



Synthesis, characterization and chemistry of platinum complexes derived from bicyclic cyclopropanes
by John Ole Hoberg

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

Montana State University

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Abstract:

Platinum(IV)cyclobutanes were prepared by the reaction of Zeise's dimer ($\text{Pt}\pi$) with cyclopropyl methyl ketal. An insoluble precipitate was formed that could be solubilized by reaction with pyridine or bipyridine ligands. Hydrolysis of the ketal producing acetyl platinum(IV)cyclobutanes were achieved in excellent yields.

Mechanistic studies on the ring expansion of norbornyl molecules via Pt(II) were achieved by the use of deuterium, carbon-13 and phenyl substituents. From these studies a mechanism was postulated involving two competitive pathways which incorporated isomerizations and β -hydride abstraction.

Reaction of 1-alkoxybicyclo[X.1.0]systems with catalytic Zeise's dimer yielded methylated cyclic ketones in good yields. A mechanism on the formation of the ketones was postulated from labelling studies that were performed. Platinum(II) olefin complexes were prepared from the reaction of Zeise's dimer with 1-alkoxybicyclo[4.1.0]hept-3-ene. This led to the insertion of Pt(II) into a tetra substituted cyclopropane (7-methyl-1-methoxybicyclo [4.1.0]hept-3-ene).

A platinum(II) complex was also prepared from the reaction of bicyclo[4.1.0]hept-2-ene and Zeise's dimer. Reaction with pyridine, PPh₃, and other ligands produced novel platinum complexes. Furthermore, organic molecules could be produced in good yields and excellent regio- and stereoselectivity. This was achieved by the reaction of the initial complex with ROH, AcOH, H₂O followed by H₂, PPh₃ or CO. Bicyclo[3.1.0]hex-2-ene and bicyclo[5.1.0]oct-2-ene produced similar results on reaction with Pt(II).

SYNTHESIS, CHARACTERIZATION AND CHEMISTRY OF
PLATINUM COMPLEXES DERIVED FROM
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by

John Ole Hoberg

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in

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APPROVAL

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John Ole Hoberg

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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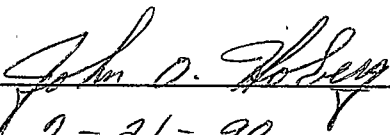
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ABSTRACT

Platina(IV)cyclobutanes were prepared by the reaction of Zeise's dimer (Pt^{II}) with cyclopropyl methyl ketal. An insoluble precipitate was formed that could be solubilized by reaction with pyridine or bipyridine ligands. Hydrolysis of the ketal producing acetyl platina(IV)cyclobutanes were achieved in excellent yields.

Mechanistic studies on the ring expansion of norbornyl molecules via $\text{Pt}(\text{II})$ were achieved by the use of deuterium, carbon-13 and phenyl substituents. From these studies a mechanism was postulated involving two competitive pathways which incorporated isomerizations and β -hydride abstraction.

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INTRODUCTION

Transition metal organometallic chemistry has been growing immensely since its inception in the 1950's. The chemistry that has developed has led to new methods of organic synthesis as well as a number of unique organometallic molecules. A number of industrial processes, such as the Ziegler Natta catalysis, have employed transition metals in catalytic synthesis. Also the long-sought after molecule, cyclobutadiene, was formed by stabilization with metals. Not only have novel complexes been made but surprising mechanisms have been discovered in the study of transition metal chemistry.

When defining organometallic chemistry it is important to note that a metal-carbon bond must exist, by either a σ or π bond. Metal complexes having ligands such as amines and halides do not "qualify" as organometallic compounds. Transition metal ions are also Lewis acids, which means that they can bind to the lone pairs of ligands. Carbon monoxide is an example of a ligand that bonds with its pair of electrons and produces an organometallic compound, while water also bonds with a pair of electrons it is not classified as an organometallic compound.

The area of organometallic chemistry which this author has undertaken is organoplatinum chemistry. Starting in the late 1960's, a number of articles were reported on highly strained organic molecules rearranging upon exposure to a transition metal. Platinum is particularly adept at this when the organic molecule is a cyclopropane. Quite an interest was taken in this chemistry until most felt that it had run its course and was finished. P.W. Jennings revived the area in the early 1980's with the norbornyl system and has since expanded the platinum cyclopropane area. Platinum also undergoes chemistry

other than that with cyclopropanes. It has long been used as a hydrogenation catalyst and is particularly good at complexing with sites of unsaturation, especially olefins.

The material in the introduction has been covered to familiarize the reader (and author) with basic bonding, mechanisms, reactions and history that is needed to help understand the research presented in the discussion. Usually each section of the introduction will begin with a very brief history of platinum in that specific area and some basic bonding concepts using frontier molecular orbitals. This is most often followed by known reactions using either platinum or another transition metal that will serve as an analogy. Structure determination of known platinum complexes will also be presented to add precedence to structures presented in the discussion.

Platinum Carbonyl Complexes

Structure and Bonding

The discovery of the first organotransition-metal compound, $K^+[(C_2H_4)PtCl_3]EtOH$ was first reported by Zeise in 1827¹. Forty years later Schutzenberger² prepared the first metal carbonyl, $[PtCl_2(CO)_2]$, and since then a whole host of platinum pi complexes have been prepared. By virtue of the C-O multiple bond, CO is an unsaturated ligand. Known as a soft ligand because of its capability of accepting metal d_π electrons, CO is called a π acceptor or π acid. Sigma bonding between platinum and CO consists of the donation of a lone electron pair on the carbon, shown in Figure 1, to an empty hybrid metal orbital. The CO ligand having empty π^* orbitals interact and accept electrons from the filled metal d orbitals. This delocalization of electron density from the metal to the carbonyl ligand, known as back bonding, compensates for excess electron density donated to the metal. A composite picture is shown at the bottom of Figure 1.

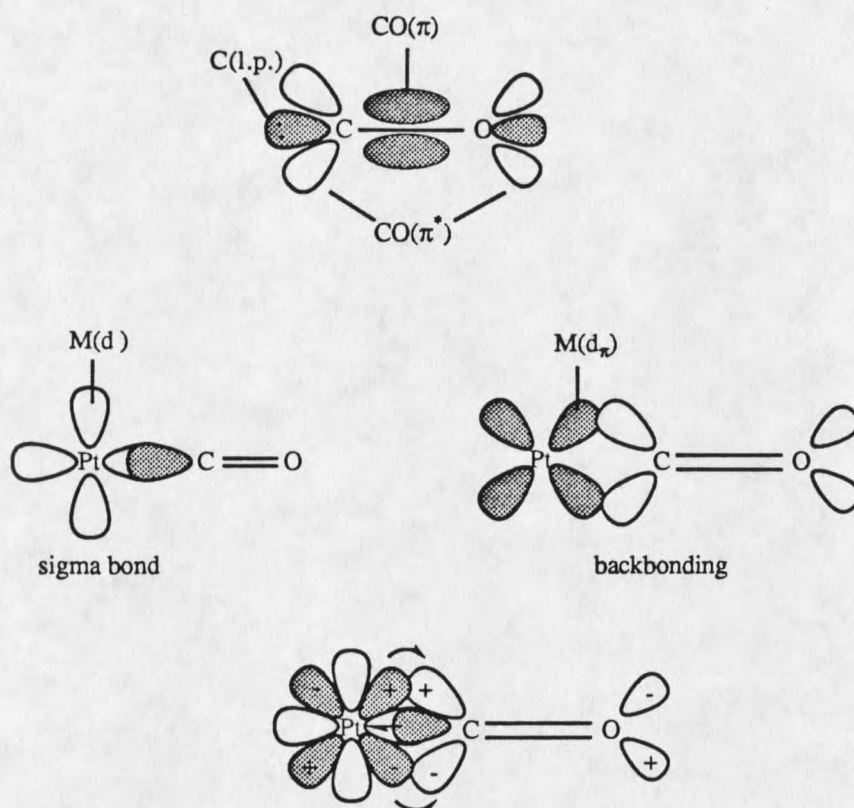


Figure 1. Pt-CO Bonding Scheme (bottom). The shading represents occupied orbitals and the plus and minus signs the phasing. Only one of the two π orbitals is shown in the structure of CO (top).

Formation and Characterization of Pt-Carbonyl Complexes

The presence of electrons in the antibonding orbitals of CO causes weakening of the C-O bond. This weakening causes a shift in the C-O stretching frequency due to CO resembling an electronically excited state. Free CO has a resonance frequency in the infrared spectrum at 2155 cm^{-1} . Table 1 shows the CO stretching frequencies of some Pt compounds. As the electronegativity of the halogen decreases so does the frequency reflecting the increase of back-donation from Pt(II) to CO.

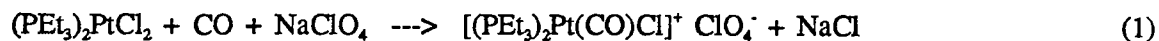
The electronic effects that ligands in Pt complexes have on $^1J_{\text{Pt,C}}$ and ^{13}CO NMR chemical shifts have also been studied. Changes in both the cis and trans ligands relative to the CO can have a marked affect on the chemical shift and Pt-C coupling. For complexes

such as $\text{trans-[PtX(CO)L}_3\text{]BF}_4$ ($\text{X} = \text{H, C}_6\text{H}_4\text{Cl, CH}_2\text{Ph, NCS, NO}_3, \text{Cl, Br or I}$) ^{13}C measurements have been made. If X has a high trans influence, the platinum carbon (CO) coupling is between 960-990 Hz but if X has a low trans influence, the range is between 1660 and 1820 Hz¹⁰.

Table 1. C-O Stretching Frequencies (cm^{-1}) in some Pt(II) Carbonyls

	Cl	Br	I
$\text{cis-[Pt(CO)X}_3\text{]}^+$	2132	2112	2088
$[\text{PtX}_2(\text{CO})_2]$	2152	2130	2112
$[\text{Pt(bipy)(CO)X}]$	2145	2132	2120
$\text{cis-[(PEt}_3\text{)PtX}_2(\text{CO})]$	2100	2094	2085

In recent years, extensive chemical studies have been made on platinum(II) carbonyls. Preparative routes to simple platinum carbonyls are as follows⁹: (a) Displacement of a chlorine ligand in a solution containing a counter ion resulting in the formation of cationic carbonyl complexes, Equation 1. Similar reactions also go in the presence of silver nitrate which abstracts a chloride. (b) Olefins and acetylenes can also be displaced by carbon monoxide to form complexes as shown in Equation 2. (c) Chlorine bridged compounds can also be cleaved by carbon monoxide, Equation 3. When CO is passed through solutions of halogen-bridged platinum-olefin complexes in carbon tetrachloride, mixed complexes containing olefins are formed.



Reactions Involving Pt-Carbonyls

CO shows a strong tendency to insert into metal alkyl bonds. With Pd^4 , pressures as low as 1 atmosphere will insure insertion. Platinum on the other hand needs much higher pressures such as 70 atmospheres⁵. The actual mechanism for the reaction is thought to be migration of the alkyl group to a cis CO. Evidence for this migration can be seen in experiments using ^{13}C labelled CO. After the migration, an empty site develops at the metal, Figure 2⁶. When the incoming ligand is ^{13}CO , the observed product contains only one labelled ^{13}CO . This shows that the methyl group migrates to a coordinated CO, instead of free CO inserting into the metal-methyl bond. By using microscopic reversibility, the reverse reaction also sheds light on the mechanism, Figure 3. Elimination of CO from $\text{Me}^{13}\text{COMn}(\text{CO})_5$ followed by migration of methyl showed the ^{13}CO was cis to the methyl group.

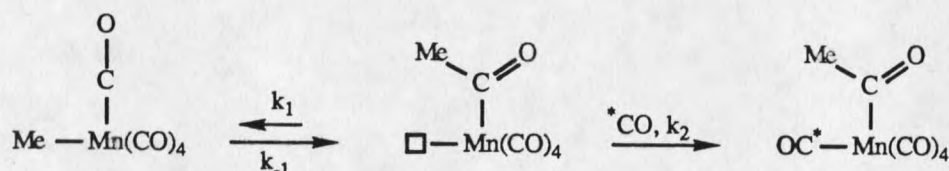


Figure 2. Migratory Insertion Mechanism (squares indicate vacant sites).

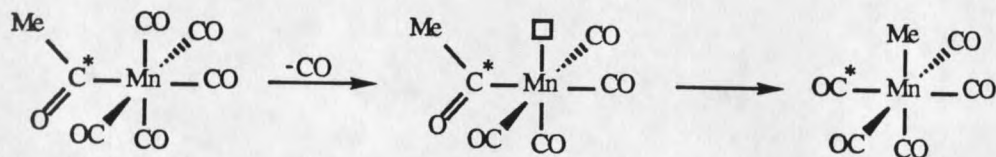
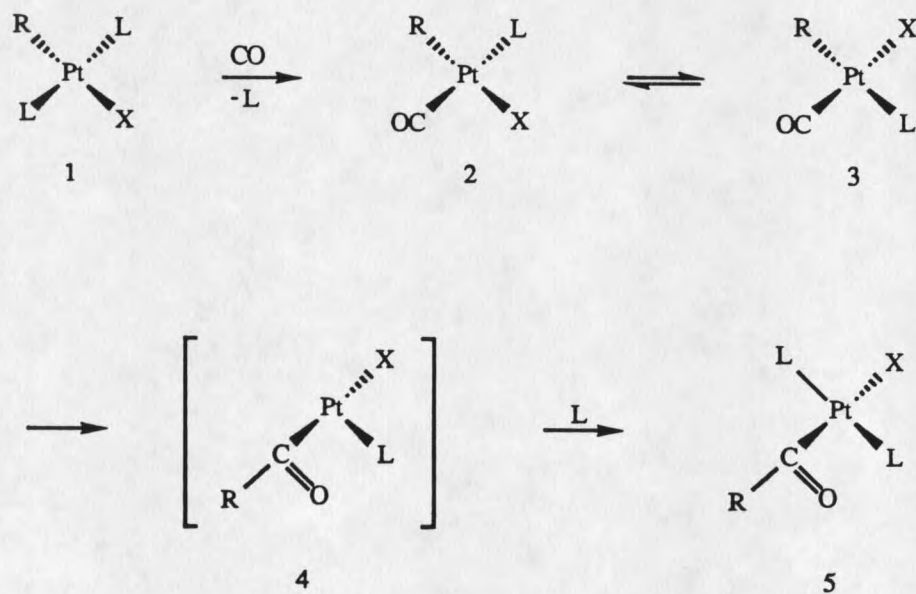


Figure 3. Reversible CO Insertion.

As stated cis coordination is required, and this is clearly shown in these experiments, but the question, does the alkyl group migrate to a cis CO or does the CO insert into the M-alkyl bond, is not shown. In all actuality both have been observed, but the former is much more prevalent⁷ and is the accepted pathway with CO insertion being an exception to the rule.

Carbonylation of four-coordinate d^8 complexes have also been studied⁸, 1-5. In the first step carbon monoxide replaces a ligand to form complex 2. The alkyl group does have a CO cis to it but does not undergo migratory insertion instead it rearranges to 3. After rearrangement the Pt-R bond is weakened due to the trans effect of the phosphine ($L=PR_3$). This then enables migration to the CO giving the intermediate 4, which then picks up a ligand to give the Pt-acetyl 5.



Complexes containing a metal-carbon bond have found extensive application in organic synthesis. After formation of the metal-acetyl, the complex can reductively eliminate to give an organic product and regenerate the starting metal complex. Quite often this process can

be made catalytic. As can be seen in Figure 4¹¹ metal-acyl groups can be carbonylated to esters in the presence of alcohols, to amides with amines, acids with water and aldehydes with H_2 present. When Pd is the metal, a tertiary amine is necessary to absorb the HX. Figure 5 outlines how the reaction is thought to proceed. Exactly what the mechanism is after CO insertion is as yet unclear. The three prevalent ideas for decomposition are as follows:

- Reductive elimination to form RCOX which then reacts with alcohol to produce the acid derivative.
- Alcohol reacts with the metal acetyl directly at the carbonyl carbon forming the ester.
- Finally, the alcohol can add to the metal by exchanging with the halide, which after reductive elimination gives the ester.

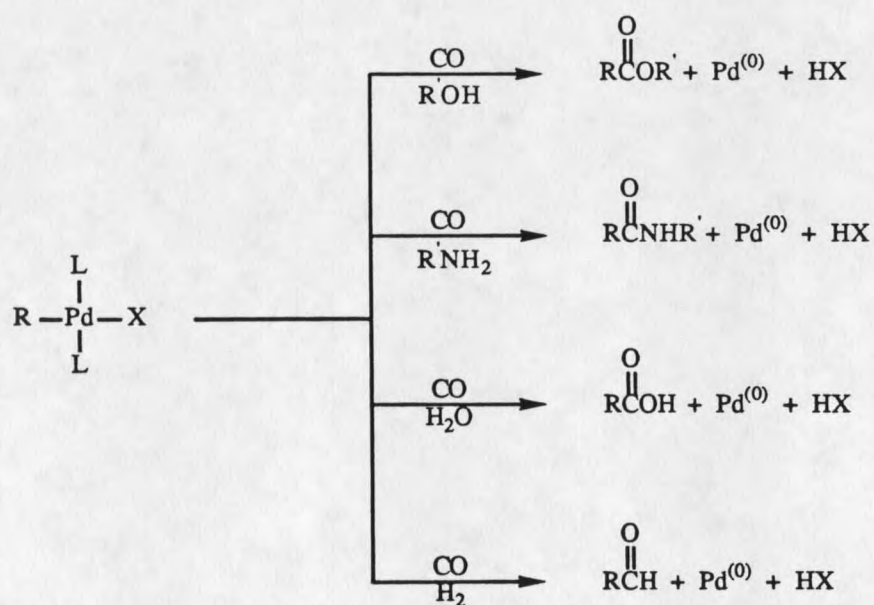


Figure 4. Palladium Catalyzed Reaction Pathways.

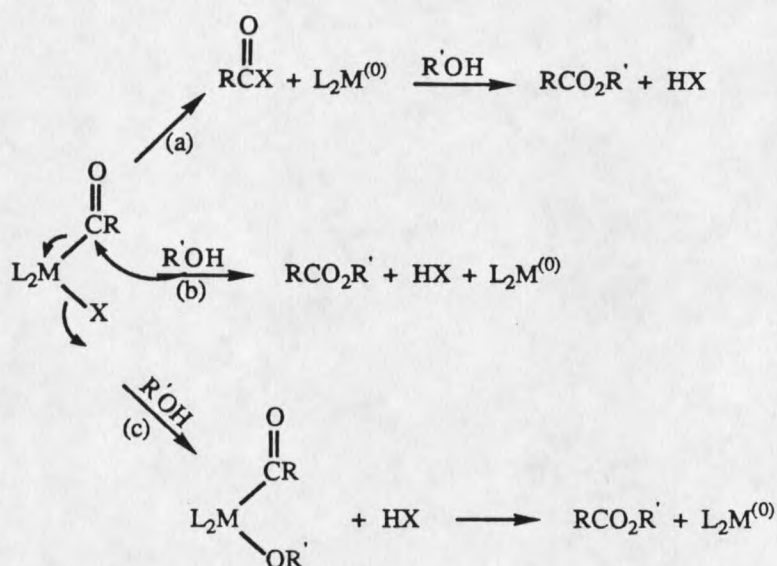


Figure 5. Proposed Pathways to Ester Formation.

Carbonylation reactions are also useful for the formation of heterocycles. Intramolecular alcohols will act as the incoming nucleophile forming heterocyclic systems. Stille¹² has shown this in the formation of the lactone shown in Figure 6.

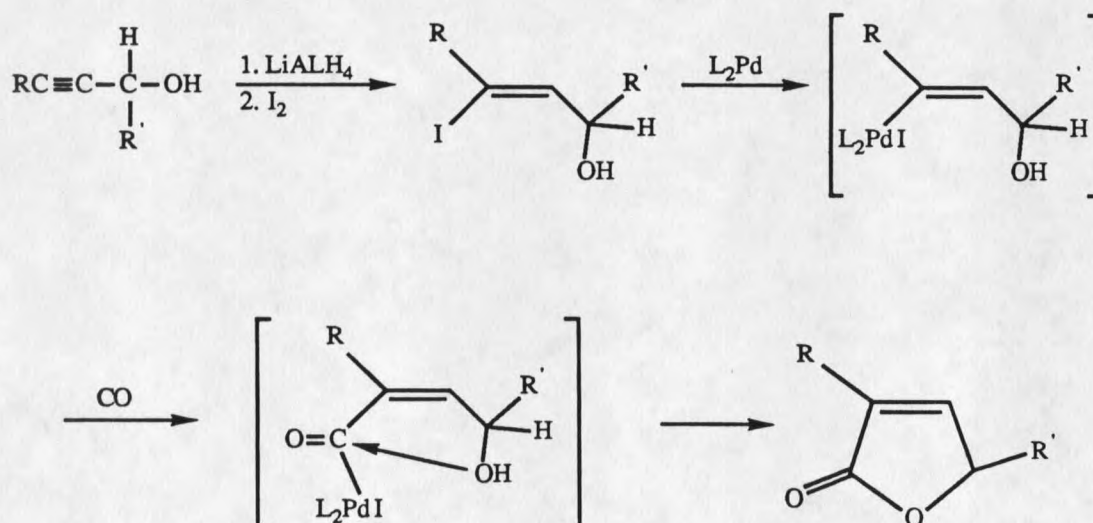


Figure 6. Palladium Catalyzed Lactone Formation.

Carboalkoxylation of olefins is also a very useful process undergoing reactions shown in Equation 4¹³. Conditions for these types of reactions are typically about 140-170°C under 100-200 atmospheres carbon monoxide. The mechanism for the reaction is shown below in Figure 7. The first step is coordination of the olefin to the metal followed by insertion into the M-H bond, which then undergoes typical carbonylation chemistry.

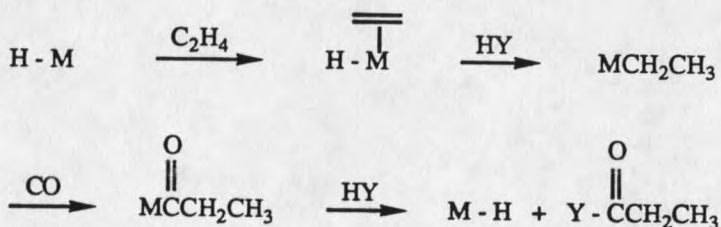
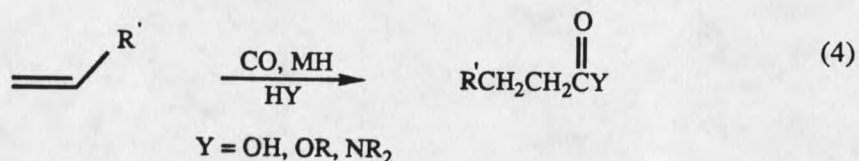


Figure 7. Carboalkoxylation of Ethylene

Platinum-Olefin Complexes

Structure and Bonding

Earlier it was mentioned that Zeise discovered the first complex. This was later shown to be $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\cdot\text{H}_2\text{O}$ which formed by dehydration of ethanol. The alkene on Zeise's salt is oriented as shown in Structure 6. This perpendicular orientation to the coordination plane of the complex allows for efficient bonding of the metal to the alkene electrons. In the CO bonding scheme a lone pair was donated to the metal through a σ bond, but ethylene

has no lone pairs, and so the next most available electron pair, the C=C π -bonding electrons are used. Chatt, Dewar, and Duncanson¹⁴ have described the bonding picture for metal-olefins. Like the M-CO picture this consists of a σ interaction and π interaction, Figure 8. The σ interaction results in the ethylene π electrons donating to an empty d_σ orbital on the metal. The π interaction is the result of filled metal d_π orbitals backdonating to the empty C=C π^* orbitals. The overall scheme is shown at the bottom of Figure 8.

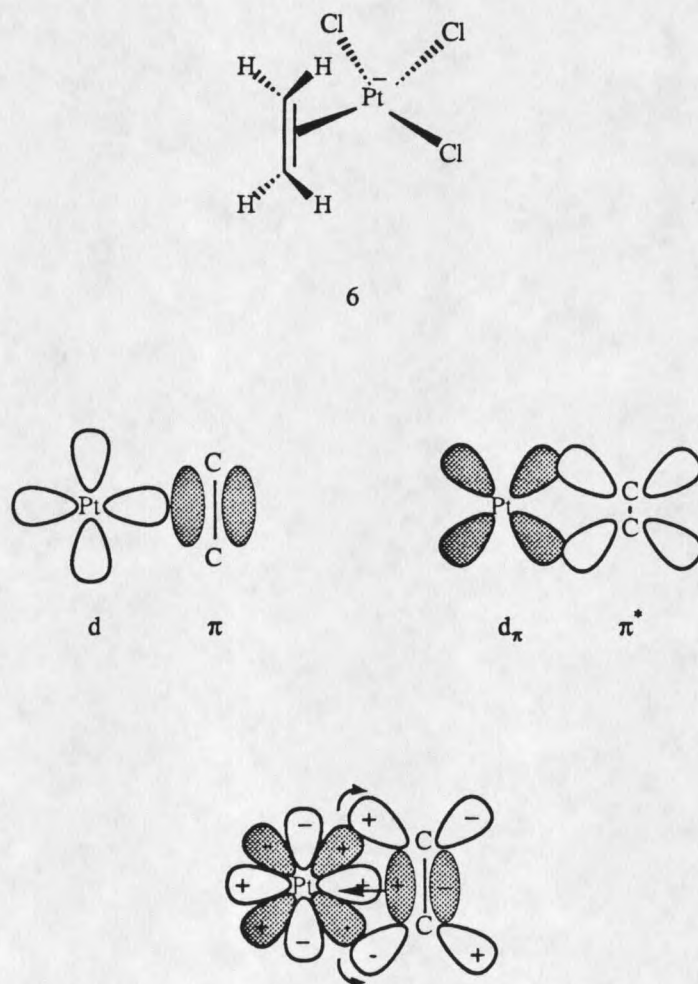


Figure 8. Bonding Scheme between Platinum and an Olefin. The shading represents occupied orbitals and the plus and minus signs the symmetry.

Olefins that bind to metals undergo lengthening of the C=C bond. The formation of the metal-alkene σ bond weakens the C=C bond by depleting the carbon π orbitals, thereby inducing elongation. The degree of back bonding from the metal also determines the amount of C=C bond lengthening. By filling the π^* orbital the C-C bond order can be reduced almost to a single bond. Zeise's salt, for example, is predominantly σ and its C-C length is 1.375Å, compared to free alkene (1.337Å). This would then be drawn as complex 7 which is the extreme of minimal back bonding. The other extreme is shown in complex 8 where back donation from the metal is very large. $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)^{15}$ has a C-C distance of (1.43Å) inducing the substituents on the carbons to bend back away from the metal. When electron withdrawing groups are present on the olefin back donation is enhanced even more, such as $\text{Pt}(\text{PPh}_3)_2(\text{C}_2(\text{CN})_4)$, which has a C-C bond distance of 1.49Å¹⁶.



Characterization of Pt-Olefins

Infrared, Raman and NMR spectroscopies furnish valuable insight into the nature of platinum-olefin π -bonding. Most often, the C-C stretching shifts to lower wave numbers when the platinum-olefin bond strength increases. Examples of this are listed in Table 2¹⁷. However, the C-C stretching frequency can combine with other modes thereby influencing the frequency. Consequently, the C-C frequency must be used with discretion. However, the platinum-olefin stretching frequency is very indicative of bond strength Table 3¹⁷ lists various Pt-olefin stretching frequencies which usually come between 410 and 380 cm^{-1} .

Table 2. C-C Stretching Frequencies of Pt(II)-Olefins

Compound	cm ⁻¹
H ₂ C=CH ₂	1623 (Raman)
K[Pt(C ₂ H ₄)Cl ₃]	1516
trans[Pt(C ₂ H ₄)(NH ₃)Cl ₂]	1521
trans[Pt(C ₂ H ₄)(NH ₃)Br ₂]	1517
[Pt(C ₂ H ₄)Cl ₂] ₂	1516

Table 3. Pt-Olefin Stretching Frequencies.

Complex	cm ⁻¹
K[Pt(C ₂ H ₄)Cl ₃]H ₂ O	407
K[Pt(C ₂ D ₄)Cl ₃]H ₂ O	387
K[Pt(C ₂ H ₄)Br ₃]H ₂ O	395
K[Pt(C ₃ H ₆)Cl ₃]	393
K[Pt(trans-C ₄ H ₈)Cl ₃]	387
K[Pt(cis-C ₄ H ₈)Cl ₃]	405
trans[Pt(C ₂ H ₄)(NH ₃)Cl ₂]	383
trans[Pt(C ₂ H ₄)(NH ₃)Br ₂]	383

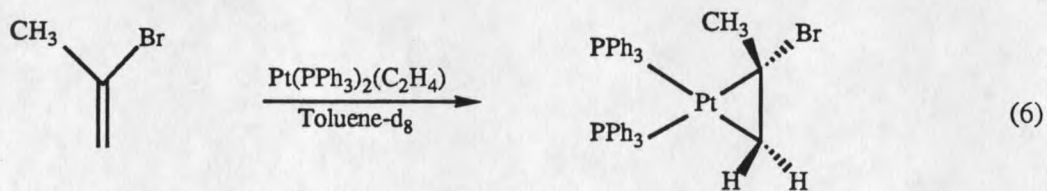
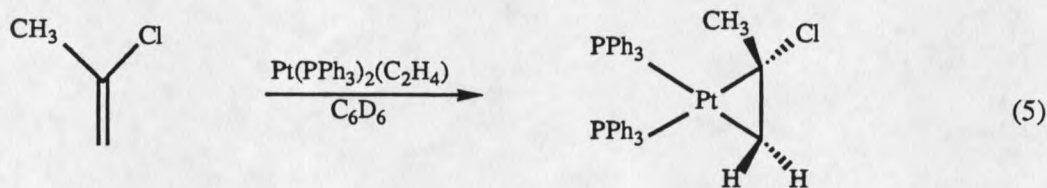
As was mentioned, ¹H and ¹³C NMR spectroscopy can be used to determine the difference between complexes such as 7 and 8. The vinyl protons and carbons shift significantly upfield depending on the amount of back donation from the metal. Carbon-13 resonances of platinum bound olefins will usually appear upfield of free olefins. The farthest upfield shift has been reported at 7 ppm and a downfield shift at 126 ppm in the ¹³C NMR. Platinum also has the nice attribute of being 33% spin 1/2 in its 195 isotope. This allows the coupling constants to be used as a gage of the relative bond strength¹⁸. Ranges of 40-400 Hz have been reported, with ligands playing a noticeable effect on these values.

Ligands with high trans influence that are trans to the olefin lower the coupling constant pushing the complex to a platinum-olefin as exhibited by structure 7. Ligands with low trans influence raise the coupling and influence the complex to a platinacyclopropane such as structure 8. Table 4¹⁹ lists some resonances and coupling constants of selected compounds.

Table 4. Platinum(II)-Olefin ¹³C Resonances and Coupling Constants.

Complex	ppm	¹ J _{Pt,C}
Pt(C ¹ H ₂ =C ² H ³ CN)Me(HBpZ ₃)	7.4 (C ²)	
Pt(t-NCCH=CHCN)Me(HBpZ ₃)	7.8	
[Pt(cod)(C ₈ H ₁₃)] ⁺	126.9	
t-Pt(C ₂ H ₄)py Cl ₂	75.0	180 Hz
t-Pt(C ₂ H ₄)(CD ₃ CN)Cl ₂	74.8	163 Hz

¹H NMR data can also lend insight into the bonding of platinum-olefin complexes. Stang²⁰ has reported on the reaction of olefins with Pt(0) to form platinacyclopropanes, Equations 5 and 6.



The vinyl protons of free vinyl chloride in Equation 5 resonate at 4.18 and 4.94 ppm. Upon complexation to platinum they are shifted upfield to 2.82 and 2.18 ppm. In Equation 6, the same trend is observed. Table 5 lists the NMR data for the two complexes.

Table 5. NMR Data for Equations 5 and 6 in ppm.

	^1H (free olefins)	^1H (complex)	^{13}C (complex)
5)	4.18 4.94	2.18(m, $^2J_{\text{Pt,H}} = 62$ Hz) 2.82(m, $^2J_{\text{Pt,H}} = 62$ Hz)	
6)	5.06 5.15	2.22(m, $^2J_{\text{Pt,H}} = 62$ Hz) 3.00(m, $^2J_{\text{Pt,H}} = 62$ Hz)	42.6 64.6

As can be seen in Table 5 there is also a large upfield shift of the vinyl carbon signal for the complexes in Equation 6 (free alkene resonates at 137 and 117 ppm). As stated by Stang, the complexes in Equation 5 and 6 would be best represented as platinacyclopropanes from the NMR data. It should be noted though that ^1H NMR data and its platinum coupling constants are not always the best tool or easiest for assigning bond strength. Quite often the resonances are broadened and no coupling is observed.

Reactions of Pt(II)-Olefins

The characteristic reaction of platinum-olefin complexes is nucleophilic attack at the olefin to give a σ bonded alkyl platinum complex. Two mechanisms can be postulated for the attack. The first, and by far most prevalent, is trans attack (anti to the metal) of the nucleophile on the olefin without prior coordination to the platinum. If the olefin is substituted the nucleophile will attack at the most substituted position with the platinum "slipping"²¹ to a σ bonding position at the least substituted terminus, Equation 7. The second mechanism involves coordination of the nucleophile to the platinum which then undergoes

insertion of the olefin into the platinum nucleophile bond. Insertion occurs at the less-substituted position of the olefin and gives cis addition of the nucleophile, Equation 8. A competing step in this reaction is displacement of the olefin in cases where the nucleophile works as a good ligand, Equation 8. Both of these mechanisms can be distinguished by stereochemistry and regioselectivity. For example, Figure 9 shows the work of Panunzi²². In this experiment (+)-cis-dichloro[(S)-1-butene][(S)- α -methyl benzyl amine] platinum(II) was attacked by diethyl amine. The result Panunzi observed was that the amine attacked trans to the platinum without prior coordination to the metal.

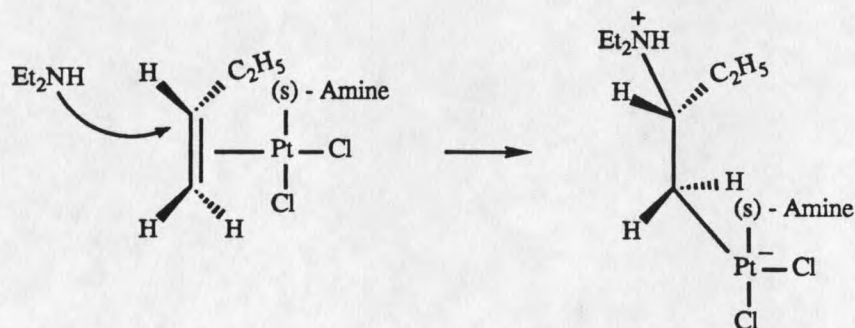
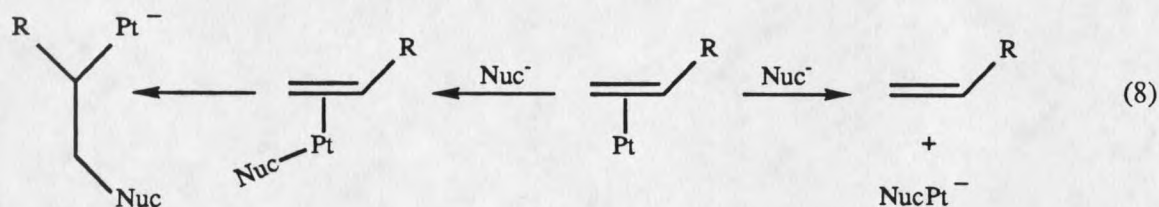


Figure 9. Amine Attack on a Pt(II)-Olefin

Most studies are done on mono or disubstituted olefins, as more highly substituted olefins coordinate weakly and are easily displaced. Nucleophiles that are used range from primary and secondary amines which add directly to the olefin, soft nucleophiles like dimethyl sulfide and phosphines that coordinate to the platinum first, and pyridine which is capable of attacking either the olefin or the platinum. A variety of nucleophiles, such as methoxide²³, amines²⁴, azide²⁵, and stabilized carbanions²⁶, will attack chelated platinum-olefins generating stable (α -alkyl)-platinum complexes as shown in Figure 10. Complexes of chelated platinum-olefins include norbornadiene, 1,5-cyclooctadiene and straight chain dienes. In almost all of these examples, after addition of the first nucleophile the remaining platinum olefin is resistant to further attack²⁷. Furthermore, a typical reaction involves trans attack and displacement of the remaining olefin is not observed.

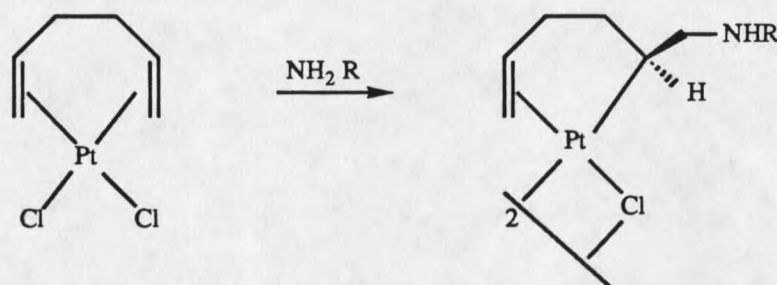


Figure 10. Nucleophilic Attack on a Platinum-chelated Olefin.

Platinum π -Allyls

Structure and Bonding

Metal π -allyls are very common in organometallic chemistry. These η^3 -allyl complexes are proven to be very useful as nucleophilic attack occurs at the termini of the allylic group. The orientation of the allyl group is shown in complex 9, which shows the anti unhindered face for nucleophilic attack. The bonding scheme for π -allyls is shown in Figure 11²⁸.

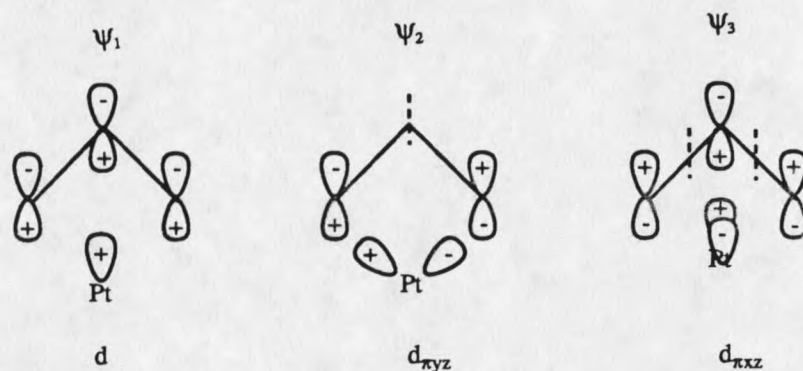
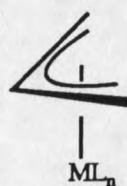


Figure 11. Pt- π -allyl Bonding Scheme. Nodes are shown as dotted lines.

It can be seen from ψ_2 why nucleophilic attack occurs at the termini of the allyl fragment and not at the center carbon (for an exception see ref. 29). For nucleophilic attack to occur, the fragment must be electrophilic. Thus, a two electron, cationic π -allyl complex is needed. Being ψ_2 , the LUMO, has a node at the center carbon the nucleophile will attack at the terminal carbons of the π -allyl. Most often nucleophilic attack occurs in a trans manner, from the face opposite the metal, producing a neutral η^2 olefin complex³⁰, Figure 12.

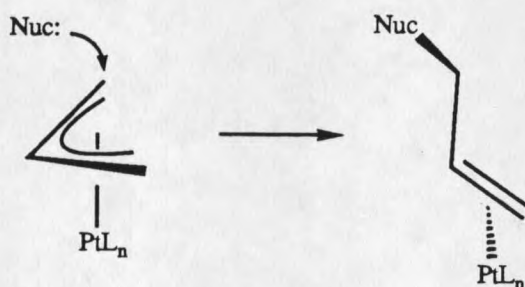


Figure 12. Nucleophilic Attack on Pt- η^3 -allyl.

Formation and Reaction

Metal η^3 -allyl can be generated by a variety of methods some of which are shown below.

1. From an alkene³¹:

$$\text{ML}_2(\text{propene}) \rightarrow \text{ML}_2(\text{allyl})\text{H}$$
2. From an allyl compound by nucleophilic attack on the metal³²:

$$\text{CH}_2=\text{CHCH}_2\text{SnMe}_3 + \text{ML}_n\text{X} \rightarrow (\eta^3\text{-CH}_2\text{CHCH}_2)\text{ML}_2 + \text{XSnMe}_3$$
3. From an allyl compound by electrophilic attack^{33,34}:

$$\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{ML}_5^- \rightarrow (\eta^1\text{-CH}_2=\text{CHCH}_2)\text{ML}_5 \rightarrow (\eta^3\text{-CH}_2\text{CHCH}_2)\text{ML}_4$$

As was just mentioned, nucleophiles attack η^3 -allyl to give η^2 -metal complexes. With the broad range of this reaction, the only example that will be discussed is the reaction of Kurosawa³⁵, Figure 13. Using an excess of phosphine ligand, Kurosawa has induced nucleophilic attack on the η^3 -allyl which eventually leads to the organic product shown.

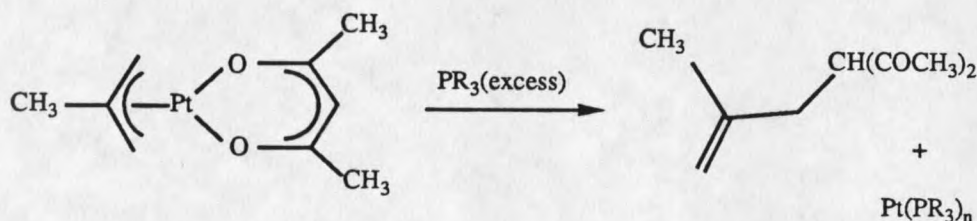


Figure 13. C-C Coupling Reaction of Methallyl and Acetylacetonate Ligands.

The mechanism that has been proposed for this reaction is shown below in Figure 14 and is believed to be an intramolecular nucleophilic attack by the platinum ligand. The first PPh_3 causes formation of the η^1 -allyl by addition as a ligand. The second PPh_3 kicks off the acetylacetonate as the counter ion causing reformation of the η^3 -allyl to fill the empty coordination site. This anion is then capable of nucleophilic attack on the π -allyl

forming the η^2 complex. Excess PPh_3 releases the observed products. Kurosawa has also used chlorine as the ligand and observed ionic dissociation in chloroform. Use of benzene suppresses chlorine dissociation.

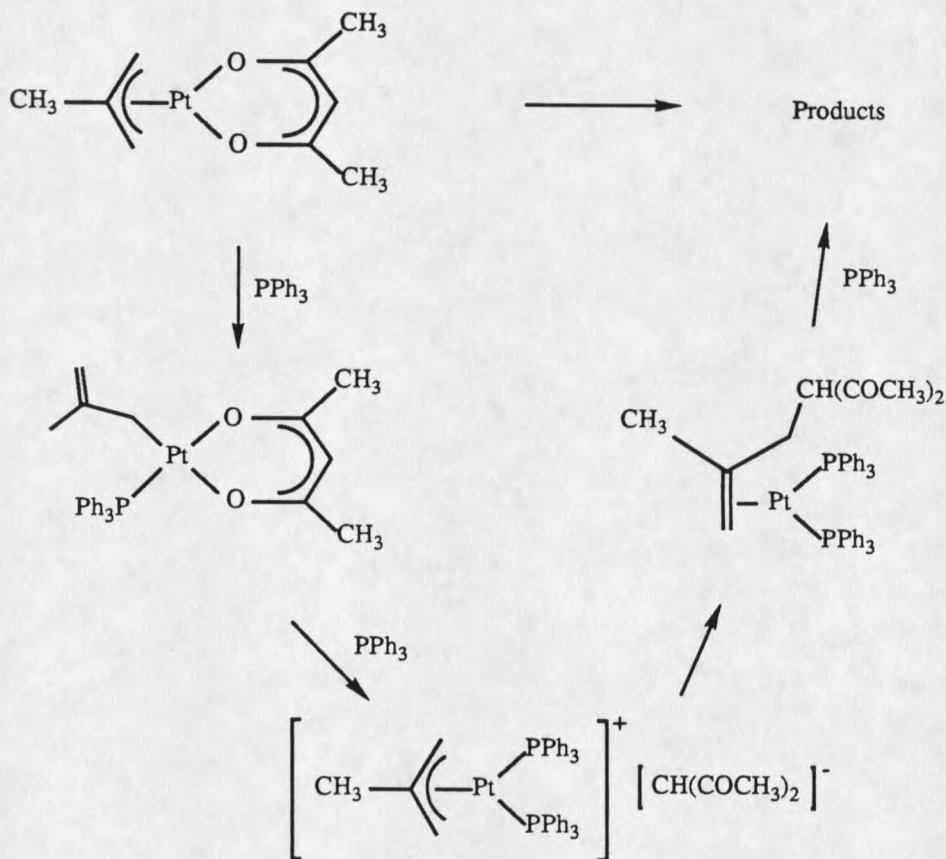
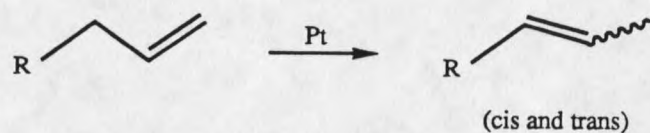


Figure 14. Mechanism of C-C Coupling

Platinum Olefin Isomerization

Platinum is one of the many metals capable of catalyzing the migration of hydrogen in olefins. This has the effect of isomerizing the carbon double bond, Equation 9. The two most prevalent mechanisms are shown in Figure 15³⁶: One going by alkyl intermediates (upper drawing) and the other by η^3 -allyl intermediates (lower drawing). All the steps are reversible in both mechanisms and so there is a thermodynamic ratio of alkenes.



(9)

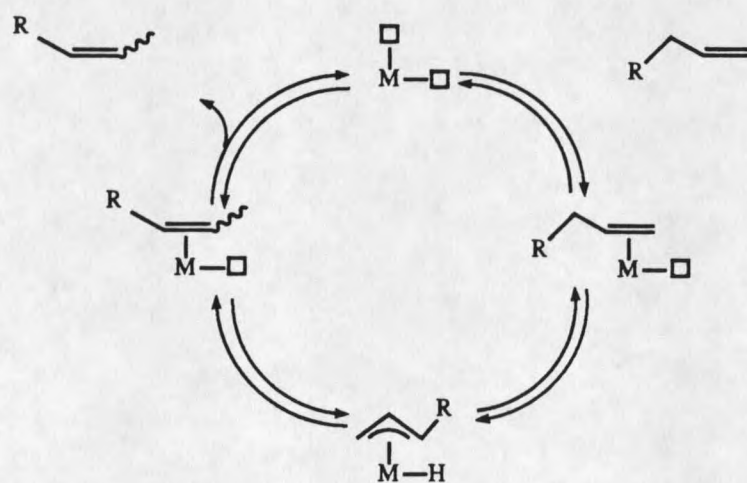
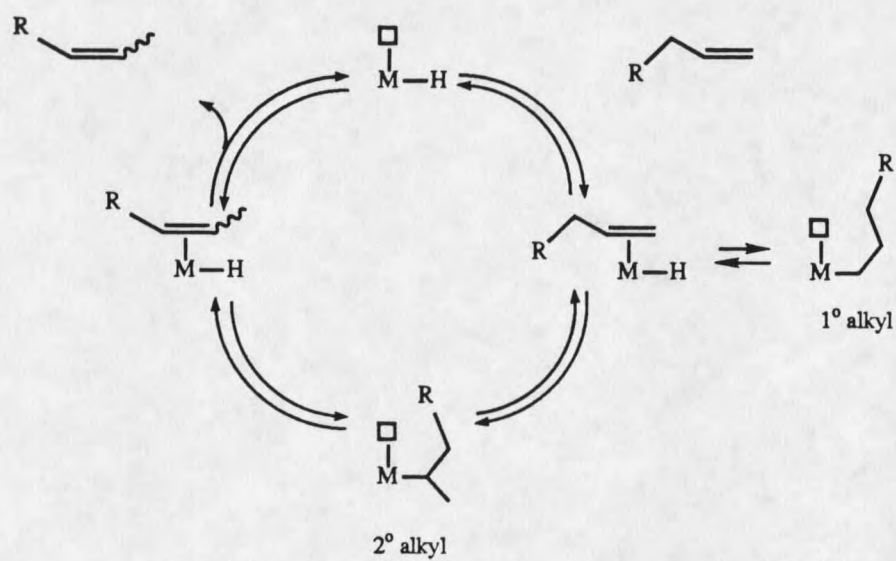


Figure 15. Alkene Isomerization Mechanisms (open box represents a vacant site).

In the alkyl pathway, there must be an M-H bond as well as a vacant site. After alkene complexation the metal undergoes insertion to give either a primary or secondary alkyl complex. The primary alkyl structure reverts back to the original complex by undergoing a β -elimination, while the secondary alkyl can give a new complex yielding a new alkene after β -elimination.

The second pathway, involving a π -allyl intermediate, does not need a hydride but does require two vacant sites on the metal. In this mechanism, an activated allylic C-H bond undergoes oxidative addition to the metal. The resulting η^3 -allyl hydride undergoes reductive elimination to back a new alkene.

Alkene isomerization with platinum is normally heterogeneous³⁷ as homogeneous catalysis is an inferior method compared to other transition metals³⁸. Platinum(II)-olefins³⁹⁻⁴², sodium tetrachloroplatinate⁴³, π -allyls⁴⁴ and preformed platinum(II) hydrides⁴⁵ are some heterogeneous catalysts used for isomerization. Figure 16 shows a few examples of platinum hydride generating reactions⁴⁰. In (a) the complex abstracts a hydrogen intramolecularly, while Zeise's Dimer (Pt^{II}) can use alcohols, acids and H_2 as hydrogen sources for either (b) or (c).

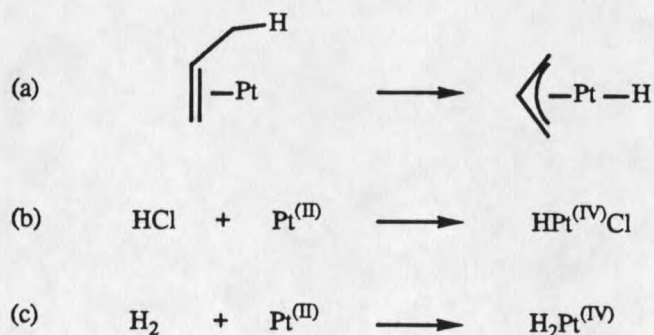


Figure 16. Hydride-Generating Reactions.

Alkene Hydrogenation

Hydrogenation catalysts add molecular hydrogen to olefins to give alkanes. Figure 17 depicts a proposed mechanism⁴⁶ of hydrogenation while Equations 10-12 show three modes of hydrogen activation⁴⁷. The first step in hydrogenation is oxidative addition of H_2 followed by olefin complexation. After alkene insertion, the metal alkyl reductively eliminates to give the alkane. Both Equations 10 and 11 exhibit oxidative addition of hydrogen. In Equation 11, the metal loses HX after the oxidative addition step. Equation 12 shows heterolytic hydrogen activation but it could also be an oxidative addition followed by deprotonation.

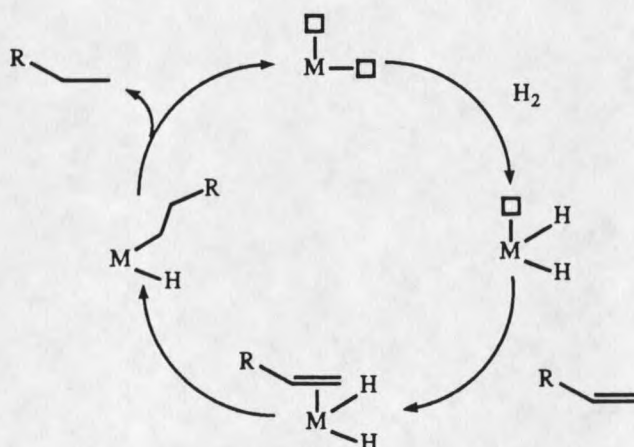
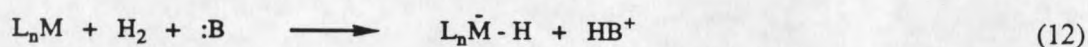
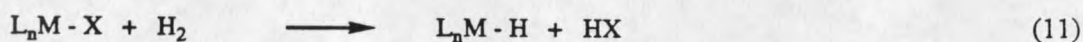
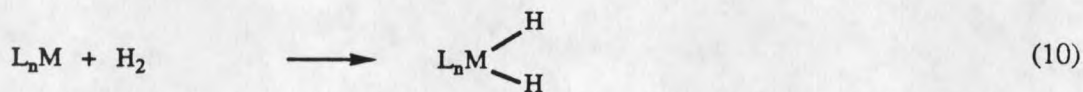


Figure 17. Hydrogenation Mechanism of an Alkene by Oxidative Addition of H_2 (squares represent an open site or labile ligand).



Platina(IV)cyclobutane Complexes

Structure and Bonding

The chemical behavior and physical data for cyclopropane and its derivatives are unlike those of other cyclic or acyclic alkanes. In fact, they are more similar to those of alkenes. For example, cyclopropanes are resistant to substitution⁴⁸. They also undergo ring-opening by electrophiles⁴⁹. In 1947 two bonding models were published to explain these results: one by Walsh^{50,51}, which is shown in Figure 18, postulates the three bonding orbitals. The other, Figure 19, is an update of the Forster⁵² model done by Coulson and Moffitt⁵³ (F.C.M. basis). In the F.C.M. theory, there are three bent bonds that describe the electronic structure making up the bonding orbitals. The Walsh theory is the more frequently used due to its ease of application, although there are arguments for⁵⁴ and against⁵⁵ it being the correct model.

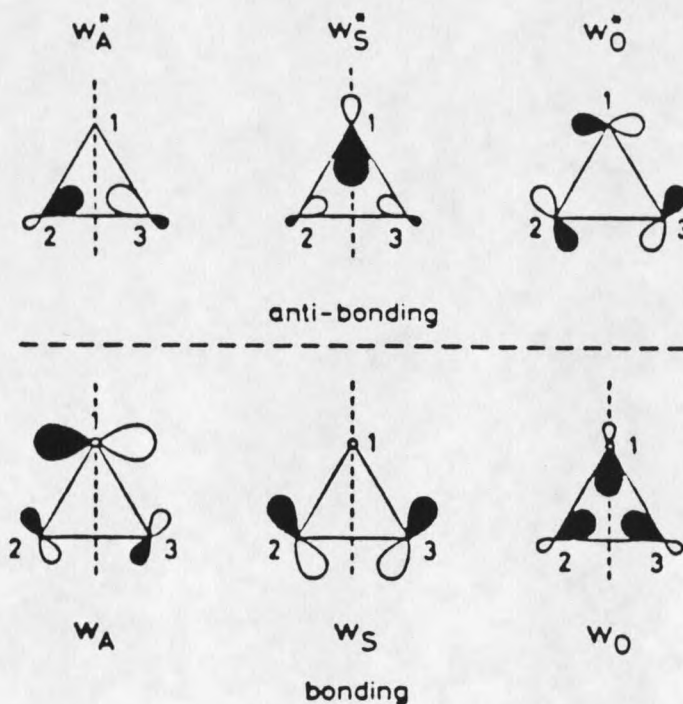


Figure 18. The Walsh-basis.

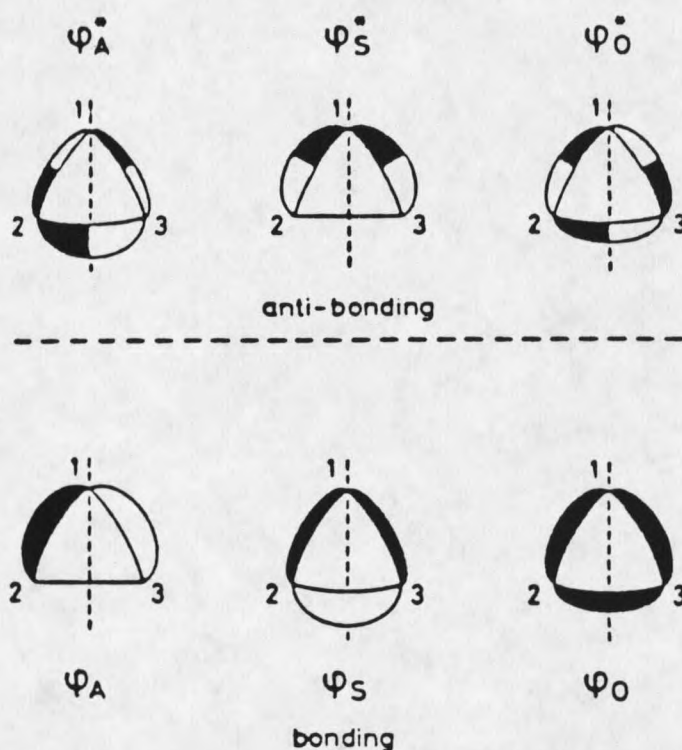
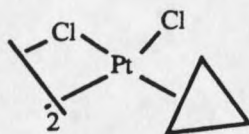
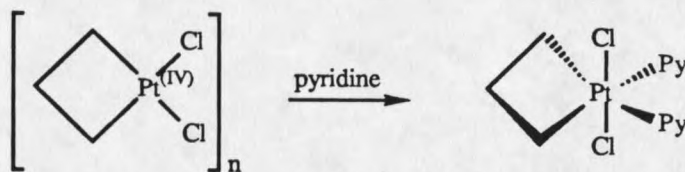


Figure 19. The (F.C.M.)-basis.

Tipper⁵⁶, using the analogy that transition metals complex with ethylene, reacted cyclopropane with hexachloroplatinic(IV) acid H_2PtCl_6 in acetic anhydride. Tipper's conclusion was that the dimeric cyclopropane complex **10** had formed. He compared this to Zeise's Dimer. Some years later Chatt⁵⁷, using more sophisticated techniques, deduced that the cyclopropane had opened to give the platinacyclic derivative **11**. Reaction of this with pyridine would be expected to give the octahedral complex **12**, which was later confirmed by Gillard⁵⁸ using x-ray analysis.



10



11

12

The bonding scheme of platinum to cyclopropane is of much interest but is still in question. The simplest model would involve anionic ligand $C_3H_6^{2-}$ (where the carbon atoms are sp^3 -hybridized) and a d^6 platinum (d^2sp^3 -hybridized). The platinum and three carbon atoms form four two-center, two-electron σ bonds. This has the value of simplicity but does not describe the chemistry or differences in geometry in various molecules. Looking for a better model, McGinnety³⁹ postulated four-center molecular orbitals comprised from the carbon atoms in the sp^2 -hybridized state (much like the Walsh cyclopropane) and a dsp^3 platinum. This would give σ orbitals in a trigonal bipyramidal array with a d-orbital in the equatorial plane. Figure 20 depicts the four occupied orbitals comprised from the eight bonding electrons. McGinnety lists several advantages of his model but the shortcoming is that the MO's lead to no net platinum-cyclopropane bonding interaction. The picture he draws for us though is that there is the probability of bent bonds in platinacyclobutanes.

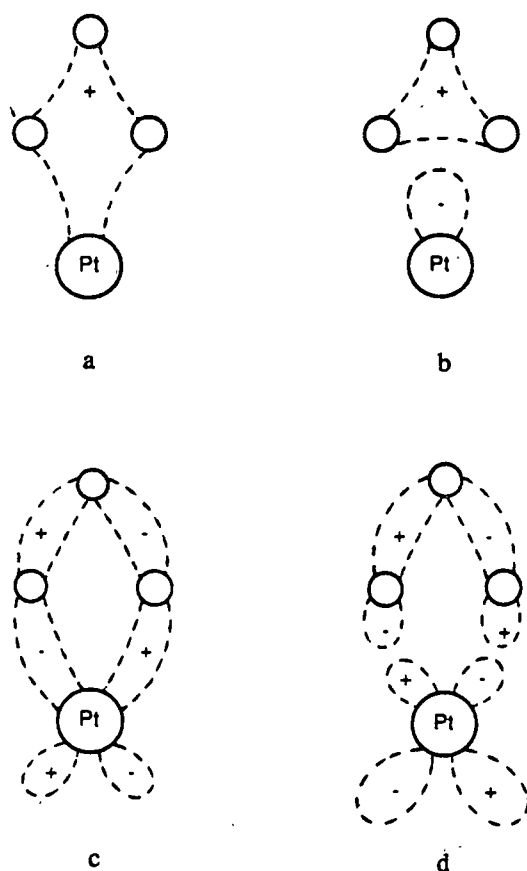


Figure 20. McGinnety Platinacyclobutane Bonding Scheme. (a) and (b) are constructed from available σ -orbitals while (c) and (d) are from the metal d-orbital and p-orbitals of the carbon atoms.

McQuillin⁶⁰ also used the Walsh orbital picture to envision a bonding scheme. Insertion of Pt can be a process of rehybridization. Electrons from the carbon bonds will overlap with a hybrid vacant orbital of the platinum. Using a bonding orbital and a non-bonding orbital, see Figure 18, McQuillan describes his scheme as a σ -donor component from the lowest cyclopropane orbital along with π back donation from the metal into the antibonding cyclopropane orbitals, Figure 21. This can be compared to the platinum-ethylene picture and could rationalize the downfield shift of the methylene protons in the platinacyclobutane complexes.

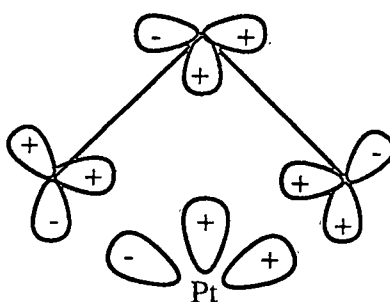


Figure 21. McQuillin Platinacyclobutane Orbital Model

Characterization of Platinacyclic Compounds

Insertion of platinum into cyclopropanes usually results in an insoluble precipitate (initially precipitated complex-IPC). Three methods have been employed in the characterization of this solid: mass spectrum, infrared and solid state (CP/MAS) NMR. The mass spectrum of $[(\text{PtCl}_2\text{C}_3\text{H}_6)_n]$ has been taken⁶¹, and the observation of a peak at m/e 1232 is believed to be the parent ion which corresponds to the tetramer **13**. The IR spectrum of these solids also displayed the presence of bridging and terminal chlorines. Comparison of the polymeric $[\{\text{PtY}_2(\text{CH}_2\text{CH}_2\text{CH}_2)\}_n]$ and the proposed tetramer show similar stretching frequencies. IR spectroscopy also identified the C_3H_6 unit as a platinacyclobutane. Table 6⁶² gives the stretching frequencies of two complexes in comparison to cyclopropane, indicating opening of the ring.

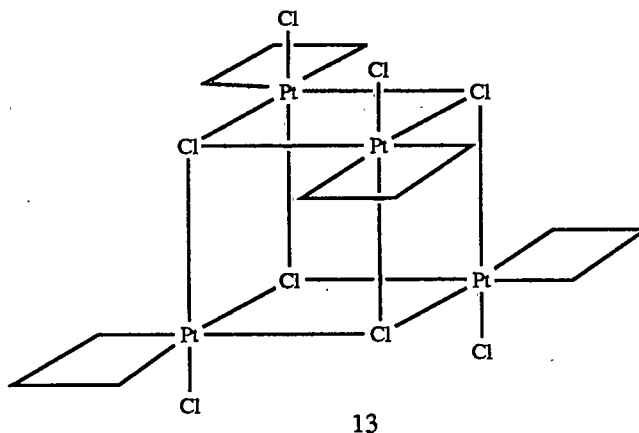


Table 6. Stretching Frequencies for Platinacyclobutanes.

C_3H_6 unit	$Pt(C_3H_6)Cl_2Py_2$	$[Pt(C_3H_6)Cl_2]_4$	C_3H_6
C-H	2992 2938 2917	3025 2954 2948	3103
CH_2 wag	1238	1255 1237	
CH_2 deformation	1437	1414	1442
CH_2 twist	1217	1165	
ring deformation	1134 1087	1149 1125	
CH_2 rock	1038	1087 1022	1029
ring deformation	980	981	
CH_2 rock	976 892	948 890 663	869
Pt-C ring deformation		563	

Solid state NMR has also been used to show platinacyclobutane formation in the IPC. Because of the broadening of lines in the spectrum, solid state NMR data is most useful when compared to solution NMR spectra (see section on solution ^{13}C NMR spectroscopy). Waddington⁶³, Figure 22, and Parsons⁶⁴ have both used solid state ^{13}C NMR spectroscopy to characterize the initially precipitated platinacyclobutanes. The chemical shift difference in the NMR is a result of a ligand change. It should be remembered that as a solid it is believed to be a tetramer (see 11, page 25). This would put a chlorine atom trans to a σ -bound carbon atom. In the solution NMR spectra, pyridine is trans to the σ -bound carbon atoms (see 12, page 25).

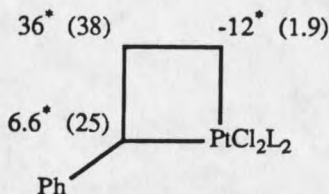
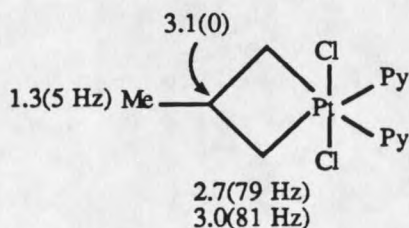


Figure 22. CP/MAS Resonances of a Platinacyclobutane (numbers in parentheses). The * Numbers are Solution ^{13}C Resonances.

Treatment of the solid tetramer with ligands such as pyridine break apart the tetramer giving the platinacyclobutane monomer. These monomers are extremely soluble in solvents such as chloroform making their characterization much easier. Solution state NMR and X-ray studies are now applicable to the platinacyclobutanes. ^1H , ^{13}C and ^{195}Pt NMR are very convenient methods to characterize platinacyclic compounds.

^1H NMR spectra of simple cyclobutanes such as **14**⁵⁷ ($J_{\text{Pt,H}}$ in parentheses) are relatively simple to interpret. Platinum proton coupling has a range of 60-110 Hz for $^2J_{\text{Pt,H}}$, 0-50 Hz for $^3J_{\text{Pt,H}}$ and 0-10 Hz for $^4J_{\text{Pt,H}}$ ⁶⁵⁻⁶⁸. This is usually a good model for simple and complex platinacycles. Complex molecules have the problem of overlapping signals which make assignments difficult, but with today's high field NMR spectrometers and sophisticated techniques, proton NMR data is extremely useful in characterization. Moving from 60 or 100 MHz to a 500 MHz magnet has the advantage of spreading out what was once a cluttered spectrum.



^{13}C NMR spectroscopy is perhaps a better method for the identification of platinacycles. Platina(IV)cyclobutanes exhibit characteristic resonances for the platinum ring carbons. Figure 23 shows the range for a substituted and nonsubstituted rings. Platinum-carbon coupling is also very typical for platinacyclobutanes. This is usually 335-460 Hz for $^1J_{\text{Pt,C}}$, 0-25 Hz for $^2J_{\text{Pt,C}}$ and 20-65 Hz for $^3J_{\text{Pt,C}}$ ^{65,66,69,70}.



Figure 23. ^{13}C NMR Resonance Ranges in PPM.

^{13}C NMR spectra are also very useful for the characterization of platinum complexes other than platinacyclobutanes. Some characteristic chemical shift ranges for various platinum compounds and their $^1J_{\text{Pt,C}}$ are given in Table 7. These values can be extremely indicative of what type of platinum compound is present.

Given that Platinum-195 is NMR active, it too can be observed and used as an indicator for the oxidation state of the platinum. Platinum(IV) complexes usually resonate at a lower field than platinum(II) complexes. Sodium tetracyanoplatinate(II) and $[\text{PtCl}_6]^{2-}$ have both been used as standards with $[\text{PtCl}_6]^{2-}$ being the more common. This standard decomposes with time and also is very dependent on solvent and temperature⁷⁵. The advantage it has, is it is a well known reference in platinum chemistry. $\text{Na}_2\text{Pt}(\text{CN})_4$ on the other hand is less sensitive to solvents and temperature⁷⁶ as well as resonating at a higher field than most platinum species. This is a less well known standard in the field however. Table 8 lists the resonances for various Pt(IV) complexes which can be compared to the Pt(II)-Olefin complexes in Table 9.

Table 7. ^{13}C NMR Shifts and 1J Constants for Various Complexes.

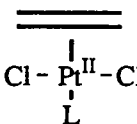
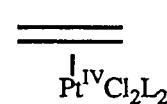
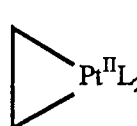
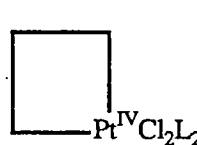
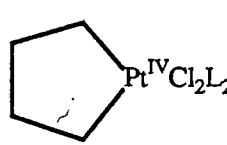
COMPLEX	in PPM	$^1J_{\text{Pt,C}}$ in Hertz	Ref.
 $\text{Cl}-\text{Pt}^{\text{II}}-\text{Cl}$ $\quad \quad \quad \text{L}$	70 - 110	50 - 200	71, 72
 $\text{Pt}^{\text{IV}}\text{Cl}_2\text{L}_2$	120	94	71
 $\text{Pt}^{\text{II}}\text{L}_2$	40 - 65	not reported	20
 $\text{Pt}^{\text{IV}}\text{Cl}_2\text{L}_2$	(-20) - 20	335 - 460	65, 66, 69, 70
 $\text{Pt}^{\text{IV}}\text{Cl}_2\text{L}_2$	15 - 45	490 - 560	73, 74
$\text{L}_2\text{Pt}^{\text{IV}}(\text{Alkyl})_4$	(-5) - 20	660 - 730	74

Table 8. Pt(IV) NMR Shifts Relative to 1M Na₂Pt(CN)₄ in D₂O at 25° C.

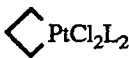
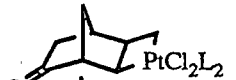
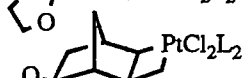
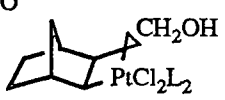
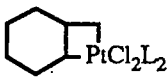
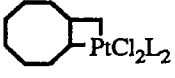
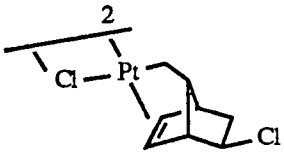
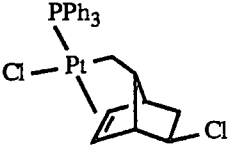
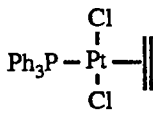
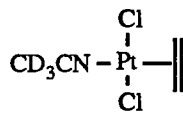
COMPLEX	LIGAND	SOVENT	SOLVENT (ppm)
	Py	CDCl ₃	3317
	Py	CDCl ₃	3308
	Py	CDCl ₃	3350
	THF	THF	3278
	THF	THF	3365
	Py	CDCl ₃	3368
	Py	CDCl ₃	3390
	Py	CDCl ₃	3333
	Py	CDCl ₃	3322
	Py	CDCl ₃	3334
	Py	Py - d ₅	3315
	Py	Py - d ₅	3300

Table 9. Pt(II) NMR Shifts Relative to 1M Na₂Pt(CN)₄ in D₂O at 25° C.

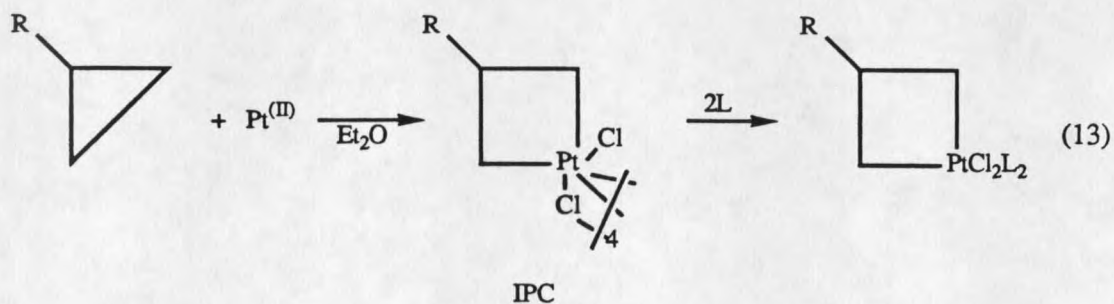
COMPLEX	SOLVENT	SHIFT (ppm)
	DMSO	1635
	CDCl ₃	723
	CDCl ₃	732
	CDCl ₃	687
	CD ₃ CN	1726

A myriad of X-ray crystal structures of platinacyclobutanes have been reported. Most of these show a substantial puckering of the platinacyclobutane ring, from 12-28°. This compares well to cyclobutane hydrocarbon derivatives of 20-35°⁷⁷. The carbon-carbon bond lengths are also elongated in the platinum complexes presumably due to covalent radii of platinum⁷⁸.

Formation of Platinacycles

Tipper's original reaction of cyclopropane with platinum was done in acetic acid, but this has proven to be quite unsuccessful with substituted cyclopropanes. The solvent of choice, using the methods below, is most often diethyl ether and occasionally tetrahydrofuran. Usually platinacyclobutanes are formed from the displacement of ethylene from Zeise's dimer^{79,80}, although a cyclopropane can exchange with a different platinum-bound cyclopropane⁸¹. 1,3-di-Grignards will also react to form platinacyclobutanes^{82,83} by oxidative addition.

When platinacyclobutanes are prepared in diethylether, the orange Zeise's dimer is consumed to give yellow precipitates which are the platinacyclobutane tetramers. These yellow solids are usually referred to as IPC's (initially precipitated complexes). Usually the complexes are studied as monomeric complexes, however, a few solvents have been found which will slightly solubilize the IPC's. Formation of the monomeric species can be achieved by reaction of the IPC's with nitrogen or oxygen ligands, an example is shown below in Equation 13. Nitrogen ligands, such as pyridine, bipyridyl and acetonitrile, have become the most popular. Oxygen ligands, such as THF, are used less frequently because the ligand can be lost when the solvent is removed. Finally use of soft ligands such as cyanide ions and phosphines cause decomposition, usually back to starting cyclopropanes.



Cis-1,2-Dialkylcyclopropanes were believed to either fail to react with Zeise's dimer⁸⁴ or yield π -allyl complexes⁸⁵, as shown in Figure 24. In the case of norbornyl cyclopropanes, they were believed to form the bis(edge-complex) **15**⁸⁶.

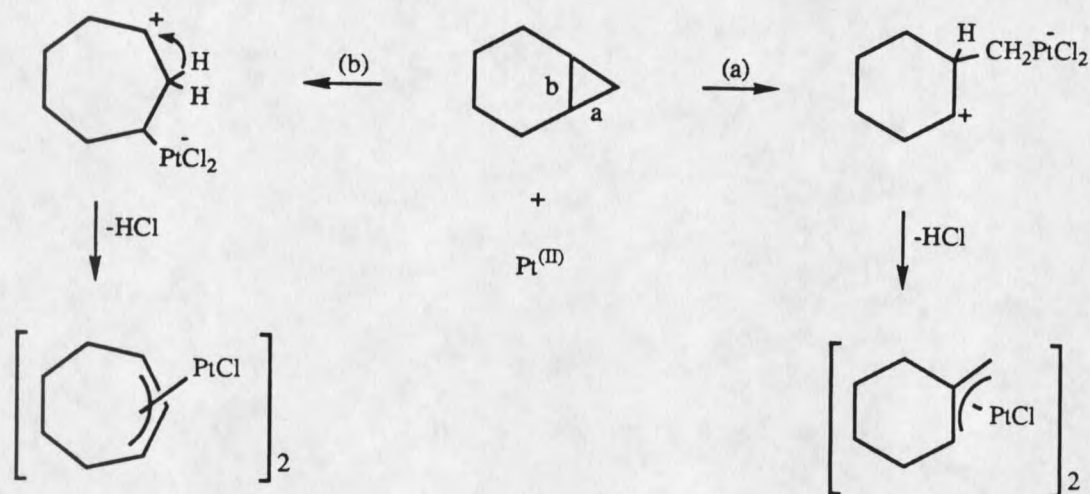
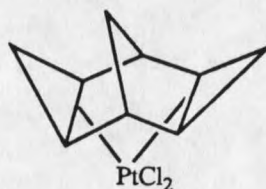


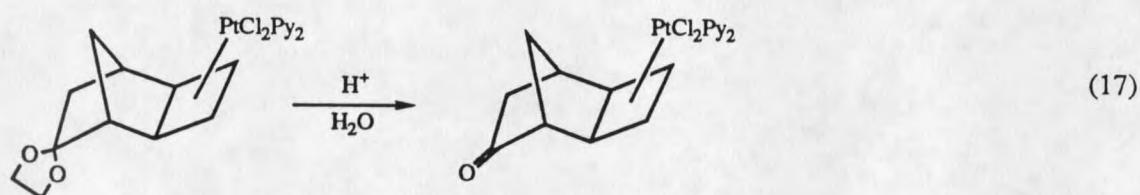
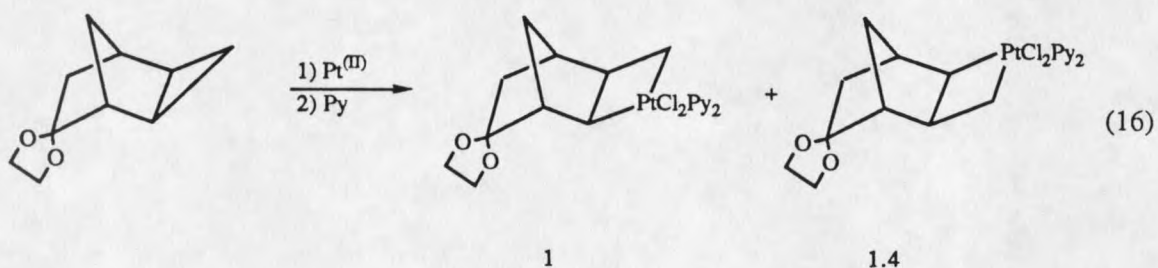
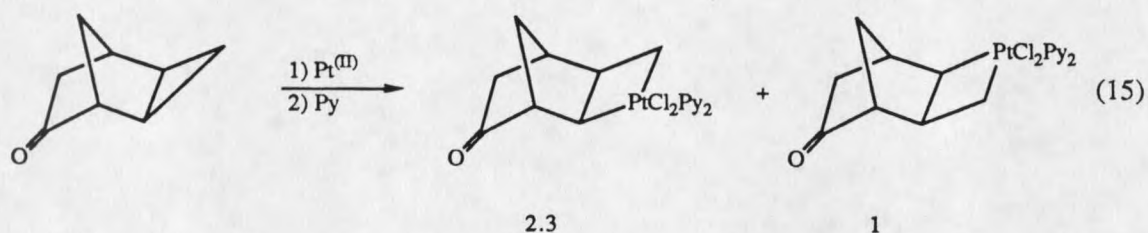
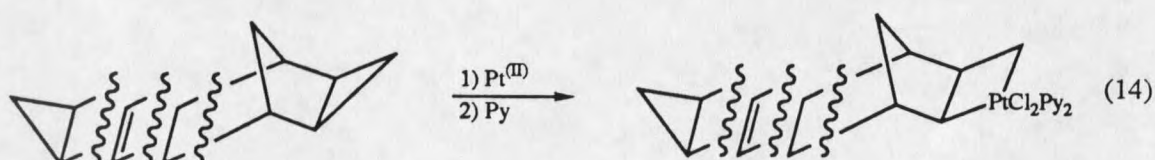
Figure 24. π -Allyl Formation from Norcarane and Pt(II).



15

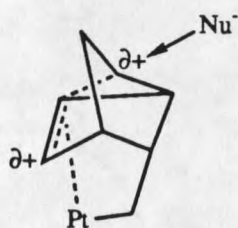
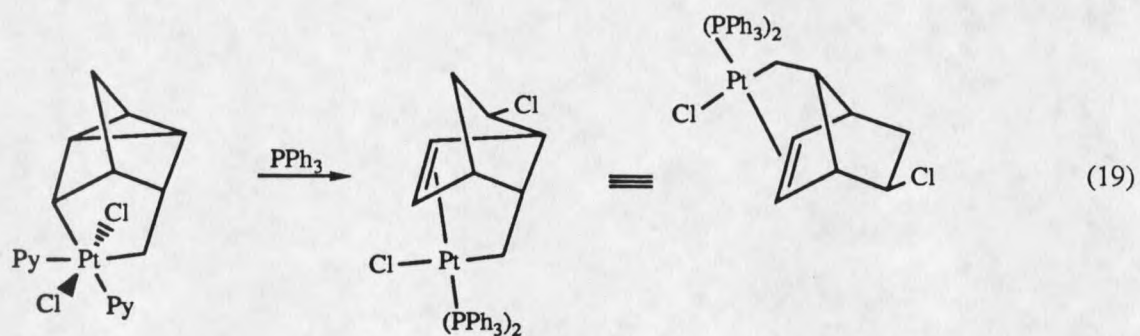
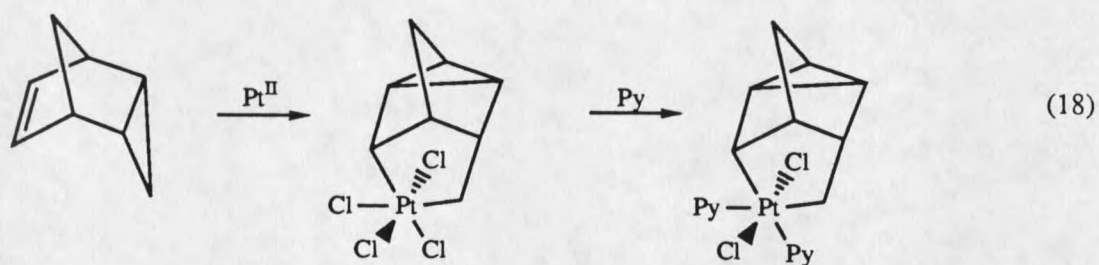
However, Jennings and Waddington⁶⁹, in 1982, showed that reaction of Zeise's dimer with norbornyl cyclopropanes did in fact insert platinum to form stable platinacyclobutanes in excellent yields, Equation 14. Ekeland and Jennings⁷⁰ extended the exo-norbornyl system list by putting functionality on the norbornyl fragment, Equation 15 and 16. They observed that protection of the ketone increased reactivity almost 2-fold as well as changing the

regioselectivity of insertion. Finally, they were able to deprotect the ketones, Equation 17, but observed that these ketones were relatively inert to reactions which are generally operative in analogous platinacylcobutanes.



Jennings⁸⁷ has also studied the endo-norbornyl system. This system provided new and insightful chemistry into cyclopropane reactions. Equation 18 outlines the observed results. Presumably, a platinacyclobutane is formed first followed by a pseudo 1,3 sigmatropic shift.

This is probably due to the close proximity of the olefin to the platinacycle. Treatment of the pyridine analogue with triphenyl phosphine resulted in a rearrangement to the chlorine adduct, Equation 19. Presumably this is going through the intermediate cation **16**. One of the positive charges is stabilized by the platinum while charge density increases at the bridgehead carbon. Nucleophilic attack at this carbon is then preferred. In order to gain insight on the ionic character of this reaction, it was conducted in a more polar solvent methanol. This resulted in capture of both Cl and MeO at the same position.



Steric effects also play a role in platinum insertion. Cushman and Brown⁸⁸ have reported on a trisubstituted platinacyclobutane, Figure 25. Neilsen and Jennings⁸⁹ have since expanded this to 2,3,4-trisubstituted platinacyclobutanes, Figure 26, in which platinum inserts stereospecifically. Previous to the work done by this author, no examples of tetrasubstituted cyclopropanes were found to insert platinum and were thought to be impervious to insertion. An example of this, 1,1,2,2-tetramethyl cyclopropane failed to react with Zeise's dimer on the basis of steric hinderance by the methyl groups⁹⁰. An example of insertion of Pt(II) into a tetrasubstituted cyclopropane will be presented in a chapter of the discussion.

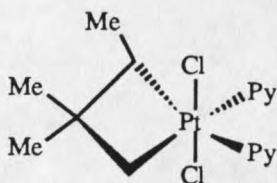


Figure 25. 2,3,3-Trisubstituted Platinacyclobutane.

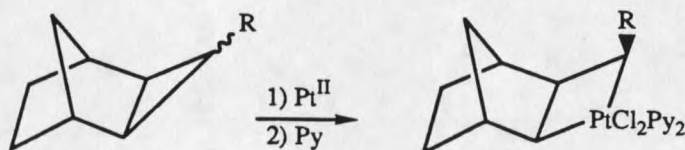
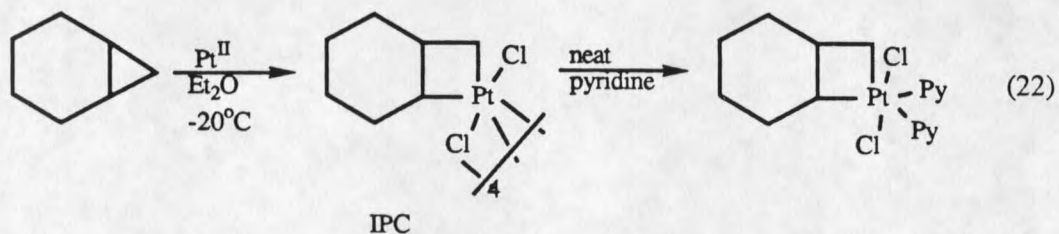
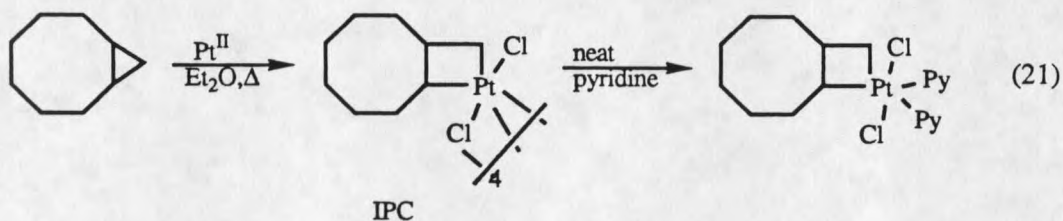


Figure 26. 2,3,4-Trisubstituted Platinacyclobutane.

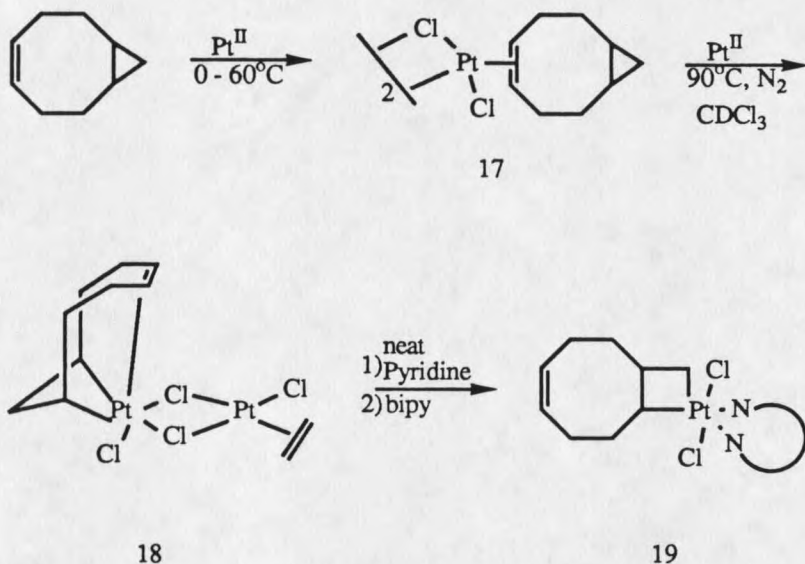
The type of functionality on the cyclopropane also plays a key role in insertion of platinum(II). Electron-releasing groups accelerate the reaction of cyclopropanes with platinum^{77,85}. On the other hand, electron-withdrawing groups such as CO_2Me , CN or COMe completely stopped insertion of platinum(II) into cyclopropanes (McQuillin)⁸⁵. In one example, a norbornyl cyclopropane bearing a CO_2Et substituent has inserted platinum(II). This was developed by Moats⁹¹ and is shown in Equation 20.



As was mentioned previously, McQuillin stated that norcarane reacted with Zeise's dimer to give π -allyl complexes. After the discovery that norbornyl cyclopropane produced platinacyclobutanes, the bicyclo[X.1.0] hydrocarbons were reinvestigated by Parsons and Jennings⁶⁴. The initial molecule used was bicyclo[6.1.0]nonane and the results are shown in Equation 21. As can be seen, the cyclopropane moiety inserts platinum to give a platinacyclobutane as the IPC which was characterized by CP/MAS. This could be reacted with pyridine forming a stable monomer which was characterized by solution NMR spectroscopy. With these results in hand, norcarane was reacted with Zeise's dimer. Reaction at room temperature resulted in the formation of a mixture of olefins. In order to obtain the platinacyclobutane analogue, the reaction had to be carried out at low temperatures resulting in an IPC which was unstable at room temperature and required immediate reaction with neat pyridine, Equation 22.

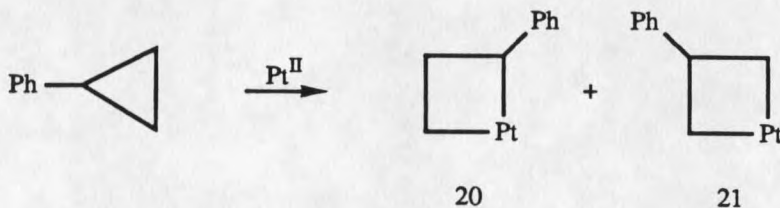


Incorporation of an olefin into the bicyclo[6.1.0]nonane resulted in the formation of platinum-olefin complex **17**. Treatment of the complex with an additional equivalent of Pt(II) and high temperatures resulted in the formation of the first Pt(IV)-olefin complex **18**⁹². This could be treated with pyridine and then bipyridyl to give **19**.

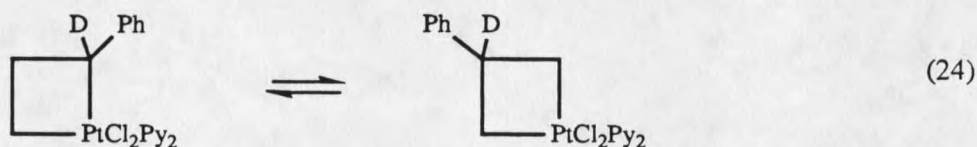
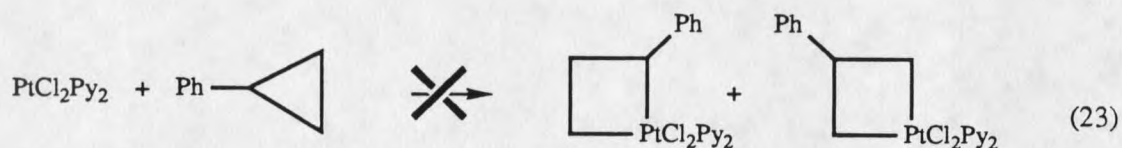


Isomerization of Platinacyclobutanes

Insertion of platinum into phenylcyclopropane followed by conversion to the monomer gives complex **20**. When **20** is allowed to equilibrate, it rearranges to a mixture of **20** and **21**^{93,94}. This has been shown to be general for many platinacyclobutanes and has come to be known as the Puddephatt rearrangement.



Puddephatt was able to show that when labelled phenylcyclopropane was added to the monomer complex **20**, none or very little labelled cyclopropane had been incorporated into **20** and **21**^{95,96} after isomerization. Also, reaction of *cis* or *trans*-PtCl₂(C₅H₅N)₂ with phenylcyclopropane does not give insertion products, Equation 23^{94,96}. Both of these results rule out the possibility of dissociation of platinum and then reinsertion, thereby asserting that the rearrangement is intramolecular. Migration of the phenyl group was ruled out by the lack of scrambling in the isomerization experiments involving 1-deuterio-1-phenylplatinacyclobutane, Equation 24⁹⁴. Finally a chelating ligand will completely stop the isomerization indicating that an initial loss of ligand is necessary.



The mechanisms for this rearrangement that have been postulated are shown in Figure 27. Mechanism (i) involves a carbene-alkene in which free rotation with both alkene and carbene give isomerization. Two results that have shown mechanism (i) to be incorrect are: 1) thermal decomposition would be expected to give ethylene and RCH=CH₂ which have not been observed^{93,97,98}. 2) Incorporation of an R and R' into the platinacyclobutane would give *cis-trans* isomers after rotation, which has also not been observed^{95,99}. The isomerization has been shown to occur with complete retention of stereochemistry.

Mechanism (ii) has not been disproved but is held in doubt. It involves reductive elimination to form an "edge" complex followed by an edge to edge isomerization, reinsertion yielding the isomeric complex. The earlier mentioned crossover experiment with labelled cyclopropane has shown that the platinum is strongly bound to the cyclopropane. The situation in (ii) is thus thermodynamically unfeasible and has no precedence¹⁰⁰.

Mechanism (iii), proposed by Puddephatt⁹³, is a concerted process in which the bond cleavage and reformation are all concerted. Complete C-C bond cleavage (as in mechanism i) must never occur in (iii).

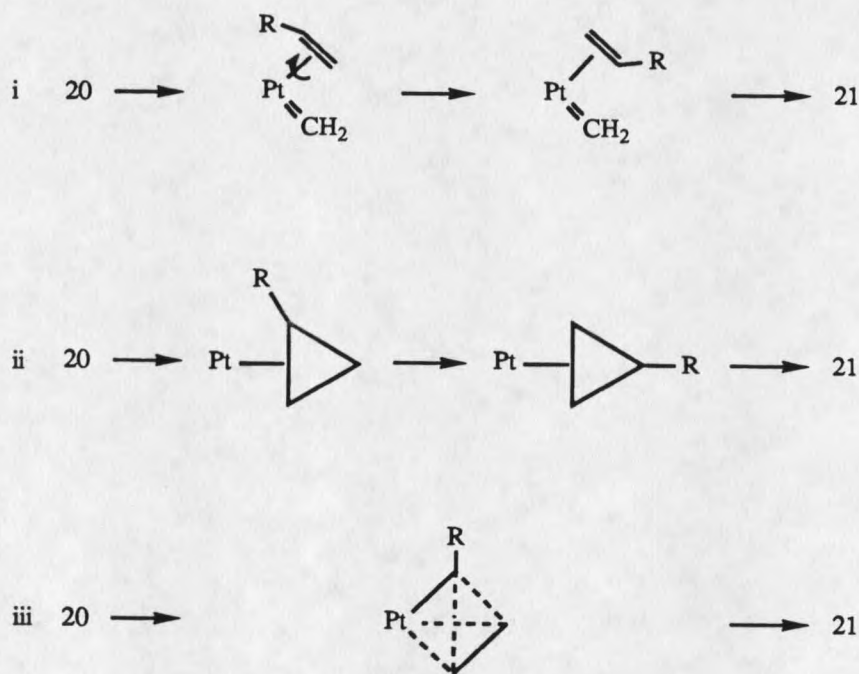


Figure 27. Proposed Mechanisms for the Puddephatt Rearrangement.

Mechanism (iii) can also be compared to a cyclobutyl cation which proceeds as shown in Figure 28. This was developed by Hoffman^{100,101} as an extension of Puddephatt's mechanism. After initial loss of a ligand, the LPtCl_2 fragment rearranges to pyramidal geometry which is isolobal to CH^+ . The $\text{LCl}_2\text{Pt}(\text{C}_3\text{H}_6)$ can then be compared to C_4H_7^+ , a non

classical carbonium ion. Both Puddephatt's and Hoffman's mechanisms explain the existing experimental data, but cannot be differentiated experimentally, if in fact, there is any difference.

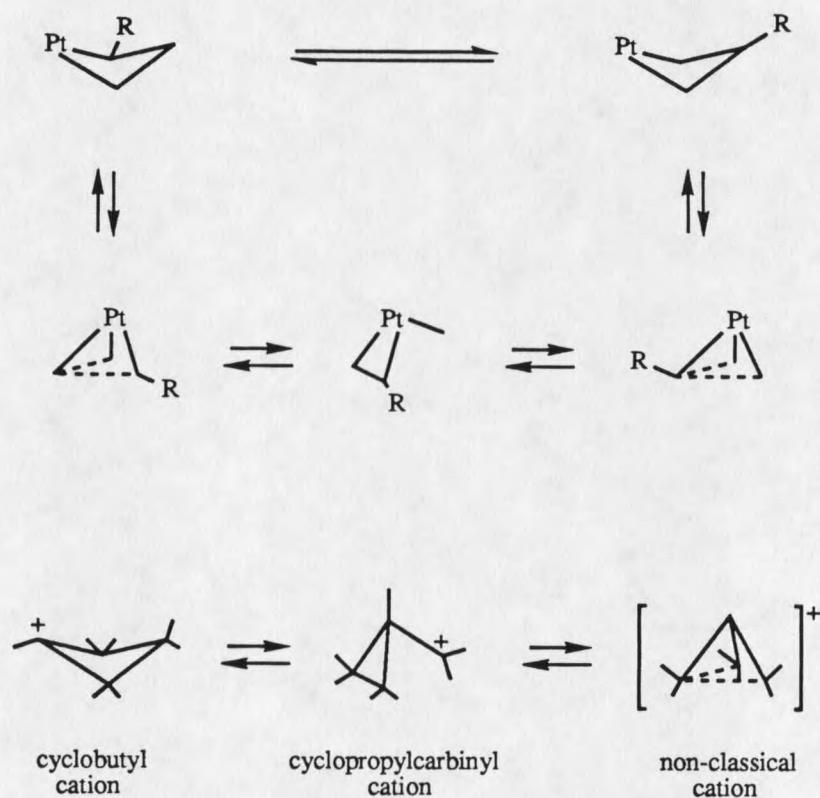
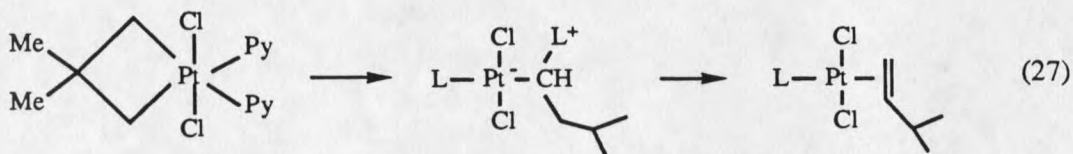
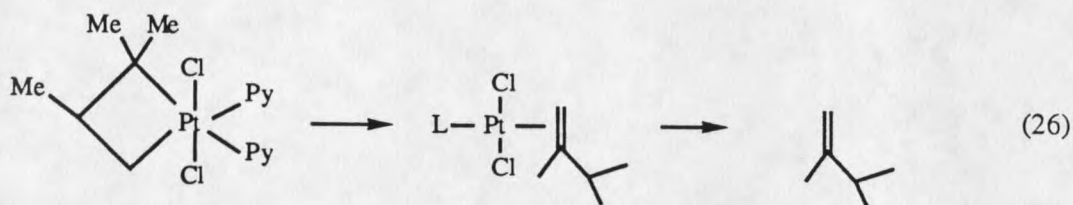
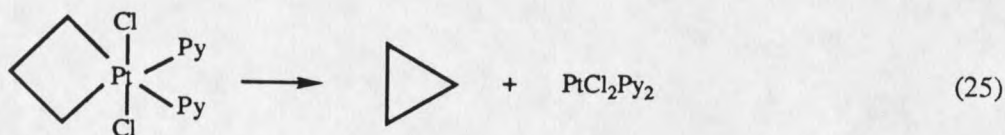


Figure 28. Comparison of $\text{LCl}_2\text{Pt}(\text{C}_3\text{H}_6)$ (top diagram) to the Nonclassical Carbonium Ion (lower diagram).

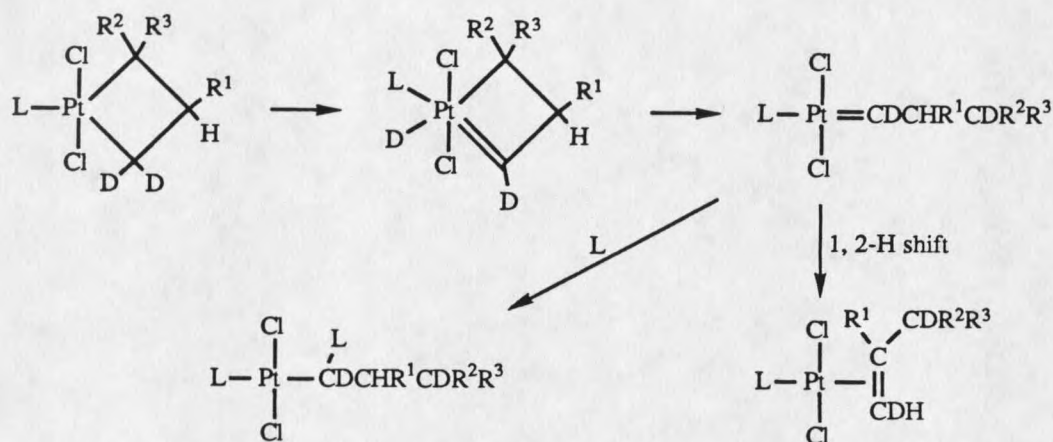
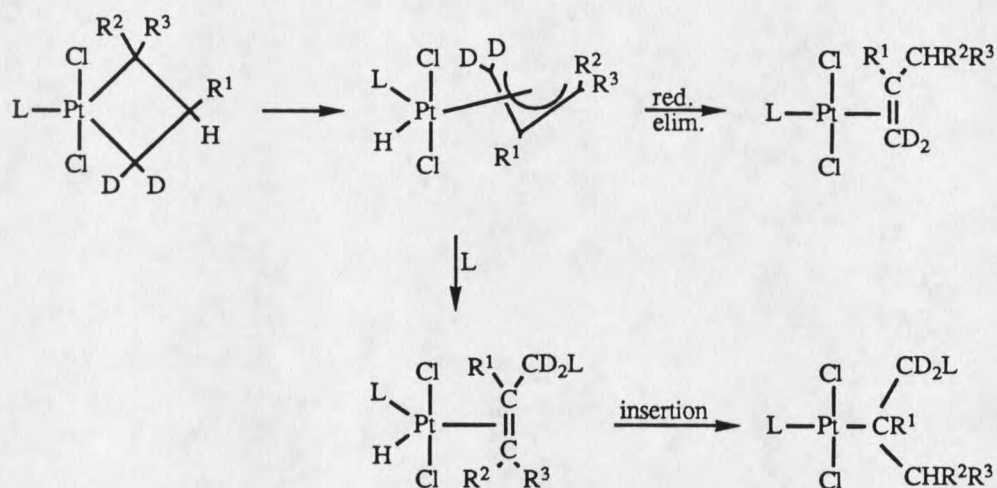
Platinacyclobutane Chemistry

Platina(IV)cyclobutanes are known to decompose to organic products or platinum complexes that are different from the original platinacycle. Reductive elimination results in starting cyclopropane, Equation 25. Dissociation of a ligand produces an alkene complex which yields free olefin, Equation 26. Dissociation of a ligand can result in rearrangement to produce an ylide complex which also yields an olefin, Equation 27.

Reductive elimination to form cyclopropanes can be achieved by the use of soft ligands such as PPh_3 , KCN and DMSO . These can be added to the tetrameric or monomeric platinacyclobutane. In the case of the monomeric species, the soft ligand must compete with the ligand already bound to the platinum.



In both alkene and ylide formation, prior dissociation of a ligand must occur to give a five-coordinate intermediate^{93,96}. When excess pyridine is added as the ligand, the formation of ylide and alkenes is retarded¹⁰². After dissociation of a ligand the complex can undergo an alpha or beta hydrogen abstraction to yield the alkene or ylide complexes. Both the alpha and beta mechanistic pathways are shown in Figure 29 and Figure 30¹⁰³ respectively.

Figure 29. α -Elimination Mechanism.Figure 30. β -Elimination Mechanism.

In the alpha mechanism, Figure 29, a proton on the carbon alpha to the platinum is abstracted by the platinum forming a platinacyclocarbene. The hydride is then transferred to the opposite side of the ring to give the open chain carbene. This is followed by a 1,2 shift of a proton from the original beta carbon to give an olefin. In the beta mechanism, Figure 30, the first step involves abstraction of a hydrogen from a carbon beta to the platinum, which produces the π -allyl intermediate. Olefin formation is again the result of

hydride transfer from the platinum. In both of these mechanisms, ylide formation results when plausible intermediates are intercepted by a ligand.

Both the alpha and beta elimination pathways have precedence in the literature¹⁰⁴. Johnson¹⁰⁵ examined the reaction that was shown in Equation 27 and found that a β -pathway was followed, Puddephatt re-examined¹⁰³ the reaction and found that an α -pathway was actually followed. However, the same reaction conditions were not used and so it would seem that conditions may alter the pathway.

Upon closer look at the β -mechanism it can be seen that two possible olefins can be formed, this is dependent on where the proton is transferred to, via the platinum. As can be seen in Figure 31, pathway (a) gives the least substituted olefin while (b) leads to the more substituted olefin. Johnson¹⁰⁶ studied various substituted platinacyclobutanes and was able to show that the least substituted olefin is formed almost exclusively when a β -mechanism is employed, i.e. pathway (a) in Figure 31. The explanation for this observance is that decomposition to olefins seems to prefer formation along the least-substituted edge of the platinacyclobutane. This would lead to the less-substituted olefin-platinum complex which is more stable than a highly substituted olefin-platinum complex.

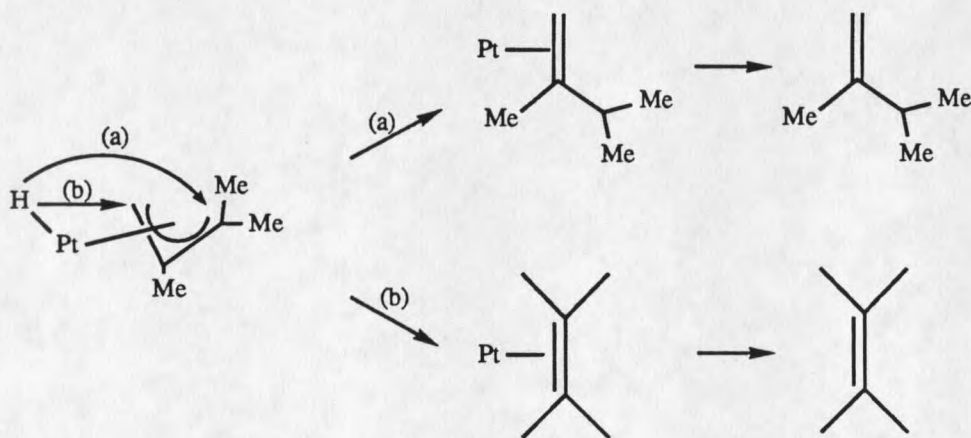


Figure 31. Pathways in Olefin Formation from the β -Mechanism.

Reactions of Norbornyl Platinacyclobutanes

Norbornyl platinacyclobutanes will also form olefins by reaction with CO^{107} , as shown in Figure 32, or by ring expansion, Figure 33, when treated with DMSO^{107} . The mechanism for the ring expansion is proposed to proceed via the Puddephatt rearrangement shown in Figure 34.

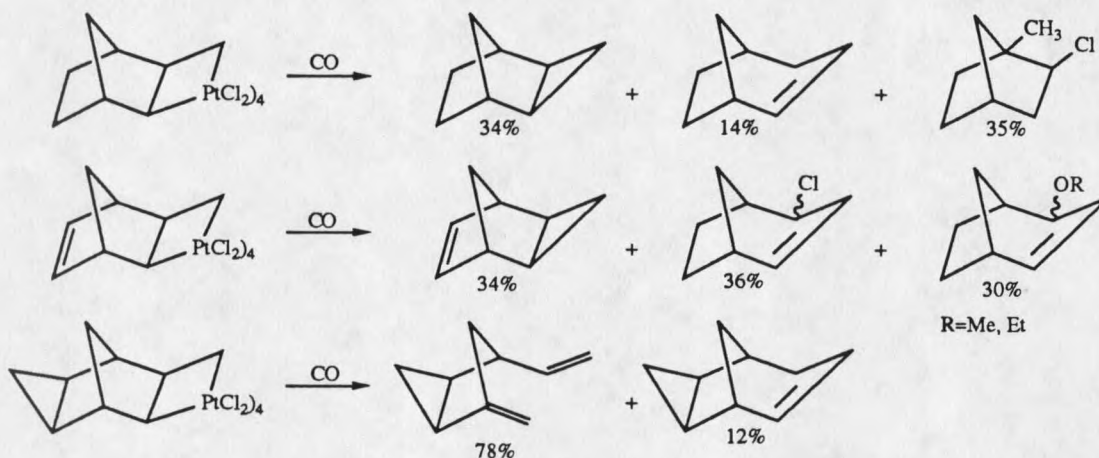


Figure 32. Reaction of CO with Norbornyl Platinacyclobutanes

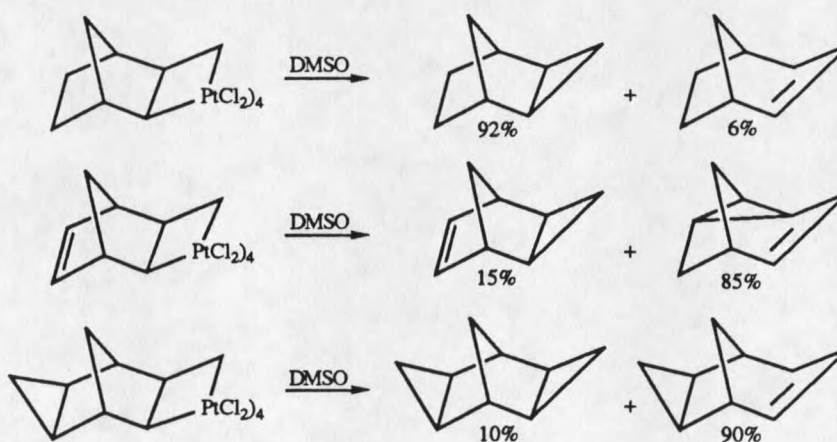


Figure 33. Ring Expansion with DMSO

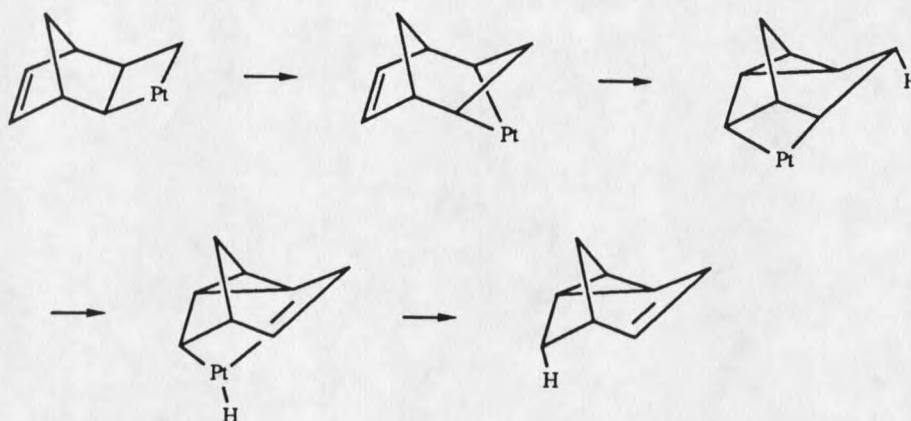


Figure 34. Proposed Ring Homologation Mechanism.

Katz's^{109,110} work with rhodium on the norbornyl system lends precedence to the proposed mechanism. He proposes a Puddephatt rearrangement as well for the ring homologation with rhodium, Figure 35.

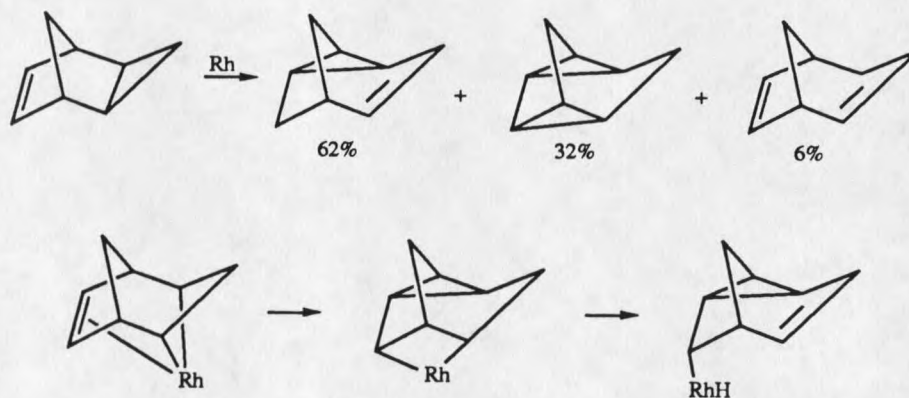


Figure 35. Rhodium Ring Expansion and Mechanism.

Norbornyl platinacyclobutanes will also form olefins by the addition of diazo compounds to the monomers, Figure 36^{89,107}. In the case of ethyl diazoacetate, no stereochemistry about the olefin has been achieved. The other sites of stereochemistry have

been set when platinum inserts into the cyclopropane and is carried through into the products. The proposed mechanism, Equation 28, suggests that a symmetric platinacyclopentane is formed which decomposes to the dienes.

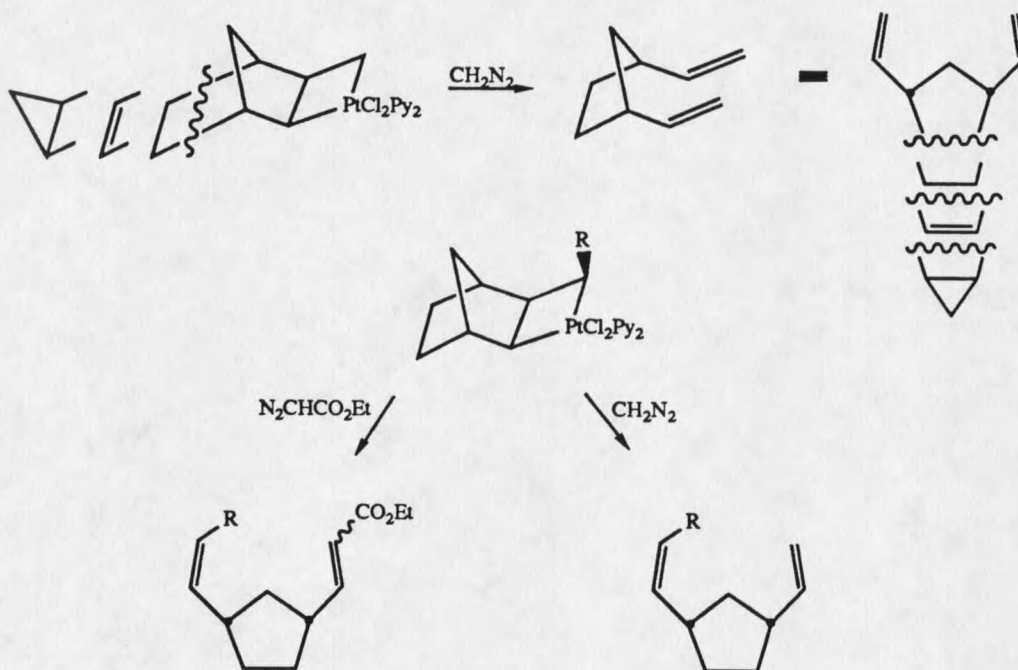
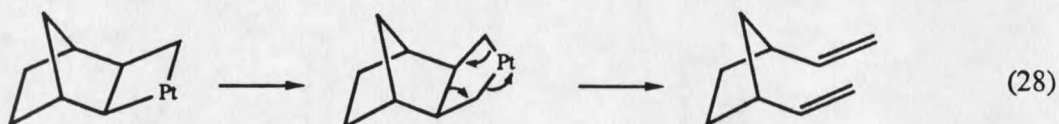


Figure 36. Olefin Formation via Diazo Compounds, $\text{R} = \text{CH}_2\text{OH}$, $-\text{CH}_3$, $-\text{COH}$, when R is anti to the norbornyl bridge the resulting olefin has trans stereochemistry.



Bicyclo Platinacyclobutane Chemistry

The chemistry of the bicyclo system is also dominated by olefin formation. Parsons and Jennings^{64,111} reported on the chemistry of the bicyclo[6.1.0] and bicyclo[4.1.0] platinacyclobutanes observing mixtures of olefins and cyclopropanes. Warming of the

platinacycle formed from norcarane followed by reaction with KCN gave a mixture of eight olefins and starting cyclopropane, Figure 37. Reaction of the [6.2.0] platinacyclobutane gave a mixture of three olefins and the starting cyclopropane, Equation 29.

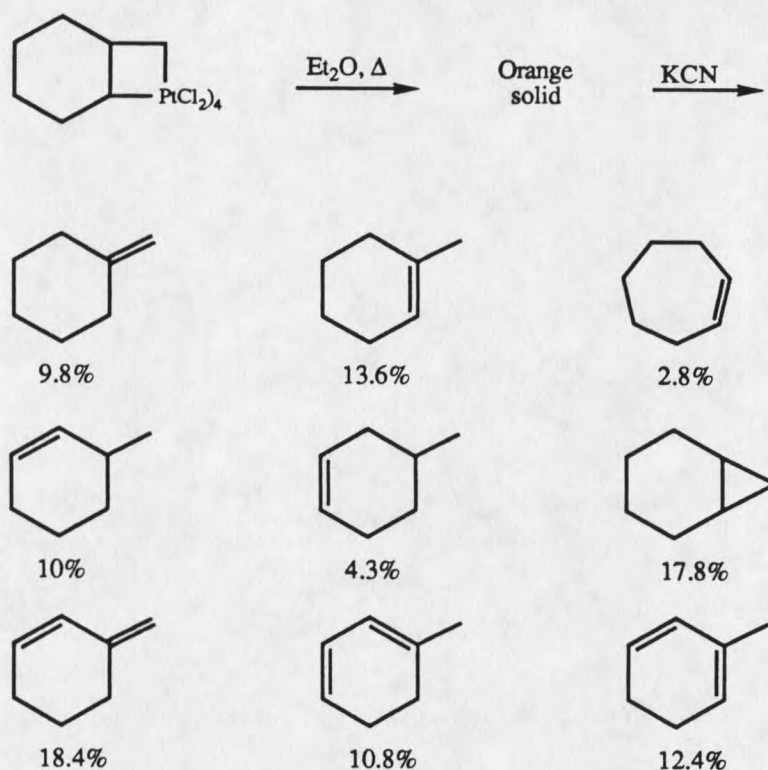
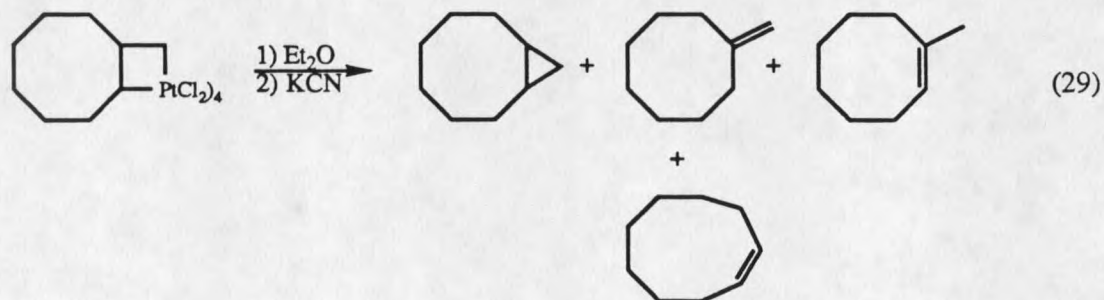
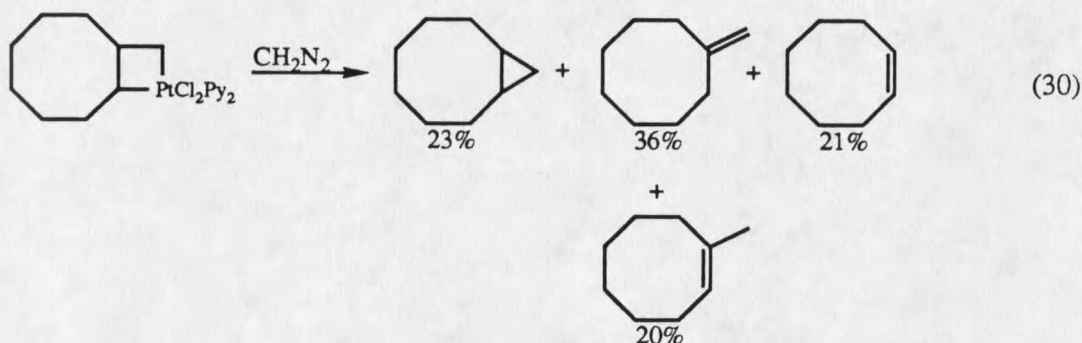


Figure 37. Olefin Formation from the Bicyclo[4.1.0] System.



Previously, it was shown that the norbornyl platinacyclobutanes ring expanded upon treatment with DMSO. It was therefore anticipated that the bicyclo[6.1.0] system would also expand to cyclononene. However, treatment of the IPC with DMSO initiated reductive elimination to the starting cyclopropane exclusively.

Reaction of the bicyclo[6.1.0] IPC with diazomethane also gave results similar to those observed in Equation 29. Unlike the reaction of diazomethane with norbornyl systems, the bicyclo system yielded no synthetically useful results but did give an interesting product by the formation of cyclooctene, Equation 30. This product can be rationalized by ring expansion to an unsymmetric platinacyclopentane which upon decomposition results in cyclooctene and ethylene.



Earlier it was mentioned that the bicyclo[6.1.0.] platinacyclobutane monomer required excess pyridine to prevent rearrangement. If only 2 equivalents of pyridine are added to the tetramer, an almost quantitative yield of exo-cyclic olefin is obtained, Equation 31. Deuterium labelling studies showed that an alpha hydride mechanism is the major pathway in this reaction. Figure 38 shows the proposed pathway and observed results.

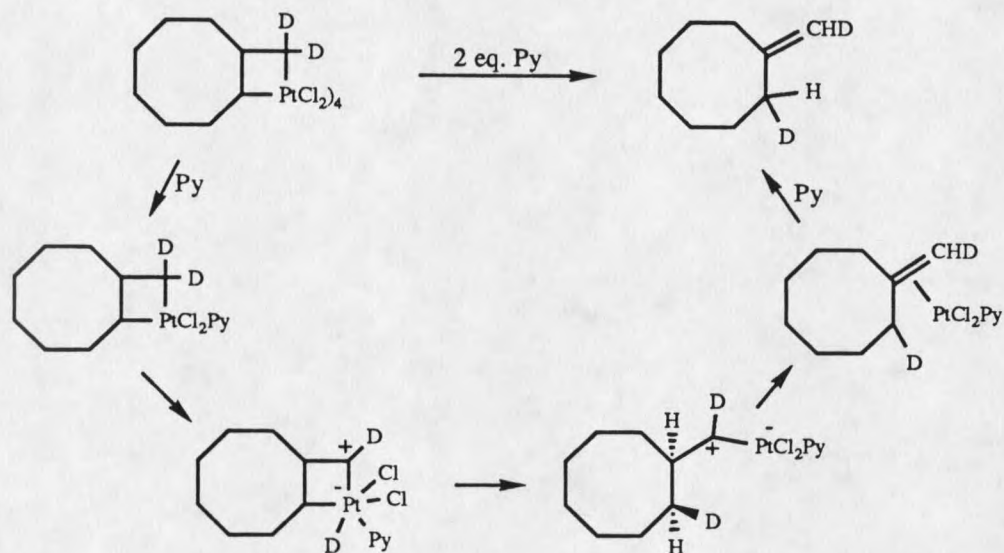
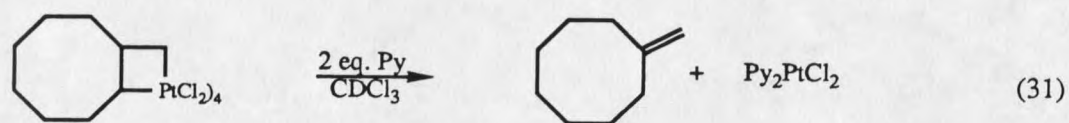
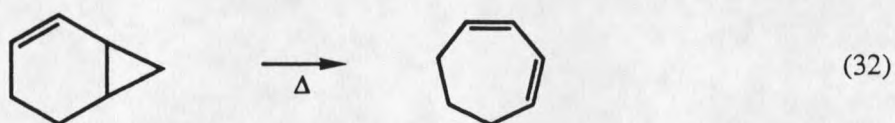


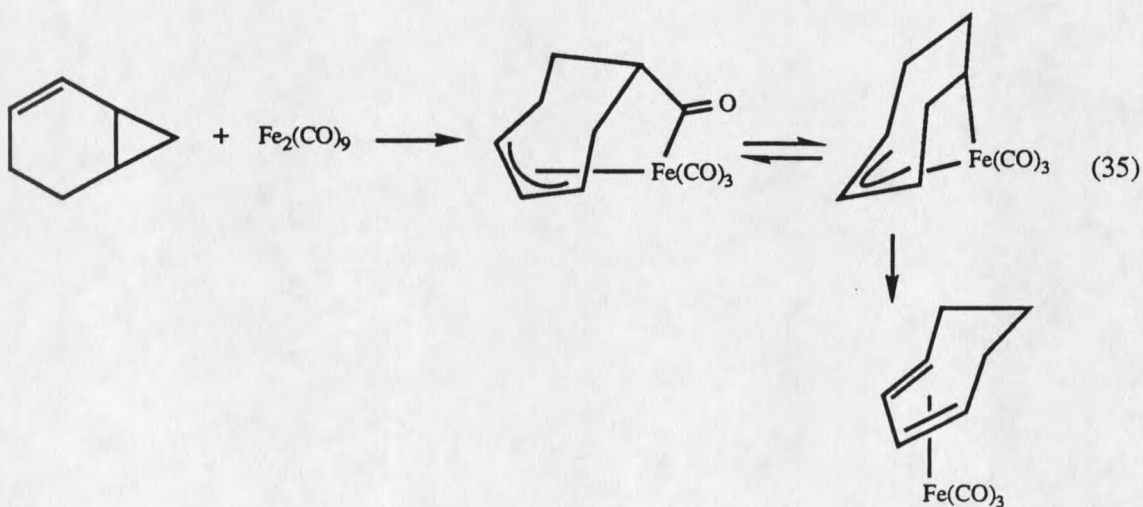
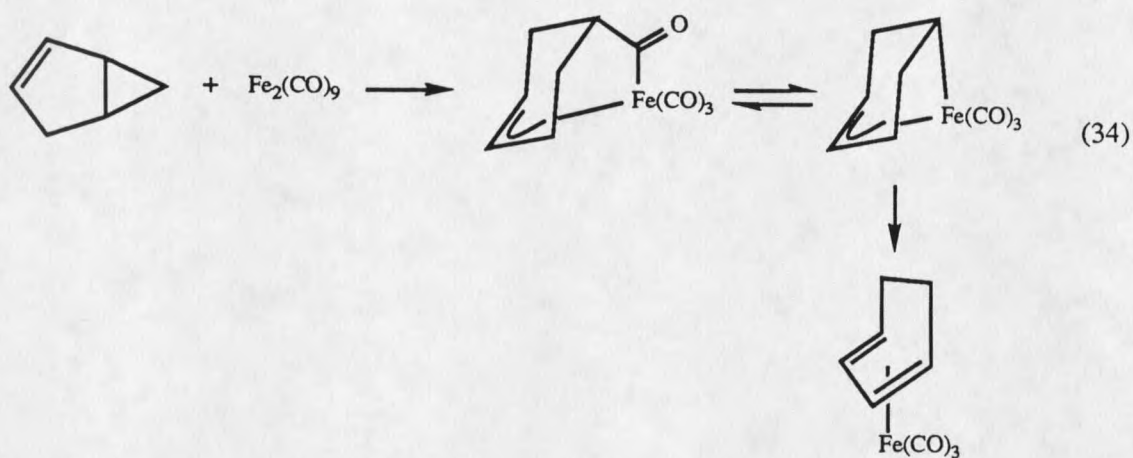
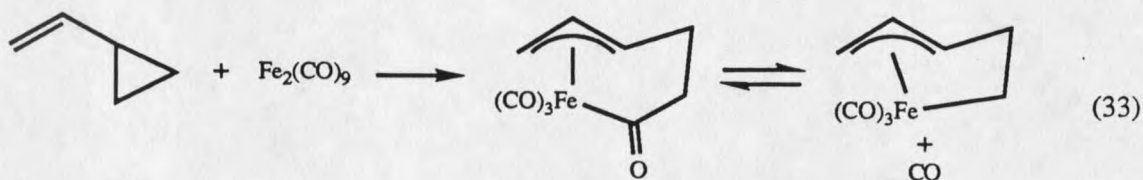
Figure 38. Mechanistic Pathway with Deuterium Results.

History of Vinyl Cyclopropanes in Organometallic Chemistry

Vinyl cyclopropanes are in effect a conjugated system, and as a result have been the object of much study from both thermal chemistry and transition metal chemistry. Gassman¹¹² studied the reaction of 2-norcarene with heat and found isomerization to 1,3-heptadiene, Equation 32.



Aumann¹¹³ studied the reaction of $\text{Fe}_2(\text{CO})_9$ with vinylcyclopropane, bicyclo[3.1.0]hex-2-ene and bicyclo[4.1.0]hept-2-ene, as shown in Equations 33-35. With vinylcyclopropane, a π -allylic complex is formed via cyclopropane insertion and rearrangement. Bicyclo systems go through π -allylic intermediates to form the stable η^4 -diene complexes.



Other transition metals that have been reacted with 2-norcarene include rhodium, titanium, chromium, nickel and palladium. Of these rhodium¹¹⁴ was found to catalyze the isomerization to 1-methyl-1,3-cyclohexadiene at 75°C. The rest of the metals ¹¹⁵ mentioned did not cause any change in the 2-norcarene and it was concluded that no insertion into the cyclopropane had occurred.

RESULTS AND DISCUSSION

Statement of Problem

Insertion of Pt(II) into cyclopropanes bearing electron withdrawing groups has proven to be next to impossible. This has blocked what could be a very rich area of organoplatinum chemistry. One goal of this research was to develop methodology to circumvent this problem.

As shown in the introduction, DMSO facilitates ring expansion of norbornyl platinacyclobutanes. Since its discovery, the mechanism of this reaction has been in question. Labelling studies on this reaction were hoped to resolve the pathway of the mechanism.

Since the discovery that platinum(II) inserts into cyclopropanes with cis alkyl groups, bicyclo[X.1.0] systems have also been shown to insert platinum. Although platinacyclobutanes were found to be formed the chemistry of these systems was dominated by olefin formation, often in complex mixtures. The main focus of this research has been to develop the bicyclic system such that a wider range of chemistry could be developed. At the same time a simplification of the products giving single isomers was a primary goal. The further development of this system would hopefully lead to intermediates or pathways to natural products.

Formation and Characterization of Platinacyclobutanes

Complexes from Cyclopropane 22

Reaction of cyclopropanes with electron withdrawing substituents decreases the reactivity of platinum insertion^{67,68}. Ekeland⁷⁰ showed the effects of platinum insertion into a cyclopropane with a strong electron withdrawing group present in the molecule, Figure 39. By changing from a ketone to a ketal, the relative ratio of products was altered. It should be noted however, that the initial insertion products may not be the ones eventually isolated. Nevertheless, even if insertion followed by isomerization might be taking place, the end result of using the ketal group is still evident.

In cases where strong electron withdrawing groups are directly attached to the cyclopropane, insertion is completely inhibited, Figure 40. Using conditions similar to those for Ekeland's norbornyl ketone, refluxing diethyl ether, no insertion products were obtained. Elevated temperature and longer reaction times did not accomplish any insertion and often left intractable mixtures.

Failure to achieve reactions of the type shown in Figure 40 limits the range of the reaction. To date, the chemistry that has been performed on platinacyclobutanes has not involved electron withdrawing groups positioned directly on the platinacyclic ring. Positioning an electron withdrawing substituent onto a platinacyclobutane could have a directing influence and thus alter the ensuing chemistry. It would seem then that a methodology enabling insertion into cyclopropanes would be extremely useful.

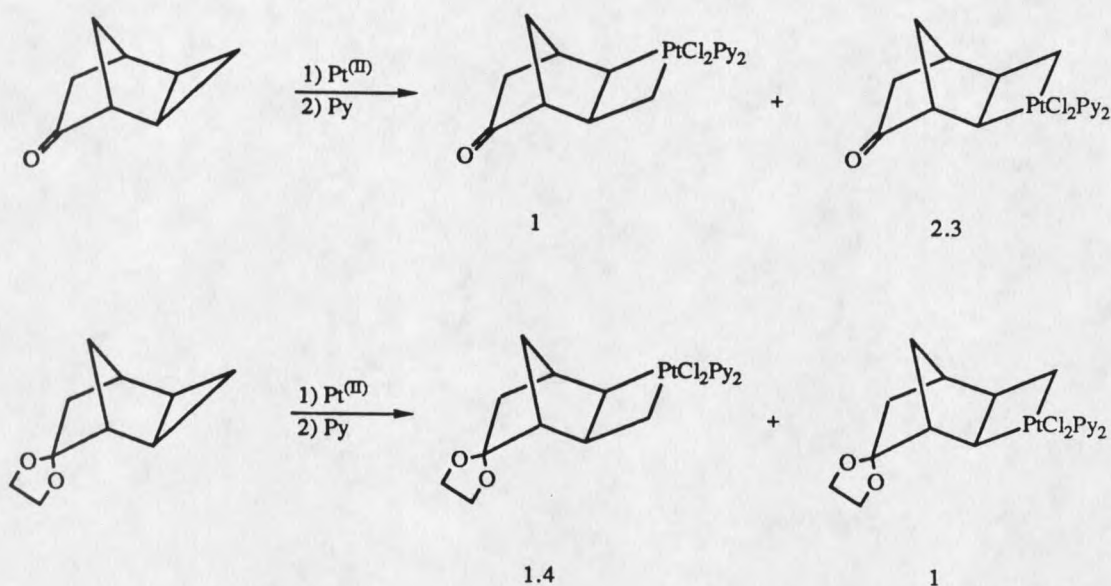


Figure 39. Effects of Ketal Protection on Platinum Insertion.

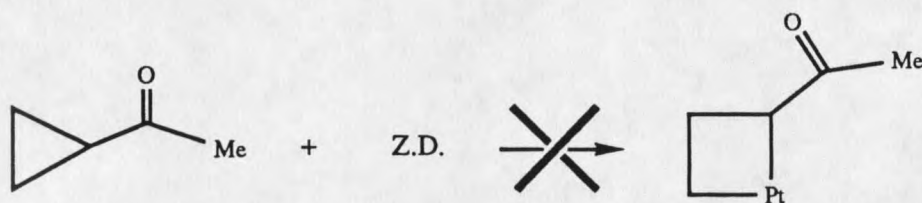


Figure 40. Reaction of Pt(II) with Cyclopropyl Methyl Ketone.

The approach used by Ekeland involved protection of the ketone followed by platinum insertion and then removal of the protecting group, Figure 41. This was felt to be a viable pathway for completion of the reaction in Figure 40. Protection of aldehydes and ketones are easily catalyzed by acids but not by bases, making this very useful when basic ligands are required with platinum ligation. Reaction of the cyclopropyl ketal with platinum(II) would then lead to platinacyclobutane products. Two possible isomers for the resulting platinacyclobutanes would be conceivable, symmetrical and unsymmetrical, as shown in Figure 42. Generally it is felt that platinum inserts into the most substituted bond. After the addition of ligands, it rearranges to some equilibrium mixture, thereby giving two

isomers. After generation of a platinacyclobutane, hydrolysis of the ketal would provide the platinacyclobutane with a strong electron withdrawing group directly on the ring. The overall pathway for the formation of the acetyl platinacyclobutane is diagrammed in Figure 42.

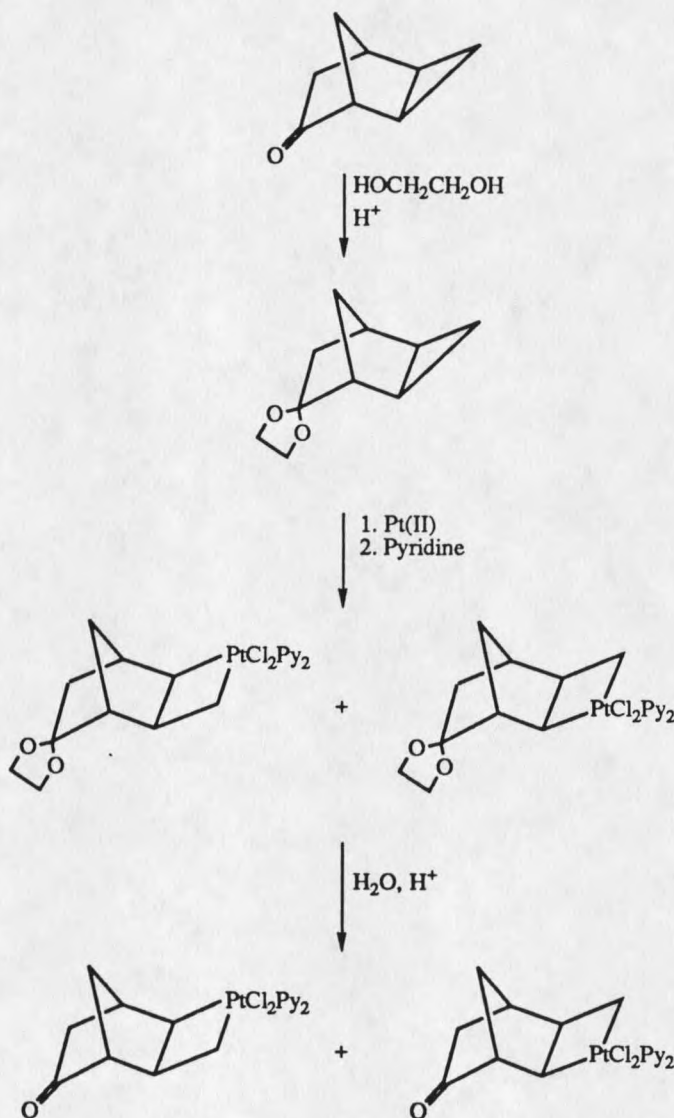


Figure 41. Synthetic Pathway to Norbornyl Platinum Complexes.

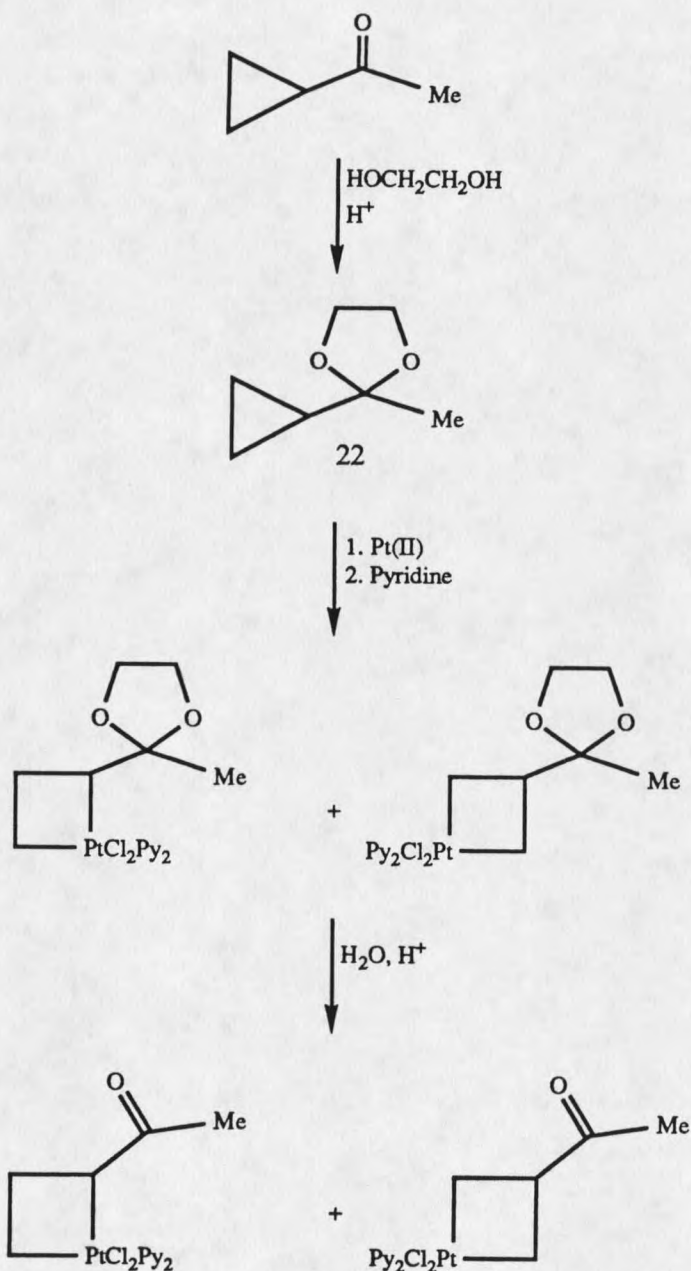
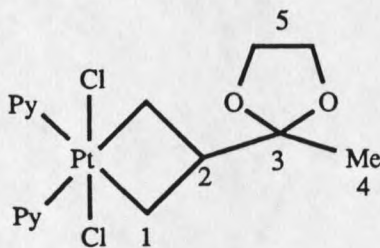


Figure 42. Synthetic Pathway to Platinacyclobutane Acetyl Complexes.

Formation of ketal **22** was accomplished by a procedure taken from Curran *et.al.*¹¹⁶ and gave an average yield of 70%. Reaction with Zeise's dimer in refluxing ether for 8 hours gave a yellow solid **23**, in quantitative yield, which upon isolation was stable in air for up to two hours. Addition of pyridine and CDCl_3 to this IPC (Initially Precipitated Complex)

gave a yellow solution which was characterized by NMR spectroscopy. The ^{13}C NMR spectrum showed only one isomer of a platinacyclobutane complex that was assigned as structure **24**. Figure 43 shows the proton decoupled ^{13}C NMR spectrum of **24**. As would be expected for a symmetrical platinacyclobutane, only five resonances appear, excluding pyridine resonances. Additional proof for a symmetrical complex are the resonances at -10.5 ppm, $^1J_{\text{Pt,C}} = 358$ Hz, which appears as a methylene in the ^1H -coupled ^{13}C spectrum and the peak at 51.5 ppm, $^2J_{\text{Pt,C}} = 97.8$ Hz, appearing as a methine. For an unsymmetrical complex to be viable, the ^{13}C NMR spectrum would have to contain upfield methylene and methine peaks with large $^1J_{\text{Pt,C}}$ coupling in the range of 335-460 Hz (see Table 7, pg 31). Furthermore, the resonance at 51.5 ppm with $^2J_{\text{Pt,C}}$ coupling would have to be a methylene instead of a methine for the unsymmetrical complex to be reasonable. Further evidence for the symmetrical complex was gained from the proton NMR spectrum which is listed with the ^{13}C assignments in Table 10.



24

Two possibilities exist that can explain insertion into the ketal but not into the ketone. First coordination of the platinum to the carbonyl oxygen is prevented upon protection. Second, greater electron density may exist at the cyclopropane when the carbonyl is protected, thus enhancing the nucleophilic attack of the cyclopropane at the platinum. One or both of these possibilities could be in effect.

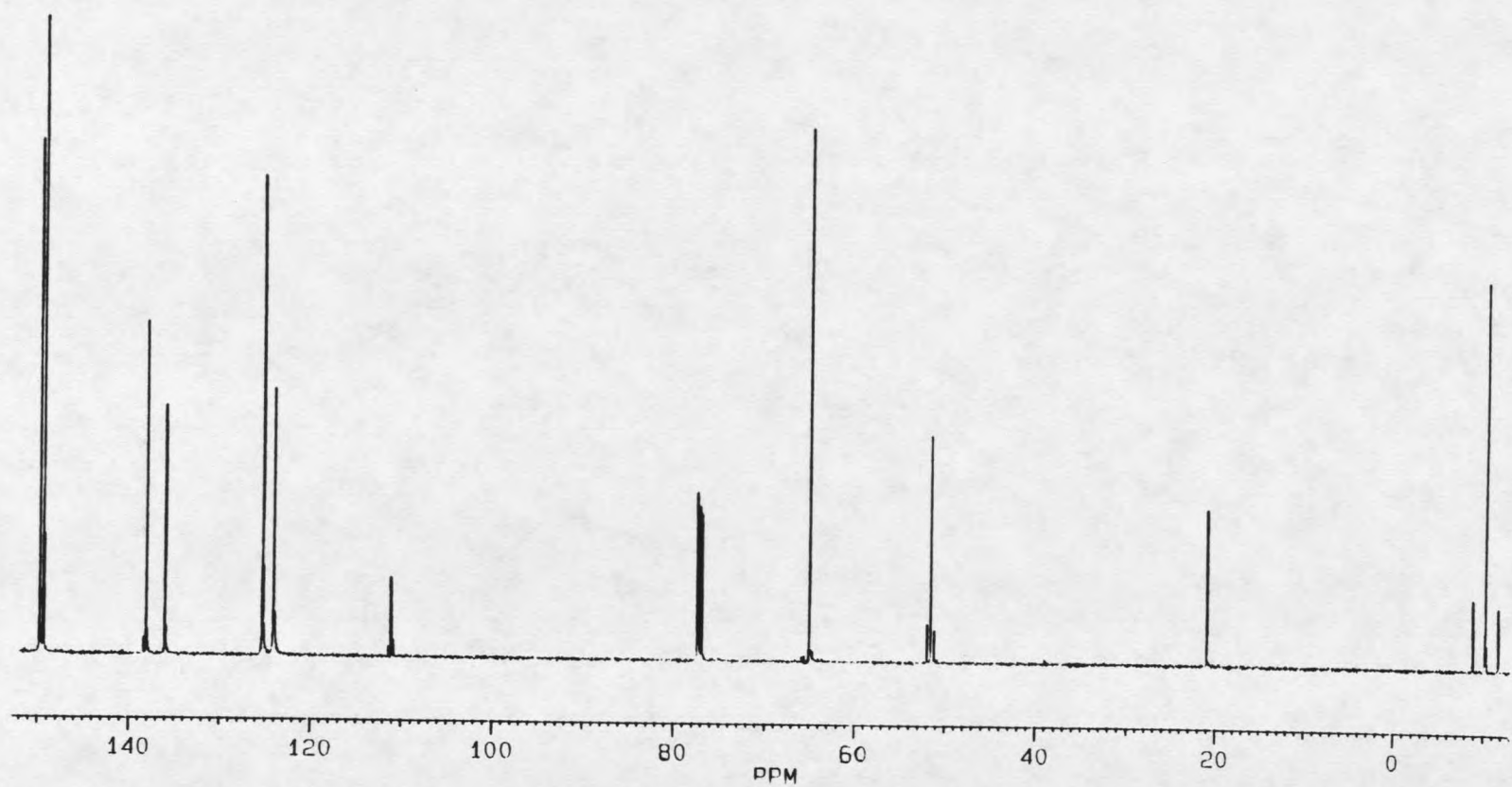


Figure 43. ^{13}C NMR Spectrum of 24.

Table 10. NMR Data for Compound 24.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{H,H}}$ **	$J_{\text{Pt,H}}$ **
1	-12.5	358.1	2.41 (dd) 2.74 (dd)	9.5,4.4 9.5,4.4	84.9 79.8
2	49.7	97.8	3.14 (t)	9.5	37.3
3	109.0	58.9			
4	19.0	0.0	1.23 (s)		
5	62.9	0.0	3.91 (d)	3.2	

 $^{195}\text{Pt}^{***}$ - 3326 ppm* Relative to CDCl_3

** Coupling in Hertz

*** Relative to 1M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25° C.

() Multiplicity

Although the platinacyclobutane monomer was isolated as the symmetrical isomer, the IPC does not have to be symmetrical. The isolated IPC could well have been the unsymmetrical complex which rearranged upon dissolution with pyridine. With most of the past work in the literature showing insertion into the most substituted bond and without contrary experimental data, the most logical way to picture the IPC is as an unsymmetrical complex. On page 40, it was stated that the Puddephatt rearrangement requires loss of a ligand to open a coordination site. Use of a chelating ligand effectively stops ligand loss and hence stops the rearrangement.

In hopes of obtaining more insight into the structure of **23**, bipyridine was reacted with the IPC and the resulting monomer was characterized by NMR spectroscopy. Both the proton-decoupled and proton-coupled ^{13}C spectra of this product are shown in Figure 44. Upon comparison of the pyridine and bipyridine spectra, the structure of the bipyridine complex was also assigned to the symmetrical platinacyclobutane **25**. Table 11 lists the NMR data for complex **25** with the assignments.

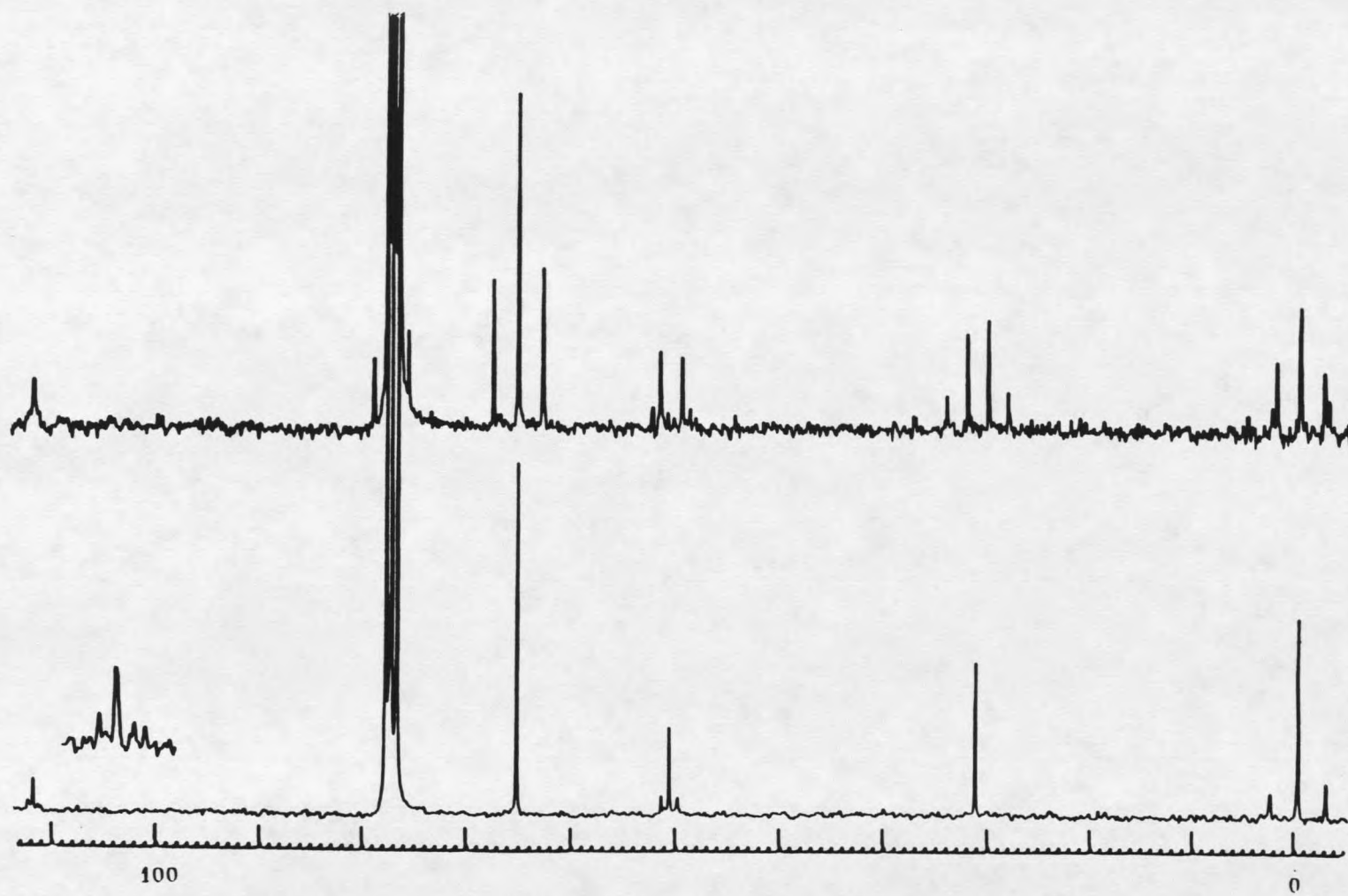
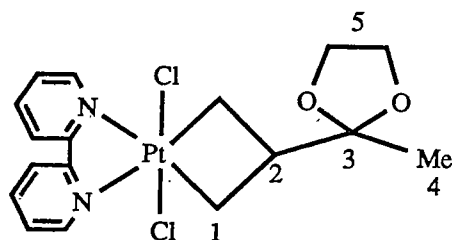


Figure 44. Gated (top) and BB ^{13}C NMR Spectra of 25.



25

Table 11. NMR Data for Compound 25.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{H,H}}$ **	$J_{\text{Pt,H}}$ **
1	-10.6	349.2	2.67 (dd) 2.50 (dd)	9.4,4.3 9.2,4.3	80.1 72.0
2	50.5	95.0	3.24 (t)	9.5	36.0
3	111.6	57.0			
4	20.9	0.0	1.32 (s)		
5	65.0	0.0	4.00 (d)	3.0	

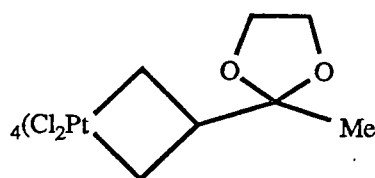
 $^{195}\text{Pt}^{***}$ - 2910 ppm* Relative to CDCl_3

** Coupling in Hertz

*** Relative to $1\text{M Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25°C .

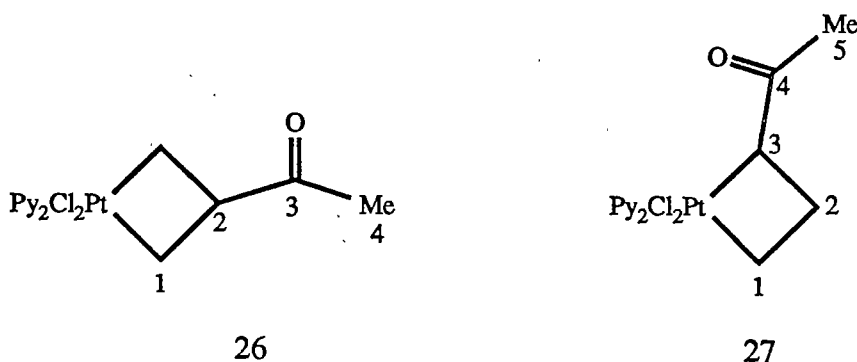
() Multiplicity

With the assignment of complex 25 as a symmetrical structure and any rearrangement prevented, it is logical to conclude that the IPC 23 (shown below) is a symmetrical complex as well. This is contrary to prevailing thoughts but electronic or steric effects could be influencing the complexes to prefer a symmetrical orientation. Nevertheless, although 23 is symmetrical, insertion could still be into the most substituted bond with isomerization taking place before precipitation as the IPC.



23

The next step in the synthesis shown in Figure 42 was hydrolysis of the ketal, to generate the ketone functionality. To accomplish this, **24** was treated in a manner analogous to that employed by Ekeland. Shaking a chloroform mixture with a dilute aqueous solution of p-toluenesulfonic acid solution resulted in complete recovery of **24**. If, however, a concentrated p-toluenesulfonic acid solution was used, complete hydrolysis was observed. ^{13}C NMR spectroscopy, Figure 45, reveals two carbonyl resonances (211 and 209) and three resonances at 3.3, -10.4 and -12.4 which exhibit platinum-carbon coupling of 353.6, 328.5 and 362.6 Hz, respectively. These coupling constants are in the range of a platina(IV)cyclobutane. This suggests two isomers of a platinacyclobutane and are assigned as **26** and **27**. Further proof is the appearance of carbonyl bands at 1700.9 and 1683.3 cm^{-1} in the IR spectrum. Integration of the methyl ^1H resonances demonstrated that **26** was the major isomer in a 1.5:1 ratio. Table 12 and 13 contain the NMR data with the assignments. Apparently electronic effects are coming into play causing some isomerization to form **27**.



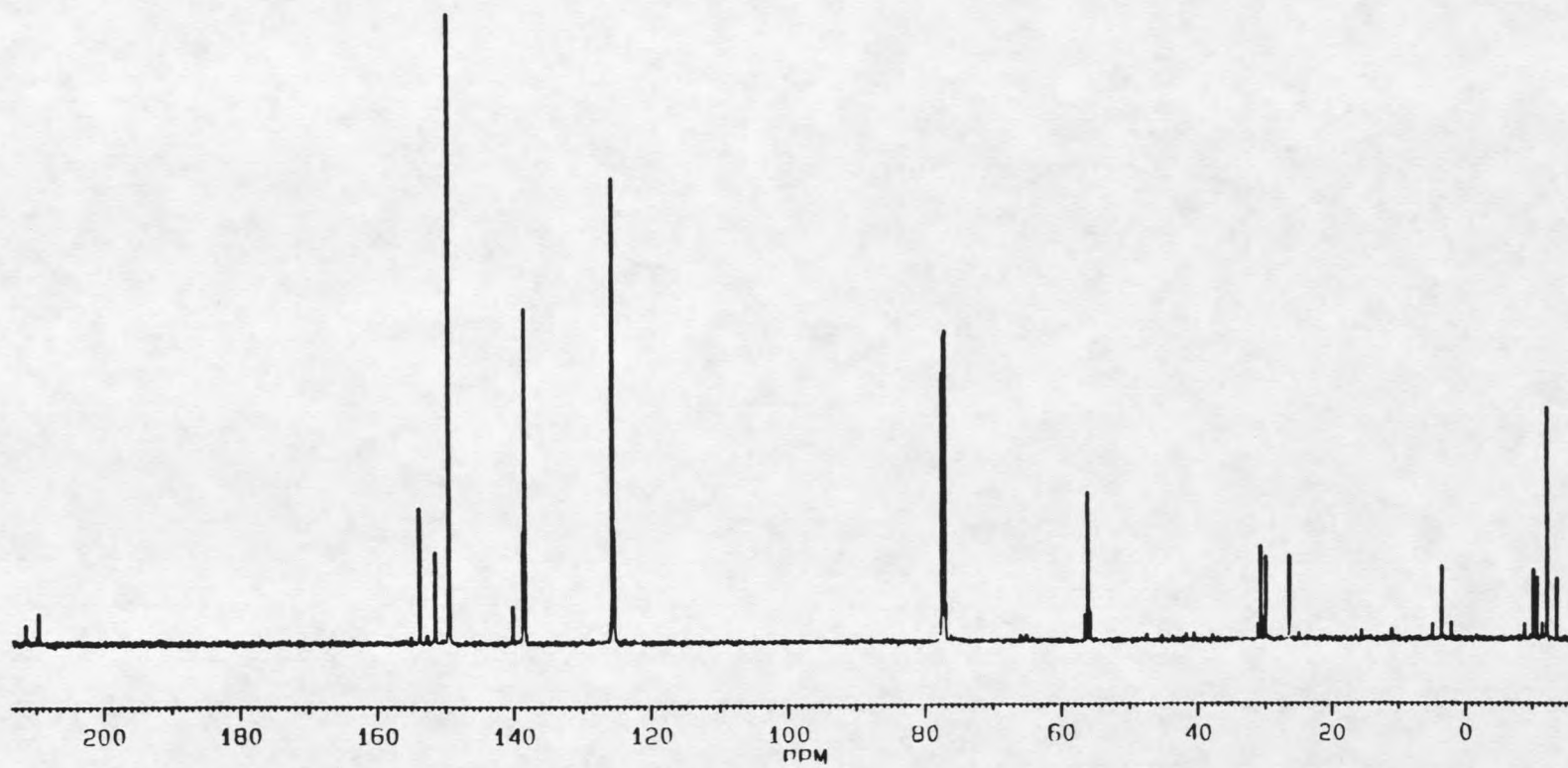


Figure 45. ^{13}C NMR Spectrum of 26 and 27.

Table 12. NMR Data for Complex 26.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{H,H}}$ **	$J_{\text{Pt,H}}$ **
1	-12.5	364.3	2.93 (dd) 2.64 (dd)	9.3,4.8 9.3,4.8	80.5 83.8
2	55.9	103.0	3.76 (t)	9.3	
3	209.4	54.5			
4	26.1		2.1 (s)		

* Relative to CDCl_3

** Coupling in Hertz

() Multiplicity

Table 13. NMR Data for Complex 27.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{H,H}}$ **	$J_{\text{Pt,H}}$ **
1	-10.4	328.0	2.90 (m) 2.61 (m)		72.0 81.6
2	30.5	106.8	3.24 (m) 2.52 (m)		
3	3.2	351.0	4.50 (dd)	6.2,6.2	108.1
4	211.3	48.1			
5	29.7	0	1.55 (s)		

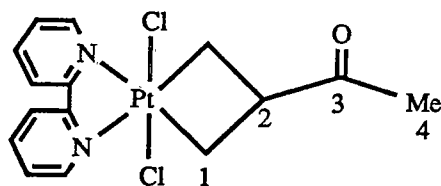
 $^{195}\text{Pt}^{***}$ - 3441 (26), 3307 (27) ppm* Relative to CDCl_3

** Coupling in Hertz

*** Relative to 1M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25°C .

() Multiplicity

Similarly 25 could be hydrolyzed using acidic conditions. Because a chelating ligand was present on the platinum, the Puddephatt rearrangement was prevented. This resulted in the formation of only one isomer of the ketone, 28. NMR data for 28 are listed below in Table 14 and the ^{13}C spectrum is shown in Figure 46. Only one resonance with large 1J platinum-carbon coupling is observed at -12.4 ppm. In addition, only one absorption frequency appears in the IR spectrum at 1700 cm^{-1} for the carbonyl band.



28

Table 14. NMR Data for Complex 28*.

#	^{13}C ppm**	$J_{\text{Pt,C}}$ ***	^1H ppm**	$J_{\text{H,H}}$ **	$J_{\text{Pt,H}}$ **
1	-12.4	356.7	2.87 (dd)	8.6,4.3	80.0
			2.69 (dd)	8.6,4.3	84.6
2	55.0	99.2	3.84 (t)	8.6	
3	210.3	51.5			
4	26.1	0	2.17 (s)		

* Pt NMR data in Experimental

** Relative to CDCl_3

*** Coupling in Hertz

() Multiplicity

The strategy described here shows the ease with which platinum can be inserted into cyclopropanes bearing strong electron withdrawing groups. A method has not been developed for cyclopropanes with groups such as esters, however, the present method should work fairly well with ketones and aldehydes. In the case of the simple cyclopropanes, rearrangement observed with pyridine as a ligand was prevented when bipyridine was used as a ligand. The disadvantage of using bipyridine is that the chelating effect also prevented any additional chemical reactions. Chemistry of platinacyclobutanes usually requires loss of a ligand and bipyridine prevents this. Although the final ketones **26** and **27** were formed as a mixture of isomers, they do show quite well that platinum insertion is not always obstructed with electron withdrawing groups present. In the future, cyclopropanes impervious to isomerization should be employed, thus avoiding the isomerization observed with **26** and **27**.

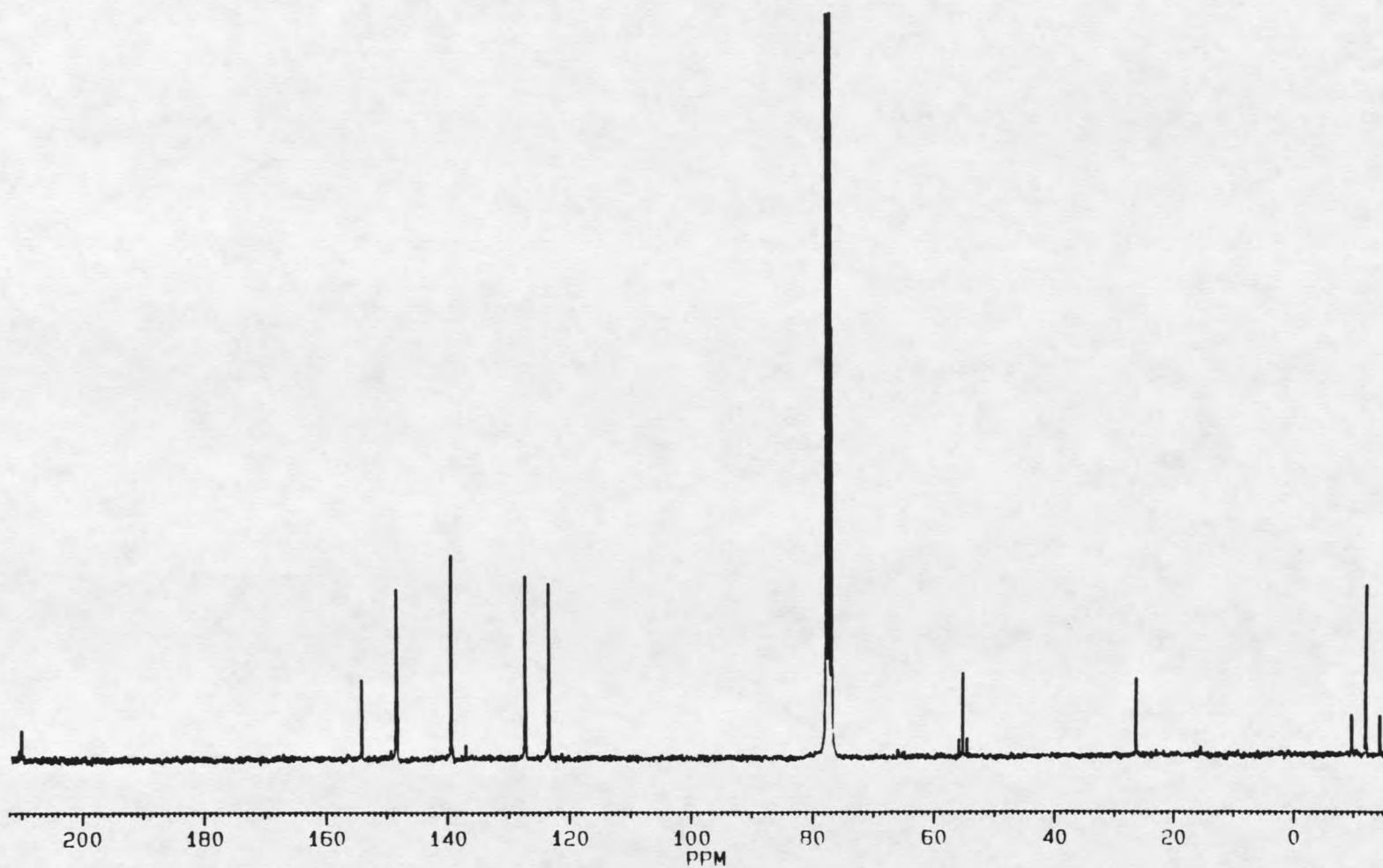


Figure 46. ^{13}C NMR Spectrum of 26.

On the Mechanism of the Norbornyl Ring Expansion Reaction

Norbornyl IPC's, such as those shown in Figure 47, undergo ring homologation on treatment with DMSO¹⁰⁷. These examples represent a significant methodology for ring homologation with very good yields. Understanding the mechanism of the homologation can provide an opportunity to facilitate the transformation. Thus, in an effort to ascertain the mechanism, labelling of the starting cyclopropanes was carried out.

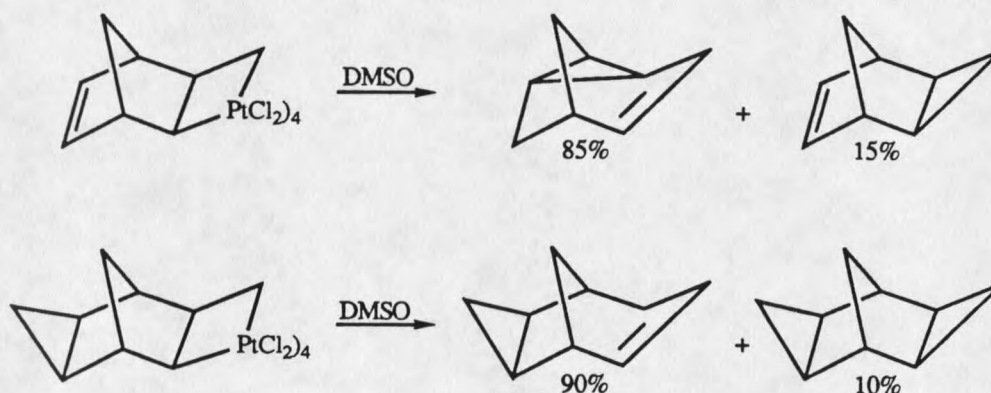


Figure 47. Ring Homologation of Norbornyl IPC's.

Incorporation of deuterium and ^{13}C at the cyclopropyl methylene moiety could eventually give the best insight into the mechanism, Figure 48. Deuterium-labelled sites can be readily observed by ^2H NMR spectroscopy. Similarly, ^{13}C labelling at a carbon increases the natural abundance of ^{13}C from 1.1% to 100% which is then readily observed by ^{13}C NMR spectroscopy.

Compounds **29** and **30** were prepared by cyclopropanation of norbornadiene with deuterium labelled diiodomethane (99.4%- d_2) using Simmons-Smith conditions. Separation of **29** from **30** by gas chromatography afforded the pure labelled substrates. Compounds **31**

and **32** were derived by cyclopropanation of norbornadiene with ^{13}C labelled diazomethane (99% ^{13}C) and a Pd(II) catalyst. Compound **31** could be collected via GC in pure form. However, **32** had to be used as a mixture with **31**.

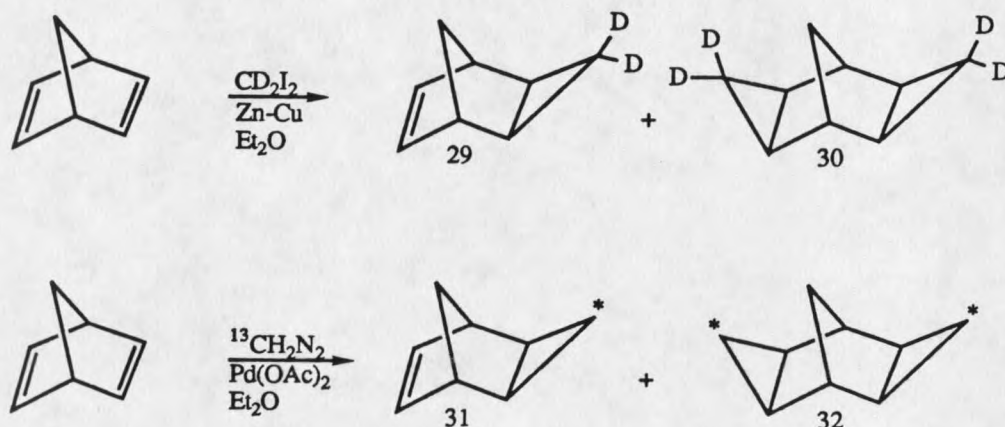


Figure 48. Synthesis of **29**, **30**, **31** and **32**; 99% labelling at each site.

Reaction of **29-32** with Zeise's dimer resulted in formation of IPC's **33**, **34**, **35** and **36**, Figure 49. The unlabelled IPC's had been characterized by Waddington using CP/MAS⁶³. He was able to show that the platinacyclobutane structure was intact in the solid tetramer. IPC's **33-36** were subsequently reacted with DMSO. Results of the transformations are shown in Figure 49. ^1H , ^2H , and ^{13}C NMR and GCMS were used to ascertain the labelled positions. As can be seen, the results of **34** to **38** and **36** to **40** are relatively straight forward. Figure 50 is the ^2H NMR spectrum of **38**. A resonance at 5.1 ppm demonstrates the presence of a deuterium on an olefin, as well as another deuterium in an upfield position at 2.0 ppm which is due to the endo deuterium in **38**. Resonances at -0.1 to 0.4 ppm are due to deuterium on the cyclopropane in **38** and **30**, with the two major peaks resulting from **38**. Resonances at 0.2 and 0.4 ppm are a result of 10% reductive elimination to give starting cyclopropane **30**.

^{13}C NMR spectroscopy of **40** also exhibits obvious labelled positions by the increased resonances for the olefin and cyclopropane methylene. Comparisons of unlabelled NMR data to labelled data are listed in Appendix A.

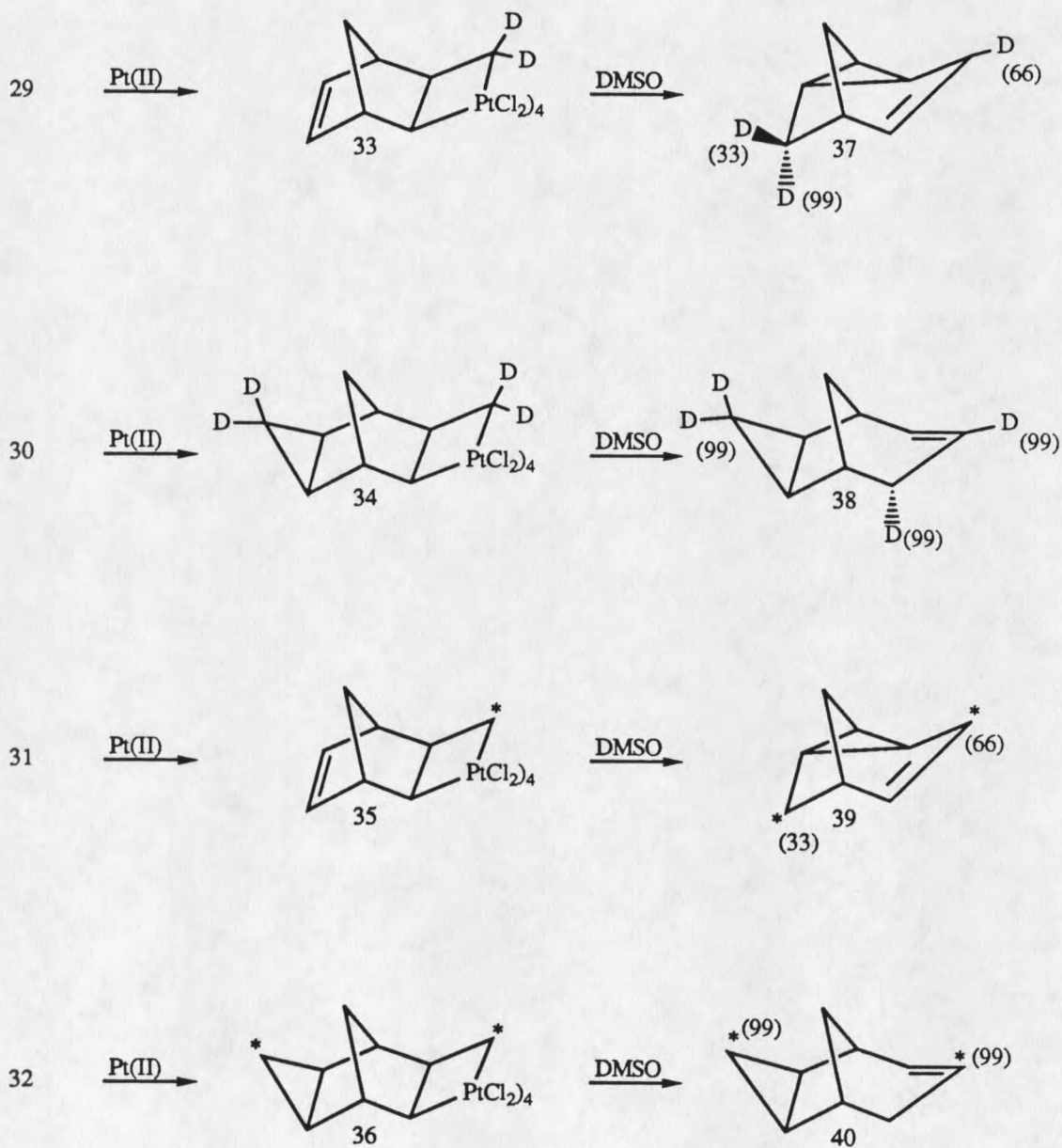


Figure 49. Formation and Reaction of IPC's 33, 34, 35 and 36.

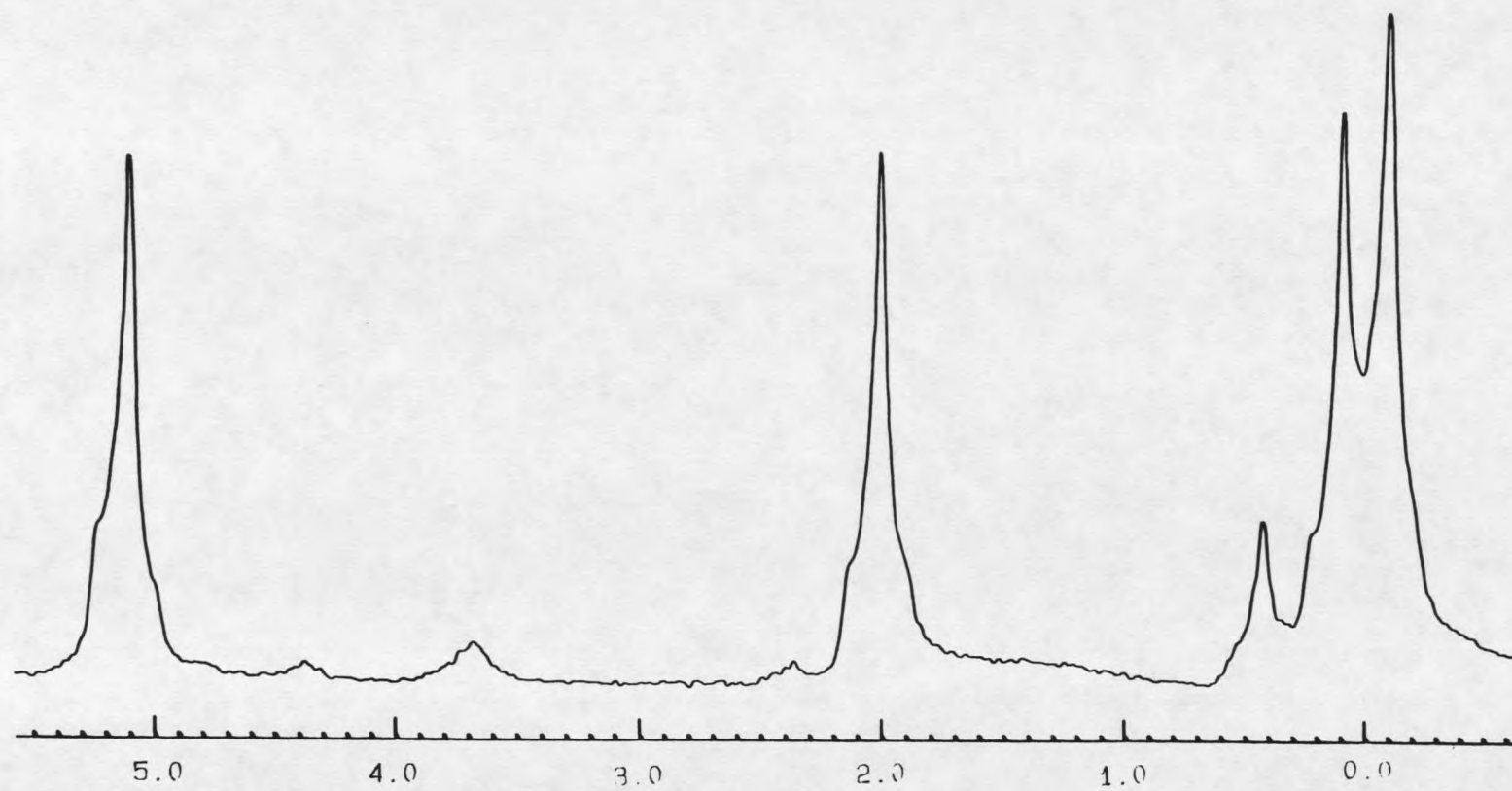


Figure 50. ^2H NMR Spectrum of 38.

Figure 51 depicts the proposed mechanism for the reaction of **30** and **32**. Reaction of the IPC with DMSO induces isomerization, via a Puddephatt rearrangement, to give **41**. Subsequent abstraction of a deuterium cis to the platinum yields π -allyl **42** which collapses to compound **43**. This final step may be viewed in more detail by invoking **44** as an intermediate. Prior to deuterium transfer to the endo position, a σ platinum-carbon bond is formed. Reductive-elimination will then form **43**.

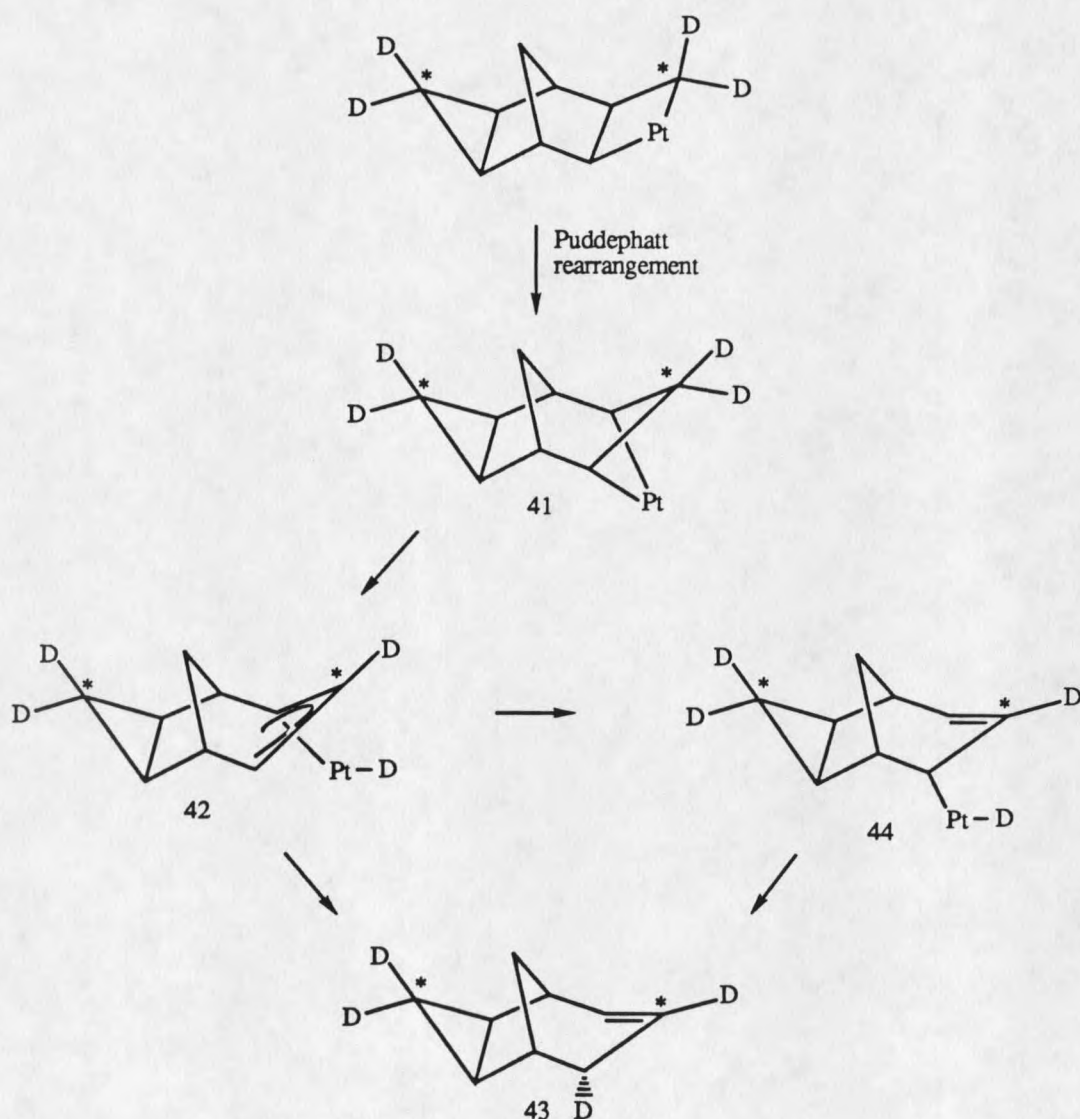


Figure 51. Proposed Mechanism for Ring Expansion of **30** and **32**.

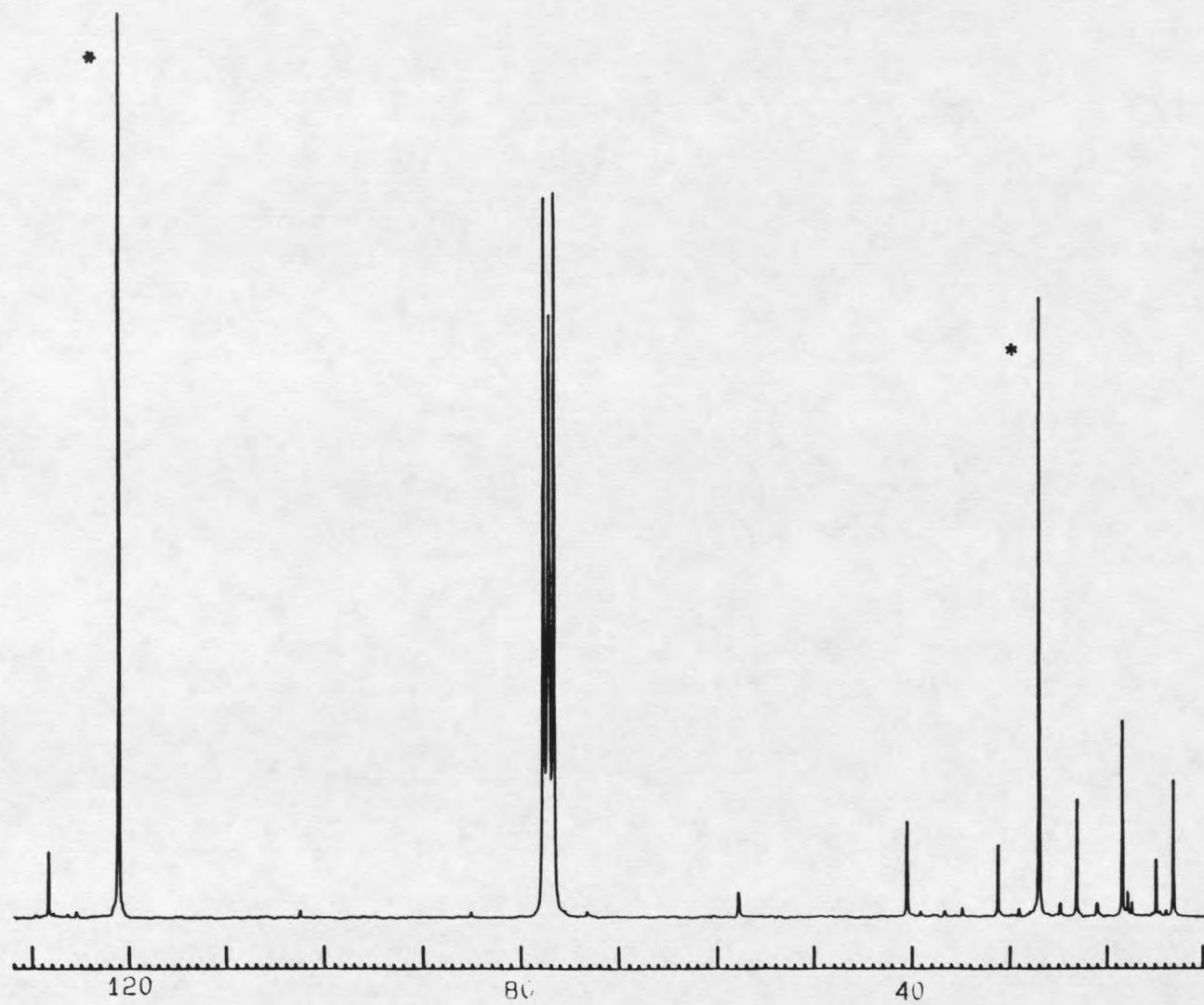


Figure 52. ^{13}C NMR Spectrum of 39.

Explanations for the ring expansions of **29** and **31** to produce **37** and **39** are not as clear cut. From the ^{13}C labelling results shown in Figure 52, it is evident that the previously outlined pathway (Figure 51) does not adequately rationalize the result. Had Figure 51 been followed only one ^{13}C labelled carbon would have been observed. As can be seen, two carbons are labelled. The resonance at 121 ppm has increased dramatically as expected due to ^{13}C labelling. This resonance can be compared to the resonance at 128 ppm which is the unlabelled olefin. In the upfield region at 27 ppm, an unanticipated second ^{13}C labelled carbon is evident, although not as abundant. A 2:1 ratio of labelled olefin to labelled methylene was deduced by integration and chemical shift interpretation of the ^{13}C spectrum. This splitting of the ^{13}C labelling provides evidence for a different or a dual pathway in the formation of **39**. Further evidence was gained by labelling with deuterium, the results of which were previously shown in Figure 49 for the formation of **37**. Again labelling occurred in several sites, which cannot be accounted for by the mechanism shown in Figure 51 or by one mechanism. Therefore, a mechanism involving a dual pathway must be invoked.

Deuterium labelling in both the olefinic and the endo methylene moieties can be explained by pathway A in Figure 53. Once again, a Puddephatt rearrangement is suggested in this case generating **45**. Subsequent olefin migration, forming a new platinacyclobutane, produces **46**. Deuterium abstraction, followed by olefin formation, leads to **47** with the platinum in the endo position. Reductive elimination yields **48** where deuterium labelling is at the olefinic moiety and in the endo position of the appropriate methylene moiety.

Pathway A adequately explains some of the deuterium labelling. However, Path A does not explain the observance of an exo deuterium or ^{13}C at the methylene carbon (Figure 49: **37** and **39**). A mechanism to account for these results is shown as pathway B in Figure 53. Instead of initial olefin migration, the bridge migrates yielding **49**. Formation of platinacyclobutane **50** now produces a new olefin which reductively eliminates to give **51**,

in which no labelling occurs at the olefinic position. Upon redrawing **51**, one can see that the exo position of the methylene unit is now labelled with deuterium, as well as with ^{13}C and is in concert with the observed results. Path A would be responsible for 66% of the product and B for 33%.

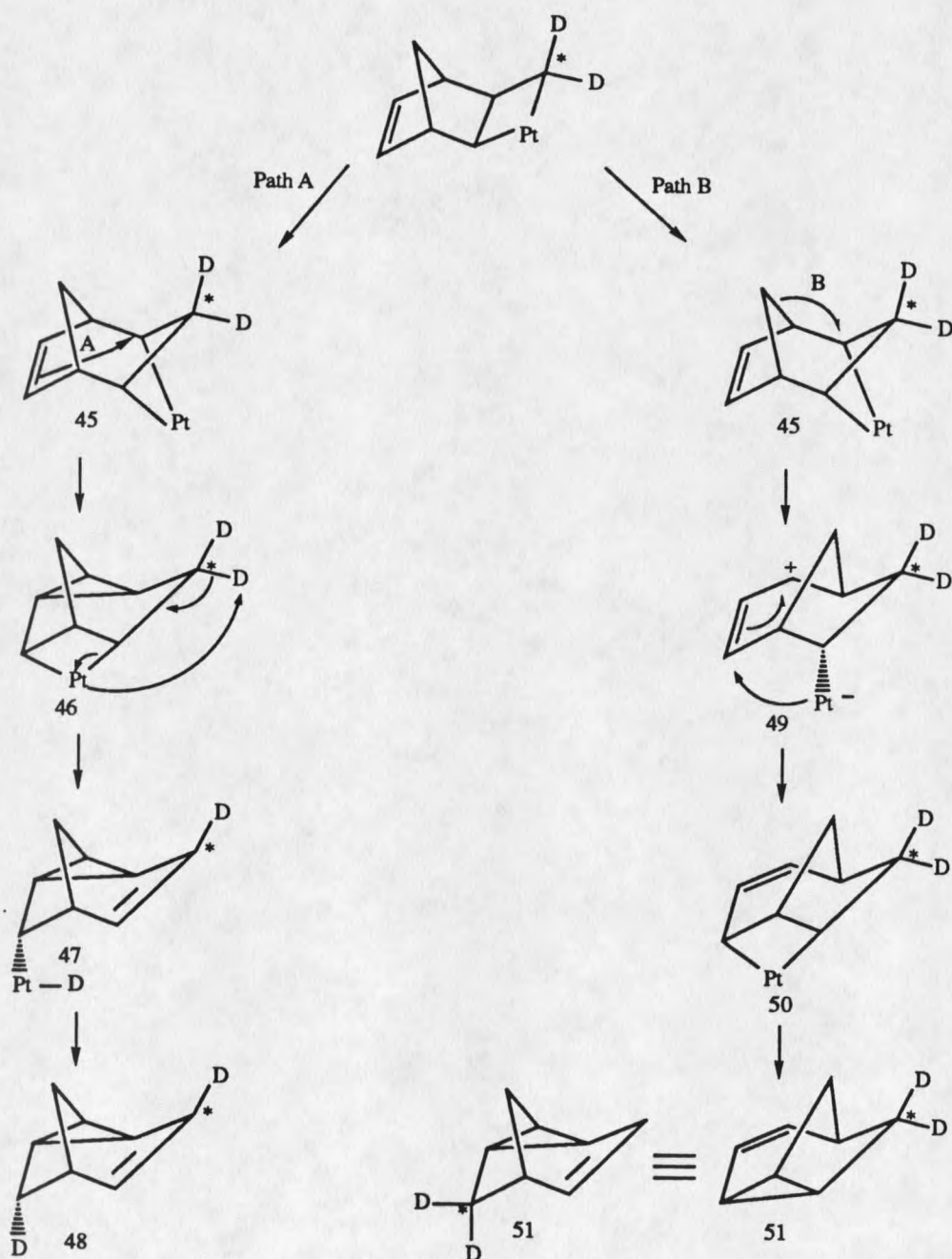


Figure 53. Proposed Mechanism for Formation of **37** and **39**.

An alternative pathway for the formation of the minor labelled products **51d₂** or **51¹³C** can also be proposed, Figure 54¹⁷. Like Path A in Figure 53, this pathway uses structure **46** as a common intermediate. Platinacyclobutane **46** can undergo a degenerate Puddephatt rearrangement generating **52**. Once again the platinum can abstract a β -hydrogen forming **53**. Reductive elimination will then lead to the ring expansion product that is the equivalent of **51**. Upon closer scrutiny of the transformation of **46** to **52** one can see two different bonds which might be involved in the Puddephatt rearrangement, i and ii. Reaction of bond i will give rise to product **51**. Isomerization into bond ii would be more sterically hindered than that of bond i. Figure 55 diagrams the transformation of **46** to **51** in more detail. In this representation, complex **46** has been rotated to display the ease of which isomerization can take place. As can be seen, isomerization between **46** and **52** is very accessible, while isomerization into bond ii is evidently sterically hindered. To get a better understanding for the isomerization, structure **54** is illustrated displaying only the organic portion of **46**. This clearly shows the equivalency between **46** and **52**.

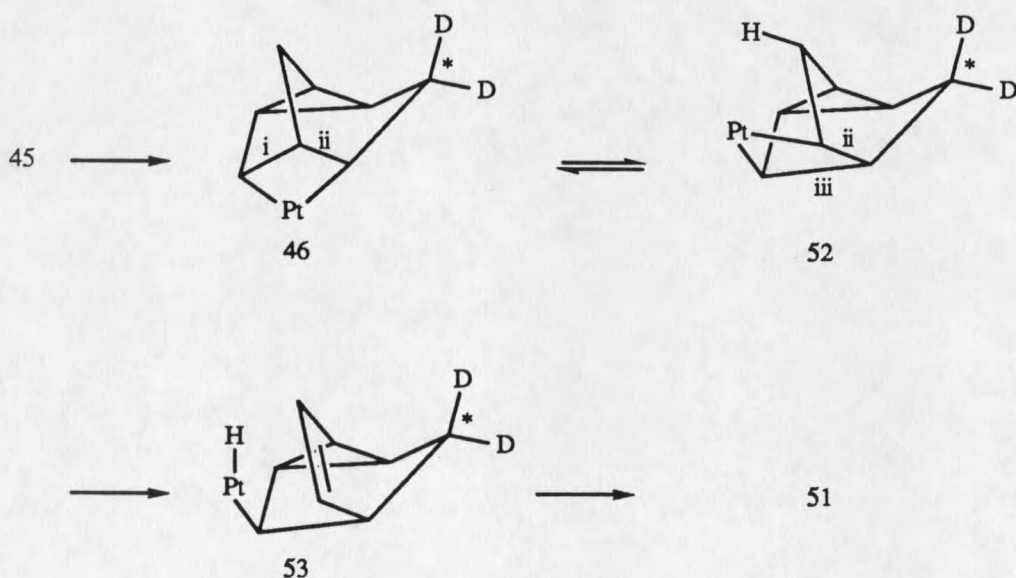


Figure 54. Alternative Pathway for Formation of **51**, Path C.

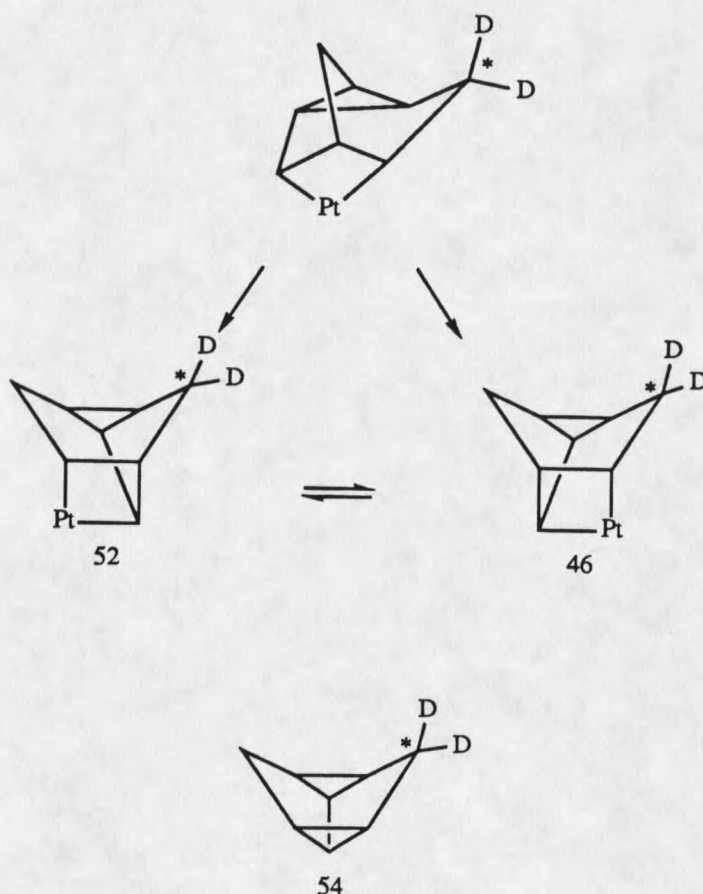


Figure 55. Isomerization of **46** to **52**.

Although the labelling experiments have provided significant insight into the mechanism, they cannot distinguish between Path B and the alternative in Figure 54, path C. A number of different labelling studies can provide a distinction. However, synthesizing cyclopropanes with different labelling requires multi-step procedures. An alternative idea was to block the pathway of one of the proposed mechanisms, path C or path B. Two possibilities exist: one is to exchange or replace the bridge proton in question with an R group, the other is to obstruct bridge migration which would inhibit path B. Obviously the most convenient of the two is replacement of the proton.

Figures 56 and 57 diagram the use of a phenyl group at the bridge carbon and its expected effects on the pathways. As can be seen in Figure 56, the presence of the phenyl substituent does not stop either pathway. However, the presence of the phenyl does result in the formation of two isomers, **57** and **59**. Compound **59** is a result of bridge migration in **55** to form **58** followed by reductive elimination. Compound **57** is formed via a mechanism analogous to path A to yield **56** and on to **57**. However, the phenyl group has a marked effect on the alternative pathway C, Figure 57. Complex **55** can again lead to **57** via path A giving rise to one isomer. At this point the path C chemistry is altered. Performing the Puddephatt rearrangement on **56** still leads to **60**; however, in this system a β -hydrogen is no longer present. Complex **60** has no recourse but to revert back to **56** and eventually lead to **57**, resulting in only one isomer.

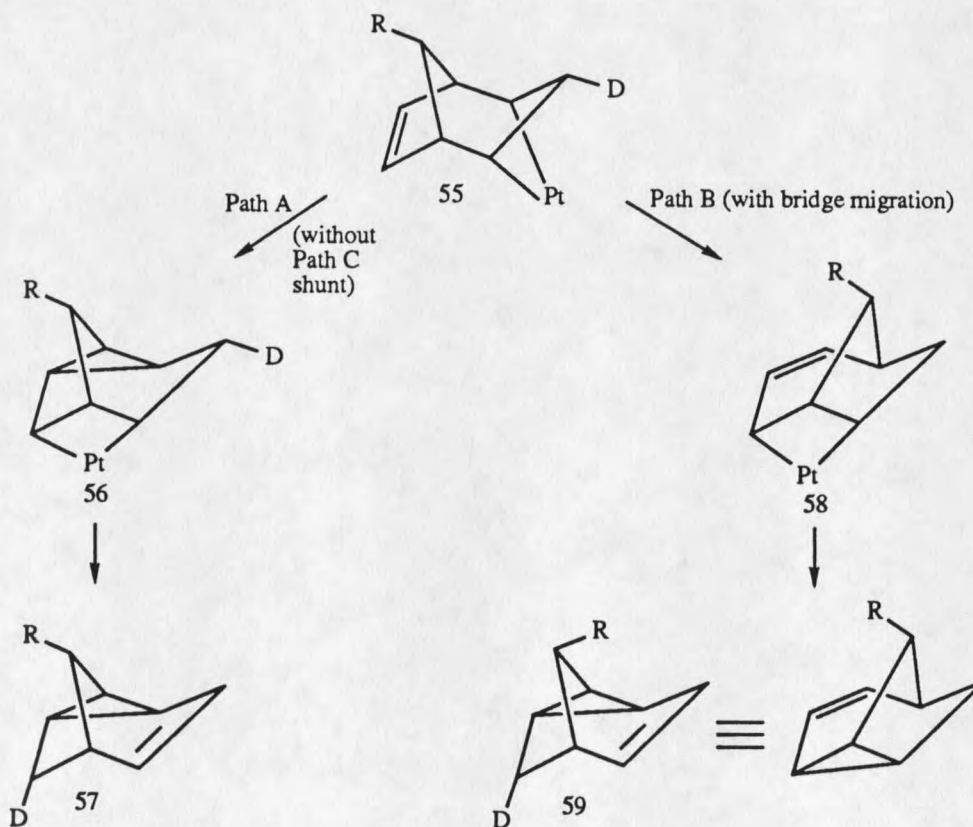


Figure 56. Postulated Products from Paths A and B.

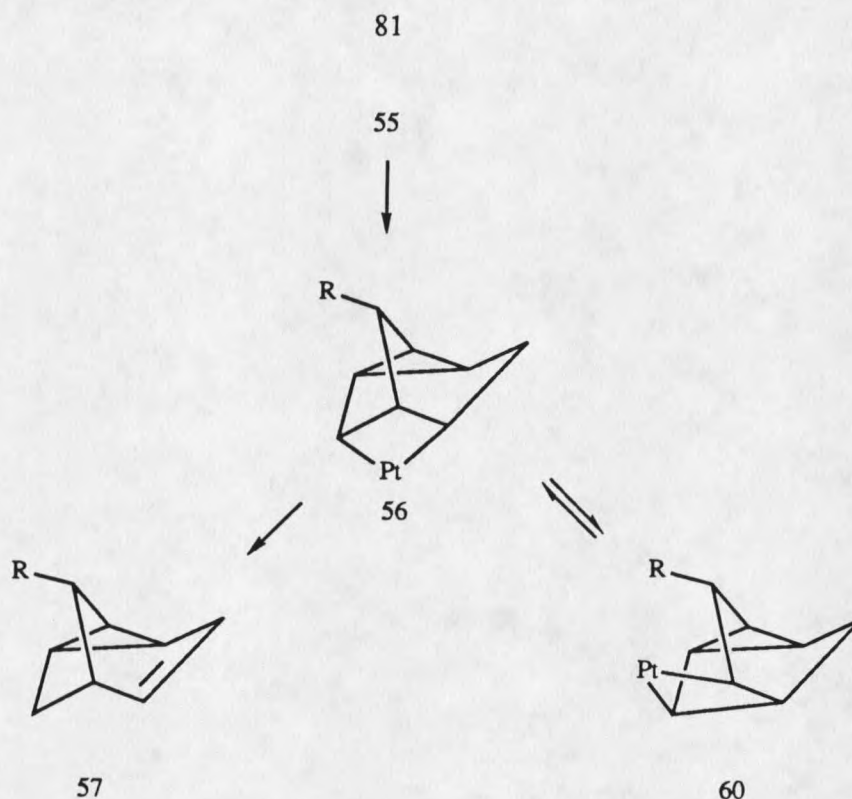
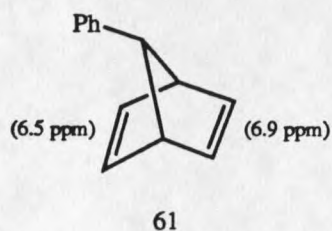


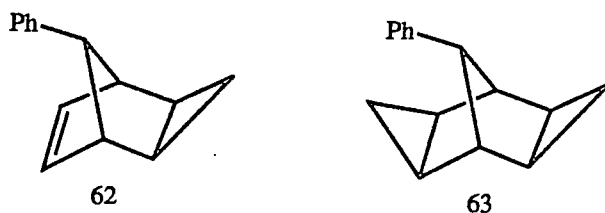
Figure 57. Expected Product from Alternate Mechanism.

The criterion for paths A and C with the phenyl substituted substrate then is that only one isomer is formed, Figure 57. The process outlined in Figure 56, on the other hand, would give two isomers which can be observed by spectroscopic means. It is anticipated that the phenyl group over the olefin moiety in **59** would shield the olefin protons¹¹⁸, resulting in an observable upfield shift of the resonances compared to **57**. A good model for this is 7-phenylnorbornadiene, **61**. As can be seen, the olefinic protons are separated by 0.4 ppm, with those on the phenyl side more highly shielded. This gives evidence that the olefins in **57** and **59** will also show different resonances.

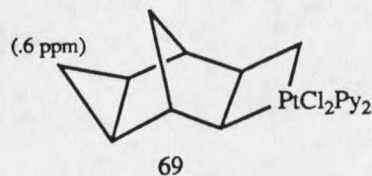
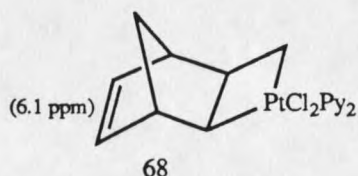
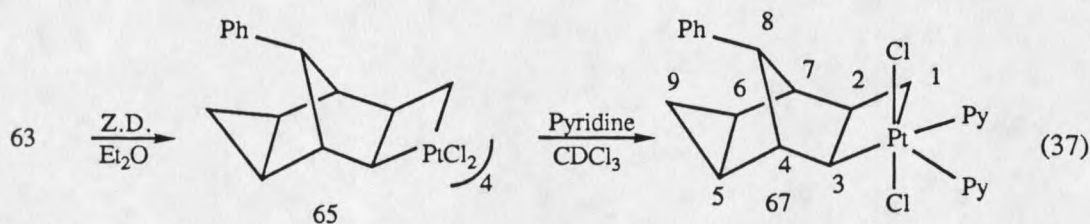
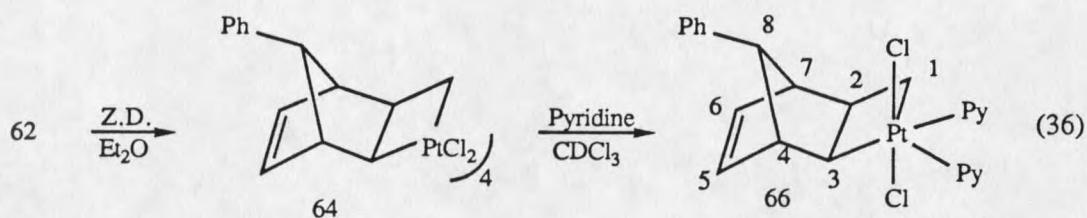


Synthesis and Reaction of 8-Phenyl-exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene

Cyclopropanation of **61** was achieved using diazomethane and Pd(OAc)₂. With 5 equivalents of diazomethane, 50% cyclopropanation of **61** was achieved (by NMR). Product **62** is believed to be the major isomer formed, based on steric arguments. Attempts to separate **62** from **61** by preparative GC failed. **62** and **61** were thus submitted to further diazomethane until **61** was completely consumed. Under the conditions used, the bis cyclopropanated product **63** was also produced. Small amounts of endo cyclopropanes were also formed. Again separation was not achieved so an excess of the mixture of **62** and **63** (2:1 ratio) was reacted with Pt(II).



Stirring in diethyl ether resulted in the formation of a yellow precipitate believed to be the IPC's **64** and **65**, Equations 36 and 37. Isolation of the IPC's and reaction with pyridine in CDCl₃ gave the platinacyclobutanes **66** and **67** (3:1 ratio). Evidently the platinum is moderately selecting **62** over **63**. Proof of the stereochemistry comes from two arguments. First, the olefinic and cyclopropane protons under the phenyl substituent are shifted upfield relative to the model compounds **68** and **69** (see Table 15 and 16 for NMR data). The second argument is based on steric factors. Shown below is **66** with its octahedral geometry. In an apical position is a chlorine atom, which would be impossible to maintain were a phenyl group syn to the platinum. It should be mentioned that x-ray studies have been performed on various norbornyl platinacyclobutanes. These x-ray data have shown that the bridge proton is in very close proximity to the axial chlorine. Thus, the syn phenyl of **66** and **67** is likely to be precluded.



Tables 15 and 16 give the ^{13}C and ^1H NMR for **66** and **67**. Norbornyl platinacyclobutanes have been previously characterized in detail⁶⁹. Data for both **66** and **67** agree extremely well with past examples. A problem that did arise was assignment of the phenyl carbon resonances as a result of using pyridine as a ligand. The sp^2 region of the NMR was very cluttered. Simplification of this region was achieved by using d_5 -pyridine and a 135° DEPT experiment. In the DEPT experiment, all solvent and quaternary carbon resonances are suppressed into the baseline. With the d_5 -pyridine ligands, the carbon resonances are seen as quaternary peaks and are, therefore, suppressed in the DEPT experiment. All that remains in the unsaturated region are the norbornyl phenyl and two olefin resonances. These were assigned by consideration of integration ratios.

Table 15. NMR Data for Complex 66.

#	^{13}C ppm*	$J_{\text{P,C}}$ **	^1H ppm*
1	-2.5	374.6	***
2	52.1	84.2	***
3	10.7	406.2	***
4	41.7	0.0	***
5	131.0	27.9	5.81(m)
6	132.8	0.0	5.96(m)
7	41.9	22.2	***
8	56.8	0.0	4.53(s)
Ph	142.4		7.0-7.35
Ph	128.8		7.0-7.35
Ph	127.3		7.0-7.35
Ph	124.8		7.0-7.35

* Relative to CDCl_3

** Coupling in Hertz

*** Resonates between 2.5-3.2

() Multiplicity

Table 16. NMR Data for Complex 67.

#	^{13}C ppm*	$J_{\text{P,C}}$ **	^1H ppm*
1	-8.6	363.0	***
2	57.3	95.3	***
3	13.7	398.6	***
4	41.8	8.3	***
5	14.8	38.2	0.88
6	15.4	0.0	***
7	44.3	25.1	***
8	42.1	0.0	4.23
9	5.9	0.0	0.24
			-0.38
Ph	144.3		
Ph	128.0		
Ph	126.8		
Ph	124.2		

* Relative to CDCl_3

** Coupling in Hertz

*** Resonates between 2.5-3.2

() Multiplicity

Reaction of IPC's **64** and **65** with DMSO, Figure 58, for 24 hours in d_6 -DMSO gave complete reaction of the IPC's. ^1H NMR of the resulting solution show a complex mixture. However, expansion of the olefinic region, Figure 59, results in a relatively simple spectrum. Resonances at 5.45 and 6.27 ppm are due to ring expansion yielding **70**. Assignments were established by comparison of integrations of the olefinic proton peaks to the integrated cyclopropane peaks of **70**. Added proof is garnered by proton-proton correlation (COSY) spectroscopy and decoupling experiments. These experiments established that the cyclopropane protons and olefin protons at 5.45 and 6.27 were on the same molecule.

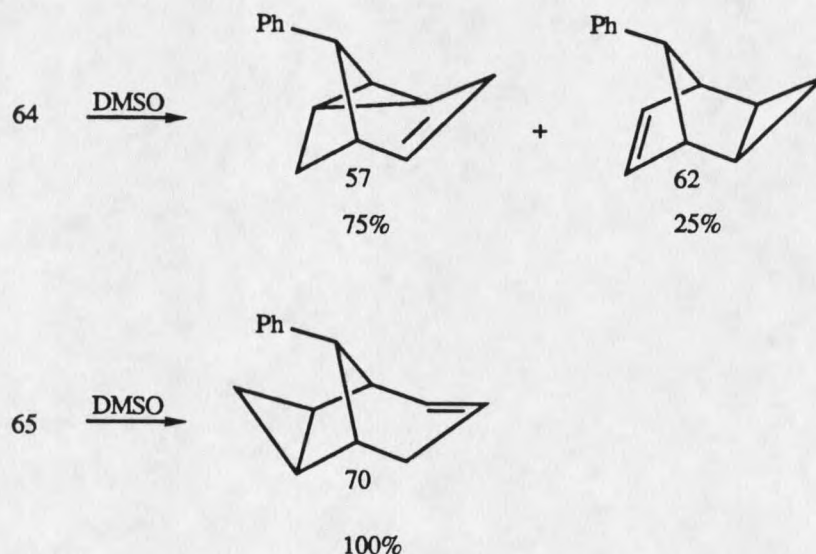


Figure 58. Ring Homologation of **64** and **65**.

A side reaction in the ring expansion to form **57** is reductive elimination producing **62**. By comparison with the spectrum of the starting cyclopropane **62**, the resonance at 6.18 was assigned to olefinic protons of **62**. Using the same NMR techniques as above, the remaining peaks at 5.92 and 6.08 ppm were assigned to **57**. It's now very evident that only one ring expansion product arises from **62**. This results from following pathway A in Figure 53. This experiment rules out the pathway shown as pathway B in Figures 53 and 56. Path C is inhibited as described earlier.

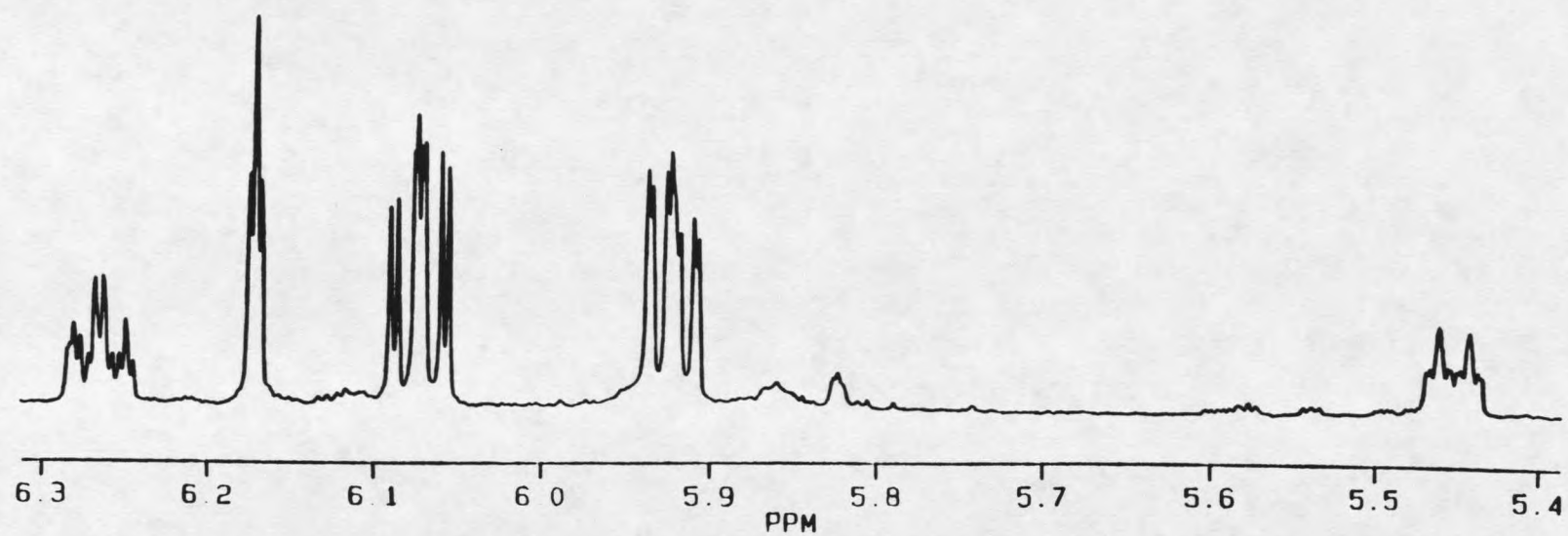


Figure 59. Expanded ^1H NMR Spectrum of 57, 62 and 70.

To assure that the formation of **57** was following the proposed pathway A in Figure 53, **62** was also labelled with ^{13}C . Results of this experiment are provided in Figure 60. Appearance of ^{13}C labelling at the olefin carbon, only, further corroborates that the transformation is indeed proceeding by the proposed mechanism.

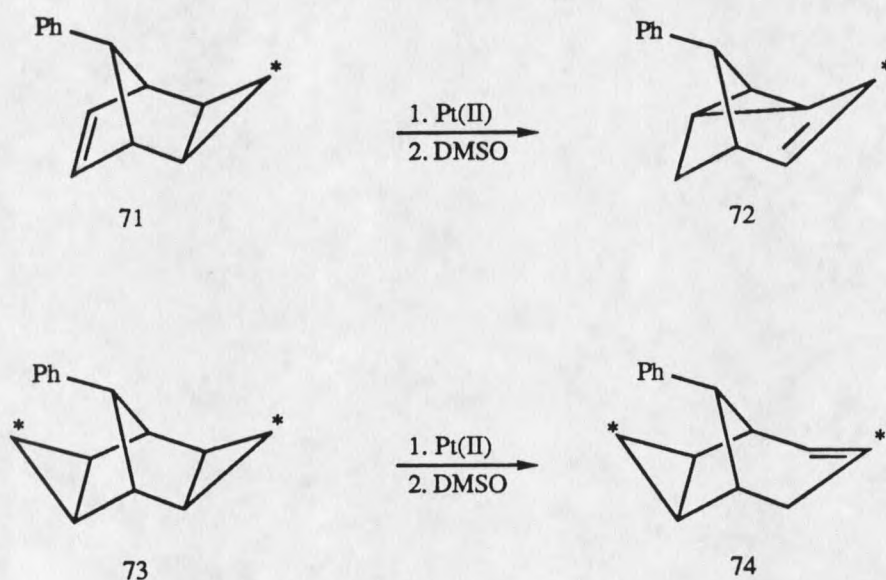


Figure 60. ^{13}C Labelling Results on **71** and **73**.

In conclusion, use of the 8-phenylnorbornyl system has ruled out mechanistic pathway B. The mechanism shown in Figure 61 is consistent with the evidence garnered to date. This invokes a degenerate Puddephatt rearrangement to achieve 33% of the product, path C, whereas 66% of the product is formed via an initial β -hydride abstraction, path A. It is the feeling of this author that abstraction of the hydride is faster than the second Puddephatt rearrangement, thus accounting for the observed ratio in the pathways.

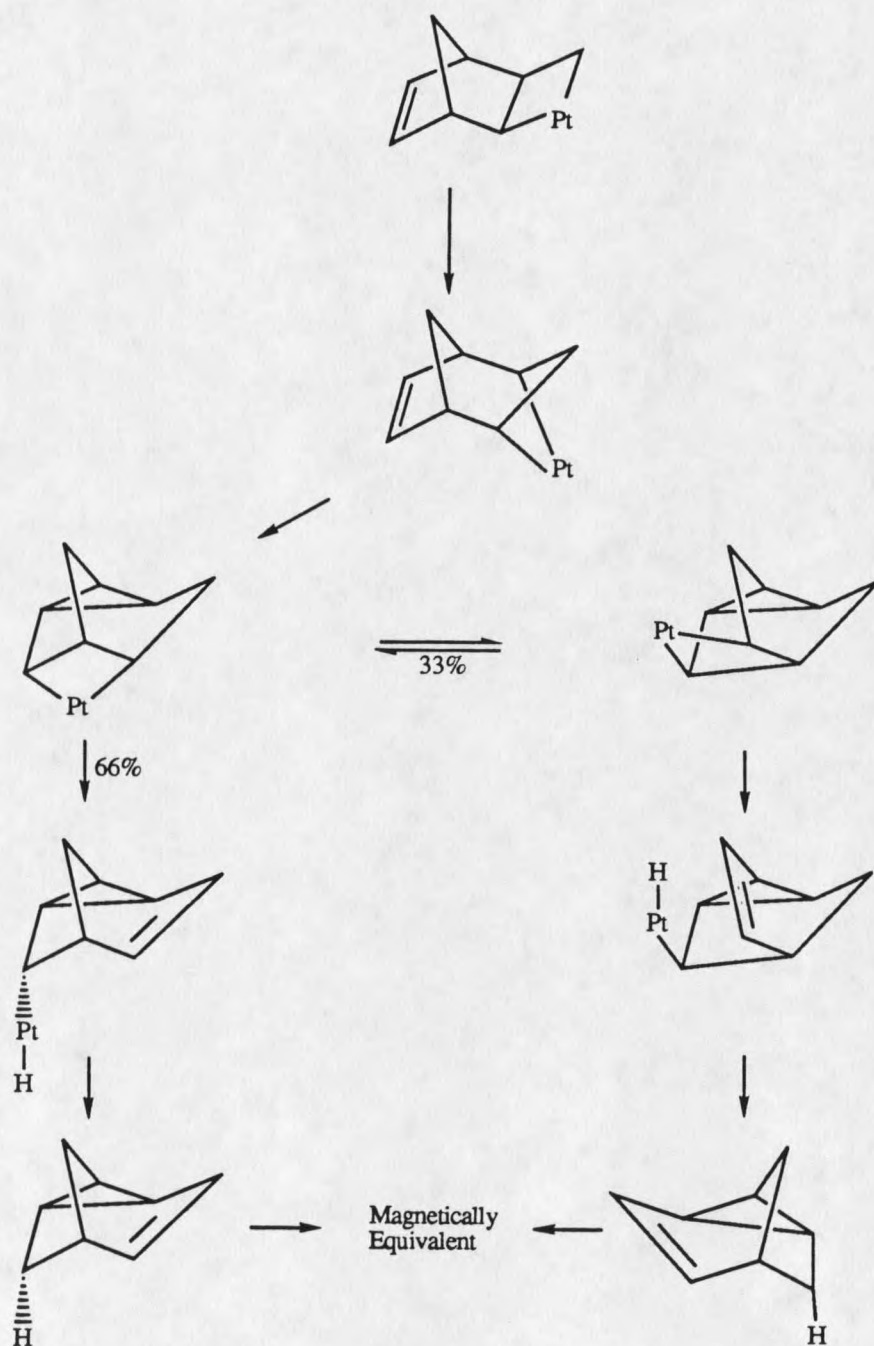


Figure 61. Mechanism for Ring Homologation in Unsaturated Norbornyl Systems.

Substituted Bicyclo[X.1.0] Systems: Ether Substituents

Saturated Ether Systems

Chemistry of the bicyclo[X.1.0] hydrocarbons has been limited. Although platinacyclobutanes have been isolated⁶⁴, Figure 62, a myriad of olefinic products is usually obtained¹¹¹. For the most part, these results can be attributed to the instability of the bicyclo system. In attempts to change the outcome, the starting bicyclo cyclopropane has been altered.

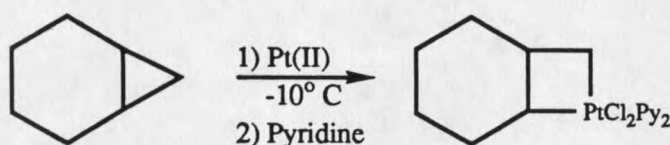
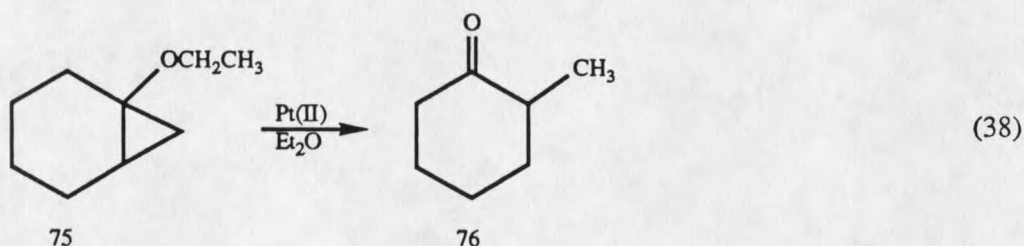


Figure 62. Formation of a Bicyclo Platinacyclobutane.

Incorporation of an ether group at the ring junction was the first modification made. On the surface, this may not seem reasonable, because an ether group will act as an activating group to a system already very reactive. However, it should also have a regioselective directing influence. Therefore, platinum insertion and subsequent rearrangements could be guided by this influence. Placement of an ether substituent at the ring juncture was accomplished quite easily. Structure 75, Equation 38, was synthesized by cyclopropanation of the corresponding enol ether in very good yields. Reaction with one equivalent of Zeise's dimer in diethyl ether at room temperature resulted in the formation of 76, in quantitative yields (by NMR). Isolated yields were in the 75-85% range. Structure 76 was initially proposed due to the presence of a peak at 1702 cm^{-1} in the IR spectrum,

presumably as a result of the carbonyl functionality. In the ^1H NMR spectrum, a resonance at 1.0 ppm appearing as a doublet is assigned to the methyl moiety. Both a carbonyl (211.9 ppm) and methyl resonance (14.6 ppm) appear in the ^{13}C NMR spectrum. Final verification was made by comparison of the acquired NMR data to literature data¹¹⁹ which proved the assigned structure to be correct.



At the time of the initial discovery, the mechanism in Figure 63 was postulated. This involves platinum insertion, with loss of ethylene, to form an intermediate platinacyclobutane. Rearrangement of **77** produces **78**. By β -hydride abstraction, **78** yields **79** which undergoes reductive elimination forming **76**. More important, however, is the initial catalyst remains intact, which is significant. If in fact Zeise's dimer is generated, the process should be catalytic. To test this proposition, cyclopropane **75** was reacted with 2 mol% of Zeise's dimer. ^1H NMR of the resulting reaction product exhibited the presence of both **75** and **76**. However, integration revealed an abundance of **75**. Further manipulation of the conditions revealed that 10 mol% of Zeise's dimer would quantitatively convert **75** to **76**. Formation of **76** can thus be achieved using a catalytic amount of Zeise's dimer.

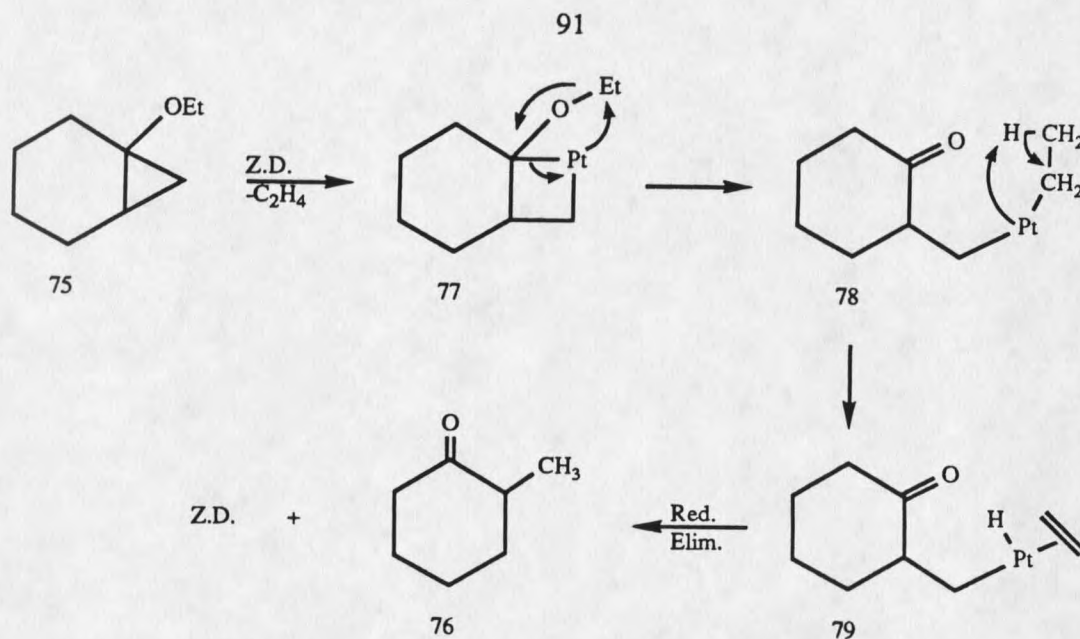
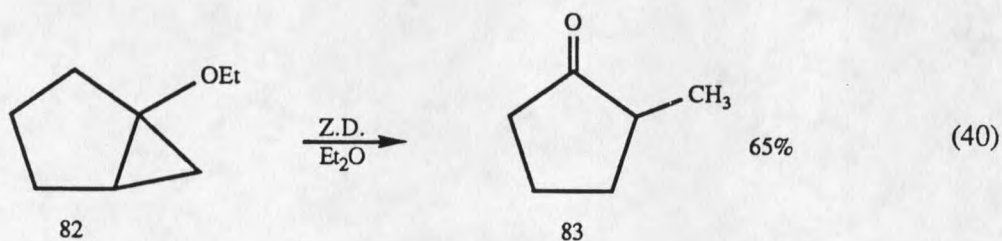
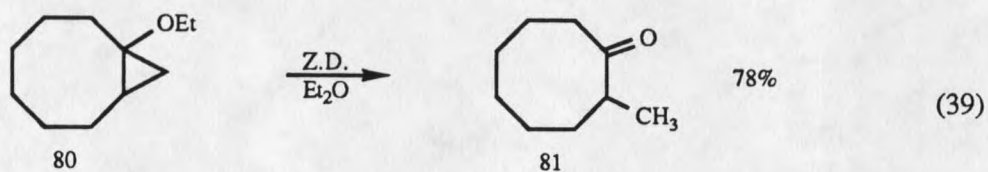


Figure 63. Initially Proposed Mechanism for 1-Methylcyclohexanone Formation.

Because the conversion of **75** to **76** occurred under mild conditions, the procedure was felt to be applicable to additional substrates. Use of an eight-membered ring in a reaction with Zeise's dimer gave good results, Equation 39. This reaction was also shown to be catalytic in Zeise's dimer. 1-Methylcyclopentanone, as shown in Equation 40, could also be synthesized via the platinum catalyst. Both **81** and **83** gave the characteristic methyl doublet in the ^1H NMR spectrum, as well as a carbonyl stretching frequency in the IR spectrum.



An ethoxy group is not required for the transformation. Methylcyclohexanone can also be formed from **84** and **85**, as shown in Figure 64. Initially both were treated with stoichiometric amounts of Zeise's dimer. However, it was later discovered that a catalytic amount of Zeise' dimer would suffice in the conversion of **85**. Diethyl ether is also not the only compatible solvent. THF and chloroform can be used for the transformation.

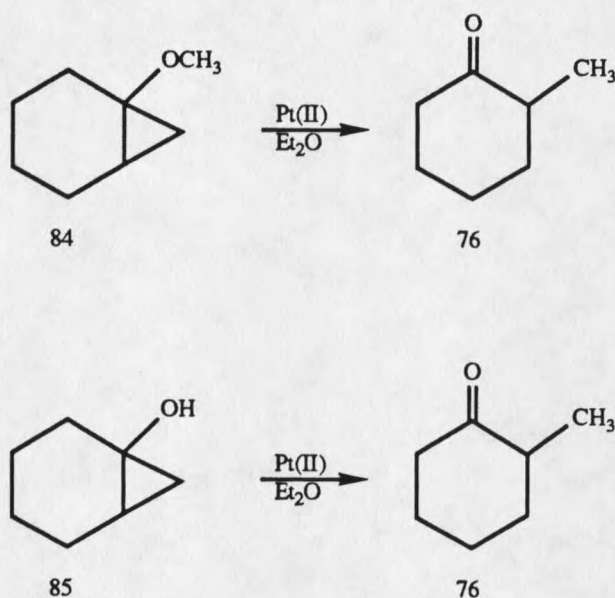


Figure 64. Synthesis of **76** from **84** and **85**.

However, with the discoveries shown in Figure 64, the mechanism originally proposed seemed questionable because **85** is not capable of regenerating a platinum-ethylene complex. The question must be asked, is it platinum that is causing the transformation, or an adventitious proton source? Conversion of **75** to **76** can be accomplished as shown in Figure 65, by addition of H_2O to the cyclopropane to yield **86**, which subsequently loses ROH ¹²⁰. In the experiment¹²¹, **84** was treated with concentrated hydrochloric acid and methanol. This solution was then refluxed for two hours to yield **76**. However, in the case of platinum-associated rearrangement, the conditions are much milder. This suggests that the platinum is responsible and not an adventitious proton source. To test this, **75** was run in the absence

of Zeise's dimer and a trace amount of HCl and no conversion to **76** was achieved. Furthermore, **84** was reacted with a catalytic amount of Zeise's dimer in oven dried glassware in the absence of solvent. Nevertheless, the platinum could be acting as a Lewis acid, implying that platinum never actually inserts into the cyclopropane ring.

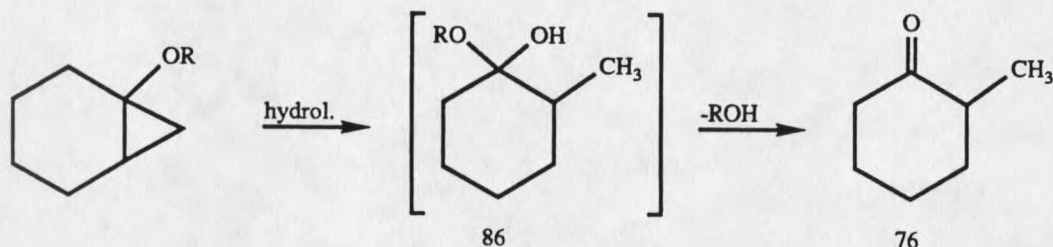


Figure 65. Alternative Formation of **76**.

In an effort to intercept a platinacyclobutane or comparable species, low temperature reactions were undertaken. Cyclopropane **75** was reacted with an equivalent of platinum in CDCl_3 at -20°C . NMR spectroscopy revealed **76** as the only observable species. Decreasing the reaction times produced no observable changes. Due to the reactivity of the norcarane system, this outcome was not altogether surprising. With a less reactive system, an intermediate might still be intercepted. Shown in Figure 66 are conditions used for the synthesis of two different platinacyclobutanes⁶⁶. It is evident that **89** is much less reactive than **87**. In order to isolate a platinacyclobutane from **87**, a reaction temperature of -10°C was required. Reaction at room temperature resulted in formation of olefins. Cyclopropane **89**, on the other hand, gave a stable platinacyclobutane at room temperature. Thus it would seem that reaction of **80** in Equation 39 at lower temperature might, in fact, yield a platinacyclobutane. Reaction of **80** at -20°C with one equivalent of platinum in CDCl_3 generated a product with a very complex spectrum. Resonances for starting cyclopropane as well as methyl ketone could be observed in the spectrum. Aside from the presence of **80** and **81**, several resonances with platinum coupling appeared. However, because of the

complexity of the spectrum, no structure could be confidently postulated. Thus proof of platinum insertion has yet to be accomplished.

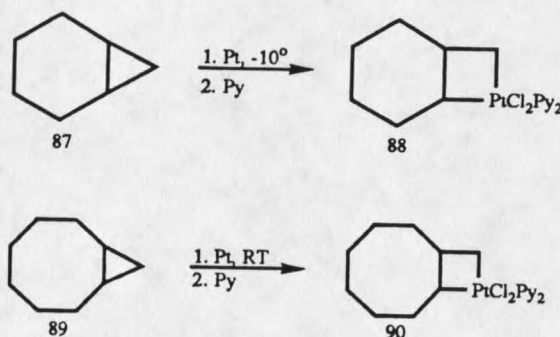
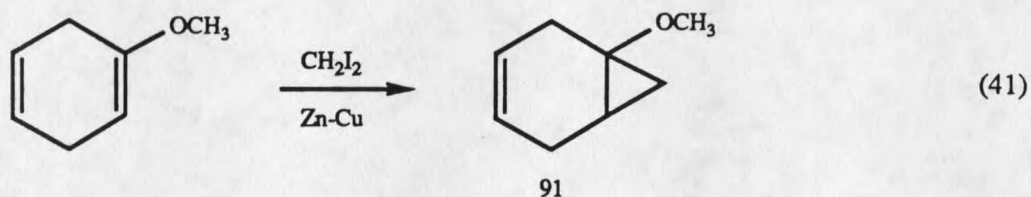


Figure 66. Effect of Ring Size on Platinum Insertion.

Unsaturated Ether Systems

To provide another substrate to prove platinum insertion, **91** was synthesized, Equation 41. Cyclopropanation was achieved using Simmons-Smith techniques. In this case, two different olefins were available for cyclopropanation. The electron-donating effect of the ether group was expected to make the adjacent alkene more electron rich than the other olefin. Therefore, more cyclopropanation would be expected to occur at the enol ether olefin. Indeed, examination of the reaction products revealed **91** in greater than 95% yield.



Reaction of **91** with platinum resulted in the formation of an orange solid, Figure 67. It is the opinion of this author that the texture and color of solid **92** resemble those of Zeise's dimer. Dissolution of **92** in neat pyridine at room temperature produced a yellow

solution which immediately formed an orange precipitate. Neither the resulting solid nor solution gave an informative NMR spectrum. THF appeared not to react in any way with **92**. However, treatment of **92** with CD_3CN resulted in a yellow solution. No appreciable precipitation occurred over several days, making analysis by NMR spectroscopy possible. Based on NMR and IR spectroscopy **93**, was assigned as the acetonitrile adduct. Shown in Figure 68 is the CPD ^{13}C NMR spectrum of **93**. As can be seen, a resonance appears at 205 ppm which is attributed to the carbonyl. IR spectroscopy confirmed this with a band at 1702 cm^{-1} . Proof of a platinum olefin bond is garnered from the resonances at 87 and 80 ppm. An upfield shift, along with platinum coupling of 249 and 254 Hertz, signifies a platinum olefin bond. Finally, proof of platinum insertion into the cyclopropane ring is solidified by the resonance at -3 ppm. Gated ^{13}C NMR spectroscopy revealed this to be a methylene. Moreover platinum carbon coupling of 588 Hertz and the large upfield shift substantiate assignment of the carbon platinum-sigma bond. Assignments for **93** are listed on page 104.

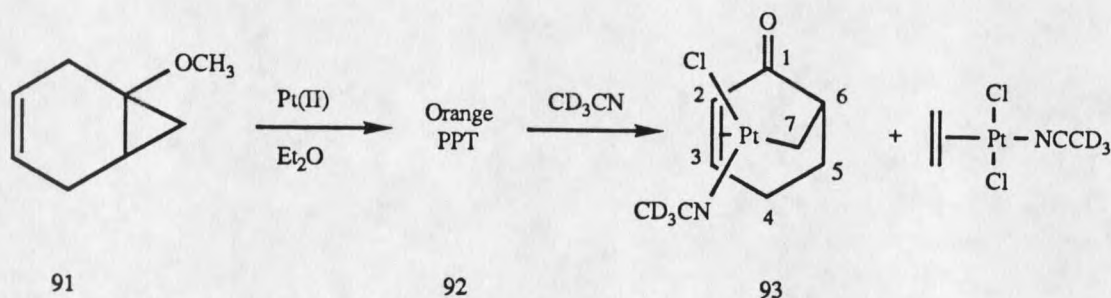


Figure 67. Reaction of **91** with Platinum.

Further evidence for platinum insertion was obtained with deuterium labelling. Labelling at the cyclopropane apex in **91** resulted in deuterium at the sigma bonded carbon, Figure 69. The oxidation state of the platinum was derived by ^{195}Pt NMR spectroscopy. A resonance at 1213.6 ppm is indicative of a Pt(II) . At this point, it would seem that a chlorine and a methyl group have been lost. This probability will be addressed later.

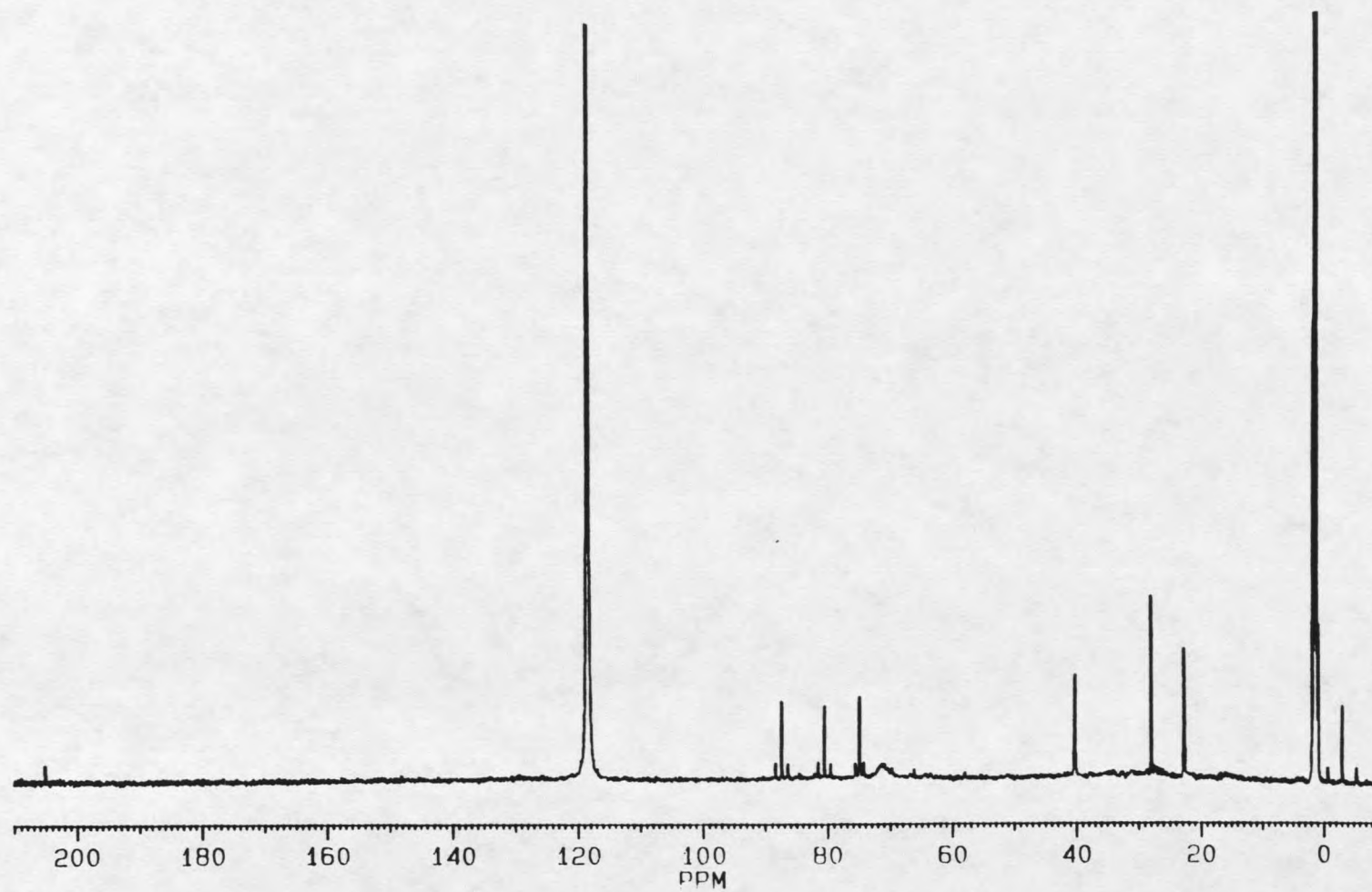


Figure 68. CPD ^{13}C NMR Spectrum of 93.

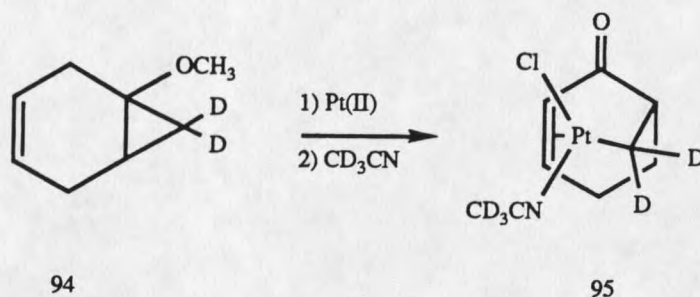


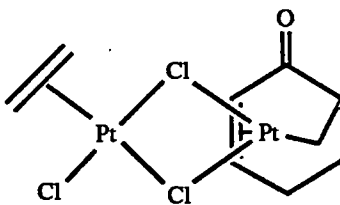
Figure 69. Deuterium Labelled Platinum Complex.

The regiochemistry of **93** and a resonance at 75 ppm in the ^{13}C NMR spectrum remain to be discussed, Figure 67. By ^{13}C NMR spectroscopy, the regiochemistry of the olefin can not be readily assigned. However, ^1H NMR spectroscopy reveals the stereochemistry very easily. One olefinic proton resonance appears as a doublet of triplets and is assigned to proton three. H-2 appears as a doublet, coupled only to H-3. Moreover, H-2 resonates at 4.1 ppm which is upfield of H-3 (5.4 ppm). This difference in chemical shift is due to anisotropy from the carbonyl moiety. Additional evidence comes from comparison of the ^1H NMR spectrum of **93** with that of 2-cyclohexenone. Aside from the effect of platinum on the chemical shift and platinum coupling, the olefinic regions are identical.

A side product in the reaction of **91**, Figure 67, is formation of the platinum ethylene monomer which accounts for the resonance at 75 ppm in the ^{13}C spectrum. Substantiation of this was achieved by addition of acetonitrile to Zeise's dimer. Both platinum coupling and chemical shifts in the ^{13}C NMR spectrum were identical for products from this reaction and that in Figure 67. Dichloroplatinum-ethylene monomer could be produced from unreacted Zeise's dimer carried over to the addition of acetonitrile. Alternatively, ppt **92** could liberate the ethylene complex. Integration of an INVGATED ^{13}C NMR spectrum of **93** gave much insight into the question. Relative to a resonance assigned to complex **93**, integration of the resonance at 75 ppm indicated the presence of two carbons. Had the ethylene complex been an impurity, integration would have given contrary results. Repetition of the experiment

proved it to be reproducible, thus ruling out the chance of fortuitous results. It would seem then, that the ethylene monomer is being formed via precipitate **92**. It should be noted that the ethylene group is carried over from Zeise's dimer. Characterization of **92** was therefore the next logical step.

Using CP/MAS, the ^{13}C spectrum shown in Figure 70 was produced. With this data the structure of **92** is proposed as shown below. The most conclusive piece of evidence for a carbonyl moiety in **92** is derived from the resonance at 214 ppm. A band at 1702 cm^{-1} in the IR spectrum further supports the presence carbonyl functionality in **92**. Equally obvious is the fact that the platinum olefin bond has also been formed. No resonance is present where free olefin would be expected (resonances at 178, 134 and 130 were shown to be spinning side bands). On the other hand, a large resonance at 74 ppm is apparent. However, the regiochemistry of the olefin is not apparent nor does any of the above data rigorously prove an α,β regiochemistry. Realistically, isomerization can happen at two stages, before or after formation of **92**. If isomerization occurs before **92** is formed, then addition of acetonitrile only breaks apart the dimer, path A in Figure 71. However, **92** could be generated as a β,γ -unsaturated complex, path B in Figure 71. Isomerization would then take place upon addition of acetonitrile.



92

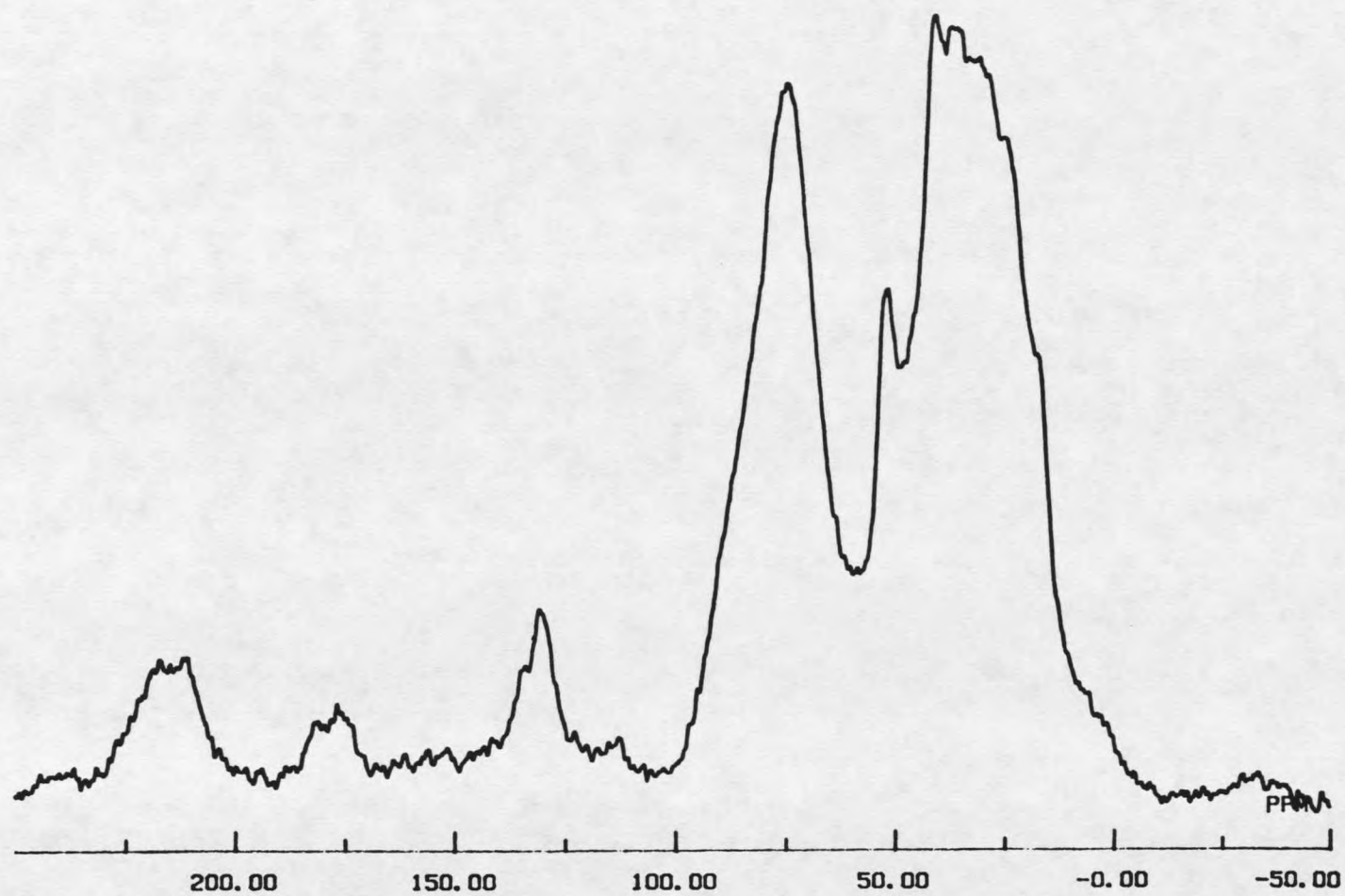


Figure 70. CP/MAS ^{13}C NMR Spectrum of 92.

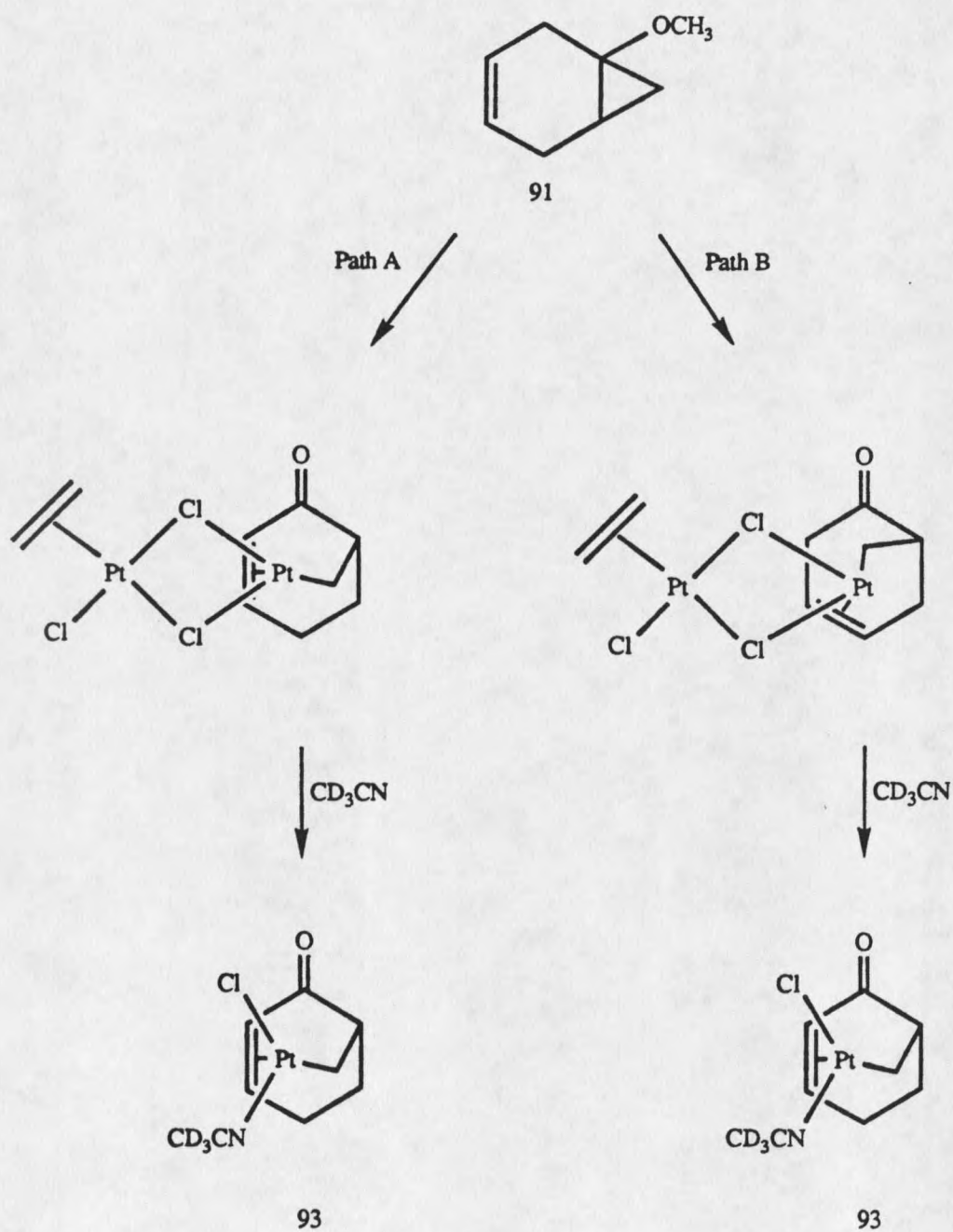
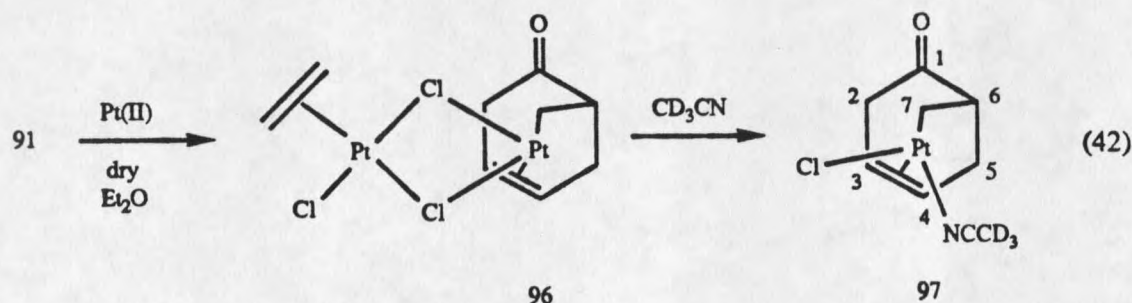


Figure 71. Alkene Isomerization Alternatives.

NMR spectroscopy was used in an attempt to deduce which pathway was operable. If isomerization is slow on the NMR timescale, then isomerization in path B could be observed. Addition of CD_3CN and immediate observation of the ^1H NMR spectrum showed **93** exclusively. Two conclusions are available: isomerization is too fast to be observed or path A is being followed. Assuming that path A is actually being followed, attempts were made to arrest isomerization. Using scrupulously dry and pure reagents, precipitate **96** was formed. Dissolution with CD_3CN yielded **97** as shown in Equation 42. Proof of the structure and regiochemistry was derived from proton and carbon NMR spectroscopy. First, the difference in the chemical shift of the olefinic proton resonances in **97** are small as compared to **93**. Second, the complex splitting pattern of both olefinic protons in **97** show coupling to upfield protons. One and two-dimensional, Figure 72, NMR spectroscopy showed that H-3 was coupled to H-2 and H-4 was strongly coupled to H-5. Further evidence is the downfield shift of the carbonyl resonance in the ^{13}C NMR spectrum, Figure 73. As one would expect, the lack of conjugation has shifted the resonance downfield. Again ^{195}Pt NMR spectroscopy revealed a Pt(II) moiety with a resonance at 1026.5 ppm. NMR data for **93** and **97** are listed in Tables 17 and 18. Comparison of the data will demonstrate the difference in the two isomers.



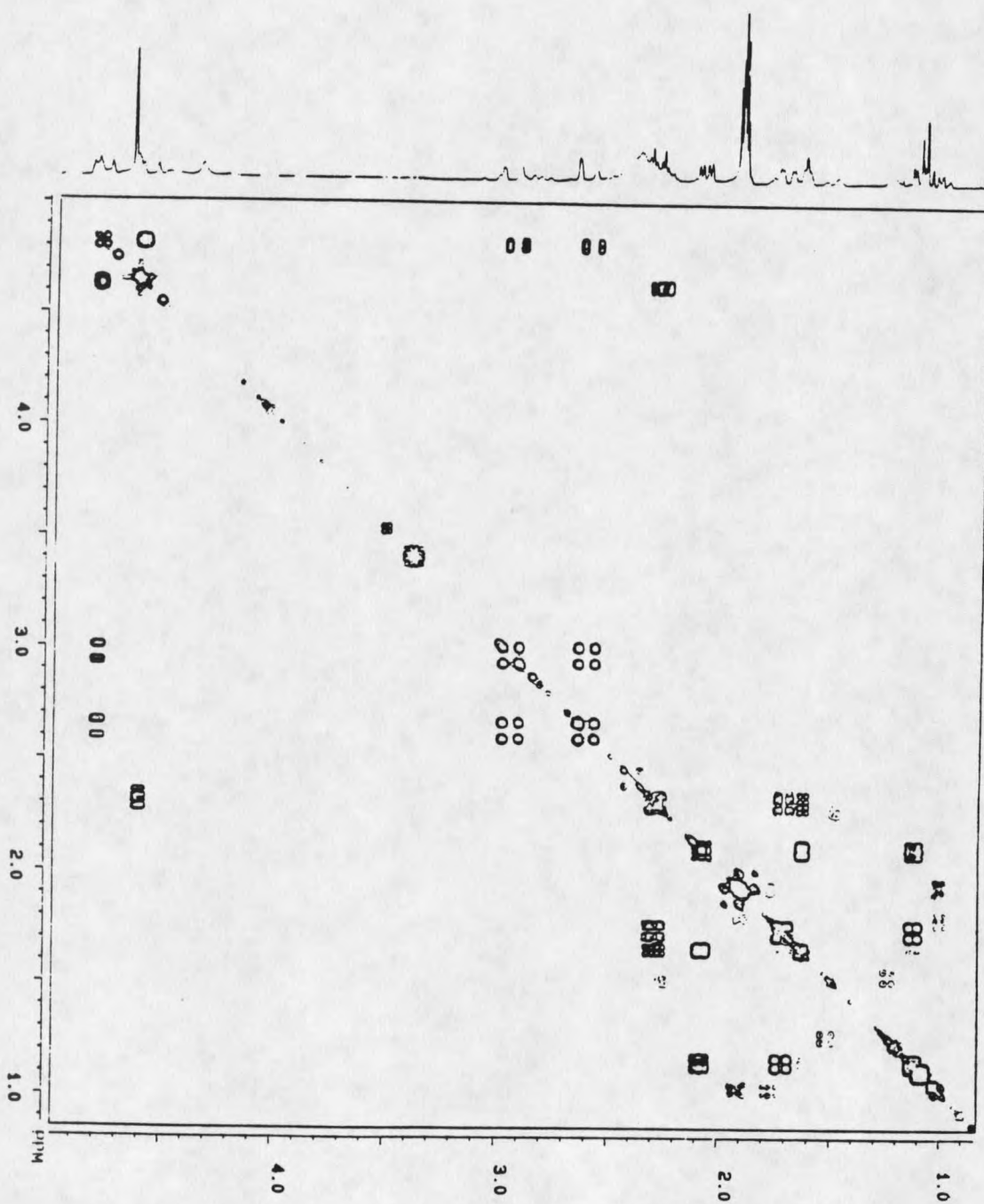


Figure 72. 2-Dimensional (COSY) ^1H NMR Spectrum of 97.

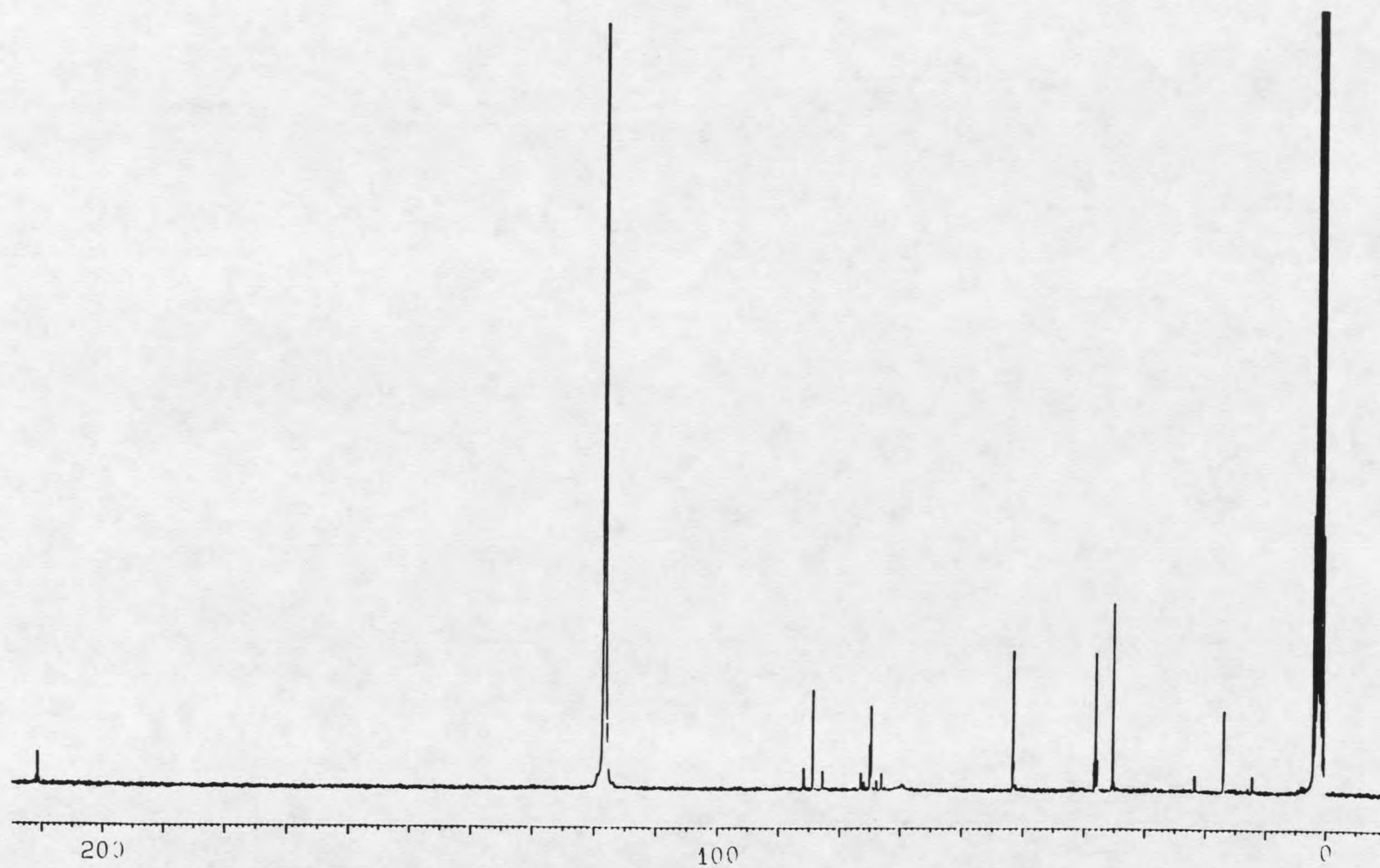


Figure 73. CPD ^{13}C NMR Spectrum of 97.

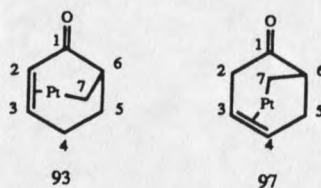


Table 17. NMR Data for Complex 93.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ *
1	205.0	0.0	-	-	-
2	80.4	254.3	4.08 (d)	60.2	7.3
3	87.3	249.4	5.35 (dd)	60.6	7.3, 3.6
4	22.6	37.2	2.5-2.6 (m)	0.0	
			2.25-2.32 (m)		
5	27.9	0.0	1.95-2.0 (ddd)	0.0	
			2.05-2.18 (m)		
6	40.1	29.4	1.25-1.31(hrs)	66.5	
7	-3.2	588.8	1.00 (d)	107.5	11.0
			1.80 (ddd)	98.0	11.0

* Relative to CD_3CN

** Coupling in Hertz

() Multiplicity

Table 18. NMR Data for Complex 97.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ *
1	210.6	27.3	-	-	-
2	38.0	33.8	2.61 (dd)	0.0	21.7, 1.8
			2.97 (dd)	0.0	21.7, 2.2
3	74.7	257.2	4.80 (ddd)	76.3	1.8, 2.2, 10.5
4	84.3	233.2	4.65 (dd)	80.9	10.6, 2.0
5	35.2	0.0	1.72 (m)	0.0	2.0
			2.31 (m)		
6	51.5	< 5.0	1.64 (hrs)	85.0	
7	17.0	720.4	1.13 (d)	113.4	3.7
			2.10 (dd)	unres.	3.7, 7.0

* Relative to CD_3CN

** Coupling in Hertz

() Multiplicity

Insertion of Pt(II) into a tetra-substituted cyclopropane has never been accomplished. However, with the activating effect of the methoxy group, insertion might be possible. To test this hypothesis, **98** was synthesized. Stereochemistry of the methyl group was assigned by ^1H NMR. Reaction of **98** with Zeise's dimer resulted in formation of a solid, Figure 74. Addition of CD_3CN , CDCl_3 and pyridine resulted in formation of **100** in 50% yield. With the formation of **100**, the first example of Pt(II) insertion into a tetrasubstituted cyclopropane has been accomplished. Proof for the structure of **100** comes from NMR data, listed in Table 19, and an X-ray structure shown in Figure 75.

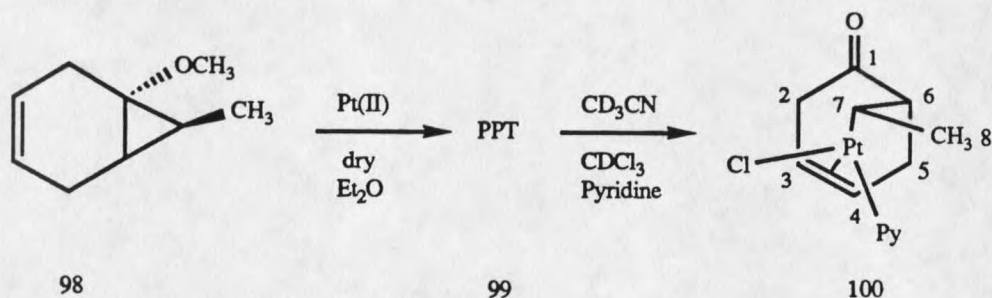


Figure 74. Pt(II) Insertion into a Tetra-Substituted Cyclopropane.

Table 19. NMR Data for Complex **100**°.

#	^{13}C ppm**	$J_{\text{P,C}}$ ***	^1H ppm**	$J_{\text{P,H}}$ ***
1	211.0	****		
2	39.2	26	2.4-3.0 (m)	0
3	75.1	271	5.5 (m)	67
4	81.0	277	4.8 (m)	66
5	31.0	0	2.4-3.0 (m)	0
6	60.8	28	1.6 (brs)	****
7	25.7	723	2.0 (m)	****
8	22.9	37	0.6 (d)	

* Not rigorously determined

** Relative to CDCl_3

*** Coupling in Hertz

**** Not Resolved

() Multiplicity

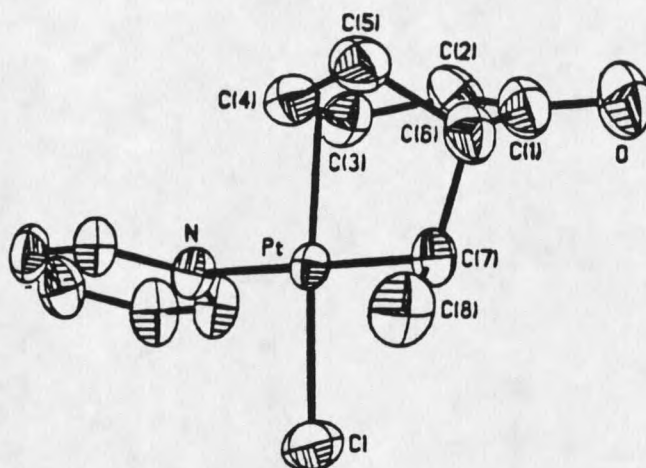


Figure 75. X-ray Crystal Structure for Complex **100**.

Attainment of the X-ray structure for **100** solidifies the regiochemistry of not only complex **100**, but also of **93** and **97**. Comparison of NMR data for **97** and **100** shows very good agreement. In complex **100**, pyridine has presumably replaced acetonitrile as a ligand. Crystallization of the pyridine adduct proved to be very easy. However, all attempts to form crystals with acetonitrile as a ligand failed.

Interesting comparisons can be made with **93** and **97**. In complex **93**, carbon 7 resonates at -3.2 ppm with 589 Hertz platinum coupling. However, **97** resonates at 17.0 ppm and has 720 Hertz coupling for its carbon 7. This is a dramatic difference. The chemical shifts for the carbonyl carbons in these compounds are also of interest. With a resonance at 210.6 ppm compound **97** is very similar to cyclohexanone (210.3¹²²). However, the carbonyl resonance in **93** is at 205 ppm, whereas its model, 2-cyclohexenone has a resonance at 197 ppm. It would thus seem that the platinum is having an effect on the carbonyl resonance in **93**.

In an approximate description of the three main terms that contribute to ¹³C NMR shifts, Equation 43: a diamagnetic shielding term, σ_a , a paramagnetic shielding term, σ_p , and contributions from neighboring-group nuclei, σ_n . The diamagnetic term is due to currents

involving electrons on the nucleus being considered. Contributions of higher electronic states (especially low-level "excited states") to the description of the ground state make up the paramagnetic term. Finally, σ_a accounts for electron circulations on neighboring atoms and specific anisotropic groups such as phenyl rings, carbonyl groups and acetylenes. Anisotropic terms are relatively insignificant in ^{13}C NMR spectroscopy. σ_p has been shown to be dominant for most ^{13}C chemical shifts, although σ_d has been suggested to be important, especially in interpretation of small changes¹²³.

$$\sigma = \sigma_d + \sigma_p + \sigma_a \quad (43)$$

With a 20 ppm difference in carbonyl resonances between **93** and **97**, σ_p is most likely responsible. In the opinion of this author, the chemical shifts and $^1J_{\text{Pt,CH}_2}$ coupling in **97** are expected values. Complex **93**, however, has unusual values. As a result of more angle strain, **93** is in a higher electronic state and therefore a resonance at -3 ppm is observed. A downfield shift of eight ppm has occurred in the carbonyl resonance of **93** versus that of 2-cyclohexenone. With a small change such as this, the diamagnetic term can be considered. If electrons are flowing away from the carbonyl to the platinum, the carbonyl would be deshielded and the resonance would move downfield. With the assumption that electron density is moving to the platinum, the lower $^1J_{\text{Pt,C}}$ coupling can be explained as well. The platinum, with more electron density, is less capable of accepting sigma donation from the carbon. Hence, less s character and lower coupling is observed.

As in the saturated system, the methoxy unsaturated system will react with Pt(II). Figure 76 shows the results when an ethyl group is used. As can be seen, complexes **93** and **97** can be derived via the cyclopropane **101**. Identical NMR spectra were obtained when using a methoxy or an ethoxy substituent. Thus, it would seem that, upon reaction with

Zeise's dimer, ethyl chloride or methyl chloride would be liberated. To test this, the deuterium-labelled substrate **102** was synthesized. Reaction with Zeise's dimer followed by acetonitrile gave complete loss of all labelling, demonstrating the loss of the ethyl group, Figure 77. Exactly what happens to the leaving group was shown with **103**. Initially the reaction was run in diethyl ether which resulted in the formation of a precipitate. Addition of CD_3CN to the precipitate yielded **93**. Next the reaction was run in a sealed vial in the absence of solvent. ^1H NMR Spectroscopy of the liquid and GCMS of the head gas revealed the formation of butyl chloride. Presumably methyl chloride and ethyl chloride are liberated when the methoxy or ethoxy cyclopropanes are used.

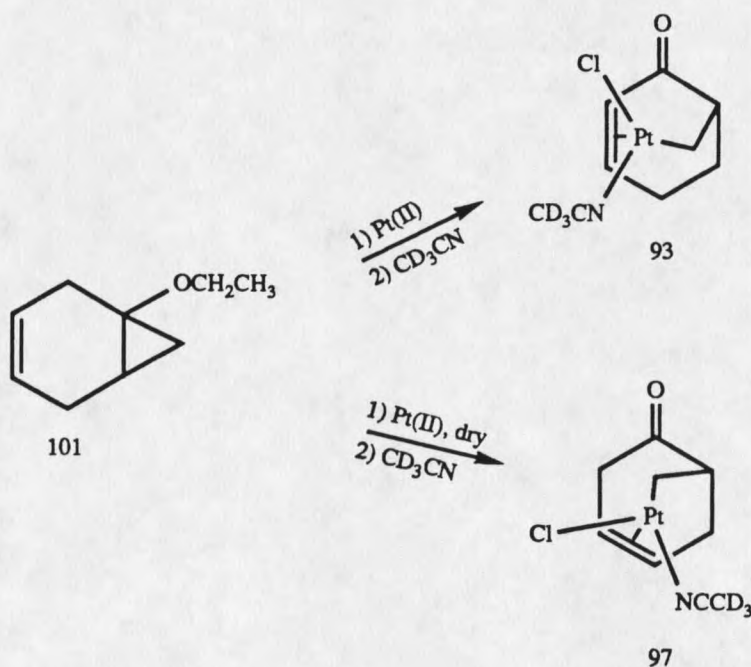


Figure 76. Reaction of **101** with Pt(II).

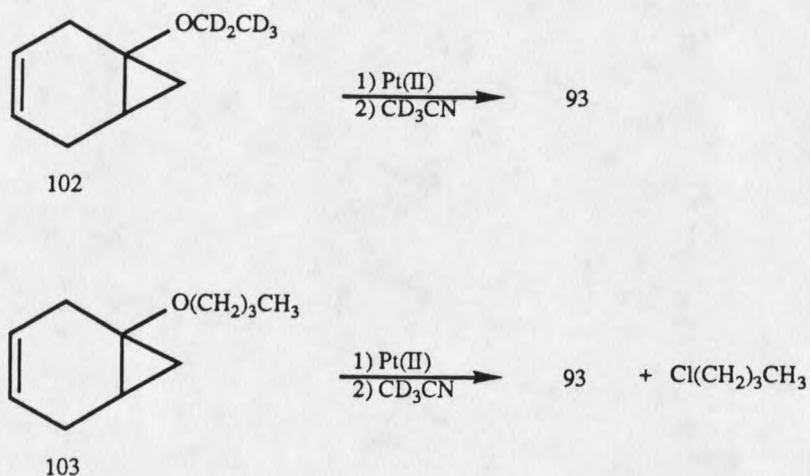


Figure 77. Reaction of **102** and **103** with Pt(II) .

Finally, removal of the platinum from complexes **92** and **96** can be achieved. Treatment of either **92** or **96** with triphenyl phosphine yielded 6-methyl-2-cyclohexenone, Figure 78. The mechanism of formation has not been tested. However, in speculating on the mechanism, an orthometallation could be proposed, Equation 44. The initial step in this mechanism is coordination of phosphine to platinum. Insertion of platinum into an ortho hydrogen bond yields a platinum hydride. From this, reductive elimination yields **104**. In the case of **96** an isomerization must be occurring at one point prior to product formation.

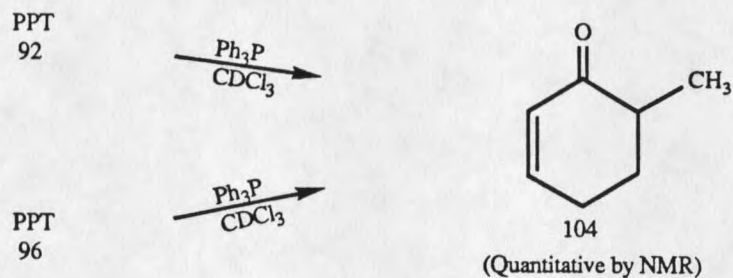
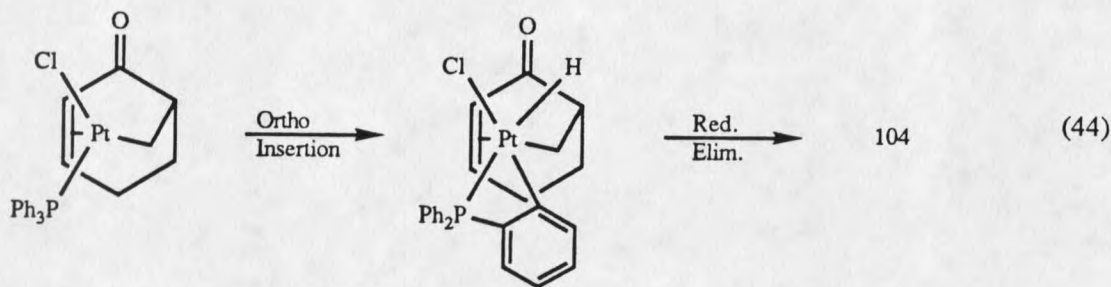


Figure 78. Formation of 6-Methyl-2-cyclohexenone.



Mechanism for the Formation of 1-Methylcyclohexanone.

Several possible mechanisms exist for the formation of methyl cyclohexanone. Figure 79 displays three mechanisms that can be postulated. Considering the results presented in the previous section, insertion of platinum into the cyclopropane to form **105** is now a reasonable step. Compound **105** can then rearrange to **106** which can proceed along several paths. One such path involves abstraction of a proton from the ethyl group, Path I. Reductive elimination would give **76**. However, loss of butyl chloride, seen in the reaction of **103**, could potentially rule this out. Thus, two other mechanisms have been proposed, both using **107** as an intermediate. Mechanism II is quite simple. Platinum can obtain an adventitious proton from the solvent with subsequent reductive elimination to give **76**. Mechanism III involves abstraction of an acidic ring proton followed by reductive elimination yielding the platinum enolate **108**, which again requires a proton source to produce **76**.

At this point, substantiation or disputation of mechanisms I-III was undertaken. Labelling of the cyclohexyl ring, Equation 45, would resolve mechanism III. If mechanism III is followed, a deuterium atom would be expected on the methyl group, Equation 46. However, reaction of **109** with platinum resulted in the formation of **110**, Equation 47. Thus, it would seem that mechanism III is inoperable.

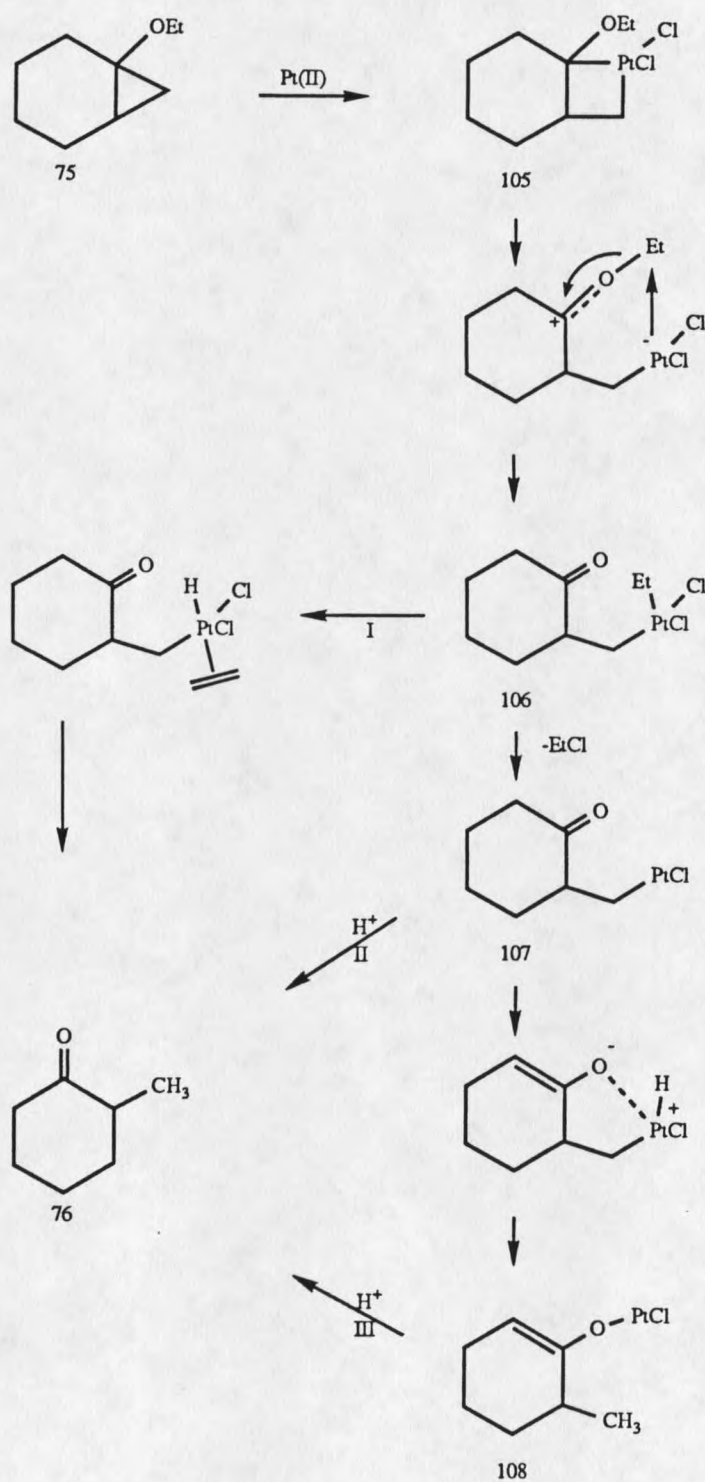
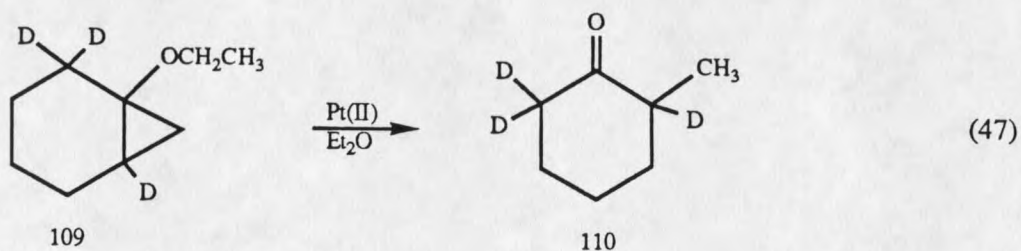
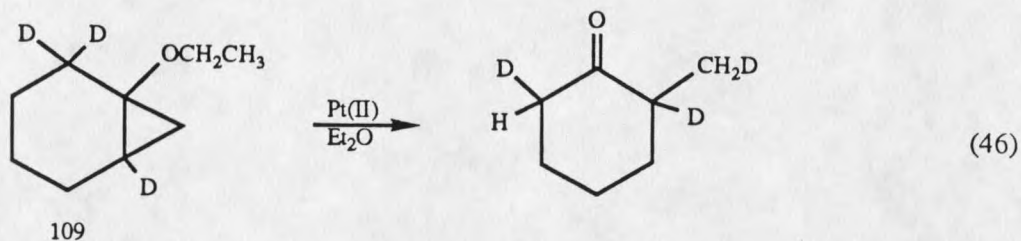
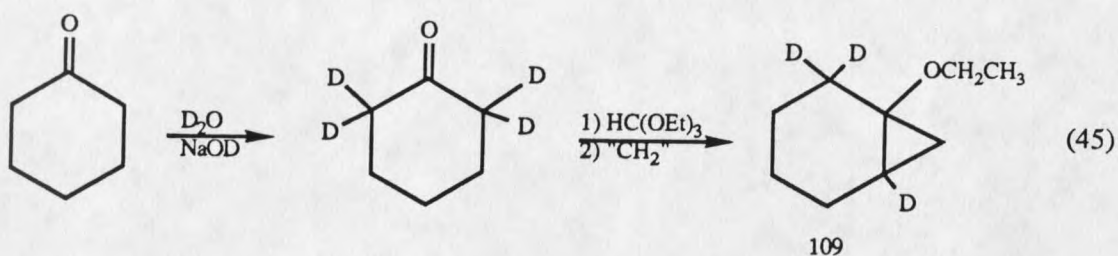
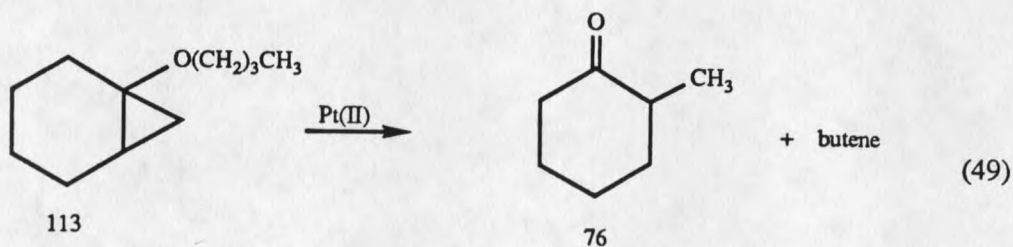
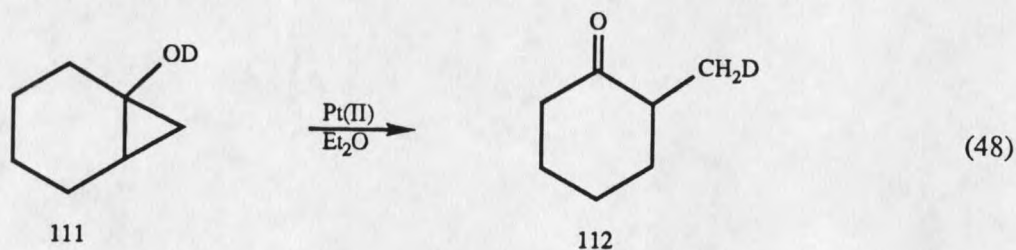


Figure 79. Possible Mechanisms in the Formation of 76.



The validity of mechanism II can also be tested. Removal of all extraneous proton sources would suppress formation of **76**. Formation of olefins or platinum complexes, such as **107**, might then be expected. Cyclopropane **75** was thus reacted with platinum under stringent conditions. Oven dried glassware, a nitrogen atmosphere and an absence of solvent were employed in the reaction. Under these conditions **76** was formed quantitatively (by NMR) when using a catalytic amount of platinum. Thus, it would seem that mechanism II is also inoperable.

With the two results above, mechanism I would seem more plausible. Labelling of the ethyl group with deuterium would determine if mechanism I is followed. However, a more convenient and less expensive substrate is the alcohol **111** used previously. Exchange of the proton with a deuterium will give results analogous to a labelled ethyl group. Results of the reaction with platinum are shown in Equation 48. Proof of a deuterium on the methyl group comes from ^2H NMR spectroscopy and GCMS. Structure **112** has a M^+ of 113 as well as an initial loss of 16. Furthermore, a resonance appears at 1.01 ppm in the ^2H NMR spectrum. This chemical shift coincides with the shift of the methyl doublet in the ^1H NMR spectrum. Further potential proof for mechanism I is shown in Equation 49. Reaction of **113** with Zeise's dimer yielded **76** in quantitative yield by NMR spectroscopy as well as butene. Performing the reaction in a sealed container and analysis of the head gas by GCMS indicated the formation of butene, however rigorous proof for butene was not obtained.



Shown in Figure 80 is a proposed catalytic cycle for the formation of **76**. In the first step, insertion of platinum with loss of ethylene occurs. Rearrangement will lead to the zwitterion. This species can follow two pathways. In the cases where the olefin was present in the ring, coordination of the platinum was observed succeeded by loss of EtCl. When the saturated system is employed a platinum ethyl moiety is formed. Subsequent hydrogen abstraction and reductive elimination produces methylcyclohexanone. Thus, use of the unsaturated cyclopropanes has intercepted the catalytic cycle.

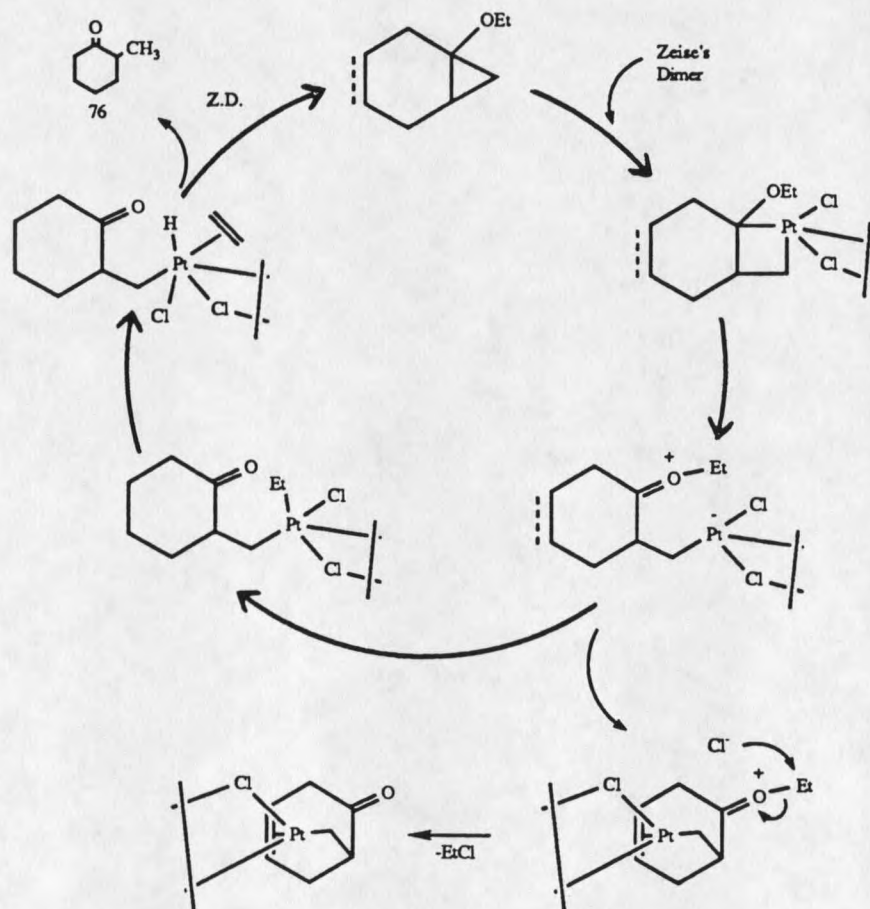
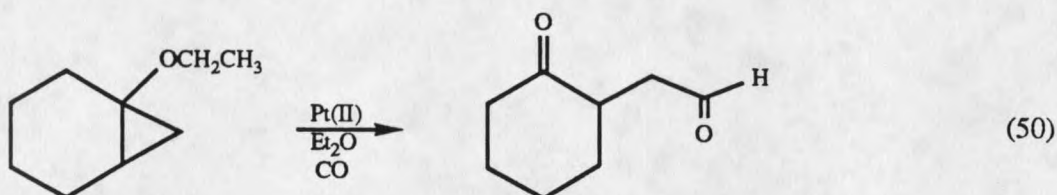


Figure 80. Mechanism for the Synthesis of 1-Methylcyclohexanone.

When an ethoxy or butoxy cyclopropane is used, ethylene or butene, respectively, would be regenerated on the platinum as shown in Figure 80 (with ether group). However, when methoxy cyclopropane is used a platinum carbene is generated. At this point, catalysis is no longer possible and hence the reason for a stoichiometric amount of Pt(II). In the case of the hydroxy cyclopropane, a platinum-olefin complex cannot be regenerated but a Pt(II) species with an open site for coordination is probably available for catalysis.

Finally, in attempts to broaden the scope of the reaction, carbon monoxide was added as a reagent. It was hoped that this would lead to the product shown in Equation 50. However, using CO pressures from 100 up to 1000 psi, no reaction was observed. Elevated temperatures also proved to be fruitless. In all cases, starting cyclopropanes were recovered.

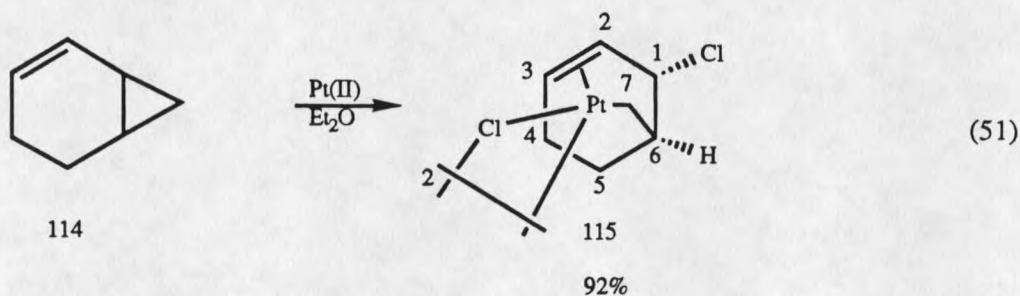


Even though the reaction in Equation 50 failed, a useful procedure for hydrolysis of alkoxy cyclopropanes has been developed. Compared to hydrolysis using concentrated HCl, the use of platinum requires very mild conditions. Furthermore the complexes developed in this investigation will further enhance the understanding of platinum chemistry.

Bicyclo[X.1.0] hydrocarbons: Vinyl Cyclopropanes

Reaction of bicyclo[4.1.0]hept-2-ene with Pt(II).

The reaction of bicyclo[4.1.0]hept-2-ene (**114**) with Zeise's dimer at room temperature resulted in the formation of a white precipitate which was characterized by several techniques, Equation 51. The solid state ^{13}C NMR spectrum, reproduced in Figure 81, showed resonances between 82.7 and 7.9 ppm suggesting that (a) the olefin moiety is coordinated to the platinum causing its resonance to be shifted upfield and (b) the cyclopropane is no longer intact. If the cyclopropane was intact a large resonance upfield of 16 ppm would be apparent. The small resonance at 7.9 ppm is assigned as a platinum satellite to the resonance at 16 ppm. The small spikes at -9 and 182 ppm are assigned as spinning sidebands.



Additional evidence for **115** comes from solution state NMR spectroscopy. Complex **115** was slightly soluble in CDCl_3 , making attainment of the NMR data listed in Table 21 possible. A resonance at 58.26 ppm is attributed to C-1. This resonance is in the region for a carbon bearing a chlorine. C-7 resonates at 14 ppm and has 618 Hertz platinum coupling which compares well with the solid state resonance at 16 ppm, 615 Hertz coupling.

Solid state IR spectroscopy exhibited strong bands between 700 and 800 cm^{-1} , further supporting a carbon-chlorine bond. Complex **115** gave good elemental analysis results as well.

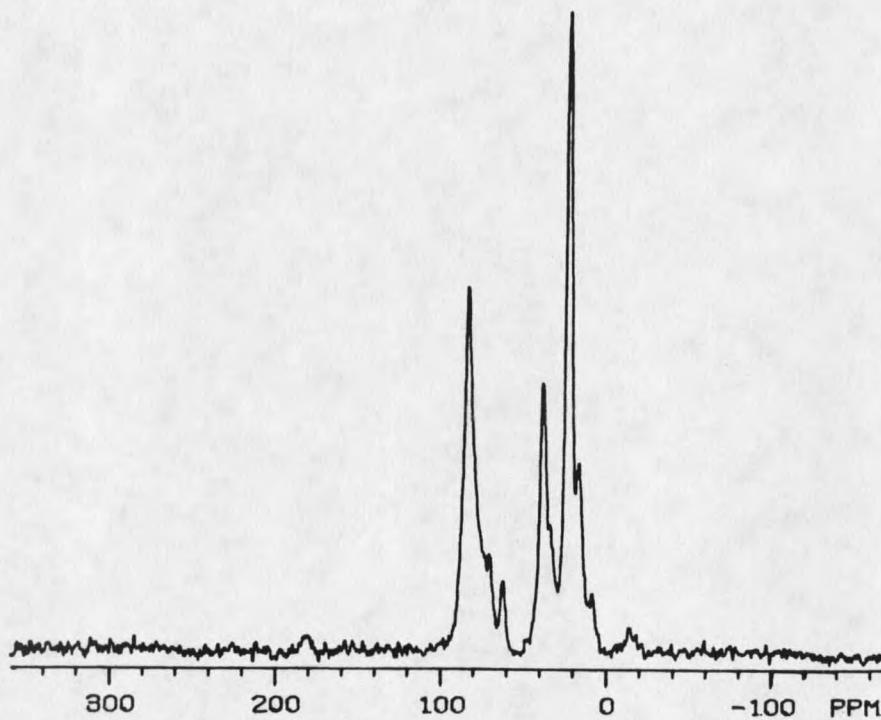


Figure 81. CP/MAS ^{13}C NMR Spectrum of **115**.

Table 20. CP/MAS ^{13}C Resonances for **115**.

#	^{13}C ppm	
1	70.0	
2	82.7	
3	82.7	
4	22.6	
5	22.6	
6	37.6	
7	16.1	$J_{\text{P,C}} = 615$

Table 21. Solution NMR Data for **115**.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ **
1	58.3	82.0	4.46(dd)	unres.	3.81, 4.31
2	80.2	248.3	4.42(dd)	95.2	4.31, 8.5
3	80.2	248.3	4.78(dt)	81.6	
4	20.4	38.8	2.65(m)	0	
			2.50(m)	0	
5	20.3	0	1.50(m)	0	
			2.27(m)	0	
6	35.5	<10	1.10(bris)	113.0	
7	13.9	618.6	1.28(d)	82.4	10.3
			2.05(brd)	104.6	10.3

^{195}Pt NMR*** - 1267, 1269, 1252, 1254 ppm

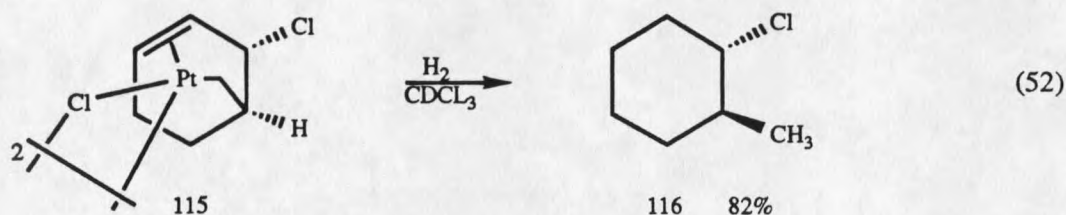
* Relative to CDCl_3

** Coupling in Hertz

*** Relative to 1.0 M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25° C

() Multiplicity

The stereochemistry of the chlorine in **115** was deduced by two methods. A proton coupling of 3.8 Hertz between H-1 and H-6 might indicate cis stereochemistry. However, complex **115** has the configuration similar to a norbornyl system suggesting that a value of 3.8 is actually indicative of trans stereochemistry. A second result was derived from treatment of **115** with hydrogen at 50 psi in chloroform. This yielded the chlorine adduct **116** shown in Equation 52. Assuming that no isomerization takes place during hydrogenation, compound **116** further corroborates the stereochemistry in **115**.



NMR data for **116** matches with the literature values for 2-methyl-chlorocyclohexane having trans stereochemistry¹²⁴. Isomerization in the hydrogenation process is unlikely due to the mild conditions.

A suggested mechanism for the formation of **115** is outlined in Figure 82. Insertion into bond **a** of **114** is evidently directed by the olefin. Normally in platinacyclobutane formation, the cyclopropane is thought of as the nucleophile and platinum the electrophile. Thus, bond **a** is likely more electron rich than bond **b** causing insertion to be centered at bond **a**. Insertion into bond **c** has been observed only once⁹² in the bicyclic or norbornyl systems as a result of steric hindrance. Platinacyclobutanes are very unstable in these bicyclic systems, consequently a rearrangement occurs. Migration of the platinum to the olefin would lead to the chlorine transferring to C-1. This however would place the chlorine syn to the platinum. Hence, a π -allyl intermediate is proposed. Presumably because of steric effects, the chlorine attacks anti to the platinum. The observed regiochemistry of the chlorine is a result of the platinum sliding toward C-3 on account of normal bond geometries. This results in more positive charge at C-1. Precedence for an internal ligand attacking a platinum π -allyl was presented on pages 18 and 19.

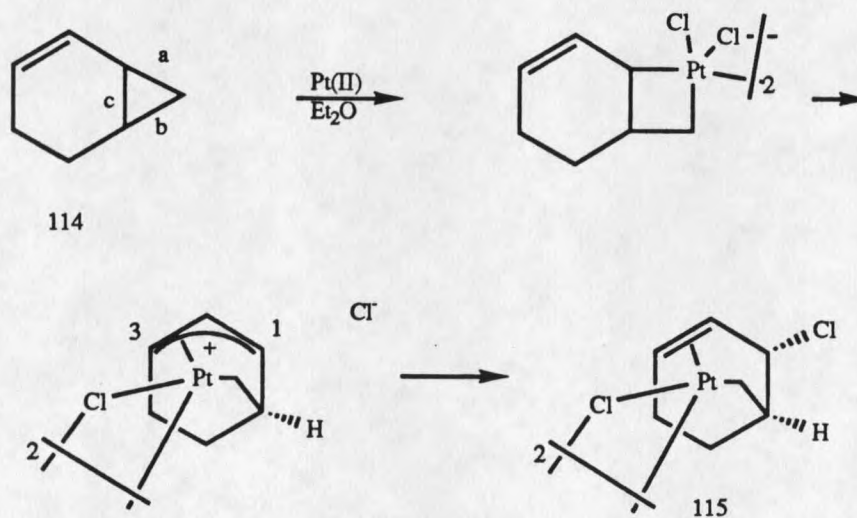


Figure 82. Mechanism for the Formation of **115**.

^{195}Pt NMR spectroscopy was used to demonstrate that a dimeric structure is present in **115**. Shown in Figure 83 is the ^{195}Pt NMR spectrum for **115**. Two major and two minor resonances are present in the Pt(II) region. This can be compared to the spectrum for Zeise's dimer, Figure 84. Major and minor resonances are a result of the two isomers pictured next to the resonances. In the major isomer, the ethylene groups are anti to each other, whereas the ethylenes are syn in the minor isomer. Complex **115** has this same attribute. Shown in Figure 85 are four isomers postulated to be responsible for the resonances in Figure 83. In the major isomers, the olefins are anti to each other. Because the ring chlorines can also be syn or anti to each other, there are two major isomers. Minor isomers have the olefins syn to each other and again the ring chlorines are both syn and anti. A test for the validity of the proposed isomers is to break the dimeric structure by reaction with a ligand. This should result in a product with only one resonance in the ^{195}Pt NMR spectrum.

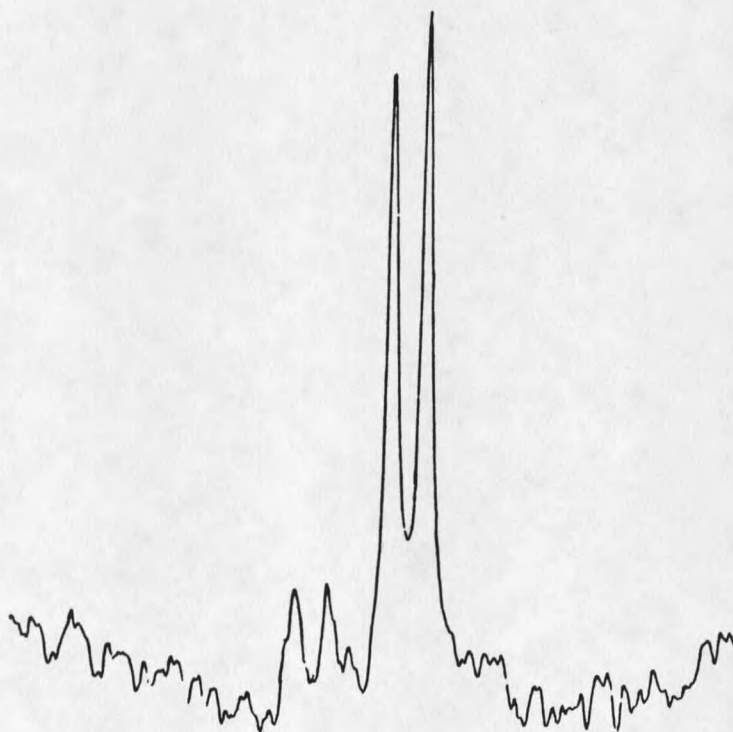


Figure 83. ^{195}Pt NMR Spectrum of **115** in CDCl_3 .

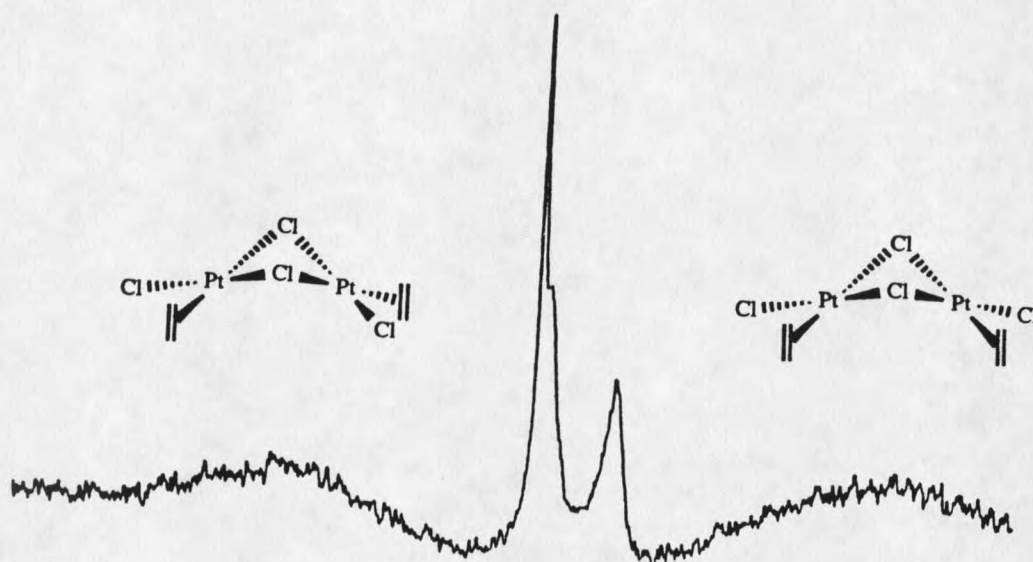


Figure 84. ^{195}Pt NMR Spectrum of Zeise's Dimer in CDCl_3 .

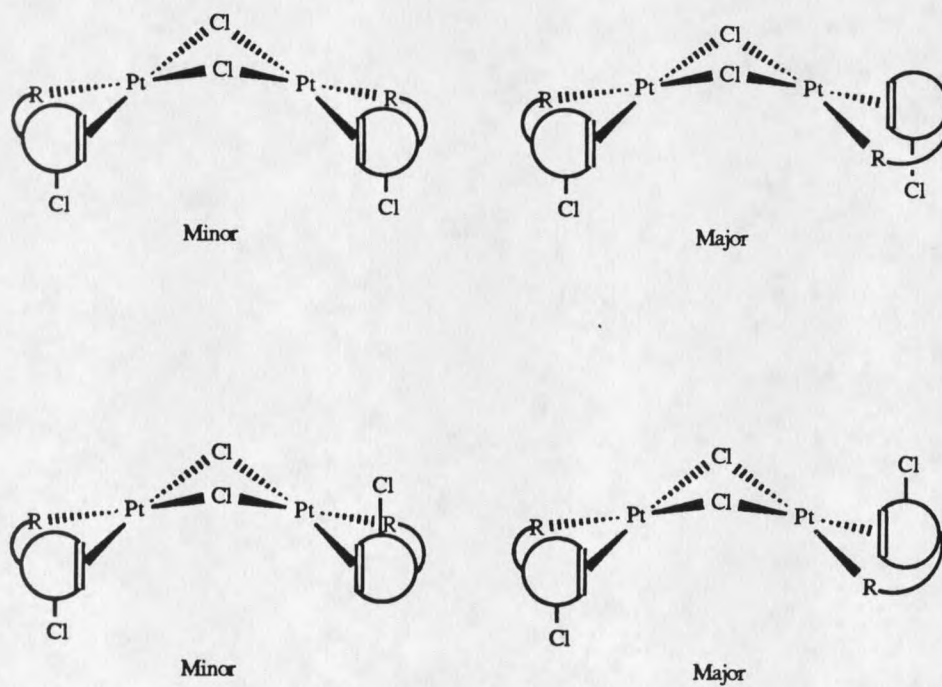
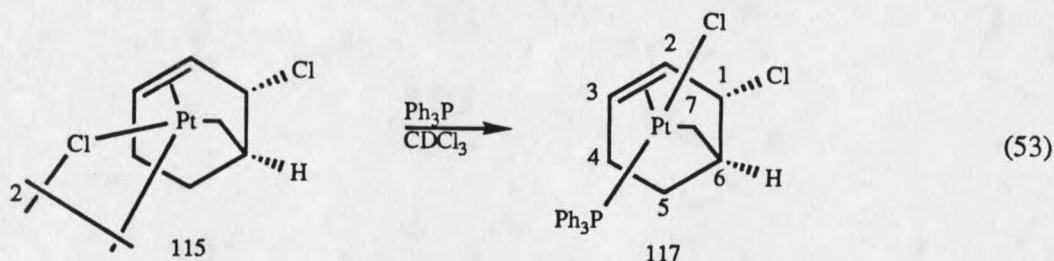


Figure 85. Proposed Isomers of Complex 115.

Reaction of Ligands with Complex **115**

Reaction of **115** with triphenylphosphine in CDCl_3 resulted in the formation of **117** as a colorless solution, Equation 53. Complex **117** is indefinitely stable at 0°C but decomposes at room temperature over three days. The decomposition products will be discussed later. ^{195}Pt NMR spectroscopy of **117** exhibited a doublet at 641 ppm due to phosphorus coupling of 4255 Hertz. Phosphorus-31 NMR spectroscopy revealed a triplet as a result of platinum coupling, also with a value of 4255 Hertz. As a result of the ^{195}Pt NMR study for **117**, the postulation of four isomers for **115** is solidified. A doublet in the ^{195}Pt NMR spectrum indicates that there is only one phosphine on the platinum.



Ligands that are trans to phosphorus groups have larger phosphorus coupling than those with cis phosphorus groups. Figure 86 displays the ^{13}C spectrum of **117**, while Table 22 lists the assignments. Both olefins appear as doublets due to phosphorus coupling whereas C-7 is only a singlet (excluding the ^{195}Pt coupling). Employing this data, the triphenyl phosphine ligand is determined to be trans to the olefin and the chlorine trans to C-7 in a square planar geometry. Detailed assignment of ^{13}C and ^1H NMR spectra was aided by two-dimensional spectroscopy. Figures 87 and 88 exhibit ^1H - ^1H and ^1H - ^{13}C correlated spectra for **117**. Utilizing Figure 88, each proton resonance was assigned to the proper carbon. For example, the resonances at 105 and 110 ppm on the ^{13}C axis displays connectivity to the

resonances at 5.7 and 6.2 ppm on the proton axis. These resonances were shown to be correlated to each other in Figure 87. Another example in Figure 87 is the connectivity of H-1 to H-6 which is shown with the large square. A coupling constant of 3.8 Hertz between these protons (attained from 1-D NMR spectroscopy) again signifies the chlorine anti to the platinum in 117. As was previously mentioned, the resonance for C-1 is shifted downfield as a result of being bonded to the chlorine. Figure 86 also displays this with a resonance at 57 ppm.

Table 22. NMR Data for Complex 117.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ **	$J_{\text{C,P}}$ **
1	57.0	64.4	4.50(dd)	0	3.81, 4.31	
2	104.75 104.64	96.6	5.67(brs)	51.1	4.31, 8	13.8
3	110.63 110.55	86.6	6.20(brs)	42.0		10.9
4	22.6	25.4	2.6(dd) 2.8(m)	0 0		
5	20.1	0	1.36(t) 2.25(m)	0 0		
6	36.9	37.3	1.74(brs)	95.9		
7	13.5	625.6	0.61(d) 1.2(brd)	62.6 105.7	11.0 11.0	

^{195}Pt NMR*** - 680, 602 ppm (4255 Hz = $J_{\text{P,Pt}}$)

^{31}P NMR**** - 21.4 ppm (4255 Hz = $J_{\text{P,Pt}}$)

* Relative to CDCl_3

** Coupling in Hertz

*** Relative to 1.0 M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25° C

**** Relative to 1.0 M H_3PO_4 in D_2O at 25° C

() Multiplicity

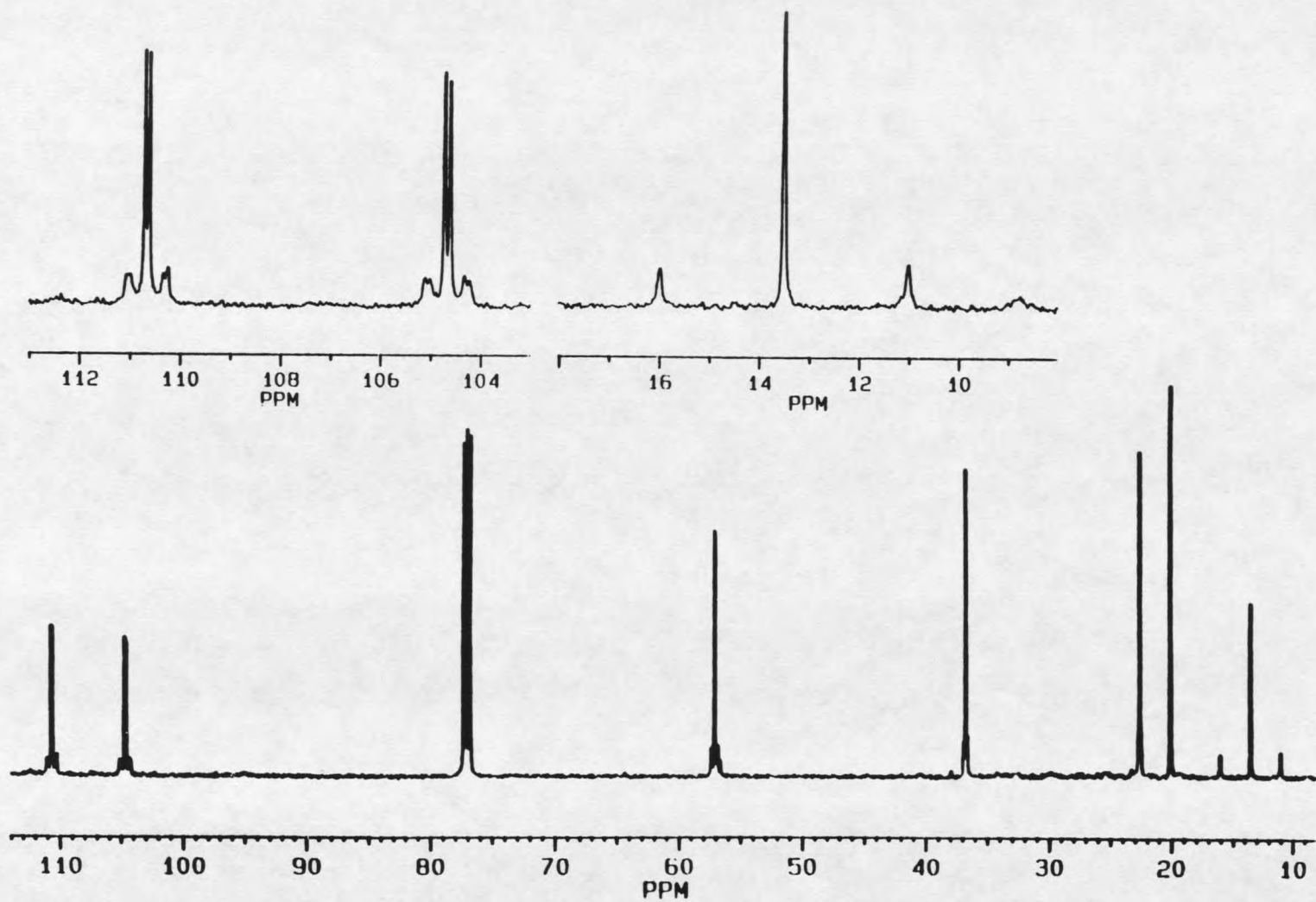


Figure 86. CPD ^{13}C NMR Spectrum of 117 (excluding PPh_3 Resonances).

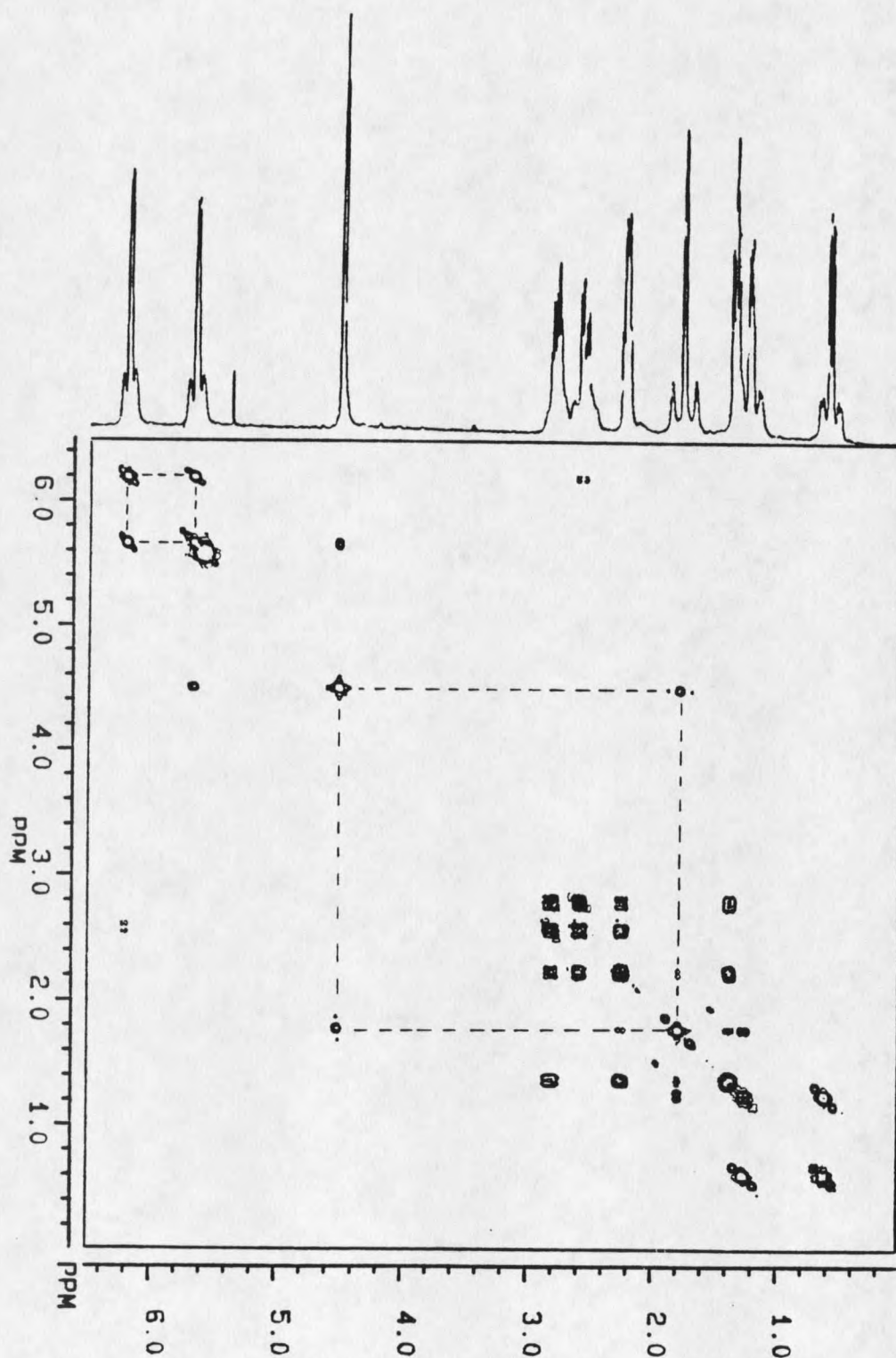


Figure 87. ^1H - ^1H Correlated (COSY) Spectrum of 117 (1-D ^1H spectrum on top axis).

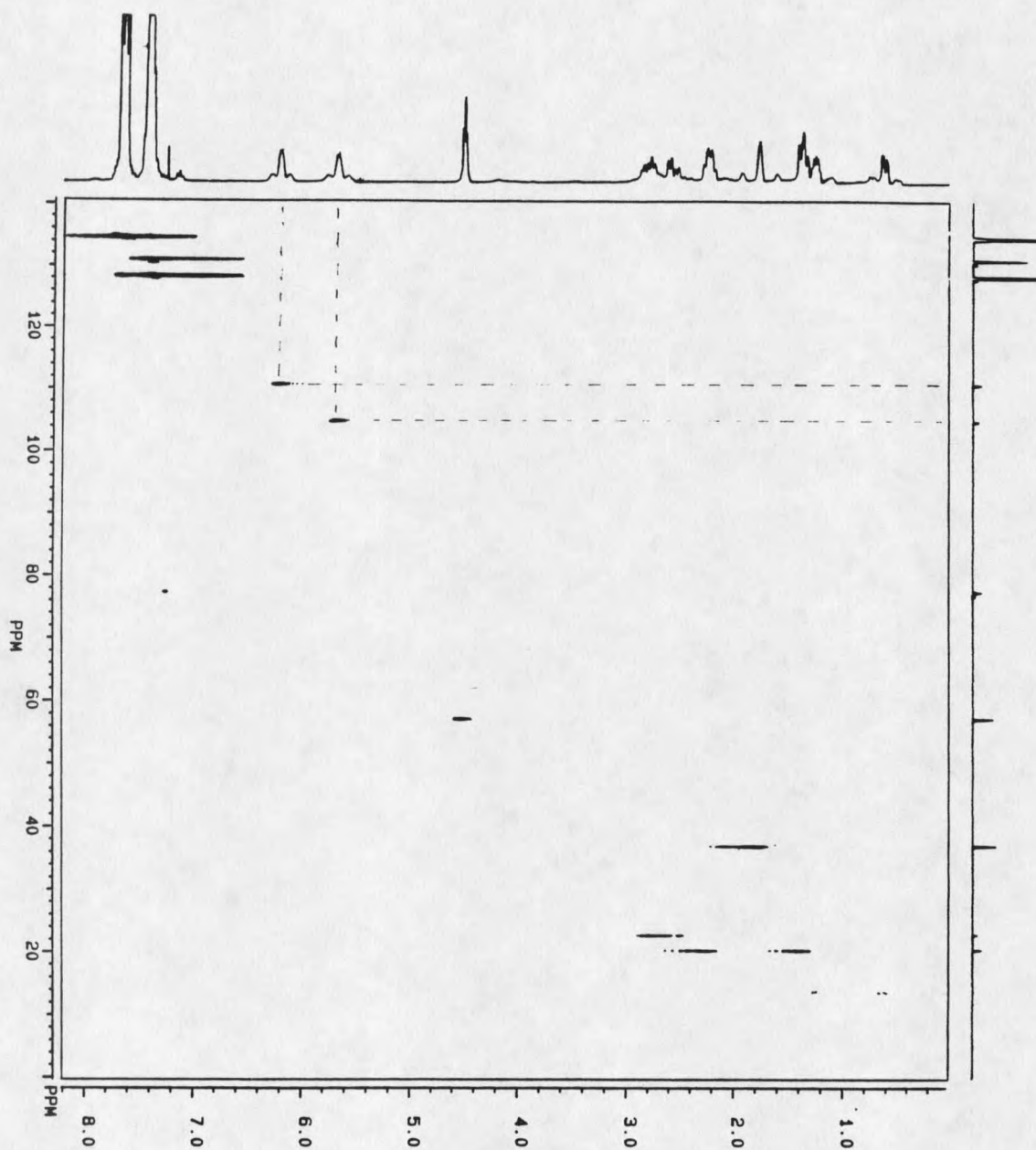
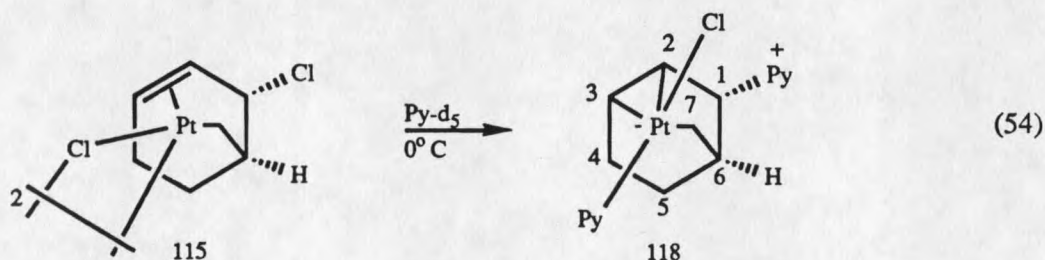


Figure 88. ^1H - ^{13}C Correlated (XHCORR) Spectrum of 117.

Reaction of **115** with pyridine had a marked effect on the complex, Equation 54. Complex **118** was formed as a yellow solution that decomposed over several days. The addition of 1 mL d_5 -pyridine at 0°C resulted in replacement of the chlorine. Furthermore, a large upfield chemical shift in the olefins to 53.9 and 57.2 ppm was observed, as seen in Figure 89. As a result of this chemical shift and large platinum-carbon coupling, the platinacyclopropane moiety in **118** is proposed. Additional evidence was garnered from ^{195}Pt NMR spectroscopy. A resonance at 1888 ppm signifies a Pt(IV) when compared to 641 ppm for complex **117**. Table 23 lists the NMR data for complex **118**. Assignments were made using two-dimensional NMR techniques. Comparison of ^{13}C NMR data of **118** and **117** shows a significant difference. Carbons 1,2 and 3 are of main interest. C-1 shifted downfield to 72.9 ppm from 57.0 ppm (to 6.2 from 4.5 in the ^1H spectrum) as a result of the attachment of pyridine. Additional evidence for a pyridine at C-1 comes from the six pyridine resonances in the ^{13}C spectrum (excluding solvent resonances). Integration of the spectrum exhibited the presence of two pyridines, one which is assigned to the ligand pyridine and the other on C-1. C-2 and C-3 in **118** resonate at 53.9 and 57.2 ppm with 377 and 342 Hertz platinum coupling. These can be compared to C-2 and C-3 in **117** which resonate at 104 ppm (97 Hertz platinum coupling) and 100 ppm (87 Hertz platinum coupling).



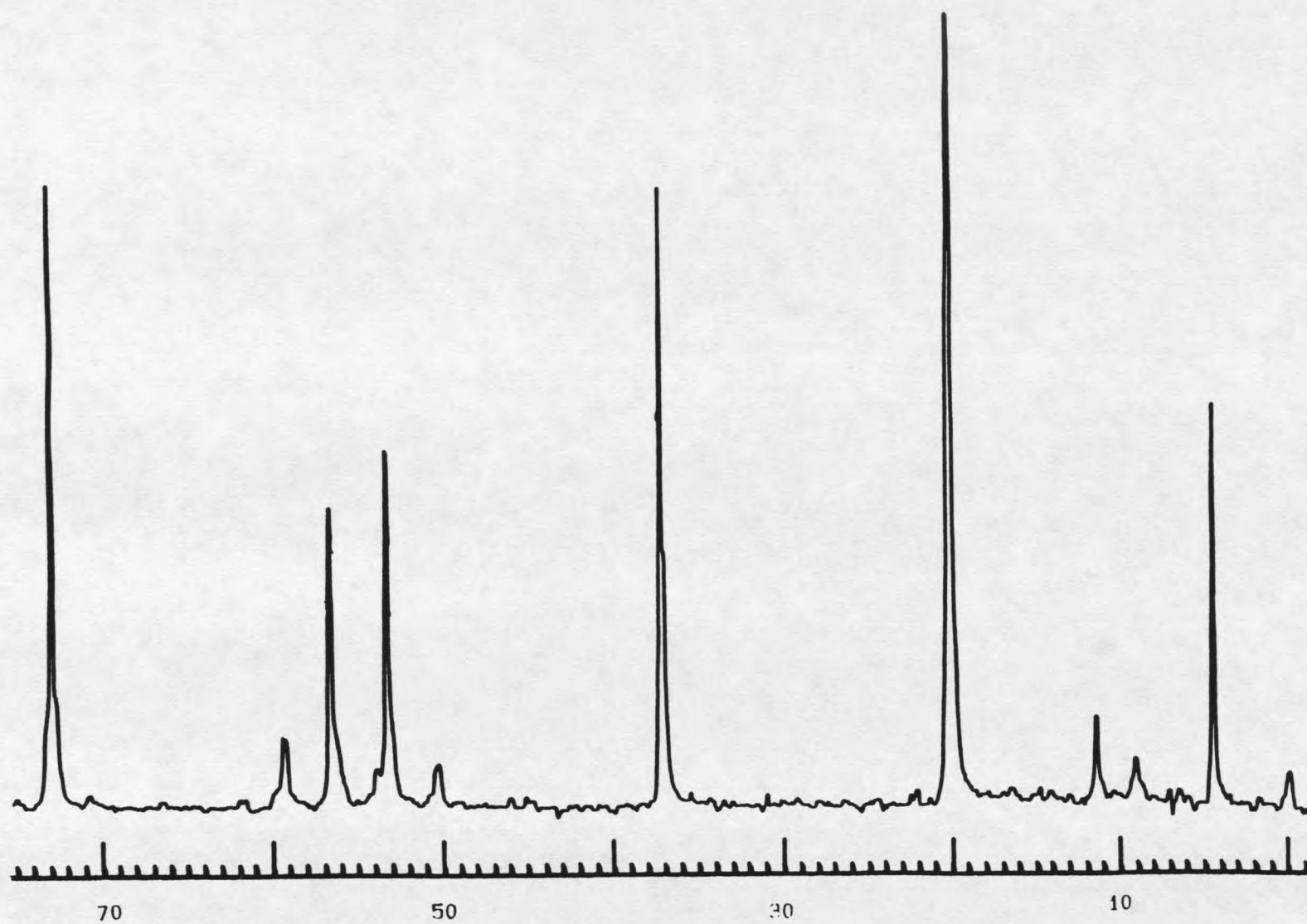


Figure 89. CPD ^{13}C NMR Spectrum of **118** (excluding Py resonances).

Table 23. NMR Data for Complex 118.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ **
1	72.9	40.7	6.24(dd)	0	4.7
2	53.9	377.2	4.00(dd)	88.0	
3	57.2	341.8	3.94(dt)	unres.	
4	20.0	unres.	2.30(m)	0	
5	20.0	unres.	2.55(m)	0	
			1.35(m)	0	
			0.90(m)	0	
6	37.3	27.9	1.86(brs)	63.4	4.7
7	4.5	577.7	1.80(d)	90.4	9.5
			2.70(ddd)	93.1	9.5
py!	125.9				
py!	128.1				
py!	138.2				
py!	143.8				
py!	145.1				
py!	150.8				

 ^{195}Pt NMR*** - 1888 ppm* Relative to Pyridine- d_5

** Coupling in Hertz

*** Relative to 1.0 M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25° C

() Multiplicity

! Pyridine Resonance on Complex

Complexes 117 and 118 represent the two bonding extremes of a platinum-olefin bond. Triphenylphosphine is an excellent trans labilizer, while pyridine is very poor. In the case of 117, electron density has moved from the platinum to the phosphine. This results in a loss of backbonding from the platinum d orbitals to the olefin π^* orbitals. Pyridine, on the other hand, does not withdraw electron density from the platinum as well. This enables platinum to backbond to the olefin resulting in the shielded carbons and large coupling.

Acetonitrile has an effect similar to pyridine, although not as extreme. Treatment of 115 with 1 mL CD_3CN at room temperature results in the formation of 119 as a yellow solution, Equation 55. Complex 119 is depicted as the platinum-olefin bonding extreme as

a result of NMR data listed in Table 24. C-2 and C-3 are shifted upfield and have large platinum coupling compared to analogous carbons in **117**. However, the ^{13}C NMR values still come within the range assigned to platinum-olefin bonds, (see Table 7, page 31). Further proof for a platinum-olefin bonding extreme comes from ^{195}Pt NMR spectroscopy. A resonance at 1172 ppm is within the range of a Pt(II). Replacement of the chlorine has evidently not occurred with acetonitrile. As can be seen in Table 24, C-1 NMR shifts resonate in the same region as did **117** with a chlorine attached (60.5 versus 57 ppm).

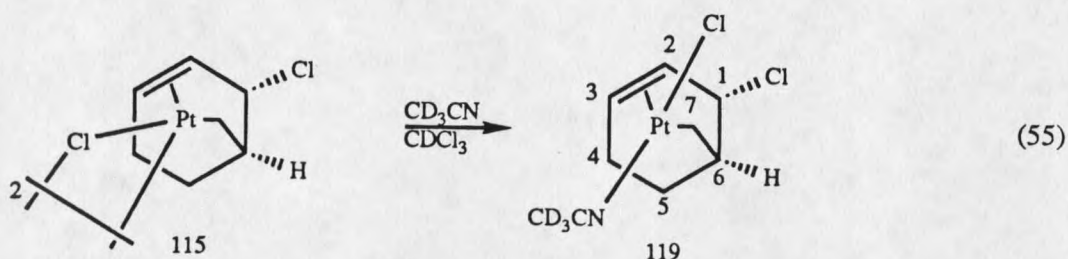


Table 24. NMR Data for Complex **119**.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ **
1	60.5	75.4	4.17(dd)	16.1	4.1, 4.3
2	80.3	240.6	4.07(m)	79.2	4.3, 6.3
3	79.1	237.0	4.42(dt)	71.1	6.3
4	21.6	38.3	2.00(m)- 2.30(m)	0 0	
5	21.4	10.8	1.15(m) 1.90(m)	0 0	
6	36.3	29.3	1.02(m)	94.4	
7	8.4	636.7	0.95(d) 1.55(ddd)	96.4 99.2	12.4 12.4

^{195}Pt NMR*** - 1172 ppm

* Relative to CD_3CN

** Coupling in Hertz

*** Relative to 1.0 M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25° C

() Multiplicity

Reaction of **115** with 1 mL CD_3OD for 30 minutes resulted in the formation of complex **120-d₇**, Equation 56. Complex **120-d₇** was formed as a colorless solution that is indefinitely stable. Figure 90 displays the ^{13}C NMR spectrum of **120**. The assignments for ^{13}C and ^1H data are listed in Table 25. As in the complexes discussed previously, two-dimensional NMR spectroscopy was used in the NMR assignments. Again a platinum-olefin is assigned from the NMR data. Proof of the stereochemistry at C-1 is derived, in part, from the proton coupling constant. A coupling of 4.3 Hertz between H-1 and H-6 is indicative of a trans stereochemistry.

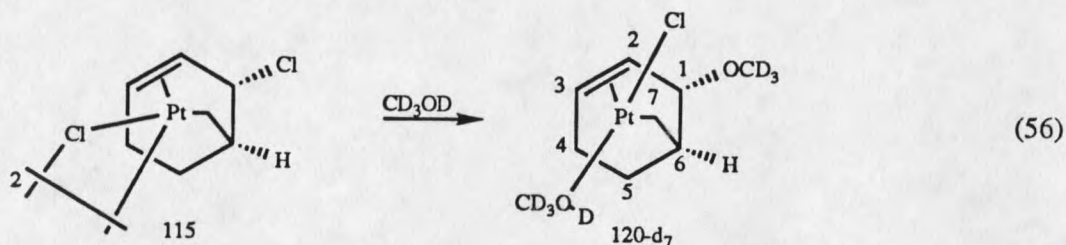


Table 25. NMR Data for Complex **120**.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ **
1	81.2	50.4	3.18(dd)	<10	3.8, 4.3
2	76.7	237.7	3.72(brs)	88.7	3.8
3	78.9	255.8	4.32(brs)	75.8	
4	22.0	40.2	1.80(m)	0	
			1.95(m)	0	
5	20.6	0	0.85(t)	0	
			1.50(m)	0	
6	32.3	31.5	0.65(brs)	113.5	
7	7.1	646.4	0.60(d)	92.5	9.1
			1.35(brdd)	103.9	9.1, 3.0
CD_3	55.8				

^{195}Pt NMR*** - 1245 ppm

* Relative to CD_3OD

** Coupling in Hertz

*** Relative to 1.0 M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25° C

() Multiplicity

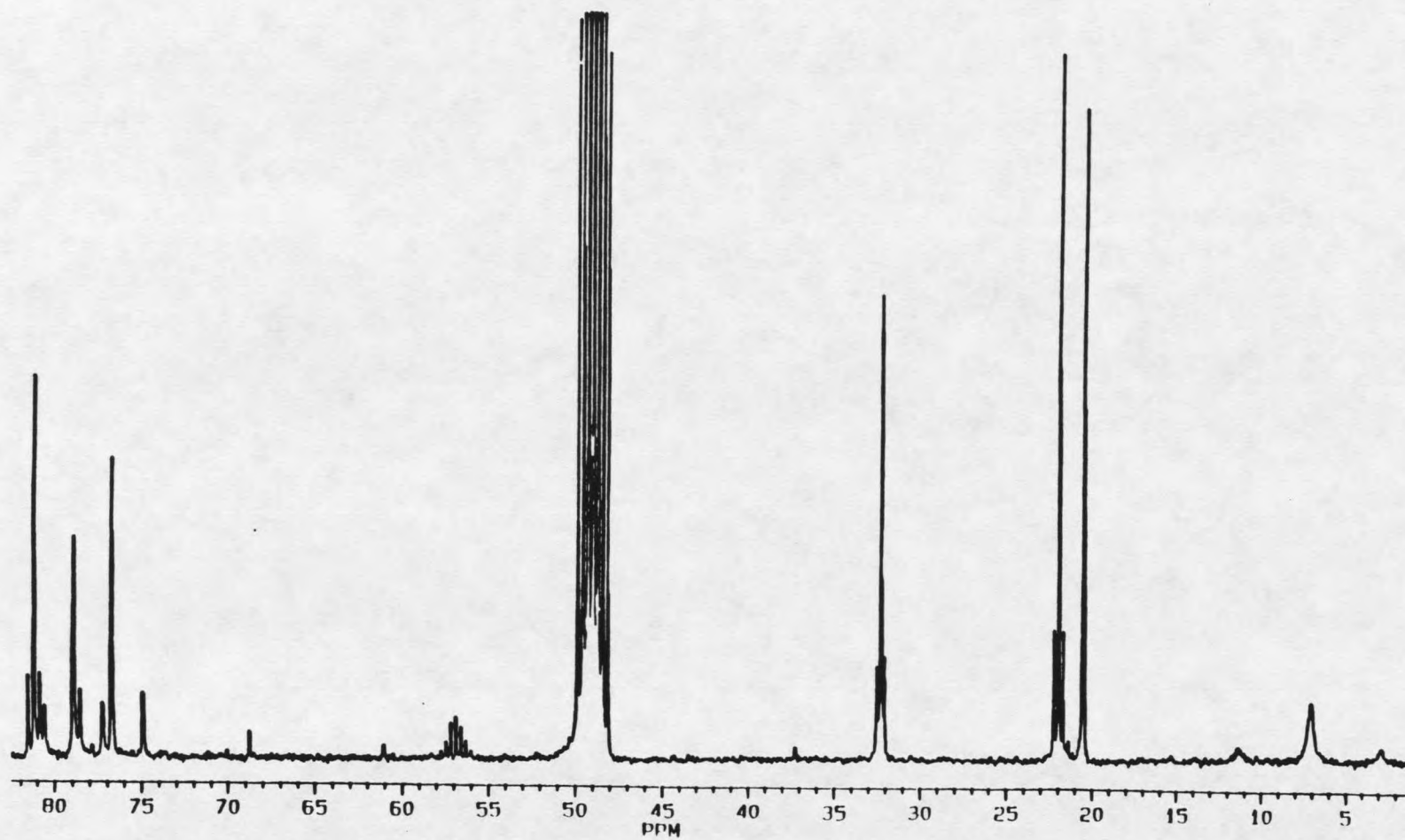
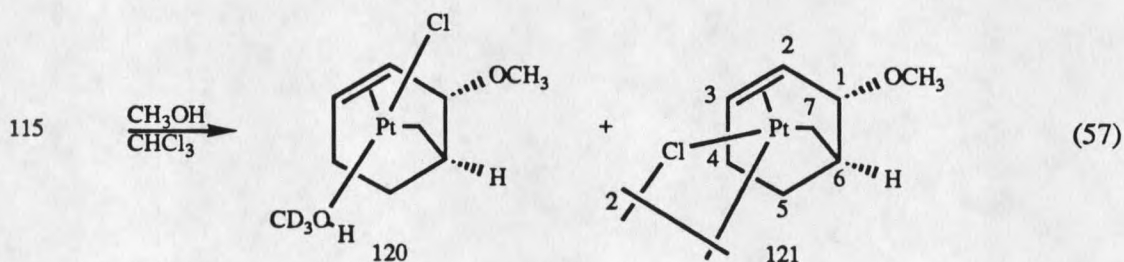


Figure 90. CPD ^{13}C NMR Spectrum of 120- d_7 .

Dissolution of **115** in 2 mL methanol and 2 mL chloroform followed by immediate rotoevaporation yielded two isomers, Equation 57. ^{13}C NMR data for complex **121** is listed in Table 26. Complex **121** results from modifying the concentration of methanol and time of reaction. It should be noted that addition of chloroform also increases the rate of dissolution of complex **115**. In the previous cases reaction of **115** with ligands, such as PPh_3 , resulted in complete formation of monomeric complexes. Formation of **121** occurs because methanol is a poor ligand compared to other ligands such as PPh_3 . However, prolonged exposure to methanol will eventually result in conversion to **120**. Proof for **121** comes from two parts. Comparison of ^{13}C NMR data in Table 26 and Table 21 (Complex **115**) shows very similar chemical shifts as a result of both **115** and **121** being dimers. A second test for **121** is reaction of triphenylphosphine with the mixture of **120** and **121**, Figure 91. Only one product is observed. This results from breaking the dimer in **121** and displacing the methanol ligand in **120**. NMR data for **122** is listed in Table 27. Complex **122** did not show any sharp $J_{\text{Pt,C}}$ coupling. However, the olefin resonances were broadened presumably because of the phosphorus. Hence, the Ph_3P ligand is assigned as trans to the olefin. Again data in Table 27 can be compared to that in Table 22, for the chlorine adduct **117**.



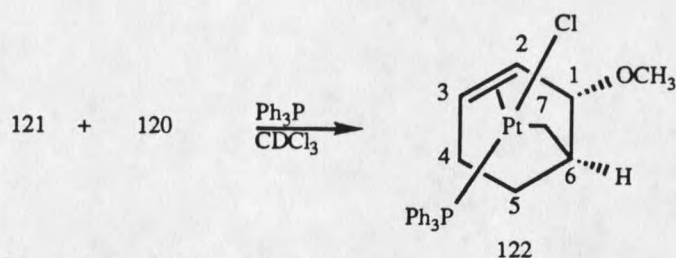


Figure 91. Formation of Complex 122.

Table 26. ^{13}C NMR Data for 121.

#	^{13}C ppm*	$J_{\text{P,C}}$ **
1	78.7	45.0
2	80.1	unres.
3	80.1	unres.
4	20.4	0
5	20.2	0
6	35.4	28.1
7	13.6	650.9
Me	58.3	0

* Relative to CDCl_3

** Coupling in Hertz

Table 27. ^1H and ^{13}C NMR Data for Complex 122.

#	^{13}C ppm*	$J_{\text{P,C}}$ **	^1H ppm*	$J_{\text{P,H}}$ **	$J_{\text{H,H}}$ **
1	77.3	38.6	3.70(dd)	0	4.3
2	104.6	109.2	5.70(brs)	57.4	
3	113.5	94.8	6.25(brs)	43.4	
4	23.3	20.0	2.58(dd)	0	
			2.76(m)	0	
5	19.6	0	1.28(t)	0	
			2.02(m)	0	
6	32.5	36.9	1.74(brs)	101.9	
7	11.1	618.4	0.44(d)	67.3	11.8
			1.11(brd)	81.6	
Me	57.4	0	3.36	0	12.0

* Relative to CDCl_3

** Coupling in Hertz

() Multiplicity

Ethanol could be used in place of methanol. Dissolution of **115** in 1 mL d_5 -ethanol yielded **123** as a colorless solution, Equation 58. Stirring for 30 minutes gave **123** as a single isomer. NMR data for complex **123** is listed in Table 28. Again two dimensional techniques were used to assign the structure. In both complexes **120** and **123**, the incoming alcohol bonds anti to the platinum. The steric bulk of platinum and its ligands are most likely the reason for this.

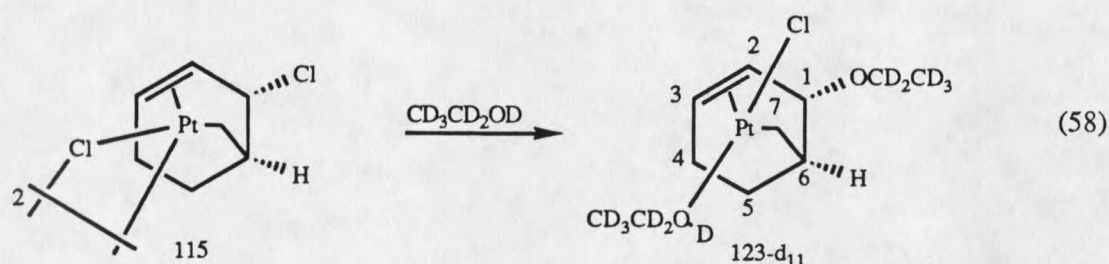


Table 28. ^1H and ^{13}C NMR Data for Complex **123**.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ **
1	79.2	51.1	3.68(dd)	0	4.3
2	77.2	273.3	4.24(brs)	90.0	
3	78.4	254.8	4.72(brs)	75.0	
4	21.7	39.8	2.20(m)-	0	
			2.60(m)	0	
5	20.5	0	1.35(m)	0	
			2.00(m)	0	
6	32.5	30.6	0.30(brs)	unres.	
7	6.9	640.2	0.40(d)	unres.	
			1.00(brs)	unres.	
CD_2	64.8	0			
CD_3	14.7				

* Relative to $\text{CD}_3\text{CD}_2\text{OD}$

** Coupling in Hertz

() Multiplicity

Figure 92 depicts a mechanism for the formation of **120**. Solvolysis of **115** results in the formation of **124**. Structure **124** is essentially the same as the π -allyl **125**. As a result of normal bond geometries the platinum is closer to C-3 than C-1, thus a partial positive charge occurs at C-1. Nucleophilic attack of methanol at C-1 followed by addition of another methanol as a ligand yields **120**. Loss of HCl, arising from the chlorine on C-1 and the proton on the incoming methanol, is also believed to occur in this process.

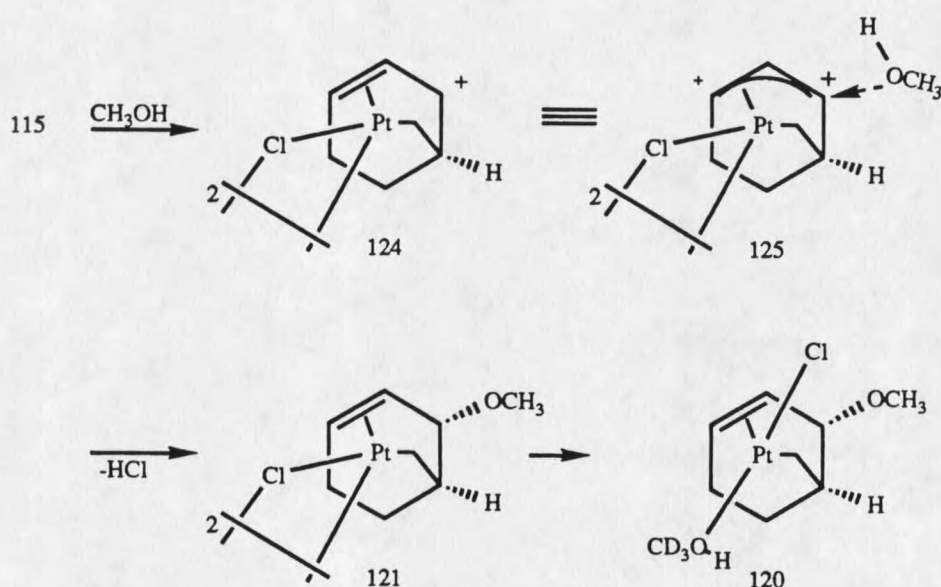
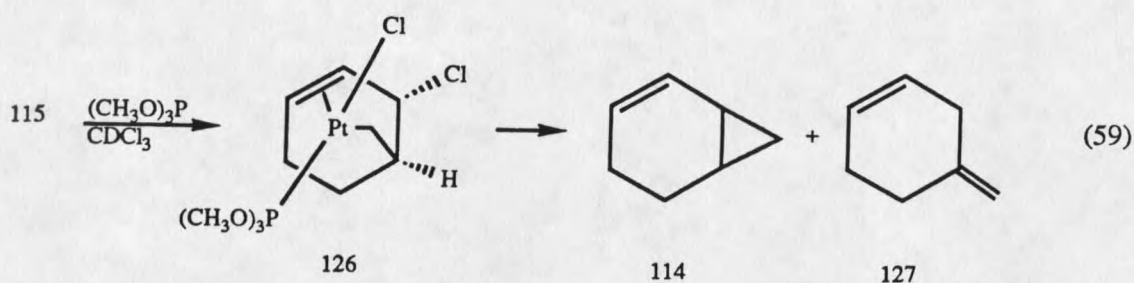


Figure 92. Mechanism for Formation of **120**.

Reaction of complex **115** with trimethylphosphite, $(\text{MeO})_3\text{P}$, led to the formation of **126**. However, decomposition began immediately to yield **114** and **127**, Equation 59. Complex **126** was deduced by ^1H NMR and compared to ^1H NMR data for **117**. Stirring for 24 hours led to complete formation of **114** and **127** in a 1:1.5 ratio, respectively. Comparison of NMR data for **127** to literature values proved the structure to be correct¹²⁵. Complex **117**, the Ph_3P adduct discussed earlier, also decomposes to **114** and **127**. However, decomposition is much slower. The reason for this difference is that $(\text{MeO})_3\text{P}$ is a better trans labilizer than Ph_3P .



Two mechanisms, an alpha and beta pathway, for decomposition of platinum complexes are generally accepted. These were discussed on pages 44-46. In order to deduce the mechanism for formation of 127, deuterium labelling was used. Figure 93 diagrams the expected labelling results for 127 when either an alpha or beta mechanism is followed. A beta mechanism would result in both deuterium atoms on the exocyclic methylene carbon, while an alpha mechanism would transfer one deuterium.

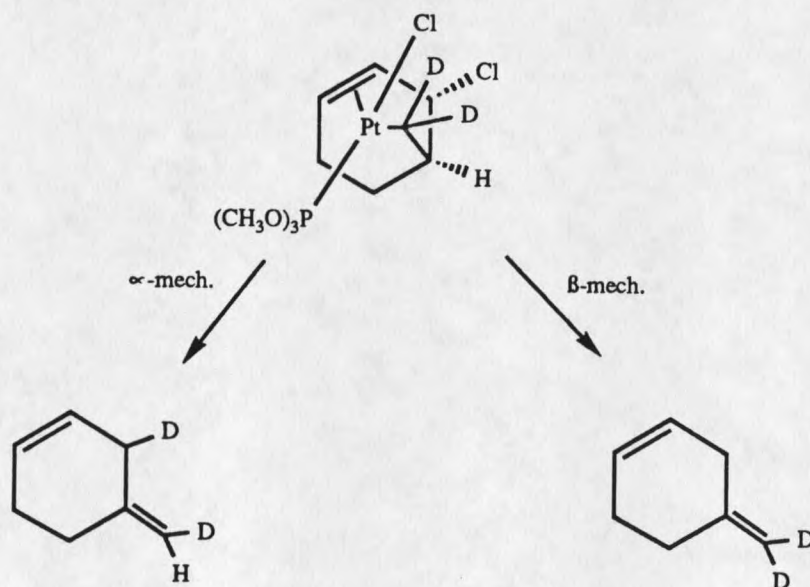


Figure 93. Expected Results for Alpha and Beta Pathways.

Reaction of cyclopropane **128** with Zeise's dimer resulted in formation of **129** as a white solid, Figure 94. ^2H NMR spectroscopy of **129** in CHCl_3 showed two resonances at 1.30 and 2.02 ppm. Since in the nondeuterated complex **115**, the protons resonate at 1.28 and 2.05 ppm, it would seem that **129** is assigned correctly. Reaction of **129** with trimethyl phosphite yielded **128** and **130**. ^1H , ^{13}C , and ^2H NMR spectroscopy were used to assign the deuterium atoms in **130**. Integration of the ^1H spectrum showed reduced area at the exocyclic methylene in **130**. Furthermore, deuterium coupling to the exocyclic methylene carbon was observed whereas no deuterium coupling was seen elsewhere in **130**. Finally, the ^2H spectrum gave a resonance at 4.7 which is assigned to the exocyclic methylene. Hence, it seems that a beta mechanism is employed in the formation of **127** and **130**.

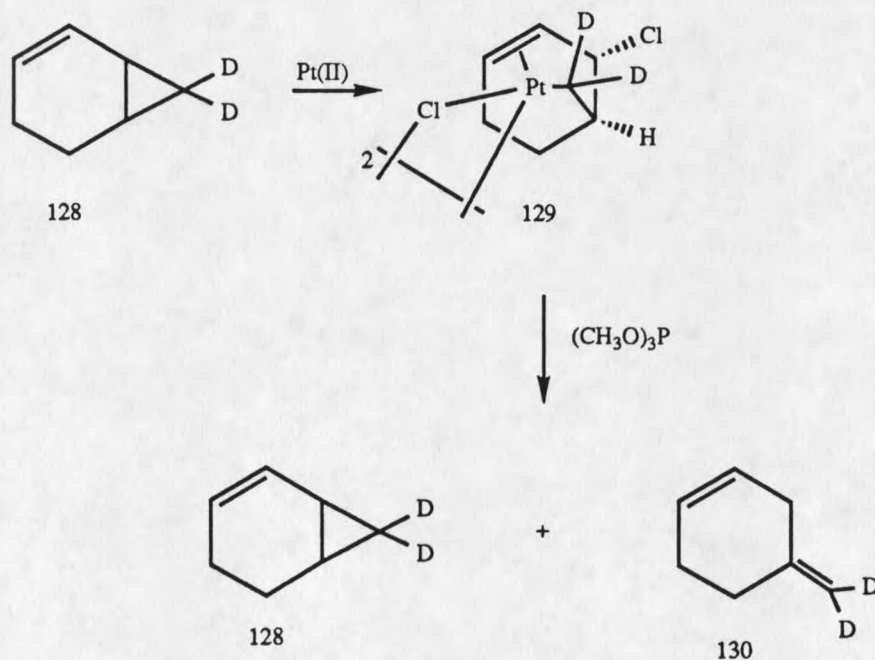


Figure 94. Deuterium Labelling Results in the Reaction of **129** with $(\text{MeO})_3\text{P}$.

A proposed mechanism for the formation of **114** and **127** from complex **115** is outlined in Figure 95. Formation of a coordinatively unsaturated platinacyclobutane can follow two pathways. In one route, reductive elimination yields cyclopropane **114**. In the second

pathway, abstraction of a beta hydride produces a π -allyl. At this point it would seem that two products would be possible. Transfer of the hydride to carbon a would lead to the observed product **127**. However, if the hydride is transferred to terminus b, 1-methyl-1,3-cyclohexadiene would be observed. The reason for formation of **127** over 1-methyl-1,3-cyclohexadiene was postulated by Johnson¹⁰⁶. Decomposition to olefins prefers formation along the least-substituted edge of the platinacyclobutane, thus leading to the less-substituted platinum-olefin complex.

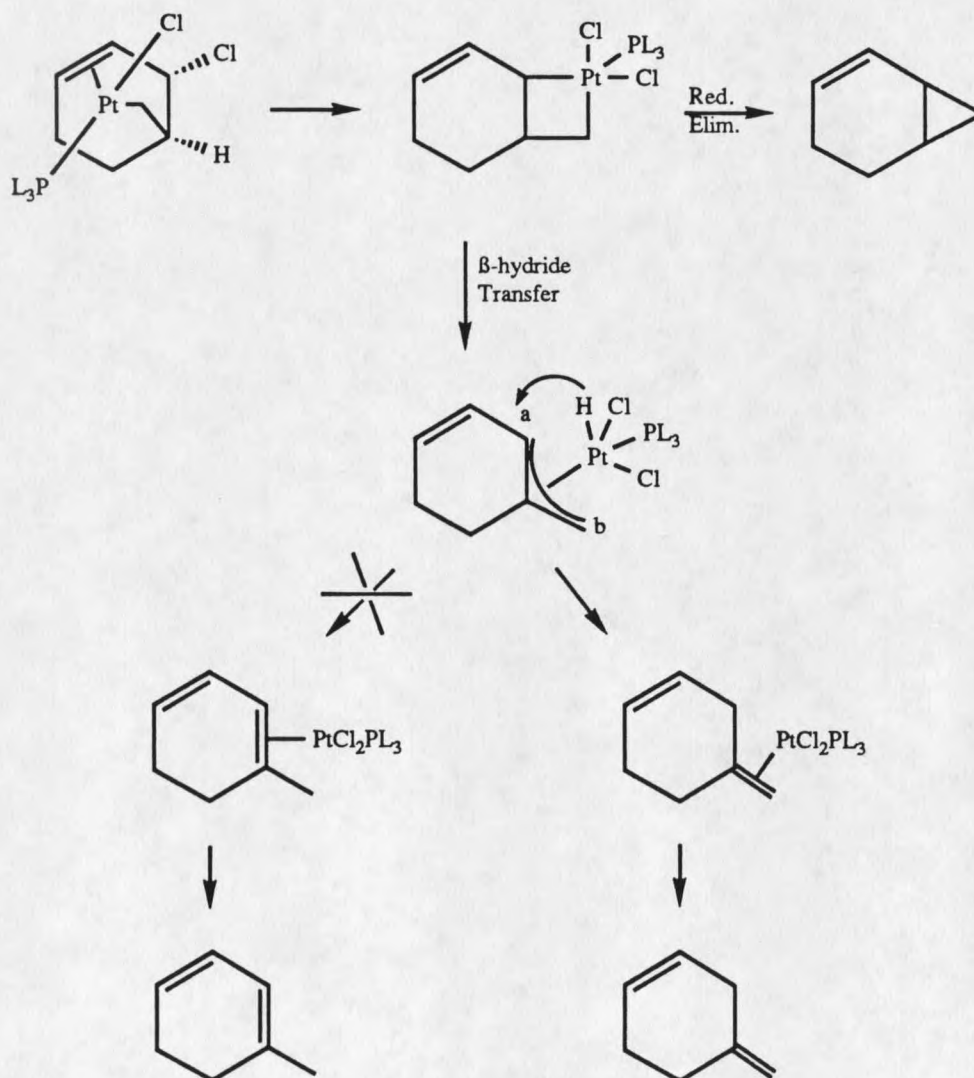


Figure 95. Mechanistic Pathway for the Formation of **114** and **127**.

Finally, Kurosawa, *et. al.*, discovered that the use of benzene suppressed chlorine transfer from a platinum to form a π -allyl (see pages 18 and 19). However, use of d_5 -benzene as a solvent in the reaction of **114**, followed by treatment with Ph_3P , gave complex **117**, Equation 60. NMR data for complex **117** in benzene is listed in Table 29. Comparison of **117** in benzene to CDCl_3 shows very close correlation.

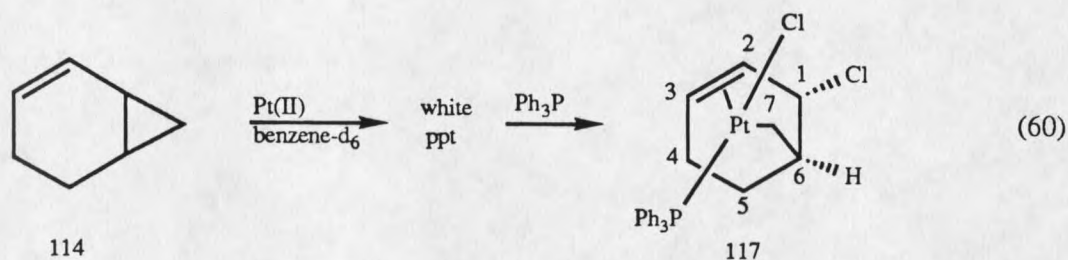


Table 29. ^1H and ^{13}C NMR Data for Complex **117** in Benzene.

#	^{13}C ppm*	$J_{\text{P,C}}$ **	^1H ppm*	$J_{\text{P,H}}$ **	$J_{\text{H,H}}$ **	$J_{\text{P,C}}$ **
1	57.2	84.1	4.34(brs)	0		
2	105.2	100.7	5.88(brs)	50.3		13.8
	105.3					
3	110.2	91.6	6.41(brs)	40.0		10.7
	110.8					
4	22.8	29.0	2.20(m)	0		
			2.63(m)	0		
5	20.7	0	1.16(m)	0		
			2.26(m)	0		
6	37.4	39.7	1.73(brs)	86.4		
7	13.7	615.0	0.65(d)	66.6	11.0	
			1.23(dd)	59.6	11.0	

* Relative to Benzene- d_6

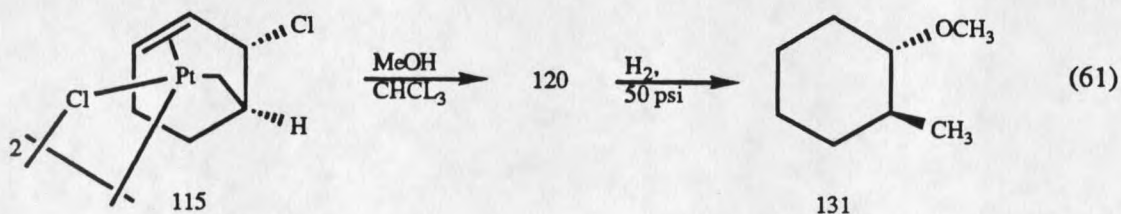
** Coupling in Hertz

() Multiplicity

Organic Transformations using Complex 115.

In the Statement of Problem, it was mentioned that one goal of this research was to develop organic products from bicyclo[X.1.0] systems. This section will discuss results in pursuit of this goal. Unless otherwise stated, complex 115 was used for all the transformations. The structure of 115 will be pictured in the first diagram and then referred to by number only. All compounds were characterized by one and two dimensional proton and carbon NMR techniques, as well as IR and mass spectroscopy. Yields are reported from the starting cyclopropane 114.

In the previous section, it was shown that reaction of 115 with methanol yielded the complex 120, Equation 61. Treatment of 120 with hydrogen at 50 psi produced 131 in 84.3 % isolated yield. The stereochemistry of 131 was deduced by ^1H NMR spectroscopy and comparison to analogous compounds¹²⁶. Furthermore, 131 could be synthesized independently by methylation of trans-2-methylcyclohexanol. NMR data for products resulting from both procedures exhibited identical resonances. A H-H coupling constant of 9.1 Hertz between the carbinol and methine protons, which is indicative of a trans stereochemistry, was observed. Ethanol and isopropanol were also used producing similar results, Figure 96. Proton coupling constants in the nine Hertz range were observed in each case, signifying a trans stereochemistry. Workup of the reactions was very easy. Chromatography with silica gel and diethyl ether resulted in products that gave very clean NMR spectra.



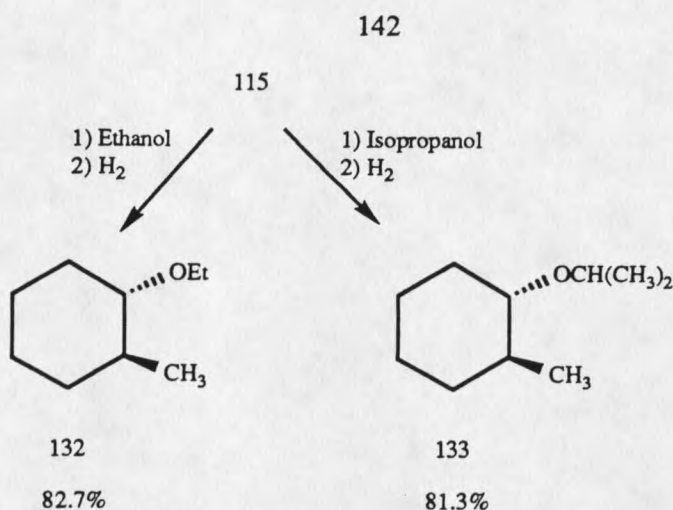


Figure 96. Formation of 132 and 133.

A suggested mechanism for the formation of the above products is diagrammed in Figure 97. Oxidative addition of hydrogen leads to hydrogenation of the olefin. Addition of another molecule of hydrogen followed by reductive elimination yields the observed products. An alternative to this mechanism involves reductive elimination of the platinum-carbon sigma bond occurring before hydrogenation of the alkene. Exactly what the ligands are on the final platinum species is also unknown. In the experiment, the platinum was produced as a black precipitate and characterization was not attempted.

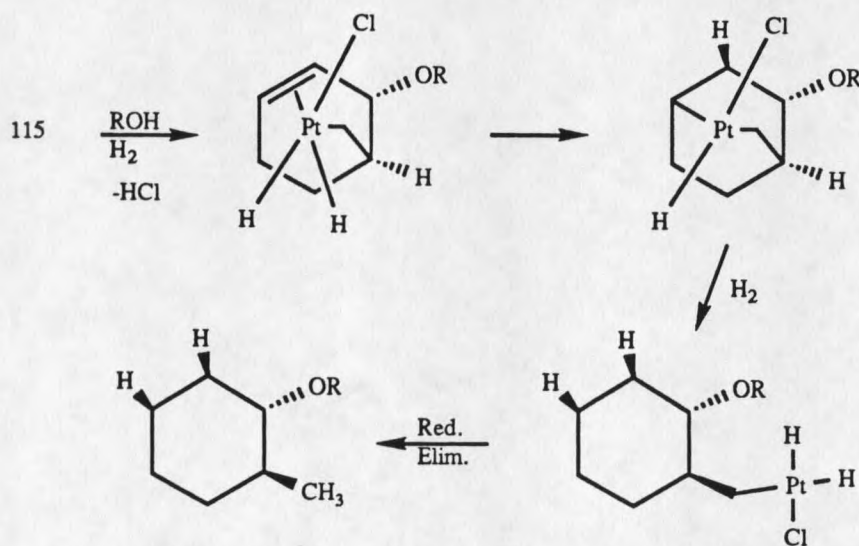
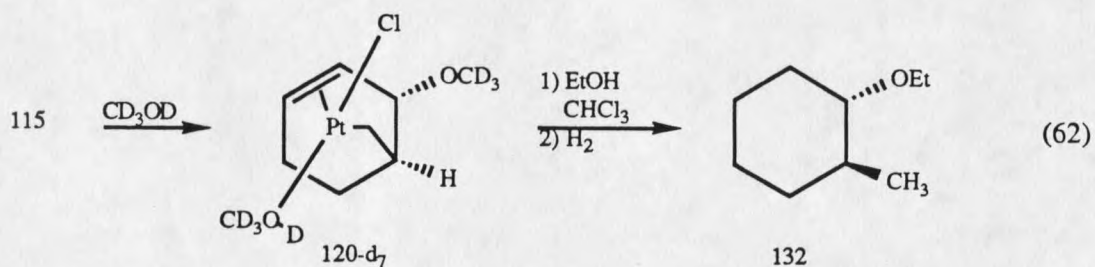


Figure 97. Mechanism for the Formation of 131-133.

The observed stereospecific production of compounds **131-133** further supports the stereochemical assignment in complex **120**. Further proof that the incoming nucleophile prefers an anti relationship to the platinum is shown in Equation 62. Reaction of **115** with CD_3OD gave complex **120**. Removal of the solvent methanol and treatment with ethanol and hydrogen yielded **132**. Mass spectroscopy and ^1H NMR showed the trans ethoxy functionality to be present. Therefore, it would seem that the platinum moiety, with its steric bulk, has very good directing capabilities.



Even though the reaction with hydrogen produces excellent results, the olefin functionality has been lost. Use of triphenylphosphine instead of hydrogen preserved the olefin and resulted in formation of substituted cyclohexene products, Figure 98. Stirring at room temperature for 28 hours produced **134-136**. A proton coupling constant of 6.4 Hertz for **134** was observed between the methine and carbinol protons. This is indicative of a trans stereochemistry when compared to analogous compounds in the literature¹²⁷. In the reactions in Figure 98, an orange platinum precipitate was formed as a by product. Again no attempts were made to characterize it.

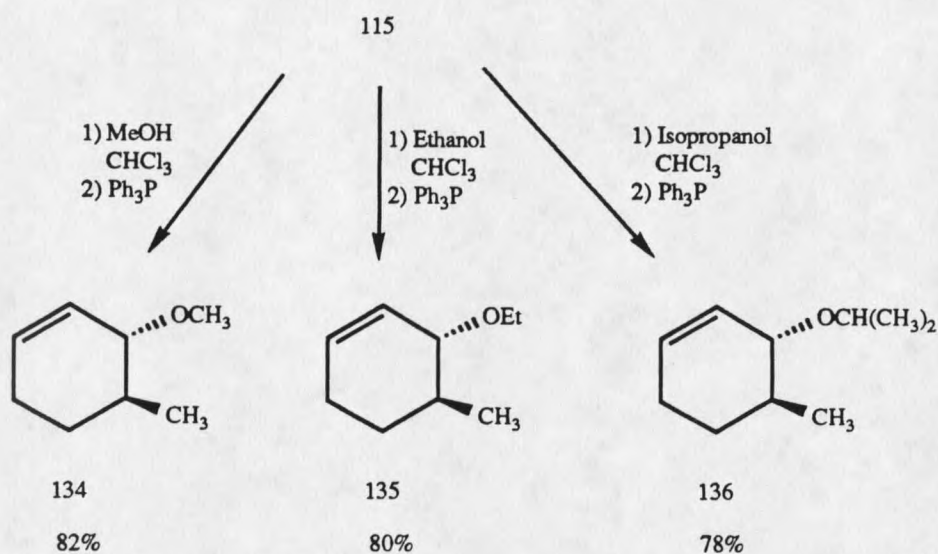
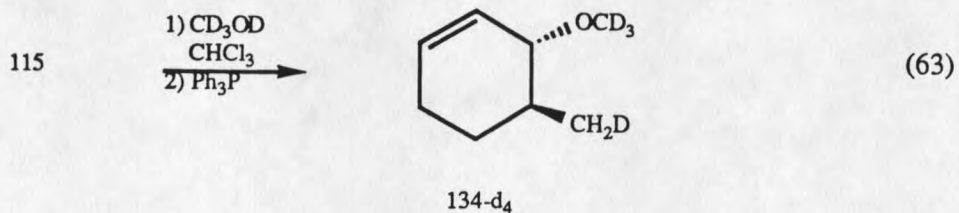


Figure 98. Formation of 134-136.

Determination of the proton source in the formation of the methyl group was done with the use of CD₃OD. Reaction of 115 with CD₃OD and triphenylphosphine yielded 134-d₄, Equation 63. The structure of compound 134-d₄ was assigned using ¹H, ²H, ¹³C NMR and mass spectroscopy. For example, in the ²H NMR spectrum, a resonance appeared at 1.0 ppm due to the CH₂D, while the OCD₃ resonated at 3.4 ppm and has three times the intensity of the 1.0 ppm resonance. A mechanism for the formation of 134 is postulated in Figure 99. Monitoring the reaction by ¹H NMR spectroscopy revealed the formation of 122-d₃ from 120-d₇. Oxidative addition of DCl (which results upon formation of 120) is preceded by breaking of the platinum-olefin bond. Reductive elimination will then give 134-d₄. Again the alternative is reductive elimination occurring before breaking of the platinum-olefin bond.



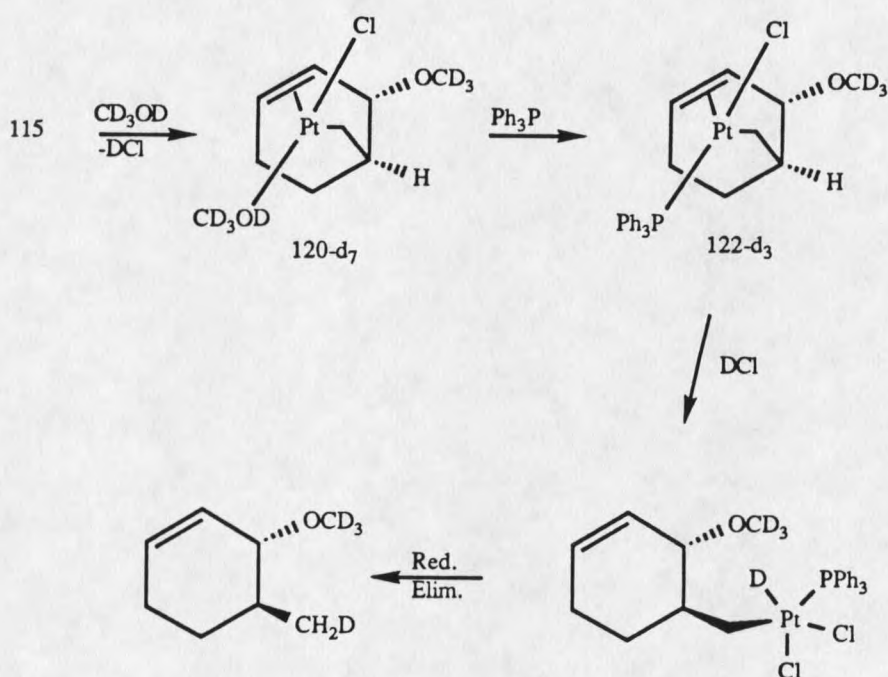


Figure 99. Mechanism for the Formation of **134**.

Functionality at the platinum-carbon sigma bond has so far been limited to production of a methyl group. Reaction with carbon monoxide could theoretically alter this by insertion of CO into the platinum-methylene bond. Complex **115** was thus treated with 2 mL methanol and 3 mL chloroform, followed by carbon monoxide at 325 psi. Reaction at room temperature for 4-5 days gave the products shown in Figure 100. Workup of the reaction was quite simple and accomplished by chromatography on silica gel with diethyl ether. The resulting oil displayed very clean NMR spectra. The ester moiety was deduced from a carbonyl band at 1732.4 cm^{-1} in the IR spectrum. Further verification of the ester was made by ^{13}C NMR spectroscopy. Resonances at 173.4, 172.7 and 172.9 ppm are indicative of the three ester carbonyls. GCMS verified the molecular weights as well the ratios of products. Integration of the GC and ^{13}C NMR spectra furnished the ratios of the products. Assignments of stereochemistry were achieved using one and two dimensional NMR techniques. Using proton-carbon (XHCORR) correlations, the resonances in the proton NMR

could be assigned to the major and minor isomers. The stereochemistry and proton connectivity were then deduced by decoupling and two dimensional proton (COSY) techniques. For example, **137** showed a vicinal coupling constant of 6.25 Hertz between H-1 and H-6. However, **138** and **139** exhibited vicinal coupling of H-1 to H-2 and H-6 but not to H-4. A disproportionate ratio of **138** and **139** was observed, however, a distinction between the two was not made.

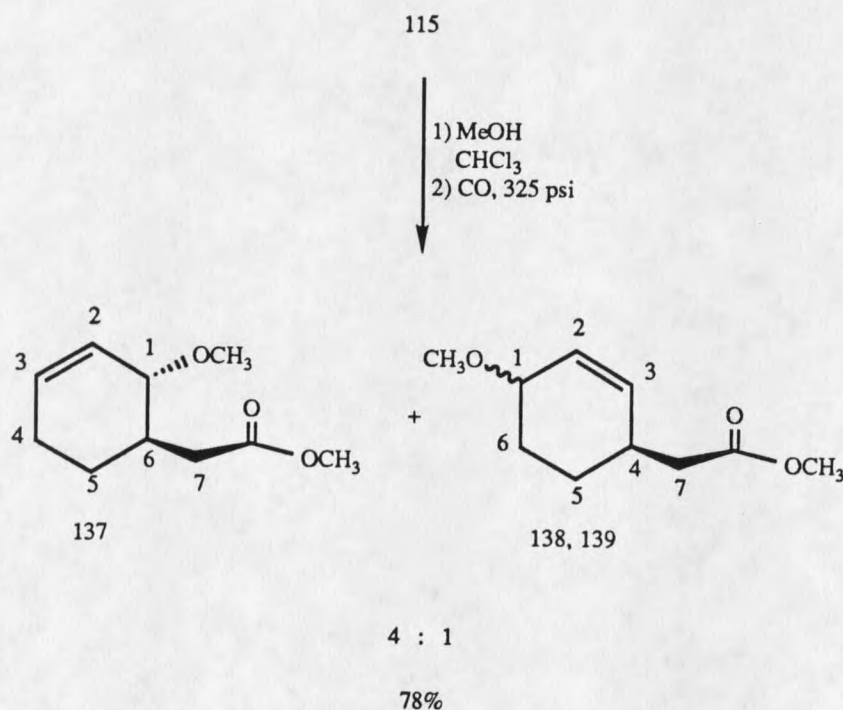


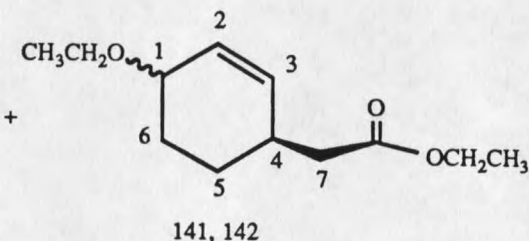
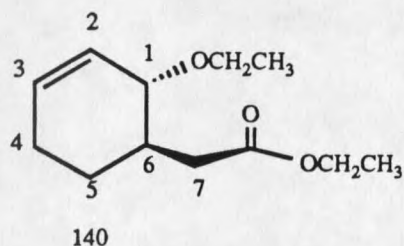
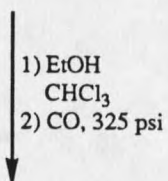
Figure 100. Formation of **137-139** by Esterification of **115**.

Formation of the ester functionality is a significant achievement in platinum chemistry. Carbon-carbon bond formation with platinum is generally quite difficult. Even though three isomers were produced reasonable selectivity was observed. A few points should be made about the reaction. The pressure under which the reaction is run is important. Pressures less than 325 psi CO result in intractable mixtures. The amount of methanol is also important. Use of 3 mL, as compared to 2 mL methanol, increases the amount of **138** and **139**

produced. However, enough methanol must be used in order to replace the chlorine. Although elevated pressure is used, the conditions are actually quite mild. Normally, vigorous conditions must be used in order to accomplish esterification reactions with platinum, as shown in Equation 64¹²⁸. In this example undesirably high temperatures and pressures were used. Esterification was also accomplished in the presence of ethanol as shown in Figure 101. Assignments of the structures of the compounds were made using the same techniques as in the methanol reaction.



115



4.1 : 1

77%

Figure 101. Esterification of 115 using Ethanol.

A mechanism for the formation of the above esters is proposed in Figure 102. As described earlier, addition of methanol to **115** forms complex **120**. In the presence of carbon monoxide the methanol ligand can be replaced by CO. The next step is migratory insertion of the methylene into a CO-platinum bond which is followed by addition of a second CO. Attack of methanol can occur in several ways which were outlined on page 8. Figure 102 depicts one theory in which attack by methanol at the carbonyl carbon results in formation of a platinum-olefin bonded ester. Formation of **138** and **139** can occur by generation of a π -allyl complex. Attack of methanol will then occur at the terminus farthest from the ester moiety as a result of steric effects.

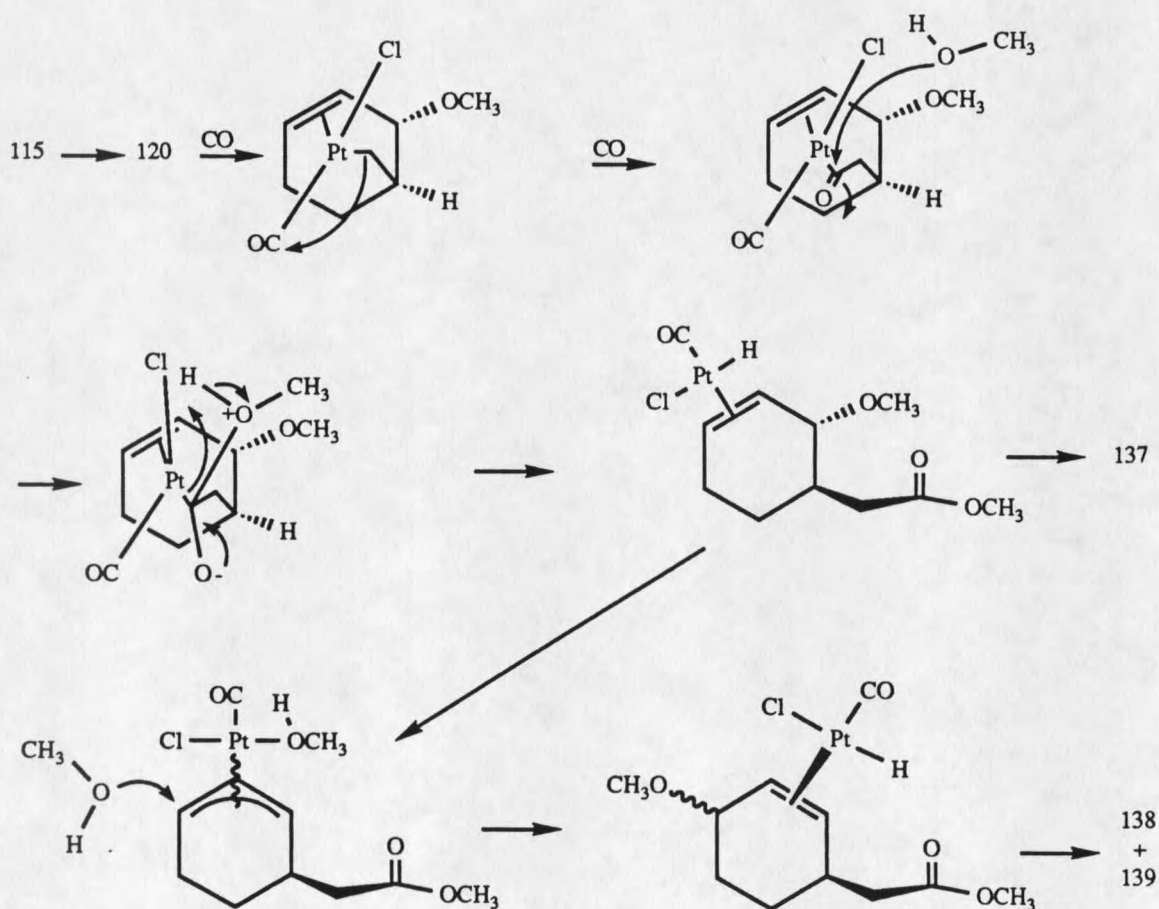


Figure 102. Proposed Mechanism for the Formation of **137**, **138** and **139**.

Complex **115** can also be reacted with carbon monoxide with only 5 equivalents of alcohol present. Formation of an equal mixture of olefins was observed, as shown in Figure 103. In the case of **143** and **144** mass spectroscopy revealed a molecular weight of 154. Additionally, proton and carbon NMR spectroscopy exhibited only one methoxy resonance which is assigned to the ester. IR spectroscopy verified the presence of the ester with a carbonyl band at 1732.8 cm^{-1} . Moreover, two resonances at 173.3 and 173.1 ppm for the carbonyls were present in the ^{13}C NMR spectrum.

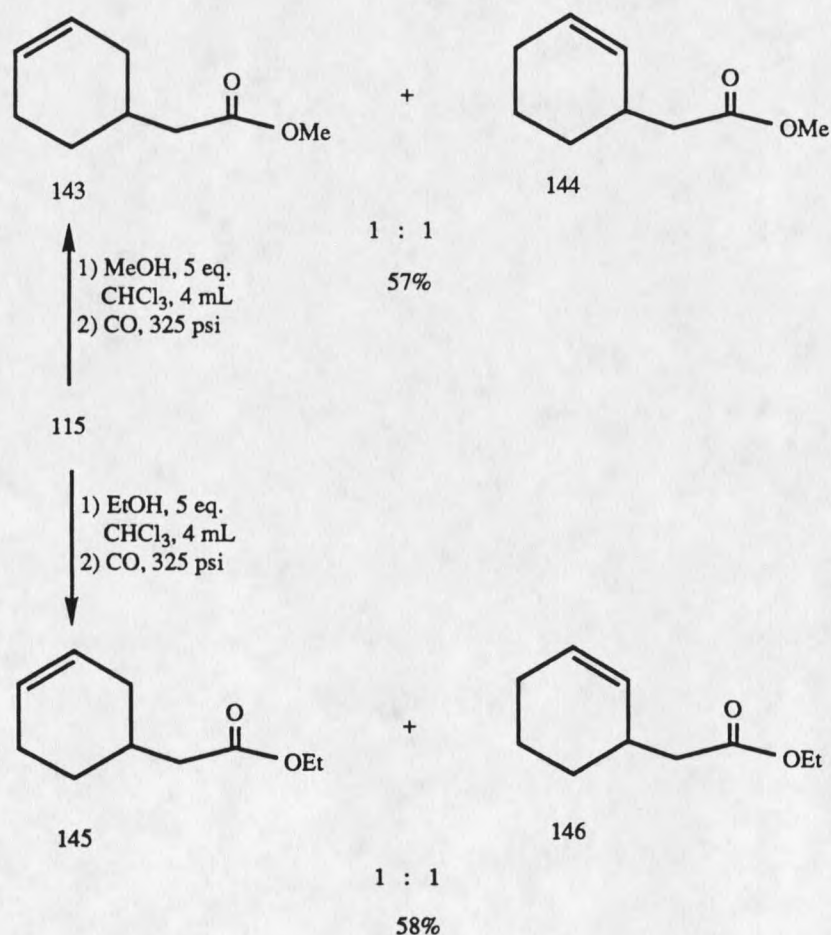


Figure 103. Formation of **143**, **144**, **145** and **146**.

A mechanism for the formation of the above esters is diagrammed in Figure 104. NMR experiments showed that replacement of the chlorine does not take place with only 5 equivalents of methanol. The first steps are similar to the mechanism proposed in Figure 102, although formation of a platinum π -allyl from a vinyl chloride is much easier. Upon formation of the π -allyl a new pathway is suggested. With only small amounts of alcohol present, transfer of a hydride to either terminus of the π -allyl is prevalent. Steric considerations are evidently not in effect when a smaller group such as a proton is transferred. Furthermore, the hydride is most likely coming from the platinum and attacking the positively-charged π -allyl.

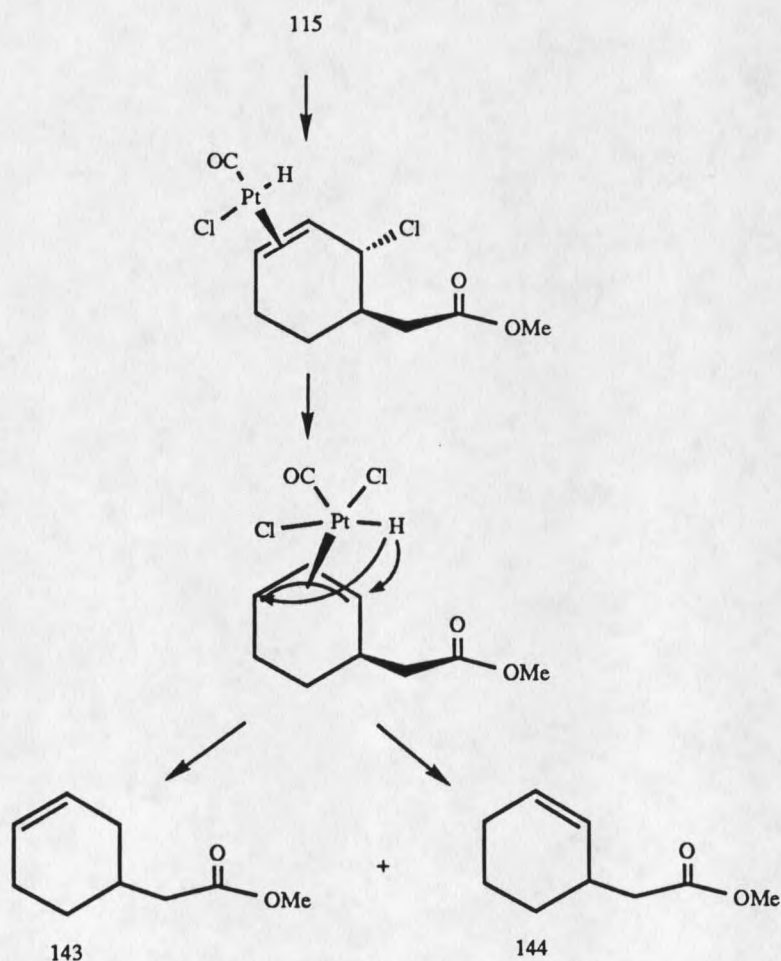


Figure 104. Proposed Mechanism for the Formation of 143-146.

With the replacement of the chlorine in **115** by alcohols, acids were potential reagents as well. Treatment of **115** with acetic acid in an aqueous solution followed by Ph_3P yielded **147** and **148**, Figure 105. Assignments of the structures **147** and **148** were accomplished by ^1H NMR spectroscopy. H-1 in **148** was coupled only to H-2 whereas H-1 in **147** was coupled to H-6 and H-2. Integration of the ^1H NMR spectrum showed **147** to be the major isomer. Addition of acetone, water and chloroform were necessary to solubilize **115**. However, formation of the exocyclic methylene was achieved by removal of all the aqueous solution before addition of the Ph_3P .

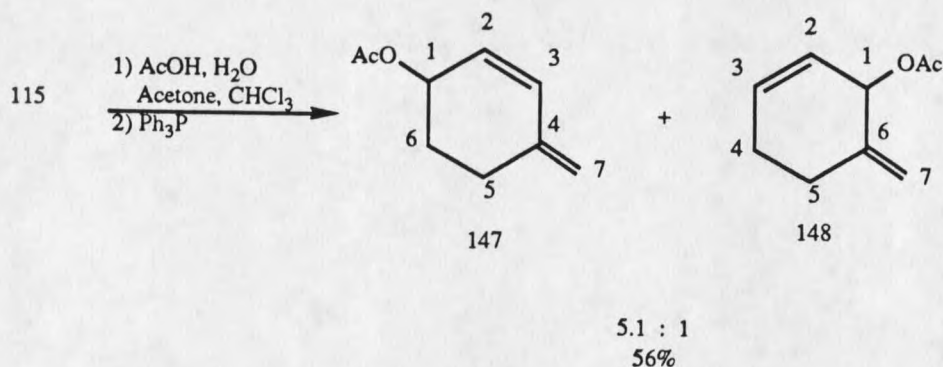
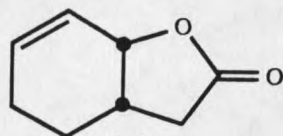
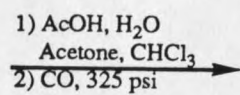


Figure 105. Formation of **147** and **148**.

Reaction of **115** in an aqueous solution with carbon monoxide resulted in formation of **149** as shown in Equation 65. Complete spectroscopic analysis and comparison to literature values¹²⁹ established **149** as a lactone with *cis* stereochemistry. Formation of **149** is postulated as shown in Figure 106. Generation of the anhydride can be accomplished in much the same way as the previously discussed esters. Hydrolysis of the anhydride followed by $\text{S}_{\text{N}}2$ attack yields **149**.

115



(65)

149

84%

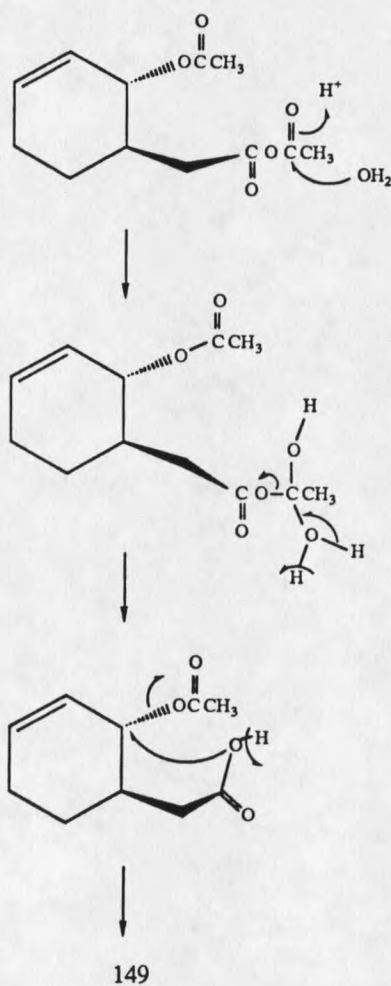


Figure 106. Mechanism for the Formation of 149.

Reaction of **115** with only water, acetone and carbon monoxide gave the results shown in Figure 107. Structures of the acids were not rigorously determined by two dimensional NMR spectroscopy, but rather the NMR data was compared to the ester results.

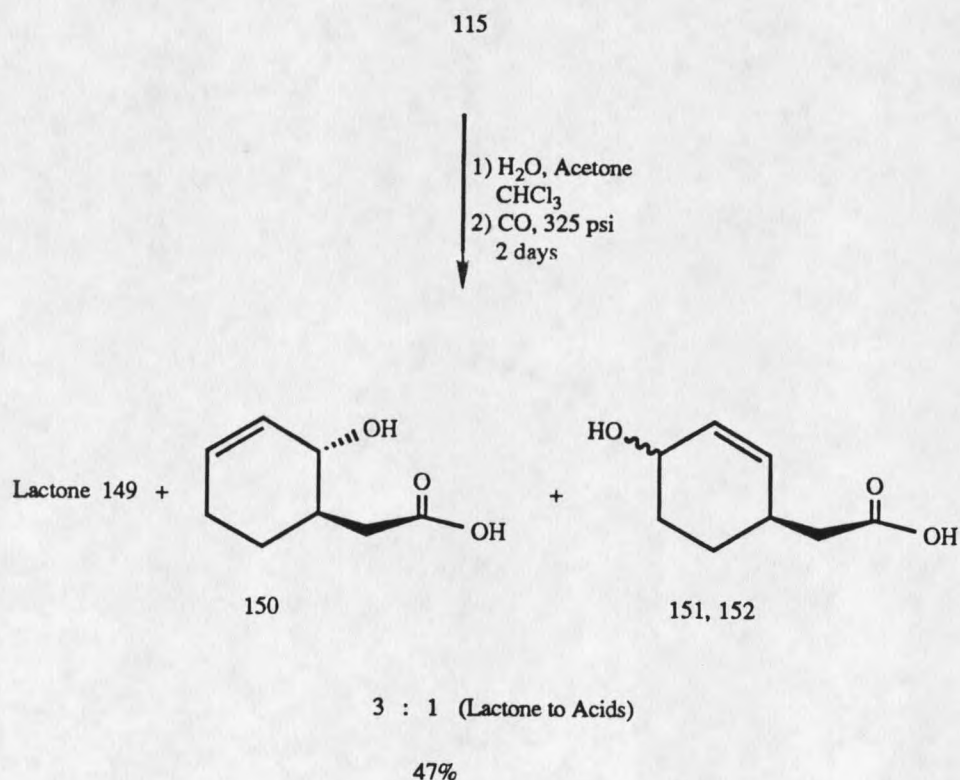
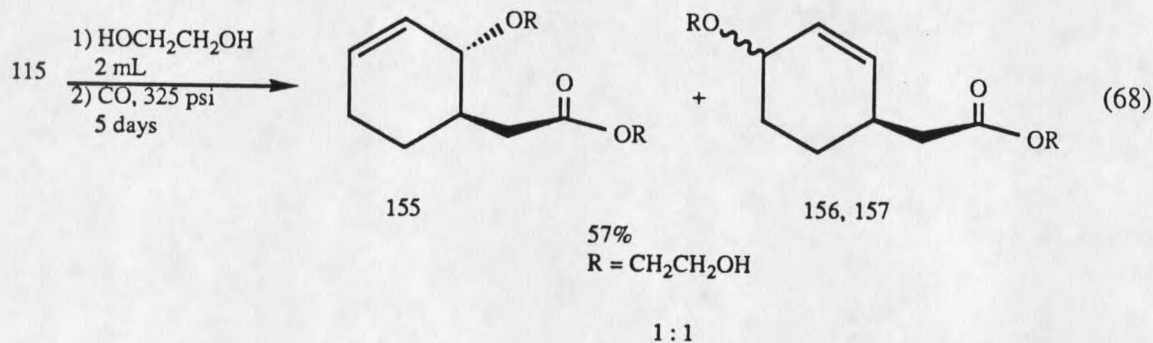
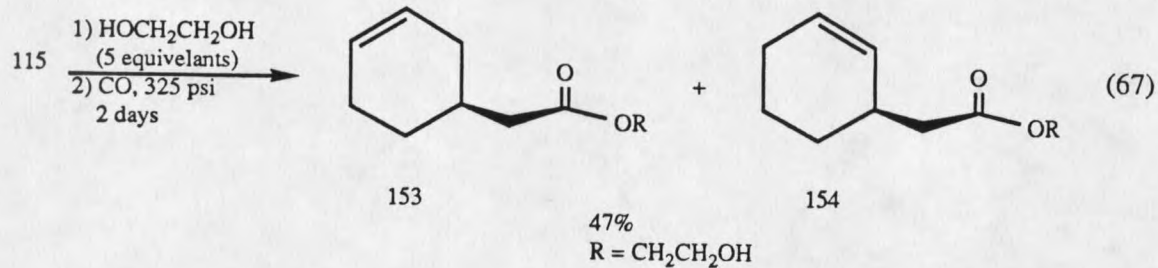
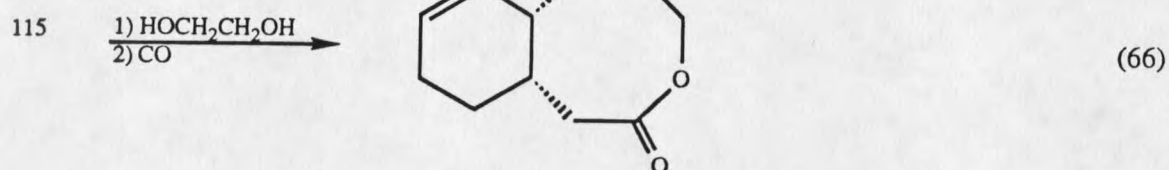


Figure 107. Formation of Acids **150-152**.

With the formation of lactone **149**, the possibility exists for further cyclizations. Reaction with di-alcohols could lead to cyclizations such as those in Equation 66. Initially the experiment was run with a limited amount of ethylene glycol. As expected, a mixture of the olefins **153** and **154** was produced, Equation 67. Increasing the amount of ethylene glycol and adding water yielded the products shown in Equation 68. Hence, it would seem that cyclizations of the type presented in Equation 66 are unattainable.

154



Expansion of the Bicyclo-vinylcyclopropane System

Reaction of bicyclo[3.1.0]hex-2-ene (158) with Zeise's dimer at room temperature produced 159 as a white solid, Equation 69. Shown in Figure 108 is the ¹³C NMR spectrum of 159 and the numerical data is listed in Table 30. Reaction of bicyclo[5.1.0]oct-2-ene

(160) with Zeise's dimer at room temperature yielded **161** as a white solid, Equation 70. NMR data for **161** is listed in Table 31. Comparison of data for **159** and **161** to **115** (Table 21) reveals very good correlation. Complex **161** also produces chemistry similar to **115**. Reaction of **161** with CD_3CN produced **162**, Equation 71. Figure 109 displays the ^{13}C NMR spectrum for **162** while Table 32 lists the NMR data for **162**.

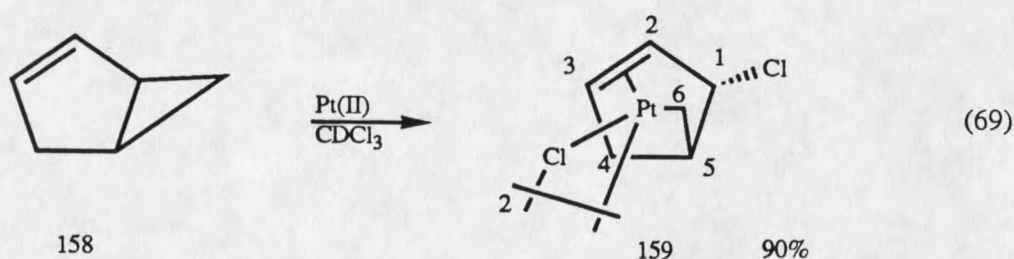


Table 30. NMR Data for Complex **159**.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ **	$J_{\text{H,H}}$ **
1	64.9	61.0	4.46(brs)	unres.	3.8, 4.3
2	83.0	305.2	4.28(brs)	87.2	
3	87.3	300.6	4.43(brs)	unres.	
4	38.7	0	1.69(dd)	0	13.6
			1.97(d)	0	13.6
5	44.5	<10	1.16(brs)	80.5	
6	25.6	671.4	0.76(brs)	113.2	
			1.45(d)	106.2	8.1

^{195}Pt NMR*** - Major = 1087 (broad), Minor = 1109 (broad) ppm

* Relative to CD_3Cl

** Coupling in Hertz

*** Relative to 1.0 M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25°C

() Multiplicity

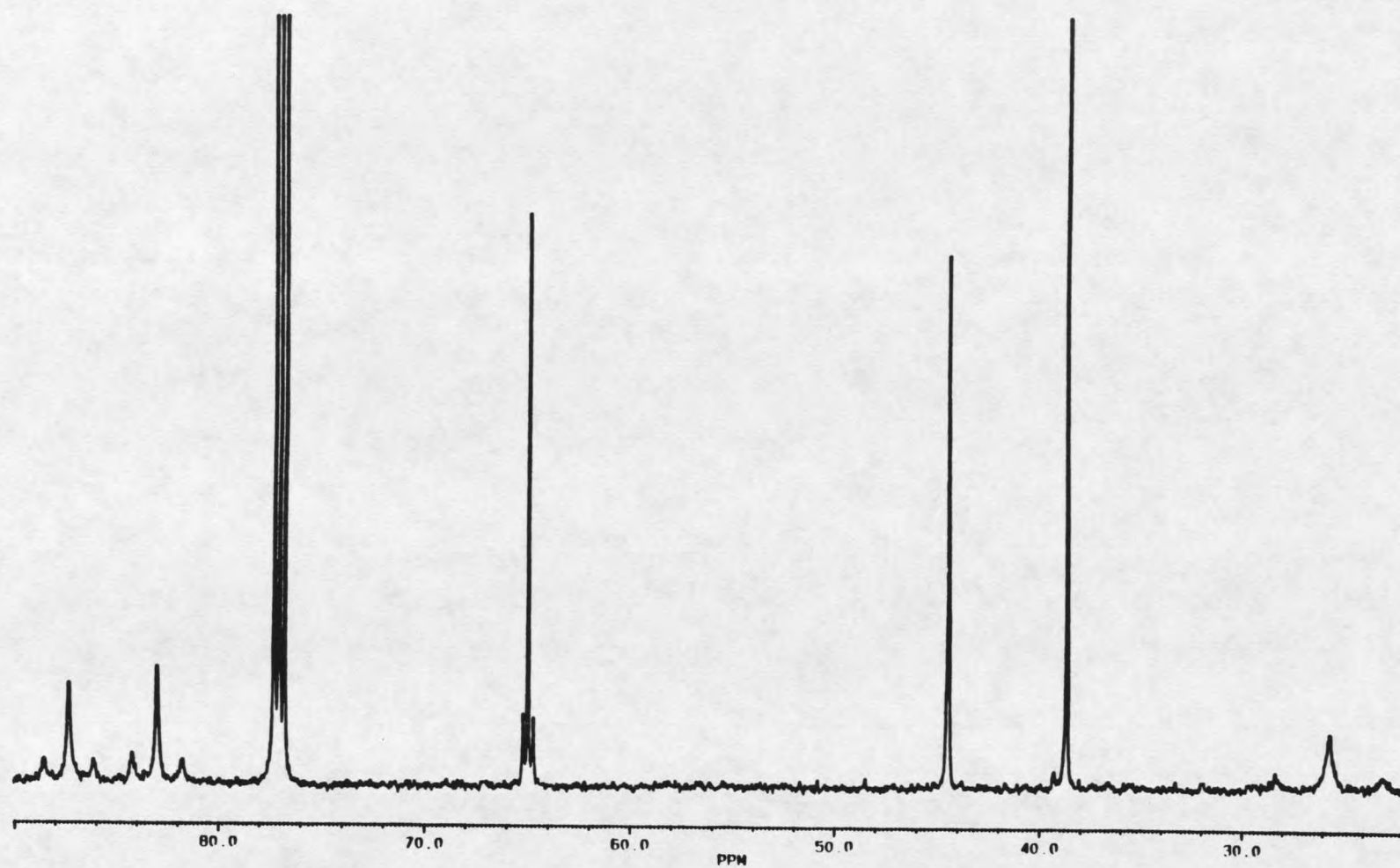
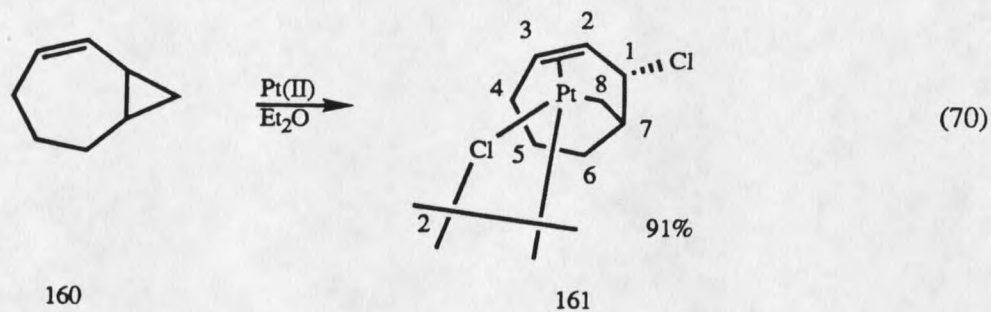


Figure 108. CPD ^{13}C NMR Spectrum of 159.

Table 31. ^1H and ^{13}C NMR Data for Complex 161.

#	^{13}C ppm*	$J_{\text{Pt,C}}$ **	^1H ppm*	$J_{\text{Pt,H}}$ ***	$J_{\text{H,H}}$ **
1	64.6	93.2	4.82(dd)		3.8
2	82.8	249.0	4.66(brd)		
3	82.8	249.0	4.73(brd)		
4	28.9	20.0	****		
5	26.8	0	****		
6	23.0	30.5	****		
7	41.6	<10	****		
8	13.1	628.0	****		

* Relative to CD_3Cl

** Coupling in Hertz

*** All $J_{\text{Pt,H}}$ were unresolved

**** Resonates between 1.3-2.1

() Multiplicity

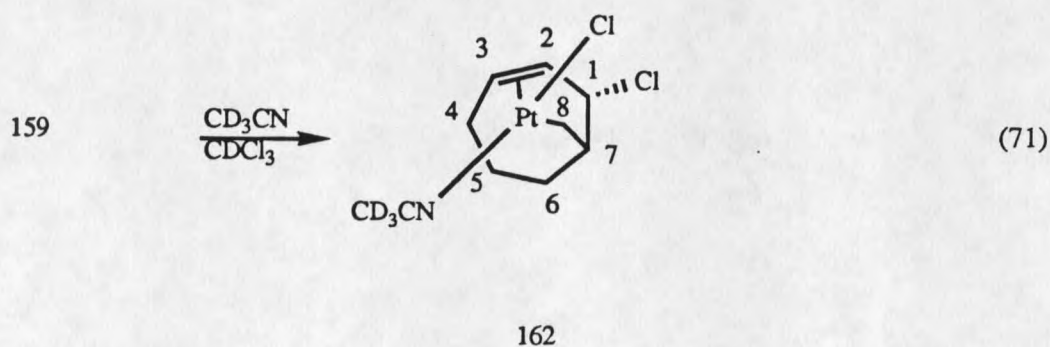


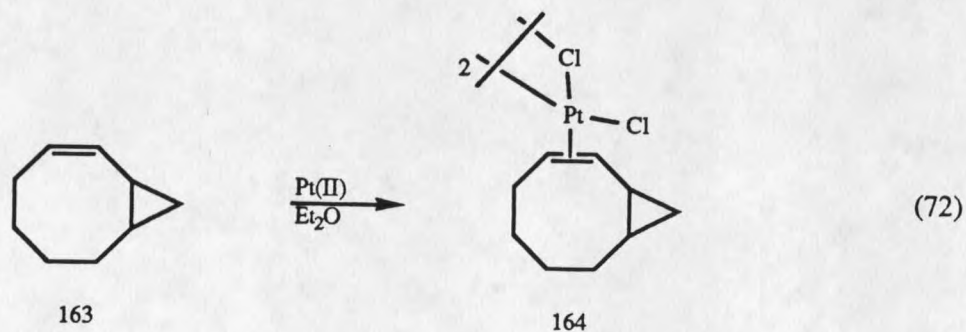
Table 32. ^1H and ^{13}C NMR Data for Complex **162**.*

#	^{13}C ppm**	$J_{\text{Pt,C}}$ ***	^1H ppm**	$J_{\text{Pt,H}}$ ***
1	66.8	92.6	4.5-4.9	
2	86.8	255.4	4.5-4.9	
3	83.5	231.5	4.5-4.9	
4	30.1	25.0	1.5-2.5	
5	28.4	0	1.5-2.5	
6	23.9	31.4	1.5-2.5	
7	42.5	14.7	1.5-2.5	
8	8.0	636.9	1.5-2.5	
			1.42(d)	90.0

 ^{195}Pt NMR**** - 1062 ppm

- * Assigned by comparison to Complex **119**
 ** Relative to CD_3CN
 *** Coupling in Hertz
 **** Relative to 1.0 M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25°C
 () Multiplicity

Reaction of bicyclo[6.1.0]non-2-ene (**163**) with Zeise's dimer at room temperature resulted in the formation of the platinum olefin complex as a yellow solid **164**, Equation 72. Table 34 lists the NMR data for **164**. Comparison of NMR data to complexes **115**, **159** and **161** shows significant differences. Most noticeable is the lack of an upfield methylene with large platinum coupling (600 Hertz range). Using two equivalents of platinum and increased temperatures (60°C) still did not result in insertion into the cyclopropane.



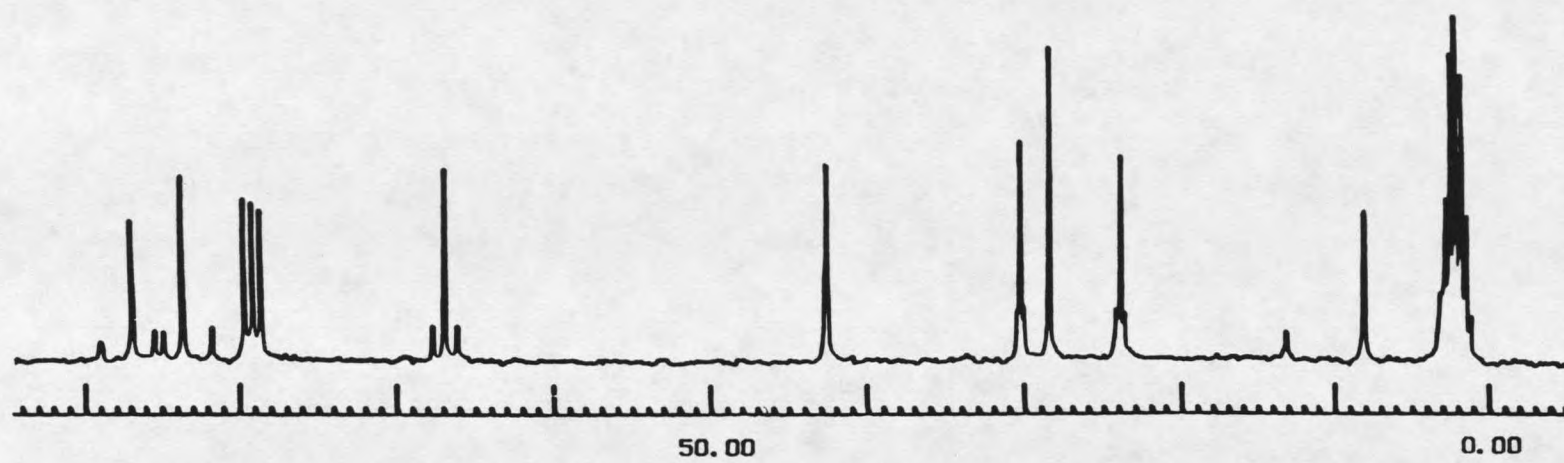


Figure 109. CPD ^{13}C NMR Spectrum of 162.

Table 33. ^1H and ^{13}C NMR Data for Complex **164***

^{13}C ppm**	$J_{\text{Pt,C}}$ ***	^1H ppm**	$J_{\text{Pt,H}}$ ***
96.9	152.6	5.8(m)	70
90.6	156.0	5.3(dd)	69
31.1	0	2.68(m)	
30.9	0	2.4(m)	
28.6	0	1.85(m)	
22.9	0	1.55(q)	
14.9	0	1.0(m)	
13.6	0	0.2(dd)	
		0.7(m)	

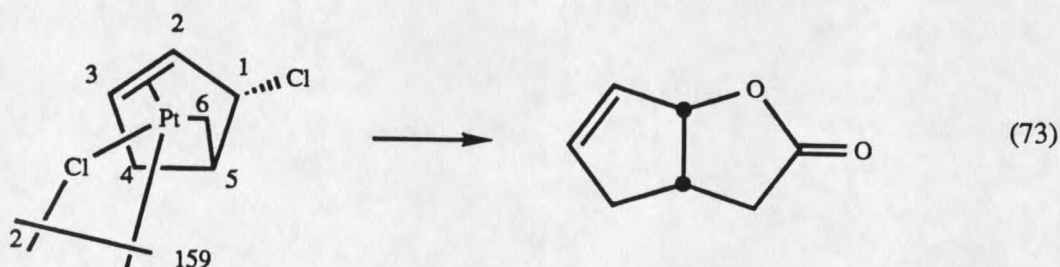
* Not rigorously determined

** Relative to CD_3Cl

*** Coupling in Hertz when pyridine is added

() Multiplicity

In summary, reaction of bicyclo[4.1.0]hept-2-ene with platinum(II) has produced some very interesting and novel complexes. Additionally, synthesis of organic products have been accomplished in excellent yields and stereoselectivity. Furthermore, the system appears to be ubiquitous to five membered and seven membered rings. Application to natural product syntheses is also a possibility. Complex **159** could potentially form the lactone shown in Equation 73. Lactones of this type have been used as precursors in natural product syntheses¹³⁰. Finally, the research that has been presented opens new avenues in platinum chemistry. Synthesis of organic molecules with various ring sizes containing a wide range of functionalities are certainly feasible.



EXPERIMENTAL

General

^1H NMR spectra were obtained on a Bruker AM500, AC300 or WM250-MHz instrument. Chemical Shifts are reported in units of parts per million (ppm) (δ) downfield from tetramethylsilane (TMS). ^1H NMR shifts are relative to residual protiated solvent in: CDCl_3 -7.24, CD_3OD -3.30, pyridine-7.19, CD_3CN -1.93. ^{13}C NMR spectra were recorded at 62.9, 75.5 or 125.8 MHz and chemical shifts are reported relative to the solvent resonance: CDCl_3 -77.0, CD_3OD -49.0, pyridine-123.5, CD_3CN -118.2. Multiplicities () in carbon spectra are referred to gated ^1H -coupled experiments. ^{195}Pt NMR spectra were recorded at 53.66 MHz and chemical shifts are given relative to external 1M $\text{Na}_2\text{Pt}(\text{CN})_4$. $^2\text{H}\{^1\text{H}\}$ NMR were recorded at 38.38 MHz and are referenced to CDCl_3 . $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 101.27 MHz and chemical shifts are given relative to external 1M H_3PO_4 . All coupling constants are reported in Hertz. Mass spectral data were collected on a Varian MM-16 spectrometer. Infrared spectra were obtained on a Nicolet 5DX FT-IR spectrometer. X-ray data was collected on a Nicolet R3ME automated diffractometer and structure determinations and refinement calculations were carried out with SHELXTL software on a Nicolet R3ME crystallographic system. Preparative GC collections were made with a Varian 3300 FID equipped with a 10' x .25" column packed with SE30 on Chromosorb W. Unless otherwise stated, injector and detector temperatures were set at 250° C. Analyses were done by Galbraith Laboratories. Column chromatography was performed on silica gel unless otherwise stated. High pressure reactions were run in a Parr Instrumental bomb no. 4702 type T304 SS with a glass insert.

Unless otherwise stated, all solvents and reagents were purchased from commercial suppliers and used without further purification. Diethyl ether was distilled from sodium benzophenone, chloroform was washed with water 5 times, distilled from CaCl_2 and stored in the dark over 4Å molecular sieves for use in bomb reactions. Pentane was distilled from LiAlH_4 and benzene was distilled from CaH_2 . Simmon-Smith cyclopropanations were done using analogous conditions unless otherwise stated, for an example see the cyclopropanation of 1,3-cycloheptadiene.

Formation of Platinacyclobutanes

Synthesis of Methyl Cyclopropyl Ketal 22. To a 100 mL flask fitted with a Dean-Stark water trap and condenser was added 2.50 mL (25.2mmol) cyclopropyl methyl ketone, 60 mL benzene, 5.50 mL (100mmol) ethylene glycol, 5.50 mL (50mmol) trimethyl orthoformate and p-toluenesulfonic acid (5 mg). The mixture was stirred at reflux for two days and allowed to cool. After cooling the mixture was poured into 50 mL saturated aqueous NaHCO_3 . Layers were separated and the organic layer was subsequently washed two times with 25 mL water, once with 25 mL brine and dried over MgSO_4 . Removal of solvent under vacuum yielded 2.19 grams **22** as a colorless oil (68%). I.R. (CDCl_3) 3156, 2987, 1797, 1472, 1385, 1098 cm^{-1} ; ^1H NMR (CDCl_3) 3.81 (s, 4H), 1.25 (s, 3H), 1.00 (m, 1H), 0.3 (m, 4H); ^{13}C NMR (CDCl_3) 109.1 (s), 64.9 (t), 24.3 (q), 18.4 (d), 1.1 (t); MS, m/e (%) 128 (M^+ , 2.9), 113 (13.1), 87 (89.7), 85 (29.0), 69 (15.4), 55 (28.7), 43 (100).

Reaction of 22 with Zeise's dimer yielding 23. To a 25 mL round bottom with 15 mL dry diethyl ether was added 73.6 mg (0.575mmol) Zeise's dimer. The mixture was refluxed with stirring for six h at which time a yellow solid had formed. The ether was reduced to 5 mL and the solid was washed 2 times with 15 mL pentane and dried under vacuum to yield **23** in quantitative yield. Decomposition occurs within two h.

Reaction of IPC 23 with pyridine yielding 24. To a stirred solution of 50-150 mg IPC 23 at room temperature in 3 mL CDCl_3 was added 2.5-3 equivalents pyridine yielding 24 as a yellow solution. Chromatography on florisil with chloroform could be performed resulting in sharpening of the NMR signals, otherwise chromatography was not necessary. See Table 10 for NMR data.

Reaction of IPC 23 with 2,2'-bipyridine yielding 25. To a stirred solution of 50-150 mg IPC 23 in 3 mL CDCl_3 was added 1 equivalent bipy at room temperature yielding 25 in 80-85% yields. Complex 25 was formed in a yellow solution with small amounts of pink precipitate (bipyplatinum dichloride) which could be filtered out. Removal of the chloroform resulted in increased formation of the precipitate. See Table 11 for NMR data.

Hydrolysis of 24 yielding 26 and 27. 100 mg 24 in 3 mL chloroform was shaken with 1 gram p-toluenesulfonic acid in 2 mL water for 10 minutes. The aqueous layer was removed and the chloroform layer was washed with 2 mL NaHCO_3 (sat.), 2 mL brine and then dried over K_2CO_3 . ^1H NMR displayed a ratio of 1.5:1 in favor of 26. I.R. (CDCl_3) 1700.9 (s), 1473, 1383, 1097, 990 - assigned to 26; 1683.3 (s), 1605, 1487, 1450, 1356, 1217, 1173, 1075, 1013 - assigned to 27; See Tables 12 and 13 for NMR data.

Hydrolysis of 25 yielding 28. 100 mg 25 in 5 mL chloroform was shaken frequently over 8 h with 1 gram p-toluenesulfonic acid in 2 mL water. The aqueous layer was removed and the chloroform was washed with 2 mL NaHCO_3 (sat.), 2 mL brine and dried over K_2CO_3 . I.R. (CDCl_3) 1700.4 (s), 1472.9, 1448, 1381.6, 1097, 990; ^{195}Pt NMR resonance at 3118 ppm relative to 1M $\text{Na}_2\text{Pt}(\text{CN})_4$ in D_2O at 25° C. See Table 14 for ^1H and ^{13}C NMR data.

Mechanistic Studies on the Norbornyl Ring Expansion Reaction

Synthesis of 29 and 30. Cyclopropanes 29 and 30 were prepared from norbornadiene by the method of Rawson and Harrison using CD_2I_2 . Separation of the resulting diene, tricycle

and tetracycle were achieved by preparative GLC (column temperature = 125° C) with solvent and diene eluting first followed by **29** and **30**, respectively.

29- ^1H NMR (CDCl_3) 0.85 (brd, 1H), 1.11 (brd, 1H), 2.72 (brs, 2H), 6.38 (brt, 2H), methylene cyclopropane resonances absent; ^{13}C NMR (CDCl_3) 18.7 (split and broadened due to deuterium coupling), 21.4 (d), 37.1 (t), 40.98 (d), 140.87 (d); ^2H NMR (CDCl_3) 0.80, 1.45; MS m/e (%) 108 (m^+ , 31), 107 (43.8), 106 (31.3), 105 (12.5), 93 (66.7), 92 (74.9), 91 (51.0), 81 (24.6), 80 (66.5), 79 (100), 78 (93.5).

30- ^1H NMR (CDCl_3) 0.38 (brs, 2H), 0.96 (brs, 2H), 2.24 (brs, 2H), methylene cyclopropane resonances absent; ^{13}C NMR (CDCl_3) 6.0 (split and broadened due to deuterium coupling), 14.3 (d), 18.6 (d), ^2H NMR (CDCl_3) 0.17, 0.66; MS m/e (%) 124 (m^+ , 0.6), 108 (15.6), 107 (56.9), 106 (48.4), 105 (21.8), 94 (39.8), 93 (71.9), 92 (71.6), 91 (31.1), 81 (95.2), 80 (100), 79 (97.8).

Synthesis of 31 and 32. Cyclopropanes **31** and **32** were prepared by reaction of $^{13}\text{CH}_2\text{N}_2$ with 0.5 mL norbornadiene in dry ether in the presence of a catalytic amount of $\text{Pd}(\text{OAc})_2$. The $^{13}\text{CH}_2\text{N}_2$ was generated by addition of 0.31 g MSD Isotopes 99% ^{13}C Diazald in 20 mL dry Et_2O to 0.3 g NaOH in 1 mL H_2O and 2.2 mL 2-(2-ethoxyethoxy) ethanol as solvent. Preparative GC eluted pure **31** in reasonable amounts, **32** could not be collected as such and had to be used as a mixture with **31**.

31- ^{13}C NMR (CDCl_3) 19.16 (extremely large resonance due to 99% ^{13}C labelling), 21.8 (d), 37.4 (t), 41.3 (d), 141.1 (d).

32- ^{13}C NMR (CDCl_3) 6.15 (extremely large due to ^{13}C labelling), 15.0 (t) 18.5 (d), 35.4 (d); MS m/e (%) 122 (m^+ , 0.75), 106 (16), 93 (19.7), 92 (23.5), 91 (13.7), 80 (100)

Reaction of 29 or 31 with Zeise's dimer yielding 33 or 35. To a vial containing 40.2 mg (0.372 mmol) of **29** or **31** in 5 mL dry ether was added 109.4g Zeise's dimer (0.186 mmol) with stirring at room temperature. The orange dimer was consumed in less than one h being

replaced by the yellow platinacyclobutane complex. The ether was reduced to 1 mL and 10 mL of pentane was added with stirring. The complex was allowed to settle and the pentane washing was removed. Two additional pentane washings were performed and the complex was dried under vacuum. For yields and analytic data see: (Waddington, M.D.; Ph.D. Thesis, pp 190)

Reaction of 30 or 32 with Zeise's dimer yielding 34 or 36. IPC 34 was formed as 33 and 35 were, using 100.8 mg Zeise's dimer (0.172 mmol) and 43.2 mg (0.343 mmol) 30. IPC 36 was formed as a mixture with 35 using the same procedure.

Reaction of IPC's 33, 34 and 35 with DMSO-Formation of 37, 38 and 39. To complexes 33, 34 and 35 was added 1 mL of DMSO at room temperature with stirring for 20-24 h. ^2H NMR spectroscopy was performed on samples 33 and 34 showing the formation of 37 and 38 respectively. Vacuum distillation was performed on 37 and 39. See Appendix A for NMR and MS data.

Reaction of IPC 36 with DMSO-Formation of 40. To a mixture of IPC containing 36 and 35 was added 1 mL of DMSO-d_6 at room temperature for 20-24 h with stirring. ^{13}C NMR spectroscopy was then performed showing the formation of 40 and 39. Vacuum distillation of the sample was carried out for GCMS analysis. See Appendix A for NMR and MS data.

Cyclopropanation of 7-Phenyl Norbornadiene. 1 mL (6.0 mmol) of 7-phenyl norbornadiene was placed in a 250 mL flask with 10 mL Et_2O . A catalytic amount of $\text{Pd}(\text{OAc})_2$ was added and the mixture was cooled to -10°C . 12 equivalents of diazomethane was added dropwise with stirring over 2 h. Diazomethane was generated by addition of 15.3 g (72.0 mmol) diazald to 2 g KOH in 6 mL carbital. The mixture was warmed to room temperature and stirred for an additional 12 h. Chromatography on silica gel and Et_2O , followed by rotoevaporation yielded 62 and 63 in a 2.5:1 ratio by (^1H NMR) with 85-90%

yields. Small amounts of endo isomers were also obtained (<5%). Attempts to separate **62** and **63** by GC failed, **62** and **63** were thus used as a mixture.

62- ^1H NMR (CDCl_3) 1.05 (dd, 1H anti CH_2), 1.25 (m, 2H, CH), 1.92 (dd, 1H, syn CH_2), 2.95 (brs, 1H, bridge), 3.1 (brs, 2H, bridgehead), 6.25 (brs, 2H, olefin), 7.0-7.6 (phenyl); ^{13}C NMR (CDCl_3) 20.6 (t), 23.9 (d), 45.7 (d, bridgehead), 50.2 (d, bridge), 137.8 (d, olefin), 124.8-128.7 (phenyl); MS m/e (%), 182 (m^+ , 13.1), 181 (8.3), 167 (23.1), 166 (10.7), 165 (14.3), 154 (11.4), 153 (11.5), 141 (22.3), 128 (16.9), 117 (11.6), 115 (24.0), 104 (71.5), 103 (14.2), 91 (100).

63- ^1H NMR (CDCl_3) 0.0 (dd, 1H, anti CH_2), 0.4 (dd, 2H, syn and anti CH_2), 0.95 (dd, 1H, syn CH_2), 1.15 (2H, m, CH), 1.23 (m, 2H, CH), 2.13 (brs, 1H, bridge), 2.95 (brs, 2H, bridgehead), 7.0-7.6 (phenyl); ^{13}C NMR (CDCl_3) 6.0 (t), 11.7 (t), 20.5 (d), 20.6 (d), 34.2 (bridge), 38.0 (bridgehead), 124.8 - 128.7 (phenyl); MS m/e (%) 196 (m^+ , 18.4), 181 (30.0), 178 (8.8), 168 (23.8), 167 (41.3), 166 (19.4), 165 (30.6), 156 (16.2), 155 (86.9), 154 (24.9), 153 (27.5), 152 (22.5), 142 (45.0), 141 (37.2), 130 (37.5), 129 (61.3), 128 (47.4), 127 (19.9), 118 (63.2), 117 (52.5), 116 (25.0), 115 (62.5), 105 (85.7), 104 (24.9), 103 (28.0), 102 (12.5), 92 (57.5), 91 (100).

Reaction of **62** and **63** with Zeise's dimer yielding **64** and **65**. 0.325 g of **62** and **63** were reacted as a mixture with 72.8 mg (0.124 mmol) Zeise's dimer in 5 mL dry Et_2O . The mixture was stirred at room temperature for 0.5 h yielding a yellow solid. The Et_2O was reduced and the solid was washed three times with 10 mL pentane. Drying under vacuum left IPC's **64** and **65** as a yellow powder in quantitative yields.

Dissolution of IPC's **64** and **65** in pyridine. 1 mL CDCl_3 was added to **64** and **65**, formed above, followed by 40 μL pyridine- d_5 (0.495 mmol, 2 eq. per platinum). Stirring for 15 minutes yielded **66** and **67** as a yellow solution. Integration of the ^1H NMR spectrum showed a 3:1 ratio of **66** to **67**. See Tables 15 and 16 for NMR data.

Reaction of IPC's 64 and 65 with DMSO-Formation of 57 and 70. 1 mL DMSO- d_6 was added to IPC's 15 and 16 at room temperature. Stirring was continued for 24 h forming a yellow solution. ^1H NMR displayed formation of 57, 62 and 70. Integration of the ^1H NMR spectrum showed 59% 57, 16% 62 and 25% 70 in the mixture. See Appendix A for NMR data.

Synthesis of 71 and 73. 71 and 73 were formed in an analogous procedure as 62 and 63 were using 0.07 g of 8-phenyl norbornadiene and 1 g $^{13}\text{CH}_2\text{N}_2$. ^1H NMR of 71 and 73 displayed ^{13}C coupling to the cyclopropane methylene protons. ^{13}C NMR displayed increased intensity to peaks at 20.6 ppm for 71; and at 6.0 and 11.7 ppm for 73.

Formation of 72 and 74. To 50.0 mg 71 and 73 was added 58.2 mg Zeise's dimer in 2 mL Et_2O . The mixture was stirred at room temperature for 1 h producing a yellow solid. The solid was washed 2 times with pentane and dried. A small amount (5 mg) of the solid was removed and put in pyridine- d_5 . ^{13}C NMR (140 scans) displayed three resonances at 5.7, -2.4 ($J_{\text{P,C}} = 375$) and -8.6 ($J_{\text{P,C}} = 360$). These are assigned to ^{13}C labelled complexes 66 and 67. Dissolution of the remaining solid into DMSO- d_6 at room temperature with stirring for 24 h yielded 72 and 74. See Appendix A for ^{13}C NMR data on 72. ^1H NMR of 72 and 74 displayed ^{13}C coupling to the olefinic protons. ^{13}C NMR of 74 displayed increased intensity at 125.7 and 20.4 ppm.

Bicyclo System: Ether Substituents.

Synthesis of cyclopropanes 75 and 84. 75 and 84 were prepared from cyclohexanone by the method of Wohl¹³¹ (formation of the enol ether) and Rawson and Harrison (cyclopropanation using Simmon-Smith techniques)¹³². Chromatography on silica gel with pentane yielded 75 and 84 as yellow oils. Preparative GC (col temp = 120, inj. temp = 120) could be performed but was usually not necessary.

84- ^1H NMR (CDCl_3) 3.2 (s, 3H), 1.86-2.1 (m, 3H), 1.38-1.5 (m, 2H), 1.05-1.25 (m, 4H), 0.8 (dd, 1H), 0.2 (dd, 1H); ^{13}C (CDCl_3) 61.2 (s), 43.8 (q), 27.4 (t), 25.0 (t), 22.1 (t), 21.8 (t), 19.0 (d), 17.3 (t); MS, m/e (%) 126 (m^+ , 44.4), 125 (13.2), 112 (6.1), 111 (74.9), 98 (41.0), 97 (100).

75- ^1H NMR (CDCl_3) 3.38-3.6 (m, 2H), 1.84-2.1 (m, 3H), 1.32-1.5 (m, 2H), 1.0-1.3 (m, 7H), 0.82 (dd, 1H), 0.22 (dd, 1H); ^{13}C NMR (CDCl_3) 62.2 (t), 59.9 (s), 28.1 (t), 24.5 (t), 21.9 (t), 21.3 (t), 18.8 (d), 17.3 (t), 15.7 (q); MS, m/e (%) 140 (m^+ , 41.9), 125 (22.1), 112 (33.9), 111 (19.2), 97 (59.4), 84 (52.7), 83(100).

Synthesis of cyclopropane 85. 85 was prepared by the method of Murai, et al.¹³³

^1H NMR;¹³³ I.R.¹³³

Synthesis of cyclopropane 80. 80 was prepared from cyclooctanone by the method of Wohl¹³¹ and Rawson and Harrison.¹³² ^1H NMR (CDCl_3) 3.5-3.65 (dq, 1H), 3.2-3.36 (dq, 1H), 2.24-2.37 (m, 1H), 1.9-2.03 (m, 1H), 0.65-1.8 (m, 15H), 0.15 (dd, 1H); MS, m/e (%) 168 (m^+ , 40.0), 139 (42.3), 125 (81.4), 97 (75.5), 83 (100).

Synthesis of cyclopropane 82. 82 was prepared from cyclopentanone by the method of Wohl¹³¹ and Rawson and Harrison¹³². ^1H NMR (CDCl_3) 3.5 (q, 2H), 1.25-2.0 (m, 6H), 1.2 (t, 3H), 1.0-1.2 (m, 1H), 0.8 (m, 1H), 0.5 (t, 1H); MS m/e (%) 126 (m^+ , 41.7), 111 (5.6), 99 (62.0), 98 (79.0), 97 (11.0), 70 (100).

Reaction of 75 with Zeise's dimer: (General Procedure for 75, 85, 80 and 82). In a 10 mL round bottom was placed 20.0 mg (0.155 mmol) of 75 and 4 mL of freshly distilled ether. Zeise's dimer (0.0091g, .0155 mmol) was added and the mixture was stirred at room temperature for 24 h. The mixture was filtered and then chromatographed on silica gel with 75:25 Et_2O /pentane yielding 2-methyl cyclohexanone 76 as a yellow oil (78-84% yields).

76- ^1H NMR (CDCl_3) 2.4-1.2 (m, 9H) 1.0 (d, $J = 6.6$, 3H); ^{13}C NMR (CDCl_3) 213.3 (s), 45.4 (d), 41.8 (t), 36.2 (t), 27.9 (t), 25.2 (t), 14.7 (q); IR (CDCl_3) 1700 cm^{-1} ; MS, m/e (%) 112 (m^+ , 48.4), 84 (26.7), 70 (10.8), 69 (51.0), 68 (100).

81- (77-82% yields) ^1H NMR (CDCl_3) 2.52-2.52 (m, 1H), 2.4-2.3 (m, 2H), 1.95-1.15 (m, 10H), 1.05 (d, 3H); ^{13}C NMR (CDCl_3) 206 (s), 46.1 (d), 40.8 (t), 33.1 (t), 26.9 (t), 26.5 (t), 25.6 (t), 24.5 (t), 16.8 (q); IR 1702 cm^{-1} ; MS, m/e (%) 140 (m^+ , 18.7), 112 (21.8), 98 (65.8), 84 (28.7), 83 (25.0), 41 (100).

83- (65% yield) ^1H NMR (CDCl_3) 2.5-1.2 (m, 7H), 1.0 (d, 1H); IR (CDCl_3) 1700 cm^{-1} .

Reaction of 84 with Zeise's dimer in Diethyl Ether. To 19.1 mg (0.152mmol) of **84** in 4 mL Et_2O was added 89.4 mg (0.152mmol, stoichiometric amount of Pt) Zeise's dimer. The mixture was stirred at room temperature for 24 h and treated in an analogous manner as **75** yielding **76** in 75-85% yields.

Reaction of neat 84 with Zeise's dimer. To 19.1 mg (0.152mmol) of **84** was added 8.9 mg (0.015mmol) Zeise's dimer in oven dried glassware without Et_2O under nitrogen. The mixture was stirred for 24 h and 0.5 mL CDCl_3 was added. ^1H NMR spectroscopy showed a mixture of products (including olefins) that was not identified except for starting cyclopropane **84**.

Synthesis of cyclopropane 91. **91** was prepared by the method of Rawson and Harrison.¹³²

In a typical reaction, 2.0 mL (1.88 g 17.1 mmol) 1-methoxy-1,4-cyclohexadiene (Aldrich) and 1.5 mL (18.7 mmol) CH_2I_2 were added to 1.68g (25.6 mmol) Zn dust, 2.54g (25.6 mmol) CuCl and 60mL Et_2O . After 30 h of refluxing, the mixture was filtered and washed with 30 mL aq. NH_4Cl , NaHCO_3 , water and then dried (MgSO_4). Chromatography on silica gel with pentane yielded a yellow oil (68-80%). ^1H NMR (CDCl_3) 5.3-5.58 (m, 2H), 3.28 (s, 3H), 2.58-2.73 (m, 1H), 2.35-2.55 (m, 2H), 2.1-2.28 (m, 1H), 1.2- 1.32 (m, 1H), 0.78 (dd, 1H), 0.48 (dd, 1H); ^{13}C NMR (CDCl_3) 123.5 (d), 123.4 (d), 60.8 (s), 53.6 (q), 27.1 (t), 25.6 (t), 17.9 (d), 13.6 (t); MS, m/e (%) 124 (m^+ , 48.8), 123 (27.9), 110 (8.8), 109 (100).

Synthesis of cyclopropane 101. **101** was prepared by Birch reduction¹³⁴ of phenetole (Aldrich) followed by cyclopropanation using Simmon-Smith conditions. A 500 mL three-

neck flask was equipped with a dry-ice condenser, an ammonia inlet and a septum. Lithium metal (3.38g, 0.488 mol) was added portionwise to a solution of 12.4 mL (11.92g, 97.6 mmol) of phenetole in 20 mL of ether and 200 mL of liquid ammonia at reflux. After 30 min, 28.2 mL (0.488 mol) of ethanol was added via a dropping funnel over 0.5 h. After 15 min, 20 mL of ethanol was added to the still blue mixture and the ammonia was allowed to evaporate from the colorless mixture. The residue was partitioned between 100 mL of water and 50 mL of ether. Layers were separated and the aqueous layer was extracted with ether (3 x 50 mL). The organic phase was washed with 50 mL of brine and dried (MgSO_4). Evaporation of solvent afforded 12.4 g (99%) 1-ethoxy-1,4-cyclohexadiene as a colorless oil. Comparison of the ^1H NMR to 1-methoxy-1,4-cyclohexadiene showed it to be correct. The diene was then put in a 300 mL three-neck flask equipped with condenser and glass stoppers and cyclopropanated under Simmon-Smith conditions² using 9.88g CuCl (1eq), 6.53g Zn (1eq, and 8.0 mL CH_2I_2 (1 eq)) and refluxed for 30 h. The mixture was cooled, filtered and washed successively with cold aqueous NH_4Cl , aqueous NaHCO_3 , water and dried (MgSO_4). Chromatography on silica gel with pentane afforded 11.0 g of 1-ethoxybicyclo[4.1.0]hept-3-ene. See Appendix E for MS and NMR assignments. Note: some formation of phenetole is observed after cyclopropanation and preparative GC.

Reaction of 91 or 101 with Zeise's dimer yielding 92. In a 10 mL round bottom was placed 0.435 mmol of nonprep GC'ed 91 or 101 and 3 mL of Et_2O . Zeise's dimer (123.2 mg, 0.2095 mmol) was added and the mixture was stirred at room temperature for 3 h. The resulting orange-yellow solid was washed 3 times with 5 mL of pentane and dried under vacuum (60-70% yields based on Pt). I.R. (KBr) 1702 cm^{-1} .

Reaction of 92 with acetonitrile yielding 93. Addition of 0.5 mL CD_3CN to 25-100 mg 92 at room temperature yielded a yellow solution within 2 minutes. ^{195}Pt NMR (CD_3CN) 1213. See Table 17 for NMR data. Note: The ratio of 97 to 93 is dependent on the presence of trace impurities which could be removed by preparative G.C.

Formation of 96. In a 10 mL round bottom was placed 0.435 mmol of pure **91** or **101** and 3 mL of dry ether. Zeise's dimer (0.1232 g, 0.2095 mmol) was added and the reaction was stirred under nitrogen at room temperature for 1 h yielding an orange-yellow solid. The resulting precipitate was washed two times with 5 mL of pentane and dried under vacuum (60-70% yields based on Pt, 85-95% regioselectivity). ^{13}C CP/MAS NMR 209.9, 75.3, 50.2, 39.9, 27.4, 16.9; IR (KBr) 1715 cm^{-1} .

Reaction of 96 with acetonitrile yielding 97. Addition of 0.5 mL CD_3CN to 25-100 mg **96** at room temperature with stirring yielded a yellow solution within 2 minutes. IR (CD_3CN) 1715 cm^{-1} ; ^{195}Pt NMR (CD_3CN) 1026.5. See Table 18 for NMR data.

Synthesis of 94. **94** was prepared by the addition of 2.27 mL (18.5 mmol) 1-methoxy-1,4-cyclohexadiene and 5g CD_2I_2 (18.5 mmol) to 1.21g (18.5 mmol) Zn dust and 1.83g (18.5 mmol) CuCl in 60 mL Et_2O . Workup was performed in manner analogous to **91** and **101** resulting in deuterium labelling at C-7. ^1H NMR (CDCl_3) 5.38-5.58 (m, 2H), 3.28 (s, 3H), 2.1-2.7 (m, 4H), 1.22 (t, 1H); ^2H NMR (CCl_4) 0.9, 0.4.

Reaction of 94 with Zeise's dimer and acetonitrile yielding 95. To 39.1 mg (0.310 mmol) **94** in 3 mL dry Et_2O was added 91.2 mg (0.155 mmol) Zeise's dimer at room temperature with stirring. After 5 h the resulting precipitate was washed 3 times with 10 mL pentane and dried. Addition of 0.5 mL CD_3CN gave **95** d_2 . ^1H NMR (CD_3CN) 5.35 (dd, 1H), 4.08 (d, 1H), 2.25-2.6 (m, 2) 1.99-2.18 (m, 2H), 1.25-1.3 (brs, 1H); ^2H NMR (CH_3CN) 1.75, 0.94;

Synthesis of cyclopropane 98. Cyclopropanation of 2.9 mL (24.8 mmol) 1-methoxy-1,4-cyclohexadiene was achieved using 3 mL (24.8 mmol) 1,1-diiodoethane, 2.0 g (30.3 mmol) Zn dust and 3.0 g (30.3 mmol) CuCl under Simmon-Smith conditions for 30 h. The cooled solution was filtered, worked up with NH_4Cl , NaHCO_3 and water, dried and chromatographed on silica gel with pentane yielding **98** as a yellow oil (61%). ^1H NMR (CDCl_3) 5.35- 5.52

(m, 2H), 3.27 (s, 3H), 2.1-2.63 (m, 4H), 1.2-1.3 (m 1H), 1.19 (d, 3H), 0.8 (m, 1H) ^{13}C NMR (CDCl_3) 123.5 (d), 124.1 (d), 63.3 (s), 54.2 (q), 27.3 (t), 25.5 (t), 23.9 (q), 19.8 (d), 11.8 (d).

Reaction of 98 with Zeise's dimer yielding 99. In a 10 mL round bottom with reflux condenser was placed 54.3 mg (.394 mmol) of **98** and 5mL of dry ether. Zeise's dimer (115.5 mg, 0.197 mmol, was added, and the mixture was refluxed for 24 h yielding an orange-yellow precipitate. The ether was reduced to 2 mL and then was washed three times with 6 mL of pentane and dried (50% yield).

Formation of 100. An excess of CD_3CN and CDCl_3 and 1 eg. of pyridine was added to **99** at room temperature yielding a yellow solution. See Table 19 for NMR data.

X-ray Structure Determination of 100. Crystals suitable for crystallographic data collection were grown by slow evaporation from a chloroform solution. A pale yellow crystal (approximately 0.31 X 0.40 X 0.52 mm) was mounted on a glass fiber for data collection on a Nicolet R3mE automated diffractometer at 25° C with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The unit cell was triclinic with dimensions of $a = 7.165(1)$, $b = 9.734(2)$, $c = 10.538(3)$, $\alpha = 114.08(2)$, $\beta = 98.00(2)$, and $\gamma = 96.14(2)$, obtained by least squares refinement using 25 centered reflections for which $20^\circ < 2\theta < 30^\circ$. Omega scans were used to collect intensity data for 6877 unique reflections in the range $4^\circ < 2\theta < 75^\circ$. Data reduction, including corrections for Lorentz and polarization effects gave 3809 reflections with $I > 3\sigma(I)$, which were used for structure solution and refinement. Based on cell volume ($653.4(3) \text{ \AA}^3$), the centric space group $\text{P}1'$ was assumed and subsequently confirmed by successful structure solution and refinement. The platinum position was determined from a Patterson synthesis, and a difference map revealed the remaining non-hydrogen positions. Absorption corrections were calculated by Gaussian integration using crystal dimensions and indices for crystal faces, $\mu = 110.4 \text{ cm}^{-1}$; transmission factor range was 0.034 to 0.111. Calculated density for $\text{C}_{13}\text{H}_{16}\text{NOClPt}$, $Z = 2$, is 2.20 gm/cm^3 ($F(\text{OOO})$)

= 408). All atoms were refined with anisotropic thermal parameters, except hydrogens, which were assigned to idealized positions with a common refined isotropic thermal parameter. The orientation of the methyl group was taken from a difference map. Statistical weighting was used in the least-squares refinement of 155 parameters, and no corrections for extinction were needed. The final R value for structure refinement was 0.0578 (R_w = 0.0589).

Synthesis of 102. 102 was prepared by O-Alkylation of phenol¹³⁵ using 10 g (87.8 mmol) BrCD_2CD_3 resulting in d_5 -phenetole. Birch reduction followed by cyclopropanation yielded 102. ^1H NMR (CDCl_3) 5.4-5.52 (m, 2H), 2.1-2.7 (m, 4H), 1.2 -1.3 (m, 1H), 0.7-0.8 (ddd, 1H), 0.45 (dd, 1H); ^2H NMR (CHCl_3) 3.5, 1.1.

Reaction of 102 with Zeise's dimer and acetonitrile yielding 93. To 12.2 mg (.085 mmol) 102 in Et_2O was added 50 mg (.085 mmol) Zeise's dimer with stirring at room temperature. After 4 h the resulting precipitate was washed 3 times with 10 mL pentane and dried. Addition of 0.5 mL CH_3CN gave 93 with no observable deuterium detected using ^1H and ^2H NMR spectroscopy.

Synthesis of 103. 103 was synthesized by Birch reduction of phenyl butyl ether (92.6% yield) followed by cyclopropanation (68% yield) under Simmon-Smith conditions (see synthesis of 101). ^1H NMR (CDCl_3) 5.45 (m, 2H), 3.4 (m, 2H), 2.2-2.7 (m, 4H), 1.2-1.5 (m, 5H), 0.96 (t, 3H), 0.8 (dt, 1H), 0.5 (dd, 1H); ^{13}C NMR (CDCl_3) 123.8 (d), 123.6 (d), 66.1 (t), 59.8 (s), 32.3 (t), 28.2 (t), 25.8 (t), 19.5 (t), 18.2 (d), 13.9 (q), 13.8 (t); MS m/e (%) 166 (m^+ , 14.3), 111 (13.5), 110 (100), 109 (25.9), 95 (95).

Reaction of 103 with Zeise's dimer. To 25 mg (0.151mmol) 103 in a 1 mL volumetric flask was added 26 mg (0.044mmol) Zeise's dimer. The flask was sealed with a rubber septum and stirred without any solvent for 3 h at room temperature. GCMS of the head gas revealed chlorobutane. Addition of CD_3CN to the brown liquid that had formed produced a yellow solution. ^1H NMR revealed 93 and chlorobutane present.

Reaction of 92 and 96 with Ph_3P . To 10-25 mg **92** or **96** in CDCl_3 was added 1 equivalent of triphenylphosphine per platinum with stirring at room temperature for 20 h. Chromatography on silica gel with diethyl ether afforded **103** as the only organic product (by ^1H NMR). ^1H NMR (CDCl_3) 1.13 (d, $J = 6.5$, 3H), 2.05 (m, 2H), 2.38 (m, 3H), 5.97 (d, $J = 10.0$, 1H), 6.92 (dt, $J = 10.2$, 1H); MS m/e (%) 110 (m^+ , 29.6), 69 (4.8), 68 (100), 67 (2.1), 55 (2.1), 53 (2.9), 42 (2.7), 41 (4.1).

Synthesis of 109. **109** was prepared from cyclohexanone by repeated treatment with D_2O and NaOD. The labelled cyclohexanone- d_4 was then treated in an analogous manner that afforded **75**. Deuterium percent of **109** was 99% by ^1H NMR spectroscopy. ^1H NMR (CDCl_3) 3.2 (s, 3H), 2.1-1.86 (m, 1H), 1.5-1.38 (m, 2H), 1.25-1.05 (m, 3H), 0.8 (d, 1H), 0.2 (d, 1H); ^{13}C (CDCl_3) 61.2 (s), 53.3 (t), 24.4 (t), 21.8 (t), 21.3 (t), 17.1 (t), deuterium coupling appeared to the resonances at 19.0 and 27.4; ms, m/e (%) 129 (m^+ , 29.2), 128 (48.7), 127 (18.2), 113 (70.4), 99 (100); ^2H NMR (CCl_4) 1.99 (2D), 1.13 (1D).

Formation of 110. Reaction of **109** was performed in analogous manner as reaction of **75** with Zeise's dimer. Workup yielded **110**. ^1H NMR (CDCl_3) methyl doublet at 1.0 resonates as a singlet; ^2H NMR (CHCl_3) 2.30, 2.00, 1.70.

Synthesis of 111. **111** was prepared by shaking of the hydroxy substrate **85** with D_2O in a biphasic mixture in Et_2O . Separation of the Et_2O layer followed by drying (MgSO_4) gave the deuterium labelled substrate **111**. ^1H NMR OH resonance absent; ^2H NMR (CHCl_3) 3.30.

Formation of 112. To 140 mg (1.25mmol) **111** was added 73.0 mg (1.25mmol, 10 mol %) Zeise's dimer without any solvent. The neat mixture was stirred for 24 h. Workup yielded **112**. ^2H NMR (CHCl_3) 1.0 ppm; MS m/e (%) 113 (m^+ , 21.1), 112 (15.0), 97 (10.5), 84 (11.3), 70 (24.7), 69 (40.5), 68 (100).

Synthesis of 113. **113** was synthesized in an analogous manner as **75** using tri-*n*-butyl orthoformate in the formation of the enol ether. Cyclopropanation gave **113** in 60% yield.

^1H (CDCl_3) 3.44 (m, 2H), 1.9 (m, 3H), 1.0-1.7 (m, 9H), 0.95 (m, 1H), 0.86 (t, 3H), 0.7 (dd, 1H), 0.2 (dd, 1H); MS m/e (%) 168 (m^+ , 19.0), 113 (22.3), 112 (100), 97 (85.1), 84 (63.6), 83 (80.4), 55 (60.6), 41 (86.4).

Reaction of 113 with Zeise's dimer. To 28.5 mg (0.170 mmol) 113 in a 1 mL volumetric flask was added 10.0 mg (0.017 mmol) Zeise's dimer. The flask was sealed with a rubber septum and stirred 24 h. GCMS of the head gas revealed butene. ^1H NMR (CDCl_3) of the yellow oil displayed 76.

Bicyclo system: Vinyl Cyclopropanes

Synthesis of 114. 3.0 mL (31.5 mmol) of 1,3-cyclohexadiene at 10° was reacted with CH_2N_2 in dry diethyl ether in the presence of a catalytic amount of PdCl_2 over 3 h. The CH_2N_2 was generated by addition of 15 g Aldrich Diazald to 2 g KOH in 5 mL water and 12 mL 2-(2-ethoxyethoxy) ethanol as a solvent. The mixture was allowed to stir 12 h and then was filtered. The solvent was removed by distillation yielding 114 in 60-65% yields by NMR spectroscopy. Preparative GC yielded pure 114 as the third eluent (trace solvent and cyclohexadiene eluting first). See Appendix E for MS and NMR assignments.

Reaction of 114 with Zeise's dimer yielding 115. In a 5 dram vial was placed 25.5 μL (23.3 mg, 0.247 mmol) 114 and 4 mL of dry diethyl ether. 72.7 mg (0.124 mmol) of Zeise's dimer was added and the mixture was stirred at room temperature for 1 h yielding a white ppt. The precipitate was washed one time with 6 mL pentane and dried under vacuum yielding 115 in 90%. Anal. Calc. for $\text{C}_{14}\text{H}_{20}\text{Cl}_4\text{Pt}_2$: C 23.33; H 2.77; Found: C 22.89; H 2.71; I.R. (KBr) 868.0, 816.7, 786.0, 734.7, 560.4 (s); See Table 20 for CP/MAS ^{13}C NMR data, Table 21 for solution NMR data.

Reaction of 115 with H_2 yielding 116. A suspension of the dimer (42 mg) in 3 mL chloroform was placed in a pressure reaction bomb under 50 psi of hydrogen with stirring

at room temperature. After 24 h the reaction mixture was removed and a black precipitate was filtered out leaving a yellow solution. The chloroform was removed by distillation and the yellow oil was chromatographed on silica gel with diethyl ether. Distillation of solvent yielded a yellow oil (**116**) in 82% yield. ^1H NMR (CDCl_3) 3.5 (ddd, $J_{\text{HH}} = 11.0$, 1H), 2.18 (m, 1H), 1.5-1.82 (m, 6H), 1.25-1.32 (m 2H), 1.06 (d, $J_{\text{HH}} = 6.2$, 3H); ^{13}C NMR (CDCl_3) 67.78 (d), 41.21 (d), 37.57 (t), 34.85 (t), 26.55 (t), 25.46 (t), 20.29 (q) MS m/e (%) 134 (1.2), 132 (2.1), 96 (65.4), 81 (95.9), 55 (100).

Reaction of **115** with Ph_3P yielding **117**. To 34.0 mg (0.047 mmol) **115** in 0.5 mL CDCl_3 was added 24.8 mg Ph_3P (0.094mmol) at room temperature to give **117** as a light yellow solution. See Table 22 for NMR data.

Formation of **118**. 42.0 mg **115** and 1.0 mL pyridine- d_5 were cooled to -10°C and then mixed yielding **118** as a yellow solution in quantitative yields (by NMR). The solution of **118** was stable at room temperature for 1-2 days. See Table 23 for NMR data.

Formation of **119**. 1 mL CD_3CN was added to 50 mg **115** at room temperature with stirring yielding **119** as a yellow solution. The solution of **119** was stable for 1-2 weeks. See Table 24 for NMR data.

Reaction of **115** with CD_3OD yielding **120-d**. CD_3OD (0.5 mL) was added to 50.0 mg of **115** at room temperature. Stirring was continued until all the dimer was taken up (0.5-1 h) to yield **120-d**. See Table 25 for NMR data.

Formation of the mixture **120**, **121** and **122**. 2 mL methanol and 2 mL chloroform was added to **115** at room temperature with stirring for 2 minutes. The solvent was removed under vacuum and CDCl_3 was added. NMR spectroscopy displayed the appearance of 2 isomers. See Table 26 for NMR data on **121**. Addition of 1 equivalent of PPh_3 per platinum produced **122** in quantitative yields (by NMR). Table 27 lists the NMR data for **122**.

Formation of 123-d₁₁. 123 was formed in an analogous manner as 120-d₇. Table 28 lists the NMR data for 123.

Reaction of 115 with (MeO)₃P. To 115, formed from 16.0 mg (0.170mmol) 114 and 50.0 mg (0.085mmol) Zeise's dimer, was added 22.0 μ L (0.170mmol) of (MeO)₃P in 1 mL CDCl₃ at room temperature. Formation of 126 was deduced by ¹H NMR spectroscopy. ¹H NMR (CDCl₃) 6.16 (brs, J_{P,H} = 40, 1H), 5.70 (brs, J_{P,H} = 48, 1H) 4.43 (dd, J_{H,H} = 3.8, 1H) 2.9-2.5 (m, 2H), 2.05 (brs, 1H) 1.8-1.1 (m, 4H). Stirring of the solution for 24 h yielded 114 and 127 in a 1:1.5 ratio, respectively. 127: ¹H NMR (CDCl₃) 5.73-5.55 (m, 2H), 4.71 (d, 2H), 2.75-2.68 (brs, 2H), 2.3-2.2 (m, 2H), 2.15-2.06 (m, 2H); ¹³C NMR (CDCl₃) 145.6 (s), 128.8 (d), 122.6 (d), 107.4 (t), 33.5 (t), 31.5 (t), 27.5 (t); MS m/e (%) 94 (m⁺, 69.6), 93 (25.5), 91 (28.8), 79 (100).

Synthesis of 128 and 129. 128 was synthesized in an analogous manner as 114. The CD₂N₂ was generated by addition of diazald to 30% NaOD in D₂O with 2-(2-Ethoxyethoxy)ethan(ol-d) (97%-d) as solvent. 128 was 70% deuterium labelled. ¹H NMR showed decreased intensity as the cyclopropane methylenes (0.7 and 0.6 ppm); ¹³C NMR (CDCl₃) deuterium coupling appeared to the resonance at 10.1 ppm; ²H NMR (CCl₄) 0.7, 0.6 ppm. 16.7 mg (0.174mmol) 128 and 51.1 (0.087mmol) Zeise's dimer were stirred in dry ether forming 129; ²H NMR (CHCl₃) 1.30 and 2.02 ppm.

Reaction of 129 with (MeO)₃P. 21.0 μ L (0.174mmol) (MeO)₃P was added to 129, formed above, and stirred for 24 h at room temperature yielding 128 and 130. ¹H NMR (CDCl₃) Resonance at 4.71 integrated to 25% of one proton; ²H NMR (CHCl₃) 4.7 ppm; ¹³C NMR (CDCl₃) deuterium coupling appeared to the resonance at 107.4.

Formation of 117 in benzene. 114 was reacted with Zeise's dimer in 0.5 mL benzene-d₆ forming a white precipitate. Addition of 1 eq. PPh₃ to the benzene solution yielded 117. See Table 29 for NMR data.

Formation of 131, 132 and 133. To 115, formed from 29.0 mg 114 and 90.6 mg Z.D. was added 2 mL chloroform and 3 mL methanol to form 120. 120 was stirred in a pressure reaction vessel with 50 psi hydrogen. After 24 h the mixture was removed and filtered to give a yellow solution, filtering out a black precipitate. The solvent was removed by distillation and the resulting yellow oil chromatographed on silica gel with diethyl ether, distillation of solvent yielded 131 in 84.3% yield. ^1H NMR (CDCl_3) 3.3 (s, 3H), 2.63 (ddd, $J_{\text{HH}} = 9.1$; coupling of the carbinol proton resonance when methylene protons are irradiated, 1H), 2.06 (m, 1H) 0.98 - 1.74 (m, 8H), 0.953 (d, $J_{\text{HH}} = 6.2$, 3H); ^{13}C NMR (CDCl_3) 85.37 (d), 56.23 (q), 38.22 (d), 33.87 (t), 30.48 (t), 25.57 (t), 24.92 (t), 18.68 (q); MS m/e (%) 128 (m^+ , 29.1) 96 (26), 85 (52), 71 (100).

The same procedure was used for 132 and 133 in 82.7 and 81.3% yields, respectively.

132- ^1H NMR (CDCl_3) 3.62 (dq, 1H), 3.45 (dq, 1H), 2.71 (ddd, $J_{\text{HH}} = 9.5$, 1H), 2.04 (m, 1H) 1.05 - 1.78 (m, 11H), 0.952 (d, $J_{\text{HH}} = 6.2$, 3H) ^{13}C NMR (CDCl_3) 83.83 (d), 63.99 (t), 38.41 (d), 34.06 (t), 31.57 (t), 25.67 (t), 25.12 (t), 18.78 (q), 15.69 (q) MS m/e (%) 142 (m^+ , 57.6, 99 (72.6), 85 (100).

133- ^1H NMR (CDCl_3) 3.6 (qq, 1H), 2.73 (ddd, $J_{\text{HH}} = 9.1$, 1H), 1.94 (m, 1H), 1.05 - 1.73 (m, 14H), 0.934 (d, $J_{\text{HH}} = 6.2$, 3H); ^{13}C NMR (CDCl_3) 81.87 (d), 69.76 (d), 38.71 (d) 34.16 (t), 32.92 (t), 25.70 (t), 25.25 (t), 23.68 (q), 22.33 (q), 18.94 (q); MS m/e (%) 156 (m^+ , 43), 114 (88.9), 57.0 (100).

Formation of 132 via 120-d₇ (equation 62). To 134.7 mg of 115 was added 1 mL CDCl_3 and 2 mL CD_3OD to form 120-d₇, deduced by ^1H NMR. Rotoevaporation of the solvent left 120-d₇ as a yellow oil. 3 mL ethanol and 2 mL chloroform was added to 120-d₇ with stirring for 0.5 h at room temperature. The solution was reacted with 50 psi H_2 for 24 h at room temperature with stirring. Work-up was performed in an analogous manner as in the formation of 131. GCMS and ^1H NMR data were identical to that reported for 132.

Formation of 134, 135 and 136. To 115, formed from 35.0 mg 114 and 103.9 mg Z.D., was added 7 mL methanol and 2 mL chloroform with stirring for 10 minutes at room temperature to give 120 as a yellow solution. 92.7 mg Ph_3P (0.35 mmol) was added at room temperature and stirring was continued for 28 h. The solution was filtered leaving a yellow precipitate and the solvent was removed by distillation. Chromatography of the resulting oil on silica gel with 10% Et_2O /pentane followed by distillation of the solvent gave 134 in 82% yield. ^1H NMR (CDCl_3) 5.69-5.83 (m, 2H), 3.36 (d, $J_{\text{HH}} = 6.44$, residual coupling of the carbinol proton resonance when the vinyl proton is irradiated, 1H), 3.34 (s, 3H) 1.95-2.06 (m, 2H), 1.64-1.76 (m, 1H), 1.14-1.41 (m, 2H), 0.984 (d, $J_{\text{HH}} = 6.2$); ^{13}C NMR (CDCl_3) 130.08 (d), 126.68 (d), 81.43 (d), 55.65 (q), 33.11 (d), 28.19 (t), 24.39 (t), 18.24 (q); MS m/e (%) 126 (m^+ , 19.9), 111 (10.9), 94 (7.8), 84 (100).

The same procedure was used for 135 and 136 in yields of 79.8% and 78.0%, respectively.

135- ^1H NMR (CDCl_3) 5.65-5.79 (m, 2H), 3.38-3.64 (m, 3H, $J_{\text{HH}} = 6.6$, for carbinol proton), 1.95-2.06 (m, 2H), 1.65-1.74 (m, 2H), 1.14-1.4 (m, 4H), 0.98 (d, 3H); ^{13}C NMR (CDCl_3) 129.58 (d), 127.52 (d) 80.09 (d), 63.60 (t), 33.64 (d), 28.42 (t), 24.47 (t), 18.34 (q), 15.69 (q); MS m/e (%) 140 (m^+ , 19.1), 112 (12.1), 99 (8.3), 98 (100).

136- ^1H NMR (CDCl_3) 5.58-5.77 (m, 2H), 3.6-3.72 (m, 1H), 3.45 (brd, $J_{\text{HH}} = 7.1$, 1H), 1.94-2.05 (m, 2H), 1.6-1.78 (m, 2H), 1.1-1.4 (m, 7H), 0.98 (d, 3H); MS m/e (%) 154 (m^+ , 3.0), 112 (79.4), 95 (36.7), 79 (22.9), 70 (100).

Formation of 134- d_4 . 134- d_4 was synthesized using the same procedure used for 134 using CD_3OD in replace of CH_3OH . ^1H NMR (CDCl_3) 3.34 resonance gone (OCD_3), 0.98 resonance split due to deuterium coupling; ^2H NMR (CHCl_3) 3.36, 1.0 ppm; ^{13}C NMR (CDCl_3) 18.0 (split into a triplet from deuterium coupling), OCD_3 resonance gone; MS m/e (%) 130 (m^+ , 18.1), 114 (9.2), 88 (5.5), 87 (100).

Formation of 137, 138 and 139. To 115, formed from 18.0 uL (16.4 mg, 0.175mmol) 114 and 51.3 mg Zeise's dimer, was added 2 mL chloroform and 3 mL methanol at room temperature. After 0.5 h the yellow solution was placed in a pressure reaction bomb and CO (325 psi) was introduced. The mixture was stirred for 4.5 days at room temperature. After venting the bomb the mixture was removed and the yellow solution was filtered leaving a black precipitate. The solvent was removed by simple distillation leaving a yellow oil which was chromatographed on silica gel with diethyl ether. Removal of the ether by distillation yielded 137, 138 and 139 in a 78% average yield with 137 as the major isomer. See Appendix E for NMR, IR and MS data.

Formation of 140, 141 and 142. 140, 141 and 142 were formed in an analogous manner as 137-139 using ethanol as a solvent in 77% average yield with 140 as the major isomer. IR (CDCl₃) 1732 cm⁻¹; ¹H NMR (CDCl₃) 5.6-5.9 (m, 6H), 3.4-4.1 (m, 15H), 1.3-2.7 (m, 21H), 1.23 (t, 9H), 1.14 (t, 9H); ¹³C NMR (CDCl₃) 140: 172.9 (s), 129.8 (d), 127.0 (d), 77.4 (d), 63.5 (t), 60.1 (t), 37.5 (t), 35.8 (d), 25.8 (t), 24.2 (t), 15.6 (q), 14.2 (q); 141, 142: 171.1 (s), 134.0 (d), 129.5 (d), 76.6 (d), 63.4 (t), 60.3 (t), 40.5 (t), 32.7 (d), 28.0 (t), 26.8 (t), 15.7 (q), 14.2 (q); 171.6 (s), 133.7 (d), 128.1 (d), 71.3 (d), 63.9 (t), 59.9 (t), 40.0 (t), 32.3 (d), 26.1 (t), 24.6 (t), 15.7 (q), 14.2 (q); MS m/e (%) 140: 212 (m⁺, 1.2), 183 (9), 166 (10), 137 (19), 98 (34), 91 (100); 141, 142: 212 (m⁺, 1.1) 166 (20), 124 (23), 61 (56), 60 (100); 212 M⁺, 1.6), 166 (12), 124 (13), 91 (100).

Formation of 143 and 144. To complex 115, formed from 51.0 mg Zeise's dimer and 17.9 uL (16.3 mg) 114, was added 4 mL chloroform and 35 uL (5 eq.) methanol. The mixture was stirred at room temperature for .2 h and placed in a glass lined pressure reaction bomb and CO (325psi) was introduced. Stirring was continued for 4.5 days when the bomb was vented and the mixture removed. The mixture was filtered and the solvent removed by distillation. Chromatography on silica gel with diethyl ether followed by distillation of the

ether yielded **143** and **144** as a yellow oil in 57% average yield. The two products were not separated but characterized as a mixture. IR (CDCl₃) 2900, 1732.8 cm⁻¹; ¹H NMR (CDCl₃) 5.42-5.72 (m, 4H), 3.65 (s, 6H), 0.8-2.7 (m, 18H); MS m/e (%) 154 (m⁺, 11.2), 123 (10.9), 122 (24), 94 (16.9), 93 (4.5), 80 (100), 79 (47.2), 78 (11.3), 77 (10.4), 74 (26.6); ¹³C NMR (CDCl₃) one isomer: 173.3 (s), 130.1 (d), 126.8 (d), 51.3 (q), 40.8 (t), 31.3 (t), 30.7 (d), 28.9 (t), 25.0 (t); 2nd isomer: 173.1 (s), 128.1 (d), 125.7 (d), 51.3 (q), 40.6 (t), 32.3 (d), 28.5 (t), 24.7 (t), 21.0 (t).

Formation of 145 and 146. **145** and **146** were formed in an analogous manner as **143** and **144** using 5 eq. of ethanol in 56% average yield. IR (CDCl₃) 1726 cm⁻¹; ¹H NMR (CDCl₃) 5.43-5.7 (m, 4H), 4.1 (dq, 4H), 1.4-2.7 (m, 16H), 1.2 (t, 6H), 0.95 (m, 2H); MS m/e (%) 168 (m⁺, 12.6), 123 (18.7), 122 (26.2), 95 (16.0), 94 (27.8), 93 (12.6), 89 (14.4), 88 (23.5), 81 (44.1), 80 (100), 79 (69.0), 78 (12.6), 77 (12.8); ¹³C NMR (CDCl₃) 1 isomer 173.0 (s), 130.2 (d), 122.1 (d), 60.3 (t), 41.0 (t), 31.7 (t), 31.2 (d), 29.2 (t), 25.3 (t), 14.2 (q); 2nd isomer 172.8 (s), 128.0 (d), 126.0 (d), 60.3 (t), 40.8 (t), 32.4 (d), 28.8 (t), 25.0 (t), 21.2 (t), 14.2 (q).

Formation of 147 and 148. To **115**, formed from 100.6 mg Zeise's dimer and 35.3 uL (32.3 mg, 0.344mmol) **114**, was added 4 mL chloroform, 2 mL acetic acid, 1 mL water and 2 mL acetone. The mixture was stirred at room temperature for 0.5 h when 6 mL of chloroform was added and the layers were separated. The water layer was washed 2 times with 5 mL chloroform. The chloroform washings were combined and reduced in volume under vacuum to 3 mL. 89.7 mg (0.344mmol) PPh₃ was added at room temperature and the mixture was stirred for 28 h. Filtration of an orange solid gave a yellow solution which was reduced by distillation. Chromatography on silica gel with diethyl ether followed by distillation of solvent yielded a mixture of **147** and **148** (29.6 mg, 56% yield). IR (CDCl₃) 1733, 1718 cm⁻¹; **147**: ¹H NMR (CDCl₃) 6.25 (d, J_{HH} = 9.9, 1H), 5.75 (dd, J_{HH} = 9.9, 2.6,

1H), 5.33 (dt, $J_{HH} = 2.6, 5.9$, 1H), 4.90 (brs, 2H), 2.44-2.54 (m, 1H), 2.31-2.38 (m, 1H), 2.04 (s, 3H), 1.92-2.00 (m, 1H), 1.73-1.83 (m, 1H); ^{13}C NMR (CDCl_3) 170.7 (s), 141.4 (s), 132.9 (d), 127.4 (d), 113.6 (t), 68.1 (d), 28.3 (t), 26.8 (t), 21.3 (q); MS m/e (%) 110 ($m^+ - 42$, 7.4), 92 (49.0), 91 (73.2), 65 (11.4), 60 (12.1), 45 (14.8), 44 (20.1), 43 (30.2); 148: ^1H NMR (CDCl_3) 6.15 (d, 1H), 5.83 (dd, 1H), 5.33 (dt, 1H), 4.82 (brs, 1H), other protons obscured; MS m/e (%) 138 ($m^+ - 14$, 7.2), 110 (6.3), 109 (4.0), 95 (8.1), 92 (10.9), 91 (21.1), 77 (6.8), 65 (4.5), 44 (13.1).

Formation of 149. To 115, formed from 51.0 mg Zeise's dimer and 17.9 μL (16.3 mg) 114, was added 2 mL chloroform, 3 mL acetic acid, 1 mL water and 1 mL acetone with stirring at room temperature. The mixture was placed in a glass lined high pressure bomb and CO (325 psi) was introduced. Stirring was maintained at room temperature for 4.5 days when the bomb was vented. The mixture was transferred to a separatory funnel and washed 3 times with 10 mL chloroform and dried (MgSO_4). The chloroform was removed by distillation and the resulting oil was chromatographed on silica gel and diethyl ether. Removal of the ether by distillation yielded 149 as a yellow oil in 84% average yield. IR (CDCl_3) 1771.6 cm^{-1} ; See Appendix E for NMR and MS data.

Formation of 150, 151 and 152. 150, 151 and 152 were formed in an analogous manner as 149 with the following exceptions: reaction time went for 2 days and acetic acid was omitted. Lactone 149 was formed as the major isomer in a 3:1 ratio, 47% yield. IR (CDCl_3) $2800, 1710\text{ cm}^{-1}$; ^1H NMR (CDCl_3) 5.88 (m, 3H), 5.64 (m, 3H) 4.43 (brd, $J_{HH} = 6.8$, 1H), 4.12 (dt, 2H), 1.3-2.3 (m, 21H); ^{13}C NMR (CDCl_3) 191.9 (s), 158.7 (s), 158.6 (s), 131.2 (d), 131.0 (d), 130.4 (d), 130.1 (d), 129.8 (d), 125.8 (d), 81.9 (d), 78.5 (d), 78.1 (d), 42.1 (d), 41.6 (d), 41.4 (d), 36.0 (t), 29.9 (t), 28.1 (t, 2C), 26.0 (t), 25.0 (t), 24.0 (t), MS m/e (%) 138 ($m^+ - 18$, 4.7), 106 (15.2), 105 (15.0), 91 (30.7), 79 (52.6), 78 (100);

Formation of 153 and 154. 153 and 154 were synthesized in an analogous manner as 143-146 using 5 eq. of ethylene glycol in 47% yield. IR (CDCl_3) 3418 (broad), 1734 1472, 1382, 1095 cm^{-1} ; ^1H NMR (CDCl_3) 5.5-5.72 (m, 4H), 4.3 (t, 4H), 4.1 (2H), 3.65 (t, 4H), 1.2-2.6 (m, 18H); ^{13}C NMR (CDCl_3) 172.5 (s), 172.3 (s), 129.9 (d), 128.3 (d), 126.8 (d), 125.6 (d), 63.8 (t), 41.6 (t), 40.6 (t), 32.3 (d), 31.3 (t), 30.7 (d), 29.7 (t), 29.1 (t), 25.0 (t), 24.7 (t), 21.0 (t).

Formation of 155, 156 and 157. To 30.0 mg 115 was added 2 mL ethylene glycol, 1 mL water and 1 mL acetone at room temperature. The mixture was placed in a high pressure bomb and submitted to CO (325 psi) for 4.5 days. The bomb was vented and the mixture washed with 10 mL chloroform 3X. The chloroform layer was dried (MgSO_4) and chromatographed on silica gel. Removal of the solvent under vacuum yielded 155, 156 and 157 as a mixture in 40% yield. ^{13}C NMR (CDCl_3) 173.8 (s), 173.6 (s), 133.4 (d), 130.1 (d), 129.0 (d), 126.3 (d), 79.4 (d), 74.2 (d), 74.0 (d), 69.3 (t), 69.1 (t), 65.8 (t), 61.9 (t), 60.8 (t), 60.6 (t), 40.1 (t), 38.6 (t), 36.5 (t), 31.2 (d), 30.6 (d, 2C), 27.7 (d), 26.7 (t), 26.5 (t), 24.6 (t), all other carbons unres.

Formation of 158. 158 was synthesized by a modification of Tomilov et al¹³⁶. 1.6 g (24mmol) of cyclopentadiene was reacted at -10°C with CH_2N_2 in the presence of a catalytic amount of $(\text{PhCN})_2\text{PdCl}_2$ over a period of 1 h. The CH_2N_2 was generated by addition of 5.5 g (25.1mmol) Aldrich diazald in CH_2Cl_2 to 2 g KOH in 5 mL water and 12 mL carbital as a solvent. Over the course of the reaction 3 increments of Pd catalyst were added. The mixture was allowed to stir an additional 8 h and then an equal amount of pentane was added to the CH_2Cl_2 solution. The solution was chromatographed on silica gel and the solvent removed by spinning band distillation. Preparative GC (col. temp. = 80°C) yielded 156 as the 2nd eluent (50% of mixture). ^1H NMR (CDCl_3) 5.9 (m, 1H), 5.35 (dd, 1H), 2.56

(dd, 1H), 2.26 (dd, 1H), 1.74 (m, 1H), 1.52 (m, 1H), 0.75 (ddd, 1H), -0.2 (dd, 1H); ^{13}C NMR (CDCl_3) 134.8 (d), 127.5 (d), 35.8 (d), 23.5 (t), 16.5 (d), 15.0 (t).

Formation of 159. To 10.0 mg (0.125mmol) **158** in 0.5 mL CDCl_3 was added 36.5 mg (0.061mmol) Zeise's dimer at room temperature with stirring for 0.5 h. NMR spectroscopy revealed **159** in quantitative yield. Addition of pentane caused precipitation of a white solid in 90% isolated yield. See Table 30 for NMR data.

Formation of 160. 11.5 g (116.2mmol) CuCl and 7.6 g (116.2mmol) Zn dust were placed in a three-necked round bottom containing 150 mL dry diethyl ether. The flask was fitted with 2 glass stoppers and a condenser with nitrogen line. The mixture was charged with nitrogen and refluxed for 0.5 h with stirring. After 30 minutes 4.75 mL (58.1mmol) 1,3-cycloheptadiene was pipetted into the flask followed by 5.15 mL (63.9mmol) of diiodomethane. The flask was recharged with nitrogen and refluxed for 26 h. The mixture was cooled to room temperature and filtered into a separatory funnel. 0.1N HCl is slowly added and the mixture washed 2 times with acid and once with water. The ether layer was dried (K_2CO_3) and reduced under vacuum. Preparative GC (col. temp. = 120°C) yielded **160** as the 2nd eluent (50% of the mixture). ^1H NMR (CDCl_3) 5.72 (m, 1H), 5.38 (m, 1H), 2.0 (m, 2H), 1.85 (m, 1H), 1.6 (m, 1H), 1.45 (m, 2H), 1.28 (m, 1H), 1.12 (m, 1H), 0.75 (ddd, 1H), 0.1 (dd, 1H); MS m/e (%) 108 (m^+ , 33.6), 93 (75.7), 91 (90.9), 80 (55.9), 79 (100).

Formation of 161. In a 5 dram vial was placed 61.7 mg (0.571mmol) **160**, 4 mL dry diethyl ether and 161.7 mg (0.275mmol) Zeise's dimer. The mixture was stirred for 2 h at room temperature at which time a white precipitate had formed. The solid was washed 2 times with 5 mL pentane and dried under vacuum. See Table 31 for NMR data.

Formation of 162. To **161**, formed above, 0.5 mL CD_3CN and 0.5 mL CDCl_3 was added at 0°C producing a yellow solution. Yields were quantitative by NMR. See Table 32 for NMR data.

Formation of 163. 5.0 mL (40.2mmol) 1,3-cyclooctadiene and 3.5 mL (44.0) diiodomethane were added to 10.4 g (104.5mmol) CuCl and 6.8 g (104.5mmol) Zn dust in diethyl ether using Simmon-Smith conditions. The mixture was washed 2 times with 0.1N HCl and once with water and dried (K_2CO_3). The ether was removed under vacuum and the yellow oil prep GC (col. temp. = 120° C, 2nd peak). 1H NMR ($CDCl_3$) 5.67 (m, 1H), 5.40 (brd, J_{HH} = 12, 1H), 2.42 (m, 1H), 1.95 (m, 3H), 1.6 (m, 2H), 1.2-1.45 (m, 2H), 0.75-1.0 (m, 2H), 0.7 (ddd, 1H), -0.2 (dd, 1H); ^{13}C NMR ($CDCl_3$) 134.5 (d), 126.7 (d), 31.3 (t), 29.6 (t), 28.0 (t), 25.8 (t), 19.2 (d), 14.6 (d), 10.5 (t); MS m/e (%) 122 (m^+ , 43.7), 107 (13.2), 94 (18.7), 93 (54.7), 91 (15.6), 81 (70.3), 80 (59.4), 79 (100).

Formation of 164. 124.7 mg (0.212mmol) Zeise's dimer was added to a 25 mL round bottom containing 56.9 mg (0.466) 163 and solvent. The following conditions were tried: (A) Diethyl ether at room temperature for 8 h. (B) Refluxing diethyl ether for 8 h. (C) Refluxing chloroform under nitrogen for 18 h. (D) Refluxing toluene for 2 h under nitrogen. (E) 250 mg Zeise's dimer in refluxing diethyl ether for 10 h. The above experiments were all run with 10-15 mL solvent with continuous stirring. At the end of the reaction pentane was added precipitating a yellow solid. The solid was generally washed a total of 3 times and then dried under vacuum. The precipitate could be characterized by NMR in $CDCl_3$ which gave broad resonances due to the platinum. Pyridine could be added which sharpened the signal and enabled platinum coupling to be measured. The pyridine solutions were unstable and fell apart to Py_2PtCl_2 and 163. See Table 33 for NMR data.

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APPENDICES

APPENDIX A

NMR AND MS DATA FOR 37, 38, 39, 40, 57, 70, 72
AND
UNLABELLED 37 AND 40

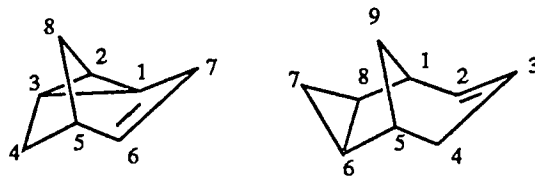


Table 34. NMR Data for Compound 37.

^1H NMR*	^2H NMR*
1) 1.5-1.65 (m)	
2) 1.35-1.5 (m)	
3) 1.35-1.5 (m)	
4) 1.6-exo (m)	1.6
endo absent	0.8
5) 2.50 (brs)	
6) 5.8-5.9 (m)	
7) 5.8-5.9 (m)	5.9
8) 1.5-1.65	

* Relative to CDCl_3

() Multiplicity

MS, m/e (%) 108 (m^+ , 3.3), 107 (33.7), 106 (62.2), 105 (23.6), 92 (48.4), 91 (99.7), 80 (25.6), 79 (77.9), 78 (100).

Table 35. ^{13}C NMR Data for Compound 39.

^{13}C NMR*
1) 15.0
2) 13.1
3) 13.1
4) 27.0 (increased intensity)
5) 31.1
6) 128.2
7) 122.0 (increased intensity)
8) 27.0

* Relative to CDCl_3

() Multiplicity

MS, m/e (%), 107 (m^+ , 33.7), 106 (62.1), 105 (27.1), 103 (11.4), 93 (12.5), 92 (59.1), 91 (94.9), 80 (26.9), 79 (72.0), 78 (100).

Table 36. NMR Data for Compound 38 and Compound 40.

38 ² H NMR*		40 ¹³ C NMR**
1)		32.0
2)	2.0	33.8
3)	5.2	124.2 (intensity increased 20-fold)
4)		135.3
5)		32.5
6)		26.7
7)	0.4 0.2	5.1 (intensity increased 20-fold)
8)		20.0
9)		24.9

* Relative to CDCl₃** Relative to DMSO-d₆

40 MS, m/e (%) 122 (m⁺, 11.8), 121 (18.2), 120 (19.4), 107 (11.3), 106 (34.6), 105 (23.9), 94 (10.9), 93 (32.6), 92 (49.2), 91 (34.8), 81 (33.7), 80 (78.3), 79 (100).

Table 37. NMR Data for Compound 57.

¹ H NMR*		¹³ C NMR*
1)	1.79 (brs) 1H	18.1
2)	1.55 (m) 1H	17.2
3)	1.95 (m) 1H	14.0
4)	1.74 (brd) 1H	23.7
	1.55 (m) 1H	
5)	2.23 (brs) 1H	40.6
6)	6.05 (dt) 1H	130.0
7)	5.90 (dt) 1H	122.2
8)	0.5 (d) 1H	45.1

* Relative to DMSO-d₆

() Multiplicity

Table 38. ^1H NMR Data for Compound 70.

^1H	
1)	1.55 (m)
2)	2.30 (exo)
	2.0 (endo)
3)	5.4 (dt)
4)	6.2 (ddd)
5)	3.0
6)	1.49 (m)
7)	-0.1 (dd, anti)
	0.06 (dt, syn)
8)	1.04 (m)
9)	0.72 (d)

* Relative to DMSO- d_6

() Multiplicity

Table 39. NMR Data for Compound 72.

^1H NMR*	^{13}C NMR*
1) 1.79 (brd) 1H	18.1**
2) 1.55 (m) 1H	17.2**
3) 1.95 (brdd) 1H	14.0**
4) 1.74 (brd) 1H	23.7
1.55 (m) 1H	
5) 2.23 (brs) 1H	40.6
6) 6.05 (dt) 1H	130.0
7) 5.90 (dt) 1H***	122.2***
8) 0.5 (d) 1H	45.1

* Relative to DMSO- d_6

** Not rigorously determined

*** ^{13}C labelling observed

() Multiplicity

Table 40. NMR Data for Compound 37-nonlabelled*.

	^1H ppm**	^{13}C ppm**
1)	1.59 (m)	15.4
2)	1.39 (d)	13.4
3)	1.59 (m)	13.4
4)		27.5
5)	2.50 (brs)	32.4
6)	5.90 (m)	122.2
7)	5.82 (m)	128.8
8)	0.7 (d)	27.5
	1.53 (dd)	

* Taken from Waddington M. D.; Ph. D. Thesis; M.S.U. pp 172 and 240.

** Relative to CDCl_3

() Multiplicity

Table 41. NMR Data for Compound 40-nonlabelled*.

	^1H **	^{13}C **
1)	2.24 (m)	33.5
2)	2.30 (exo)	35.7
	2.0 (endo)	
3)	5.24 (m)	125.2
4)	6.07 (ddd)	136.5
5)	2.20	33.7
6)	1.44 (m)	25.6
7)	0.38 (syn)	6.1
	0.19 (anti)	
8)	0.98 (m)	17.7
9)	1.25	26.9
	1.30	

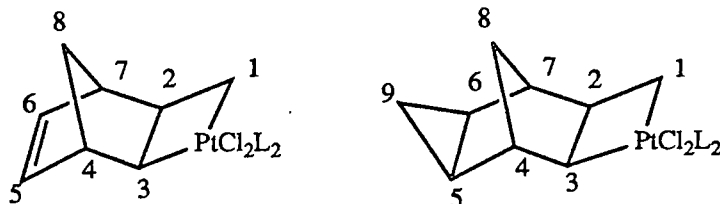
* Taken from Waddington, M. D., Ph. D. Thesis; M.S.U.; pp 174 and 240.

** Relative to CDCl_3

() Multiplicity

APPENDIX B

^{13}C NMR SHIFTS FOR NORBORNYL PLATINACYCLOBUTANES

Table 42. ¹³C NMR Data for Unsaturated Norbornyl Platinacyclobutane.

Solvent- #	CDCl ₃ L = pyridine*	pyridine-d ₅ L = pyridine	CDCl ₃ L = 2,2'-bipyridine
1	-2.2 (371)	-2.7 (376.4)	-3.1 (362)
2	51.5 (83)	52.0 (85.9)	50.2 (84)
3	10.7 (403)	9.7 (408.3)	8.9 (391)
4	45.7 (<10)	46.2 (0)	45.1 (0)
5	134.9 (37)	135.5 (37.5)	135.0 (37)
6	136.3 (0)	136.4 (0)	136.2 (0)
7	46.9 (24)	47.4 (23.9)	46.2 (21)
8	44.4 (0)	45.1 (0)	44.0 (0)

* Taken from Ekeland, R. A., Ph. D. Thesis; M. S. U., pp 91.

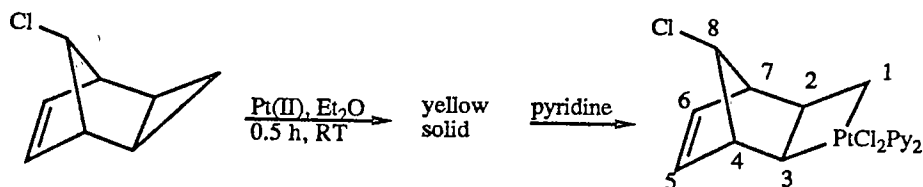
Table 43. ¹³C NMR Data for Cyclopropyl Norbornyl Platinacyclobutane.

Solvent- #	CDCl ₃ L = pyridine*	pyridine-d ₅ L = pyridine	CDCl ₃ L = 2,2'-bipyridine
1	-9.0 (359)	-9.7 (363.5)	-10.3 (348)
2	56.7 (93)	57.0 (94.3)	55.2 (91)
3	13.8 (396)	12.7 (400.0)	11.8 (385)
4	39.2 (<10)	39.5 (0)	38.7 (0)
5	13.2 (39)	13.9 (40.0)	13.6 (38)
6	13.7 (0)	14.2 (0)	13.6 (0)
7	41.7 (22)	42.0 (24.0)	41.2 (21)
8	22.5 (0)	23.1 (0)	22.4 (0)
9	1.6 (0)	1.8 (0)	1.4 (0)

* Taken from Ekeland, R. A., Ph. D. Thesis; M. S. U., pp 91.

APPENDIX C

CHLORO-NORBORNYLPLATINACYCLOBUTANE

Table 44. NMR Data for 8-chloro-tricyclo[3.2.1.0^{2,4}]oct-6-ene*.

	¹³ C ppm	¹ H ppm
CH ₂	20.8	0.99 (dd) 1.18 (dd)
CH	23.5	1.82 (m)
bridgehead	48.6	2.93 (brs)
bridge	68.4	3.91 (brs)
olefin	137.7	6.36 (brs)

* Relative to CDCl₃

() Multiplicity

Table 45. NMR Data for Chloro-Norbornyl Platinacyclobutane.

#	¹³ C ppm*	J _{Pt,C} **	¹ H ppm*	J _{Pt,H} **	J _{H,H} **
1	-3.2	374.7	2.72 (brs)	85.6	
2	50.3	84.8	2.53 (dd)	unres.	8.1, 7.8
3	5.72	412.0	2.65 (d)	99.6	8.1
4	52.4	0	2.90 (s)	19.0	
5	131.7	39.0	5.94 (brs)	0	
6	131.9	0	5.94 (brs)	0	
7	54.0	23.7	2.72 (brs)	0	
8	72.4	0	5.38 (brs)	0	

¹⁹⁵Pt NMR - 3214***.* Relative to CDCl₃

** Coupling in Hertz

*** Relative to 1M Na₂Pt(CN)₄ in D₂O at 25° C.

() Multiplicity

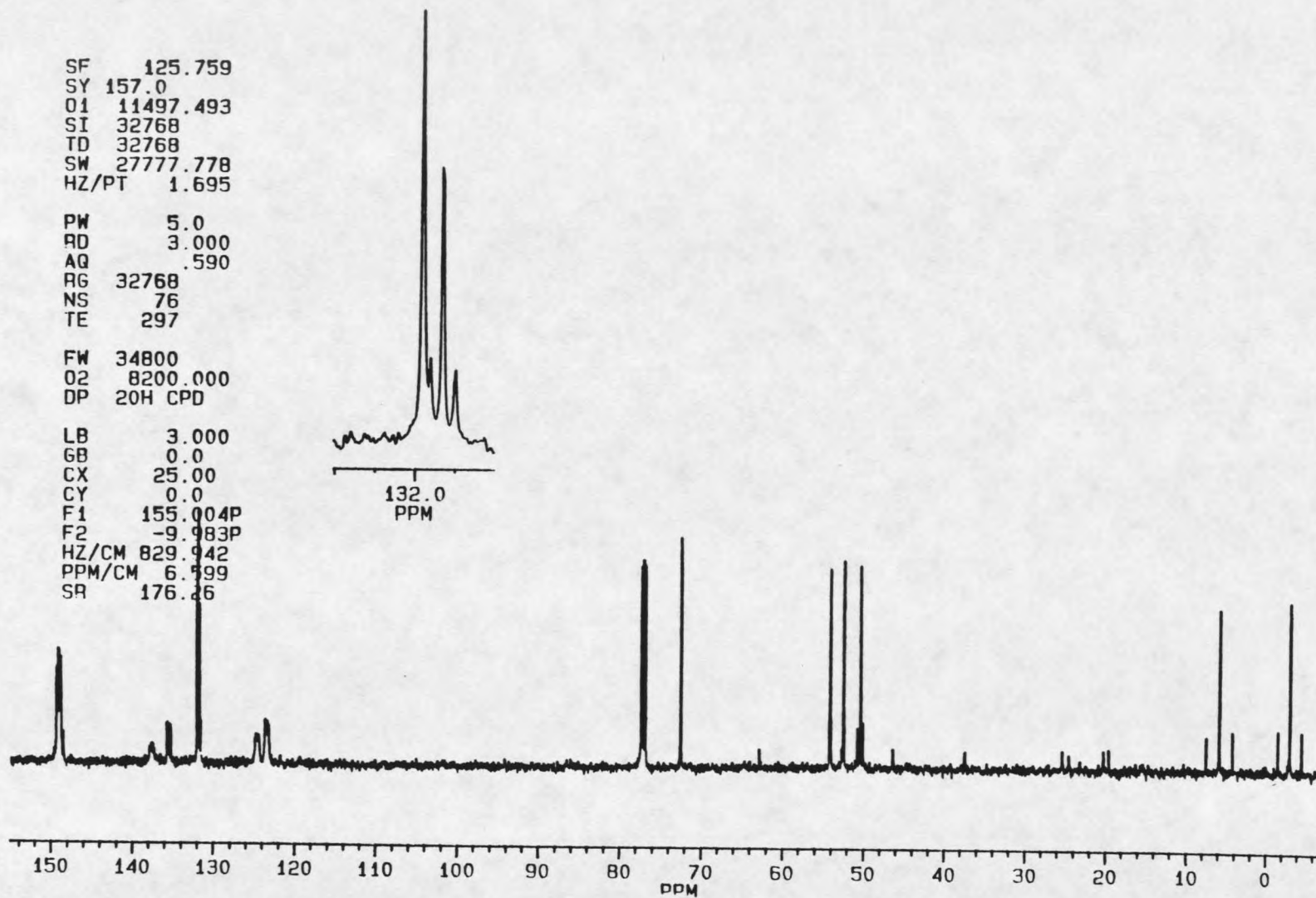
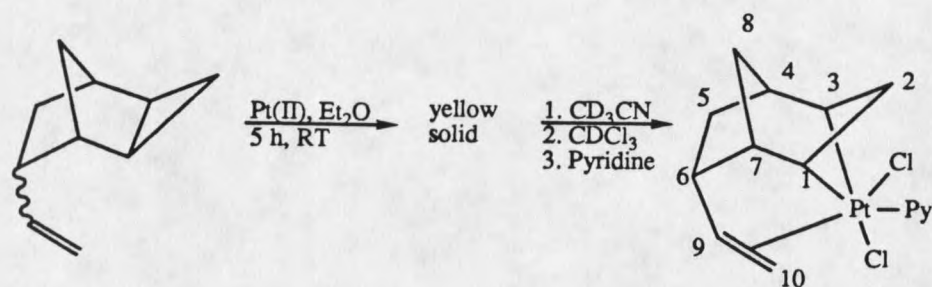


Figure 110. CPD ^{13}C NMR Spectrum of Chloro-Norbornyl Platinacyclobutane.

APPENDIX D

POSTULATION OF A
NOVEL PLATINACYCLOBUTANE-OLEFIN COMPLEX

Table 46. NMR Data for Platinacyclobutane-Olefin Complex[!].

	¹³ C ppm [*]	J _{Pt,C} ^{**}	¹ H ppm [*]	J _{Pt,H} ^{**}	J _{H,H} ^{**}
1	28.3	336.6	1.6 (dd)	unres.	
2	30.3	39.9	1.6 (dd)	unres.	
3	28.3	336.6	1.9 (brs)		
4	42.7	0	2.8 (brs)		
5	32.8	22.3	2.2 (brs)		
6	44.7	16.6	2.9 (brs)		
7	81.2	15.8	5.4 (brs)	24.1	
8	41.6	20.2	2.85 (brs)		
9	92.5	231.6	4.52 (dd)	55	7.3, 12.8
10	60.4	244.0	3.34 (d)	76.1	7.3
			3.81 (d)	78.2	13.0

¹⁹⁵Pt NMR - 1297^{***}.[!] Assignments not rigorously determined^{*} Relative to CDCl₃^{**} Coupling in Hertz^{***} Relative to 1M Na₂Pt(CN)₄ in D₂O at 25° C.

() Multiplicity

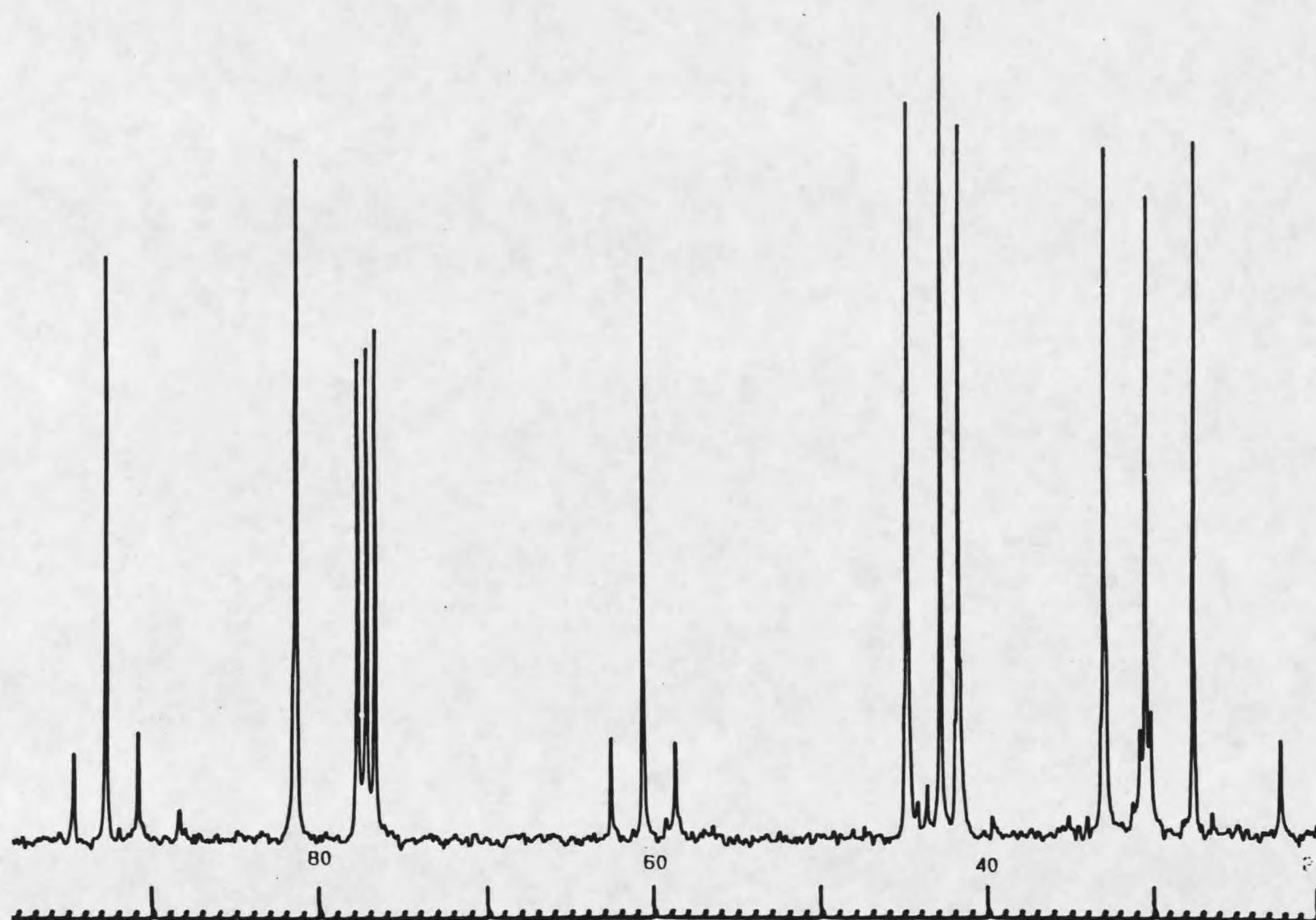
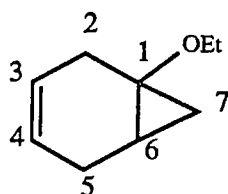


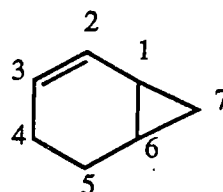
Figure 111. BB ^{13}C NMR Spectrum of Platinacyclobutane-Olefin Complex.

APPENDIX E

NMR ASSIGNMENTS FOR COMPOUNDS
101, 114, 137, 138, 139, 149



101



114

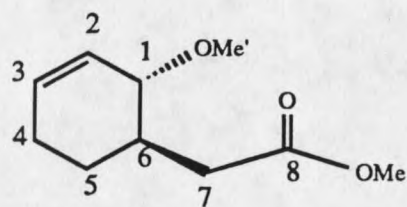
Table 47. NMR Assignments for 101 and 114.

#	<u>101</u>		<u>114</u>	
	¹³ Cppm*	¹ Hppm*	¹³ Cppm*	¹ Hppm*
1	59.7		9.7	1.1-1.2 (m)
2	28.0	2.37-2.53 (m) 2.6-2.7 (m)	128.9	6.0 (m)
3	123.6	5.4-5.52 (m)	122.8	5.3-5.4 (m)
4	123.5	5.35-5.4 (m)	20.7	1.65-1.80 (m) 1.9-2.0 (m)
5	25.6	2.1-2.2 (m) 2.37-2.53 (m)	18.6	1.5-1.62 (m) 1.9-2.0 (m)
6	18.0	1.2-1.25 (m)	13.9	1.2-1.32 (m)
7	13.8	0.45-0.5 (dd) 0.73-0.80 (dt)	10.1	0.55-0.62 (dd) 0.65-0.75 (dt)
CH ₂	61.5	3.45 (m)		
Me	15.7	1.13 (t)		
MS**	138 (m+, 41.8)		94 (m+, 44.5)	
	123 (33.7)		91 (16.6)	
	110 (69.9)		79 (100)	
	109 (37.4)			
	95 (90.0)			
	55 (100.0)			

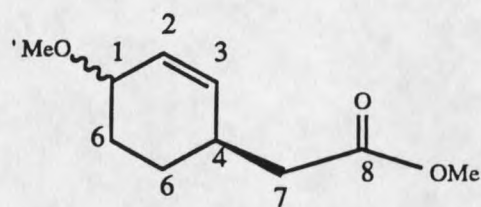
* Relative to CDCl₃

** m/e (%)

() Multiplicity



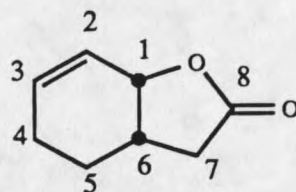
137



138, 139

Table 48. NMR Assignments for 137, 138 and 139*.

	<u>137</u>		<u>138 and 139</u>			
#	¹³ Cppm	¹ Hppm	¹³ Cppm	¹ Hppm	¹³ Cppm	¹ Hppm
1	78.9	3.49(d, J=6.25)	74.9	3.75(m)	72.9	3.62(m)
2	126.1	5.72(brd)	128.9	5.74	127.6	5.78
3	130.2	5.79(brd)	132.8	5.63	134.0	5.70
4	24.2	1.98(m)	32.5	2.60	32.4	2.60
		2.04(m)				
5	25.8	1.38(m)	26.5	1.2	24.3	1.40
		1.80(m)		1.90		unres.
6	35.4	2.13(m)	27.2	1.5	29.7	1.63
				2.0		1.78
7	37.3	2.18(dd)**	40.1	2.2	39.6	unres.
		2.50(dd)**		2.28		unres.
8	173.4		172.7		172.9	
Me'	55.4	3.30(s)	55.6	3.32	56.0	3.32
Me	51.4	3.63(s)	51.5	3.64	51.4	3.63
MS***	184 (m+, 2.6)		184 (m+, 1.3)		184 (m+, 0.4)	
	169 (10.2)		153 (17.8)		152 (1.0)	
	153 (5.7)		152 (14.5)		111 (82.6)	
	152 (7.8)		111 (78.6)		110 (97.6)	
	137 (11.1)		110 (100)		91 (60.1)	
	124 (16.1)		91 (40)		79 (75.2)	
	110 (74.7)		79 (39.0)		74 (100)	
	84 (100)		74 (52.7)			
!	Columns 6 and 7 list data for smallest isomer, 2 and 3 the major isomer.					
*	Relative to CDCl ₃					
**	J=14.1, 5.5 Hertz					
***	m/e (%)					
()	Multiplicity					



149

Table 49. NMR Assignments for 149*.

#	¹³ Cppm	¹ Hppm
1	75.4	4.77 (dd, J = 6.2)
2	123.3	5.86 (m)
3	134.0	6.10 (m)
4	22.6	2.0-2.14 (m)
5	23.5	1.40-1.53 (m)
		1.67-1.76 (m)
6	33.5	2.56 (m)
7	35.0	2.23 (dd, J = 4.3, 16.7)
		2.68 (dd, J = 3.8, 16.7)
8	176.4	

MS** 138 (m+, 100) IR - 1771.6 cm⁻¹
 110 (92.1)
 93 (12.7)
 82 (15.7)
 79 (80.7)
 77 (27.8)
 67 (32.5)
 55 (33)

* Relative to CDCl₃

** m/e (%)

() Multiplicity

APPENDIX F

REACTION OF 115 WITH ETHYLENE-CO, AMINES AND FORMIC ACID

Reaction of **115** with a mixture of formamide and formic acid yielded a yellow solution. The solution was submitted to carbon monoxide, 500 psi for 7 days at room temperature. The solution was washed 3X with CHCl_3 and chromatographed on silica gel, producing **165** in 75-80% yields, Equation 65. Data for **163** is listed in Table 50. Coordination of the nitrogen atom to the platinum was felt to be preventing CO insertion, therefore formation of a methyl group is occurring by a reductive elimination.

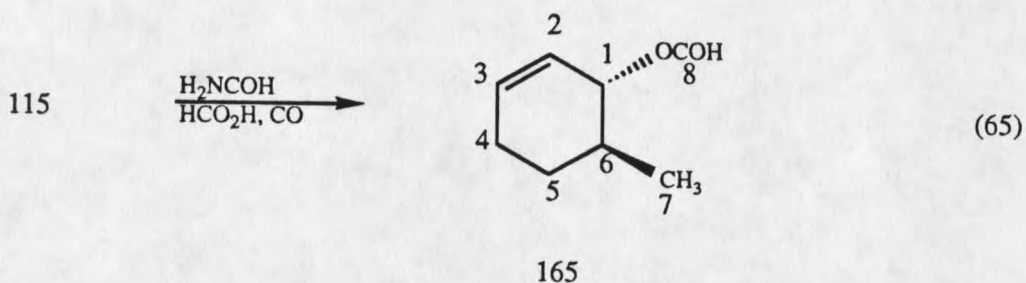


Table 50. NMR Data for **165***

#	^{13}C ppm	^1H ppm	$J_{\text{H,H}}$
1	74.9	5.10 (dd)	2.4, 7.1
2	125.4	5.57 (ddd)	10.1, 2.4, 2.0
3	131.9	5.89 (dt)	10.1, 2.8
4	24.0	2.0-2.1 (m)	
5	27.7	1.44 (m)	
		1.77 (m)	
6	33.2	1.83 (m)	
7	17.8	0.96 (d)	6.7
8	161.2	8.10 (s)	

MS** $\text{C}_8\text{H}_{12}\text{O}_2$
 IR 1716 cm^{-1}

- * Assignments made by COSY, XHCORR, DEPT and decoupling techniques.
 * Relative to CDCl_3
 ** High Resolution MS
 () Multiplicity

Reaction of **115** with methanol (3 mL), ethylene and carbon monoxide (800 psi at 85° C, 4 days), respectively, was performed in an attempt to extend the carbon chain by two methylene units. However, polymerization appeared to have occurred. Gas chromatography revealed as many as 40 products apparent, ^{13}C NMR spectroscopy displayed a myriad of olefinic, carbonyl and upfield resonances. Two groups of carbonyl resonances appeared, one at around 210 ppm and another at 170 ppm. These chemical shifts are indicative of saturated and α,β -unsaturated esters and ketones. The region from 10 ppm to 80 ppm was a forest of resonances indicating a host of ether and hydrocarbon functionalities. Finally, IR spectroscopy displayed strong bands at 1214, 1719, 1732 and 3020 cm^{-1} . Figure 112 depicts three types of possible compounds. The upper left structure is formed by continuous insertion of ethylene into the platinum-carbon bond, while insertion of one ethylene and a CO followed by propagation will give the lower left structure. The right hand structure results from C-H bond activation producing α,β -unsaturated compounds, this is the least likely of the three. Another possibility not shown is simple copolymerization of ethylene and CO by the platinum, not involving the cyclohexene ring. With the multitude of products obtained, the reaction was not pursued any farther.

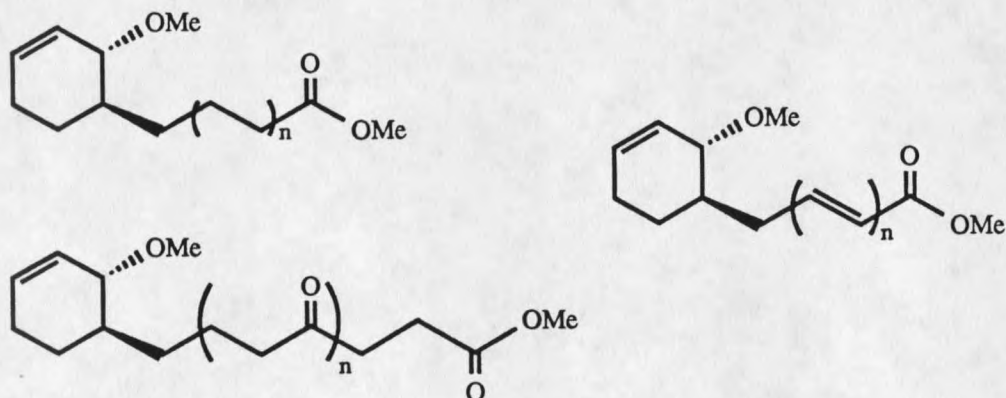


Figure 112. Possible Products in the Reaction of **115** with CO, C_2H_4 and MeOH.

Reaction of amines with **115** was undertaken to further broaden the range of organic products formed. Complex **115** dissolves easily into numerous amines, however, after stirring for 30 hours no precipitation of platinum occurred. Moreover, separation of 20-30 mg of organic products from the solution proved quite difficult. In a final attempt to overcome the above problems **115** was reacted with one equivalent of triphenylphosphine per platinum, 5 equivalents of isopropyl amine in 3 mL CHCl_3 . This mixture was stirred for 30 hours resulting in a yellow solution. Distillation of the chloroform produced an orange solid in a small amount of liquid. Chromatography on silica gel with diethyl ether yielded a yellow oil. GCMS of the oil displayed 3 peaks all with a m^+ of 153. ^{13}C NMR spectroscopy revealed 6 olefinic resonances (excluding the Ph_3P) and 3 resonances between 60 and 70 ppm. Furthermore, resonances appeared between 15 and 51 ppm. In the ^1H NMR spectrum a set of resonances appeared at 5.5 and 5.8 ppm, 3-4 ppm and 0.7 to 2.0 ppm. With this data, the structures are proposed as shown in Figure 113.

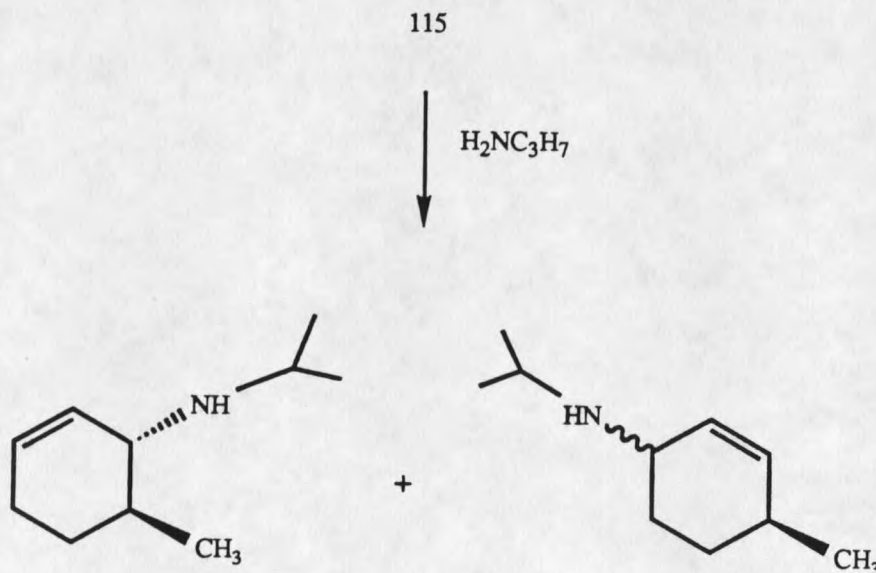


Figure 113. Reaction of **115** with Isopropyl Amine.

APPENDIX G

X-RAY DATA FOR COMPLEX 100

Table 51. Atomic Coordinates ($\times 10^3$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with Standard Deviations in Parenthesis.

	x/a	y/b	z/c	U ^a
Pt	412.0(1)	506.7(1)	260.8(1)	30(1)
C(1)	203(2)	141(1)	129(1)	54(5)
C(2)	104(2)	248(1)	230(1)	58(5)
C(3)	125(2)	402(1)	236(1)	48(4)
C(4)	145(2)	421(1)	112(1)	49(4)
C(5)	166(2)	285(1)	-17(1)	52(4)
C(6)	293(2)	194(1)	36(1)	47(4)
C(7)	480(2)	307(1)	127(1)	38(3)
C(8)	609(2)	331(2)	29(1)	55(5)
O	212(2)	14(1)	125(1)	79(5)
Cl	730.5(4)	603.7(4)	371.1(4)	56(1)
N	339(1)	719(1)	399(1)	40(3)
C(9)	359(2)	759(1)	539(1)	51(4)
C(10)	319(2)	890(1)	630(1)	62(5)
C(11)	258(2)	993(1)	580(2)	59(5)
C(12)	238(2)	956(1)	439(2)	55(5)
C(13)	282(2)	820(1)	351(1)	45(4)
H(2a) ^b	160	258	335	69 ^c
H(2b)	-47	199	201	
H(3)	126	500	334	
H(4)	145	531	110	
H(5a)	27	215	-73	
H(5b)	233	322	-86	
H(6)	317	97	-54	
H(7)	560	262	190	
H(8a)	612	221	-56	
H(8b)	752	383	89	
H(8c)	552	404	-15	
H(9)	410	681	579	
H(10)	333	916	741	
H(11)	227	1101	651	
H(12)	188	1032	397	
H(13)	270	793	240	

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor

^bHydrogen atom coordinates were calculated in idealized positions

^cA common isotropic thermal parameter was refined for all H atoms

Table 52. Bond Angles (deg).

C(7)-Pt-Cl	91.3(3)	C(7)-Pt-N	178.8(4)
Cl-Pt-N	89.1(2)	C(2)-C(1)-C(6)	117.2(1)
C(2)-C(1)-O	120.7(2)	C(6)-C(1)-O	122.1(1)
C(1)-C(2)-C(3)	114.9(1)	C(2)-C(3)-C(4)	119.2(1)
C(3)-C(4)-C(5)	118.8(1)	C(4)-C(5)-C(6)	107.1(1)
C(1)-C(6)-C(5)	110.8(1)	C(1)-C(6)-C(7)	107.3(1)
C(5)-C(6)-C(7)	106.5(1)	Pt-C(7)-C(6)	108.9(1)
Pt-C(7)-C(8)	112.6(1)	C(6)-C(7)-C(8)	109.6(1)
C(3)-Pt-C(4)	38.7(6)	C(4)-Pt-C(7)	82.6(4)
C(4)-Pt-Cl	164.7(4)	C(3)-Pt-N	87.3(4)
Pt-C(3)-C(2)	114.7(9)	Pt-C(4)-C(5)	109.1(8)
Pt-N-C(13)	121.8(7)	N-C(9)-C(10)	123.1(1)
C(3)-Pt-C(7)	92.8(4)	N-C(13)-C(12)	121.7(1)
C(3)-Pt-Cl	156.2(4)	C(4)-Pt-N	96.8(4)
Pt-C(3)-C(4)	71.2(7)	C(9)-C(10)-C(11)	119.3(1)
Pt-C(4)-C(3)	70.1(6)	C(11)-C(12)-C(13)	119.8(1)
Pt-N-C(9)	120.5(1)	C(10)-C(11)-C(12)	118.5(1)
C(9)-N-C(13)	117.6(1)		

Table 53. Bond Lengths (Å).

Pt-C(3)	2.123(1)	Pt-C(4)	2.138(1)
Pt-C(7)	2.041(1)	Pt-Cl	2.314(3)
Pt-N	2.158(1)	C(1)-C(2)	1.484(2)
C(1)-C(6)	1.474(2)	C(1)-O	1.225(2)
C(2)-C(3)	1.472(2)	C(3)-C(4)	1.413(2)
C(4)-C(5)	1.497(2)	C(5)-C(6)	1.527(2)
C(6)-C(7)	1.546(1)	C(7)-C(8)	1.541(2)
N-C(9)	1.339(2)	N-C(13)	1.354(2)
C(9)-(10)	1.340(2)	C(10)-C(11)	1.393(2)
C(11)-C(12)	1.354(2)	C(12)-C(13)	1.370(2)

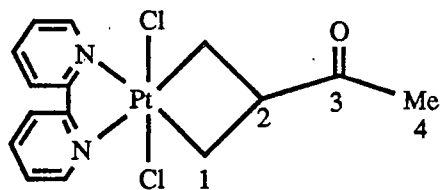
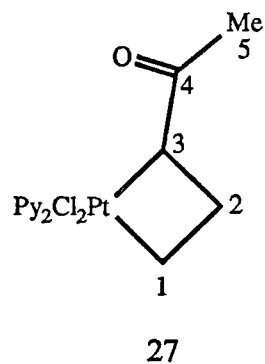
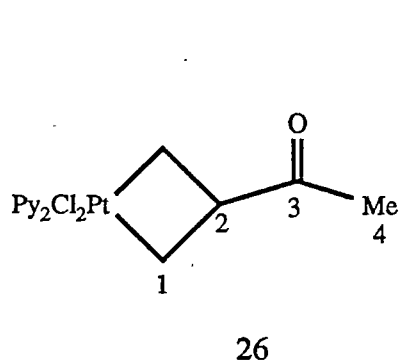
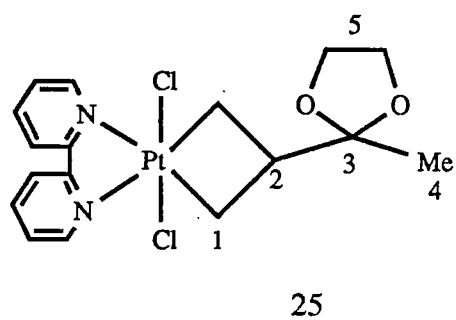
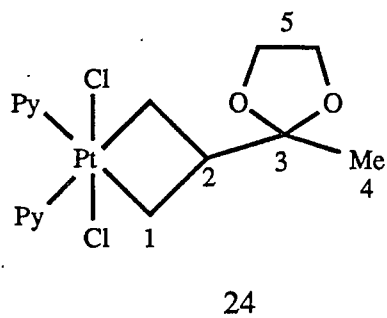
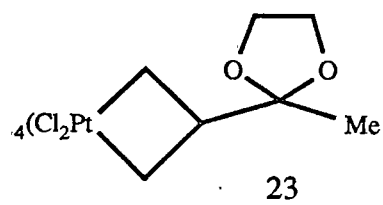
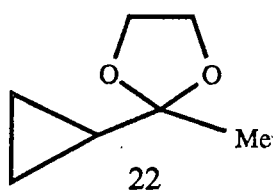
Table 54. Anisotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with Standard Deviations.

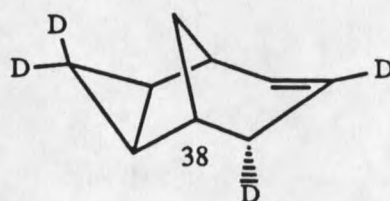
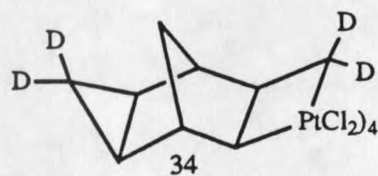
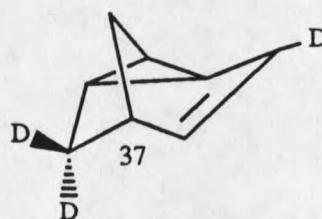
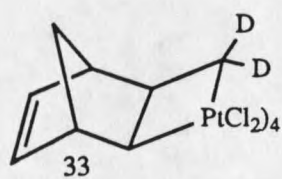
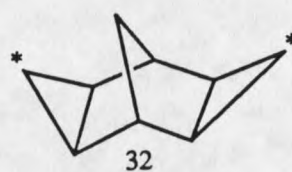
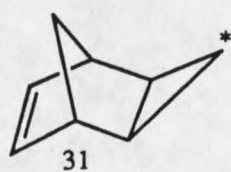
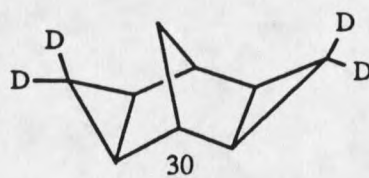
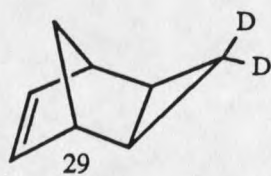
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13} U_{12}
Pt	36(1)	27(1)	29(1)	12(1)	8(1)10(1)
C(1)	67(7)	42(5)	50(6)	21(5)	7(5) 4(5)
C(2)	66(7)	49(6)	59(7)	25(6)	21(6)-6(5)
C(3)	42(5)	55(6)	55(6)	25(5)	21(5)19(5)
C(4)	40(5)	49(6)	54(6)	20(5)	5(4) 8(4)
C(5)	58(6)	51(6)	42(5)	21(5)	-4(5)-2(5)
C(6)	65(6)	35(5)	34(5)	12(4)	4(4) 6(5)
C(7)	48(5)	30(4)	37(4)	13(3)	15(4)13(4)
C(8)	64(7)	58(7)	53(6)	23(6)	31(6)24(6)
O	96(8)	54(5)	103(8)	52(6)	21(7) 9(5)
Cl	41(1)	51(1)	59(2)	11(1)	2(1)11(1)
N	46(4)	38(4)	38(4)	15(3)	15(3)16(3)
C(9)	80(8)	48(6)	35(5)	20(4)	23(5)27(6)
C(10)	102(10)	47(6)	39(5)	14(5)	32(6)27(7)
C(11)	78(8)	40(5)	65(8)	20(5)	32(7)19(6)
C(12)	63(7)	42(5)	75(8)	34(6)	18(6)23(5)
C(13)	61(6)	39(5)	43(5)	22(4)	18(5)16(5)

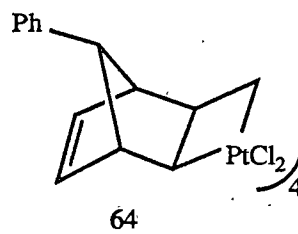
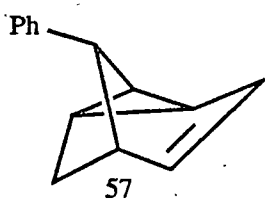
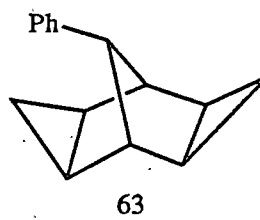
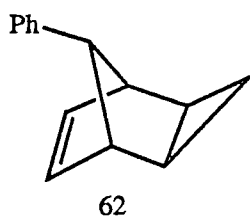
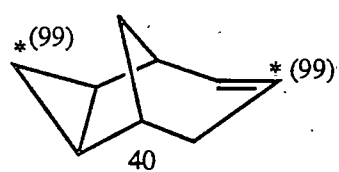
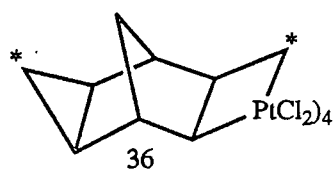
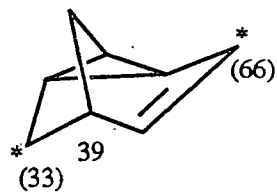
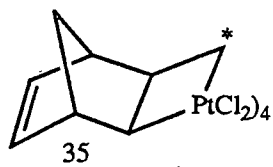
The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})$.

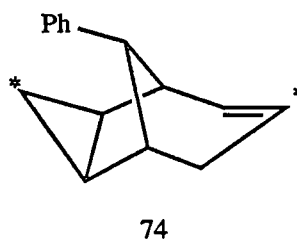
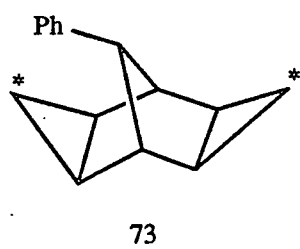
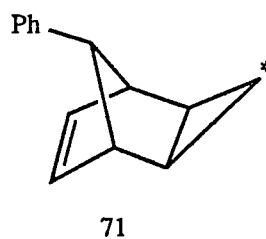
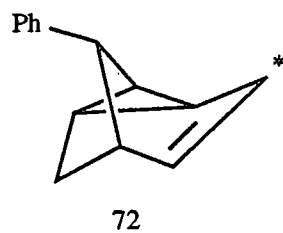
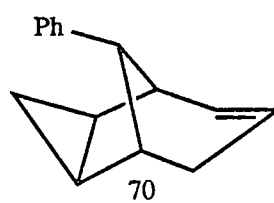
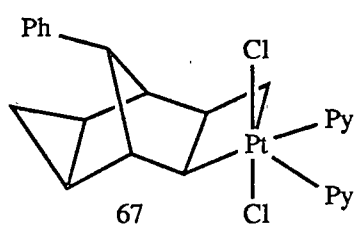
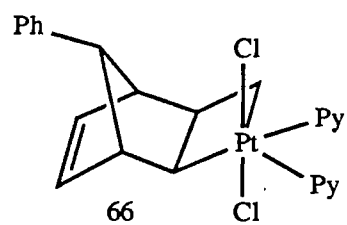
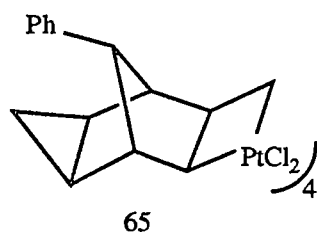
APPENDIX H

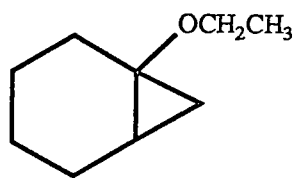
STRUCTURES



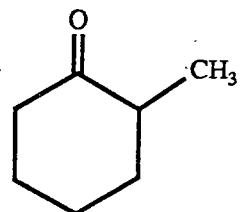




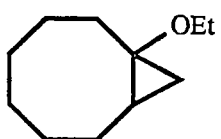




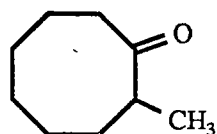
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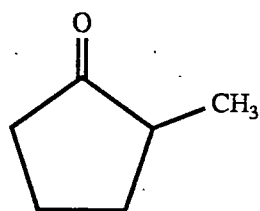
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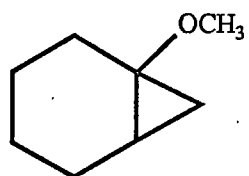
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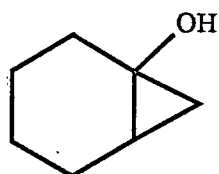
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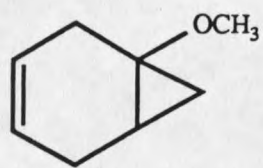
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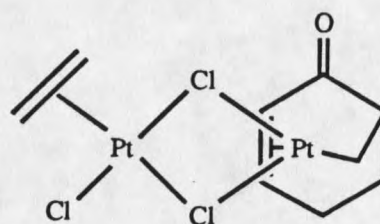
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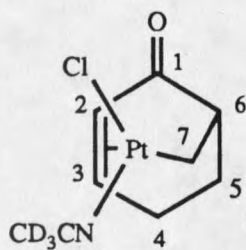
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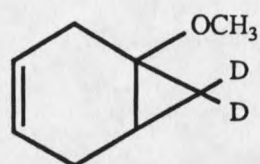
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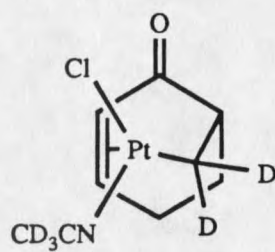
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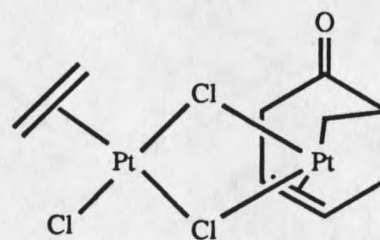
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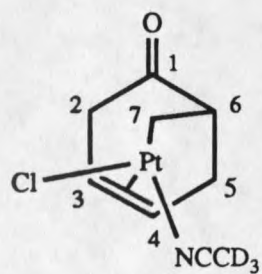
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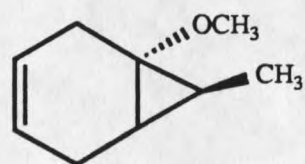
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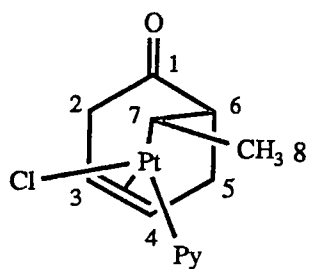
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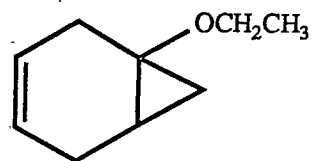
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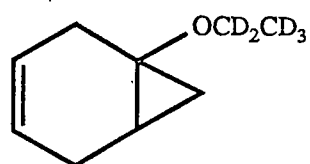
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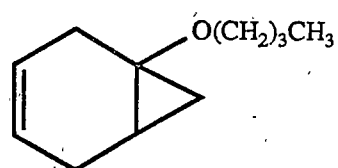
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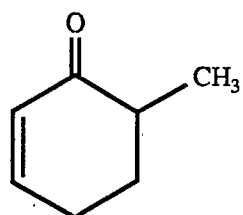
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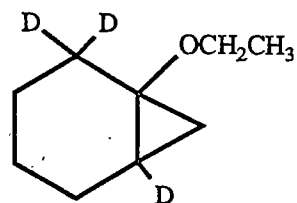
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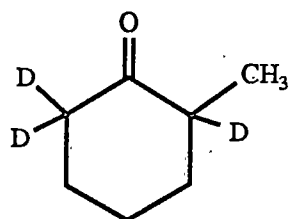
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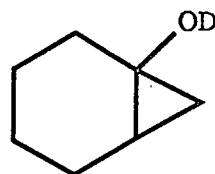
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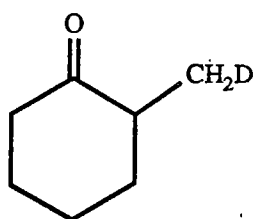
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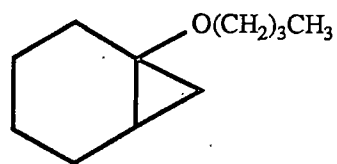
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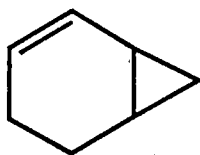
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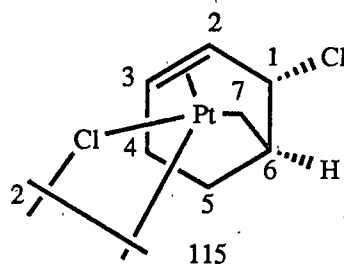
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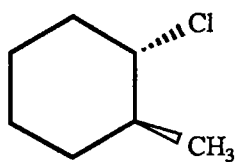
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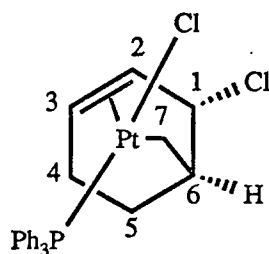
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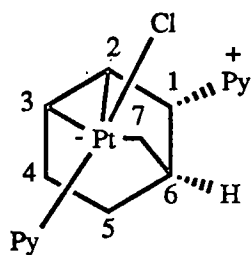
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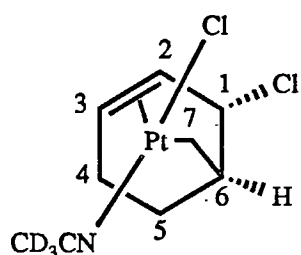
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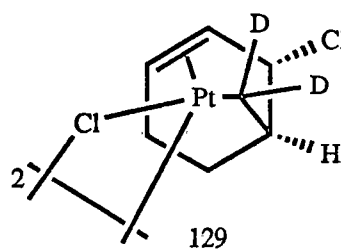
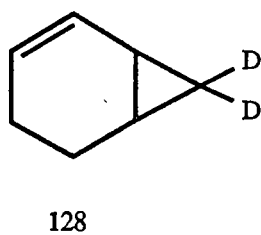
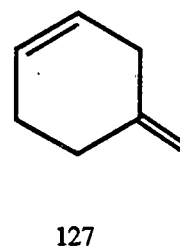
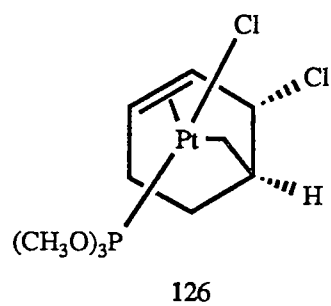
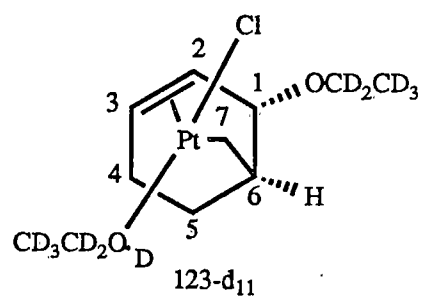
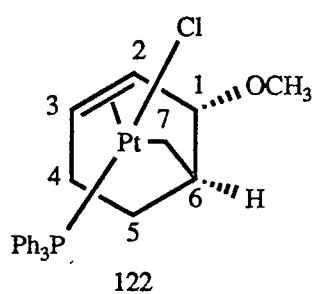
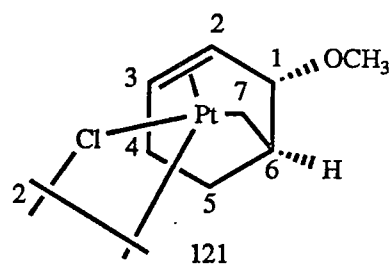
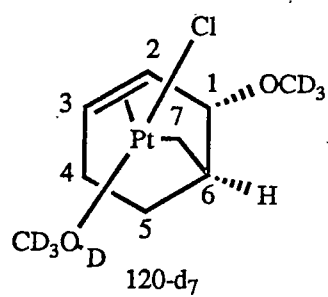
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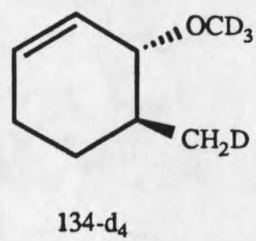
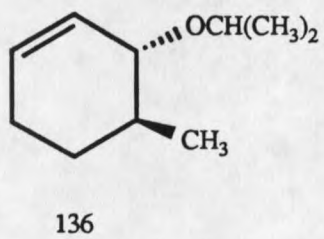
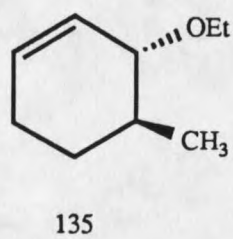
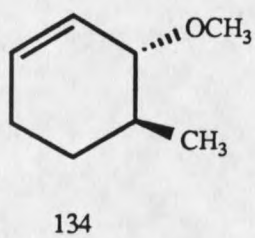
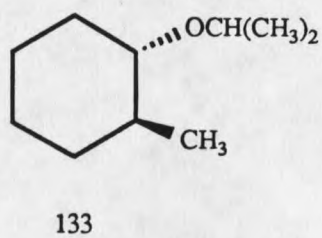
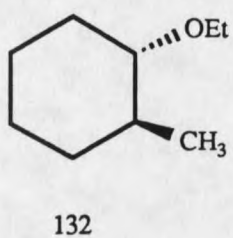
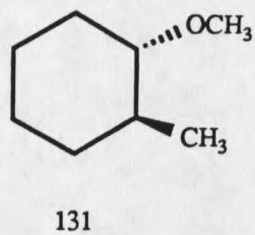
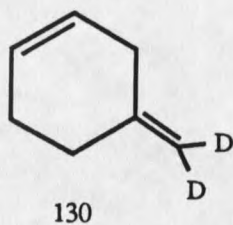


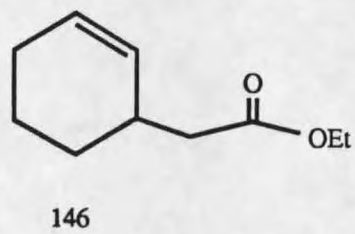
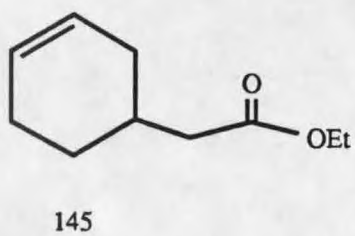
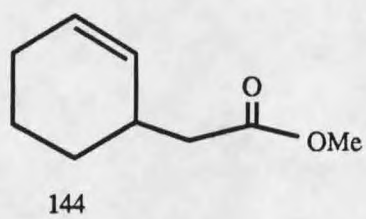
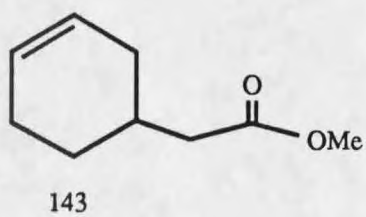
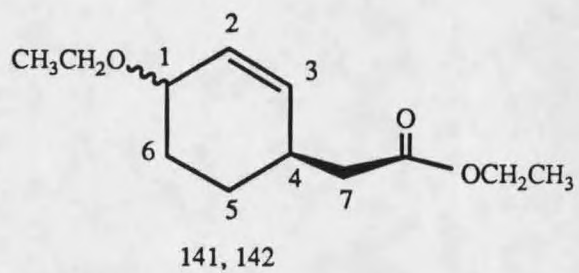
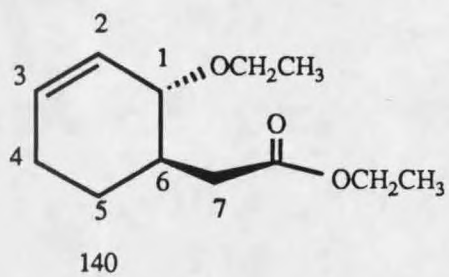
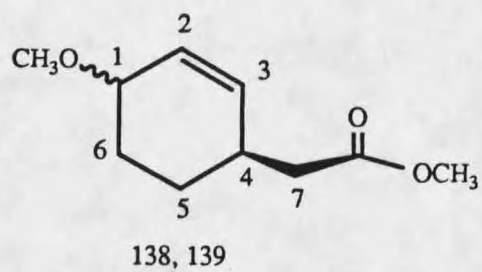
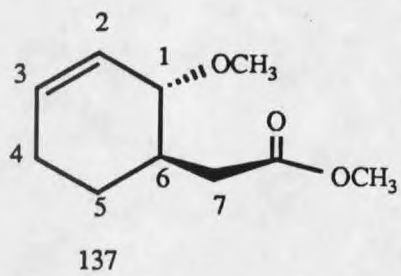
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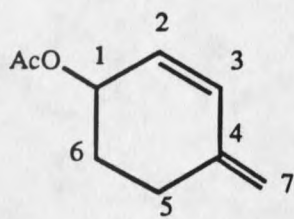


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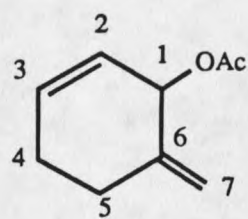




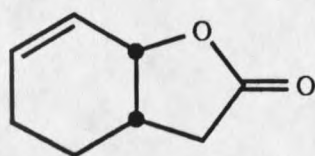




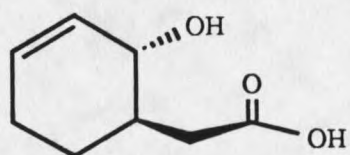
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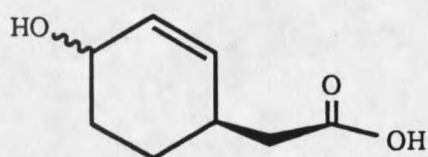
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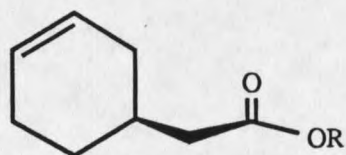
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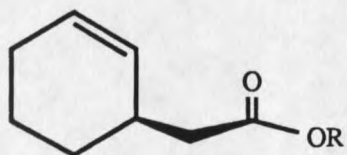
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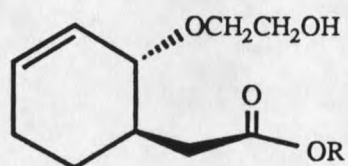
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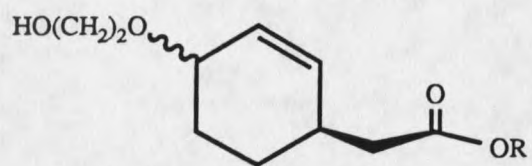
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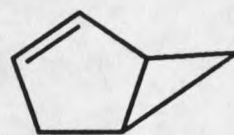
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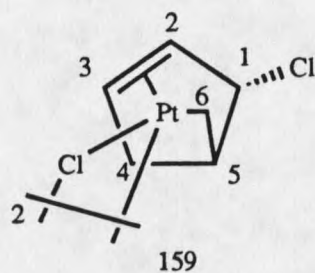
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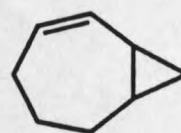
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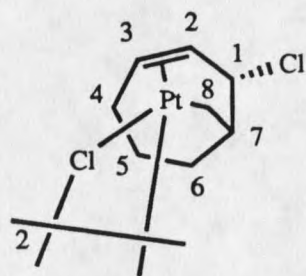
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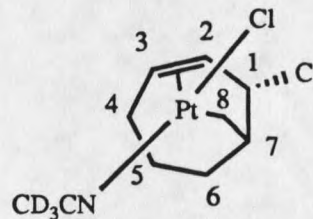
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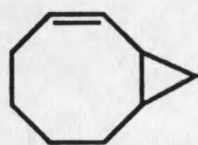
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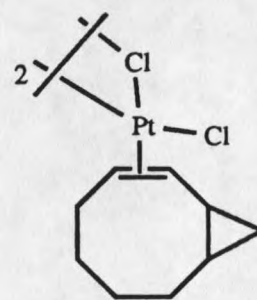
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