The Synthesis of \((\eta^5\text{-Indenyl})(\text{TMED})\) trichlorozirconium(IV)

An Honors Thesis
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Abstract

This paper is a summary of the organometallic chemistry research that has been accomplished after two years of work with Dr. Robert Morris' research group. A description of the long term goals of this project and of my particular contribution is as followed. My intent is to describe the basic background on why this particular research was initiated and to describe the chemistry in an understandable but in-depth manner, which will include a step-by-step description of chemical procedures.
Table of Contents

List of Figures .................................................. ii

I. Introduction .................................................. 1

II. 1-(Tributylstannyl)indene ................................. 7

III. (η⁵-Indenyl)trichlorozirconium(IV) ...................... 7

IV. (η⁵-Indenyl)(TMED)trichlorozirconium(IV) ............... 8

V. Acknowledgments ............................................. 11

References ...................................................... 12
List of Figures

1. $\eta^5$- Binding Ligands. .................................................. 1
2. $\eta^5$- $\eta^3$ Slippage Mechanism of Indene. ......................... 2
3. Polymer for ($\eta^5$-Indenyl) trichlorozirconium(IV) ............. 3
4. Structures of DME and DMPE Ligands. ............................... 3
5. Structure of TMED Ligand. ............................................... 4
6. Structure of TMS-Indene. ................................................ 4
7. $^1$H NMR Spectrum of 1-(Tributylstannyl)indene ................. 7
8. $^1$H NMR Spectrum of ($\eta^5$-Indenyl) trichlorozirconium(IV). 8
9. $^1$H NMR Spectrum of ($\eta^5$-Indenyl)(TMED) trichlorozirconium(IV). 9
10. $^{13}$C($^1$H)NMR Spectrum of ($\eta^5$-Indenyl)(TMED) trichlorozirconium(IV). 9
11. X-ray structure of ($\eta^5$-Indenyl)(TMED) trichlorozirconium(IV). 9
12. Structure of Fac and Mer Isomers of ($\eta^5$-Indenyl)(TMED) trichlorozirconium(IV). .......................... 9
13. $^{13}$C($^1$H)NMR Spectrum of TMED carbons from figure 10 ...... 10
I. Introduction:

Over the last several decades, the metallocene complexes of Group 4 metals have become an important class of homogeneous catalyst.\(^1\)\(^-\)\(^2\) Most of the earlier known reactions where performed with cyclopentadienyl (Cp) and 1,2,3,4,5-pentamethylcyclopentadienyl (Cp\(^*\)) group 4 complexes. Due to the many similarities between Cp/Cp\(^*\) and indenyl rings, the production of group 4 indenyl complexes of Ti, Hf, and Zr are an important consideration for chemist. The indenyl group 4 complexes have been shown to have greater polymerization activity due to the greater electron-donating ability of the indenyl ring relative to the Cp ligand.\(^3\) To find an inexpensive and effective way of synthesizing these complexes will be highly beneficial due to the many uses of plastics and other polymers in industry.

The similarities between Cp, Cp\(^*\) and indenyl (Ind) complexes can be seen in the metal bonding of these complexes. These complexes bind a metal atom to the five carbons of the ring, this called \(\eta^5\).

![Figure 1](image-url)
It is the \( \eta_5 \) chemistry that allows for the polymerization of olefins to occur more readily due to the indenyl ligands ability to slip for \( \eta_5 \) to \( \eta_3 \). The slippage of the indenyl ligand is a special case. When the indenyl ligand slips into the \( \eta_3 \) state, the non-binding segment of the ligand re-aromatizes to form a benzene component, which is known to be stable.\(^4\)

\[ \begin{align*}
&\text{[Diagram showing the slippage from } \eta_5 \text{ to } \eta_3 \text{]} \\
&\text{Figure 2}
\end{align*} \]

Due to the stability of the indenyl complex by the aromaticity of the benzene, it is assumed that Group 4 indenyl complexes will be more readily active than Cp and Cp*, making it easier to accomplish the intermediate necessary for polymerization to begin. The proposed indenyl catalysts should produce plastics and other polymers more rapidly than the current Cp and Cp* analogs.

Earlier research groups of Dr. Morris' have done initial experimentation with the catalytic abilities of the indenyl complexes. In their research they found that direct methylation
of indenylzirconium chloride complex is unsuccessful due to the polymer structure:

\[
\begin{array}{c}
\text{Ind} \quad \text{Cl} \\
\text{Cl} \quad \text{Zr} \\
\text{Cl} \quad \text{Ind} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{Zr} \\
\text{Cl} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{Ind} \\
\text{Cl} \\
\end{array}
\]

**Figure 3**

Methylation of this complex was then modified. The polymer had to be broken apart into separate monomers that would be more susceptible to methylation. Two monomers had earlier been found for zirconium using two different chelating ligands. The two chelating ligands

\[
\begin{array}{c}
\text{Me}_2 \quad \text{P} \\
\text{P} \\
\text{Me}_2
\end{array}
\]

DMPE

\[
\begin{array}{c}
\text{Me} \quad \text{O} \\
\text{O} \\
\text{Me}
\end{array}
\]

DME

**Figure 4**

are bis(dimethylphosphino)ethane (DMPE) and dimethoxyethane (DME). Both of these chelating ligands have two metal binding sites.

These two chelating ligands were made and tested by groups that did their work prior to me. As a result it was found that both
DME and DMPE are not good ligands to use for this particular reaction. DME is fluxional and hard to alkylate, ruling it out for large-scale use. DMPE is not fluxional but if is very expensive (approx. $50/g), also ruling it out for large-scale use. We then moved on to other chelating ligands, nitrogen containing compounds. Tertamethylethylenediamine(TMED) was our ligand of choice.

\[
\text{Me}_2N \quad \text{NMe}_2
\]

TMED

Figure 5

Certain starting materials must be synthesized before the catalyst can be produced. The procedure determined by previous Morris groups was used to prepare 1-(trimethylsilyl)inden (TMS-indene).

\[
\text{SnBu}_3
\]

TMS-indene

Figure 6

This compound reacts well with the Group 4 tetrachlorides to create Group 4 indenyl trichloride complexes by the substitution of indene for a chloride. The exact synthesis of this indenyl trichloride complex will be explained in greater
detail in the following sections, as well as the synthesis of TMS-indene.

Several of the compounds used to due this type of chemistry are extremely air- and water- sensitive. Do to the nature of inorganic chemistry in general, it is necessary to learn to work with Schlenk lines in order to accomplish air-sensitive chemistry. Schlenk lines are glass assemblies that allow one to connect a reaction flask to either a vacuum pump or an argon tank. The preparation of a reaction, the transfer of reagents, and the recrystallization of products can be accomplished without exposure to air or water by careful technique on a Schlenk line with appropriate Schlenk-adapted flasks. Also, characterization with NMR requires special Schlenk line techniques in order to prepare a sample without air or water in the sample tube.

Along with the Schlenk techniques, a dry box is used in the handling of air- and water- sensitive compounds. A dry box is a large air-tight metal box that is filled with argon. Compounds and glassware are imported into the box through a vacuum port when transporting materials into the box, the vacuum port must have all the outside atmosphere evacuated and be refilled with argon before allowing the materials to enter. Two rubber gloves are attached to the transparent glass allowing the user to work with the equipment inside the box. In some cases reactions are
performed in dry boxes, but Ball State's dry box is strictly for storing starting materials and the weighing and transporting of products in an inert atmosphere.

Due to the repeated use of the NMR; it is necessary to have a brief introduction to NMR. This instrumental technique was used in determining the structure and purity of all the compounds that were made. The instrument allows one to observe the protons and the carbons of complex depending one which experiment was ran. On the proton NMR the indenyl protons are usually designated around 7.0 ppm, the methyl protons around 1.5ppm and there is a peak around 0.05ppm which corresponds to grease and a peak at 0ppm which is the reference peak, TMS. A further detailed explanation of the NMR spectra will follow in later sections. All NMR spectra were taken in deuterated chloroform.
1-((Tributylstannyl)indene)

\[
\text{Indene} + \text{Li}(\text{Bu}^n) \quad \text{butane} \quad \text{Li}(\text{C}_9\text{H}_7) \rightarrow \text{ClSnBu}_3
\]

Production of 1-((Tributylstannyl)indene) (TBT-indene) (1) was carried out according to the method published by Robert Morris et al in *Inorganic Syntheses*. The (Tributylstannyl)indene is a clear, pale yellow liquid with 65% yield. The proton NMR spectrum of this complex can be seen in Figure 7. The spectra shows indenyl peaks at $\delta$ 6.8 ppm to $\delta$ 7.7 ppm and butyl peaks at $\delta$ 0.6 ppm to $\delta$ 1.5 ppm.

(Tributylstannyl)indene is then used to produce (η⁵-Indenyl) trichlorozirconium(IV).

(η⁵-Indenyl) trichlorozirconium(IV)

\[
\text{Indene} + \text{ZrCl}_4 \rightarrow [\eta^5-C_9H_7\text{ZrCl}_3]_x
\]

Production of (η⁵-Indenyl) trichlorozirconium(IV) (2) was accomplished by reacting TBT-indene and zirconium.
tetrachloride according to the preparation procedure published in *Inorganic Syntheses*, by Robert Morris et al.\(^5\) The product was a yellow powder with 82% yield. The proton NMR spectrum of this complex can be seen in Figure 8. The spectra shows indenyl peaks at \(\delta 6.3\text{ppm}\) to \(\delta 7.7\text{ppm}\), the tms peak at \(\delta 0.0\text{ ppm}\) and a grease peak at \(\delta 1.0\text{ ppm}\). This product is a polymer in which the metal centers are bridged by Cl. This structure can be seen in figure 8.

\[(\eta^5\text{-Indenyl})(\text{TMED})\text{ trichlorozirconium}^{\text{IV}}\]

\[\begin{align*}
(\text{IndZrCl}_3)_x & + \begin{array}{c}
\text{Me}_2\text{N} \\
\text{NMe}_2
\end{array} \rightarrow \text{Toluene} \\
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me}
\end{array}
\end{align*}\]

The production of \((\eta^5\text{-Indenyl})(\text{TMED})\) (3) trichlorozirconium(IV)(3) was accomplished by reacting \((\eta^5\text{-Indenyl})\text{ trichlorozirconium}(\text{IV})\) and TMED in a one to one ratio in ether. The solution was then allowed to stir overnight to produce a bright yellow solution. The supernatant was then removed through vacuo leaving a yellow solid on the walls of the flask. The yellow solid was then scraped off the sides on
the flask and dissolved in a minimum amount of degassed toluene. The solution was then transferred into a shlenk flask and placed into the freezer overnight. The product was yellow crystals with 37% yield. The proton and carbon NMR spectrum of this complex can be seen in Figures 9 & 10. This product was then sent to Indiana University for X-ray crystallography to be preformed. This structure can be seen in figure 11.

The NMR spectra of \((n^5\text{-Indenyl})(\text{TMED})\) trichloroziirconium(IV) were then used to determine basic structural properties of the compound. Looking at the proton NMR the indenyl peaks can be seen at \(\delta 6.5-7.8\text{ppm} \) with the peak for the solvent at \(\delta 7.25\text{ppm} \). The proton NMR also shows the peaks for the four methyl groups at \(\delta 2.7\text{ppm} \). Just by looking at the proton NMR the structure of the compound can be one of two isomers. It could be the mer configuration or the fac configuration.

![Figure 12](image-url)
The Fac isomer has a mirror plane passing through the TMED, causing to have three different carbons for TMED. The Mer isomer has no mirror plan causing it to have four different carbons associated with TMED. Looking at the carbon NMR we see that there are four peaks for the TMED carbons (Figure 13 - a blown up spectra of TMED carbons). This tells us that our compound is the mer isomer. This was then confirmed by the X-ray analysis.
V. Acknowledgements:

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References:


