



Synthesis, characterization, chemistry and intermediacy of metallacyclobutane derivatives of the group eight transition metals
by Lynette Louise Johnson

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

A review article, intended for publication, was written on metallacyclobutane derivatives of the Group VIII transition metals. To begin this project a complete search of the literature was performed both by manual means and by utilizing a computerized literature search. Once the desired published material was gathered, the information was compiled into one article and is summarized below.

The synthesis of metallacyclobutane derivatives of the Group VIII transition metals invokes a few common methodologies which have been used to prepare a variety of metallacyclobutane derivatives. Other methodologies have been employed to create isolated examples of metallacyclic species. The characterization of these complexes includes the use of ^1H NMR and ^{13}C NMR spectroscopy and, for relatively few examples, x-ray crystallographic analysis.

The reported reaction chemistry of the metallacyclobutane derivatives of the Group VIII transition metals yields a surprisingly limited number of products. However, these products can be generated using a variety of reagents and techniques.

Metallacyclobutane derivatives have been suggested as intermediates in a number of different reactions involving Group VIE metals. The metal often serves as a catalyst in these reactions.

SYNTHESIS, CHARACTERIZATION, CHEMISTRY AND INTERMEDIACY
OF METALLACYCLOBUTANE DERIVATIVES OF
THE GROUP EIGHT TRANSITION METALS

by

Lynette Louise Johnson

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of a thesis submitted by

Lynette Louise Johnson

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ABSTRACT

A review article, intended for publication, was written on metallacyclobutane derivatives of the Group VIII transition metals. To begin this project a complete search of the literature was performed both by manual means and by utilizing a computerized literature search. Once the desired published material was gathered, the information was compiled into one article and is summarized below.

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INTRODUCTION

The publication of review articles has become an essential factor in the progress of research. The amount of time researchers spend searching the literature for work relevant to their interests can be considerably reduced by the publication of an updated, thorough review article. The purpose of a review article, therefore, is to compile either all, or the most recent results, in a chosen area and concisely report the known work as well as any new ideas the author may have.

Chemical Reviews is a journal published monthly by the American Chemical Society. This publication was first issued in April 1924 and includes current review articles in all areas of chemistry. A number of other journals exist that publish only review material such as Coordination Chemistry Reviews and Topics in Current Chemistry.

The interest of our research group in organometallic chemistry, more specifically organo-platinum chemistry and metallacyclic complexes, led to the vision of creating a review article on metallacyclobutane derivatives of the group eight transition metals. Although related review material has been published, we viewed the previous work to be either incomplete or outdated. The benefit to our research of an updated, complete compilation of literature in the chosen area would be enormous.

STATEMENT OF PROBLEM

The literature on metallacyclobutane derivatives covers over 35 years and is included in over 50 different journals and books. The large scope and locale of the literature makes searching for material in this area difficult and time consuming.

The intent of this research project was to concisely compile all of the reported literature on the synthesis, characterization, chemistry and intermediacy of metallacyclobutane derivatives of the Group VIII transition metals into one article to be submitted for publication in Chemical Reviews. The following text is the result of this research, the completed review article.

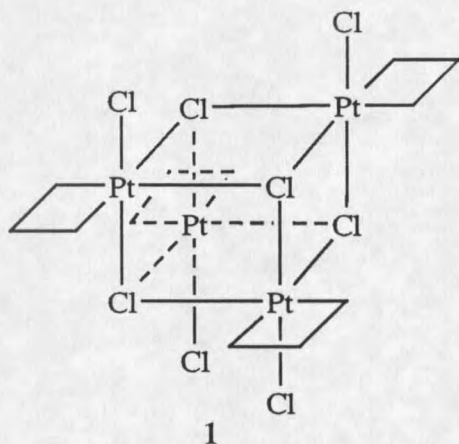
RESULTS AND DISCUSSION

Introduction

The chemistry of metallacyclic compounds is a major area of organometallic chemistry. Within the past two decades these intriguing systems have been explored in depth and their study has attracted considerable attention. Metallacyclic compounds play an important role in a number of catalytic transformations. They have been suggested as key intermediates in olefin and acetylene metathesis¹⁻¹¹, cycloadditions of alkenes¹²⁻¹⁵ and cyclotrimerizations of acetylenes¹⁶⁻¹⁸, dimerization of alkenes¹⁹⁻²¹, oligomerization of alkynes^{22,23}, oligomerization of dienes²⁴⁻²⁷, polymerization of olefins and acetylenes²⁸⁻³¹, and isomerizations of strained carbocyclic ring systems³²⁻³⁵. In addition to being key intermediates in catalytic reactions, metallacycles also have been used successfully in organic synthesis³⁶.

The first metallacyclic compound was discovered in 1955 by Tipper³⁷. While studying the similarities in electron delocalization between cyclopropanes and olefins suggested by Walsh in 1949³⁸, Tipper examined the ability of cyclopropane to form complexes with transition metals analogous to known olefin-metal complexes. He treated cyclopropane with hexachloroplatinic acid, (H_2PtCl_6), in acetic anhydride and found the reaction product to have empirical formula $\text{PtCl}_2\text{C}_3\text{H}_6$ 1. Further reaction of 1 with pyridine formed a stable compound of formula $(\text{C}_5\text{H}_5\text{N})_2\text{PtCl}_2\text{C}_3\text{H}_6$. Tipper believed the cyclopropane ring remained intact and that the new complex was a dimer analogous with

Zeise's Dimer. The structure of **1** was not accurately identified as a platinacyclobutane however, until 1960 when Chatt and co-workers further examined the compound³⁹. Chatt observed that the solubility properties and the IR data of Tipper's complex suggested a polymeric species, rather than a dimer, and that the cyclopropane ring had opened forming a platina(IV)cyclobutane complex. This conclusion was subsequently confirmed by Gillard et.al. in 1966⁴⁰ and the structure of compound **1** was suggested to be tetrameric in 1969.⁴¹

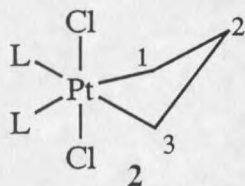


A number of transition metals since have been found to form stable metallacyclic compounds from a variety of methodologies. Other comprehensive and semi-comprehensive reviews that include discussions on metallacyclic compounds have appeared emphasizing topics such as the preparations and properties of metallacyclic compounds⁴²⁻⁴⁴, metallabenzenes⁴⁵, pallada(II)- and platina(II)cyclobutanes⁴⁶, platina(II)- and -(IV)cyclobutanes⁴⁷, cyclometallation reactions^{48,49}, the chemistry of alkanes⁵⁰, acetylenes⁵¹ and cycloproparenes⁵², and metallacycles as intermediates in olefin metathesis¹⁻⁸ and other metal-catalyzed reactions^{34,53-59}. This review will deal specifically with the preparation, characterization, chemistry, and intermediacy of metallacyclobutane derivatives of the Group VIII transition metals (Groups VIII, IX, and X). The discussion is limited to mono-metallic systems and to ring systems consisting only of metal and carbon atoms.

Synthesis of Metallacyclobutane Derivatives

Oxidative Addition of C-C Bond Methodology

Oxidative addition of a C-C bond of cyclopropane to a metal center provides a facile synthesis of metallacyclic complexes of a variety of transition metals. As stated in the introduction, Tipper initiated this methodology when he allowed chloroplatinic acid and cyclopropane to react in acetic anhydride³⁷. The resulting tetramer can further react with several nitrogen donor ligands (L= Py, 2-,3- and 4-Mepy, 2,6-diMepy, bipy and en) to obtain the platina(IV)cyclobutane derivative 2. Although this method provides a facile



route to an unsubstituted platina(IV)cyclobutane, it has been ineffective in the synthesis of alkyl or aryl substituted platina(IV)cyclobutanes⁶⁰.

There exists a more general synthetic procedure involving the reaction of cyclopropane with Zeise's Dimer 3 as the platinum(II) source to form a tetrameric platina(IV)cyclobutane⁶¹⁻⁶³. Subsequent addition of ligands forms the platina(IV)cyclobutane monomer 4 in high yields (equation 1). Nitrogen donor ligands have been found most effective in obtaining the monomeric species 4. Oxygen donor ligands, such as THF or 1,4-dioxane, may form 4 in solution but are rarely isolated^{39,41,64}. Addition of soft ligands, such as PR_3 , DMSO, and CO, to the tetrameric complex results in reductive elimination of the cyclopropane^{39,61,62,65}.

