



Synthesis, characterization and chemistry of platinum complexes derived from cyclopropanes with electron donors  
by Mark Thomas Dimke

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry  
Montana State University  
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Abstract:

It has long been known that Zeise's Dimer inserts into cyclopropanes to form platinacyclobutanes. However, not all platinacyclobutanes are stable, and several have been shown to form novel organic products. It has also been shown that pi electron donors on the cyclopropane will stabilize the incipient carbocation formed by the platinacyclobutane. Various tactics can then be used to further direct the chemistry.

The first thrust of this research utilized strained ring systems to affect the chemistry about the platinacyclobutane. In the first example, 2,7,7-trimethyltricyclo[4.1.1.0<sup>2,4</sup>]octane forms a platinacyclobutane in the presence of Zeise's Dimer which subsequently undergoes a carbocation mediated bond migration to form 1,7,7-trimethyl-2-methylidene-endo-6-chlorobicyclo[2.2.1]heptane. In the second case, cis tricyclo[5.1.0.0<sup>2,4</sup>]octane undergoes a novel transformation upon treatment with Zeise's Dimer and triphenyl phosphine to form 3-(chloromethyl)-6-methylidene-1-cyclohexene. This is thought to be due to the proximity of the second cyclopropane to the first cyclopropane.

A second method utilized in the stabilization of the incipient carbocation generated by a platinacyclobutane is the use of an olefin alpha to the cyclopropane. Platinacyclobutanes from these systems undergo a rearrangement to form methylene tethered pi allylic complexes which have the unique ability to undergo a variety of regio and stereo-selective nucleophilic additions without decomposition of the complex. These complexes can then be decomposed utilizing a variety of methods yielding a plethora of interesting organic products based on the original diene that the cyclopropane was generated from.

A third method used to direct the chemistry resulting from platinacyclobutanes is the use of the lone pair of electrons on a heteroatom, in this case sulfur and nitrogen.

Both demonstrate the ability of a hetero atom to direct the chemistry of platinacyclobutanes. However in the case of amino cyclopropane, the nitrogen complexes to one platinum atom before a second inserts and thereby prevents chemistry alpha to the amine. In the case of phenyl cyclopropyl sulfide, the addition of Zeise's Dimer yields a rearrangement of the cyclopropane to a propenyl moiety.

In all cases, it was shown that the nature of the platinum carbon bond polarization in a platinum(IV)cyclobutane is platinum minus carbon plus. Also, this thesis helps define how pi donating substituents on cyclopropanes direct the subsequent chemistry of platinacyclobutanes formed from these cyclopropanes.

**SYNTHESIS, CHARACTERIZATION AND CHEMISTRY OF PLATINUM  
COMPLEXES DERIVED FROM CYCLOPROPANES  
WITH ELECTRON DONORS**

by

**Mark Thomas Dimke**

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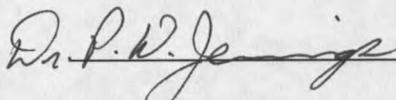
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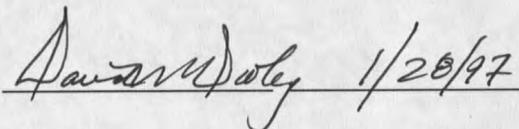
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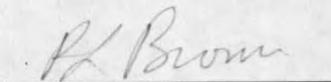


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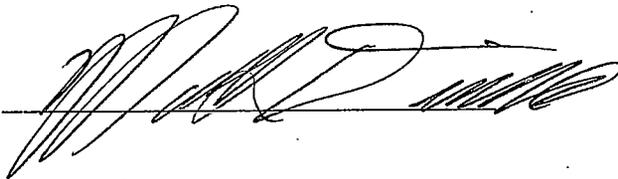
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## TABLE OF CONTENTS

|  | Page |
|--|------|
| <u>LIST OF TABLES</u> .....  | viii |
| <u>LIST OF FIGURES</u> .....   | ix   |
| <u>ABSTRACT</u> .....  | xiv  |
| <u>INTRODUCTION</u> .....  | 1    |
| Historical Preface .....   | 1    |
| Bonding .....  | 2    |
| $\pi$ Bonding in Organoplatinum Complexes .....  | 2    |
| Bonding of $\pi$ Allylic Metal Systems .....   | 5    |
| $\pi$ Allylic Complexes .....  | 7    |
| Reaction of Metal $\pi$ Allylic Systems .....  | 7    |
| Formation of $\pi$ Allylic Complexes .....   | 8    |
| Oxidative Addition and Reductive Elimination .....   | 8    |
| Formation of Platinacyclobutanes via Oxidative Addition .....  | 9    |
| Platinacyclobutane Complexes .....   | 11   |
| Discovery and Structure Elucidation of Platinacyclobutanes .....   | 11   |
| McQuillin's Method of Platinacyclobutane Formation .....   | 13   |
| Puddephatt Rearrangement .....   | 14   |
| Diversity and Limitations of Platinacyclobutane Formation .....  | 16   |
| Cis-1,2-Disubstituted Platinacyclobutanes .....  | 18   |
| Trisubstituted Platinacyclobutanes .....   | 23   |
| NMR Spectroscopy of Organoplatinum Complexes .....   | 25   |
| Reactions of Organoplatinum Complexes .....  | 27   |
| Addition of Hydrogen Gas Liberating the Organic Moiety .....   | 27   |
| Olefin Products from Platinacyclobutanes The Unstable Nature of Cis-1,2<br>disubstituted Platinacyclobutanes ..... | 29   |
| Platinum Complexes Derived from Cyclopropanes with Electron Donors .....   | 33   |
| Cyclopropanes with Oxygen Based Electron Donors .....  | 33   |
| Olefin Stabilized Platinacyclobutanes / Metallacyclobutanes .....  | 35   |
| Vinylcyclopropane and Zeise's Dimer .....  | 38   |
| <u>RESULTS AND DISCUSSION</u> .....  | 44   |
| Statement of Problem .....   | 44   |

|  |    |
|--|----|
| Zeise's Dimer Induced Rearrangement of 2,7,7-Trimethyltricyclo[4.1.1.0 <sup>2,4</sup> ]octane<br><b>125</b> .....  | 45 |
| Cyclopropanation of $\alpha$ Pinene and Establishment of Stereochemistry.....  | 45 |
| Reaction of Zeise's Dimer <b>2</b> with 2,7,7-Trimethyltricyclo[4.1.1.0 <sup>2,4</sup> ]octane <b>125</b> .....  | 47 |
| The Reaction of <b>128</b> and Zeise's Dimer <b>2</b> .....  | 49 |
| Interactions of Tricyclo[5.1.0.0 <sup>2,4</sup> ]octane <b>132</b> and Zeise's Dimer .....   | 53 |
| Formation of Tricyclo[5.1.0.0 <sup>2,4</sup> ]octane <b>132</b> and Establishment of its<br>Stereochemistry .....  | 53 |
| Reaction of cis-Tricyclo[5.1.0.0 <sup>2,4</sup> ]octane <b>132</b> and Zeise's dimer <b>2</b> .....  | 54 |
| Structure Elucidation of <b>133</b> .....  | 55 |
| Proposed Mechanisms for the formation of <b>133</b> .....  | 57 |
| <i>Trans, trans</i> -2,4-hexadiene-1-ol <b>134</b> Based Transformations.....  | 61 |
| Introduction.....  | 61 |
| Syntheses of <i>trans</i> -1-(Methoxymethyl) -2-(1-E-propenyl)cyclopropane <b>137</b> .....  | 62 |
| Reaction of <b>137</b> with Zeise's Dimer <b>2</b> to form <b>138</b> .....  | 64 |
| Characterization of (Acetonitrile-d <sub>3</sub> )chloro[(1,4,5- $\eta$ )-2-(methoxymethyl)-3-<br>chloride-4-hexenyl- platinum, <b>139</b> .....   | 64 |
| Mechanism of di- $\mu$ -chlorobis [(1,4,5- $\eta$ )-3-chloro-2-methoxymethyl)-4-<br>hexenyl]di-platinum, <b>138</b> Formation.....   | 66 |
| Characterization of the dimer <b>138</b> .....   | 68 |
| Addition of Oxygen Nucleophiles to <b>138</b> .....  | 70 |
| Addition of Ethanol to <b>138</b> to form di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-ethoxy-2-<br>methoxymethyl)-4-hexenyl]di-platinum, <b>145</b> .....  | 70 |
| Addition of <i>iso</i> -Propanol to <b>138</b> to form Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-<br><i>isopropoxide</i> -2-methoxymethyl)-4-hexenyl]di-platinum, <b>147</b> .....                   | 74 |
| Addition of Potassium <i>tert</i> -Butoxide to <b>138</b> to form Di- $\mu$ -chlorobis<br>[(1,4,5- $\eta$ )-3- <i>tert</i> -butoxide-2-methoxymethyl)-4-hexenyl]di-platinum, <b>149</b> .....        | 75 |
| Addition of Sodium Acetate to <b>138</b> to form <b>152</b> .....  | 78 |
| Addition of Sodium Benzoate to <b>138</b> to form <b>154</b> .....   | 79 |
| Addition of Carbon Nucleophiles to <b>138</b> .....  | 81 |
| Addition of <b>157</b> to <b>138</b> to form Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-(2-<br>propanoyl)-2-methoxymethyl)-4-hexenyl]di-platinum, <b>158</b> .....                                    | 81 |
| Addition of <b>160</b> to <b>138</b> to form Di- $\mu$ -chlorobis[(1,4,5- $\eta$ )-3-[2-ethoxy-1-1-<br>(ethoxycarbonyl)-2-oxoethyl]-2-(methoxymethyl)-4-hexenyl]di-platinum,<br><b>161</b> .....     | 84 |
| Addition of Nitrogen Nucleophiles to <b>138</b> .....  | 86 |
| Addition of Tosylamide <b>163</b> to <b>138</b> to form Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-<br>[[[4-methylphenyl)sulfonyl]amino]-2-methoxymethyl)-4-hexenyl]di-<br>platinum, <b>164</b> ..... | 86 |
| Addition of Sulfur Nucleophiles to <b>138</b> .....  | 88 |
| Addition of Ethyl Mercaptan to <b>138</b> .....  | 88 |
| Mechanism of Formation of 3-Ethylthio-1-methoxy-2-methyl-4-hexene <b>168</b> ....  | 89 |

|  |     |
|--|-----|
| Liberation of Organic Substrates in $\sigma$ $\pi$ bound Platinum (II) Complexes.....  | 90  |
| Hydrogenation of <b>145</b> .....  | 90  |
| Hydrogenation of <b>164</b> .....  | 91  |
| Liberation of the Organic Moiety by Addition of Triphenylphosphine .....   | 93  |
| Summary .....  | 94  |
| Platinacyclobutanes with a $\alpha$ Hetero Atom.....   | 95  |
| $\alpha$ Sulfur Substituted Cyclopropanes .....  | 95  |
| Addition of Zeise's Dimer <b>2</b> to Cyclopropyl Amine <b>175</b> .....   | 99  |
| Conclusions .....  | 101 |
| <b>EXPERIMENTAL</b> .....  | 103 |
| General.....   | 103 |
| Chemicals .....  | 103 |
| Instrumentation.....   | 104 |
| Procedures.....  | 104 |
| Reaction of $\alpha$ -Pinene <b>124</b> with Trimethylaluminum and Diiodomethane to form (2 <i>R</i> *, 4 <i>S</i> *)-2,7,7-Trimethytricyclo[4.1.1.0 <sup>2,4</sup> ]octane <b>125</b> .....   | 104 |
| Reaction of 1,3-cyclohexadiene <b>130</b> with Zinc-copper Couple and Diiodomethane to Yield (1 <i>S</i> *, 2 <i>R</i> *, 4 <i>S</i> *, 7 <i>R</i> *)-Tricyclo[5.1.0.0 <sup>2,4</sup> ]octane <b>132</b> and (1 <i>S</i> *, 2 <i>S</i> *, 4 <i>R</i> *, 7 <i>R</i> *)-Tricyclo[5.1.0.0 <sup>2,4</sup> ]octane <b>131</b> ..... | 105 |
| Reaction of (1 <i>S</i> *, 2 <i>R</i> *, 4 <i>S</i> *, 7 <i>R</i> *)-Tricyclo[5.1.0.0 <sup>2,4</sup> ]octane <b>132</b> with Zeise's Dimer <b>2</b> to Yield 3-(Chloromethyl)-6-methylidenyl-1-cyclohexene <b>137</b> .....  | 107 |
| Reaction of 2,4-hexadien-1-ol <b>134</b> with Zinc-copper Couple and Diiodomethane yielding (1 <i>S</i> *, 2 <i>S</i> *)-1-(Hydroxymethyl)-2-(1- <i>E</i> -propenyl) cyclopropane <b>135</b> .....   | 108 |
| Synthesis and isolation of (1 <i>S</i> *, 2 <i>S</i> *)-1-(Methoxymethyl)-2-(1- <i>E</i> -propenyl) cyclopropane <b>137</b> from <b>134</b> and <b>135</b> .....   | 109 |
| Reaction of <b>137</b> with Zeise's Dimer <b>2</b> to form -Di- $\mu$ -chlorobis [(1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> .....   | 111 |
| Formation of <b>138</b> with Subsequent Treatment with Ethanol to form Di- $\mu$ -chlorobis [(1,4,5- $\eta$ )-3-ethoxy-2-methoxymethyl]-4-hexenyl]di-platinum, <b>145</b> .....  | 111 |
| Formation of <b>138</b> with Subsequent Treatment with <i>iso</i> -Propanol to form Di- $\mu$ -chlorobis[(1,4,5- $\eta$ )-3- <i>isopropoxy</i> -2-methoxymethyl]-4-hexenyl]di-platinum, <b>147</b> .....   | 113 |
| Formation of <b>138</b> with Subsequent Treatment with Potassium <i>tert</i> -Butoxide to form Di- $\mu$ -chlorobis [(1,4,5- $\eta$ )-3- <i>tert</i> -butoxy-2-methoxymethyl]-4-hexenyl]di-platinum, <b>149</b> .....  | 114 |
| Formation of <b>138</b> with Subsequent Treatment with Sodium Acetate to form <b>152</b> .....   | 115 |
| Formation of <b>138</b> with Subsequent Treatment with Sodium Benzoate to form <b>154</b> .....  | 116 |
| Formation of <b>138</b> with Subsequent Treatment with the Trimethylsilyl enol   |     |

|   |     |
|---|-----|
| ether of Acetone <b>157</b> to form Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-(2-propanoyl)-2-methoxymethyl)-4-hexenyl]di-platinum, <b>158</b> .....  | 117 |
| Formation of <b>138</b> with Subsequent Treatment with the Sodium Salt of Ethylmalonate <b>160</b> to form Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-[2-ethoxy-1-1-(ethoxycarbonyl)-2-oxoethyl]-2-(methoxymethyl)-4-hexenyl]di-platinum, <b>161</b> ..... | 118 |
| Formation of <b>138</b> with Subsequent Treatment with <i>p</i> -Toluenesulfonamide <b>163</b> to form Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-[[4-methylphenyl)sulfonyl]amino]-2-methoxymethyl)-4-hexenyl]di-platinum, <b>164</b> .....                | 119 |
| Formation of <b>138</b> with Subsequent Treatment of Ethanethiol to form 3-Ethylthio-1-methoxy-2-methyl-4-hexene <b>168</b> .....   | 120 |
| Formation of <b>145</b> with Subsequent Treatment of Hydrogen to form 3-Ethoxy-1-methoxy-2-methylhexane <b>170</b> .....  | 121 |
| Formation of <b>164</b> with Subsequent Treatment of Hydrogen to form 2-methyl, 3-[[4-methylphenyl)sulfonyl]amino) 1-methoxyhexane <b>171</b> .....   | 122 |
| Formation of <b>145</b> with Subsequent Treatment of Triphenylphosphine to form 3-Ethoxy-2-(methoxymethyl)-1,4-hexadiene <b>172</b> .....   | 124 |
| Reaction of Cyclopropyl Phenyl Sulfide <b>173</b> with Zeise's Dimer <b>2</b> to form <b>174</b> .....  | 125 |
| Reaction of Cyclopropyl amine <b>175</b> with Zeise's Dimer <b>2</b> to form <b>176</b> .....   | 125 |
| <u>REFERENCES CITED</u> .....   | 127 |
| <u>APPENDIX A NMR FIGURES</u> .....   | 139 |
| <u>APPENDIX B STRUCTURES</u> .....  | 152 |

LIST OF TABLES

|   | Page |
|---|------|
| Table 1. Tricyclic Platinacyclobutanes.....   | 22   |
| Table 2. Trisubstituted Platinacyclobutanes.....  | 24   |
| Table 3. NMR Data for 3-(chloromethyl)-6-methylidencyclohexene <b>133</b> .....   | 57   |
| Table 4. NMR Data for and (Acetonitrile-d <sub>3</sub> )chloro[ (1,4,5-η)-2-(methoxymethyl)-3-chloride-4-hexenyl-platinum, <b>139</b> , and (Acetonitrile-d <sub>3</sub> ) chloro [η <sup>3</sup> -(chloro-3-cyclohexen-1-yl)methyl]-platinum, <b>115</b> ..... | 66   |
| Table 5. NMR Data for (Acetonitrile-d <sub>3</sub> )chloro[ (1,4,5-η)-2-(methoxymethyl)-3-chloride-4-hexenyl-platinum, <b>146</b> .....   | 73   |
| Table 6. NMR Data for (Acetonitrile-d <sub>3</sub> )Chloro[(1,4,5-η)-2- (methoxymethyl)-3- <i>iso</i> -propoxide-4-hexenyl-platinum, <b>148</b> .....   | 75   |
| Table 7. NMR data for (Acetonitrile-d <sub>3</sub> )Chloro[(1,4,5-η)-2-(methoxymethyl)-3- <i>t</i> -butoxide-4-hexenyl-platinum, <b>150</b> .....   | 77   |
| Table 8. NMR data for (Acetonitrile-d <sub>3</sub> )chloro[(1,4,5-η)-2-(methoxymethyl)-3-acetate-4-hexenyl-platinum, <b>155</b> and (Acetonitrile-d <sub>3</sub> )Chloro[ (1,4,5-η)-2-(methoxymethyl)-3-benzoate-4-hexenyl-platinum, <b>156</b> .....           | 80   |
| Table 9. NMR data for (Acetonitrile-d <sub>3</sub> )chloro[(1,4,5-η)-2-(methoxymethyl)-3-(2-propanoyl)-4-hexenyl-platinum, <b>159</b> .....   | 82   |
| Table 10. NMR Data for (Acetonitrile-d <sub>3</sub> ) chloro [ (1,4,5-η)-2-(methoxymethyl)-3-[2-ethoxy-1-(ethoxycarbonyl)-2-oxoethyl]-2-(methoxymethyl)-4-hexenyl]-platinum, <b>162</b> .....   | 85   |
| Table 11. NMR Data for (Acetonitrile-d <sub>3</sub> ) Chloro [ (1,4,5-η)-2-(methoxymethyl)-3-[[4-methylphenyl)sulfonyl]amino]-4-hexenyl-platinum, <b>165</b> .....  | 88   |
| Table 12. NMR Data for Allyl Portion of Platinum Complexed Allyl Phenyl Sulfide.....  | 99   |

LIST OF FIGURES

|  | Page |
|--|------|
| Figure 1. Zeise's Salt 1.....  | 2    |
| Figure 2. The Olefin Orbital Electron Donation to an Unfilled $d_{sp}^2$ hybrid Orbital..... | 3    |
| Figure 3. Donation of d Electrons Into $\pi^*$ Orbital.....                                  | 4    |
| Figure 4. Combined Bonding Interaction.....  | 4    |
| Figure 5. Bonding Extremes.....  | 5    |
| Figure 6. $\pi$ Allyl Resonance Structures.....  | 5    |
| Figure 7. $\pi$ Allyl Orbital Interactions.....  | 6    |
| Figure 8. Nucleophilic Attack of a $\pi$ Allylic Complex.....                                | 7    |
| Figure 9. Three Center Oxidative Addition.....   | 9    |
| Figure 10. Example of Oxidative Addition.....  | 10   |
| Figure 11. Walsh Orbitals for Cyclopropane.....  | 12   |
| Figure 12. Suggested Tetrameric Structure (IPC) for Platinacyclobutanes.....                 | 13   |
| Figure 13. Oxidative Addition and Monomer Formation.....                                     | 14   |
| Figure 14. Puddephatt Rearrangement.....   | 15   |
| Figure 15. Formation of Phenalene 10.....  | 16   |
| Figure 16. Formation of Acetyl Substituted Platinacyclobutanes.....                          | 17   |
| Figure 17. Volger's Proposed Structures.....   | 18   |
| Figure 18. Insertions into Norbornyl Cyclopropanes.....                                      | 19   |

|   |    |
|---|----|
| Figure 19. Stable Cis Disubstituted Platinacyclobutane.....                                   | 20 |
| Figure 20. Bicyclic Platinacyclobutanes.....  | 21 |
| Figure 21. Insertion of Z.D. 2 into a Cyclopropane with an Electron<br>Withdrawing Group..... | 23 |
| Figure 22. Results of Hydrogenation.....  | 28 |
| Figure 23. Formation of Olefinic Products from Norcarane.....                                 | 30 |
| Figure 24. Formation of Olefinic Products from Bicyclo[6.1.0]nonane.....                      | 31 |
| Figure 25. Wiberg's Skeletal Rearrangement.....   | 31 |
| Figure 26. Jennings' Norbornyl Rearrangement.....   | 32 |
| Figure 27. Zeise's Dimer 2 Catalyzed Ketone Formation.....                                    | 33 |
| Figure 28. Stabilization of the Platinum Intermediate Forming 98.....                         | 34 |
| Figure 29. Mechanism for the Catalytic Synthesis of 1-Methylcyclohexanone 96.....             | 35 |
| Figure 30. Aumann's Iron Vinylcyclopropane Reactions.....                                     | 37 |
| Figure 31. Zeise's Dimer 2 Reaction with Norcarene 110.....                                   | 38 |
| Figure 32. Proposed Mechanism of Norcarene 110 Addition of Zeise's Dimer 2.....               | 39 |
| Figure 33. Alkoxide Substitution for Chloride.....  | 40 |
| Figure 34. Solvolysis of 114.....   | 41 |
| Figure 35. Methodologies Releasing the Organic Moiety.....                                    | 41 |
| Figure 36. Five, Seven and Eight Membered Organoplatinum Complex Rings.....                   | 42 |
| Figure 37. Vinylcyclopropane Addition Methodology.....  | 43 |
| Figure 38. Olefin Transformation Via Platinacyclobutanes Methodology.....                     | 44 |
| Figure 39. Cyclopropanation of Pinene 124.....  | 46 |

|  |    |
|--|----|
| Figure 40. NOE Data for 2,7,7-Trimethyltricyclo[4.1.1.0 <sup>2,4</sup> ]octane 125.....  | 47 |
| Figure 41. Insertion of Zeise's dimer into 2,7,7-Trimethyltricyclo[4.1.1.0 <sup>2,4</sup> ]octane<br>125.....  | 48 |
| Figure 42. Formation of 1,7,7-trimethyl-2-methylidenyl- <i>endo</i> -6-<br>chlorobicyclo[2.2.1]heptane 127 and 1,7,7-trimethyl- <i>endo</i> -2-methyl- <i>endo</i> -6-<br>chlorobicyclo[2.2.1]heptane 126..... | 48 |
| Figure 43. Formation of 1,7,7-trimethyl-2-methylidenyl- <i>endo</i> -6-<br>chlorobicyclo[2.2.1]heptane 127.....  | 49 |
| Figure 44. Zeise's Dimer 2 Catalyzed Formation of Allyl Silyl Ethers.....  | 49 |
| Figure 45. The Proposed Mechanisms of Zeise's Dimer 2 Rearrangement. ....  | 51 |
| Figure 46. Formation of Tricyclo [5.1.0.0 <sup>2,4</sup> ] octanes 131 and 132. ....   | 54 |
| Figure 47. Formation of 3-(chloromethyl)-6-methylidenyl-1-cyclohexene 133. ....  | 54 |
| Figure 48. Proposed Mechanisms for the Formation of 133.....   | 59 |
| Figure 49. Synthesis of <i>trans</i> -1-(methoxymethyl) -2-(1-E-propenyl)cyclopropane<br>137.....  | 63 |
| Figure 50. Formation of Di- $\mu$ -chlorobis[(1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-<br>hexenyl]di- platinum, 138. ....  | 64 |
| Figure 51. Mechanism of Formation of Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-<br>methoxymethyl]-4-hexenyl]di-platinum,138.....  | 67 |
| Figure 52. Cis and Trans Zeise's Dimer 140, 2.....   | 69 |
| Figure 53. The Four Possible Isomers of Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-<br>methoxymethyl]-4-hexenyl]di-platinum, 138. ....   | 70 |
| Figure 54. Substitution of Chloride for Ethoxide.....  | 71 |
| Figure 55. Proposed Mechanism for the Formation of Di- $\mu$ -chlorobis [(1,4,5- $\eta$ )-3-<br>ethoxide-2-methoxymethyl]-4-hexenyl]di-platinum, 145. ....   | 71 |
| Figure 56. Addition of Iso-Propanol to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-<br>methoxymethyl]-4-hexenyl]di-platinum, 138. ....  | 74 |

|   |     |
|---|-----|
| Figure 57. Addition of Potassium <i>tert</i> -butoxide to Di- $\mu$ -chlorobis[(1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> .....                       | 76  |
| Figure 58. Sodium acetate addition to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> .....   | 78  |
| Figure 59. Addition of Sodium Benzoate to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> .....                                     | 79  |
| Figure 60. Addition of the trimethylsilyl enol ether of acetone <b>157</b> to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> ..... | 81  |
| Figure 61. Addition of Sodium ethyl Malanate <b>160</b> to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> .....                    | 84  |
| Figure 62. Addition of Tosylamide <b>163</b> to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> .....                               | 87  |
| Figure 63. Addition of Ethyl Mercaptan to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-chloro-2-methoxymethyl]-4-hexenyl]di-platinum, <b>138</b> .....                                     | 89  |
| Figure 64. Proposed Mechanism for the formation of 3-ethylthio-1-methoxy-2-methyl-4-hexene, <b>168</b> .....  | 90  |
| Figure 65. Hydrogenation of Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-ethoxy-2-methoxymethyl]-4-hexenyl]di-platinum, <b>145</b> .....   | 91  |
| Figure 66. Hydrogenation of Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-[[4-methylphenyl)sulfonyl]amino]-2-methoxymethyl]-4-hexenyl]di-platinum, <b>164</b> .....                         | 93  |
| Figure 67. Addition of Triphenylphosphine to Di- $\mu$ -chlorobis [ (1,4,5- $\eta$ )-3-ethoxy-2-methoxymethyl]-4-hexenyl]di-platinum, <b>145</b> in Ethanol.....                        | 94  |
| Figure 68. Utility of Vinyl Cyclopropane Methodology.....   | 95  |
| Figure 69. Addition of Zeise's Dimer <b>2</b> to Phenyl Cyclopropyl Sulfide <b>173</b> .....  | 97  |
| Figure 70. Proposed Mechanism for the Formation of Allyl Phenyl Sulfide.....  | 98  |
| Figure 71. Addition of Zeise's Dimer <b>2</b> to Cyclopropyl Amine <b>175</b> .....   | 100 |

|   |     |
|---|-----|
| Figure 72. $^1\text{H}$ NMR Spectrum of 139.....    | 140 |
| Figure 73. $^{13}\text{C}$ NMR Spectrum of 139..... | 141 |
| Figure 74. $^1\text{H}$ NMR Spectrum of 146.....    | 142 |
| Figure 75. $^{13}\text{C}$ NMR Spectrum of 146..... | 143 |
| Figure 76. $^1\text{H}$ NMR Spectrum of 148.....    | 144 |
| Figure 77. $^{13}\text{C}$ NMR Spectrum of 148..... | 145 |
| Figure 78. $^{13}\text{C}$ NMR Spectrum of 150..... | 146 |
| Figure 79. $^{13}\text{C}$ NMR Spectrum of 155..... | 147 |
| Figure 80. $^{13}\text{C}$ NMR Spectrum of 156..... | 148 |
| Figure 81. $^{13}\text{C}$ NMR Spectrum of 162..... | 149 |
| Figure 82. $^1\text{H}$ NMR Spectrum of 165.....    | 150 |
| Figure 83. $^{13}\text{C}$ NMR Spectrum of 165..... | 151 |

ABSTRACT

It has long been known that Zeise's Dimer inserts into cyclopropanes to form platinacyclobutanes. However, not all platinacyclobutanes are stable, and several have been shown to form novel organic products. It has also been shown that pi electron donors on the cyclopropane will stabilize the incipient carbocation formed by the platinacyclobutane. Various tactics can then be used to further direct the chemistry.

The first thrust of this research utilized strained ring systems to affect the chemistry about the platinacyclobutane. In the first example, 2,7,7-trimethyltricyclo[4.1.1.0<sup>2,4</sup>]octane forms a platinacyclobutane in the presence of Zeise's Dimer which subsequently undergoes a carbocation mediated bond migration to form 1,7,7-trimethyl-2-methylidyl-*endo*-6-chlorobicyclo[2.2.1]heptane. In the second case, *cis* tricyclo[5.1.0.0<sup>2,4</sup>]octane undergoes a novel transformation upon treatment with Zeise's Dimer and triphenyl phosphine to form 3-(chloromethyl)-6-methylidyl-1-cyclohexene. This is thought to be due to the proximity of the second cyclopropane to the first cyclopropane.

A second method utilized in the stabilization of the incipient carbocation generated by a platinacyclobutane is the use of an olefin alpha to the cyclopropane. Platinacyclobutanes from these systems undergo a rearrangement to form methylene tethered pi allylic complexes which have the unique ability to undergo a variety of regio and stereo-selective nucleophilic additions without decomposition of the complex. These complexes can then be decomposed utilizing a variety of methods yielding a plethora of interesting organic products based on the original diene that the cyclopropane was generated from.

A third method used to direct the chemistry resulting from platinacyclobutanes is the use of the lone pair of electrons on a heteroatom, in this case sulfur and nitrogen. Both demonstrate the ability of a hetero atom to direct the chemistry of platinacyclobutanes. However in the case of amino cyclopropane, the nitrogen complexes to one platinum atom before a second inserts and thereby prevents chemistry alpha to the amine. In the case of phenyl cyclopropyl sulfide, the addition of Zeise's Dimer yields a rearrangement of the cyclopropane to a propenyl moiety.

In all cases, it was shown that the nature of the platinum carbon bond polarization in a platina(IV)cyclobutane is platinum minus carbon plus. Also, this thesis helps define how pi donating substituents on cyclopropanes direct the subsequent chemistry of platinacyclobutanes formed from these cyclopropanes.

## INTRODUCTION

### Historical Preface

The history of organometallic chemistry is quite rich and older than might be expected originating in 1827 with a compound discovered by a Danish pharmacist Zeise, commonly known as Zeise's salt, **1**.<sup>1</sup> The true nature of this salt was not understood unambiguously until Wunderlich and Mellor reported the first X-ray crystal structure in 1954 (See Figure 1).<sup>2</sup> Zeise's salt **1** launched a branch of chemistry, and even though this branch is nearly two centuries old, the chemistry has not seen its utility exhausted.

Indeed this thesis relies entirely on the novel chemistry that a closely related complex, Zeise's dimer, **2**, ( see Figure 10) exhibits when it is allowed to interact with cyclopropanes to form platinacyclobutanes. Platinacyclobutanes were initially discovered in the fifties and received a good deal of attention at the time. However, by the late sixties it appeared that interest had waned. In the early eighties, interest in this area was revitalized by Jennings for its mechanistic and synthetic potential. His work with platinacyclobutanes took a general course. First, an olefin is cyclopropanated using standard organic methods. Second, Zeise's dimer **2** is reacted with the cyclopropane to form a platinacyclobutane. Third, the platinacyclobutane is treated with a series of reagents to effect the release of the organic substrate, yielding an organic product. When one examines the overall effect of this method, a ubiquitous olefin undergoes a novel

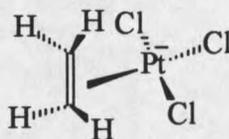
organic transformation while yielding mechanistic insights into all of organometallic chemistry. This thesis further examines the chemistry of platinacyclobutanes which have an electron donor in the  $\alpha$  position. Before launching into a discussion of that chemistry, it would be useful to the reader to present an overview of bonding, common mechanistic pathways, and structure elucidation in the organometallic/organoplatinum arena.

## Bonding

### $\pi$ Bonding in Organoplatinum Complexes

In the preface to this thesis, it was mentioned that Zeise's salt **1** was the first organometallic complex to be described. In addition, it was the first complex known to exhibit transition metal  $\pi$  bonding to an olefin. In this case, the  $\pi$  bonding is between platinum and ethylene (Figure 1).

Carbon monoxide and other related ligands such as nitrosyl and the isocyanides are probably the most common  $\pi$  bonding ligands. However, since  $\pi$  bound olefins are important to the chemistry discussed in this thesis, the discussion will center on this ligand.

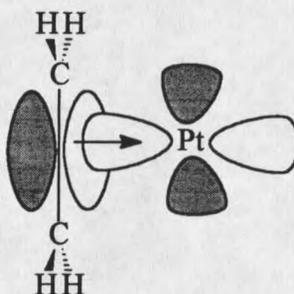


**1**

**Figure 1. Zeise's Salt 1.**

The first thing that should be noted in the bonding of ethylene or any other olefin to a transition metal is that the carbon-carbon bond of the olefin is most often perpendicular to the plane of square planar complexes. The predominate factor influencing the orientation of the olefin is the steric effect from the other ligands.<sup>3</sup> However, one rare example where the olefin (styrene) is coplanar to the other ligands is a compound described by Miki et al.<sup>4</sup> Before engaging in further discussion of the  $\pi$  backbonding, an overview of the general orbital interactions of  $\pi$  bonding to metals would be useful.

The orbital picture for organometallic  $\pi$  bonds goes back to the Chatt, Duncanson, and Dewar model.<sup>5,6</sup> This involves two interactions, the first of which is a  $\sigma$  type interaction where the electrons in the  $\pi$  bond of the olefin are donated into the empty  $d_{sp}^2$  hybrid orbital on the metal as shown in Figure 2.



**Figure 2. The Olefin Orbital Electron Donation to an Unfilled  $d_{sp}^2$  hybrid Orbital.**

The second interaction is the back donation of the filled  $d_{yz}$ ,  $d_{xz}$  or  $d_{xy}$  orbital on the metal to the  $\pi^*$  orbital on the olefin as shown in Figure 3.



































































































































































































































































































































