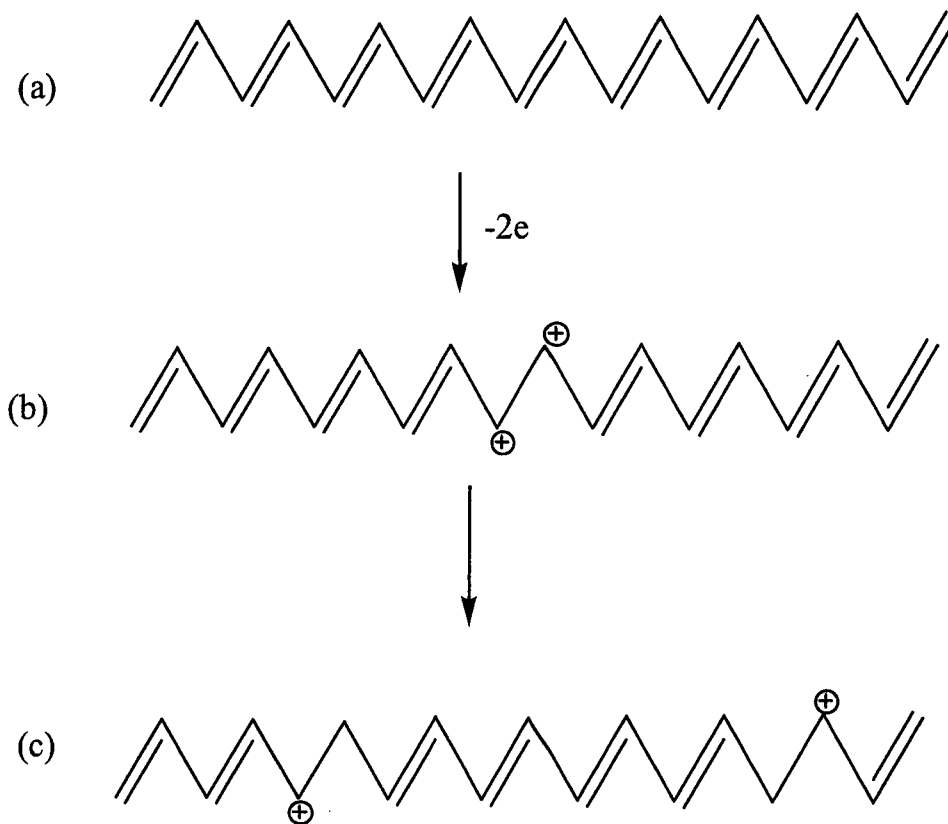


Figure 5. Illustration of the formation of two charged solitons on a chain of polyacetylene.¹¹

II. EXPERIMENTAL

The standard organic synthetic techniques were carried out under air unless otherwise noted. CDCl_3 (Cambridge Isotopes) was used without further purification. The $[\text{Re}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{CO-p-C}_6\text{H}_4\text{-OMe})_2\}]$ (**3A**), $[\text{Re}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{C-p-C}_6\text{H}_4\text{-OMeN})(\text{C-p-C}_6\text{H}_4\text{-OMeN})\}]$ (**4A**), were prepared according to modified literature methods. Tetrahydrofuran, methanol thallium(I) ethoxide (Aldrich) and rhenium pentacarbonyl bromide (Strem) were used without further purification. Benzene was dried over sodium benzophenone ketyl.

^1H 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.

Characterization Data of $[\text{Tl}\{1,2\text{-C}_5\text{H}_3(\text{CO-p-C}_6\text{H}_4\text{-OMe})_2\}]$ (2A**).**

IR (KBr, cm^{-1}): 1602 (C=O), 2942 (Me). ^1H and ^{13}C NMR data could not be obtained due to its insolubility in all available NMR solvents.

Synthesis of $[\text{Re}(\text{CO})_3\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{CO-p-C}_6\text{H}_4\text{-OMe})_2\}]$ (3A**).**

In a 100-mL Schlenk flask $[\text{ReBr}(\text{CO})_5]$ (114 mg, 0.280 mmol) was added to a stirred suspension of $[\text{Tl}\{1,2\text{-C}_5\text{H}_3(\text{CO-p-C}_6\text{H}_4\text{-OMe})_2\}]$ (150 mg, 0.280 mmol) in dry benzene (40 mL). The solution was allowed to reflux for 4 hours. The reaction was cooled and passed through a thin pad of Celite to yield an orange solution. The volatiles

were removed in vacuo, and then triturated with cold pentane to give a red powder (105 mg, 0.175 mmol, 62.4%). **Mp:** 56-61 °C. **¹H NMR (500 MHz, CDCl₃, ppm):** δ 3.83 (s, 6H, OCH₃), 5.40 (t, 1H, ³J = 2.7 Hz, CHCHCH), 5.85 (d, 2H, ³J = 2.7 Hz, CHCHCH), 6.86 (d, 4H, ³J = 8.6 Hz, CHCHCOMe), 7.78 (d, 4H, ³J = 8.6 Hz, CHCHCOMe). **¹³C NMR (125 MHz, CDCl₃, ppm):** δ 55.6 (OCH₃), 81.7 (CHCHCH), 88.7 (CHCHCH), 106.8, 114.0, 129.5, 131.6 (Ar), 163.9 (C=O), 191.5 (ReCO). **IR (KBr, cm⁻¹):** 1599 (C=O), 1927, 2030 (ReCO), 2964 (Me).

Synthesis of [Re(CO)₃{η⁵-1,2-C₅H₃(C-p-C₆H₄-OMeN)(C-p-C₆H₄-OMeN)}] (4A).

In a 125-mL Schlenk flask [Re(CO)₃{η⁵-1,2-C₅H₃(CO-p-C₆H₄-Cl)₂}] (105 mg, 0.175 mmol) was added to a solution of hydrazine hydrate (1 mL, 1.03 g, 20.6 mmol) and methyl alcohol (30 mL). The solution was allowed to stir at room temperature overnight. To the reaction, water (20 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3 x 30 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 pentane to give [Re (CO)₃{η⁵-1,2-C₅H₃(C-p-C₆H₄-OMeN)(C-p-C₆H₄-OMeN)}] (25 mg, 0.042 mmol, 24.0%) as a red powder. **Mp:** 162-167 °C. **¹H NMR (500 MHz, CDCl₃, ppm):** δ 3.90 (s, 6H, OCH₃), 7.00 (d, 4H, ³J = 8.6 Hz, NCCCCH), 7.06 (d, 2H, ³J = 4.0 Hz, CHCHCH), 7.48 (t, 1H, ³J = 4.0 Hz, CHCHCH), 7.87 (d, 4H, ³J = 8.6 Hz, CHCO). **¹³C NMR (125 MHz, CDCl₃, ppm):** δ 55.4 (OCH₃), 108.9 (CHCHCH), 114.4 (CHCHCH), 120.3, 130.0, 132.0 (Ar), 161.1 (C=N), 186.4 (ReCO). **IR (KBr, cm⁻¹):** 1607 (C=N), 1900, 2014 (ReCO) 2957, 2833 (Csp³-H).

Synthesis of [Ti-1,2-C₅H₃(COC₆H₄-Cl)(CO-C₆H₄-Cl)] (2B).

In a 100-mL Schlenk flask TiOC₂H₅ (0.160 g, 0.0454 mL, 0.644 mmol) was added to a stirred suspension of [1, 2-C₅H₃(CO-p-C₆H₄-Cl)(COH-p-C₆H₄-Cl)] (200 mg, 0.585 mmol) in THF (30 mL). The solution was allowed to stir at room temperature for 4 hours producing a yellow precipitate. The solution was filtered and washed with cold ethyl ether yielding a yellow solid (327 mg, 0.599 mmol, 51.3%). **Mp:** 164°C (dec). **IR (KBr, cm⁻¹):** 1585 (C=O). ¹H and ¹³C NMR could not be obtained due to its insolubility in our NMR solvent.

Synthesis of [Re (CO)₃{η⁵-1, 2-C₅H₃ (CO-p-C₆H₄-Cl)₂}] (3B).

In a 100-mL Schlenk flask [Re(CO)₅Br] (186 mg, 0.458 mmol) was added to a stirred suspension of [Ti{1,2-C₅H₃(CO-p-C₆H₄-OCl)₂}] (250 mg, 0.458 mmol) in dry benzene (40 mL). The solution turned orange after 10 minutes and then was allowed to reflux for 6 hours. The reaction was cooled and passed through a thin pad of Celite to yield a solution. The volatiles were removed in vacuo, then triturated with cold pentane to give a powder (157 mg, 0.257 mmol, 55.9%). **Mp:** °C. **¹H NMR (500 MHz, CDCl₃, ppm):** δ 5.44 (t, 1H, ³J = 2.3 Hz, CHCHCH), 5.87 (d, 2H, ³J = 2.3 Hz, CHCHCH), 7.39 (d, 4H, ³J = 8.0 Hz, CHCHCl), 7.71 (d, 4H, ³J = 8.0 Hz, CHCHCl). **¹³C NMR (125 MHz, CDCl₃, ppm):** δ 82.1 (CHCHCH), 89.2 (CHCHCH), 105.6, 114.0, 129.2, 130.2, 130.3 (Ar), 187.4 (C=O), 190.8 (ReCO). **IR (Nujol, cm⁻¹):** 1635 (C=O), 1962, 2035 (ReCO).

Synthesis of [Re(CO)₃{η⁵-1,2-C₅H₃(C-p-C₆H₄-ClN)(C-p-C₆H₄-ClN)}] (4B).

In a 125-mL Schlenk flask [Re(CO)₃{h⁵-1,2-C₅H₃(CO-p-C₆H₄-Cl)₂}] (105 mg, 0.175 mmol) was added to a solution of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) and methyl alcohol (30 mL). The solution was allowed to stir at room temperature overnight. To the reaction, water (20 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3 x 30 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 pentane to give [Re(CO)₃{h⁵-1,2-C₅H₃(C-p-C₆H₄-OMeN)(C-p-C₆H₄-OMeN)}] (25 mg, 0.042 mmol, 24.0%) as a red powder. **Mp:** 162-167 °C. **¹H NMR (500 MHz, CDCl₃, ppm):** δ 7.05 (d, 1H, 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). **¹³C NMR (125 MHz, CDCl₃, ppm):** δ 109.3 (CHCHCH), 120.4 (CHCHCH), 129.4, 129.9, 133.4 (Ar), 176.2 (C=N), 178.3 (ReCO). **IR (KBr, cm⁻¹):** 1633 (C=N), 1904, 2028 (ReCO).

Synthesis of [Tl{1,2-C₅H₃(COC₄H₃O)₂}] (2C).

Thallium (I) ethoxide was added to a solution of 1,2-C₅H₃(COC₄H₃O)(COHC₄H₃O) (1, 1.15 g, 3.93 mmol) in THF (25 mL). An orange precipitate formed after 5 minutes. The solution was stirred for 3 hours at 22°C. The precipitate was filtered and washed with cold hexane (3 x 10 mL) providing [Tl{1,2-C₅H₃(COC₄H₃O)₂}] (2, 60.4%, 1.25 g, 1.93 mmol) as a yellow solid. **dec.** 136–150 °C. **IR (KBr, cm⁻¹):** 1572, 1537 (CO), 3112 (CH). NMR analysis could not be obtained due to compound's insolubility in all available NMR solvents.

Synthesis of [Re{ η^5 -1,2-C₅H₃(COC₄H₃O)₂}(CO₃)] (3C).

To a solution of [Ti{1,2-C₅H₃(COC₄H₃O)₂}] (2, 482 mg, 1.05 mmol) in dry benzene (30 mL) was added [ReBr(CO)₅] (473 mg, 1.16 mmol). The solution was allowed to reflux for 5 hours. The solution was filtered through a Celite plug using benzene. The solvent was removed under reduced pressure to leave a red semi-solid. The semi-solid was triturated with pentane (2 x 5 mL) to provide a red powder (3B, 65.7%, 330 mg, 0.693 mmol). **Mp.** 82–86 °C. **¹H NMR (500 MHz, CDCl₃, ppm):** δ 5.42 (t, 1H, ³J = 2.9 Hz, CHCHCH), 6.11 (d, 1H, ³J = 2.9 Hz, CHCHCH), 7.25–7.52 (m, 6H, CHCHCHO). **¹³C NMR (125 MHz, CDCl₃, ppm):** δ 82.2 (CHCHCH), 89.6 (CHCHCH), 102.9 (CCO), 128.3, 146.8, 157.9 (Fr), 175.3 (CO), 191.4 (ReCO). **IR (KBr, cm⁻¹):** 3136 (CH), 2030, 1932 (ReCO), 1645 (CO). **MS:** *m/z* 524 (M⁺ + 1), 288 (M⁺ - C₁₅H₉O₄). **Anal. Calcd. for C₁₈H₉O₄Re:** C, 45.45; H, 1.89. **Found:** C, 31.50; H, 1.62.

Synthesis of [Re(CO₃)- η^5 -1,2-C₅H₃(CC₄H₃ON)(CC₄H₃ON)] (4C).

To a 50 mL round-bottom flask, [Re{ η^5 -1,2-C₅H₃(COC₄H₃O)₂}(CO₃)] (3B, 200 mg, 0.382 mmol) was dissolved in 30 mL of methanol. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was then added to the solution. The solution was stirred 24 hours at room temperature. To the reaction, water (5 mL) was added and the aqueous suspension was washed with ethyl ether (3 x 2 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 [Re(CO₃)- η^5 -1,2-C₅H₃(CC₄H₃ON)(CC₄H₃ON)] (4B, 19.0 mg, 0.0644 mmol, 76.0%) as red solid. **M.p.** 125–130 °C. **¹H NMR (500**

MHz, CDCl₃, ppm): δ 7.44 (t, 1H, $^3J = 7.45$ Hz, CHCHCH), 7.59 (d, 2H, $^3J = 7.45$, CHCHCH), 7.25–7.76 (m, 6H, CHCHCHO). **¹³C NMR (125 MHz, CDCl₃, ppm):** δ 108.5 (CHCHCH), 110.0 (CHCHCH), 117.5 (CCN), 127.2, 128.8, 141.9, 144.6 (Fr), 150.9 (CCN), 221.6 (ReCO). **IR (KBr, cm⁻¹):** 1604 (CN), 1890, 2004 (ReCO), 3056 (C–H). **MS:** m/z 250 ($M^+ - C_{15}H_5O_4$).

III. RESULTS AND DISCUSSION

Thallium salts **2A–C** were synthesized by the addition of thallium (I) ethoxide to fulvenes **1A–C** in dry THF at room temperature for 3 hours (Scheme 1). The percent yields were 51.3% (**2B**) and 60.4% (**2C**) for the new thallium compounds. Thallium salt **2A** was used directly from our lab and its characterization data has been previously reported. IR spectroscopy confirmed the delocalized C=O stretches found between 1585–1602 cm^{-1} for **2A–C**. ^1H and ^{13}C NMR spectroscopy data could not be obtained due to the thallium salt being insoluble in all available NMR solvents. Additionally, thallium salts **2A–C** decomposed when obtaining a melting point, which is typical for thallium Cp salts.

Rhenium complexes **3A–C** were synthesized by the addition of rhenium pentacarbonyl bromide to thallium Cp salts **2A–C** in dry benzene (Scheme 1). The solution was allowed to reflux for 4–6 hours producing a red solution. For each reaction the percentage yields ranged from 55.9–65.7%. IR spectroscopy confirmed the ReCO carbonyl stretches at 2030 and 2035 cm^{-1} . ^1H NMR spectroscopy showed the Cp signals at δ 5.40–5.44 (t, 1H, CHCHCH), and δ 5.85–6.11 (d, 2H, CHCHCH), for rhenium complexes **3A–C**. ^{13}C NMR spectroscopy showed the ReCO signals between δ 190.8–191.5 for rhenium complexes **3A–C**.

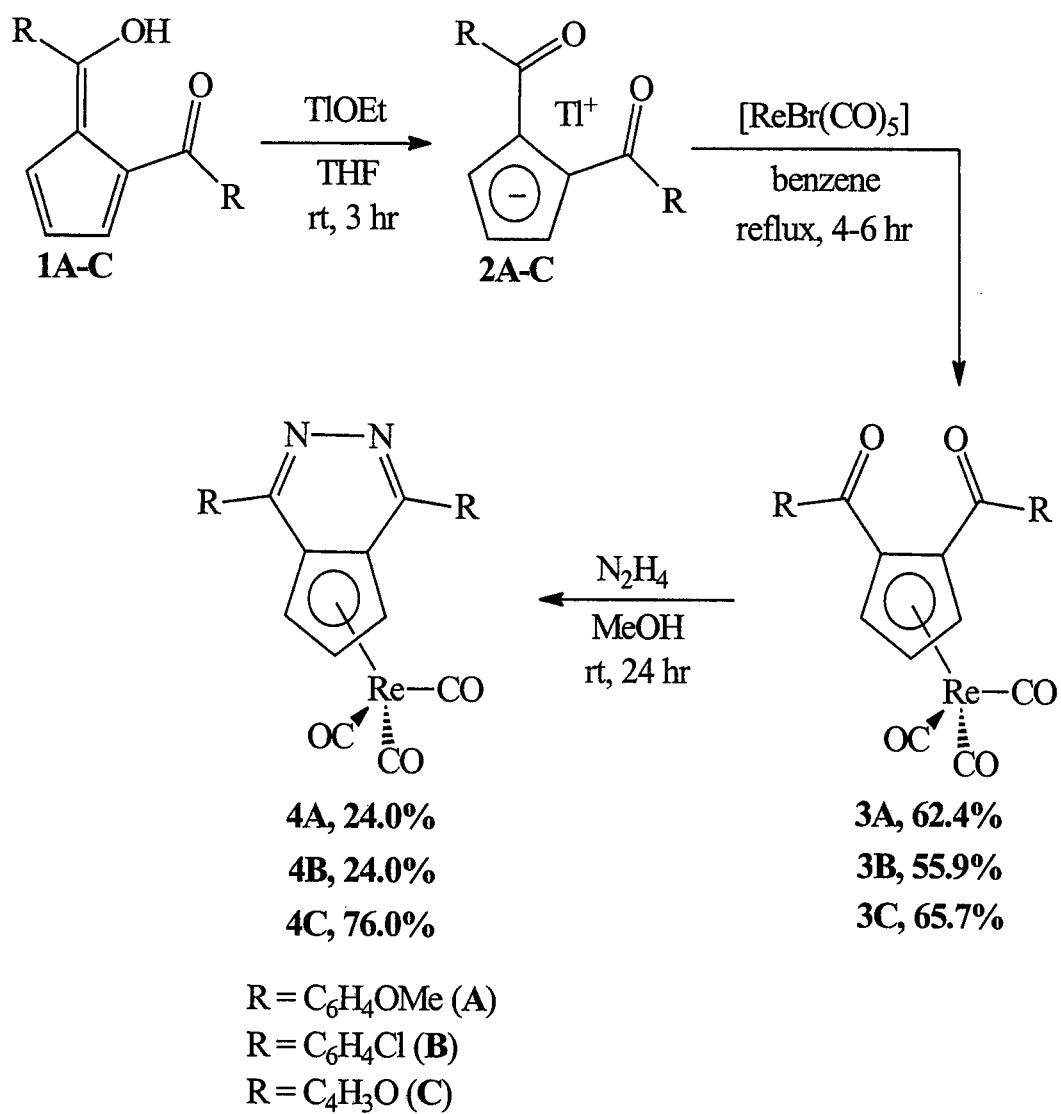
Pyridazyl complexes **4A–C** were synthesized by addition of excess hydrazine hydrate in methanol to a solution of diacyl **3A–C** and were allowed to stir for 24 hours at room temperature (Scheme 1). A red powder was obtained after purification with yields ranging from 24.0–76.0% for **4A–C**. IR spectroscopy showed the imine stretches around 1607 cm^{-1} (C=N), and ReCO around 1900–2014 cm^{-1} . ^1H NMR spectroscopy confirmed

the presence of cyclopentadiene signals around δ 7.08–7.87 with a coupling constant of $^3J = 4.0\text{--}4.55$ Hz. ^{13}C NMR spectroscopy for all three complexes confirmed Cp carbon signals ranging from δ 110.0–120.4 (CHCHCH), δ 108.5–109.3 (CHCHCH), δ 150.9–176.2 (C=N), and δ 178.3–221.6 (ReCO). Spectroscopic data and selected characterization tables are presented in Figures 6–12 and Tables 1–5.

The structure of $[\text{Re}\{\eta^5\text{-1,2-C}_5\text{H}_3(\text{COC}_4\text{H}_3\text{O})_2\}(\text{CO}_3)]$ (**3C**) was determined by X-ray crystallographic methods and the plot of the molecular structure is shown in Figure 13. Full crystallographic data is presented in Table 6-11. The crystals for which data were collected were typical of others in the batch, which had been grown by slow evaporation from methylene chloride 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.¹⁸ Hydrogen atoms were placed in geometrically calculated positions. Crystal data and a summary of experimental details are given in Table 5.

Recrystallization of **3C** affords the diacyl complex as yellow-orange, block crystals. The diacyl complex **3C** crystallizes in a triclinic *P*-1 space group, with two molecules in the unit cell. The Re–C Cp bonds are highly uniform for **3C**, with the deviations from the average length of 2.305(1) Å no more than 0.014 Å. X-ray analysis shows the two sets of carbonyls, the acyl C=O and the ReCO, having average bond lengths of 1.228(9) Å and 1.146(4) Å, respectively. In the solid state, the furoyl rings are highly asymmetric with respect to each other. The acyl portion involving O4, C12–C15

is nearly planar with respect to the central Cp ring, with the C9–C10–C11–C12 torsion angle at $-6.0(5)^\circ$. Conversely, the acyl moiety involving O1, C1–C4 is highly twisted out of plane of the Cp ring, with the C4–C5–C6–C7 torsion angle at $108.1(3)^\circ$.



Scheme 1. On-metal synthetic route to $[\text{Re}(\text{CO})_3\text{-}1,2\text{-C}_5\text{H}_3(\text{CNR})_2]$ (**4A-C**).

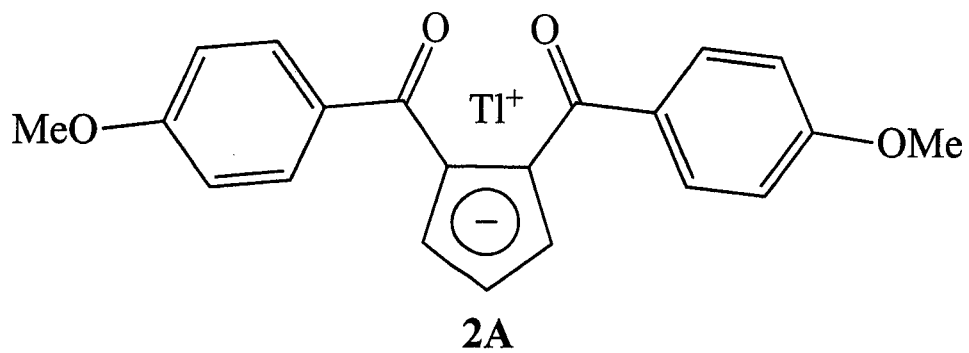


Table 1. Selected data for [Tl {1, 2-C₅H₃(CO-p-C₆H₄-OMe)₂}] (**2A**).

2A	R = PhOMe
% Yield	100%
M.P.	Decomposed
IR	1602 (C=O), 2942 (Me).

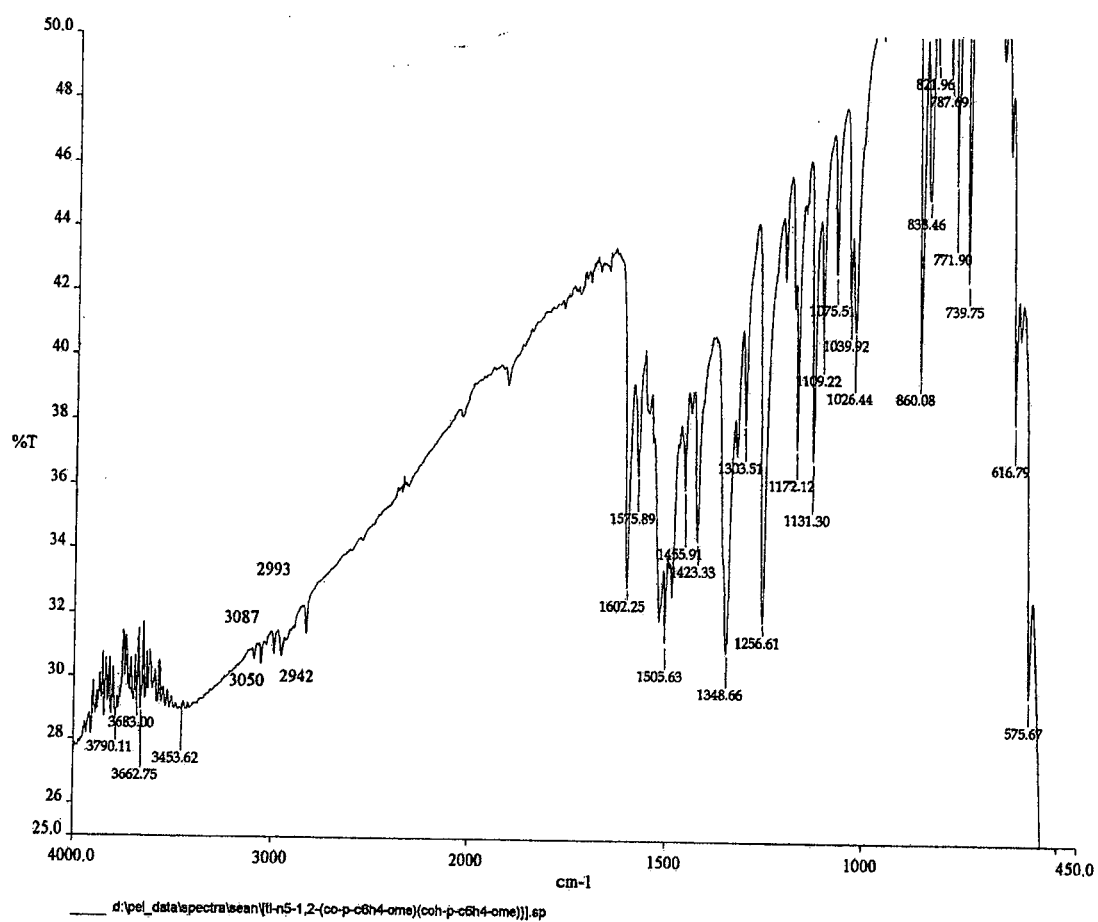
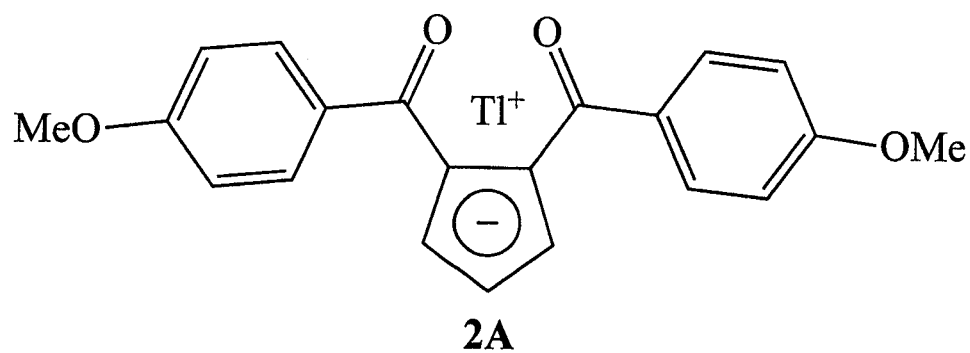


Figure 6. IR Spectrum of Tl complex 2A.

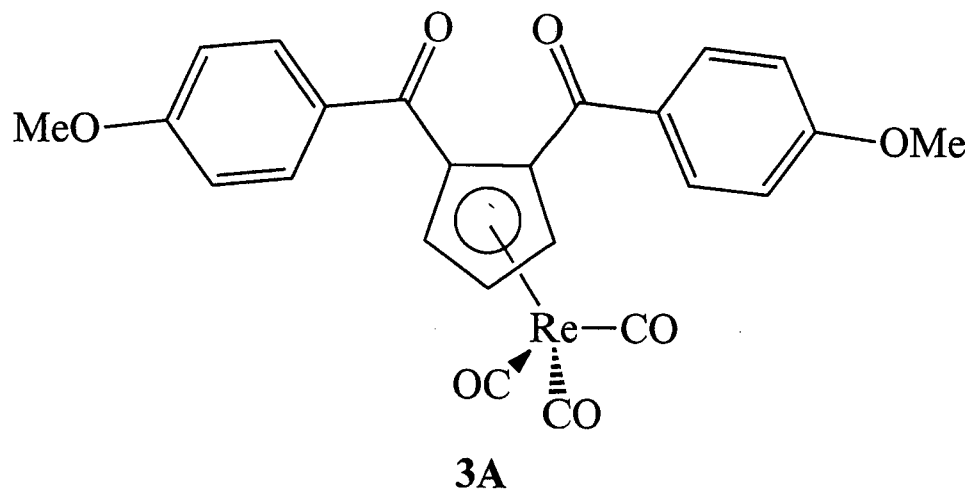


Table 2. Selected characterization data of $[\text{Re}(\text{CO})_3\{\eta^5\text{-}1,2\text{-C}_5\text{H}_3(\text{CO}\text{-}p\text{-C}_6\text{H}_4\text{-OMe})_2\}]$ (3A).

3A	R = PhOMe
% Yield	62.4%
M.P.	56-61°C
IR	1599 (C=O), 1927, 2030 (ReCO), 2964 (Me)
^{13}C NMR	δ 81.7 (CHCHCH)
	δ 124.5 (ReCO)
	δ 131.6 (Ar)
	δ 163.9 (CO)
^1H NMR	δ 5.40 (t, 1H, $^3J = 2.7$ Hz, CHCHCH)
	δ 5.85 (d, 2H, $^3J = 2.7$ Hz, CHCHCH)
	δ 6.86 (d, 4H, $^3J = 8.6$ Hz, CHCHCOMe),
	δ 7.78 (d, 4H, $^3J = 8.6$ Hz, CHCHCOMe).

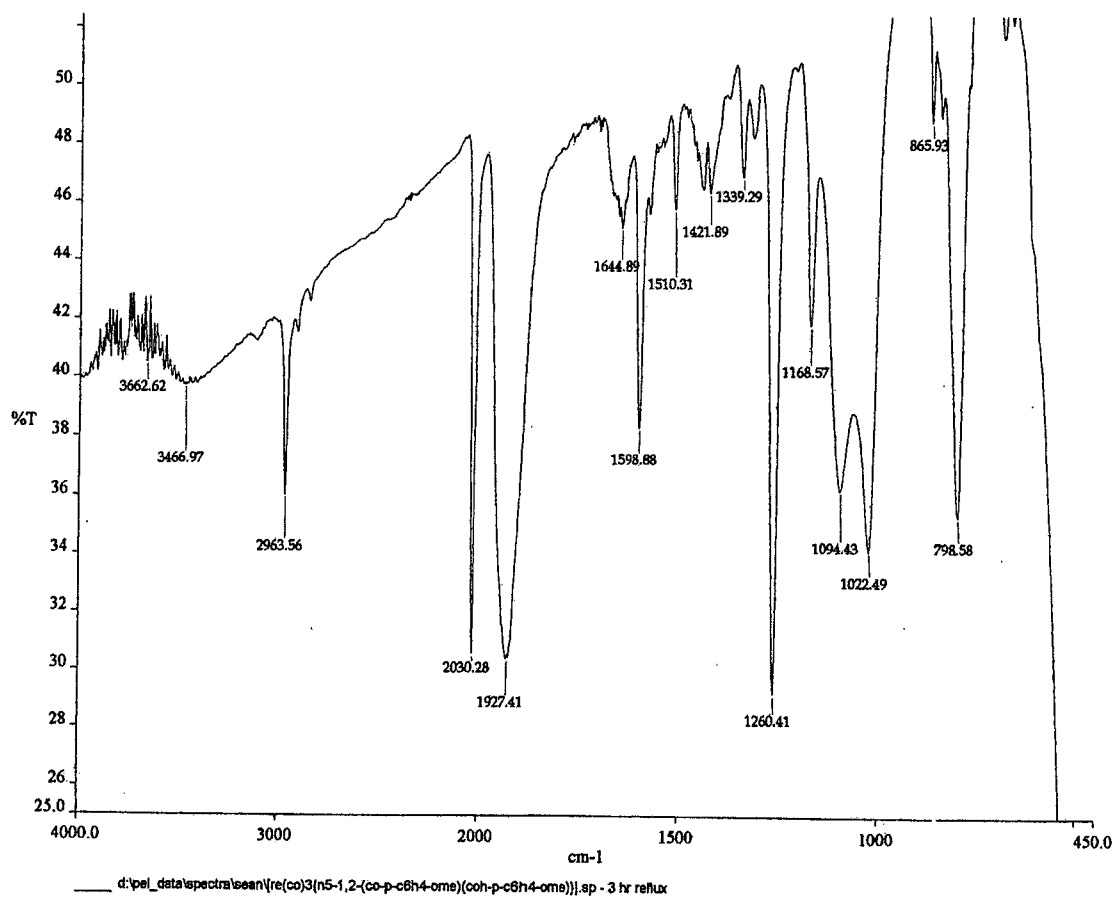
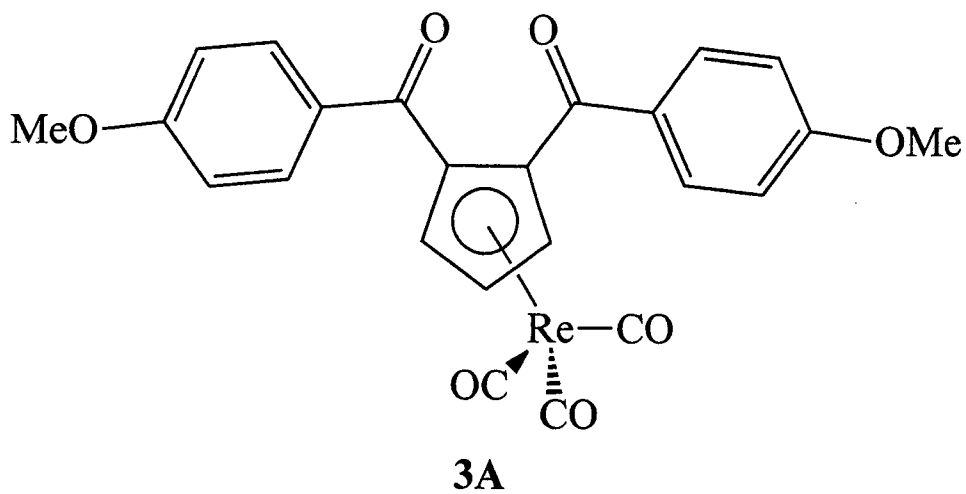


Figure 7. IR spectrum of rhenium complex 3A.

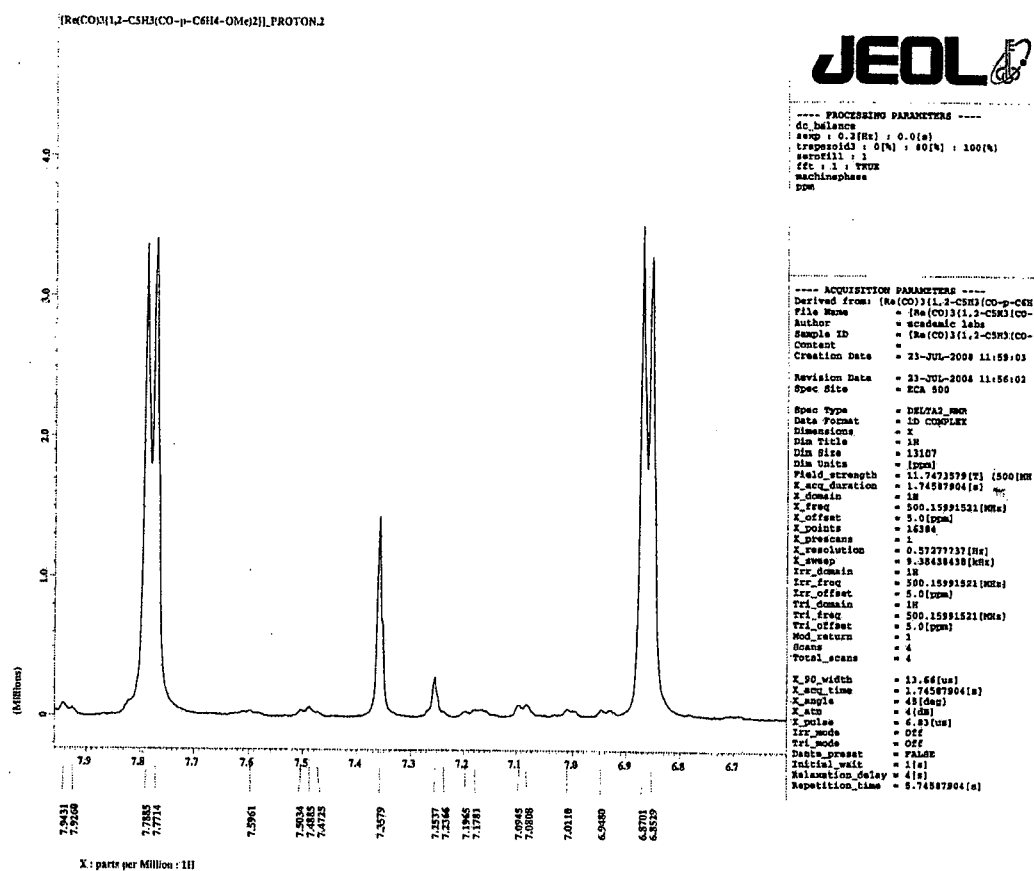
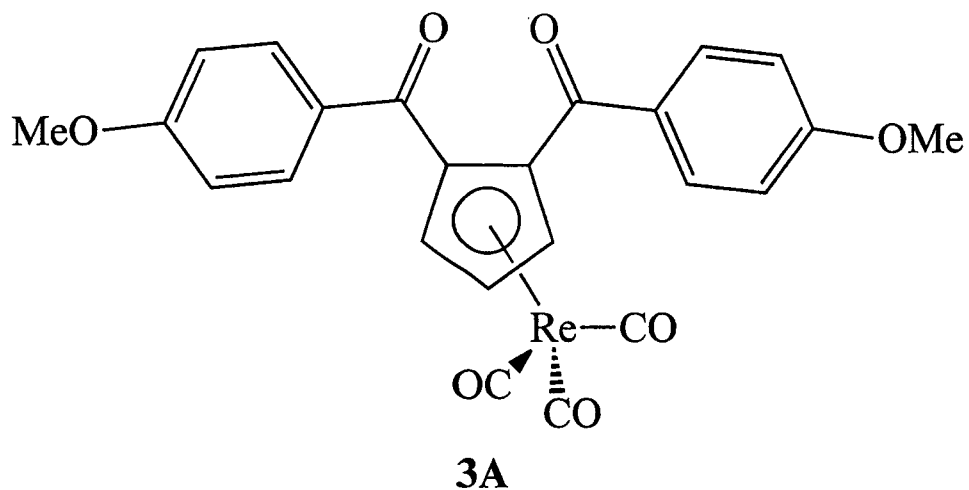


Figure 8. ¹H NMR of rhenium complex 3A.

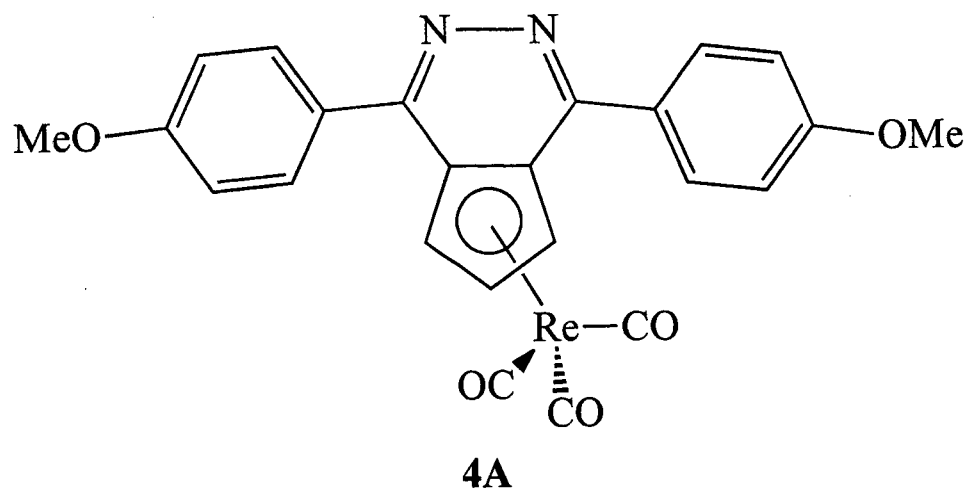


Table 3. Selected characterization of $[\text{Re}(\text{CO})_3\{\eta^5\text{-}1,2\text{-C}_5\text{H}_3(\text{C-p-C}_6\text{H}_4\text{-OMeN})(\text{C-p-C}_6\text{H}_4\text{-OMeN})\}]$ (**4A**).

4A	R = PhOMe
% Yield	24%
M.P.	56-61°C
IR	1607 (C=N), 2014 (ReCO), 2957, 2833 (Csp ³ -H)
¹³C NMR	δ 108.9(CHCHCH) δ 186.4(ReCO) δ 132.0(Ar) δ 163.9 (C=N)
¹H NMR	δ 7.48 (t, 1H, ³ J = 4.0 Hz, (CHCHCH)) δ 7.06 (d, 2H, ³ J = 4.0 Hz, (CHCHCH)) δ 7.00 (d, 4H, ³ J = 8.6 Hz, (NCCCH)) Δ 7.87 (d, 4H, ³ J = 8.6 Hz, (CHCO))

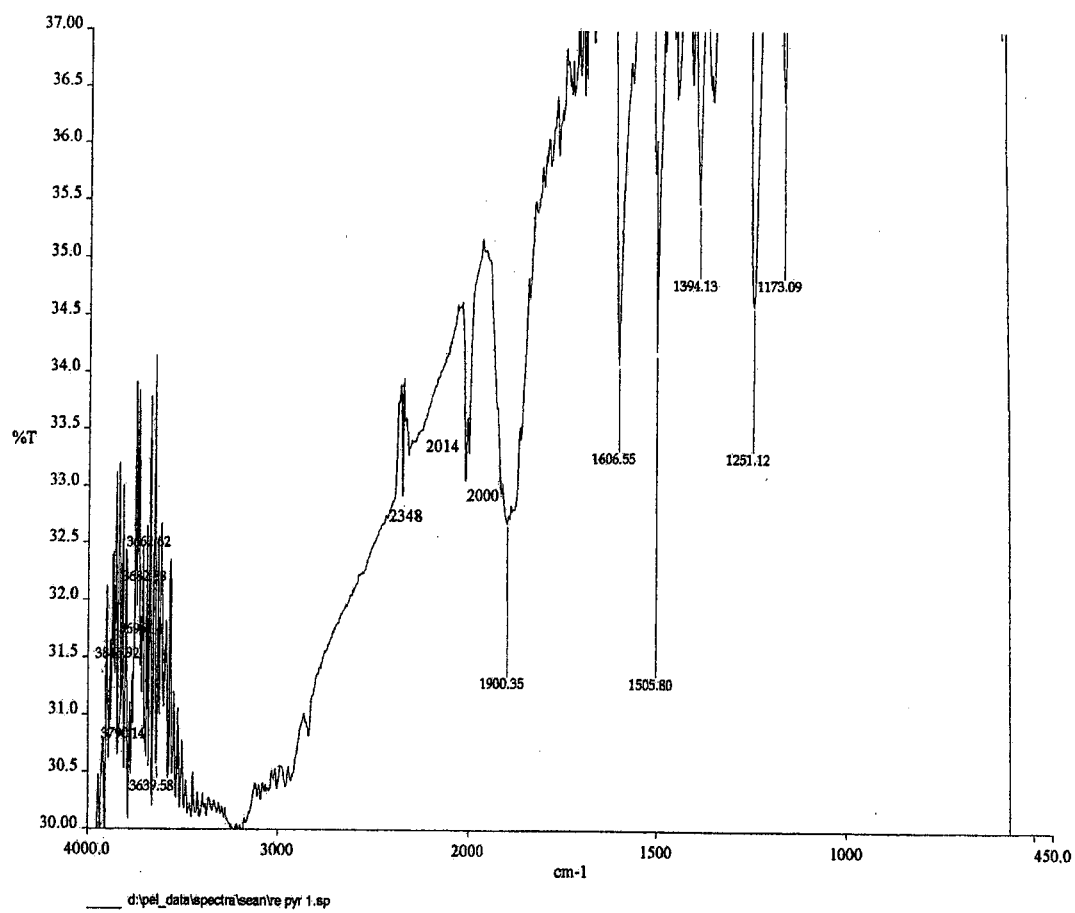
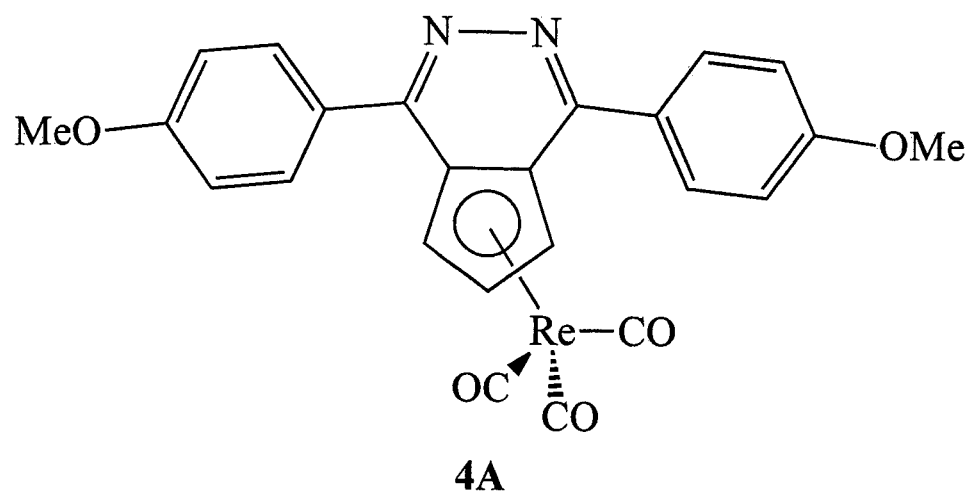


Figure 9. IR spectrum of rhenium pyridazyl complex 4A.

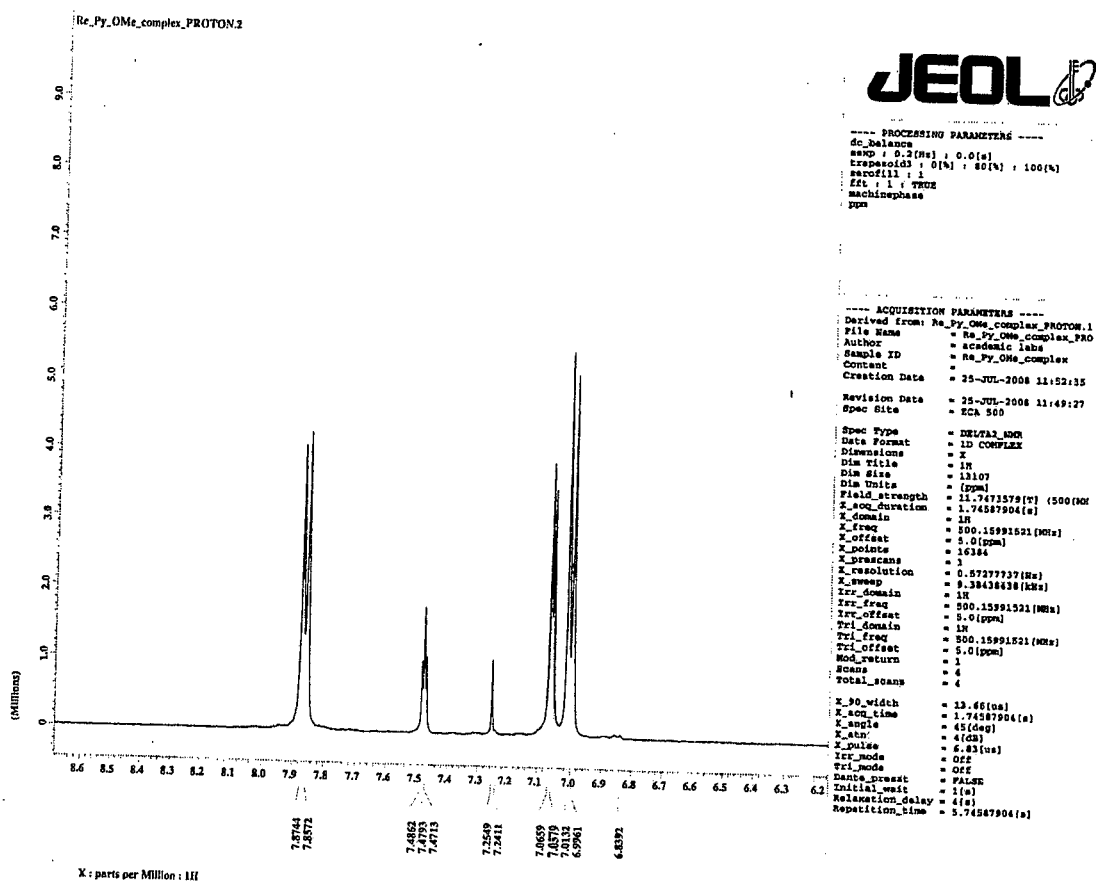
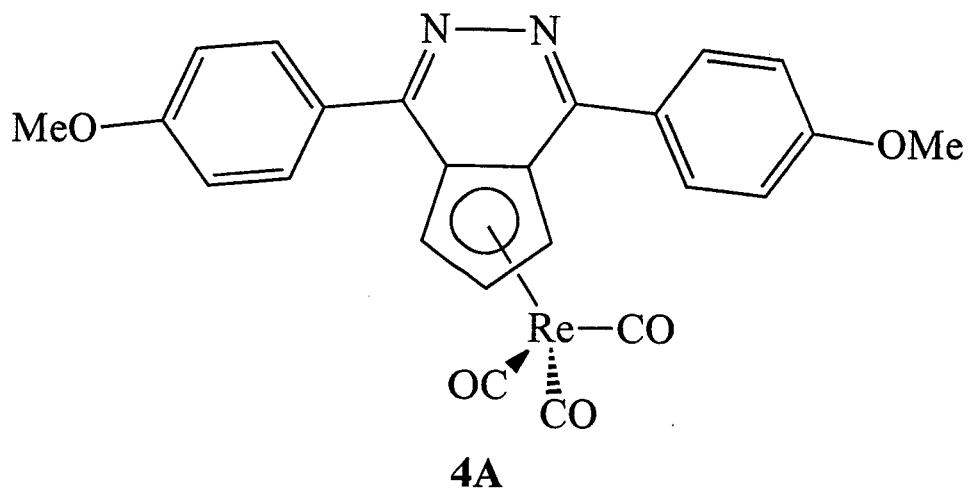


Figure 10. ^1H NMR of rhenium pyridazolyl complex 4A.

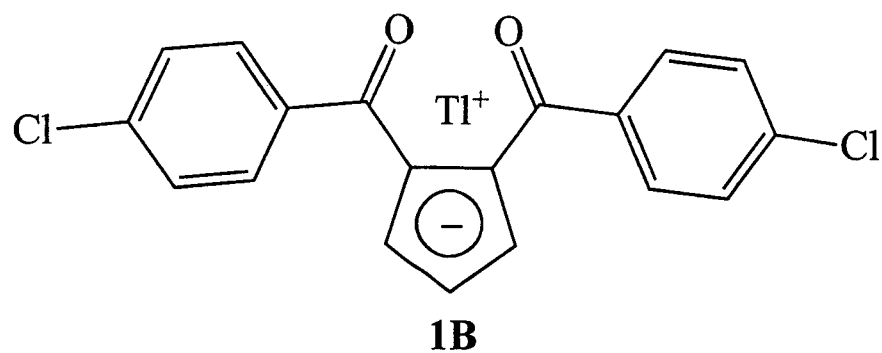


Table 4. Selected Characterization of $[\text{Ti}-1,2-\text{C}_5\text{H}_3(\text{COC}_6\text{H}_4\text{-Cl})(\text{COH}-\text{C}_6\text{H}_4\text{-Cl})]$ (**1B**).

1B	R = PhCl
% Yield	51.3%
M.P.	164°C (decomposition)
IR	1607 (C=O)
¹³C NMR	Cannot obtain due to insolubility
¹H NMR	Cannot obtain due to insolubility

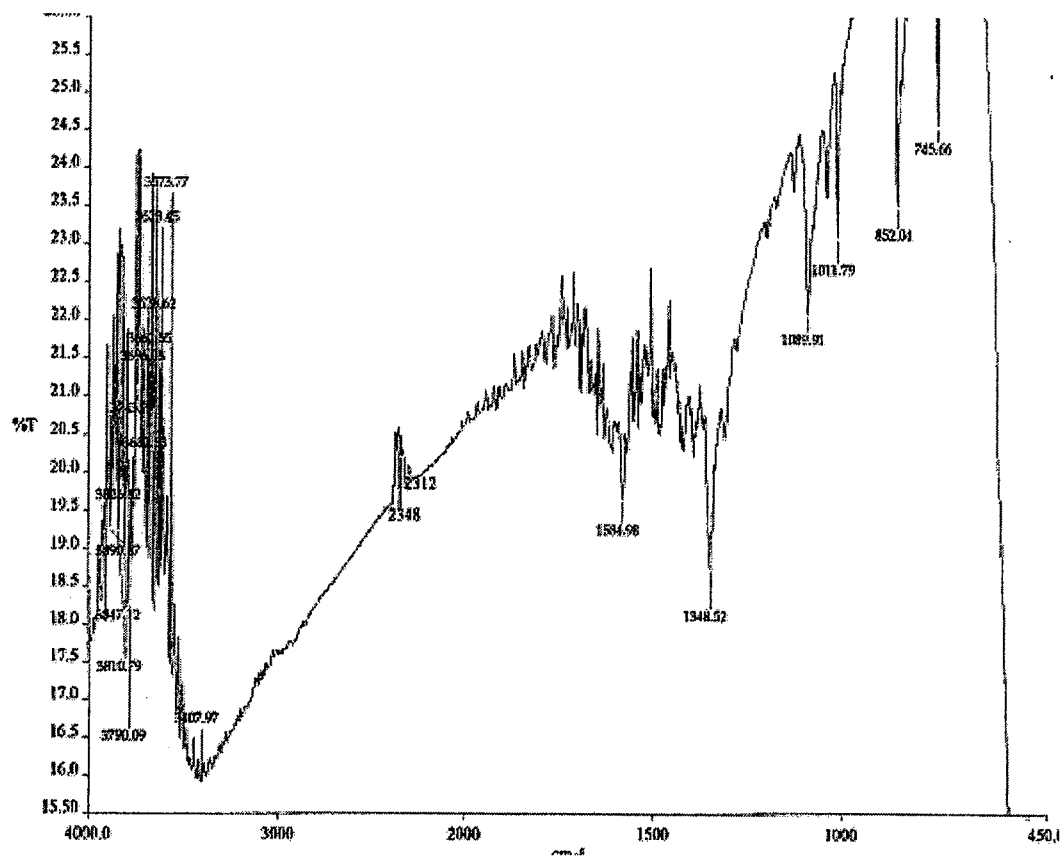
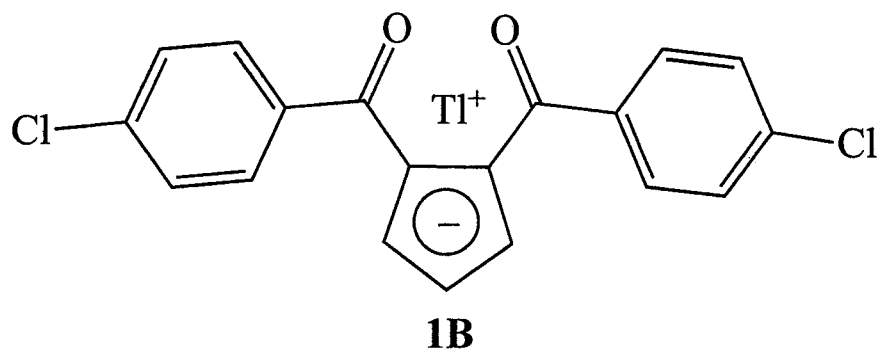


Figure 11. IR spectrum of Tl^+ complex 1B.

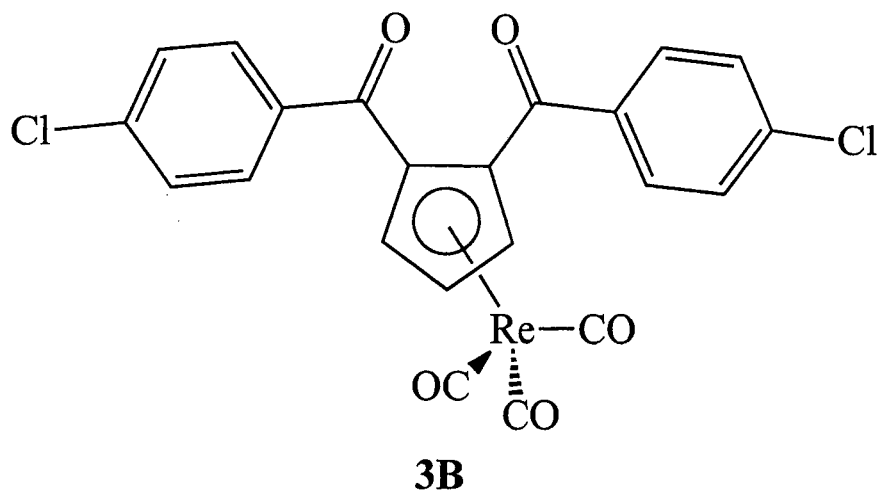


Table 5. Selected characterization of $[\text{Re}(\text{CO})_3\{\eta^5\text{-}1,2\text{-C}_5\text{H}_3(\text{CO-p-C}_6\text{H}_4\text{-Cl})_2\}]$ (**3B**).

	R = PhCl
% Yield	
M.P.	
IR	1635 (C=O), 1962, 2035 (ReCO).
^{13}C NMR	δ 82.1 (CHCHCH)
	δ 89.2 (CHCHCH)
	δ 130.2 (Ar)
	190.8 (ReCO)
^1H NMR	δ 5.44 (t, 1H, $^3J = 2.3$ Hz, CHCHCH)
	δ 5.87 (d, 2H, $^3J = 2.3$ Hz, CHCHCH)
	δ 7.39 (d, 4H, $^3J = 8.0$ Hz, CHCHCl),
	δ 7.71 (d, 4H, $^3J = 8.0$ Hz, CHCHCl).

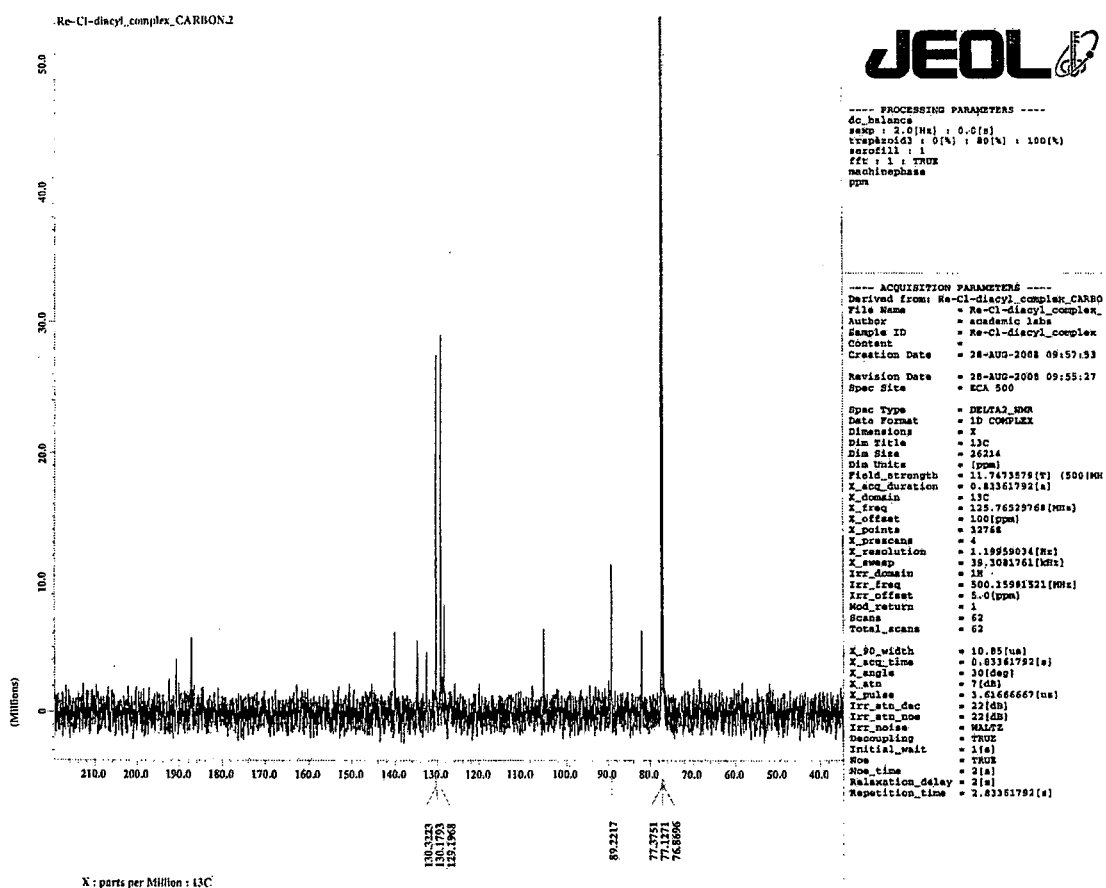
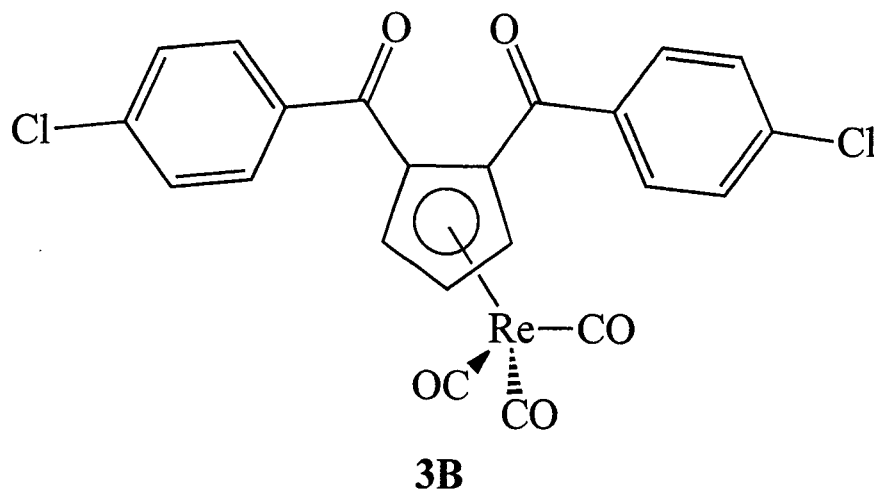


Figure 12. ^{13}C NMR of rhenium complex 3B.

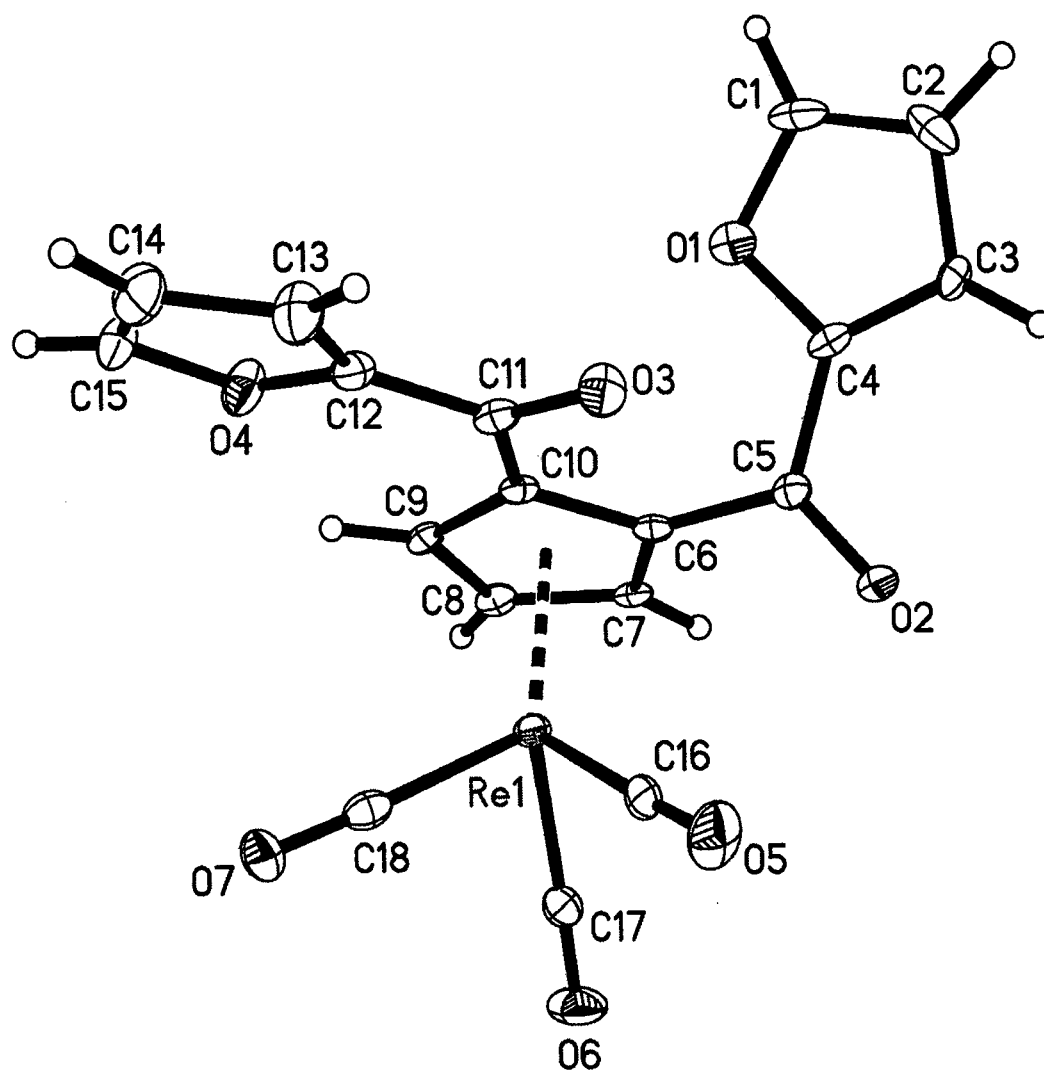


Figure 13. Molecular structure for 3C.

Table 6. Crystal data and structure refinement for **3C**.

Identification code	3C
Empirical formula	C ₁₈ H ₉ O ₇ Re
Formula weight	523.45
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P $\bar{1}$
Unit cell dimensions	a = 7.7072(1) Å b = 7.7210(1) Å c = 14.7324(3) Å α = 92.3941(7) $^\circ$ β = 96.3070(7) $^\circ$ γ = 112.9205(7) $^\circ$
Volume	799.15(2) Å ³
Z, Calculated density	2, 2.175 Mg/m ³
Absorption coefficient	7.643 mm ⁻¹
F(000)	496
Crystal size	0.21 x 0.12 x 0.10 mm
Theta range for data collection	1.40 to 25.00 $^\circ$
Limiting indices	-9 \leq h \leq 9, -9 \leq k \leq 9, -17 \leq l \leq 17
Reflections collected / unique	16433 / 2814 [R(int) = 0.0360]
Completeness to theta = 25.00	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.515 and 0.335
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2814 / 0 / 236
Goodness-of-fit on F ²	1.077
Final R indices [I > 2 σ (I)]	R1 = 0.0151, wR2 = 0.0336
R indices (all data)	R1 = 0.0163, wR2 = 0.0341
Extinction coefficient	0.00081(17)
Largest diff. peak and hole	1.393 and -0.698 e.Å ⁻³

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3C. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	Y	Z	U(eq)
Re(1)	4810(1)	4199(1)	2270(1)	12(1)
O(1)	3245(3)	8872(3)	4144(2)	21(1)
O(2)	2783(3)	4155(3)	4396(1)	17(1)
O(3)	834(3)	5967(3)	2534(2)	20(1)
O(4)	3280(3)	8162(3)	709(2)	22(1)
C(1)	2557(5)	9911(4)	4667(2)	23(1)
C(2)	1683(5)	8901(5)	5329(2)	24(1)
C(3)	1801(4)	7116(4)	5224(2)	13(1)
C(4)	2745(4)	7167(4)	4506(2)	15(1)
C(5)	3249(4)	5707(4)	4096(2)	12(1)
C(6)	4489(4)	6231(4)	3359(2)	13(1)
C(7)	6424(4)	6461(4)	3487(2)	12(1)
C(8)	7242(4)	7149(4)	2682(2)	14(1)
C(9)	5822(4)	7355(4)	2052(2)	14(1)
C(10)	4095(4)	6800(4)	2460(2)	12(1)
C(11)	2166(4)	6641(4)	2089(2)	15(1)
C(12)	1792(4)	7258(4)	1188(2)	16(1)
C(13)	128(5)	7027(5)	679(2)	25(1)
C(14)	591(5)	7822(5)	-159(2)	27(1)
C(15)	2487(5)	8470(5)	-111(2)	23(1)
C(16)	2551(5)	2088(4)	2463(2)	17(1)
O(5)	1184(4)	875(3)	2584(2)	31(1)
C(17)	6260(5)	2659(4)	2420(2)	19(1)
O(6)	7157(4)	1774(3)	2503(2)	29(1)
C(18)	4271(4)	3397(4)	984(2)	17(1)
O(7)	3938(3)	2964(3)	209(2)	23(1)

Table 8. Bond lengths [Å] and angles [deg] for **3C**.

Re(1)–C(18)	1.916(3)
Re(1)–C(16)	1.925(3)
Re(1)–C(17)	1.928(3)
Re(1)–C(10)	2.294(3)
Re(1)–C(6)	2.297(3)
Re(1)–C(9)	2.300(3)
Re(1)–C(7)	2.317(3)
Re(1)–C(8)	2.319(3)
O(1)–C(4)	1.369(4)
O(1)–C(1)	1.374(4)
O(2)–C(5)	1.226(3)
O(3)–C(11)	1.231(4)
O(4)–C(15)	1.366(4)
O(4)–C(12)	1.376(4)
C(1)–C(2)	1.346(5)
C(1)–H(1)	0.9500
C(2)–C(3)	1.419(4)
C(2)–H(2)	0.9500
C(3)–C(4)	1.342(4)
C(3)–H(3)	0.9500
C(4)–C(5)	1.457(4)
C(5)–C(6)	1.490(4)
C(6)–C(7)	1.421(4)
C(6)–C(10)	1.450(4)
C(7)–C(8)	1.429(4)
C(7)–H(7)	0.9500
C(8)–C(9)	1.417(4)
C(8)–H(8)	0.9500
C(9)–C(10)	1.439(4)
C(9)–H(9)	0.9500
C(10)–C(11)	1.483(4)
C(11)–C(12)	1.466(4)
C(12)–C(13)	1.356(4)
C(13)–C(14)	1.420(5)
C(13)–H(13)	0.9500
C(14)–C(15)	1.340(5)
C(14)–H(14)	0.9500
C(15)–H(15)	0.9500
C(16)–O(5)	1.143(4)
C(17)–O(6)	1.147(4)
C(18)–O(7)	1.148(4)
C(18)–Re(1)–C(16)	89.40(1)
C(18)–Re(1)–C(17)	88.71(13)

C(16)–Re(1)–C(17)	90.08(14)
C(18)–Re(1)–C(10)	107.05(11)
C(16)–Re(1)–C(10)	105.17(12)
C(17)–Re(1)–C(10)	157.87(12)
C(18)–Re(1)–C(6)	143.23(11)
C(16)–Re(1)–C(6)	94.65(12)
C(17)–Re(1)–C(6)	127.74(12)
C(10)–Re(1)–C(6)	36.81(10)
C(18)–Re(1)–C(9)	94.04(12)
C(16)–Re(1)–C(9)	140.38(12)
C(17)–Re(1)–C(9)	129.40(12)
C(10)–Re(1)–C(9)	36.51(10)
C(6)–Re(1)–C(9)	60.69(11)
C(18)–Re(1)–C(7)	151.06(12)
C(16)–Re(1)–C(7)	118.43(12)
C(17)–Re(1)–C(7)	98.38(11)
C(10)–Re(1)–C(7)	60.39(10)
C(6)–Re(1)–C(7)	35.88(10)
C(9)–Re(1)–C(7)	59.90(10)
C(18)–Re(1)–C(8)	115.35(12)
C(16)–Re(1)–C(8)	153.56(12)
C(17)–Re(1)–C(8)	99.17(12)
C(10)–Re(1)–C(8)	60.31(10)
C(6)–Re(1)–C(8)	60.16(11)
C(9)–Re(1)–C(8)	35.72(10)
C(4)–O(1)–C(1)	105.6(3)
C(15)–O(4)–C(12)	106.2(3)
C(2)–C(1)–O(1)	110.2(3)
C(2)–C(1)–H(1)	124.9
O(1)–C(1)–H(1)	124.9
C(1)–C(2)–C(3)	107.0(3)
C(1)–C(2)–H(2)	126.5
C(3)–C(2)–H(2)	126.5
C(4)–C(3)–C(2)	106.1(3)
C(4)–C(3)–H(3)	127.0
C(2)–C(3)–H(3)	127.0
C(3)–C(4)–O(1)	111.2(3)
C(3)–C(4)–C(5)	129.2(3)
O(1)–C(4)–C(5)	119.7(3)
O(2)–C(5)–C(4)	120.9(3)
O(2)–C(5)–C(6)	121.6(3)
C(4)–C(5)–C(6)	117.4(3)
C(7)–C(6)–C(10)	107.8(3)
C(7)–C(6)–C(5)	123.0(3)
C(10)–C(6)–C(5)	128.8(3)

C(7)–C(6)–Re(1)	72.81(16)
C(10)–C(6)–Re(1)	71.49(15)
C(5)–C(6)–Re(1)	126.64(19)
C(6)–C(7)–C(8)	108.5(3)
C(6)–C(7)–Re(1)	71.31(16)
C(8)–C(7)–Re(1)	72.14(16)
C(6)–C(7)–H(7)	125.7
C(8)–C(7)–H(7)	125.7
Re(1)–C(7)–H(7)	122.5
C(9)–C(8)–C(7)	108.2(3)
C(9)–C(8)–Re(1)	71.37(16)
C(7)–C(8)–Re(1)	71.94(16)
C(9)–C(8)–H(8)	125.9
C(7)–C(8)–H(8)	125.9
Re(1)–C(8)–H(8)	122.4
C(8)–C(9)–C(10)	108.5(3)
C(8)–C(9)–Re(1)	72.91(16)
C(10)–C(9)–Re(1)	71.55(16)
C(8)–C(9)–H(9)	125.7
C(10)–C(9)–H(9)	125.7
Re(1)–C(9)–H(9)	121.5
C(9)–C(10)–C(6)	107.0(3)
C(9)–C(10)–C(11)	131.1(3)
C(6)–C(10)–C(11)	121.7(3)
C(9)–C(10)–Re(1)	71.94(16)
C(6)–C(10)–Re(1)	71.70(15)
C(11)–C(10)–Re(1)	118.37(18)
O(3)–C(11)–C(12)	118.6(3)
O(3)–C(11)–C(10)	120.2(3)
C(12)–C(11)–C(10)	121.3(3)
C(13)–C(12)–O(4)	109.6(3)
C(13)–C(12)–C(11)	130.5(3)
O(4)–C(12)–C(11)	119.8(3)
C(12)–C(13)–C(14)	106.7(3)
C(12)–C(13)–H(13)	126.6
C(14)–C(13)–H(13)	126.6
C(15)–C(14)–C(13)	106.6(3)
C(15)–C(14)–H(14)	126.7
C(13)–C(14)–H(14)	126.7
C(14)–C(15)–O(4)	110.8(3)
C(14)–C(15)–H(15)	124.6
O(4)–C(15)–H(15)	124.6
O(5)–C(16)–Re(1)	177.8(3)
O(6)–C(17)–Re(1)	178.5(3)
O(7)–C(18)–Re(1)	178.0(3)

Table 9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3C.

The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$.

Atom	U11	U22	U33	U23	U13	U12
Re(1)	14(1)	10(1)	12(1)	1(1)	1(1)	5(1)
O(1)	24(1)	19(1)	23(1)	3(1)	4(1)	10(1)
O(2)	21(1)	13(1)	20(1)	4(1)	6(1)	9(1)
O(3)	25(1)	21(1)	4(1)	3(1)	9(1)	15(1)
O(4)	19(1)	28(1)	21(1)	10(1)	2(1)	10(1)
C(1)	27(2)	14(2)	28(2)	-4(1)	-5(2)	14(2)
C(2)	21(2)	37(2)	20(2)	-5(2)	4(1)	17(2)
C(3)	9(2)	13(2)	17(2)	6(1)	3(1)	2(1)
C(4)	15(2)	10(1)	18(2)	3(1)	-1(1)	6(1)
C(5)	12(2)	13(2)	12(2)	1(1)	-2(1)	6(1)
C(6)	16(2)	7(1)	15(2)	-2(1)	2(1)	5(1)
C(7)	14(2)	8(1)	14(2)	-1(1)	-2(1)	6(1)
C(8)	12(2)	7(1)	18(2)	-2(1)	-1(1)	1(1)
C(9)	17(2)	7(1)	17(2)	3(1)	4(1)	4(1)
C(10)	13(2)	8(1)	14(2)	1(1)	2(1)	5(1)
C(11)	16(2)	10(1)	18(2)	1(1)	0(1)	6(1)
C(12)	17(2)	15(2)	20(2)	3(1)	3(1)	8(1)
C(13)	19(2)	34(2)	22(2)	6(2)	1(1)	12(2)
C(14)	27(2)	34(2)	21(2)	4(2)	-3(2)	15(2)
C(15)	31(2)	24(2)	16(2)	8(1)	3(2)	13(2)
C(16)	24(2)	16(2)	9(2)	-1(1)	0(1)	7(2)
O(5)	30(2)	20(1)	29(1)	4(1)	6(1)	-4(1)
C(17)	25(2)	16(2)	13(2)	-2(1)	0(1)	7(2)
O(6)	39(2)	26(1)	30(1)	-3(1)	-5(1)	24(1)
C(18)	13(2)	12(2)	25(2)	3(1)	2(1)	4(1)
O(7)	29(1)	25(1)	14(1)	-2(1)	0(1)	11(1)

Table 10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **3C**.

Atom	x	Y	z	U(eq)
H(1)	2681	11162	4575	27
H(2)	1097	9306	5781	29
H(3)	1311	6093	5589	16
H(7)	7065	6200	4018	14
H(8)	7421	2585	16	8518
H(9)	5984	7786	1461	16
H(13)	-1109	6446	850	29
H(14)	-274	7882	-656	32
H(15)	3185	9063	-584	28

Table 11. Torsion angles [deg] for 3C.

C(4)–O(1)–C(1)–C(2)	0.5(4)
O(1)–C(1)–C(2)–C(3)	–0.4(4)
C(1)–C(2)–C(3)–C(4)	0.1(4)
C(2)–C(3)–C(4)–O(1)	0.2(3)
C(2)–C(3)–C(4)–C(5)	–179.5(3)
C(1)–O(1)–C(4)–C(3)	–0.4(3)
C(1)–O(1)–C(4)–C(5)	179.3(3)
C(3)–C(4)–C(5)–O(2)	1.1(5)
O(1)–C(4)–C(5)–O(2)	–178.5(3)
C(3)–C(4)–C(5)–C(6)	–173.6(3)
O(1)–C(4)–C(5)–C(6)	6.7(4)
O(2)–C(5)–C(6)–C(7)	–66.6(4)
C(4)–C(5)–C(6)–C(7)	108.1(3)
O(2)–C(5)–C(6)–C(10)	121.1(3)
C(4)–C(5)–C(6)–C(10)	–64.1(4)
O(2)–C(5)–C(6)–Re(1)	25.9(4)
C(4)–C(5)–C(6)–Re(1)	–159.3(2)
C(18)–Re(1)–C(6)–C(7)	–130.1(2)
C(16)–Re(1)–C(6)–C(7)	134.63(18)
C(17)–Re(1)–C(6)–C(7)	40.9(2)
C(10)–Re(1)–C(6)–C(7)	–116.1(2)
C(9)–Re(1)–C(6)–C(7)	–78.15(18)
C(8)–Re(1)–C(6)–C(7)	–36.87(17)
C(18)–Re(1)–C(6)–C(10)	–14.0(3)
C(16)–Re(1)–C(6)–C(10)	–109.24(18)
C(17)–Re(1)–C(6)–C(10)	157.05(18)
C(9)–Re(1)–C(6)–C(10)	37.97(17)
C(7)–Re(1)–C(6)–C(10)	116.1(2)
C(8)–Re(1)–C(6)–C(10)	79.26(18)
C(18)–Re(1)–C(6)–C(5)	111.1(3)
C(16)–Re(1)–C(6)–C(5)	15.9(3)
C(17)–Re(1)–C(6)–C(5)	–77.8(3)
C(10)–Re(1)–C(6)–C(5)	125.1(3)
C(9)–Re(1)–C(6)–C(5)	163.1(3)
C(7)–Re(1)–C(6)–C(5)	–118.8(3)
C(8)–Re(1)–C(6)–C(5)	–155.6(3)
C(10)–C(6)–C(7)–C(8)	–0.4(3)
C(5)–C(6)–C(7)–C(8)	–174.1(2)
Re(1)–C(6)–C(7)–C(8)	62.95(19)
C(10)–C(6)–C(7)–Re(1)	–63.38(19)
C(5)–C(6)–C(7)–Re(1)	123.0(3)
C(18)–Re(1)–C(7)–C(6)	108.9(3)
C(16)–Re(1)–C(7)–C(6)	–53.8(2)

C(17)-Re(1)-C(7)-C(6)	-148.42(19)
C(10)-Re(1)-C(7)-C(6)	38.23(17)
C(9)-Re(1)-C(7)-C(6)	80.56(18)
C(8)-Re(1)-C(7)-C(6)	117.5(2)
C(18)-Re(1)-C(7)-C(8)	-8.6(3)
C(16)-Re(1)-C(7)-C(8)	-171.24(17)
C(17)-Re(1)-C(7)-C(8)	94.09(19)
C(10)-Re(1)-C(7)-C(8)	-79.25(18)
C(6)-Re(1)-C(7)-C(8)	-117.5(2)
C(9)-Re(1)-C(7)-C(8)	-36.92(17)
C(6)-C(7)-C(8)-C(9)	0.2(3)
Re(1)-C(7)-C(8)-C(9)	62.59(19)
C(6)-C(7)-C(8)-Re(1)	-62.42(19)
C(18)-Re(1)-C(8)-C(9)	58.3(2)
C(16)-Re(1)-C(8)-C(9)	-99.6(3)
C(17)-Re(1)-C(8)-C(9)	151.25(19)
C(10)-Re(1)-C(8)-C(9)	-37.62(17)
C(6)-Re(1)-C(8)-C(9)	-80.28(19)
C(7)-Re(1)-C(8)-C(9)	-117.1(3)
C(18)-Re(1)-C(8)-C(7)	175.42(17)
C(16)-Re(1)-C(8)-C(7)	17.5(3)
C(17)-Re(1)-C(8)-C(7)	-91.64(18)
C(10)-Re(1)-C(8)-C(7)	79.48(18)
C(6)-Re(1)-C(8)-C(7)	36.83(16)
C(9)-Re(1)-C(8)-C(7)	117.1(3)
C(7)-C(8)-C(9)-C(10)	0.2(3)
Re(1)-C(8)-C(9)-C(10)	63.11(19)
C(7)-C(8)-C(9)-Re(1)	-62.95(19)
C(18)-Re(1)-C(9)-C(8)	-129.56(19)
C(16)-Re(1)-C(9)-C(8)	136.5(2)
C(17)-Re(1)-C(9)-C(8)	-37.9(2)
C(10)-Re(1)-C(9)-C(8)	116.9(3)
C(6)-Re(1)-C(9)-C(8)	78.65(19)
C(7)-Re(1)-C(9)-C(8)	37.12(17)
C(18)-Re(1)-C(9)-C(10)	113.50(18)
C(16)-Re(1)-C(9)-C(10)	19.5(3)
C(17)-Re(1)-C(9)-C(10)	-154.85(18)
C(6)-Re(1)-C(9)-C(10)	-38.29(17)
C(7)-Re(1)-C(9)-C(10)	-79.82(18)
C(8)-Re(1)-C(9)-C(10)	-116.9(3)
C(8)-C(9)-C(10)-C(6)	-0.4(3)
Re(1)-C(9)-C(10)-C(6)	63.56(18)
C(8)-C(9)-C(10)-C(11)	-176.2(3)
Re(1)-C(9)-C(10)-C(11)	-112.3(3)
C(8)-C(9)-C(10)-Re(1)	-63.99(19)

C(7)-C(6)-C(10)-C(9)	0.5(3)
C(5)-C(6)-C(10)-C(9)	173.7(3)
Re(1)-C(6)-C(10)-C(9)	-63.72(19)
C(7)-C(6)-C(10)-C(11)	176.8(2)
C(5)-C(6)-C(10)-C(11)	-10.0(4)
Re(1)-C(6)-C(10)-C(11)	112.6(2)
C(7)-C(6)-C(10)-Re(1)	64.24(19)
C(5)-C(6)-C(10)-Re(1)	-122.6(3)
C(18)-Re(1)-C(10)-C(9)	-73.11(19)
C(16)-Re(1)-C(10)-C(9)	-167.24(18)
C(17)-Re(1)-C(10)-C(9)	60.6(4)
C(6)-Re(1)-C(10)-C(9)	115.6(2)
C(7)-Re(1)-C(10)-C(9)	78.36(18)
C(8)-Re(1)-C(10)-C(9)	36.80(17)
C(18)-Re(1)-C(10)-C(6)	171.28(17)
C(16)-Re(1)-C(10)-C(6)	77.16(19)
C(17)-Re(1)-C(10)-C(6)	-55.0(4)
C(9)-Re(1)-C(10)-C(6)	-115.6(2)
C(7)-Re(1)-C(10)-C(6)	-37.25(17)
C(8)-Re(1)-C(10)-C(6)	-78.80(18)
C(18)-Re(1)-C(10)-C(11)	54.5(3)
C(16)-Re(1)-C(10)-C(11)	-39.6(2)
C(17)-Re(1)-C(10)-C(11)	-171.7(3)
C(6)-Re(1)-C(10)-C(11)	-116.8(3)
C(9)-Re(1)-C(10)-C(11)	127.6(3)
C(7)-Re(1)-C(10)-C(11)	-154.0(3)
C(8)-Re(1)-C(10)-C(11)	164.4(3)
C(9)-C(10)-C(11)-O(3)	173.3(3)
C(6)-C(10)-C(11)-O(3)	-2.0(4)
Re(1)-C(10)-C(11)-O(3)	83.1(3)
C(9)-C(10)-C(11)-C(12)	-6.0(5)
C(6)-C(10)-C(11)-C(12)	178.7(3)
Re(1)-C(10)-C(11)-C(12)	-96.2(3)
C(15)-O(4)-C(12)-C(13)	-0.4(3)
C(15)-O(4)-C(12)-C(11)	177.0(3)
O(3)-C(11)-C(12)-C(13)	-8.6(5)
C(10)-C(11)-C(12)-C(13)	170.7(3)
O(3)-C(11)-C(12)-O(4)	174.5(3)
C(10)-C(11)-C(12)-O(4)	-6.1(4)
O(4)-C(12)-C(13)-C(14)	0.0(4)
C(11)-C(12)-C(13)-C(14)	-177.0(3)
C(12)-C(13)-C(14)-C(15)	0.4(4)
C(13)-C(14)-C(15)-O(4)	-0.7(4)
C(12)-O(4)-C(15)-C(14)	0.7(4)
C(18)-Re(1)-C(16)-O(5)	-110(7)

C(17)-Re(1)-C(16)-O(5)	161(7)
C(10)-Re(1)-C(16)-O(5)	-2(7)
C(6)-Re(1)-C(16)-O(5)	34(7)
C(9)-Re(1)-C(16)-O(5)	-14(7)
C(7)-Re(1)-C(16)-O(5)	62(7)
C(8)-Re(1)-C(16)-O(5)	50(7)
C(18)-Re(1)-C(17)-O(6)	81(11)
C(16)-Re(1)-C(17)-O(6)	170(100)
C(10)-Re(1)-C(17)-O(6)	-56(11)
C(6)-Re(1)-C(17)-O(6)	-94(11)
C(9)-Re(1)-C(17)-O(6)	-14(11)
C(7)-Re(1)-C(17)-O(6)	-71(11)
C(8)-Re(1)-C(17)-O(6)	-35(11)
C(16)-Re(1)-C(18)-O(7)	112(8)
C(17)-Re(1)-C(18)-O(7)	-158(8)
C(10)-Re(1)-C(18)-O(7)	6(8)
C(6)-Re(1)-C(18)-O(7)	15(8)
C(9)-Re(1)-C(18)-O(7)	-29(8)
C(7)-Re(1)-C(18)-O(7)	-53(8)
C(8)-Re(1)-C(18)-O(7)	-59(8)

IV. CONCLUSIONS

Fulvene 1 was synthesized in higher yields and greater purity than what was previously reported by Snyder and Tice. Thallium 2C salt was unusually soluble in DMSO-d₆ which allowed for ¹H and ¹³C NMR characterization. TICp salts are well-known to be insoluble in NMR solvents. Additionally, it is difficult to obtain the M⁺ for TICp salts. Thallium compound 2C displayed a strong M⁺ signal in its MS.

Pyridazyl complexes [Re(CO)₃{η⁵-1,2-C₅H₃(RN)₂] (R = C₆H₄OMe, C₆H₄Cl, and C₄H₃O) are red in color and were synthesized by a series of organic and organometallic reactions. The percent yields for the products 4A–C were moderately good having a range between 24.0–76.0%. Their overall stability is low as they degrade in the presence of air over the course of 3-4 days.

¹H and ¹³C NMR analysis confirmed the structures for 3A–C and 4A–C complexes. Single-crystal x-ray analysis also confirmed the molecular structure for diacyl complex 3C. IR spectroscopy confirmed the presence of carbonyls (3A–C; 4A–C) and imines (4A–C); where applicable.

Diacyl complexes 3A-C were relatively easy to synthesize and each proved to be stable to air and moisture over the course of several days.

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