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SYNTHESIS AND STRUCTURE OF TRANS-DIALKENE COMPLEXES OF PLATINUM(II)

A Thesis
Submitted to the School of Graduate Studies and Research
in Partial Fulfillment of the
Requirements for the Degree
Master of Science

Jeremy Jon Hay
Indiana University of Pennsylvania
March 2012
Indiana University of Pennsylvania  
School of Graduate Studies and Research  
Department of Chemistry

We hereby approve the Thesis of

Jeremy Jon Hay

Candidate for the degree of Master of Science

__________________________________________
John C Woolcook, Ph.D.  
Professor of Chemistry, Advisor

__________________________________________
John C. Ford, Ph.D.  
Professor of Chemistry

__________________________________________
Keith S. Kyler, Ph.D.  
Professor of Chemistry

__________________________________________
Charles H. Lake, Ph.D.  
Professor of Chemistry

ACCEPTED

__________________________________________
Timothy P. Mack, Ph.D.  
Dean  
School of Graduate Studies and Research
This thesis examines the synthesis and characterization of trans-dialkene platinum complexes with cycloalkenes. The first step was to synthesize trans-[PtCl₂(η²-cot)]₂ (cot = cyclooctene) which have been previously reported in the literature to be sure we have mastered the techniques to prepare this unusual type of complex. Once this compound was synthesized we used a similar strategy to react 2 and 4 molar equivalents of the Z-cyclohexene, Z-cycloheptene, E-cyclodecene, and E/Z-cyclododecene with Zeise’s dimer. We also reacted 2 and 4 molar equivalents of rigid ring-bridged cycloalkenes such as bicyclo[2.2.1]hept-2-ene, and bicyclo[3.2.1]oct-2-ene with Zeise’s dimer. As a result of this research we successfully synthesized the trans-dialkene compound of E-cyclodecene and its Zeise’s dimer analogue. We also synthesized Zeise’s dimer analogues of E/Z-cyclododecene and bicyclo[2.2.1]hept-2-ene which have not been previously reported in the literature.
ACKNOWLEDGMENTS

I would like to thank God for granting me the ability and understanding to step forward and take my education to the master’s level. I would like to thank my advisor for his helpful and understanding guidance throughout this research. Finally I would like to thank my family and friends for all the moral boosts during my studies while at IUP.
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CHAPTER I
REVIEW OF THE LITERATURE

1.1 The History of Zeise’s Salt and Zeise’s Dimer

To synthesize trans-dichlorobis(η^2-cyclooctene)platinum(II), which is a primary focus of this thesis, you must first synthesize Zeise’s salt K[Pt(C_2H_4)Cl_3], which is shown in Figure 1.1.

![Figure 1.1: Zeise’s Salt](image)

Zeise’s salt, named after its creator William Christopher Zeise, was first prepared in 1825 when he refluxed a mixture of PtCl_4 and PtCl_2 in ethanol with the addition of KCl. Zeise’s dimer, [Pt(C_2H_4)Cl_2]_2, was also synthesized during this time by a similar method. However, this product was not as pure, and was not immediately characterized. The salt of the anion Zeise obtained from his reaction were yellow needle-like crystals, that he theorized contained an ethylene group based on its elemental analysis. A proposed structure for metal-olefin bonding was first published in 1951 by M. J. S. Dewar which contained a normal dative bond via overlap between the filled π-orbitals of ethylene and the empty orbitals of the metal. Dewar applied this bonding model to silver-alkene compounds and proposed its use in platinum olefin structures. The bonding for Zeise’s salt, based on Dewar’s π-bonding model, was designed by Joseph Chat and L.A. Duncanson in 1953 and was the first published diagram of this model (shown in Figure 1.2). In 1954 x-ray crystallography confirmed this bonding model and the structure of
Zeise’s salt was found to be square planar with three chloride ligands and the ethylene positioned at the fourth corner of the square plane and perpendicular to the plane of chlorides.\textsuperscript{1} Zeise’s salt according to the Donor Pair electron counting method follows the 16/18 rule with a 16 electron count. Since Pt(+) is d\textsuperscript{8} it contributes 8 electrons, the chlorides provide 6 electrons, as 2 electron donors each, the ethylene contributes 2 electrons for a total of 16 electrons per complex.

\textbf{Figure 1.2: Dewar-Chatt-Duncanson Model of M-Alkene Bonding (from ref 4)}
1.2 Modern Synthesis of Zeise’s Salt and Zeise’s Dimer

The modern synthesis of Zeise’s salt is found in *Inorganic Syntheses* 1973, 14, 90. Similarly the modern method for synthesis of Zeise’s dimer, trans-[PtCl₄(η²-C₂H₄)]₂ can be found in *Inorganic Syntheses* 1977, 18, 181-185.

Potassium trichloro(η²-ethene)platinate(II) or Zeise’s salt is synthesized in the following reaction, shown below in Figure 1.3.

\[
\text{K}_2\text{PtCl}_4 + \text{C}_2\text{H}_4 + \text{H}_2\text{O} \xrightarrow{\text{SnCl}_2} \text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\cdot\text{H}_2\text{O} + \text{KCl}
\]

**Figure 1.3: Zeise’s Salt Synthesis (From ref 6)**

In the above reaction, deoxygenated 5M hydrochloric acid is mixed with the K₂PtCl₄ and a catalytic amount of SnCl₂. Any gas can be used for deoxygenation; however, it is a much easier to use ethylene gas since this will be the reagent gas. One thing to note when deoxygenating and adding ethylene gas, it is best to use long stem glass pipettes rather than syringe needles, due to corrosion from the 5 M HCl. The catalyst for the reaction, SnCl₂·2H₂O, is first mixed with deoxygenated distilled water. The dissolved deoxygenated tin(II) chloride solution is transferred using a hypodermic syringe to a flask containing a deoxygenated solution of K₂PtCl₄ in 5 M HCl. Then a steady stream of ethylene gas is bubbled through the solution until it changes to yellow. It can take up to 4-8 hours to dissolve the platinum salt. Once fully reacted, the mother liquor is decanted from the initial crop of crystals and placed in a refrigerator. The flask with the mother liquor is scratched to provide nucleation points for crystal growth. Once a second crop of crystals have formed, they are filtered. The remaining mother liquor is then placed under flowing argon gas to obtain the last remaining product by evaporation.
The mother liquor crystals are then dissolved in methanol and then vacuum filtered to separate them from the KCl. Evaporation of the methanol yields a third crop of product. The overall yield is 86%.

The synthesis of Zeise’s dimer starts with a reaction of Zeise’s salt and an equal molar ratio of pyridine to obtain the compound shown in Figure 1.4, using the reaction shown in Figure 1.5.

![Figure 1.4: Dichloro-η²-ethylenepyridineplatinum(II)](image)

To synthesize the pyridine complex, Zeise’s salt is dissolved in water and stirred until it is fully dissolved. Pyridine is then slowly added, dropwise over two minutes. Once the pyridine is added, a thick yellow cloud of precipitate is observed. The solution is allowed to stir for 30 minutes to ensure a full reaction. Once the reaction is complete the compound is then vacuum filtered and the bright yellow solids are left to dry. The typical yield is 89%.
The pyridine complex is next mixed vigorously with diethyl ether and acidic Dowex 50W-X8 resin, for an hour’s time, which removes the pyridine and forms Zeise’s dimer. To obtain a maximum yield, the solution is vacuum filtered and the resin rinsed with diethyl ether. The treatment with fresh Dowex resin is repeated for a total of 3 cycles. The solution after the third treatment is mixed with anhydrous MgSO₄ (to remove any water) and stored overnight in a refrigerator. The MgSO₄ is then filtered off and rinsed with diethyl ether. The final solution is then placed in a rotovap to remove the ether and the dry, orange solid of Zeise’s dimer is obtained. The overall yield is 40% based on the moles of platinum.

Many Zeise’s dimer analogs have been synthesized using both acyclic and cyclic alkenes such as styrene and 1-dodecene. The synthesis of cyclopentene, cyclohexene, cycloheptene, and cyclooctene analogues of Zeise’s dimer is shown in Figure 1.6 below using a generic cycloalkene (L) as an example. In this reaction two equivalents of the cycloalkene is reacted with Zeise’s dimer in either a chloroform or benzene solvent to synthesize the dimer analog.
Figure 1.6: Synthesis of the Cycloalkene Dimer
1.3 Structure and Bonding in Zeise’s Salt and Zeise’s Dimer

Zeise’s salt anion is a d^8 platinum(+2) compound with three Pt-Cl bonds at three corners of a square plane and the Pt-(η^2-C2H4) bond at the fourth corner. The ethylene is coordinated perpendicular to the Pt-Cl plane. This perpendicular coordination was also found to be preferred by Hoffmann et. al. in Molecular Orbital studies on M-L_4 ethylene complexes. The results showed this is due largely to steric repulsions between the ethylene and the cis-chlorides when the ethylene is forced into the Pt-Cl plane.

The alkene is perpendicular to the square plane in the crystal structure; however, in solution it is in constant motion. Temperature dependent NMR spectra of coordinated alkens, such as [PtCl(cis-but-2-ene)acac] (acac = acetylacetone), shown in Figure 1.7 (a), has two alkene proton resonances at low temperatures. These resonances are attributed to the two cis-but-2-ene isomers, with one isomer having the 1-methyl and 4-methyl positions of the butene angled toward the platinum center (b), and the other isomer having the methyls facing away (c). However, upon warming it was found that these signals coalesce. This coalescence was explained as being due to the rotational spin of the olefin around the Pt-olefin bond. Variable temperature NMR experiments found the energy barrier of rotation to be between 41.8 and 62.8 kJ mol^-1, and independent of the olefin.

![Figure 1.7: Rotation of the Olefin Bond (from ref. (10))](image)
The bond between ethylene and the metal is explained by the Dewar-Chatt-Duncanson model. In this model there is a sigma-bond between the \( \pi \) cloud of the ethylene and an empty d-orbital of the metal. There is also a \( \pi \)-back donation of electron density from the metal’s filled d orbitals to the empty \( \pi^* \) orbital of the ligand.\(^1\) Evidence for sigma donation and \( \pi \)-backbonding includes the facts that the hydrogens on the ethylene are bent away from the normal C=\( \text{C} \)-H plane by 32.5\(^\circ\)\(^\text{10}\) and that the C=C bond length of coordinated ethylene is longer when compared to free ethylene by 0.053 Å.\(^\text{12}\) Figure 1.8 below, shows the neutron diffraction structure of Zeise’s salt. The Pt-Cl \( \text{cis} \) bonds at 2.302(2) and 2.303(2) Å are slightly shorter than the Pt-Cl \( \text{trans} \) bond at 2.340(2) Å\(^\text{16}\), due to the \( \text{trans} \)-influence, which will be discussed later in this thesis. The Pt-C bond lengths are of similar length at 2.128(3) and 2.135(3) Å, with the bond length of coordinated ethylene at 1.375(4) Å.\(^\text{16}\)

![Figure 1.8: Structure of Zeise’s Salt (from ref 16)](image)

As shown in Figure 1.9, the single crystal X-ray structure of Zeise’s dimer shows this compound has a square planar structure with two terminal and two Pt-Cl bridge bonds and the ethyleses are perpendicular to the square plane as indicated by the following bond angles: Cl(1)-Pt(1)-Cl(11) =90.94\(^\text{9}\)\(^\circ\), C(11)-Pt(1)-Cl(1) =90.9\(^\circ\), and C(12)-Pt(1)-Cl(1) =92.3\(^\text{14}\)\(^\circ\). Also it has been found that the Pt-Cl bonds that are \( \text{trans} \) to the
bridging chloride bonds are shorter than the Pt-Cl bridged bonds: Pt(1)-Cl(1) 2.257 Å and Pt(1)-Cl(11) 2.328 Å respectfully.\textsuperscript{14} This is due to the ground state \textit{trans} influence of alkenes and a weakened \textit{trans} influence of the bridged chlorides.\textsuperscript{15} Zeise’s dimer has Pt-C bond lengths of 2.108 (18) and 2.157 (18) Å\textsuperscript{14}, while Zeise’s salt has Pt-C bond lengths of 2.16 and 2.15 Å.\textsuperscript{13} So, the bond lengths in these two compounds are very similar. The C=C bond lengths for Zeise’s dimer and Zeise’s salt are 1.41 (3) Å\textsuperscript{14} and 1.375 (4) Å\textsuperscript{15} respectively, while the C=C bond length for free ethylene is 1.337 (2) Å.\textsuperscript{16} This lengthening is reflective of the C=C bond weakening resulting from π-back donation of electrons from the platinum upon coordination.

\textbf{Figure 1.9:} Zeise’s Dimer (from ref 14)

The structure of Zeise’s dimer analogues have been reported in the literature.\textsuperscript{6,7,8} They are also square planer with the cycloalkene coordinated perpendicularly to the Pt-Cl plane.\textsuperscript{7,8} The cycloheptene analog of Zeise’s dimer has Pt-Cl bond distances of 2.257(6), 2.328(6), 2.362(6) Å, and Pt-C distances of 2.14(2) and 2.10(2) Å.\textsuperscript{7} The cyclopentene analog has Pt-Cl bond distances of 2.264(6), 2.320(5), and 2.349(5) Å, and Pt-C distances of 2.20(2) Å.\textsuperscript{7} These distances are similar to those of Zeise’s dimer. The bond distance of
the cyclooctene analogs of Zeise’s dimer will be discussed later in this thesis since they
are used to make trans-dialkene complexes of platinum(II).

1.4 Trans-Influence Versus Trans-Effect in Platinum Complexes

The trans influence and the trans effect are two distinctly separate properties of
square planar complexes. However both of these properties focus on the effect of a ligand
that is trans or opposite to the ligand of interest. Sometimes the trans effect is referred to
as the ‘trans-kinetic-effect’ to avoid confusion with trans influence, which will be
discussed later and is a thermodynamic effect.

In 1926 Russian scientist I. I. Chernyaev, introduced the concept of the trans-
effect, based his studies of the rates of square planar substitution reactions of Pt(II)
complexes.\(^1\) What he found was that when substitution occurred, the ligand trans to the
leaving group had an effect on the reaction rate. For example the rate constant for a
substitution reaction with a trans trialkylphosphine was 10,000 times larger than if the
trans ligand was chloride. After numerous studies of the rates of reaction of square planar
complexes of Pd(II) and Pt(II), the relative order of the trans effect, was found to be as
show in figure 1.10 below.\(^1\)

\[
\text{CN}^- \sim \text{CO} \sim \text{C}_2\text{H}_4 > \text{PR}_3 > \text{SH}_2 > \text{NO}_2^- > \Gamma > \text{Br}^- > \text{Cl}^- > \text{NH}_3 \sim \text{py} > \text{OH}^- > \text{H}_2\text{O}
\]

**Figure 1.10: Trans Effect Series**

This order means that for a complex such as the one shown below in Figure 1.11,
the anion of Zeise’s salt, [Pt(C\(_2\)H\(_4\))Cl\(_3\)]\(^-\), the substitution of the chloride trans to the C\(_2\)H\(_4\)
will be faster than the chlorides that are cis to it. This is why the trans isomer is
produced, when this compound is reacted with pyridine as shown in Figure 1.5.
Two factors that have been suggested as sources of the \textit{trans} effect. The effect of the \textit{trans} ligand on the ground state of the complex and the effect of the \textit{trans} ligand on the transition state.\textsuperscript{1} Of these two, the latter is the most plausible. The transition state rationale is based on the assumption that the \textit{trans} ligand stabilizes the trigonal bipyramidal transition state through π-bonding. This stabilization lowers the energy of the transition state and provides a stereochemical preference for substitution at the \textit{trans} position. The stereochemical preference comes from the assumption that π-bonding ligands prefer the trigonal plane of the trigonal bipyramidal transition state.\textsuperscript{1} This is shown in Figure 1.12. This rationale is supported by the fact that ligands that are high in the \textit{trans} effect such as CO and C\textsubscript{2}H\textsubscript{4}, have π-backbonding and overlap best with the d-orbitals in the trigonal plane of the trigonal bipyramidal transition state.\textsuperscript{15}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure11.png}
\caption{[Pt(C\textsubscript{2}H\textsubscript{4})Cl\textsubscript{3}]\textsuperscript{-}}
\end{figure}

\textbf{Figure 1.12:} Square Planar Associative Reaction (from ref 17)

The ground state rationale for the \textit{trans} effect is often called the \textit{trans} influence. This rationale is based on the fact that a ligand \textit{trans} to the leaving group weakens the leaving group’s bond to the metal because it more successfully competes for the same d-
orbitals of the metal. Using this rationale, ligands with strong σ-donor abilities will be high in the *trans* effect and destabilize the complex at this position.

The *trans*-influence is still a recognized property of square planar complexes. For example the bond length of the chloride *trans* to ethylene in Zeise’s salt is 2.340 (2) Å while the chloride *cis* to it is 2.302 (2) Å. By examining the structures of a number of series of *trans* complexes of the type *trans*-[PtL₂XY] a *trans*-influence series has been determined and is shown in Figure 1.13 below. Note that π-bonding ligands such as CO and CN⁻ are lower in the *trans*-influence series than strong sigma bonding ligands such as H⁻, which is also consistent with a ground state, thermodynamic model.

\[
\text{H}^- > \text{PR}_3 > \text{SCN}^- > \text{I}^- > \text{CH}_3^- > \text{CO} > \text{CN}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 > \text{OH}^-
\]

**Figure 1.13: Trans Influence Series**
1.5 NMR Spectroscopy of Alkene Complexes of Platinum

Nuclear magnetic resonance spectroscopy is one of the primary methods for characterization of organometallic compounds since both hydrogen and carbon nuclei in the ligands can be detected. For organometallic complexes of platinum there is an added benefit in that one of the isotopes of platinum, $^{195}$Pt, is also NMR active and is present in 33% abundance. So, in platinum-alkene complexes, $^1$H, $^{13}$C, and $^{195}$Pt NMR spectroscopy can be used to characterize the hydrocarbon ligands and their bonding with the metal center. The resonances that are linked to the bond between platinum and the ligand can also be identified by the coupling of platinum to the hydrogens on carbon and indicated in the literature as, $J_{Pt-H}$ and $J_{Pt-C}$.1 Another added benefit of NMR spectroscopy is that the magnitude of the chemical shift and the coupling constants (when compared to the uncoordinated ligand) also provide a qualitative measure of the platinum carbon bond strength. The larger the chemical shifts and coupling constants, the stronger the bond. A summary of NMR and X-ray crystallography data for selected platinum-alkene complexes is presented in Table 1.1. The chemical shifts presented in the table are of the C=C bond of the ligand.
Table 1.1: Summary of the NMR and Pt-C Bond Length Data for Selected Alkene Complexes of Platinum(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR H-C=C-H (ppm)</th>
<th>$^{13}$C NMR H-C=C-H (ppm)</th>
<th>$^{195}$Pt NMR (ppm)</th>
<th>Pt-C Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeise’s Salt$^{14}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PtCl$_3$-(η$^2$-C$_2$H$_4$)]$^-$</td>
<td>4.43</td>
<td>67</td>
<td>-2994</td>
<td>2.16/2.15</td>
</tr>
<tr>
<td>Diene Complexes$^{10,18}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis- PtCl$_2$(η$^2$-C$<em>8$H$</em>{12}$)</td>
<td>5.6</td>
<td>100.6</td>
<td>-3337</td>
<td>2.176/2.178</td>
</tr>
<tr>
<td>trans-PtCl$_2$-(η$^2$-C$<em>8$H$</em>{14}$)$_2$</td>
<td>5.58</td>
<td>113.3</td>
<td>-2747</td>
<td>2.26</td>
</tr>
<tr>
<td>Zeise’s Dimer and Analogs$^{12-15}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-[PtCl$_2$(η$^2$-C$<em>8$H$</em>{14}$)]$_2$</td>
<td>5.47</td>
<td>109.5</td>
<td>-2434, -2453</td>
<td>2.132/2.143</td>
</tr>
<tr>
<td>trans-[PtCl$_2$-(η$^2$-C$<em>7$H$</em>{12}$)]$_2$</td>
<td>5.78</td>
<td></td>
<td>2.14/2.10</td>
<td></td>
</tr>
<tr>
<td>trans-[PtCl$_2$-(η$^2$-C$<em>6$H$</em>{10}$)]$_2$</td>
<td>6.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-[PtCl$_2$-(η$^2$-C$<em>5$H$</em>{8}$)]$_2$</td>
<td>6.05</td>
<td></td>
<td></td>
<td>2.20</td>
</tr>
<tr>
<td>trans-[PtCl$_2$-(η$^2$-C$_2$H$_4$)]$_2$</td>
<td>4.88</td>
<td>82</td>
<td>-2525</td>
<td>2.114/2.132</td>
</tr>
</tbody>
</table>

The $^1$H NMR of Zeise’s salt and Zeise’s dimer have the lowest chemical shift compared to those of the cycloalkenes (C$_5$H$_8$, C$_6$H$_{10}$, C$_7$H$_{12}$, C$_8$H$_{12}$, C$_8$H$_{14}$). The $^1$H NMR chemical shifts of the alkene protons show that the cycloalkene complexes in Zeise’s dimer analogs have a gradual downfield chemical shift from cyclooctene to cyclopentene. It should be noted that, with respect to the complexes, the $^1$H chemical shift value of uncoordinated ethylene is 5.4 ppm in CDCl$_3$ solvent$^{19}$ and the $^1$H chemical shift values for uncoordinated cyclooctene are 5.618, 1.526, and 1.492 ppm in CDCl$_3$ solvent.$^{20}$ So, while the chemical shift of uncoordinated ethylene is downfield when compared to the analogous platinum compounds, this is not true for the cyclooctene or cyclooctadience complexes. There are no observable coupling between the cyclooctene hydrogens and the platinum due to fast exchange with excess cyclooctene (cot) in solution.$^{18}$ The $J_{Pt-H}$ values
for Zeise’s salt and Zeise’s dimer are 66 Hz and 71 Hz respectively and the $J_{\text{Pt-H}}$ coupling for $\text{PtCl}_2(\eta^2-\text{C}_8\text{H}_{12})$ is 67 Hz.\textsuperscript{8,15,18} This shows that there is little difference in $J_{\text{Pt-H}}$ coupling from the platinum-carbon bond and that there is no apparent trend with the various compounds of platinum(II).

The $^{13}\text{C}$ NMR data in Table 1.1 shows that the chemical shift of free ethylene in CDCl$_3$ (123 ppm) decreases significantly when coordinated to platinum (67 for Zeise’s salt and 82 ppm for Zeise’s dimer) indicative of deshielding by $\pi$-backbonding resulting in a strong platinum olefin bond. This is also true for the cyclooctene and cyclooctadiene compounds. The trans-[$\text{PtCl}_2(\eta^2-\text{cot})]_2$ and the trans-$\text{PtCl}_2(\eta^2-\text{cot})_2$ compounds have similar $^{13}\text{C}$ chemical shifts, with those of 1,5-CODPtCl$_2$. In uncoordinated cyclooctene the $^{13}\text{C}$ chemical shift values are 130.098 (C=C), 29.241 (CH$_2$), 26.200 (CH$_2$), and 25.521 (CH$_2$), ppm in CDCl$_3$.\textsuperscript{20} The [PtCl$_3(\eta^2-\text{C}_2\text{H}_4)]^-$ chemical shift value is noticeably smaller than in Zeise’s dimer, and both are smaller than the cyclooctene or cyclooctadiene complexes. However, there appears to be no correlation of chemical shifts with the corresponding Pt-C bond lengths in these complexes as shown in Table 1.1.\textsuperscript{10}

Table 1.2 lists $^{195}\text{Pt}$ NMR for some selected alkene complexes of platinum(II). The chemical shift values show that the monomeric compounds have an upfield shift of the alkene when compared to their dimeric counterparts.\textsuperscript{8,10,18} However, as with the carbon NMR, there appears to be no relatable trend between the $^{195}\text{Pt}$ NMR chemical shifts and the Pt-C bond lengths in determining whether the compounds contains an ethylene or a cycloalkene ring.
Table 1.2: $^{195}$Pt NMR Chemical Shift Values

<table>
<thead>
<tr>
<th>$^{195}$Pt NMR, ppm</th>
<th>Solvent: CDCl$_3$</th>
<th>Monomer or Dimer</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[PtCl$_2$(η$^2$-C$_2$H$_4$)]$_2$</td>
<td>-2525</td>
<td>dimer</td>
<td>8</td>
</tr>
<tr>
<td>[PtCl$_3$(η$^2$-C$_2$H$_4$)]$^-$</td>
<td>-2994</td>
<td>monomer</td>
<td>8</td>
</tr>
<tr>
<td>1,5-CODPtCl$_2$</td>
<td>-3337</td>
<td>monomer</td>
<td>10,18</td>
</tr>
<tr>
<td>trans-[PtCl$_2$(η$^2$-cot)]$_2$</td>
<td>-2434 and -2452</td>
<td>dimer</td>
<td>18</td>
</tr>
<tr>
<td>trans-PtCl$_2$(η$^2$-cot)$_2$</td>
<td>-2747</td>
<td>monomer</td>
<td>18</td>
</tr>
</tbody>
</table>
1.6 Trans-Dialkene Complexes of Platinum(II)

There are only a few reports of trans-dialkene complexes of platinum(II) in the literature. This is in contrast to the large amount of research done on cyclic cis-dialkene complexes such as cis-dichloro(η^4–1,5-cyclooctadiene)platinum(II). These cyclic cis-dialkene are not only commercially available, but take advantage of the chelate effect to provide a more stable product. Because of the large distance between the trans coordination positions of a square plane, no cyclic trans-dialkene complexes have been reported, as these would require specially designed ligands. Therefore, the current examples of trans-dialkene complexes all involve monodentate coordination of an alkene to the metal. An example of a generic trans-dialkene complex of platinum is shown in Figure 1.14. In the literature there are three different alkenes that appear most often in trans-dialkene complexes of platinum(II). These are complexes of a) ethene; b) styrene; and c) cyclooctene which are described in this section

![Figure 1.14: Generic trans-Di-Alkene Complex of Platinum](image)

The most recent studies of trans-bisethene complexes of platinum were done by Plutino et. al.\(^\text{18}\) in 1999 and Otto et.al.\(^\text{22}\) in 2006. In both of these literature reports, the trans-dichlorobis(η^2-ethene)platinum(II) was synthesized as shown in Figure 1.15.
In this reaction, Zeise’s dimer (1) is reacted with excess ethene in chloroform at room temperature. The initial product (2) was obtained as a yellow solid and proposed to be the *trans*-monomer (2) based on $^1$H NMR, $^{195}$Pt NMR and mass spectrometry. NMR data for compound (2), the *trans* complex are: $^1$H: 4.71 ppm, 55 Hz $^1$H-$^1$H; $^{195}$Pt: $-$2994 ppm. Compound (2) decomposes at room temperature and or isomerizes to the *cis*-complex (3) when the solvent is evaporated. The *cis*-complex was previously reported by Huang et. al. and is more thermodynamically stable than its *trans* counterpart. The more stable *cis*-isomer was characterized by NMR, mass spectrometry and single crystal x-ray diffraction. NMR data for compound (3), the *cis* product: $^1$H: 4.709 ppm, 56 Hz $^1$H-$^1$H; $^{195}$Pt: $-$3645 ppm.

The large difference in the $^{195}$Pt NMR chemical shifts of compounds (2) and (3) may be due to the different geometries of the two compounds as well as the *trans* isomer having alkenes that are competing for the same d-orbitals on the metal for bonding and π-backbonding. Zeise’s dimer has a larger downfield $^1$H NMR chemical shift (4.88 ppm) than compounds (2) and (3) while Zeise’s salt has a smaller chemical shift (4.43) than compounds (2) and (3). The Pt-H coupling constant of Zeise’s dimer at 71.8 Hz is larger than the 55, 56 Hz for compounds (2) and (3), respectively while the coupling for Zeise’s salt is larger (66Hz). There appears to be no pattern to these proton NMR values from one complex to another, which is also the case with the $^{195}$Pt chemical shifts.
NMR data is also not correlated to the Pt-C bond lengths in the x-ray structures of Zeise’s salt, Zeise’s dimer and compound (3) which range from 2.11/2.157 in Zeise’s dimer to 2.16/2.15 in Zeise’s salt to 2.17/2.15 in compound (3).

Figure 1.16: X-Ray Crystal Structure for Complex (3) (from ref 22)

The x-ray structure of compound (3) is shown in Figure 1.16 along with a summary of the bond lengths and angles. Compounds (1) and (3) have square planar geometries with the alkene coordinated perpendicular to the Pt-Cl plane. It is also important to note that there is little difference in Pt-C bond lengths of Zeise’s salt, Zeise’s dimer, and (3). A slight difference is noted when comparing the C=C bond lengths of 1.375(4) Å for Zeise’s salt, 1.41(3) Å for Zeise’s dimer, and 1.384(14)/1.390(16) Å for (3).

The second type of trans-dialkene complexes in the literature are those derived from styrene. These complexes were studied by Hupp in 1976, by Albinati et. al. in 1976.
1987 and by Caseri\textsuperscript{26} in 1988. In these reports the \textit{trans}-bis-styrene complex was synthesized by reacting the styrene dimer with an excess of styrene in dichloromethane (Figure 1.17) or by adding PtCl\textsubscript{2} to liquid styrene.

**Figure 1.17:** \textit{Trans}-bis Styrene Synthesis

Hupp et. al.\textsuperscript{24} reported that a \textit{trans} bis-styrene complex is the most plausible product based on the presence of as a new peak at 370 nm in the UV spectrum. Caseri, et. al.\textsuperscript{26} reported that the \textit{trans} isomer is the initial product formed from the reaction of PtCl\textsubscript{2} with liquid styrene. This was identified by a \textsuperscript{195}Pt NMR peak at -2609 ppm and a single Pt-Cl vibration in the IR at 332 cm\textsuperscript{-1}, since the \textit{cis}-product has a chemical shift of -3100 ppm,\textsuperscript{25,24} and \textit{cis}-PtCl\textsubscript{2} complexes have two Pt-Cl vibrations. The initial \textit{trans} product is unstable above -6°C, and soon isomerizes into the \textit{cis} form. According to Albirati et. al.\textsuperscript{25}, only the \textit{cis} isomer (4) can be isolated from the reaction of PtCl\textsubscript{2} with styrene; \textsuperscript{195}Pt NMR reveals three possible conformations (a, b, c) as shown in Figure 1.18. The three chemical shifts are at c = -3169 ppm, a = -3290 ppm, b = -3310 ppm in a 2:1:1 ratio. Conformation (a) was found in a single crystal X-ray diffraction of the solid and was suggested to be the most stable since it would pack best into a crystal, due to the orientation of the phenyl groups.\textsuperscript{25}
As described above, the first two trans-dialkene complexes synthesized from ethylene and styrene are unstable and isomerize easily to the cis form. On the other hand, trans-biscyclooctene complexes are quite stable. This type of complex has been investigated by Shaver et. al. in 2000 and Otto et. al. in 2003. This trans-dialkene compound can be prepared either by reacting K₂PtCl₄ and SnCl₂ in an isopropanol-water mixture with an excess of cyclooctene or by using the reaction shown in Figure 1.19. This is preferred over the isopropanol-water method since it provides higher yields and has a shorter reaction time.

In the reaction shown in Figure 1.19, the cyclooctene (cot) analogue of Zeise’s dimer is reacted with 2.2 molar equivalents of cyclooctene in dichloromethane and the monomer (6) is obtained. The NMR data for compound (5) and (6) are summarized in Table 1.1 and 1.2 and were discussed earlier. Table 1.3 below, shows x-ray
crystallography bond lengths and angles for the compounds compounds (5) and (6) as well as a cycloctene analogue to Zeise’s salt, compound (7). Table 1.3 and Figure 1.20 below, come from Otto et. al. in *Dalton Trans.* (2003), p. 2519.\(^\text{15}\)

All three compounds have the expected square planar geometry. Compound (5) has a Cl(1)-Pt-Cl (1)’ bond angle of 83°, compound (6) has a Cl(1)-Pt-Cl(1)’ bond angle of 180°, and compound (7) has a Cl(1)-Pt-Cl(3) bond angle of 86°.\(^\text{15}\)

The bond angle between the Pt-Cl square plane and the alkenes are 89.8°, 88.2°, and 88.9° for compounds (5), (6), and (7) respectively. This shows the alkenes are coordinated perpendicular to the Pt-Cl plane in accordance with previous literature studies conducted on metal olefin bonding angles by Hoffman et.al.\(^\text{9}\) and the structures of Zeise’s salt and Zeise’s dimer.

In compound (5) the Pt-Cl bond lengths for the terminal and bridging chlorides are 2.265 Å and 2.355 Å respectively. These bond lengths are similar to those in Zeise’s dimer which has terminal and bridging Pt-Cl bond lengths of 2.257 Å and 2.347 Å.\(^\text{14}\)

The *trans* Pt-Cl bond length of compound (7) is similar to the one in Zeise’s salt (2.36 Å versus 2.34 Å respectively). The *cis*-Pt-Cl bond lengths in compounds (6) and (7) are similar to each other at ~2.30 Å, however, in compound 5 there is a noticeable *trans* influence with the *trans* Pt-Cl bond length of 2.36 Å.\(^\text{16}\)

The Pt-C bond lengths of compound (5) are 2.132 and 2.143 Å,\(^\text{15}\) and are similar to its chemically analogous compound, Zeise’s dimer, which has Pt-C bond lengths of 2.108 and 2.157 Å.\(^\text{14}\) Compound (7) has Pt-C bond lengths of 2.160 and 2.161 Å\(^\text{15}\) which are slightly longer than Zeise’s salt, which has Pt-C bond lengths of 2.128 and 2.135 Å.\(^\text{16}\)

This difference in bond length is almost within experimental error. Compound (6) has the
longest Pt-C bond lengths at 2.259 and 2.287 Å.\textsuperscript{15} These weak bonds, according to the authors\textsuperscript{15} is due to labilization of the trans-cyclooctene ligands since they share the same d-orbital’s of the platinum metal\textsuperscript{15}.

Table 1.3: Selected bond lengths (Å) and angles (°)

| Symmetry related atoms primed (From ref. 15) |
|---|---|---|
| Bond/angle | 5 | 6 | 7 |
| Pt-C1(1) | 2.340(3) | 2.3068(18) | 2.3632(12) |
| Pt-C1(1)' | 2.371(3) | 2.3068(18) | 2.3632(12) |
| Pt-C1(2) | 2.265(4) | 2.3022(12) | 2.3022(12) |
| Pt-C1(3) | 2.2913(12) | 2.2913(12) | 2.2913(12) |
| Pt-C1(1) | 2.132(13) | 2.259(6) | 2.160(4) |
| Pt-C1(2) | 2.145(13) | 2.287(6) | 2.161(4) |
| C1(1)-C2(1) | 1.41(2) | 1.375(8) | 1.399(6) |
| C1(1)-Pt-C1(1)' | 83.84(12) | 180 | 90.68(5) |
| C1(1)-Pt-C1(2) | 173.74(12) | 90.68(5) | 90.68(5) |
| C1(1)-Pt-C1(3) | 86.81(5) | 173.74(12) | 173.74(12) |
| C1(2)-Pt-C1(1) | 96.2(4) | 86.04(17) | 86.04(17) |
| C1(2)-Pt-C1(2) | 96.5(4) | 86.19(18) | 86.19(18) |
| C1(2)-Pt-C1(3) | 89.9(4) | 88.80(12) | 88.80(12) |
| C1(3)-Pt-C1(1) | 94.0(4) | 87.64(13) | 87.64(13) |
| C1(3)-Pt-C1(2) | 94.30(13) | 94.30(13) | 94.30(13) |
| C1(1)'-Pt-C1(1) | 157.0(4) | 93.96(17) | 93.96(17) |
| C1(1)'-Pt-C1(2) | 164.5(4) | 93.81(18) | 93.81(18) |
| C1(1)-C2(1)-PtC1(2) | 91.8(8) | 88.5(4) | 88.5(4) |
| C1(1)-C2(1)-PtC1(3) | 90.7(8) | 90.0(3) | 90.0(3) |
| C1(1)-C2(1)-PtC1(3) | 91.1(3) | 91.1(3) | 91.1(3) |

Figure 1.20: Molecular diagrams of structures (5), (6), and (7). (From ref. 15)
CHAPTER 2.
STATMENT OF THE PROBLEM

The objective of this research is to synthesis trans-dialkene complexes of platinum(II). Since there have been few reports of these trans-dialkene structures compared to numerous cis-chelate complexes already presented in literature, the extent of their characterization is limited. These trans-dialkene complexes will be synthesized by reacting various cycloalkenes with Zeise’s dimer in solution. The trans-dialkene complex of Z-cyclooctene has already been reported in the literature. This will be used as a benchmark for successful synthesis and characterization of other cycloalkene complexes. Then other cycloalkenes will be used including Z-cyclohexene, Z-cycloheptene, Z-cyclooctene, E-cyclodecene, and E/Z-cyclododecene. Rigid bridged cycloalkenes such as bicyclo[2.2.1]hept-2-ene and bicyclo[3.2.1]oct-2-ene will also be reacted with Zeise’s dimer in attempts to obtain the corresponding trans-dialkene compounds.
CHAPTER 3.
EXPERIMENTAL SECTION

All reactions were done at room temperature in the presence of air unless otherwise discussed. All of the chemicals, equipment, and materials used in this research were available in the Science Storeroom in Weyandt Hall and Dr. Woolcock’s research lab, Weyandt 239C. This includes basic laboratory equipment and glassware, stirring hot plates, rotaory evaporator, freezer, fume hood, balances, inert atmosphere glassware, etc. Basic laboratory chemicals and solvents that are not available from the Science Storeroom or are not currently available in Dr. Woolcock’s research lab that were purchased were E-cyclodecene, and E and Z-cyclododecene. Chemicals that were purchased to synthesize 1,2-cyclononadiene, include: methyllithium, HBr, ethylmagnesium bromide, CHBr₃, and cyclooctene. These materials came from Sigma Aldrich and Acros Chemical. The platinum starting material for the synthesis of all these organometallic complexes, K₂PtCl₄, was purchased from Sigma-Aldrich and Pressure Chemical. A 300 MHz Bruker/Tecmag NMR spectrometer was used for ¹H, ¹³C, and ¹⁹⁵Pt NMR spectroscopy. Single crystal and powder X-ray diffraction was done in The Multidisplinary X-ray Facility in Weyandt 65-66.

3.1. Synthesis of Zeise’s Salt

Zeise’s salt was synthesized following Inorganic Syntheses 1973, 14, 90-91⁵. This is a modernized and more efficient method based on the original synthesis (see Figure 1.3). In the Reaction 3.0 g of K₂PtCl₄ (7.23 mmol) were placed in 50 mL pear shaped flask with 30.0 mL of 5 M HCl, this flask is then stoppered and deoxygenated by bubbling ethylene gas through the solution for 30 minutes. Deoxygenation is done with
ethylene gas since it is also the reagent gas in the reaction. Another flask with 3.30 ml of water is deoxygenated and transferred by syringe to a flask containing 26.0 mg of catalyst, SnCl₂ that has also been deoxygenated. Once fully mixed the catalyst is transferred to the flask containing K₂PtCl₄ by syringe and ethylene is then bubbled into the red solution. When bubbling in ethylene, two glass pipettes are used as the gas-inlet and gas-outlet. Glass is used due to the acidic nature of the solution since the acid will dissolve metal needles and contaminate the mixture. The solution is bubbled until all particulates are dissolved and the solution changes from red to yellow in color, usually ~8 hrs. The solution was then refrigerated and scratched to promote further crystal growth. The mother liquor was then decanted, evaporated, and the solid that remained is rinsed with methanol to remove any impurities such as KCl. The mixture was then vacuum filtrated and then evaporated to obtain Zeise’s salt. The crystals were weighed to obtain a total mass of 2.578 g for an 86% yield.

3.2 Synthesis of Zeise’s Dimer

The synthesis of Zeise’s dimer follows the reaction diagram shown below in Figure 3.1 and is adapted from Inorganic Syntheses 1977, 18, 181-185.⁶ In the reaction 2.00 g of Zeise’s salt (5.43 mmol) is placed in a 100 mL Erlenmeyer flask with 50.0 mL of water and magnetically stirred until it was completely dissolved. Next, 0.44 mL (5.46 mmol) of pyridine was added dropwise via a syringe over two minutes. Once added a thick yellow cloud of precipitate was formed and the reaction was magnetically stirred for 30 minutes.
Figure 3.1: Synthesis of Zeise’s Dimer (1)

The solid was separated by vacuum filtration using a sintered glass frit (medium pore size), washed three times with 10.0 mL portions of water, dried, weighed, and stored till further use. A typical yield was 1.702 g (96%). In all cycloalkene synthesis reactions 0.400 g of the pyridine compound was used to make Zeise’s dimer unless otherwise noted. A 1.07 mmol (0.400 g), amount of trans-dichloro(ethylene)(pyridine)platinum(II) is weighed out and dissolved in 25.0 mL of anhydrous diethyl ether. Then 7.5-8.0 g (12 equivalents) of Dowex 50W-X8 H⁺ Resin, was added and stirred vigorously with a magnetic stirrer for one hour. Once stirred, the mixture was vacuum filtrated using a sintered glass frit (medium) and rinsed twice with 5.0 mL portions of diethyl ether. The filtrate was collected and stirred with fresh 7.5-8.0 g of new Dowex H⁺ Resin for another hour. This process is repeated for a total of three times. After the third time the filtrate was stored overnight in a refrigerator with anhydrous MgSO₄ to remove any water. The solution is rotovaped to dryness to obtain the orange solid of Zeise’s dimer; yield was 0.304 g (0.517 mmol), or 96%. The yield was based on the moles of platinum present. The maximum yield possible for Zeise’s dimer from the pyridine compound is 0.315 g
from a 0.400 g sample. The Dowex H⁺ Resin can be regenerated by rinsing it first with water, than three times with an equal volume of 4.0 M H₂SO₄. It is then stored in a tightly closed jar until needed.

3.3 Synthesis of trans-Dialkene Complexes

The main scheme used is shown below in Figure 3.2 with cyclooctene as an example ligand. However, any cycloalkene ligand can be used in its place. This procedure was adapted from Inorganic Syntheses 1973, 14, 90-91, 1977, 18, 181-185, and Dalton Transactions 2003, 2519-2525. This synthetic process for the cyclooctene trans-dialkene was the same general procedure used with all other ligands to obtain a trans-dialkene compound unless otherwise noted.

The method used to obtain the trans-dialkene compounds in this thesis follow pathway A. These syntheses used between 0.340-1.06 mmol of Zeise’s dimer as the starting material, 4.4 molar equivalents of the ligand, 10.0 mL of toluene as the solvent, and 2.0 mL of acetone to fully dissolve the dimer in a 50 mL round bottom flask. The solutions were stirred with a magnetic stirrer for half an hour without heating. If no changes were observed, gentle heating by convection (the flask is positioned above a hot plate) was commenced. If after two hours there was no noticeable change, the heat was gradually increased to a slight reflux and argon gas was gently bubbled into solution using a glass pipette to drive off ethylene gas. This process was continued for an additional 2 hours. Then the flask was then cooled and stoppered and placed in a freezer to promote crystal growth. Any solid obtained was collected using vacuum filtration over a sintered glass frit (medium pore size) and rinsed three times with equal 3 mL portions
of toluene. The solid obtained was placed in the freezer to prevent breakdown of the product.

Another possible synthetic route to obtain the trans-dialkene compound is shown as path B. This route reacts the pyridine compound with the desired cycloalkene to form the dimer analog, then a further 2 equivalents of ligand is added to synthesize the trans-dialkene compound.

A third synthetic route, path C, can be used to obtain the desired trans-dialkene compound as well. This is done in two stages; Zeise’s dimer is first reacted with two equivalents of the desired cycloalkene to obtain the dimer analog. Another 2 equivalents are then used to break the bridging Pt-Cl bond to obtain the trans-dialkene compound.

Path A was used first since there are fewer steps in this synthesis. Path C was used for the reaction of cyclohexene, cycloheptene, E-cyclodecene, cis/trans-cyclododecene and bicyclo[2.2.1]hept-2-ene where only 2.2 molar equivalents were mixed with Zeise’s dimer. Path B was also used with the bicycle[2.2.1]hept-2-ene ligand in an attempt to produce the trans-dialkene compound.
Figure 3.2: Synthesis Pathway for trans-[PtCl$_2$-(η$^2$-cot)$_2$] (6)

3.4 Synthesis of the Cyclooctene trans-Dialkene Compound: Path A

In this reaction 1.06 mmol (0.621 g) of Zeise’s dimer was dissolved in 10 mL of dichloromethane, with 4 molar equivalents 4.21 mmol (0.465 g) of cyclooctene, the solution was stirred with a magnetic stirrer, after 40 minutes another half equivalent 0.529 mmol (0.058 g) was added to speed up or force the reaction to completion$^{15}$. After
reacting, the yellow solution was placed in a freezer and a yellow solid was observed the next day. The reaction mixture was left for 2 more days in the freezer to promote crystal growth. The liquid was decanted from the solid and rinsed two times with 5.0 mL portions of hexanes. The solid had a slight orange color with a mass of 0.431 g (0.573 mmol), for a 54% yield. Further cooling of the mother liquor in a freezer afforded precipitation of a yellow solid. The liquid was decanted from the solid and rinsed with hexanes, to give a mass of 0.376 g (0.773 mmol), for a 36% yield. For NMR analysis 0.020 g of each solid was dissolved in 1.0 mL of CDCl₃ and ¹H NMR data was collected. After sitting in solution for 3 months in the NMR tube, the solvent was allowed to slowly evaporate to obtain single crystals that were cut, mounted, and analyzed by single crystal X-ray diffraction. The yellow solid was also analyzed by X-ray powder diffraction. The X-Ray analysis were done during the 2011 ACA (American Crystallography Association) summer course held at IUP.

3.5 Synthesis of Zeise’s Dimer Analogs: Path B

Pathway B was used with bicyclo[2.2.1]hept-2-ene, in which 0.535 mmol (0.200 g) of the pyridine compound was added to one molar equivalent 0.535 mmol (0.051 g) of the ligand in CDCl₃ (12 mL). The reaction was initially set in an ice bath according to literature procedures.²⁷ A sample of the reaction mixture was analyzed using ¹H NMR after the reaction was allowed to mix for 3 hours.
3.6 Synthesis of Zeise’s Dimer Analogs: Path C

The method to obtain the Zeise’s dimer analog of the various cycloalkenes, *trans*-[PtCl₂(η²-CₓH₂y)]₂ where x = 6-10, 12; y = 12-18, 22 compounds follow pathway C shown in Figure 3.2. These syntheses used 0.340-0.524 mmol (0.200-0.308 g) of Zeise’s dimer as the starting material and 2.2 molar equivalents of the ligand. This amount of ligand is sufficient in replacing the ethylene of Zeise’s dimer with the desired cycloalkene. The solvents used, the reaction steps, and product work up, were the same as for the synthesis of the *trans*-dialkene complexes on page 28.

3.7 Crystal Growth

Two methods were used to grow crystals. The first was a two solvent method in which the solid was added to a solvent in which it was soluble. A second, less volatile solvent was added to slow evaporation for better crystal growth. The solvent choice was varied on which solvent dissolved the solid the best. Toluene and acetone worked well in most cases. This mixture of two solvents in a beaker was covered with Parafilm with several needle holes poked through to allow for evaporation. The beaker is then placed in a freezer and left undisturbed. This method was used to grow the crystals of: *trans*- [PtCl₂(η²-C₇H₁₂)]₂ (9), *trans*- [PtCl₂(η²-C₁₀H₁₈)]₂ (10), and *trans*- PtCl₂(η²-C₁₀H₁₂)₂ (11).

The second crystal growth method was evaporation in an NMR tube over time. This method was facilitated by the slow evaporation of CDCl₃ from the already saturated solution. Crystals obtained this way needed more work-up (cutting and cleaning) compared to the other method. The NMR tubes were cut in half to allow a needle access in to remove the crystals. Once removed the crystals were cut with an Exacto knife to obtain a single crystal. The crystal was glued to the end of a glass fiber with a silicon
based adhesive and placed in a brass mounting pin for analysis. This method was used to mount crystals of trans-[PtCl$_2$(η$^2$-C$_8$H$_{16}$)]$_2$ (5), trans-PtCl$_2$(η$^2$-C$_8$H$_{16}$)$_2$ (6), and, trans-[PtCl$_2$(η$^2$-C$_7$H$_{12}$)]$_2$ (9).

3.8 Synthesis of the Cyclohexene Analog of Zeise’s Dimer

The synthesis of trans-[PtCl$_2$(η$^2$-C$_6$H$_{10}$)]$_2$ (12) followed path C (shown in Figure 3.2) in which 2.2 molar equivalents 1.15 mmol (0.095 g), of cyclohexene were used. Zeise’s dimer (0.524 mmol, 0.304 g), was dissolved in solution with the ligand. The reaction followed the general procedure for path B on page 31. After reacting the solution was decanted into a beaker and placed in a freezer to precipitate a solid. After sitting in the freezer overnight, the dark orange solution was evaporated to afford a brown solid, 0.309 g (0.444 mmol), or 85% yield. For NMR analysis 0.016 g of product was dissolved in CDCl$_3$ and the $^1$H NMR spectral analysis was obtained, (see Figure 4.4).

3.9 Reaction of 4 Molar Equivalents of Z-Cyclohexene with Zeise’s Dimer

The attempted synthesis of trans-PtCl$_2$(η$^2$-C$_6$H$_{10}$)$_2$ followed path A in which 4.4 molar equivalents 2.27 mmol (0.187 g), of cyclohexene was reacted with Zeise’s dimer 0.517 mmol (0.304 g), in solution. The reaction followed the general procedure for path A on page 28. No solids were observed so the orange solution was placed in a freezer when the reaction was completed. After 5 days the orange solution did not precipitate crystals or solid so the solution was placed in a Petri dish and the solvent allowed to evaporate in a fume hood with the sash closed enough to allow constant air flow. After 4 hours a brown colored solid was obtained (0.197 g) on the bottom of the dish, with a ring of solid (0.089 g) at the evaporated solvent level on the side. The solid was collected and
placed back into a freezer. Yield 0.286 g (0.411 mmol), or 80% based on molar amounts of platinum. For $^1$H $^{13}$C and $^{195}$Pt NMR analysis 0.035 g of the brown product was dissolved in 1.0 mL of CDCl$_3$ and spectral analysis of the solution was obtained.

3.10 Synthesis of the Cycloheptene Analog of Zeise’s Dimer

The synthesis of $trans$-[PtCl$_2$(η$_2$-C$_7$H$_{12}$)]$_2$ (9) followed path B in which 2.2 molar equivalents 1.10 mmol (0.106 g), of cycloheptene were reacted with Zeise’s dimer 0.505 mmol (0.297 g) in solution. The reaction followed the general procedure for path B on page 32. After 30 minutes a cloudy precipitate was noticed in the yellow-orange solution, and the reaction was continued. A bright orange colored solid was obtained. Both the solid and mother liquor were placed in a freezer. After sitting in the freezer overnight more orange solid precipitated from solution. The solid obtained was weighed to give 0.230 g (0.318 mmol), for a 63% yield. For NMR analysis 0.035 g of product was dissolved in 1.0 mL CDCl$_3$. The $^1$H, $^{13}$C, $^{195}$Pt NMR spectral analysis, and single crystal x-ray diffraction date was obtained.

3.11 Reaction of 4 Molar Equivalents of Z-Cycloheptene with Zeise’s Dimer

The attempted synthesis of $trans$-PtCl$_2$(η$_2$-C$_7$H$_{12}$)$_2$ followed path A in which 4.4 molar equivalents 2.25 mmol (0.216 g), of Z-cycloheptene were used. Zeise’s dimer 0.512 mmol (0.301 g), was dissolved in and the ligand was added. The reaction followed the general procedure for path A on from page 28. After reacting for an hour, a cloudy precipitate was noticed in the yellow-orange solution. A bright orange solid was obtained. Both the solid and mother liquor were placed in a freezer. After sitting in the freezer overnight, further orange solid precipitated from solution and was weighed, and the
mother liquor was left in the freezer to slowly evaporate to afford further solid. We obtained a total mass of 0.258 g (0.356 mmol), for a 70% yield. For NMR analysis 0.015 g of product was dissolved in CDCl₃ and \(^1\)H, \(^{13}\)C, \(^{195}\)Pt NMR spectral analysis was obtained.

Another method used in an attempt to synthesize \(\text{trans-PtCl}_2(\eta^2\text{-C}_7\text{H}_{12})_2\) following path C, was to take 0.019 mmol \(\text{trans-[PtCl}_2(\eta^2\text{-C}_7\text{H}_{12})_2]\) (9), (0.014 g), fully dissolved in 1.0 mL of CDCl₃ and add 2.0 molar equivalent 0.042 mmol (0.004 g), of Z-cycloheptene. This method allowed for kinetic time study on the reaction by analysis using \(^1\)H NMR. Spectra were obtained at time intervals of 5 minutes, 30 minutes, 1 hour, 4 hours, 16 hours and 32 hours.

3.12 Synthesis of the E-Cyclodecene Analog of Zeise’s Dimer

The synthesis of \(\text{trans-[PtCl}_2(\eta^2\text{-C}_{10}\text{H}_{18})]\) (10) followed path C in which 2.2 molar equivalents 1.135 mmol (0.157 g), of E-cyclodecene was reacted with Zeise’s dimer 0.515 mmol (0.303 g), in solution. While heating, the solution turned a yellow-orange, and the reaction was continued following the general procedure for path C on page 31. After reacting the flask was placed in a freezer. After sitting in the freezer overnight orange crystals were observed in solution and separated from the mother liquor by filtration. We obtained 0.371 mmol (0.300 g), for a 72% yield. For NMR analysis 0.121 g of product was dissolved in 1.0 mL CDCl₃ and the \(^1\)H, \(^{13}\)C, and \(^{195}\)Pt NMR spectral analysis was obtained.

3.13 Synthesis of the E-Cyclodecene \(\text{trans-dialkene Compound}\)
The synthesis of \( \text{trans-PtCl}_2(\eta^2-\text{C}_{10}H_{18})_2 \) (11) followed path A in which 4.4 molar equivalents 2.24 mmol (0.309 g), of E-cyclodecene was reacted with Zeise’s dimer 0.508 mmol (0.299 g), in solution. The reaction followed the general procedure for path A on page 28. While heating, the solution turned a yellow-orange. After reacting the solution was placed in a freezer. After sitting in the fridge overnight yellow solid was present in solution the next day and was vacuum filtrated and rinsed two times with 5.0 mL portions of toluene. The solid reflected light under a microscope indicating that they were crystalline in nature. The initial product mass was 0.271 g. Evaporation of the mother liquor afforded an additional 0.131 g, for a total mass of 0.741 mmol (0.402 g), or a 73% yield. For NMR analysis 0.131 g was dissolved in 1 mL of CDCl\(_3\) and analyzed by \(^1\)H, \(^{13}\)C, and \(^{195}\)Pt NMR.

3.14 Synthesis of the Bicyclo[2.2.1]hept-2-ene Analog of Zeise’s Dimer

The synthesis of \( \text{trans-[PtCl}_2(\eta^2-\text{C}_7\text{H}_{10})]_2 \) (13) followed path C in which 2.2 molar equivalents 1.13 mmol (0.106 g), of solid bicyclo[2.2.1]hept-2-ene was weighed out and reacted with Zeise’s dimer 0.515 mmol (0.303 g). The reaction followed the general procedure for path C on page 28. While reacting the solution changed color to yellow from a red-orange. After reacting, a yellow precipitate (0.015 g) was filtrated out of solution. Both the solid and mother liquor were placed in a freezer to precipitate further solid that was filtrated out of solution. A total obtained mass of 0.142 mmol (0.102 g), gave a 27% yield. For \(^1\)H NMR analysis 5.0 mg was dissolved in 1.0 mL of CDCl\(_3\) and the spectrum was obtained.
3.15 Reaction of 4 Molar equivalents of Bicyclo[2.2.1]hept-2-ene with Zeise’s Dimer

The attempted synthesis of trans-PtCl₂(η²-C₇H₁₀)₂ followed path A in which 4.4 molar equivalents 2.17 mmol (0.203 g) of solid bicyclo[2.2.1]hept-2-ene was weighed out and added to with Zeise’s dimer 0.479 mmol (0.281 g), in solution. The reaction followed the general procedure on page 28. While heating, the solution changed color from yellow to orange and the reaction was allowed to continue, a cloudy precipitate was present in solution after reacting. A yellow solid (0.050 g) was decanted from the solution. Both the solid and mother liquor were then placed in a freezer to precipitate any further solid. The solid was studied to find a solvent which it would dissolve into.

3.16 Reaction of 2 Molar Equivalents of Bicyclo[3.2.1]oct-2-ene with Zeise’s Dimer

The attempted synthesis of trans-[PtCl₂(η²-C₈H₁₂)]₂ followed path B in which 2.2 molar equivalents, 1.17 mmol (0.126 g), of bicycle[3.2.1]oct-2-ene was reacted with Zeise’s dimer, 0.267 mmol (0.157 g), in solution. The mixture was stirred in an inert argon atmosphere without heating for 4 hours to determine if heat and oxygen plays a role in reaction. After mixing, the dark brown solution was placed in a freezer. After sitting in the freezer overnight a tar like solid (0.053 g) was obtained and dissolved in 1.0 mL of CDCl₃ and analyzed by ¹H NMR.

3.17 Reaction of 4 Molar Equivalents of Bicyclo[3.2.1]oct-2-ene with Zeise’s Dimer

The attempted synthesis of trans-[PtCl₂(η²-C₈H₁₂)]₂ followed path A in which 4.4 molar equivalents, 1.09 mmol (0.118 g) of bicycle[3.2.1]oct-2-ene was reacted with Zeise’s dimer, 0.248 mmol (0.146 g), in solution. The reaction followed the general procedure on page 28. The mixture was gently heated by convection resulting in a
yellow-orange solution. After reacting the dark brown solution was placed in freezer. After sitting in the freezer overnight a tar like substance (0.010 g) was filtrated and dissolved in 1.0 mL of CDCl$_3$ and analyzed by $^1$H NMR.

3.18 Reaction of 2 molar equivalents of cis/trans-cyclododecene with Zeise’s Dimer

A mixture of cis and trans-cyclododecene was reacted using pathway B in which 2.2 molar equivalents 0.583 mmol (0.097 g), of the ligand was reacted with Zeise’s dimer 0.265 mmol (0.156 g) in acetone (2.0 mL) and dichloromethane (10.0 mL). When mixed the red solution took on an orange hue. After heating by convection for 25 minutes a solid was seen in solution. The reaction was stopped and the yellow solid was decanted from the mother liquor, rinsed 3 times with equal portions of hexanes, dried and weighed (0.081 g). The product was placed in a freezer and the remaining mother solution was vacuum filtrated (0.054 g). Total mass obtained was 0.135 mmol (0.117 g), for a 51% yield. For $^1$H NMR analysis 10.0 mg was dissolved in 1.0 mL of CDCl$_3$ and the spectrum was obtained.

3.19 Reaction of 4 molar equivalents of cis/trans-cyclododecene with Zeise’s Dimer

A mixture of cis and trans-cyclododecene was reacted using pathway A in which 4.4 molar equivalents 1.04 mmol (0.173 g), of the ligand was reacted with Zeise’s dimer 0.236 mmol (0.139 g), in acetone and dichloromethane. When mixed the red solution took on an orange hue. After heating by convection for 25 minutes, a solid was seen in solution. The reaction was stopped and the yellow solid was decanted from the mother liquor, rinsed 3 times with equal portions of hexanes and weighed (0.056 g). The product was placed in a freezer and the remaining mother solution was vacuum filtrated (0.067 g).
Total mass obtained was 0.123 g, for a 60% yield. For $^1$H and $^{195}$Pt NMR analysis 5.0 mg was dissolved in 1.0 mL of CDCl$_3$ and the spectrum was obtained.

3.20 Synthesis of 1,2-cyclononadiene

Due to the inability to purchase cyclononene, the organic synthesis below was attempted to obtain a C$_9$-cycloalkene to react it with Zeise’s dimer. The synthesis is an adaption from literature procedures found in *Organic Synthesis*, 1973, Coll. Vol. 5, 306$^{28}$, *Tetrahedron* 2008, 64, 5497-5501$^{29}$, and *Journal of Organic Chemistry C*, 1969, 1803-1808$^{30}$. The multistep synthesis to obtain 1,2-cyclononadiene (14) is shown below in Figure 3.3.

![Synthesis Diagram](attachment:diagram.png)

**Figure 3.3:** Synthesis of 1,2-cyclononadiene (14)

In step one, a three neck 250 mL round bottom flask was equipped with a dropping funnel, a water cooled condenser with gas out-let, and an rubber septum with needle as an Argon gas inlet source. The dropping funnel was filled with 60.0 mL of 50% NaOH, while 25.0 mL of cyclooctene, 1.0 mL of ethanol, 58.0 mL of bromoform, and 3.502 g of centramide were mixed together in the round bottom flask. The reaction was stirred and the container purged and cooled in an ice bath for 15 minutes before the NaOH was slowly added dropwise. After 40 minutes the mixture became warm. The reaction was allowed to stir till the next day (~20 hours), after which the yellow colored
solution was neutralized with 20.0 mL of 6.0 M HCl and the organic layer separated using a separatory funnel and dried over MgSO$_4$. The MgSO$_4$ was filtrated off, and the golden-amber solution was placed in a round bottom flask for fractional vacuum distillation with two dewer cold traps in liquid nitrogen.

After the ether was removed partial vacuum fractional distillation (15 mm) was set up using the bottom of a Bunsen burner as a pressure regulator connected to two adjustable three-way T-joints. These T-joints connected the regulator and distillation column with the vacuum line and pressure meter. Two dewer cold traps in liquid nitrogen were used to remove any low boiling solvents and to protect the vacuum pump. The fractions came at, 26 - 36$^\circ$C, and 110 - 125$^\circ$C. $^1$H and $^{13}$C NMR of each fraction were obtained. The first fraction was found to be bromoform. The second fraction was determined to be 9,9-dibromobicyclo[6,1,0]nonane by $^1$H NMR chemical shifts$^{28,29,30}$ 2.01, 1.58, 1.41, 1.47, 1.12 ppm (31.513 g, for a 58% yield).

In the next step the 9,9-dibromobicyclo[6,1,0]nonane, 0.053 moles (14.84 g), was mixed with 15.0 mL of ether in a 50 mL three neck round bottom flask, which had a dropping funnel charged with 34.0 mL of 1.6 M (0.054 moles) methylolithium in ethyl ether, using a double needle to transfer it to the funnel with argon gas. The other two necks were sealed with rubber septums, with one septum serving as an argon gas inlet to create an inert atmosphere. The flask was cooled to -40$^\circ$C with a methanol-liquid nitrogen ice bath. The methylolithium solution was added slowly over 40 minutes. After addition, the reaction was stirred for 2 hours. Twenty milliliters of ether was then added to rinse any excess MeLi into solution. This was followed by 25.0 mL H$_2$O and 10.0 mL of 1 M HCl to quench any excess MeLi and to neutralize any LiOH that has formed. The mixture
was separated using a separatory funnel and the organic layer was collected. The translucent yellow solution was then dried over MgSO₄. The MgSO₄ was filtrated off, and the solution was placed in a round bottom flask for atmospheric distillation to remove the ether solvent. The ether fraction came off at 30–36 °C. After the ether was removed partial vacuum fractional distillation (30 mm) was set up using the bottom of a Bunsen burner as a pressure regulator connected to two adjustable three-way T-joints. These T-joints connected the regulator and distillation column with the vacuum line and pressure meter. Two dewer cold traps in liquid nitrogen were used to remove any low boiling solvents and to protect the vacuum pump. Three fractions were collected at: 70–75 °C, 80–86 °C, and 118–130 °C. ¹H and ¹³C NMR analysis showed that the second fraction (80-86 °C) was the desired 1,2-cyclononadiene (14) compound, 6.41 mmoles (0.816 g), for a 13%. The first and third fractions were determined by ¹H NMR to be impurities derived from 1,2-cyclononadiene, their full characterization is not necessary for this thesis.

Another method to synthesize 1,2-cyclononadiene from 9,9-dibromobicyclo[6,1,0]nonane comes from Baird et. al³¹. One deviation from this method was the use of diethyl ether solvent instead of THF, due to availability. In this synthesis the 9,9-dibromobicyclo[6,1,0]nonane (0.112 moles) is treated with a 2 molar ratio of 1.0 M methylmagnesium bromide (0.224 moles) in diethyl ether. An equal amount of diethyl ether solvent is added (74.5 mL). The glassware, reaction and addition of the solvent is the same set-up as the MeLi reaction except that this reaction is done at room temperature. The reaction was left to stir overnight (~15 hours). Water (25.0 mL) and 3M HCl (35.0 mL) were added to quench any excess EtMgBr and to dissolve any magnesium
salts that may have formed. The mixture was separated using a separatory funnel and the organic layer was collected. The solution was then dried over anhydrous MgSO$_4$. The MgSO$_4$ was filtrated off, and the solution was placed in a round bottom flask for atmospheric distillation to remove the ether solvent. A partial vacuum distillation (15mm) was set up as described above for the MeLi reaction. Four fractions were collected at: 60–110$^\circ$C, 110–115$^\circ$C, 115–120 $^\circ$C, and 125–135 $^\circ$C. $^1$H NMR chemical shifts 5.24, 2.18, and 1.1- 1.8 ppm$^{29}$ showed that the first fraction (60-110 $^\circ$C) was the desired 1,2-cyclononadiene compound (14), 0.056 moles (7.222 g), for a 53% yield. The other fractions were determined by $^1$H NMR to be impurities derived from 1,2-cyclononadiene, their full characterization is not necessary for this thesis. Although not a primary ligand of this research, since it is a dialkene, 1,2-cyclononadien (14) was reacted with Zeise’s dimer in an attempt to synthesize a characterizable compound.

3.21 Reaction of 2 molar equivalents of 1,2-cyclononadiene with Zeise’s Dimer

The 1,2-cyclononadiene (14) was then reacted using pathway B in which 2.2 molar equivalents 0.769 mmol (0.094 g) of the diene was dissolved in solution with Zeise’s dimer 0.349 mmol (0.205 g). This reaction followed the process on page 28. The solution was mixed for half an hour then gentle heating was added with argon gas purge. Heating was suspended after 30 minutes and a yellow solid (0.087 g), was decanted from the mother liquor and placed in a freezer along with the remaining mother liquor solution for slow evaporation. The solid (0.035 g) was then dissolved in 1.0 mL of CDCl$_3$ and NMR results were obtained.
3.22 Reaction of 4 molar equivalents of 1,2-cyclononadiene with Zeise’s Dimer

The 1,2-cyclononadiene (14) was then reacted using pathway A in which 4.4 molar equivalents 2.32 mmol. (0.284 g), of the diene was dissolved in solution with Zeise’s dimer 0.528 mmol. (0.311 g). This reaction followed the process on page 28. After reacting, a yellow solid was filtrated from the mother liquor, rinsed 3 times with equal portions of hexanes, weighed (0.153 g), and placed in a freezer along with the remaining mother liquor solution for slow evaporation. The solid (0.035 g) was then dissolved in 1.0 mL CDCl₃ and ¹H NMR results were obtained.
4.1 Characterization of \( \text{trans-}[\text{PtCl}_2(\eta^2-\text{C}_8\text{H}_{14})]_2 \) and \( \text{trans-PtCl}_2(\eta^2-\text{C}_8\text{H}_{14})_2 \)

The \(^1\text{H}\) NMR spectrum of the orange solid from the reaction of 4.4 equivalents of Z-cyclooctene with Zeise’s dimer is shown in Figure 4.1, below. The spectrum had broad peaks that made assigning chemical shifts to individual protons difficult, except for the alkene at 5.46 ppm which matched closely with previously reported literature values for \( \text{trans-}[\text{PtCl}_2(\eta^2-\text{C}_8\text{H}_{14})]_2 \)\(^1\). These broad peaks are indicative of fast exchange with excess cyclooctene. Upon coordination to platinum via \(\pi\)-backbonding the trend in \(^1\text{H}\) NMR for the alkene is a downfield shift. This is not true for this compound since the uncoordinated alkene of Z-cyclooctene is at 5.62 ppm, this indicates that the compound has higher shielding of the protons.\(^2\) The –CH\(_2\)- protons have broad peaks with shifts at 2.17, 1.69, and 1.37 ppm. Integration of the two sets of peaks gave a ratio of 2:13 which can be explained by the inclusion of the peak at 1.54 ppm seen in the spectra which is the ubiquitous water peak present in the deuterated solvent\(^1\) CDCl\(_3\). However a chemical shift at 1.55 ppm is also reported in the literature\(^1\) as a peak for the Zeise’s dimer analog of Z-cyclooctene. Addition of 4A molecular sieves to the deuterated solvent before the sample is prepared decreased the intensity of the water resonance. Taking this into account, an actual ratio of the peak integrations would be closer to 2:12 which accounts for all hydrogens present.

Characterization of the orange product as the Zeise’s dimer analog was provided by single crystal x-ray diffraction. A red rectangular crystal that was, 8.23 mm x 5.94 mm x 20.98 mm, was mounted on a metal probe with a Teflon loop under an inert atmosphere for data collection. The X-ray intensity and crystal dimension data were measured at -73
on a Bruker SMART X2S X-ray diffractometer equipped with a Mo-Ka radiation source (\(\lambda = 0.71073\ \text{Å}\)). Lattice determination and data collection were carried out using SMART software. The structure determination was conducted using SHELXTL\textsuperscript{32} software. This gave unit cell parameters for the dimer compound which were previously reported by Otto et. al. 2003.\textsuperscript{15}

The \(^1\text{H}\) NMR spectrum of the yellow solid is shown below in Figure 4.2. The chemical shifts were compared to previously reported literature values for the trans-dialkene compound of cyclooctene\textsuperscript{15}. Due to similarities between the chemical shifts of the synthesized product matching peaks from both compounds, further characterization methods were needed. Table 4.1 below shows the chemical shift comparison of the synthesized yellow solid to the literature values.

**Table 4.1: \(^1\text{H}\) NMR Chemical shift (ppm) Comparison of the yellow solid to Literature (from Ref 15)**

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</table>

X-ray powder diffraction analysis was conducted on the yellow product to confirm the structure. By comparison of the obtained diffractogram with previous literature reports from the Cambridge Structural Database\textsuperscript{33} it was determined using JADE\textsuperscript{34} software that three compounds are present in the powder. They are: \(\text{trans-}[\text{PtCl}_2(\eta^2-C_8\text{H}_{14})]_2\) (5), \(\text{trans-PtCl}_2(\eta^2-C_8\text{H}_{14})_2\) (6), and a still yet unknown compound. The diffractogram is shown below in Figure 4.3.
Figure 4.1: $^1$H NMR of $\text{trans-[PtCl}_2(\eta^2-\text{C}_8\text{H}_{14})\text{]}_2$ (5)
Figure 4.2: $^1$H NMR of trans-PtCl$_2$(η$^2$-C$_8$H$_{14}$)$_2$ (6)
4.2 Cyclohexene Analog of Zeise’s Dimer

The $^1$H NMR of the Zeise’s dimer analog of cyclohexene, $\textit{trans}$-$[$PtCl$_2$(η$^2$-C$_6$H$_{10}$)]$_2$ (12), dissolved in CDCl$_3$ is shown in Figure 4.4 below. A coordinative chemical shift of the alkene at 5.97 ppm is seen, which is in agreement with the literature value. This has lower shielding than that of the uncoordinated cyclohexene at 5.66 ppm. The alkene peak also shows a 75.4 Hz J$_{\text{Pt-C}}$ coupling indicative of coordination and this also corresponds with previous literature results. The -CH$_2$- protons show a slight shift from those reported for the free ligand. Also present in the spectrum is the chemical shift for Zeise’s dimer at 4.74 ppm. This indicates that the product is a mixture of both Zeise’s dimer and $\textit{trans}$-$[$PtCl$_2$(η$^2$-C$_6$H$_{10}$)]$_2$ (12). A longer reaction period is warranted for a complete transition of Zeise’s dimer to $\textit{trans}$-$[$PtCl$_2$(η$^2$-C$_6$H$_{10}$)]$_2$ (12). The ratio the alkene peak, set at 2.00 hydrogens, verses aliphatic hydrogens from 2.5-1.6 ppm is 2:8.

The $^{13}$C NMR of $\textit{trans}$-$[$PtCl$_2$(η$^2$-C$_6$H$_{10}$)]$_2$ (12) is shown below in Figure 4.5. In the spectrum the alkene shift of cyclohexene has a chemical shift shift of 91.5 ppm,
which is more shielded compared to the free ligand at 127.2.\textsuperscript{20} Also seen shifted are the two peaks from the CH\textsubscript{2}’s of the cycloalkene ring at 27.2 and 20.9 ppm, compared to their uncoordinated shifts at 25.2 and 22.7 ppm\textsuperscript{20} respectively. The chemical shift peak at 137.5 ppm present in the spectrum maybe due to toluene, which has a shift of 137.9 in CDCl\textsubscript{3}.\textsuperscript{19} The toluene shift appears due to its presence as the solvent in the synthesis of this compound.

The $^{195}$Pt NMR of trans-$[\text{PtCl}_2(\eta^2-(\text{C}_6\text{H}_{10}))_2$ (12) shows a chemical shift at -2385 ppm which is agreement with the literature values for other Zeise’s dimer analogs shown in Table 1.1.

4.3 Cyclohexene trans-diaklene Compound

The $^1$H, $^{13}$C, and $^{195}$Pt NMR of the 4 molar equivalents reaction of cyclohexene with Zeise’s dimer were virtually identical with those of (12). Therefore there was no formation of the trans-diaklene product from this reaction.
Figure 4.4: $^1$H NMR of $\text{trans-}[\text{PtCl}_2(\eta^2-C_6H_{10})]_2$ (12)
Figure 4.5: $^{13}$C NMR of trans-[PtCl$_2$(η$^2$-C$_6$H$_{10}$)]$_2$ (12)
4.4 Z-Cycloheptene Analog of Zeise’s Dimer \textit{trans}-[PtCl}_2(\eta^2-C_7H_{12})]\_2

The \textit{^1H} NMR spectrum of the orange solid was obtained and is shown in Figure 4.6. The spectrum showed the alkene peak at 5.70 ppm which is slightly lower in shielding compared to that of the uncoordinated ligand at 5.78 ppm.\textsuperscript{20} A \textit{J}_{\text{Pt-H}} coupling constant of 11.5 Hz was also observed in the \textit{^1H} NMR spectrum, indicative of coordination. This coupling appears on the shoulders of the alkene peak. Integration of the peaks gave the correct ratio of 2:10 for the alkene and aliphatic hydrogens respectively.

The \textit{^{13}C} NMR is shown below in Figure 4.7. A coordinative chemical shift of the alkene is seen at 91.6 ppm, compared to the uncoordinated free ligand which has a peak at 132.3 ppm.\textsuperscript{20} Also seen in the spectrum are the chemical shifts of the three \textit{CH}_2’s from the cycloalkene ring at 32.8, 28.6, and 23.9 ppm. There is no \textit{J}_{\text{Pt-C}} visible in this spectrum.

The \textit{^{195}Pt} NMR spectrum (Figure 4.8) shows a single chemical shift peak at -2527 ppm. This shift fits with other Zeise’s dimer analogs mentioned in Table 1.1.

Single crystal X-Ray diffraction of this compound was performed at the Chemistry Department of Duquesne University in Pittsburgh Pennsylvania. A translucent yellow rectangular crystal that was 0.239 mm x 0.513 mm x 0.181 mm, was mounted on glass fiber under an inert atmosphere for data collection. Structural analysis of the data collected gave unit cell parameters for the Zeise’s dimer analog which were previously reported by Bordner et. al.\textsuperscript{7}
Figure 4.6: $^1$H NMR of trans-[PtCl$_2$(η$^2$-C$_7$H$_{12}$)]$_2$ (9)
Figure 4.7: $^{13}$C NMR of trans-[PtCl$_2$(η$^2$-C$_7$H$_{12}$)]$_2$ (9)
Figure 4.8: $^{195}\text{Pt}$ NMR of trans-$[\text{PtCl}_2(\eta^2-\text{C}_7\text{H}_{12})]_2$ (9)
4.5 Reaction of 4 Molar equivalents of Z-cycloheptene with Zeise’s Dimer

The $^1$H NMR Spectrum of the 4.4 molar equivalent reaction of Z-cycloheptene and Zeise’s dimer is shown in Figure 4.9. The alkene peak was set at 2.00 hydrogens verses aliphatic hydrogens from 2.4-1.2 ppm for a ratio of 2:10. The alkene chemical shift is at 5.70 ppm, a slightly higher shielding compared to the uncoordinated Z-cycloheptene alkene at 5.78 ppm. The reported literature value of the alkene shift is 5.78 ppm for the $trans$-$[PtCl_2(\eta^2-C_7H_{12})]_2$ compound. A 10.7 Hz $J_{Pt-H}$ coupling constant is also observed in the spectrum on the shoulders of the alkene, and suggests ligand exchange.

The $^1$H NMR results for the NMR tube reaction of $trans$-$[PtCl_2(\eta^2-C_7H_{12})]_2$ with two molar equivalents of Z-cycloheptene showed no chemical change in the spectrum over time. There was no change in the chemical shift of the alkene which would be expected if the $trans$-dialkene compound was present.

The $^{195}$Pt NMR has the same chemical shift as $trans$-$[PtCl_2(\eta^2-C_7H_{12})]_2$ (9) indicating that there is no $trans$-dialkene product in solution. This is further confirmed by the similarities of the compared $^1$H NMR’s.
Figure 4.9: $^1$H NMR of 4.4 Equivalents of Z-cycloheptene with Zeise’s Dimer
4.6 Characterization of trans-[PtCl₂(η²-C₁₀H₁₈)₂]₂

The ¹H NMR is shown in Figure 4.10. Analysis of the spectrum shows the alkene peak at 5.22 ppm, has a higher shielding compared to literature reports of 5.4 ppm for the free ligand.³⁶ It’s not clear why this is the case since coordination to platinum typically results in a downfield shift for alkene resonances. The ratio of the alkene peak, set at 2.00 hydrogens verses aliphatic hydrogens from 2.5-1.2 ppm is 2:16, which agrees with the 18 CH₂ protons of the E-cyclodecene ligand. Also seen in the spectrum are the toluene solvent aryl ring and methyl chemical shifts at 7.17 and 2.34 ppm, respectfully. Also seen is the chemical shift for water in CDCl₃ at 1.5 ppm.

The ¹³C NMR (Figure 4.11) shows the alkene chemical shift peak at 94.8 ppm which is consistent with a coordinative shift from the uncoordinated chemical shift of E-cyclodecene at 131.3 ppm.³⁶ The ¹⁹⁵Pt NMR (Figure 4.12) shows the chemical shift of the platinum at -2514 ppm, which is similar to Zeise’s dimer at -2525 ppm.
Figure 4.10: $^1$H NMR of $\text{trans-}[\text{PtCl}_2(\eta^2-\text{C}_{10}\text{H}_{18})_2]_2$ (10)
Figure 4.11: $^{13}$C NMR of trans-$[\text{PtCl}_2(\eta^2-C_{10}H_{18})_2]_2$ (10)
Figure 4.12: $^{195}$Pt NMR of trans-$[\text{PtCl}_2(\eta^2-\text{C}_{10}\text{H}_{18})_2]_2$ (10)
4.7 Characterization of \textit{trans}-PtCl$_2$(\(\eta^2\)-C$_{10}$H$_{18}$)$_2$

The \(^1\)H NMR spectra is shown in Figure 4.13. The alkene shift is at 6.22 ppm which has lower shielding compared to uncoordinated E-cyclodecene at 5.40 ppm.\(^36\) Broad peaks prevented observations of Pt-H coupling. The ratio of the alkene peak, set at 2.00 hydrogens verses aliphatic hydrogens from 2.5-1.2 ppm is 2:16, which agrees with the 18 CH$_2$ protons of the E-cyclodecene ligand. Also seen in the spectrum are the toluene and acetone solvent chemical shifts at 2.33 and 2.15 ppm, respectfully. The chemical shift of the aryl hydrogens of toluene can be seen at 7.15 ppm.

The \(^{13}\)C NMR (Figure 4.14) has a coordinative shift of 119.1 ppm from the free ligand of 133.3 ppm\(^36\). The CH$_2$’s are slightly shifted when compared to the chemical shifts of the free ligand.\(^37,38\)

The \(^{195}\)Pt NMR spectrum is shown in Figure 4.15. In the spectrum two peaks are seen at -2820 and -2948 ppm. These shifts correspond to reported literature values of other \textit{trans}-dialkene compounds mentioned earlier in this thesis in Table 1.1. Previously reported literature results\(^15,18,22\) show that \textit{trans}-dialkene compounds have a lower shielding value when compared to their dimer analogs. Multiple chemical shifts have been reported for \(^{195}\)Pt NMR of similar compounds, such as \textit{trans}-[PtCl$_2$(\(\eta^2\)-C$_8$H$_{16}$)$_2$]$_2$ (10)\(^15\) shown in Table 1.1.
Figure 4.13: $^1$H NMR of trans-PtCl$_2$(η$^2$-C$_{10}$H$_{18}$)$_2$ (11)
Figure 4.14: $^{13}$C NMR of trans-PtCl$_2$(η$^2$-C$_{10}H_{18})_2$ (11)
Figure 4.15: $^{195}$Pt NMR of $trans$-PtCl$_2$(η$^2$-C$_{10}$H$_{18}$)$_2$ (11)
4.8 Characterization of \(\text{trans-}[\text{PtCl}_2\eta^2-(\text{C}_7\text{H}_{10})_2]\)

The \(^1\text{H}\) NMR Spectrum of the bicyclo[2.2.1]hept-2-ene analog of Zeise’s dimer is shown in Figure 4.16. The ratio of the alkene peak, set at 2.00 hydrogens verses aliphatic hydrogens from 2.8-0.8 ppm is 2:8, which fits with the 10 \(\text{CH}_2\) protons of the bicyclo[2.2.1]hept-2-ene ligand. The alkene chemical shift is at 5.61 ppm, a slightly higher shielding compared to the uncoordinated alkene at 5.99 ppm.\(^{20}\) A \(J_{\text{Pt-H}}\) coupling constant of 83.6 Hz is observed for the alkene resonance. This is slightly larger than the coupling of Zeise’s dimer at 67.3 Hz.\(^{18}\) The peak at 4.74 ppm indicates that there is still some unreacted Zeise’s dimer in solution. A longer reaction time might convert the unreacted Zeise’s dimer to the bicyclo[2.2.1]hept-2-ene analog. Also seen in the spectrum are the chemical shifts of the solvents, toluene (7.25, 7.15 and 2.33 ppm) and acetone (2.15 ppm). Due to the low solubility of this compound \(^{13}\text{C}\) and \(^{195}\text{Pt}\) NMR could not be obtained.

Pathway B was attempted to find a more efficient process in obtaining the desired \(\text{trans-}\)dialkene compound of bicyclo[2.2.1]hept-2-ene. Results from \(^1\text{H}\) NMR analysis of the pathway B reaction of bicyclo[2.2.1]hept-2-ene with \(\text{trans-}[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5\text{N})]\), showed that the alkene shift of ethylene was still present after 3 hours. Further attempts to produce the desired product, such as refluxing for 30 minutes as used by Busse et. al.\(^{16}\) and extend magnetic stirring (12 hrs), showed no change in the \(^1\text{H}\) NMR.
Figure 4.16: $^1$H NMR of trans-[PtCl$_2$(η$_2$-C$_7$H$_{10}$)$_2$]$_2$ (13)
4.9 Reaction of 4 Molar Equivalents of Bicyclo[2.2.1]hept-2-ene with Zeise’s Dimer

NMR analysis of the reaction was difficult due to the low solubility of the yellow solid. Ten milligrams the solid was added to 1.0 mL of d_1-choloform, d_6-acetone, d_2-dichloromethane, and d_6-benzene. In each case the ^1H NMR showed only the peaks for the reaction solvent (toluene), the deuterated solvent, and the water peak in the deuterated solvent. Due to the insoluble nature of the product the compound remains un-characterized at this time.

4.10 Reaction of 2 Molar Equivalents of Bicyclo[3.2.1]oct-2-ene with Zeise’s Dimer

The reaction of bicyclo[3.2.1]oct-2-ene with Zeise’s dimer to obtain the dimer analog using this method did not produce a characterizable product. The ^1H NMR analysis of the reaction showed the chemical shift for Zeise’s dimer at 4.75 ppm and a broad set of peaks from 2.4-1.3 ppm.

4.11 Reaction of 4 Molar Equivalents of Bicyclo[3.2.1]oct-2-ene with Zeise’s Dimer

NMR analysis of the reaction was difficult due to the low solubility of the yellow solid obtained. The ^1H NMR showed peaks for toluene (the solvent), the peak for the CDCl_3 solvent, and the water peak in the deuterated solvent. Due to the insoluble nature of this product and the difficulties in crystal growth, the structure remains undetermined at this point. Other deuterated solvents such as acetone, benzene, and dichloromethane were used but did not dissolve the product. Due to the low solubility of the solid ^13C and ^195Pt NMR could not be obtained.
4.12 Characterization of \( \text{trans-}[\text{PtCl}_2-\eta^2-(\text{C}_{12}\text{H}_{22})_2]_2 \)

The \( ^1H \) NMR is shown in Figure 4.17. Analysis of the spectrum shows the alkene peak at 5.36 ppm, which is the same chemical shift of the free ligand.\(^{20}\) The ratio of the alkene peak, set at 2.00 hydrogens verses aliphatic hydrogens from 2.8-0.8 ppm is 2:20, which fits with 22 CH\(_2\) protons of the cyclododecene ligand. The \( ^1H \) NMR of both the 2.2 and 4.4 molar equivalents reactions of cyclododecene with Zeise’s dimer gave the same chemical shifts. Due to the low solubility of the compound, and after 30,000 scans the \( ^{13}C \) NMR could not be obtained. The \( ^{195}Pt \) NMR shows a chemical shift at -2438 ppm. This shift is similar to the other Zeise’s dimer analogs shown in Table 1.1.
Figure 4.17: $^1$H NMR of trans-$[\text{PtCl}_2(\eta^2-\text{C}_{12}H_{22})_2]_2$ (15)
4.13 Synthesis of 1,2-cyclononadiene

The synthesis of cyclononene was not completed due to the low yield of the 1,2-cyclononadiene compound from both the MeLi and EtMgBr reactions. The yield (58%) for 9,9-dibromobicyclo[6.1.0]nonane in the reaction prior to the 1,2-cyclononadiene synthesis were in agreement with the literature method yield of 52-65%.\textsuperscript{28} The EtMgBr reaction with 9,9-dibromobicyclo[6.1.0]nonane afforded a better yield at 53%, compared to the same reaction using MeLi (13%). The reason for the difference between these yields and the expected yield of 81-93%\textsuperscript{28,29} has not been determined.

4.14 Reaction of 2 Molar Equivalents of 1,2-cyclononadiene with Zeise’s Dimer

NMR analysis showed no alkene shift of 1,2-cyclononadiene (14) when mixed with Zeise’s dimer. The $^1$H NMR analysis of the solid showed the chemical shifts for the toluene solvent at 7.25, 7.15, and 2.36 ppm and a broad set of peaks from 2.2-1.3 ppm. Further analysis by broadband and DEPT 45 $^{13}$C NMR at 30,000 scans and 30,000 scans for $^{195}$Pt NMR yielded no spectra. Reasons for the apparent unreactivity of this compound have not been determined and will be a focus of future research.

4.15 Reaction of four Equivalents of 1,2-cyclononadiene with Zeise’s Dimer

The $^1$H NMR analysis of the reaction showed the chemical shifts for the alkene at 5.68 ppm a downfield shift compared to that of 1,2-cyclononadiene at 5.26 ppm. Also seen in the spectrum was Zeise’s dimer at 4.83 ppm. Integration was impossible due to broad peaks. Further analysis by broadband and DEPT 45 $^{13}$C NMR at 30,000 scans and 30,000 scans for $^{195}$Pt NMR yielded no spectrum.
For the synthesis of trans-dialkene compounds, pathway A afforded results, with the synthesis of both the Z-cyclooctene and E-cyclodecene ligands. The reactions of Z-cyclohexene, Z-cycloheptene, E/Z-cyclododecene, and bicyclo[2.2.1]hept-2-ene ligands afforded only their Zeise’s dimer analogs using the trans-dialkene synthetic methods.

Table 4.2 below shows a tabulation of the obtained results from this research (bold faced values) and previously reported values for some selected compounds of platinum. The NMR values are of the C=C bond in the ligand.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR H-C=C-H (ppm)</th>
<th>$^{13}$C NMR H-C=C-H (ppm)</th>
<th>$^{195}$Pt NMR (ppm)</th>
<th>Pt-C Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zeise’s Salt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{PtCl}_3(\eta^2-C_2H_4)]^-$</td>
<td>4.43</td>
<td>67</td>
<td>-2994</td>
<td>2.16/2.15</td>
</tr>
<tr>
<td><strong>Diene Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-$\text{PtCl}<em>2(\eta^2-C_8H</em>{12})$</td>
<td>5.6</td>
<td>100.8</td>
<td>-3337</td>
<td>2.176/2.178</td>
</tr>
<tr>
<td>trans-$\text{PtCl}<em>2(\eta^2-C_8H</em>{14})_2$</td>
<td>5.58</td>
<td>113.3</td>
<td>-2747</td>
<td>2.26</td>
</tr>
<tr>
<td>trans-$\text{PtCl}<em>2(\eta^2-C</em>{10}H_{18})_2$</td>
<td><strong>6.22</strong></td>
<td><strong>119.1</strong></td>
<td><strong>-2820, -2948</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Zeise’s Dimer Analogs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-$[\text{PtCl}<em>2(\eta^2-C</em>{12}H_{22})]_2$</td>
<td>5.36</td>
<td></td>
<td>-2438</td>
<td></td>
</tr>
<tr>
<td>trans-$[\text{PtCl}<em>2(\eta^2-C</em>{10}H_{18})]_2$</td>
<td><strong>5.22</strong></td>
<td><strong>94.9</strong></td>
<td><strong>-2514</strong></td>
<td></td>
</tr>
<tr>
<td>trans-$[\text{PtCl}<em>2(\eta^2-C_8H</em>{14})]_2$</td>
<td>5.47</td>
<td>109.5</td>
<td>-2434, -2453</td>
<td>2.132/2.143</td>
</tr>
<tr>
<td>trans-$[\text{PtCl}<em>2(\eta^2-C_7H</em>{12})]_2$</td>
<td>5.78</td>
<td><strong>91.6</strong></td>
<td><strong>-2527</strong></td>
<td>2.14/2.10</td>
</tr>
<tr>
<td>trans-$[\text{PtCl}<em>2(\eta^2-C_6H</em>{10})]_2$</td>
<td>6.06</td>
<td><strong>91.5</strong></td>
<td><strong>-2385</strong></td>
<td></td>
</tr>
<tr>
<td>trans-$[\text{PtCl}_2(\eta^2-C_5H_8)]_2$</td>
<td>6.05</td>
<td></td>
<td></td>
<td>2.20</td>
</tr>
<tr>
<td>trans-$[\text{PtCl}_2(\eta^2-C_4H_4)]_2$</td>
<td>4.88</td>
<td>82</td>
<td>-2525</td>
<td>2.114/2.132</td>
</tr>
</tbody>
</table>
These results show that the Zeise’s dimer analogs are more readily synthesized than the trans-dialkene counterparts. This can be expected since the dimer analog is synthesized first in the reaction and then if enough ligand is added the bridging Pt-Cl bond can be broken to form the trans-dialken compound. It is possible that with longer reaction times the trans-dialkene compound could be obtained, suggestive of a kinetic mechanism. Further studies would be needed to confirm this idea.

There appears to be no general trend in the $^1$H and $^{13}$C NMR results to compare the chemical shift of the alkene, and directly correlate it to a specific ligand. However, in $^{195}$Pt NMR a trend can be noticed when comparing the trans-dialkene compound to the corresponding Zeise’s dimer analog of the same ligand. The $^{195}$Pt NMR for trans-PtCl$_2$(η$^2$-C$_{10}$H$_{18}$)$_2$ shows an upfield chemical shift when compared to trans-[PtCl$_2$(η$^2$-C$_{10}$H$_{18}$)]$_2$. The upfield chemical shift of the alkene on the bicyclo[2.2.1]hept-2-ene can be explained by the higher shielding of the protons due to the strained nature of the rigid bridge. The flexible cycloalkene compounds show a coordinative downfield shift upon coordination to platinum with exception to both the trans-dialkene and Zeise’s dimer analog compounds of cyclooctene.
CHAPTER 5.
CONCLUSIONS

The synthesis of the trans-dialkene analogs of compound (6) made from Z-cyclooctene, and (11) made from E-cyclodecene, was successful. Compound (6) has previously been reported in literature; however, compound (11) has not been synthesized before. Also synthesized in this research were the Zeise’s dimer analogs: (5) made from Z-cyclooctene, (9) from Z-cyclohexene, (10) from E-cyclodecene, (12) from Z-cyclohexene, and (15) from E/Z-cyclododecene. Compounds (10) and (15) have not been previously reported in the literature. $^{13}$C and $^{195}$Pt NMR data for compounds (9) and (12) have also not been reported in the literature, and are presented here as further characterization of these compounds. Compound (13) made from bicyclo[2.2.1]hept-2-ene, showed coordinative coupling of the alkene in $^1$H NMR and a $^{195}$Pt NMR similar to Zeise’s dimer. However, due to low solubility further characterization was not possible.

Cycloalkenes such as Z-cyclohexene, Z-cycloheptene, and E/Z-cyclododecene, when reacted in 4.4 molar equivalents with Zeise’s dimer produced only their Zeise’s dimer analogs. Two and four molar equivalents of the rigid ring bicyclo-alkene ligands produced insoluble products that could not be characterized, with exception to two molar equivalents of bicyclo[2.2.1]hept-2-ene (13), with Zeise’s dimer. This gave a mixture of Zeise’s dimer and the Zeise’s dimer analogue trans-[PtCl$_2$(η$^2$-C$_7$H$_{10}$)$_2$].

Compound (14) 1,2-cyclononadiene, was synthesized as part of a synthetic scheme to make cyclononene. This ligand was also reacted with Zeise’s dimer. When 4.4 molar equivalents of compound (14) were used, a coordinative alkene shift was present in the $^1$H NMR spectrum. However, due to low solubility further characterization has not been obtained.
REFERENCES.


http://www.britannica.com/EBchecked/topic/492733/reaction-mechanism,
accessed May 2011.


33. The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK., 2004-2012.
34. JADE, version 6.5; X-ray Powder Diffraction Software, Rigaku Corporation, 20012.