



Organic transformations derived from the reaction of platinum (IV) metallacycles with nucleophilic reagents

by Frederick Forrest Stewart

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:

Platinum can form many stable complexes that can be compared, by analogy, to catalytically active systems. The study of platinum complexes and the chemistry derived from them can give new organic products with intriguing novel reaction mechanisms. Various pathways of chemistry were garnered by the reaction of platinum (IV) metallacycles with nucleophiles. Reaction of platinum (IV) metallacyclopentanes with hydride gives liberated organic substrates where the metal has effected carbon-hydrogen bond formation. The products were methyl norbomyl alcohols or ethers. Reaction of iodide with platinum(IV)cyclobutylcarbinol was observed to give 2-norbomyl acetaldehyde in good yield. Product formation is attributed to (3-hydride elimination, this the first time that this mechanism has been observed with this substrate. Reaction of platinumacyclobutanes and platinumacyclopentanes with azide have been found to undergo ligand substitution giving stable complexes. Platinumacyclobutanes were observed to be more labile in this substitution pathway, substitutions were conducted at room temperature where the analogous platinumacyclopentanes required refluxing methanol.

The reaction of diazo-derivatives with platinum(IV) metallacyclobutanes involves a novel metal mediated carbon-carbon bond forming process. The products observed are cis-divinylcyclopentanes which exhibit high degrees of stereocontrol. The process was studied through modification of the substrate and use of alternate diazo-reagents. Norbomyl analogs, benzofuran derived systems, allow for bridgehead substitution readily. This substituted substrate was found to give stereospecific product upon reaction with mono-substituted diazo-reagent, thus giving support to the proposed mechanism. In addition, diazo-reagents with electron donating groups were found to halt the reaction. Attachment of electron withdrawing groups, on the otherhand, was found to give products in good yield.

Platinumacyclobutanes are known to ring expand upon solvolysis to give platinumacyclopentanes with stereo- and regiospecificity. These bis-pyridyl complexes were found to undergo substitution reactions with various phosphine and phosphite ligands. Studies of these complexes were conducted in excess ligand. Removal of the ligand began decomposition of the complexes, this decomposition was found to be complete in one hour at reflux. The organic products were found to be cyclobutanes formed with total stereospecificity in excellent yield.

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in

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APPROVAL

of a thesis submitted by

Frederick Forrest Stewart

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.

6/15/92
Date

Dr. P. W. Jennings
Chairperson, Graduate Committee

Approved for the Major Department

6/15/92
Date

John R. Owens
Head, Major Department

Approved for the College of Graduate Studies

June 18, 1992
Date

Henry S. Parsons
Graduate Dean

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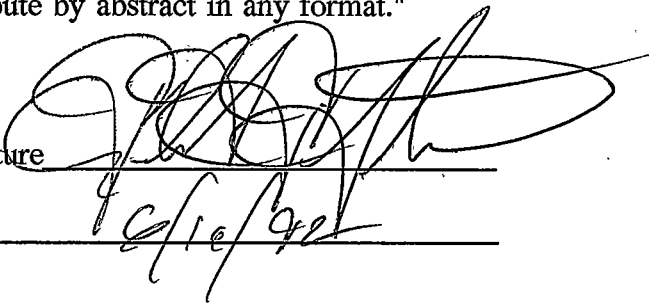
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ABSTRACT

Platinum can form many stable complexes that can be compared, by analogy, to catalytically active systems. The study of platinum complexes and the chemistry derived from them can give new organic products with intriguing novel reaction mechanisms. Various pathways of chemistry were garnered by the reaction of platinum(IV) metallacycles with nucleophiles. Reaction of platinum(IV) metallacyclopentanes with hydride gives liberated organic substrates where the metal has effected carbon-hydrogen bond formation. The products were methyl norbornyl alcohols or ethers. Reaction of iodide with platinum(IV)cyclobutylcarbinol was observed to give 2-norbornyl acetaldehyde in good yield. Product formation is attributed to β -hydride elimination, this the first time that this mechanism has been observed with this substrate. Reaction of platinacyclobutanes and platinacyclopentanes with azide have been found to undergo ligand substitution giving stable complexes. Platinacyclobutanes were observed to be more labile in this substitution pathway, substitutions were conducted at room temperature where the analogous platinacyclopentanes required refluxing methanol.

The reaction of diazo-derivatives with platinum(IV) metallacyclobutanes involves a novel metal mediated carbon-carbon bond forming process. The products observed are cis-divinylcyclopentanes which exhibit high degrees of stereocontrol. The process was studied through modification of the substrate and use of alternate diazo-reagents. Norbornyl analogs, benzofuran derived systems, allow for bridgehead substitution readily. This substituted substrate was found to give stereospecific product upon reaction with mono-substituted diazo-reagent, thus giving support to the proposed mechanism. In addition, diazo-reagents with electron donating groups were found to halt the reaction. Attachment of electron withdrawing groups, on the otherhand, was found to give products in good yield.

Platinacyclobutanes are known to ring expand upon solvolysis to give platinacyclopentanes with stereo- and regiospecificity. These bis-pyridyl complexes were found to undergo substitution reactions with various phosphine and phosphite ligands. Studies of these complexes were conducted in excess ligand. Removal of the ligand began decomposition of the complexes, this decomposition was found to be complete in one hour at reflux. The organic products were found to be cyclobutanes formed with total stereospecificity in excellent yield.

INTRODUCTION

The use of metals in organic synthesis has exploded over the past three decades. Likewise, the complexity of the transformations either catalyzed or mediated by metals has also seen tremendous growth. Simple procedures like catalytic hydrogenation with platinum (IV) oxide have given way to asymmetric hydrogenations and carbon-carbon bond formation with high enantiomeric excesses. In fact, the study of the interactions of metals with carbon, organometallics, has grown from a gray-area between the long established disciplines of organic and inorganic chemistry into a recognized field of study in its own right.

The main impetus for the study of organometallics is that metals, upon reaction with organic molecules, give numerous novel reactions with innovative reaction mechanisms. In understanding these mechanisms, it allows these reactions to be modified to obtain better stereochemical control and overall utility.

Synthesis and Chemistry of Metallacyclopentanes of the Late Transition Metals

Metallacyclopentanes are often thought of as fleeting intermediates in many organometallic transformations. However, stable metallacycles may be viewed as models for these intermediates and can be treated in a variety of ways to give new products while gaining insight into the nature of the metallacycle itself.

Numerous intriguing syntheses of metallacyclopentanes have appeared in the literature and the purpose of this part of the introduction is to acquaint the reader with some of the intricacies of their formation and chemistry.

Metallacyclopentanes from Olefin Coupling

It was shown by Osborn et. al.¹ in 1973 that norbornadiene could be coupled in the presence of Iridium (I) giving an irida(III)cyclopentane. This process can be thought of as a six electron electrocyclic reaction where two electrons are donated from the

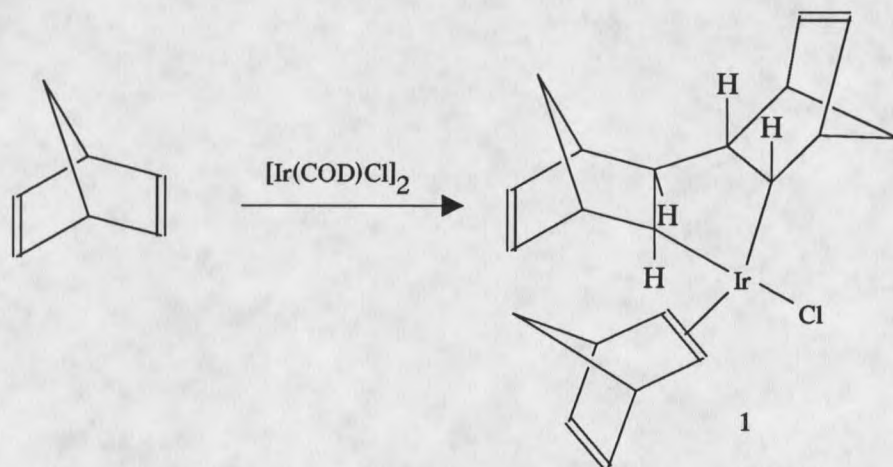


Figure 1. Coupling of Norbornadiene with Iridium (I).

metal. Complex 1 is an assumed structure, as the author states², the complex is sparingly soluble, thus a definitive structure determination was not possible. However, complex 1 was derivatized using acetyl acetonate (Figure 2). The proposed structure was verified through the use of X-ray crystallographic analysis. This evidence firmly

established the presence of a five membered heterocyclic ring for complex **2** and implied the same for complex **1**. Complex **1** was also found to undergo carbonyl insertion when exposed to carbon monoxide followed by treatment with triphenylphosphine (Figure 2).

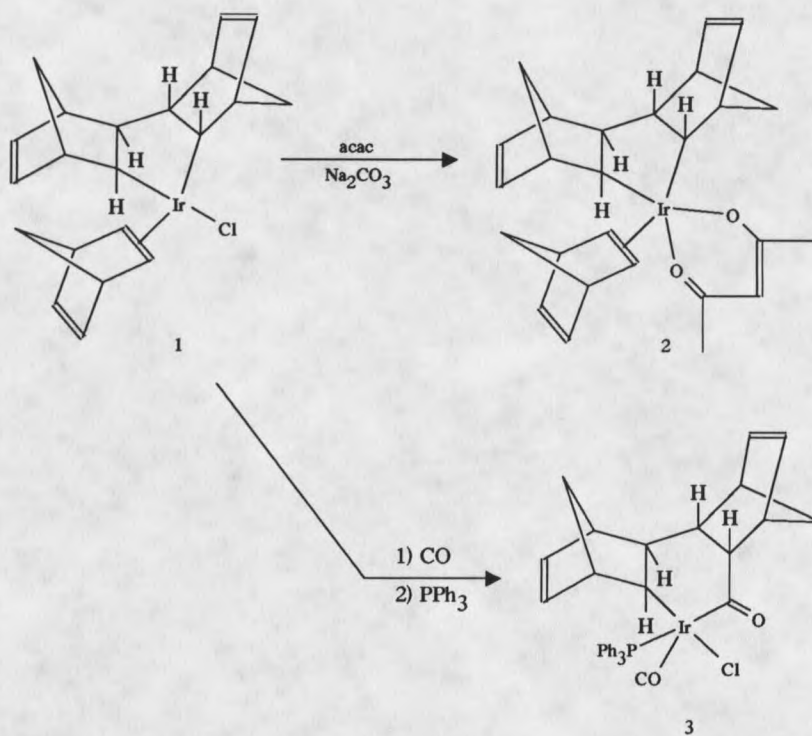


Figure 2. Reaction of Complex 1 with Acetylacetonate and Carbon Monoxide.

Determination of the stereochemistry at the juncture of the two norbornyl rings also was obtained by reaction of **1** with excess triphenylphosphine. Under these conditions, the complex decomposed to the hydrocarbon shown in Figure 3.

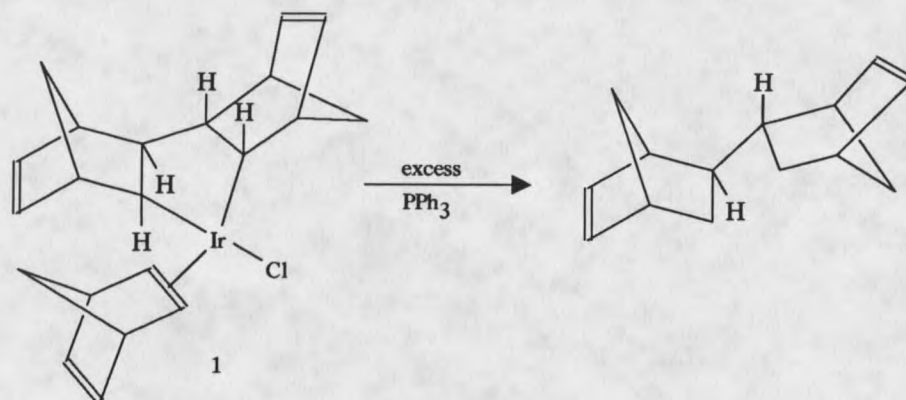


Figure 3. Reaction of Complex 1 with excess Triphenylphosphine.

Methylenecyclopropane, another strained olefin, was shown in 1972³ to dimerize in the presence of bis-1,5-cyclooctadiene nickel(0). It was proposed that this

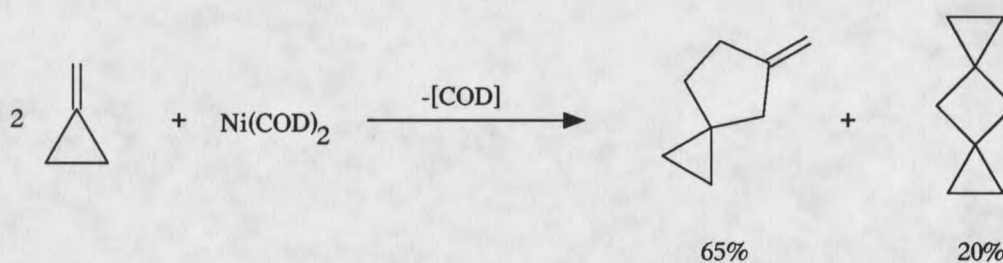


Figure 4. Dimerization of Methylene Cyclopropane.

dimerization passed through a nickelacyclopentane intermediate that either directly underwent reductive elimination to form the minor product shown in Figure 5 or rearranged and then underwent reductive elimination to give the major product as shown below.

