Structure and chemical reactivity of selected platinacyclobutanes
by Robert Alan Ekeland

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

Abstract:
This thesis describes the preparation, characterization and reactivity of a number of platinacyclobutane complexes.

The electronic factors influencing platinum insertion into 1,2-cis disubstituted cyclopropanes is examined. The remarkable inertness of some new complexes is explored.

The reactions of novel strained bicyclic platinacyclobutanes is evaluated for carbon monoxide and also diazomethane. Carbon monoxide appears to initiate Pt-C bond heterolysis. The use of the norbornyl hydrocarbon system facilitated the observation of rearrangement mechanims promoted by CO. The reaction of platinacyclobutanes with diazomethane is clean and results in the production of a CH2 addition product.

X-ray crystallographic studies on 4 different platinum containing compounds were performed. The Karplus type relationship in 3JPtC couplings was emperically fitted using 13C NMR spectral data and crystal dihdral angles for 3 bis-pyridine platinacycloalkanes.

The fourth structure was that of a novel platinum methylidene complex generated by the action of diazomethane on a platinacyclobutane.

STRUCTURE AND CHEMICAL REACTIVITY OF

SELECTED PLATINACYCLOBUTANES

by

Robert Alan Ekeland

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1985

APPROVAL

of a thesis submitted by

Robert Alan Ekeland

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.

1/2/85
Date

Dr. P. W. Jennings
Chairperson, Graduate Committee

Approved for the Major Department

1/2/85
Date

Edwin H Abbott
Head, Major Department

Approved for the College of Graduate Studies

3-25-85
Date

M. S. Malone
Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute copies of the dissertation in and from microfilm and the right to reproduce and distribute by abstract in any format."

Signature Robert Alan Steele

Date Feb 24, 1985

ACKNOWLEDGEMENTS

The author wishes to extend his gratitude to Dr. P.W. Jennings, for his continued encouragement and support. I am deeply indebted to Dr. Jennings for opening my eyes to some of the more intriguing aspects of chemistry. I would also like to thank Dr's. Jim Campbell and Ken Emerson for their energetic assistance in the area of x-ray diffractometry. I also wish to thank the other faculty members and graduate students who have made my stay here stimulating and generally enjoyable. I would like to thank my parents for their love, understanding and encouragement. Many thanks also to Georgia Ziemba for her assistance with the statistical and computational work. I wish to thank my wife, Kari Dawson Ekeland, for her endless energy and support which has proved invaluable to me during the completion of this manuscript.

TABLE OF CONTENTS

TABLE OF CONTENTS-Continued

LIST OF TABLES

LIST OF FIGURES

Key Abbreviations

X = halogen

R = alkyl group

Me = methyl

Et = ethyl

Ph = phenyl

bpy = 2,2′ bipyridine

py = pyridine

THF = tetrahydrofuran

NMR = nuclear magnetic resonance

IR = infra red

GC = gas chromatography

XPS = x-ray photoelectron spectroscopy (ESCA)

Hz = hertz

ppm = parts per million

IPC = initially precipitated complex

MS = mass spectroscopy

HPLC = high performance liquid chromatography

FAB = fast atom bombardment (mass spectroscopy)

M = transition metal

OM = organometallic

ref. = reference

ABSTRACT

This thesis describes the preparation, characterization and reactivity of a number of platinacyclobutane complexes.

The electronic factors influencing platinum insertion into 1,2-cis disubstituted cyclopropanes is examined. The remarkable inertness of some new complexes is explored.

The reactions of novel strained bicyclic platinacyclobutanes is evaluated for carbon monoxide and also diazomethane. Carbon monoxide appears to initiate Pt-C bond heterolysis. The use of the norbornyl hydrocarbon system facilitated the observation of rearrangement mechanims promoted by CO. The reaction of platinacyclobutanes with diazomethane is clean and results in the production of a CH_2 addition product.

X-ray crystallographic studies on 4 different platinum containing compounds were performed. The Karplus type relationship in $^3J_{PtC}$ couplings was emperically fitted using ^{13}C NMR spectral data and crystal dihdral angles for 3 bis-pyridine platinacycloalkanes. The fourth structure was that of a novel platinum methylidene complex generated by the action of diazomethane on a platinacyclobutane.

CHAPTER 1

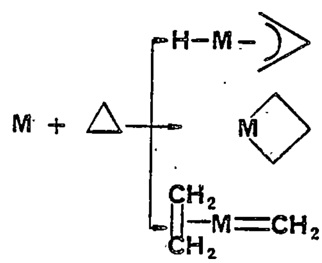
INTRODUCTION

Organometallics

Some of the benefits mankind has received from the study of chemistry are: The eradication of some diseases through the implementation of medicine and the fabrication and manipulation of chemicals to enhance man's comfort and productivity. Increasingly some of those benefits are coming from the study of the interactions between metals and organic moieties. Organometallic chemistry, focusing specifically on the chemistry of carbons bonded to metals has experienced much growth in the last 30 years. As is with any emerging science, there still is much to learn. More specifically, many organometallic reactions and transformations have been observed. However, less is known about such things as reaction mechanisms, regioselectivity, stereochemistry, and possible synthetic utility. Hence a scientist searching for a valid and justified research project, need not search long in organometallics to find that goal.

One such transformation which has received significant interest is the reaction of cyclopropane containing compounds with transition metals. These reactions have been shown to be either catalytic or stoichiometric. Vaska's catalyst, an iridium compound, has been shown to react catalytically in its reactions with cyclopropane.[1]

Platinum (II) complexes, conversely, react stoichiometrically.[2] Some general reactions of cyclopropane with transition metals are shown in Figure 1. These product complexes; 1, pi-allyl, 2, metallacyclobutane, and 3, metallocarbene olefin, illustrate the wide variety that have been observed. This thesis means to explore some of these pathways, examining what effects different substituted cyclopropanes have on the formation of intermediates and probing the possiblity of their synthetic utility. This introduction is intended to provide a brief overview of platinum and its reactions with cyclopropanes and other olefin-like substrates.



1

2

3

Figure 1. Possible Products of Metal Cyclopropane Interactions.

Platinum

Platinum, first used in organometallic chemistry by Zeise[3] to form the salt $PtCl_3(C_2H_4)$, owes much of its popularity to its ability to form many complexes which are stable under ambient conditions. Platinum exists in oxidation states, 0, +1, +2, +3, +4, and higher but its organometallic complexes are mainly limited to the 0, +2, +4 states. These stable $\underline{d}^{10}$, $\underline{d}^{8}$, and $\underline{d}^{6}$ configurations make the common 2 electron processes of oxidative-addition and reductive-elimination favorable. Table 1 lists some of the properties and representative complexes of Pt.

Table 1.

Properties and Usual Coordination Numbers
Of Common Oxidation States of Platinum

Pt	at. wt.	195.09
	at. no.	78.00

Stable Isotopes	% Natural Abundance
$_{78}Pt^{194}$	32.9
$_{78}PT^{195}$	33.8
$_{78}Pt^{196}$	25.3
$_{78}Pt^{198}$	7.2

^{195}Pt NMR spin 1/2

receptivity $/^{13}C$ = 19.1

gyromagnetic ratio = 5.7412

chemical shift range (ppm)*	oxidation state
0 - 15,000	Pt (IV)
0 - 5,000	Pt (II)
0 - 2,000	Pt (0)

*relative to K_2PtCN_6

Oxidation State (d^n)	Coordination Number	Geometry	Examples	Ref.
Pt(0) d^{10}	4	Tetr.	$Pt(PPh_3)_3CO$	31
Pt(II) d^8	4	Sq. pl.	$[PtCl_2(C_2H_4)]_2$	1
Pt(IV) d^6	6	O_h	$Pt\text{-}CH_2CH_2CHPhCl_2py_2$	7

Platinum-Olefin Complexes

As was stated earlier, platinum has the ability to form many stable complexes. Platinum forms stable olefin complexes in the 0 and +2 oxidation states which can be formed from reaction of a salt with an olefin as in equation 1.1.

$$K_2PtCl_4 + C_2H_4 \xrightarrow{H_2O} K[Pt(C_2H_4)Cl_3] + KCl \qquad (1.1)$$

Likewise, once a platinum-olefin complex is formed, another olefin can be substituted for it as shown in equation 1.2.

$$K\{Pt(C_2H_4)CL_3\} + PhCH{=}CH_2 \longrightarrow K[Pt(PhCH{=}CH_2)Cl_3] + C_2H_4 \quad (1.2)$$

Ethylene complexes provide a facile means of promoting substitutional reactivity in platinum-olefin complexes since it is easily removed from reaction mixtures eliminating reversibility.

Bonding in Platinum-Olefins

Dewar, Chatt, and Duncanson have provided a reasonable picture of the bonding interactions believed to occur between a transition metal and a coordinated olefin.[4] This bonding arrangement arises from two contributions. The σ component of the overall bond is formed through the interaction of an empty π acceptor orbital on the metal and a filled π-bonding orbital on the olefin. The π-backbonding component of the metal olefin bond arises from the interaction of filled d orbital on the metal and empty π^*-antibonding orbital of the olefin. These features are shown in

Figure 2. This model adequately describes most of the physical characteristics observed in metal olefins. Low or negatively valent metals are more receptive to pi backbonding.

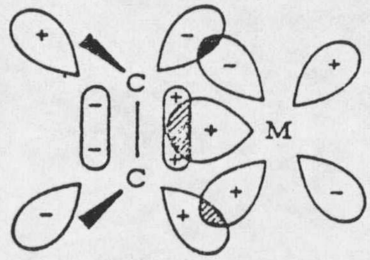


Figure 2. Metal-Olefin Orbital Interactions.

It is apparent that the two contributions must be compared. The first can be described as the metals' ability to accept electrons from the olefin p orbital, and the second the metals' ability to donate electrons from its d_{xy} orbital. The former may be approximated from the metals' electron affinity and the latter by its promotion energy. Table 2 presents the promotion energies and electron affinities for selected compounds. A high promotion energy indicates the metal will be a poor electron donor. A large electron affinity indicates the metal will be a good electron acceptor. Combination of these two factors allows one to anticipate the olefin bonding ability of a metal.

Table 2. Data for Selected Transition Metals[5]

Metal	d^n	Promotion Energy[a]	Electron Affinity
Ni 0	d^{10}	1.72	1.2
Pd 0	d^{10}	4.23	1.3
Pt 0	d^{10}	3.28	2.4
Pd II	d^8	3.05	18.56
Pt II	d^8	3.39	19.42
Zn II	d^{10}	17.10	17.96
Hg II	d^{10}	12.82	18.75

[a] $nd^{10} \rightarrow nd^9(n+1)p$; $nd^8 \rightarrow nd^7(n+1)p$.

Pd (II) and Pt (II) show the ideal characteristics for metal olefin bonding as high electron affinity and low promotion energy indicate excellent bonding capabilities. Also, the platinum olefin complex may range from only a slightly perturbed olefin to the other extreme which is indistinguishable from a metallacyclopropane. These two cases are shown in Figure 3.

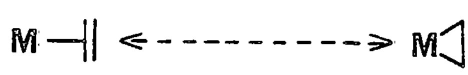
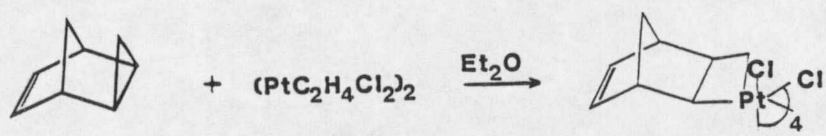


Figure 3. Metal-Olefin Bonding Extremes.

The similarities between olefins and cyclopropanes will be discussed later. However, the excellent ability of Pt (II) to bond to olefins may be reduced by the characteristics of the olefin itself. The compound 4 shown in equation 1.3 contains both a cyclopropane and an olefin. The product of the reaction would be expected to be simple olefin exchange.



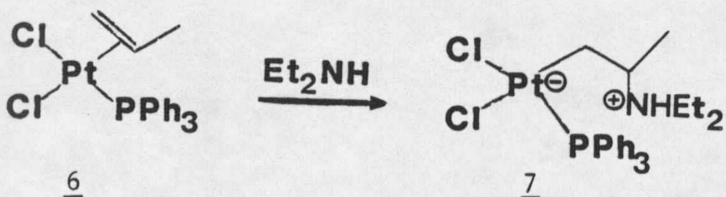
(1.3)

4 5

In fact, what is observed is an insertion of Pt into the cyclopropane. The reasons for this unexpected reaction are unknown. However, the olefin system, which has the greatest electron density on the exo side, may be sterically hindered by the bridge hydrogen, precluding bonding orientation of the platinum. Further, this norbornyl system presents severe steric difficulty for the endo side as well.

Chemistry of Metal Bound Olefins

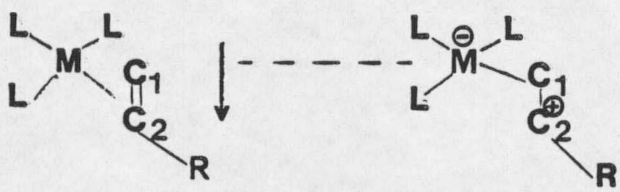
There are some important similarities between the reactions of Pt olefins and those of platinacyclobutanes. To enumerate those similarities a short discussion of the chemistry of metal olefins will be given. The bonding picture described previously suggests that the electron density of a coordinated olefin may be reduced which is corraborated by the fact that metal bound olefins undergo attack by nucleophiles. In most cases, the attack by the nucleophile is trans to the complex and occurs without prior coordination to the metal. As is illustrated in equation 1.4, the most substituted carbon is captured by the nucleophile(7).[6]



(1.4)

6 7

The mechanism for this type of reaction has been rationalized by Hoffmann and Eisenstein.[7] A slipping motion of the alkene out of the ML_3 plane prior to attack on the olefin by the nucleophile is shown in Figure 4a.



a b

Figure 4. Metal-Olefin Orientations Promoting Nucleophilic Attack.

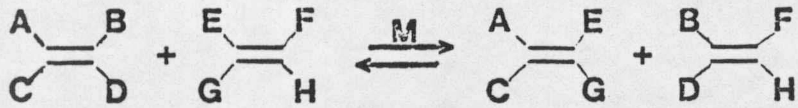
X-ray crystal data on substituted metal-alkenes show that the distance between the metal and C_1 is shorter than the $M-C_2$ distance. The extreme case of slipping in a metal bound olefin is depicted in Figure 4b. This is a zwitterion or metal stabilized carbonium ion. In the absence of overriding steric effects this illustration accounts for the observed products. Other nucleophiles such as OH^-, CH_3COO^-, CH_3O^-, Cl^-, amines, and amides react similarly with Pt olefins.

Another significant synthetic reaction of metal bound olefins is that of hydrogenation. The proposed mechanisms are important but simply beyond the scope of this discussion. Another important reaction of metal bound olefins is olefin dimerization. The cases studied by Schrock using Ta complexes provide the most interesting chemistry of this type.[8] Other insertion, polymerization, and addition types of reactions with metal-olefins have received some attention.

Olefin Metathesis

Olefin metathesis is another type of metal bound olefin chemistry which deserves special note. On page 2 in Figure 1., some of the products of metal cyclopropane interactions were enumerated. Olefin metathesis has been thought to involve the second and third intermediates. One of the significant driving forces in platinacyclobutane chemistry has been its possible role in the understanding of the olefin metathesis reaction. Although metathesis has only been observed in early transition series metals, its stable reaction products have been examined as possible models.

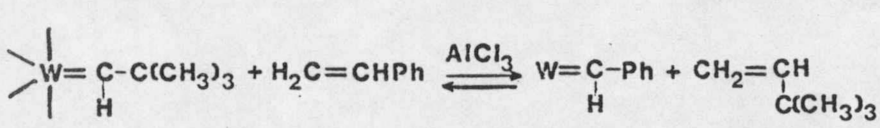
Olefin metathesis, simply described, equilibrates alkylidene units of olefins as illustrated in equation 1.5.



(1.5)

The metathesis mechanism is illustrated in Figure 5. It is basically that which was proposed by Herison and Chauvin in 1970.[9] The important intermediates in relation to platinacyclobutane chemistry are the metallocarbene-olefin, (8), and also the metallacyclobutane itself (9). Hence, if a recoverable metal-carbene complex could catalyze metathesis and a metallacyclobutane intermediate could be proven, the mechanism would be credible. Recently some of the pertinent features of this reaction have been elucidated and are summarized below.

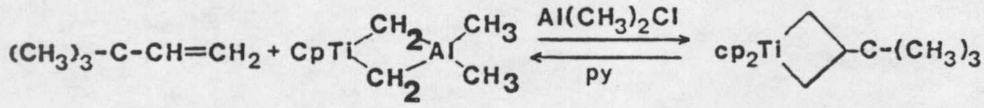
Schrock reported that both the initial (10) and metathesis exchanged metallocarbenes (11) had been isolated and characterized for the reaction shown in equation 1.6.[7] This data supports the first argument in favor of the mechanism.



(1.6)

10 11

Grubbs has prepared metallocyclobutanes from a metal carbene olefin reaction and characterized the products by X-ray.[10] Part of this reaction is illustrated in equation 1.7. Thus, the mechanism proposed in 1970 has been strengthened by the recent literature.

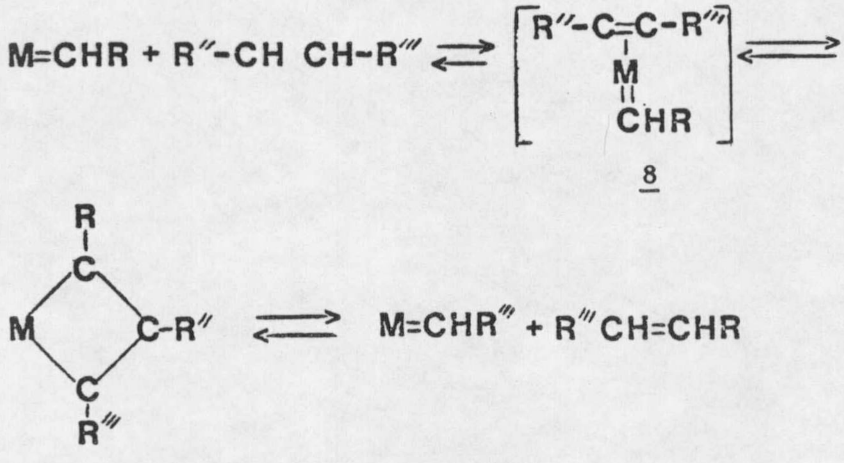


(1.7)

INITIATION

$$M + R\text{-}CH{=}CH\text{-}R' \rightleftharpoons M{=}CHR\ (M{=}CHR')$$

PROPAGATION



8

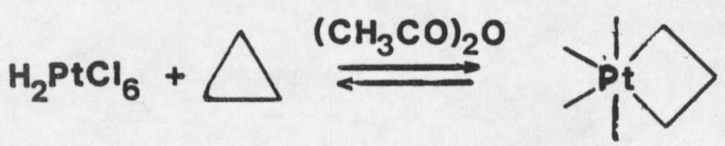
9

Figure 5. The Mechanism of Olefin Metathesis.

Bonding and Reactions of Platinum and Cyclopropanes

In 1949 Walsh published his theory on the electronic structure of cyclopropane, ethylene oxide and related molecules.[11] In it he suggested that the unusual properties of cyclopropane could be rationalized by looking at cyclopropane as being closely related to ethylene. Since then there have been a steady stream of reports by theorists and experimentalists basically supporting those initial tenets. This similarity prompted Tipper in 1955[12] to react cyclopropane with chloroplatinic acid (H_2PtCl_6). The resulting complex was postulated to be an edge bound analog of Zeise's dimer $[(PtC_2H_4Cl_2)_2]$. This was further supported by both IR spectroscopic evidence and the fact that cyclopropane was produced when the complex was reacted with aqueous KCN.

Chatt reinvestigated Tipper's early work and on the basis of IR and NMR spectroscopy, suggested that the structure was a platinacyclobutane (equation 1.8).[13]



(1.8)

This structure was expected to be a six coordinate chlorine bridged polymer analogous to the alkyl platinum (IV) halides. These initially precipitated complexes of platinacyclobutanes have been further investigated. A peak in the electron ionization MS, due to the tetrameric formula $[(PtCl_2C_3H_6)_4]$ at m/e 1232, was noted by Gillard and co-workers.[14] This formula led to the proposed structure in Figure 6.