



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
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Abstract:

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

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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.

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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 possibility 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.

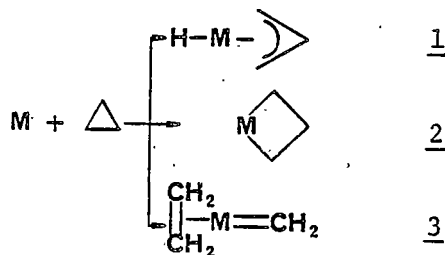


Figure 1. Possible Products of Metal Cyclopropane Interactions.

Platinum

Platinum, first used in organometallic chemistry by Zeise³ to form the salt $\text{PtCl}_3(\text{C}_2\text{H}_4)$, 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 d^{10} , d^8 , and 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

$^{78}\text{Pt}^{194}$ 32.9
 $^{78}\text{Pt}^{195}$ 33.8
 $^{78}\text{Pt}^{196}$ 25.3
 $^{78}\text{Pt}^{198}$ 7.2

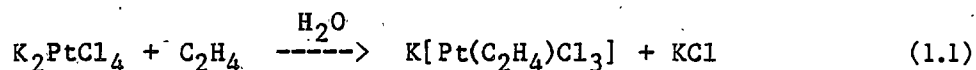
^{195}Pt NMR spin 1/2
 receptivity / ^{13}C = 19.1
 gyromagnetic ratio = 5.7412

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.	$\text{Pt}(\text{PPh}_3)_3\text{CO}$	31
Pt(II) d^8	4	Sq. pl.	$[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$	1
Pt(IV) d^6	6	O_h	$\text{Pt}-\text{CH}_2\text{CH}_2\text{CHPhCl}_2\text{py}_2$	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.



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

