Synthesis and Characterization of (*o*-Amidobenzenethiolato)indium Complexes as Green Redox Active Catalysts

by

Michael Mosher

A thesis submitted to the
Department of Chemistry and Biochemistry
Mount Allison University
in partial fulfillment of the requirements for the
Bachelor of Science degree with Honours
April, 2020

Thesis Committee

Supervisor

Dr. Glen Briand
Associate Professor of Chemistry

Reviewer

Dr. Greg Sandala
Assistant Professor of Chemistry
Acting Director, Office of Research Services

Table of Contents

Acknowledgments

I would like to express my deep gratitude to Dr. Briand for his patience, guidance, and encouragement throughout this research project. My improvement as a student can be greatly attributed to working in the Metalheads lab and I wanted to thank you so much for this. I would like to also thank Dr. Sandala for his assistance as a second reader for my thesis. My grateful thanks are also extended to Dan Durant, Philip Cormier, Eva Zhou and Susan Wheaton for their technical training and mentorship throughout my time at Mount Allison.

I would like to thank the Department of Chemistry and Biochemistry at Mount Allison University for providing me with the opportunity to conduct research in my undergraduate degree. I would also like to say thank you to my fellow lab mates Viv, Alex, Sam and Cyler for their assistance and company in the lab. Best of luck with your future endeavors.

Finally, I would like to thank my friends and family for their continuous love and support throughout my years at Mount Allison. The things you have all done for me will not be forgotten and I truly appreciate everything you have all done for me.

Kind regards,

Mike

List of Figures

List of Schemes

List of Spectra in Appendix

Glossary of Abbreviations and Symbols

amu – atomic mass units

cm – centimeter

d – doublet

g – grams

h – hour

Me – methyl

Mes – mesityl

mL – milliliter

M – molarity

mmol – millimole

mol – mole

m – multiplet

NMR – nuclear magnetic resonance

ppm – parts per million

py – pyridine

s – singlet

t – triplet

THF – tetrahydrofuran

$^{\circ}C$ – degrees Celsius

^{1}H – hydrogen-1 nuclei

^{13}C – carbon-13 nuclei

Abstract

Green Chemistry is an area of interest currently receiving significant attention from both industrial and academic communities. This area aims to develop chemical products and processes that reduce or eliminate the use and generation of substances hazardous to human health and the environment. Designing environmentally benign catalysts capable of performing redox reactions has been at the centre of Green Chemistry initiatives. Traditional catalysis is dominated by precious metals, such as palladium and platinum, due to their ability to achieve variable oxidation states and perform redox chemistry. However, significant environmental concerns exist with their use and disposal. Indium could offer an appealing alternative to traditional precious metals due to its environmentally benign nature and tolerance towards various functional groups. By incorporating a redox active ligand, the possibility to create a benign, base-metal-centered redox active catalyst exists. To this end, the objectives of this research project are to synthesize and characterize a series of molecular indium complexes incorporating a redox active amidobenzenethiolate (abt) ligand and test their redox capabilities through use of cyclic voltammetry. The target compound MeIn(abt) (**1**) has been successfully synthesized via a hydrocarbon elimination reaction of Me_3In and $H_2(abt)$ and spectroscopically characterized. Synthesis of organoindium reactants Ph_3In and Mes_3In has required modification of literature procedures, with the latter being successfully isolated in a yield of 47%. Significant progress has been made on the synthesis of MesIn(abt) (**3**). Further work is required in order to isolate crystals of target compounds for X-ray crystallography and subsequently test their redox properties.

1. Introduction

1.1. Green Chemistry

Green Chemistry initiatives are currently receiving significant attention from both industrial and academic activities. Green Chemistry can be defined as the invention, design, development and application of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and environment.[1] Not only does Green Chemistry aim to be economically beneficial for modern day industry by reducing energy demands and the cost of waste treatment, it also addresses fundamental scientific challenges of protecting human health and the environment.[2]

The foundation of Green Chemistry originates from concern of the environmental consequences of chemical synthesis. Chemical synthesis has applications in pharmaceuticals, electronics, petrochemicals amongst other industries, yet these processes can have a negative impact on the sustainability and toxicity of the environment. An initiative beginning in 1990 helped create a modus operandi for addressing pollution in an innovative way; a defining moment in this period was ratification of the Pollution Prevention Act by the United States, which sought to minimize environmental harm caused directly or indirectly from chemical synthesis.[1] The waste prevention movement sparked by this formative legislature has led to the creation of scientific journals such as *Green Chemistry* and *Green Chemistry Letters and Reviews*, which focus on chemical research aimed at minimizing environmental waste from chemical processes.[3] As a multifaceted field, Green Chemistry has sparked the development of novel synthetic methodologies which can maximize desired products while minimizing by-products and waste.[1]

The Pollution Prevention Act paved the way for researchers Paul Anastas and John Warner to coin the term 'Green Chemistry' and create the 12 principles of Green Chemistry (Figure 1). Developments made by these environmental pioneers have led to sustainable development now being recognized by governments, industry, and the public as necessary for achieving societal, economic and environmental goals.[2] The principles of Green Chemistry are meant to work as one all-encompassing unit when conducting chemical synthesis and must be carefully considered early in a given process if truly sustainable and environmentally friendly chemistry is desired.

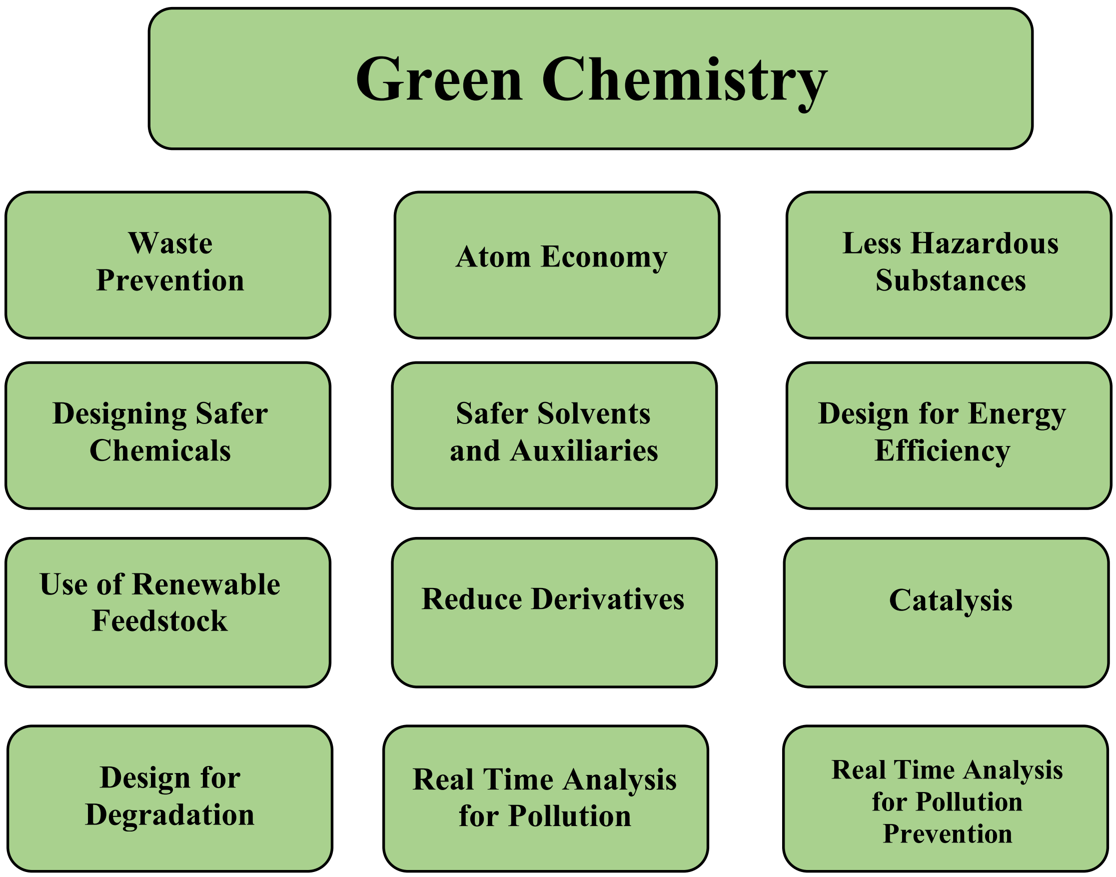


Figure 1. The 12 Principles of Green Chemistry as stated by Anastas and Warner.[2]

Although significant improvements within chemical syntheses have surfaced since the first Green Chemistry initiatives, estimates provided by the United Nations Environment Programme indicate that more than 400 million tonnes of hazardous waste are produced worldwide every year.[4] It is established universally that the best way to address hazardous waste is to prevent its formation in the first place.[5] With this in mind, there has been considerable progress made in redesigning industrial processes that minimize the generation of hazardous waste, are economically feasible, and are 100% sustainable through the practices of Green Chemistry.

1.2.History of Catalysis

One principle of Green Chemistry that has led to incredible advances in global chemical synthesis is catalysis. Catalysis has been an ever-improving area of research for centuries since its discovery by Swedish chemist Jöns Berzelius. Berzelius defined a catalyst as any substance present in a reaction that increases the rate of a chemical reaction without itself being consumed.[6] The benefit of catalyst regeneration in reactions, combined with causing a decrease in the required energy input for reaction, lowering of environmental impact, and increasing of the financial benefit to industry makes catalysis an extremely valuable branch of chemical research today. The benefits of catalysis have proven to be extremely economical, so much so that 90% of all commercial chemicals are produced by methods that involve at least one catalytic step.[7]

Homogenous catalysis predominantly consists of transition metal compounds.[6] The extensive use of homogenous catalysts can be attributed to a combination of their efficiency, reactivity, and predictability for both activity and selectivity in synthesis. Transition metals have the ability to withstand oxidation state changes through interactions of d-orbitals, which is a valuable asset in catalysis to promote redox reactions.[7] Due to the electronic structures of traditional metal catalysts, two-electron redox reactions that promote bond formation are typical for these complexes. The limitless diversity available to these catalysts arises from the ability to modify the oxidation state of the metal centre itself, or change the ligand environment of the complex.[6] Through alterations such as these, there exists innumerable possibilities for designing novel catalysts with unique chemical properties.

Despite the widespread use of precious metal catalysts, problems arising from their continuous use in industry continue to grow. By definition, since precious metals are scarce, costly, and can withstand supply fluctuations, their use is of concern. Economic issues aside, environmental implications of precious metal use is also a major concern when applied to Green Chemistry principles as the sustainability of these valuable metals is jeopardized with their use. Further, the removal of these metals from reaction products also requires measures that are accompanied by the production of significant amounts of waste.[6] In order to eliminate unsustainable demands and hazardous waste from precious metal complexes, further research using environmentally benign base metals is an extremely important area of modern research.

1.3. Indium

Indium (In) is the 49th element in the periodic table with a molecular weight of 114.82 amu. This semi-precious post-transition metal normally exists in its trivalent oxidation state since these complexes are the most stable.[8] Indium was first discovered in 1863 by Ferdinand Reich through the use of spectral emission. Reich observed a novel blue-violet line in the spectral emission of a zinc ore sample, which he rightly deduced was a new element; he coined it indium, after the Latin word for violet.[9]

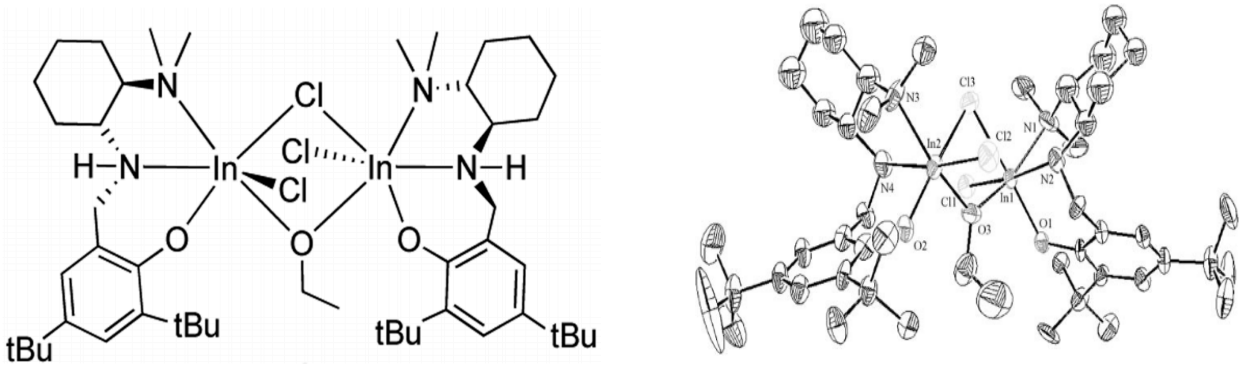
Indium is commonly found associated with zinc minerals and iron, lead and copper ores, and is largely produced as a by-product of zinc metal processing operations. The most common use of indium is as indium tin oxide, a semi-conductor used widely in touch screens and LCD disks.[8] Indium is an attractive choice for such applications because it conducts electricity and adheres strongly to glass. Due to the precious nature of indium and recent increases in LCD use, both the demand and price of indium have increased in recent years owing to wide fluctuations in delivered price.[10]

The large number of scrap LCDs has gradually become an important part of sustainable indium reservoirs. While accumulation of electronics has historically been problematic, recycling indium from scrap LCDs has become an economically and environmentally justifiable means of obtaining indium. Since 2007, more indium has been produced from secondary sources like recycled LCDs than primary raw materials.[10] LCD recycling has made great advancements to the sustainability of indium since less mining of primary environmental sources are needed to obtain this metal.

1.4. Indium Catalysis

Catalysis catering to Green Chemistry is amongst the most vibrant fields in chemical research. Indium(III) salts have received considerable attention as green Lewis acid catalysts in recent years due to their stability when coordinating to atoms in organic substrates while in sub-stoichiometric quantities.[11] Indium salts have also been shown to be stable in aqueous solutions, enabling water to be used as the reaction solvent. Solvents often account for ~75% of the cumulative life cycle environmental impacts of chemical processes; thus, the ability of water to serve as the reaction solvent supports the use of indium in Green Chemistry practices.[3]

Although indium is not unique in its ability to catalyze reactions, the benefits of indium compounds being cheaper and more environmentally benign relative to alternatives have led to a dramatic increase of interest in indium-mediated processes.[12] Indium compounds also have great potential as catalysts because they demonstrate selectivity and functional group tolerance in catalysis. For example, indium(III) complexes have emerged as useful Lewis acid initiators for the controlled polymerization of lactide and other cyclic esters.[12] Research performed by Douglas *et al*. (2008) generated the first indium-based catalysts for ring-opening polymerization (ROP) of cyclic esters (Figure 2). This initial discovery has itself become a catalyst for designing commercially relevant indium-based catalysts that are superior to the industry standards while being more environmentally benign.



A **B**

Figure 2. Chemical (**A**) and crystal (**B**) structures of indium-based ring-opening polymerization catalyst [{(NNO)InCl}$_2$(μ-OEt)(μ-Cl)].[12, 13]

Using green catalysts to perform this ROP is an exciting field of research because it has the potential of developing new biodegradable polymers, and further highlights the unique value of indium-based catalysis.[12] Compared with traditional transition metal catalysts, recent developments in indium catalysis have only provided a glimpse of more environmentally friendly catalysts that are aligned with the 12 principles of Green Chemistry.

1.5. Redox Active Ligands

Traditionally, the steric and electronic properties of ligand systems are used to control the performance of redox catalysts. For electron transfer, ligands often play a spectator role as this reactivity normally occurs at the metal center.[14] Recent approaches deviate from this concept and make use of ligand systems that can play an active role in the elementary bond activation steps in a catalytic cycle.[14] Through incorporation of redox active moieties within the ligand, the oxidation state of the metal centre can remain unchanged while the ligand itself facilitates vital multi-electron catalytic transformations.[15]

One example of a redox active moiety is that of Smith *et al*., who synthesized a cobalt-based redox system for Negishi-type C-C cross-coupling reactions (Figure 3).[15] In this system, a square planar cobalt(III) complexed with redox active amidophenolate ligands is reacted with alkyl halides to generate stable square pyramidal alkylcobalt(III) complexes. The net electrophilic addition reaction formally requires two-electron oxidation of the metal fragment, yet there is no change in metal oxidation state, since the reaction proceeds with one-electron oxidation of each amidophenolate ligand.[16] The metal center maintains its formal 3^+ oxidation state throughout this process, with each amidophenolate moiety providing one electron to afford the final product with a cobalt-carbon bond.

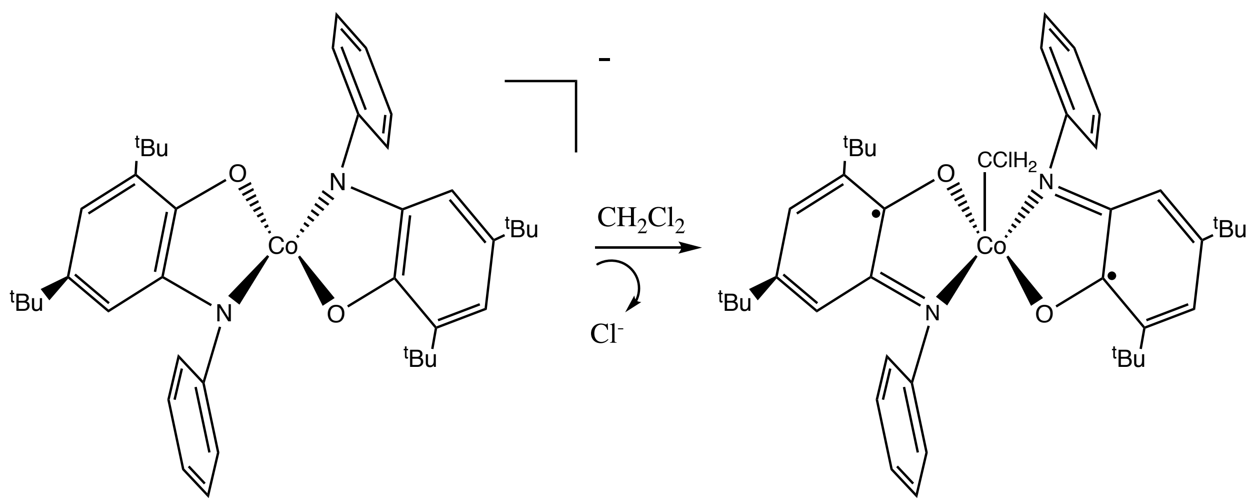
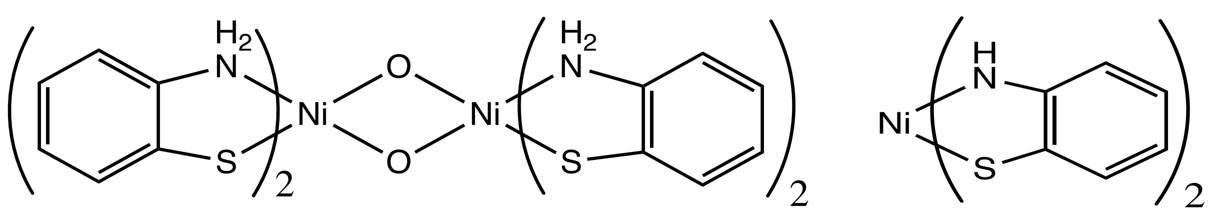


Figure 3. Redox active cobalt amidophenolate complex.[16]

Unfortunately, the majority of catalytic transformations using redox-active ligands still rely on precious metal centres. By drawing on the use of redox active moieties to perform redox chemistry rather than the metal itself, the development of catalysts based on environmentally benign and abundant base metals could address the environmental, health, and financial issues associated with the use of precious metal catalysts.[15] Further investigation into the area of base-metal coordination chemistry and catalysis would be indispensable for modern global Green Chemistry initiatives.

1.6. *o*-Aminobenzenethiol Ligands

o-Aminobenzenethiolate (abt)$^{-1}$ ligands are N,S-coordinated, aromatic mono-anionic ligands.[17] These ligands were initially synthesized in the 1960s due to their similarity to 1,2-benzenedithiol ligands in the sense that they are redox non-innocent.[18] Significant confusion existed around initial *o*-aminobenzenethiolate complexes when they were first synthesized due to their air sensitivity.[19] Preliminary reports described the first *o*-aminobenzenethiolate complexes as oxygen-bridged compounds (Figure 4, compound **C**) . These initial complexes were later identified to be the oxidized product of such systems. The true structure was discovered to possess the (amidobenzenethiolate)$^{2-}$ ligand (Figure 4, compound **D**).[19] In (aminobenzenethiolate)$^{1-}$ complexes, wherein the amine retains its fully protonated form, the similarity to dithiolene complexes is lost as redox activity is not possible. However, (amidobenzenethiolate)$^{2-}$ ligands have the ability to transfer or exchange protons as well as electrons.[20]



C **D**

Figure 4. Initially postulated (**C**) and later confirmed (**D**) structures of Ni(abt) complex.[19]

o-Amidobenzenethiolate ligands are able to assist in single electron-transfer reactions (Figure 5). While ligands capable of two-electron redox chemistry are favoured in terms of bond breaking/formation, *o*-amidobenzenethiolate ligands carry an additional benefit in that they can be doubly or singly protonated, as well as alkylated, which allows for a great variety of ligands with unique intermolecular bonding.[18] The incorporation of an *o*-amidobenzenethiolate redox active ligand could potentially provide a pathway for redox chemistry in redox innocent base metals that would otherwise not be possible. The advantage of N,S coordination about a metal centre is also of interest to human biochemistry as it resembles numerous biological systems, in particular, the nitrogenases.[18]

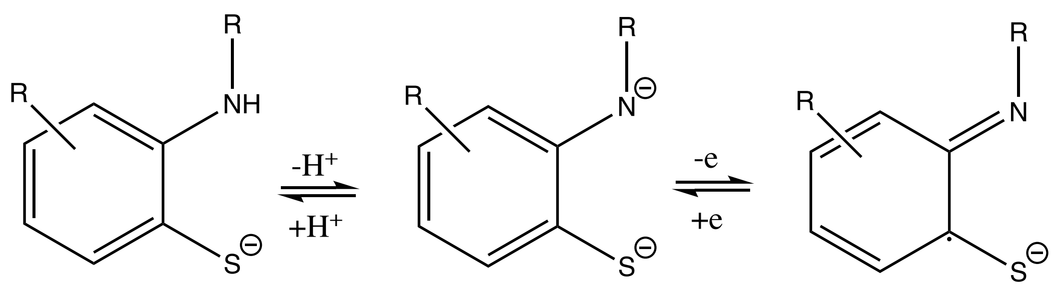


Figure 5. Deprotonation and electronic resonance structures of the *o*-aminobenzenethiolate $(abt)^-$ ligand.[18]

1.7. Current Study

The focus of this study is to synthesize a series of indium complexes incorporating a redox active *o*-amidobenzenethiolate ligand. These novel compounds will then be studied electrochemically to determine their stability and potential as green redox active catalysts. The amidobenzenethiolate ligand used for this study is 2-amidobenzenethiolate (Figure 6). Target compounds (Figure 7) will possess one 2-amidobenzenethiolate ligand to promote redox activity and one organic ligand to alter the steric bulk and solubilities of the compounds. The final products will be characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, elemental analysis, melting point, FT-IR spectroscopy, FT-Raman spectroscopy, and X-ray crystallography. Following characterization, these novel complexes will be tested for redox properties using cyclic voltammetry.

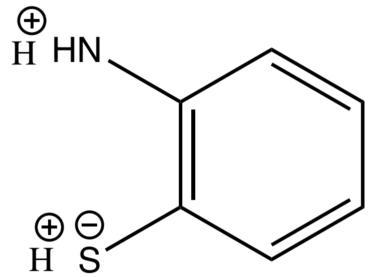
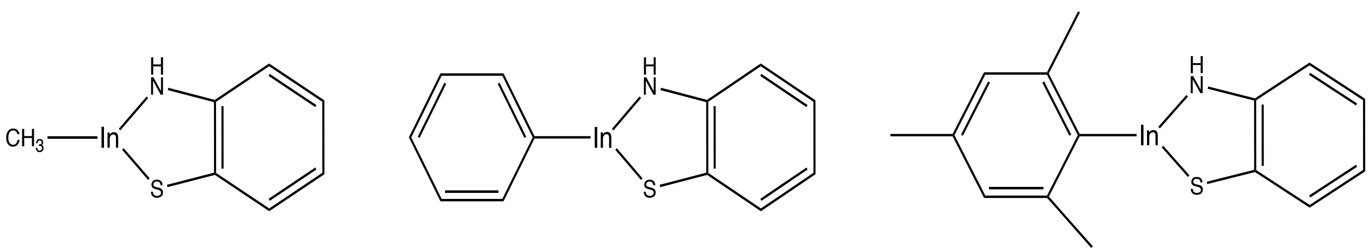


Figure 6. 2-Aminobenzenethiol H_2(abt).



1 **2** **3**

Figure 7. Target indium complexes for this study: MeIn(abt) (**1**), PhIn(abt) (**2**) and MesIn(abt) (**3**).

2. Experimental

2.1. Instrumentation

All reactions were performed under an atmosphere of dinitrogen using standard Schlenk techniques or an Innovative Technology glove box. All ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Varian Mercury 200 MHz+ spectrometer (^{1}H: 200 MHz; $^{13}C\{^{1}H\}$: 50.3 MHz) at room temperature (23 ºC). FT-IR spectra were obtained with a Thermo Nicolet diamond ATR spectrometer. FT-Raman were recorded using a Thermo Nicolet NXR 9600 series FT-Raman spectrometer between 3900–100 cm^{-1}. Melting points were obtained on an Electrothermal MEL-TEMP apparatus.

2.2. Reagents

2-Aminobenzenethiol (99%), trimethylindium (98%), indium(III) chloride (98%), 2-mesitylmagnesium bromide solution 1.0 M in diethyl ether, and triphenylmagnesium bromide solution 3 M in diethyl ether were used as received from Sigma Aldrich. Activated molecular sieves were added to pyridine (anhydrous 99.8%), tetrahydrofuran (anhydrous, ≥99.9%, inhibitor-free), toluene (anhydrous, 99.8%), hexanes (anhydrous, 95%), diethyl ether ACS reagent (anhydrous, ≥99%) and pentane (anhydrous, ≥99%) as received from Sigma Aldrich.

2.3. Synthesis of Mes_3In[21, 22]

Under an atmosphere of dinitrogen, $InCl_3$ (1.002 g, 4.53 mmol) was added to diethyl ether (20 mL) and cooled to 0 ºC in an ice bath. MesMgBr (14.2 mL, 1 M in Et_2O) was added dropwise, and the reaction was stirred and heated at reflux for 18 h in the dark. The removal of solvent under vacuum gave a gray solid. The product was extracted with toluene (30 mL) and gravity filtered to yield a colorless solution. The solution was placed at -15 ºC for 18 h and gravity filtered to separate a white powder from the solution. The filtered solution was concentrated to ~2 mL and layered with pentane (5 mL). The solution was placed at -15 ºC for 18 h and colourless crystals of Mes_3In were collected by filtration and dried under vacuum. Yield: 1.405 g, 2.97 mmol, 47.0%. Elemental analysis: Calculated: C, 68.65%; H, 7.04%. Found: C, 68.88%, H, 7.21%.

2.4. Attempted Synthesis of Ph_3In

Under an atmosphere of dinitrogen, $InCl_3$ (2.002 g, 9.05 mmol) was added to diethyl ether (40 mL) and cooled to -100 ºC in an ethanol bath. PhMgBr (9.0 mL, 3 M in Et_2O, 27.00 mmol) was added dropwise, and the reaction was stirred and heated at reflux for 2 h in the dark. The removal of solvent under vacuum gave a gray solid. The product was extracted twice with hot toluene (2 × 25 mL). The mixture was filtered, and the solvent was concentrated to ~2 mL and stored at -15 ºC for 10 h. Colorless crystals were collected by filtration and dried under vacuum. Yield: 1.409 g, 4.07 mmol, 45.2%. Preliminary X-ray crystallography data suggested the presence of bromine, which indicated the material was not pure.

2.5. Synthesis of MeIn(abt) (1)

Under an atmosphere of dinitrogen, 2-aminobenzenethiol (0.198 g, 1.58 mmol) in toluene (4 mL) was added dropwise to a solution of Me_3In (0.255 g, 1.58 mmol) in toluene (3 mL). The mixture was left to stir for 1 h, and then heated at reflux for 3 h. The solution was initially dark blue in colour and then turned a reddish purple colour after heating. The reaction mixture was then filtered to yield a purple microcrystalline material. The dark purple solution was concentrated to ~3 mL and left at 23 ºC for 72 h, yielding a purple powder. Yield: 0.321 g, 1.27 mmol, 80.3%. Melting point: >300 ºC. ^1H NMR (DMSO-d_6, ppm): 6.82–6.53 (4 H, m, C_6H_4), 4.98 (1 H, s, NH), -0.347 (3 H, s, CH_3).

2.6. Attempted Synthesis of MeIn(abt)(py)$_2$

Compound (**1**) (0.321 g, 1. 27 mmol) was dissolved in toluene (15 mL) and pyridine (0.499 g, 6.32 mmol) to yield a cloudy purple slurry. After heating near reflux for 2 h, the product dissolved in solution yielding a clear dark purple solution. This solution was concentrated to 4 mL and allowed to sit at 23 °C. After 72 h, a purple microcrystalline product precipitated from solution. ^{1}H NMR spectroscopy data showed peaks corresponding to **1** and the absence of peaks corresponding to the presence of pyridine.

2.7. Attempted Synthesis of MesIn(abt)

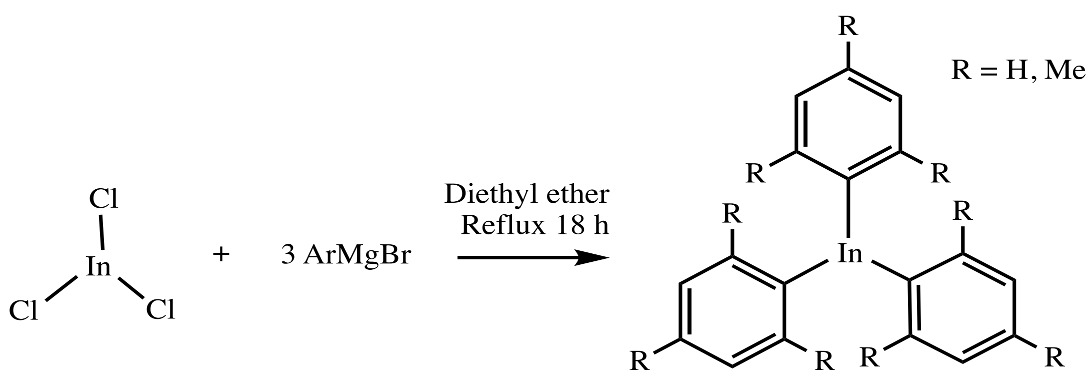
Attempt 1. Under an atmosphere of dinitrogen, 2-aminobenzenethiol (0.105 g, 0.84 mmol) in toluene (4 mL) was added dropwise to a solution of Mes$_3$In (0.397 g, 0.84 mmol) in toluene (3 mL). The yellow solution was heated at reflux for 3 h yielding a brown slurry. Following heating, pyridine (0.266 g, 3.36 mmol) was added to the mixture and the brown slurry persisted. The solvent was removed under vacuum, and THF (7 mL) and pyridine (0.266 g, 3.36 mmol) were added in an attempt to dissolve the product. The mixture was heated near reflux for 2 h yielding a brown slurry. ^{1}H NMR spectroscopic results concluded that the pyridine adduct was not formed, however spectroscopy data showed mesitylene peaks corresponding to **3**.

Attempt 2. Under an atmosphere of dinitrogen, 2-aminobenzenethiol (0.105 g, 0.839 mmol) in THF (4 mL) and pyridine (0.266 g, 3.36 mmol) were added dropwise to a solution of Mes$_3$In (0.397 g, 8399 mmol) in toluene (3 mL). The clear yellow solution was heated at reflux for 18 h yielding a dark purple solution. The solution was filtered and concentrated to ~5 mL and stored at 23 °C for 72 h yielding light colourless needle crystals. X-ray crystallography determined the product to be MgBr$_2$(py)$_3$(THF).

3. Results and Discussion

3.1. Synthesis of Mes_3In and Ph_3In

Me_3In is available commercially but Mes_3In and Ph_3In had to be synthesized. The synthesis of Mes_3In was achieved by following modified literature procedures by Leman and Barron (1989) and Blumel (1997) (Scheme 1).[21,22] A similar procedure was used for the synthesis of Ph_3In. Indium trichloride in diethyl ether was cooled using an ice bath and the appropriate aryl Grignard was added dropwise. The solution turned a murky grey and was heated at reflux. The first attempts of this synthesis involved heating the reaction mixture at reflux for 3 h. However, upon multiple unsuccessful attempts, the reaction mixture was heated at reflux for 18 h and yielded the desired product.



Scheme 1. General synthesis for Mes_3In and Ph_3In, R = Me and H respectively.[21,22]

In the synthesis of Mes_3In, removal of the solvent under vacuum yielded a grey solid which was then extracted with 30 mL of pentane. In subsequent syntheses, two separate extractions of 15 mL were used in an attempt to increase the reaction yield. Notably, the two extractions increased the yield from 16% to 37%. Following extraction, the clear solution was decanted and stored at -15 ºC for 18 h, which gave colorless crystals. Results from elemental analysis provided a carbon percentage of 36%. By comparison, the literature suggests the %C should be 69%. Due to the extreme difference, it was concluded that Mes_3In was not being synthesized and other reaction routes would have to be tested to correctly synthesis the desired product.

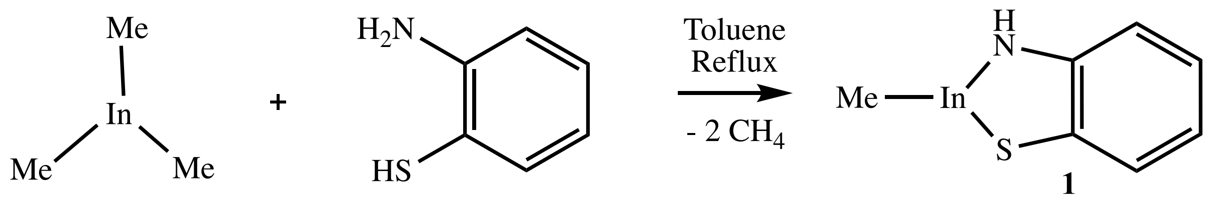
In subsequent Mes_3In syntheses, removal of the solvent under vacuum yielded a grey solid, which was then extracted with 30 mL of toluene. Following extraction, the filtered solution was decanted and stored at -15 ºC for 18 h, giving a white precipitate. The reaction mixture was gravity filtered, the solution was concentrated, and layered with pentane to promote crystallization. Colorless crystals were obtained in a percent yield of 47%, and elemental analysis yielded results of 68.88% %C and 7.21% %H. When compared to the calculated %C of 68.65% and %H of 7.04%, it was confirmed the Mes_3In product was correctly synthesized. The compound began to decompose at 165 ºC and completely decomposed upon heating to 180 ºC, which is similar to the melting point of 178-179 ºC reported in the literature.

For the preparation of Ph_3In, removal of the solvent under vacuum yielded a dark grey solid, which was extracted twice with 20 mL of toluene. Following extraction, the clear solutions were decanted, concentrated to 10 mL, and stored at -15 ºC for 18 h, giving colorless crystals in a 45% yield. Preliminary X-ray crystallography results suggested the presence of a magnesium bromide salt. It was therefore concluded that this product was impure and alternate extraction/purification steps would be required. Future attempts in synthesizing this material should follow the same modified procedure as that used in the successful synthesis of Mes_3In.

3.2. Synthesis of MeIn(abt) (1)

Me_3In and 2-aminobenzenethiol were reacted in a 1:1 ratio in toluene in an attempt to prepare the target compound MeIn(abt) (Scheme 2, compound 1). Early trials of this synthesis involved heating the reaction mixture at 50 ºC for 1 h, which yielded a purple solution. The solution was concentrated and stored at 23 ºC for 18 h to afford purple crystals in a 27% yield.

The product was submitted for X-ray crystallography. However, the results were inconclusive as the product was determined to be an amorphous powder. When a similar procedure was carried out in THF, purple needles formed from the reaction mixture. An attempt to crystallize the product by layering the THF reaction mixture with diethyl ether at room temperature resulted in precipitation of a purple powder in a 52% yield. An identical reaction using diethyl ether gave purple needles in a 21% yield.



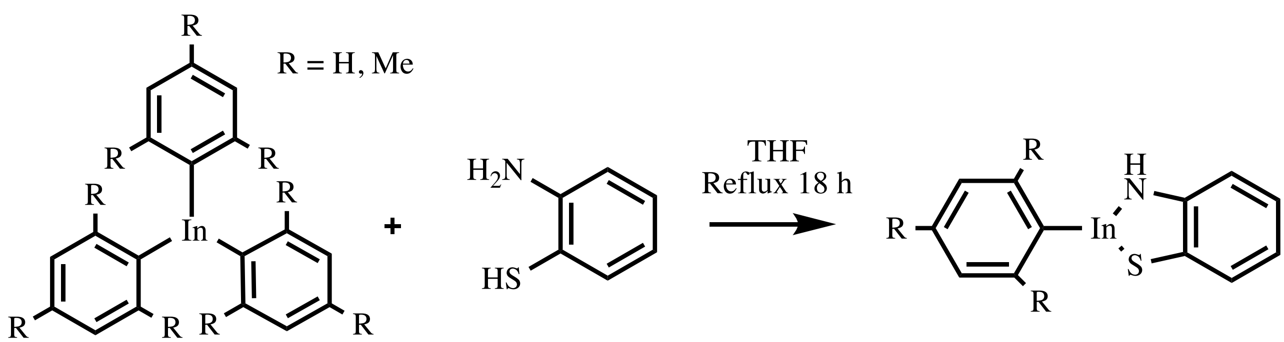
1

Scheme 2. General synthesis of MeIn(abt) (**1**).

Results from ^{1}H NMR spectroscopy suggest that **1** was not being synthesized in these reactions. In the desired product, the ratio of aromatic protons (6.82–6.53 ppm) to methyl protons (-0.347 ppm) to amine protons (4.98 ppm) in MeIn(abt) should be 4:3:1. However, the ^{1}H NMR spectroscopy data suggest that a different unidentified product with a doubly protonated amine was formed since the ratio of aromatic protons to methyl protons to amine protons was 4:2:2 rather than the desired 4:3:1 in the target compound (Appendix, A.1). Therefore, an analogous reaction was carried out but heated at reflux for 3 h to facilitate deprotonation of the amine group. After carrying out this reaction in both THF and toluene, the resultant purple solutions were filtered to yield small purple crystals from each reaction mixture. The purple filtrates were left at 23 ºC for 72 h and yielded a purple powder in both solvents. The crystals and powders were collected and gave a percent yield of 25% in THF and 80% in toluene. ^{1}H NMR spectra confirm single deprotonation of the amine group in the toluene reaction but not the THF reaction (Appendix, A.2). It was concluded that since toluene has a higher boiling point than THF, the reaction mixture can be sufficiently heated to permit deprotonation of the amine via elimination of methane in the reaction with Me_3In. The product (**1**) was re-dissolved in toluene with four equivalents of dry pyridine in an attempt to recrystallize the product as a pyridine adduct. The compound did not dissolve at room temperature but did so after heating the solution to a gentle boil, yielding a purple solution. The solution was left at 23 ºC for 48 h and yielded a purple powder. The solution was decanted, concentrated, and layered in hexane (3 mL) and left at 23 ºC for 72 h to crystallize. No crystals suitable for X-ray crystallography were obtained by any of these methods.

3.3. Synthesis of MesIn(abt) (3)

Mes_3In was reacted in a 1:1 ratio with 2-aminobenzenethiol in toluene in an attempt to synthesize compound **3** (Scheme 3).



Scheme 3. General synthesis of MesIn(abt) (**3**, R = Me).

Initially, the light yellow reaction solution was heated at 50 ºC for 3 h. However, it was determined that the amino group was not being deprotonated and subsequent reactions of the MesIn(abt) product were heated at reflux for 3 h. The solution went from being an initially cloudy-yellow colour to a cloudy-brown colour over the course of heating. The mixture was filtered yielding a light brown pellet and colorless solution. Four equivalents of pyridine were added in an attempt to dissolve the pellet into solution. The brown mixture retained its cloudiness, so the solvent was removed under vacuum and THF was added. The product did not dissolve, so four additional equivalents of pyridine were added. The mixture was heated near reflux for 2 h to encourage dissolution. Although this approach turned the mixture slightly purple, no dissolution occurred.

In a subsequent MesIn(abt) synthesis, Mes_3In was reacted in a 1:1 ratio with 2-aminobenzenethiol in THF and four equivalents of pyridine in THF. The clear yellow solution was heated at reflux for 18 h to ensure amine deprotonation, yielding a dark purple solution. The solution was filtered and concentrated to ~5 mL and stored at 23 ºC for 72 h, yielding colourless needle crystals. X-ray crystallography shows that much of the sample was $MgBr_2(py)_3(THF)$. This suggests that the Mes_3In reactant is impure despite previous attempts to isolate pure material. Further attempts to crystallize this compound are needed. Notably, ^1H NMR spectroscopy of the colourless crystals confirms the presence of the mesitylene moiety, suggesting the correct product was indeed synthesized.

4. Conclusion

With modern pressures to reduce energy consumption, protect the environment, and conserve natural resources, the synthesis of novel green catalyst alternatives is an extremely important area of research. Significant progress has been made on the synthesis and characterization of MeIn(abt) (**1**) and MesIn(abt) (**3**), which possess environmentally benign indium metal centres and redox active amidobenzenethiolate ligands. These were prepared through the hydrocarbon elimination reaction of the appropriate triorganoindium reagent and 2-aminobenzenethiol. Although the organoindium reagent Me_3In is commercially available, successful synthesis of Mes_3In, as confirmed by ^1H NMR spectroscopy and elemental analysis, required modification of literature methods. Further work will be required for the isolation of the Ph_3In reagent. MeIn(abt) (**1**) has been isolated in an 80% yield and has been spectroscopically characterized. Preliminary evidence suggests that Mes_3In(abt) (**3**) has been successfully prepared but has yet to be isolated.

5. Future Directions

Future work on this project would be to continue attempts to isolate adequate crystals of compounds **1** and **3** for X-ray crystallographic analysis. Also, further synthetic methods attempting to isolate pure Ph_3In should be undertaken in order to test how this aryl substituent influences the solubility of these indium compounds. Additional complexes of indium with alternate bulky substituents on the indium metal centre (R = Mes*, 4-tBuC_6H_4) should be synthesized as changes in steric bulk of the indium substituent will alter the solubility of the complexes and facilitate crystallization. Further, alterations to the amine moiety, or within the aryl ring of the ligand should also be investigated as these modifications could influence the redox properties of these complexes. Once these compounds are synthesized, another important step in their full characterization is assessing their redox potentials using cyclic voltammetry to determine their applicability as redox catalysts.

6. References

1) Chanshetti, U. *Int. J. Adv. Res. Chem. Sci.* **2014**, 1, 110–115.

2) Anastas, P.; Heine, L.; Williamson, T. *Green Chemical Syntheses and Processes: Introduction* **2000**, 1–6.

3) Bhandari, M.; Raj, S. *Int. J. Pharm. Pharm. Sci.* **2017**, 9, 10–26.

4) Schmidt, C. *Environ. Health Perspect.* **1999**, 107, 410–413.

5) Orloff, K.; Falk, H. *Int. J. Hyg. Environ. Health* **2003**, 206, 291–302.

6) Ludwig, J.; Schindler, C. *Chem.* **2017**, 2, 313–316.

7) Zhou, Q. *Angew. Chem. Int.* **2016**, 55, 5352–5353.

8) Alfantzi, A.; Moskalyk, R. *Miner. Eng.* **2003**, 16, 687–694.

9) Venetskii, S. *Metallurgist* **1971**, 15, 148.

10) Ruan, J.; Guo, Y.; Qiao, Q. *Procedia Environ. Sci.* **2012**, 16, 545–551.

11) Frost, C.; Hartley, J. *Mini-Reviews in Organic Chemistry* **2004**, 1, 1–7.

12) Osten, K.; Mehrkhodavandi, P. *Acc. Chem. Res.* **2017**, 50, 2861–2869.

13) Douglas, A. F.; Patrick, B. O.; Mehrkhodavandi, P. *Angew. Chem. Int. Ed.* **2008**, 47, 2290–2293.

14) Lyaskovskyy, V.; de Bruin, B. *ACS Catal.* **2012**, 2, 270–279.

15) Praneeth, V.; Ringenburg, M.; Ward, T. *Angew. Chem. Int. Ed.* **2012**, 51, 10228–10234.

16) Smith, A.; Hardcastle, K.; Soper, J. *J. Am. Chem. Soc.* **2010** 132, 14358–14360.

17) Ghosh, P.; Begum, A.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2013**, 42, 3208–3215.

18) Sproules, S.; Wieghardt, K. *Coord. Chem. Rev.* **2010**, 13, 1358–1382.

19) Larkworthy, L. F.; Murphy, J. M.; Phillips, D. *J. Inorg. Chem.* **1968**, 7, 1436.

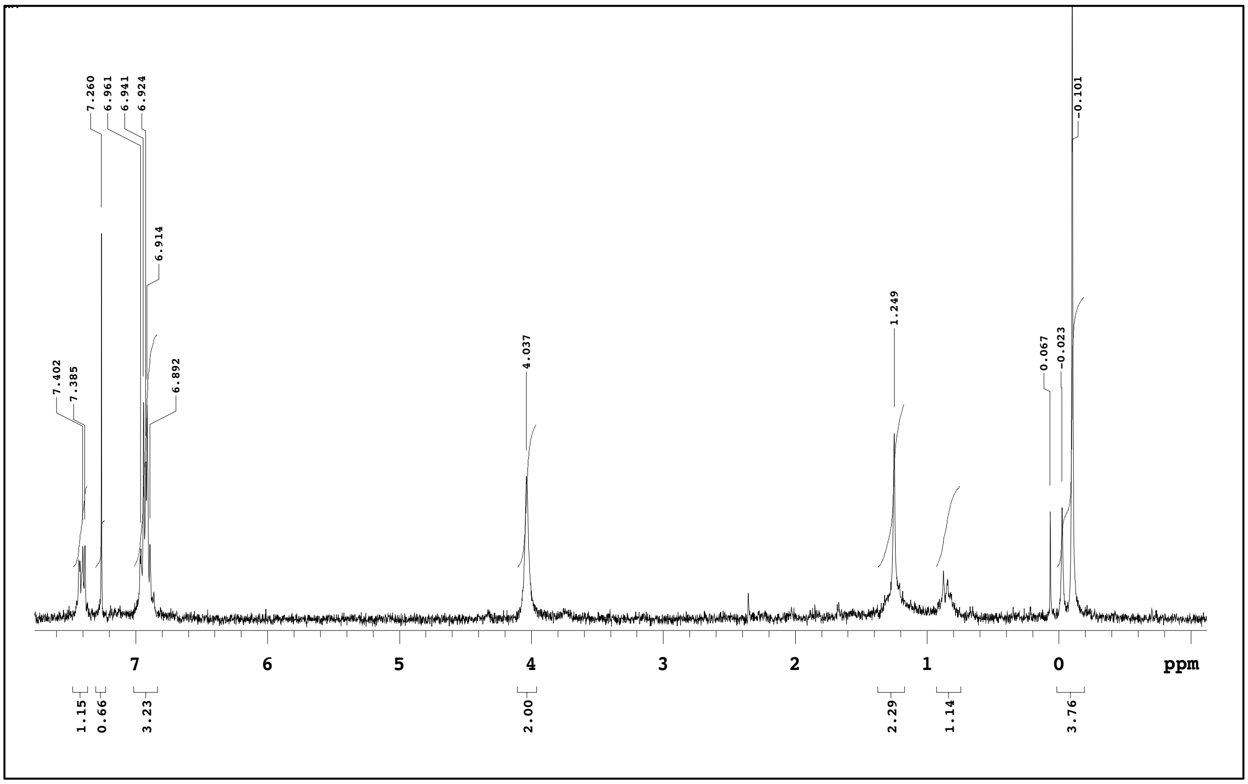
20) Gardner, J.; Pariyadath, N.; Corbin, J.; Stiefel, E. *Inorg. Chem.* **1978**, 17, 897–904.

21) Leman, J.; Barron, A. *Organometallics* **1989**, 8, 2214–2219.

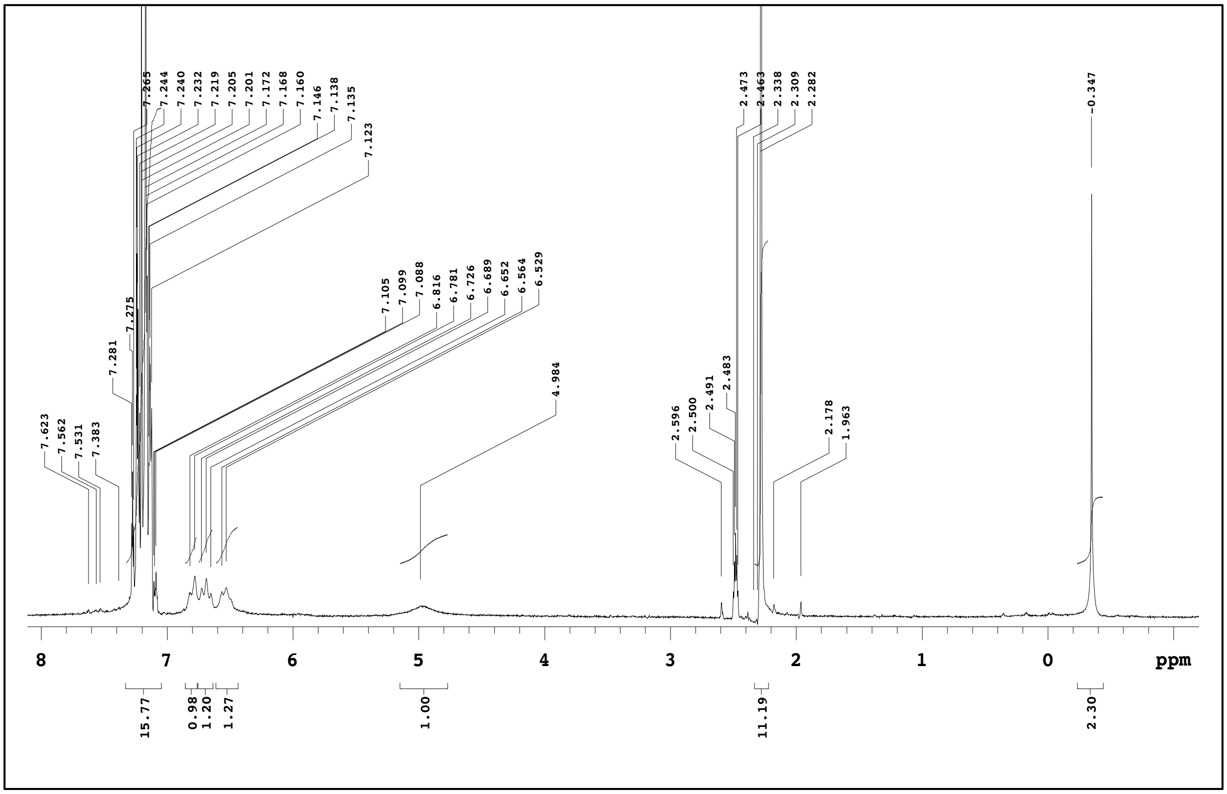
22) Blumel, J. *Z. Anorg. Allg. Chem.* **1997**, 623, 309–315.

7. Appendix

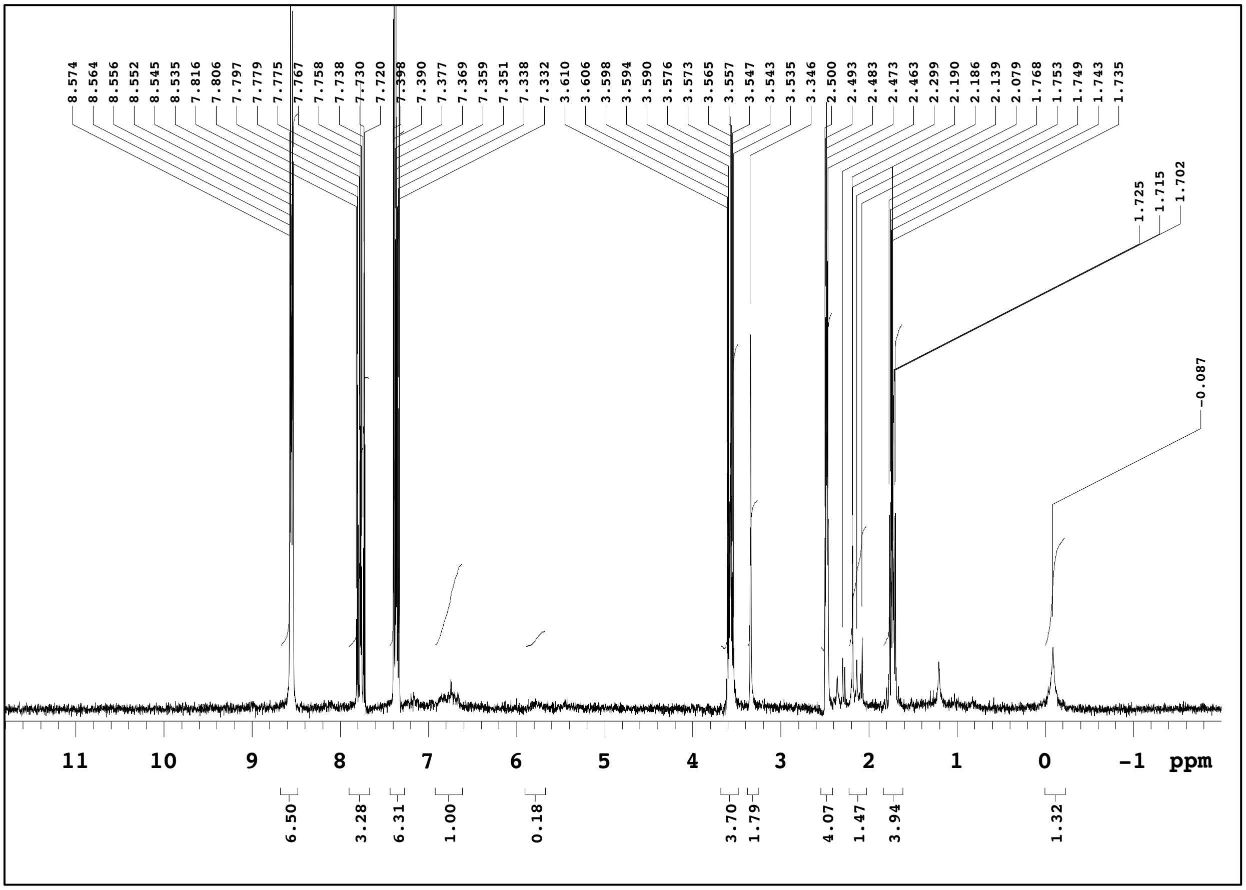
A.1. ^{1}H NMR spectrum of the product from the attempted synthesis of MeIn(abt) heated at 50 ^{o}C.



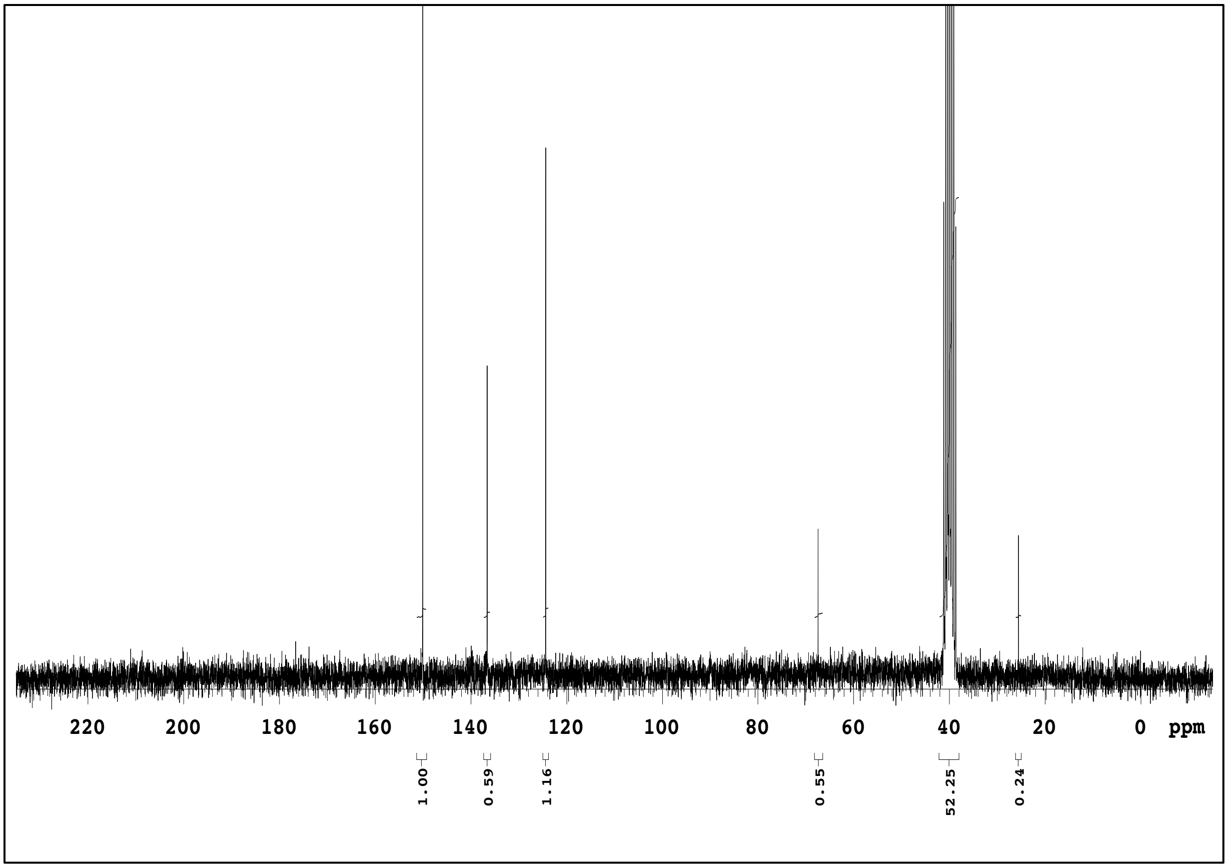
A.2. [1]H NMR spectrum of confirmed MeIn(abt) product heated at reflux.



A.3. [1]H NMR spectrum of MesIn(abt).



A.4. $^{13}C\{^{1}H\}$ NMR spectrum of MesIn(abt).



A.5. [1]H NMR spectrum of the product from the attempted synthesis of PhIn(abt).