



Synthetic and mechanistic studies on the thermal reactions of platinum (II) and rhodium (I) with substituted cyclopropanes and the homologation of alkenes
by Brian David Williams

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:

A new methodology for the homologation of alkenes was examined. Novel platinum(IV)cyclobutanes were prepared by the reaction of platinum(II) in the form of Zeise's dimer with a variety of substituted cyclopropanes. The alkenes formed from the thermal decomposition of the platinum(IV)cyclobutanes were characterized and yields of chain extended and ring expanded products were determined. Mechanistic techniques have been employed in an effort to determine the pathway for the alkene homologation process. Included in these mechanistic studies were; ^2H and ^{13}C isotopic labeling studies, determination of kinetic isotope effects, acquisition and analysis of thermodynamic parameters, ligand exchange experiments, and solvent effects. Conclusions based on results were used to develop a plausible reaction mechanism.

SYNTHETIC AND MECHANISTIC STUDIES ON THE THERMAL REACTIONS
OF PLATINUM(II) AND RHODIUM(I) WITH SUBSTITUTED CYCLOPROPANES
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Brian David Williams

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

A new methodology for the homologation of alkenes was examined. Novel platina(IV)cyclobutanes were prepared by the reaction of platinum(II) in the form of Zeise's dimer with a variety of substituted cyclopropanes. The alkenes formed from the thermal decomposition of the platina(IV)cyclobutanes were characterized and yields of chain extended and ring expanded products were determined. Mechanistic techniques have been employed in an effort to determine the pathway for the alkene homologation process. Included in these mechanistic studies were; ^2H and ^{13}C isotopic labeling studies, determination of kinetic isotope effects, acquisition and analysis of thermodynamic parameters, ligand exchange experiments, and solvent effects. Conclusions based on results were used to develop a plausible reaction mechanism.

INTRODUCTION

Discovery and Structure of Platina(IV)cyclobutanes

The history of Platina(IV)cyclobutanes began in 1955 with a discovery by Tipper¹. Inspired by the work of Walsh² which suggested that there are similarities in electron delocalization between cyclopropanes and olefins, Tipper reasoned that it might be possible to synthesize metal-cyclopropane complexes similar to complexes known to exist for metal-alkenes. Tipper reported that cyclopropane reacted with hexachloroplatinic acid, H_2PtCl_6 , in acetic anhydride to form a brown solid with composition $\text{C}_3\text{H}_6\text{Cl}_2\text{Pt}$, which on treatment with pyridine (Py) gave a white compound $[\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{Py})_2]$ (Figure 1). The white substance was later identified as a platina(IV)cyclobutane.³⁻⁵

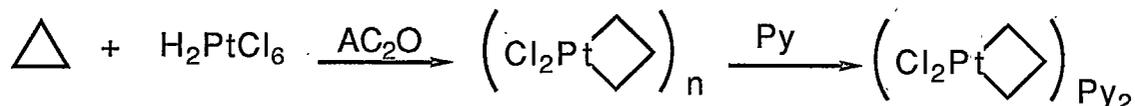


Figure 1. Discovery of Platina(IV)cyclobutanes.

Tipper's method for the preparation of platina(IV)cyclobutanes is limited by the use of hexachloroplatinic acid and was found not to be useful in the preparation of substituted analogues.⁶ A more general synthetic route, discovered by McQuillin, involved the reaction of cyclopropane derivatives with Zeise's Dimer (Figure 2).⁷

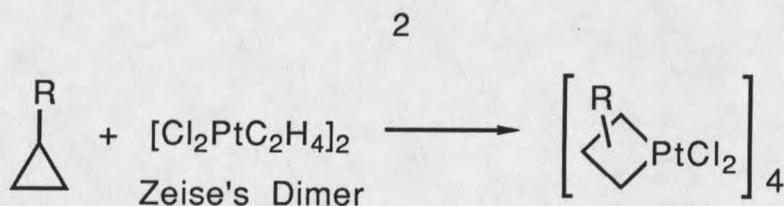


Figure 2. General Method for Platina(IV)cyclobutane Synthesis.

The reaction of Zeise's Dimer with cyclopropane can often be monitored visually by the disappearance of the orange colored Zeise's Dimer and the formation of the yellow initially precipitated complexes (IPC).⁸ An IPC is only sparingly soluble in any solvent in which it does not react and the first attempts to characterize it were made by R.D. Gillard in 1969.⁹

Gillard proposed two possible structures for an IPC derived from cyclopropane based on IR, mass spectrum and x-ray powder diffraction and the analysis of monomers derived from reactions of the IPC with good donor ligands like pyridine (Figure 3).

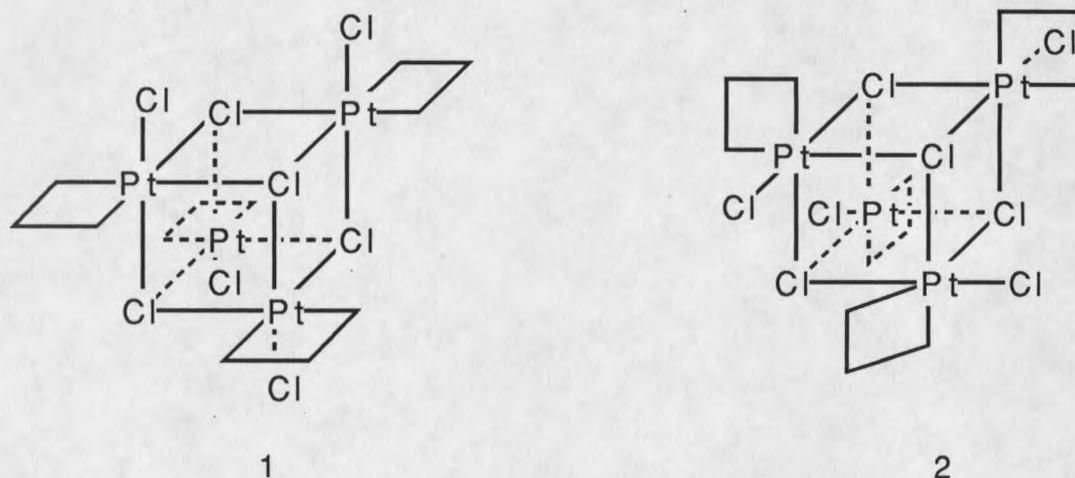


Figure 3. Possible Structures of Tetrameric Platina(IV)cyclobutanes.

Gillard further argued that structure 1 (Figure 3) was most probable based on an analysis of the products derived from the reaction of the I.P.C. with dioxane. Dioxane attack trans to the methylene groups in structure 1 would give either compound 3 or 4, whereas similar attack on structure 2 would give only compound 4 (Figure 4).

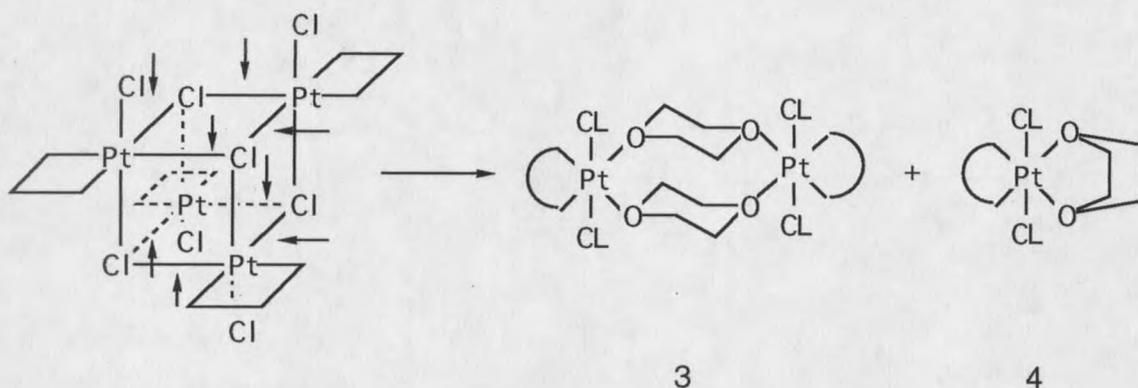


Figure 4. Reactions of Tetrameric Platina(IV)cyclobutanes with Dioxane.

Gillard found that the IR spectrum due to the product resulting from the reaction of the I.P.C. with dioxane is virtually identical with the spectrum of other complexes containing dioxane in the chair conformation and also with the spectrum of free dioxane which is known to have a chair conformation. It was therefore concluded that the dioxane derivative has the bridging chair form and that the I.P.C. is most likely structure 1.

Treatment of the I.P.C.'s with pyridine or a variety of other coordinating ligands produces monomeric platina(IV)cyclobutanes $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ where $x = \text{Cl}$ or Br . These monomeric complexes are easily isolated and are readily soluble in many common solvents including chloroform, methylene chloride,

benzene and acetonitrile. Due to the enhanced solubilities relative to the tetrameric complexes, the monomers have been well characterized. With few exceptions, X-ray crystal structure analysis has shown them to be octahedral complexes with the cyclopropane moiety trans to the pyridine or other coordinating ligands (L) and the halogens are trans to one another as shown in Figure 6.³⁻⁵

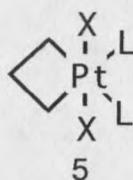


Figure 5. Structure of Monomeric Platina(IV)cyclobutanes.

Synthesis of Platina(IV)cyclobutanes

The most versatile and frequently used method for preparing substituted platina(IV)cyclobutanes is reaction of cyclopropanes with Zeise's Dimer. In this method, diethyl ether is the most frequently used solvent, but tetrahydrofuran, chloroform and methylene chloride have also been employed successfully.¹⁰ Tetrahydrofuran has mild ligating abilities with platinum and provides increased solubility of both the starting materials and the products.

The platina(IV)cyclobutane monomers are stable when X = Cl or Br and L is an oxygen or nitrogen-donor ligand. Replacement of the platinum bound ligands (L) have been observed in the order; tetrahydrofuran, pyridine, 4-methylpyridine, and ethylene diamine. All of these displacement reactions were observed to occur without the elimination of the cyclopropane.¹¹ When strong ligands with a high trans-effect, such as tertiary phosphines are coordinated to

