



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  $^1\text{H}$  NMR and  $^{13}\text{C}$  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 VI 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

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in

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Bozeman, Montana

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APPROVAL

of a thesis submitted by

Lynette Louise Johnson

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## TABLE OF CONTENTS

	Page
APPROVAL.....	ii
STATEMENT OF PERMISSION TO USE.....	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	vi
ABSTRACT.....	x
INTRODUCTION.....	1
STATEMENT OF PROBLEM.....	2
RESULTS AND DISCUSSION.....	3
Introduction.....	3
Synthesis of Metallacyclobutane Derivatives.....	5
Oxidative Addition of C-C Bond Methodology.....	5
Oxidative Addition of C-H Bond Methodology.....	25
Nucleophilic Addition to Metal $\eta^3$ -Allyl Complexes Methodology.....	29
Other Methodologies.....	35
Characterization of Metallacyclobutane Derivatives.....	49
$^1\text{H}$ NMR Spectroscopy.....	49
$^{13}\text{C}$ NMR Spectroscopy.....	71
X-ray Crystallographic Analysis.....	90
Chemistry of Metallacyclobutane Derivatives.....	104
Reactions Yielding Alkane Products.....	104
Reactions Yielding Cyclopropane Products.....	108
Reactions Yielding Olefinic Products.....	113
Reactions Yielding Alkene-Metal Complexes.....	121
Reactions Yielding $\eta^3$ -Allyl-Metal Complexes.....	125
Reactions Yielding Ring Expanded Products.....	125
Reactions Yielding Ligand Exchange Products.....	130
Reactions Yielding Ylide Products.....	132
Intramolecular Rearrangement Yielding Isomeric Products.....	136

TABLE OF CONTENTS-Continued

	Page
Metallacyclobutane Derivatives as Intermediates.....	138
Ferra(II)cyclobutane Derivatives as Intermediates.....	138
Cobalta(II)- and -(III)cyclobutane Derivatives as Intermediates.....	142
Rhoda(III)cyclobutane Derivatives as Intermediates.....	144
Irida(III)cyclobutane Derivatives as Intermediates.....	150
Nickela(II)cyclobutane Derivatives as Intermediates.....	153
Pallada(II)cyclobutane Derivatives as Intermediates.....	156
Platina(II)- and -(IV)cyclobutane Derivatives as Intermediates.....	160
EXPERIMENTAL.....	169
Conducting the Literature Search.....	169
Indexing the References.....	171
REFERENCES.....	173

## LIST OF TABLES

Table	Page
1. Monosubstituted platina(IV)cyclobutanes via oxidative addition.....	8
2. 2,2-disubstituted platina(IV)cyclobutanes via oxidative addition.....	9
3. Trans-1,2-disubstituted platina(IV)cyclobutanes via oxidative addition.....	10
4. Cis-disubstituted platina(IV)cyclobutanes via oxidative addition.....	13
5. 1,2,3-trisubstituted platina(IV)cyclobutanes via oxidative addition.....	15
6. Pallada(II)- and platina(II)cyclobutanes via oxidative addition.....	19
7. Rhoda(III)-, irida(III)- and platina(II)cyclobutanes via nucleophilic addition to metal $\eta^3$ -allyl complexes.....	31
8. Cobalta(II)-, rhoda(III)-, pallada(II)- and platina(II)cyclobutanes via transannular ring closure reactions.....	34
9. Pallada(II)- and platina(II)cyclobutanes via reaction with acidic substrates.....	37
10. $^1\text{H}$ NMR chemical shift data (ppm) of ferra(II)-, ruthena(II)-, osmia(II)-, rhoda(III)-, irida(III)-, nickela(II)-, pallada(II)- and platina(II)cyclobutanes.....	50
11. $^1\text{H}$ NMR chemical shift data (ppm) of pallada(II)- and platina(II)cyclobutanes.....	53
12. $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant data (Hz) of platina(II)cyclobutanes.....	54
13. $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of unsubstituted platina(IV)cyclobutanes.....	55
14. $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of monosubstituted platina(IV)cyclobutanes.....	56

LIST OF TABLES-Continued

Table	Page
15. $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of 2,2-disubstituted platina(IV)cyclobutanes.....	59
16. $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of trans-1,2-disubstituted platina(IV)cyclobutanes.....	61
17. $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of cis-disubstituted platina(IV)cyclobutanes.....	62
18. $^1\text{H}$ NMR chemical shift (ppm) data of 1,2,3-trisubstituted platina(IV)cyclobutanes.....	64
19. Low Temperature $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of pallada(II)- and platina(II)cyclobutanones.....	65
20. $^1\text{H}$ NMR chemical shift data (ppm) of pallada(II)cyclobutanones.....	66
21. $^1\text{H}$ NMR chemical shift (ppm) and Pt-H coupling constant data (Hz) of platina(II)cyclobutanones.....	67
22. $^1\text{H}$ NMR chemical shift (ppm) data of other metallacyclobutanones.....	68
23. $^1\text{H}$ NMR chemical shift (ppm) data of rhoda(III)-, irida(III)-, nickela(II)- and platina(II)cyclobutabenzenes.....	70
24. $^{13}\text{C}$ NMR chemical shift (ppm) data of ruthena(II)-, osmia(II)-, rhoda(III)-, irida(III)-, and platina(II)cyclobutanes.....	72
25. $^{13}\text{C}$ NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data of unsubstituted platina(IV)cyclobutanes.....	74
26. $^{13}\text{C}$ NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data of monosubstituted platina(IV)cyclobutanes.....	75
27. $^{13}\text{C}$ NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data for trans-1,2-disubstituted, trans-1,3-disubstituted and 2,2-disubstituted platina(IV)cyclobutanes.....	77

LIST OF TABLES-Continued

Table	Page
28. $^{13}\text{C}$ NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data for cis-disubstituted platina(IV)cyclobutanes.....	78
29. $^{13}\text{C}$ NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data for 1,2,3-trisubstituted platina(IV)cyclobutanes.....	82
30. $^{13}\text{C}$ NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data for pallada(II)- and platina(II)cyclobutanones.....	85
31. $^{13}\text{C}$ NMR chemical shift (ppm) data of other metallacyclobutanones.....	86
32. $^{13}\text{C}$ NMR chemical shift (ppm) data for nickela(II)cyclobutabenzenes.....	87
33. $^{13}\text{C}$ NMR chemical shift (ppm) data of other metallacyclobutabenzenes.....	88
34. Bond length (Å) data for ferra(II)-, ruthena(II)-, cobalta(II)-, rhoda(III)-, irida(III)- and nickela(II)cyclobutanes.....	92
35. Bond angle (°) data for ferra(II)-, ruthena(II)-, cobalta(II)-, rhoda(III)-, irida(III)- and nickela(II)cyclobutanes.....	94
36. Bond length (Å) data for platina(II)- and platina(IV)cyclobutanes.....	95
37. Bond angle (°) data for platina(II)- and platina(IV)cyclobutanes.....	97
38. Bond length (Å) data for ruthena(II)-, irida(III)-, pallada(II)-, and platina(II)cyclobutanones.....	98
39. Bond angle (°) data for ruthena(II)-, irida(III)-, pallada(II)- and platina(II)cyclobutanones.....	99
40. Bond length (Å) data for irida(III)- and platina(II)cyclobutenes.....	100
41. Bond angle (°) data for irida(III)- and platina(II)cyclobutenes.....	101
42. Bond length (Å) data for rhoda(III)-, nickela(II)- and platina(II)cyclobutabenzenes.....	102

LIST OF TABLES-Continued

Table	Page
43. Bond angle ( $^{\circ}$ ) data for rhoda(III)-, nickela(II)- and platina(II)cyclobutabenzenes.....	103
44. Hydrogenolysis products of mono- and disubstituted platina(IV)cyclobutane tetramers.....	106
45. Platinum(IV) ylide complexes.....	133

## 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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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 VIII metals. The metal often serves as a catalyst in these reactions.

## 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.

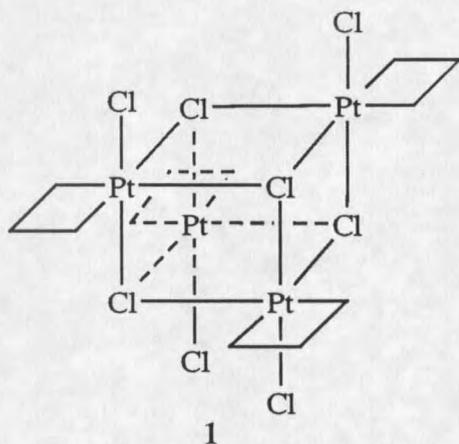
## RESULTS AND DISCUSSION

### 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 metathesis<sup>1-11</sup>, cycloadditions of alkenes<sup>12-15</sup> and cyclotrimerizations of acetylenes<sup>16-18</sup>, dimerization of alkenes<sup>19-21</sup>, oligomerization of alkynes<sup>22,23</sup>, oligomerization of dienes<sup>24-27</sup>, polymerization of olefins and acetylenes<sup>28-31</sup>, and isomerizations of strained carbocyclic ring systems<sup>32-35</sup>. In addition to being key intermediates in catalytic reactions, metallacycles also have been used successfully in organic synthesis<sup>36</sup>.

The first metallacyclic compound was discovered in 1955 by Tipper<sup>37</sup>. While studying the similarities in electron delocalization between cyclopropanes and olefins suggested by Walsh in 1949<sup>38</sup>, Tipper examined the ability of cyclopropane to form complexes with transition metals analogous to known olefin-metal complexes. He treated cyclopropane with hexachloroplatinic acid,  $(\text{H}_2\text{PtCl}_6)$ , 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 compound<sup>39</sup>. 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 1966<sup>40</sup> and the structure of compound **1** was suggested to be tetrameric in 1969.<sup>41</sup>

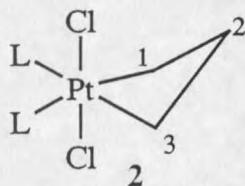


A number of transition metals since have been found to form stable metallacyclic compounds from a variety of methodologies. Other comprehensive and semi-comprehensive reviews that include discussions on metallacyclic compounds have appeared emphasizing topics such as the preparations and properties of metallacyclic compounds<sup>42-44</sup>, metallabenzenes<sup>45</sup>, pallada(II)- and platina(II)cyclobutanes<sup>46</sup>, platina(II)- and -(IV)cyclobutanes<sup>47</sup>, cyclometallation reactions<sup>48,49</sup>, the chemistry of alkanes<sup>50</sup>, acetylenes<sup>51</sup> and cycloproparenes<sup>52</sup>, and metallacycles as intermediates in olefin metathesis<sup>1-8</sup> and other metal-catalyzed reactions<sup>34,53-59</sup>. 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

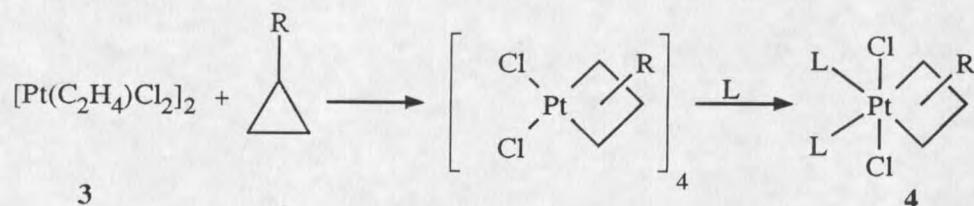
Oxidative addition of a C-C bond of cyclopropane to a metal center provides a facile synthesis of metallacyclic complexes of a variety of transition metals. As stated in the introduction, Tipper initiated this methodology when he allowed chloroplatinic acid and cyclopropane to react in acetic anhydride<sup>37</sup>. 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)cyclobutanes<sup>60</sup>.

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)cyclobutane<sup>61-63</sup>. 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<sup>39,41,64</sup>. Addition of soft ligands, such as  $\text{PR}_3$ , DMSO, and CO, to the tetrameric complex results in reductive elimination of the cyclopropane<sup>39,61,62,65</sup>.

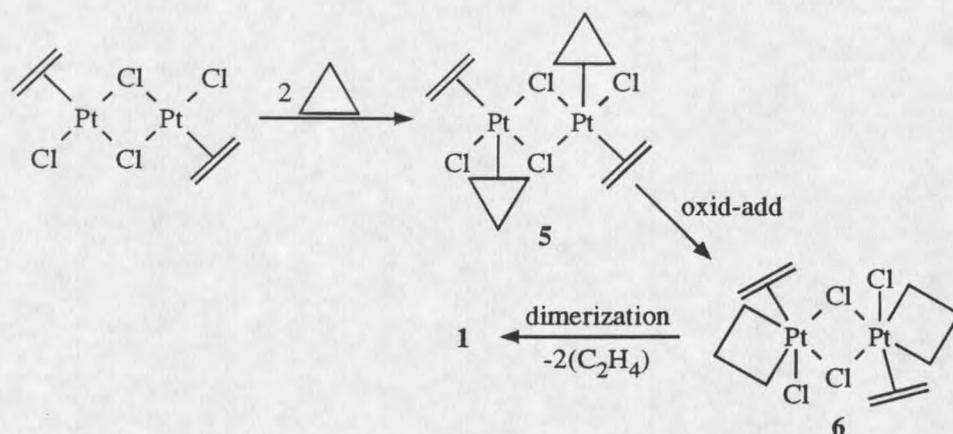
(1)



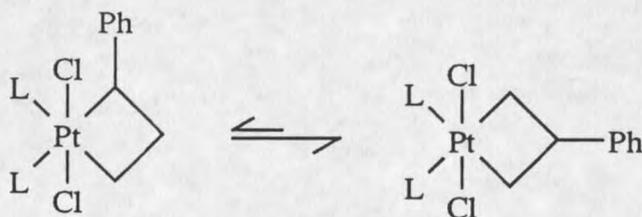
The proposed pathway for platina(IV)cyclobutane formation, shown in Scheme I, invokes initial coordination of a nucleophilic cyclopropane to an electrophilic Pt(II) center to form a Pt-cyclopropane "edge-complex" intermediate 5. Subsequent ring opening of the cyclopropane occurs to form 6, which upon loss of ethylene and dimerization forms the observed platina(IV)cyclobutane tetramer 1. An alternative mechanism, resulting from the suggestion that platinum(IV) is unable to coordinate to olefins, proposed that ethylene is lost from intermediate 5 to form an intermediate analogous to 6 with ethylene removed and solvent inhabiting the open coordination sites<sup>64</sup>. However, a platina(IV)cyclobutane recently has been synthesized that also accommodates a Pt(IV)-olefin bond (see equation 7)<sup>66</sup>. Further, a recent report on a Zeise's Dimer catalyzed reaction that invokes a platina(IV)cyclobutane intermediate suggests that ethylene remains intact upon ring opening<sup>67</sup> (see Scheme XLVII). Both of these observations lend credence to the mechanism proposed in Scheme I.

Tables 1, 2, and 3 include examples of platina(IV)cyclobutanes prepared by this method which is both more convenient than Tipper's synthesis and effective for alkyl and aryl substituted cyclopropanes. Table 1 illustrates monosubstituted platina(IV)-cyclobutanes. In many of the aryl substituted examples both a 1- and 2-substituted isomer are present. These two species result from the known isomerization of platina(IV)-cyclobutanes shown in equation 2 for the phenyl substituted example<sup>68</sup>.

Scheme I.



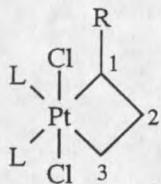
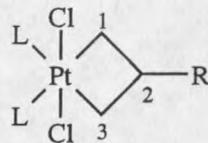
(2)



The most recent studies suggest that Pt(II) inserts into the cyclopropane at the more highly substituted C-C bond forming a 1-substituted platina(IV)cyclobutane. Subsequent isomerization then leads to the predominant 2-substituted isomer. Although the presence of both isomers in the aryl substituted examples readily support this theory, in most of the alkyl substituted examples only the 2-substituted isomer is observed<sup>69</sup>. However, Pt(II) insertion into the more highly substituted bond in these examples followed by rapid isomerization to the observed species cannot be excluded.

When 1,1-disubstituted cyclopropanes are treated with Zeise's Dimer, the 2,2-disubstituted platina(IV)cyclobutanes shown in Table 2 result. (Another example of a 2,2-disubstituted platina(IV)cyclobutane, formed by an alternate methodology, is shown in Scheme XI<sup>70</sup>). Although in no instance is the 1,1-disubstituted platina(IV)cyclobutane isomer observed in these reactions, it again is not possible to exclude initial insertion of

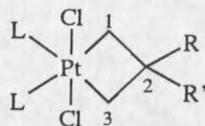
Table 1. Monosubstituted platina(IV)cyclobutanes via oxidative addition.

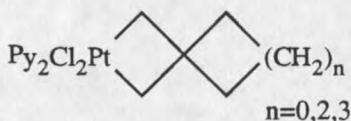
L	R	ref.	L	R	ref.
py	H	63	4-Mepy	2-Me <sup>a</sup>	47,74
py	2-Me <sup>a</sup>	47,71,74	4-Mepy	1-Ph	75
py	2-Et	69	4-Mepy	2-Ph	75
py	2-i-Pr	69	2-Mepy	2-Ph	75
py	2-Bu	47,71,74	3-Mepy	2-Me <sup>a</sup>	47,74
py	2-CH <sub>2</sub> CO <sub>2</sub> Me	76	½(bipy)	1-Ph	75
py	2-CH <sub>2</sub> OH	77	½(bipy)	2-Ph	75
py	2-CHMeOH	77	½(bipy)	2-CH <sub>2</sub> OMs	78,79
py	2-CMe <sub>2</sub> OH	77	½(tmed)	1-Ph	68,75
py	2-CH <sub>2</sub> OMs	78,79	½(tmed)	2-Ph	75
py	2-CH <sub>2</sub> OPNB	79	½(tmed)	1-Me	80
py	2-CMe <sub>2</sub> OPNB	79	½(tmed)	2-Me	80
py	1-Ph	68,75	½(tmed)	2-Et	80
py	2-Ph	61-63	½(phen)	2-Me	47,74
py	2-PhCH <sub>2</sub>	61-63	THF	2-Me <sup>a</sup>	71
py	1-p-MeC <sub>6</sub> H <sub>4</sub>	62,63,75	THF	1-Ph	64,75
py	2-p-MeC <sub>6</sub> H <sub>4</sub>	75	THF	2-Ph	75
py	2-o-MeC <sub>6</sub> H <sub>4</sub> <sup>a</sup>	75	THF	1-p-MeC <sub>6</sub> H <sub>4</sub>	75
py	2-n-C <sub>6</sub> H <sub>13</sub>	61-63	THF	2-p-MeC <sub>6</sub> H <sub>4</sub>	75
py	2-o-NO <sub>2</sub> Ph	62,63			
py	2-(4-MeOC <sub>6</sub> H <sub>4</sub> ) <sup>a</sup>	75			
py	2-(4-EtOC <sub>6</sub> H <sub>4</sub> ) <sup>a</sup>	75			
py	2-NH <sub>2</sub>	81			
complex					
					84
82,83					

<sup>a</sup> Found as a mixture with the substituent at the 1 position, the isomer shown being predominant in a ratio greater than 8 to 1.

Table 2. 2,2-disubstituted platina(IV)cyclobutanes via oxidative addition.

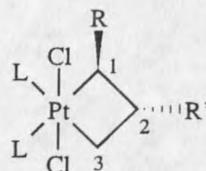


L	R	R'	ref.
py	Me	Me	69
py	Me	CH <sub>2</sub> OH	77
py	Me	CH <sub>2</sub> OMs	78,79
py	Ph	CH <sub>2</sub> OMs	79
½(bipy)	Me	Me	47
½(bipy)	Ph	CH <sub>2</sub> OMs	79
½(phen)	Me	Me	47
½(tmed)	Me	Me	80
<u>complex</u>			85



Pt(II) into the more highly substituted bond, followed by rapid isomerization, as the synthetic pathway.

When Zeise's Dimer is added to *trans*-1,2-diarylcyclopropanes, two platina(IV)-cyclobutane isomers result (Table 3). The *trans*-1,3-diaryl isomer is initially observed followed by isomerization to the predominant *trans*-1,2-diarylplatina(IV)-cyclobutane, strongly supporting Pt(II) insertion into the more highly substituted bond<sup>71-73</sup>. The *trans*-1,2-dialkylcyclopropanes are observed to form only the *trans*-1,2-dialkyl-1,3-propanediyl

Table 3. Trans-1,2-disubstituted platina(IV)cyclobutanes via oxidative addition.

L	R	R'	ref.
py	Me	Me	69,71,73
py	Ph	Ph <sup>a</sup>	61-63,73
py	Me	Ph	71,73
py	Ph	Me	71,73
py	Me	n-Butyl	62,63
4-(t-Butylpy)	Ph	Ph <sup>a</sup>	71,73
4-(t-Butylpy)	p-MeC <sub>6</sub> H <sub>4</sub>	p-C <sub>6</sub> H <sub>4</sub> <sup>a</sup>	73,75
½(phen)	Me	Me	73
CD <sub>3</sub> CN <sup>b</sup>	Me	Me	73
PhCN <sup>b</sup>	Me	Me	73
2-Mepy <sup>b</sup>	Me	Me	73

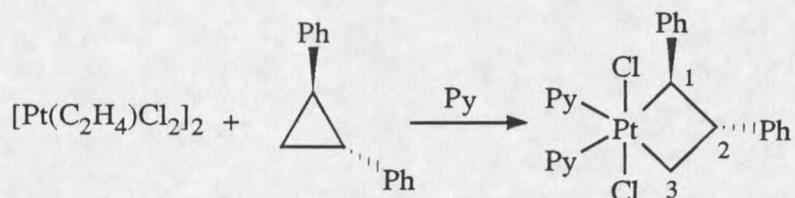
<sup>a</sup> Found as a mixture with the 1,3-disubstituted isomer, the 1,2-disubstituted isomer being predominant. <sup>b</sup> Isolated at -78°C.

platinum(IV) product.

Insertion of Pt(II) into cyclopropane derivatives has been shown to proceed stereospecifically with retention of configuration of the cyclopropane ring substituents <sup>61,62,86</sup>. For example, trans-1,2-diphenylcyclopropane oxidatively adds to the Pt(II) center of Zeise's Dimer to form a 1,2-diphenylplatina(IV)cyclobutane, along with the 1,3-diphenyl isomer, each with trans stereochemistry (equation 3).

Despite the versatility of this methodology limitations exist. All of the examples of 1,2-disubstituted platina(IV)cyclobutanes shown in Table 3 were derived from substrates with trans stereochemistry. However, cis-disubstituted cyclopropanes

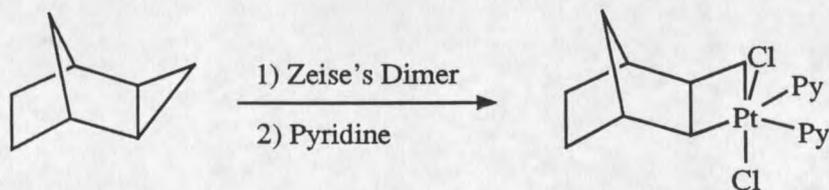
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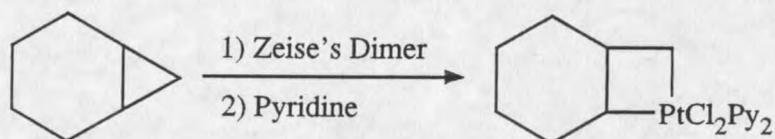
treated with Zeise's dimer behaved quite differently. Upon reaction of *cis*-1-*n*-butyl-2-methylcyclopropane with Zeise's Dimer no platinum(IV)cyclobutane derivative was observed<sup>62</sup>. The resulting products were instead a mixture of olefins. Similar results were obtained from other *cis*-disubstituted cyclopropanes and initially led investigators to conclude that either *cis*-disubstituted cyclopropanes failed to react with Zeise's Dimer or an unstable platinum(IV)cyclobutane was formed enroute to the observed olefinic products<sup>47,69,73</sup>. The latter explanation most accurately describes the observed results.

However, a variety of *cis*-disubstituted platinum(IV)cyclobutanes recently have been synthesized, in high yield, from Zeise's Dimer and *cis*-disubstituted cyclopropanes. Two examples are shown in equations 4<sup>87</sup> and 5<sup>88,89</sup>. The final products of these two reactions depict platinum(II) introduced into the less substituted bond of the cyclopropane ring. Similar products are illustrated in Table 4. Two *cis*-1,3-disubstituted examples also exist in which platinum(II) is incorporated into the more highly substituted bond of the three-membered ring (equations 6<sup>90</sup> and 7<sup>66</sup>).

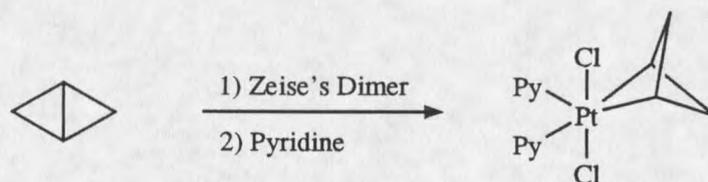
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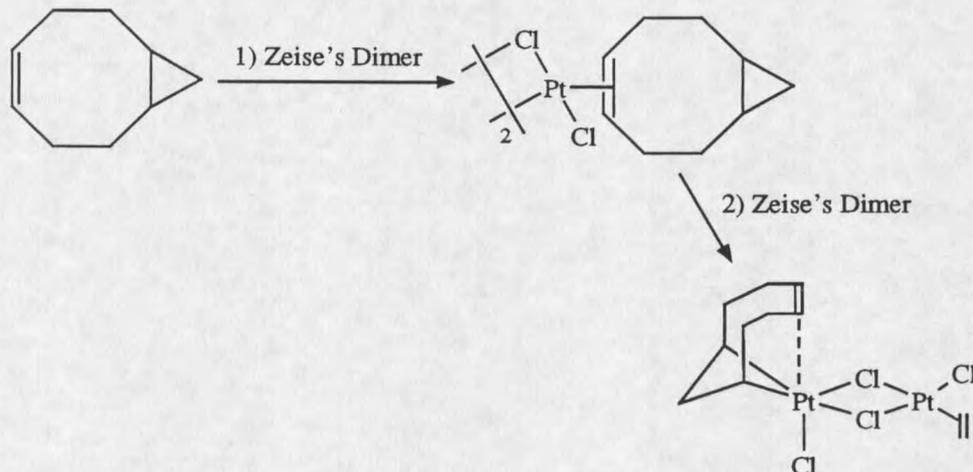
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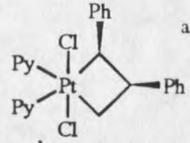
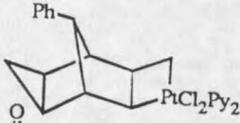
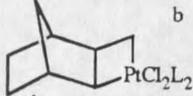
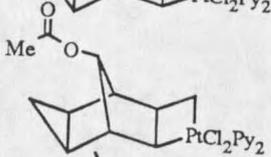
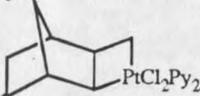
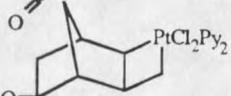
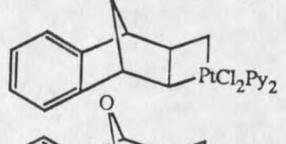
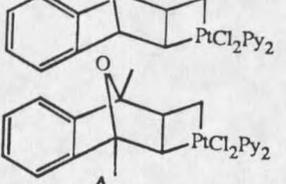
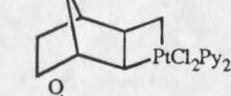
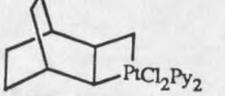
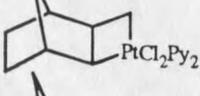
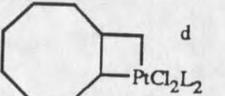
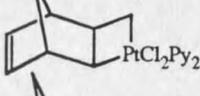
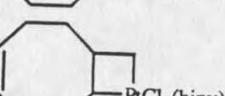
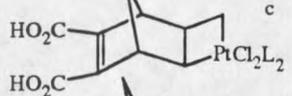
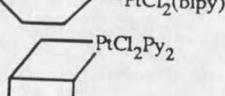
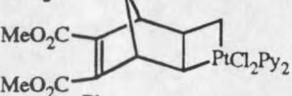
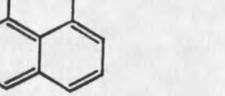
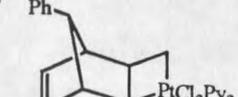
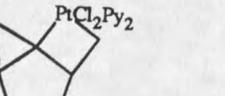
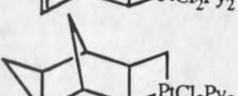
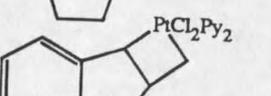


(7)



1,1,2,2-tetramethylcyclopropane forms a relatively minute amount of platina(IV)cyclobutane upon reaction with Zeise's Dimer suggesting that steric effects also inhibit the oxidative addition of cyclopropane to Pt(II). When 1,1,2-trimethylcyclopropane is treated with Zeise's Dimer a tetrameric platina(IV)cyclobutane is formed. However upon addition of pyridine, isomerization to a platinum-olefin species occurs and no monomeric platina(IV)cyclobutane is observed. The bispyridine adduct of 1,1,2-trimethylplatina(IV)cyclobutane can be prepared, however,

Table 4. Cis-disubstituted platina(IV)cyclobutanes via oxidative addition.

complex	ref.	complex	ref.
	61,72,73		91
	81,92		81
	93		76
	93		76
	81		81
	81		92
	81		88
	87		88
	76		76,94
	76		76,94
	91		95
	87		94

<sup>a</sup> Found as a mixture with the 1,3-disubstituted isomer, the 1,2-disubstituted isomer being predominant. <sup>b</sup> L=4-Mepy, 2,5-diMepy, 3,6-diMepy, Aniline, p-Cl-Aniline, DMAP, 2-Mepyrzine, en, bipy <sup>c</sup> L=Py, en, (4-pyridyl)carbinol <sup>d</sup> L=Py, bipy

if pyridine is added to the corresponding tetramer at low temperatures ( $-40^{\circ}\text{C}$ )<sup>69</sup>.

Recently, a variety of 1,2,3-trisubstituted platina(IV)cyclobutanes have been synthesized from 1,2,3-trisubstituted cyclopropanes and Zeise's Dimer under mild conditions. Examples of these systems are exhibited in Table 5.

The oxidative addition of cyclopropane to the platinum center of Zeise's Dimer is further limited since the ease of platina(IV)cyclobutane formation rapidly decreases as the cyclopropane's substituents become more electron withdrawing<sup>62</sup>. In fact, when the cyclopropane is substituted with  $\text{CO}_2\text{Me}$ ,  $\text{COMe}$  or  $\text{CN}$  groups no direct platina(IV)-cyclobutane formation is observed. One example does exist, however, where  $\text{Pt}(\text{II})$  is inserted into a cyclopropane bearing an electron withdrawing  $\text{CO}_2\text{Et}$  substituent (equation 8)<sup>76</sup>. Presumably, the double bond of the norbornyl moiety contributes enough additional electron density to the electron poor cyclopropane to allow insertion of the electrophilic  $\text{Pt}(\text{II})$ . In addition, an indirect methodology for preparing a platina(IV)cyclobutane bearing electron withdrawing groups recently has been achieved (equation 9)<sup>98</sup>.

(8)

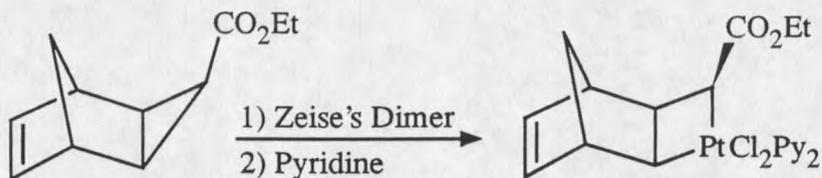
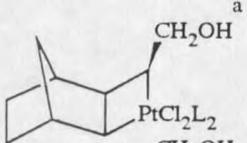
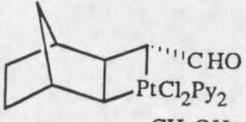
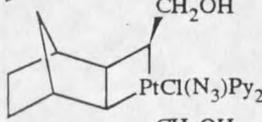
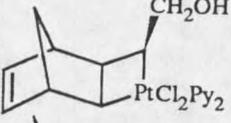
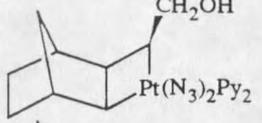
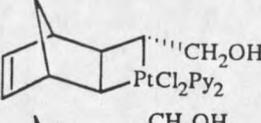
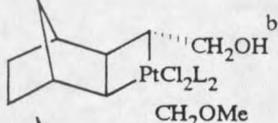
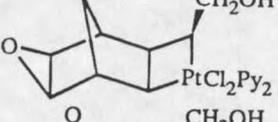
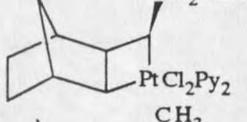
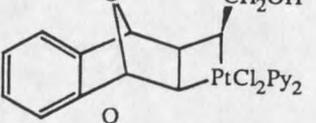
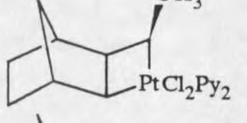
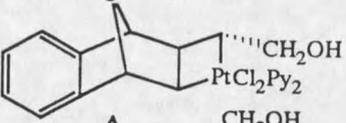
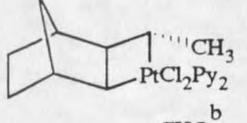
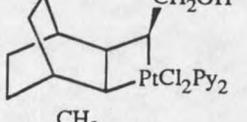
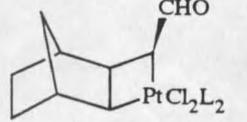
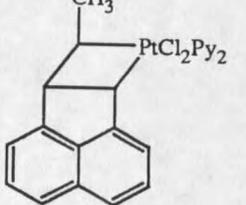
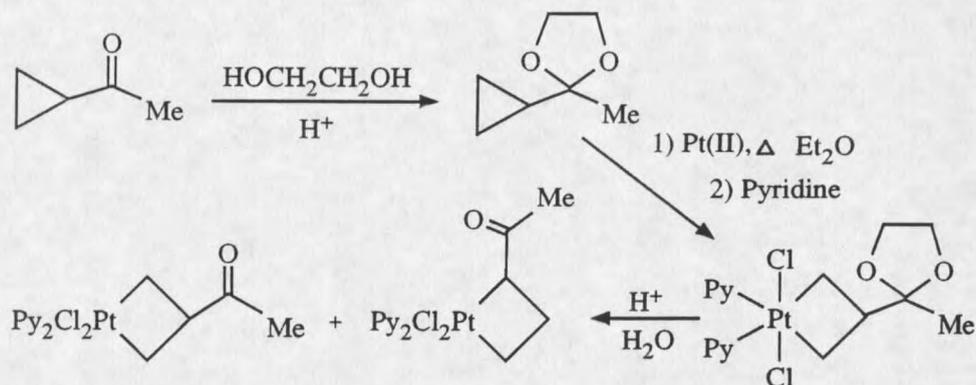


Table 5. 1,2,3-trisubstituted platina(IV)cyclobutanes via oxidative addition.

complex	ref.	complex	ref.
	81,96,97		92
	81		76
	81		76
	96,97		76
	81		76
	92		76
	92		81
	92,97		94

<sup>a</sup> L=Py, DMAP, bipy, en <sup>b</sup> L=Py, bipy, en

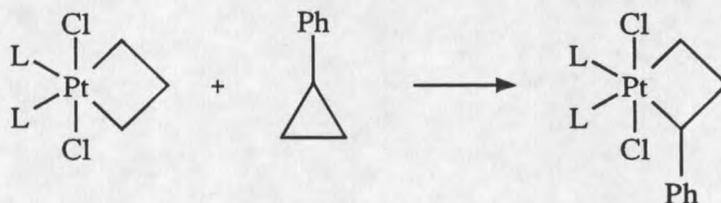
(9)



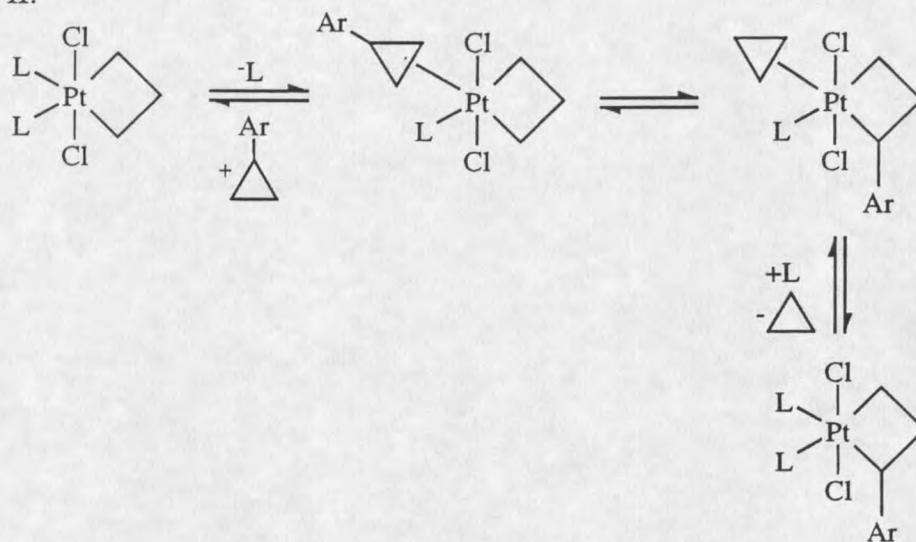
The formation of the stable platina(IV)cyclobutanes shown in equations 8 and 9, suggests that the inability of cyclopropanes with electron withdrawing substituents to oxidatively add to Pt(II) must result from a lack of electron density on the cyclopropane. This provides further evidence that Pt(II) is acting as an electrophile while cyclopropane behaves as a nucleophile in this methodology.

Another example of a platina(IV)cyclobutane synthesized by oxidative addition of a C-C bond is shown in equation 10<sup>99</sup>. Scheme II illustrates the mechanistic pathway for this displacement process<sup>64</sup>. Initial formation of an edge-bound cyclopropane-Pt complex is proposed as was inferred previously for platina(IV)cyclobutane formation (see Scheme I).

(10)



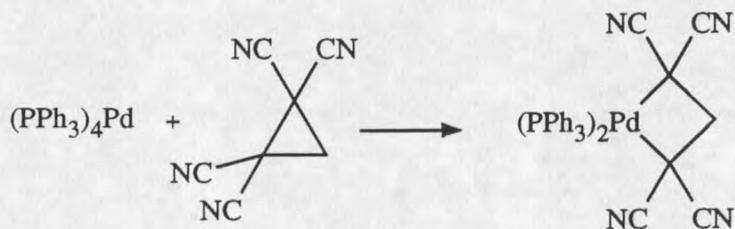
Scheme II.



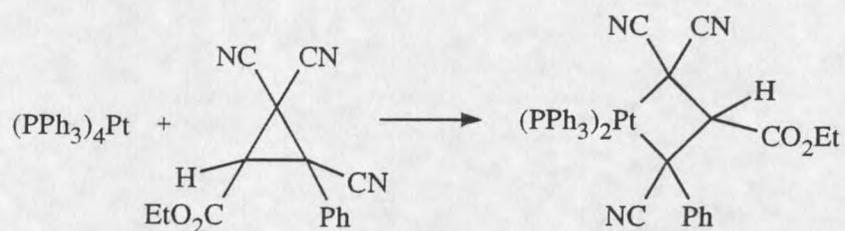
As demonstrated above, Pt(II) insertion into a C-C bond of cyclopropanes to form platina(IV)cyclobutanes is quite common. However, Pt(0) and other group eight transition metals also can be inserted into cyclopropanes to form their respective metallacyclobutanes.

For example, Pd(0) and Pt(0) are inserted effectively into cyclopropanes bearing strong electron-withdrawing groups (equations 11, 12, and 13)<sup>46,100-102</sup>.

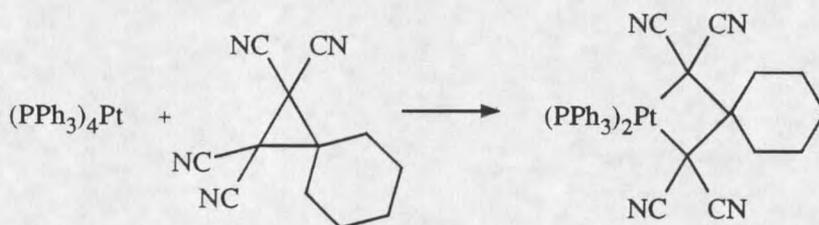
(11)



(12)

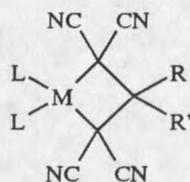


(13)



It has been proposed that the electron withdrawing groups create electrophilic character in the cyclopropane ring. The metal species then acts as a nucleophile and is inserted into the site of lowest electron density. This explanation is further supported by the observation that  $\text{Pt}(\text{PPh}_3)_4$  does not form a platina(II)cyclobutane upon reaction with the less electrophilic 1,2-dicyanocyclopropane<sup>102</sup>. That  $\text{Pt}(0)$  behaves as a nucleophile contrasts the proposed mechanism of insertion of  $\text{Pt}(\text{II})$  into cyclopropane, discussed earlier, where the metal exhibited electrophilic character and the cyclopropane was the nucleophile. Other pallada(II)- and platina(II)cyclobutanes formed by this methodology, in 20%-80% yield, are listed in Table 6.

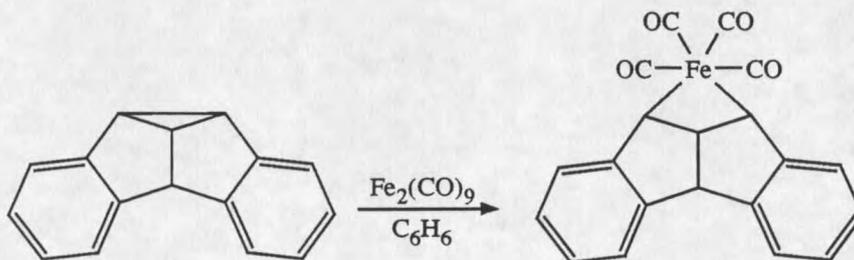
Table 6. Pallada(II)- and platina(II)cyclobutanes via oxidative addition.



M	L	R	R'	ref.
Pd	PPh <sub>3</sub>	Me	Me	102
Pd	PPh <sub>2</sub> Me	Me	Me	102
Pt	PPh <sub>3</sub>	H	H	100,102,103
Pt	PPh <sub>3</sub>	Me	Me	102
Pt	PPh <sub>3</sub>	H	Ph	101
Pt	PEt <sub>3</sub>	H	H	102
Pt	PPh <sub>2</sub> Me	H	H	102
Pt	PPh <sub>2</sub> Me	Me	Me	102
Pt	AsPh <sub>3</sub>	H	H	102
Pt	AsPh <sub>3</sub>	Me	Me	102

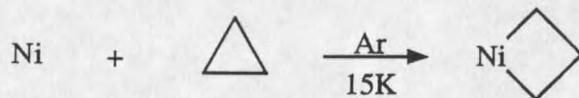
Dibenzosemibullvalene reacts with diiron nonacarbonyl, according to equation 14, to form ferretane in 25% yield<sup>104</sup>. The rhodium analogue also has been prepared, in 85% yield, from Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> and dibenzosemibullvalene and appears to be dimeric in nature<sup>105</sup>. The stability of these complexes may be attributed to the lack of β-elimination or C-C σ-bond rearrangement pathways.

(14)



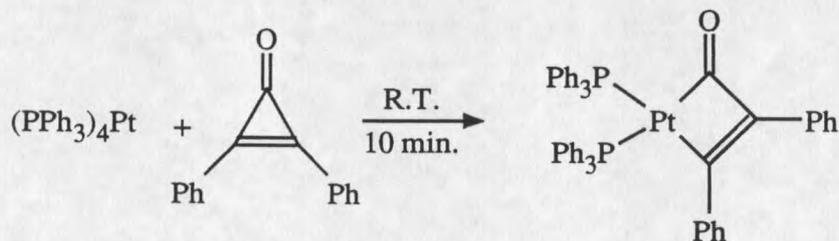
Atomic nickel, when cocondensed in an argon matrix, can be inserted into cyclopropane to form an unligated nickela(II)cyclobutane (equation 15)<sup>106</sup>.

(15)

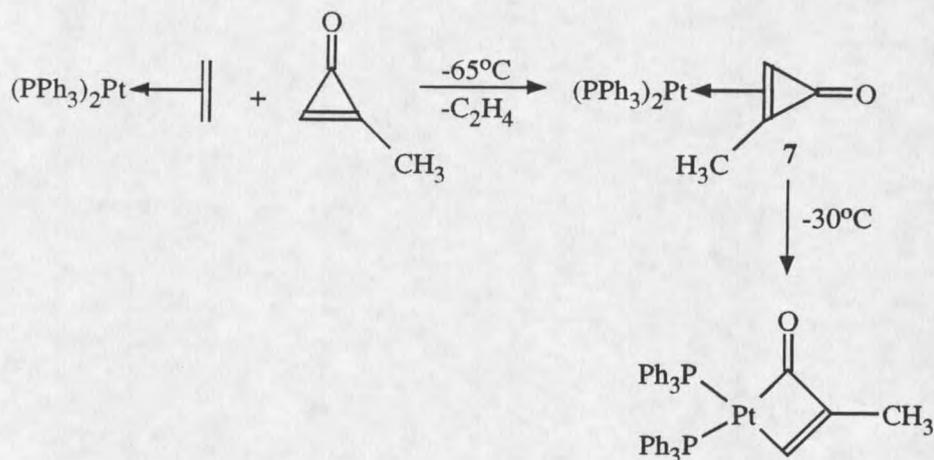


A second type of metallacyclobutane derivative, metallacyclobutenones can be synthesized by metal insertion into cyclopropenones. Platina(II)cyclobutenones were the first complexes of this type to be prepared utilizing Pt(0) which readily can be inserted into the C-C single bond of the organic substrate (equations 16 and 17). Equation 16 reports a direct synthesis of a diphenyl substituted platina(II)cyclobutenone formed in 60% yield<sup>107</sup>. In the reaction shown in equation 17 an isolated intermediate 7 is initially formed, which upon further reaction at -30°C yields the platina(II)cyclobutenone<sup>108</sup>. The possibility of trapping the platinum-olefin complex 7 seemingly depends on the ring substituents. So although dimethyl- and diphenylcyclopropenone formed platina(II)cyclobutenones under the reaction conditions of equation 17, no olefin complex was detected.

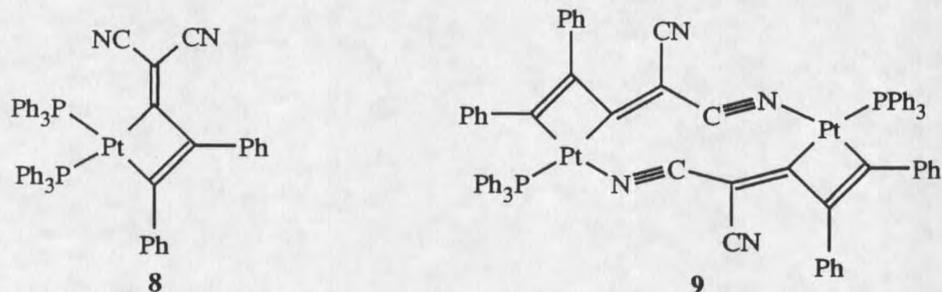
(16)



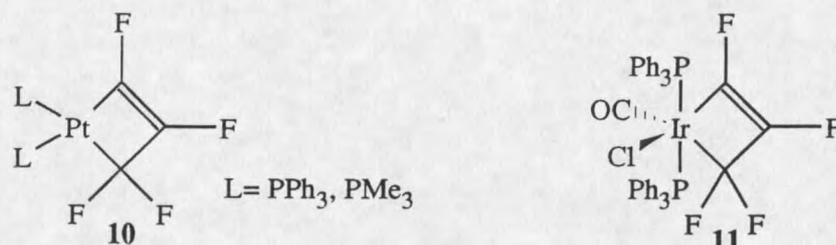
(17)



A metallacyclobutene of Pt(II) was prepared by treating 1,2-diphenyl-3-dicyanomethylenecyclopropane with bis(triphenylphosphine)(ethylene)platinum. Pt(0) cleaves the strained  $\sigma$ -bond of the cyclopropane to form the platina(II)cyclobutene monomer and dimer shown as 8 and 9<sup>109</sup>.

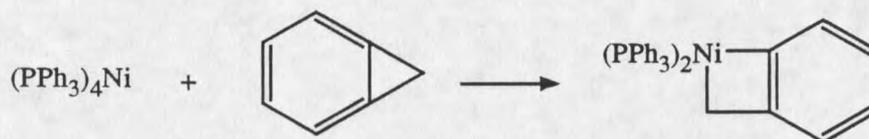


Tetrafluorinated cyclopropenes also can oxidatively add to the metal center of Pt(0) and Ir(I) complexes to form tetrafluorinatedplatina(II)- and irida(III)cyclobutenes, respectively. Two examples are shown as 10<sup>110</sup> and 11<sup>111</sup>.



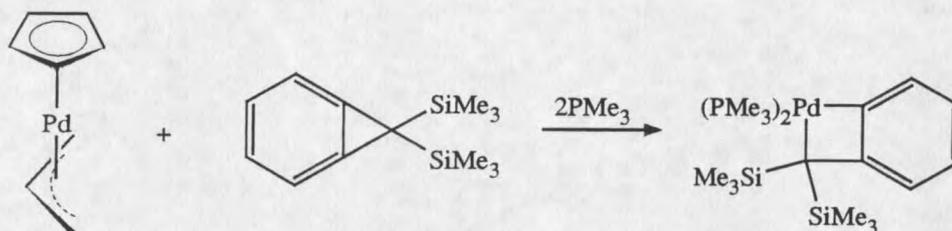
Metallacyclobutabenzene derivatives are a fourth class of metallacyclobutanes that can be prepared by the oxidative addition of a C-C bond methodology. Nickela(II)cyclobutabenzene was the first of this class of compounds to be synthesized in this manner by treating cyclopropabenzene with (PPh<sub>3</sub>)<sub>4</sub>Ni (equation 18)<sup>112</sup>. Other nickel(0) sources that can be utilized effectively in this reaction include (Et<sub>3</sub>P)<sub>2</sub>Ni(COD), (n-Bu<sub>3</sub>P)<sub>2</sub>Ni(COD) or Ni(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> in TMED.

(18)

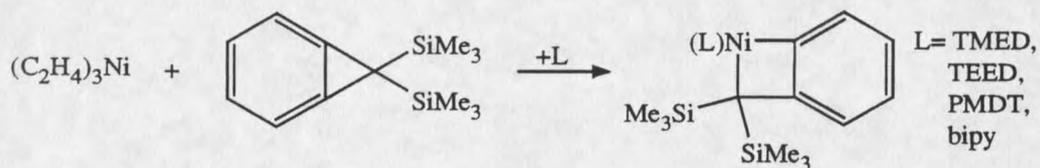


The synthesis described above also led to the preparation of bis(trimethylsilyl) substituted pallada(II)- and nickela(II)cyclobutabenzenes (equations 19<sup>113</sup> and 20<sup>114</sup>). In equation 19, both the allyl and cyclopentadienyl ligands are displaced and Pd(0) is inserted into one of the single bonds of the three-membered ring of 7,7-bis(trimethylsilyl)cyclopropabenzene. The analogous nickel complex is formed, in 61%-82% yield, with tris(ethylene)nickel and the cyclopropabenzene in the presence of a chelating ligand. When L=TMED in this example a ligand exchange reaction can occur to form the analogous nickela(II)cyclobutabenzene compounds with phosphorous ligands

(19)



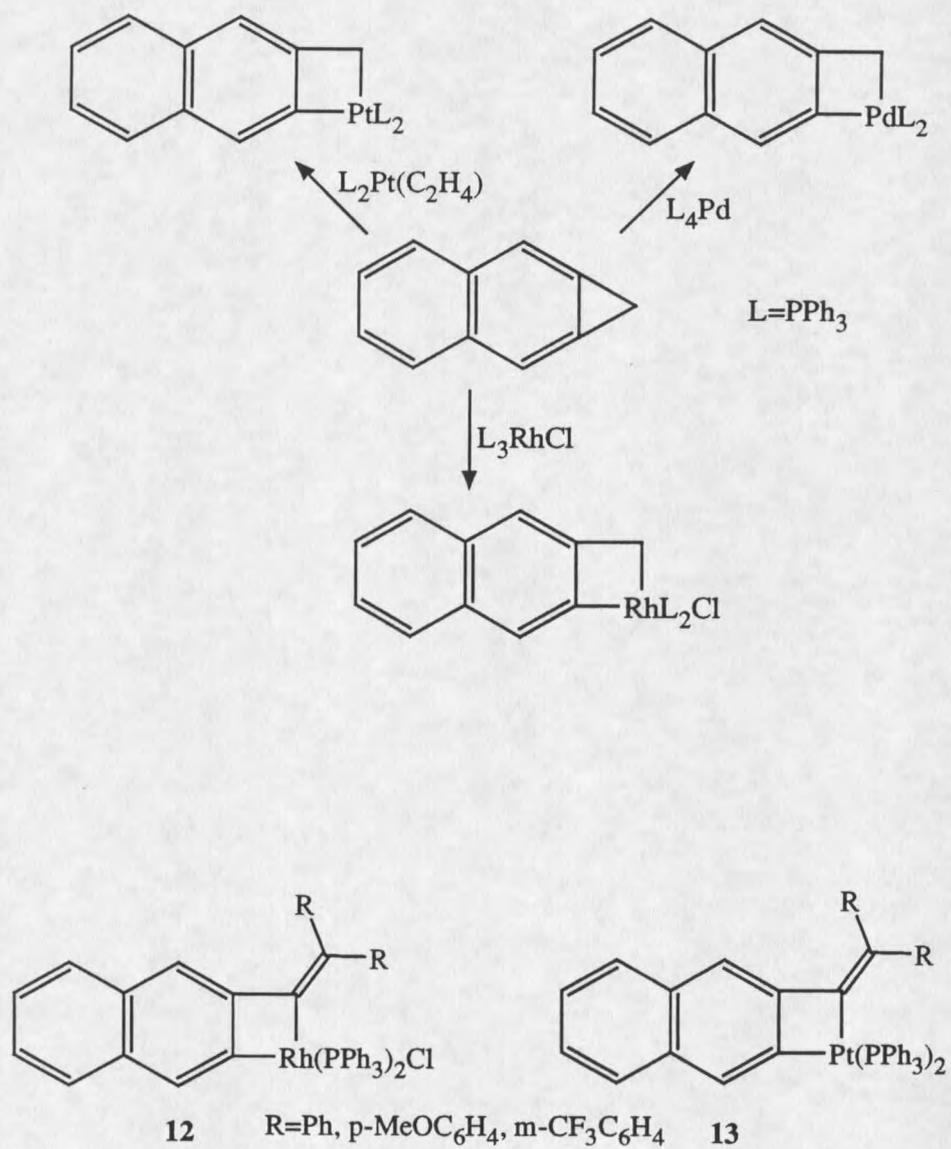
(20)



$\text{PMe}_3$ , dcpe, and dppe.

Further investigations of metal insertions into cyclopropenes led to the preparation of metallacyclobutanes of Rh(III) (74% yield), Pd(II), and Pt(II) (92% yield) as illustrated in Scheme III<sup>115</sup>. Alkylidene-1-rhoda(III)- 12 and -platina(II)cyclobutanes 13 also have been prepared from (diarylmethylene)cyclopropenes and  $(\text{PPh}_3)_3\text{RhCl}$  and  $(\text{PPh}_3)_4\text{Pt}$ , respectively (60%-85% yield)<sup>116</sup>.

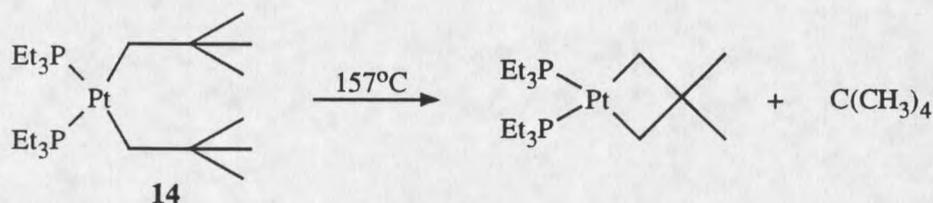
Scheme III.



### Oxidative Addition of C-H Bond Methodology

The intramolecular oxidative addition of C-H bonds to a central metal atom, commonly referred to as a cyclometallation reaction, can form an assortment of metallacyclic complexes including metallacyclobutanes, -butanones, and -butabenzenes. The most thoroughly studied example of this methodology involves the thermal decomposition of dineopentylbis(triethylphosphine)platinum(II) to form bis(triethylphosphine)-2,2-dimethylplatina(II)cyclobutane in 70% yield (equation 21)<sup>117</sup>.

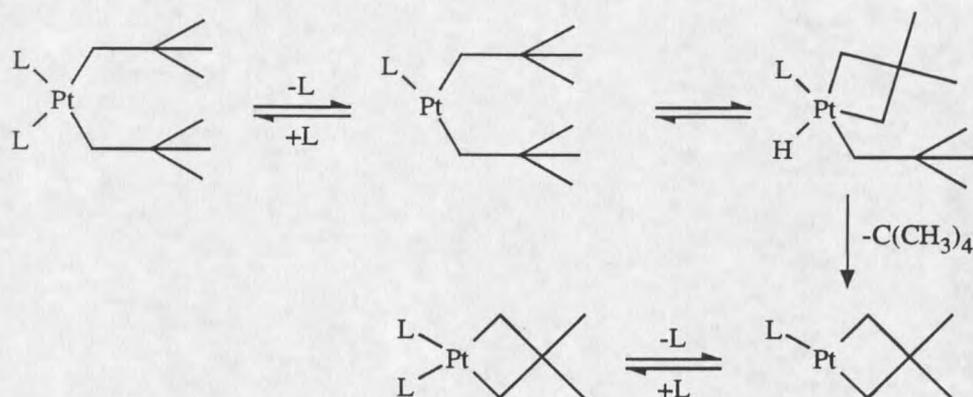
(21)



In this reaction, an unactivated  $\gamma$  C-H bond is cleaved by the platinum moiety under vigorous conditions to form the platina(II)cyclobutane. The mechanism has been investigated and is outlined in Scheme IV<sup>117-120</sup>. Studies have indicated relief of steric congestion in the dineopentylplatinum complex as the driving force of the reaction.

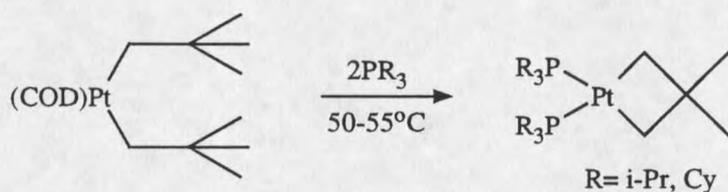
Compound **14**, shown above, was prepared in good yield by treating (1,5-COD)PtCl<sub>2</sub> with neopentylmagnesium bromide forming cis-dineopentyl-1,5-cyclooctadieneplatinum(II), (1,5-COD)Pt[CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, followed by addition of triethylphosphine. The corresponding reactions of (1,5-COD)Pt[CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> with triisopropylphosphine and tricyclohexylphosphine do not form the expected analogues to **14**, however, but lead directly to platina(IV)cyclobutane formation in 19% and 17% yields, respectively (equation 22)<sup>121</sup>. The difference in products in these reactions is presumably due to

Scheme IV.



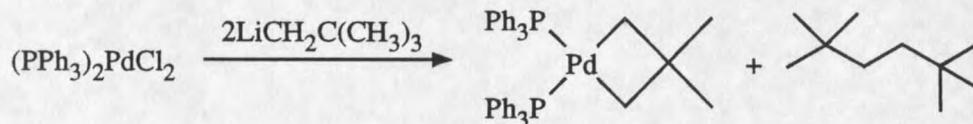
the increased steric bulk of triisopropyl- and tricyclohexylphosphine, relative to triethylphosphine, making formation of a stable square planar Pt(II) dineopentyl complex unlikely.

(22)

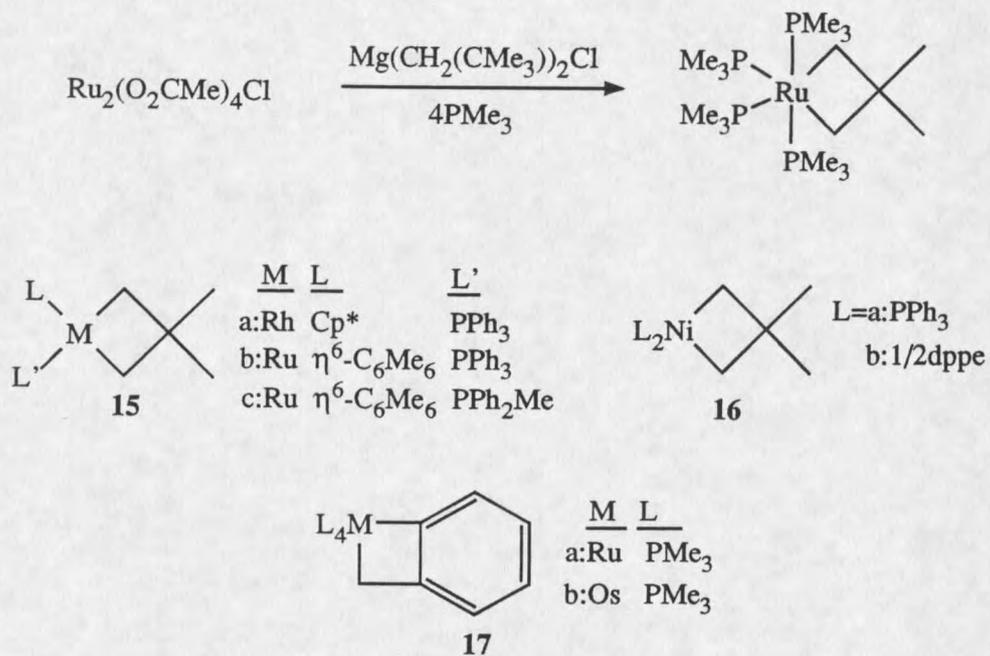


The mechanism shown in Scheme IV for 2,2-dimethylplatinum(II)cyclobutane formation also is invoked in the preparation of the 2,2-dimethylmetallacyclobutanes formed in equations 23<sup>122</sup> and 24<sup>123</sup>. Other metallacyclobutane and -butabenzene compounds that have been prepared by this methodology, in yields ranging from 12%-70% are shown as 15a-c<sup>124-127</sup>, 16a and b<sup>122</sup> and 17a<sup>128,129</sup> and b<sup>130</sup>.

(23)

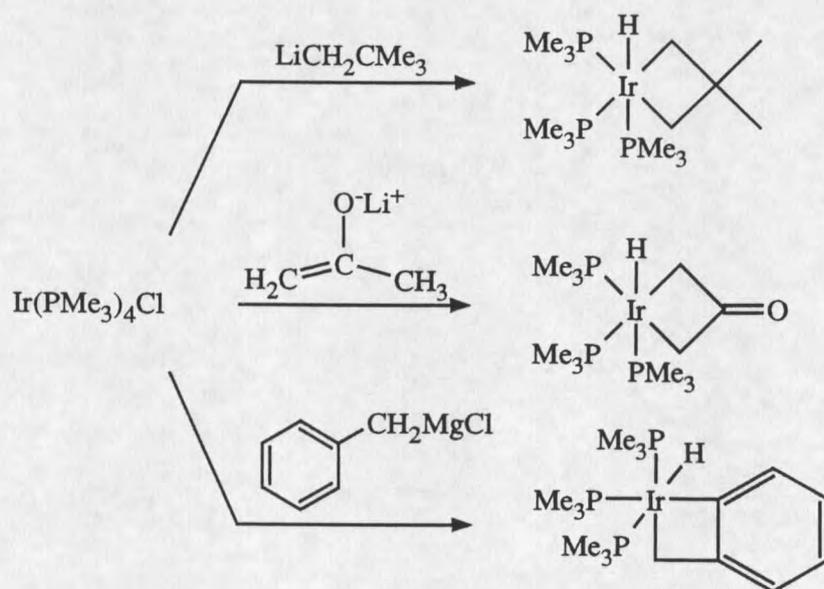


(24)



Irida(III)cyclobutane, -butanone, and -butabenzene all have been prepared via cyclometallation reactions according to Scheme V<sup>128,131</sup>.

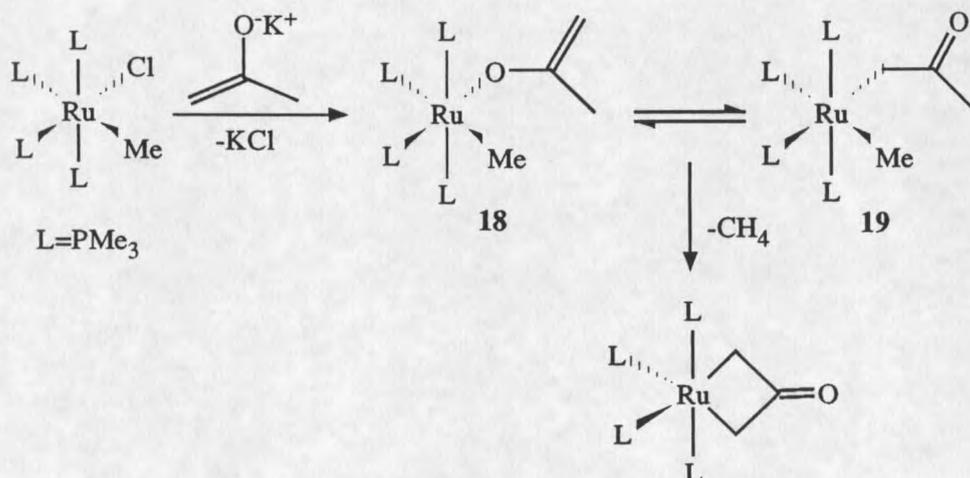
Scheme V.



Each reaction shown in Scheme V involves the insertion of iridium(I) into a  $\gamma$  C-H bond of the alkyl or aryl moiety. The cyclometallation mechanism of the iridium examples slightly differs, however, from the cyclometallation pathway outlined in Scheme IV, since no sacrificial alkyl ligand is present to reductively eliminate with the abstracted hydrogen. A later mechanistic study revealed that ligand dissociation did not occur prior to oxidative addition of the C-H bond to iridium suggesting direct oxidative addition of the C-H bond to a square planar monoalkyl (or aryl) iridium intermediate<sup>132</sup>.

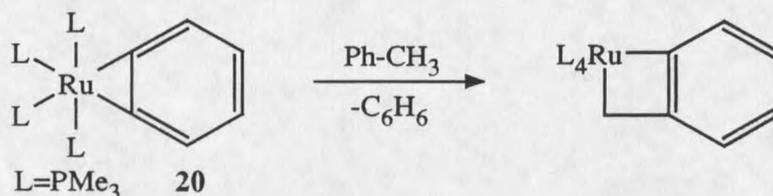
An analogous product to the irida(III)cyclobutanone formed in Scheme V can be prepared for ruthenium as illustrated in equation 25<sup>133</sup>. An equilibrium is first established between the ruthenium enolate complexes **18** and **19** which exist in both the C- and O-bound forms in a 70:30 ratio. Thermolysis of this mixture leads to loss of methane and formation of the ruthena(II)cyclobutanone product in 74% yield as determined by <sup>1</sup>H NMR spectroscopy at -20°C. The metallacyclobutanone formed is extremely unstable but was isolated and characterized at low temperatures.

(25)



A ruthena(II)cyclobutabenzene results from the reaction of a ruthenium-benzynes complex with toluene under the conditions described in equation 26<sup>134</sup>. It has not been determined whether the metallacyclic product results from initial reaction of 20 with the ortho position of toluene followed by metallation of the benzylic methyl group or by initial reaction with the benzylic C-H bond followed by orthometallation.

(26)

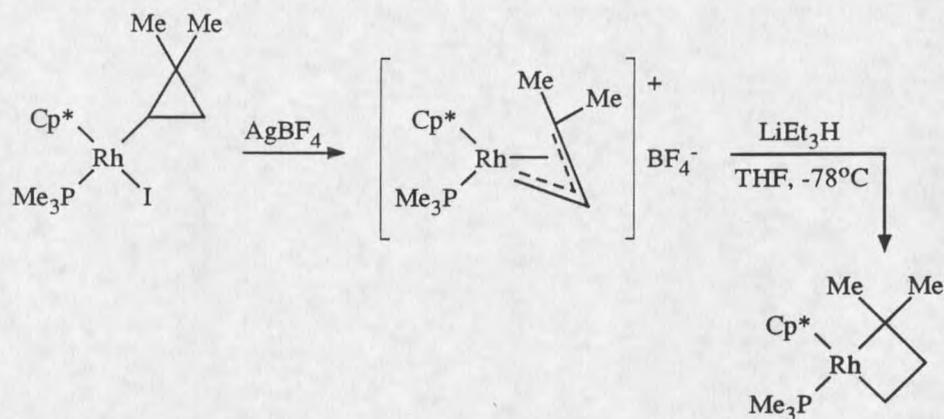


#### Nucleophilic Addition to Metal $\eta^3$ -allyl Complexes Methodology

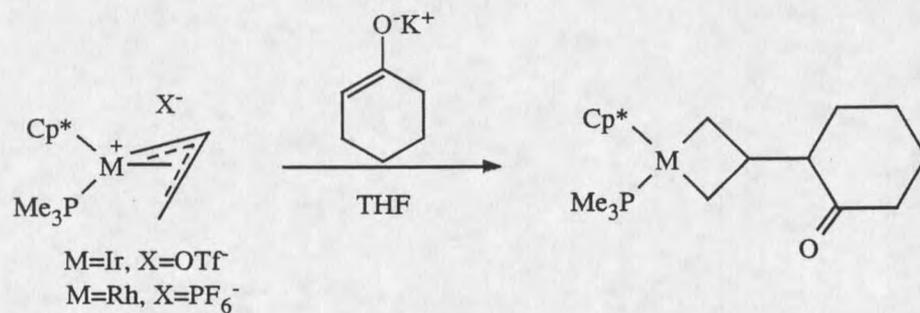
Nucleophilic addition to the central carbon of  $\eta^3$ -allyl transition metal complexes can form two types of metallacyclobutane products. Simple metallacyclobutanes can be synthesized from an isolated metal- $\eta^3$ -allyl complex and a tricyclic ring closure product, containing a metallacyclobutane moiety, results from nucleophilic attack on a suggested metal- $\eta^3$ -allyl intermediate.

Four examples of metallacyclobutanes prepared from isolated  $\eta^3$ -allyl metal complexes are shown in equations 27<sup>135</sup>, 28<sup>136,137</sup>, 29<sup>138</sup> and 30<sup>139</sup>. Other metallacyclobutanes synthesized by this methodology are exhibited in Table 7. That the nucleophile attacks at the central carbon, rather than the terminal carbon, of the  $\pi$ -allyl system is unusual and is reportedly the result of frontier orbital control as well as charge control<sup>140-142</sup>. In addition, the reactions shown in equations 29 and 30 indicate that  $\beta$ -alkyl substitution on the allylic group does not prevent nucleophilic attack at the central carbon.

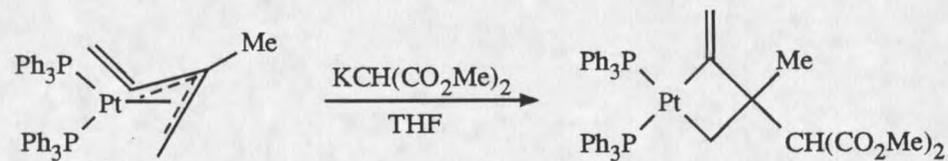
(27)



(28)



(29)



(30)

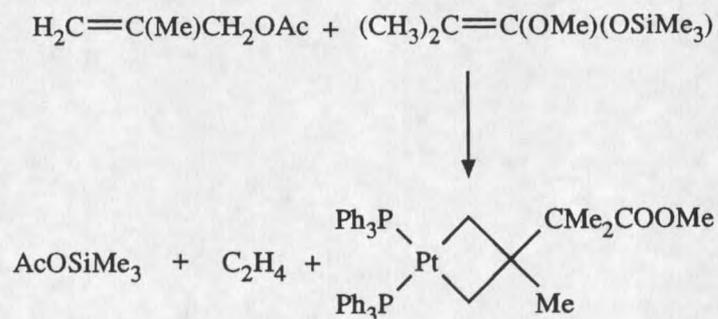
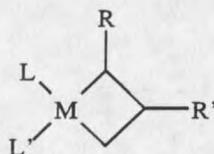
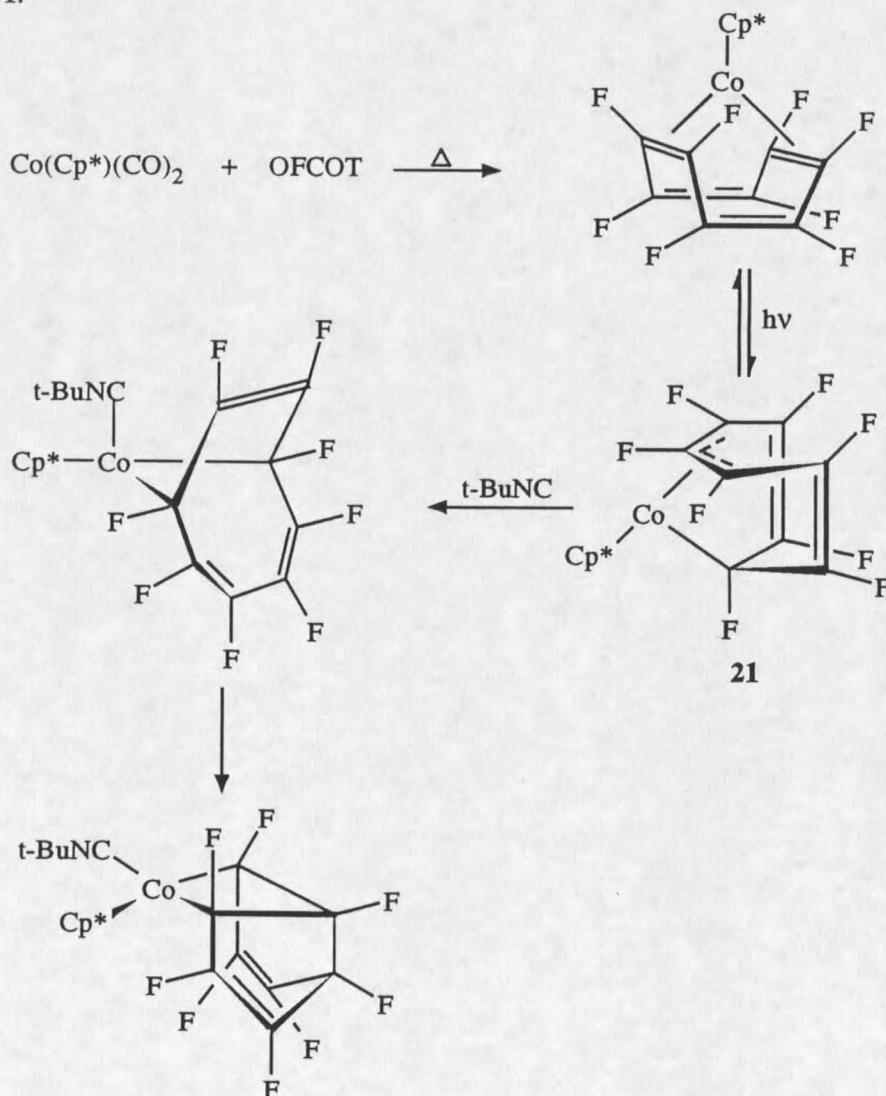


Table 7. Rhoda(III)-, irida(III) and platina(II)cyclobutanes via nucleophilic addition to metal  $\eta^3$ -allyl complexes.

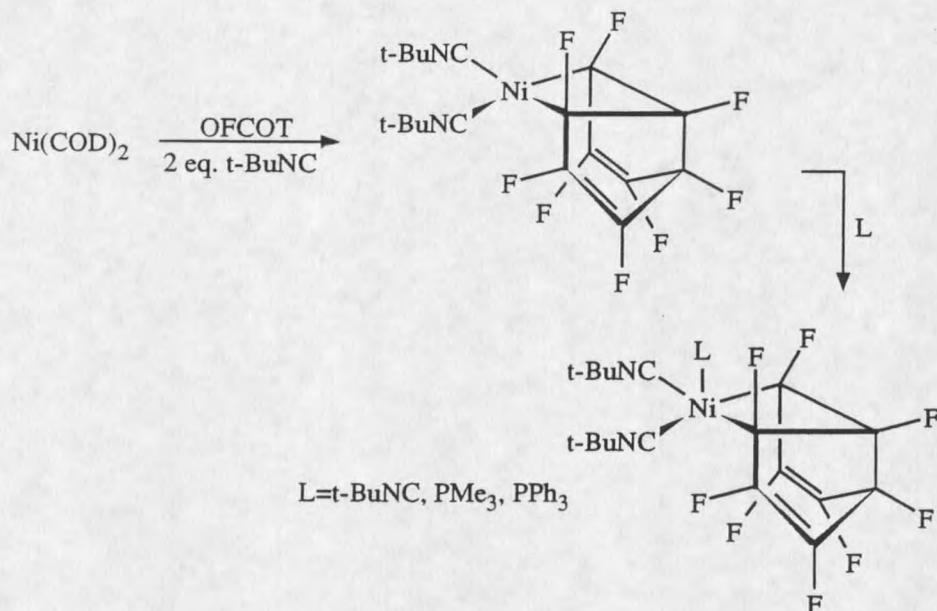
M	L	L'	R	R'	ref.
Rh	Cp*	PMe <sub>3</sub>	H	H	135
Rh	Cp	PMe <sub>3</sub>	Me	H	143
Rh	Cp	P(i-Pr) <sub>3</sub>	Me	H	144
Rh	Cp	P(i-Pr) <sub>3</sub>	H	CHCl <sub>2</sub>	144
Rh	Cp	PMe <sub>3</sub>	Me	Me	143
Rh	Cp	P(i-Pr) <sub>3</sub>	Me	Me	144
Rh	Cp	P(i-Pr) <sub>3</sub>	Me	CHCl <sub>2</sub>	143
Rh	Cp	P(i-Pr) <sub>3</sub>	Me	CCl <sub>3</sub>	143
Rh	Cp*	PMe <sub>3</sub>	H	CHMeC(O)Ph	136
Ir	Cp*	PMe <sub>3</sub>	H	H	145
Ir	Cp*	C <sub>2</sub> H <sub>4</sub>	H	H	142
Ir	Cp*	C <sub>2</sub> Ph <sub>2</sub>	H	H	146
Ir	Cp*	PMe <sub>3</sub>	H	Me	145
Ir	Cp*	CO	H	CH(CO <sub>2</sub> Me) <sub>2</sub>	147
Ir	Cp*	CO	H	CN	147
Ir	Cp*	CO	H	CHMeC(O)Ph	147
Ir	Cp*	PMe <sub>3</sub>	H	CHMeC(O)Ph	136
Ir	Cp*	C <sub>2</sub> H <sub>4</sub>	H	CHMeC(O)Ph	136
Ir	Cp*	C <sub>2</sub> Ph <sub>2</sub>	H	CHMeC(O)Ph	146
Ir	Cp*	C <sub>2</sub> Me <sub>2</sub>	H	CHMeC(O)Ph	146
Pt	PPh <sub>3</sub>	PPh <sub>3</sub>	H	CMe <sub>2</sub> CO <sub>2</sub> Me	139
Pt	P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	H	CMe <sub>2</sub> CO <sub>2</sub> Me	139
Pt	PPh <sub>3</sub>	PPh <sub>3</sub>	Me	CMe <sub>2</sub> CO <sub>2</sub> Me	139
Pt	½(dppe)		H	CHMeCO <sub>2</sub> Me	139

Three examples of the second type of metallacyclobutane product formed by nucleophilic attack on the central carbon of a proposed  $\eta^3$ -allyl metal intermediate are shown in Scheme VI<sup>148</sup> and equations 31<sup>149,150</sup> and 32<sup>151</sup>. In each example, a metal complex is treated with octafluorocyclooctatetraene, (OFCOT), under varying conditions, to generate a transannular ring closure product containing a metallacyclobutane moiety. Other metallacyclobutane products resulting from this methodology are shown in Table 8.

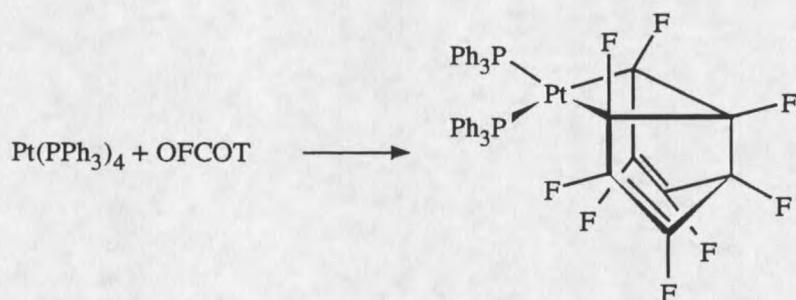
Scheme VI.



(31)

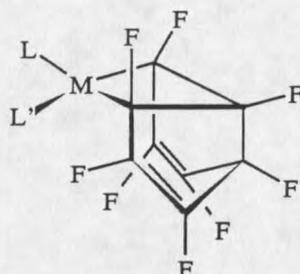


(32)

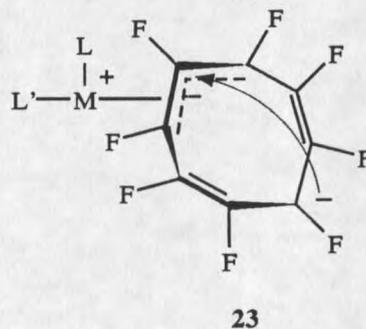
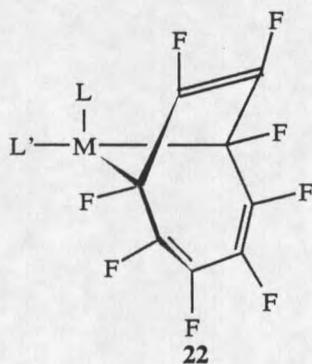


Although the various metal complexes utilized in the reactions in Scheme VI, equations 31 and 32, and to generate the products shown in Table 8, require different reaction conditions to arrive at the observed ring closure product, a common metallacyclopentene intermediate **22** is suggested for each reaction and actually was isolated and characterized in the cobalt and rhodium examples. It is this intermediate that can be transformed into a zwitterionic species **23** containing an  $\eta^3$ -allyl metal moiety. Attack of the negatively charged carbon on the central carbon of the allyl leads to the observed metallacyclobutane products<sup>152</sup>.

Table 8. Cobalta(II)-, rhoda(III), pallada(II)- and platina(II)cyclobutanes via transannular ring closure reactions.

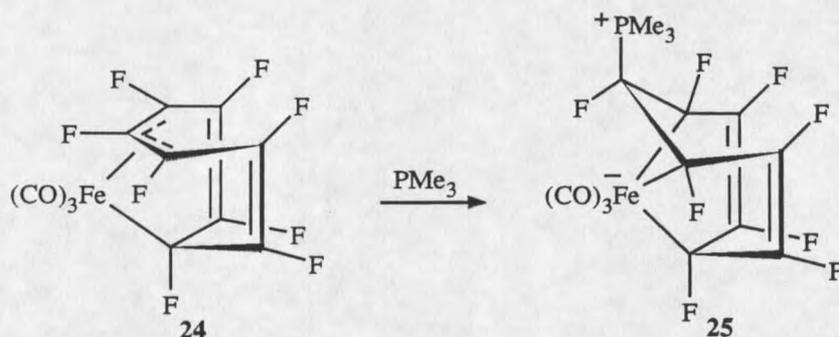


M	L	L'	ref.
Co	CO	Cp*	151
Rh	t-BuNC	Cp*	148
Rh	PMe <sub>3</sub>	Cp*	148
Rh	t-BuNC	indenyl	148
Pd	PPh <sub>3</sub>	PPh <sub>3</sub>	149
Pd	t-BuNC	t-BuNC	149
Pt	PPhMe <sub>2</sub>	PPhMe <sub>2</sub>	151
Pt	PPh <sub>2</sub> Me	PPh <sub>2</sub> Me	151
Pt	AsPh <sub>3</sub>	AsPh <sub>3</sub>	151
Pt	t-BuNC	t-BuNC	149



A similar reaction of Fe(0) with OFCOT leads to a different type of metallacyclobutane product as external nucleophilic attack at the central carbon of an iron  $\eta^3$ -allyl complex occurs. In this case, when  $\text{Fe}_2(\text{CO})_9$  is treated with OFCOT an allylic iron complex **24** results. (A similar structure to **21** in Scheme VI). Subsequent addition of  $\text{PMe}_3$  leads to formation of the trialkyltricarboxyl iron(IV) complex **25** presumably via attack of  $\text{PMe}_3$  on the internal allylic carbon (equation 33)<sup>153</sup>. Further, treatment of **24** with the anionic nucleophile  $[(\text{Me}_2\text{N})_3\text{S}]^+[\text{Me}_3\text{SiF}_2]^-$  adds an additional fluorine at the center carbon of the allylic moiety to form the analogous anionic nonafluoro complex.

(33)



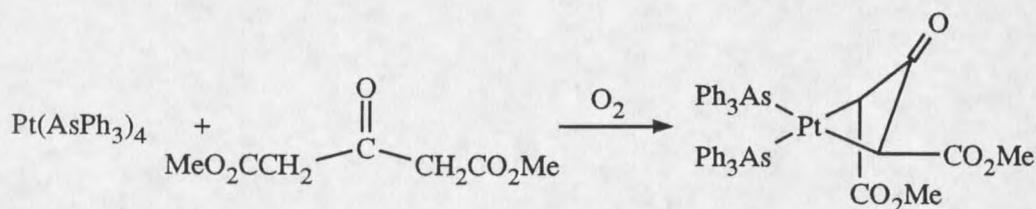
### Other Methodologies

The synthesis of metallacyclobutane derivatives is not limited, however, to the previously described methodologies. A number of other procedures also have proven effective.

Metallacyclobutanones can be prepared by three different methodologies in addition to the cyclometallation reactions described previously. Reaction of Pt(0) and Pd(0) species,  $\text{Pt}(\text{PR}_3)_4$ ,  $\text{Pt}(\text{AsPh}_3)_4$ ,  $\text{Pt}(\text{CO}_3)(\text{PR}_3)_2$ ,  $\text{cis-Pt}(\text{OCOPh})_2$ ,  $\text{cis-PtCl}_2(\text{PPh}_3)$ ,  $\text{Pd}(\text{PR}_3)_2$  or  $\text{Pd}(\text{dba})_2$ , with esters of 3-oxopentanedioic acid or 2,4,6-heptatrione, under various reaction conditions, produces pallada(II)- and platina(II)cyclobutanones, in high

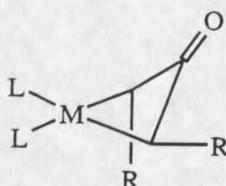
yield. One example of this methodology is shown in equation 34<sup>154</sup>. Other examples of metallacyclobutanones synthesized from the metal species and reagents discussed above are listed in Table 9. In each case, one substituent occupies an equatorial position, while the other is found to be axial as shown.

(34)



The silyl complex, 3-chloro-1-(trimethylsilyl)propane-2-one, can be utilized as a reagent to generate osmia(II)- and irida(III)cyclobutanones, as well as the Pt(II) analogue, according to Scheme VII<sup>161</sup>. The reaction is suggested to proceed from the silylenol ether rather than the respective ketone and to follow the oxidative addition pathway shown in equation 35<sup>162</sup>.

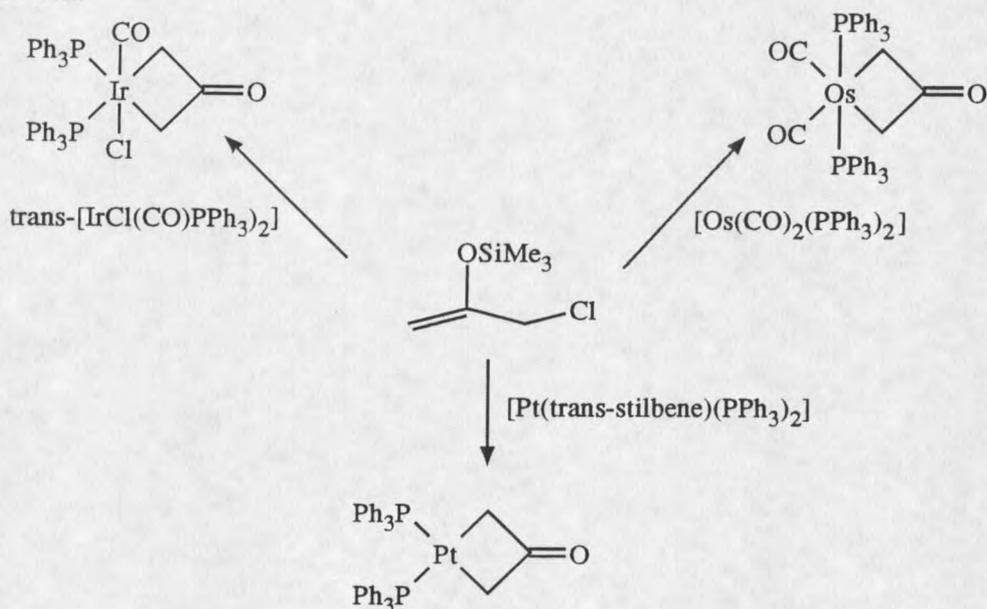
Table 9. Pallada(II)- and platina(II)cyclobutanones via reaction with acidic substrates.



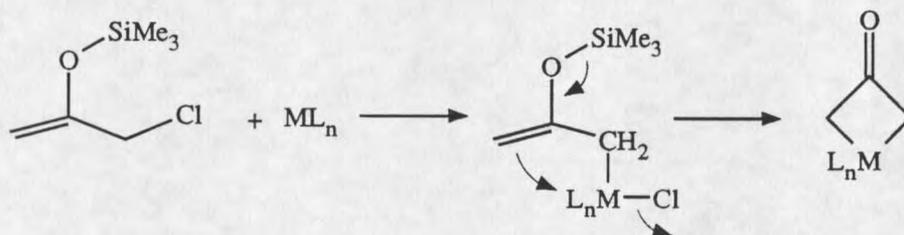
M	L	R	ref.
Pd	PPh <sub>3</sub>	CO <sub>2</sub> Me	154-158
Pd	PPh <sub>3</sub>	CO <sub>2</sub> Et	157,158
Pd	PPh <sub>2</sub> Me	CO <sub>2</sub> Me	156,157
Pd	PPhMe <sub>2</sub>	CO <sub>2</sub> Me	156,157
Pd	PEt <sub>3</sub>	CO <sub>2</sub> Me	157
Pd	AsPh <sub>3</sub>	CO <sub>2</sub> Me	156,157
Pd	AsPh <sub>3</sub>	CO <sub>2</sub> Et	157
Pd	½(bipy)	CO <sub>2</sub> Me	156-158
Pd	½(bipy)	CO <sub>2</sub> Et	157
Pd	½(bipy)	CO <sub>2</sub> n-Pr	157
Pt	PPh <sub>3</sub>	CO <sub>2</sub> Me	154,155,158 <sup>b</sup>
Pt	PPh <sub>3</sub>	CO <sub>2</sub> Et	154
Pt	PPh <sub>3</sub>	CO <sub>2</sub> n-Pr	154
Pt	PPh <sub>3</sub>	COMe	159,160
Pt	PPh <sub>3</sub>	CO <sub>2</sub> Et, CO <sub>2</sub> n-Pr <sup>a</sup>	159
Pt	PPh <sub>2</sub> Me	CO <sub>2</sub> Me	154,155,158 <sup>b</sup>
Pt	PPhMe <sub>2</sub>	CO <sub>2</sub> Me	154,155,158 <sup>b</sup>
Pt	½(dppe)	CO <sub>2</sub> Me	154,158,159
Pt	AsPh <sub>3</sub>	CO <sub>2</sub> Et	154
Pt	AsPh <sub>3</sub>	CO <sub>2</sub> n-Pr	154
Pt	AsPh <sub>3</sub>	COMe	159,160

<sup>a</sup> Each group occupies one R position <sup>b</sup> Also found in ref. 159.

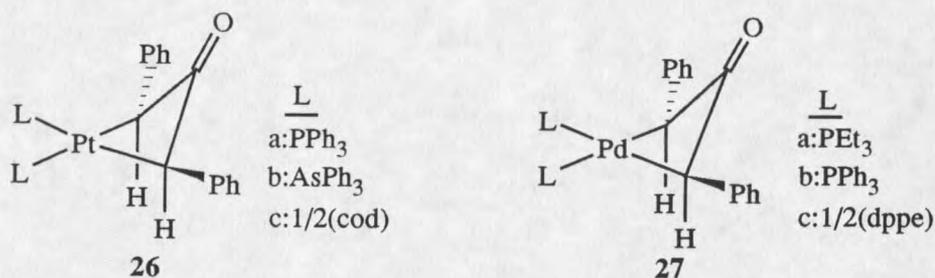
Scheme VII.



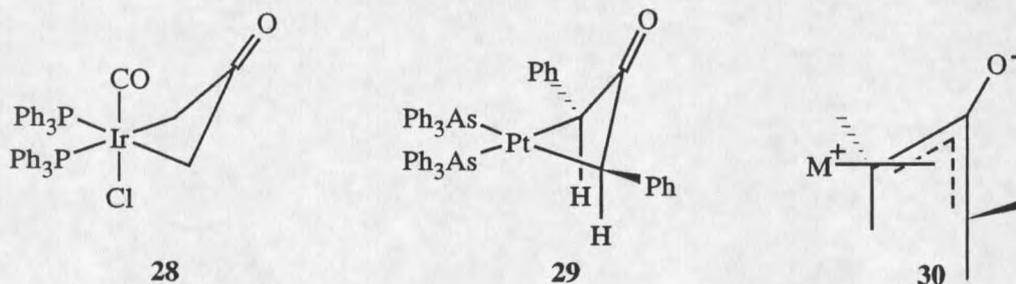
(35)



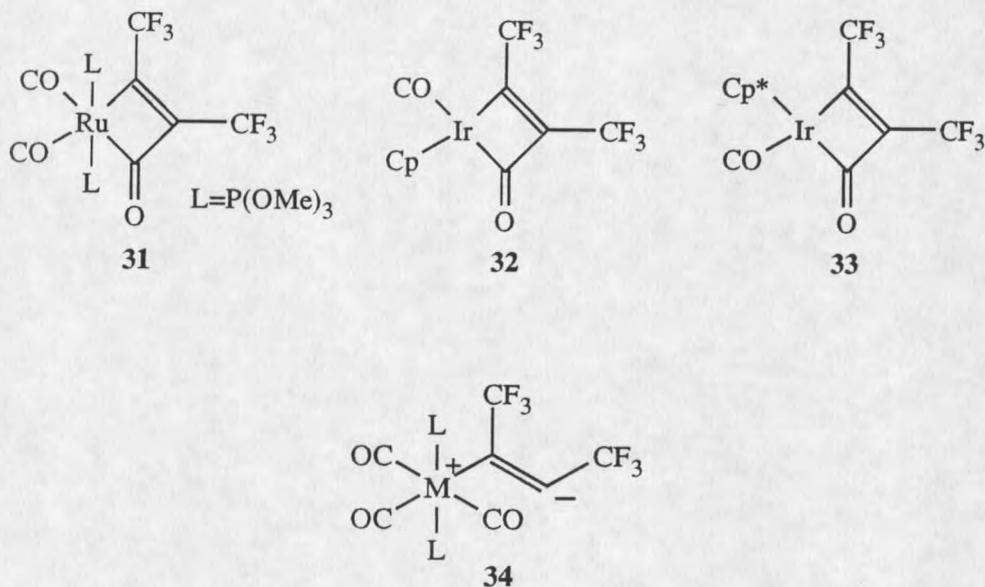
Metallacyclobutanones of Pt(II), 26a-c, and Pd(II), 27a-c, bearing phenyl substituents can be synthesized from the dianion of 1,3-diphenylacetone in yields ranging from 42%-93%<sup>163</sup>. In contrast to the substitution of the metallacyclobutanones of Table 9, both of the phenyl substituents on 26a-c, and 27a-c adopt equatorial positions. This novel substitution is best explained by the increased conjugation that can be achieved between the phenyl groups and the  $\pi$ -system of the oxodimethylene ligand when an equatorial orientation is adopted.



Characterization of the metallacyclobutanones prepared by the three methodologies described above has revealed a highly puckered ring system. The degree of puckering ranges from 41° in **28**<sup>157</sup> to 56.7° in **29**<sup>163</sup> and is believed to result from a transannular attraction between the metal and the β-carbonyl group. In fact, the bonding description of these metallacycles should include considerable contribution from an η<sup>3</sup>-oxodimethylenemethane structure **30**, and in the most highly puckered cases is more logically suggested as such. The amount of allylic contribution in these systems is related to variations in the metal, the ligands, and the ring substituent.



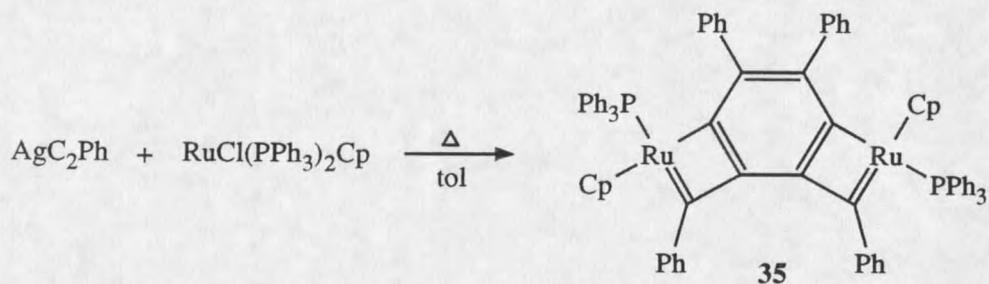
Metallacyclobutenones **31**, **32**, and **33** can be synthesized from the reaction of alkynes bearing strong electron withdrawing CF<sub>3</sub> groups with trans-(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)<sub>2</sub>Ru, Cp(CO)<sub>2</sub>Ir, and Cp<sup>\*</sup>(CO)<sub>2</sub>Ir, respectively<sup>164-166</sup>. The reaction pathway for the synthesis of **31** suggests initial formation of an ionic intermediate **34** followed by nucleophilic attack by the carbanion on the coordinated carbon monoxide to give the



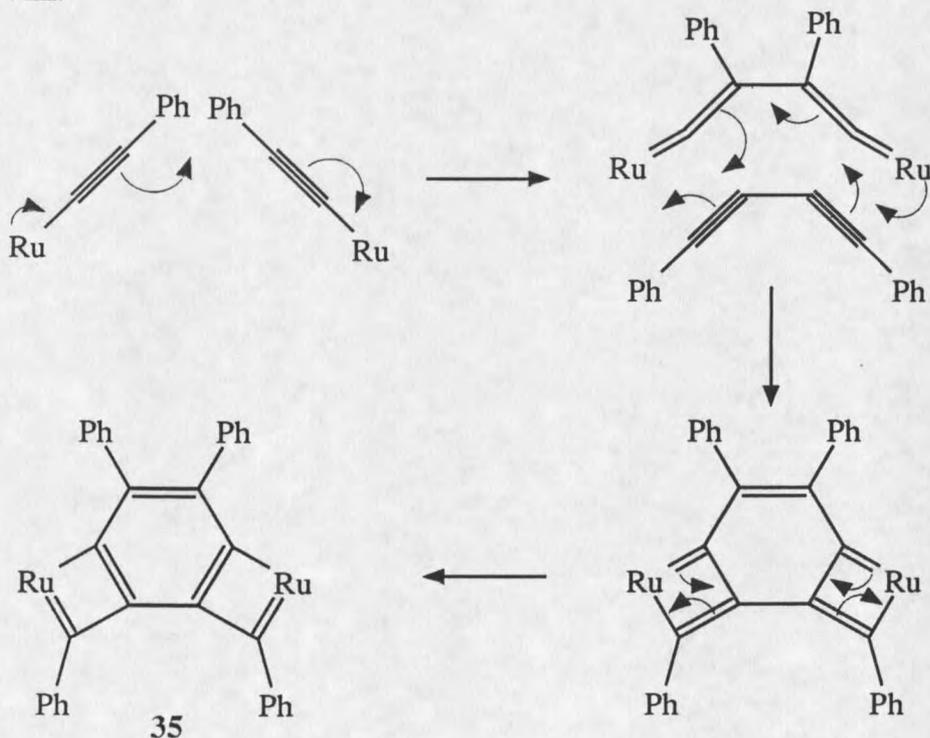
ruthena(II)cyclobutene product.

The unusual tetramerization of alkynes is proposed for the formation of the diruthenadicyclobutadiene[*a,c*]benzene complex **35**, in 24% yield, from the reaction of  $\text{AgC}_2\text{Ph}$  and  $\text{RuCl}(\text{PPh}_3)_2$  as shown in equation 36<sup>167</sup>. Also isolated in small yields from this reaction was a diruthenapentacyclic pentalene system. The formation of both products is attributed to the oligomerization of phenylacetylide units on ruthenium. The proposed pathway for the formation of **35** is shown in Scheme VIII. Initial formation of two ruthenium  $\sigma$ -phenylacetylide complexes is followed by oxidative coupling to form the ruthenium divinylidene complex. Further coupling with 1,4-diphenylbuta-1,3-diyne, which also is formed by oxidative coupling of phenylacetylide units, leads to **35** as shown.

(36)



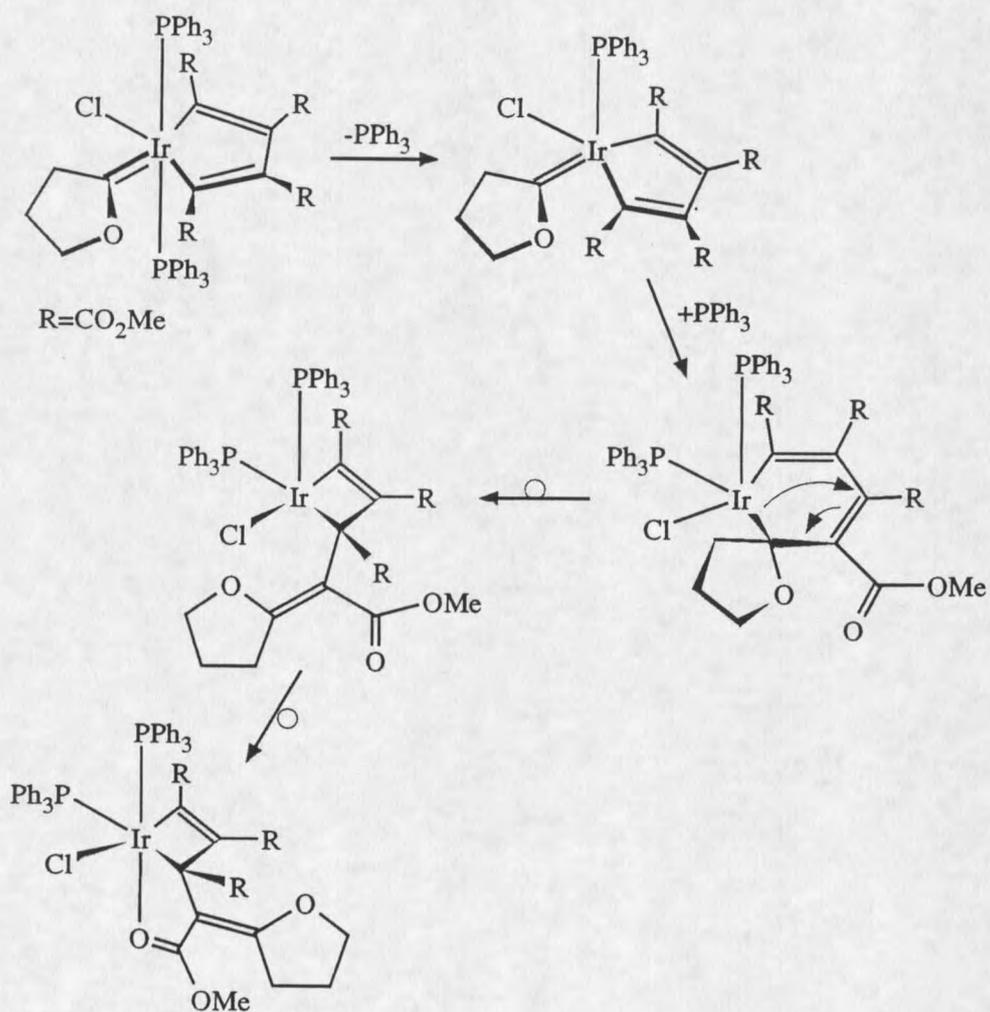
Scheme VIII.



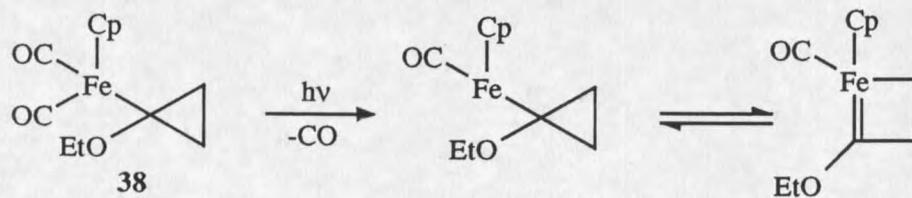
Another methodology incorporating alkynes involves conversion of a (methoxymethyl)iridium(I) acetylene complex **36** to an irida(III)cyclobutene presumably by the pathway shown in equation 37<sup>168</sup>. The C-O bond of the methoxy group is easily cleaved by the electrophilic reagent bromotrimethylsilane to form the suggested iridium-carbene intermediate **37**. The iridium-carbene then can undergo a [2+2] cycloaddition to the  $\pi$ -bound acetylene to form the observed metallacyclobutene product in 66% yield.



Scheme IX.

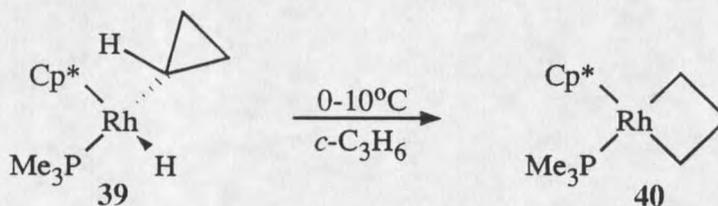


(38)



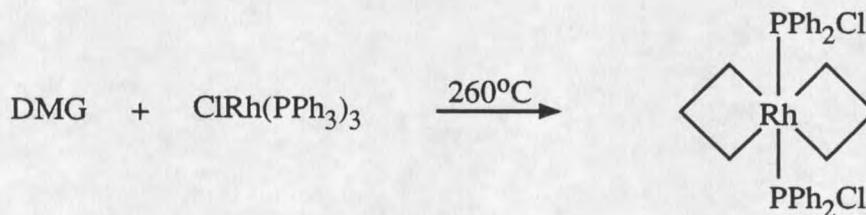
An intramolecular rearrangement of a cyclopropyl  $\sigma$  complex of rhodium **39** to form a rhoda(III)cyclobutane has been suggested for the reaction shown in equation 39<sup>135,172</sup>. Kinetic and <sup>13</sup>C labeling studies have indicated that the cyclopropyl moiety and the rhodium remain intact during conversion of **39** to **40**, and that rearrangement occurs by regiospecific insertion of Rh(III) into an  $\alpha$  C-C bond of the cyclopropyl ring thus supporting an intramolecular rearrangement pathway.

(39)



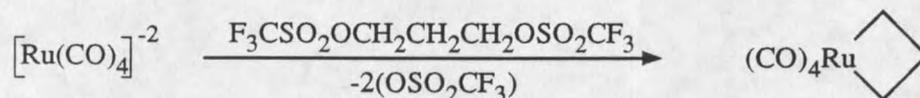
An unusual rhoda(IV)cyclobutane reportedly is produced in the reaction shown in equation 40<sup>173</sup>. The pyrolysis of dimethylglutarate, DMG, with Wilkinson's salt, ClRh(PPh<sub>3</sub>)<sub>3</sub>, produces a large number of products. Six rhodium containing compounds were isolated, one being the rhoda(IV)cyclobutane shown. Initial oxidative addition into the C-O bond of DMG, followed by additional reactions, accounts for the formation of the Rh compounds. However, the additional reactions necessary to form the rhoda(IV)-cyclobutane are not obvious.

(40)

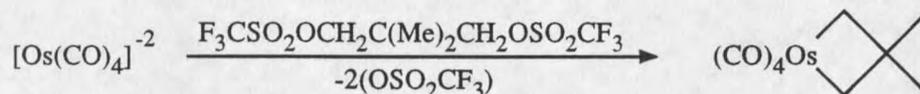


Ruthena(II)- and osmia(II)cyclobutanes can be synthesized by nucleophilic elimination-cycloaddition on the alkanediyl bis(trifluoromethanesulfonate) with the divalent anions  $[M(\text{CO})_4]^{-2}$  according to equations 41 and 42<sup>174</sup>. An analogous unsubstituted osmia(II)cyclobutane also can be synthesized by the reaction shown in equation 41 and is found to be considerably more thermally stable than the ruthenium homologue.

(41)



(42)

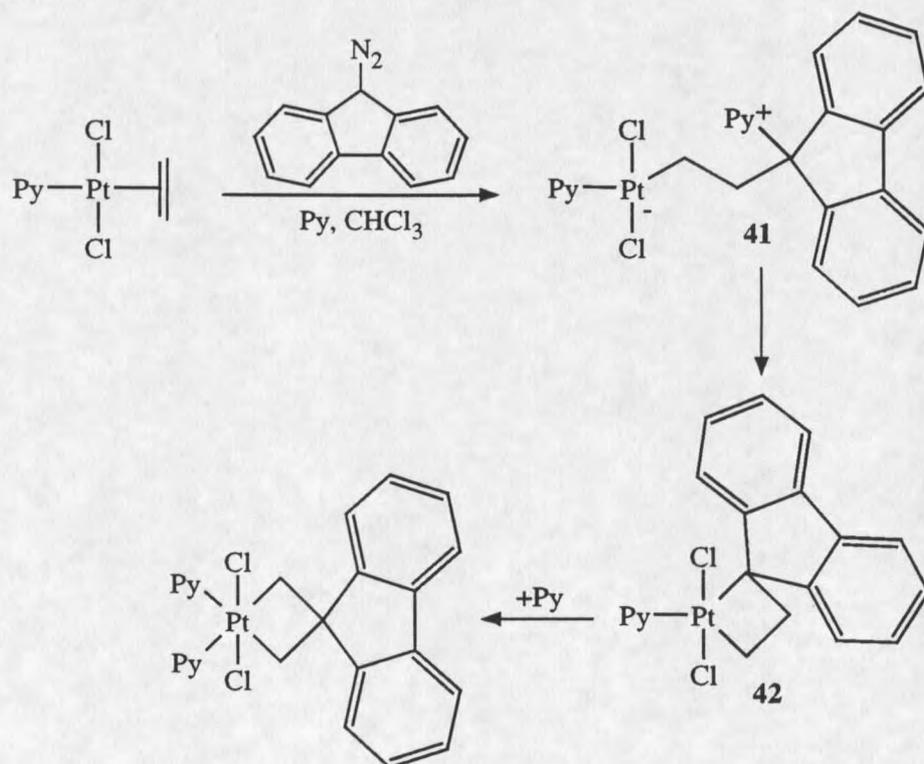


Both the sodium amalgam reduction, (or the less convenient cathodic reduction), of platina(IV)cyclobutane, equation 43<sup>175,176</sup>, and the reaction of a 1,3-diGrignard reagent with a Pt(II) species, equation 44<sup>177</sup>, can be used to prepare platina(II)cyclobutanes in high yield. These methodologies are useful in preparing platina(II)cyclobutanes without the electronegative substituents required for Pt(0) insertion into cyclopropanes (see equations 12 and 13). Both the bipyridyl and COD ligands are labile and can be displaced readily by monodentate ligands to form platina(II)cyclobutanes with  $\text{L}=\text{PPh}_3$ ,  $\text{PMe}_3$ ,  $\text{PEt}_3$ ,  $\text{P}(\text{t-Bu})_3$  and  $\text{t-BuNC}$ .



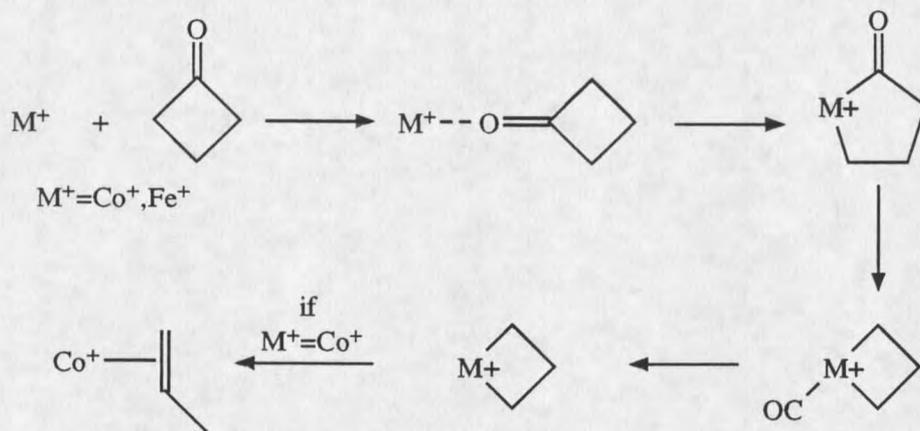
A platina(IV)cyclobutane can be formed in 94% yield by reacting diazofluorene with Zeise's pyridine monomer according to Scheme X<sup>70</sup>. The pathway for this transformation suggests initial formation of intermediate **41** which subsequently cyclizes to form an  $\alpha$ -substituted platina(IV)cyclobutane **42**. A Puddephatt type rearrangement and addition of pyridine lead to the observed product. Intermediate **41** was observed by NMR spectroscopy from reactions run at low temperatures ( $-40^{\circ}$  to  $0^{\circ}\text{C}$ ) and was found to form the platina(IV)cyclobutane upon warming. Intermediate **42** was not observed but ample precedent is reported for the rearrangement of  $\alpha$ -substituted platina(IV)cyclobutanes to their  $\beta$ -substituted counterparts.

Scheme X.



Metallacyclobutane ions can be formed in the gas phase with  $\text{Fe}^+$  and  $\text{Co}^+$  according to equation 46<sup>179,180</sup>. The ferra(III)cyclobutane ion formed is stable whereas the corresponding cobalta(III)cyclobutane ion has been found to isomerize to a  $\pi$ -complexed propene product.

(46)



### Characterization of Metallacyclobutane Derivatives

The use of  $^1\text{H}$  NMR spectroscopy,  $^{13}\text{C}$  NMR spectroscopy and x-ray crystallographic analysis has aided the characterization of metallacyclobutane derivatives tremendously. This section provides an extensive  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and x-ray crystallography database for those metallacyclobutane derivatives for which this information has been reported.

#### $^1\text{H}$ NMR Spectroscopy

Tables 10 through 23 display the reported  $^1\text{H}$  NMR chemical shift (ppm) and metal-proton coupling constant (Hz) data (where applicable) for metallacyclobutane complexes. The effect of the metal on the proton chemical shift in these systems is evident when comparing the data for analogous rhoda(III)- and irida(III)cyclobutanes found in Table 10. The chemical shift of the  $\alpha$  protons in the irida(III)cyclobutanes consistently are found further downfield. A similar effect is observed in Table 11 when comparing the  $\beta$  proton chemical shifts of analogous pallada(II)- and platina(II)cyclobutanes. The decreased shielding caused by Ir(III) and Pt(II) is attributable to their increased ability to accept electron density from the carbon ring system.

The data for the platina(II)cyclobutanes in Table 12 illustrate the substantial influence that the coordinated ligands have on the proton chemical shifts. When a phosphorus ligand is coordinated to the platinum(II) in the unsubstituted examples, the  $\alpha$  proton chemical shift value ranges from 0.35 ppm to 0.47 ppm. However, when the

Table 10.  $^1\text{H}$  NMR chemical shift data (ppm) of ferra(II)-, ruthena(II)-, osmia(II)-, rhoda(III)-, irida(III)-, nickela(II), pallada(II)- and platina(II)cyclobutanes.

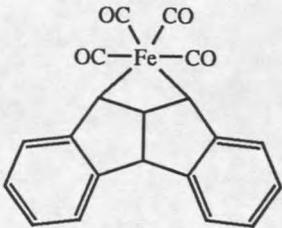
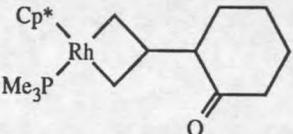
complex	$\text{H}^\alpha$	$\text{H}^\beta$	ref.
	3.04	4.55	104
$(\eta^6\text{-C}_6\text{H}_6)(\text{PPh}_3)\text{Ru}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	0.22,0.53	-	127
$(\eta^6\text{-C}_6\text{H}_6)(\text{PPh}_2\text{Me})\text{Ru}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	0.26,0.41	-	127
$(\text{CO})_4\text{Os}[\text{CH}_2\text{CH}_2\text{CH}_2]$	0.63	3.73	174
$(\text{Cp}^*)(\text{PMe}_3)\text{Rh}[\text{CH}_2\text{CH}_2\text{CH}_2]$	0.20,0.38	3.20,3.48	172
$(\text{Cp}^*)(\text{PMe}_3)\text{Rh}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	0.23,0.32	-	172
$(\text{Cp}^*)(\text{PMe}_3)\text{Rh}[\text{CMe}_2\text{CH}_2\text{CH}_2]$	0.53,0.81	2.52,3.41	172
$(\text{Cp}^*)(\text{PPh}_3)\text{Rh}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	0.41	-	124,125
$(\text{Cp})(\text{P}(i\text{-Pr}_3))\text{Rh}[\text{CHMeCH}_2\text{CH}_2]$	2.06 <sup>a</sup>	2.55,3.71	144
	0.27,0.98 <sup>b</sup>		
	0.50-0.60 -0.08-(-0.38)	2.85	137

Table 10. (continued)

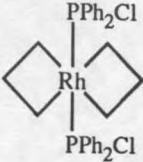
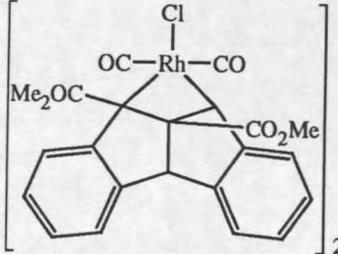
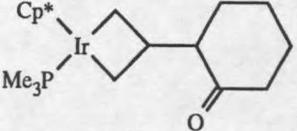
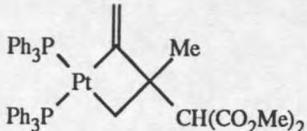
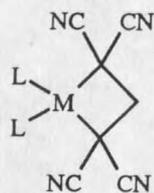
	1.00	1.3	173
	5.70	-	105
$(Cp^*)(C_2H_4)Ir[CH_2CH_2CH_2]$	0.96	2.80,4.14	142
$(AsMe_3)_3Hr[CH_2CMe_2CH_2]$	0.92	-	131
$(Cp^*)(C_2H_4)Ir[CH_2CH(CHMeC(O)Ph)CH_2]^c$	0.48,1.12	2.34	137
$(Cp^*)(C_2H_4)Ir[CH_2CH(CHMeC(O)Ph)CH_2]^d$	0.35,1.45	2.57	142
$(Cp^*)(PMe_3)Ir[CH_2CH(CHMeC(O)Ph)CH_2]^d$	0.93,1.05 <sup>e</sup> 0.42-0.52 <sup>f</sup>	2.84	137
	0.92,0.96 <sup>e</sup> 0.32,0.55 <sup>f</sup>	2.79	137
$(PPh_3)_2Ni[CH_2CMe_2CH_2]$	1.07	-	122
$(dppe)Ni[CH_2CMe_2CH_2]$	1.14	-	122

Table 10. (continued)

$(\text{PPh}_3)_2\text{Pd}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	0.85	-	122
$(\text{PPh}_3)_2\text{Pt}[\text{CH}_2\text{CH}(\text{CMe}_2\text{COOMe})\text{CH}_2]$	0.10, 0.44 <sup>g</sup>	3.02	139
$(\text{P}(\text{C}_6\text{H}_{11})_3)_2\text{Pt}[\text{CH}_2\text{CH}(\text{CMe}_2\text{COOMe})\text{CH}_2]$	-0.01, 0.66 <sup>h</sup>	2.84	139
$(\text{dppe})\text{Pt}[\text{CH}_2\text{CH}(\text{CHMeCOOMe})\text{CH}_2]$	-0.04, -0.20, 0.74 <sup>i</sup>	3.04	139
$(\text{PPh}_3)_2\text{Pt}[\text{CH}_2\text{C}(\text{Me})(\text{CMe}_2\text{COOMe})\text{CH}_2]$	0.11, 0.56 <sup>j</sup>	-	139
$(\text{PPh}_3)_2\text{Pt}[\text{CH}(\text{Me})\text{CH}(\text{CMe}_2\text{COOMe})\text{CH}_2]$ <sup>i</sup>	0.00, 0.34 <sup>k</sup> 0.60 <sup>k</sup>	3.06	139
	0.95, 1.66	-	138

<sup>a</sup> RhCHMe <sup>b</sup> RhCH<sub>2</sub> <sup>c</sup> Ring substituent syn to Cp\* <sup>d</sup> Ring substituent anti to Cp\* <sup>e</sup> H<sup>α</sup> trans to Cp\* <sup>f</sup> H<sup>α</sup> trans to PMe<sub>3</sub>.  
<sup>g</sup> <sup>2</sup>J<sub>Pt-H</sub>=80,84 <sup>h</sup> <sup>2</sup>J<sub>Pt-H</sub>=70,78 <sup>i</sup> <sup>2</sup>J<sub>Pt-H</sub>=78,81 <sup>j</sup> <sup>2</sup>J<sub>Pt-H</sub>=83 <sup>k</sup> Ring substituents trans, <sup>2</sup>J<sub>Pt-H</sub>=80,90, δ=0.60ppm CHMe, no <sup>2</sup>J<sub>Pt-H</sub> data for this proton.

Table 11.  $^1\text{H}$  NMR chemical shift data (ppm) of pallada(II)- and platina(II)cyclobutanes.

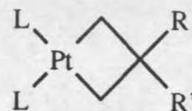
M	L	$\text{H}^\beta(^3J_{\text{Pt-H}})$	ref.
Pd	$\text{PPh}_3$	3.96	102
Pd	$\text{PPh}_2\text{Me}$	4.0	102
Pt	$\text{PEt}_3$	4.34(28)	102
Pt	$\text{PPh}_3$	4.38(38)	102
Pt	$\text{PPh}_2\text{Me}$	4.40(30)	102
Pt	$\text{PPhMe}_2$	4.49(26)	102
Pt	$\text{AsPh}_3$	4.39(44)	102

ligand is *t*-BuNC or bipy, the chemical shift value is 1.52 ppm and 1.29 ppm, respectively. A similar influence is observed in the 2,2-dimethylplatina(II)cyclobutanes and is explained best by the increased donating ability of the phosphorus ligands which pushes electron density into the carbon ring system, resulting in a more shielded proton environment and a lower chemical shift value.

The chlorine and bromine ligands coordinated to the platinum in the platina(IV)-cyclobutanes in Table 13 also influence the chemical shift of the  $\alpha$  protons. As illustrated, each platina(IV)cyclobutane bearing a bromine has an  $\alpha$  proton chemical shift slightly downfield of its chlorine analogue.

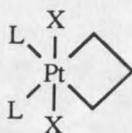
The effect of the ring substituents on the chemical shift value is a useful tool in determining the substituents position on the ring. This influence is illustrated for the

Table 12.  $^1\text{H}$  NMR chemical shift (ppm) and Pt-H coupling constant data (Hz) of platina(II)cyclobutanes.



L	R	R'	$\text{H}^\alpha(^2J_{\text{Pt-H}})$	$\text{H}^\beta(^3J_{\text{Pt-H}})$	$\text{Me}(^4J_{\text{Pt-H}})$	ref.
$\frac{1}{2}(\text{cod})$	Me	Me	1.19(108.8)	-	1.40(2.7)	177
$\frac{1}{2}(\text{bpy})$	H	H	1.29(115)	3.32(110)	-	175,176
t-BuNC	H	H	1.52 (80)	4.58 (90)	-	175
$\text{PPh}_3$	H	H	0.37 (88)	3.51(112)	-	175,176
$\text{PEt}_3$	H	H	0.35 (80)	3.75 (94)	-	175,176
$\text{PMe}_3$	H	H	0.47 (83)	3.74 (95)	-	175,176
$\text{P}(\text{C}_2\text{D}_5)_3$	Me	Me	0.73 (74)	-	-	117
$\text{PMe}_3$	Me	Me	0.88 (77.4)	-	1.57(5.0)	177
$\text{PEt}_3$	Me	Me	0.73 (75.1)	-	1.57(4.4)	177
$\text{P}(\text{i-Pr})_3$	Me	Me	0.86 (75.2)	-	1.49	121
$\text{PBu}_3$	Me	Me	0.85 (76.3)	-	1.56(4.1)	177
$\text{PCy}_3$	Me	Me	0.98 (75.1)	-	1.58	121
$\text{PPh}_3$	Me	Me	0.87 (84.5)	-	1.40(4.6)	177

Table 13.  $^1\text{H}$  NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of unsubstituted platina(IV)cyclobutanes.

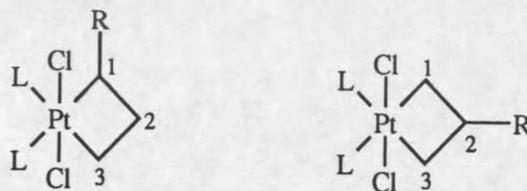


L	X	$\text{H}^\alpha(^2J_{\text{Pt-H}})$	$\text{H}^\beta(^3J_{\text{Pt-H}})$	ref.
py	Cl	2.64(83)	2.64	39,41
py	Br	2.80(88)	2.44	181
4-Mepy	Cl	2.58(83)	2.58	181
4-Mepy	Br	2.84(88)	2.61	181
$\text{NH}_3$	Cl	2.07(82)	2.40	181
$\text{NH}_3$	Br	2.44(81)	2.61	181
$\frac{1}{2}(\text{en})$	Cl	2.17(78)	2.40	181
$\frac{1}{2}(\text{en})$	Br	2.43(83)	2.43	181

platina(IV)cyclobutanes shown in Table 14. A drastic change occurs in the chemical shift value when a proton is bonded to a carbon bearing an alkyl or aryl substituent. For example, the  $\alpha$  proton chemical shift of a platina(IV)cyclobutane with a phenyl substituent changes from 4.93 ppm when the phenyl is also at the  $\alpha$  position to 2.97 ppm when the phenyl group is at the  $\beta$  position.

The identification of platinacyclobutanes is aided by the Pt-H coupling constants as shown in tables 12 through 17. This information is particularly useful in determining the position of ring substituents. For example, when a methyl group is located  $\alpha$  to the platinum the  $^3J_{\text{Pt-H}}$  coupling to the methyl protons ranges from 22-45 Hz (Table 14). However, if the methyl is found  $\beta$  to platinum the  $^4J_{\text{Pt-H}}$  coupling observed ranges from 4-8 Hz, making identification of isomers facile.

Table 14.  $^1\text{H}$  NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of monosubstituted platina(IV)cyclobutanes.



L	R	$\text{H}^\alpha(^2J_{\text{Pt-H}})$	$\text{H}^\beta(^3J_{\text{Pt-H}})$	$\text{Me}(J_{\text{Pt-H}})$	ref.
PY	1-Me	-	-	0.84(22)	71,74
PY	2-Me	2.67,3.02(79,81)	3.08	1.30(5)	71,74
PY	2-Et	2.49,2.80(78)	-	-	69
PY	2-i-Pr	2.69(90)	-	-	69
PY	2-n-Bu	2.73(80,82)	-	-	74
PY	2- $\text{CH}_2\text{OH}$	2.47,2.61(82.5,84.0)	3.06	-	77
PY	2- $\text{CHMeOH}$	2.64,2.74(84.8,85.0)	3.63	-	77
PY	2- $\text{CMe}_2\text{OH}$	2.57,2.87(80.8,84.6)	2.75	-	77
PY	2- $\text{CH}_2\text{OMs}$	2.36,2.58(81.5)	-	-	79
PY	2- $\text{CHMeOPNB}$	2.2-3.2	-	-	79
PY	2- $\text{CMe}_2\text{OPNB}$	2.54-3.02(80,77)	-	-	79
PY	1-Ph	4.93(101) <sup>a</sup>	-	-	75
PY	2-Ph	2.97(82)	4.05	-	62,71,75
PY	1-(p-MeC <sub>6</sub> H <sub>4</sub> )	4.93(102) <sup>a</sup>	2.95	-	62,75
		2.95(102) <sup>b</sup>	-	-	
PY	2-(p-MeC <sub>6</sub> H <sub>4</sub> )	3.00(80)	3.67	-	75
PY	1-(o-MeC <sub>6</sub> H <sub>4</sub> )	4.90 <sup>a</sup>	-	-	75

Table 14. (continued)

py	2-(o-MeC <sub>6</sub> H <sub>4</sub> )	2.97(80)	3.6	-	75
py	2-(CH <sub>2</sub> Ph)	2.97(81)	3.21	-	62,74
py	2-(n-C <sub>6</sub> H <sub>13</sub> )	2.42,2.75	3.75	-	62
py	2-(o-NO <sub>2</sub> Ph)	2.98(82)	4.56	-	62
py	1-(4-MeOC <sub>6</sub> H <sub>4</sub> )	5.03(100) <sup>a</sup>	-	-	75
py	2-(4-MeOC <sub>6</sub> H <sub>4</sub> )	2.96(83)	-	-	75
py	1-(4-EtOC <sub>6</sub> H <sub>4</sub> )	4.90(100) <sup>a</sup>	-	-	75
py	2-(4-EtOC <sub>6</sub> H <sub>4</sub> )	2.90(82)	3.65	-	75
2-Mepy	2-Ph	3.05(80)	3.60	-	75
3-Mepy	1-Me	-	-	0.60(22)	74
3-Mepy	2-Me	1.83,2.87(76,78)	2.83	1.15	74
4-Mepy	1-Me	4.88(100) <sup>a</sup>	-	0.68(22)	74,75
4-Mepy	2-Me	2.06,2.69(83,79)	2.72	1.00(7)	74
4-Mepy	2-Ph	2.94(81)	4.05	-	75
NH <sub>3</sub>	2-Me	-	-	0.95	74
CD <sub>3</sub> CN	1-Me	-	-	0.70(36)	71,74,80
CD <sub>3</sub> CN	2-Me	2.35,2.70	-	0.93(4)	71,74,80
CD <sub>3</sub> CN	2-Et	2.71	-	-	80
C <sub>4</sub> D <sub>8</sub> O	1-Me	-	-	0.46(45)	74
C <sub>4</sub> D <sub>8</sub> O	2-Me	2.36,2.78(109,108)	2.82	0.85(8)	74
C <sub>4</sub> D <sub>8</sub> O	1-Ph	5.17(113) <sup>a</sup>	-	-	75
C <sub>4</sub> D <sub>8</sub> O	2-Ph	3.10	-	-	75
C <sub>4</sub> D <sub>8</sub> O	1-(p-MeC <sub>6</sub> H <sub>4</sub> )	5.00(120) <sup>a</sup>	-	-	75
C <sub>4</sub> D <sub>8</sub> O	2-(p-MeC <sub>6</sub> H <sub>4</sub> )	3.07(80)	3.67	-	75
½(bipy)	2-CH <sub>2</sub> OMs	2.37,2.61(81.5,85)	-	-	79
½(tmed)	1-Me	-	2.6	0.62(26.0)	80
½(tmed)	2-Me	-	2.6	0.89(4.0)	80

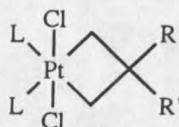
Table 14. (continued)

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½(tmed)	2-Et	-	2.25	-	80
½(tmed)	1-Ph	5.10(101) <sup>a</sup>	-	-	75
½(tmed)	2-Ph	3.43(84)	4.07	-	75
½(phen)	2-Me	2.44,2.72(79,81)	2.74	-	74

---

<sup>a</sup>PtCHR <sup>b</sup>PtCH<sub>2</sub>

Table 15.  $^1\text{H}$  chemical shift (ppm) and Pt-H coupling constant (Hz) data of 2,2-disubstituted platina(IV)cyclobutanes.

L	R	R'	$\text{H}^\alpha(^2J_{\text{Pt-H}})$	ref.
py	Me	Me	2.64(85.5)	69
py	Me	$\text{CH}_2\text{OMs}$	2.36(85)	79
py	Ph	$\text{CH}_2\text{OMs}$	2.95,3.23(85,86)	79
$\text{CD}_3\text{CN}$	Me	Me	2.54(96.0)	80
$\frac{1}{2}(\text{bipy})$	Ph	$\text{CH}_2\text{OMs}$	2.96,3.20(86.5,87)	79
$\frac{1}{2}(\text{tmed})$	Me	Me	2.40(84.0)	80
<u>complex</u>				
			2.72(82)	85
			2.71(85)	85
			2.61(84)	85
			3.17(88)	182

Table 16 illustrates the reported  $^1\text{H}$  NMR data of trans-1,2-disubstituted platina(IV)cyclobutanes. A few trans-1,3-disubstituted platina(IV)cyclobutanes also have been observed, however,  $^1\text{H}$  NMR data is reported only for the trans-1,3-p-tolyl-platina(IV)cyclobutane **41** shown below. In this example the  $\alpha$  protons at positions 1 and 3 have a chemical shift value of 5.29 ppm and  $^2J_{\text{Pt-H}}=102$  Hz. The chemical shift of the protons  $\beta$  to platinum are reported as 3.29 ppm<sup>73</sup>.

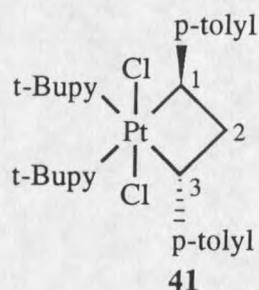


Table 18 reports the  $^1\text{H}$  NMR data of 1,2,3-trisubstituted platina(IV)cyclobutanes. Data also is reported for two 1,2,2-trimethylplatina(IV)cyclobutanes. In complex **42** the  $\alpha$  proton at the 1 position has a chemical shift value of 3.45 ppm. For the  $\alpha$  protons at the 3 position,  $\delta=2.67$  ppm<sup>69</sup>. For complex **43**, the  $\alpha$  proton at position 1 has a chemical shift of 3.27 ppm, while the chemical shift value of the  $\alpha$  protons at position 3 is reported as 2.43 ppm<sup>80</sup>.

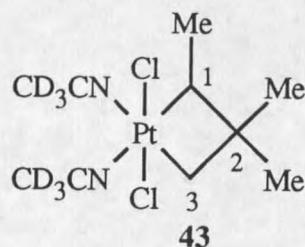
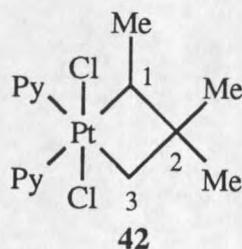
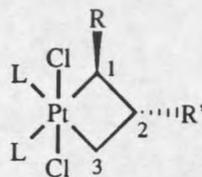


Table 16.  $^1\text{H}$  NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of trans-1,2-disubstituted platina(IV)cyclobutanes.



L	R	R'	$\text{H}^\alpha(^2J_{\text{Pt-H}})^a$	$\text{H}^\beta(^3J_{\text{Pt-H}})$	$\text{H}^{\alpha'}(^2J_{\text{Pt-H}})^b$	$\text{Me}(J_{\text{Pt-H}})$	ref.
py	Me	Me	2.98(88)	2.95	2.28,2.32(79.5)	0.58(22.8) <sup>c</sup> 0.94(7.2) <sup>d</sup>	73
py	Ph	Ph	5.12(98)	4.75	3.2(77,84.5)	-	62,73
py	Ph	Me	4.56(99)	-	2.67(80)	0.96	71,73
py	Me	Ph	-	-	-	0.61(24)	71,73
2-Mepy	Me	Me	-	-	-	0.40(32) <sup>c</sup> 0.83 <sup>d</sup>	73
t-Bupy	Ph	Ph	5.13(98)	4.78	3.26(80.5)	-	73
t-Bupy	p-tol	p-tol	5.11(97)	4.76	3.27(80.5)	-	73
PhCN	Me	Me	-	-	-	0.60(38) <sup>c</sup> 0.78 <sup>d</sup>	73
$\text{CD}_3\text{CN}$	Me	Me	-	-	-	0.60(37) <sup>c</sup> 0.73(14) <sup>d</sup>	73
$\frac{1}{2}(\text{phen})$	Me	Me	-	-	-	1.15(22) <sup>c</sup> 1.05 <sup>d</sup>	73

<sup>a</sup>  $\text{H}^\alpha$  is bonded to carbon labeled 1. <sup>b</sup>  $\text{H}^{\alpha'}$  is bonded to carbon labeled 3. <sup>c</sup> 1-Me <sup>d</sup> 2-Me

Table 17.  $^1\text{H}$  NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of cis-disubstituted platina(IV)cyclobutanes.

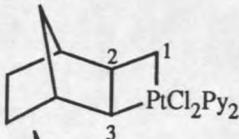
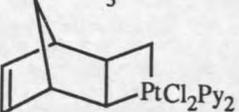
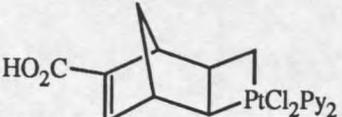
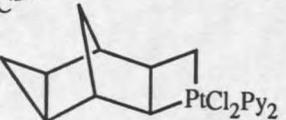
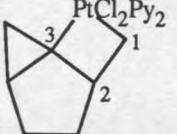
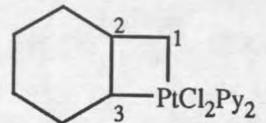
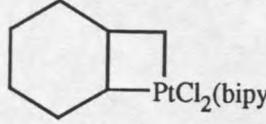
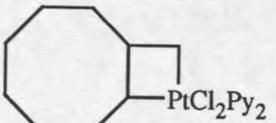
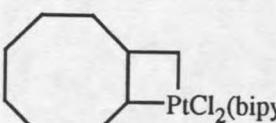
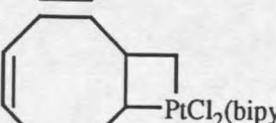
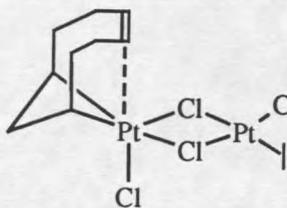
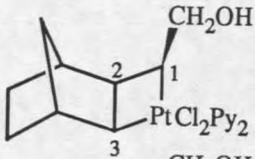
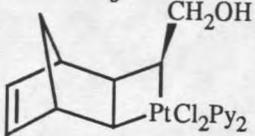
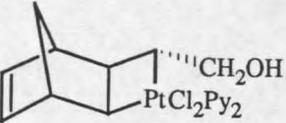
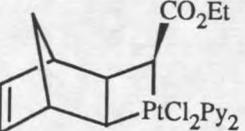
complex	$\text{H}^\alpha(^2J_{\text{Pt-H}})^a$	$\text{H}^\beta(^3J_{\text{Pt-H}})$	$\text{H}^{\alpha'}(^2J_{\text{Pt-H}})^b$	ref.
	2.47,2.51	2.77	2.74	76
	2.72,2.76	2.48	2.34	76
	2.8	2.7	2.5	97
	2.35	2.40	2.04	97
	2.55-2.65	2.93	2.79	183
	2.87,3.10(80,76)	3.05	-	95

Table 17. (continued)

	2.8,3.0	3.0	3.7(93)	89
	2.4,2.7(80,85)	3.1	3.3(92)	89
	2.5,2.66	2.7	3.6(96)	184
	2.4,2.6(91)	2.9	3.5(98)	184
	1.8-2.5,2.6(91)	3.15	3.6(95)	184
	1.28(108)	2.22-2.6,2.96(92)	—	184

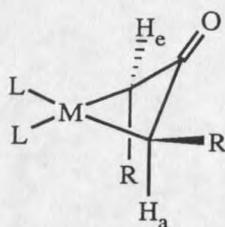
<sup>a</sup> H<sup>α</sup> is bonded to carbon labeled 1. <sup>b</sup> H<sup>α'</sup> is bonded to carbon labeled 3.

Table 18.  $^1\text{H}$  NMR chemical shift (ppm) data of 1,2,3-trisubstituted platina(IV)cyclobutanes.

complex	$\text{H}^{\alpha\text{ a}}$	$\text{H}^{\beta}$	$\text{H}^{\alpha'\text{ b}}$	ref.
	3.55	2.89	2.70	76
	3.90	2.45	2.52	76
	4.12	2.85	3.06	76
	5.16	2.80	2.85	76

<sup>a</sup>  $\text{H}^{\alpha}$  is bonded to carbon labeled 1. <sup>b</sup>  $\text{H}^{\alpha'}$  is bonded to carbon labeled 3.

Table 19. Low Temperature<sup>a</sup> <sup>1</sup>H NMR chemical shift (ppm) and Pt-H coupling constant (Hz) data of pallada(II)- and platina(II)cyclobutanones.



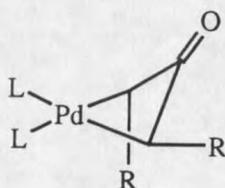
M	L	R	H <sup>axial</sup> ( <sup>2</sup> J <sub>Pt-H</sub> )	H <sup>equat</sup> ( <sup>2</sup> J <sub>PtH</sub> )	ref.
Pd	PPh <sub>3</sub>	CO <sub>2</sub> Me	4.54	3.71	156
Pd	PEt <sub>3</sub>	CO <sub>2</sub> Me	4.22	3.67	157
Pd	PPh <sub>2</sub> Me	CO <sub>2</sub> Me	4.36	3.78	157
Pd	PPhMe <sub>2</sub>	CO <sub>2</sub> Me	4.45	3.96	157
Pd	½(bipy)	CO <sub>2</sub> Me	4.49	3.67	157
Pd	AsPh <sub>3</sub>	CO <sub>2</sub> Me	4.48	4.00	157
Pt	PPh <sub>3</sub>	H	2.25(48.4)	2.01,2.25	162
Pt	PPh <sub>3</sub>	CO <sub>2</sub> Me	4.05(74)	3.24(23.8)	159
Pt	PPh <sub>3</sub>	COMe	4.53(49.9)	3.80(29.0)	159
Pt	AsPh <sub>3</sub>	CO <sub>2</sub> Me	4.02(83.2)	3.67(36.0)	159
Pt	AsPh <sub>3</sub>	COMe	4.52(81.2)	4.09(51.2)	159

<sup>a</sup>-50° to -100°C

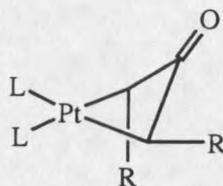
The reported <sup>1</sup>H NMR data for metallacyclobutanones is exhibited in Tables 19 through 22. Table 19 reports the <sup>1</sup>H NMR data of the α protons of pallada(II)- and platina(II)cyclobutanones. The puckered structure of these metallacyclic complexes causes the ring substituents at the two α positions to adopt an equatorial and an axial configuration. This in turn forces one α proton into an axial position while the other becomes equatorial. If the <sup>1</sup>H NMR data spectrum is collected at low temperatures it is possible to identify the individual chemical shifts of the axial and equatorial protons.

However, if the data is recorded at room temperature the peaks formed from these two non-equivalent protons become indistinguishable (Tables 20 and 21). This data is consistent with inversion of the ring through a planar structure causing rapid inter-conversion of protons.

Table 20.  $^1\text{H}$  NMR chemical shift data (ppm) of pallada(II)cyclobutanones.

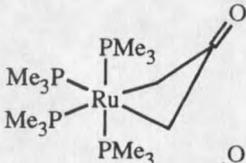
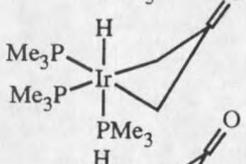
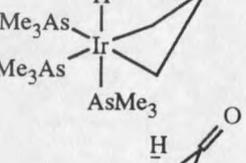
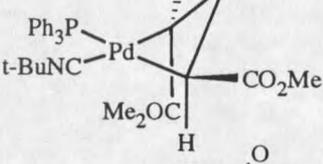
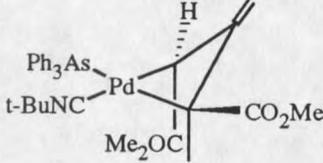
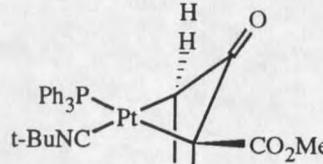
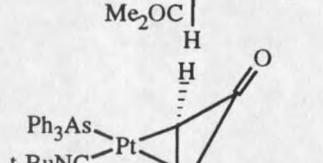


L	R	H $^{\alpha}$	ref.
PEt <sub>3</sub>	CO <sub>2</sub> Me	3.98	157
PEt <sub>3</sub>	Ph	3.87	163
PPh <sub>3</sub>	CO <sub>2</sub> Me	4.11	157
PPh <sub>3</sub>	CO <sub>2</sub> Et	4.09	157
PPh <sub>3</sub>	Ph	4.15	163
PPh <sub>2</sub> Me	CO <sub>2</sub> Me	4.00	157
PPhMe <sub>2</sub>	CO <sub>2</sub> Me	4.26	157
½(bipy)	CO <sub>2</sub> Me	4.07	157
½(bipy)	CO <sub>2</sub> Et	3.82	157
½(bipy)	CO <sub>2</sub> Pr <sup>n</sup>	3.86	157
½(dppe)	Ph	3.99	163
AsPh <sub>3</sub>	CO <sub>2</sub> Me	4.22	157
AsPh <sub>3</sub>	CO <sub>2</sub> Et	4.33	157

Table 21.  $^1\text{H}$  NMR chemical shift (ppm) and Pt-H coupling constant data (Hz) of platina(II)cyclobutanones.

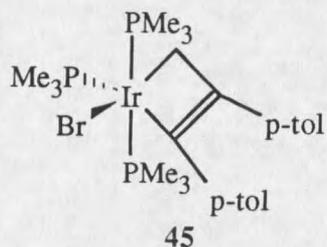
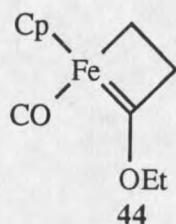
L	R	$\delta\text{H}^\alpha(^2J_{\text{Pt-H}})$	ref.
$\text{PPh}_3$	$\text{CO}_2\text{Me}$	3.73(54.17)	154
$\text{PPh}_3$	$\text{CO}_2\text{Et}$	3.90(52.2)	154
$\text{PPh}_3$	$\text{CO}_2\text{Pr}^n$	3.92(52.8)	154
$\text{PPh}_3$	$\text{COMe}$	4.20(47.8)	160
$\text{PPh}_3$	Ph	4.01(84.2)	163
$\text{PPh}_2\text{Me}$	$\text{CO}_2\text{Me}$	3.96(55.5)	154
$\text{PPhMe}_2$	$\text{CO}_2\text{Me}$	4.07(55.2)	154
$\frac{1}{2}(\text{dppe})$	$\text{CO}_2\text{Me}$	4.37(53.6)	154
$\text{AsPh}_3$	$\text{CO}_2\text{Me}$	4.16(71.64)	154
$\text{AsPh}_3$	$\text{CO}_2\text{Et}$	4.09(69.9)	154
$\text{AsPh}_3$	$\text{CO}_2\text{Pr}^n$	4.12(69.6)	154
$\text{AsPh}_3$	$\text{COMe}$	4.31(65.6)	160
$\text{AsPh}_3$	Ph	4.14(100.29)	163
$\frac{1}{2}(\text{cod})$	Ph	3.99(104.4)	163

Table 22.  $^1\text{H}$  NMR chemical shift (ppm) data of other metallacyclobutanones.

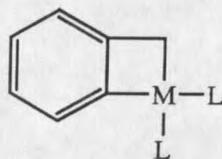
complex	$\text{H}^\alpha$	ref.
	1.54	185
	2.20,3.10	131
	2.49,3.10	131
	4.02 <sup>a</sup> ,4.62 <sup>b</sup>	158
	3.69,4.64	158
	3.69 <sup>a e</sup> ,4.46 <sup>b f</sup>	158
	3.90 <sup>c g</sup> ,4.44 <sup>d h</sup>	158

<sup>a</sup> equatorial proton trans to t-BuNC <sup>b</sup> axial proton trans to PPh<sub>3</sub> <sup>c</sup> equatorial proton trans to AsPh<sub>3</sub> <sup>d</sup> axial proton trans to t-BuNC <sup>e</sup>  $^2J_{\text{Pt-H}}=46.0$  <sup>f</sup>  $^2J_{\text{Pt-H}}=71.8$  <sup>g</sup>  $^2J_{\text{Pt-H}}=49.3$  <sup>h</sup>  $^2J_{\text{Pt-H}}=88.7$

Only two metallacyclobutene complexes have reported  $^1\text{H}$  NMR data. The data for the ferra(II)cyclobutene **44** reports a multiplet at 2.5-1.7 ppm assignable to the  $\text{CH}_2$  groups of the metallacyclic ring<sup>170</sup>. The data for the irida(III)cyclobutene **45** reports the chemical shift of the  $\alpha$  protons to be 1.16 ppm<sup>168</sup>.

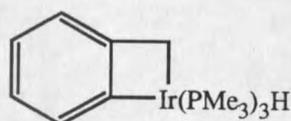


The reported  $^1\text{H}$  NMR data of metallacyclobutabenzenes is displayed in Table 23. The data for the Pt(II) and Ni(II) examples are indicative of the effect of the metal on proton chemical shifts.

Table 23.  $^1\text{H}$  NMR chemical shift (ppm) data of rhoda(III)-, irida(III)-, nickela(II)- and platina(II)cyclobutabenzenes.

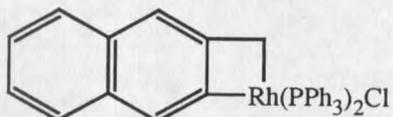
M	L	$\text{H}^\alpha$	ref.
Ni	$\text{PEt}_3$	0.41	112
Ni	$\text{PBu}^n_3$	0.38	112
Ni	$\text{PPh}_3$	0.55	112
Ni	$\frac{1}{2}(\text{tmed})$	-0.26	112
Pt	$\text{PMe}_3$	1.13 <sup>a</sup>	178
Pt	$\text{PMe}_3$	2.06 <sup>b</sup>	178
Pt	$\text{PEt}_3$	1.57 <sup>c</sup>	178
Pt	$\text{PPh}_3$	1.61	178

\_\_\_\_\_ complex

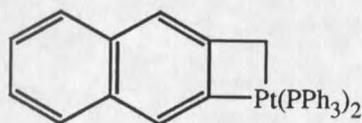


2.16

131

2.16<sup>d</sup>

115

1.23<sup>e</sup>

115

<sup>a</sup>  $^2J_{\text{Pt-H}}=67.9$  in  $d_8$ -dioxane <sup>b</sup> in  $d_6$ -benzene <sup>c</sup>  $^2J_{\text{Pt-H}}=78.3$  <sup>d</sup>  $^2J_{\text{Rh-H}}=3.9$  <sup>e</sup>  $^2J_{\text{Pt-H}}=79$

$^{13}\text{C}$  NMR Spectroscopy

Tables 24 through 33 display the reported  $^{13}\text{C}$  NMR chemical shift (ppm) and metal-carbon coupling constant (Hz) data (where applicable) for metallacyclobutane derivatives. Again, the data repeatedly confirms the utility of this form of spectroscopy in the characterization of metallacyclic complexes.

As was apparent in the reported  $^1\text{H}$  NMR data, the amount of  $^{13}\text{C}$  NMR data is largest for platina(IV)cyclobutanes. This information is particularly valuable for distinguishing between isomers of platina(IV)cyclobutanes. Table 26 depicts platina(IV)-cyclobutanes that are substituted at either the 1 or 2 position. It is apparent that three unique ring carbon peaks are present when the ring substituent is found at the 1 position whereas only two carbon ring resonances are observed, due to symmetry, when the substituent is located on the carbon  $\beta$  to the platinum. This pattern also is observed when 1,2- and 1,3-disubstituted isomers are present as shown in Table 27. The 1,2-disubstituted isomers give three unique ring carbon resonances while the 1,3-disubstituted isomers show two ring carbon resonances.

The Pt-C coupling constants observed in the spectra of platina(II)- and -(IV)cyclobutanes invoke further characterization of these complexes. The large coupling constant values are identified easily from the  $^{13}\text{C}$  NMR spectrum and facilitate complex identification. Tables 28 and 29 illustrate the characteristic Pt-C coupling constant values for a variety of norbornyl systems containing a platina(IV)cyclobutane moiety.

Table 24.  $^{13}\text{C}$  NMR chemical shift (ppm) data of ruthena(II)-, osmia(II)-, rhoda(III)-, irida(III)- and platina(II)cyclobutanes.

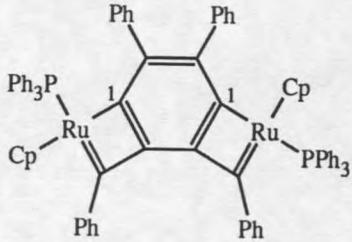
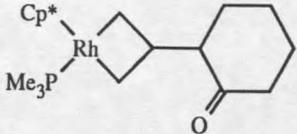
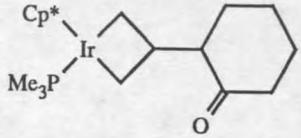
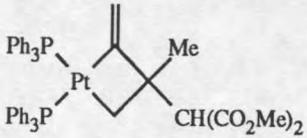
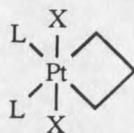
complex	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	ref.
	138.3	-	-	167
$(\text{CO})_4\text{Os}[\text{CH}_2\text{CH}_2\text{CH}_2]$	-38.01	39.04	-	174
$\text{Cp}^*(\text{PMe}_3)\text{Rh}[\text{CH}_2\text{CH}_2\text{CH}_2]$	-22.85	31.33	-	172
$\text{Cp}^*(\text{PMe}_3)\text{Rh}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	-23.1	43.21	-	172
$\text{Cp}^*(\text{PPh}_3)\text{Rh}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	-1.85	38.50	-	125
$\text{Cp}(\text{P}(i\text{-Pr})_3)\text{Rh}[\text{CHMeCH}_2\text{CH}_2]$	-30.9 <sup>a</sup>	43.9 <sup>a</sup>	-10.6 <sup>a</sup>	144
	-11 <sup>b</sup>	43.4	-11.5 <sup>b</sup>	137
$\text{Cp}^*(\text{C}_2\text{H}_4)\text{Ir}[\text{CH}_2\text{CH}_2\text{CH}_2]$	-31.7	31.3	-	142
$(\text{PMe}_3)_3\text{HfIr}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	-17.87	45.75	-	131
$(\text{AsMe}_3)_3\text{HfIr}[\text{CH}_2\text{CMe}_2\text{CH}_2]$	-20.96	47.28	-	131
$\text{Cp}^*(\text{C}_2\text{H}_4)\text{Ir}[\text{CH}_2\text{CH}(\text{CHMeC}(\text{O})\text{Ph})\text{CH}_2]^c$	-23.0	-	-24.1	142
$\text{Cp}^*(\text{C}_2\text{H}_4)\text{Ir}[\text{CH}_2\text{CH}(\text{CHMeC}(\text{O})\text{Ph})\text{CH}_2]^d$	-19.3	-	-20.7	142
$\text{Cp}^*(\text{PMe}_3)\text{Ir}[\text{CH}_2\text{CH}(\text{CHMeC}(\text{O})\text{Ph})\text{CH}_2]^d$	-28.6	-	-29.2	137

Table 24. (continued)

	-29.7	46.8	-30.3	137
(PPh <sub>3</sub> ) <sub>2</sub> Pt[C(CN) <sub>2</sub> CH <sub>2</sub> C(CN) <sub>2</sub> ]	-	48.1 <sup>e</sup>	-	181
(PMePh <sub>2</sub> ) <sub>2</sub> Pt[C(CN) <sub>2</sub> CH <sub>2</sub> C(CN) <sub>2</sub> ]	-	47.4 <sup>f</sup>	-	181
(AsPh <sub>3</sub> ) <sub>2</sub> Pt[C(CN) <sub>2</sub> CH <sub>2</sub> C(CN) <sub>2</sub> ]	-	54.7 <sup>g</sup>	-	181
(PPh <sub>3</sub> ) <sub>2</sub> Pt[CH <sub>2</sub> CH(CMe <sub>2</sub> COOMe)CH <sub>2</sub> ]	-7.3 <sup>h</sup>	50.8 <sup>h</sup>	-	139
(P(C <sub>6</sub> H <sub>11</sub> )) <sub>2</sub> Pt[CH <sub>2</sub> CH(CMe <sub>2</sub> COOMe)CH <sub>2</sub> ]	-10.2 <sup>i</sup>	51.2 <sup>i</sup>	-	139
(dppe)Pt[CH <sub>2</sub> CH(CHMeCOOMe)CH <sub>2</sub> ]	-8.7 <sup>j</sup>	47.4 <sup>j</sup>	-7.1	139
(PPh <sub>3</sub> ) <sub>2</sub> Pt[CH <sub>2</sub> C(Me)(CMe <sub>2</sub> COOMe)CH <sub>2</sub> ]	1.5 <sup>k</sup>	50.3 <sup>k</sup>	-	139
(PPh <sub>3</sub> ) <sub>2</sub> Pt[CH(Me)CH(CMe <sub>2</sub> COOMe)CH <sub>2</sub> ] <sup>l</sup>	-2.8 <sup>l</sup>	60.0 <sup>l</sup>	-10.3 <sup>l</sup>	139
(PPh <sub>3</sub> ) <sub>2</sub> Pt[CH(Me)CH(CMe <sub>2</sub> COOMe)CH <sub>2</sub> ] <sup>m</sup>	9.9	53.7 <sup>m</sup>	-6.8	139
	141.2 <sup>n</sup>	58.5 <sup>n</sup>	9.2 <sup>n</sup>	138

<sup>a</sup> Me is bonded to C<sup>1</sup>, <sup>1</sup>J<sub>Rh-C1</sub>=19.3, <sup>2</sup>J<sub>Rh-C</sub>=6.6, <sup>1</sup>J<sub>Rh-C3</sub>=19.5, <sup>b</sup> <sup>1</sup>J<sub>Rh-C</sub>=10.2, <sup>c</sup> Ring substituent is syn to Cp\*, <sup>d</sup> Ring substituent is anti to Cp\*, <sup>e</sup> <sup>2</sup>J<sub>Pt-C</sub>=160, <sup>f</sup> <sup>2</sup>J<sub>Pt-C</sub>=152, <sup>g</sup> <sup>2</sup>J<sub>Pt-C</sub>=202, <sup>h</sup> <sup>1</sup>J<sub>Pt-C</sub>=413, <sup>2</sup>J<sub>Pt-C</sub>=128, <sup>i</sup> <sup>1</sup>J<sub>Pt-C</sub>=430, <sup>2</sup>J<sub>Pt-C</sub>=128, <sup>j</sup> <sup>1</sup>J<sub>Pt-C</sub>=398, <sup>2</sup>J<sub>Pt-C</sub>=139, <sup>k</sup> <sup>1</sup>J<sub>Pt-C</sub>=415, <sup>2</sup>J<sub>Pt-C</sub>=116, <sup>l</sup> Ring substituents trans, Me is bonded to C<sup>1</sup>, <sup>1</sup>J<sub>Pt-C1</sub>=459, <sup>2</sup>J<sub>Pt-C</sub>=128, <sup>1</sup>J<sub>Pt-C3</sub>=420, <sup>m</sup> Ring substituents cis, Me is bonded to C<sup>1</sup>, <sup>2</sup>J<sub>Pt-C</sub>=130, <sup>n</sup> Methylene is bonded to C<sup>1</sup>, <sup>2</sup>J<sub>Pt-C</sub>=130, <sup>1</sup>J<sub>Pt-C3</sub>=437.5

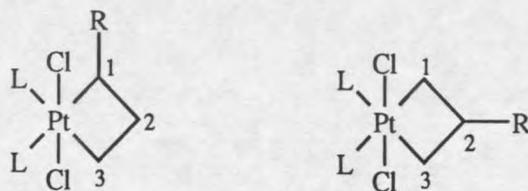
Table 25.  $^{13}\text{C}$  NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data of unsubstituted platina(IV)cyclobutanes.



L	X	$C^1(^1J_{\text{Pt-C}})$	$C^2(^2J_{\text{Pt-C}})$	ref.
py	Cl	-15.2(335)	30(105)	181
py	Br	-17.9(325)	30.4(110)	181
4-Mepy	Cl	3.77(338)	29.9(105)	181
4-Mepy	Br	-18.5(323)	30.5(103)	181
$\frac{1}{2}(\text{en})$	Cl	-18.9(332)	29.6(108)	181
$\frac{1}{2}(\text{en})$	Br	-21.4(317)	30.4(105)	181

Pallada(II)- and platina(II)cyclobutanones also exhibit characteristic  $^{13}\text{C}$  NMR data as demonstrated in Table 30. Two ring carbon resonances are observed. The chemical shift values range from 48.8 ppm to 67.06 ppm for  $C^1$  and from 171.21 ppm to 183.8 ppm for  $C^2$ . The substituent, R, seemingly has the greatest effect on the peak location. The  $^{13}\text{C}$  NMR data of other metallacyclobutanones is shown in Table 31. Notice that the pallada(II)- and platina(II)cyclobutanes found in Table 31 have two different ligands coordinated to the metal, therefore making the  $\alpha$  ring carbons non-equivalent and resulting in three unique carbon resonances.

Table 26.  $^{13}\text{C}$  NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data of monosubstituted platinum(IV)cyclobutanes.



L	R	$C^1(^1J_{\text{Pt-C}})$	$C^2(^2J_{\text{Pt-C}})$	$C^3(^1J_{\text{Pt-C}})$	ref.
py	1-Me	5.65	45.2	-8.0	71,74
py	2-Me	1.0(344)	42.6(98)	-	71,74
py	1-Bu	11.8	-	-7.9	74
py	2-Bu	-5.2(344)	43.4(95)	-	71,74
py	2-CH <sub>2</sub> OH	-11.3(350.1)	45.6(99.1)	-	77
py	2-CHMeOH	-11.1(351.0)	51.1(96.2)	-10.5(349.2)	77
py	2-CMe <sub>2</sub> OH	-10.5(352.3)	54.1(94.1)	-	77
py	2-CH <sub>2</sub> CO <sub>2</sub> Me	-7.64(349.2)	39.13(101.5)	-	76
py	1-CH <sub>2</sub> COMe	3.2(351)	30.5(107)	-10.4(328)	98
py	2-CH <sub>2</sub> COMe	-12.5(364)	55.9(103)	-	98
py	2-CH <sub>2</sub> OMs	-13.7(356)	42.1(104)	-	78,79
py	2-CHMeOPNB	-11.6(358)	48.5(101)	-10.6(355)	79
py	2-CMe <sub>2</sub> OPNB	-9.8(361)	54.8(97.5)	-	79
py	1-Ph	5.6(326)	35.1(112)	-11.3(354)	68,75
py	2-Ph	-4.9(369)	48.1(100.5)	-	68,75
py	1-(p-MeC <sub>6</sub> H <sub>4</sub> )	5.80(323)	35.3(112)	-11.5(366)	75
py	2-(p-MeC <sub>6</sub> H <sub>4</sub> )	-4.30(370)	47.8(99)	-	75

Table 26. (continued)

py	1-(4-EtOC <sub>6</sub> H <sub>4</sub> )	5.75(320)	35.5(115)	-11.9(360)	75
py	2-(4-EtOC <sub>6</sub> H <sub>4</sub> )	-4.30(360)	46.97(105)	-	75
py	2-NH <sub>2</sub>	-11.6(466)	60.4(107.7)	-	81
4-Mepy	1-Ph	4.29(330)	37.6(114)	-11.8(372)	75
4-Mepy	2-Ph	-5.13(358)	48.11(99)	-	75
½(bipy)	2-CH <sub>2</sub> OMe	-12.4(357)	55(99)	-	98
½(tmed)	1-Ph	7.15(329)	38.0(112)	-7.6(359)	75
½(tmed)	2-Ph	-3.10(370)	-	-	75
C <sub>4</sub> D <sub>8</sub> O	1-Me	5.5	40.6	-12.8	74
C <sub>4</sub> D <sub>8</sub> O	2-Me	-5.1(398)	37.6(109)	-	74
C <sub>4</sub> D <sub>8</sub> O	1-(p-MeC <sub>6</sub> H <sub>4</sub> )	6.07(397)	34.9(127)	-13.9(429)	75
C <sub>4</sub> D <sub>8</sub> O	2-(p-MeC <sub>6</sub> H <sub>4</sub> )	-7.57(418)	47.0(111)	-	75

complex

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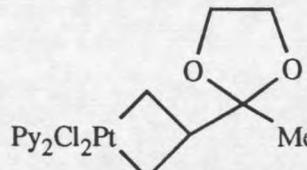
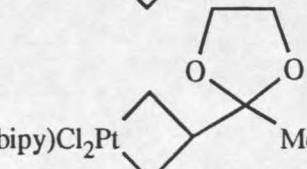
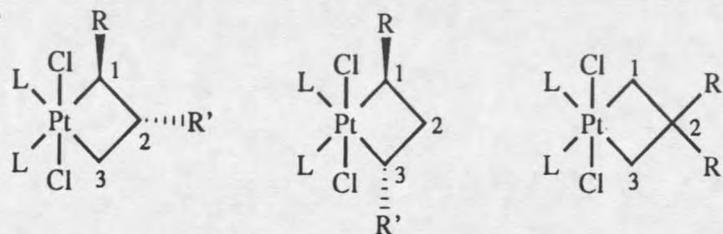
	-10.6(349)	50.5(95)	-	98
	-12.5(358)	49.7(98)	-	98

Table 27.  $^{13}\text{C}$  NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data for trans-1,2-disubstituted, trans-1,3-disubstituted, and 2,2-disubstituted platina(IV)cyclobutanes.



L	R	R'	$C^1(^1J_{\text{Pt-C}})$	$C^2(^2J_{\text{Pt-C}})$	$C^3(^1J_{\text{Pt-C}})$	ref.
py	1-Me	2-Me	10.9(336)	46.4(98)	-2.6(347)	73
py	1-Me	2-Ph	10.6(360)	57.5(100)	-2.9(370)	71,73
py	1-Ph	2-Me	16.9(333)	41.2(103)	-0.2(263.5)	71,73
t-Bupy	1-Ph	2-Ph	15.1(343)	50.6(105)	-1.8(377)	71,73
t-Bupy	1-(p-tolyl)	2-(p-tolyl)	15.7(341)	50.5(105)	-1.6(383)	71,73
t-Bupy	1-Ph	3-Ph	6.05(340)	41.2(130)	-	71,73
t-Bupy	1-(p-tolyl)	3-(p-tolyl)	6.3(338)	41.6(125)	-	71,73
py	2-Me	2-CH <sub>2</sub> OH	-3.0(355.7)	48.7(92.2)	-	77
py	2-Me	2-CH <sub>2</sub> OMs	-4.9(361)	46.9(95)	-	79
py	2-Ph	2-CH <sub>2</sub> OMs	-6.7(367)	56.0(90)	-	79
			-4.65(376)	60.9(95)	-	182

Table 28.  $^{13}\text{C}$  NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data for cis-disubstituted platina(IV)cyclobutanes.

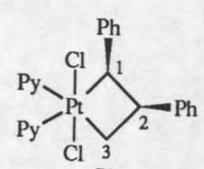
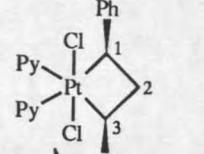
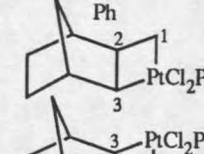
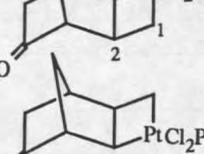
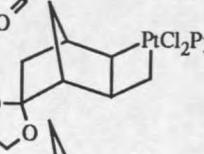
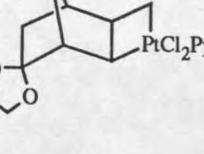
complex	$\text{C}^1(^1J_{\text{Pt-C}})$	$\text{C}^2(^2J_{\text{Pt-C}})$	$\text{C}^3(^1J_{\text{Pt-C}})$	ref.
	14.9(353.4)	51.7(109.93)	-8.6(364.4)	94
	10.5(347.2)	39.5(116.6)	-	94
	-12.1(352)	55.6(95)	12.4(391)	183
	-13.56(362)	47.16(100)	5.20(412)	93
	-10.65(351.5)	52.71(98.3)	-2.21(429.3)	93
	-12.9(355.8)	54.0(97.6)	9.5(399.3)	93
	-11.2(352.3)	47.8(98.4)	2.7(408.2)	93

Table 28. (continued)

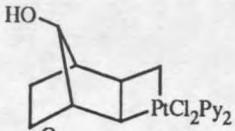
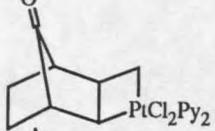
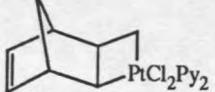
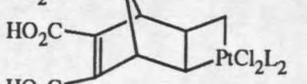
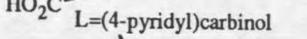
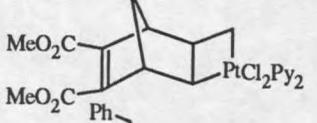
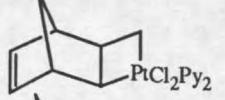
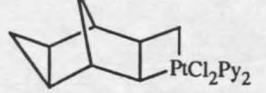
	-12.1(352)	53.9(95)	9.2(391)	81
	-12.3(351)	51.1(99)	2.7(405)	81
	-2.2(371)	51.4(83)	10.7(403)	87
	-3.7(366)	51.25(90)	5.8(422)	76
	-5.54(345)	51.6(87.4)	7.23(383)	76
	-3.6(373.3)	52.3(85.0)	5.9(423.2)	97
				
	-3.8(387)	51.0	5.85(430)	76
	-2.5(374.6)	52.1(84.2)	10.7(406.2)	92
	-12.1(352)	55.6(95)	12.4(391)	79,88

Table 28. (continued)

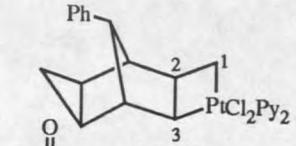
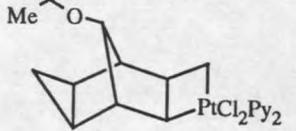
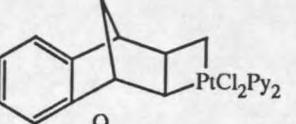
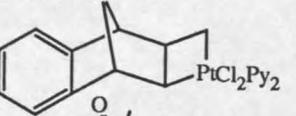
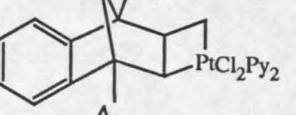
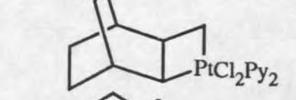
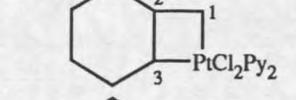
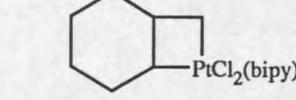
	-8.6(363.0)	57.3(95.3)	13.7(398.6)	92
	-8.6(359)	54.9(95)	8.1(406)	81
	-5.7(365)	56.6(97)	10.1(408)	76
	-6.39(364)	52.36(96)	5.37(440)	76
	-8.63(361)	58.0(94)	13.7(444)	81
	-12.9(352)	49.3(94)	11.9(387)	92
	-8.6(354)	44.6(98)	5.8(369)	88
	-7.7(342)	42.8(92)	5.2(366)	89

Table 28. (continued)

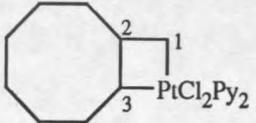
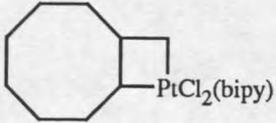
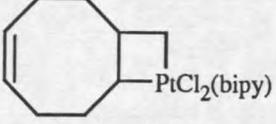
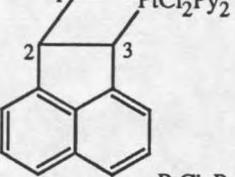
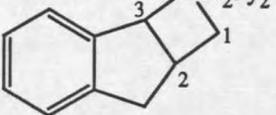
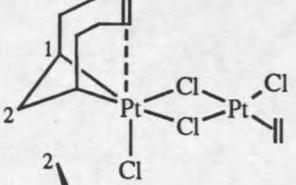
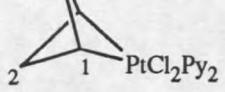
	-7.2(351)	48.6(85)	14.2(348)	88
	-6.7(364)	47.4(85)	13.3(342)	184
	-6.1(361)	47.8(82)	12.5(345)	88
	-4.99(366.2)	55.06(106.9)	5.28(363.5)	94
	-4.71(348.7)	48.23(102.4)	10.71(354.9)	94
	29.6(338)	36.8(100)	-	66
	19.7(621)	45.6	-	90

Table 29.  $^{13}\text{C}$  NMR chemical shift (ppm) and Pt-C coupling constant (Hz) data for 1,2,3-trisubstituted platina(IV)cyclobutanes.

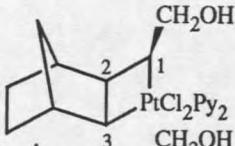
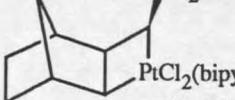
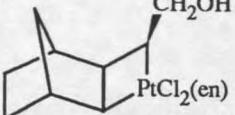
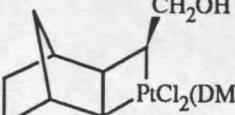
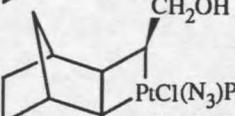
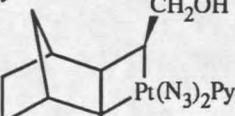
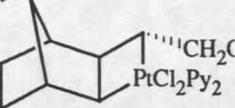
complex	$\text{C}^1(^1J_{\text{Pt-C}})$	$\text{C}^2(^2J_{\text{Pt-C}})$	$\text{C}^3(^1J_{\text{Pt-C}})$	ref.
	6.36(370)	56.7(98)	13.0(394)	96
	1.83(363.0)	56.5(95.7)	9.8(396.1)	97
	1.9(366.2)	56.3(99.2)	7.1(391.3)	97
	4.46(366)	56.5(98)	10.6(394)	81
	2.4(392)	55.7(101)	11.0(421)	81
	1.7(424)	53.5(109)	10.6(451)	81
	4.05(370)	59(98)	14.4(398)	96

Table 29.(continued)

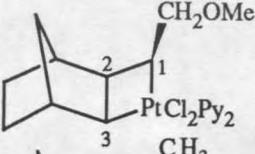
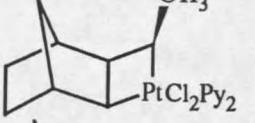
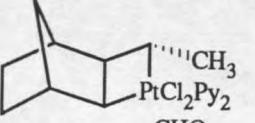
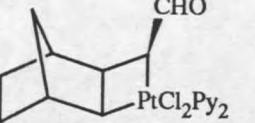
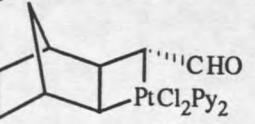
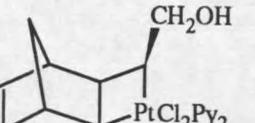
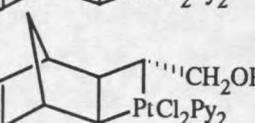
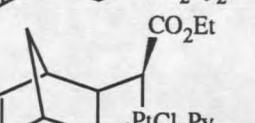
	.5(373)	57.5(97)	13.7(394)	81
	1.33(351)	59.16(97)	12.07(401)	92
	1.40(355)	64.49(97)	12.9(394)	92
	4.35(352)	55.6(106)	15.2(380)	92
	4.8(348)	53.9(103)	15.7(377)	92
	15.8(394)	52.72(86.1)	11.14(405)	76
	14.6(392)	54.24(81.3)	12.45(404)	76
	3.0(406)	53.2(87)	3.3(394)	76

Table 29. (continued)

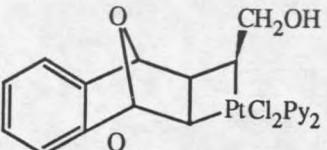
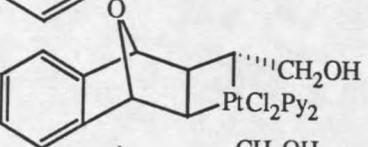
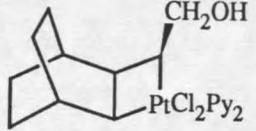
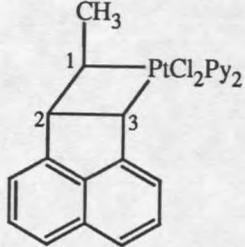
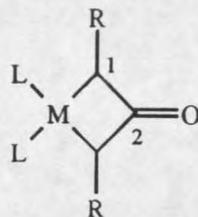
	12.3(400)	54.1(104)	6.1(450)	76
	11.2(396)	55.8(104)	7.9(458)	76
	11.0(371)	52.1(96)	11.3(395)	81
	6.38(385.8)	64.02(105.7)	10.73(372.7)	94

Table 30.  $^{13}\text{C}$  NMR chemical shift (ppm) and Pt-C coupling constant data for pallada(II)- and platina(II)cyclobutanones.



M	L	R	$C^1(^1J_{\text{Pt-C}})$	$C^2(^2J_{\text{Pt-C}})$	ref.
Pd	$\text{PPh}_3$	$\text{CO}_2\text{Me}$	61.82	174.42	157
Pd	$\text{PPh}_2\text{Me}$	$\text{CO}_2\text{Me}$	59.26	171.21	157
Pd	$\text{PPhMe}_2$	$\text{CO}_2\text{Me}$	57.34	175.52	157
Pt	$\text{PPh}_3$	$\text{CO}_2\text{Me}$	56.43(273.9)	178.30(175.5)	154
Pt	$\text{PPh}_3$	$\text{COMe}$	67.06(246.9)	176.17(173.7)	160
Pt	$\text{PPh}_3$	Ph	67.07(242.4)	173.2(155)	163
Pt	$\text{PPh}_3$	H	49.6(251.5)	183.8	162
Pt	$\text{PPh}_2\text{Me}$	$\text{CO}_2\text{Me}$	54.84(245)	179.73(170)	154
Pt	$\text{PPhMe}_2$	$\text{CO}_2\text{Me}$	53.24(229.3)	179.00(171)	154
Pt	$\frac{1}{2}(\text{dppe})$	$\text{CO}_2\text{Me}$	54.89(231.0)	178.47(161)	154
Pt	$\text{AsPh}_3$	$\text{CO}_2\text{Me}$	51.21(313.9)	179.26(195)	154
Pt	$\text{AsPh}_3$	$\text{COMe}$	63.28(298.1)	179.08(196.3)	160
Pt	$\text{AsPh}_3$	Ph	61.52(308.4)	174.39	163
Pt	$\frac{1}{2}(\text{cod})$	Ph	63.28(351.7)	178.6	163

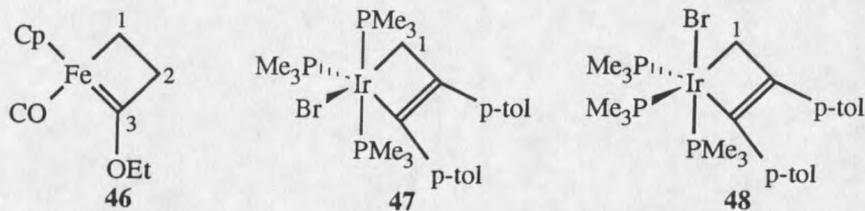
Table 31.  $^{13}\text{C}$  NMR chemical shift (ppm) data of other metallacyclobutanones.

complex	$\text{C}^1$	$\text{C}^2$	$\text{C}^3$	ref.
	29.13	184.0	-	185
	12.32	185.06	-	131
	56.9 <sup>a</sup>	175.2	55.7 <sup>b</sup>	158
	51.3 <sup>a c</sup>	179.6 <sup>c</sup>	51.0 <sup>b c</sup>	158
	48.8 <sup>a d</sup>	179.8 <sup>d</sup>	48.2 <sup>b d</sup>	158

<sup>a</sup>  $\text{C}^1$  is trans to t-BuNC <sup>b</sup>  $\text{C}^3$  is cis to t-BuNC <sup>c</sup>  $^1J_{\text{Pt-C}^1}=293$ ,  $^2J_{\text{Pt-C}}=177$ ,  $^1J_{\text{Pt-C}^3}=216.5$  <sup>d</sup>  $^1J_{\text{Pt-C}^1}=288.8$ ,  $^2J_{\text{Pt-C}}=189.4$ ,  $^1J_{\text{Pt-C}^3}=267.7$

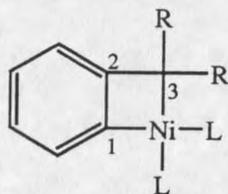
$^{13}\text{C}$  NMR chemical shift data for metallacyclobutenes of iron(II) and iridium(III) has been reported and is shown below. Complex **46** reports 61.6 ppm, 56.8 ppm, and 335 ppm for carbons labeled 1, 2 and 3 respectively. Compounds **47** and **48** report the

chemical shift for their respective  $C^1$  labeled carbons at -17.96 ppm and -8.76 ppm.



A number of nickela(II)cyclobutabenzenes have been characterized by their  $^{13}C$  NMR spectra. Table 32 exhibits this data while table 33 displays the  $^{13}C$  NMR data for other metallacyclobutabenzenes.

Table 32.  $^{13}C$  NMR chemical shift (ppm) data for nickela(II)cyclobutabenzenes.



L	R	$C^1$	$C^2$	$C^3$	ref.
PEt <sub>3</sub>	H	134.7	160.5	-6.3	112
PBu <sub>3</sub>	H	134.2	160.7	-7.1	112
PPh <sub>3</sub>	H	134.5	158.0	0.5	112
½(tmed)	H	128.6	159.1	-17.1	112
½(tmed)	SiMe <sub>3</sub>	115.5	159.8	-17.1	114
PMe <sub>3</sub>	SiMe <sub>3</sub>	127.3	162.7	-3.29	114
½(dcpe)	SiMe <sub>3</sub>	127.5	161.6	-1.68	114
½(dppe)	SiMe <sub>3</sub>	125.3	162.0	0.93	114
½(TEED)	SiMe <sub>3</sub>	113.8	158.9	-17.3	114
½(PMDTA)	SiMe <sub>3</sub>	113.8	159.5	-16.5	114
½(bipy)	SiMe <sub>3</sub>	119.0	159.6	-8.67	114

Table 33.  $^{13}\text{C}$  NMR chemical shift (ppm) data of other metallacyclobutabenzenes.

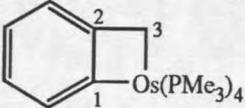
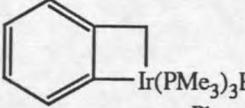
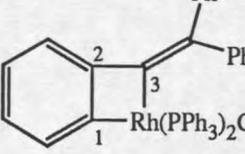
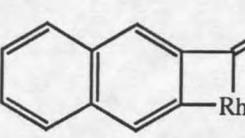
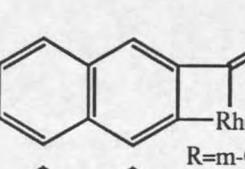
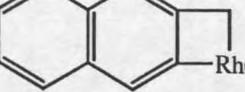
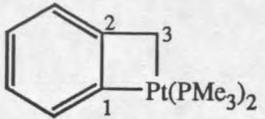
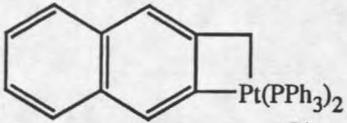
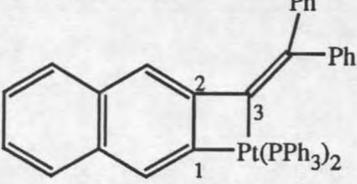
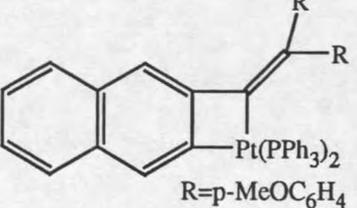
complex	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	ref.
	-	168.3	-16.5	130
	-	-	-7.15	131
	119.9, 112.3 <sup>a</sup> 124.08	156.70 <sup>a</sup>	117.7 <sup>a</sup>	116
	-	154.83 <sup>b</sup>	117.0 <sup>b</sup>	116
	-	141.72, 145.10 <sup>c</sup> 153.59	166.67 <sup>c</sup>	116
	-	150.0 <sup>d</sup>	-2.9 <sup>d</sup>	115

Table 33. (continued)

	-	-	-9.9 <sup>e</sup>	178
	-	-	-3.21	115
	147.26 <sup>f</sup>	165.64 <sup>f</sup>	113.84 <sup>f</sup>	116
	139.68	166.06	-	116

89

<sup>a</sup> Assignments for C<sup>1</sup> and C<sup>3</sup> may be interchanged, <sup>1</sup>J<sub>Rh-C1</sub>=21.0, <sup>2</sup>J<sub>Rh-C</sub>=3.9, <sup>1</sup>J<sub>Rh-C3</sub>=28.2 <sup>b</sup><sup>2</sup>J<sub>Rh-C</sub>=3.8, <sup>1</sup>J<sub>Rh-C3</sub>=28.7 <sup>c</sup><sup>2</sup>J<sub>Rh-C</sub>=3.3, <sup>1</sup>J<sub>Rh-C3</sub>=28.6 <sup>d</sup><sup>2</sup>J<sub>Rh-C</sub>=6.3, <sup>1</sup>J<sub>Rh-C3</sub>=21 <sup>e</sup><sup>1</sup>J<sub>Pt-C3</sub>=395 <sup>f</sup><sup>1</sup>J<sub>Pt-C1</sub>=86, <sup>2</sup>J<sub>Pt-C</sub>=65, <sup>1</sup>J<sub>Pt-C3</sub>=81

### X-ray Crystallographic Analysis

X-ray structure determinations have been performed on relatively few metallacyclobutane derivatives. Tables 34 through 43 display the bond length and bond angle data for the metallacyclobutane moiety of the reported structures. The written structures are all in a  $M[C_1C_2C_3]$  format, while the drawn structures are labeled appropriately. These data consistently support a metallacyclobutane structure as opposed to an edge bound cyclopropane. The reported  $C_1-C_3$  distance, ranging from 2.37 Å to 2.60 Å, most convincingly discards the notion that the cyclopropane ring remains intact and is bound edgewise to the metal species. Even a lengthening due to polarization can not explain this increase over the respective free cyclopropane bond distances of 1.501 Å to 1.524 Å.

Tables 38 and 39 include the bond lengths and bond angles of structurally characterized metallacyclobutanones. The most notable feature of these complexes is the large pucker angle, i.e. dihedral angle formed between the planes derived from  $C_1-M-C_3$  and  $C_1-C_2-C_3$ , which ranges from  $41^\circ$  to  $56.7^\circ$ . Organic cyclobutanones are only slightly nonplanar with dihedral angles of  $0-10^\circ$ . Therefore, the significant puckering of metallacyclobutanones has been attributed to a considerable transannular attraction between the metal and  $C_2$  carbonyl group which shortens the  $M-C_2$  distance substantially. In fact, the extent of non-planarity and the decreased  $M-C_2$  bond distance has led investigators to suggest that the bonding description of these molecules should include contribution from an  $\eta^3$ -allyl metal species **30** shown previously on page 39.

The dihedral angle of platina(II)- and (IV)cyclobutanes found in Table 37 ranges from  $0.0^\circ$  to  $29.7^\circ$ . The formation of the planar structures are attributed to the bidentate

bipyridyl ligand coordinated to the metal in entries numbered 11 and 19. The most highly puckered platina(II)- and (IV)cyclobutanes, entries 14, 15 and 17, each have a phenyl substituent at the  $C_2$  position suggesting a possible transannular attraction between the metal and the phenyl bearing carbon, albeit smaller than found in the metallacyclobutanones described above.

A few structures of metallacyclobutenes and metallacyclobutabenzenes also have been determined and their data is reported in Tables 40 through 43. The data is consistent with a metallacyclic structure and shows a considerable shortening of the olefinic  $C_1-C_2$  bond as expected.

Table 34. Bond length data (Å) for ferra(II)-, ruthena(II), cobalta(II)-, rhoda(III)-, irida(III)- and nickela(II)cyclobutanes.

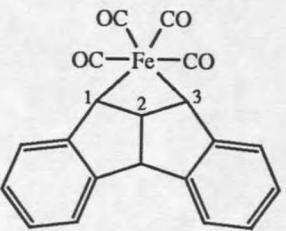
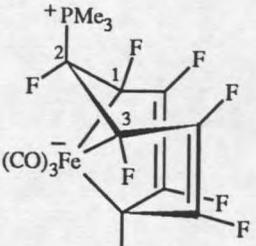
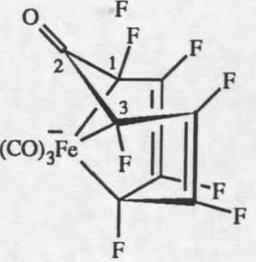
complex	#	M-C <sub>1</sub>	M-C <sub>2</sub>	M-C <sub>3</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>
	1	2.141	2.691	2.137	1.524	1.527 <sup>a</sup>
	2	2.013	-	2.006	1.536	1.519
	3	2.039	-	2.036	1.486	1.492
( $\eta^6$ -C <sub>6</sub> Me <sub>6</sub> )(PPh <sub>3</sub> )Ru[CH <sub>2</sub> CMe <sub>2</sub> CH <sub>2</sub> ]	4	2.133	-	2.144	1.537	-
( $\eta^5$ -C <sub>6</sub> Me <sub>6</sub> )(PPh <sub>2</sub> Me)Ru[CH <sub>2</sub> CMe <sub>2</sub> CH <sub>2</sub> ]	5	2.156	-	2.133	1.546	-

Table 34. (continued)

	6	2.051 2.062 <sup>b</sup>	- -	1.997 1.982	1.41 1.411	1.432 1.44
	7	1.993	-	1.986	1.525	1.526
(Cp*)(PMe <sub>3</sub> )Rh[CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ]	8	2.085	-	2.085	1.512	1.527
	9	2.126	-	2.114	1.539	1.531
	10	1.995	-	-	1.527	-

<sup>a</sup> C<sub>1</sub>-C<sub>3</sub>=2.421 <sup>b</sup> This row designates the carbons labeled prime.

Table 35. Bond angle data (°) for ferra(II)-, ruthena(II)-, cobalta(II)-, rhoda(III)-, irida(III)- and nickela(II)cyclobutanes.

#	C <sub>1</sub> -M-C <sub>3</sub>	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	M-C <sub>1</sub> -C <sub>2</sub>	M-C <sub>3</sub> -C <sub>2</sub>	dihedral <sup>a</sup>	ref.
1	68.9	105.0	93.0	93.0	0.0	186
2	-	-	-	-	-	153
3	-	-	-	-	-	153
4	65.8	-	96.6	-	0.052	127
5	66.8	-	95.4	-	0.053	127
6	64.8 <sup>b</sup>	-	-	-	-	167
7	72.87	-	-	-	4.1	151
8	67.61	99.55	96.24	96.59	0.0	135,172
9	66.3	98.1	94.2	94.9	-	137
10	-	72.98	99.2	-	5.5	150

<sup>a</sup> The angle formed between the planes of C<sub>1</sub>-M-C<sub>3</sub> and C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> <sup>b</sup> Angle of atoms labeled prime is also 64.8°.

Table 36. Bond length (Å) data for platina(II)- and platina(IV)cyclobutanes.

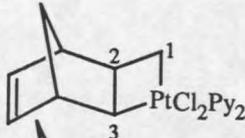
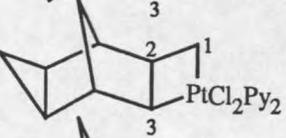
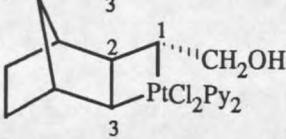
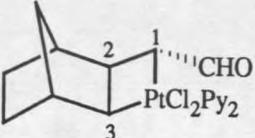
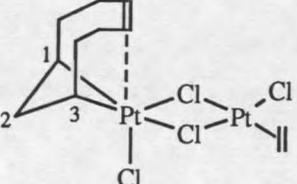
complex	#	M-C <sub>1</sub>	M-C <sub>2</sub>	M-C <sub>3</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>	C <sub>1</sub> -C <sub>3</sub>
(bipy)Pt[CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ]	11	2.030	2.665	2.037	1.534	1.534	-
(PEt <sub>3</sub> ) <sub>2</sub> Pt[CH <sub>2</sub> CMe <sub>2</sub> CH <sub>2</sub> ]	12	2.080	2.698	2.086	1.535	1.536	-
(PPh <sub>3</sub> ) <sub>2</sub> Pt[C(CN) <sub>2</sub> CH <sub>2</sub> C(CN) <sub>2</sub> ]	13	2.137	2.71	2.139	1.545	1.584	2.404
(PPh <sub>3</sub> ) <sub>2</sub> Pt[C(CN) <sub>2</sub> CH(Ph)C(CN) <sub>2</sub> ]	14	2.14	2.69	2.16	1.56	1.55	2.39
(PPh <sub>2</sub> ) <sub>2</sub> Pt[C(CN) <sub>2</sub> CH(Ph)C(CN)- CO <sub>2</sub> Et]	15	2.16	2.69	2.20	1.56	1.51	2.40
Cl <sub>2</sub> Py <sub>2</sub> Pt[CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ]	16	2.04	2.69	2.19	1.48	1.82	2.55
Cl <sub>2</sub> Py <sub>2</sub> Pt[CH(Ph)CH(Ph)CH <sub>2</sub> ] <sup>a</sup>	17	2.06	2.60	2.11	1.59	1.48	2.39
		2.05	2.62	2.17	1.59	1.71	2.60
Cl <sub>2</sub> Py <sub>2</sub> Pt[CH <sub>2</sub> C(Me)(CH <sub>2</sub> OH)CH <sub>2</sub> ]	18	2.042	2.676	2.039	1.542	1.548	-
Cl <sub>2</sub> (bipy)Pt[CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ]	19	2.07	-	-	1.63	-	-
	20	2.057	-	2.093	1.625	1.546	-
	21	2.011	-	2.097	1.587	1.547	-
	22	2.074	-	2.054	1.535	1.537	-

Table 36. (continued)

	23	2.071	-	2.074	1.532	1.528	-
	24	1.97	-	2.05	-	-	2.37

<sup>a</sup> Phenyl groups are trans to one another. Two independent molecules are present within the unit cell.

Table 37. Bond angle ( $^{\circ}$ ) data for platina(II)- and platina(IV)cyclobutanes.

#	$C_1-M-C_3$	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral <sup>a</sup>	ref.
11	69.9	98.8	95.5	-	0.0	175,176
12	67.3	97.5	95.4	95.1	22.4	119
13	68.4	100.4	93.5	92.3	24.4	103
14	67.7	100.9	92.3	-	28.6	101
15	66.9	103.2	91.2	-	29.7	101
16	74.2	100.9	99.3	84.3	12.5	41
17	70	102	90	91	28	187
	76	104	91	84	22	
18	70.15	98.75	95.55	95.54	1.0	79
19	71.9	96.2	96.0	-	0.0	175
20	70.0	97.3	94.7	95.7	-	188
21	69.8	97.2	96.7	94.6	-	188
22	68.8	98.8	94.8	95.5	-	96
23	68.7	99.8	94.7	-	-	92
24	-	-	-	-	11.0	66

<sup>a</sup> The angle formed between the planes of  $C_1-M-C_3$  and  $C_1-C_2-C_3$ .

Table 38. Bond length (Å) data for ruthena(II)-, irida(III)-, pallada(II)- and platina(II)cyclobutanones.

complex	#	M-C <sub>1</sub>	M-C <sub>2</sub>	M-C <sub>3</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>
(PMe <sub>3</sub> ) <sub>4</sub> Ru[CH <sub>2</sub> COCH <sub>2</sub> ]	25	2.217	-	2.222	1.468	1.449
(PPh <sub>3</sub> ) <sub>2</sub> (CO)ClIr[CH <sub>2</sub> COCH <sub>2</sub> ]	26	2.169	2.561	2.184	1.48	1.50
(PPh <sub>3</sub> ) <sub>2</sub> Pd[CH(CO <sub>2</sub> Me)COCH(CO <sub>2</sub> Me)]	27	2.135	2.389	2.165	1.467	1.492
(AsPh <sub>3</sub> ) <sub>2</sub> Pd[CH(CO <sub>2</sub> Me)COCH(CO <sub>2</sub> Me)]	28	2.125	2.384	2.152	1.482	1.473
(bipy)Pd[CH(CO <sub>2</sub> Me)COCH(CO <sub>2</sub> Me)]	29	2.103	2.374	2.085	1.471	1.471
(PPh <sub>3</sub> ) <sub>2</sub> Pt[CH(CO <sub>2</sub> Me)COCH(CO <sub>2</sub> Me)]	30	2.133	2.416	2.155	1.470	1.493
(PPh <sub>3</sub> ) <sub>2</sub> Pt[CH(COMe)COCH(COMe)]	31	2.183	2.486	2.153	1.496	1.491
(PPh <sub>3</sub> ) <sub>2</sub> Pt[CH <sub>2</sub> COCH <sub>2</sub> ]	32	2.145	2.422	2.119	1.473	1.496
(AsPh <sub>3</sub> ) <sub>2</sub> Pt[CH(Ph)COCH(Ph)] <sup>a</sup>	33	2.116	2.350	2.187	1.50	1.47
(AsPh <sub>3</sub> )(t-BuNC)Pt[CH(CO <sub>2</sub> Me)CO- CH(CO <sub>2</sub> Me)] <sup>b</sup>	34	2.057	2.509	2.121	1.509	1.492

<sup>a</sup> Both Ph groups occupy equatorial positions. <sup>b</sup> One substituent is equatorial, the other axial. C<sup>3</sup> is trans to AsPh<sub>3</sub>.

Table 39. Bond angle ( $^{\circ}$ ) data for ruthena(II)-, irida(III)-, pallada(II)- and platina(II)cyclobutanones.

#	$C_1-M-C_3$	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral <sup>a</sup>	ref.
25	65.72	110.8	83.5	83.5	45.6	133
26	66.5	106.6	87.1	86.0	41.0	161
27	68.5	109.5	80.8	79.2	53.2	157
28	68.7	109.5	80.6	79.9	52.3	157
29	68.8	107.1	81.2	81.8	51.3	157
30	-	108.8	82	80.7	50.4 <sup>b</sup>	154
31	67.3	107.2	82.8	84.0	48	159,160
32	68.4	107.7	-	-	51	162
33	69.2	110.4	79.0	77.2	56.7	163
34	68.1	102.6	88	86.1	42	158

<sup>a</sup> The angle formed between the planes of  $C_1-M-C_3$  and  $C_1-C_2-C_3$ . <sup>b</sup> Reported in ref. 155 as  $49.7^{\circ}$ .

Table 40. Bond length (Å) data for irida(III)- and platina(II)cyclobutenes.

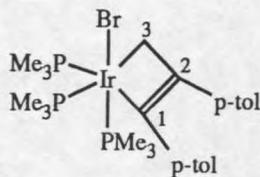
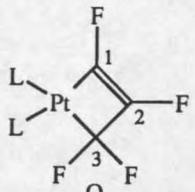
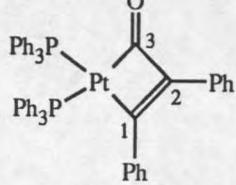
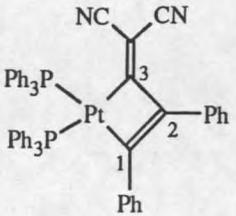
complex	#	M-C <sub>1</sub>	M-C <sub>2</sub>	M-C <sub>3</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>	C <sub>1</sub> -C <sub>3</sub>
	35	2.134	-	2.166	1.344	1.525	-
	36	2.039	-	2.08	1.35	1.47	-
	37	2.08	-	2.09	1.45	1.31	-
	38	-	-	-	-	-	-

Table 41. Bond angle ( $^{\circ}$ ) data for irida(III)- and platina(II)cyclobutenes.

#	$C_1-M-C_3$	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral <sup>a</sup>	ref.
35	72.98	99.2	-	-	5.5	168
36	65.8	104.7	97.5	-	0.0	110
37	62	100	101	97	-	107
38	63	101	-	-	23	109

<sup>a</sup> The angle formed between the planes of  $C_1-M-C_3$  and  $C_1-C_2-C_3$ .

Table 42. Bond length (Å) data for rhoda(III)-, nickela(II)- and platina(II)cyclobutabenzenes.

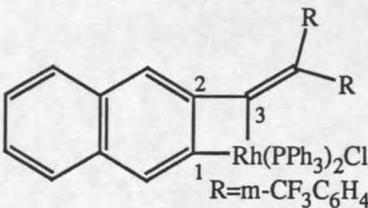
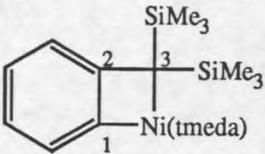
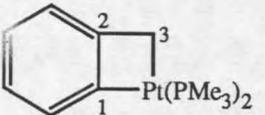
complex	#	M-C <sub>1</sub>	M-C <sub>2</sub>	M-C <sub>3</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>
	40	1.984	-	2.030	1.395	1.480
	41	1.897	-	2.075	1.38	1.534
	42	2.060	-	2.122	1.38	1.52

Table 43. Bond angle ( $^{\circ}$ ) data for rhoda(III)-, nickela(II)- and platina(II)cyclobutabenzenes.

#	$C_1-M-C_3$	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral <sup>a</sup>	ref.
39	66.2	99.3	99.5	94.6	0.0	116
40	71.7	106.0	96.9	85.3	-	114
41	66.7	104.6	97.6	90.8	-	178

<sup>a</sup> The angle formed between the planes of  $C_1-M-C_3$  and  $C_1-C_2-C_3$ .

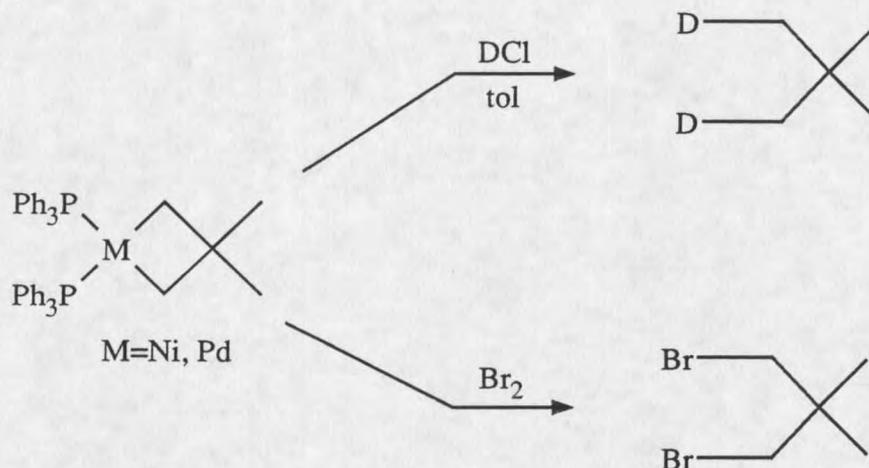
## Chemistry of Metallacyclobutane Derivatives

### Reactions Yielding Alkane Products

The formation of alkanes from metallacyclobutanes has been reported for Ni(II), Pt(II) and Pt(IV) complexes. Addition of DCl in toluene to the 2,2-dimethylmetallacyclobutanes of Ni(II) and Pd(II) results in quantitative formation of 1,3-deuterium substituted neopentane (Scheme XI)<sup>122</sup>. The same substitution pattern was observed for the analogous reaction of DCl in D<sub>2</sub>O with 2,2-dimethylplatina(II)cyclobutanes<sup>117,121</sup>. Similarly, treatment of the nickela(II)- and pallada(II)cyclobutanes, as well as a rhodium analogue<sup>125</sup>, with Br<sub>2</sub> leads to formation of 1,3-dibromo-2,2-dimethylpropane in 49%, 67% and 37% yield respectively (Scheme XI). These reactions presumably proceed by oxidative addition of the reagent to the metal, followed by reductive elimination of substituted neopentane.

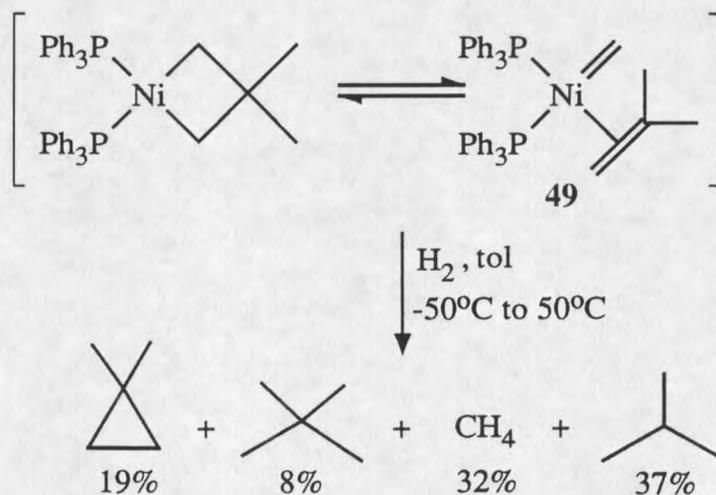
When 2,2-dimethylnickela(II)cyclobutane was pyrolyzed in the presence of hydrogen by raising the temperature from -50°C to 50°C, the products shown in Scheme XII result<sup>122,189</sup>. (Reported yields are per Ni). Although the 2,2-dimethylpropane and 1,1-dimethylcyclopropane result from reductive elimination and hydrogenolysis of the nickela(II)cyclobutane, respectively, the production of the dominant alkane species, methane and isobutane, is believed to result from a nickel-carbene intermediate **49**. In contrast, the dominant products from hydrogenolysis of the Pd(II) analogue were neopentane (69%) and dimethylcyclopropane (14%) with only small amounts of methane

Scheme XI.



and isobutane (4% and 6%, respectively).

Scheme XII.



When platinum(IV)cyclobutane tetramers are shaken in alcohol in the presence of gaseous hydrogen, a variety of alkane products, and in some cases cyclopropane, result<sup>61</sup>. One example is shown in equation 47 and Table 44 displays other hydrogenolysis products. In each case a mixture of isomeric alkane products results. It has not been determined, however, whether isomerization occurs within the platinum(IV)cyclobutane to create an isomeric mixture of tetramers which upon hydrogenolysis yield the isomeric

alkanes or whether isomerization to the observed alkane products occurs during hydrogenolysis from one tetrameric species<sup>47,75</sup>.

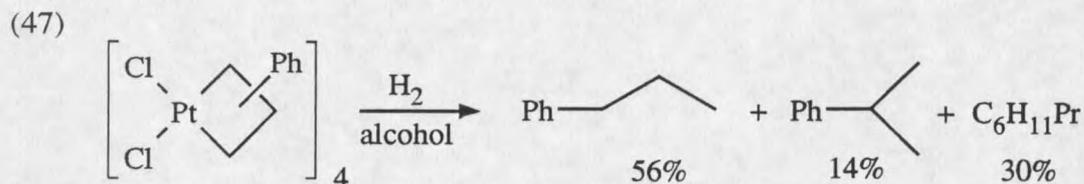


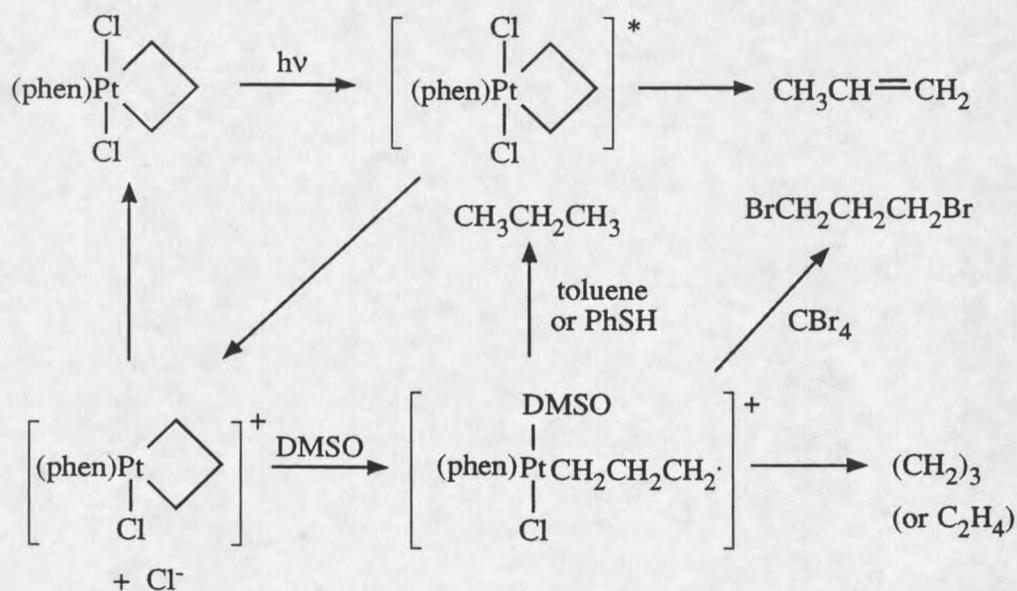
Table 44. Hydrogenolysis products of mono- and disubstituted platina(IV)cyclobutane tetramers.

R	Products			
CH <sub>2</sub> Ph				
n-C <sub>6</sub> H <sub>13</sub>				
trans-1,2-diphenyl				
cis-1,2-diphenyl				

Under certain solvent and additive conditions, it is possible to produce alkanes photolytically from platina(IV)cyclobutane, albeit cyclopropanes and alkenes are the dominant products<sup>190,191</sup>. The photolysis of (1,10-phenanthroline)dichloroplatina(IV)-cyclobutane in CH<sub>2</sub>Cl<sub>2</sub>/benzenethiol yields about 26% propane. The same reaction

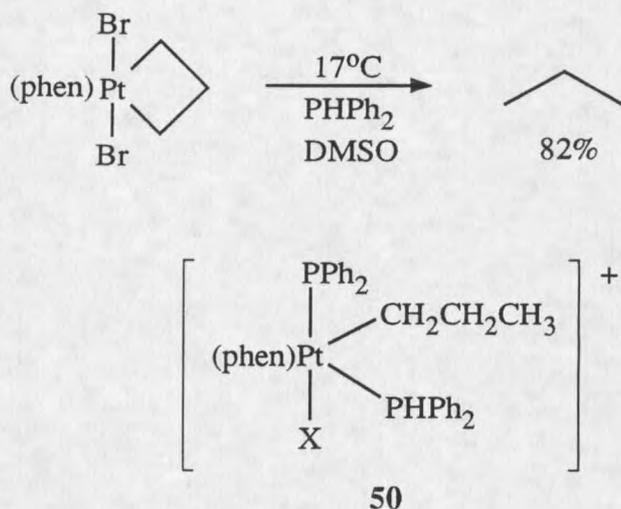
performed in DMSO/benzenethiol or DMSO/toluene yields 5% propane and 1% propane respectively. A solvent mixture of DMSO/CBr<sub>4</sub> produced 1,3-dibromopropane in small, yet detectable, amounts. The proposed reaction pathway for this photolytic process is illustrated in Scheme XIII.

Scheme XIII.



The thermal reaction of platina(IV)cyclobutane, run in the presence of diphenylphosphines, also forms propane in varying yields<sup>83</sup>. The example shown in equation 48 is the highest yielding of all the reaction conditions tested. Other phosphines also were added and were found to generate little or no propane product. The success of diphenylphosphine in generating propane is presumably due to the formation of an ionic intermediate **50** which is proposed to transfer a hydrogen from the coordinated phosphine to form propane.

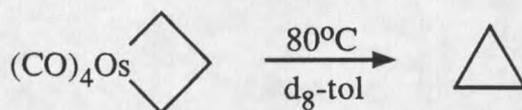
(48)



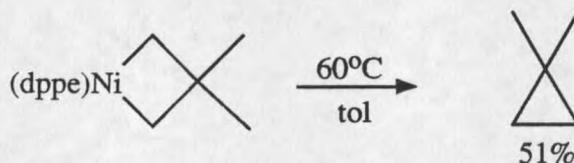
### Reactions Yielding Cyclopropane Products

Reductive elimination of metallacyclobutanes to form cyclopropane is facilitated by numerous reagents as well as heat and light. Osmia(II)- and nickela(II)cyclobutanes both decompose to cyclopropanes, and other alkene and alkane products, when heated according to equations 49<sup>174</sup> and 50<sup>122,189</sup>.

(49)

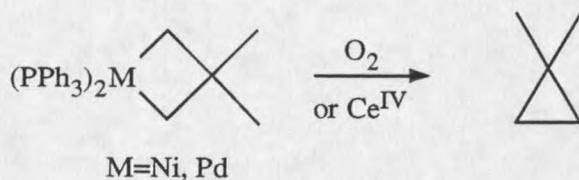


(50)



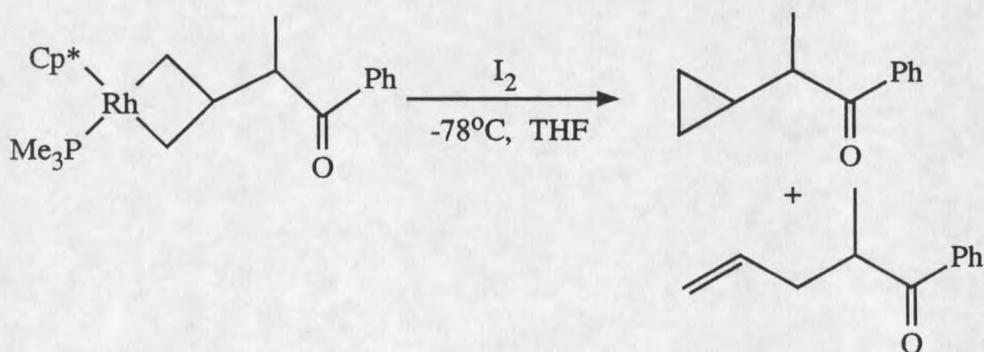
The oxidative decomposition of 2,2-dimethylnickela(II)- and pallada(II)cyclobutane with  $\text{O}_2$  or  $\text{Ce}^{\text{IV}}$  yields 1,1-dimethylcyclopropane in 80% to 87% yields as illustrated in equation 51<sup>122</sup>.

(51)

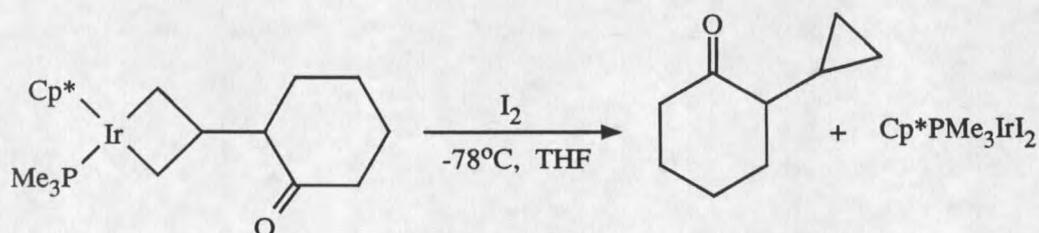


Addition of  $\text{I}_2$  in THF at  $-78^\circ\text{C}$  causes rhoda(III)- and irida(III)cyclobutanes to reductively eliminate forming cyclopropanated ketones (equations 52 and 53)<sup>136,142</sup>. Similarly, reaction of platina(II)cyclobutane with methyl iodide at  $90^\circ\text{C}$  also forms a cyclopropane product (equation 54)<sup>139</sup>. Since these metallacycles were prepared by nucleophilic attack at the central carbon of an  $\eta^3$ -allyl rhoda-, irida- or platinum complex, respectively, the overall scheme provides an alkylative cyclopropanation protocol.

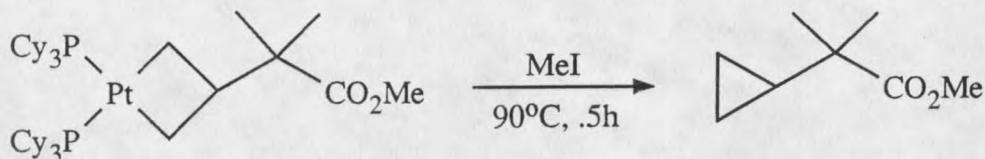
(52)



(53)

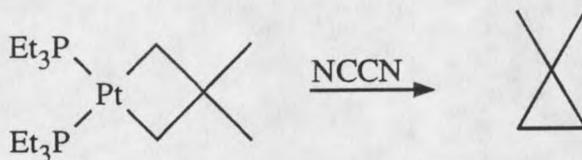


(54)



The 2,2-dimethyl platina(II)cyclobutane, shown in equation 55, forms 1,1-dimethylcyclopropane upon reaction with  $I_2$ ,  $Br_2$  and  $NCCN$ , as well as with heating<sup>117,121</sup>.

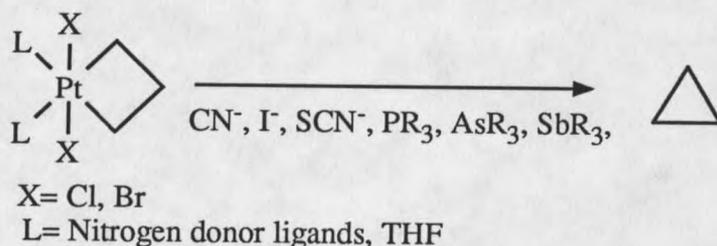
(55)



Equation 56 illustrates the most common reagents invoked for reductive elimination of platina(IV)cyclobutane tetramers and monomers<sup>37,39,41,61,62,65,73,82,83,85,88,89,190-192</sup>. The anionic ligands  $CN^-$ ,  $I^-$  and  $SCN^-$  as well as the tertiary phosphine, arsine, stibene and sulfur donor ligands, all exhibit high trans influence. The facility of these ligands in invoking reductive elimination is due to their ability to coordinate to platinum, replacing the existing coordinated ligand, L, and readily eliminating cyclopropane. Therefore a stronger ligand, such as  $PR_3$ , liberates cyclopropane faster than a weaker ligand. However, the rate of reductive elimination also depends on the halide and ligand originally on the platina(IV)cyclobutane.

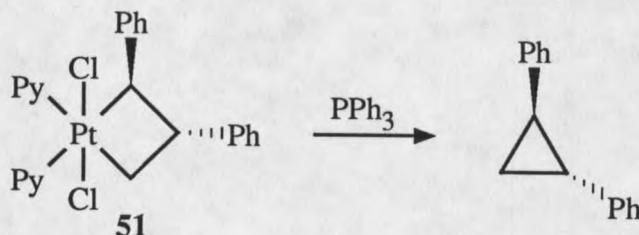
Another interesting feature of these reactions is the resulting stereochemistry of the cyclopropane product. Addition of triphenylphosphine to dichlorobis(pyridine)trans-1,2-diphenylplatina(IV)cyclobutane **51** yields trans-1,2-diphenylcyclopropane with

(56)



complete retention of stereochemistry (equation 57). However, when **51** is treated with KCN a mixture of trans and cis-1,2-diphenylcyclopropane isomers result in an 86:14 ratio, respectively. This result indicates that trans to cis isomerization occurred during reductive elimination with KCN suggesting a possible ionic intermediate for this process, in contrast to the concerted mechanism proposed for reductive elimination from addition of  $\text{PPh}_3$ <sup>73</sup>.

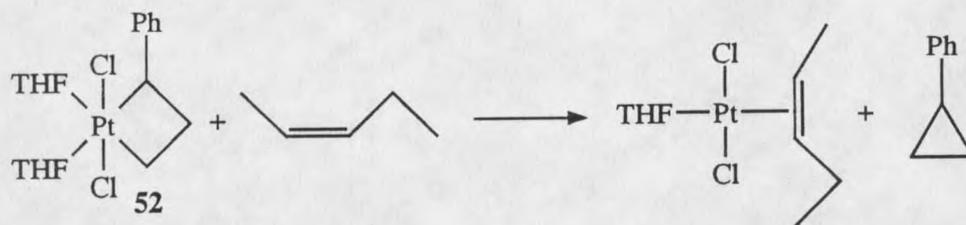
(57)



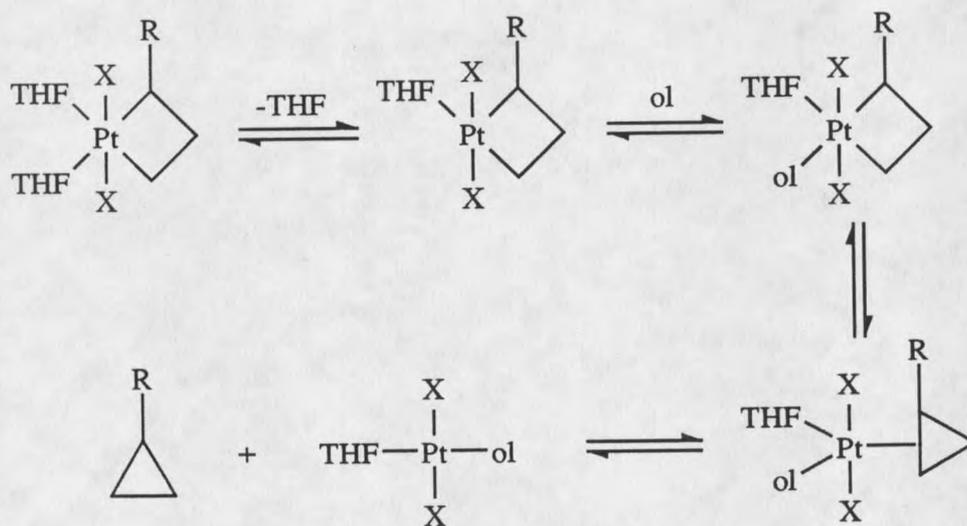
Other reagents that reportedly induce reductive elimination of platina(IV)cyclobutanes include  $\text{LiAlH}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}$ <sup>61,62,90</sup>. Displacement of cyclopropanes by olefins also occurs as is illustrated in equation 58 for the reaction of **52** with 2-pentene<sup>61,65,193,194</sup>. An olefin exhibits high trans effect but low trans influence. Therefore, the generation of cyclopropane is slower than for the ligands previously described, and does not occur if the platina(IV)cyclobutane monomer bears stronger coordinated ligands such as pyridine. However, olefins can reductively eliminate cyclopropane from platina(IV)cyclobutane tetramers or monomers in solution with a weak coordinating

solvent, such as THF. The proposed pathway for this process is shown in Scheme XIV<sup>193</sup>.

(58)



Scheme XIV.

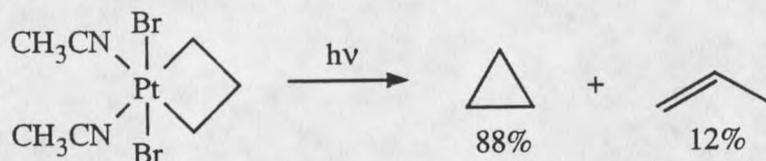


Thermal and photolytic decomposition of platina(IV)cyclobutanes also generate cyclopropane, along with other alkane and alkene products<sup>41,74,82,83,89,90,190,191,195,196</sup>. Platina(IV)cyclobutane monomers bearing high trans influence ligands yield cyclopropane in the highest yields when heated. For example, more than five times as much cyclopropane is generated upon heating a platina(IV)cyclobutane where L=ethylenediamine than when L=pyridine due to the higher trans influence of the former. The thermal

reaction of platina(IV)cyclobutanes bearing bidentate ligands also generated cyclopropane when run in the presence of phosphines. Cyclopropane yields vary from 1%-77% depending on the temperature, the solvent and the type of phosphine added.

The photodecomposition of platina(IV)cyclobutanes also varies with reaction conditions (solvent and additive) to produce cyclopropane, propene and ethylene products. The highest yield of cyclopropane formed by photolysis reportedly results from the reaction shown in equation 59<sup>191</sup>.

(59)

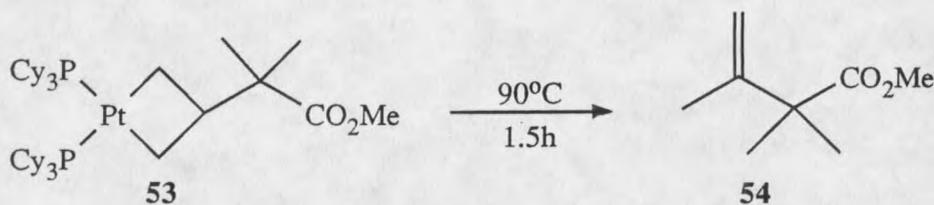


### Reactions Yielding Olefinic Products

The formation of free alkene species from metallacyclobutanes has been reported for Ni(II), Pt(II), and most commonly Pt(IV). Equation 50 in the previous section illustrates the thermal decomposition of a 2,2-dimethylnickela(II)cyclobutane to 1,1-dimethylcyclopropane. This reaction also yields the olefinic products ethylene, 2-methylpropene, and 3-methyl-1-butene in 14%, 27%, and 3% yield (per Ni) respectively<sup>122,189</sup>.

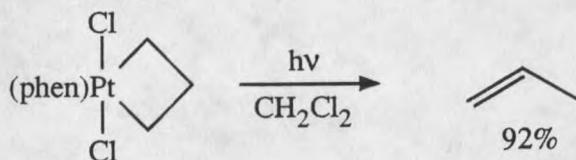
The thermal decomposition of 53 in dimethoxyethane-benzene-d<sub>6</sub> forms the olefinic product 54 exclusive of cyclopropane (equation 60)<sup>139</sup>. The β-hydride elimination and subsequent reductive elimination of the olefin is apparently a lower pathway than C-C bond formation by reductive elimination of cyclopropane.

(60)



Both thermal and photolytic decomposition of unsubstituted platina(IV)cyclobutanes form propene, along with other products, as illustrated in equation 61<sup>39,41,74,82,83,190,196</sup>. In this example propene is formed in 92% yield. However, by changing the solvent, the ligands, the temperature and other additives the distribution of products easily can be affected to yield larger amounts of ethylene, cyclopropane and other products. For example, ethylene can be formed in yields up to 70% if the decomposition conditions include DMSO or CH<sub>3</sub>CN solvents in the presence of tertiary phosphines<sup>74,83</sup>.

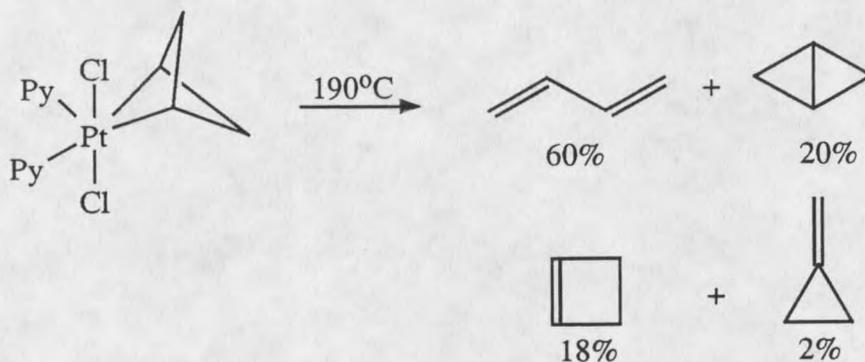
(61)



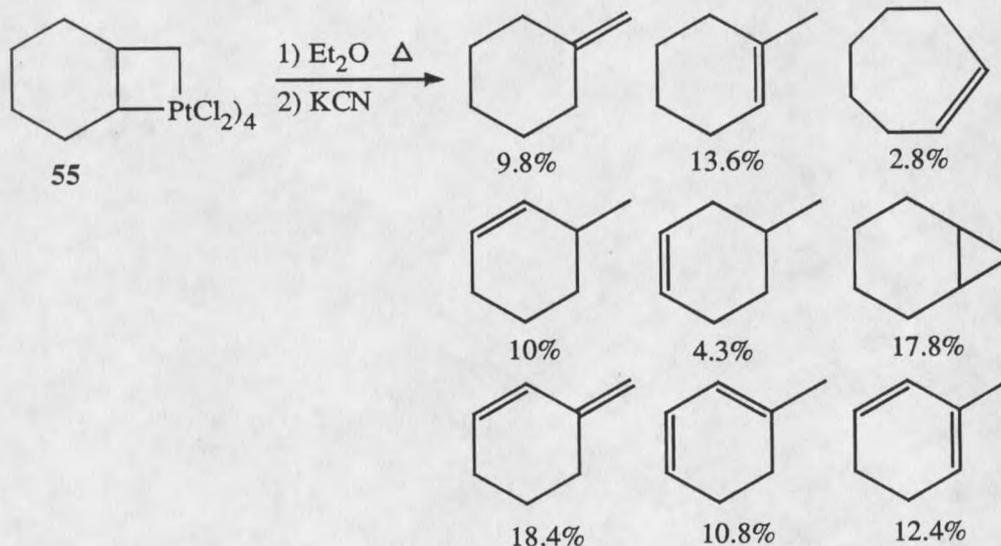
Other platina(IV)cyclobutane systems can form free alkenes. Equation 62 demonstrates the thermal decomposition of a cis-1,3-disubstituted platina(IV)cyclobutane to three different olefinic products<sup>90</sup>.

The cis-1,2-disubstituted platina(IV)cyclobutane tetramer **55** formed eight different olefinic products, along with the reductive elimination product, when heated in diethyl-ether followed by addition of KCN (equation 63)<sup>89</sup>. The same product distribution is observed when bicyclo[4.1.0]heptane is heated in the presence of platinum(II), suggesting a platina(IV)cyclobutane intermediate for the latter process.

(62)

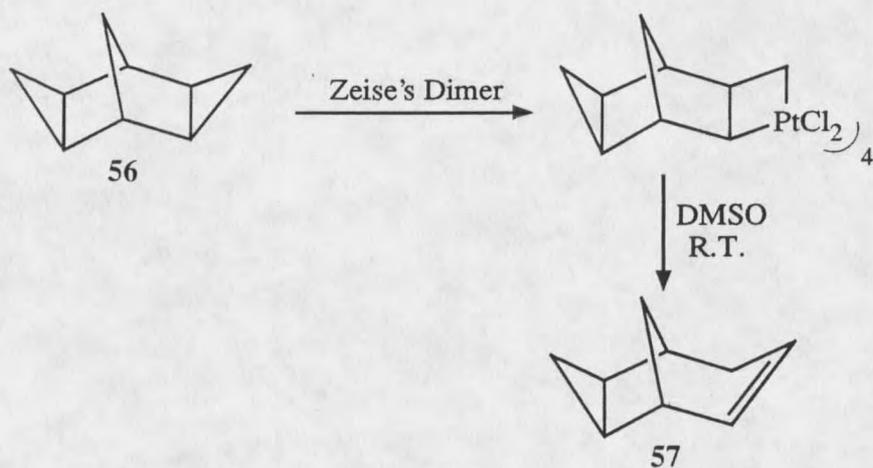


(63)

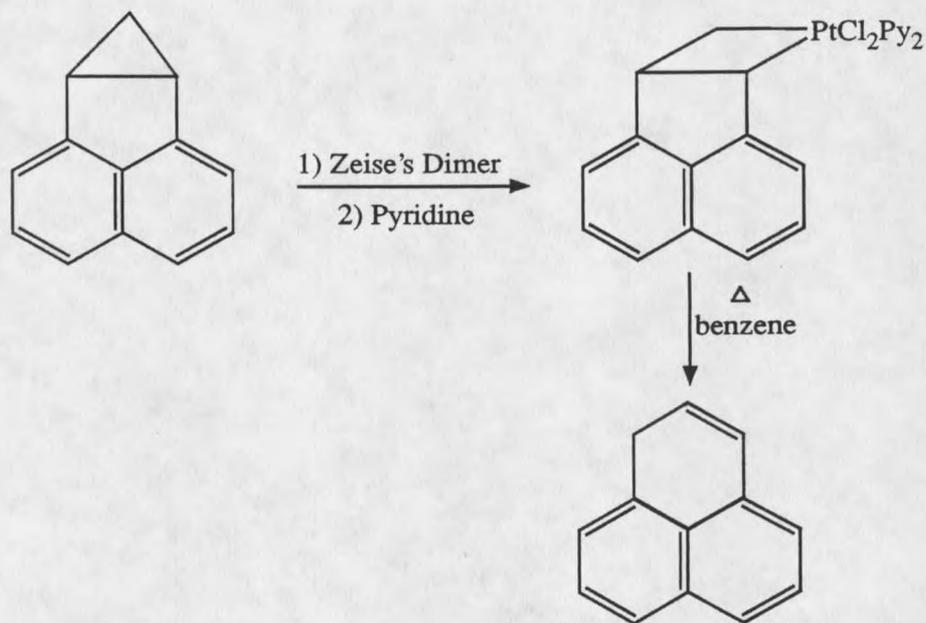


A ring homologated olefinic product results when 56 reacts with Zeise's Dimer to form a platinum(IV)cyclobutane tetramer which subsequently is treated with DMSO at room temperature to produce 57 (equation 64)<sup>197,198</sup>. Another example of this ring homologation technique is shown in equation 65<sup>94</sup>. Both of these reactions are suggested to proceed via an intermediate in which the platinum has rearranged into the disubstituted C-C bond of the cyclopropane moiety. A β-hydride elimination process, followed by reductive elimination, then leads to the observed products<sup>199</sup>.

(64)



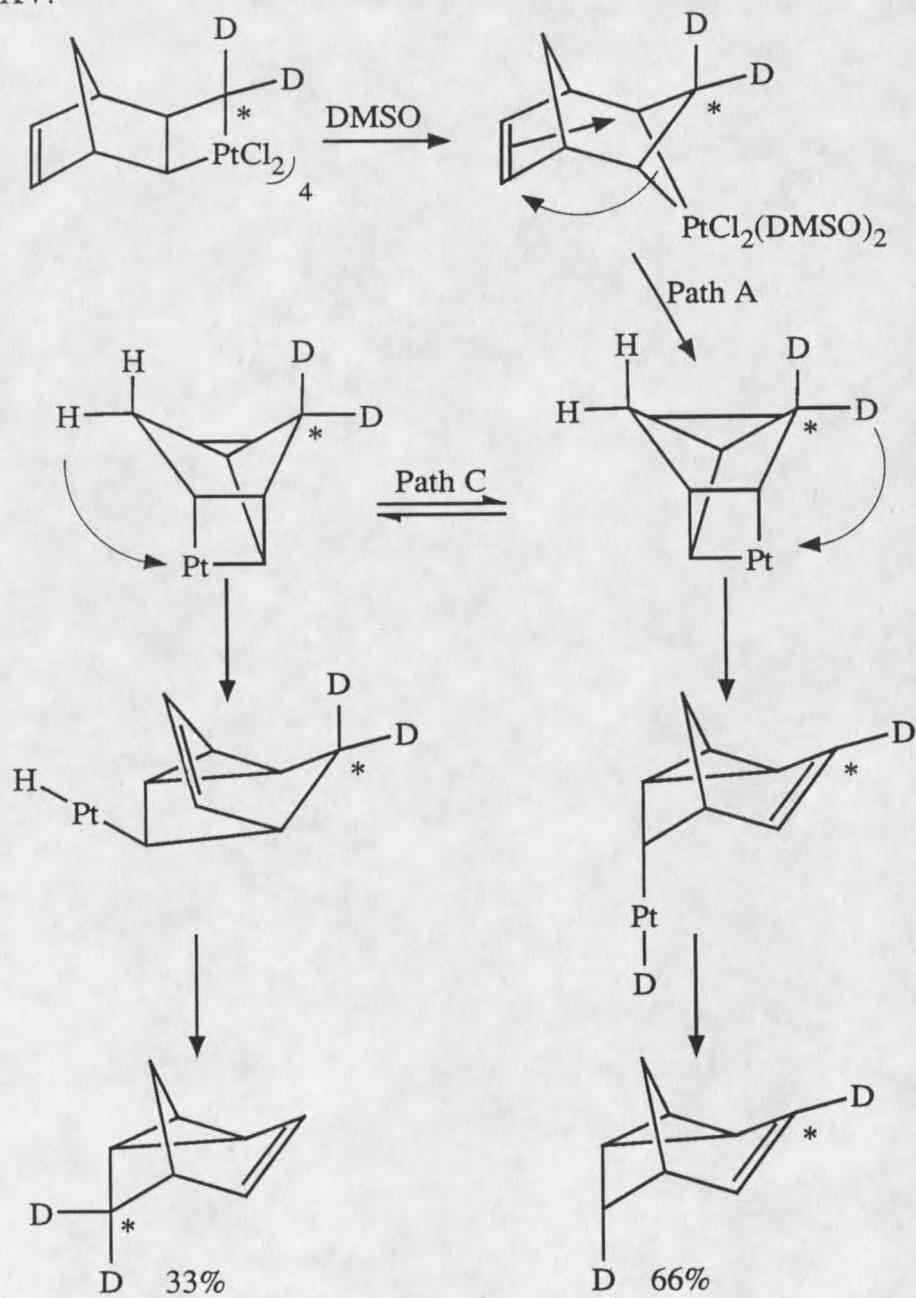
(65)



When the deuterium and  $^{13}\text{C}$  labeled unsaturated norbornyl platina(IV)cyclobutane tetramer undergoes a ring homologation, two isomers result. Scheme XV illustrates the observed products and the detailed mechanism proposed for this reaction<sup>200</sup>. Path A is suggested to form 66% of the reaction product, while path C is responsible for 33% of the product. The same reaction, utilizing a Rh(I) catalyst, results in the same nortricyclic

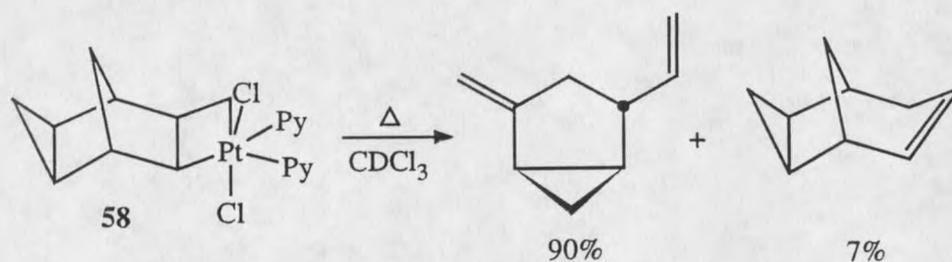
system. However,  $^{13}\text{C}$  labeling shows that only path C is followed under these conditions<sup>94,201</sup>.

Scheme XV.

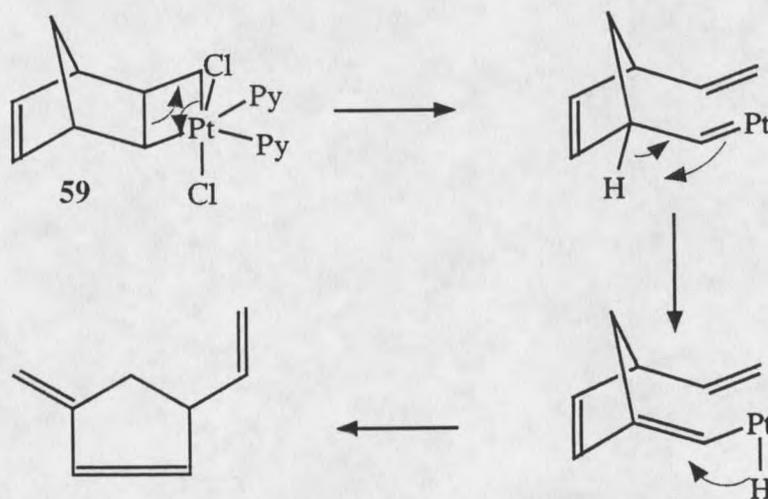


When **58** and **59** are heated in  $\text{CDCl}_3$ , a five-membered ring diene results along with the ring expanded product (equation 66 and Scheme XVI)<sup>198</sup>. The proposed pathway for the formation of the diene complex invokes cleavage of the platina(IV)-cyclobutane moiety to form a platinum-carbene olefin complex which subsequently undergoes hydrogen rearrangement followed by reductive elimination to the observed olefinic product as shown in Scheme XVI.

(66)



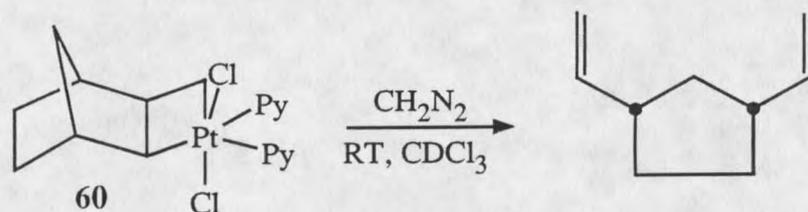
Scheme XVI.



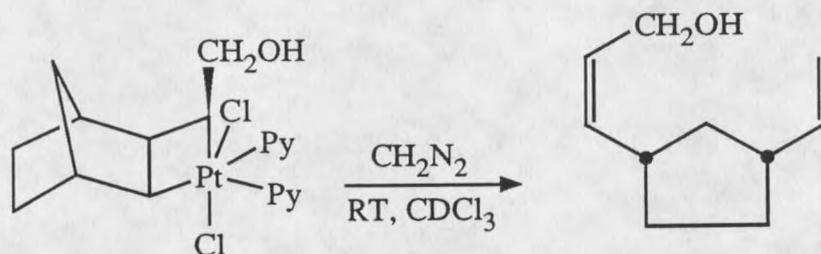
Another diene ring system results when **60** is treated with diazomethane at room temperature (equation 67)<sup>76,198</sup>. This procedure also has been performed on 1,2,3-trisubstituted platina(IV)cyclobutanes to form cis divinyl cyclopentanes with retention of stereochemistry (equation 68)<sup>96</sup>. The utility of this reaction is the stereochemical control

that can be achieved at one double bond and the two allylic centers.

(67)

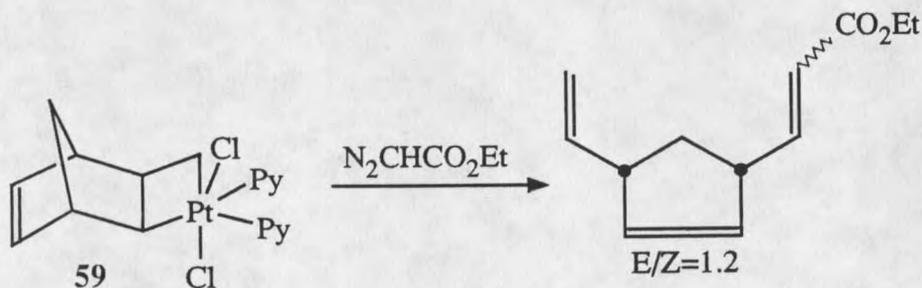


(68)

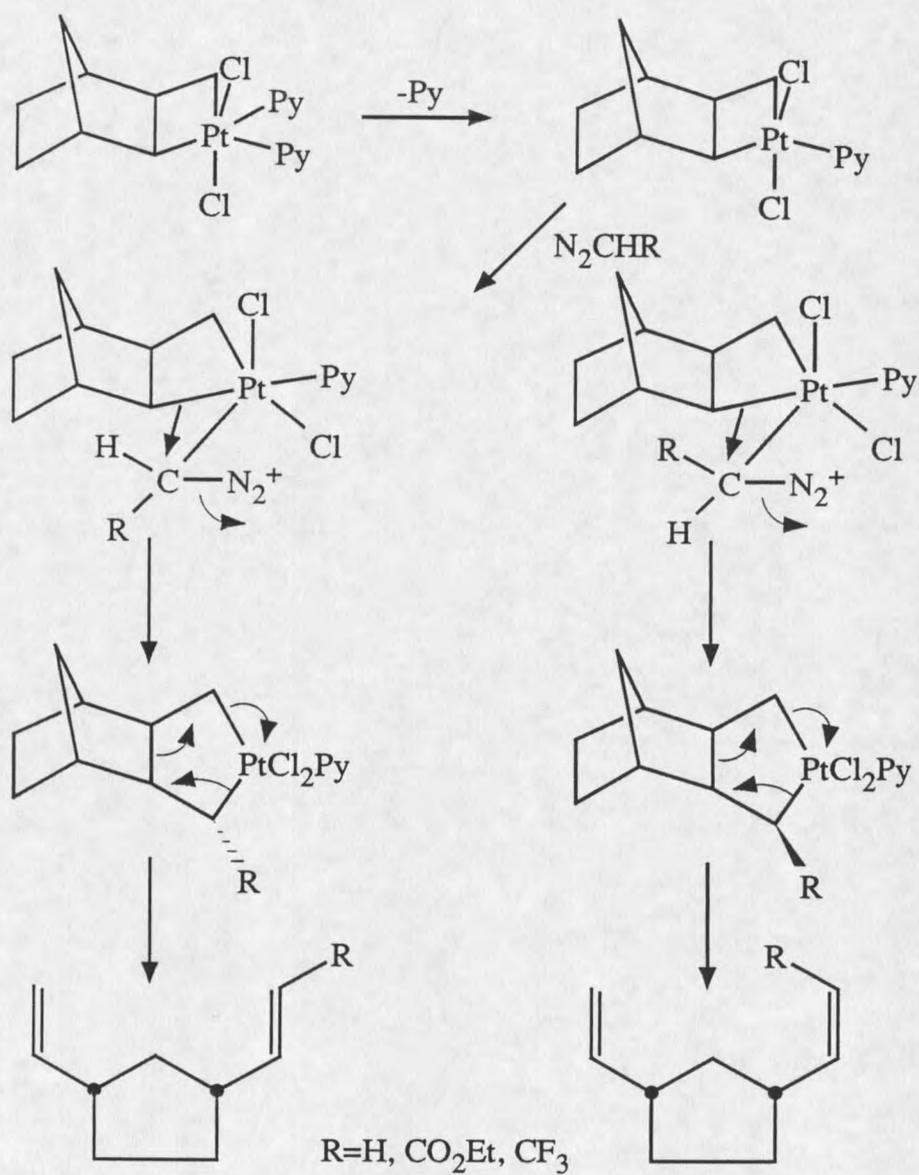


The reaction shown in equation 69 was studied with hopes of achieving stereochemical control at the second double bond as well<sup>92</sup>. However, reaction of **59** with ethyl diazoacetate results in formation of both the E and Z epimers of the carboethoxy substituted divinyl product. Scheme XVII illustrates the proposed mechanism for the reactions shown in equations 67, 68 and 69<sup>81</sup>.

(69)



Scheme XVII.

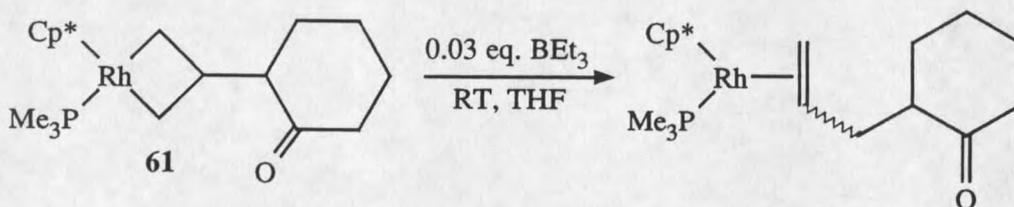


Reactions Yielding Alkene-Metal Complexes

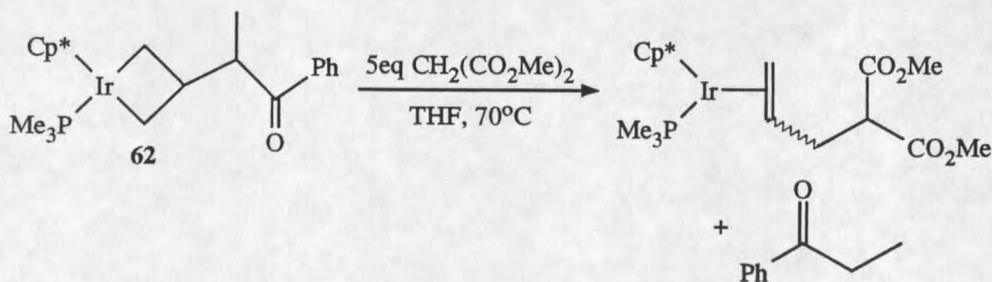
The most recent examples of metallacyclobutanes reacting to form metal-olefin complexes are shown in equations 70 and 71<sup>136</sup>. Equation 70 illustrates the mild Lewis acid, Et<sub>3</sub>B, catalyzed rearrangement of rhoda(III)cyclobutane **61** to a mixture of stereoisomers of the rhodium(I)-olefin complex. The irida(III)cyclobutane **62** however, does not rearrange to an iridium(I)-olefin complex under similar conditions presumably due to stronger metal-carbon bonding for iridium. It is possible though to form an iridium-alkene complex by heating **62** in the presence of excess dimethyl malonate.

The metallacycles **61** and **62** are formed by nucleophilic attack at the central carbon of the respective metal  $\eta^3$ -allyl complex. The mechanism for alkene-metal complex formation is suggested to result from reversible dissociation of the metallacycle to the free ion and the  $\pi$ -allylic complex, followed by nucleophilic attack at the terminal carbon of the  $\eta^3$ -allyl complex. The iridium example validates the reversible nature of this reaction by crossover substitution.

(70)

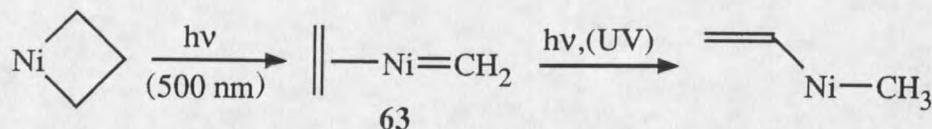


(71)



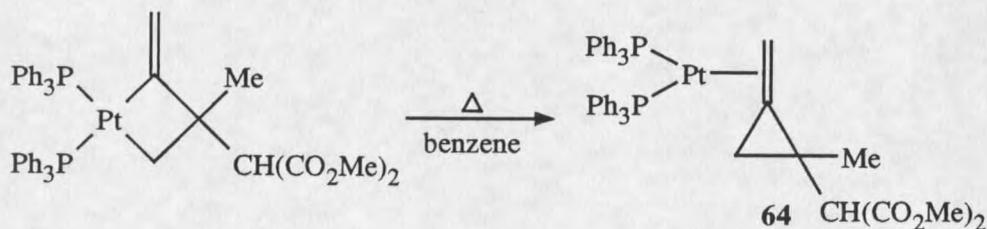
The unligated nickel(II)cyclobutane in equation 72 is irradiated at  $\lambda \geq 500\text{nm}$  to form a methylenenickel ethylene  $\pi$  complex 63. Upon further irradiation with UV photolysis 63 rearranges to a vinylnickel methyl species<sup>106</sup>.

(72)



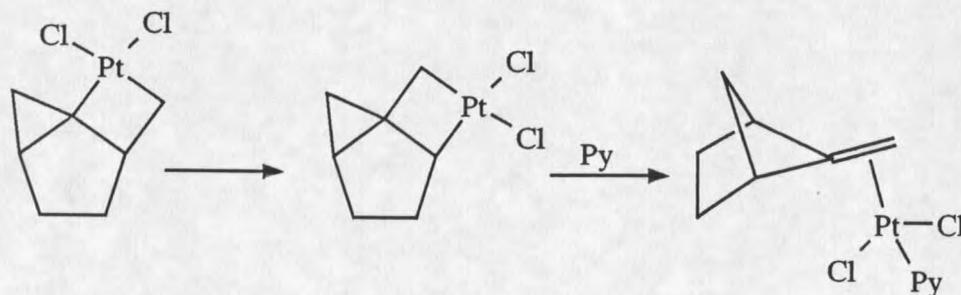
The unusual vinylidene-substituted platina(II)cyclobutane readily reductively eliminates methylenecyclopropane to form the Pt(0)-olefin complex 64 as shown in equation 73<sup>138</sup>.

(73)



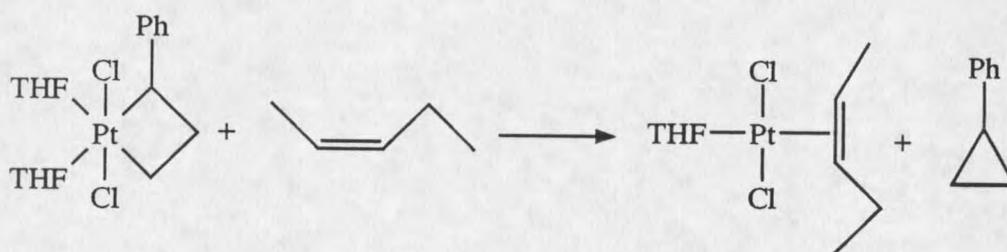
The platina(IV)cyclobutane, shown in equation 74, reportedly undergoes a skeletal rearrangement to form a bicyclic platinum(II)-olefin complex<sup>95</sup>.

74)



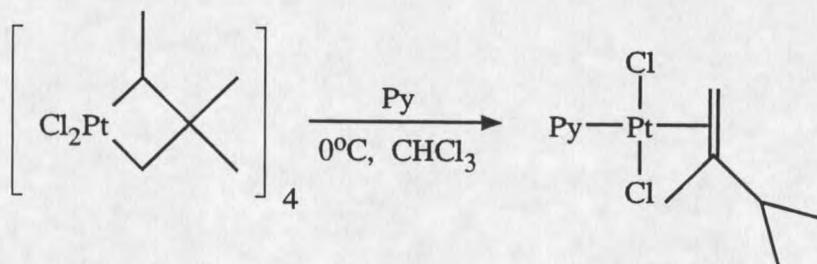
As previously shown in equation 58, platina(IV)cyclobutanes can react with olefins to reductively eliminate the cyclopropane moiety and form a Pt(II)-olefin species<sup>61,65,193,194</sup>. Another example is shown in equation 75. The olefin either can replace a weak ligand attached to the monomeric platina(IV)cyclobutane, as shown, or react directly with the tetrameric species.

(75)

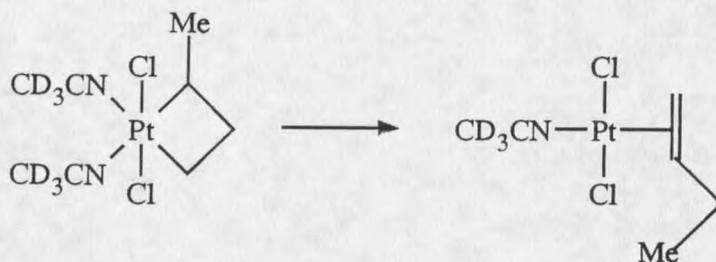


Pt(II)-olefin complexes also result from direct isomerization of tetrameric platina(IV)cyclobutanes (equation 76). Platina(IV)cyclobutanes bearing weakly coordinated or bulky nitrogen donor ligands also easily isomerize to the Pt(II)-olefin complex as illustrated in equation 77<sup>71,74,80,202-205</sup>.

(76)

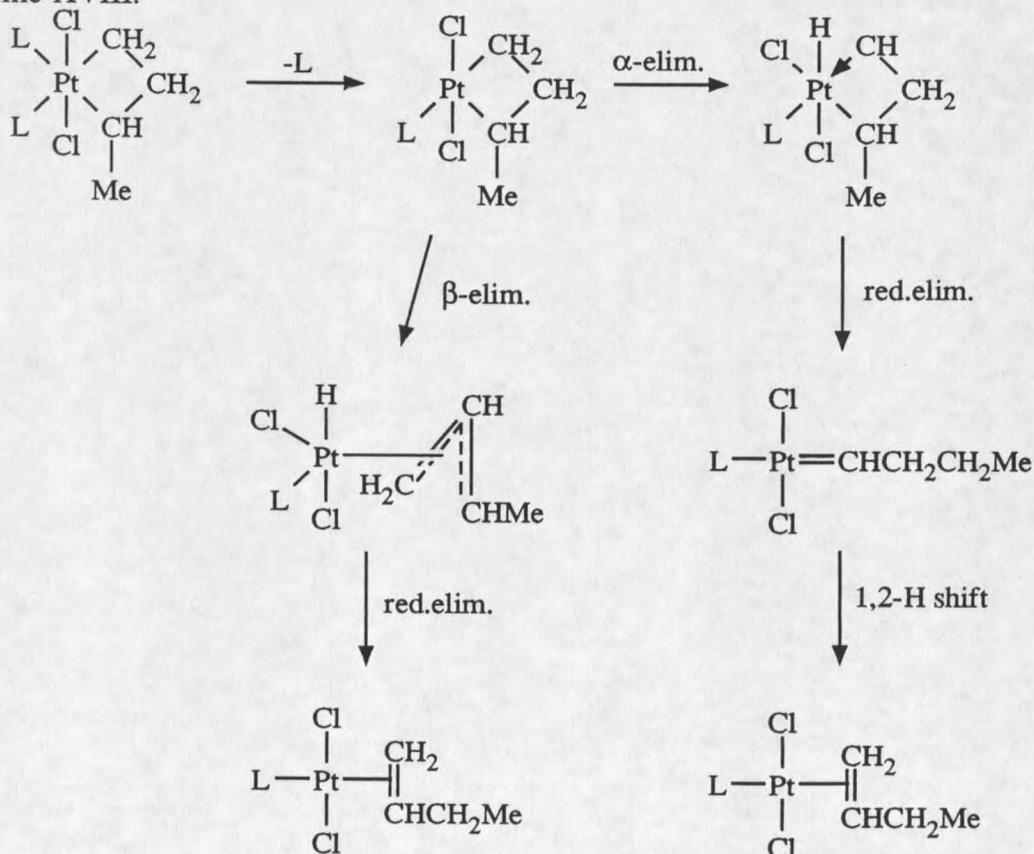


(77)



The mechanism of platinum(IV)cyclobutane isomerization to Pt(II)-olefin complexes has been extensively investigated. Scheme XVIII illustrates two possible pathways for this reaction involving either an initial  $\alpha$ - or  $\beta$ -hydride elimination<sup>199</sup>. Although some controversy exists over the correct pathway, the most recent findings support an initial  $\alpha$ -hydride elimination rather than the  $\beta$ -hydride elimination pathway.

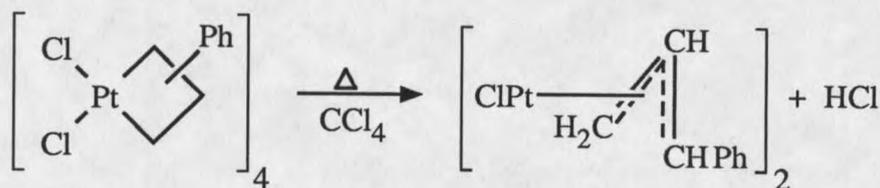
Scheme XVIII.



### Reactions Yielding $\eta^3$ -Allyl-Metal Complexes

An  $\eta^3$ -allyl-platinum(II) complex results when a phenyl substituted platina(IV)-cyclobutane tetramer is refluxed in  $\text{CCl}_4$  according to equation 78<sup>61</sup>. Other examples of  $\eta^3$ -allyl-platinum(II) complex formation from the reaction of certain cyclopropanes with Zeise's Dimer suggest a platina(IV)cyclobutane intermediate, however, the metallacycle is not actually detected<sup>62,71</sup>.

(78)

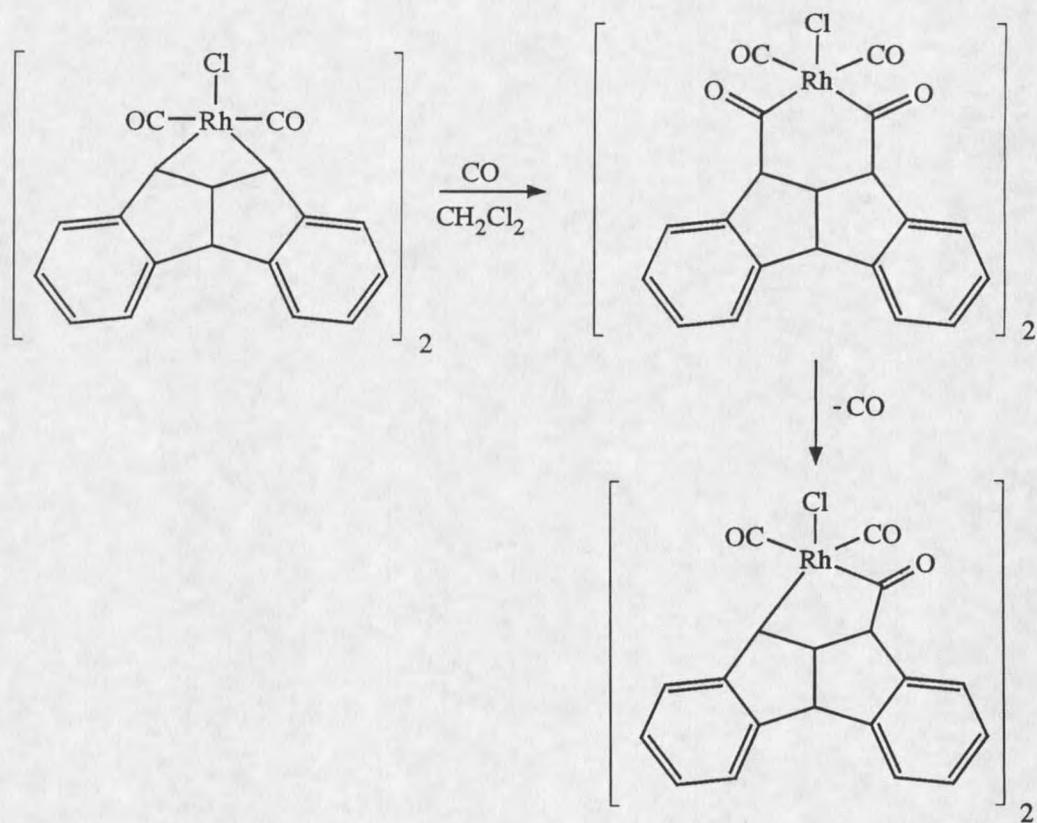


### Reactions Yielding Ring Expanded Products

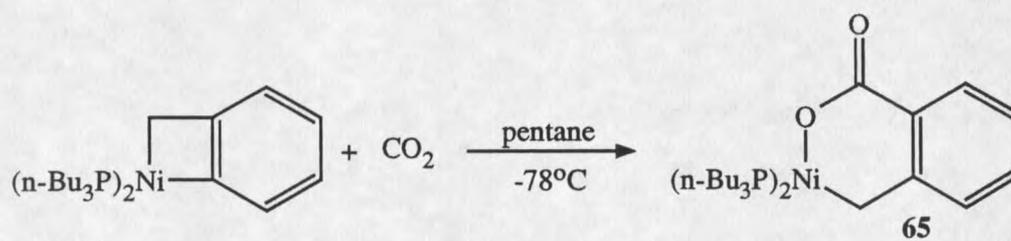
Ring expanded products have been formed from reactions of Rh(III), Ni(II), Pt(II) and Pt(IV) metallacyclobutane derivatives. When carbon monoxide is added to a rhoda(III)cyclobutane dimer a CO insertion process initially yields a rhoda(III)cyclohexadione dimer. Prolonged passage of carbon monoxide until the sample becomes dry, or evaporation to dryness, forms a rhoda(III)cyclopentanone dimer (equation 79)<sup>105</sup>.

Nickela(II)cyclobutabenzene adds carbon dioxide at  $-78^\circ\text{C}$  to form the six-membered cyclic carboxylate **65** in high yield (equation 80)<sup>112</sup>. A ring expanded product also results when the platina(II)cyclobutanone, shown in equation 81, reacts with hexafluoroacetone<sup>155</sup>.

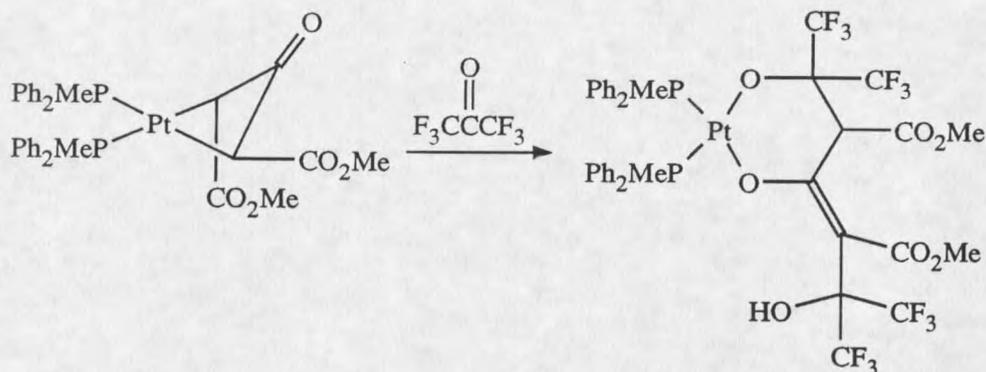
(79)



(80)

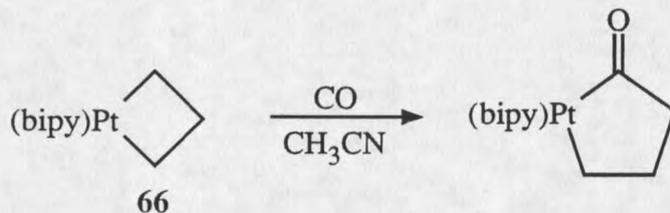


(81)

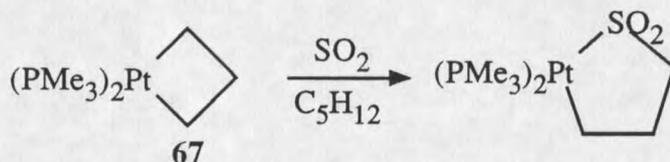


A platina(II)cyclopentanone product results when the platina(II)cyclobutane **66** is stirred in acetonitrile under 1 atm of carbon monoxide (equation 82). Similarly, exposure of **67** to 1 atm of sulfur dioxide leads to the  $\text{SO}_2$  insertion product (equation 83)<sup>175</sup>.

(82)

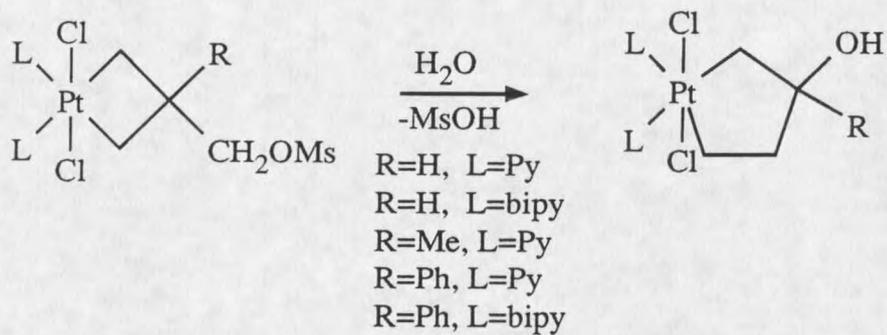


(83)

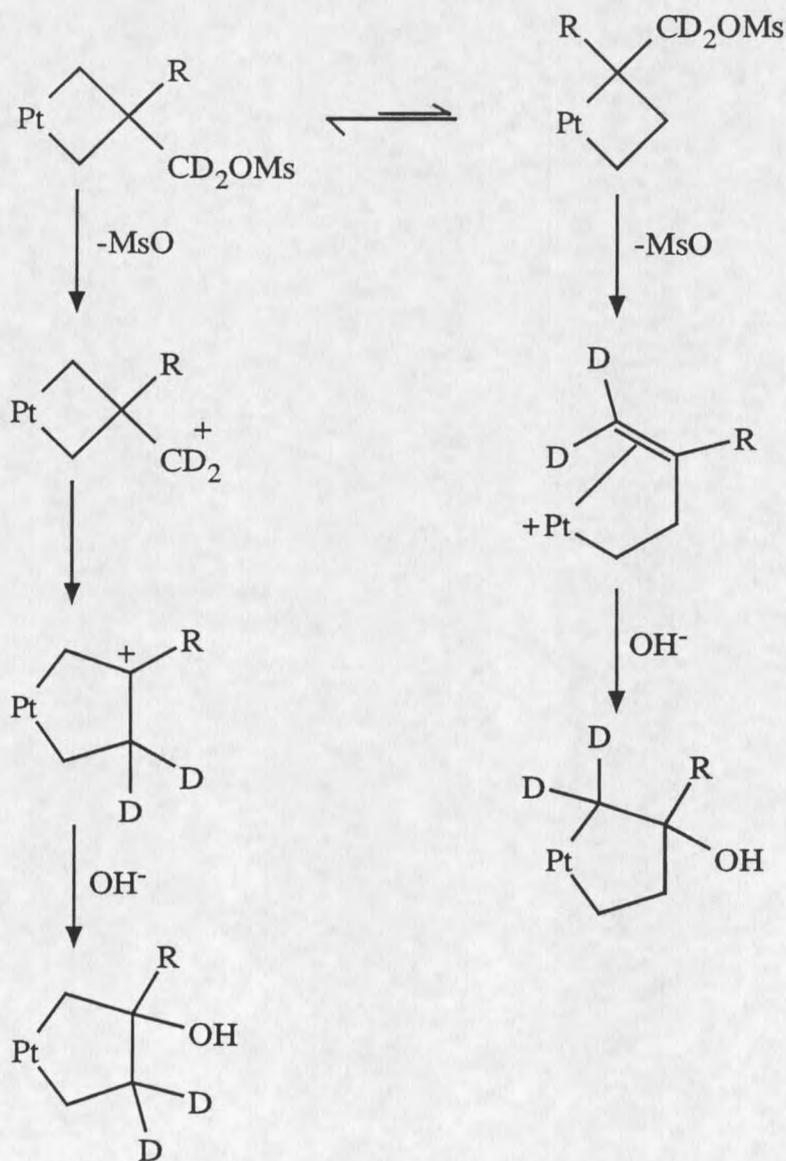


Platina(IV)cyclopentanes have been synthesized by ring expansion of platina(IV)-cyclobutanes. The solvolysis of platina(IV)cyclobutanes bearing mesylate esters produces platina(IV)cyclopentanol products according to equation 84<sup>78,79</sup>. The reaction pathway shown in Scheme XIX supports both the kinetic and labeling studies performed on this reaction.

(84)

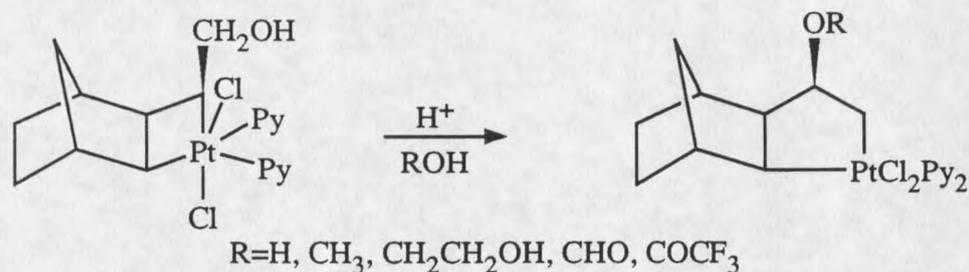


Scheme XIX.

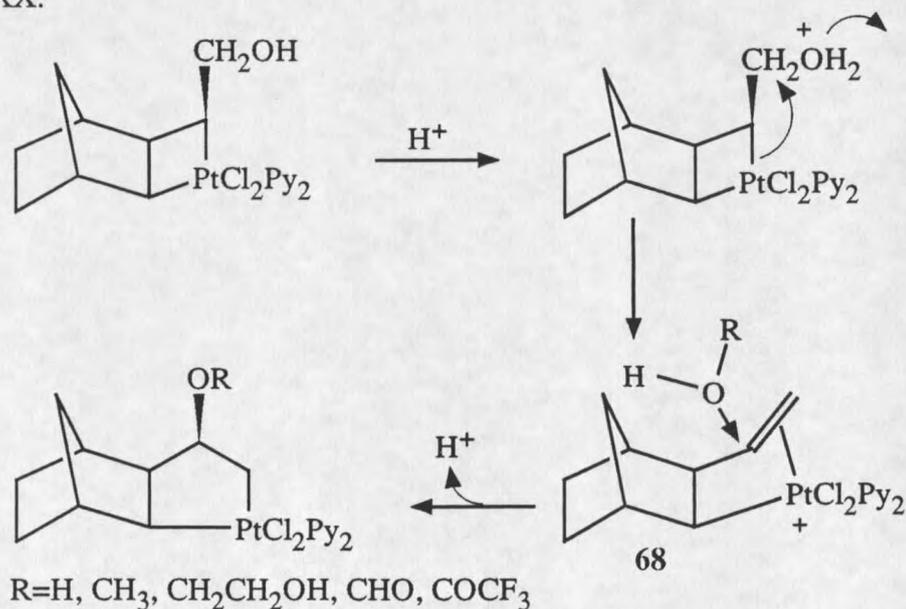


Equation 85 illustrates the facile ring expansion of 1,2,3-trisubstituted platina(IV)-cyclobutanes to trisubstituted platina(IV)cyclopentanes by acid-catalyzed hydrolysis. The suggested mechanistic pathway is shown in Scheme XX<sup>76,81,206</sup>. This ring expansion process is both regio- and stereospecific. The regioselectivity is believed to result from intermediate 68 in which formation of the cyclopentane derivative is clearly favored over the cyclobutane complex. The stereospecificity is proposed to result from nucleophilic attack of 68 at the olefinic face anti to the platinum functionality.

(85)



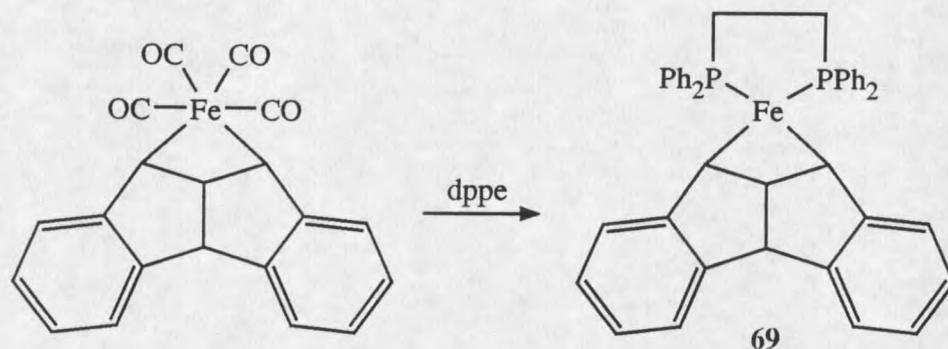
Scheme XX.



Reactions Yielding Ligand Exchange Products

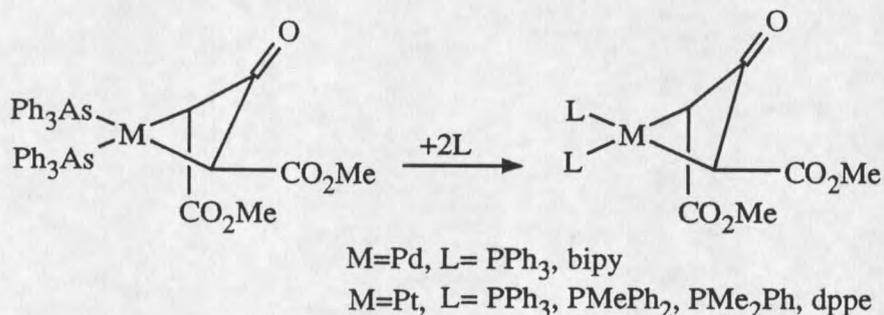
A labile ligand bound to the metal of a metallacyclobutane can be displaced by a variety of less labile ligands to create new metallacyclobutanes. The ferretane molecule, below, reacts with 1,2-bis(diphenylphosphino)ethane (dppe) to yield **69** (equation 86)<sup>104</sup>.

(86)



Pallada(II)- and platina(II)cyclobutanones bearing labile  $\text{AsPh}_3$  ligands react with various phosphorus ligands and 2,2'-bipyridine to yield the metallacyclobutanones shown in equation 87<sup>158</sup>. However, these metallacyclobutanones also can be prepared directly as shown in Table 9.

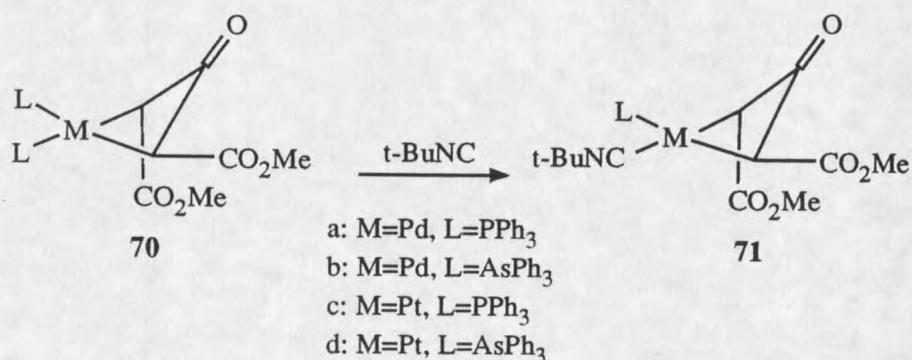
(87)



An equimolar proportion of tertiary-butyl isocyanide can displace one  $\text{AsPh}_3$  or  $\text{PPh}_3$  ligand from **70a-d** to form a high yield of the interestingly substituted complexes **71a-d** (equation 88)<sup>158</sup>. If the triphenylarsine complexes **70b** and **d** are further treated

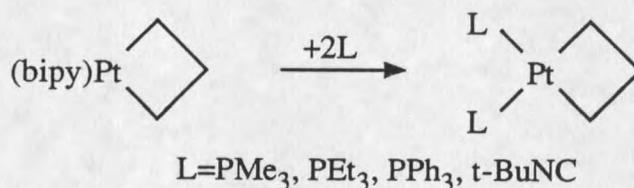
with  $\text{PPh}_3$  in dichloromethane at room temperature, displacement of  $\text{AsPh}_3$  occurs to form 71a and c. Furthermore, under forcing conditions, triphenylphosphine can displace both the  $\text{AsPh}_3$  and  $t\text{-BuNC}$  of 71b and d to form the bis(triphenylphosphine) derivatives.

(88)



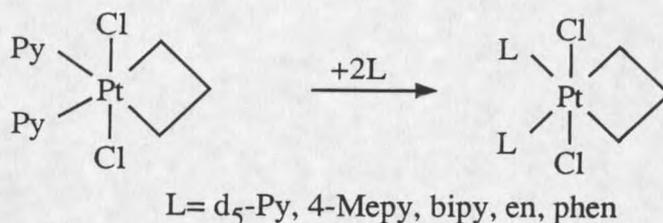
Ligand substitution of the labile 2,2'-bipyridyl ligand on the platina(II)cyclobutane, shown in equation 89, occurs readily by the monodentate ligands  $\text{PPh}_3$ ,  $\text{PEt}_3$ , and  $\text{PMe}_3$ , and to a lesser degree by  $t\text{-BuNC}$ <sup>175,176</sup>. This facile substitution contrasts with the inert behavior, under comparable experimental conditions, of the coordinatively saturated platina(IV)cyclobutane,  $\text{Cl}_2(\text{bipy})\text{Pt}[\text{CH}_2\text{CH}_2\text{CH}_2]$ .

(89)



When phosphorus ligands are added to platina(IV)cyclobutanes reductive elimination occurs rather than ligand exchange. However, labile oxygen and nitrogen donor ligands on platina(IV)cyclobutanes can be displaced by other nitrogen donor ligands according to equation 90<sup>41,65,195,207</sup>.

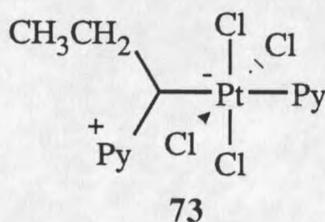
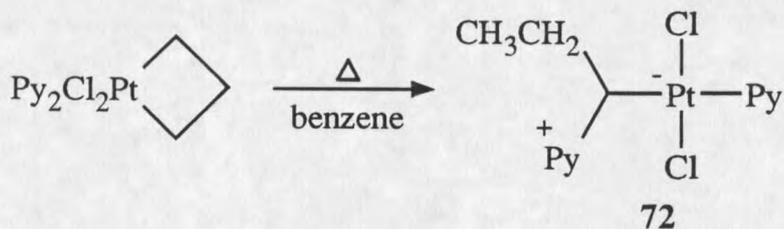
(90)



### Reactions Yielding Ylide Products

During the early investigations of platina(IV)cyclobutane chemistry, it was discovered that upon refluxing in benzene, dichlorobis(pyridine)platina(IV)cyclobutane formed a bright yellow isomeric solid<sup>39</sup>. The x-ray crystal structure later revealed the formation of an ylide complex, dichloro(pyridinium propylide)pyridineplatinum(II) **72** (equation 91)<sup>41,208</sup>. Reaction of the platina(IV)cyclobutane with CCl<sub>4</sub> in chloroform formed the analogous tetrachloro product **73**, which also can be synthesized by addition of CCl<sub>4</sub>/CHCl<sub>3</sub> to **72**<sup>40,41,208</sup>.

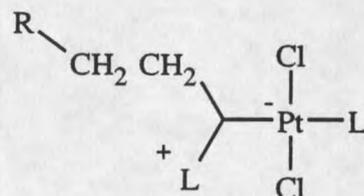
(91)



Substituted platinum ylide complexes can be formed by this methodology and are displayed in Table 45. Of particular interest is the formation of only one ylide isomer although the parent platina(IV)cyclobutanes are known to exist as an equilibrium mixture of two isomers (see equations 2 and 93). Labeling studies suggest that the reaction proceeds only from the minor platina(IV)cyclobutane isomer according to the pathway shown in Scheme XXI<sup>204</sup>. Photochemical methods also transform the minor platina(IV)cyclobutane isomer into ylide products.

When the ligand on the platina(IV)cyclobutane is 2-Mepy the reaction can proceed at room temperature. Apparently, the steric hinderance caused by the o-Me group contributes to the relative ease of ylide formation by promoting initial ligand dissociation.

Table 45. Platinum(IV) ylide complexes.

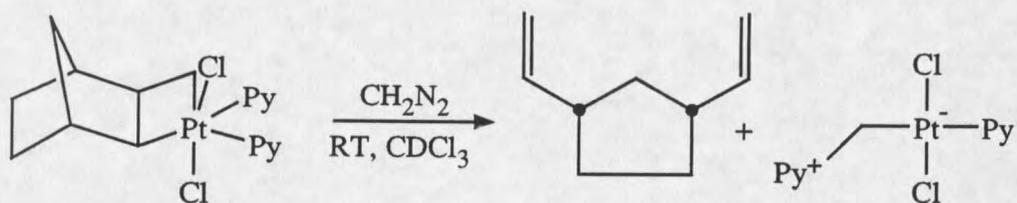


L	R	ref.	L	R	ref.
py	H	41,80	2-Mepy	Bu	47,74
py	Me	74,80	2-Mepy	Ph	47,204
py	Et	80	2-Mepy	p-tol	47
py	Bu	74	2-Mepy	Me <sub>2</sub>	47
py	Me <sub>2</sub>	47,204	3-Mepy	H	41
2-Mepy	Me	47,74	4-Mepy	H	41

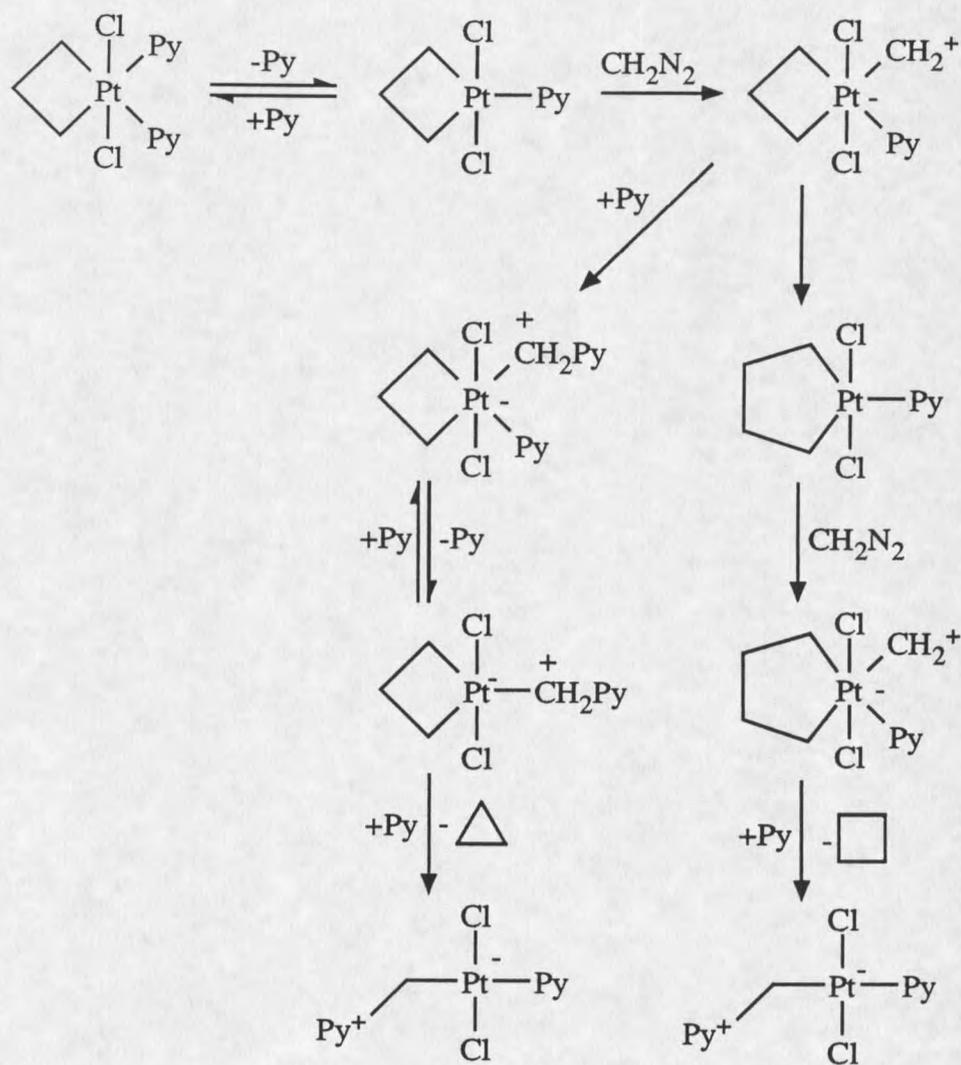


Platinum ylide complexes also have been synthesized from the reaction of norbornyl platina(IV)cyclobutanes with diazomethane, although in low yields (equation 92)<sup>198</sup>. The same ylide product results when a phenyl substituted platina(IV)cyclobutane reacts with diazomethane. The proposed reaction pathway is illustrated in Scheme XXII<sup>182</sup>. The partitioning between the two pathways shown in Scheme XXII seemingly is dependent on the platina(IV)cyclobutane starting material and the reaction temperature.

(92)



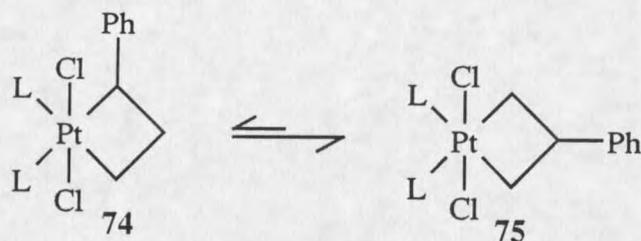
Scheme XXII.



### Intramolecular Rearrangement Yielding Isomeric Products

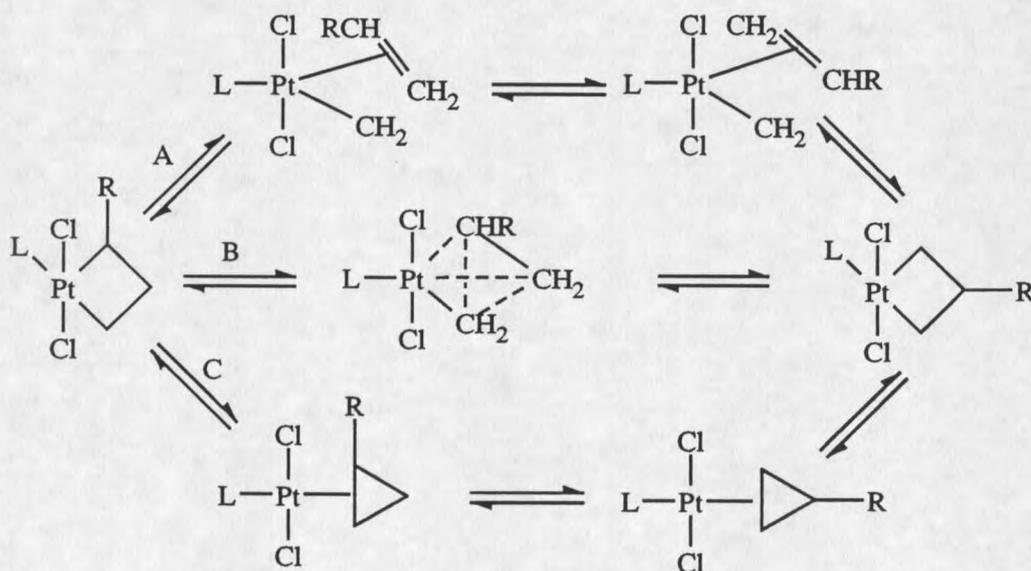
Platina(IV)cyclobutanes are known to undergo an unusual intramolecular rearrangement to form isomeric products (equation 93)<sup>68</sup>. In the case of phenylcyclopropane shown below, the Pt(II) is believed to be initially inserted into the most highly substituted cyclopropane bond to form 74 which then isomerizes to 75. The product ratio upon equilibration is 2.3 to 1, 75 to 74<sup>75</sup>.

(93)



The above isomerization has been investigated extensively with various aryl and alkyl substituents on the platinum(IV)cyclobutane, as well as numerous ligands. Three mechanisms have been proposed and are shown in Scheme XXIII<sup>68,72,75,207,209</sup>. However, the details of this rearrangement have been examined in a previous review so will not be presented here<sup>47</sup>.

Scheme XXIII.

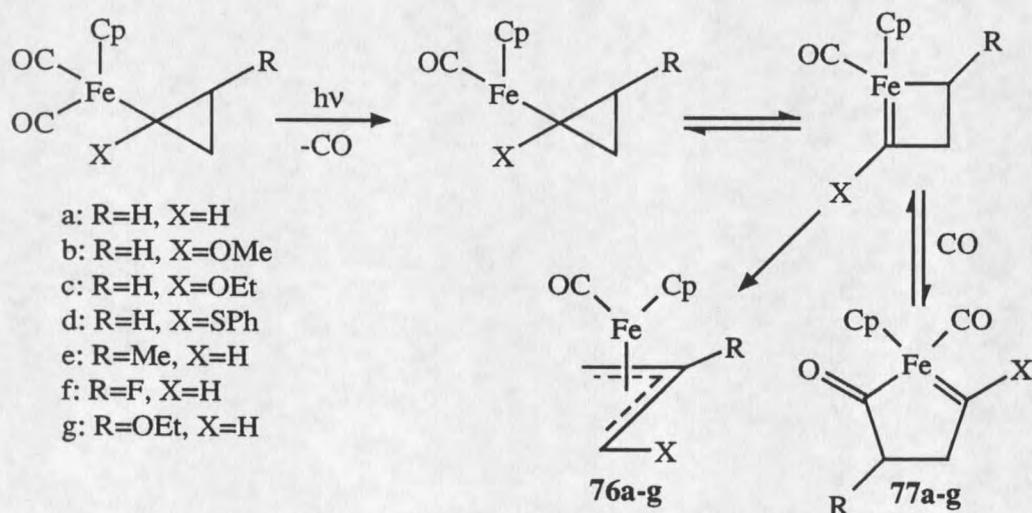


Metallacyclobutane Derivatives as Intermediates

Ferra(II)cyclobutane Derivatives as Intermediates

Ferra(II)cyclobutane and -cyclobutene intermediates have been proposed in a number of transformations involving iron complexes. Recently a ferra(II)cyclobutene was proposed for reactions involving rearrangements of cyclopropanes  $\sigma$  bonded to iron<sup>170,171, 210</sup>. Scheme XXIV illustrates the role of ferra(II)cyclobutene in formation of both the  $\pi$ -allyl iron complex **76a-g** and the ferra(II)cyclopentenones **77a-g**. Although highly unstable, the proposed ferra(II)cyclobutene intermediate reportedly has been characterized by <sup>1</sup>H NMR spectroscopy.

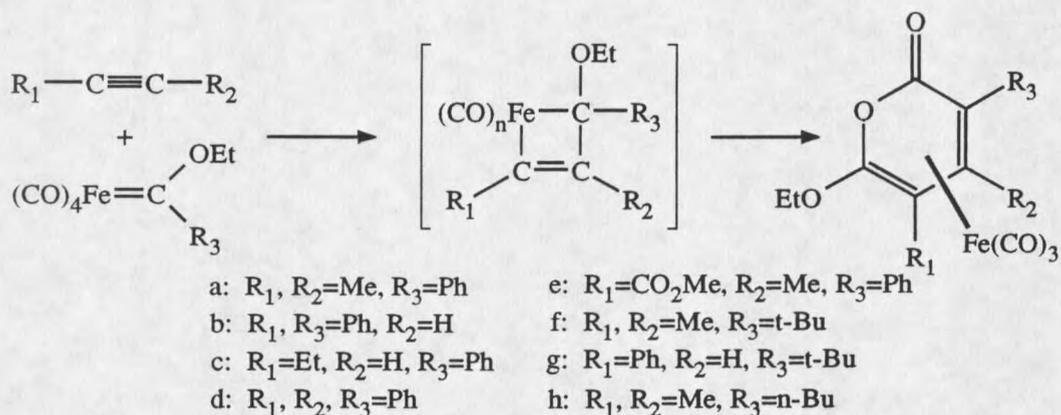
Scheme XXIV.



The synthesis of a variety of 6-ethoxy- $\alpha$ -pyrone complexes by reaction of alkynes with (ethoxyalkylidene)tetracarbonyliron(0) complexes also is believed to occur via a

ferra(II)cyclobutene intermediate according to equation 94<sup>211</sup>. Spectroscopic evidence also supports this key intermediate.

(94)



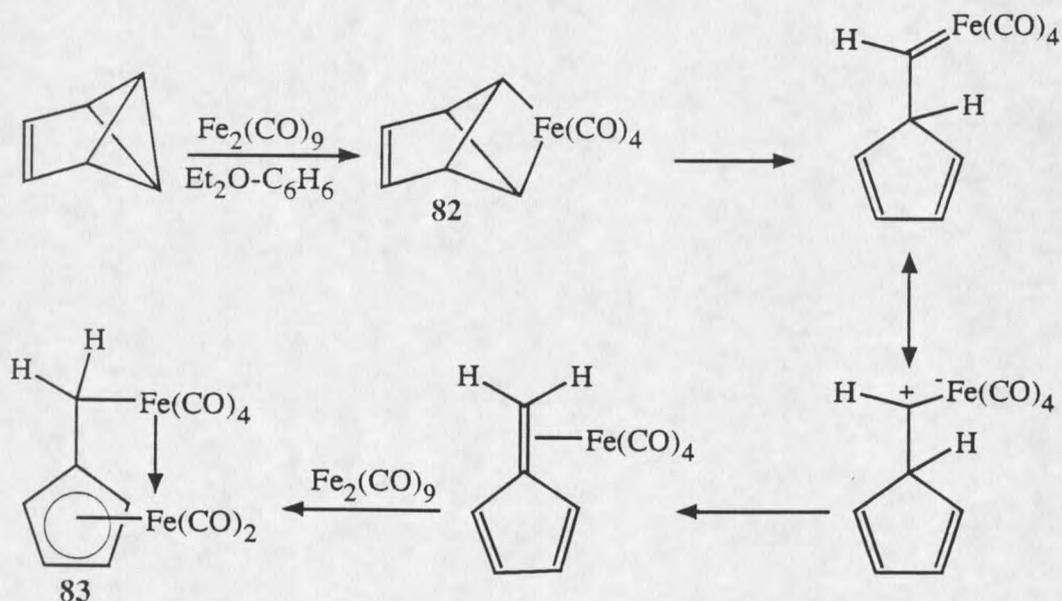
Another example of a proposed ferra(II)cyclobutene intermediate is shown in Scheme XXV for the formation of **80** from diphenylacetylene and pentakis(*t*-butylisocyanide) iron(0)<sup>212</sup>. An oxidative cyclization reaction is believed to occur from the  $\eta^2$ -bonded acetylene **78** to form the metallacyclic intermediate **79**.

In the formation of **81**, a ferra(II)cyclobutene intermediate is believed to form by insertion of Fe(0) into the most highly substituted bond of 1,3,3-trimethylcyclopropene (equation 95)<sup>213</sup>. Although having greater steric hindrance, this site may be favorable due to the increased electron density created by the methyl substituents.



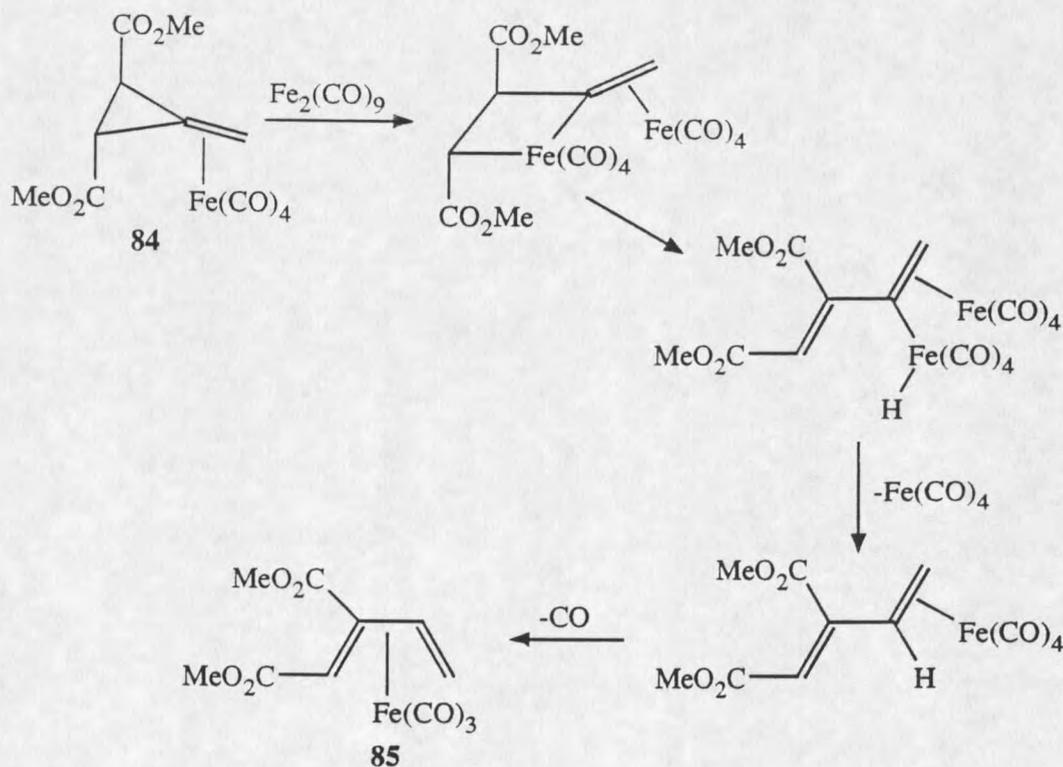
Two examples of proposed ferra(II)cyclobutane intermediates have been reported. Scheme XXVI illustrates the transformation of benzvalene to hexacarbonyl-fulvene diiron **83** via a ferretane intermediate **82**<sup>214</sup>.

Scheme XXVI.



The reaction shown in Scheme XXVII involves oxidative addition of the strained  $\text{sp}^2\text{-sp}^3$  bond of **84** to  $\text{Fe}(0)$  to form a ferra(II)cyclobutane intermediate which then proceeds as shown to form **85**<sup>215</sup>. The trans disubstituted starting material in Scheme XXVII forms exclusively syn products. Likewise, the analogous cis disubstituted starting material forms exclusively the anti product and also proceeds via a ferra(II)cyclobutane intermediate.

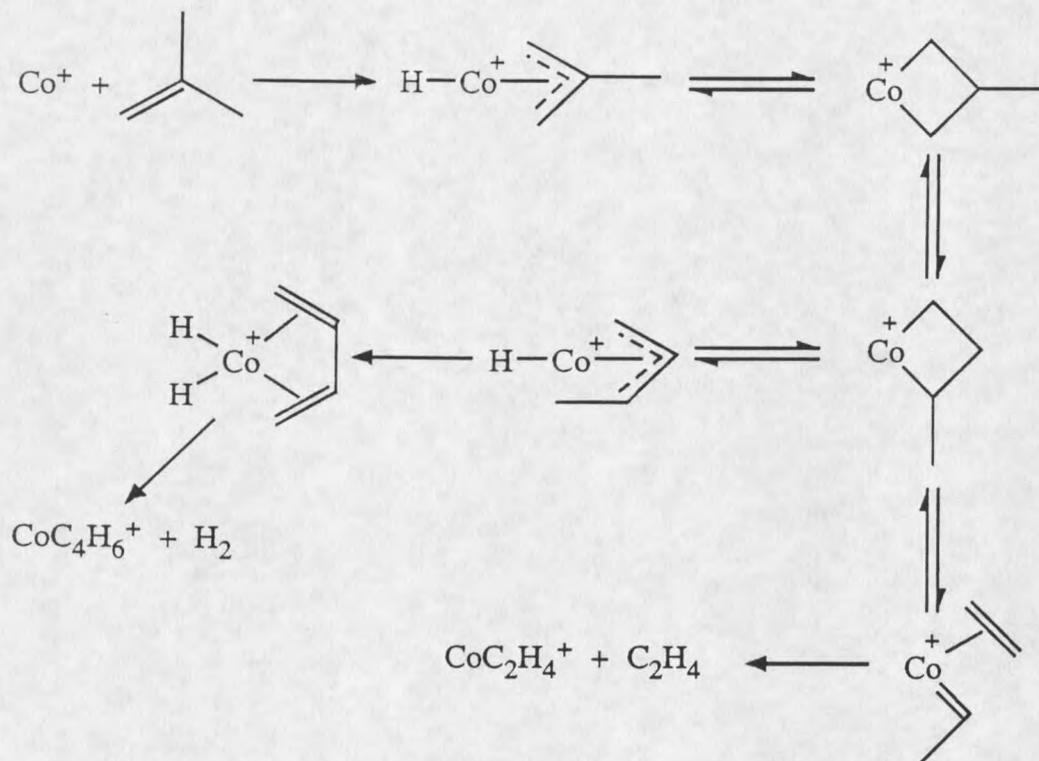
Scheme XXVII.



### Cobalta(II)- and (III)cyclobutane Derivatives as Intermediates

Cobalta(III)cyclobutane intermediates have been proposed in reactions of cobalt ions with alkenes and cycloalkanes. Reaction of cobalt in the gaseous phase with 2-methylpropene yields the cleavage products ethylene and ethylene-cobalt complexes, as well the dehydrogenation product,  $\text{CoC}_4\text{H}_6^+$ . A cobalta(III)cyclobutane ion intermediate was invoked to explain the cleavage results (Scheme XXVIII)<sup>216</sup>. The isomerization of the metallacyclic intermediate is suggested to occur through either a cobalt-carbene intermediate or by a concerted process analogous to that proposed for the rearrangement of platina(IV)cyclobutanes shown in equations 2 and 93.

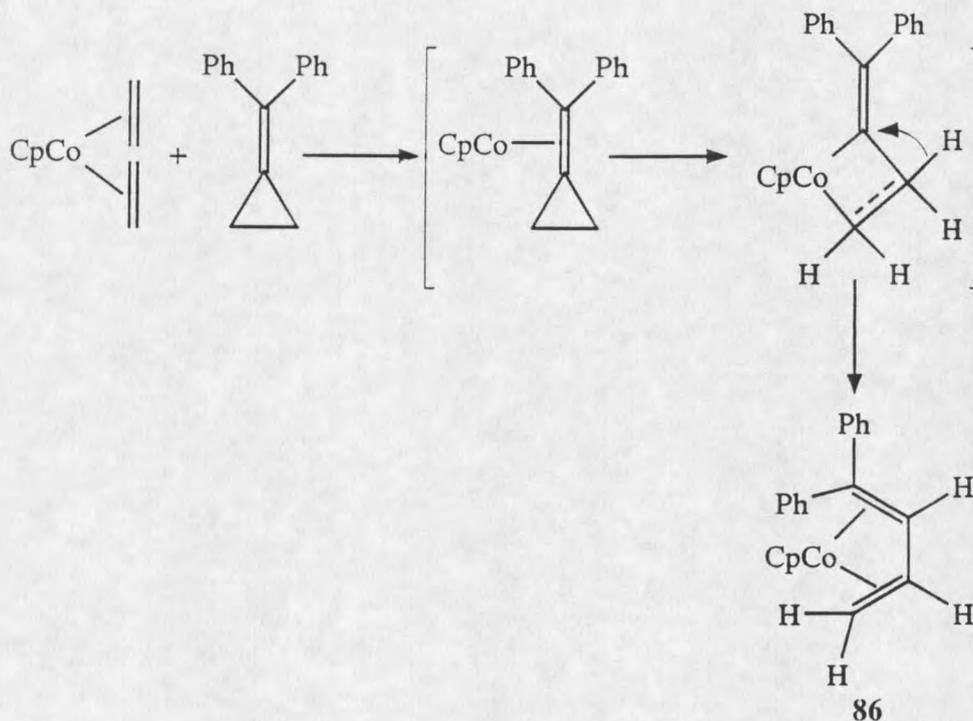
Scheme XXVIII.



Further investigations of cobalt ion reactions with cyclopropanes, cyclobutane and cyclobutanones also have led to suggestions of cobalta(III)cyclobutane ion intermediates<sup>179,180, 217</sup>.  $\text{Fe}^+$ ,  $\text{Ni}^+$ , and  $\text{Rh}^+$  also were studied with the above organic substrates and metallacyclobutane intermediates again were proposed<sup>218,219</sup>.

In addition to reactions in the gas phase, a cobalta(II)cyclobutane intermediate was invoked in the reaction of  $\text{CpCo-bis(ethylene)}$  with diphenylmethylenecyclopropane to yield 86 (equation 96)<sup>220</sup>. Minor amounts of a binuclear cobaltacyclopentadiene product also were observed.

(96)

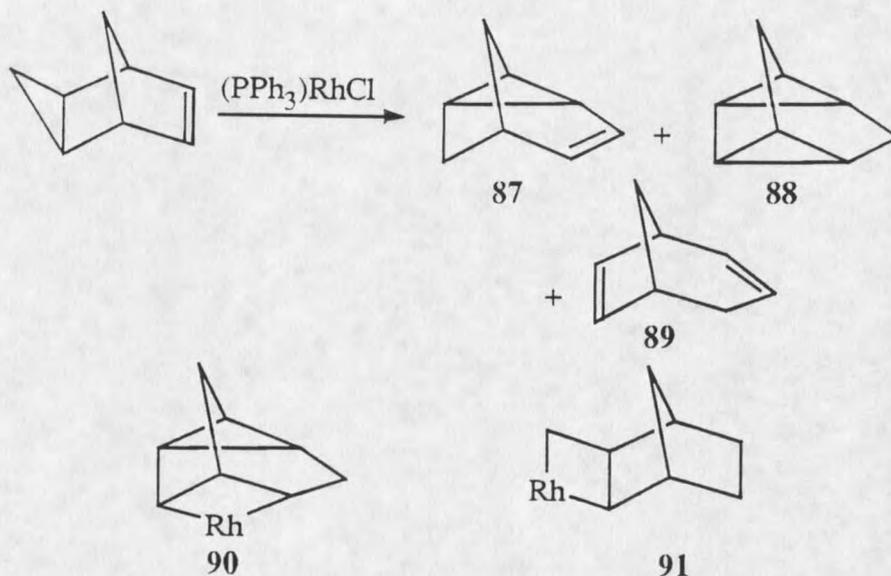


### Rhoda(III)cyclobutane Derivatives as Intermediates

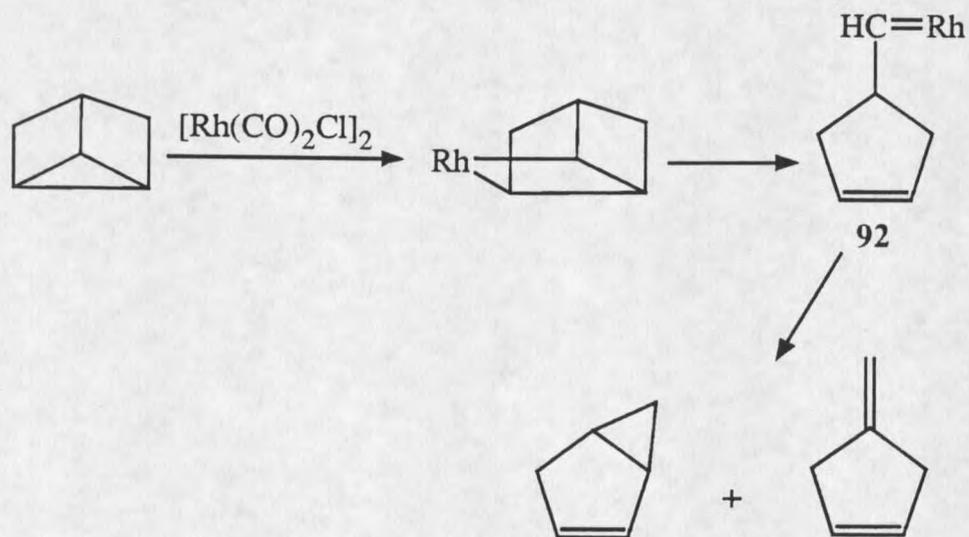
Rhodium(I) catalyzed isomerizations of strained ring systems have been suggested to occur through a rhoda(III)cyclobutane intermediate. The intermediate **90** was proposed for the isomerization of *exo*-tricyclo[3.2.1.0<sup>2,4</sup>]octene to products **87** and **88** (equation 97)<sup>201,221</sup>. A small percent of **89** also is produced in this isomerization but apparently follows an alternate pathway which is suggested to proceed via the rhoda(III)cyclobutane intermediate **91**.

A second example of a rhodium(I) catalyzed isomerization containing a proposed rhoda(III)cyclobutane intermediate is shown in equation 98<sup>222</sup>. Tricyclo[2.2.0.0<sup>2,6</sup>]-hexane is converted to 4-methylenecyclopentene via Rh(I) insertion into a carbon-carbon bond of the cyclopropane moiety to form a rhoda(III)cyclobutane intermediate which rearranges to **92** before forming 4-methylenecyclopentene, along with minor amounts of

(97)



(98)



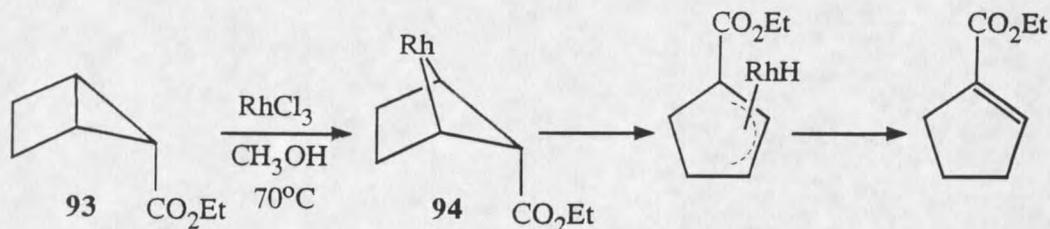
bicyclo[3.1.0]hexene.

Substituted bicyclo[2.1.0]pentanes catalytically isomerize to cyclopentenes via a rhoda(III)cyclobutane intermediate. The example shown in equation 99 produces 1-carboethoxycyclopentene, along with minor amounts of 3-carboethoxycyclopentene<sup>223</sup>.

The metallacyclic intermediate **94** is formed by oxidative addition of the central carbon

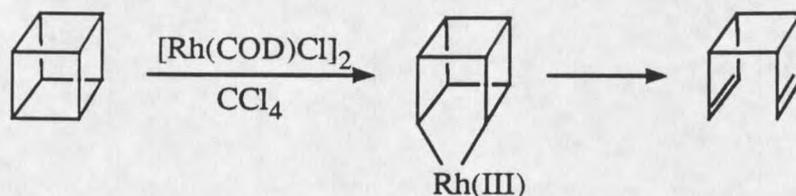
bond of 93 to the rhodium center.

(99)

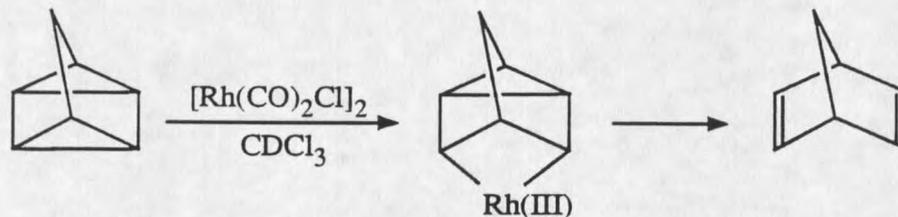


The Rh(I) catalyzed valence isomerizations of cubane and quadricyclane derivatives to form syn-tricyclooctadiene and norbornadiene are shown in equations 100<sup>224</sup> and 101<sup>225</sup>, respectively. Both isomerizations are suggested to proceed via a rhoda(III)cyclobutane intermediate as shown.

(100)

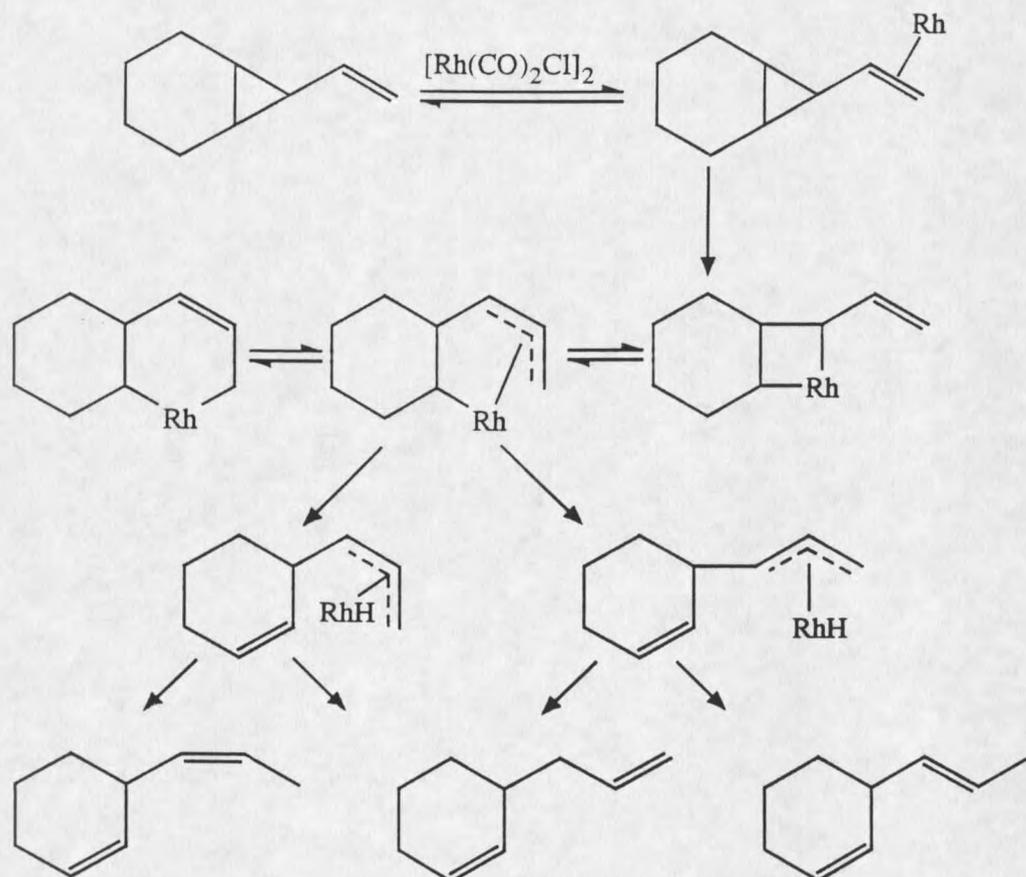


(101)



A rhoda(III)cyclobutane intermediate also is suggested for the Rh(I) catalyzed rearrangement of vinylcyclopropanes (Scheme XXIV)<sup>226,227</sup>. The regioselectivity observed for the  $\beta$ -hydride elimination is attributed to the metallacyclic structures.

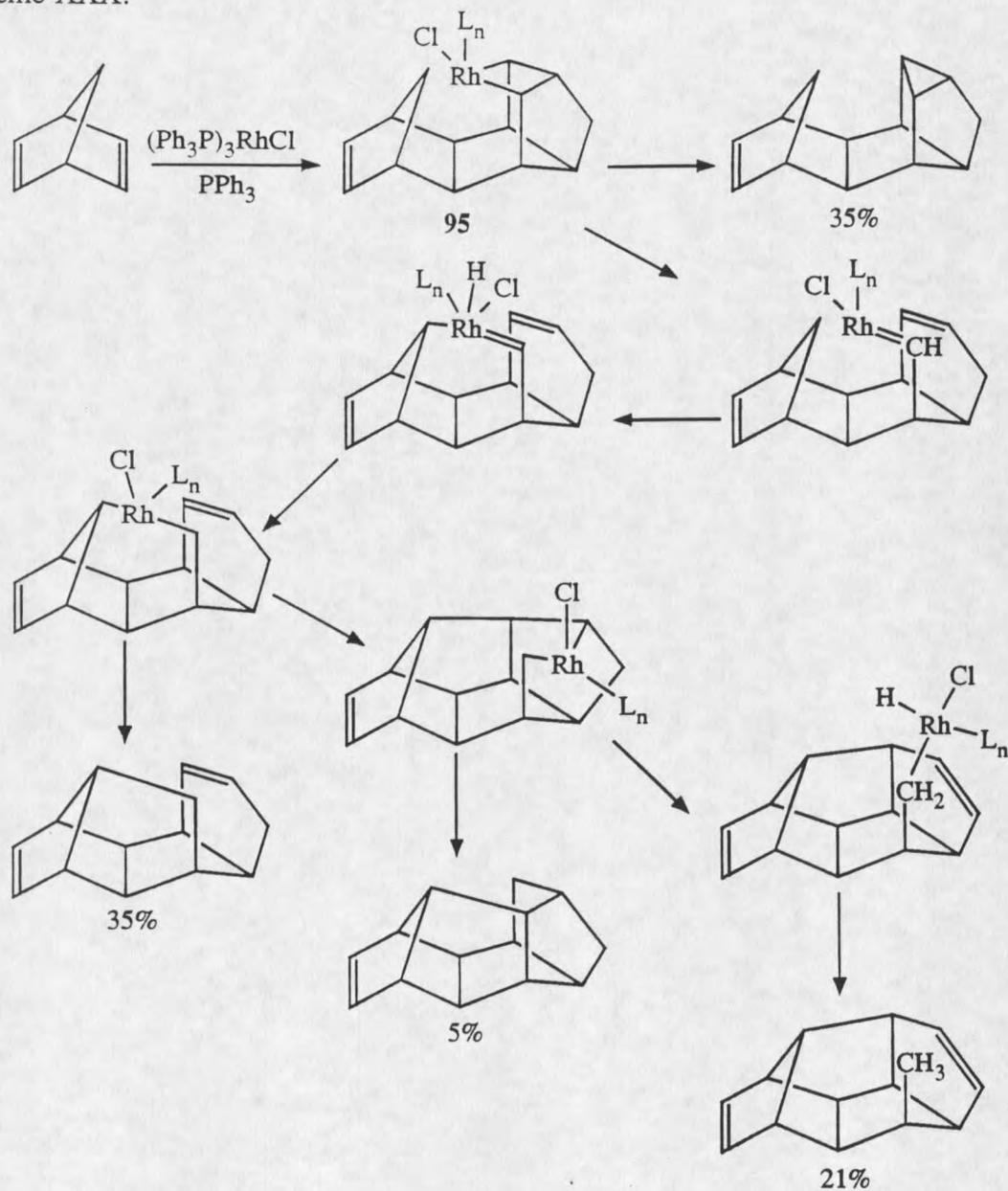
Scheme XXIV.



In addition to isomerization reactions, one rhoda(III)cyclobutane intermediate **95** has been proposed as a precursor to four different dimers, formed in 64% yield, in the oligomerization of norbornadiene<sup>228</sup>. Scheme XXX illustrates the proposed pathways suggested to obtain the resulting dimeric products.

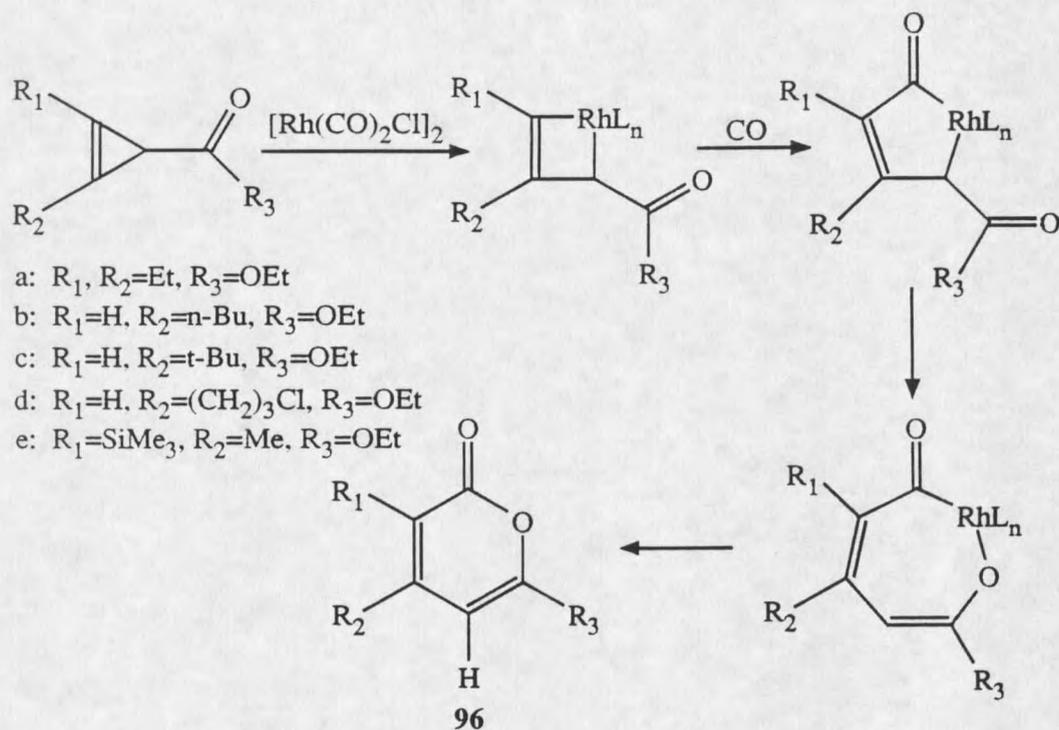
In a reaction reminiscent of that shown in equation 94, a rhoda(III)cyclobutane intermediate is invoked in the Rh(I)-catalyzed carbonylation of cyclopropenyl esters and ketones to form  $\alpha$ -pyrones (Scheme XXXI)<sup>229</sup>. A variety of substituted organic substrates have been utilized and in some instances a mixture of  $\alpha$ -pyrone isomers and formation

Scheme XXX.

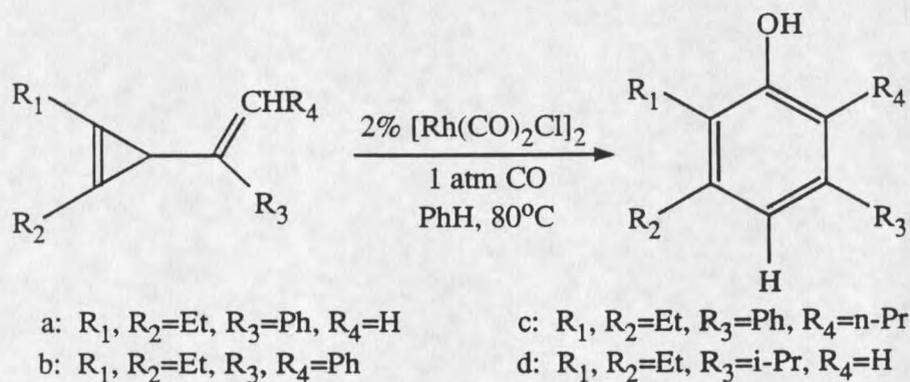


of furan isomers occurs. Scheme XXXI shows only those substituent patterns that produce 96 as the major product in greater than 60% yields. The same pathway is suggested for the formation of phenols from vinylcyclopropenes (equation 102).

Scheme XXXI.

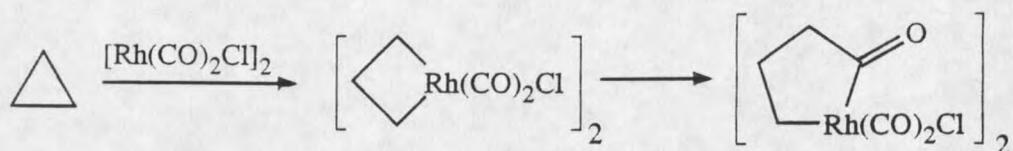


(102)



The synthesis of rhoda(III)cyclopentanone dimer also is believed to result from initial rhodium(I) insertion into cyclopropane to form a rhoda(III)cyclobutane intermediate. Subsequent migratory insertion leads to the observed metallacyclic product (equation 103)<sup>230</sup>.

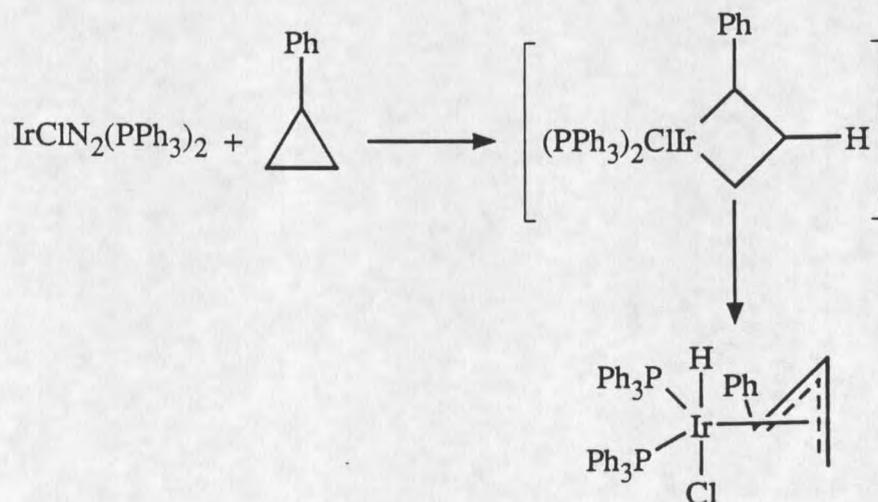
(103)



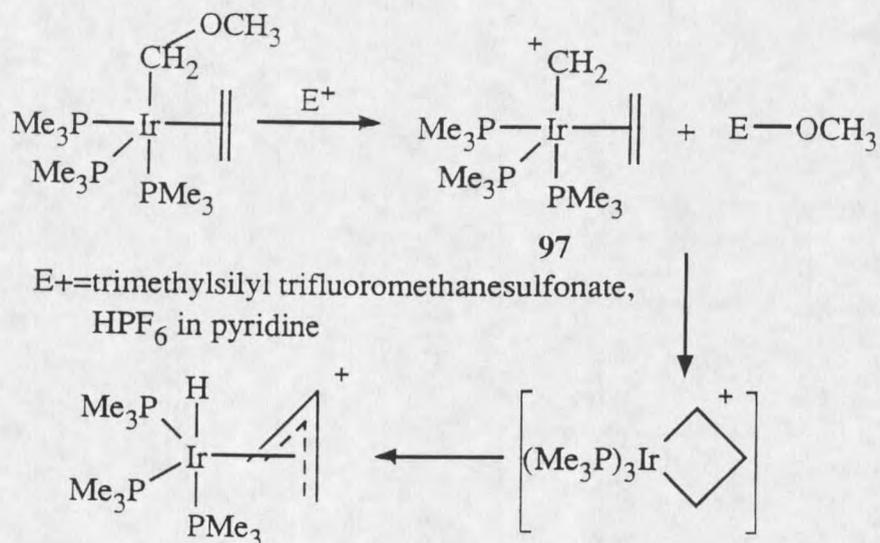
### Irida(III)cyclobutane Derivatives as Intermediates

The synthesis of  $\eta^3$ -allyl iridium hydride complexes invokes an irida(III)cyclobutane intermediate. Two examples are shown in equations 104 and 105. In equation 104, the irida(III)cyclobutane intermediate is formed by insertion of Ir(I) into the 1,2 carbon-carbon bond of phenylcyclopropane<sup>231,232</sup>. The metallacyclic intermediate formed in the reaction shown in equation 105, however, is created by rapid bond formation between the methylene ligand and the ethylene moiety of **97**<sup>24</sup>. In both cases, the irida(III)cyclobutane intermediate subsequently undergoes  $\beta$ -hydride abstraction to form the  $\eta^3$ -allyl iridium hydride product.

(104)



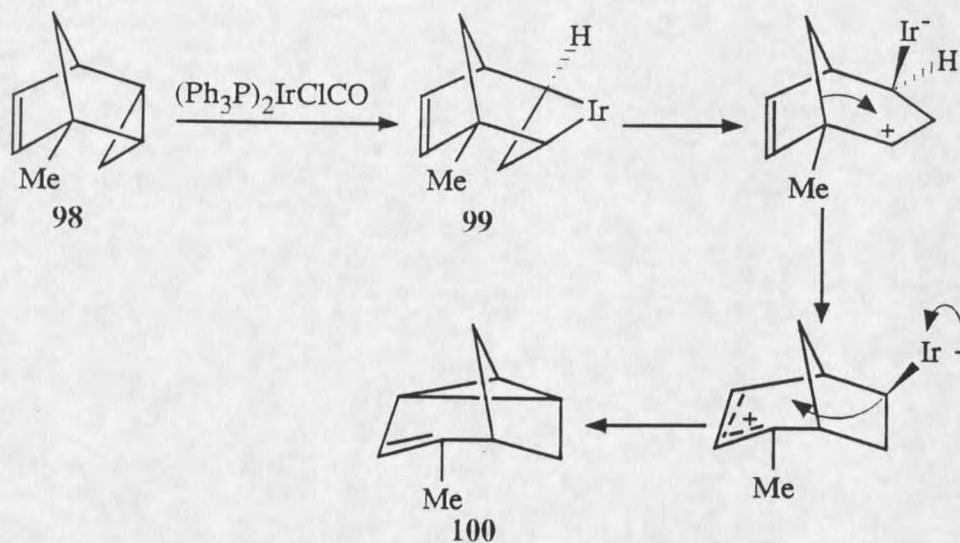
(105)



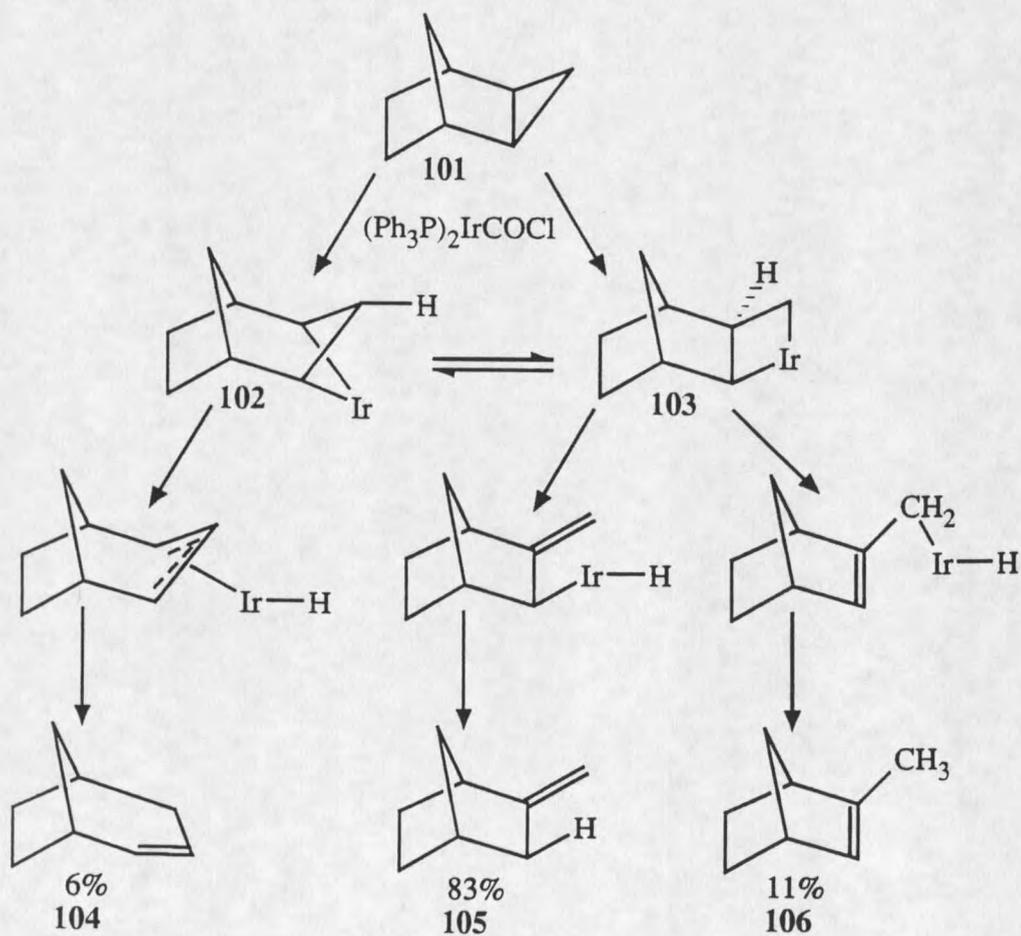
The iridium(I) catalyzed carbocyclic rearrangement of endo-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene **98** to tricyclo[3.2.1.0<sup>2,7</sup>]oct-3-ene **100** reportedly occurs via initial formation of an irida(III)cyclobutane intermediate **99**<sup>234,235</sup>. **99** is formed by iridium(I) insertion into the central carbon bond of the tricyclo ring system. The proposed rearrangement pathway for the methyl substituted substrate is outlined in Scheme XXXII.

Similarly, two irida(III)cyclobutane intermediates, **102** and **103**, are proposed for the iridium(I)-catalyzed rearrangement of exo-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene and -octane. Scheme XXXIII demonstrates the rearrangement of **101** to the observed products **104**, **105** and **106**<sup>234</sup>. It is possible that the metallacyclic intermediates are formed by initial insertion into two different edges of the cyclopropane moiety or perhaps the iridium inserts into one edge and equilibrates via a Puddephatt-type rearrangement.

Scheme XXXII.

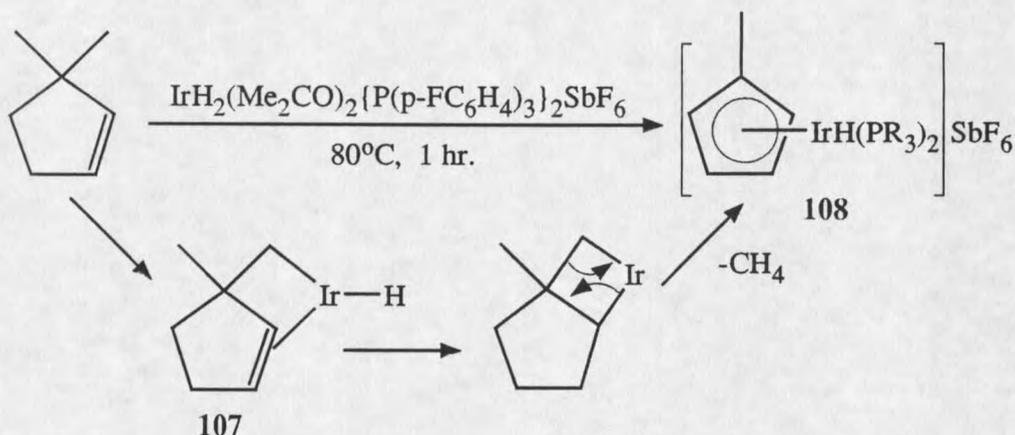


Scheme XXXIII.



The reaction of 3,3-dimethylcyclopentene with an iridium complex to form **108** also invokes an irida(III)cyclobutane intermediate (Scheme XXXIV)<sup>236</sup>. The metallacyclic intermediate is formed by olefin insertion from the iridium hydride complex **107**. A metathesis like cleavage then occurs to eventually lead to the observed product, **108**.

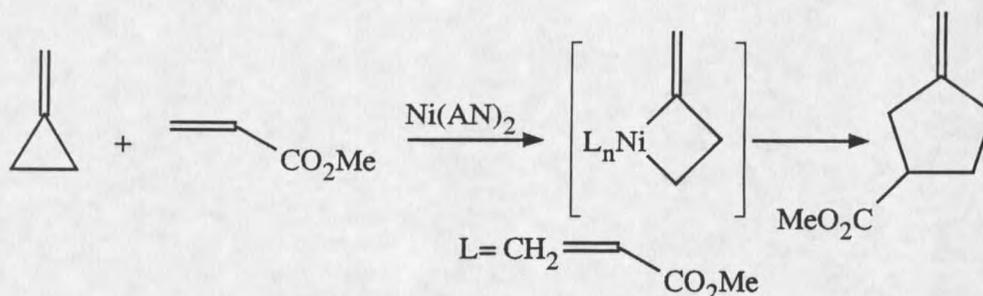
Scheme XXXIV.



#### Nickela(II)cyclobutane Derivatives as Intermediates

Nickel(0) catalyzed cycloaddition reactions often proceed through a nickela(II)-cyclobutane intermediate. The  $[2\sigma+2\pi]$  cycloaddition of methylene cyclopropane and methyl acrylate in the presence of bis(acrylonitrile)nickel(0), shown in equation 106, is one example<sup>237-239</sup>. However, a similar reaction utilizing a  $\text{Ni}(\text{COD})_2$  catalyst led to additional products and prompted investigators to suggest an alternate reaction pathway involving a nickela(II)cyclopentane intermediate<sup>240</sup>.

(106)

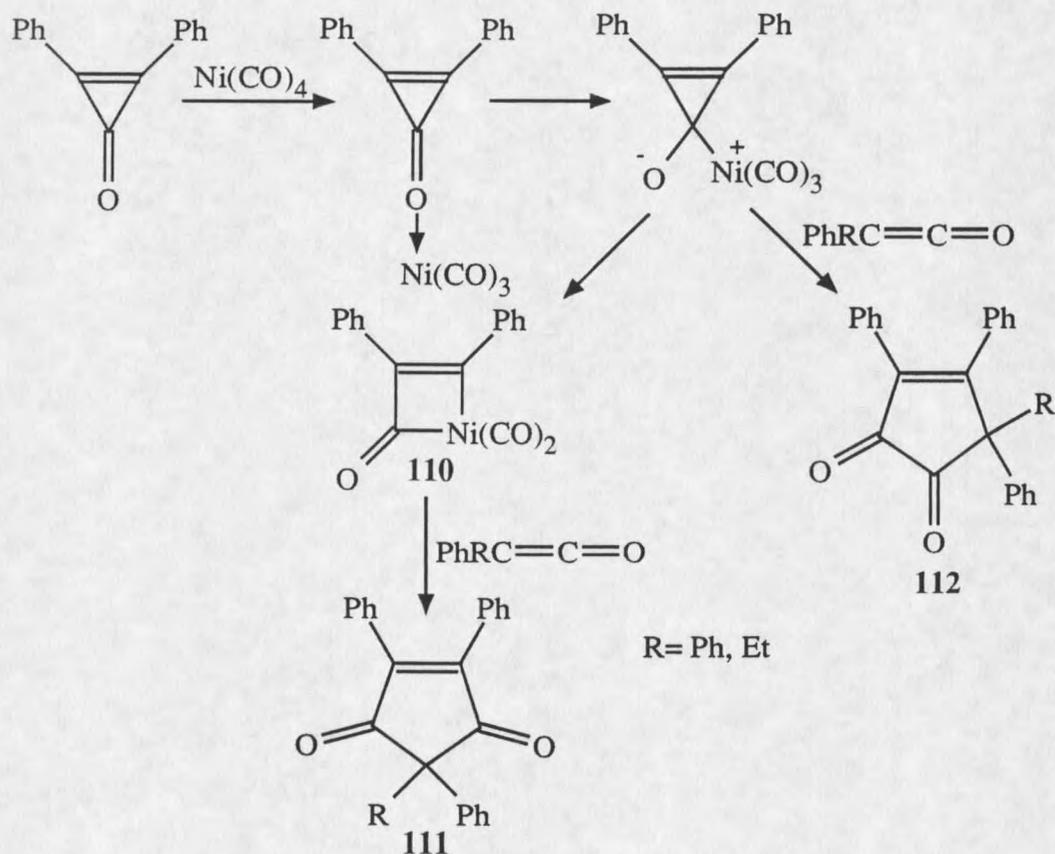


A nickela(II)cyclobutane intermediate also has been reported for the cycloadditions of bicyclo[1.1.0]butane, bicyclo[2.1.0]pentane and quadricyclane with electron deficient olefins<sup>241-243</sup>. The general reaction scheme for the deuterium labeled bicyclo[2.1.0]pentane example is shown in Scheme XXXV.

Nickela(II)cyclobutenone intermediates are proposed for the reactions shown in Schemes XXXVI and XXXVII. Scheme XXXVI illustrates the reaction of either diphenylcyclopropanone or diphenyl acetylene with (tetracarbonyl)nickel(0) and water to form 109<sup>244</sup>. In Scheme XXXVII, Ni(0) catalyzes the cycloaddition of diphenylcyclopropanone and ketene to yield 111 and 112<sup>57,245</sup>. 111 is suggested to form via a metallacyclobutenone intermediate 110 as shown.



Scheme XXXVII.

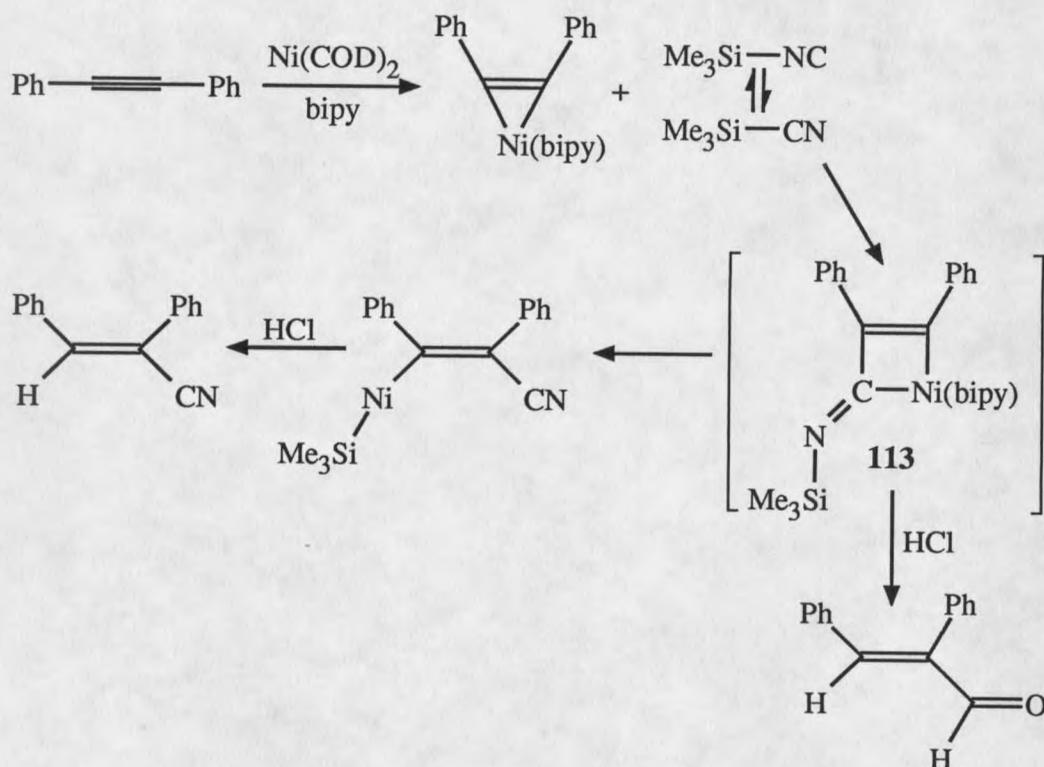


Reaction of diphenylacetylene with Ni(0) forms a nickel(II)cyclopropene that when treated with trimethylsilylisocyanide forms products which are indicative of a nickel(II)cyclobutenimine intermediate 113 (Scheme XXXVIII)<sup>246</sup>.

#### Palladium(II)cyclobutane Derivatives as Intermediates

In accordance with the reaction shown in equation 106 of the previous section, the palladium(0) catalyzed  $[2\sigma+2\pi]$  cycloaddition of methylenecyclopropane and olefins also presumably proceeds through a metallacyclic intermediate. In contrast to nickel, however, palladium(0) apparently cleaves the methylene cyclopropane at the C<sub>2</sub>-C<sub>3</sub> bond rather than

Scheme XXXVIII.

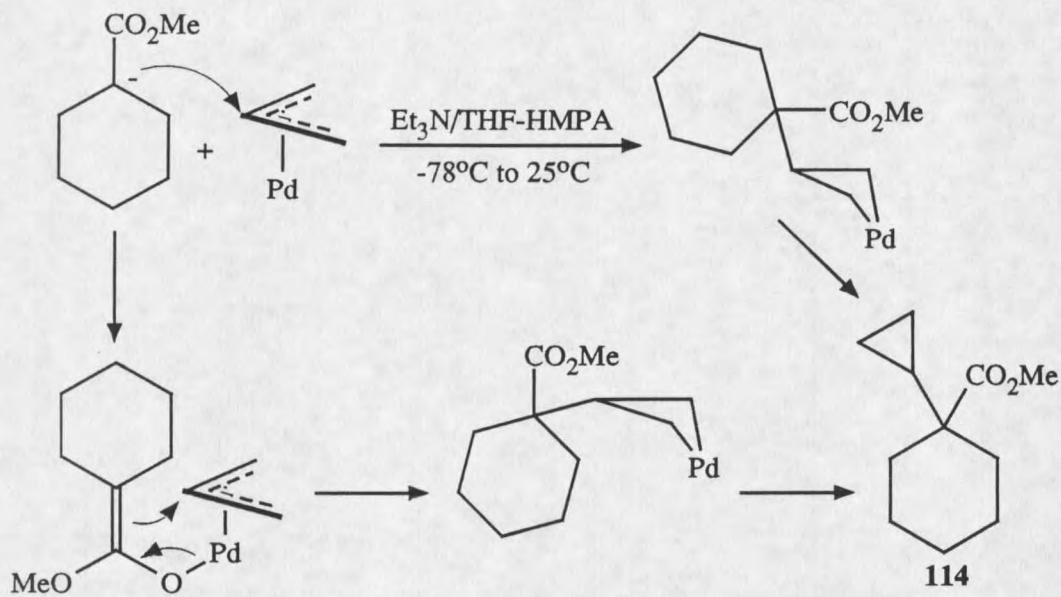


at the  $\text{C}_1\text{-C}_2$  bond to form the trimethylenemethane intermediate. An example of this process is illustrated in Scheme XXXIX<sup>247,248</sup>. Further investigations have been performed with various olefins reacting with methylene-cyclopropane and 1-methylene-2-vinylcyclopropane and reactions of  $\text{CO}_2$  with methylene cyclopropane to form  $\gamma$ -lactones<sup>249,250</sup>. In all cases, initial formation of a pallada(II)cyclobutane intermediate is suggested which subsequently leads to the observed products by various pathways.

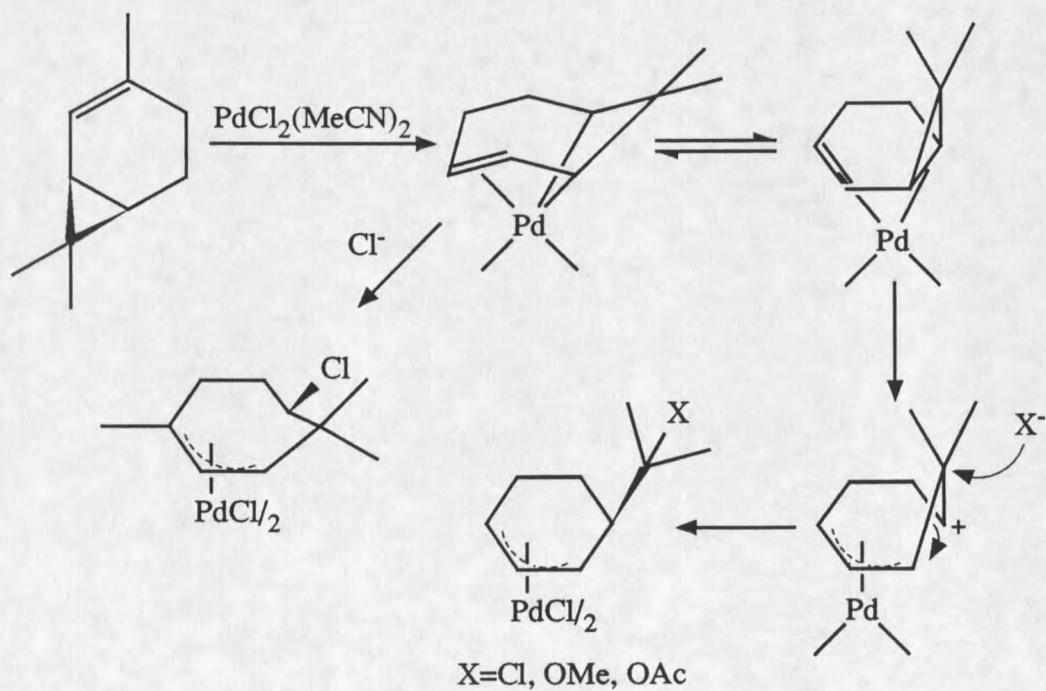
A pallada(II)cyclobutane intermediate also is invoked in the cyclopropanation of ester enolates by  $\pi$ -allyl palladium chloride complexes (Scheme XL)<sup>251</sup>. In this example, pallada(II)cyclobutane formation occurs either by direct nucleophilic attack on the central carbon of the  $\eta^3$ -allyl system or by attack at the palladium center followed by transfer to



Scheme XL.



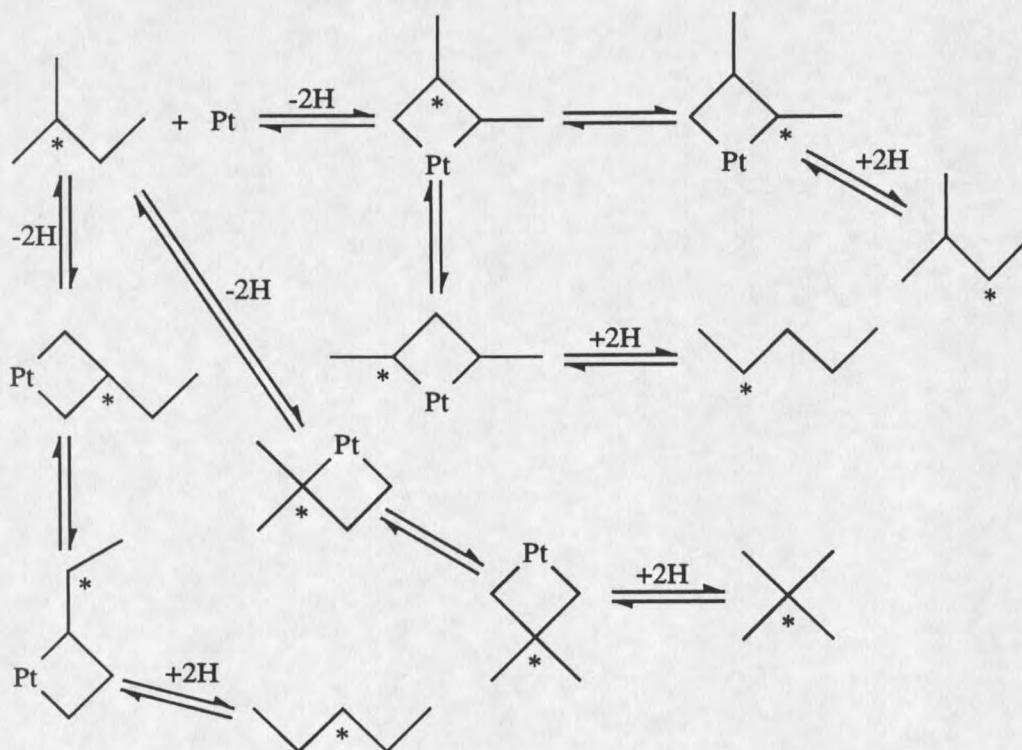
Scheme XLI.



Platina(II)- and -(IV)cyclobutane Derivatives  
as Intermediates

Both platina(II)- and platina(IV)cyclobutanes have been suggested as reaction intermediates. The isomerization of pentanes over platinum metal catalysts invokes a platina(II)cyclobutane intermediate, with possibly two or three platinum atoms interacting, to account for the observed products<sup>253</sup>. A similar mechanism has been developed for this isomerization that supports a single platinum center interacting with pentane and also employs the known skeletal isomerization of platina(IV)cyclobutanes (Scheme XLII)<sup>47,73</sup>.

Scheme XLII.

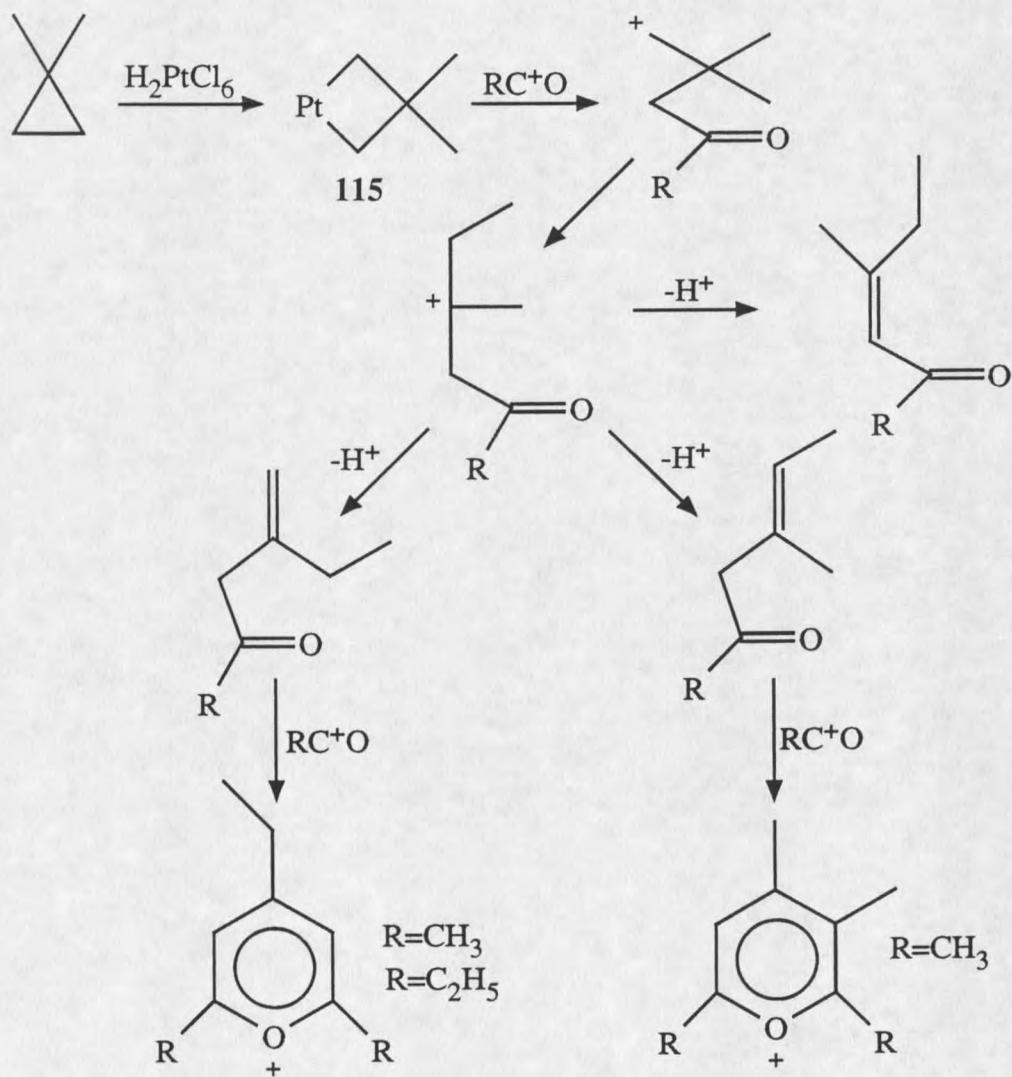


The reaction of chloroplatinic acid and methylsubstituted cyclopropanes, in acetic anhydride, failed to yield the expected stable platina(IV)cyclobutane that results from the unsubstituted cyclopropane analogues. The observed products were instead pyrilium ions

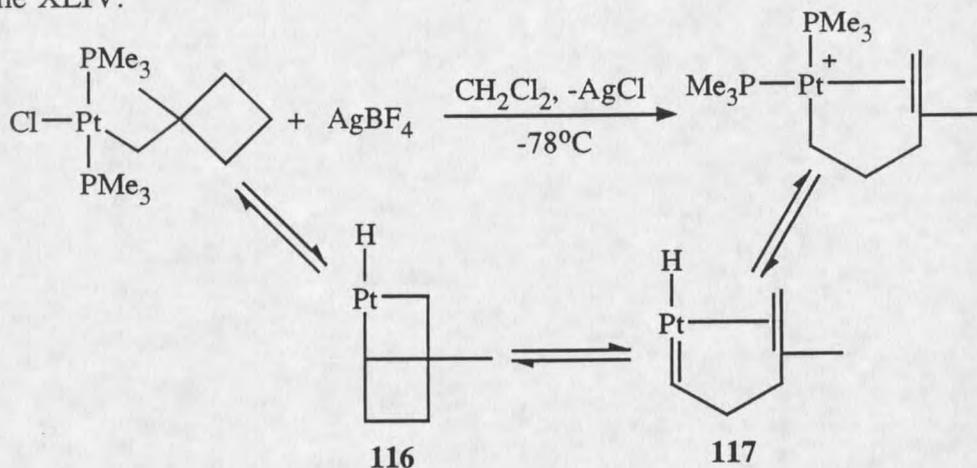
which are believed to form via a platina(IV)cyclobutane intermediate **115** according to Scheme XLIII<sup>60</sup>. It is suggested that the methyl substituted platina(IV)cyclobutane formed is more susceptible to electrophilic attack by the acyl group than its unsubstituted analogue. Therefore, acylation and subsequent pyrillium ion formation is favored over precipitation of a stable platina(IV)cyclobutane tetramer. Although a C<sub>2</sub>-C<sub>3</sub> bond cleavage of cyclopropane to form intermediate **115** is proposed, the possibility that platinum insertion into the C<sub>1</sub>-C<sub>3</sub> bond initially occurs followed by isomerization to **115** cannot be excluded. Acylation of the platina(IV)cyclobutane intermediate and cleavage of the carbon-platinum bond then occurs, followed by methyl migration and proton loss to form the  $\beta,\gamma$ -unsaturated ketones. Additional acylation of the ketone species then leads to formation of the pyrillium ions.

In a study of  $\beta$ -alkyl eliminations, the rearrangement shown in Scheme XLIV was observed enroute to the final products<sup>254</sup>. Although it appears to be a  $\beta$ -alkyl elimination, this pathway cannot be distinguished from  $\gamma$ -C-H activation process that forms a platina(IV)cyclobutane intermediate **116** as shown. Although platina(IV)cyclobutanes are normally resistant to ring cleavage, it is suggested that the intermediate **116** may be susceptible to ring cleavage to form **117** due to the strain energy from the cyclobutane moiety.

Scheme XLIII.



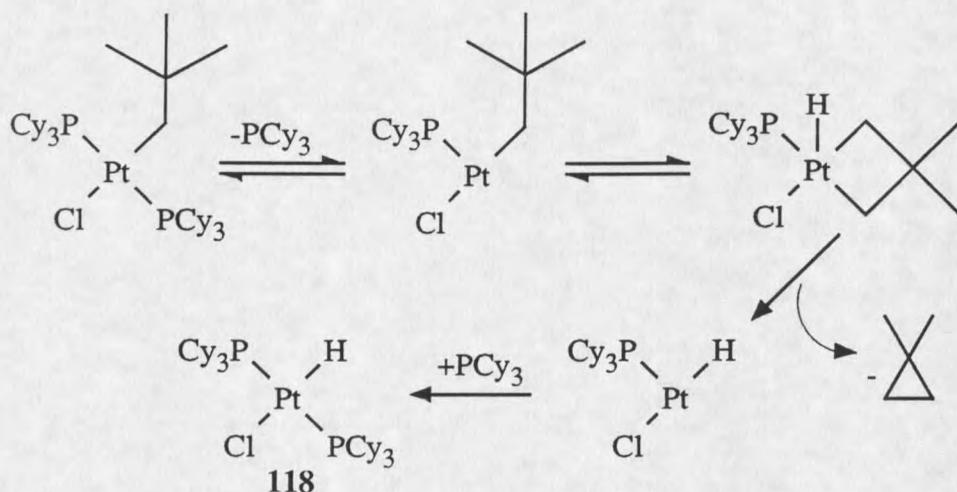
Scheme XLIV.



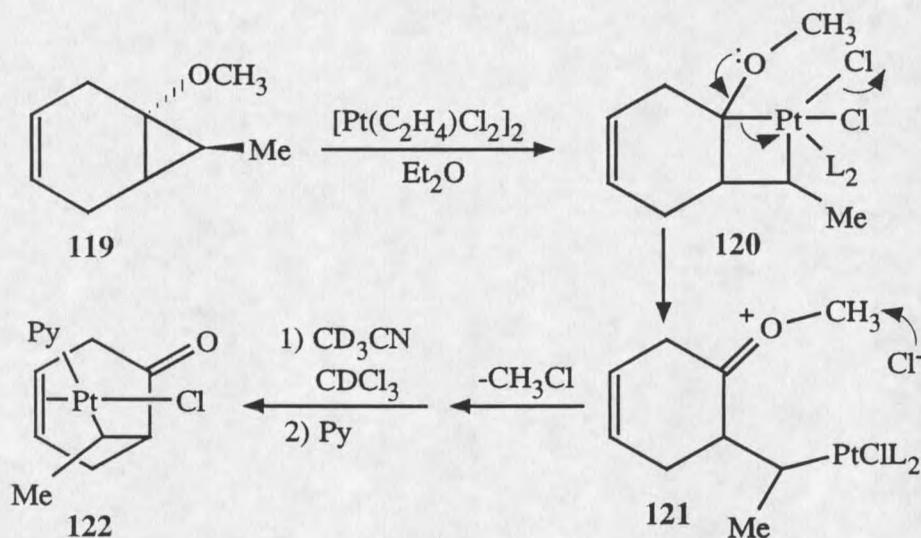
A  $\gamma$ -C-H activation to form a platina(IV)cyclobutane intermediate also is proposed for the thermal decomposition of trans-chloroneopentylbis(tricyclopentylphosphine)-platinum(II) to 1,1-dimethylcyclopropane and the platinum complex **118**<sup>255</sup>. Scheme XLV illustrates the metallacyclic intermediate formation which subsequently reductive eliminates the observed cyclopropane. Addition of ligand to the remaining platinum species creates the observed trans-chlorohydridobis(tricyclopentylphosphine)platinum(II) complex **118**.

A novel tetra-substituted platina(IV)cyclobutane intermediate is proposed for the reaction shown in equation 107<sup>256</sup>. Pt(II), in the form of Zeise's Dimer, is inserted into the most highly substituted bond of the cyclopropane moiety of **119** to form the tetra-substituted platina(IV)cyclobutane intermediate **120**. Further reaction leads to the observed platinum(II)-olefin complex **122**.

Scheme XLV.

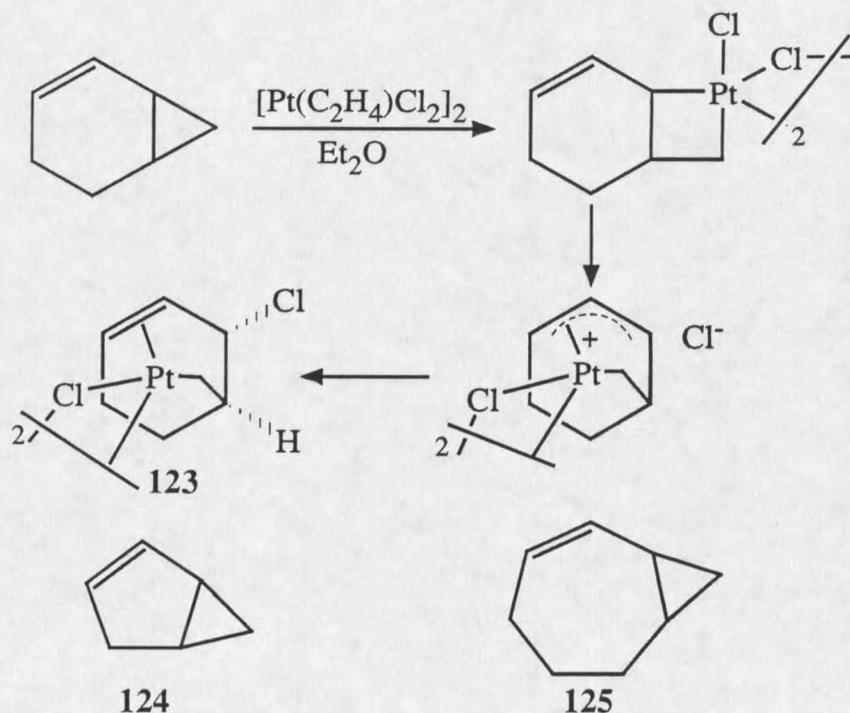


(107)



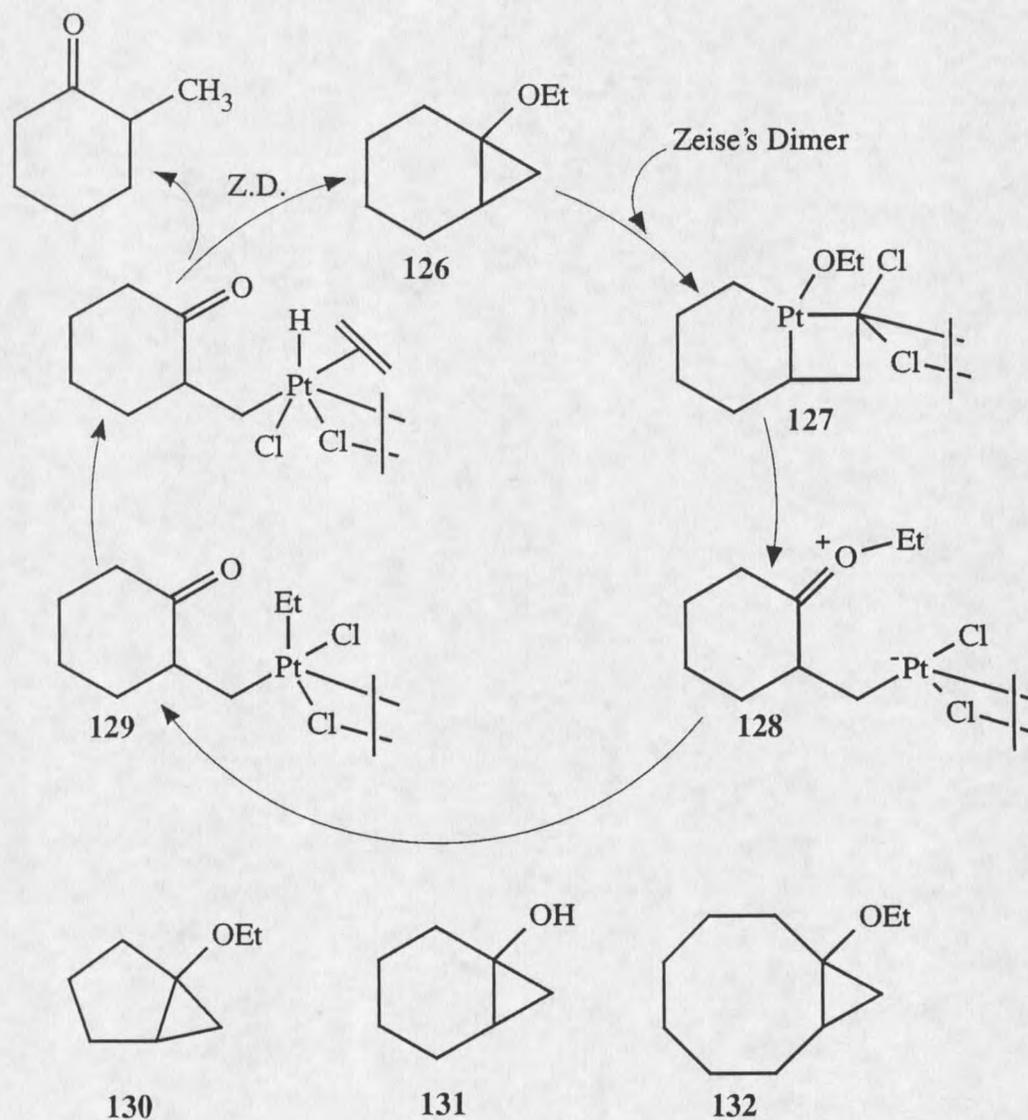
Continued investigations of unsaturated bicyclo[X.1.0] ring systems led to the formation of another platinum(II)-olefin complex **123**<sup>91</sup>. Equation 108 illustrates the proposed pathway which proceeds via initial insertion of Pt(II) into the cyclopropane moiety to form the platinum(IV)cyclobutane intermediate. The vinylcyclopropane ring systems **124** and **125** form analogous platinum(II)-olefin species.

(108)



The platinum(II) catalyzed rearrangement of 126 to form 2-methylcyclohexanone is believed to occur by the catalytic cycle shown in Scheme XLVI<sup>91</sup>. The platinum(IV)-cyclobutane intermediate 125 and intermediate 126 are analogous to intermediates 120 and 121 in equation 107. However in the absence of an olefin, a platinum-ethyl moiety is formed, 129, which upon hydrogen abstraction and subsequent reductive elimination forms the observed 2-methylcyclohexanone product. The bicyclic ring systems, 130-132, also catalytically form their respective methylcycloketones upon addition of Zeise's Dimer.

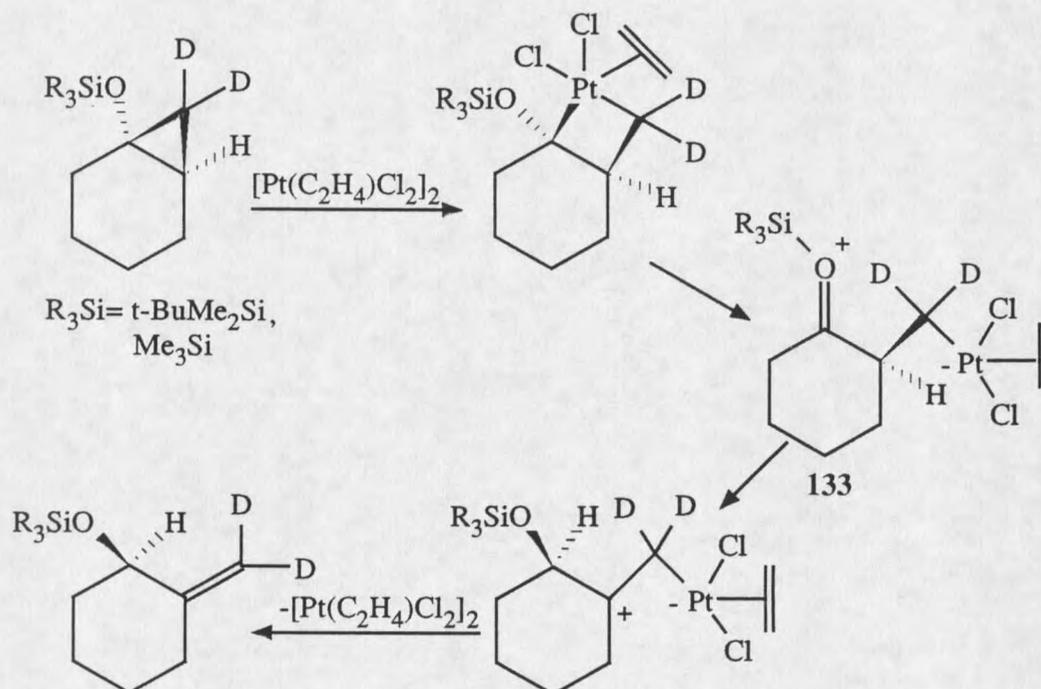
Scheme XXLVI.



Zeise's Dimer also is proposed to catalyze the isomerization of siloxycyclopropanes to exo-methylene silylethers<sup>67</sup>. The suggested reaction pathway for one example is shown in Scheme XLVII. Again, Pt(II) insertion into the most highly substituted bond of the cyclopropane moiety is proposed to form the platinum(IV)cyclobutane intermediate. Subsequent heterolytic cleavage of the platinum-siloxy carbon bond forms the zwitterion

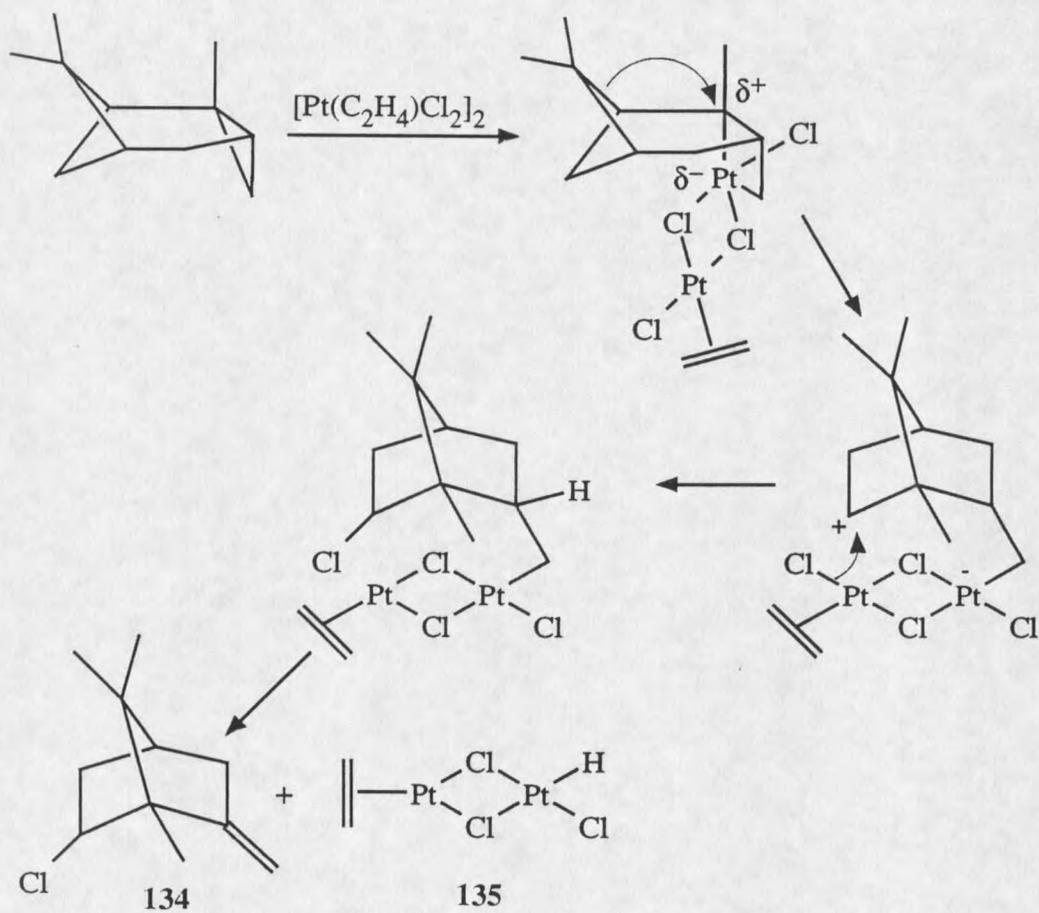
intermediate 133 which proceeds via a 1,2-H shift to the observed product. This reaction has been found to be quite general for a variety of 2-alkyl substituted siloxy cyclopropanes.

Scheme XLVII.



When cyclopropanated  $\alpha$ -pinene reacts with Zeise's Dimer, an exocyclic methylene complex also results. However, this reaction is not catalytic with Pt(II). Scheme XLVIII illustrates the proposed pathway for this reaction<sup>257</sup>. Initial formation of a platinum(IV)cyclobutane intermediate occurs followed by bridge migration. A chlorine is then believed to be transferred from the Pt(II) source to the organic substrate, however it is not certain whether this is an intramolecular process (as shown) or an intermolecular process. Subsequent  $\beta$ -hydride elimination then leads to the formation of 134 and the Pt(II) complex 135 which further decomposes to HCl, Pt(0), and PtCl<sub>2</sub>.

Scheme XLVIII.



## EXPERIMENTAL

Conducting the Literature Search

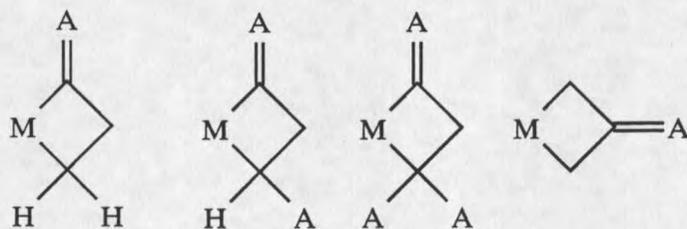
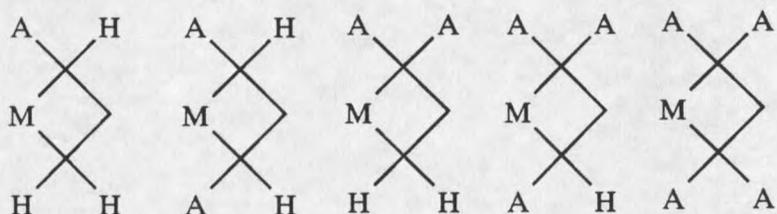
A search of the literature first began by choosing two past review articles on related work and examining each of their references for publications relevant to our article. If an article was applicable to our work, it was photocopied, read and indexed for future retrieval. By checking the references of these first two review articles and subsequently examining the references of each new publication obtained, a fairly thorough search of the literature was managed.

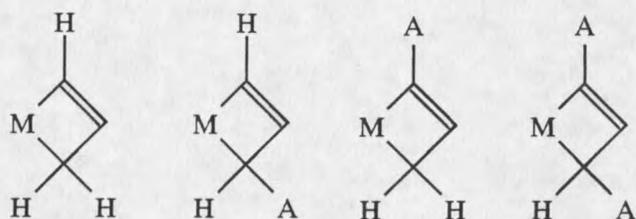
However, to complete the search and to obtain the most recent relevant publications, a computerized literature search was instigated. CAS Online, a Chemical Abstracts service available through STN International was employed for this purpose<sup>258</sup>. Upon accessing the CAS files, a structure search was performed by drawing a metallacyclobutane according to the commands of the CAS Online manual. The structure was very simple, specifying only the metals of the group eight transition metals. It was hoped that by conducting a search of a metallacyclobutane that could have either single or double bonds and any type of substitution that no metallacyclobutane derivative would be excluded from the search.

A range search was conducted on the specified structure from 1984 to the present. Upon viewing the search output, however, it became apparent that the structure searched would need to be made more specific and retrieving the desired literature would not be

quite so facile. Included in the retrieval, along with the desired metallacyclobutane derivatives, were metal- $\eta^3$ -allyl complexes and complexes with a cyclopentadienyl ligand coordinated to the metal. Both of these unexpected complexes are contained in a plethora of publications, making production of a hardcopy of the search output unrealistic.

To circumvent the inclusion of unwanted structures in our search output, it was necessary to draw structures with specific attributes. For example, by specifying a metallacyclobutane with all single bonds the  $\eta^3$ -allyl species were eliminated. So of course were any metallacyclobutene complexes but not the metal-Cp or Cp\* species. To exclude the Cp or Cp\* ligands, two substituents, two hydrogens, or a hydrogen and one substituent could be placed at any carbon. These structures did not exclude the  $\eta^3$ -allyl species, however. Examples of the structures used in the search are shown below.





A= any element except hydrogen

It was not possible to exclude both unwanted species while still obtaining all the desired metallacyclobutane derivatives by doing a single structure search. However, by searching 15-20 specific structures a successful search of the literature for metallacyclobutane derivatives of the group eight transition metals was achieved.

#### Indexing of the References

The indexing of each article gathered was done on the computer using the program Reference Manager<sup>259</sup>. After each publication was read, the authors, article title, journal name, date, volume and page numbers, notes about the article and chosen keywords were entered into the Reference Manager database entitled Metallic. By compiling this information, retrieval of a certain article was facile as was retrieval of any group of articles desired. The database also was utilized before a library search was done on any reference to be sure that the article was not already a part of the database.

A second database entitled Unused was created that included scant information on publications that were found in the library but were irrelevant to our review and therefore not obtained. Before searching new references in the library, this database also was checked to ensure that the new reference had not been already rejected. By utilizing both

databases in this manner, duplicate references were not obtained and time spent on library searching was reduced.

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