



Organic transformations derived from the reaction of platinum (IV) metallacycles with nucleophilic reagents

by Frederick Forrest Stewart

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 can form many stable complexes that can be compared, by analogy, to catalytically active systems. The study of platinum complexes and the chemistry derived from them can give new organic products with intriguing novel reaction mechanisms. Various pathways of chemistry were garnered by the reaction of platinum (IV) metallacycles with nucleophiles. Reaction of platinum (IV) metallacyclopentanes with hydride gives liberated organic substrates where the metal has effected carbon-hydrogen bond formation. The products were methyl norbomyl alcohols or ethers. Reaction of iodide with platinum(IV)cyclobutylcarbinol was observed to give 2-norbomyl acetaldehyde in good yield. Product formation is attributed to (3-hydride elimination, this the first time that this mechanism has been observed with this substrate. Reaction of platinacyclobutanes and platinacyclopentanes with azide have been found to undergo ligand substitution giving stable complexes. Platinacyclobutanes were observed to be more labile in this substitution pathway, substitutions were conducted at room temperature where the analogous platinacyclopentanes required refluxing methanol.

The reaction of diazo-derivatives with platinum(IV) metallacyclobutanes involves a novel metal mediated carbon-carbon bond forming process. The products observed are cis-divinylcyclopentanes which exhibit high degrees of stereocontrol. The process was studied through modification of the substrate and use of alternate diazo-reagents. Norbomyl analogs, benzofuran derived systems, allow for bridgehead substitution readily. This substituted substrate was found to give stereospecific product upon reaction with mono-substituted diazo-reagent, thus giving support to the proposed mechanism. In addition, diazo-reagents with electron donating groups were found to halt the reaction. Attachment of electron withdrawing groups, on the otherhand, was found to give products in good yield.

Platinacyclobutanes are known to ring expand upon solvolysis to give platinacyclopentanes with stereo- and regiospecificity. These bis-pyridyl complexes were found to undergo substitution reactions with various phosphine and phosphite ligands. Studies of these complexes were conducted in excess ligand. Removal of the ligand began decomposition of the complexes, this decomposition was found to be complete in one hour at reflux. The organic products were found to be cyclobutanes formed with total stereospecificity in excellent yield.

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

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in

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APPROVAL

of a thesis submitted by

Frederick Forrest Stewart

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.

6/15/92
Date

Dr. P. W. Jennings
Chairperson, Graduate Committee

Approved for the Major Department

6/15/92
Date

John R. Ames
Head, Major Department

Approved for the College of Graduate Studies

June 18, 1992
Date

Henry L. Parsons
Graduate Dean

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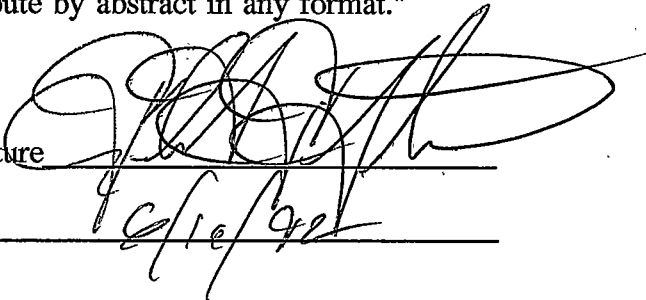
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ABSTRACT

Platinum can form many stable complexes that can be compared, by analogy, to catalytically active systems. The study of platinum complexes and the chemistry derived from them can give new organic products with intriguing novel reaction mechanisms. Various pathways of chemistry were garnered by the reaction of platinum(IV) metallacycles with nucleophiles. Reaction of platinum(IV) metallacyclopentanes with hydride gives liberated organic substrates where the metal has effected carbon-hydrogen bond formation. The products were methyl norbornyl alcohols or ethers. Reaction of iodide with platinum(IV)cyclobutylcarbinol was observed to give 2-norbornyl acetaldehyde in good yield. Product formation is attributed to β -hydride elimination, this the first time that this mechanism has been observed with this substrate. Reaction of platinacyclobutanes and platinacyclopentanes with azide have been found to undergo ligand substitution giving stable complexes. Platinacyclobutanes were observed to be more labile in this substitution pathway, substitutions were conducted at room temperature where the analogous platinacyclopentanes required refluxing methanol.

The reaction of diazo-derivatives with platinum(IV) metallacyclobutanes involves a novel metal mediated carbon-carbon bond forming process. The products observed are cis-divinylcyclopentanes which exhibit high degrees of stereocontrol. The process was studied through modification of the substrate and use of alternate diazo-reagents. Norbornyl analogs, benzofuran derived systems, allow for bridgehead substitution readily. This substituted substrate was found to give stereospecific product upon reaction with mono-substituted diazo-reagent, thus giving support to the proposed mechanism. In addition, diazo-reagents with electron donating groups were found to halt the reaction. Attachment of electron withdrawing groups, on the otherhand, was found to give products in good yield.

Platinacyclobutanes are known to ring expand upon solvolysis to give platinacyclopentanes with stereo- and regiospecificity. These bis-pyridyl complexes were found to undergo substitution reactions with various phosphine and phosphite ligands. Studies of these complexes were conducted in excess ligand. Removal of the ligand began decomposition of the complexes, this decomposition was found to be complete in one hour at reflux. The organic products were found to be cyclobutanes formed with total stereospecificity in excellent yield.

INTRODUCTION

The use of metals in organic synthesis has exploded over the past three decades. Likewise, the complexity of the transformations either catalyzed or mediated by metals has also seen tremendous growth. Simple procedures like catalytic hydrogenation with platinum (IV) oxide have given way to asymmetric hydrogenations and carbon-carbon bond formation with high enantiomeric excesses. In fact, the study of the interactions of metals with carbon, organometallics, has grown from a gray-area between the long established disciplines of organic and inorganic chemistry into a recognized field of study in its own right.

The main impetus for the study of organometallics is that metals, upon reaction with organic molecules, give numerous novel reactions with innovative reaction mechanisms. In understanding these mechanisms, it allows these reactions to be modified to obtain better stereochemical control and overall utility.

Synthesis and Chemistry of Metallacyclopentanes of the Late Transition Metals

Metallacyclopentanes are often thought of as fleeting intermediates in many organometallic transformations. However, stable metallacycles may be viewed as models for these intermediates and can be treated in a variety of ways to give new products while gaining insight into the nature of the metallacycle itself.

Numerous intriguing syntheses of metallacyclopentanes have appeared in the literature and the purpose of this part of the introduction is to acquaint the reader with some of the intricacies of their formation and chemistry.

Metallacyclopentanes from Olefin Coupling

It was shown by Osborn et. al.¹ in 1973 that norbornadiene could be coupled in the presence of Iridium (I) giving an irida(III)cyclopentane. This process can be thought of as a six electron electrocyclic reaction where two electrons are donated from the

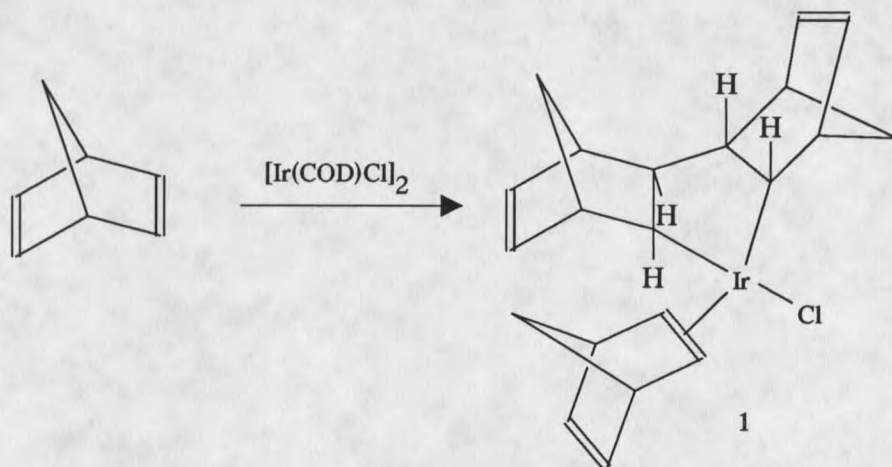


Figure 1. Coupling of Norbornadiene with Iridium (I).

metal. Complex 1 is an assumed structure, as the author states², the complex is sparingly soluble, thus a definitive structure determination was not possible. However, complex 1 was derivatized using acetyl acetate (Figure 2). The proposed structure was verified through the use of X-ray crystallographic analysis. This evidence firmly

established the presence of a five membered heterocyclic ring for complex **2** and implied the same for complex **1**. Complex **1** was also found to undergo carbonyl insertion when exposed to carbon monoxide followed by treatment with triphenylphosphine (Figure 2).

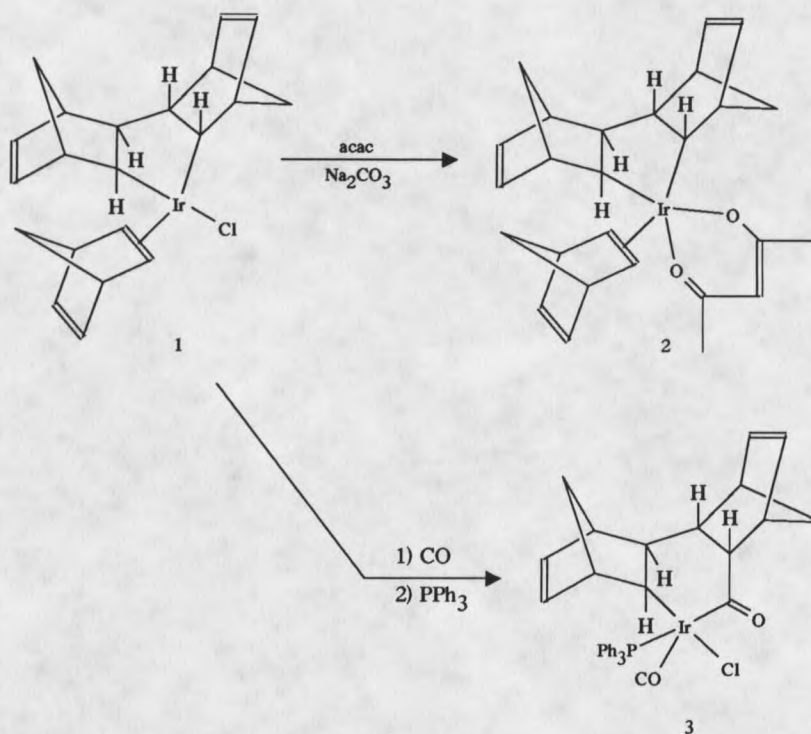


Figure 2. Reaction of Complex **1** with Acetylacetonate and Carbon Monoxide.

Determination of the stereochemistry at the juncture of the two norbornyl rings also was obtained by reaction of **1** with excess triphenylphosphine. Under these conditions, the complex decomposed to the hydrocarbon shown in Figure 3.

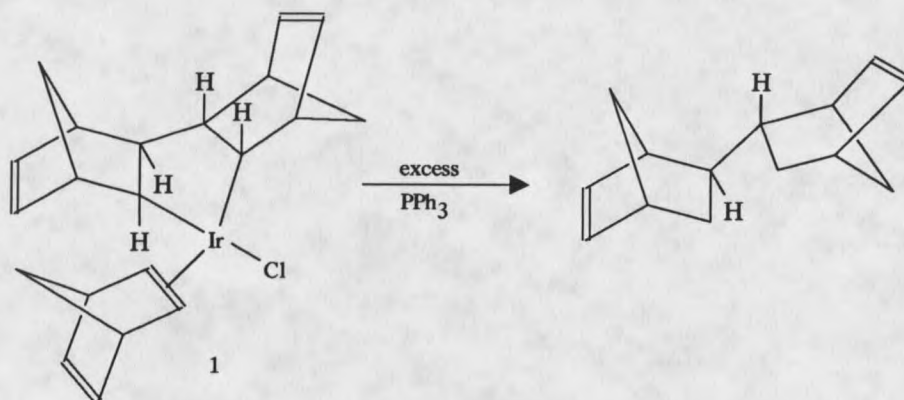


Figure 3. Reaction of Complex 1 with excess Triphenylphosphine.

Methylenecyclopropane, another strained olefin, was shown in 1972³ to dimerize in the presence of bis-1,5-cyclooctadiene nickel(0). It was proposed that this

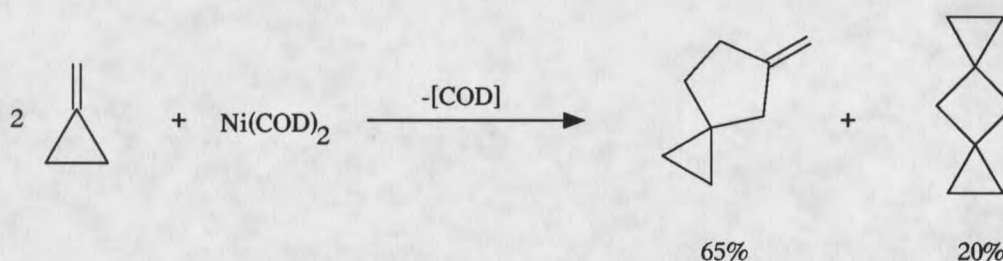


Figure 4. Dimerization of Methylene Cyclopropane.

dimerization passed through a nickelacyclopentane intermediate that either directly underwent reductive elimination to form the minor product shown in Figure 5 or rearranged and then underwent reductive elimination to give the major product as shown below.

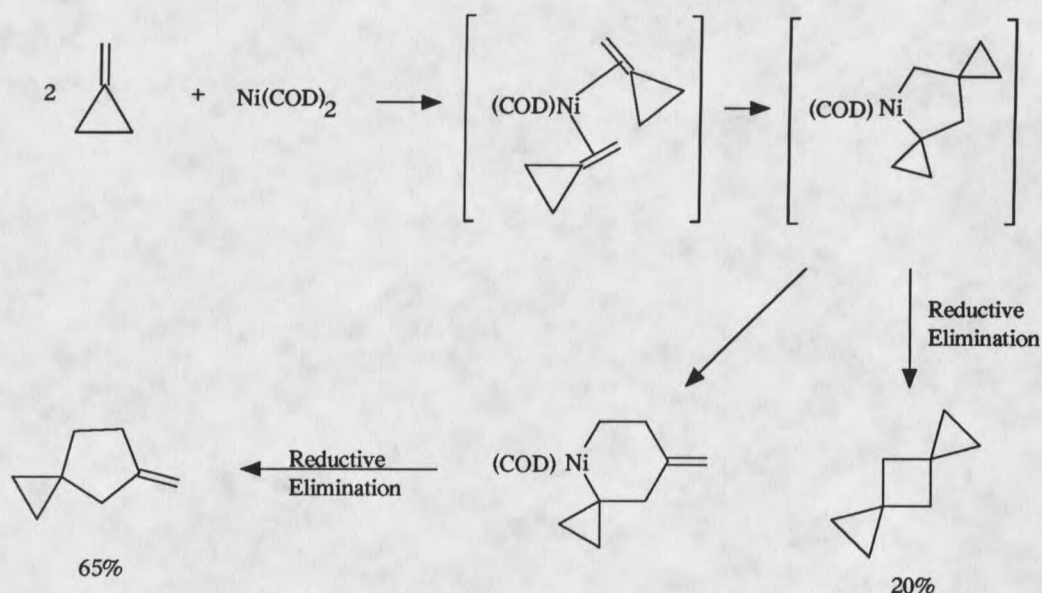


Figure 5. Proposed Mechanism for the Dimerization of Methylene Cyclopropane.

Further studies⁴ using 3,3-dimethylcyclopropene have given similar dimerized products (Figure 6). The reaction of nickel(0) with 3,3-dimethylcyclopropene was

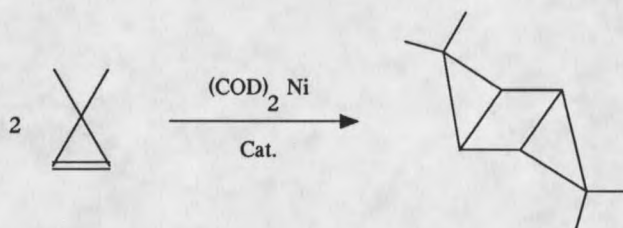


Figure 6. Catalytic Dimerization of 3,3-Dimethylcyclopropene.

found⁵ to give a stable metallacyclopentane upon subsequent treatment with one equivalent of α,α' -dipyridyl (Bipy). Complex 4 was characterized through the use of

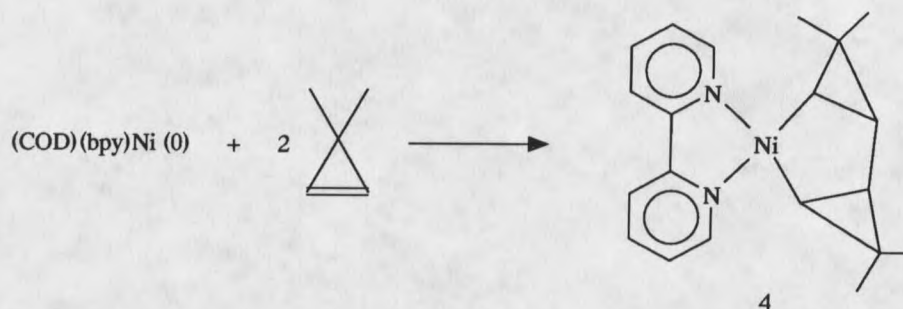


Figure 7. Capture of a Nickelacyclopentane Intermediate.

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy and by X-ray diffraction analysis. The authors state that complex **4** can be thought of as an intermediate in the catalytic process shown in Figure 6 as it reacts with O_2 to give the expected organic dimer plus an oxygen-nickel complex (Figure 8).

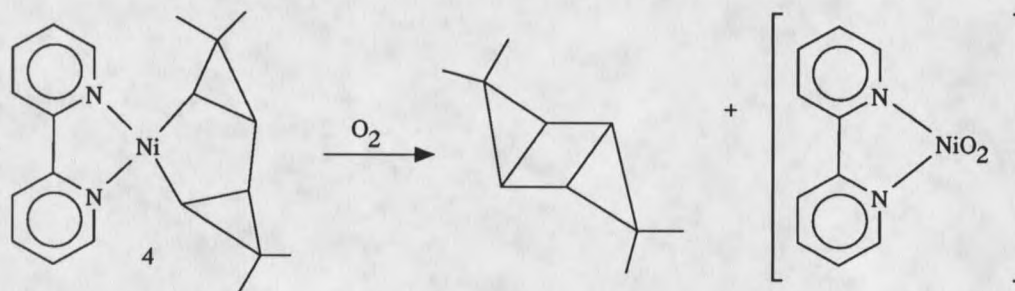


Figure 8. Oxidation of Complex **4**.

Nickel(0) also was found⁶ to dimerize norbornadiene in a manner consistent with the iridium example presented earlier.

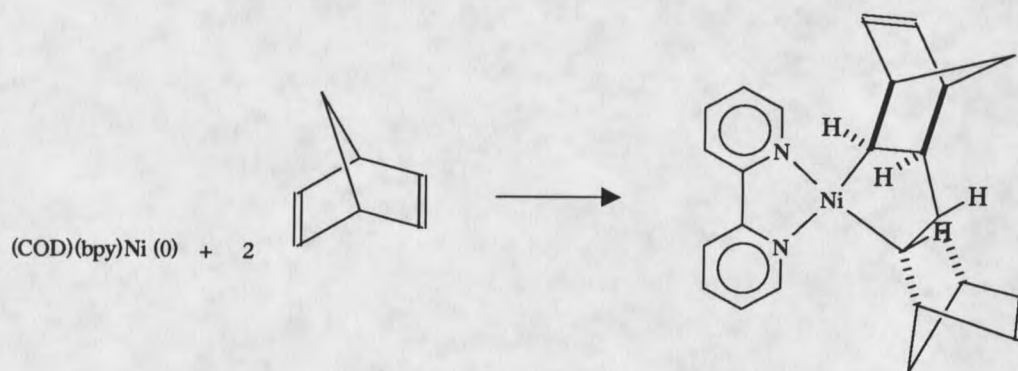


Figure 9. Nickel Mediated Coupling of Norbornadiene.

Metallacyclopentanes may also be synthesized from unstrained olefins with electron-withdrawing substituents^{7,8}.

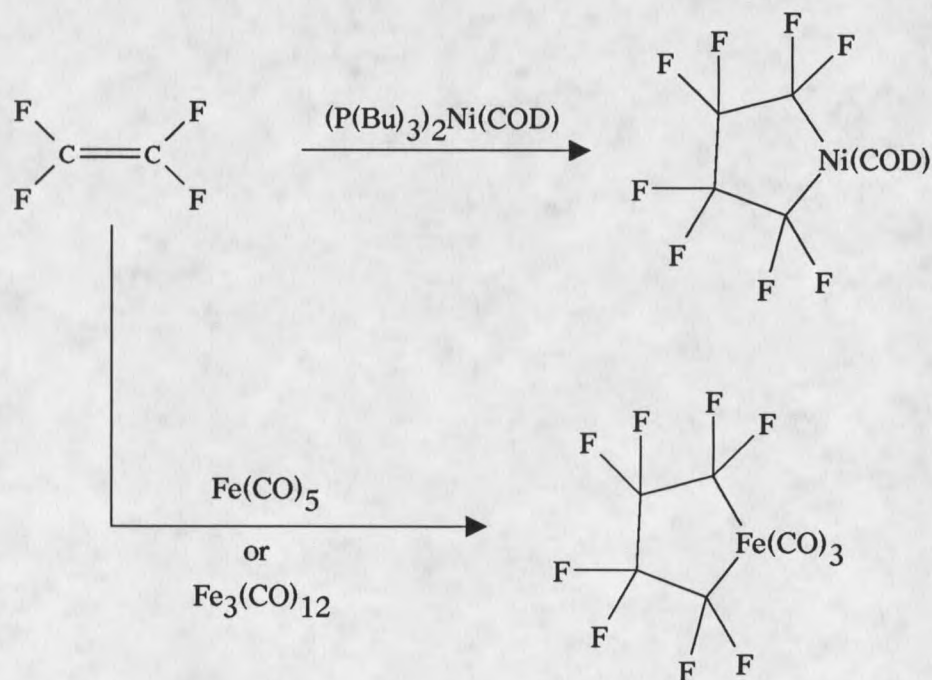


Figure 10. Coupling of 1,1,2,2-Tetrafluoroethylene with Iron (0) and Nickel (0).

Metallacyclopentanes from Grignard
and Dilithio Alkyls

Olefin coupling as a general method for the synthesis of metallacyclopentanes is limited, as shown above, to strained or activated olefins. Ethylene or other simple olefins will not react under those conditions. Successful syntheses of metallacycles without substituents on the ring have been accomplished using an alkyl digrignard or a dilithio alkyl substrate. For example, nickel(II) chloride has been found to be effective in the synthesis of a nickela(II)cyclopentane when allowed to react with 1,4-dilithiobutane^{9,10}.

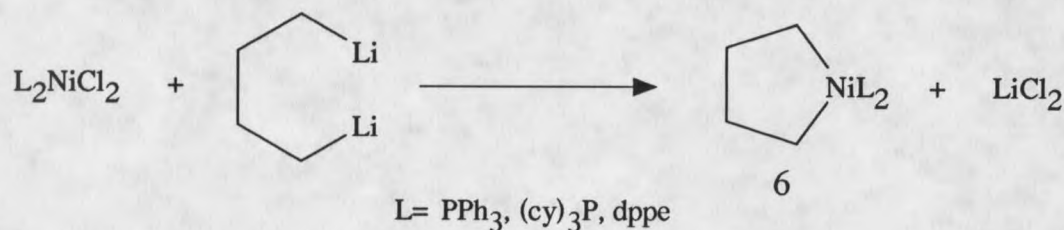


Figure 11. Reaction of 1,4-Dilithiobutane with Nickel(II).

The reaction of complex **6** with triphenyl phosphine was studied by Grubbs and it was reported in 1977^{11a,b} that an equilibrium exists between complex **6** and complexes **7** and **8** as shown in Figure 12. The decomposition pathways of complexes **6**, **7**, and **8** represent three competing mechanisms, providing early evidence of the correlation between coordination number and observed pathway for decomposition.

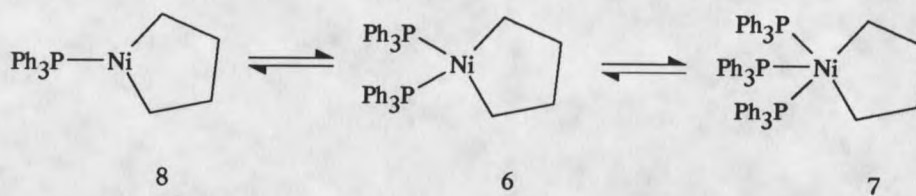


Figure 12. Ligand Equilibrium of Ni(II) Metallacyclopentanes.

The postulated mechanisms for the formation of the decomposition products are ubiquitous to organometallic chemistry and will be reviewed here to acquaint the reader with them. Reductive elimination, the first of the observed decomposition pathways, is the coupling of two ligands and the release of a reduced metal species. This is illustrated in Figure 13 for both cyclic and acyclic instances.

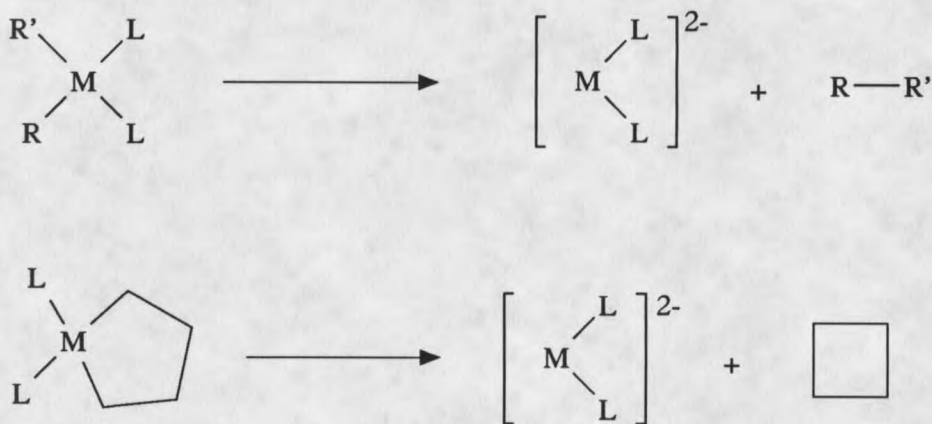


Figure 13. General Examples of Reductive Elimination.

The second pathway observed is a β -hydride elimination. This entails transfer of a hydride on the β -carbon from the substrate to the metal center. With this transfer,

the metal-carbon σ -bond is replaced by a π -bond. Subsequent reductive elimination of the σ -bonded alkyl and the hydride yield the reduced metal plus butene. This is shown in Figure 14.

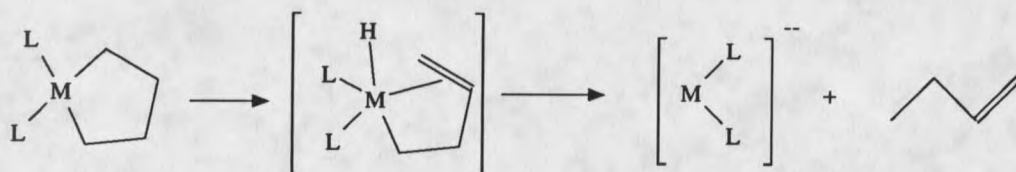


Figure 14. General Example of β -Hydride Elimination.

The third decomposition route involves the cleavage of a carbon-carbon bond. This process can also be thought of as a retro olefin-coupling reaction. The metallacycle is reduced in a manner that cleaves a β carbon-carbon bond and yields a bis-olefin complex which upon dissociation, liberates two olefins and the reduced metal center.

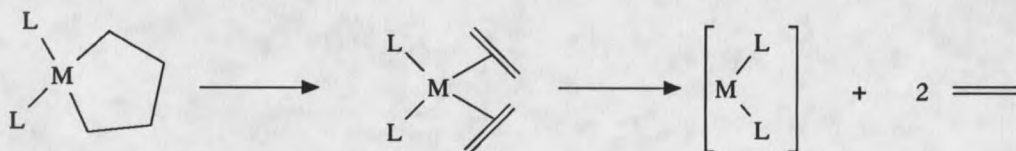


Figure 15. General Example of β Carbon-Carbon Bond Cleavage.

The pathway observed for each of the complexes, 6, 7, and 8, shows a correlation between the coordination number, the number of coordinated phosphines, and the path taken. This is one of the earliest examples of this type of correlation (Figure 16).

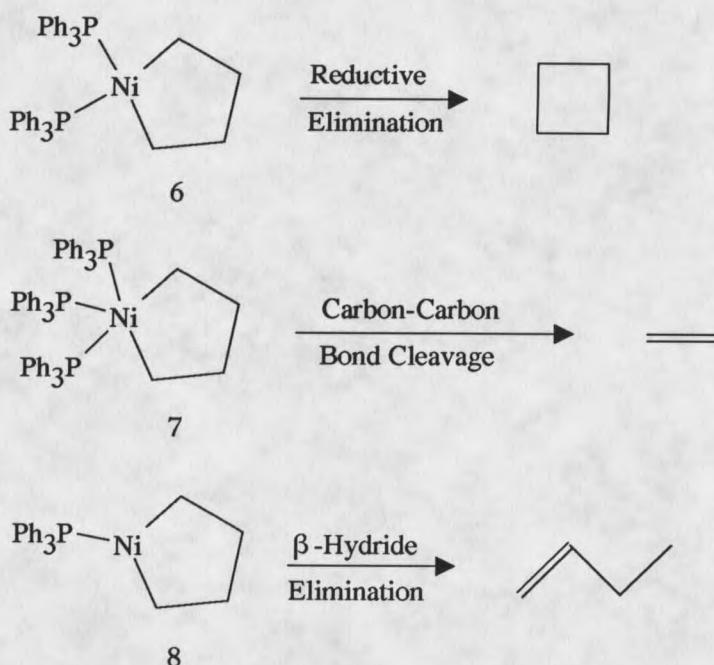


Figure 16. Observed Products from Phosphine Complexes.

Decomposition of complex 8 clearly appears to follow a β -hydride elimination pathway. For this to be viable, the complex in question must be able to assume a higher coordination number. Complex 8 is coordinatively unsaturated and production of 1-butene appears to be reasonable.

Complex 7 is a five coordinate species and ethylene formation does at first appear surprising. However, the author postulates that a rearrangement of the metallacycle that reduces the metal without changing the coordination number can be thought of as a favorable process. Subsequent liberation of ethylene is also favorable

since the experiment was performed with excess triphenyl phosphine which will displace the weaker metal-olefin bond.

Reductive elimination of cyclobutane from the bis-phosphine complex **6** is interesting if not somewhat problematic. It is generally accepted that for reductive elimination to occur, ligand dissociation must precede the process. In fact, this hypothesis has been supported by rate studies showing a significant rate enhancement of reductive elimination processes with decreasing ligand concentration^{12a}. Additional studies^{12b} indicate a significant lowering of the energy of activation for reductive elimination from a complex that has lost a ligand compared to that of a coordinatively saturated complex. Excess ligand in a system competes for open coordination sites on the metal and rate enhancement by decreasing ligand concentration would seem to indicate that an open coordination site is necessary for reductive elimination.

The problematic issue here is that reductive elimination of cyclobutane from complex **6** does not seem to be preceded by the loss of a ligand. Dissociation of a phosphine in this case would yield complex **8** and would be expected then to yield 1-butene and not cyclobutane. However, a rationalization here would be to say that complex **6** does not need to lose a ligand because it is, in fact, coordinatively unsaturated. Using this theory, cyclobutane formation would seem allowable. This is further supported by the fact that the analogous metallacyclopentane with DIPHOS as a ligand was prepared and decomposed and was shown to give cyclobutane as the major product^{11b}.

Analogous metallacyclopentane syntheses using metal hydrides and alkyl iodides have been accomplished. For example, rhenium(III) hydride has been found¹³ to react with 1,4-diiodobutane yielding a rhenia(III) metallacyclopentane.

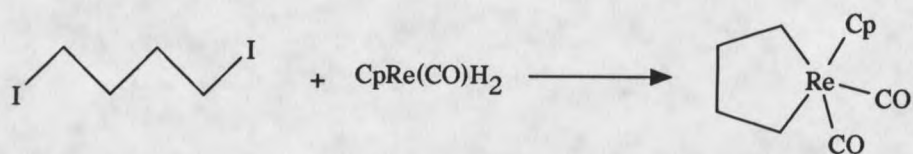


Figure 17. Reaction of 1,4-Diiodobutane with Rhenium(II)

Whitesides¹⁴ reported in 1985 a platinum(II) metallacyclopentane synthesized in 60% yield from an alkyl digrignard and platinum(II). Poisoning of complex **9** with Hg(0) in cyclohexane, Figure 19, was found to give an intriguing organic product, a cyclopropane

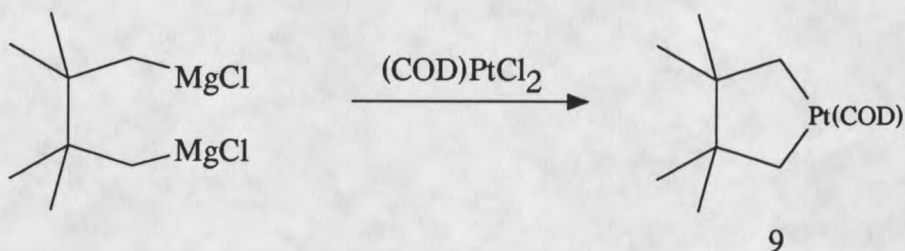


Figure 18. Reaction of Alkyl Digrignard with Platinum(II).

in quantitative yield, presumably derived from methyl group hydrogen activation by oxidative addition of a carbon-hydrogen to the metal. Furthermore, thermolysis of **9** in cyclohexane was observed to give the same cyclopropane but in much reduced yield.

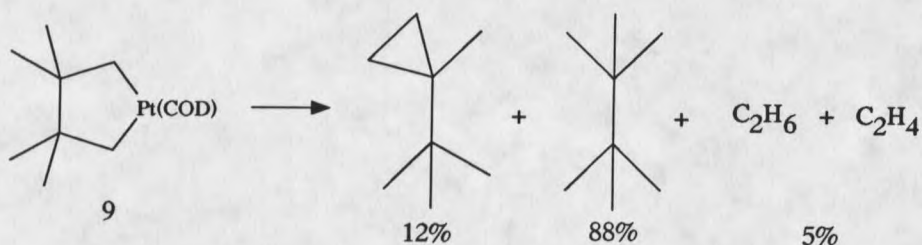


Figure 19. Thermolysis of Complex 9.

Oxidative addition, mentioned above, is a process that can be thought of as the opposite of reductive elimination. The metal is oxidized by the cleavage of a substrate bond and coordination of the cleaved portions to the metal. Whitesides proposed the

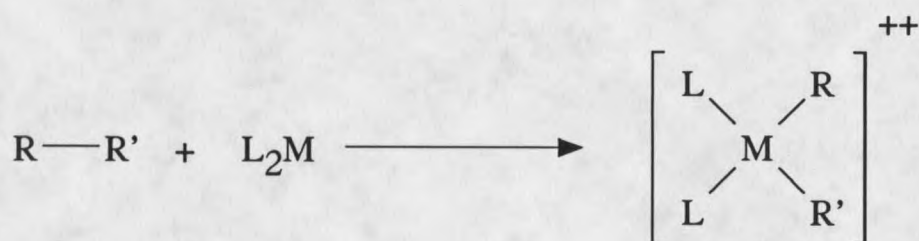


Figure 20. General Example of Oxidative Addition.

following mechanism, Figure 21, for cyclopropane formation observed in Figure 19. The first step involves oxidative addition of the platinum into a carbon-hydrogen bond followed by two reductive elimination steps.

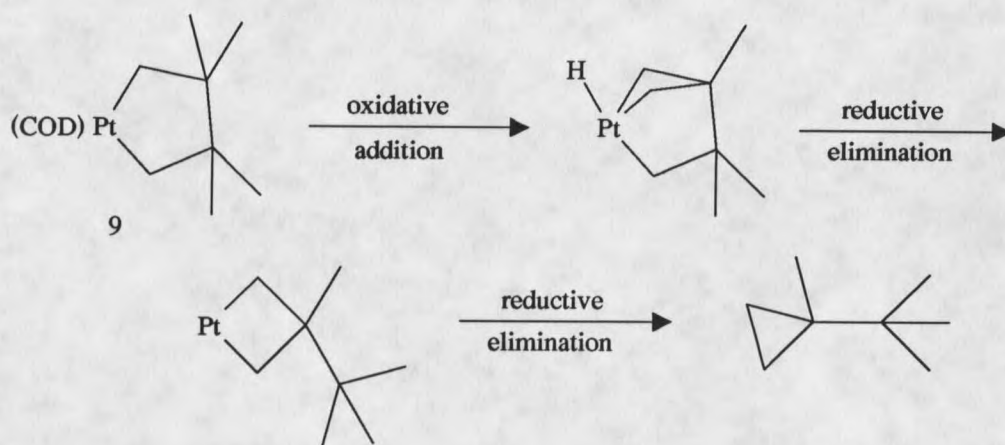


Figure 21. Proposed Mechanism for the Decomposition of Complex 9.

Platinum(IV) analogues of these platinacyclopentanes have been prepared by Puddephatt¹⁵. First, a platinum(II) metallacycle was synthesized from 1,4-dilithiobutane and cis-[bis-Dimethylphenylphosphine]platinum(II) dichloride. Subsequent oxidative addition of methyl iodide gave the platinum(IV) complex. Thermolysis of complex 11

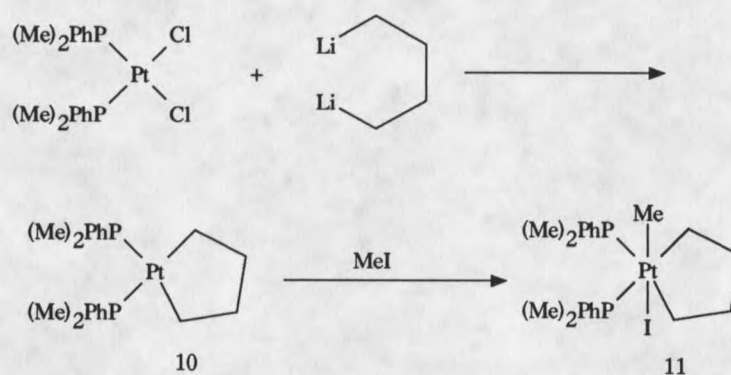


Figure 22. Synthesis of and Oxidative Addition to Complex 10.

was found to give a variety of products including methane, butene, pentenes, butane, and pentane. Oxidative addition of I_2 to complex **10** was found to yield the analogous bis-iodoplatinacyclopentane. Upon thermolysis of this complex, only one product was formed, 1-butene.

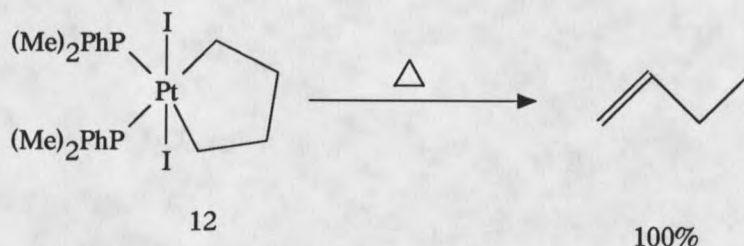


Figure 23. Thermolysis of Complex 12.

The mechanism for the thermal decomposition of **12** is explained as β -hydride elimination as shown earlier in this introduction. However, the formation of C_5 products from **11** must be addressed. As stated earlier, a β -hydride elimination mechanism first proceeds by transfer of a β -hydride to the metal center which is then transferred to σ -bonded alkyl upon reductive elimination. Complex **11** has one other possibility. The hydride on the metal, of course, can be delivered to the alkyl, but so can the σ -bonded methyl group. Delivery of the methyl group accounts for the formation of C_5 products as shown in Figure 24.

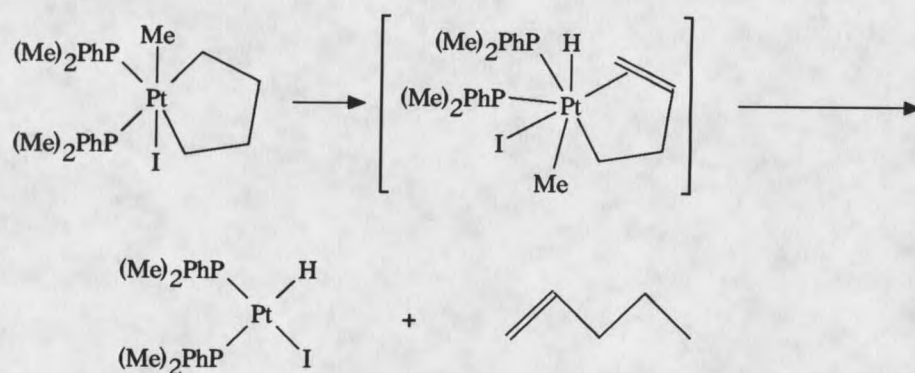


Figure 24. Mechanism for the Formation of C₅ Products.

Whitesides showed in 1978¹⁶ that solvents capable of oxidative addition to the metal center will also yield platinum(IV) metallacyclopentanes. The investigations of platinum(II) metallacycles were performed under thermolysis type conditions using methylene chloride as solvent. The products are shown in Figure 25.

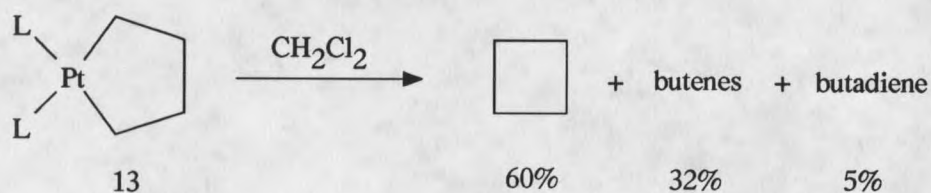


Figure 25. Distribution for the Thermal Decomposition of Complex 13 in CH₂Cl₂

No platinum(IV) metallacycle was isolated under these conditions, however the presence of methylene chloride was shown to be essential for the formation of the observed products, suggesting a platinum(IV) intermediate. Replacement of methylene chloride for trifluoromethyl iodide resulted in the isolation of a platinum(IV) complex. The chemistry of this complex is similar to the methylene chloride example, however a better yield of cyclobutane was observed. Again, no products with incorporated solvent were observed.

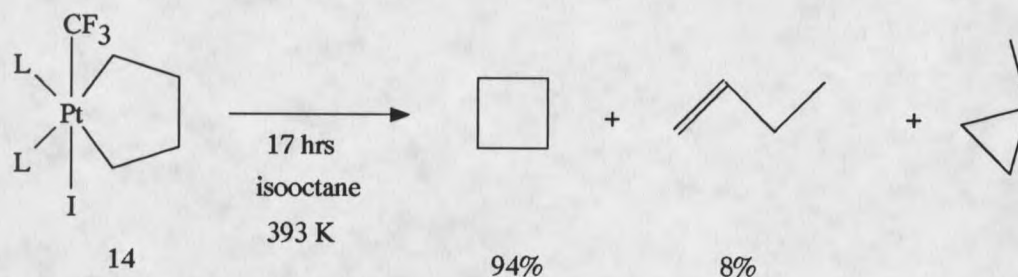


Figure 26. Thermolysis of **14**.

The observation of a platinum(IV) metallacycle, **14**, with addition of trifluoromethyl iodide can be attributed to the increased electron withdrawing character of the trifluoromethyl moiety. The proposed analogue utilizing methylene chloride could be unstable considering the decreased amount of electron withdrawing character the added methylene chloride embodies.

Metallacyclopentanes from Cyclopropanes

The interaction of platinum(II) with cyclopropanes has been well documented¹⁷. However, one such interaction has given a platinacyclopentane¹⁸. Formation of this complex was unexpected, however NMR spectral data were consistent with the proposed structure which was subsequently verified by X-ray crystallographic analysis. The transformation shown in Figure 27 is actually a multi-step process which is believed to

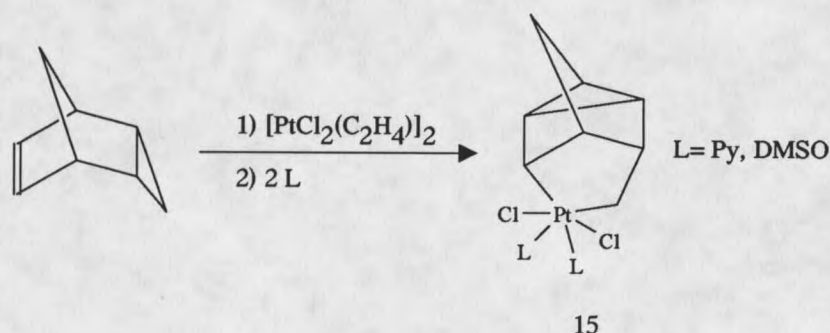


Figure 27. Reaction of *endo*-Tricyclo[3.3.1.0^{2,4}] oct-6-ene with Zeise's Dimer.

initially give a platinacyclobutane which then rearranges to the metallacyclopentane shown. The platinacyclobutane formed initially would be expected to be a tetramer based on previous data¹⁹, Figure 28. Addition of a donor ligand is thought to break the tetramer into monomeric six-coordinate species. The main reason for this step is to increase its solubility. The proposed tetrameric units have been found to be sparingly soluble in common solvents making chemistry with these molecules inconvenient. This will be discussed in more detail later in this introduction .

Assuming that the initial formation of a platinacyclobutane is correct, the question that must be addressed at this point is when does this rearrangement to the platinacyclopentane occur. The initially precipitated complex, before treatment with a donor ligand, was studied by CP/MAS solid state NMR spectroscopy and was found to be consistent with the platinacyclopentane. The key feature noted was an absence of resonances in the olefinic region. Also, it was determined that the solid state NMR spectrum was in good agreement with the liquid state NMR data obtained after pyridine was added.

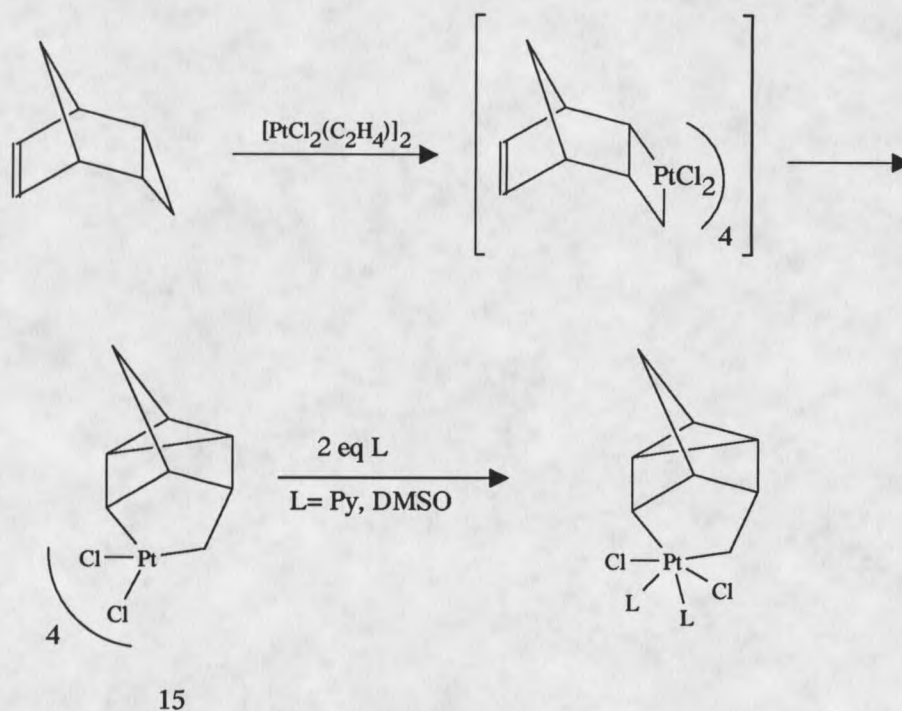


Figure 28. Reaction of *endo*-Tricyclo[3.3.1.0^{2,4}] oct-6-ene with Zeise's Dimer.

Reaction of complex **15** with triphenylphosphine was found to yield a new complex. Studies using ^1H and ^{13}C NMR indicated the presence of a platinum-olefin bond and a carbon-chlorine bond. Final determination of the connectivities and stereochemistry of **15a** was made by single crystal X-ray analysis.

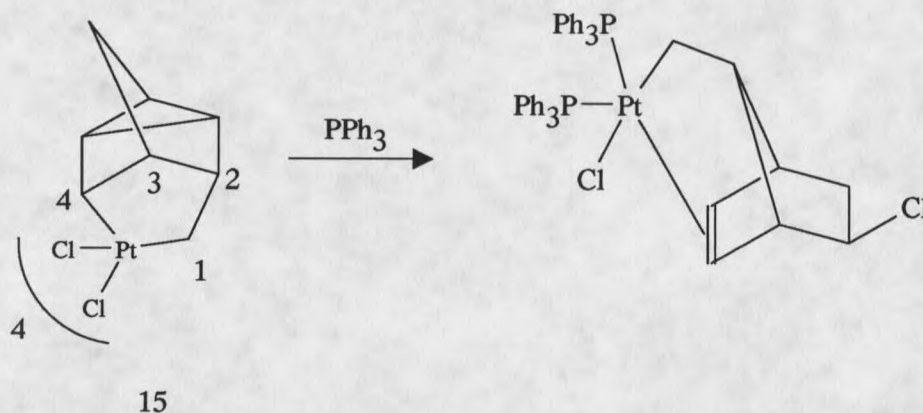


Figure 29. Reaction of Complex **15** with Triphenylphosphine.

Investigations²⁰ into the mechanism of this rearrangement indicate that carbonium ion formation at C-4 is probable. Exposure of complex **15** to an external source of nucleophile such as methanol gave the analogous methyl ether, **15b**, in 85% yield.

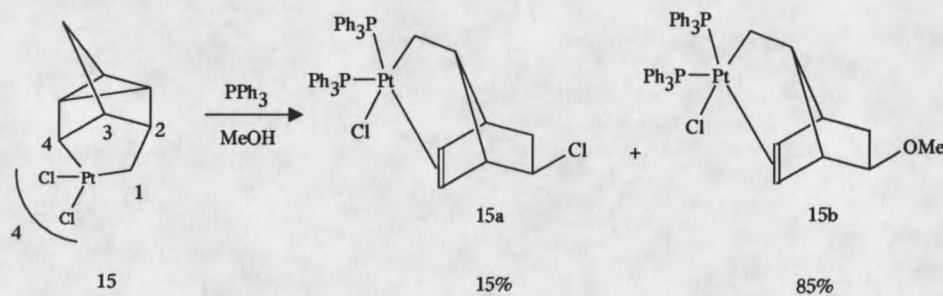


Figure 30. Reaction of Complex **15** with Triphenylphosphine in Methanol.

An alternate justification for these data invokes nucleophilic attack of the chloride complex **15a** with methoxide. Control experiments were performed and the data indicate that **15b** was formed from the organometallic intermediate. No crossover was observed in the treatment of the chloride complex with methanol. Figure 31 contains a mechanistic picture for the rearrangement as proposed by Waddington.

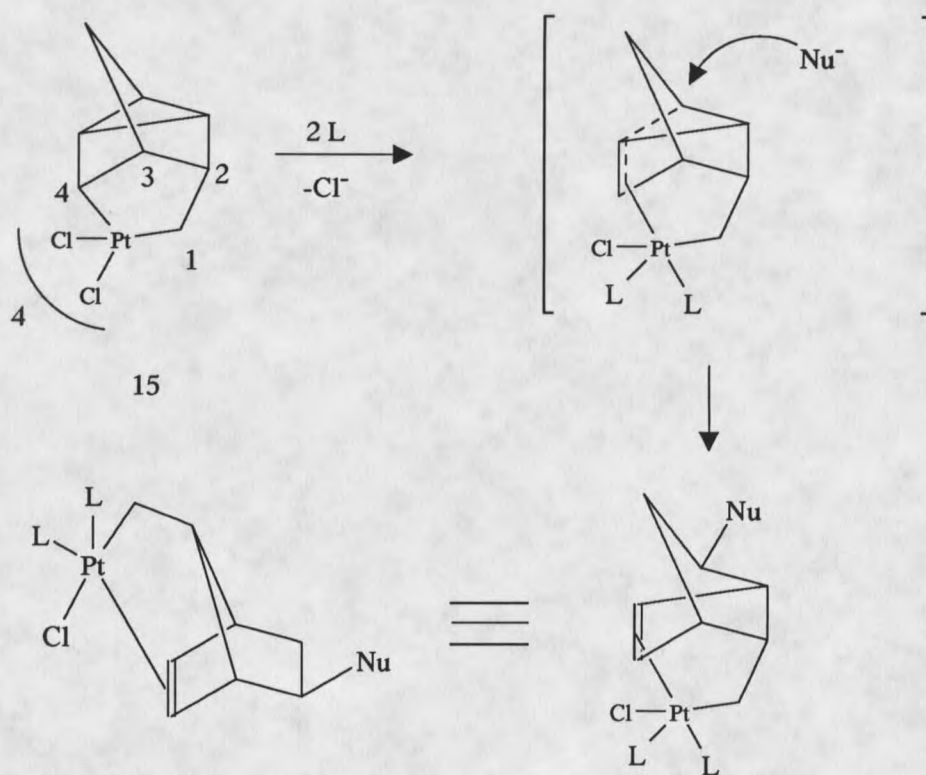


Figure 31. Proposed Mechanism for the PPh_3 Induced Rearrangement of **15**.

Metallacyclopentanes by Solvolysis
of Metallacyclobutanes

The final synthetic pathway to metallacyclopentanes to be discussed in this introduction involves ring expansion of metallacyclobutanes under solvolysis conditions. Precedent^{21,22,23} for this type of transformation was drawn by Puddephatt directly from the organic analogues shown in Figure 32.

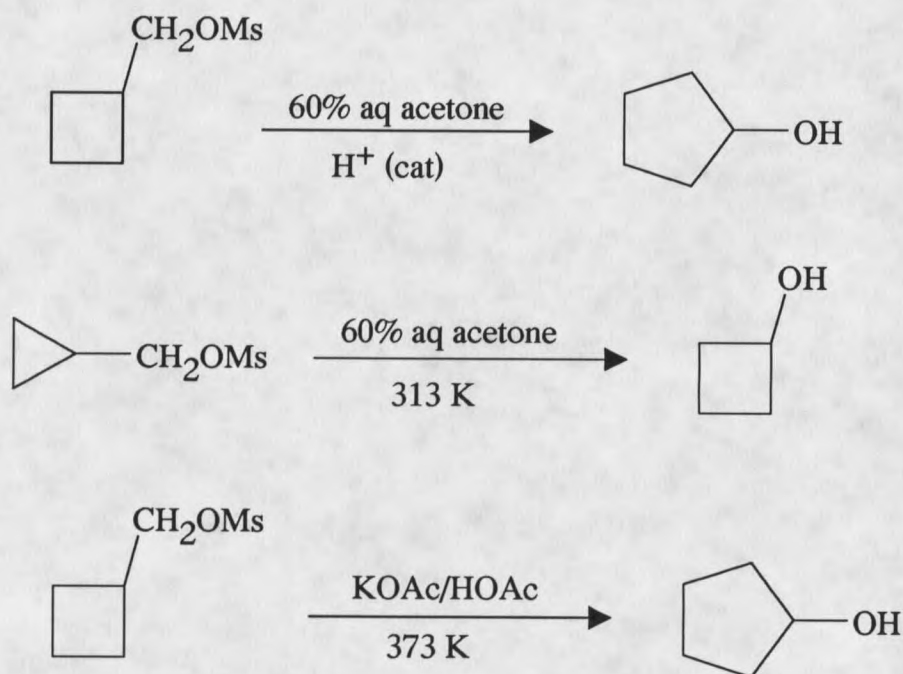


Figure 32. Examples of Organic Ring Expansion Reactions.

This methodology was applied subsequently to an organometallic system by Burton and Puddephatt and reported in 1982²⁴. They found that a platina(IV)cyclobutane could be cleanly solvolysed to a platina(IV)cyclopentane in 80% yield (Figure 33). This process was investigated by the means of isotopic labelling.

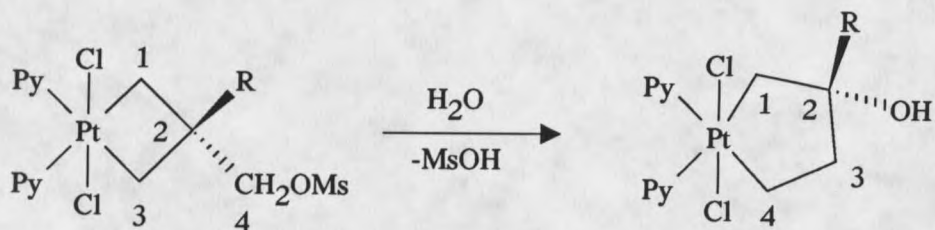


Figure 33. Ring Expansion of a Platinacyclobutane.

Enrichment of the methylene carbon indicated on complex **16**, Figure 34, with ^{13}C and observation of the reaction products by NMR showed that the final position of the labelled carbon was on the α -carbon with respect to the metal atom. This is a surprising

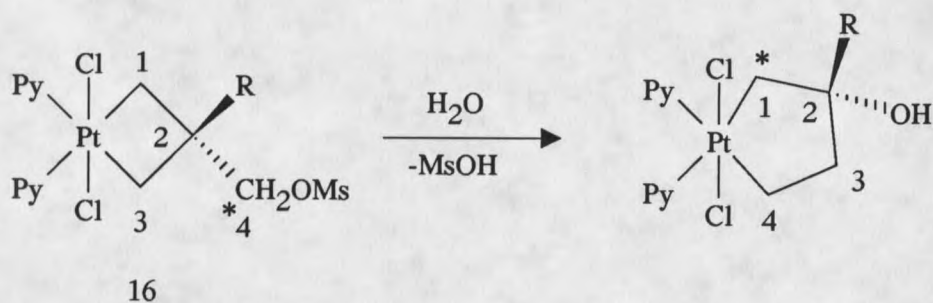


Figure 34. Ring Expansion of Complex **16** (^{13}C labelling).

result in that the bond between carbon-1 and carbon-2 of the platinacyclobutane must be cleaved. Labelling of carbon-4 with deuterium indicated that the deuterium content was conserved and was located on carbon-1 of the platinacyclopentane.

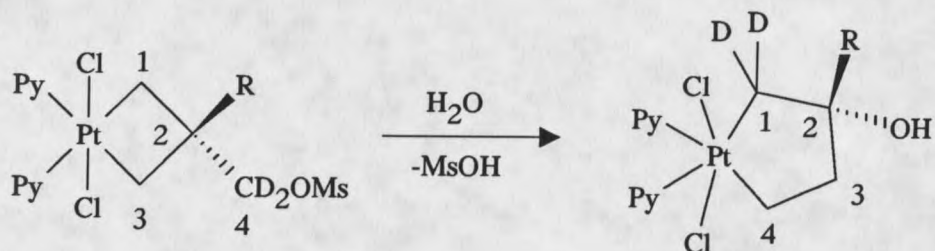


Figure 35. Ring Expansion (^2H labelling).

Mechanistically, these experiments indicate a process by which the cyclobutane is rearranged prior to expansion to give complex 17, see Figure 37. The next step presumably involves loss of mesylate to yield a metal-olefin complex that is susceptible to nucleophilic attack. This type of intermediate had been proposed by Schrock in the decomposition process of a tantalacyclopentane²⁵.

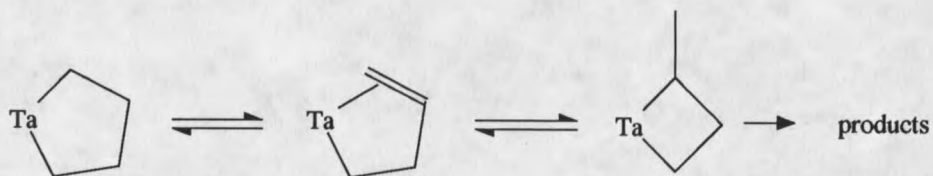


Figure 36. Proposed Decomposition Pathway for a Tantalacyclopentane.

The Puddephatt Rearrangement

The rearrangement in the initial step of the ring expansion process (Figure 37), the Puddephatt Rearrangement, deserves attention. This was first observed in the reaction between phenyl cyclopropane and platinum(II). The product formed initially

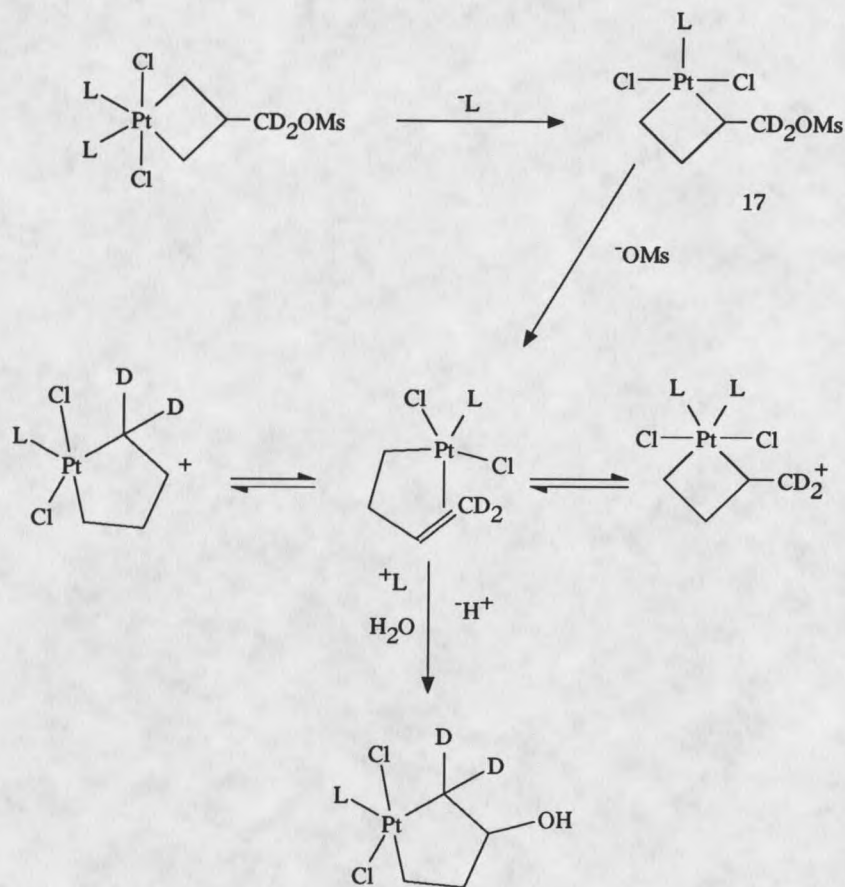


Figure 37. Proposed Mechanism for the Ring Expansion.

is complex 18, however, over time there is an equilibrium mixture observed^{26,27}, see Figure 38. Several experiments were then performed to probe the mechanism of this process.

Addition of deuterium labelled cyclopropane to the equilibrating mixture of the of the 1-phenyl and 2-phenyl platinacyclobutanes produced no labelled platinacycle²⁸. It was also found that bis-pyridyl platinum(II) dichloride, the anticipated platinum

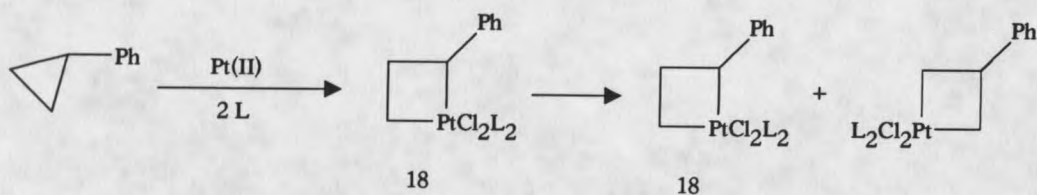


Figure 38. The Observed Puddephatt Rearrangement.

species produced from a metal-substrate separation, does not react with cyclopropanes²⁶. The conclusion from these data is that the rearrangement is intramolecular. Attachment of a chelating ligand was found to stop the rearrangement, indicating that an open coordination site is necessary. In one additional experiment using 1-phenyl-1-deuterio cyclopropane as the substrate, the resulting metallacycles were only observed to have the deuterium and the phenyl group geminal. The conclusion drawn is that the isomerization is not a result of phenyl migration from one carbon to another.

Three mechanisms have been proposed. The first is shown in Figure 39. It involves cleavage of the platinumacyclobutane to a carbene and a bound olefin. The pathway seems unlikely due to the fact that the thermal decomposition of the platinumacyclobutanes does not yield olefins^{26,29,30}. In addition, the use of disubstituted cyclopropanes would give cis and trans isomers. This was not observed²⁸.

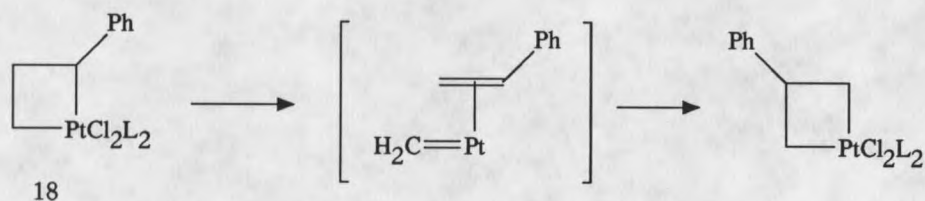


Figure 39. First Proposed Mechanism for the Puddephatt Rearrangement.

The second mechanism is a reversion to a metal-bound cyclopropane complex followed by reinsertion. This mechanism is not considered valid due to the lack of labelling incorporation in cross-over experiments as discussed earlier. If complex 19

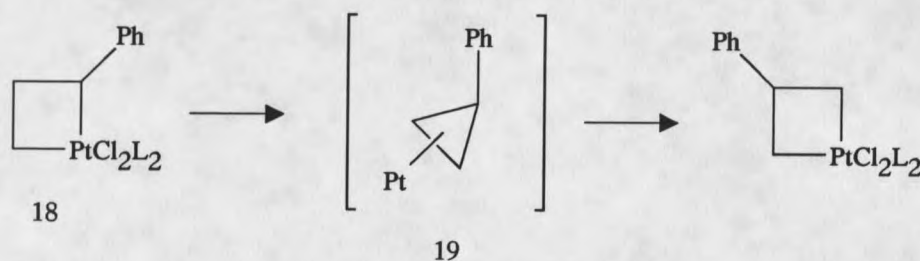


Figure 40. Second Proposed Mechanism for the Puddephatt Rearrangement.

was to be a viable intermediate, the complex would be expected to exchange cyclopropane in an analogous manner to alkenes. This was not observed.

The final mechanism to be presented here, first proposed by Puddephatt, involves a concerted rearrangement²⁶. The intermediate shown in Figure 41 involves equal bonding to all three carbons of the cyclopropane in a delocalized, non-classical manner.

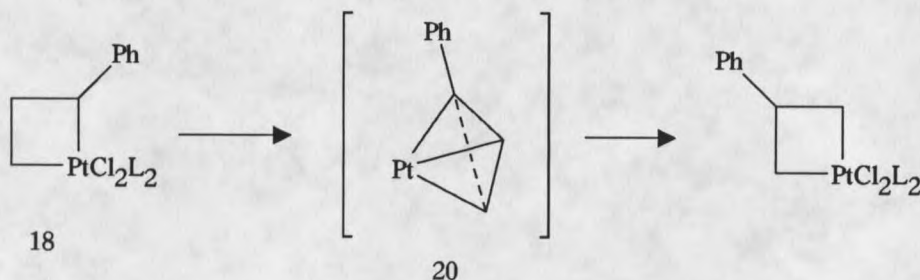


Figure 41. Third Proposed Mechanism for the Puddephatt Rearrangement.

Extended-Hückel studies reported by Hoffmann drew the analogy between intermediate 20 and the cyclopropyl carbinyl cation. This intermediate does explain the experimental data well and Hoffmann's data suggests that Figure 41 is a reasonable proposition³¹.



Figure 42. Classical and Non-classical Cyclopropyl Carbinyl Cation.

Synthesis and Chemistry of Norbornyl Platinacyclopentanes.

Puddephatt reported that attachment of mesylate to a platina(IV)cyclobutylcarbinol was not necessary to induce ring expansion. Platinacyclobutanes with hydroxymethyl substituents were found to readily expand when exposed to a catalytic amount of acid³².

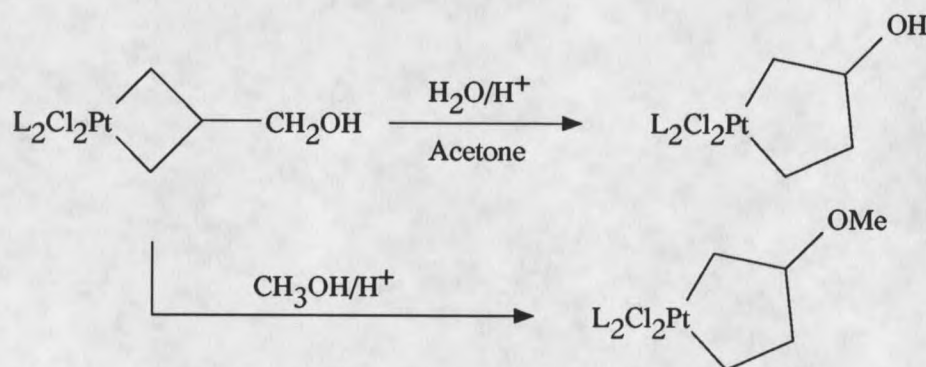


Figure 43. Acid Catalyzed Ring Expansion of Platinacyclobutanes.

Neilsen and Jennings³³ applied this methodology to platinacyclobutanes derived from norbornene. The first two steps of their synthesis, cyclopropanation and reduction, gave a mixture of epimeric alcohols that were found to react with platinum(II). Separation of the epimeric alcohols was accomplished by utilizing the fact that platinum(II) oxidatively added to the syn-epimer much faster than to the anti-epimer. Thus, the insertion reactions were performed such that there was one equivalent of platinum per equivalent of syn-epimer affording a kinetic resolution where the syn-

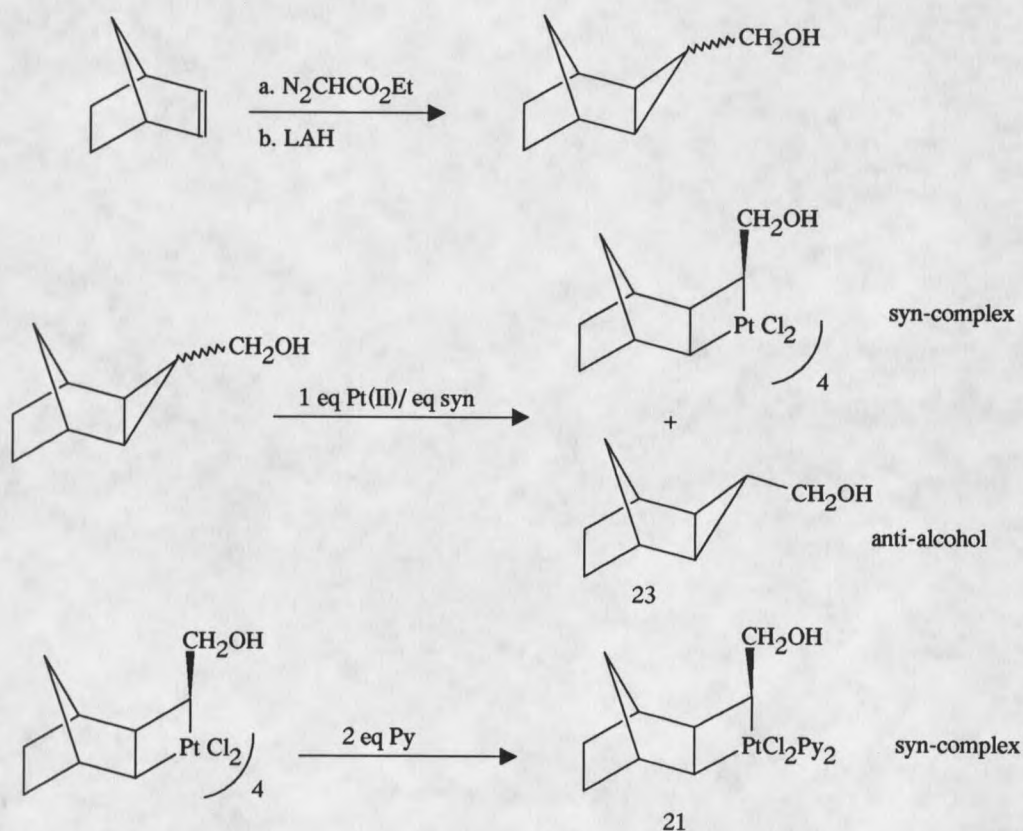


Figure 44. Pathway to Norbornyl Platina(IV)butanes.

epimer reacts preferentially and the anti-epimer can be recovered by filtration of the solid syn-epimeric complex. Treatment of the resulting platinum complex with two equivalents of a donor ligand such as pyridine gave the platina(IV)cyclobutane monomer, **21**. Treatment of the recovered anti-alcohol with Zeise's dimer resulted in the formation of the platinacyclobutane with opposite stereochemistry.

It was found that complex **21** when treated with water, acetone, and a catalytic amount of sulfuric acid will yield platina(IV)cyclopentanes³⁴. This is a process in which the product is formed with stereospecificity. The anti-isomer will also ring expand stereospecifically, Figure 45. The versatility of this reaction was shown through the use of methanol, ethylene glycol, and mannitol as nucleophiles instead of water³⁵.

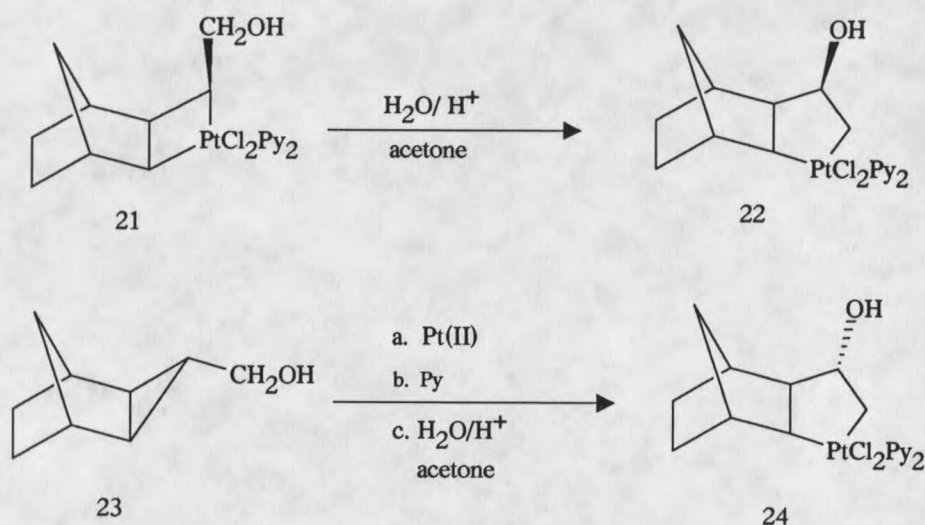


Figure 45. Ring Expansion of Norbornyl Platina(IV)cyclobutanes.

The mechanism proposed for these reactions draws upon the precedence set forth by Puddephatt, protonation, generation of a metal-olefin complex, and subsequent

nucleophilic attack. However, to rationalize the stereochemical result, it was proposed that the platinum "locks" the olefin into a single conformation allowing nucleophilic attack on only one side and, thus controlling the stereochemistry.

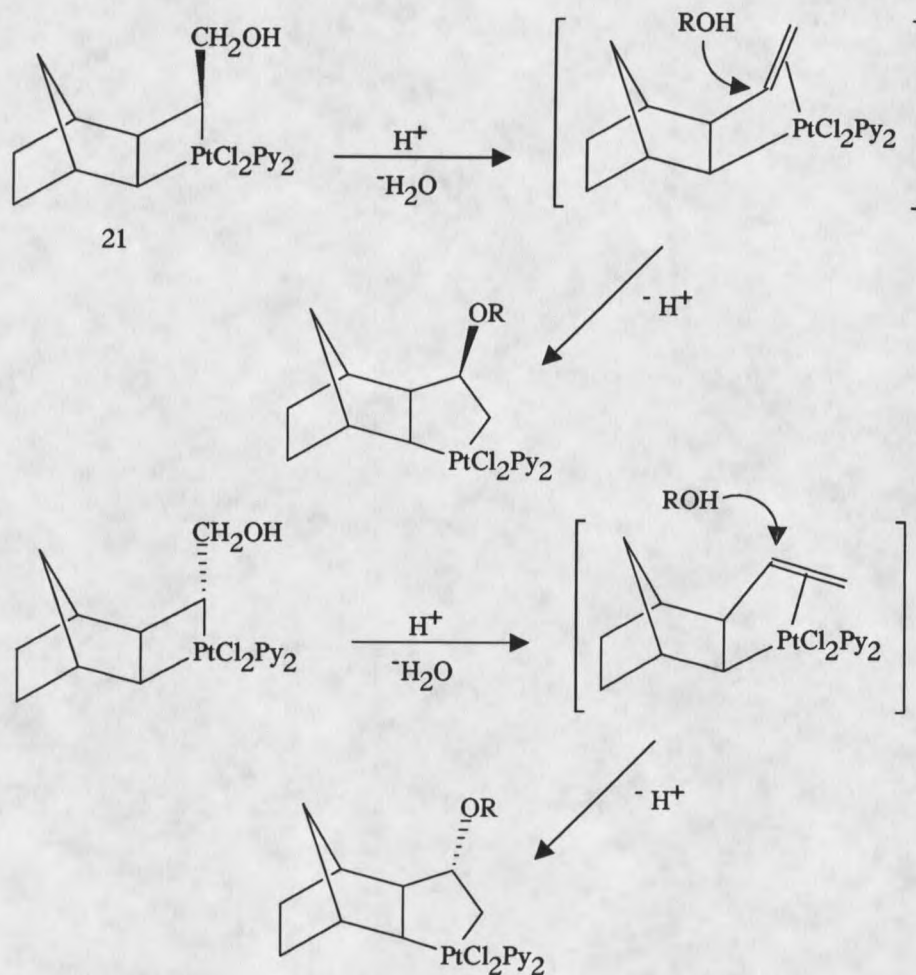


Figure 46. Proposed Mechanism of the Ring Expansion Reaction.

Formation of the metallacyclopentanes has been found to be a reversible process³⁵. Treatment of complex **22** with methanol has been found to yield the analogous methyl ether with retention of stereochemistry. Thus, it is implied that the platinum-olefin complex shown in Figure 46 is regenerated allowing the attack of nucleophile, methanol.

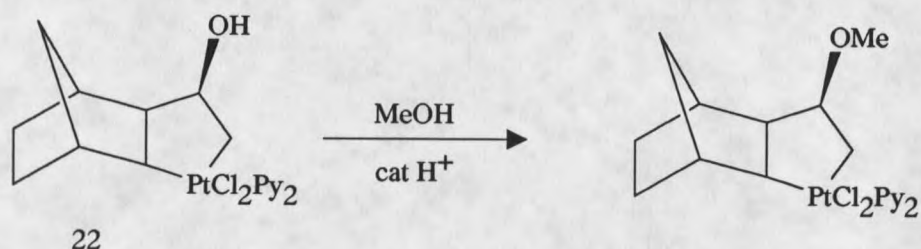


Figure 47. Nucleophilic Exchange of Platinacyclopentanes.

Ring expansion of norbornyl platinacyclobutanes under other conditions has also been performed³⁵. Treatment of complex **21** with thionyl chloride yields a short-lived chlorine-substituted platinacyclopentane that rearranges to **26** while maintaining the five-membered ring. While the stereochemistry of the chlorine in complex **25** has not been rigorously determined, the structure of the rearranged complex **26** has been confirmed by X-ray crystallographic analysis.

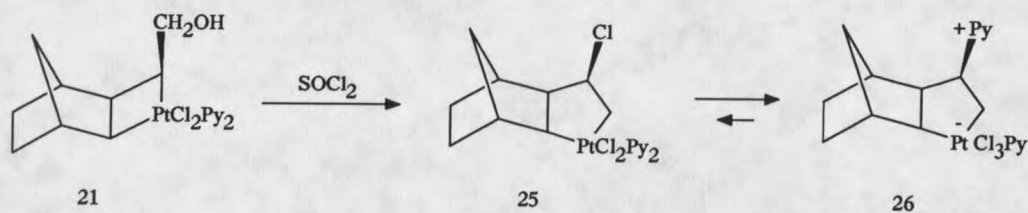


Figure 48. Reaction of 21 with Thionyl Chloride.

Ring expansion of other platinacyclobutanes has also been studied³⁵. Complex 21 can be oxidized in good yield to the corresponding aldehyde, 27, using pyridinium dichromate, Figure 49. Solvolysis of complex 27 in methanol gave a platinacyclopentane characterized as complex 28. Its stereochemistry was extensively studied by the use of ^1H NMR and the methoxy groups were found to be trans. The structure was later unambiguously determined from X-ray crystallographic data.

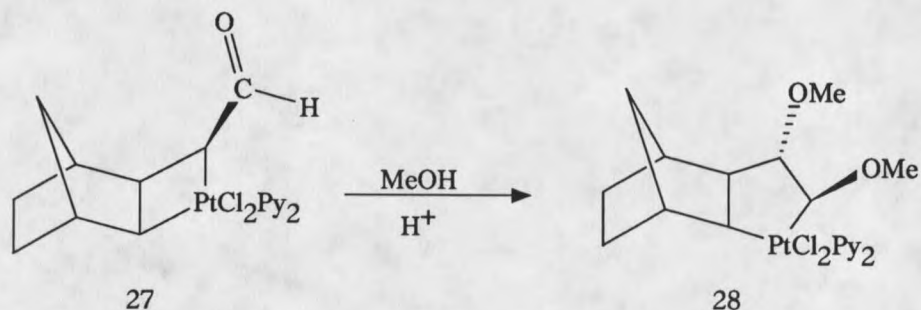


Figure 49. Ring Expansion of Complex 27.

A mechanism shown in Figure 50 has been proposed for this reaction. It commences with acid assisted nucleophilic attack at the carbonyl carbon followed by

protonation and loss of the oxygen moiety to generate of a cationic intermediate which undergoes a second nucleophilic attack to yield product.

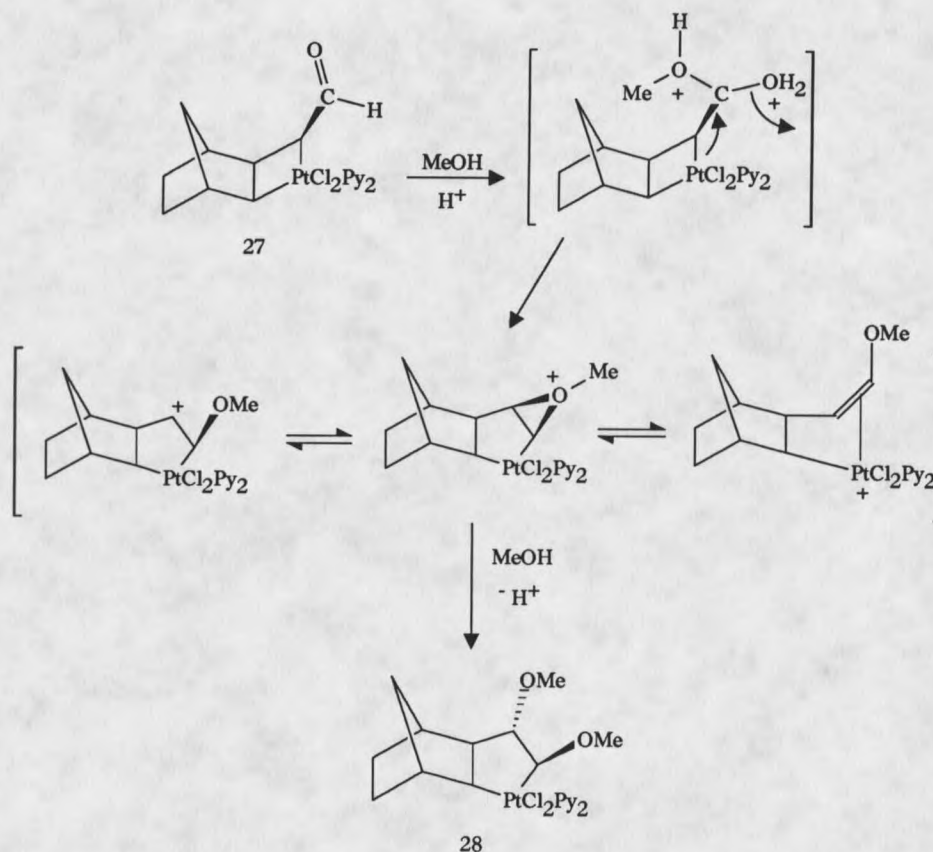


Figure 50. Proposed Mechanism for the Ring Expansion of 27.

Platinacyclopentanes have been found to be robust and capable of surviving harsh conditions³⁵. For example, complexes 22 and 24 have been shown to undergo oxidation conditions in the synthesis of a platina(IV)cyclopentanone. The significance of this structure is that it can be thought of as a platinum(IV) enolate whose possible chemistry is largely unexplored. In fact, infrared spectrophotometry revealed that the

carbonyl stretch for this complex is observed at 1692 cm^{-1} . This represents a shift to lower wavenumber when compared to cyclopentanone, found at 1710 cm^{-1} which can be rationalized as a reduction in the double bond character of the carbonyl. A possible resonance form is indicated in Figure 51.

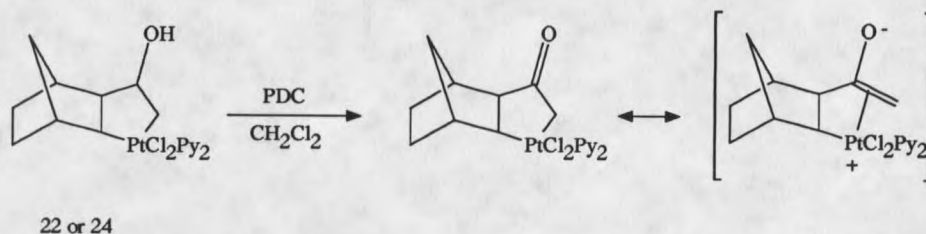


Figure 51. Reaction of **22** or **24** with Pyridinium Dichromate.

Synthesis and Structure in Platina(IV)cyclobutanes.

The results section of this thesis will present recent findings in the chemistry of platina(IV)cyclobutanes and platina(IV)cyclopentanes derived from the norbornyl system by this author. As previously shown, the pentanes discussed are synthesized from ring expansion reactions conducted using the appropriately substituted metallacyclobutanes. This necessitates a more extensive discussion into the formation and structure of platina(IV)cyclobutanes and an analysis of the interaction between platinum(II) and cyclopropanes.

The Platinum-Olefin Bond

The first organometallic compound reported in the literature³⁶ was a platinum complex containing a metal-olefin bond, $\text{K}^+[(\text{C}_2\text{H}_4)_2\text{PtCl}_3]^-$ EtOH. The bonding of an alkene to a metal has been postulated³⁷ to be a two-component bond. The first is

donation of the alkene π -electrons to the empty d_{sp^2} orbital on the metal. The second contribution consists of electron donation from a filled metal d-orbital to the empty π^* -orbital of the olefinic carbons. This second component is termed backbonding. By varying the relative contributions of each component, bonding extremes can be drawn, Figure 52. By maximizing the π -donation from the alkene and minimizing backbonding, structure 29, is clearly indicated. Reversing the relative magnitudes of each contributor, maximizing back-bonding while minimizing π -donation, yields a metallacyclopropane, 30.

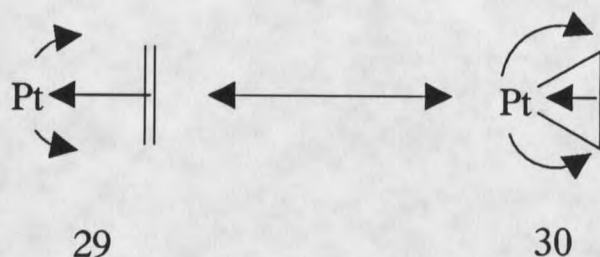


Figure 52. Metal-Olefin Bonding Extremes.

Observation of these extremes by Nuclear Magnetic Resonance spectroscopy has been proposed by Hoberg³⁸. Treatment of the dimeric complex, 31, with triphenylphosphine preserves the platinum-olefin bond character, 32. The ^{13}C NMR chemical shifts and ^1J platinum-carbon coupling constants are consistent with previously reported platinum-olefin complexes. However, treatment of complex 31 with pyridine causes a deviation in the indicative ^1J carbon resonances. These resonances are observed upfield with respect to the triphenylphosphine analog and the ^1J platinum-

carbon coupling constants increase dramatically (Table 1). This is attributed to metallacycle formation, **33**.

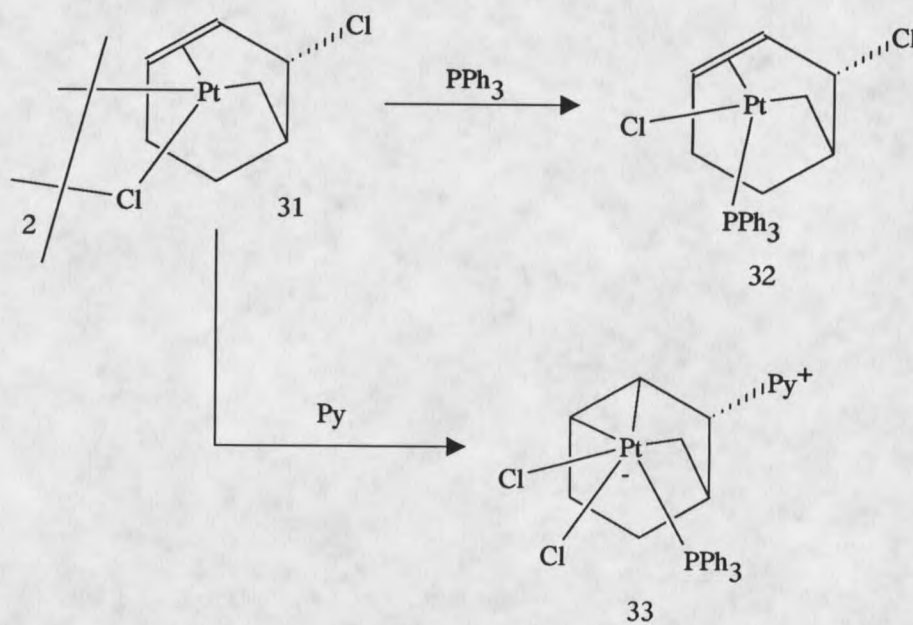


Table 1. ^{13}C NMR Data for complexes **32** and **33**.

CARBON #	PPh_3 ^{13}C NMR ppm ($^1J_{\text{Pt-C}}$)	Pyridine ^{13}C NMR ppm ($^1J_{\text{Pt-C}}$)
1	110.6 (86.6)	57.2 (341.8)
2	104.8 (96.6)	53.9 (377.2)

Since Zeise's initial discovery, platinum(II) has been shown to readily form metal-olefin bonds, however Pt(IV) does not mirror this ability. In fact, the sole example of a Pt(IV)-olefin bond was prepared by Jennings and Parsons in 1985³⁹.

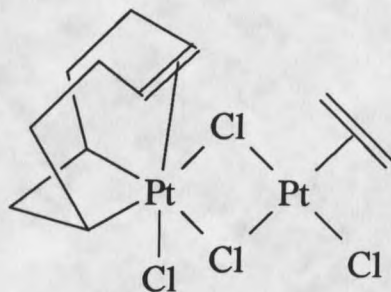


Figure 53. The First Isolated and Characterized Pt(IV) Olefin Complex.

Synthesis of Platinacyclobutanes from Cyclopropanes

Delocalization of π -electrons in olefins is key to their ability to bond to metals. This delocalization has also been proposed to occur in cyclopropanes⁴⁰. This theory was applied by Tipper⁴¹ to the possible interaction between cyclopropane and platinum. Cyclopropane was treated with hexachloroplatinic acid, H_2PtCl_6 , in acetic anhydride solvent to give what the author believed was an edge-bound platinum complex. Clarification of the actual structure was produced by Chatt⁴² who asserted that the cyclopropane had been opened to give a platinacyclobutane. Chatt also proposed that the complex was polymeric due to its apparent insolubility in common solvents.

Subsequent contributions from Gillard⁴³ gave support to Chatt's notion of the formation of a metallacycle. In addition, the polymeric nature was later proposed to be a tetramer (Figure 54). Various methods were employed to determine the molecular

weight of the complex. The conclusion drawn from mass spectrometry was that the molecular ion is 1232, which corresponds to a tetrameric unit⁴³.

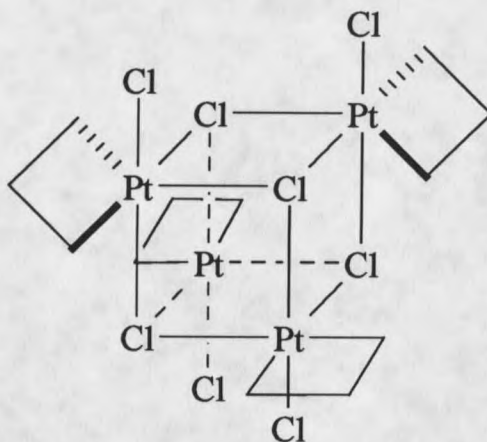
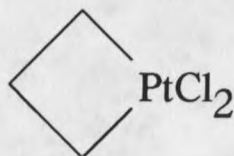


Figure 54. Proposed Structure for the Tetrameric Complex.

The tetramer is composed of four units of complex 35 and is proposed to be a cubic complex. It is diamagnetic suggesting an oxidation state of +4, a coordination number greater than four, and octahedral geometry. Additional support for a metallacycle was provided by the fact that reaction of the tetramer with donor ligands was always observed to yield complexes in the general form of complex 36.



35

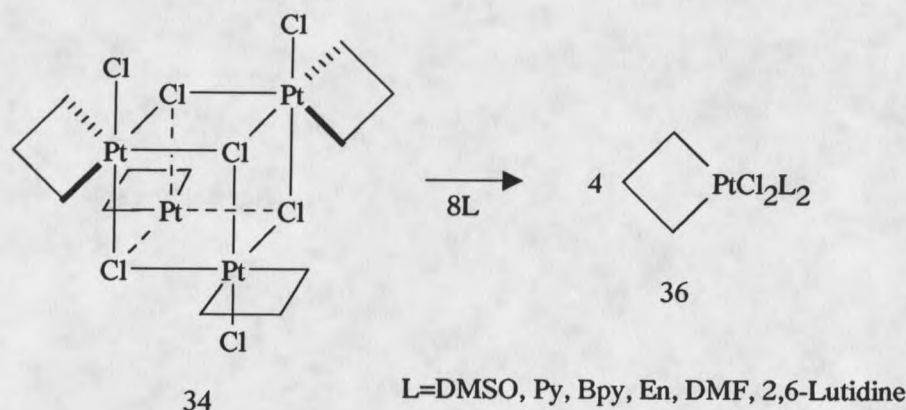


Figure 55. Reaction of 34 with Donor Ligand.

Synthesis of substituted platinacyclobutanes proved unsuccessful using Tipper's methodology⁴⁴. McQuillin⁴⁵ subsequently showed that Zeise's dimer could be used as the platinum source for the synthesis of metallacyclobutanes from substituted cyclopropanes. The effect of substituents on the reactivity of substituted cyclopropanes regarding platinacyclobutane formation were determined to be $n\text{-C}_6\text{H}_{13} > \text{PhCH}_2 > \text{Ph} > o\text{-NO}_2\text{C}_4\text{H}_6$. Also noted were the following substituents that inhibited the reaction: CN, COCH_3 , CO_2Me .

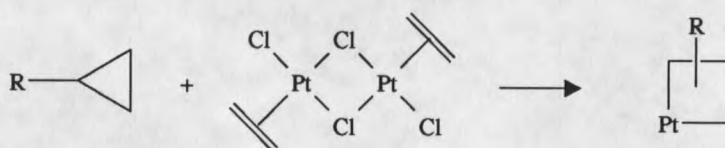


Figure 56. McQuillin's Synthesis of a Substituted Platinacycle.

The conclusion to be inferred here is that electron rich cyclopropanes enhance reaction with platinum(II) while electron poor cyclopropanes slow or halt the reaction. This suggests that the metal is acting as an electrophile while the cyclopropane acts as a nucleophile.

Synthesis of Platinacyclobutanes from Norbornyl Substrates

The reaction between platinum(II) and *exo,exo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}] nonane was reported⁴⁶ in 1969 to yield a complex where the metal is edge-bound to both cyclopropanes, complex 38. The analogous process using *exo*-tricyclo[3.2.1.0^{2,4}] oct-6-ene was also shown to give a non-inserted product, 40.

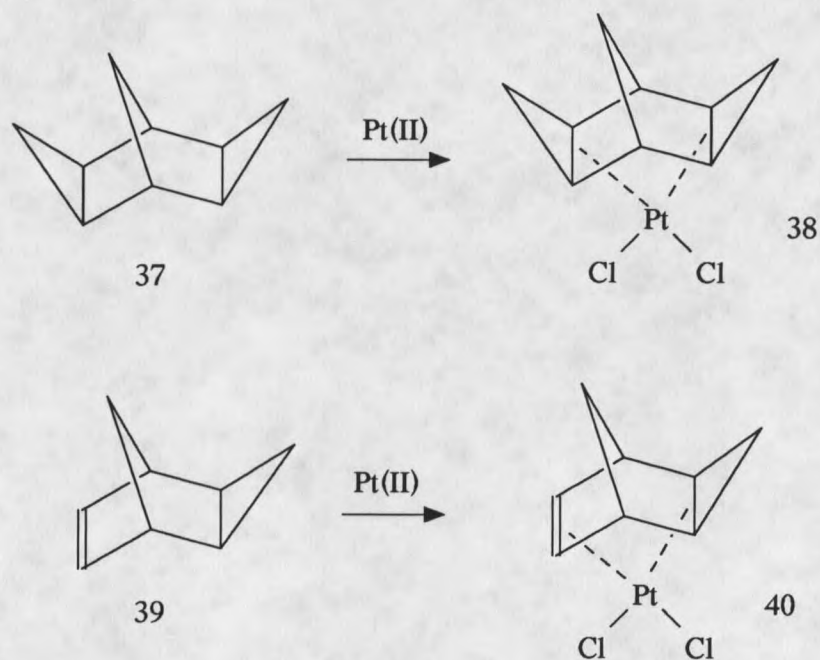


Figure 57. Proposed Product for the Reaction of 37 and 39 with Zeise's Dimer.

Further investigations by Waddington and Jennings⁴⁷ showed these structures to be incorrect. They demonstrated that the metal had inserted into the carbon-carbon bond of the cyclopropane. The product, a sparingly soluble yellow solid, was found to dissolve in d_8 THF and was studied by ^1H and ^{13}C NMR spectroscopy. The ^{13}C data was especially surprising. Nine unique resonances were observed which would not be expected if complex 38 was correct. Complex 38 would be expected to exhibit only four distinct resonances.

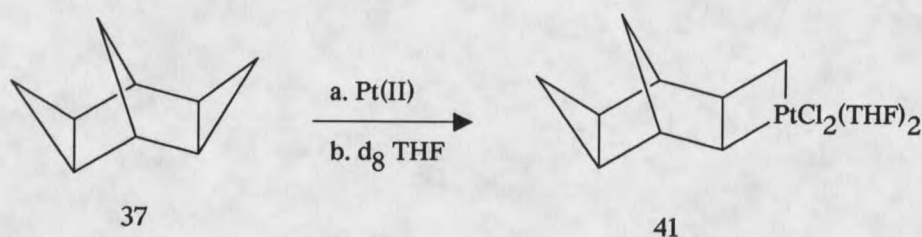


Figure 58. Platinacyclobutane Synthesis.

The dissolution of the yellow solid in tetrahydrofuran, THF, however did not allow observation of the structure in the tetrameric form. THF is a coordinating solvent that is expected to ligate the metal giving soluble monomeric products.

The above data does not discount complex 38. The possibility exists that complex 38 is initially formed and rearranges during the ligation process. However, data obtained from solid state CP-MAS spectroscopy experiments performed on the initially formed yellow solid were found to be congruent with the liquid state studies performed on the THF and pyridine monomers⁴⁸.

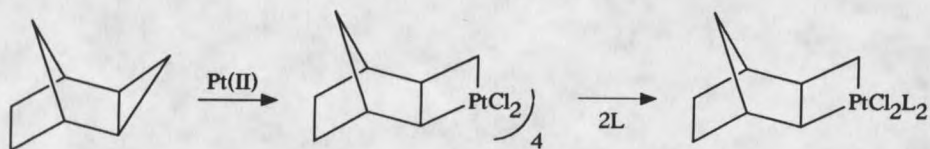


Figure 59. Proposed Reaction Sequence for Platinacyclobutane Synthesis.

In a study⁴⁹ exploring the mechanism of the insertion process, an alternate norbornyl system was prepared. This was done with two goals in mind. First, the cyclopropane derivative is remotely asymmetrical and thus allowing differentiation of the carbon-carbon bonds of the cyclopropane. Secondly, the ketone represents an electron withdrawing functionality that, although it is not directly on the cyclopropane ring, is homo-conjugated to it. Thus some effect due to the carbonyl was anticipated in the insertion process.

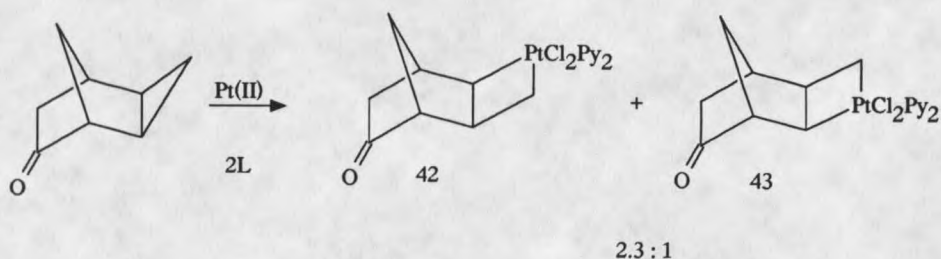


Figure 60. Insertion of Pt(II) into an Asymmetrical Cyclopropane

An effect was observed. A preponderance of complex 42 was surprising since the carbon-carbon bond cleaved is the most electron deficient. The question of whether

this is the kinetic result or a rearrangement after insertion was raised. Experiments were designed and conducted to study this question. No rearrangement was observed indicating the thermodynamic nature of the observed products.

Norbornyl analogues⁵⁰ have also proved successful in the synthesis of stable platinacyclobutanes. Cyclopropanation of 1,4-Epoxy-1,4-dihydronaphthalene with diazomethane using palladium(II) acetate as a catalyst was found to give compound **44** in excellent yield. Treatment of **44** with one equivalent of Zeise's dimer in diethyl ether at room temperature gave the familiar yellow solid. Exposure of this solid to pyridine and study of the resulting complex by NMR spectroscopy and X-ray crystallography confirmed the structure of the expected monomer, **45**.

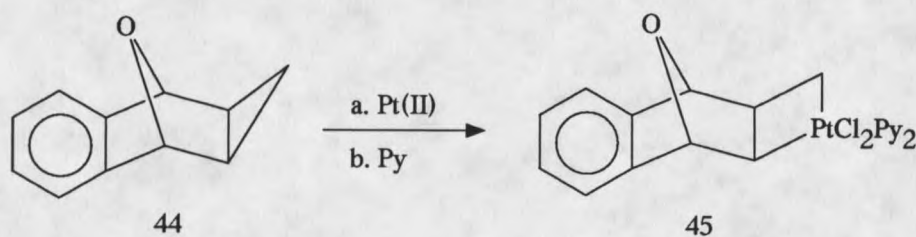


Figure 61. Synthesis of a Platinacyclobutane from 1,4-Epoxy-1,4-dihydronaphthalene

Synthesis of Platinum Complexes from Bicyclo(X.1.0) Systems.

In the attempt to extend the synthetic methodology to non-norbornyl systems, the reaction of platinum(II) with bicyclo(X.1.0) hydrocarbons was studied. Parsons and Jennings reported⁵¹ in 1988 that platina(IV)cyclobutanes could be prepared, isolated, and characterized from the reaction of bicyclo(4.1.0) heptane with Zeise's dimer. However,

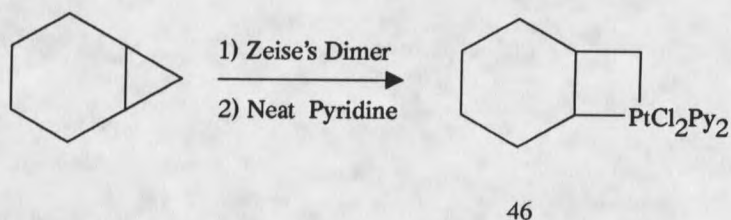


Figure 62. Synthesis of a Metallacycle from Bicyclo(4.1.0) heptane.

the inherent stability present in the norbornyl systems was not observed. Complex **46** at -10°C and decomposes at room temperature when not dissolved in neat coordinating ligand. A change of substrate to bicyclo(6.1.0) nonane also produced a platinacyclobutane that was somewhat more stable than the heptane analog, **46**, however it does not approach the level of stability witnessed in the norbornyl derivatives.

Further modifications upon this scheme were examined by Hoberg⁵². Ether substitution at the ring juncture followed by reaction with Zeise's dimer gave no stable platinacycles. However the substrate did undergo the transformation shown in Figure 63.

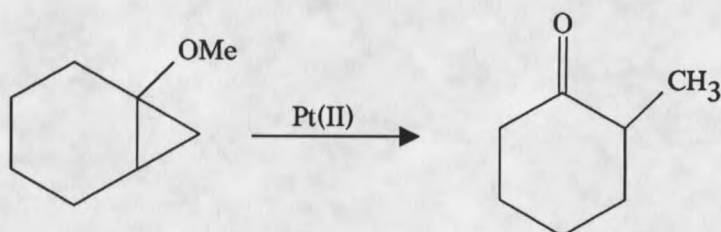


Figure 63. Platinum Mediated Formation of 2-Methylcyclohexanone.

The reaction was found to be stoichiometric when R= methyl, however it was found to be catalytic with other alkyl groups such as ethyl, butyl, etc.. Cyclopentane and cyclooctane analogues were also shown to be effective in this transformation.

Reaction of bicyclo(4.1.0) hept-2-ene with Zeise's dimer was also studied by Hoberg⁵². The product was found to be a novel platinum-olefin dimer, complex **31**.

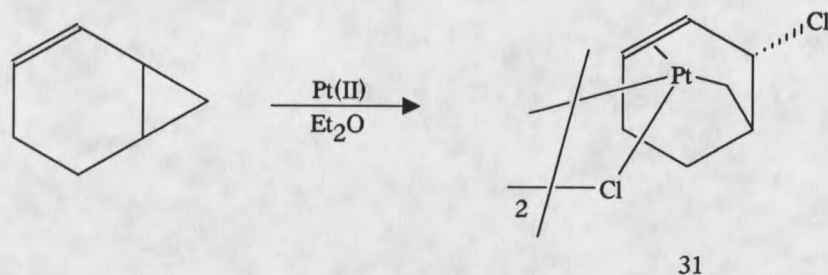


Figure 64. Reaction of Bicyclo(4.1.0) hept-2-ene with Zeise' Dimer.

The chemistry of complex **31** has been studied both in the dimeric form and in monomeric forms. Acetonitrile and triphenylphosphine have been shown to be effective in the ligation of **31** to form monomeric platinum complexes. In addition, as previously stated, pyridine as a ligand causes the formation of a platina(IV)cyclopropane.



Figure 65. Reaction of Complex **31** with Pyridine.

Characterization of Platina(IV)cyclobutanes and Platina(IV)cyclopentanes.

Characterizations of platinum(IV) metallacycles have been accomplished by using a number of analytical methods. Nuclear magnetic resonance spectroscopy is perhaps the most common technique in the elucidation of these types of complexes. However, the contributions to the early work made by infrared spectroscopy should not be ignored.

Infrared Spectroscopy

The IR spectra of the tetramer and the pyridine monomer of a simple platinacyclobutane have been thoroughly interpreted⁵⁴, see Table 2. IR spectroscopy initially was used to show that the cyclopropane ring was opened in the reaction with platinum. It was also utilized to suggest the presence of both terminal and bridging chlorines in the tetrameric structure. Table 2 contains data obtained from two complexes and cyclopropane.

Nuclear Magnetic Resonance Spectroscopy

Platinacyclic complexes can be studied extensively using NMR spectroscopy. Platinum has an isotope, 195, that has a nuclear spin of $+1/2$ in a natural abundance of 33%. Platinum-195 is termed an NMR active nucleus, meaning that nuclear coupling information can be garnered from the observation of other active nuclei in the proximity of the metal center. It also means that the metal itself may be observed by this technique. Observation of a proton that is coupled to another active nucleus with spin $+1/2$ would yield a doublet. However this is only true if the second nucleus is 100% abundant. In the case of platinum as the coupling nucleus, only 33% of the total proton

Table 2. Infrared Data for Tetramer, Monomer and Cyclopropane⁵⁴.

Bands Due to the C ₃ H ₆ Unit	[Pt(C ₃ H ₆)Cl ₂] ₄	Pt(C ₃ H ₆)Cl ₂ Py ₂	Cyclopropane C ₃ H ₆
C-H	3025m, 2954m 2948sh	2992w, 2938m 2917m	3103, 3028
CH ₂ Deformation	1414m	1437sh	1442
CH ₂ Wag	1255s, 1237sh	1238w	
CH ₂ Twist	1165w	1217m	
Ring Deformation	1149s, 1125w	1134w, 1087w	1029
CH ₂ Rock	1087vs, 1022vw	1038s	
Ring Deformation	981m	980vw	869
CH ₂ Rock	948m, 890w 663w,b	976w, 892w	
Ring Deformation- Mainly Pt-C	563m		

signal is observed to be a doublet. The remaining 66% is a single resonance. Therefore, this would make a typical proton resonance which is coupled to platinum appear as a singlet with symmetrical satellites. The combined magnitude of the satellites with respect to the central resonance reflects the natural abundance of platinum-195. The central resonance is unchanged, except for loss of 33% of its total intensity and it represents the protons in question that are in proximity of platinum isotopes other than platinum-195.

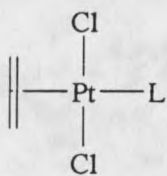
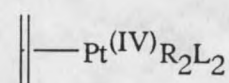
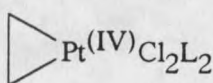
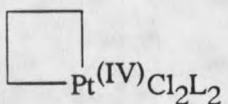
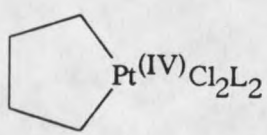
Moats⁵⁵ conducted detailed studies of the proton spectra of norbornyl platinacyclobutanes. This was no easy matter. The proton resonances in this type of

structure are often confused by the fact that the data are not clearly resolved. This limits the usefulness of ^1H NMR spectroscopy.

Carbon-13 NMR spectroscopy does not share in this impediment. Thus, proton decoupled ^{13}C NMR spectra of norbornyl platinacyclobutanes and pentanes have proven to be a powerful characterization tool. For example, some connectivities can be easily determined by observing the magnitudes of the platinum-carbon coupling constants. A general set of correlations between structure and coupling constant are shown in Table 3. Also shown in Table 3 is general chemical shift data observed for the α -carbons of various platinum-carbon complexes. Table 4 also is included to familiarize the reader with ^{13}C NMR data for selected platinacyclobutanes.

Comparisons of the ^{13}C NMR data obtained for platinacyclobutanes and platinacyclopentanes are useful as several key differences are observed, Table 5. The α -carbon resonances for platinacyclobutanes are generally found upfield near 0 part per million, ppm, for platinacyclobutanes. Platinacyclopentane α -carbons, on the otherhand, are found downfield between 20 and 60 ppm. The magnitude of the α -carbon-platinum coupling constants are also different. Generally, the coupling constants for platinacyclobutanes is 350-400 Hertz (Hz) while platinacyclopentanes usually exceed 500 Hz. These values are given for bis-pyridyl monomeric complexes. Differing ligands have been found to cause substantial variation in these values. The NMR data for a representative platinacyclobutane and platinacyclopentane are presented in Table

Table 3. Correlation Table for Structure and Coupling Constant in Platinum Complexes.

COMPLEX	α -CARBON CHEMICAL SHIFT (ppm)	$^1J_{\text{Pt-C}}$ (Hz)	Reference
	70-110	50-200	56, 57
	120	94	56
	40-65	340-380	38
	(-20)-20	335-460	47, 49, 58, 59
	5-60	350-640	34, 60

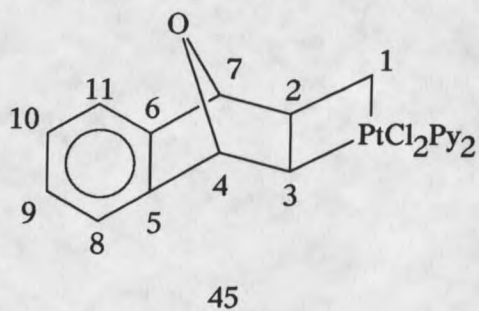
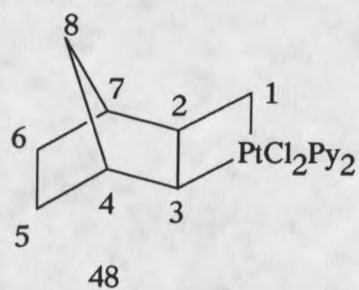
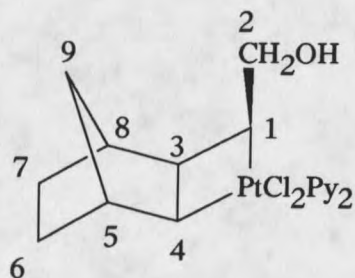
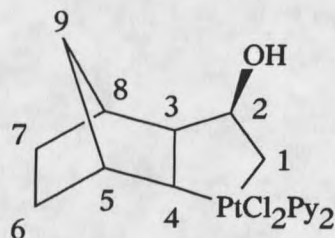


Table 4. ^{13}C NMR Data for Selected Platinacyclobutanes.

Carbon #	Complex 48 ⁶¹	Complex 45 ⁶²
1	-12.1 (352)	-6.4 (364)
2	55.6 (95)	52.4 (96)
3	12.4 (391)	5.4 (440)
4	40.9 (<10)	80.7 (16)
5	29.3 (44)	144.2
6	27.9	153.2
7	41.8 (24)	82.5 (24)
8	35.4	118.2
9	-	125.9
10	-	126.3
11	-	119.5



21



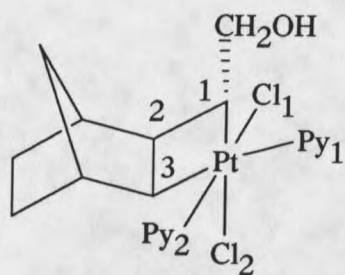
22

Table 5. ^{13}C NMR Data for Complexes 21 and 22.

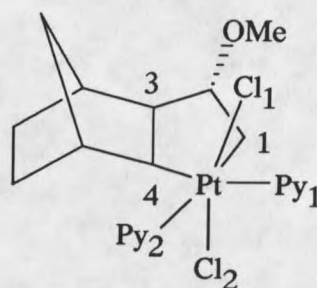
Carbon #	Complex 21 ppm ($J_{\text{Pt-C}}$) ⁶³	Complex 22 ppm ($J_{\text{Pt-C}}$) ⁶⁴
1	6.36 (370)	25.9 (548)
2	63.7 (24)	77.1
3	56.7 (98)	55.9
4	13.0 (394)	44.5 (537)
5	40.1 (10)	43.4
6	28.6	30.9
7	28.9	30.8
8	37.8 (10)	37.9
9	37.5	37.9

X-Ray Crystallography

The last analytical method to be discussed is X-ray crystallography. This process is certainly the ultimate due to the fact that it yields nuclear positions, via electron density of the molecule in question complete with bond distances and bond angles. It is important to have a conception of how the complex is oriented in space and an idea of the magnitude of the geometric perturbations of the substrate induced by the metal.



54



49

Table 6. X-ray Data for Complexes 54 and 49.

complex 21 ³³		complex 49 ³⁴	
BOND	BOND DISTANCE (Å)	BOND	BOND DISTANCE (Å)
Pt-C1	2.04	Pt-C1	2.04
Pt-C2	2.19	Pt-C2	2.08
Pt-Cl1	2.29	Pt-Cl1	2.319
Pt-Cl2	2.29	Pt-Cl2	2.325
Pt-N1	2.25	Pt-N1	2.26
Pt-N2	2.11	Pt-N2	2.24
BOND	BOND ANGLE (°)	BOND	BOND ANGLE (°)
PtC1C2	96.7	PtC1C2	110
C1C2C3	97.2	C1C2C3	111
C2C3Pt	94.6	C2C3C4	110
C3PtC1	69.8	C3C4Pt	111
Cl1PtCl2	177.4	C4PtC1	83.6
N1PtN2	90.0	Cl1PtCl2	178.6
C3PtN1	167.7	N1PtN2	87.5
C1PtN2	170.6	C4PtN1	175.9
		C1PtN2	178.2

Table 6 contains bond angle and distance data for a representative platinacyclobutane and platinacyclopentane. This data is presented in order to provide a basis for the types of molecules that were studied in the main body of this thesis.

The Chemistry of Organoplatinum Complexes Derived from Zeise's Dimer and Cyclopropanes

The reaction between Zeise's Dimer and cyclopropanes has been well documented with the synthesis of numerous complexes. The purpose of this section of the introduction is to outline some of the various pathways by which organic transformations may be accomplished using Zeise's dimer as a reagent.

Reactions with Carbon Monoxide

Insertion of carbon monoxide into a metal-carbon bond has become a ubiquitous endeavor in organometallic chemistry⁶⁵. Generally, late transition metals have been shown to insert carbon monoxide rather easily, however with platinum, the reaction is not quite so facile. Reaction⁶⁶ of the norbornyl derived platinacyclobutane shown in Figure 66 with carbon monoxide at 80 psi in a chloroform/methanol mixture gave the indicated olefinic residue.

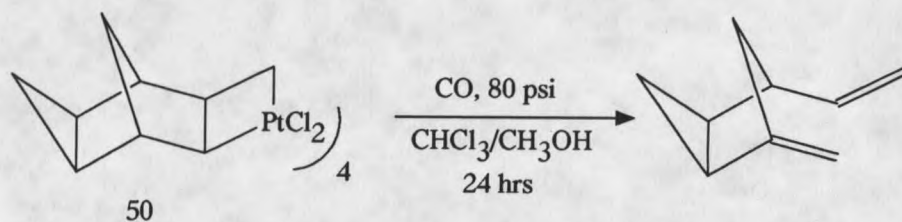


Figure 66. Reaction of a Norbornyl Platinacyclobutane, **50**, with CO.

Use of the unsaturated substrate gave several products⁶⁷. Formation of ethoxy substituted products is attributed to ethanol stabilizer commonly found in chloroform.

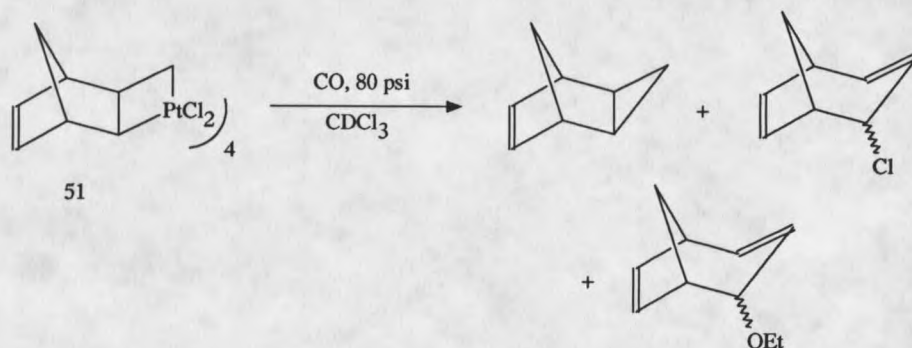


Figure 67. Reaction of Complex **51** with CO.

The importance of the previous two examples is that there was no formation of carbonyl inserted products. In contrast to these results, Hoberg⁶⁸ found that complex **31** allows for the insertion of carbon monoxide and subsequent ester formation. In addition to this, lactone synthesis was performed by altering the reaction conditions.

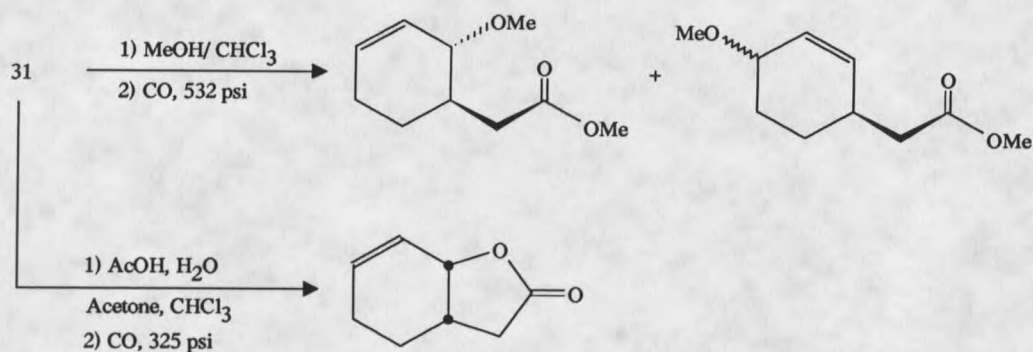


Figure 68. Reaction of Complex 31 with Carbon Monoxide.

Homologation

Thermal decomposition of norbornyl platinaacyclobutanes in chloroform is an avenue that has been explored to some degree⁶⁹. Reflux of complex 52 in chloroform was found to yield an olefinic ring homologated product. The following mechanism has

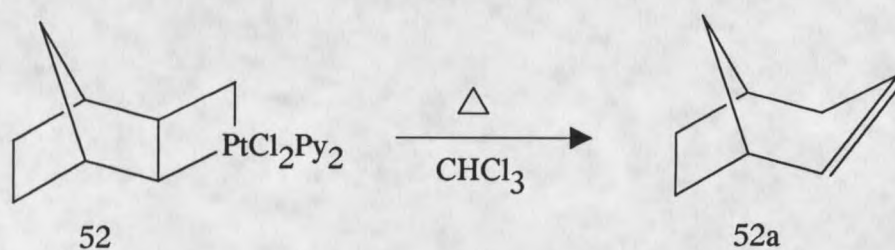


Figure 69. Thermal Homologation of Complex 52.

been proposed for this reaction, Figure 70. The first step involves loss of a ligand. This was proposed due to the fact that decomposition does not occur in excess ligand. The

next step is a Puddephatt rearrangement followed by β -hydride elimination to give the platinum-hydride that upon reductive elimination gives the homologated product, 52a.

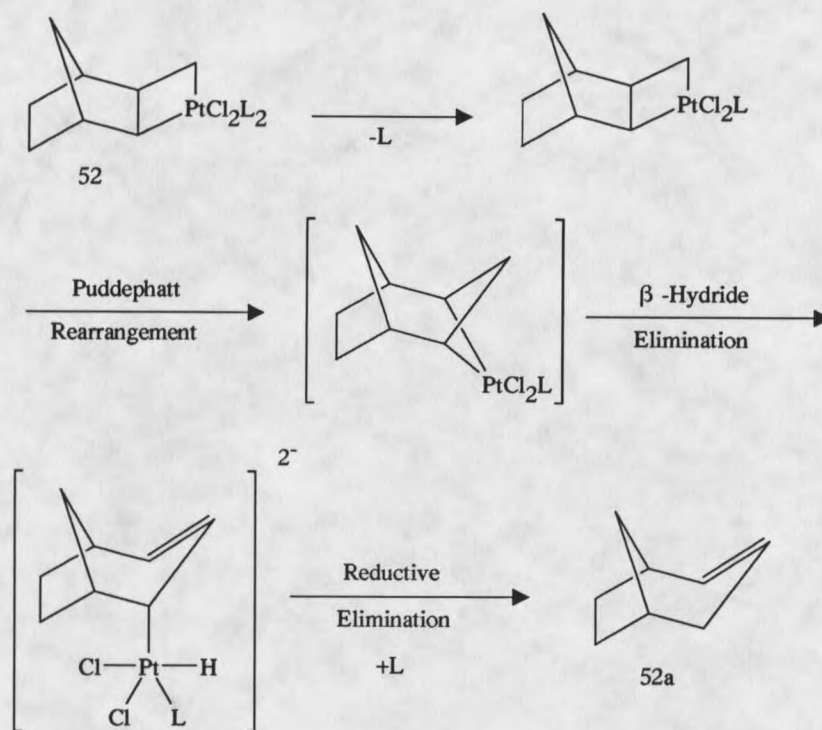


Figure 70. Proposed Mechanism for the Thermal Homologation of Complex 52.

Homologations have also been observed under other conditions⁷⁰. Complex 51 was shown to homologate upon exposure to DMSO to give the cyclic olefin in 75% yield. Better yields of homologated product were obtained by using complex 50.

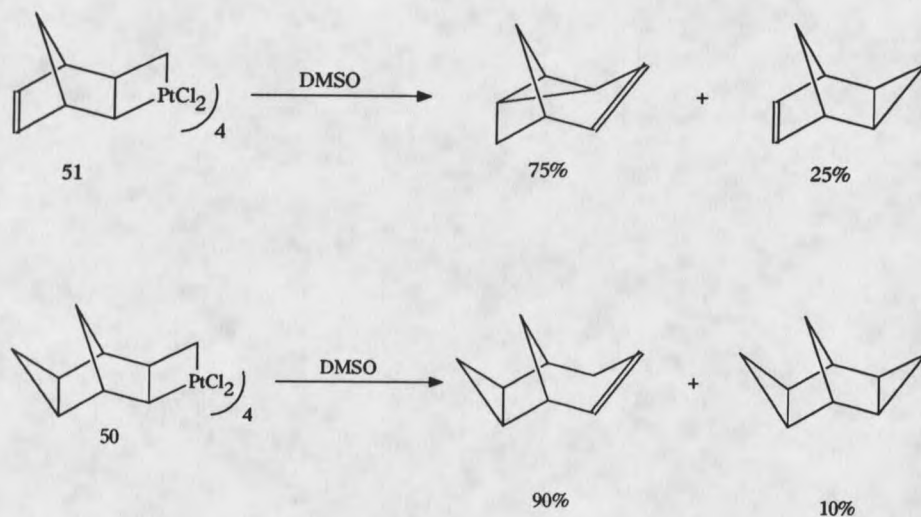


Figure 71. Reaction of Complexes 50 and 51 with DMSO.

Reactions with Diazo-derivatives

Exposure of complex 48 to diazomethane⁷¹ in chloroform was shown to give a novel platinum-mediated carbon-carbon bond forming reaction. The product from this process was determined to be cis-1,3-divinylcyclopentane. The stereochemistry of the

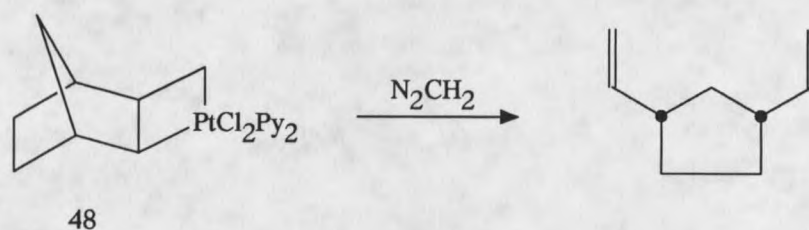


Figure 72. Reaction of Complex 48 with Diazomethane.

ring was observed as exclusively cis, which is reasonable due to the structure of the original complex.

The unsaturated analog was also observed to undergo this process. The significance of this is that it allows for a more functionalized product.

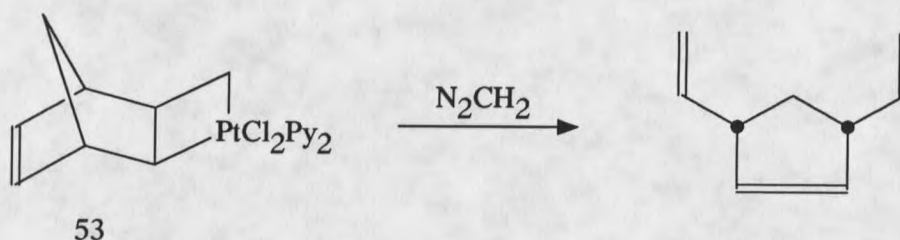


Figure 73. Reaction of Complex 53 with Diazomethane.

The reaction of substituted platinacycles with diazomethane revealed a very interesting stereochemical outcome³³. The products were observed to be stereospecific about the bis-substituted olefin. Syn substitution in the platinum complex, **21**, yields cis residues stereospecifically, while anti substituted complexes give trans substituted alkenes.

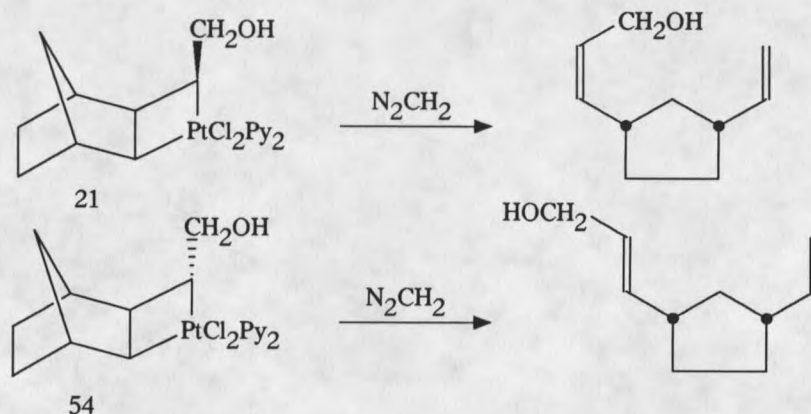


Figure 74. Reaction of Complexes 21 and 54 with Diazomethane.

A proposed pathway⁷² for this reaction is initiated with loss of a ligand, see Figure 75. Support for this supposition is provided by the fact that diazomethane fails to react in the presence of excess ligand.

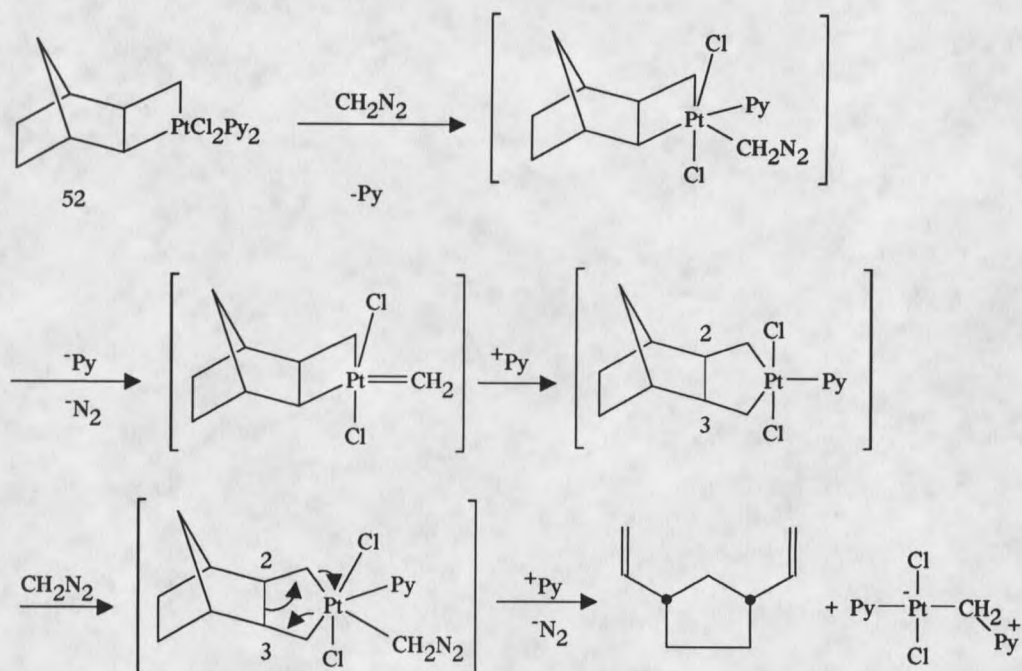


Figure 75. Proposed Mechanism of the Reaction Between 52 and N_2CH_2 .

The next step involves coordination of the reagent. The exact nature of this coordination is unknown. Resonance forms for diazomethane are shown in Figure 76.

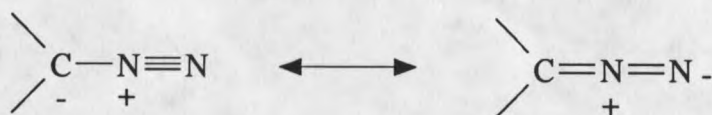


Figure 76. Resonance Forms for Diazomethane.

Theoretically, coordination could be achieved by bonding either the diazomethane-carbon or the terminal nitrogen. It is proposed that ultimately a carbon-metal bond is formed based on the fact that a metal-carbene is the product formed from either mode of bonding followed by extrusion of nitrogen. Following metal-carbene formation,

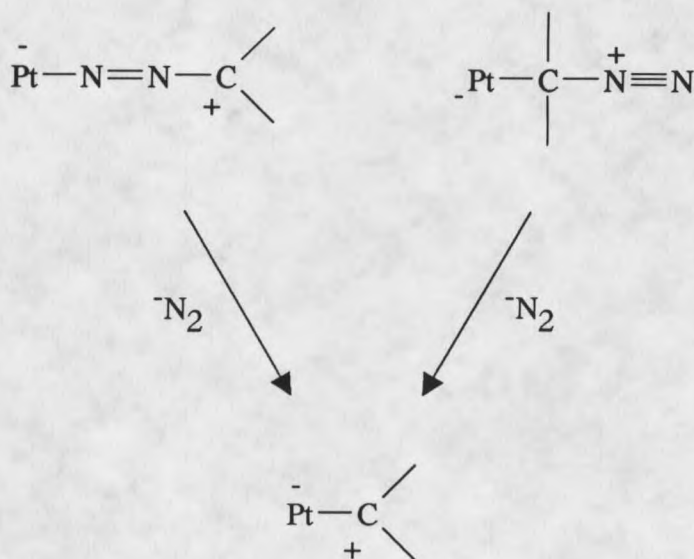


Figure 77. Formation of a Platinum-Carbene.

migratory insertion of the carbene unit into the platinum-substrate bond is envisioned. This step yields the symmetrical platinacyclopentane. Subsequent decomposition of this platinacycle gives the observed divinylcyclopentane product. The driving force for this decomposition is provided by the relief of norbornyl ring strain. It should be noted that bond migration from the α -methylene to the diazo-carbon, giving an unsymmetrical platinacyclopentane is conceivable. This unsymmetrical platinacyclopentane is analogous to stable complexes previously synthesized, however none have been detected.

A perturbation upon this mechanism is displayed in Figure 78⁷³. The key difference involves the stereochemistry of the diazo-compound attack. The diazo-compound is proposed to attack the topside of the metal. This open site is provided by initial loss of a pyridine and migration of the chlorine to a position in the plane of the ring. This pathway is more hindered sterically than the first, however it should be considered in an overall mechanistic approach.

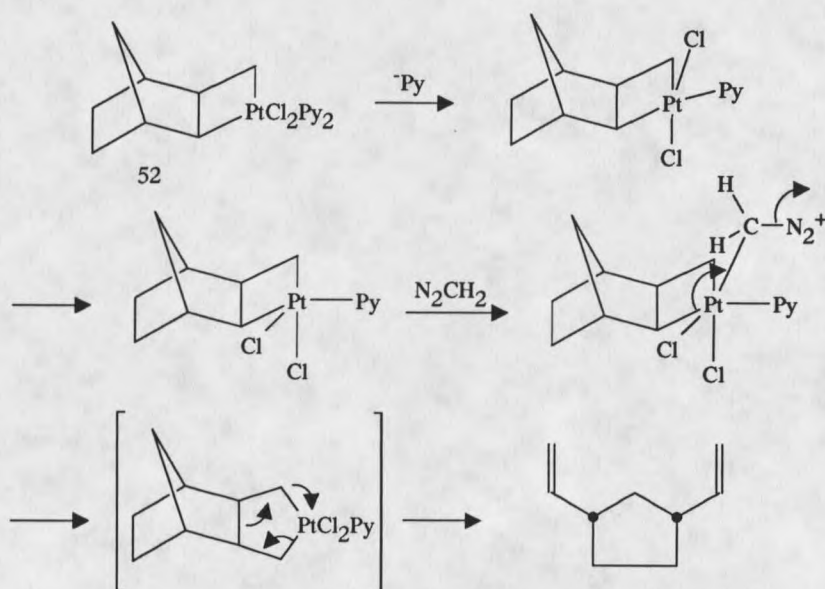


Figure 78. Proposed Mechanism for the Reaction Between Complex 52 and N_2CH_2 .

A third mechanism proposed for this process deviates somewhat from the first two, Figure 79. Coordination of the diazomethane occurs in concert with a metathesis ring opening process that liberates the a vinyl moiety. Loss of nitrogen gives a platinacyclopropane which decomposes to give the organic product and metal residue.

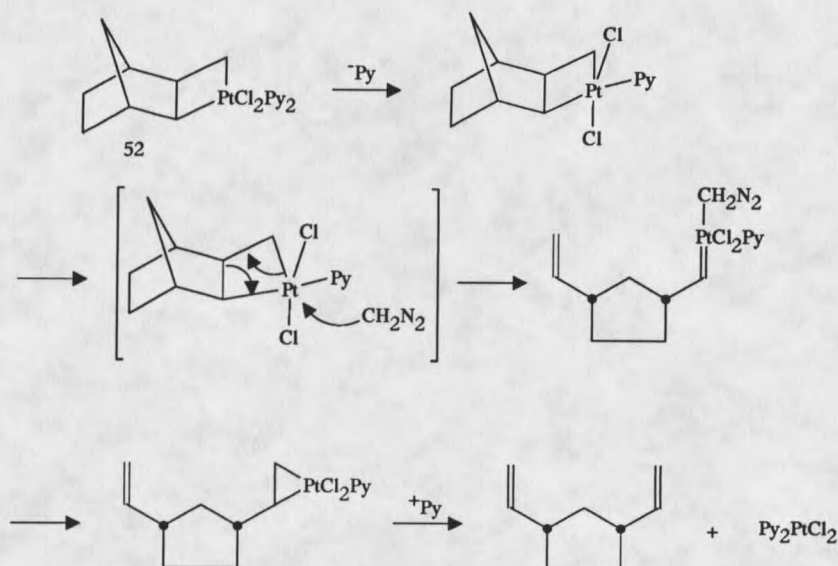


Figure 79. Proposed Mechanism for the Reaction Between Complex 52 and N_2CH_2 .

In an attempt to learn more about the reaction mechanistically, a mono-substituted diazo-reagent was employed⁷³, Figure 80. Observation of products could lead to the construction of bonding models where the orientation of the reagent onto the metal can be proposed. Treatment of the syn-hydroxymethyl platinacyclobutane, 21, with ethyl diazoacetate did give divinyl products. Stereochemistry on the hydroxymethyl portion of the product molecule was preserved. The stereochemistry of the portion derived from the diazoderivative, however, was not specific.

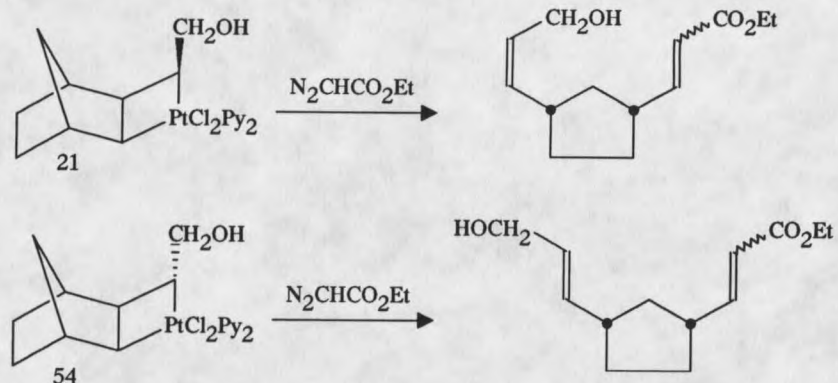


Figure 80. Reaction of **21** and **54** with Ethyl Diazoacetate.

Isomeric ratios⁷³ for the carboxylate substituted vinyl group are shown in Table 7 for various platinacyclobutanes. Significant insight into the reaction mechanism from these experiments was not garnered.

Table 7. Reaction of Various Platinacyclobutanes with $\text{N}_2\text{CHCO}_2\text{Et}$.

Platinacyclobutane (substitution)	E/Z Ratio
syn-CHO	1.0
anti-CHO	1.2
syn-Me	1.1
syn- CH_2OH	1.1
anti- CH_2OH	1.1

Operating on the assumption that only one ligand dissociates, ligand comparison studies were conducted to probe the notion that the remaining ligand would be able to influence the stereochemistry of the diazo-reagent. Table 8 contains a summary of the data. Differentiation of the three mechanisms proposed earlier was not possible based on these data⁷³.

Table 8. Ligand Effects in the Reaction Between 21 and 54 with $\text{N}_2\text{CHCO}_2\text{Et}$.

Ligand	Syn- CH_2OH (21)	Anti- CH_2OH (54)
2-methyl pyrazine	1.1	1.05
3-ethyl pyridine	0.91	1.4
3-picoline	0.91	0.83
3,5-lutidine	1.1	0.83

Platinacyclopentanes

Much of the known chemistry of these complexes has been previously discussed in this introduction. One area to note is the photochemistry of these complexes. Platinacyclopentanes will decompose upon exposure to ultraviolet radiation⁷⁴ as shown in Figure 81. The observed products were surprising. The driving force for several reactions utilizing norbornyl platinacyclobutanes is the relief of ring strain. The formation of norbornene analogs represents an unanticipated formation of products with increased ring strain.

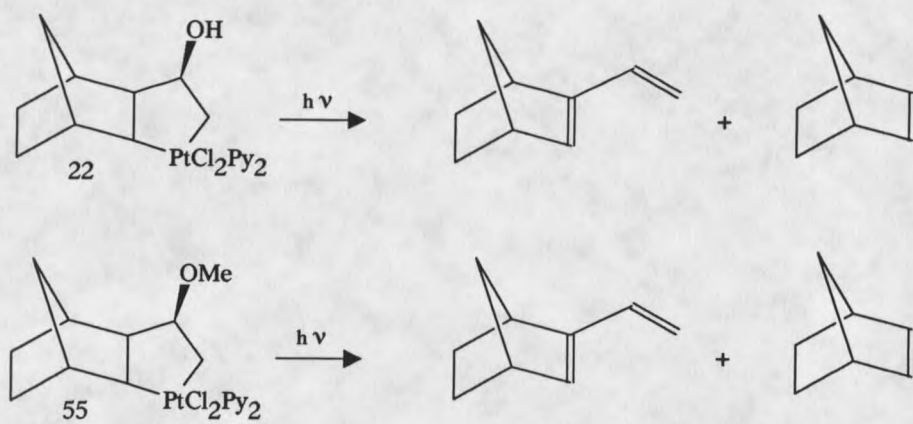


Figure 81. Irradiation of Complexes 22 and 55.

RESULTS AND DISCUSSION

Statement of Problem

The chemistry of platinum(IV) metallacyclopentanes is largely unexplored. Norbornyl platinacyclopentanes can be synthesized with stereospecific and regiospecific substitution. This represents the perfect vehicle to obtain organic products while retaining the stereocontrol. Also, manipulation of the ring-expansion process may give new platinacyclopentanes worthy of further study. In addition, ligand exchange processes and nucleophilic attack of platinum(IV) metallacycles are areas that provide much promise.

The reaction between platinum(IV) metallacyclobutanes and diazocompounds is, as previously outlined, a novel and significant transformation involving carbon-carbon bond formation mediated by platinum. The mechanism of this process requires exploration so that its versatility and synthetic usefulness may be broadened. An investigation of why a mixture of isomers is observed when the reaction is conducted with ethyl diazoacetate as the reagent may lead to modified substrates that allow for better stereocontrol. In addition to this, other diazo-reagents will be utilized in an attempt to further the versatility of the reaction.

Nucleophilic Attack of Platinum(IV) Metallacycles.

Platinacyclobutanes are known to give olefinic products upon reflux in chloroform⁷⁵. Complex **21** undergoes reductive elimination under these conditions.

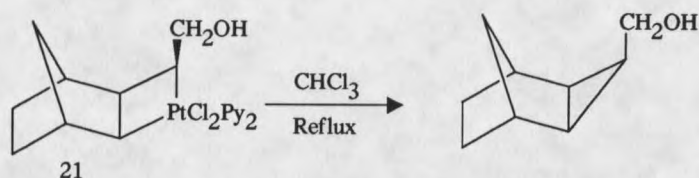


Figure 82. Reflux of Complex **21**.

Ring expansion of **21** yields the syn-platinacyclopentanol, **22**, that is stable under these conditions. In fact, reflux of **22** in benzene and toluene are observed to give no decomposition.

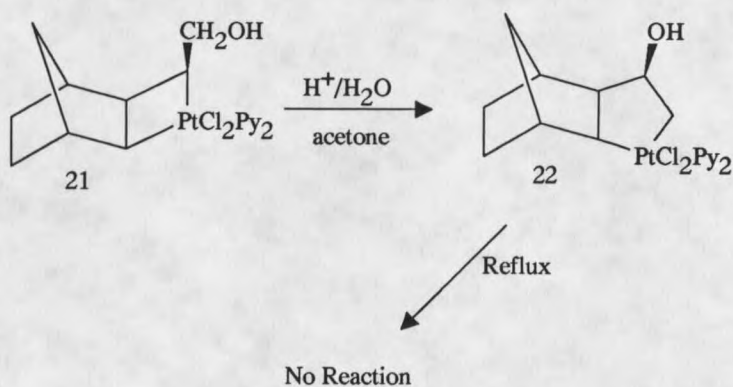


Figure 83. Reflux of Complex **22**.

As previously noted, the ^{13}C NMR spectra change considerably upon ring expansion. The coupling constants between the metal and the α -carbons are seen to increase by at least 150 Hertz. The magnitude of the coupling constant is thought to be proportional to the degree of s-bond character in the bond. Thus, the higher the coupling constant, the more s-character to the bond and the stronger the bond. Accessing chemical pathways in these systems would seem to require different methods than those utilized in metallacyclobutane chemistry.

Reaction of Platinacyclic Complexes with Hydrides

The platinacyclopentanone derived from the oxidation of **22** was dissolved in tetrahydrofuran and treated with lithium aluminum hydride with anticipation that complexes **22** and **24** would be formed. Visually, the reaction was rapid and the original golden tetrahydrofuran solution turned black in a nearly explosive manner. Immediate removal of the black precipitate by filtration and rotoevaporation of the solvent gave a pungent yellow oil. Analysis by ^1H NMR indicated that the platinacyclopentane was no longer intact and a gas chromatograph trace of the oil displayed three products. Molecular ion determinations by mass spectroscopy showed that two of the products were $m/e = 140$ and the third was $m/e = 138$. The ^{13}C NMR spectrum could be interpreted to reveal the presence of two C-OH bonds and one ketone by virtue of chemical shift.

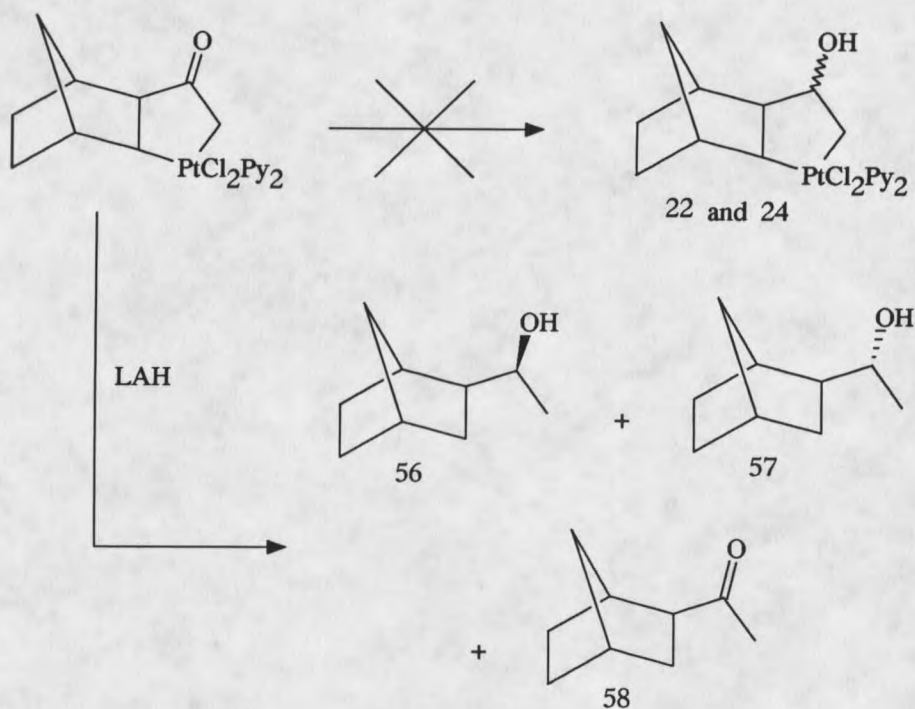


Figure 84. Reaction of the Platinacyclopentanone with LAH.

Instead of immediate analysis, the reaction was allowed to stir at room temperature for six hours prior to workup. The only products detected were the two alcohols by ^{13}C NMR spectroscopy. The ketone resonance was not observed.

Separation and characterization of the alcohols appeared to be a formidable task. However, each of the alcoholic precursors to the platinacyclopentanone, **22** and **24**, was available. Reaction of **22** with lithium aluminum under similar conditions was found to give only one of the alcohols observed in the earlier experiment, **56**, Figure 86. Yields in this process were limited to 80%. The remaining 20% consisted of several uncharacterized side products.

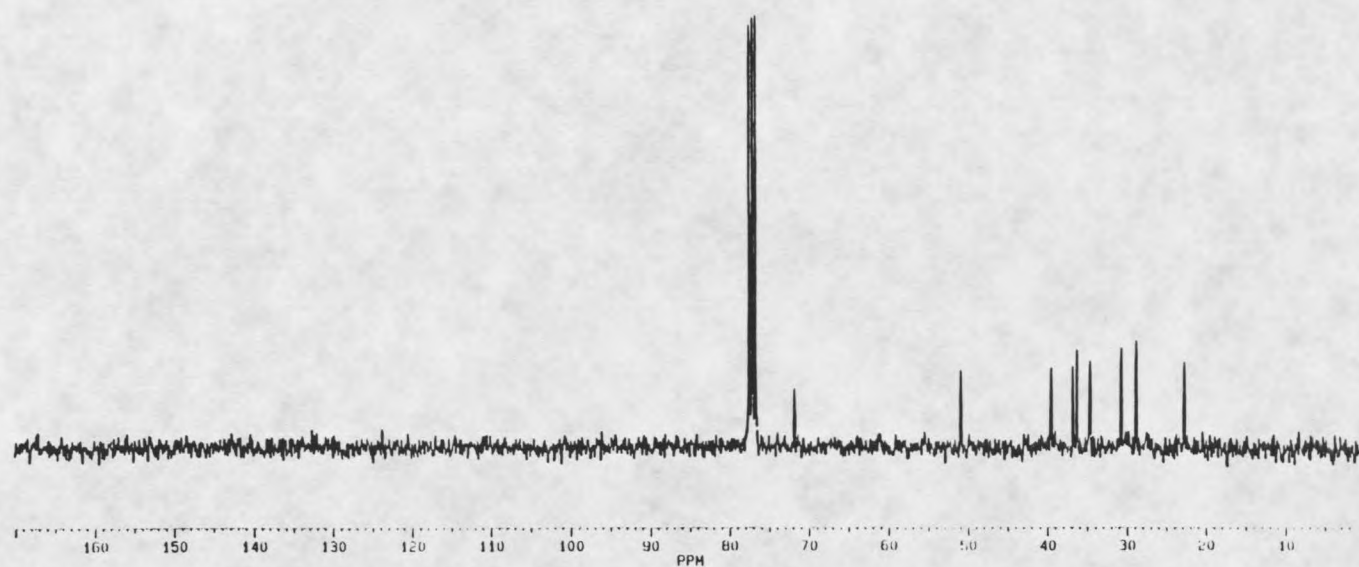


Figure 85. ^{13}C NMR Spectrum of Compound **56**.



Figure 86. Reaction of 22 with Lithium Aluminum Hydride.

Modification of this procedure by using sodium borohydride gave nearly quantitative yields of one product. The observed reaction paralleled that of lithium aluminum hydride. Filtration of the black precipitate, addition of water and extraction of the resulting solution with chloroform afforded the product. Determination of the regiochemistry of hydride addition was made by deuterium labelling.

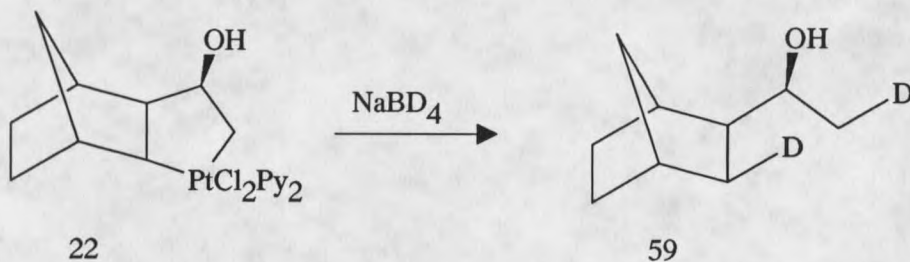


Figure 87. Reaction of 22 with NaBD_4 .

Mechanistically, the reduction of platina(IV)cyclopentane derivatives would seem to involve nucleophilic attack of hydride at the metal. In the case of the platinacyclopentanone, the observation of ketone product, 58, suggests that the metal is

the initial site of attack, liberating the platinum and giving the ketone which is subsequently reduced to the alcohols, 56 and 57.

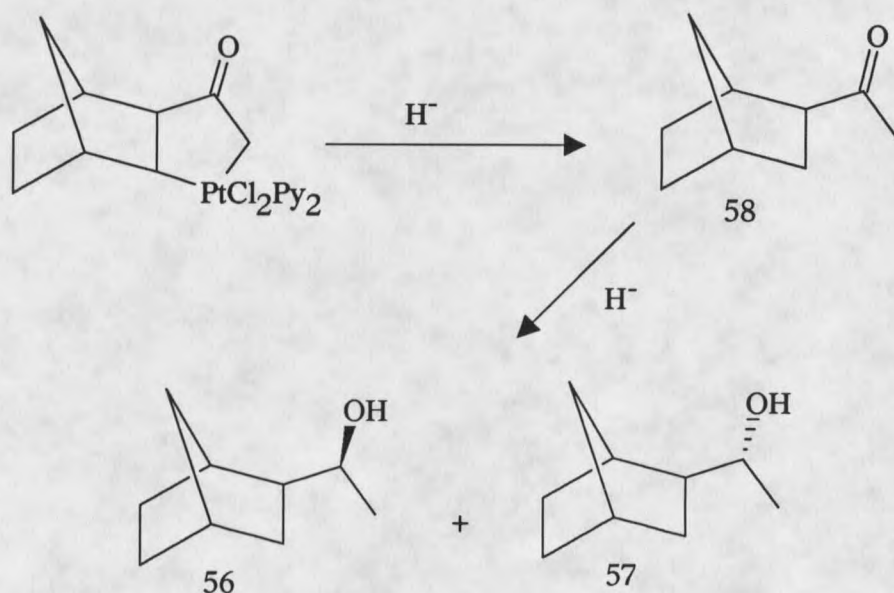


Figure 88. Proposed Reaction Sequence for Hydride Attack.

A proposed mechanism, Figure 89, begins with initial loss of a pyridine followed by attack of the hydride on the coordinatively unsaturated metal center. Reductive elimination then occurs cleaving the platinum-carbon bond and effecting the delivery of hydride to the substrate. The driving force for this reductive elimination can be thought of as a relief of electron density on the metal. Hydride is a strong σ -donor that increases the electron density on the metal substantially. Transfer of a second hydride to the substrate to give product can follow a similar course.

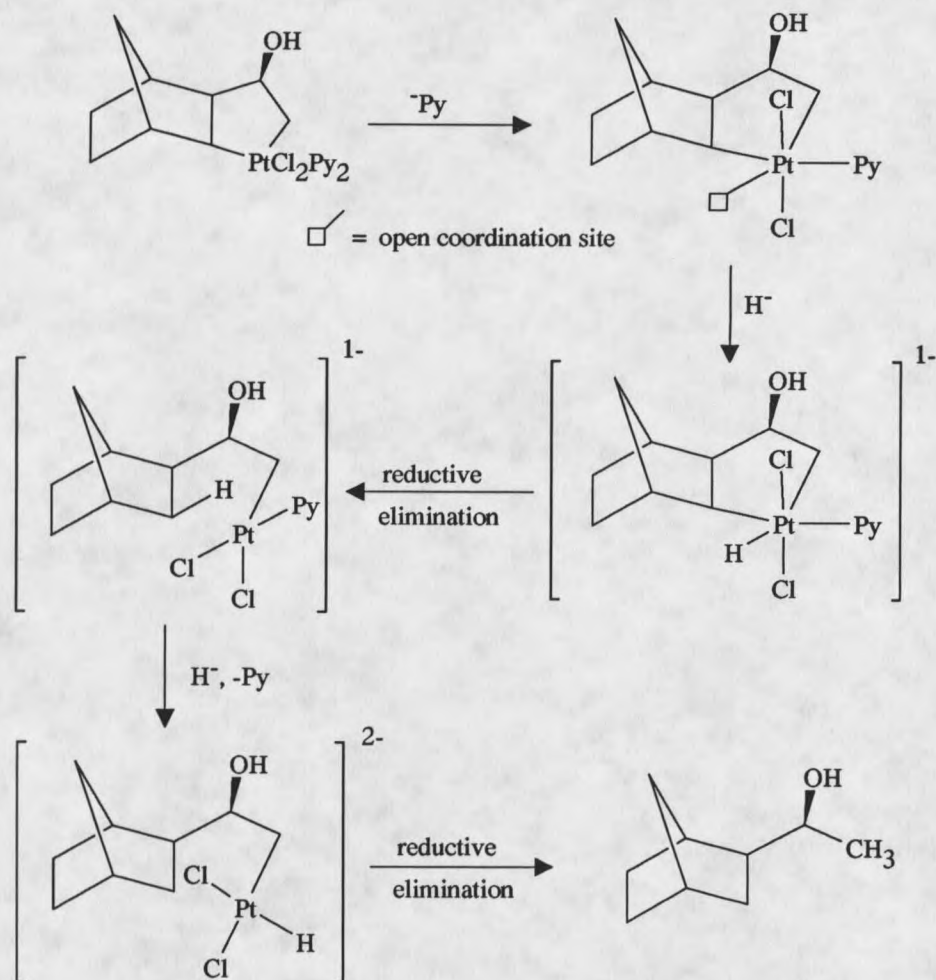


Figure 89. Proposed Mechanism for the Reaction of **22** with Hydride.

An alternate mechanism, Figure 90, has the hydride attack an α -carbon in an $\text{S}_{\text{N}}2$ manner with the platinum acting as a leaving group. Initial $\text{S}_{\text{N}}2$ attack of the α -methine is not favored due to steric concerns, however, the α -methylene is in a position for this to occur. Delivery of the second hydride would still be allowed to follow the pathway established in the first mechanism.

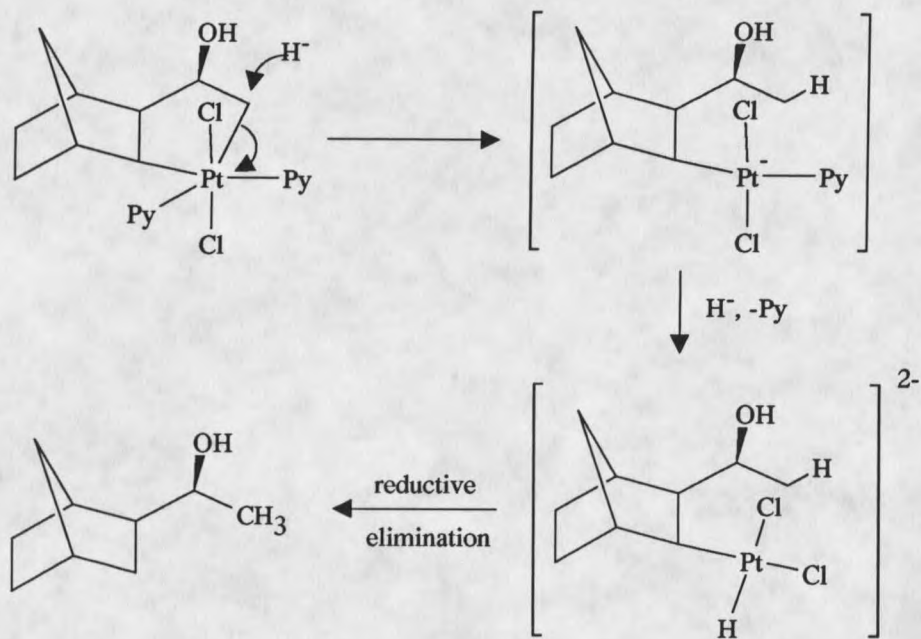


Figure 90. Proposed Mechanism for the Reaction of **22** with Hydride.

To differentiate between the two pathways presented here, complex **60** was synthesized by reaction of **22** with one equivalent of bipyridine. Complex **60** when treated with sodium borohydride, failed to react, Figure 91. Bipyridine is a bidentate

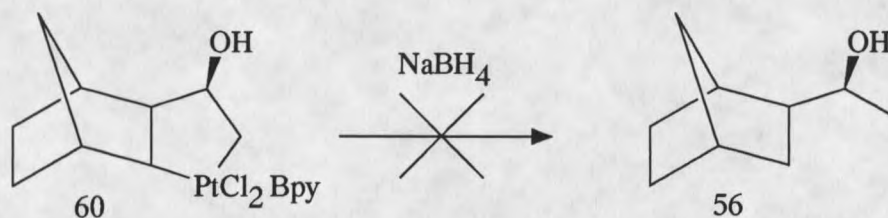


Figure 91. Reaction of **60** with Sodium Borohydride.

chelating ligand that is expected to eliminate an open coordination site on the metal which is crucial to the pathway shown in Figure 89 but not crucial to that shown in Figure 90. The lack of product formation suggests that an open coordination site is required and the first mechanism appears to have support.

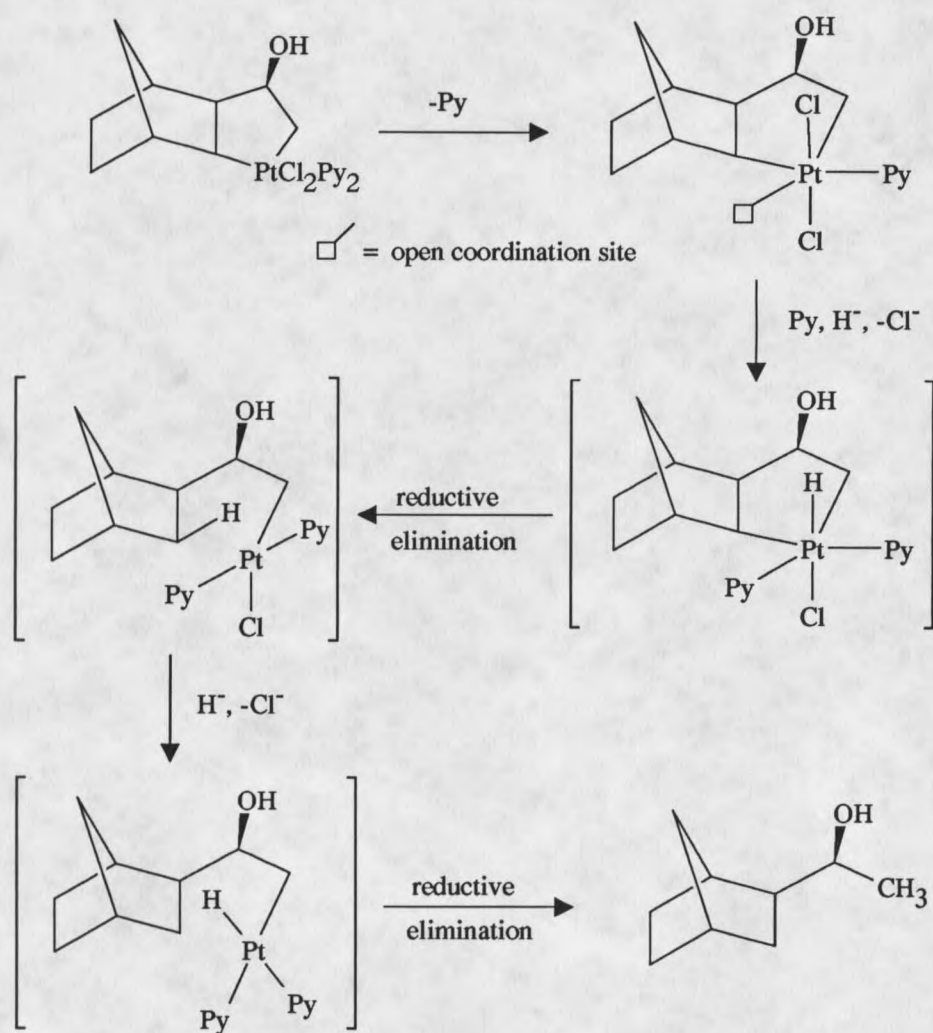


Figure 92. Proposed Mechanism for the Reaction of 22 with Hydride.

A perturbation upon the first mechanism, Figure 92, reflects a difference in the ligand on the platinum after attack of the hydride. In the first mechanism, reductive elimination occurs directly after hydride incorporation from a negatively charged 18 electron system. In Figure 92, chloride is lost forming a platinum(II) 16 electron neutral complex. This is a nucleophilic substitution that could possibly lead to barriers against extension of this methodology to other nucleophiles. Nucleophiles that can perform this transformation would be thought to have to displace chlorine, ie: it must be a better nucleophile than chlorine.

To broaden the scope of this transformation, complex **55** was treated with sodium borohydride in a manner analogous to that used for complex **22**. The result was formation of the expected methyl ether, **62**. Furthermore, this excludes any involvement of the hydroxyl moiety in the reaction sequence.

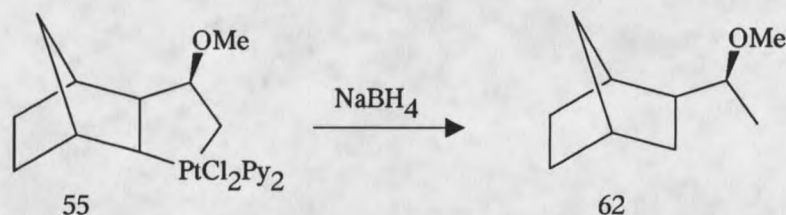


Figure 93. Reaction of Complex **55** with Sodium Borohydride.

It was envisioned that a similar product could be generated by hydrogenation of a platinacyclopentane. Typical conditions for catalytic hydrogenation of olefins with platinum(IV) oxide is one to four atmospheres of pressure at room temperature⁷⁶. Under these conditions, complex **22** was inert.

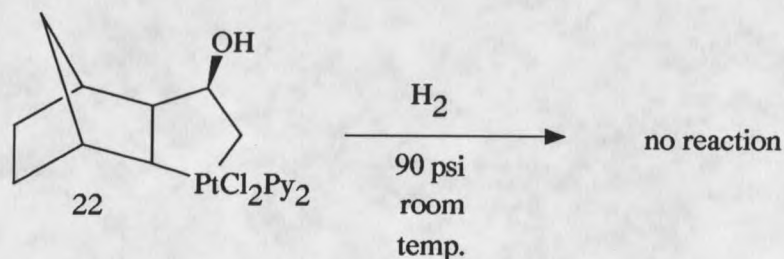


Figure 94. Reaction of 22 with Low Pressure Hydrogen Gas.

The pressure was increased to 730 psi and the reaction was stirred at room temperature for 66 hours. The formation of 56 achieved in 73% yield and was verified by comparison to a sample produced by the method previously described.

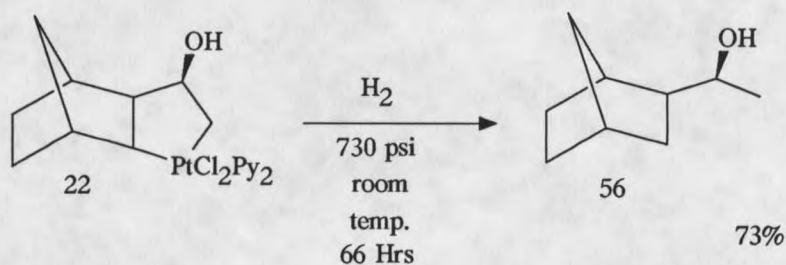


Figure 95. Reaction of 22 with Hydrogen Gas (730 psi).

The conditions under which the product was obtained is rather extreme. However, this does seem understandable considering a basic mechanism of hydrogenation. The metal is thought^{76a} to oxidatively add molecular hydrogen prior to addition of the hydrogen to the substrate, Figure 96.

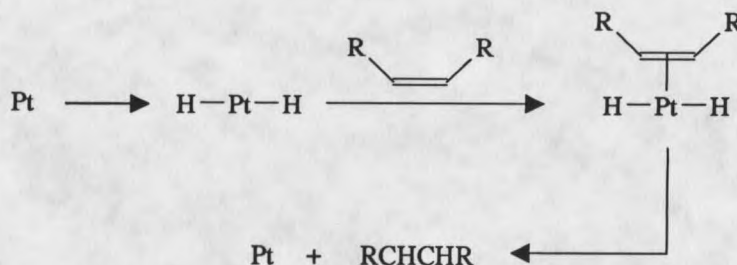


Figure 96. First Proposed Mechanism for the Hydrogenation of Alkenes.

Complex 22 is a coordinatively saturated species and oxidative addition of hydrogen to this complex would require the loss of two ligands and formation of a platinum(VI) complex which is clearly an uphill process energetically. This provides a possible explanation for the conditions required to perform this transformation.

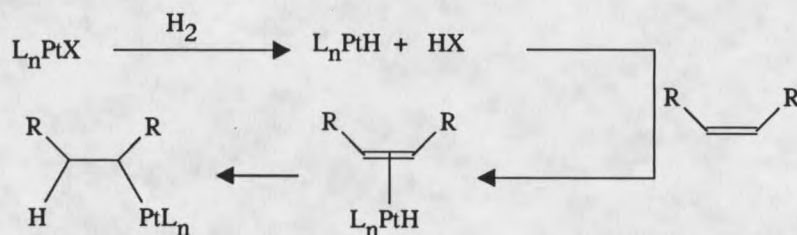


Figure 97. Second Proposed Mechanism for the Hydrogenation of Alkenes.

A second proposed mechanism, Figure 97, involves exchange of a halide for a hydride on the metal complex giving the metal hydride and corresponding acid^{76b}. This is a pathway that is viable for the transformation in question.

A third proposed mechanism, Figure 98, invokes base assisted cleavage of diatomic hydrogen^{76b}. Pyridine is present under the reaction conditions, thus this pathway must be considered. No further experiments were performed to differentiate these mechanisms.

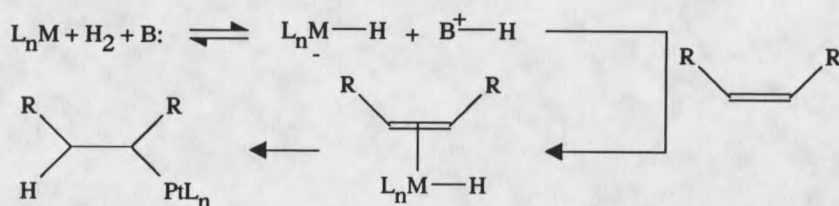


Figure 98. Third Proposed Mechanism for the Hydrogenation of Alkenes.

Reaction of Complex 22 with Sodium Acetate

In an attempt to expand the methodology outlined previously with the metal hydrides, acetate ion was employed as a nucleophile. Excess acetate was allowed to stir with complex 22 in methanol at room temperature and no reaction was observed. Elevation in temperature also was shown to give only complex 22.

Two possible conclusions can be drawn. First, no interaction between the acetate ion and the metallacycle occurred. The second scenario involves a reversible nucleophilic attack yielding only starting material.

In either case, mechanistically, the conclusion that acetate is not a potent enough nucleophile does appear to be valid. Under the first proposal, acetate ion cannot associate with the metal. The second pathway, the acetate associates with the metal, however, it is not delivered to the substrate in a manner analogous to the hydride process. Rationale for this can be either the inability of the acetate and the substrate to

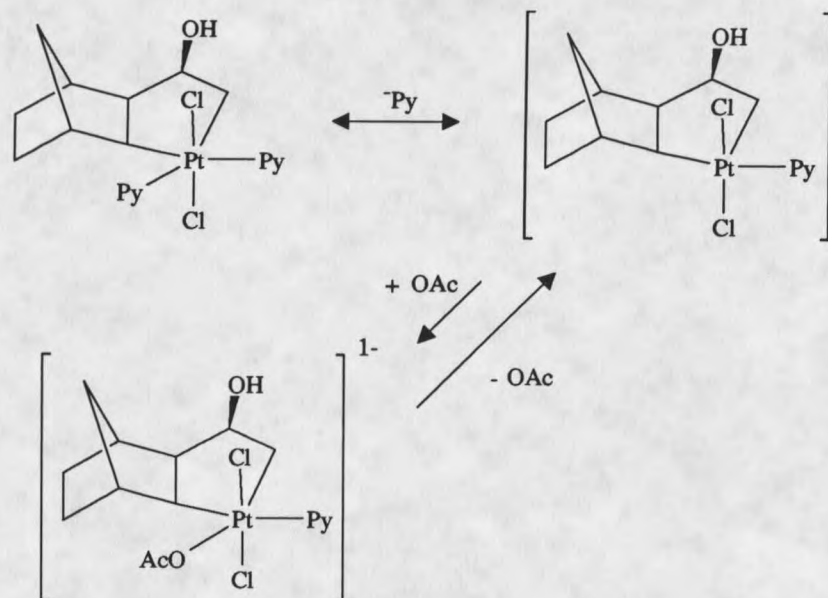


Figure 99. Proposed Reaction of **22** with Acetate Ion.

be readily coupled or the required loss of chloride as shown earlier with hydride, Figure 99. Quantitative recovery of complex **22** suggests that no chloride is lost from the complex.

This observation led to the search for a more potent nucleophile. Azide (N_3^-) ion was a natural choice. It is more nucleophilic than acetate and if it could be delivered to the substrate, alkyl azides might be formed. They are synthetically useful precursors for amines.

Reaction of Complex 22 with Sodium Azide

Treatment of complex 22 in methanol with seven equivalents of sodium azide was observed to give no reaction at room temperature. At reflux, however, products were observed to be metallacycles by ^1H and ^{13}C NMR spectroscopy. The distribution of products also appeared to change with time. Table 9 is a summary of the reaction times and the relative ratios of the two products formed, 63 and 64. The formation of products also appeared to give the following relationship.

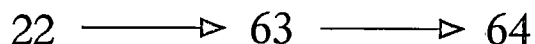


Table 9. Reaction of 22 with Sodium Azide.

Time	22(%)	63(%)	64(%)
3 hours	69	31	0
11 hours	14	67	19
23 hours	0	33	67

The ^{13}C NMR spectra of these mixtures showed some very interesting qualities. Resonances assigned to the α -carbons are most indicative. Moderate deviations in the chemical shifts were observed but they remained consistent with previous examples of platinum(IV) metallacyclopentanes. The coupling constants to platinum-195, on the other hand are seen to increase significantly in an additive manner, comparing 63 and 64 to 22, see Table 10.

The most significant way to visualize this transformation is to observe the resonances attributable to carbon #3. The ^{13}C NMR spectrum on page 86 shows the three complexes after eleven hours of reaction time. In comparison, the ^{13}C NMR spectrum on page 87, after 23 hours, indicates the disappearance of complex 22, the minimization of complex 63 and the relative enhancement of complex 64.

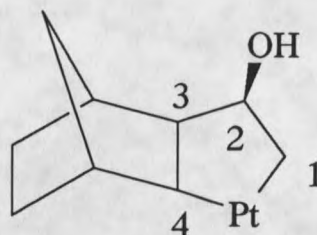


Table 10. ^{13}C NMR Data for the α -carbons of complexes 22, 63, 64.

Carbon	22 ppm ($^1J_{\text{Pt-C}}$)	63 ppm ($^1J_{\text{Pt-C}}$)	64 ppm ($^1J_{\text{Pt-C}}$)
1	25.9 (548)	30.3 (606)	31.5 (644)
3	55.9	54.9	53.8
4	44.5 (537)	42.5 (555)	45.1 (598)

The ^{13}C NMR spectra for each of the two new products contained the appropriate number of resonances, nine, attributed to the intact norbornyl platinumacyclopentane structure. Carbon #2 also appeared to have maintained the alcohol moiety by virtue of chemical shift. This would seem to suggest that the actual modification of complex 22

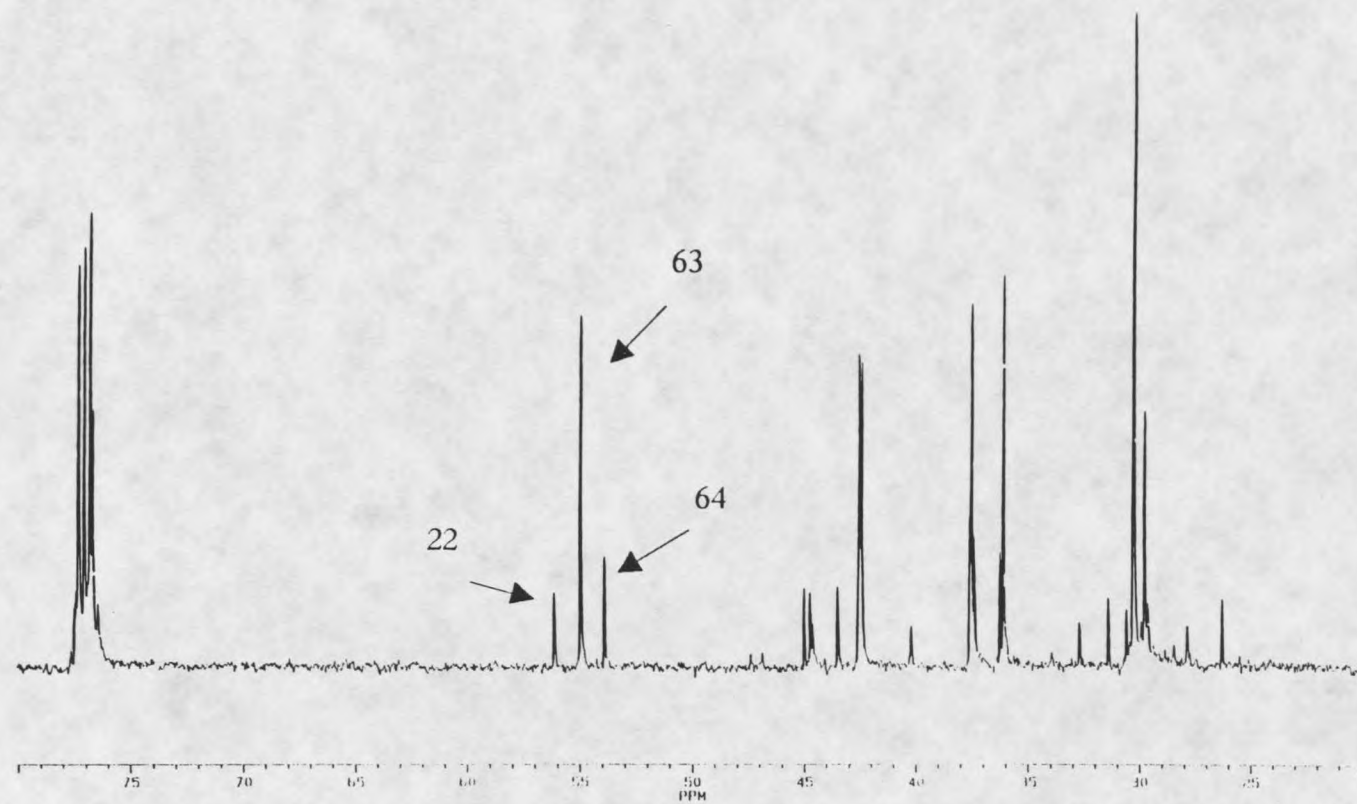


Figure 100. ^{13}C Spectrum of 22, 63, and 64 after 11 Hours at Reflux.

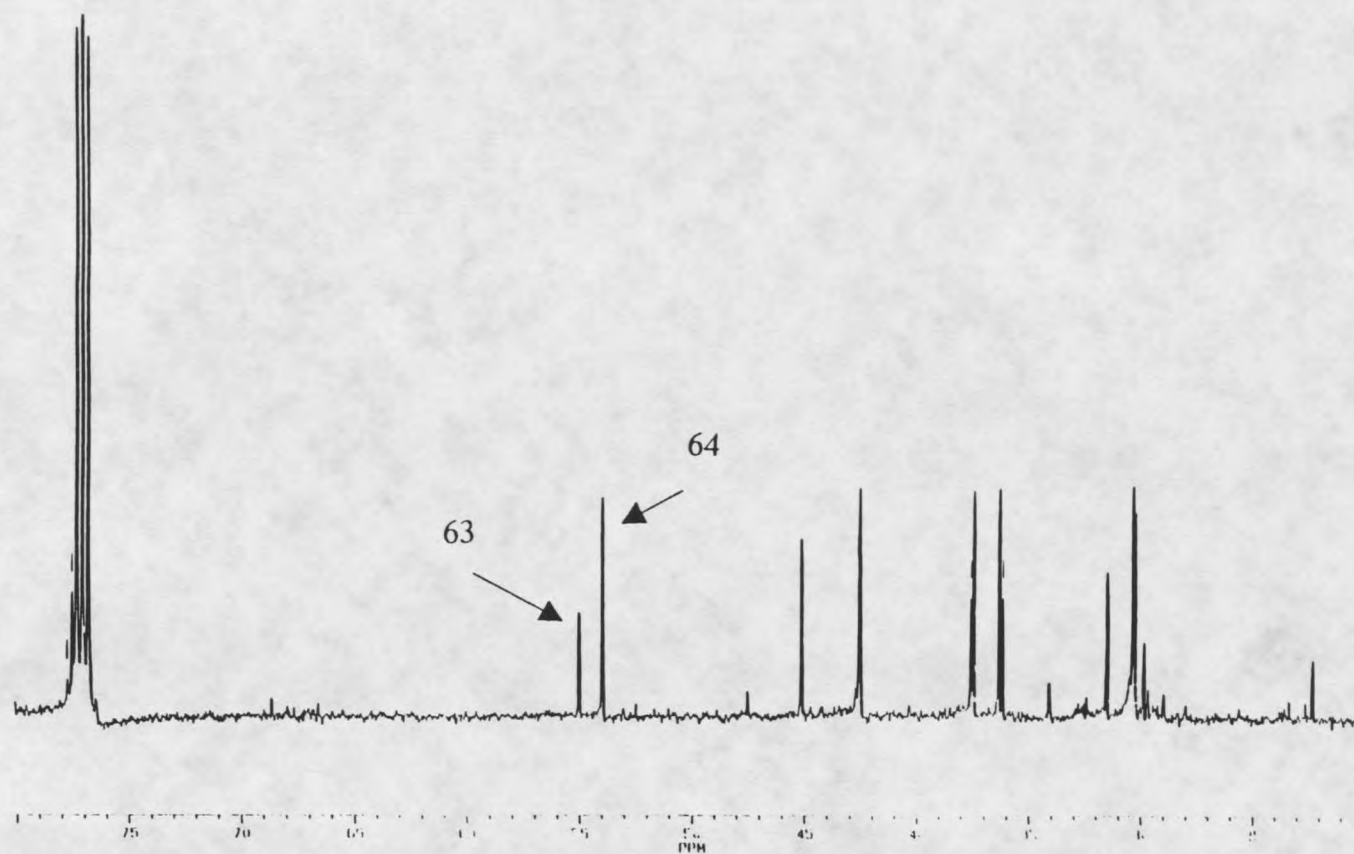


Figure 101. ^{13}C Spectrum of **63** and **64** after 23 Hours at Reflux.

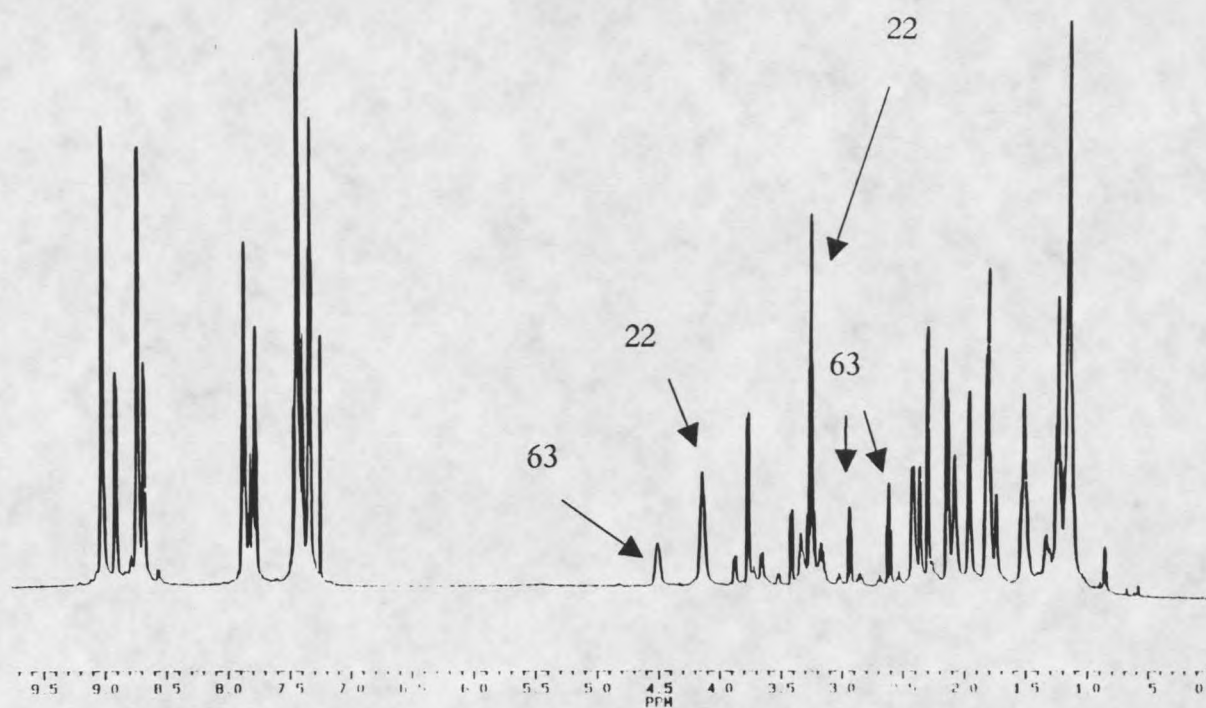


Figure 102. ^1H Spectrum of 22 and 63 after 3 Hours at Reflux.

occurred on the metal. In addition, the integratable ^1H NMR spectrum indicated that the two pyridines were still associated with the complexes. On this basis, **63** and **64** were proposed to have the structures shown in Figure 98. The stereochemistry of the azides is suggested on evidence of the platinum-carbon coupling constants. Observed for both α -carbons of each of the complexes is a symmetrical increase in magnitude of the constants. Placement of the azide in a trans position with respect to a carbon would be expected to greatly affect the chemical shift and coupling constant of the trans-carbon while the effect would be minimized on the cis-carbon. Placement of the azide cis to both carbons would be expected to give the observed NMR data. A determination of which chloride on complex **22** was replaced with azide to give complex **65** was not rigorously determined.

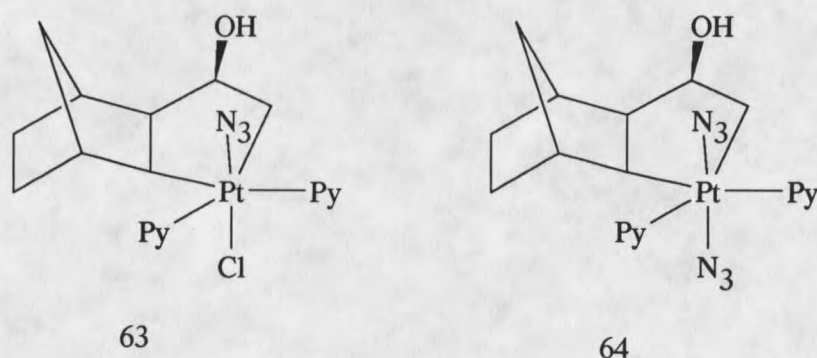


Figure 103. Proposed Structures for Complexes **63** and **64**.

Reaction of Complex **21** with Sodium Azide

It was envisioned that if platinacyclopentanes could undergo azide substitution, platinacyclobutanes should also be studied. Treatment of complex **21**, see page 94, with seven equivalents of sodium azide in methanol was also found to give substituted

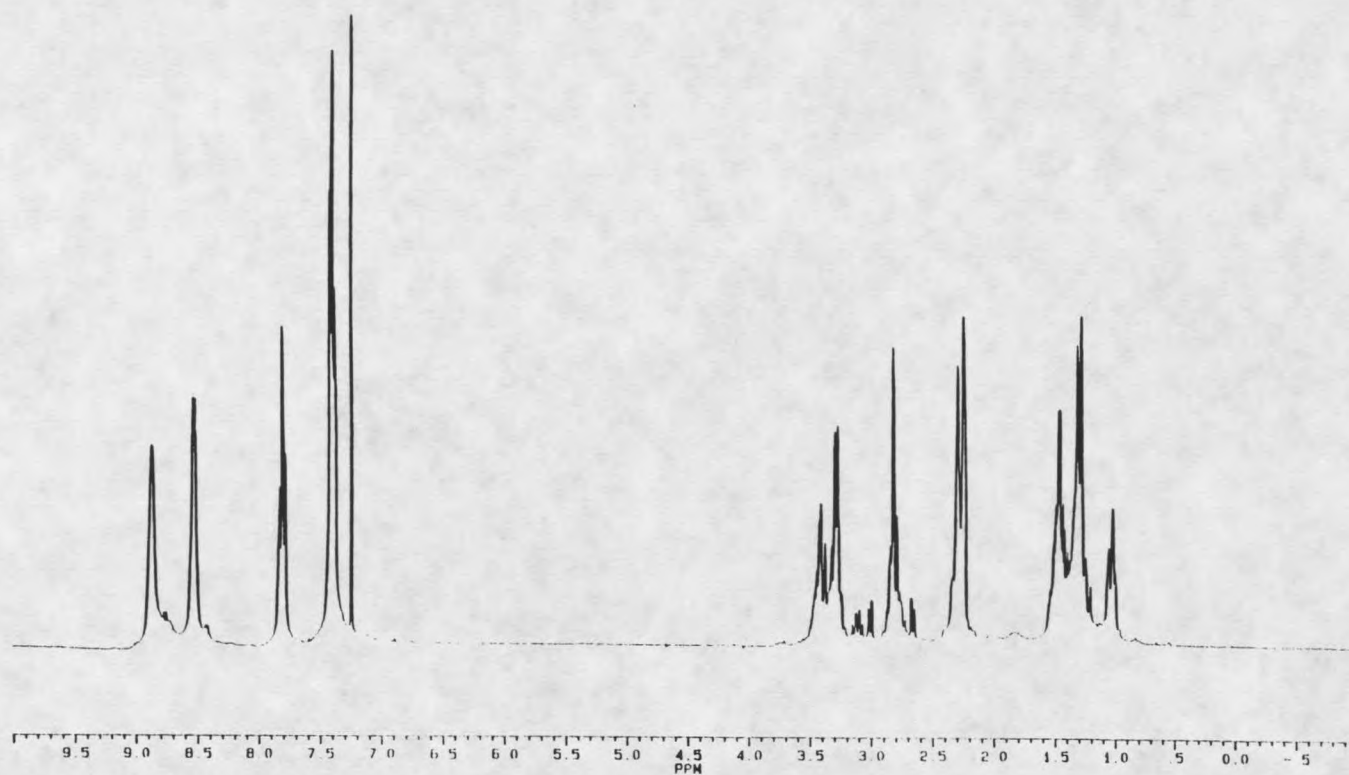


Figure 104. ^1H Spectrum of Complex 65.

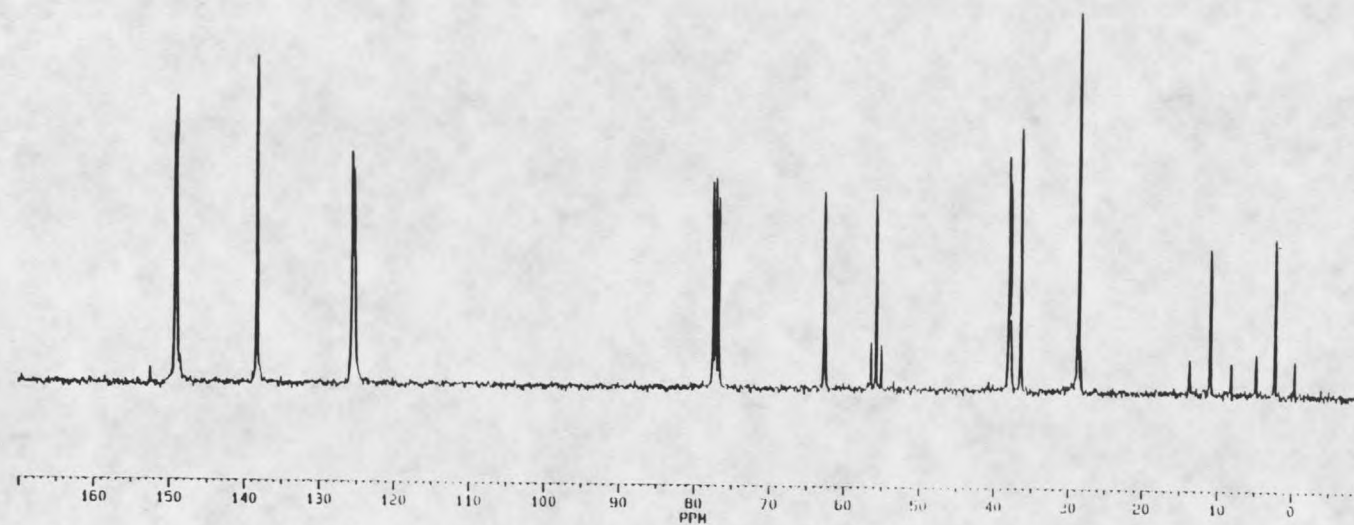


Figure 105. ^{13}C Spectrum of Complex 65.

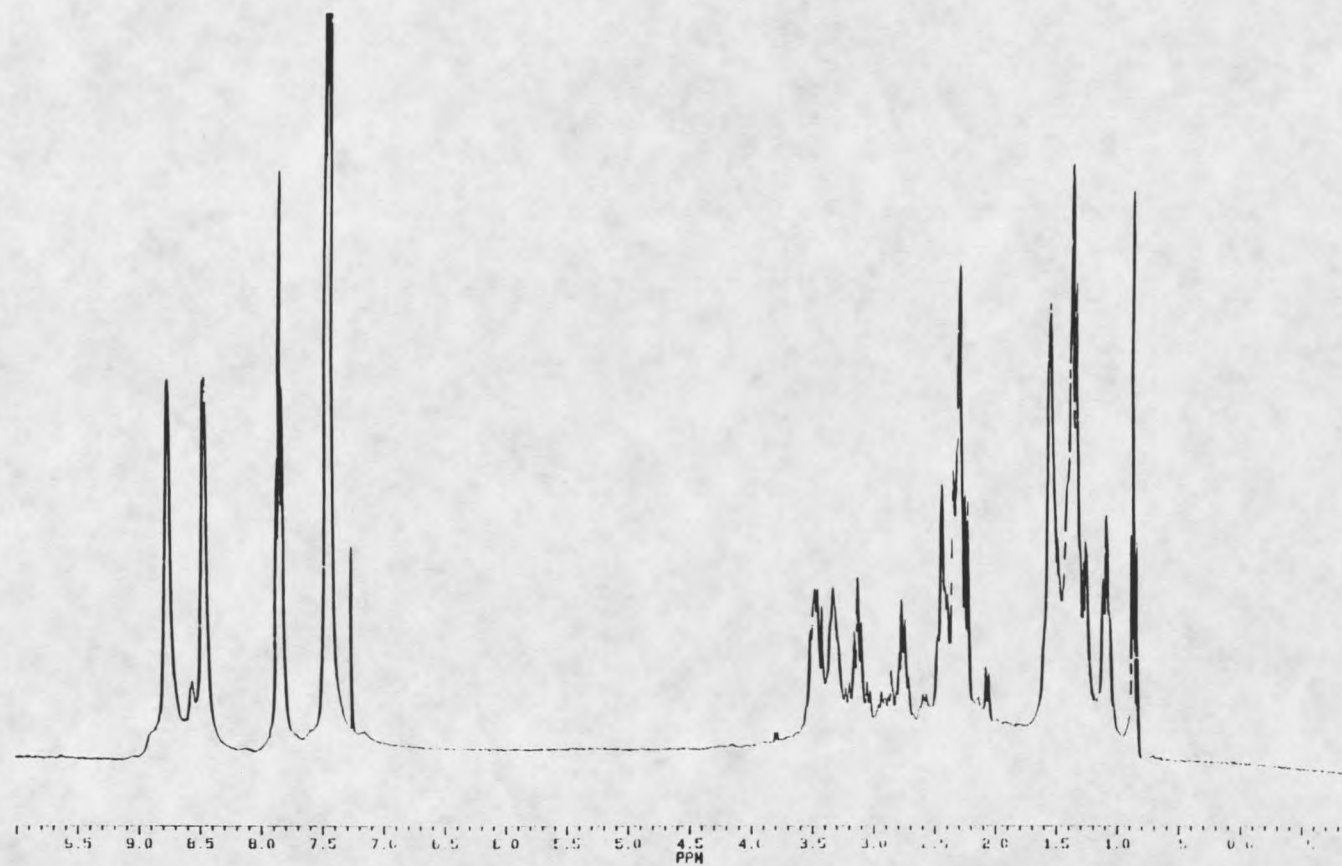


Figure 106. ^1H Spectrum of Complex 65 and 66.

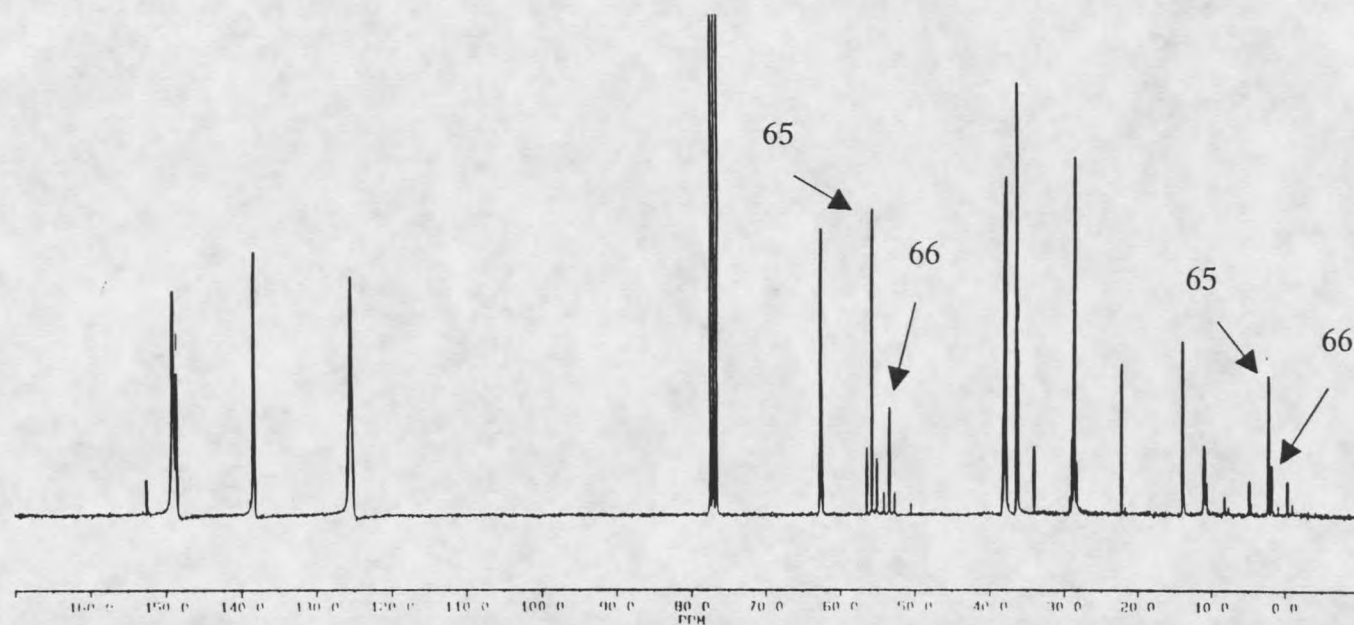


Figure 107. ^{13}C Spectrum of Complexes 65 and 66.

products similar to those observed for the platinacyclopentane complexes. Complex **21** also was more labile to ligand substitution as reflux was not required. Table 11 contains the ^{13}C NMR data for the ring carbons for complex **21** and the two product complexes, **65** and **66**. Again, a slight deviation in the chemical shifts for the ring carbons and an additive increase in the platinum-carbon coupling constants to both α -carbons was observed.

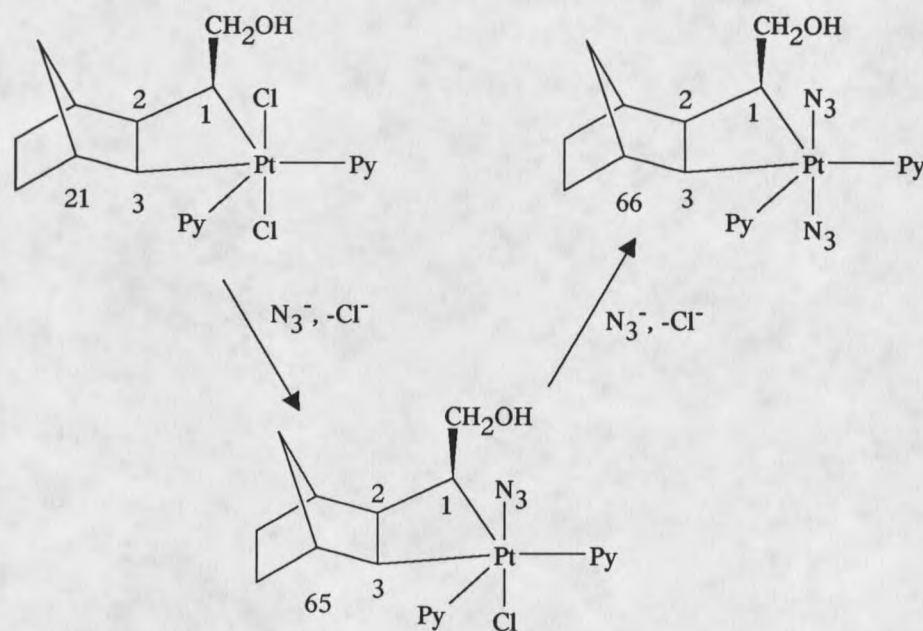


Table 11. ^{13}C NMR Data for the Ring Carbons of Complexes **21**, **65**, **66**.

Carbon #	21 ppm ($J_{\text{Pt-C}}$)	65 ppm ($J_{\text{Pt-C}}$)	66 ppm ($J_{\text{Pt-C}}$)
1	6.36 (370)	2.4 (392)	1.7 (424)
2	56.7 (98)	55.7 (101)	53.3 (109)
3	13.0 (394)	11.0 (421)	10.6 (451)

Structural determination of complexes **65** and **66** was accomplished through several observations. First, treatment of a mixture of **65** and **66** with trimethyl phosphite gave as the sole organic residue the syn cyclopropane in quantitative yield by ^1H NMR. The conclusion to be drawn here is that the reaction with azide ion does not seem to cause any alteration of the substrate. Thus, the modification must have occurred on the metal.

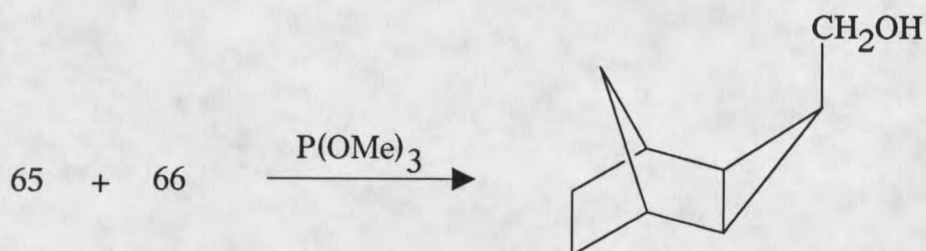


Figure 108. Reaction of Complexes **65** and **66** with Trimethylphosphite.

Second, the integratable ^1H NMR spectrum showed that the complexes contain two equivalents of pyridine and there was no liberated pyridine detected upon workup. This would allow for the drawing of a partial structure shown in Figure 108.

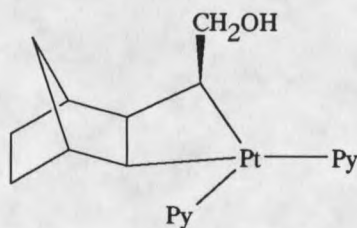


Figure 109. Partial Structure for Complexes **65** and **66**.

The logical course remaining would be to propose substitution of the chlorides on the metal center as shown for structures **65** and **66**. Synthesis of complex **65** was never accomplished without some impurity of either **21** or **66**. A sample of **65** was prepared and was determined to be approximately 96% pure. This sample was submitted for elemental analysis, and although not exact, the data appear to give support for the proposed structure. The data presented in Table 12 is the actual reported

Table 12. Elemental Data for Complex **21**.

	Carbon	Hydrogen	Nitrogen	Chlorine
Found for Complex 65	39.63%	4.33%	11.34%	6.67%
Calculated for Complex 21	40.58%	4.38%	4.98%	12.61%
Calculated for Complex 65	40.11%	4.25%	12.31%	6.23%
Calculated for Complex 66	39.65%	4.20%	19.47%	0%

percentages of elements found and calculated for complexes **21**, **65**, and **66**. Complex **66** is postulated on the fact that the platinum-carbon coupling constants are observed to increase an analogous amount with respect to the first substitution. The stereochemical placement of the ligands is suggested by the ^{13}C NMR data. A symmetrical effect is observed in both α -carbons suggesting coordination above and below the plane defined by the metallacycle. Placement of the anion trans to an α -carbon would be expected to perturb the observed ^{13}C NMR resonance of the trans carbon greatly while effect on the cis-carbon would be minimized. This is not observed. Deviation of the α -carbons is noted to be approximately equal.

The stereochemical dilemma inherent to complex **65** is the determination of which chlorine was substituted. Only one mono-substituted complex is observed. Complex **66** is discounted from being the other isomer due to the observed reaction with respect to time and the additive effect witnessed in the platinum- α -carbon coupling constants. If complex **66** were actually the other mono-substituted isomer, its ^{13}C NMR spectrum would be expected to be similar to that of complex **65**. The chemical shifts of the α -carbons would be shifted slightly however the platinum-carbon coupling constants should not deviate significantly from those observed for complex **65**.

The observation of only one mono-substituted isomer suggests that one chloride is more labile than the other. In a comparison of the two possibilities, the topside chlorine has been noticed to deviate from ideal octahedral geometry by X-ray analysis. The topside chlorine appears to be sterically hindered by the methylene located at the bridge of the norbornyl system. This hinderance causes the chloride to be bent away from the bridge. This deviation from ideal geometry might aid in the labilization of the chloride thus enhancing the likelihood of substitution at this topside site. Experimental evidence from the reaction of **65** with ethyl diazoacetate also corroborates the presented structural suggestion. This experimental evidence will be discussed in greater detail later in this chapter.

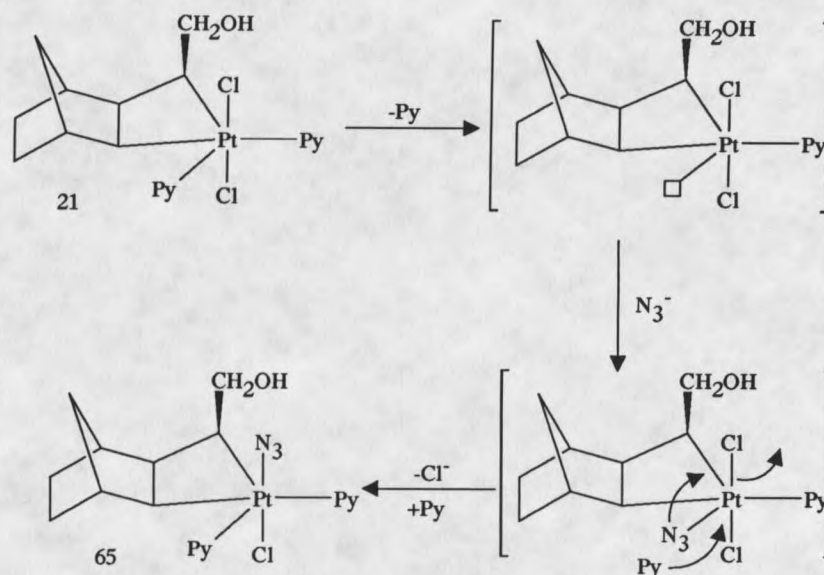


Figure 110. Proposed Mechanism for the Reaction of **21** with Sodium Azide.

The mechanism for this reaction, like most octahedral complexes, would be expected to proceed through a dissociative pathway, meaning that upon loss of a ligand the substitution can occur. Loss of pyridine is the logical first step followed by attack of the azide. At this point, the topside chloride then leaves followed by migration of the azide to the topside position. The dissociated pyridine is then free to reassociate giving complex **65**. Substitution of the bottom side chloride can occur in a similar manner to yield complex **66**.

Reaction of 21 and 22 with Iodide

Halogen nucleophiles represent a possible extension of the hydride attack methodology to give valuable alkyl halides. The reaction of complex 22 with potassium iodide in refluxing methanol was observed to decompose the metallacycle. Analysis of the organic residues proved disappointing as a complex mixture of alkyls and alkyl iodides were formed in the reaction which was not studied further.

However, complex 21 also was found, under similar reaction conditions, to react with potassium iodide, to give one organic product. The metallacycle was witnessed to decompose and give a bright yellow precipitate. Analysis of the organic residue gave one major product. Study by ^1H and ^{13}C NMR showed the nine carbon aldehyde, 67, in 73% yield.

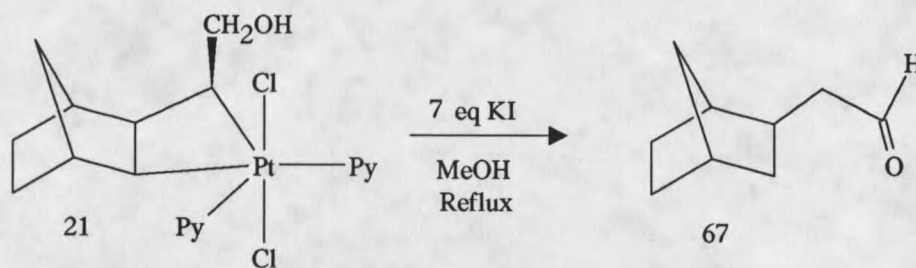


Figure 111. Reaction of Complex 21 with Potassium Iodide

Rationalization of this result is comparatively simple. Upon loss of a pyridine, iodide attacks the coordinatively unsaturated metal center followed by extrusion of a chloride. This is analogous to the azide example shown previously. However, iodide cannot move into the topside position on the metal due to overwhelming steric

hinderance. This allows for an open coordination site at the topside position that can accept a β -hydride from the hydroxymethyl giving a platinum-bound olefin complex. Reductive elimination of the hydride to the α -methine then can occur followed by dissociation of the metal and tautomerism of the vinyl alcohol.

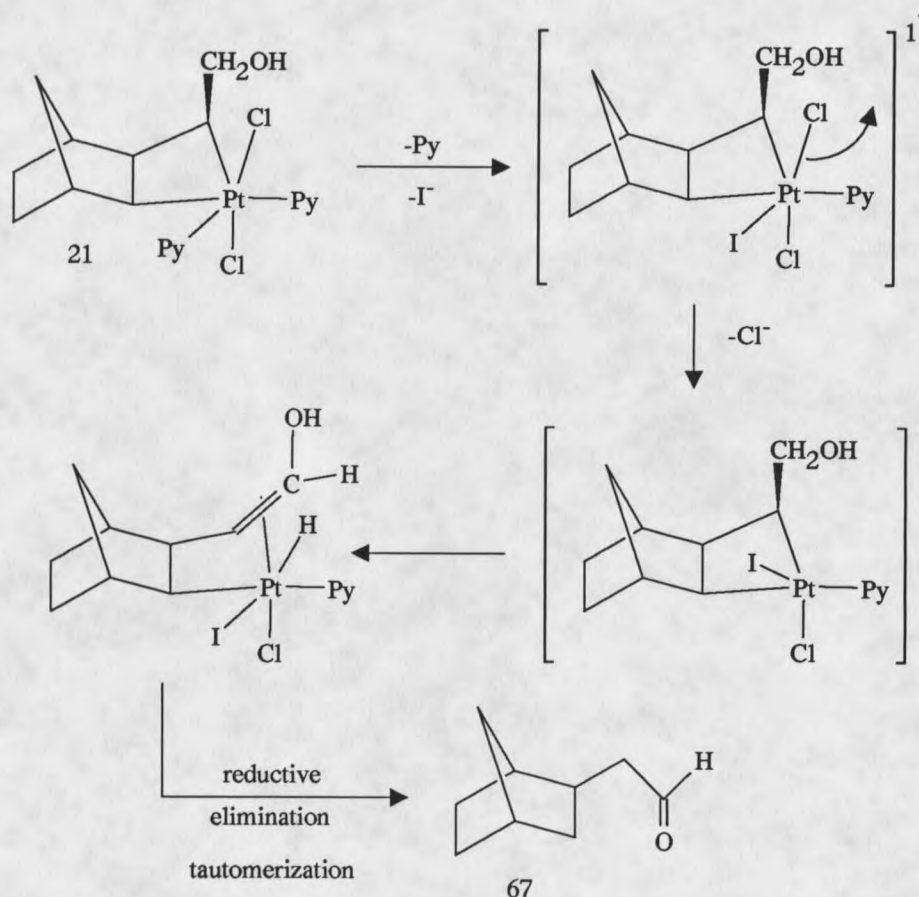


Figure 112. Proposed Mechanism for the Formation of 67.

An investigation of the role of the cation associated with the salt was conducted. If the transformation requires iodide, replacement of the iodide for another anion should

hinder product formation. If the transformation is effected using potassium only, the replacement of the anion should not cause hinderance of the formation of **67**. Reaction of complex **21** with potassium chloride gave no reaction. The conclusion here is that the iodide transformation is achieved without the participation of the cation.

The next logical step was to investigate the possibility of both the anion and the cation operating in concert. Iodide attacks the metal center and the potassium assists in the chloride extrusion from the metal. The loss of chloride in this instance could be envisioned to require the assistance of the cation. The use of lithium iodide in an analogous manner afforded the organic product in similar yield.

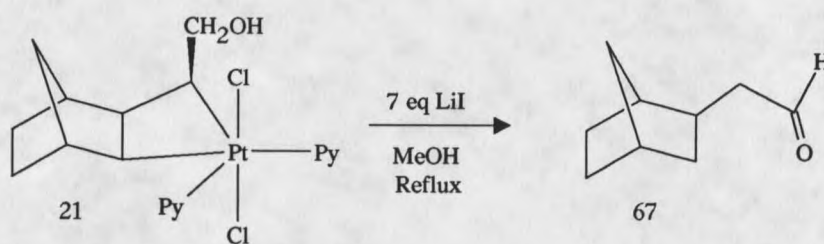


Figure 113. Reaction of Complex **21** with Lithium Iodide.

Sodium iodide, on the otherhand, was observed to promote the ring expansion of complex **21** to give **61**. Formation of complex **61** was not investigated further so no explanation of its formation will be offered.

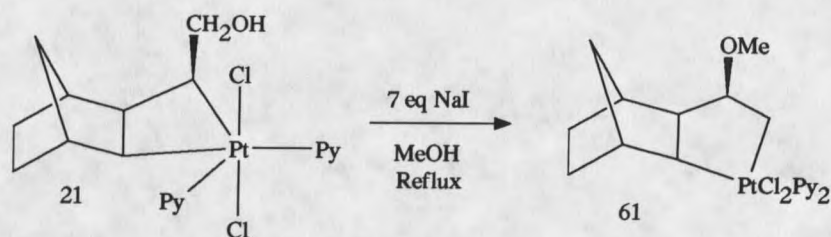


Figure 114. Reaction of Complex 21 with Sodium Iodide.

Reaction of Complex 21 with Thiocyanate

The reaction between complex 21 and potassium thiocyanate was conducted in an analogous manner as the reaction with potassium iodide. Decomposition of the complex did occur, however, the organic residue was determined to be the syn substituted cyclopropane. The conclusion drawn here is that thiocyanate is too strong a nucleophile and it deposits too much electron density onto the metal causing reductive elimination to occur.

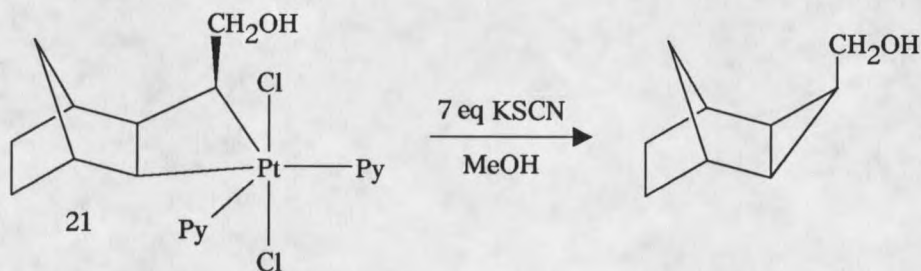


Figure 115. Reaction of Complex 21 with Potassium Thiocyanate.

Reaction of Diazo-derivatives with Platina(IV)cyclobutanes

Previous investigations⁷³ into the reaction of platinacyclobutanes with ethyl diazoacetate indicated the formation of epimeric esters with little stereoselectivity. A more rigorous analysis of the stereochemistry of the olefinic residues was conducted and the data is displayed in Table 13.

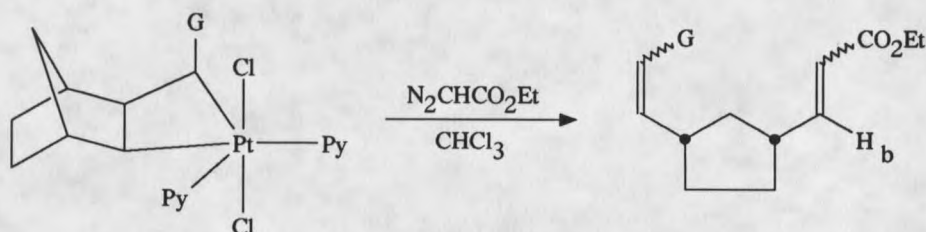


Figure 116. Scheme for the Reaction of Platinacyclobutanes with $\text{N}_2\text{CHCO}_2\text{Et}$.

The observed E/Z ratios of the carboxylates were determined by the use of ^1H NMR spectroscopy. Measurements were acquired by integration of the resonances attributable to proton H_b shown above. The resonance assigned to this proton for the trans-isomer, at 300 MHz, is partially obstructed making accurate integration

Table 13. Stereochemistry of the Carboxylate Residues.

G	E/Z
syn- CH_2OH	0.7
syn- CH_3	1.5
anti- CH_2OH	1.5

problematic. However, use of a 500 MHz instrument provided baseline resolution for both isomers. As a general rule of thumb, the *Z*-isomer is found as a doublet of doublets at 6.08 ppm while the *E*-isomer is also a doublet of doublets but it is observed at 6.88 ppm. Modification of the substituent, G, is seen to only cause deviation of these resonances on the order of 0.1 ppm.

Verification of the assignments was accomplished through the use of 1D homodecoupling and 2D homonuclear (COSY) NMR experiments. The goals were to identify which two protons were coupled to H_b of each isomer and to measure the coupling constant across the olefin.

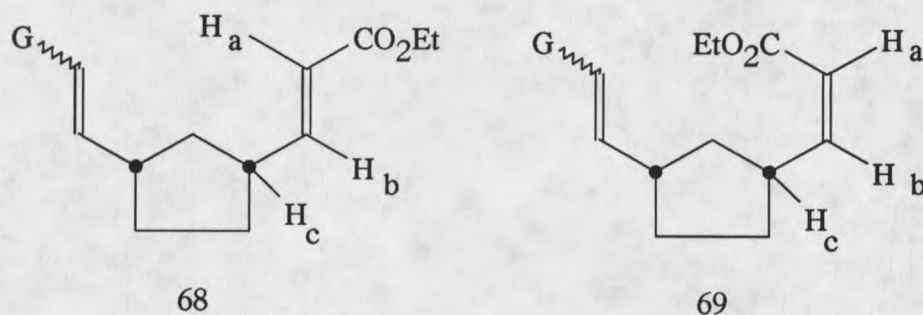


Figure 117. *Cis* and *Trans* Carboxylates.

Observation of these protons and measurement of the couplings between them is an extremely useful tool. Generally, *cis* protons across an olefin are coupled to each other in a magnitude of six to ten hertz. As opposed to this, *trans* disposed olefinic protons are coupled by eleven to sixteen Hertz. This makes this type of stereochemical determination practical by ¹H NMR.

The chemical shift of H_a of **68** is generally located at 5.7 ppm. This resonance appears as a doublet and the coupling constant was approximately 15.5 Hz. This is consistent with trans stereochemistry. Proton-c was shown to be a multiplet at about 2.6 ppm. This is also consistent with the proposed assignment.

A study of the Z-isomer, **69**, revealed, generally, that H_a was also a doublet at 5.6 ppm, however the coupling constant was measured to be 10.5 Hertz. This is also consistent with the proposed cis disubstitution.

Every example, first reported by Neilsen and then reexamined in this thesis, contained substituents on the α -carbon. The platinacyclobutane derived from the simple unsubstituted norbornyl system had not been treated with ethyl diazoacetate in this manner. Reaction of complex **48** with ethyl diazoacetate, shown in Figure 118, did give cis-divinyl cyclopentanes in an isomeric ratio of E/Z = 1.4.

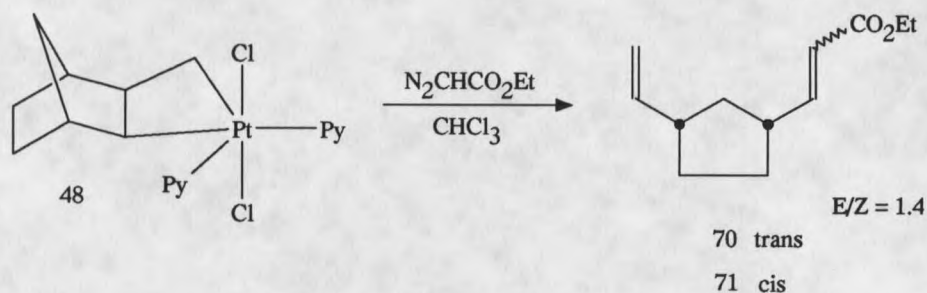
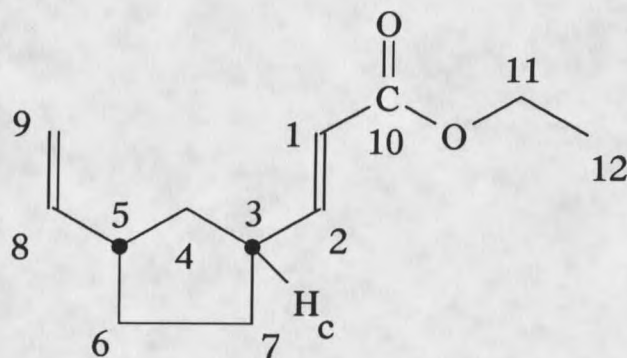


Figure 118. Reaction of Complex **48** with Ethyl Diazoacetate.

This is a significant result because it provides a basis for thought about the reaction of the substituted platinacycles. Tables 14 and 15 are summaries of the NMR spectral data for the compounds **70** and **71**.

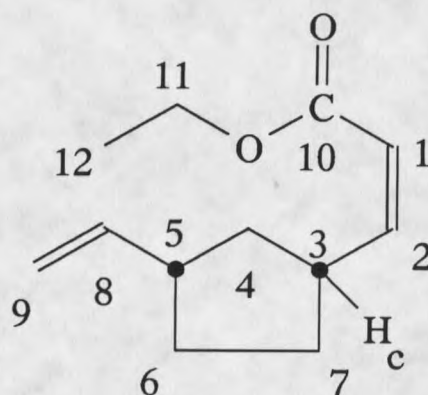


70

Table 14. NMR Data for Compound 70.

Carbon	^{13}C NMR ppm	^1H NMR ppm
1	119.5	5.77 dd, 1H
2	152.9	6.87 dd, 1H
3	44.2	2.65 m, 1H
4	39.5	*
5	42.6	2.56 m, 1H
6	44.2	*
7	31.6	*
8	142.5	5.69 m, 1H
9	112.9	4.86 d, 1H 4.90 d, 1H
10	166.9	-
11	60.1	4.17 q
12	14.0	1.30 t

* Overlapping multiplet between 1.1 and 2.0 ppm.



71

Table 15. NMR Data for Compound 71.

Carbon	^{13}C NMR ppm	^1H NMR ppm
1	118.2	5.63 dd, 1H
2	154.7	6.04 dd, 1H
3	44.4	3.66 m, 1H
4	40.6	*
5	38.9	2.56 m, 1H
6	31.8	*
7	32.1	*
8	142.7	5.69 m, 1H
9	112.7	4.86 d, 1H 4.90 d, 1H
10	166.5	-
11	59.8	4.17 q
12	14.0	1.30 t

* overlapping multiplets between 1.1 and 2.0 ppm.

Table 16 contains a summary of the isomeric ratios to this point. Interpretation of this data give one major conclusion. Use of complex **21** in this process appears to give a significant deviation when compared to the other data. Since the deviation is not mirrored in the case with syn methyl substitution, it may be concluded that the source of this deviation is not steric in nature.

Table 16. Stereochemistry of the Carboxylate Residues.

G	E/Z
syn-CH ₂ OH (21)	0.7
syn-CH ₃	1.5
anti-CH ₂ OH	1.5
H (48)	1.4

To learn more about the mechanistic process involved with this transformation, four avenues of study were adopted.

- 1) Establish the nature of the unique interaction of the diazo acetic ester and complex **21**.
- 2) Modify the substrate so that stereospecific products may be obtained.
- 3) Open the scope of the reaction to other diazo reagents.
- 4) Explore ligand dependence on the stereochemical outcome.

As noted in the introduction of this thesis, an open coordination site on the platinum appears to be a prerequisite for product formation. This means that it is reasonable to assume that the diazo reagent coordinates to the metal. Four logical intermediates can be drawn.

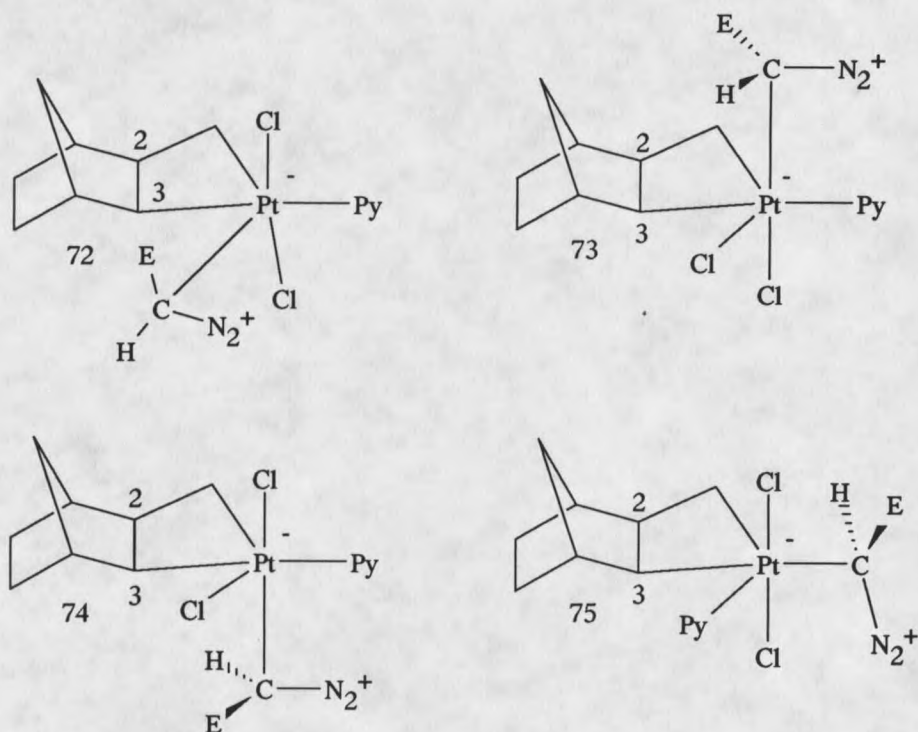


Figure 119. Four Possible Coordination Geometries for the Diazo-Reagent.

The deviation induced by a syn-CH₂OH would suggest that intermediate **73** is reasonable. This conformation allows for a maximum amount of interaction between the diazo reagent and the syn α -substituent. To obtain product, the diazo-carbon must be in the vicinity, cis disposed, to carbon-3 to allow the joining of these two. This would seem to disallow intermediate **75**. Intermediate **74** also is not considered

reasonable because of the steric interaction between the diazo-reagent and the endo protons on carbons 2 and 3. In addition to this, intermediate **74** places the syn α -substituent and the diazo-reagent too far from each other to have any interaction. Intermediate **72** also would not allow for the observed interaction.

A hydrogen-bonding interaction between the syn-CH₂OH of complex **21** and the ester carbonyl of the diazo-reagent seems reasonable. The observed effect of this interaction is that more cis-disubstituted olefins are formed. A hydrogen-bonding eight membered chelate ring is shown below. It is not implied that the chelate ring is maintained rigorously, but that the hydrogen-bonding interaction aids in the delivery of the diazo-reagent to the metal. Further reaction of this intermediate, gives a platinacyclopentane that only can give cis olefinic residues.

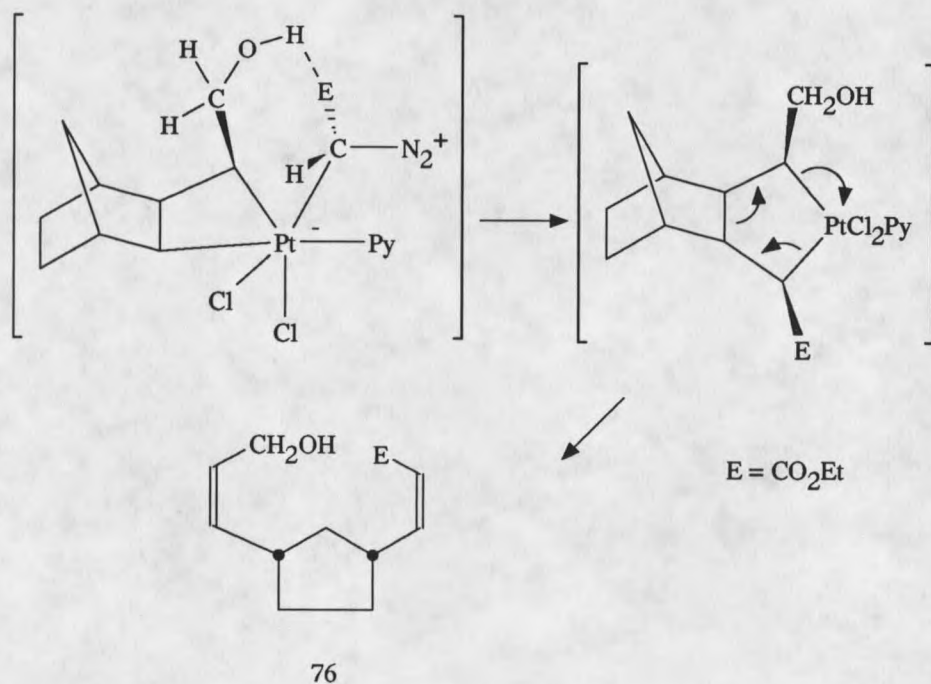


Figure 120. Proposed Formation of Compound **76**.

To study this postulate, the syn-methyl ether analog of complex **21** was prepared. Methodology utilized here was methylation of the syn and anti hydroxymethyl cyclopropanes using sodium hydride and methyl iodide under standard conditions.

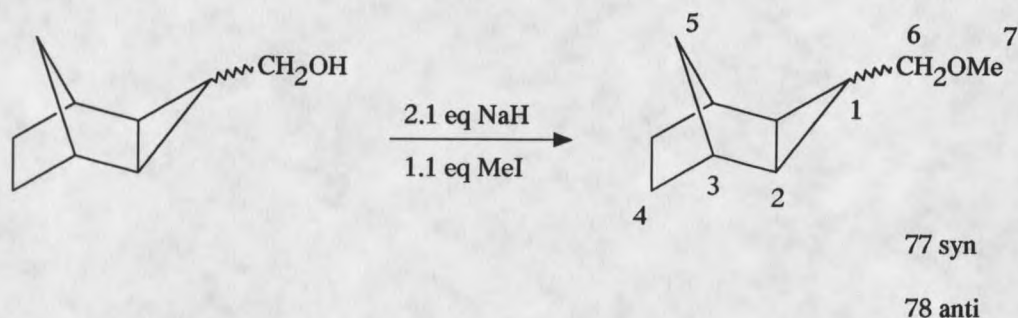


Table 17. ^{13}C NMR Data for Compounds **77** and **78**.

Carbon	77 (syn) ppm	78 (anti) ppm
1	16.6	13.6
2	21.4	20.9
3	30.6	28.5
4	29.9	29.5
5	36.0	35.7
6	70.7	75.7
7	58.1	58.3

The mixture of **77** and **78** was stirred at room temperature in diethyl ether with an amount of Zeise's dimer equal to the amount of syn-ether. Within a couple of minutes a yellow precipitate was observed and the orange color of Zeise's dimer was gone. The resulting complex was then triturated with pentane and dried under dry nitrogen. Exposure of the residue to two equivalents of pyridine in chloroform afforded

stereospecifically complex **79** in 80% yield. Complex **79** was studied by ^{13}C NMR spectroscopy and the data is summarized in Table 18.

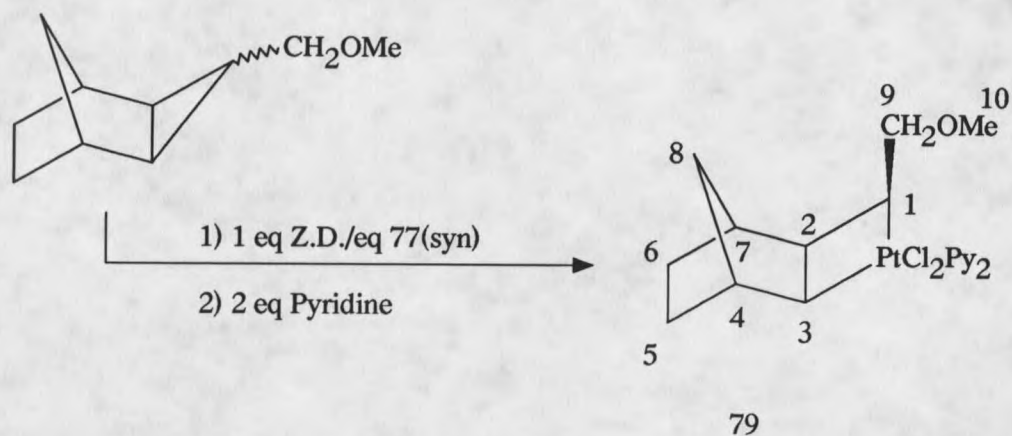


Table 18. ^{13}C NMR Data for Complex **79**.

Carbon	79 ppm ($J_{\text{Pt-C}}$)
1	0.5 (373)
2	57.5 (97)
3	13.7 (394)
4	38.3
5	29.1
6	28.8
7	37.6
8	40.5
9	73.5 (15)
10	58.0

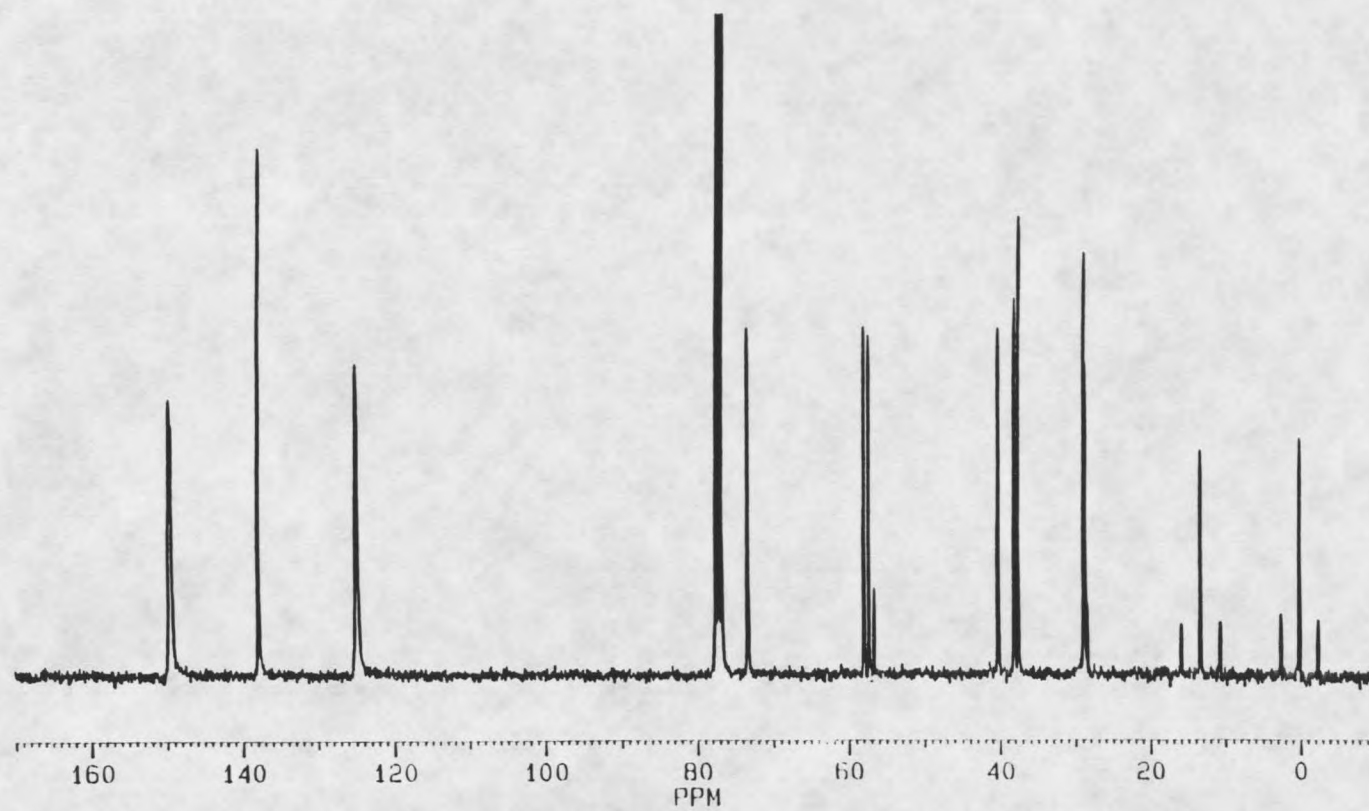


Figure 121. ^{13}C NMR Spectrum of Complex 79.

The reaction of complex **79** with ethyl diazoacetate was performed in an analogous manner to the other platinacyclobutanes. An isomeric ratio of $E/Z = 1.7$ was observed. It is noted here that the deviation to $E/Z = 0.7$ has been negated by

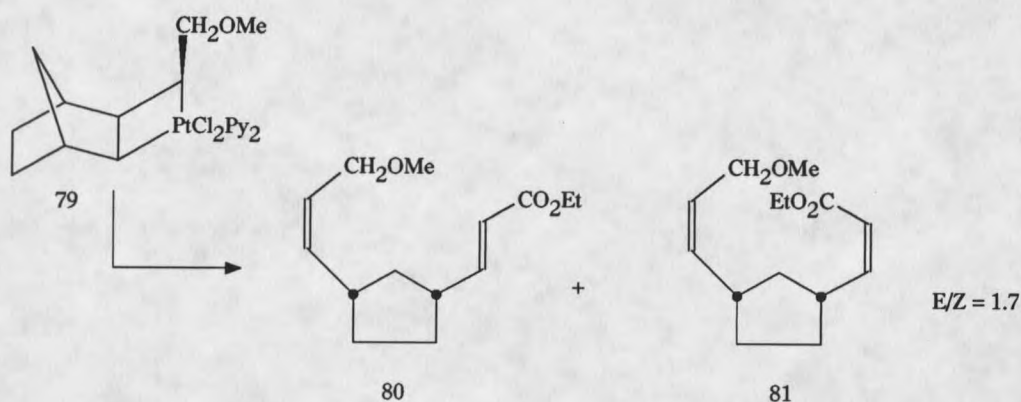
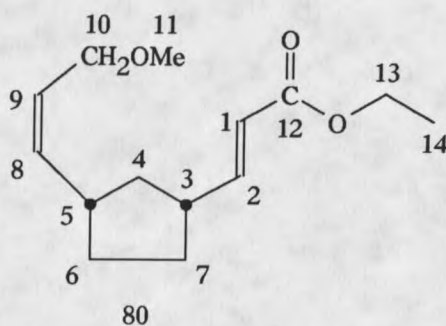


Figure 122. Reaction of **79** with Ethyl Diazoacetate.

methylation of the alcoholic substituent. This lends support to the proposed hydrogen-bonded chelate mechanism. However, the actual magnitudes of these differences are relatively small. What this suggests is that intermediate **73**, page 108, is a minor contributor to the overall outcome.

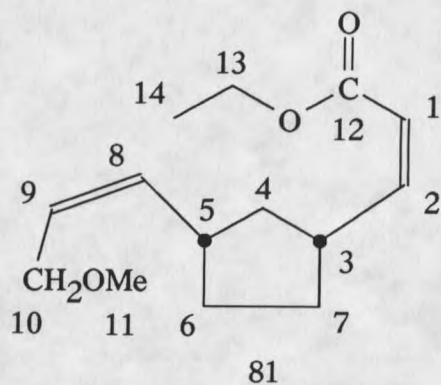
It is assumed that the diazo-reagent must be in a cis-arrangement with respect to carbon-3. If intermediate **72** is a reasonable proposition, substitution at the bridgehead position should affect the stereochemical outcome of the process.

Table 19. ^{13}C and ^1H NMR Data for Compound 80.

Carbon	^{13}C NMR ppm	^1H NMR ppm
1	118.4	5.73 d, 1H
2	154.3	6.87 dd, 1H
3	42.7	2.64 m, 1H
4	41.4	*
5	38.4	2.83 m, 1H
6	31.3	*
7	32.7	*
8	125.0	**
9	137.8	**
10	68.1	4.00 d, 1H
11	57.7	3.26 s, 3H
12	166.7	-
13	60.5	4.15 q
14	14.1	1.25 t

* overlapping multiplet between 1.1 and 2.1 ppm.

** overlapping multiplet between 5.35 and 5.5 ppm.

Table 20. ^{13}C and ^1H NMR Data for Compound 81.

Carbon	^{13}C NMR ppm	^1H NMR ppm
1	119.6	5.63 d, 1H
2	152.5	6.05 dd, 1H
3	39.1	3.79 m, 1H
4	40.4	*
5	38.5	2.83 m, 1H
6	32.2	*
7	32.5	*
8	125.1	**
9	138.0	**
10	68.2	3.92 d, 2H
11	57.7	3.26 s, 3H
12	166.4	-
13	60.5	4.15 q
14	14.1	1.25 t

* overlapping multiplet between 1.1 and 2.1 ppm.

** overlapping multiplet between 5.35 and 5.5 ppm.

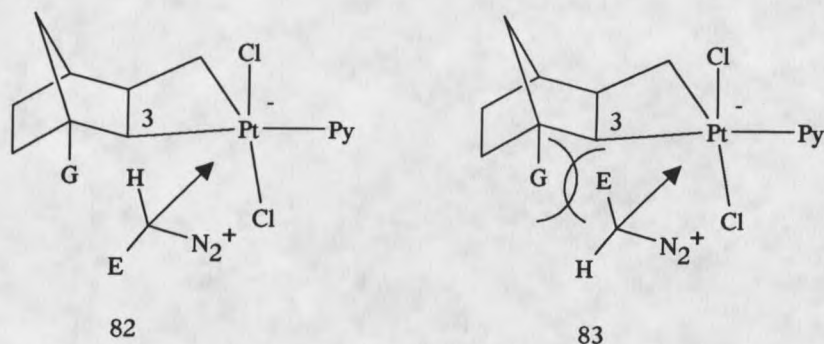


Figure 123. Bridgehead Substitution Models.

The models in Figure 123 represent the possible orientations of the diazo-reagent on the metal. The orientation as shown in complex 83 indicate severe steric hinderance between the bridgehead substituent and the carboethoxy moiety. On the otherhand, complex 82 would seem to be favored sterically.

The two orientations shown here operate on the assumption that the nitrogen acts as a leaving group and thus must be trans peri-planar to the attacking carbon, carbon-3. This assumption will be maintained.

Synthesis of Metallacycles from 2,5-Dimethylfuran

Substitution of the bridgehead position of the norbornyl system is problematic, sigmatropic shifts often ensue. Moats⁶² showed that norbornyl analogs form platinacyclobutanes of comparable stability. Reaction of ethyl diazoacetate with complex 84 was found⁷⁷ to give the analogous olefinic products in a epimeric racemic mixture.

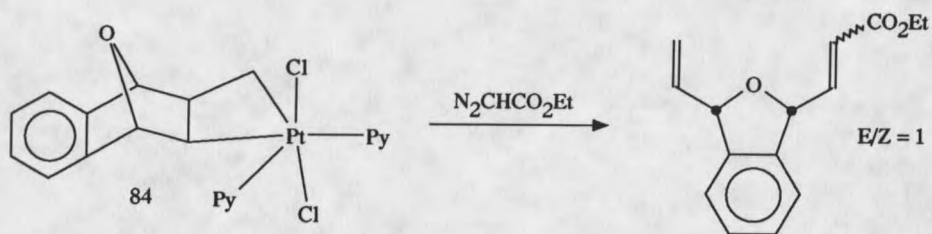


Figure 124. Reaction of Complex 84 with Ethyl Diazoacetate.

The olefinic precursor for complex 84, although commercially available, can be synthesized by the method of Wittig⁷⁸. Substitution of the furan in this instance for a furan with substituents at the two and five positions do yield suitable substrates.

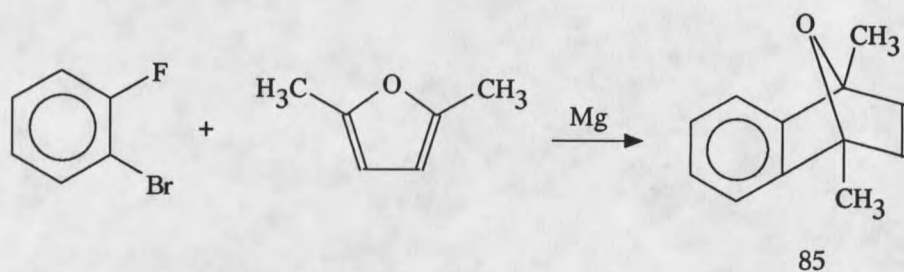
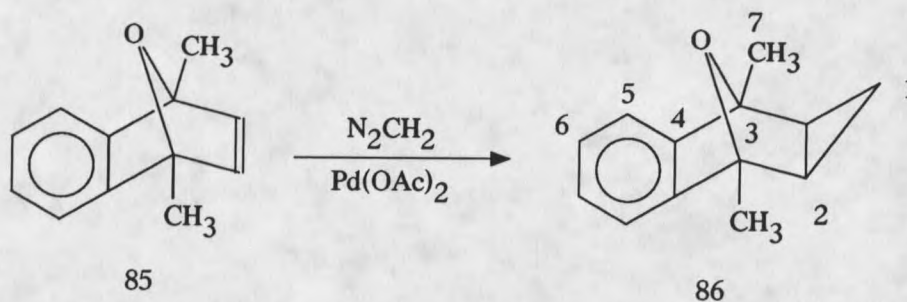


Figure 125. Synthesis of Compound 85.

Cyclopropanation of compound 85 was accomplished by using the method of Kottwitz⁷⁹. Compound 85 was treated with diazomethane using palladium(II) acetate as a catalyst giving compound 86 in 88% yield. The remainder was found to be olefinic by-products that were removed by column chromatography.

Table 21. ^{13}C and ^1H NMR Data for Compound 86.

Carbon	^{13}C NMR ppm	^1H NMR ppm
1	13.8	0.84 dd, 1H 1.59 dd, 1H
2	26.6	1.24 dd, 2H
3	83.6	-
4	151.0	-
5	125.7	*
6	117.7	*
7	15.4	1.74 s, 6H

* overlapping multiplet between 7.0 and 7.2 ppm, 4H.

Insertion of platinum into compound **86** was found to occur in refluxing diethyl ether. Treatment in the normal manner, trituration three times with pentane followed by exposure to two equivalents of pyridine, afforded the expected platinumacyclobutane, **87**, in 78% yield.

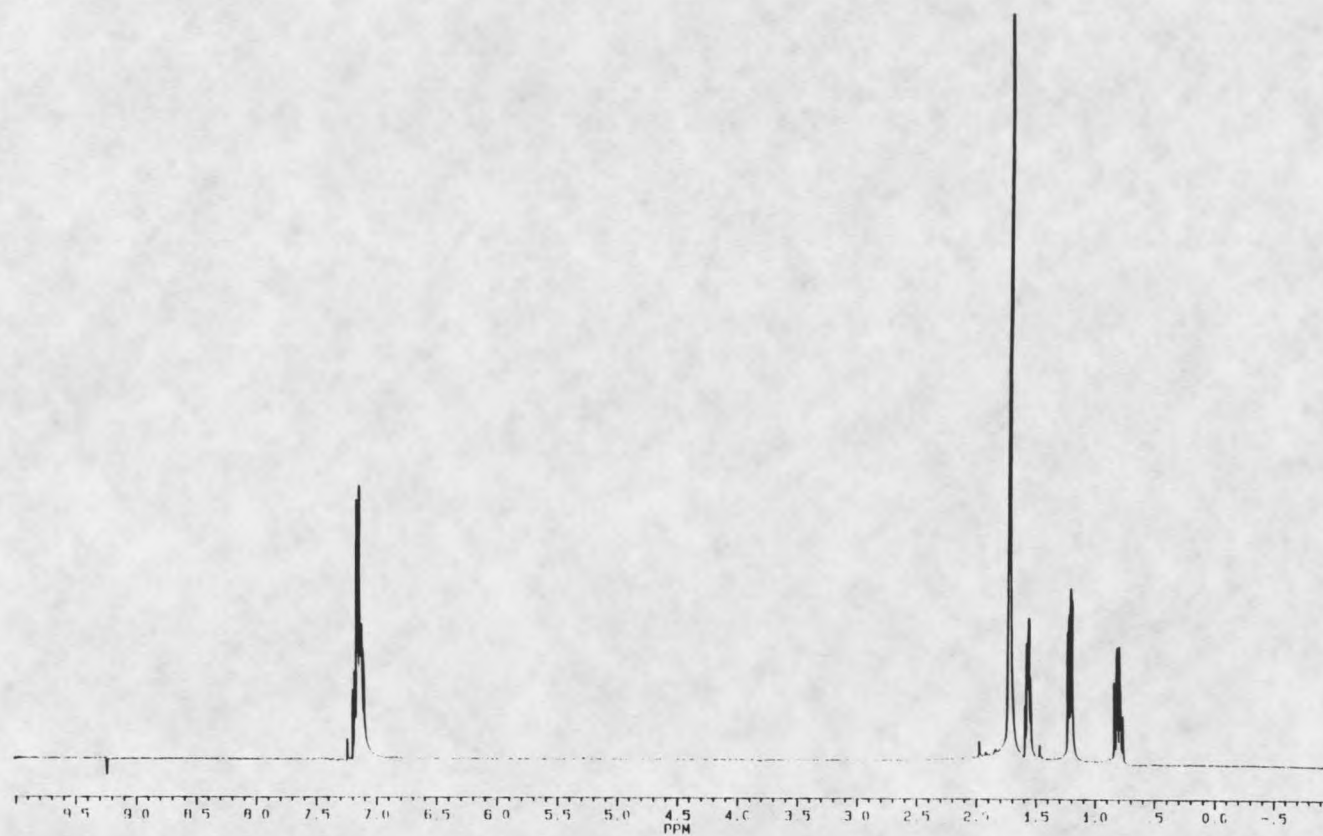
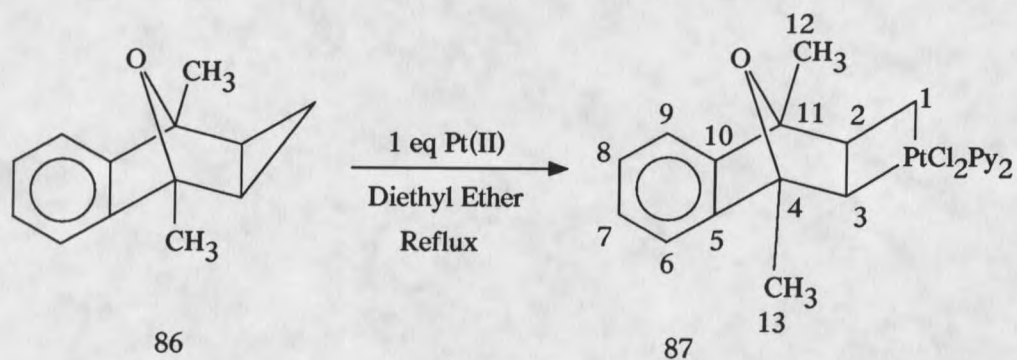


Figure 126. ^1H NMR Spectrum of Compound 86.

Table 22. ^{13}C and ^1H NMR Data for Complex 87.

Carbon	^{13}C NMR ppm ($J_{\text{Pt-C}}$)	^1H NMR ppm ($J_{\text{Pt-H}}$)
1	-8.63 (361)	2.51 (85.10) dd, 1H 3.47 (83.26) dd, 1H
2	58.02 (94)	2.66 dd, 1H
3	13.7 (444)	2.81 (96.48) d, 1H
4	86.2 (17)	-
5	147.7	-
6	117.7	*
7	126.2	*
8	126.1	*
9	117.2	*
10	148.4	-
11	86.8	-
12	13.0	1.66 s, 1H
13	15.6	1.75 s, 1H

* overlapping multiplet between 7.05 and 7.2 ppm, 4H.

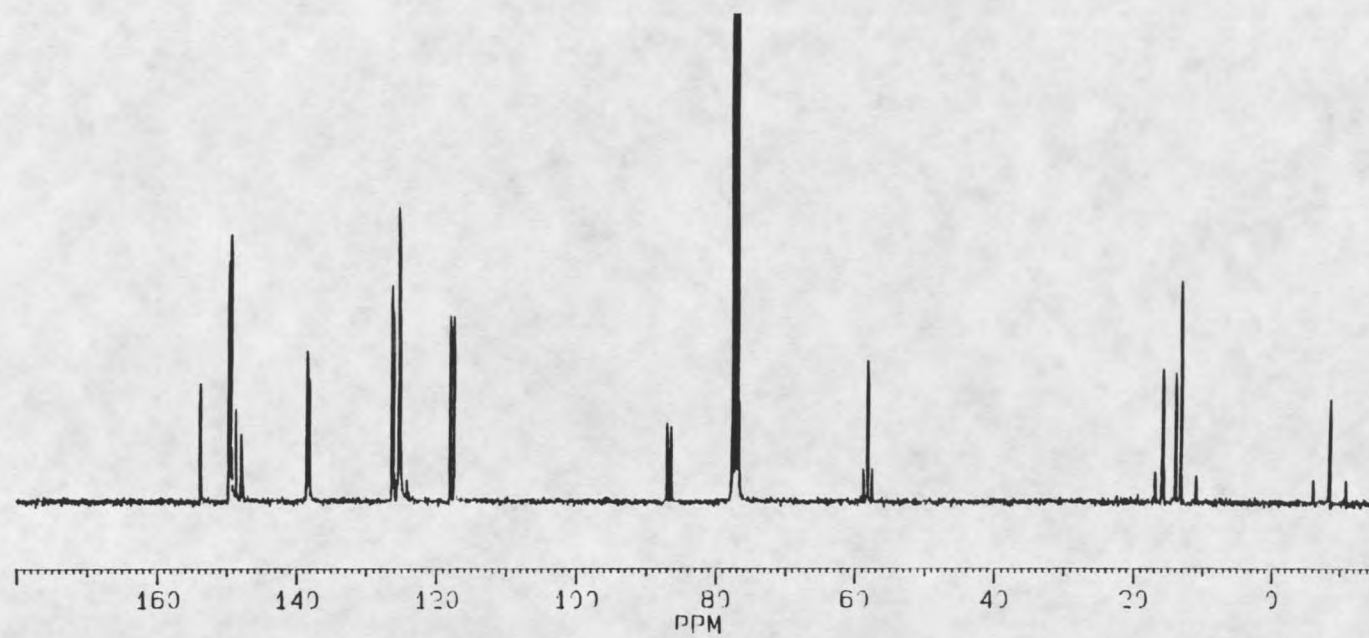


Figure 127. ^{13}C NMR Spectrum of Complex 87.

Complex **87** was reacted with diazomethane and was shown to give two organic products, the expected olefinic compound and the cyclopropane. In fact, the cyclopropane amounted to 55% of the reaction mixture. The formation of compound **88** was produced in only 15% yield.

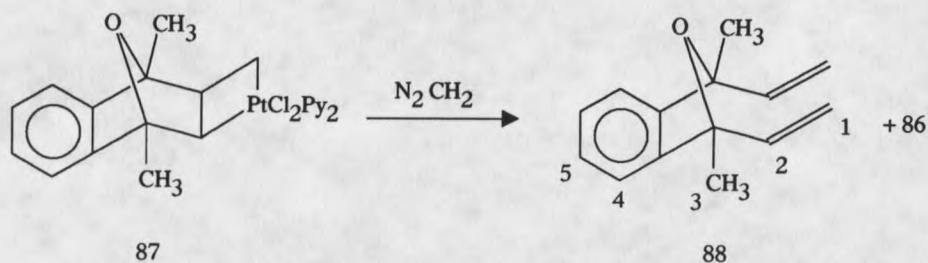


Table 23. ^1H NMR Data for Compound **88**.

Carbon	^1H NMR ppm ($J_{\text{H-H}}$)
1	5.19 d, 2H (17.1 Hz.) 5.01 d, 1H (10.3 Hz.)
2	6.08 dd, 1H (17.1 and 10.3 Hz.)
3	1.71 s, 6H
4/5	*

* overlapping multiplet between 7.0 and 7.2 ppm, 4H.

Upon further analysis of the reaction mixture, a new complex was evident. This complex was isolated through column chromatography, representing the remainder of the mixture. The ^{13}C NMR spectrum differed radically from what would be expected for a platinumacyclobutane. In fact the resonances were consistent with a platinumacyclopentane. A DEPT 135 ^{13}C NMR experiment established the presence of a methine at 45.5 ppm with 639 Hertz of coupling to ^{195}Pt and a methylene at 21.7 ppm

with 494 Hertz of coupling. The complete ^{13}C NMR data is shown in Table 24. This new complex was indeed determined to be a platinacyclopentane, complex 89.

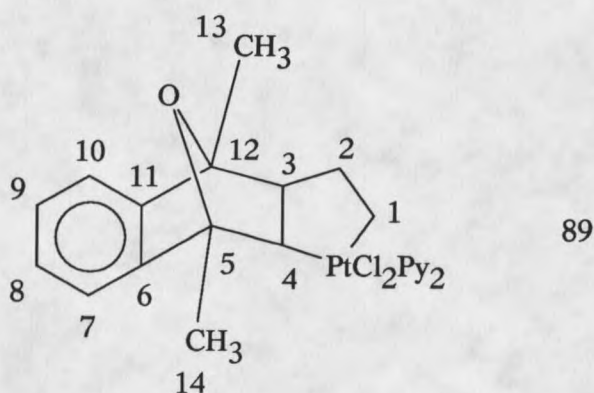


Table 24. ^{13}C NMR Data for Complex 89.

Carbon	^{13}C NMR ppm ($J_{\text{Pt-C}}$ Hz.)	Multiplicity (DEPT)
1	21.7 (494)	CH_2
2	36.1 (14)	CH_2
3	51.5 (23)	CH
4	45.5 (639)	CH
5	88.4 (11)	quaternary
6	152.9	quaternary
7	118.2	CH
8	126.0	CH
9	126.3	CH
10	118.2	CH
11	153.8	quaternary
12	84.9	quaternary
13	14.9	CH_3
14	16.3 (11)	CH_3

Suitable crystals for X-ray crystallographic analysis were grown by recrystallization from chloroform and heptane. The proposed structure for complex **89** was confirmed by X-ray analysis. An ORTEP plot is shown in Figure 129.

It is reasonable to propose the source of carbon-1 as the diazo-carbene. This was checked by the use of ^{13}C enriched diazomethane. As expected, the enrichment was observed at 21.7 ppm, the resonance assigned to carbon-1.

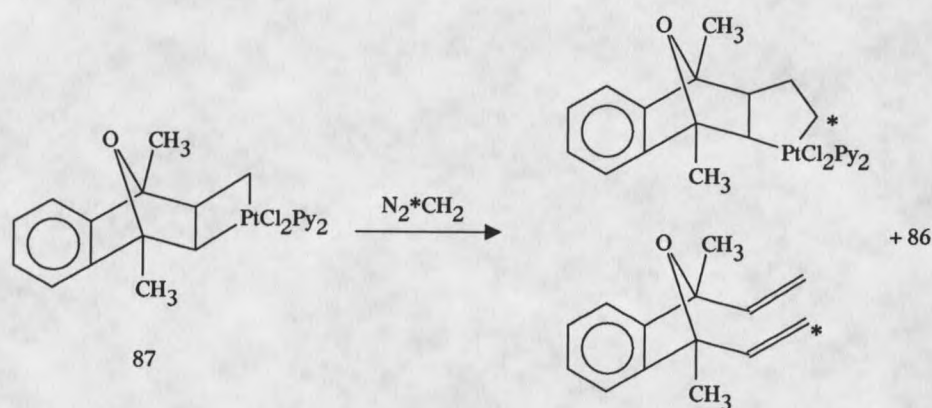


Figure 128. Reaction of Complex **87** with $\text{N}_2^{13}\text{CH}_2$.

Synthesis of a platinacyclopentane in a manner such as this is novel, it is the first ring expansion accomplished by insertion of a methylene into a metal-carbon bond. Intermediates **72** and **73**, page 108, seem insufficient in explaining the formation of this product. Intermediate **72** is unreasonable because of regiochemistry, the carbons joined in the process are trans to each other across the metal, ring expansion from this orientation is unlikely. Intermediate **73**, although ring expansion would be possible, is discounted because of steric interactions with the bridge, there is no possibility for the

pre-chelation pathway as proposed earlier for the reaction of ethyl diazoacetate with complex 21. In addition, logic would dictate that if this mechanism is utilized in the norbornyl systems, one would expect ring expansion with the norbornyl substrates as well as with the benzofuran derived substrate in question. This postulate was tested with an eye towards the formation of a platinacyclopentane, and none was observed, suggesting a new pathway utilized only in the benzofuran-derived substrates.

Intermediate 74 is still discounted on the basis of steric hinderance, interaction of the diazo-reagent with the endo protons on carbons three and four. Intermediate 75, however, is reasonable. A two part driving force can be envisioned. First, the pyridine trans to carbon-3 appears to be more labile in a substitution process when compared to the norbornyl substrates. The platinum-carbon coupling constants are elevated to carbon-3 with respect to the norbornyl substrates. This suggests a shorter and stronger bond and the net effect would be labilization of the site trans to it, occupied by a pyridine. The second factor is that the bridgehead methyl group exerts a significant steric hinderance over the site trans to carbon-1, enough to severely limit access to the metal. The net effect here would be to promote reaction at the site trans to carbon-3 and inhibit chemistry at the site trans to carbon-1. A proposed mechanism for the formation of complex 89 is shown in Figure 130.

Reaction of Complex 87 with Ethyl Diazoacetate

If intermediate 72 is in operation for the synthesis of the divinyl product, 88, it would be expected that the reaction of complex 87 with ethyl diazoacetate would yield

only a trans-disubstituted olefinic residue. The reaction was performed and analysis of the evolved organics showed a similar distribution of divinyl product and cyclopropane.

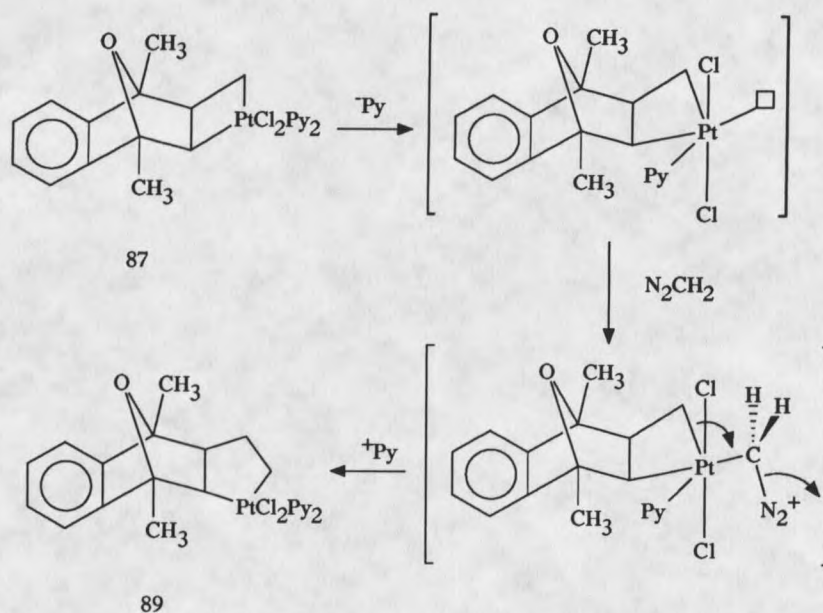


Figure 130. Proposed Mechanism for the Formation of Complex 89.

Further analysis of the divinyl product was performed. Selected ¹H homodecoupling experiments were performed and the coupling constant across the olefin was measured at 15.5 Hertz. This indicates trans stereochemistry of the divinyl product.

Integration of the olefinic resonances in the ¹H NMR spectrum was another method to assess the stereochemical result of this reaction. Using the vinyl group as an integration standard, the carboxylate olefins were shown to give good values suggesting only one olefinic compound. If the cis-isomer had been formed, the resonances for it would be expected, by analogy, to differ from those for the trans-isomer. This deviation

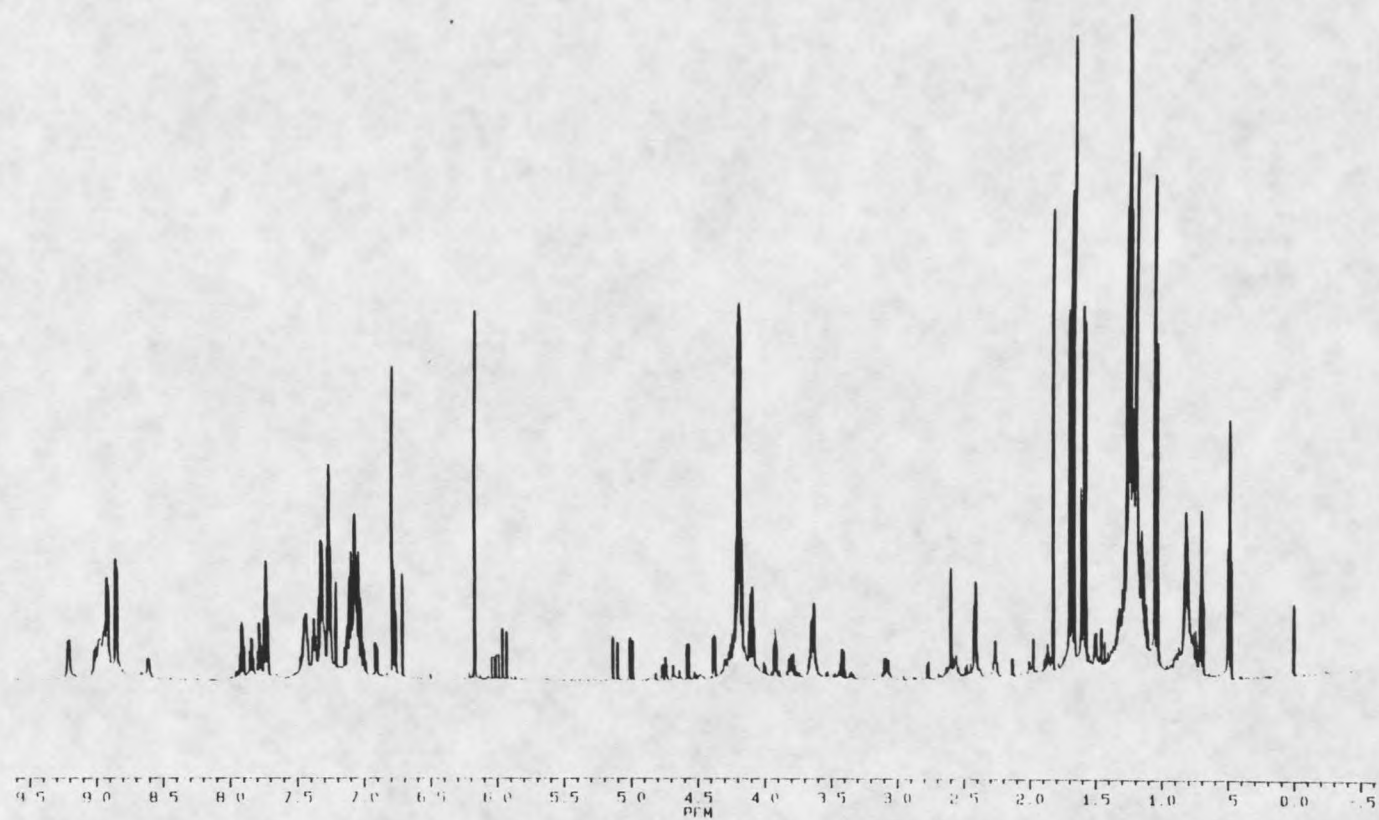
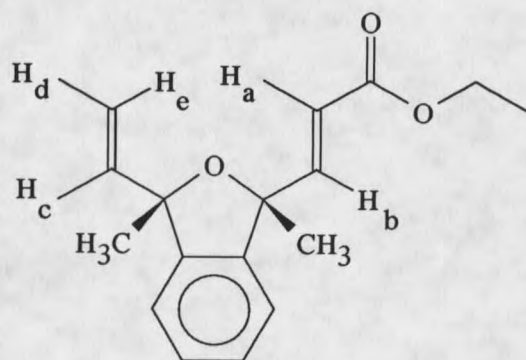


Figure 131. ^1H Spectrum of Crude Reaction Mixture of 87 with $\text{N}_2\text{CHCO}_2\text{Et}$.

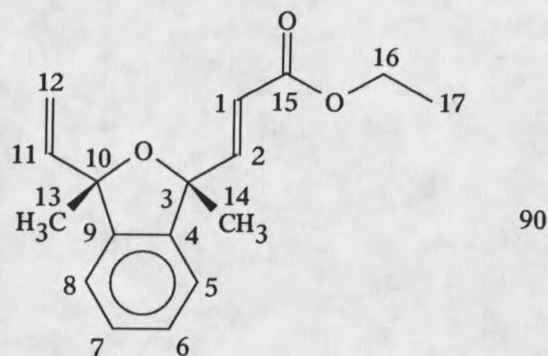
is not translated to the vinyl group, little or no change should be observed. Integration of the vinyl methine proton and the α -proton of the carboxylate gives a one-to-one ratio. Formation of cis product would lead to a larger relative amount of vinyl protons when compared to the carboxylate protons. This is not observed.



90

Figure 132. Compound **90**.

Interpretation of the proton data was not exactly straight forward. The vinyl protons, c through e, were reasonable. Protons d and e appear as doublets at 5.02 and 5.15 ppm respectively. They were found to be cleanly coupled to a doublet of doublets at 6.06 ppm. In the olefinic region, one other doublet was observed at 5.98 ppm. Based on precedence, this resonance was assigned to H_a . The location of H_b was not readily apparent. A two-dimensional homonuclear correlation experiment (COSY) revealed that the doublet at 5.98 ppm was coupled to a resonance at 7.09 ppm and direct observation of this resonance is not possible due to obstruction caused by the aromatic protons.



90

Table 25. ^{13}C and ^1H NMR Data for Compound 90.

Carbon	^{13}C NMR ppm	^1H NMR ppm
1	117.6	5.98 d, 1H
2	115.5	7.09 d, 1H
3	85.9	-
4	151.3	-
5	122.2	*
6	118.3	*
7	118.7	*
8	121.7	*
9	142.7	-
10	83.8	-
11	143.3	6.06 dd, 1H
12	112.9	5.02 d, 1H 5.15 d, 1H
13	15.1	1.61 s, 3H
14	15.3	1.63 s, 3H
15	166.9	-
16	60.8	4.20 q, 2H
17	14.0	1.30 t, 3H

* overlapping multiplet between 7.0 and 7.3 ppm.

Ring Expansion with Ethyl Diazoacetate

Analysis of the product mixture by ^{13}C NMR spectroscopy revealed platinum coupled resonances attributable, by analogy, to two platinacyclopentanes. The key feature noticed was a pair of platinum coupled ester carbonyls at 175.9 ppm and 178.7 ppm. The magnitude of the couplings suggests that the carbonyls are β to the metal. It is reasonable to propose the structures shown on page 133, complexes **91** and **92**. There was a slight preference of one isomer over the other, 1.2:1. The data was not correlated to an exact stereochemistry, syn or anti.

Mechanistically, the observation of a epimeric mixture about carbon-1 validates the proposal of intermediate **75** as an active contributor. There are no steric interactions to influence the stereochemistry of the platinacyclopentane.

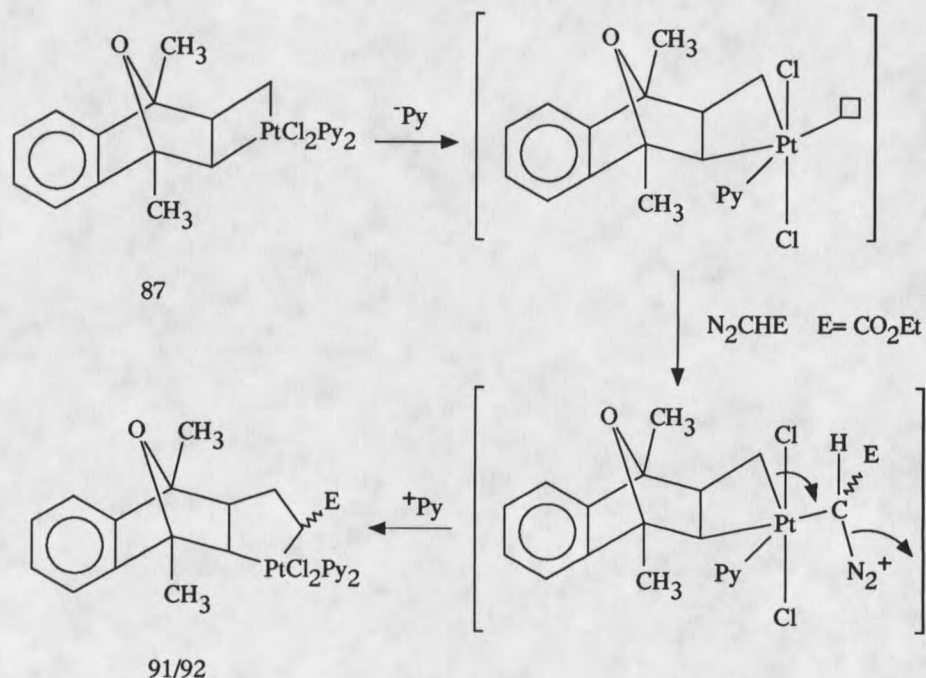
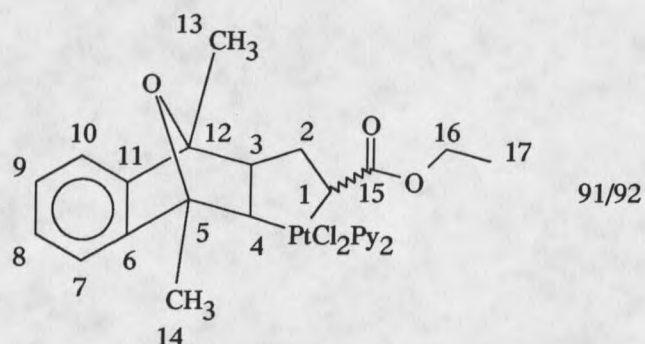


Figure 133. Proposed Mechanism for the Formation of **91** and **92**.

Table 26. ^{13}C NMR Data for Complexes **91** and **92**.

Carbon	^{13}C ppm ($J_{\text{Pt-C}}$) Major Isomer	^{13}C ppm ($J_{\text{Pt-C}}$) Minor Isomer
1	30.8 (536)	26.8 (530)
2	36.5	37.0
3	51.1 (28.9)	50.6 (12.8)
4	48.6 (604)	48.1 (610)
5	88.7	88.4
6	118.2	118.5
7	126.4	126.3
8	123.7	124.3
9	123.7	124.3
10	125.4	125.1
11	116.0	115.6
12	84.8	85.2
13	14.7	14.6
14	16.1	16.1
15	178.7 (36.9)	175.9 (32.1)
16	62.3	62.0
17	13.5	13.5

Expansion of the Transformation to Other
Diazo-Compounds

The isomeric ratios presented earlier have been interpreted to be originating from the metal mediated reaction itself. Upon review of the products of this reaction, one could envision isomerization after the product is formed catalyzed by either acid or base. In fact, under the conditions of this reaction, there is pyridine present. Pyridine has been known to readily dissociate from these types of complexes. A base catalyzed isomerization is shown below.

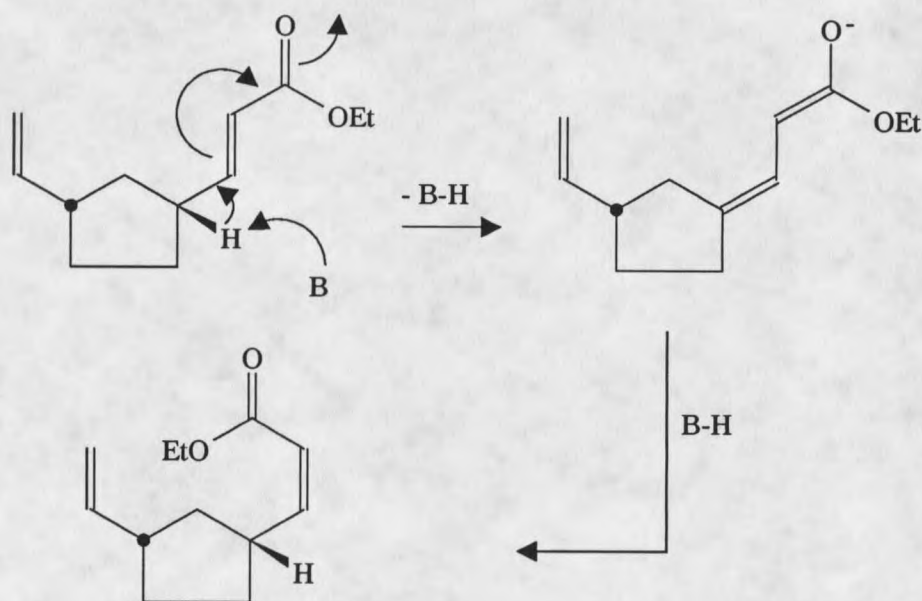


Figure 134. Base Catalyzed Isomerization of the Carboxylates.

Platinum could also act as a Lewis acid and effect the same type of isomerization. In addition, the one experiment that gave stereospecific product formation, the reaction of 87 with ethyl diazoacetate, is substituted at the bridgehead

position and cannot isomerize as shown in Figure 134. This supports the notion that the reaction of norbornyl substrates as well as those derived from benzofurans is stereospecific and that the stereocontrol is lost through isomerization after liberation of the platinum. The chosen route in the study of this problem was a search for diazo-reagents that will conduct this transformation but do not acidify the proton in question. Numerous syntheses of diazo-reagents are in the literature.

Diazoethane was allowed to react with complex 48 and was found to only give the cyclopropane, no olefinic products were formed. Phenyl diazomethane, synthesized by the method of Closs and Moss⁸⁰, was exposed to complex 48 and was also shown to cause reductive-elimination in quantitative yield. These results are problematic. This would appear to be a limitation in this methodology.

Diazomethane has been shown to give a maximum yield of 75%, while ethyl diazoacetate gives nearly quantitative conversion. The ester moiety can be thought of as electron withdrawing and its effect on the carbene is to make it relatively electron poor. The methyl group on diazoethane is electron donating, thus enhancing the electron density on the carbene. Phenyl is also electron donating inducing a similar effect on the carbene of phenyl diazomethane. Increased electron density on the carbene is donated to the metal upon coordination. This increased electron density on the metal apparently initiates reductive-elimination of the cyclopropane.

In an attempt to lower the electron density on the diazo-carbon, p-chlorophenyl and p-nitrophenyl diazomethane were prepared⁸⁰. These two reagents were found to also give reductive elimination of the cyclopropane.

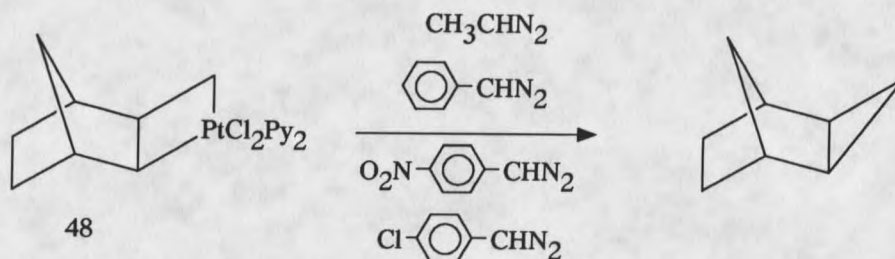


Figure 135. Reaction of Complex 48 with Various Diazo-Reagents.

The failure of *p*-chloro and *p*-nitro phenyl diazomethane to give olefinic products is understandable. The substituents on the phenyl rings serve to make the entire group electron withdrawing through the π -system while maintaining a net electron donating effect through the σ -system. The σ -system appears to be the dominating influence in this transformation.

It would appear as if electron poor diazo-reagents facilitate the transformation. As a test for this postulate, 2,2,2-trifluorodiazoethane was prepared⁸¹. This reagent is a gas at room temperature that can be made as an ethereal solution. This ethereal solution was added to a chloroform solution of complex 48 and stirred for one hour. Study of the residues, upon removal of solvents, by ^1H NMR indicated the presence of olefinic resonances. They were assigned to the expected divinyl cyclopentane products.

Proton-a for the *cis* and *trans* isomers appear as complex multiplets that partially overlap, Figure 136. The splitting is due to coupling to proton-b and coupling to the fluorines of the trifluoromethyl group. Fluorine is an NMR active nucleus with 100% natural abundance, this gives complete splitting as opposed to satellite formation as

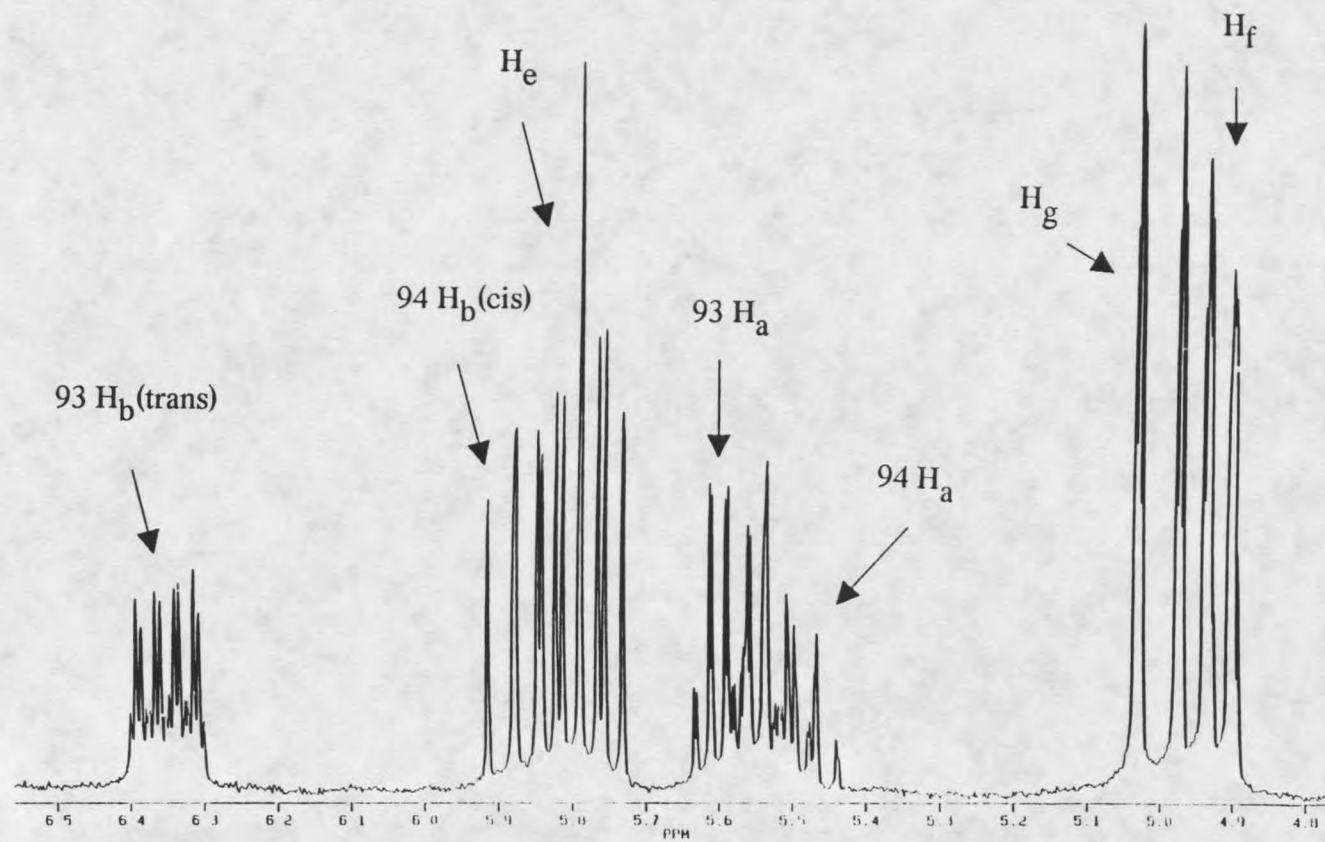


Figure 136. Olefinic Range (^1H NMR) for Compounds 93 and 94.

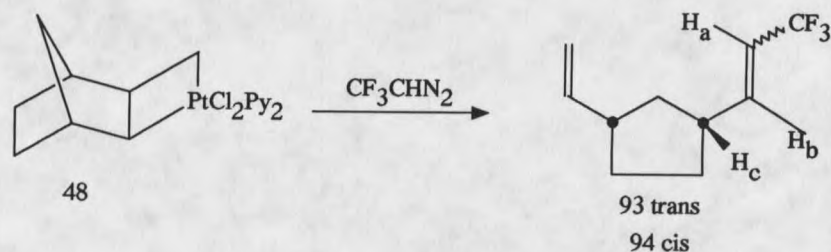
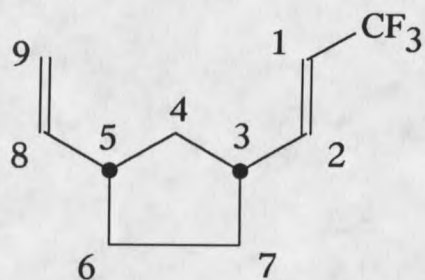


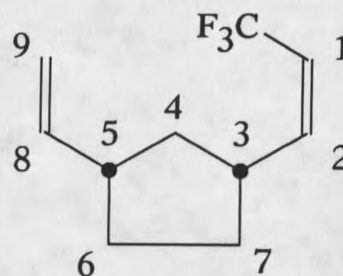
Figure 137. Reaction of Complex 48 with 2,2,2-Trifluorodiazooethane.

observed with platinum coupling. Proton-b for both isomers is unobstructed at 500 MHz. For compound 93, the proton observed at 6.3 ppm is a multiplet with discernable coupling to proton-a and proton-c. The observed coupling constant between the olefinic protons was measured to be 15.7 Hertz supporting a trans stereochemical determination. Additional coupling is due to the fluorine content in the molecule. The resonance for H_b of compound 94 appears as a simple doublet of doublets centered at 5.8 ppm with a coupling constant to H_a of 10.7 Hertz. No coupling to fluorine is observed. The vinylic protons observed for the other side of the molecules coincide with each other and are directly comparable to earlier discussed analogs synthesized from ethyl diazoacetate. The ^1H NMR assignments for compounds 93 and 94 are shown in Table 27.

Integration of the resonances attributable to H_b of each isomer gave an isomeric ratio of $\text{E/Z} = 1.3$. Therefore, production of both cis and trans isomers with a ratio comparable to those synthesized from ethyl diazoacetate appears to discount the idea of base or acid catalyzed rearrangement after the olefinic residues are formed.



93



94

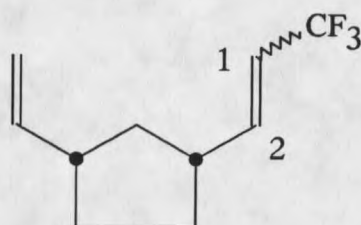
Table 27. ^1H NMR Data for Compounds 93 and 94.

Carbon	93 ppm ($J_{\text{H-F}}$)	94 ppm ($J_{\text{H-F}}$)
1	5.57 m, 1H (6.6 Hz)**	5.50 m, 1H (7.3 Hz)***
2	6.35 dd, 1H (2.6 Hz)**	5.87 dd, 1H ***
3	2.63 m, 1H	3.07 m, 1H
4	*	*
5	2.59 m, 1H	2.59 m, 1H
6	*	*
7	*	*
8	5.79 m, 1H	5.79 m, 1H
9	4.91 d, 1H 5.00 d, 1H	4.91 m, 1H 5.00 d, 1H

* overlapping multiplets between 1.0 and 1.7 ppm.

** $J_{\text{H-H}} = 15.8$ Hz.*** $J_{\text{H-H}} = 10.7$ Hz.

The ^{13}C NMR analysis performed on these molecules revealed the resonances for the olefinic carbons. As expected, both carbons of the olefins appear as quartets, coupling derived from the fluorines. Table 28 contains a summary of the observed olefinic resonances for compounds **93** and **94**. The magnitudes of the coupling constants for the ^2J and ^3J carbons are consistent with their assignment.



93 trans
94 cis

Table 28. Olefinic ^{13}C NMR Data for Compounds **93** and **94**.

Carbon	93 ppm ($J_{\text{F-C}}$)	94 ppm ($J_{\text{F-C}}$)
1	116.7 (33)	116.9 (34)
2	144.4 (6.5)	147.4 (5.5)

Reaction of Complex **21** with
2,2,2-Trifluorodiazaoethane

The question arose as to whether the E/Z ratio observed with the reaction of complex **21** with ethyl diazoacetate, presumably caused by an interaction between the diazo reagent and the syn-hydroxy methyl moiety, would be mirrored with the use of 2,2,2-trifluorodiazaoethane. An ethereal solution of 2,2,2-trifluorodiazaoethane was

prepared and introduced to a chloroform solution of complex **21** and was stirred at room temperature for one hour. Rotary evaporation of the resulting solution gave a chloroform soluble residue suitable for study by NMR spectroscopy. The ^1H NMR spectrum gave a familiar pattern of resonances indicating the formation of compounds **95** and **96**. Proton-b for the trans-isomer, **95**, was again observed as a multiplet with coupling to H_a , H_c , and to fluorine. Like the analog **94**, proton-b for compound **96** was observed to be a simple doublet of doublets.

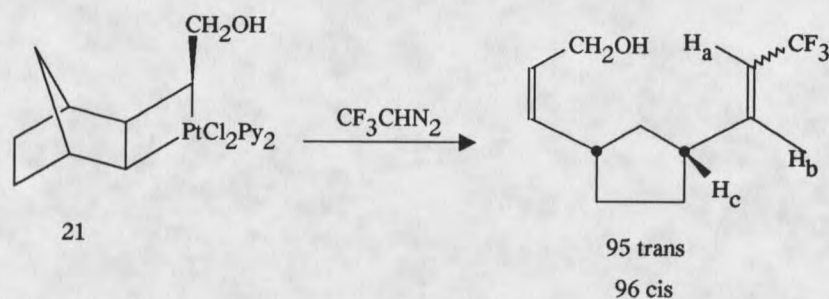


Figure 138. Reaction of Complex **21** with 2,2,2-Trifluorodiazooethane.

Integratable ^1H NMR spectroscopy was utilized in an analogous manner to obtain the isomeric ratio. A ratio of $\text{E/Z} = 1.5$ was measured. This isomeric ratio clearly provides additional evidence for a hydrogen-bonding interaction for the reaction of complex **21** with ethyl diazoacetate.

Reaction of Complex **87** with 2,2,2-Trifluorodiazooethane

In a search for any unexpected deviations from the data obtained by using ethyl diazoacetate, the reaction of complex **87** with 2,2,2-trifluorodiazooethane was conducted

in a manner analogous to the reaction of complex 48. Removal of solvents gave a chloroform soluble residue. Study of this solution by ^1H NMR revealed a large amount of reductive elimination of the cyclopropane, 72%. In the olefinic region of the spectrum there were resonances that were attributable to a vinylic product. Integration of the resonances indicated the formation of only one isomer. Selective 1D homonuclear decoupling experiments revealed a coupling constant between the indicative olefinic protons of 15.7 Hertz.

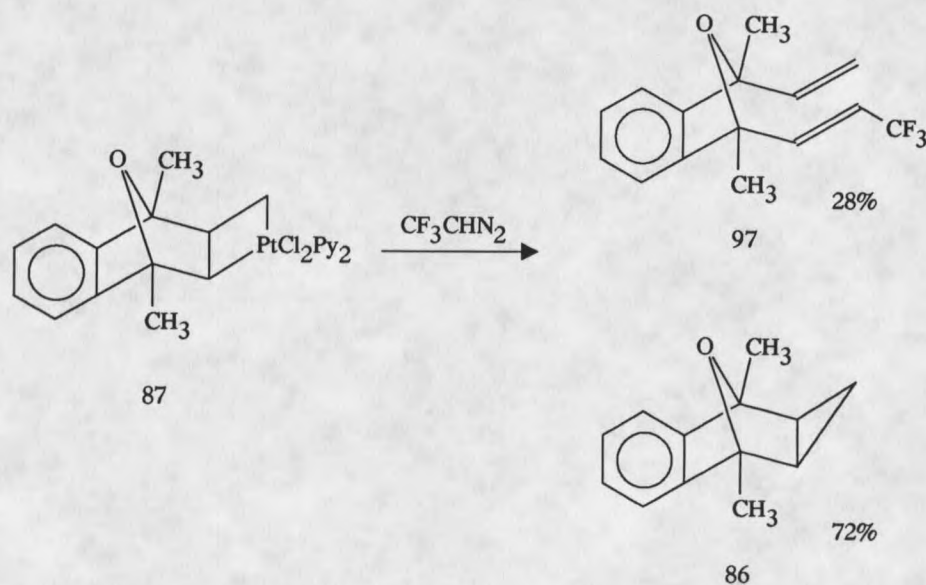
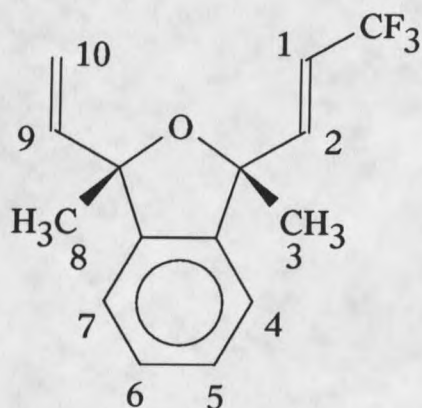


Figure 139. Reaction of Complex 87 with 2,2,2-Trifluorodiazaoethane.



97

Table 29. ¹H NMR Data for Compound 97.

Carbon	97 ppm (<i>J</i> _{H-H}) [<i>J</i> _{F-H}] Hz.
1	5.84 dq, 1H (15.7) [6.7]
2	6.57 dq, 1H (15.7) [1.7]
3	1.99 s, 3H
4	*
5	*
6	*
7	*
8	1.68 s, 3H
9	6.05 dd, 1H (10.9, 18.2)
10	5.07 d, 1H (10.9) 5.14 d, 1H (18.2)

* overlapping multiplets between 7.0 and 7.3 ppm.

The Reaction of Complex 65 with
Ethyl Diazoacetate

The reaction of complex 65 with ethyl diazoacetate is interesting because the azide, if the proposed stereochemistry about the platinum is correct, will interact with the hydroxymethyl moiety in such a way as to prevent migration of the azide to a

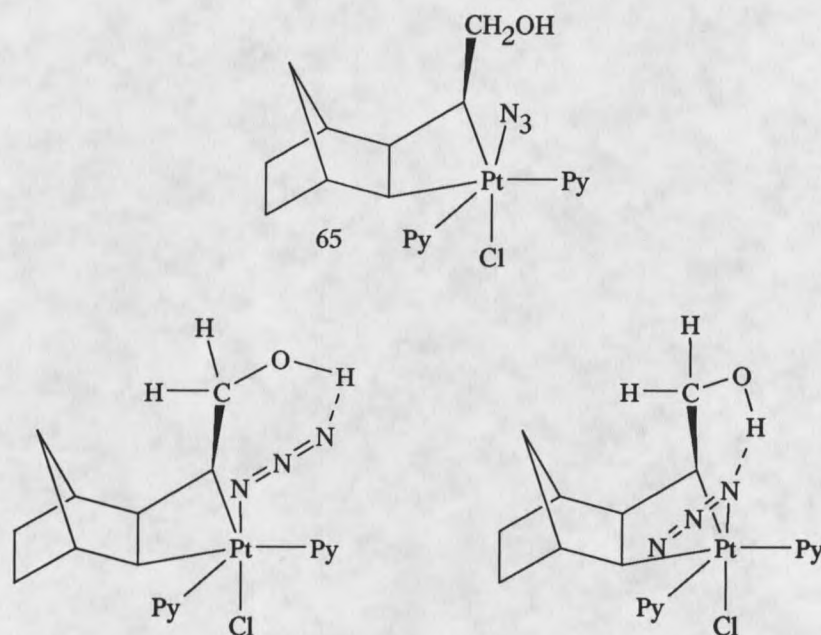


Figure 140. Proposed Interaction on Complex 65.

position trans to carbon-1, Figure 140. This only would allow for coordination of the diazo-reagent trans to carbon-1, thus an E/Z ratio of greater than 1.0 would be expected upon reaction with ethyl diazoacetate. In fact, an E/Z ratio of 1.7 was observed. This adds support to not only the proposed hydrogen bonding interaction between ethyl diazoacetate and complex 21 but to the proposed stereochemistry of the ligands on complex 65.

Ligand Effects in the Reaction of
Platina(IV)cyclobutanes with Ethyl Diazoacetate

Neilsen⁷³ employed various ligands on the syn-hydroxymethyl platinacyclobutane in an attempt to observe stereochemical deviations. A summary of these ligands is shown on page 65 of this thesis. He concluded that no significant deviations were observed.

In the course of this investigation, ligands more divorced from pyridine were chosen to gain more stereochemical perturbation. Tetrahydrofuran is a coordinating solvent that will ligate platinum tetramers. The preceding tetramer of complex 48 was dissolved in tetrahydrofuran and the resulting solution was exposed to diazomethane. The solution deepened in color. Rotoevaporation of the excess solvent gave a yellow residue. The sole organic product was the cyclopropane. It was apparent that the diazo-reagent coordinated with the metal followed by reductive elimination of the metal-carbene species, Figure 141.

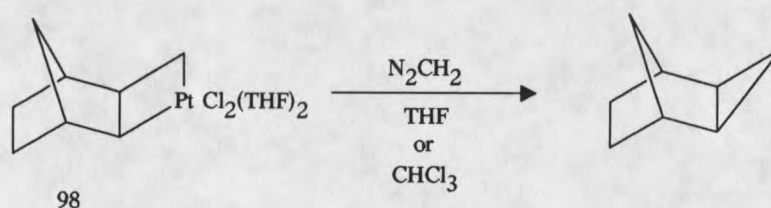


Figure 141. Reaction of Complex 98 with Diazomethane.

The analogous process was attempted using dimethyl sulfoxide (DMSO). Exposure of this system to diazomethane was shown to yield only the cyclopropane, Figure 142.

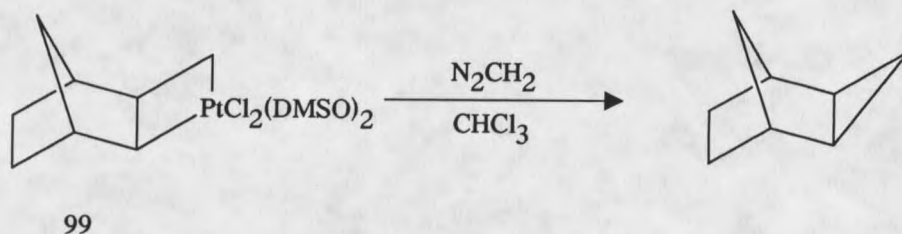
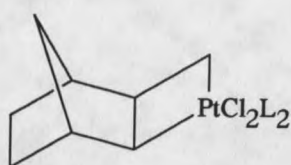


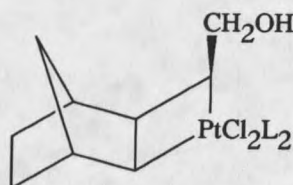
Figure 142. Reaction of Complex 99 with Diazomethane.

The conclusion was drawn that the success of this transformation appears to be limited to nitrogen donor ligands. A summary of the ligands utilized is shown in Table 30. These experiments were conducted by treating an amount of tetramer with two equivalents of the specified ligand in chloroform and stirring at room temperature until solvated. The obtained isomeric ratios are derived from the reaction of the resulting complexes with ethyl diazoacetate followed by isomeric determination by integratable ^1H NMR spectroscopy.

Several conclusions can be drawn from a review of the data, Table 30. First, this reaction, even though significant deviations were observed, is not stereospecific upon replacement of the ligands for ones with more or less steric bulk, however in some instances a greater amount of stereoselectivity is observed. The basicity of the ligand also does not appear to be a factor. This point is illustrated in the two aniline experiments. These are ligands with differing basicities but similar steric bulk and they give the same stereochemical result. Dimethylaminopyridine is also observed to give little difference when compared to the less basic pyridine.



100



101

Table 30. Isomeric Data for the Reaction of Various Complexes with N₂CHCO₂Et.

Ligand	100 E/Z	101 E/Z
Aniline	2.5	0.5
p-Chloroaniline	-	0.5
Pyridine	1.4	0.7
Dimethylaminopyridine	-	0.8
Triethylamine	-	2.4
Pyrrolidine	0.8	1.5

The result utilizing triethylamine is approaching an exciting ratio, however this should be tempered by the fact that the products are formed in extremely low yield, 5%, and that the treatment of a tetramer with triethylamine causes reductive elimination to occur in approximately 95% yield. In fact, the attempted synthesis of the triethylamine analog of complex **100** was unsuccessful giving a quantitative amount of the cyclopropane.

Pyrrolidine as a ligand gives problematic results. The apparent ratios are opposite of that measured for pyridine. This is probably best explained as steric effects of the ligand as compared to pyridine. Computational studies of these systems were made using PCMODEL, a commercial molecular modelling program designed for a personal computer. The data obtained indicates that the ligand does not act sterically as much

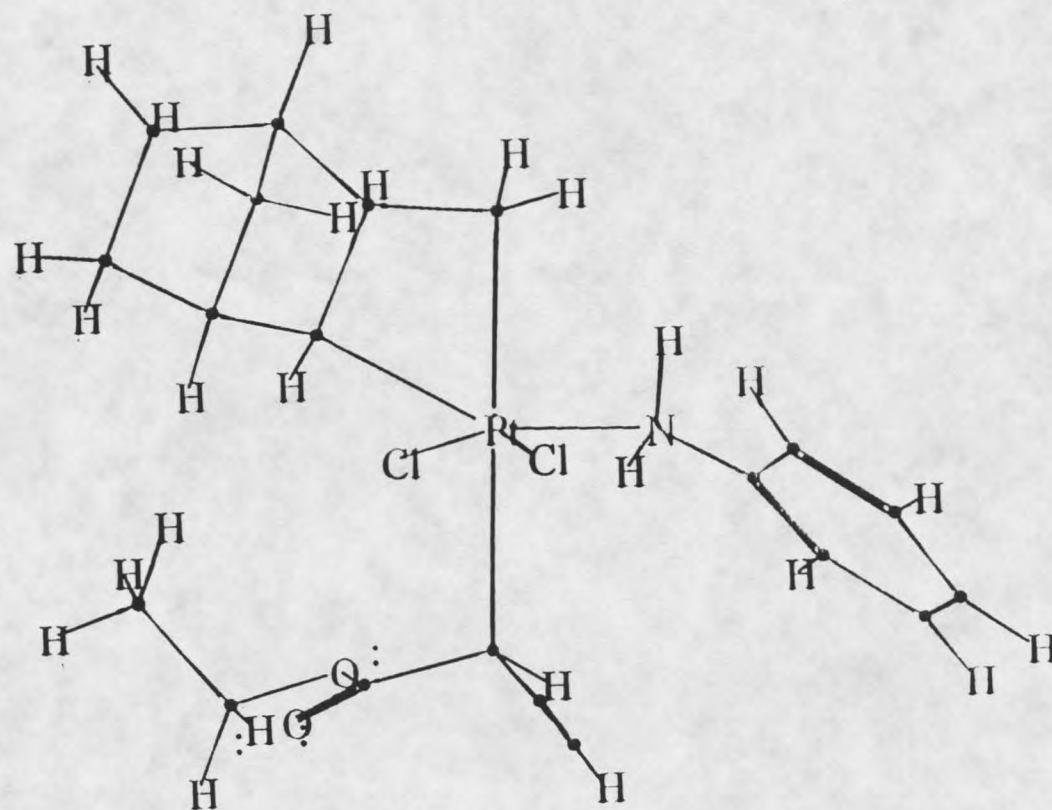


Figure 143. PCMODEL Structure for Complex **100** with Aniline as Ligands.

on the diazo-reagent as it does on the topside chlorine. Then, in turn, the chlorine influences the position of the diazo-reagent, Figure 143.

Conclusions

The data presented taken together seem to indicate a dualistic pathway by which products are obtained. The majority pathway involves coordination of the reagent, ring expansion to a platinacyclopentane, and then extrusion of the metal and the concurrent formation of the olefinic products. This pathway has the diazo-reagent coordinating trans to carbon-1 in a position so that substitution at the bridgehead may have an overwhelming influence on the stereochemistry. The stereochemical result of this mode of operation is slightly more trans compound than cis. This is probably a reflection of the marginally larger steric bulk of the upper side of the plane defined by the butane ring as compared to the lower side.

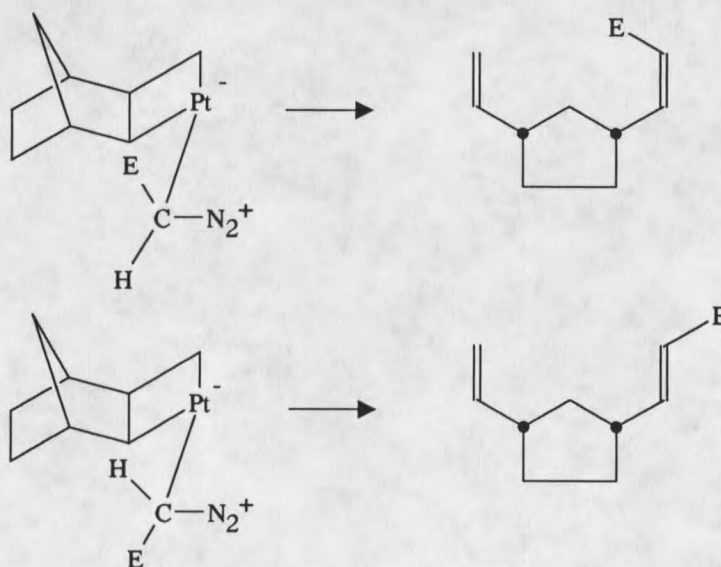


Figure 144. Formation of Cis and Trans Vinyl Cyclopentanes.

Substitution at the bridgehead rules out *cis* product formation by forcing the bulkier diazo substituent to the underside of the platinacyclobutane ring. The data also appears to support the *trans* periplanar orientation of the nitrogen and the migrating bond. If an intermediate such as shown in Figure 145 were to be in operation, one would expect a lesser influence of the bridgehead substituent and more influence of the ligand on the stereochemistry.

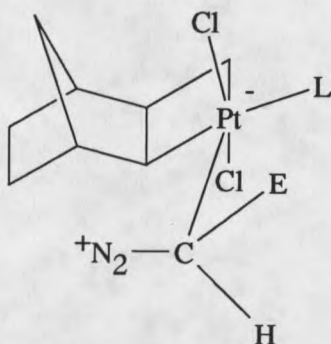


Figure 145. Non-*trans* Periplanar Orientation of the Diazo-reagent.

The minority pathway is proposed to only occur in the reaction of the syn-hydroxymethyl complex, **21**, with ethyl diazoacetate. Inducement of topside coordination of the metal is provided by pre-chelation of the diazo-group to the syn-substituent by hydrogen bonding. Masking of the proton involved in this interaction and replacement of the diazo-reagent to one that will not hydrogen bond are observed to negate the effect.

The two proposed pathways are shown in Figures 146 and 147.

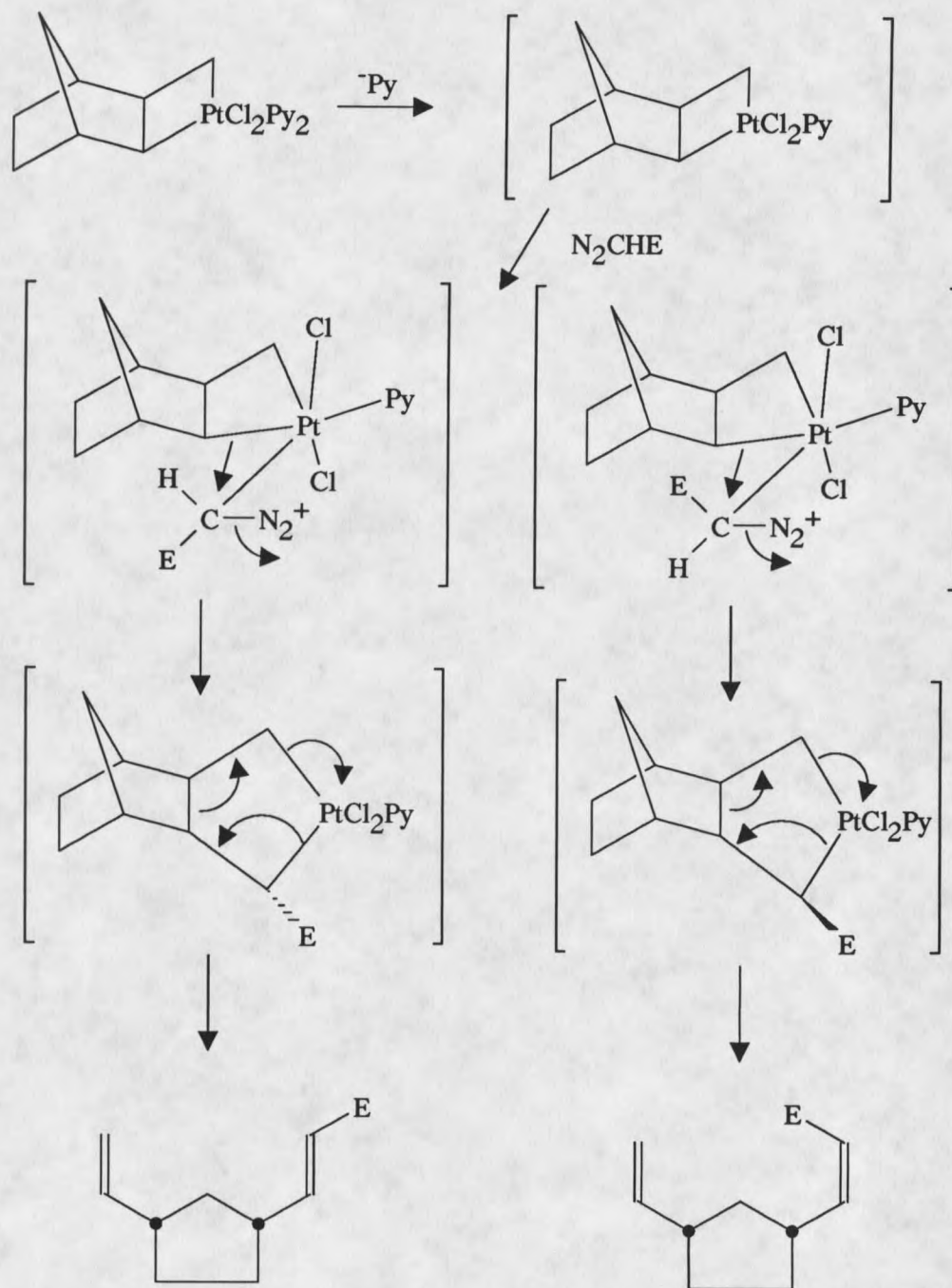


Figure 146. Majority Pathway for the Diazo-Process.

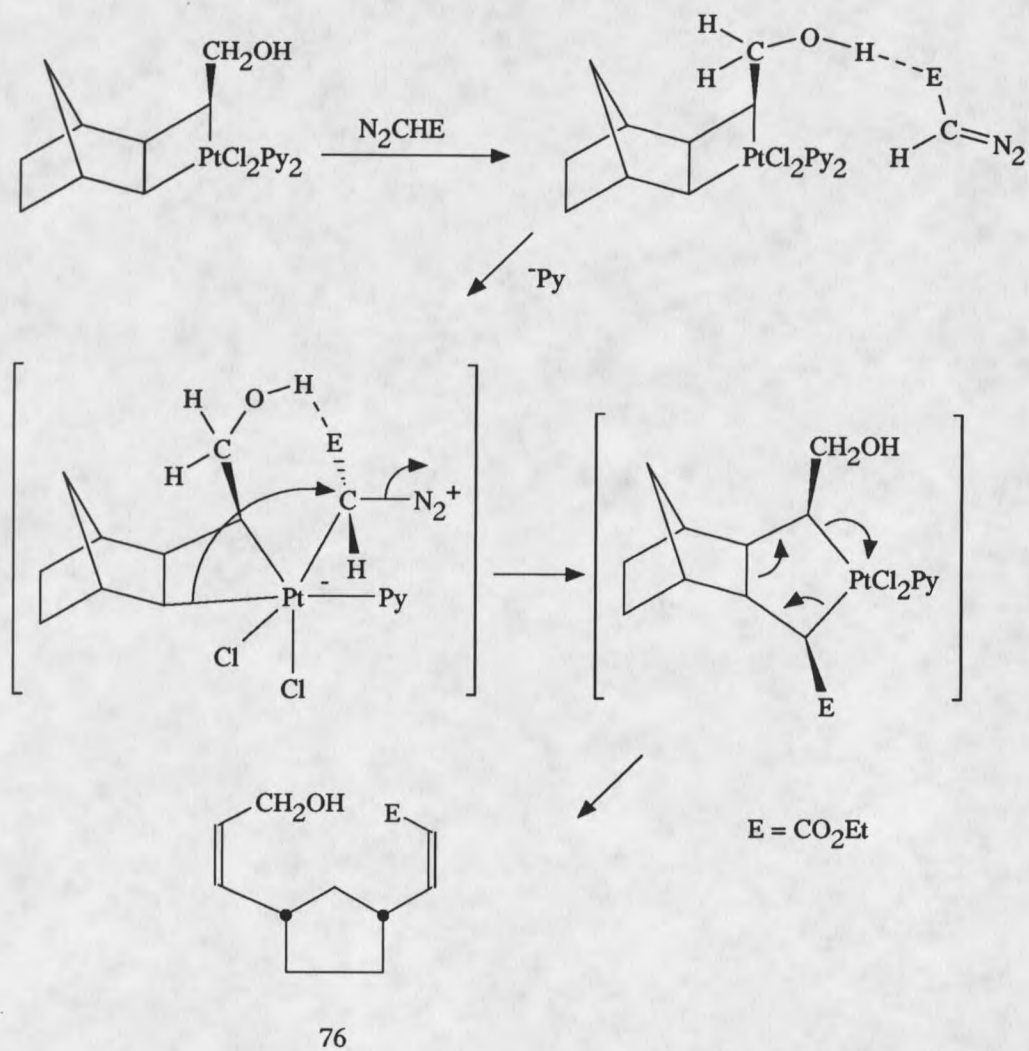


Figure 147. Minority Pathway for the Reaction of Complex 21 with $\text{N}_2\text{CHCO}_2\text{Et}$.

Exploration of the Ring Expansion Process

It was previously shown that oxygen nucleophiles, as a general class, can be substituted at carbon-2 of platinacyclopentanes. In an attempt to understand under what conditions this reaction may occur, the reaction between complex **21** and formic acid was studied. Complex **21** was treated with an 88% aqueous solution of formic acid and acetone. The resulting amber solution was clear of precipitate and was stirred at room temperature for twelve hours. At completion, the solution was neutralized with a saturated sodium bicarbonate solution and was extracted with chloroform. The collected chloroform washes were combined and the volume was reduced to one milliliter upon which the residue was triturated three times with pentane to give a yellow solid. This yellow solid was readily soluble in chloroform. Analysis of ^1H and ^{13}C NMR spectra, see Figures 149, 150, and 151, revealed the definite presence of a platinacyclopentane with formate functionality on carbon-2. Also it was indicated that the formation of this molecule was stereospecific and based on analogy, the product was determined to be complex **102**, Figure 148.

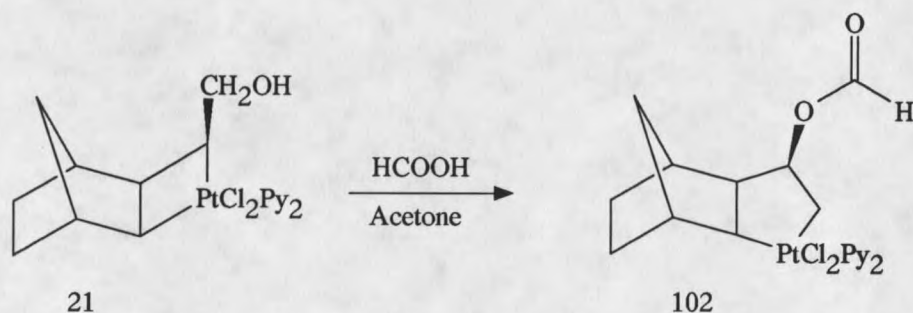
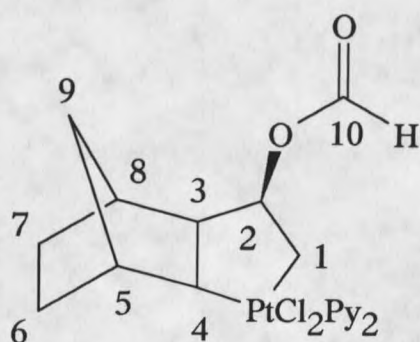


Figure 148. Synthesis of Complex **102**.



102

Table 31. ^{13}C and ^1H NMR Data for Complex **102**.

Carbon	^{13}C NMR ppm ($J_{\text{Pt-C}}$)	^1H NMR ppm ($J_{\text{Pt-C}}$)
1	18.7 (553)	3.96 dd, 1H (84.6) 2.34 dd, 1H (104.1)
2	77.7 (69.1)	5.66 dd, 1H
3	52.7	1.95 t, 1H
4	41.4 (532)	3.30 dd, 1H (85.3)
5	38.3	1.16 d, 1H
6	29.3 (32.6)	2.29 m, 1H 1.28 m, 1H
7	30.5	2.12 m, 1H 1.45 m, 1H
8	44.2	2.29 d, 1H
9	36.6	1.09 brs, 1H 1.09 m, 1H
10	160.8	7.99 s, 1H

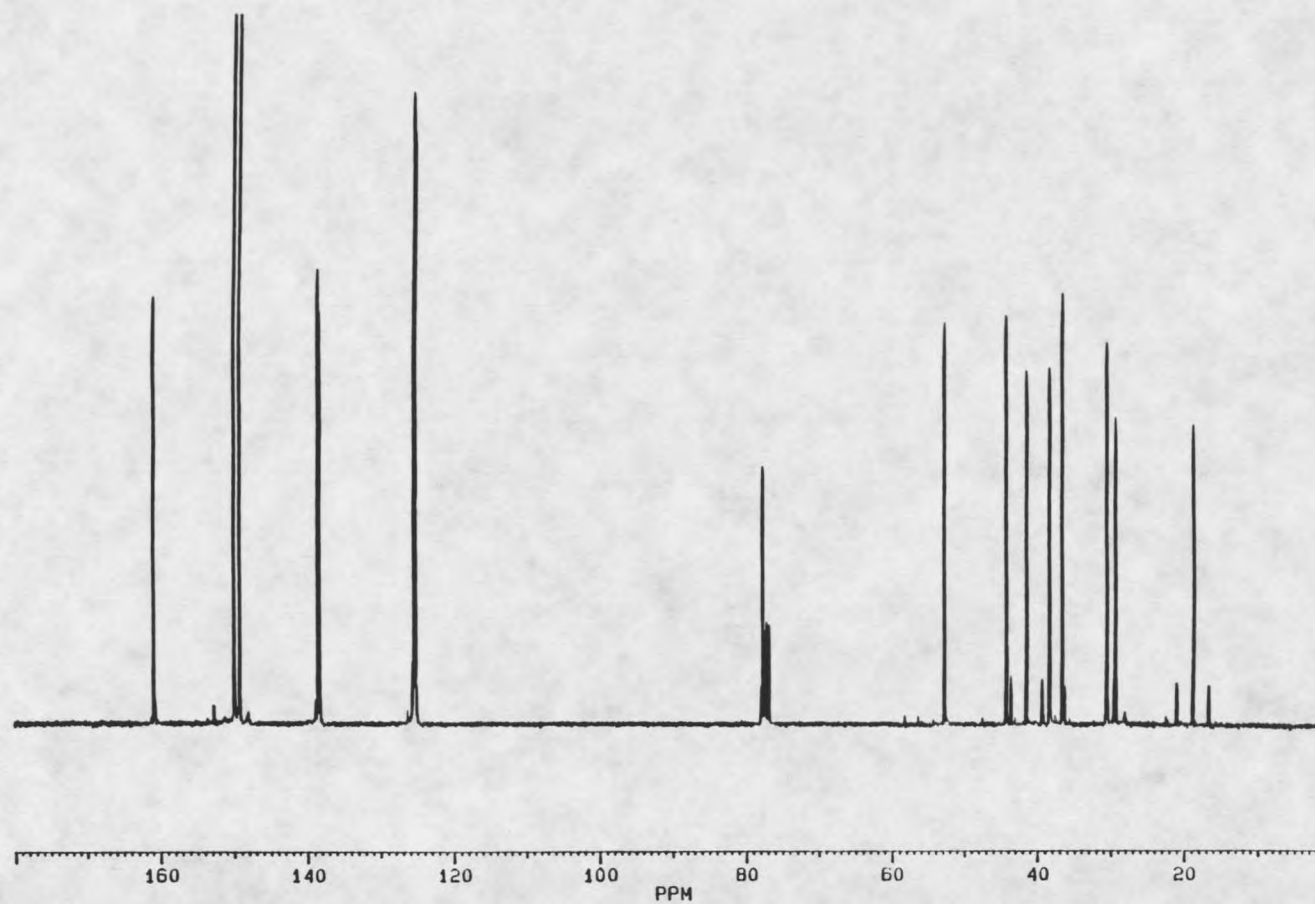
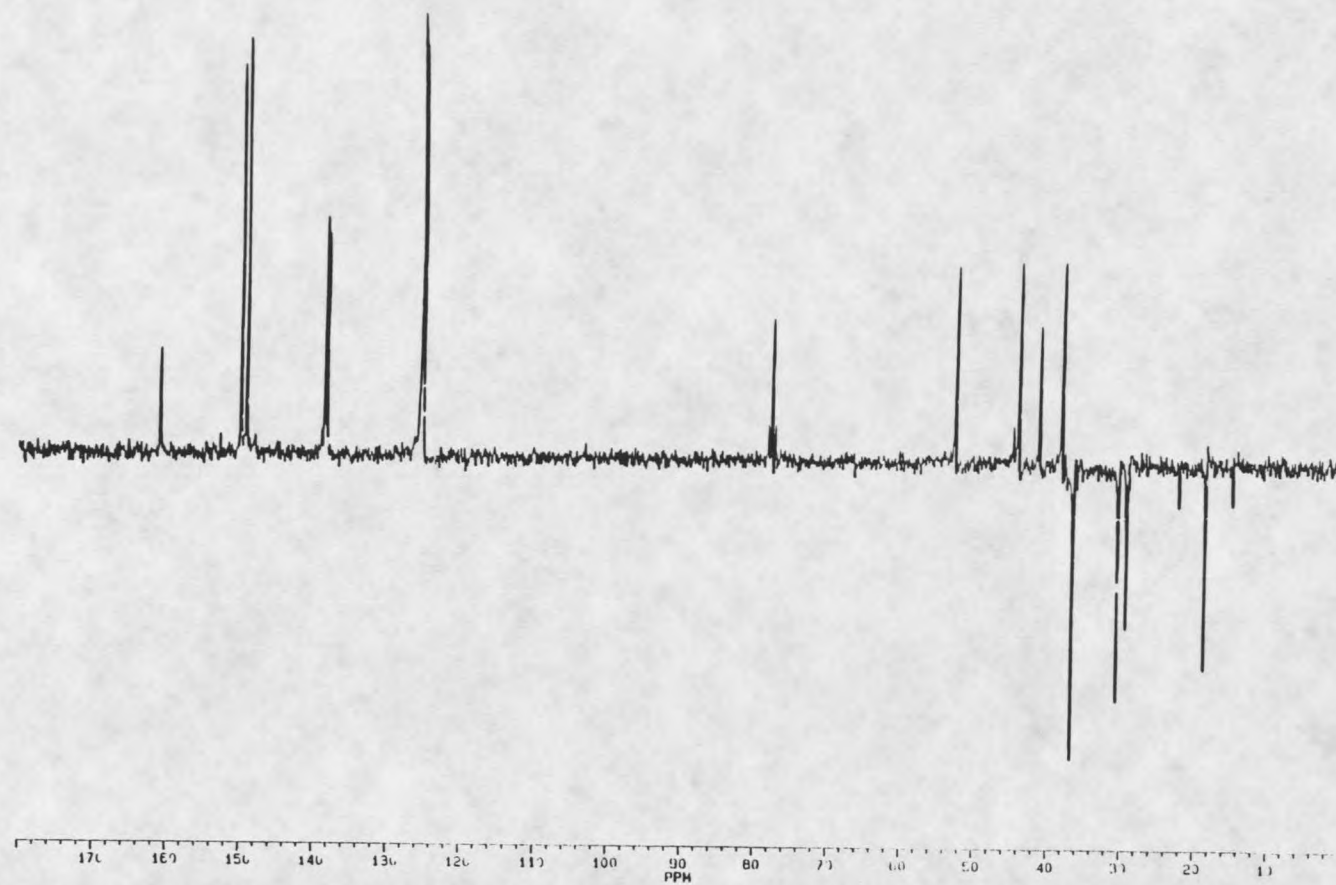


Figure 149. ^{13}C NMR Spectrum of Complex 102.



155

Figure 150. ^{13}C DEPT 135 Spectrum of Complex **102**.

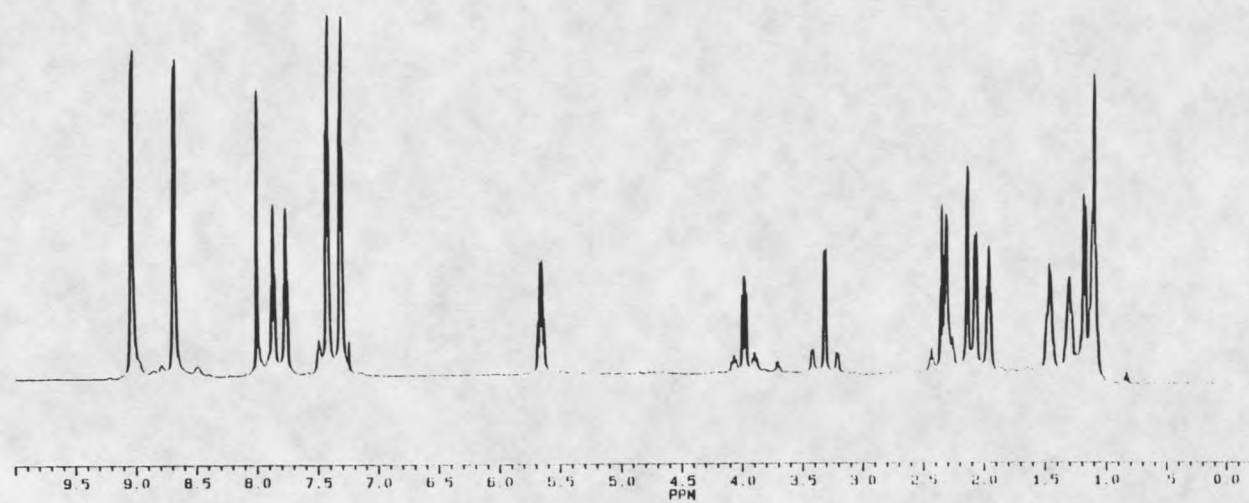


Figure 151. ^1H NMR Spectrum of Complex 102.

A comparison of complex **102** to the analogous alcohol, **22**, revealed significant differences. The resonance assignable to the proton on carbon-2 was the most dramatic, as would be expected. The multiplicity was maintained, however the chemical shift moved downfield from 4.2 ppm to 5.66 ppm. The protons on carbon-1 are also observed to shift downfield. The proton spectrum is consistent with the proposed structure.

The ^{13}C NMR spectrum also displayed differences consistent with the proposed molecule. A methine at 160.8 ppm is evident and is attributable to the formate carbonyl carbon. Carbon-2 also is seen to shift downfield slightly to 77.7 ppm.

The mechanism of the ring expansion process, as proposed by both Puddephatt and Jennings, invokes nucleophilic attack of a platinum-olefin intermediate. However, the nucleophiles capable of being delivered to carbon-2 and giving stable platinacyclopentanes appear to be limited to oxygen containing ones. To broaden the scope of platinacyclopentane synthesis, other nucleophiles were explored.

Reaction of Complex **22** with HCl

The ring expansion process, as demonstrated by Neilsen, is reversible. Treatment of complex **22** with methanol will give complex **55** with retention of stereochemistry³⁵.

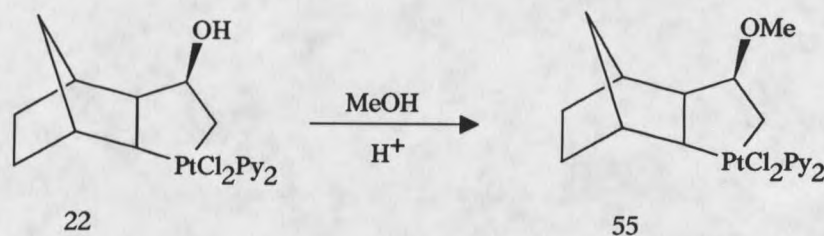


Figure 152. Reaction of Complex 22 with Methanol.

This result gives another viable pathway for substitution processes at carbon-2. Treatment of complex 22 with aqueous hydrochloric acid and acetone was found, by ^1H and ^{13}C NMR to give an analogous platinacyclopentane with a chloride situated on carbon-2.

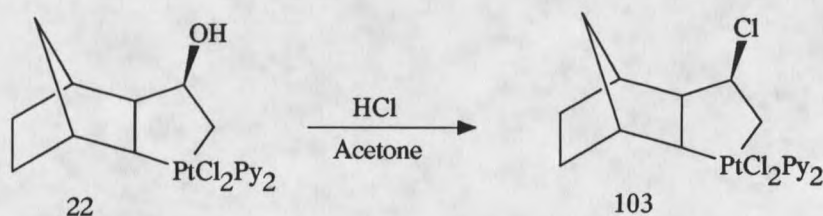


Figure 153. Reaction of Complex 22 with Hydrochloric Acid.

Conversion of complex 22 is complete and is rationalized by the enhanced nucleophilicity of chloride ion as opposed to water. Complex 103 is not novel. This complex was reported by Neilsen⁸² as the product of the reaction of complex 21 with thionyl chloride. Verification was made by comparison of ^{13}C and ^1H NMR spectral data.

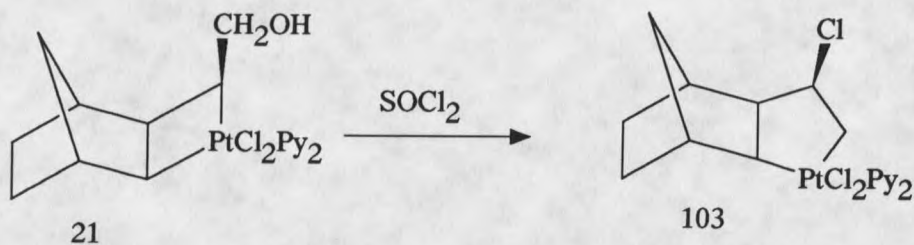


Figure 154. Reaction of Complex **21** with Thionyl Chloride.

Neilsen found this complex to be short-lived. It was observed that Complex **103** undergoes isomerization to the zwitterionic complex **104**. Characterization of this complex was accomplished through the use of ^{13}C NMR and X-ray crystallography. Complex **103** manufactured by the method of this author was also found to isomerize in a manner consistent with that reported by Neilsen.

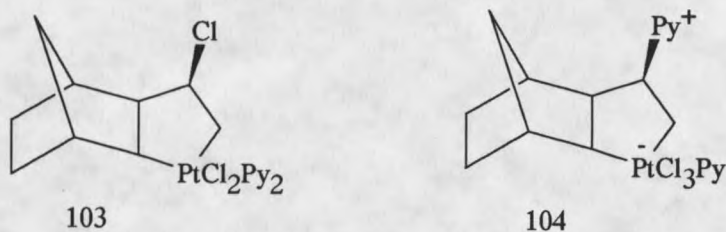


Figure 155. Proposed Structures for Complexes **103** and **104**.

Attachment of nitrogen nucleophiles to carbon-2 is another area worthy of study. Complex **55** was allowed to stir with an excess of a primary amine in an attempt to take advantage of the reversible aspect of the ring expansion process. The observed result

was maintenance of the methyl ether and substitution of the pyridine ligands for the amine. Yields appear to be quantitative by NMR spectroscopy.

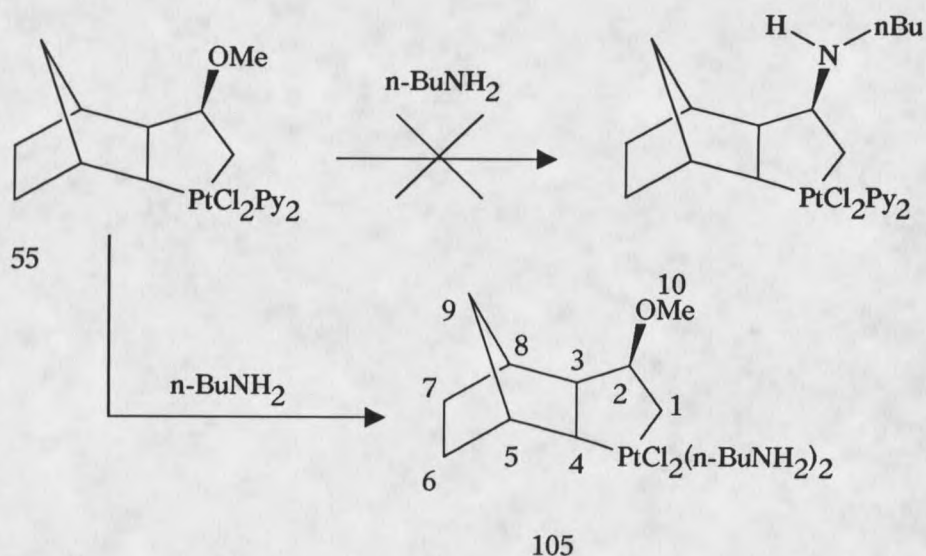


Table 32. ^{13}C NMR Data for Complex 105.

Carbon	^{13}C NMR ppm ($J_{\text{Pt-C}}$)	Multiplicity (DEPT)
1	21.1 (531)	CH_2
2	83.1 (56)	CH
3	51.8	CH
4	40.6 (502)	CH
5	44.2	CH
6	29.5 (36)	CH_2
7	31.3	CH_2
8	37.2	CH
9	37.0	CH_2
10	57.2	CH_3

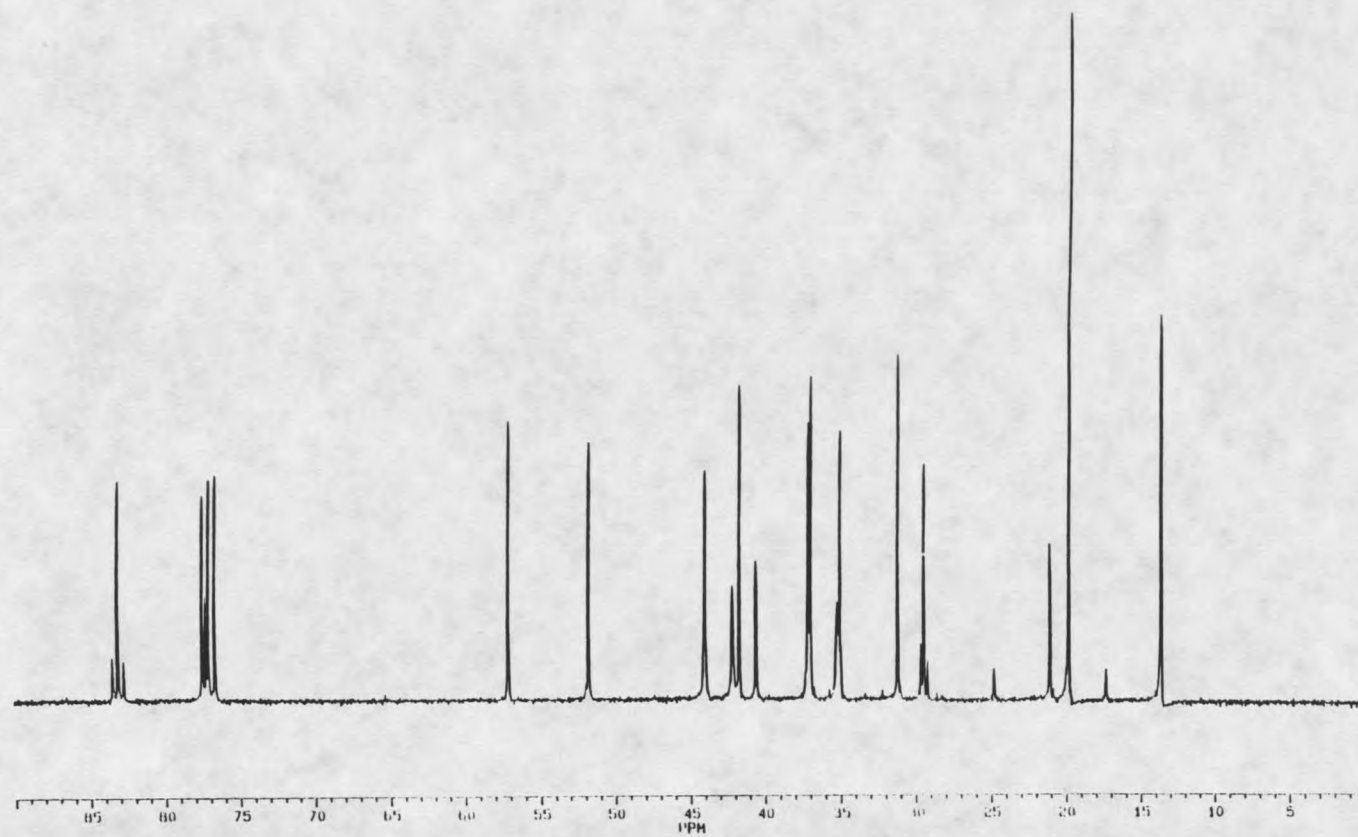


Figure 156. ^{13}C NMR Spectrum of Complex 105.

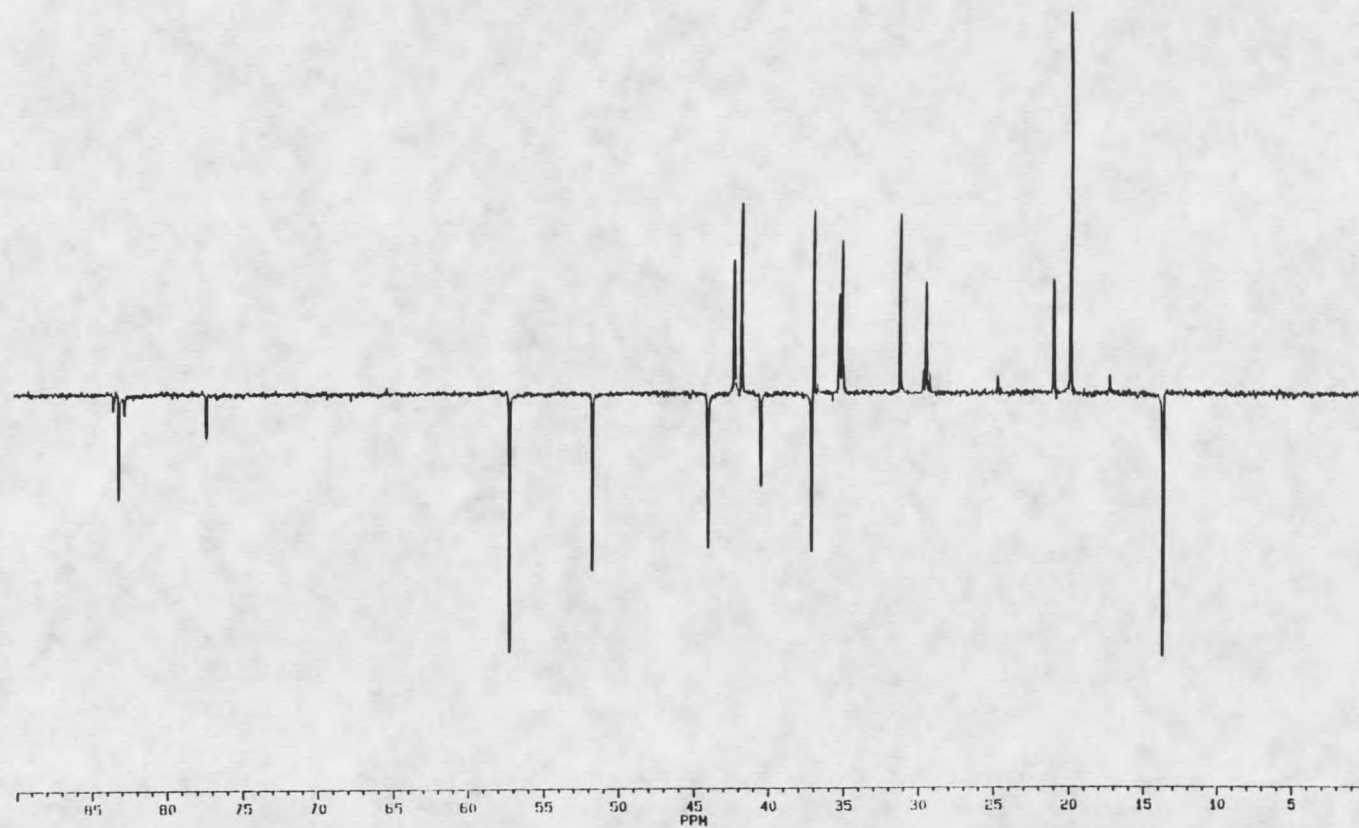


Figure 157. ^{13}C DEPT 135 Spectrum of Complex 105.

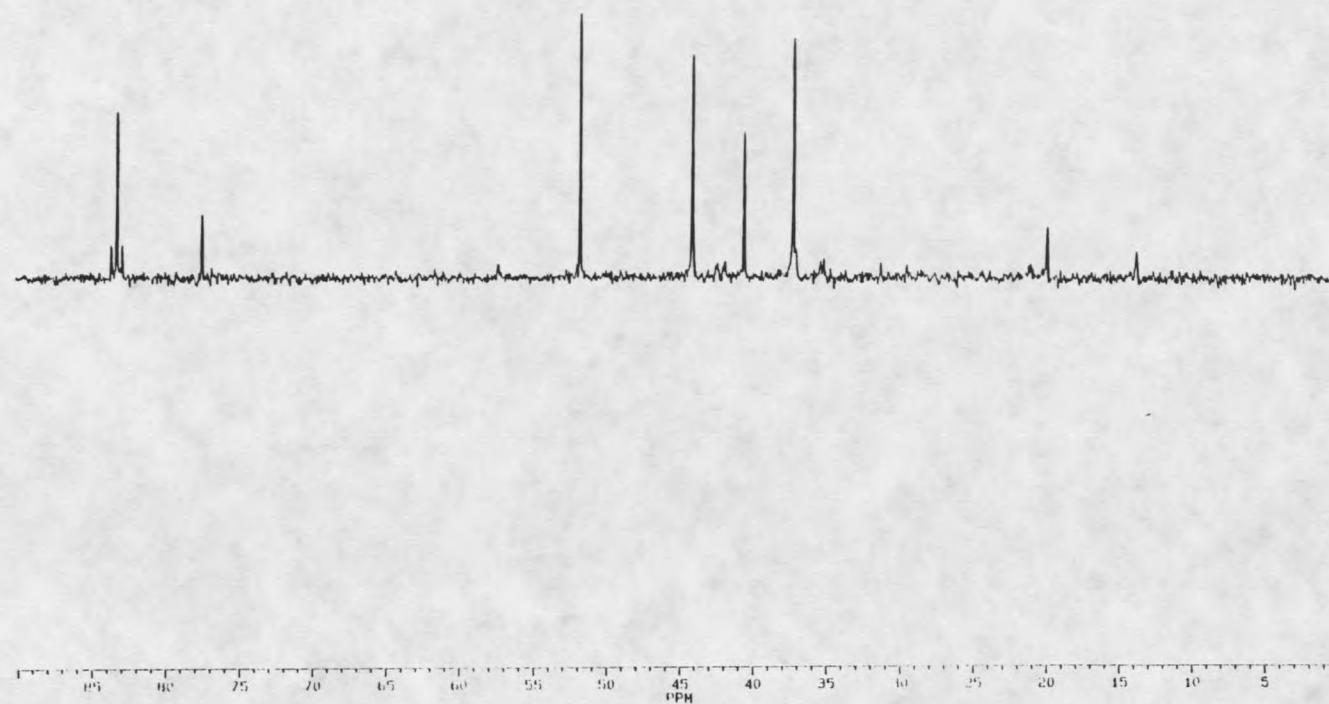


Figure 158. ^{13}C DEPT 90 Spectrum of Complex 105.

The ring expansion mechanism clearly does not seem to allow for the attachment of nitrogen. The exact reason for this is not understood but it might be possible that the amine will not deprotonate subsequent to the attachment to carbon-2 in a manner analogous to the oxygen containing instances.

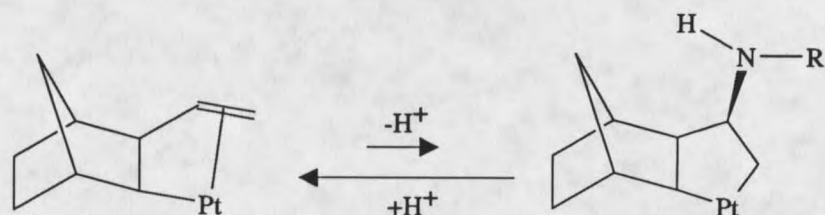


Figure 159. Model for Nitrogen Bonding.

An alternate pathway was envisioned. If an efficient leaving group could be attached to the ring at carbon-2, the site might be able to undergo nucleophilic substitution. Attachment of trifluoroacetate to the platinacyclopentane was achieved by treatment of complex **21** with trifluoroacetic acid in acetone. The resulting solution was allowed to stir for ten hours upon which it was neutralized with saturated sodium bicarbonate. Extraction of the aqueous solution with chloroform and rotoevaporation of the chloroform washes afforded the product, complex **106**, in 67% yield.

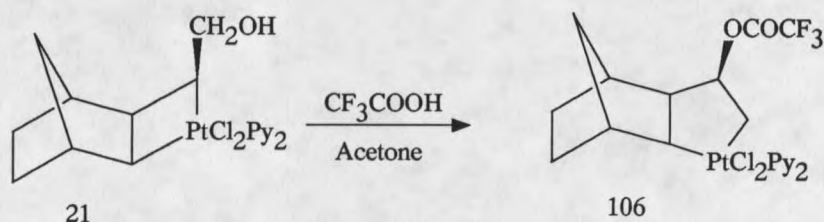


Figure 160. Synthesis of Complex **106**.

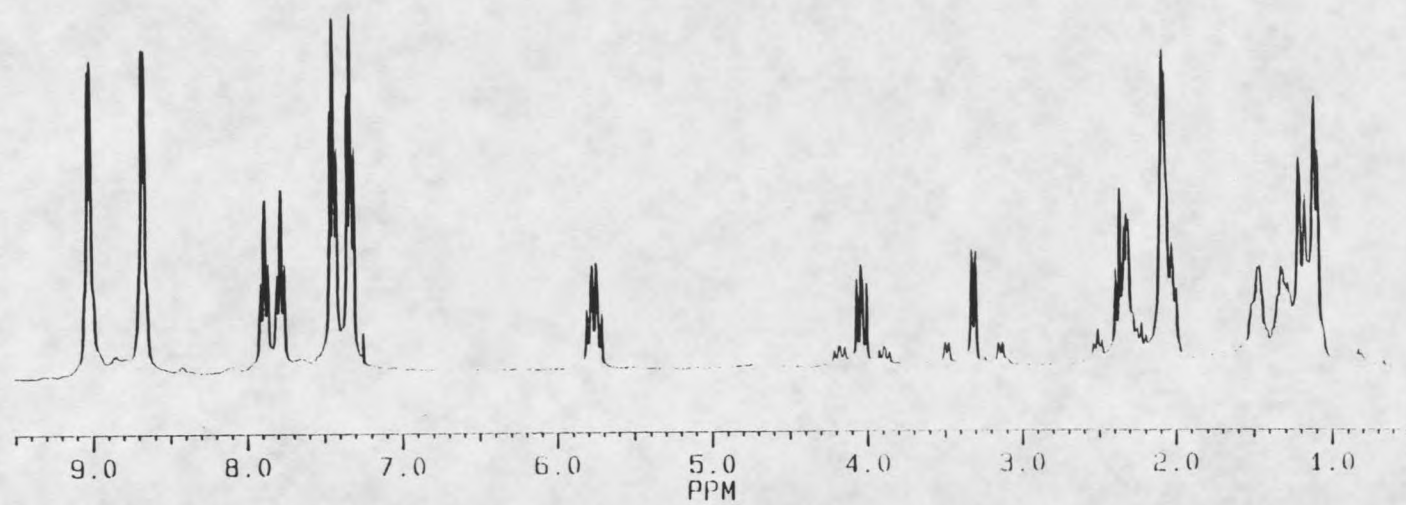


Figure 161. ^1H NMR Spectrum of Complex 106.

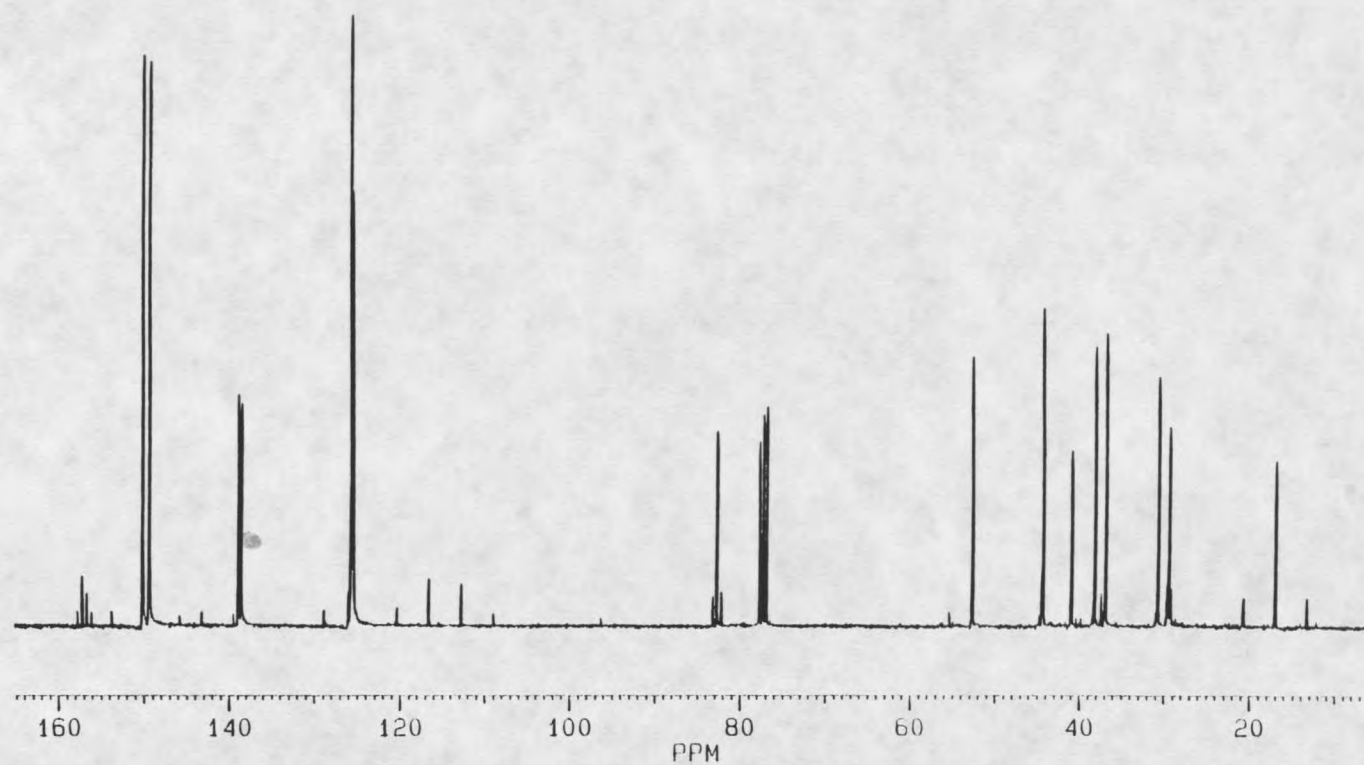
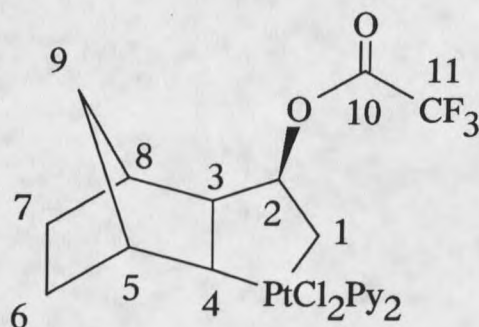


Figure 162. ^{13}C NMR Spectrum of Complex 106.



106

Table 33. ^{13}C NMR Data for Complex 106.

Carbon	^{13}C NMR ppm ($J_{\text{Pt-C}}$) [$J_{\text{F-C}}$]	Multiplicity (DEPT)
1	16.8 (557)	CH_2
2	82.4 (75.5)	CH
3	52.3	CH
4	40.7 (528)	CH
5	44.1	CH
6	29.2 (32)	CH_2
7	30.5	CH_2
8	37.9	CH
9	36.6	CH_2
10	156.7 [41.8]	-
11	114.1 [288]	-

To test the effectiveness of this leaving group on the ring, complex **106** was allowed to reflux in tetrahydrofuran with seven equivalents of sodium azide. After twelve hours at reflux, the solvent was removed from the mixture and the residue was dissolved in chloroform- d_1 and studied by ^1H NMR spectroscopy. Two new complexes were observed. The ^{13}C NMR data implied conservation of the norbornyl substrate and

the five-membered ring and the resonances attributable to the ring carbons are presented in Table 34. The platinum-carbon coupling constants are of most importance. The differences in their magnitudes, from previous experience, suggest azide substitution for chlorine on the metal.

Table 34. ^{13}C NMR Data for the Ring Carbons in the Reaction of **106** with NaN_3 .

Carbon	Complex 107 ^{13}C NMR ($J_{\text{Pt-C}}$)	Complex 108 ^{13}C NMR ($J_{\text{Pt-C}}$)
1	19.1 (556)	24.7 (623)
2	65.4 (59)	66.5 (79)
4	43.2 (533)	42.7 (556)

It was judged that an excess of sodium azide was the cause for multiple product formation so the amount was reduced to 1.1 equivalents. It was found that with a reduced amount of azide, only one product was formed corresponding to complex **107**. It was concluded that the trifluoroacetyl group had been displaced in favor of the azide.

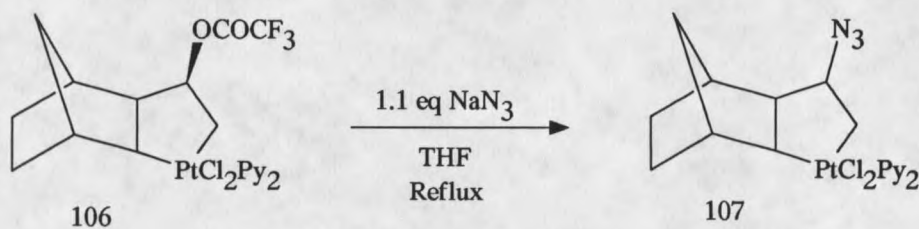


Figure 163. Reaction of Complex **106** with Sodium Azide (1.1 eq.)

The progression to complex **107** was monitored with respect to time and it was shown that a clean conversion of complex **106** to complex **107** was accomplished in sixteen hours as monitored by ^1H NMR spectroscopy.

Table 35. Conversion of **106** to **107** Monitored over Time

Time	% of Complex 106	% of Complex 107
3 Hours	52	48
16 Hours	0	100

Observation of the ^1H NMR spectrum of this new complex and comparison to complex **106** provides evidence of differing substitution at carbon-2. The proton associated with carbon-2 of complex **106** is found at 5.75 ppm. This resonance can be monitored to lose intensity as the complex is depleted. The corresponding resonance for complex **107** is found at 4.46 ppm. The significance of these values is that azide substitution on the metal would be expected to perturb the resonance in question, however, not by 1.3 ppm. This suggests substitution at carbon-2.

The ^{13}C NMR spectrum also appeared to support the conclusion drawn from the ^1H spectrum. The resonance attributable to carbon-2 of complex **106** is found at 82.4 ppm while the corresponding resonance for complex **107** was observed at 65.4 ppm. Again, this deviation is much larger than would be expected for substitution at the metal. The chemical shift of carbon-2 complex **107** is also indicative of the substitution. Substitution of trifluoroacetyl for azide should result in a upfield shift reflecting the increased shielding that would exist for a carbon bonded to an azide. This is observed and a chemical shift of 65.4 ppm is consistent with a carbon attached to a nitrogen.

One issue that needs to be addressed here is the stereochemistry of the azide. This is important from a standpoint of mechanism. If the azide were found to be syn, meaning that the stereochemistry was retained from the trifluoroacetyl complex, this would seem to indicate that the transformation occurred through a metal-olefin intermediate. Inversion of stereochemistry, meaning anti substitution, would suggest that the mechanism involves an S_N2 type displacement. Observation of only one substituted complex eliminates an S_N1 mechanism where the stereocontrol would be lost.

Determination of the stereochemistry was made by measurement of proton-proton coupling constants obtained from selected 1D homonuclear decoupling experiments.

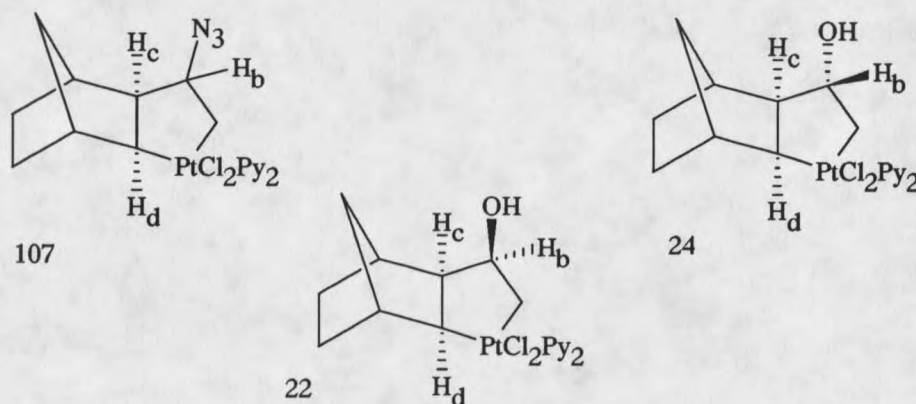


Table 36. Coupling Constant Data for Complexes 107, 22, and 24.

Complex 107	Complex 22	Complex 24
$J_{H_b-H_c} = 9.97 \text{ Hz.}$	$J_{H_b-H_c} = 8.21 \text{ Hz.}$	$J_{H_b-H_c} = 9.39 \text{ Hz.}$
$J_{H_c-H_d} = 8.63 \text{ Hz.}$	$J_{H_c-H_d} = 8.40 \text{ Hz.}$	$J_{H_c-H_d} = 7.63 \text{ Hz.}$

By comparison, it was concluded that the substitution on carbon-2 was inverted giving the anti-platinacyclopentane. This suggests that the mechanism of the

substitution was an S_N2 process. This is significant because first it represents the first formation of carbon-nitrogen bonds in these systems, and second, the mechanism by which the substitution occurs is novel to these complexes. Proton and ^{13}C NMR spectra for complex **107** are shown in Figures 165 and 166 respectfully. The conversion of complex **106** to complex **107** after six hours of reflux is displayed in the ^1H NMR spectrum shown in Figure 167.

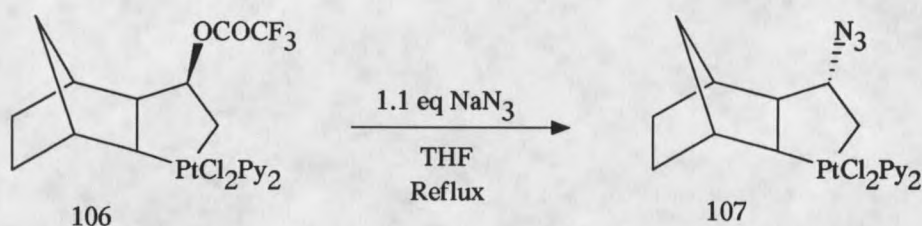


Figure 164. Reaction of Complex **106** with Sodium Azide (1.1 eq.).

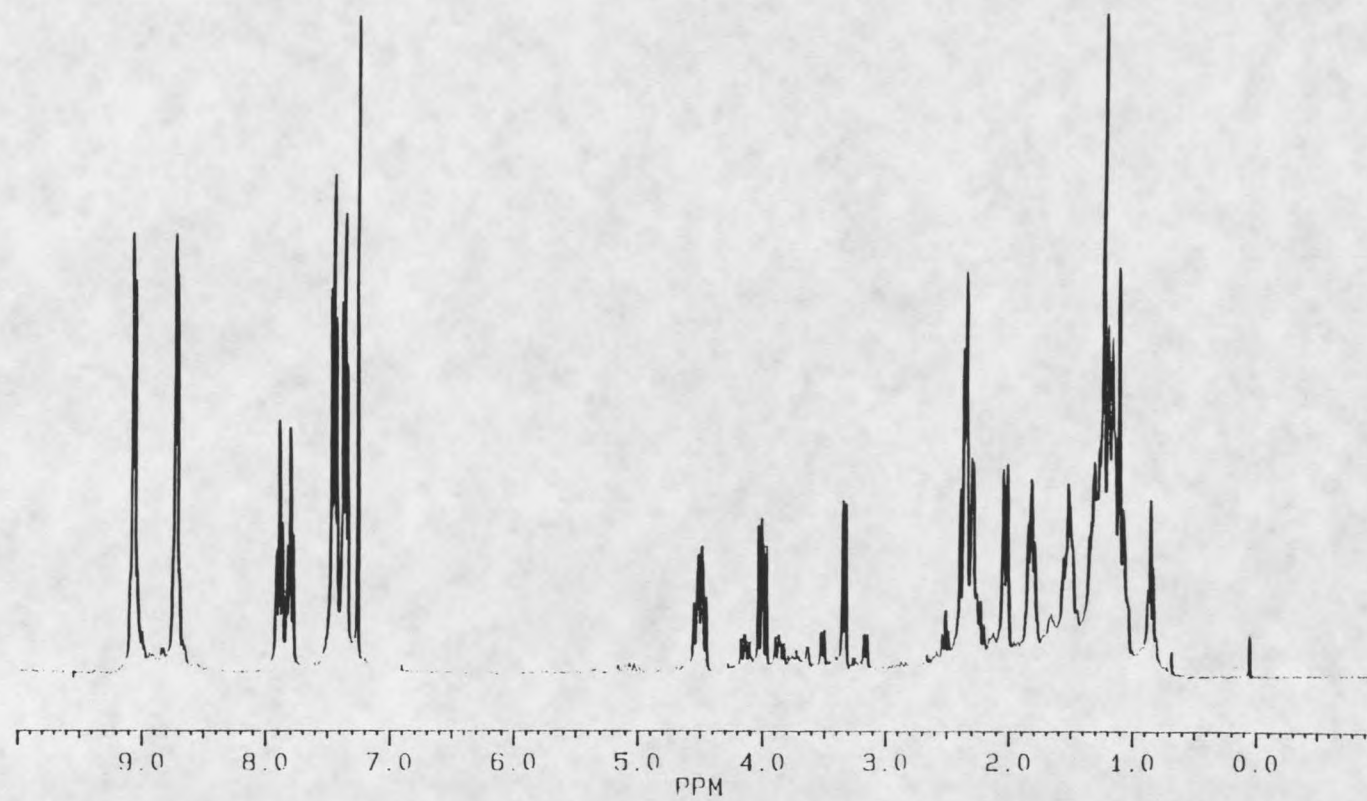


Figure 165. ^1H NMR Spectrum of Complex 107.

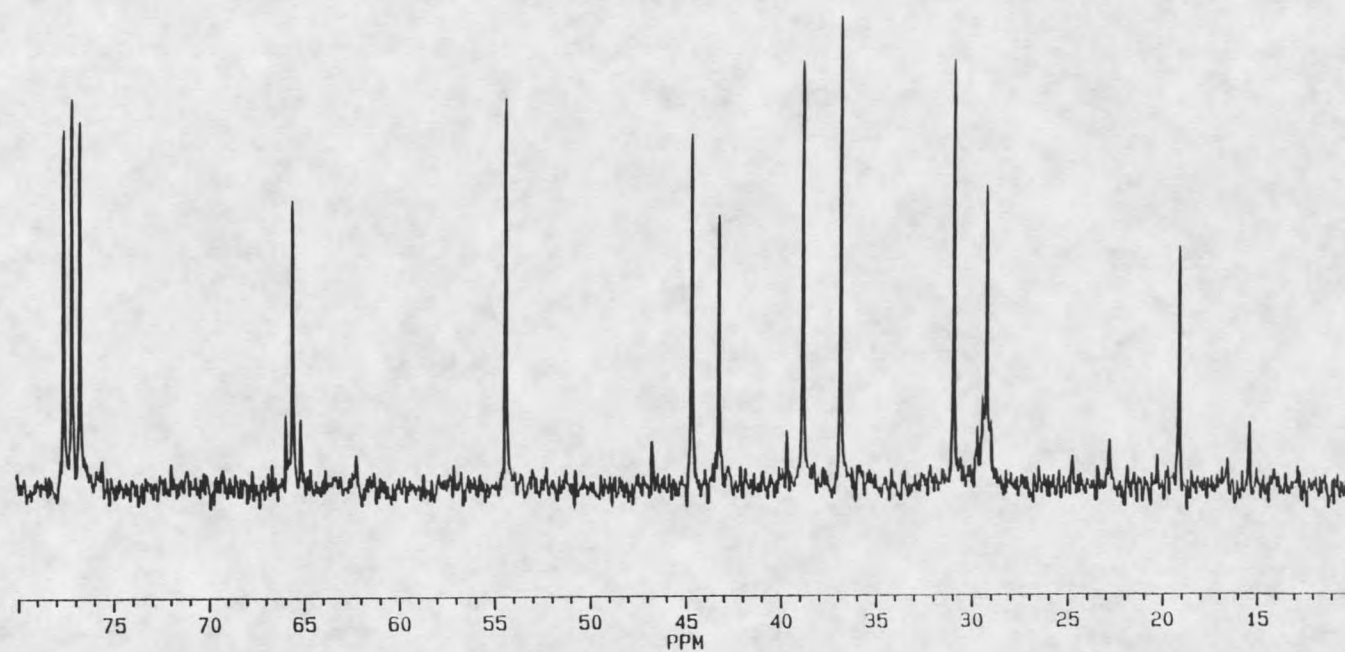


Figure 166. ^{13}C NMR Spectrum of Complex 107.

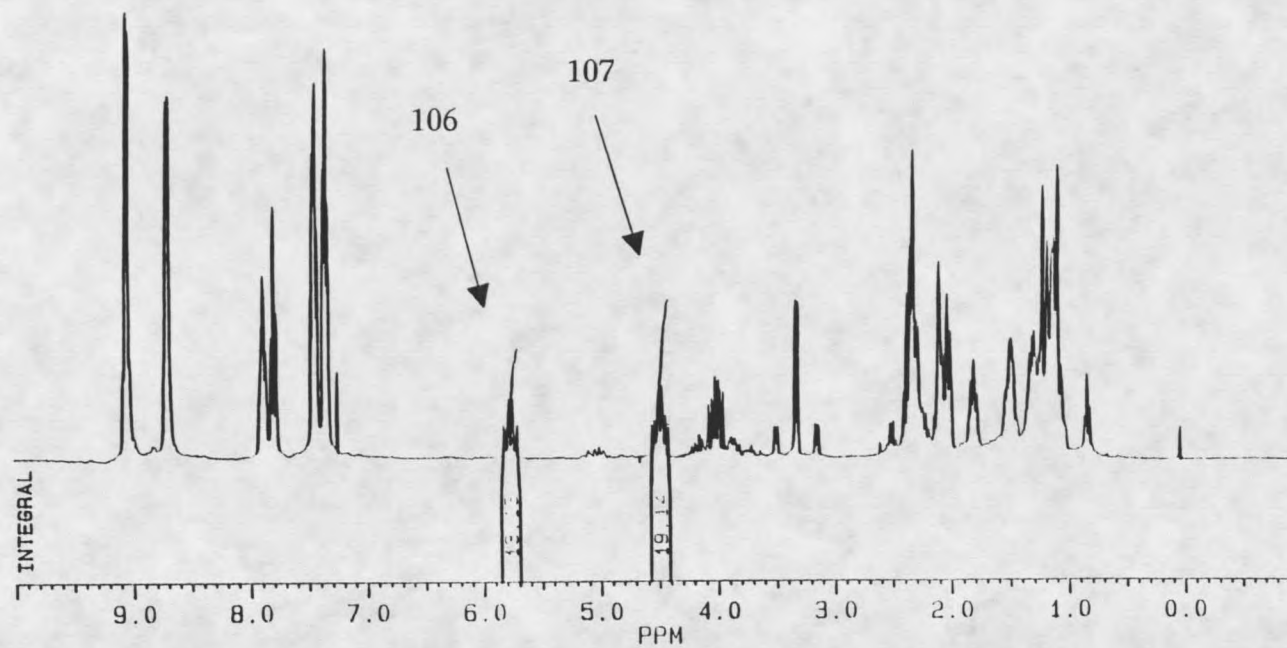


Figure 167. ^1H NMR Spectrum of Complexes **106** and **107** after Six Hours at Reflux.

Ligand Substitution Processes

Until this point, this thesis has dealt with accessing chemistry of platinum(IV) metallacycles using charged species. Treating these complexes with neutral ligands also offers a route that can lead to new complexes and organic products of interest.

Reaction of Complex 22 with Bipyridine

Bipyridine is a bidentate ligand that would be expected to chelate to the metal and halt any additional processes that may originate at this point. Treatment of 150 milligrams of complex 22 in twenty milliliters of chloroform with one equivalent of bipyridine does yield the expected chelate, 60.

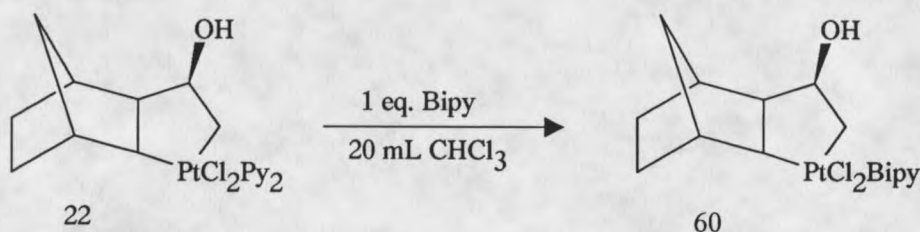
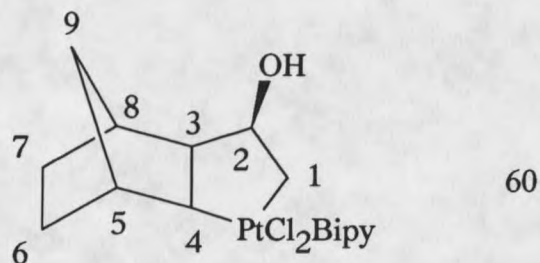


Figure 168. Reaction of Complex 22 with Bipy in 20 mL of CHCl_3 .

Modification of this experiment by reducing the solvent volume to one milliliter gave a different result. The outward appearance of the chelation experiment, in twenty milliliters of solvent, changed very slightly over twelve hours. The color deepened and no precipitate was evident. The reduced volume experiment, on the otherhand, within

Table 37. ^{13}C NMR Data for Complex **60**.

Carbon	^{13}C NMR ppm ($J_{\text{Pt-C}}$)
1	22.2 (547)
2	75.2
3	53.9
4	43.8 (536)
5	43.6
6	30.9
7	28.7
8	37.0
9	37.2

twenty minutes, turned orange and cloudy. The orange precipitate was attributed to the formation of bis-pyridylplatinum(II) dichloride and was verified by proton NMR spectroscopy. The precipitate was removed by filtration and analysis of the chloroform revealed two products. Trituration of the chloroform solution precipitated one of the products, complex **60**. Removal of solvents from the washings gave a yellow oil that was determined to be compound **109**. The best yield of organic material, 65%, was obtained by reflux of the initial reaction solution.

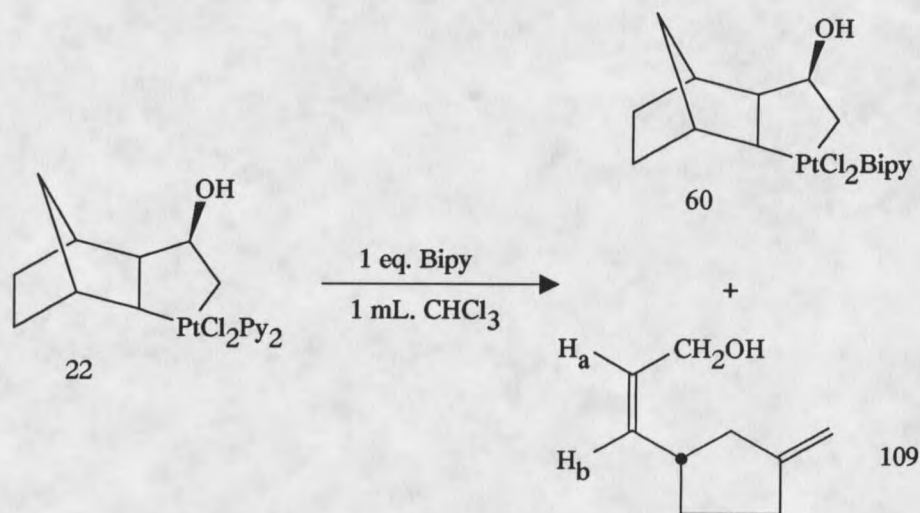


Figure 169. Reaction of Complex 22 with Bipy in One mL of CHCl_3 .

Mass spectral analysis of compound **109** gave a molecular ion peak at $m/e=138$. This is appropriate for this compound. The presence of an exocyclic methylene was established by ^{13}C NMR CPD and DEPT experiments that indicated a quaternary carbon at 151.8 ppm and a methylene at 105.4 ppm. The stereochemistry of the olefin was garnered through measurement of the coupling constant between H_a and H_b , Figure 169. This value was found to be 10.97 Hertz, which corresponds to *cis* stereochemistry.

The formation of both **109** and the chelate **60** suggest that decomposition of the platinacycle occurs only when one-half of the bipyridine is coordinated. The chelate, **60**, may be synthesized cleanly as described earlier and was shown not to decompose upon two days at reflux. This suggests that once the chelate is formed, no further chemistry can occur.

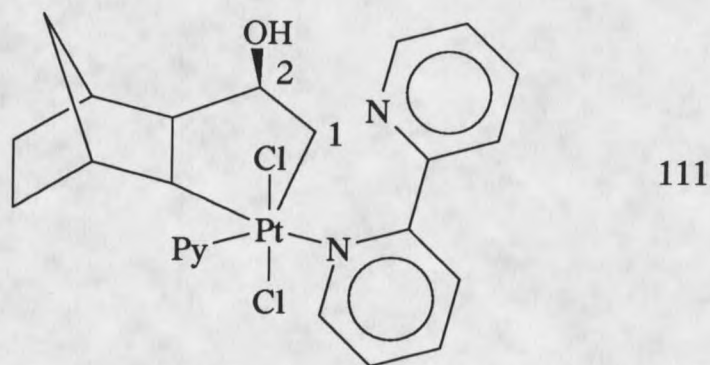


Figure 170. Proposed Intermediate in the Synthesis of Compound **109**.

To form product **109**, the hydroxyl moiety must be transferred from carbon-2 to carbon-1. To undergo this, either a proton must be removed from carbon-1 or the platinum-carbon-1 bond must be cleaved. The possibility existed for the free half of the bipyridine to orient itself in such a manner as to remove a proton from carbon-1. Reflux of complex **22** with excess pyridine gives no formation of compound **109**. The excess pyridine serves as a source of base and the lack of product formation suggests that a proton is not removed in the transformation.

Another possibility could be the steric bulk of the uncoordinated half of the bipyridine inducing the cleavage of the platinum-carbon-1 bond. To test this notion, complex **22** was allowed to reflux with excess 2-phenylpyridine. This ligand accurately simulates the steric bulk of bipyridine but is mono-dentate. Again, no formation of compound **109** was detected. This suggests that an additional electron donor on the ligand is required.

In a further attempt to probe the reaction, complex **22** was stirred at reflux in the presence of excess 1,10-phenanthroline. This ligand is a bipyridine analog that does not have the ability to rotate the bond between the rings. No product, compound **109**, was observed.

On the basis of these experiments, it is proposed that the bond between the metal and carbon-1 is cleaved followed by immediate coordination of the bipyridine. Cleavage

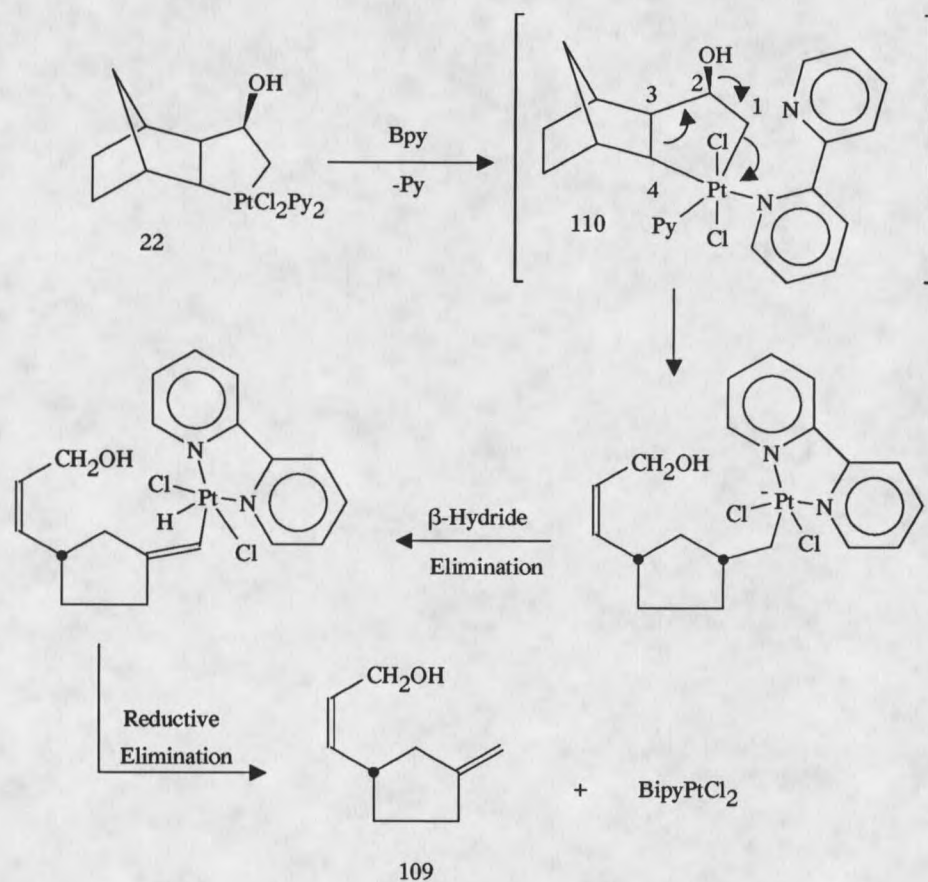


Figure 171. Proposed Mechanism for the Formation of Compound **109**.

of the bond initiates a cascade in which the hydroxyl group is transferred and the bond between carbons 3 and 4 are cleaved. The cleavage of this bond in particular provides an additional driving force because of the release of inherent norbornyl ring strain.

Reaction of Platinacyclopentane Complexes with Phosphorus Ligands

The reaction of platinacyclobutanes with trimethylphosphite has been previously established to give reductive elimination of the cyclopropane. The chemistry of platinacyclopentanes with trimethylphosphite has been largely unexplored. Treatment of complex **22** with five equivalents of trimethylphosphite was found to give the analogous bis-phosphite platinacycle in quantitative yield. Use of five equivalents was found to be necessary due to the competition for coordination sites with the pyridine. This was the minimum amount of trimethylphosphite that was found to give complete dissociation of the pyridine.

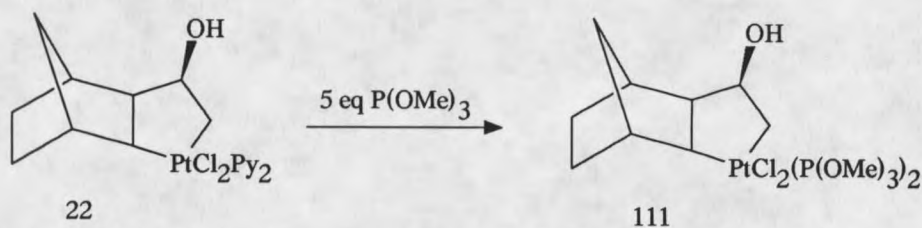
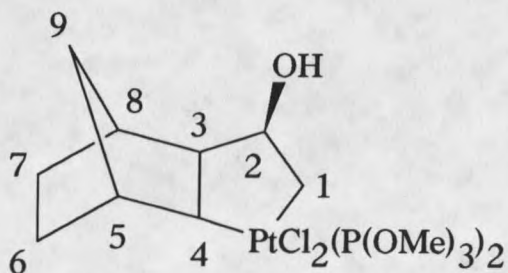


Figure 172. Reaction of Complex **22** with P(OMe)_3 .

To substantiate this claim, the new complex, **111** was studied by ^{13}C , ^{31}P , and ^{195}Pt NMR spectroscopy. The ^{13}C NMR spectrum, Figure 173, was a very complex set



111

Table 38. ^{13}C NMR Data for Complex 111.

Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	35.3	390	156	5.5
2	79.3	26.1	28.3	8.7
3	55.5			
4	52.9	375	158	3.3
5	43.2			
6	31.5	24.0	22.9	< 2
7	30.2			
8	37.0			
9	37.3			

Table 39. ^{195}Pt NMR Data for Complex 111.

111 ppm ($J_{\text{Pt-P}}$) Hz.	Standard
-3033 (2118) (1896)	$\text{K}_2\text{PtCl}_6 = 0$ ppm
1697	$\text{Na}_2\text{Pt}(\text{CN})_4 = 0$ ppm

 ^{31}P NMR Data for Complex 111.

Chemical Shift 88.3 ppm ($J_{\text{P-Pt}}=2118$ Hz.)
 99.4 ppm ($J_{\text{P-Pt}}=1896$ Hz.)

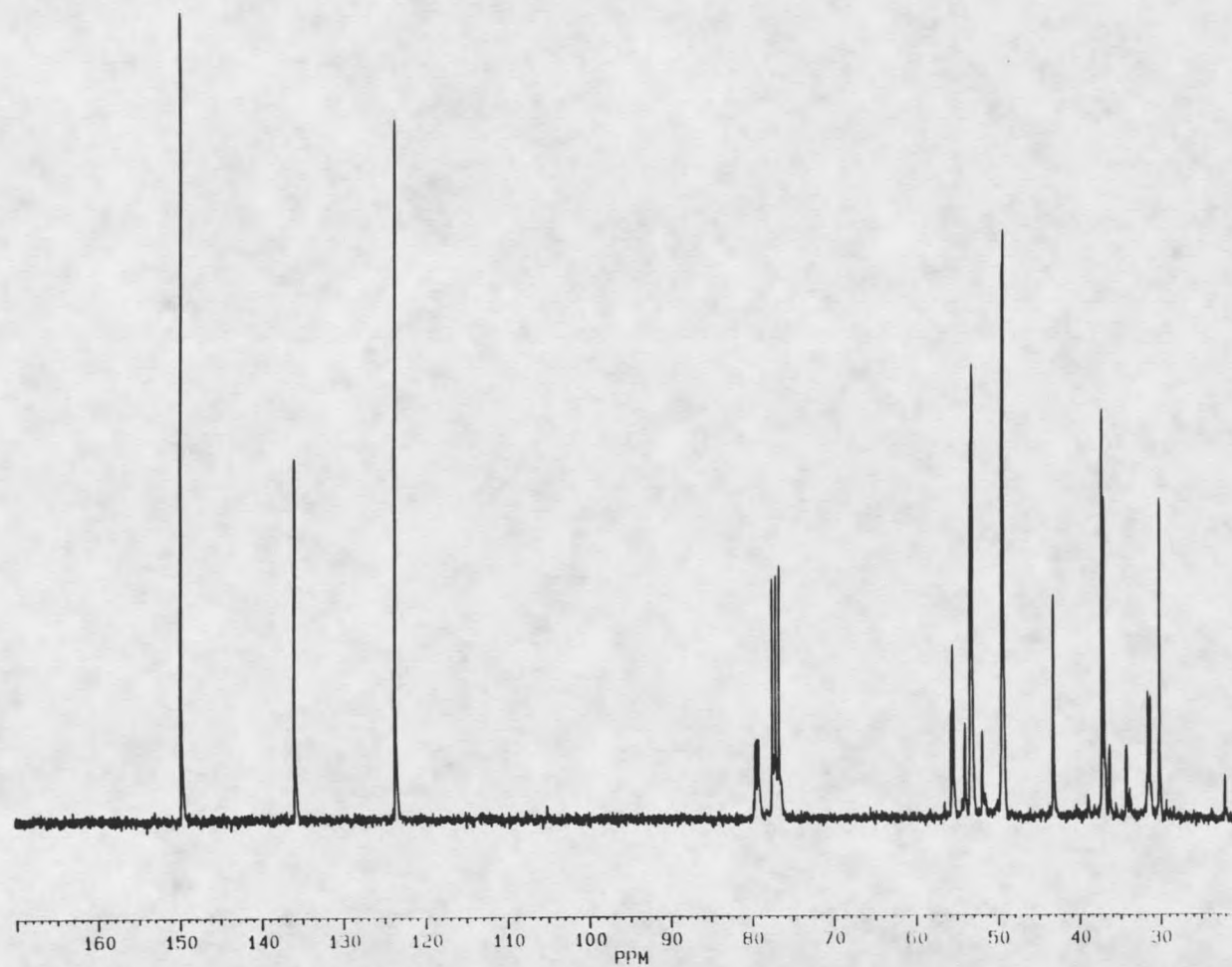


Figure 173. ^{13}C NMR Spectrum of Complex 111.

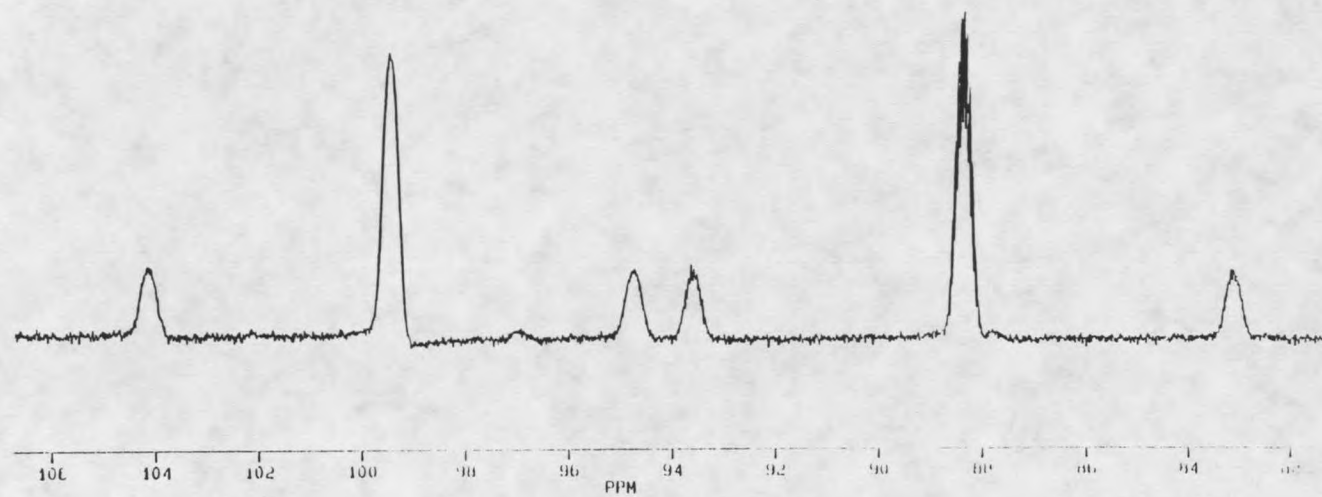


Figure 174. ^{31}P NMR Spectrum of Complex 111.

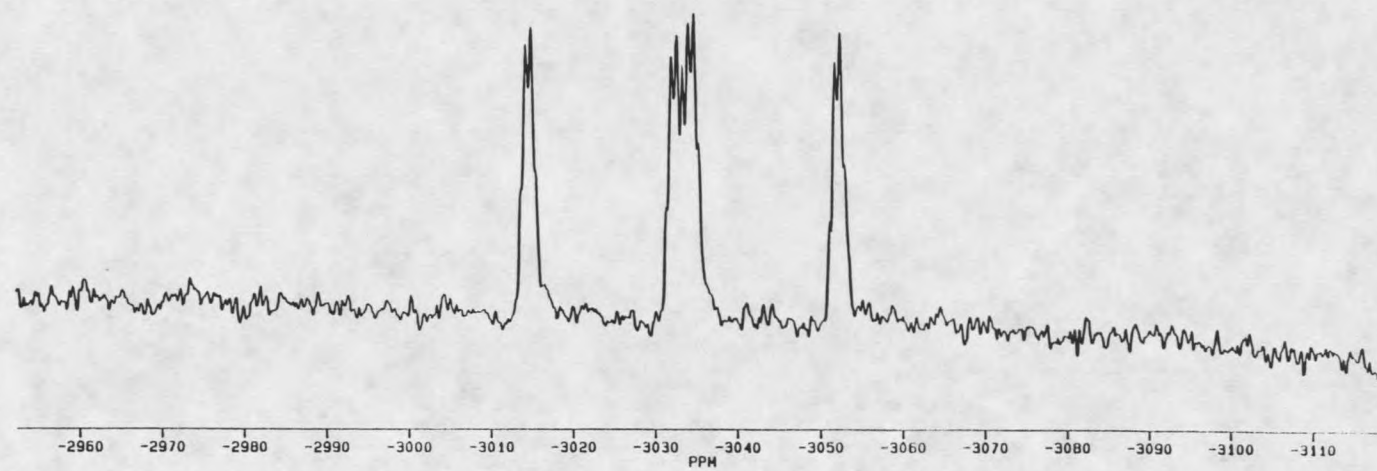


Figure 175. ^{195}Pt NMR Spectrum of Complex 111.

of resonances with many coupled to both platinum and phosphorus. The α -carbons reflect the most perturbation by the substitution. The chemical shifts are observed to move downfield approximately 10 ppm. The most dramatic change is observed in the platinum-carbon coupling constants. The coupling constants were significantly reduced from 550 Hertz for the pyridine complexes to less than 400 Hertz. The spectrum, however, was consistent with a norbornyl platinacyclopentane despite the deviations.

The ^{31}P NMR spectrum was obtained, Figure 174, and revealed the presence of two differing phosphorus ligands with coupling to platinum. This observed spectrum was expected for the proposed structure, complex 111. The magnitudes of the coupling to platinum, 2118 and 1896 Hertz, are indicative of ^1J coupling and these constants were observed to be mirrored in the ^{195}Pt NMR spectrum.

Study of the ^{195}Pt NMR spectrum, Figure 175, revealed the resonance attributable to this complex as a doublet of doublets. This is the expected multiplicity for a platinum complex with phosphorus ligands that are magnetically unequal.

An additional impetus to study this complex using ^{195}Pt NMR spectroscopy is provided by the fact the chemical shift is indicative of the oxidation state of the metal. Using sodium tetracyanoplatinate as the standard, platinum(II) complexes can be found generally at 1000 ppm. On the otherhand, platinum(IV) complexes generally resonate at approximately 3000 ppm. Complex 22 was studied using this technique and its chemical shift was measured at 2830 ppm, strongly a platinum(IV) complex. The observed chemical shift for complex 111, however, is located at 1697 ppm. This would seem to indicate increased shielding on the metal.

The Chemistry of Trimethylphosphite
Substituted Complexes

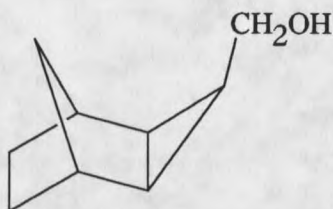
The NMR studies of complex **111** were accomplished in excess trimethylphosphite. Using five equivalents of trimethylphosphite gave the highest yield of the substituted complex. This solution in chloroform was refluxed for 24 hours and no decomposition was observed. However, removal of the excess phosphite was found to initiate the immediate decomposition of the complex. The decomposition was found to be hastened by refluxing chloroform giving a good yield of one organic product in approximately one hour. Precipitation of the platinum was accomplished by trituration of the chloroform solution with pentane. A white complex was obtained and was identified as bis(trimethylphosphite)platinum(II) dichloride using ^{195}Pt NMR spectroscopy.

The liberated organic material was isolated by chromatography of the pentane washings on a short silica gel column. The residue, a pale yellow oil, was studied by GC-MS and the molecular ion was found to be $M/Z=138$. High resolution mass spectrometry was employed to give an elemental composition. Due to the lack of intensity of the molecular ion, a reagent gas, ammonia, was utilized. The observed molecular ion using this procedure concurred with the elemental composition of $\text{C}_9\text{H}_{14}\text{O}$, the elemental formula for the substrate.

Table 40. High Resolution MS Data for the Evolved Organic Compound.

High Res. MS Data	M/Z
Calculated for $C_9H_{14}O \cdot NH_4$	156.1388
Found	156.1383

The elemental composition is consistent with the cyclopropane shown below. However, 1H and ^{13}C NMR spectroscopy indicated that the product was not the cyclopropane. The key evidence was the apparent lack of symmetry in the new compound, nine unique resonances were observed by ^{13}C NMR spectroscopy. One



would only expect six resonances for the symmetrical cyclopropane. This new compound was determined to be a cyclobutyl alcohol, **112**. This judgement was made from the ^{13}C NMR Data, both CPD and GATED were obtained. A summary of the ^{13}C NMR data is shown in Table 41.

Multiplicities of the carbon were obtained using DEPT 90 and 135 experiments. These conclusions were further supported by a proton-coupled GATED spectrum of the compound. Using this technique, ^{13}C - 1H coupling constants may be measured. Cyclobutanes have unique coupling of a magnitude of 134 Hertz and measurement of

the coupling for the methylene carbon-1 revealed the constant to be 134 Hertz. It was concluded that the bis-trimethylphosphite complex had undergone reductive elimination to give the cyclobutane, Figure 176. Carbon-13 NMR data for the cyclobutane, **112**, is shown in Table 41.

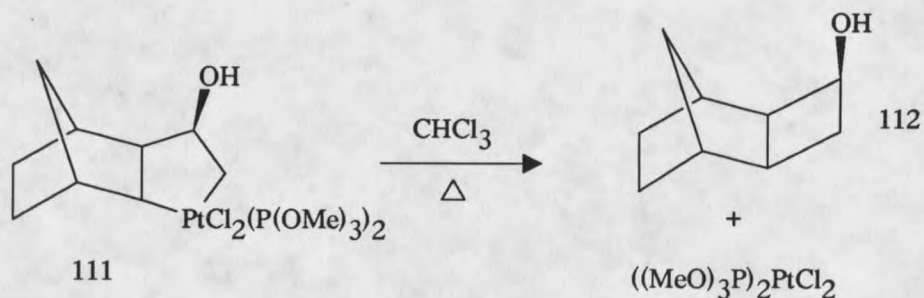
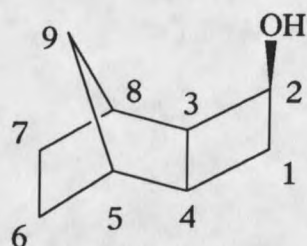


Figure 176. Decomposition of Complex **111**.

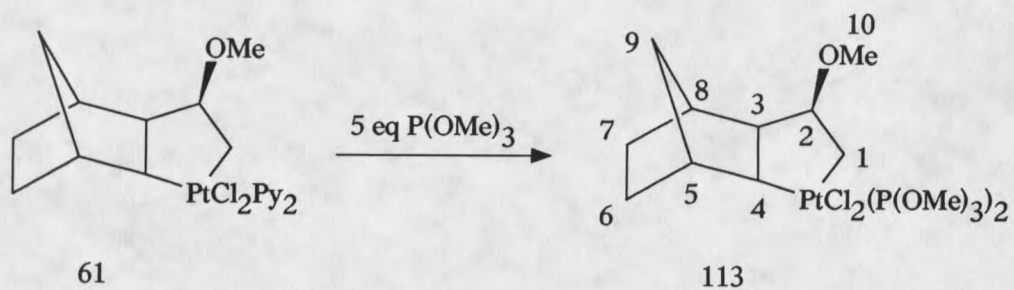
This is a significant process since it represents a general synthesis of cyclobutanes with stereospecific functionality. To demonstrate the versatility of the transformation, the bis-trimethylphosphite analogs of other platinacyclopentanes were prepared. The reactions were performed in a manner consistent with methodology previously presented, five equivalents of ligand in chloroform at room temperature.



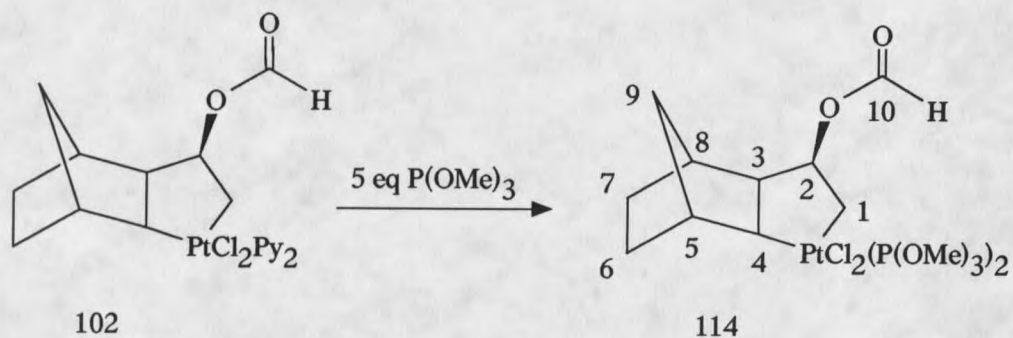
112

Table 41. ^{13}C NMR Data for Compound 112.

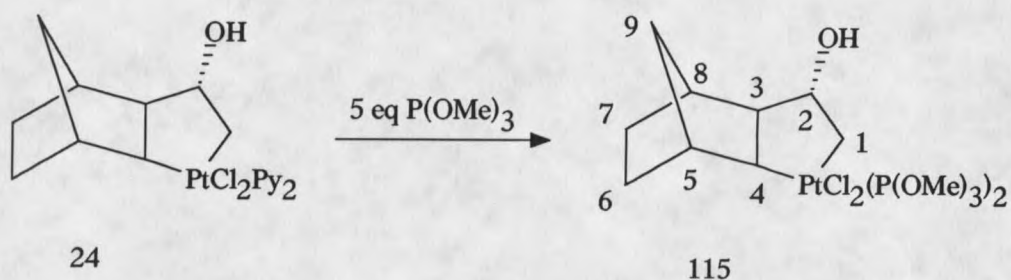
Carbon	112 ppm	multiplicity ($J_{\text{C-H}}$) Hz.
1	34.5	CH_2 (134)
2	66.9	CH (148)
3	48.9	CH (141)
4	39.4	CH (143)
5	34.6	CH
6	28.0	CH_2
7	28.3	CH_2
8	35.4	CH
9	34.0	CH_2

Table 42. ^{13}C NMR Data for Complex 113.

Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	29.3	400	156	5.2
2	85.4	38.4	25.7	4.9
3	51.4			
4	49.3	373	156.8	4.1
5	43.3			
6	30.5	25.1	22.7	< 2
7	31.0			
8	36.9			
9	36.8			
10	57.3			

Table 43. ^{13}C NMR Data for Complex **114**.

Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	27.0	399	161.3	5.5
2	80.1	48	27.3	4.3
3	51.7			
4	48.0	374	157.4	3.3
5	43.0			
6	30.1	22.5	22.5	< 2
7	30.4			
8	37.7			
9	36.4			
10	160.7			

Table 44. ^{13}C NMR Data for Complex 115.

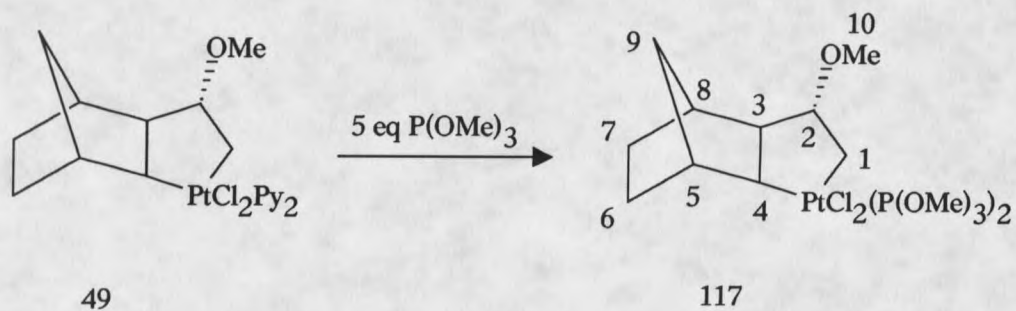
Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	36.3	375	152.6	4.8
2	80.2	32	28.9	6.4
3	59.8			
4	47.7	363	161.1	4.6
5	44.4			
6	33.5	20.9	20.9	< 2
7	27.9			
8	39.1			
9	36.6			

Table 45. ^{195}Pt NMR Data for Complex 115.

115 ppm ($J_{\text{Pt-P}}$) Hz.	Standard
-3024 (2158) (1930)	$\text{K}_2\text{PtCl}_6 = 0 \text{ ppm}$
1706	$\text{Na}_2\text{Pt}(\text{CN})_4 = 0 \text{ ppm}$

 ^{31}P NMR Data for Complex 115.

Chemical Shift 88.6 ppm ($J_{\text{P-Pt}}=2158 \text{ Hz.}$)
 99.4 ppm ($J_{\text{P-Pt}}=1930 \text{ Hz.}$)

Table 46. ^{13}C NMR Data for Complex 117.

Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	32.8	381	154	5.9
2	88.2	32	28.7	5.2
3	58.5			
4	47.4	365	160.7	4.8
5	44.6			
6	33.6	23.0		
7	27.8			
8	39.2			
9	36.6			
10	54.7			

As with complex **111**, these other substituted complexes were studied in an environment of excess ligand. Removal of the excess was found to cause a analogous decomposition giving the substituted cyclobutanes, Figure 177.

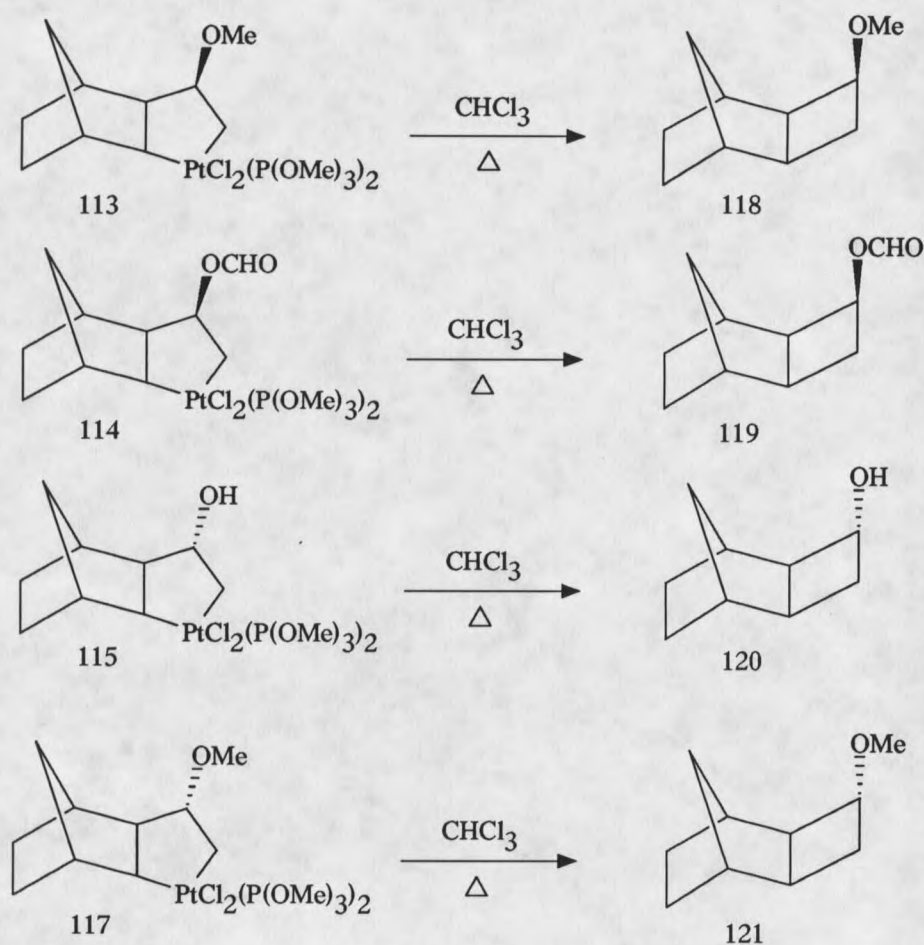
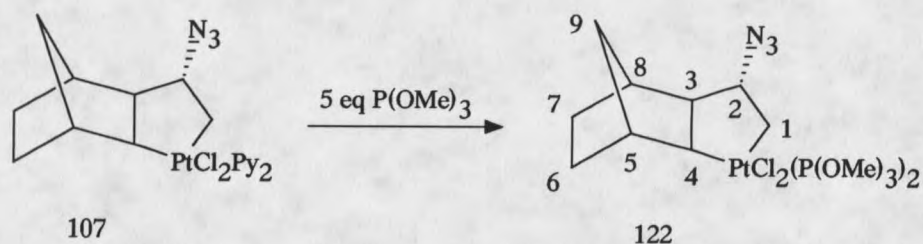


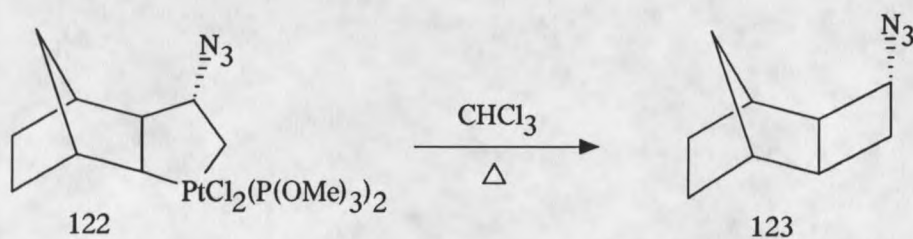
Figure 177. Decomposition of Bis-Substituted Platinacyclopentanes.

Complex **107** was also observed to react with trimethylphosphite forming the analogous adduct. The ^{13}C NMR spectral data, Table 47, is consistent with this determination.

Table 47. ^{13}C NMR Data for Complex 122.

Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	27.2	361	162	5.8
2	67.3	41.3	27.4	6.3
3	49.4			
4	49.8	497	159	3.3
5	44.4			
6	30.1	23.4	22.6	< 2
7	30.8			
8	38.2			
9	36.6			

Removal of excess ligands and reflux of the residue in chloroform gave the cyclobutane, **123**, in quantitative yield by NMR spectroscopy. The significance of this transformation is that the cyclobutane was formed with stereospecific azide substitution and is a precursor to amines.



Reaction of Complex 22 with Tri-n-butylphosphine

The reaction of complex 22 with tri-n-butylphosphine was conducted in a similar manner as the reactions involving trimethylphosphite, five equivalents in chloroform. The resulting adduct was studied by ^{13}C , ^{31}P , and ^{195}Pt NMR spectroscopy. The ^{13}C data is presented in Table 48 and is consistent with a platinacyclopentane. The ^{31}P spectrum

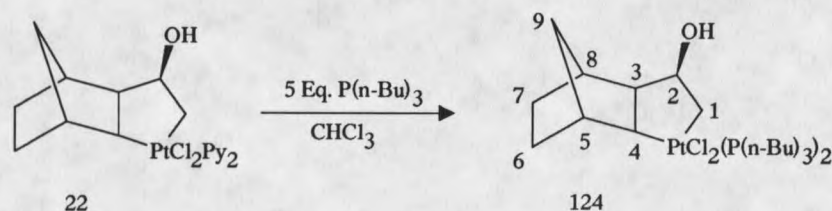


Table 48. ^{13}C NMR Data for Complex 124.

Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	35.4	427	106	< 2
2	77.8	35	19.3	4.8
3	54.3			
4	47.6	403	113	< 2
5	37.0			
6	31.1	< 2	14.5	< 2
7	30.7			
8	43.0			
9	36.9			

confirmed the presence of two phosphorus ligands in differing magnetic environments on the metal. The ^{195}Pt spectrum of this molecule indicates one resonance split into a

doublet of doublets. The chemical shift of this resonance was found at -2043 ppm relative to K_2PtCl_6 . A comparison of this value to that found for the trimethylphosphite analog is warranted. The relative electron donating and accepting properties of phosphorus ligands were studied by Tolman⁸³. In this paper, correlations of relative electronic properties were made with respect to infrared carbonyl stretching frequencies in Nickel(0) complexes. More electron donating phosphines are shown to move the carbonyl stretching frequencies to lower wavenumber. Phosphorus ligands that do not donate as strongly move the frequency to higher wavenumber.

In a further review⁸⁴ of this area, two factors influencing the chemistry of phosphorus containing metal complexes are the electronic effects, as previously described, and the cone angle of the phosphine/phosphite. The cone angle, Figure 178, is a measurement of the steric bulk of the ligand.

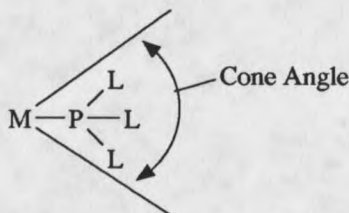


Figure 178. Measurement of Cone Angle for Phosphorus-Metal Complexes.

In the case of the platinacyclopentanes studies in this thesis, both electronic and steric effects must be taken into account. Table 49 gives cone angle values for various phosphorus ligands⁸⁴.

Table 49. Cone Angle Values for Various Ligands.

Ligand	Cone Angle (°)
P(n-Bu)_3	132
P(OMe)_3	107
PPh_3	145
P(OPh)_3	128

The basicity of these ligands fall in the following order: $\text{P(n-Bu)}_3 > \text{P(OMe)}_3 > \text{P(OPh)}_3$. Since trimethyl phosphite is less basic than tri-n-butylphosphine, it would be expected that the ^{195}Pt NMR resonance for the tri-n-butylphosphine adduct to be upfield, more shielded, and more electron rich. The net effect on the α -carbons, as observed using ^{13}C NMR spectroscopy, would be to lengthen the platinum-carbon bond and reduce the platinum-carbon coupling constants. In fact, the exact opposite is observed. By ^{195}Pt NMR spectroscopy, the trimethylphosphite adduct, **115**, reveals a more shielded metal center and this is mirrored in the platinum-carbon coupling constants. The values observed for the coupling constants are considerably less than those observed for the tri-n-butylphosphine analog, **124**.

Table 50. Comparison of ^{195}Pt NMR Data for Complexes **115** and **124**.

	115 , P(OMe)_3	124 , P(n-Bu)_3
^{195}Pt NMR Chemical Shift, ppm	-3033	-2043

The apparent reversal of what would be expected from electronic concerns is the embodiment of the cone angle influence. Trimethylphosphite has a cone angle of 107° which allows for more effective donation of electrons to the metal than what is observed for the more bulky tri-*n*-butylphosphine.

Reaction of Complex 22 with Triphenylphosphite

Triphenylphosphite was allowed to react with complex 22 in an analogous manner as the previous experiments. No displacement of pyridine was observed. Rationalization of this result is provided by both the steric and electronic nature of triphenylphosphite. The cone angle is 128° . This is less than what is indicated for tri-*n*-butylphosphine and alone does not explain the lack of coordination. Tolman⁸⁴ determined the basicity of triphenylphosphite to be relatively weak and this effect, combined with the large cone angle, work together to inhibit coordination.

Reaction of Complex 22 with Triphenylphosphine

Triphenylphosphine is a ligand with a very large cone angle, 145° . Steric influences should be overwhelming but its basicity is greater than that of trimethylphosphite. Complex 22 was allowed to react with five equivalents of triphenylphosphine at room temperature in chloroform. The solvent was removed after twelve hours stirring and the residue was studied. The ^1H spectrum was ambiguous. The ^{13}C NMR spectrum, on the otherhand, revealed only one α -carbon with coupling to phosphorus. Analysis of the obtained ^{195}Pt NMR spectrum revealed two doublets in a four to one ratio, Figure 179. The observed multiplicity, a doublet, suggests only one

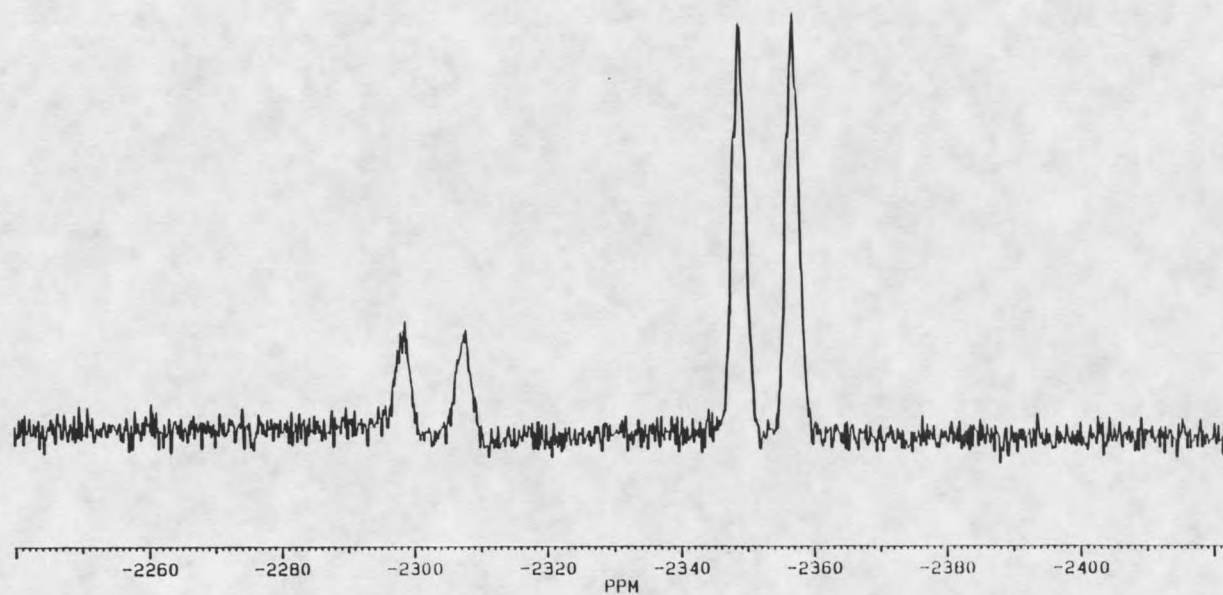


Figure 179. ^{195}Pt NMR Spectrum of Complexes 125 and 126.

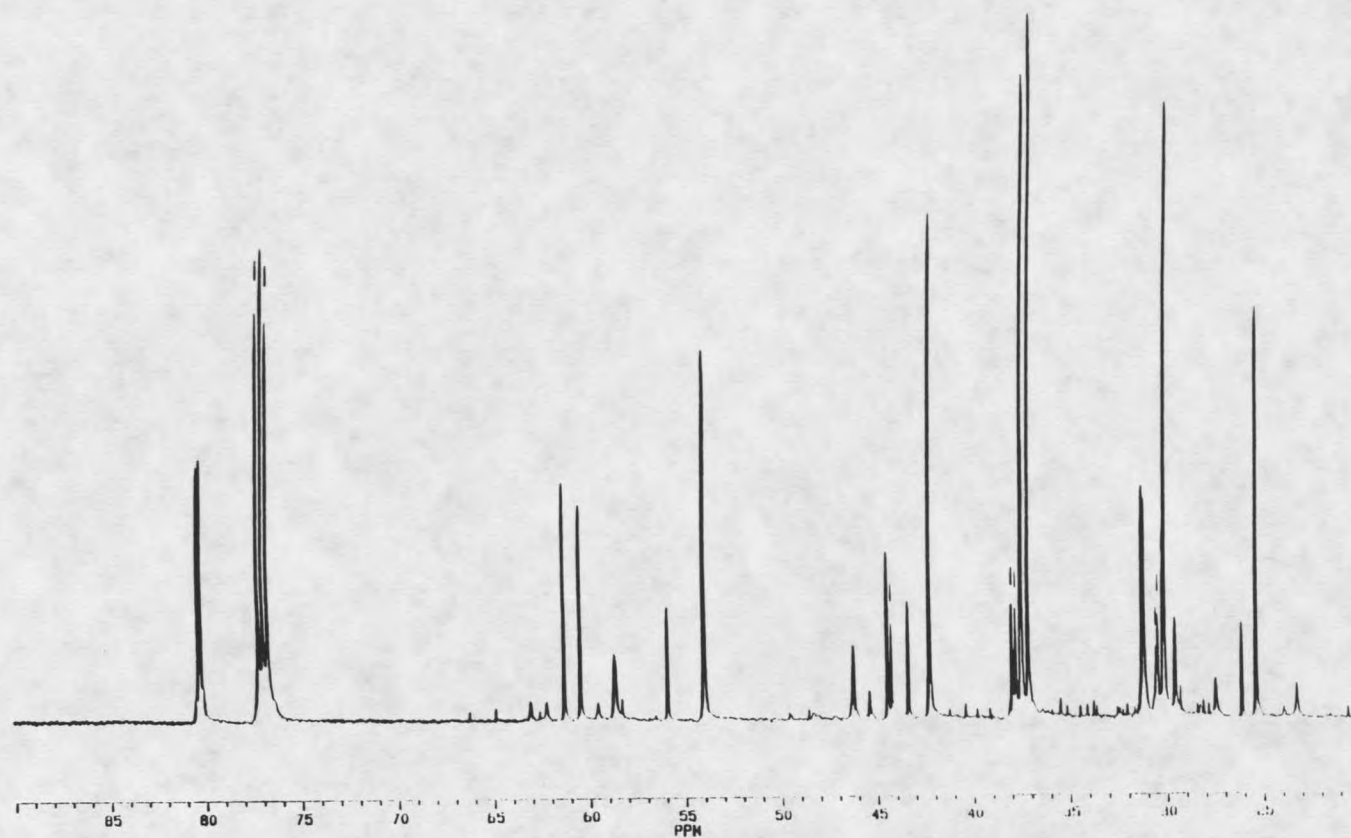


Figure 180. ^{13}C NMR Spectrum of Complexes 125 and 126.

coordinated phosphine. The difference in the intensities of the doublets suggests two different isomers, a major and a minor.

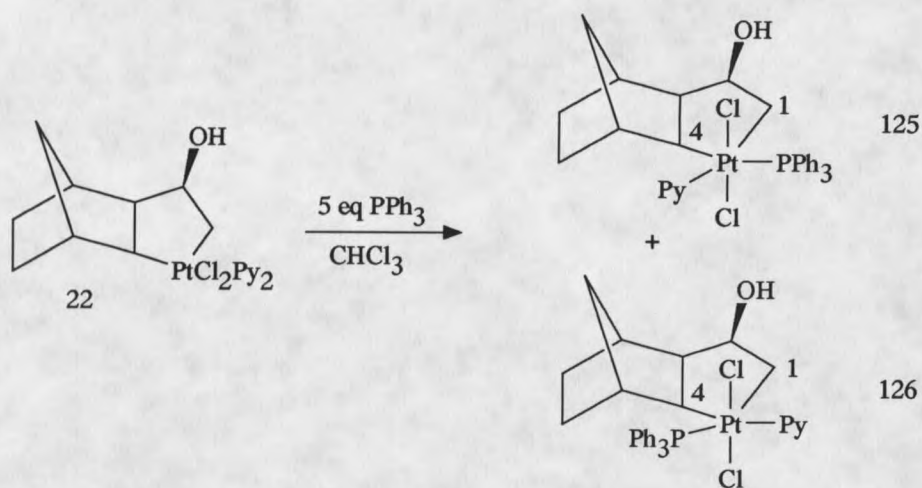
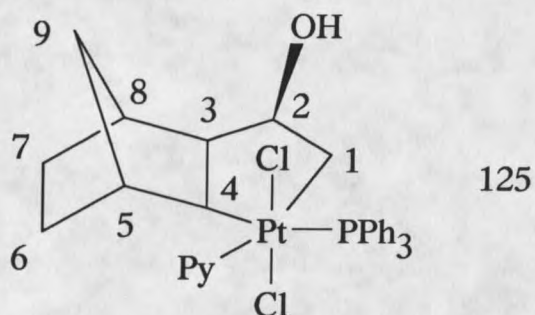


Figure 181. Reaction of Complex 22 with Triphenylphosphine.

A re-examination of the ^{13}C NMR spectrum, Figure 180, revealed low intensity resonances attributable, by chemical shift only, to the minor isomer. A DEPT 135 ^{13}C NMR experiment indicated that the α -carbon of the major isomer with phosphorus coupling was a methine. Coupling between NMR active nuclei is generally found to be greater trans across a metal than in one with a cis disposition. The conclusion drawn is that the phosphorus is trans to carbon-4, in the major isomer, as shown above, complex 125. Likewise, the minor isomer is assumed to be complex 126, with the phosphorus trans to carbon-1. This is only a presumed structure due to the lack of intensity of this complex in the ^{13}C NMR spectrum. The ^{13}C NMR data for complex 125 is shown in Table 51.

Table 51. ^{13}C NMR Data for Complex 125.

Carbon	ppm	$J_{\text{Pt-C}}$ Hz.	$J_{\text{P-C}}$ Hz.
1	25.4	529	
2	80.3	35	19.4
3	54.0		6.1
4	60.9	447	105
5	42.3		
6	31.2	14.5	13.7
7	30.2		
8	37.1		
9	37.5		

Removal of excess triphenylphosphine from these complexes was accomplished by trituration three times with 5% diethyl ether in pentane. After twelve hours of reflux of the residue in chloroform, complexes 125 and 126 completely disappeared and three compounds were formed. By precedent, these compounds were found to be the reductive-elimination product, the cyclobutanol, 112, the bis-pyridyl platinacyclopentane, 22, and bis-triphenylphosphine platinum(II) dichloride. The cyclobutane and the platinacyclopentane were identified by comparison to previously obtained ^1H and ^{13}C

NMR spectra. A ratio of these two products was determined to be 1:1 by integratable ^1H NMR spectroscopy.

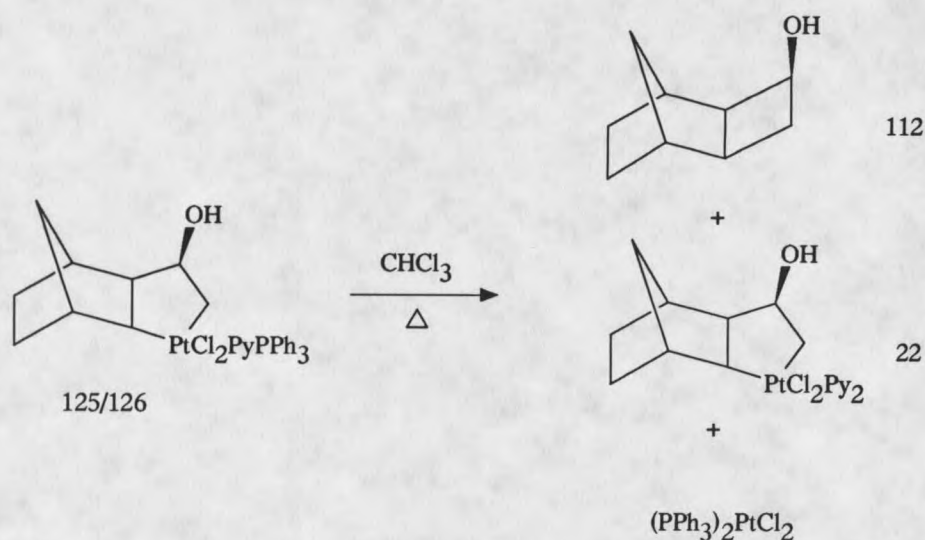
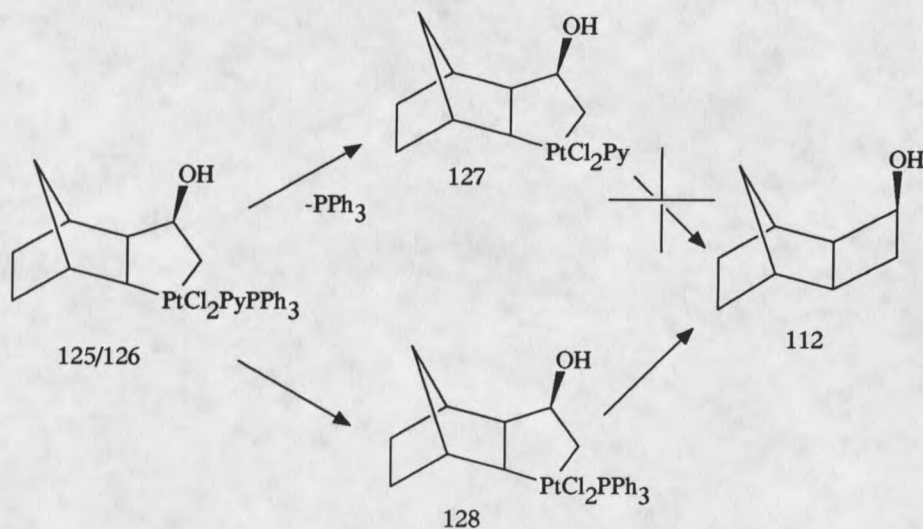


Figure 182. Decomposition of Complexes 125 and 126.

This is an intriguing result. It suggests that both pyridine and triphenylphosphine are labile and will dissociate and reassociate onto a different metal atom.

In the absence of phosphine or phosphite, complex **22** has never been shown to undergo reductive-elimination even though it is known that the pyridines readily dissociate in solution. This suggests that a five coordinate mono-pyridine complex, **127**, does not give reductive-elimination. Upon dissociation of the lone pyridine from either **125** or **126**, the mono-phosphine complex, **128**, is formed. This complex is thought to be the reactive species that initiates the reductive-elimination process. This is also



supported by the experiments presented earlier. The trimethylphosphite adducts were found to be stable in excess ligand while removal of the excess gave cyclobutane formation. Excess ligand competes for open coordination sites on the metal thus reducing the likelihood of a five-coordinate intermediate.

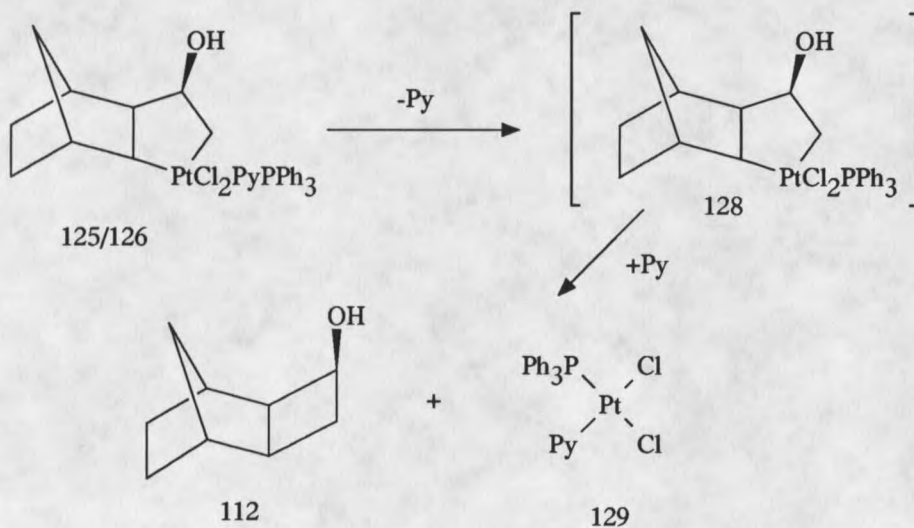


Figure 183. Proposed Decomposition Pathway for Complexes 125 and 126.

Formation of the bis-pyridyl complex, **22**, in this process was unexpected however it can be rationalized by the exchange of phosphine between the mono-phosphine complexes, **125** and **126**, and the platinum(II) residue from the reductive elimination.

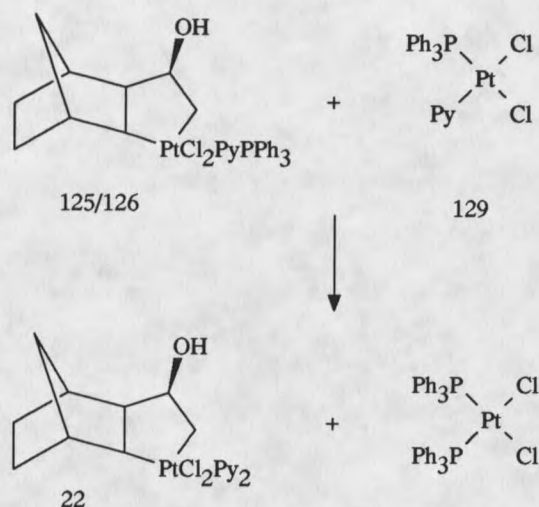


Figure 184. Proposed Exchange of Phosphine Between Complexes **125/126** and **129**.

Reaction of Complex **22** with
1,2-Bis(diphenylphosphino)ethane

The steric restraints that disallow coordination of two equivalents of triphenylphosphine were of interest. Reaction of complex **22** with 1,2-bis(diphenylphosphino)ethane (DPPE) would be an efficient test case to observe whether the steric restraints could be overcome by chelation. Treatment of complex **22** with DPPE was found to give the expected chelate in quantitative yield by NMR spectroscopy.

Table 52. ^{13}C NMR Data for Complex 130.

Carbon	ppm	J _{Pt-C}	J _{P-C}	J _{P-C}
1	36.2	405	112.4	
2	79.9		19.3	
3	55.6			
4	54.0	405		
5	37.4			
6	32.0			
7	30.0			
8	43.6			
9	37.3			

Table 53. ^{195}Pt NMR Data for Complex 130.

130 ppm ($J_{\text{Pt-P}}$) Hz.	Standard
-1723 (996) (1098)	$\text{K}_2\text{PtCl}_6 = 0$ ppm
3007	$\text{Na}_2\text{Pt}(\text{CN})_4 = 0$ ppm

³¹P NMR Data for Complex 130.

Chemical Shift -52.3 ppm ($J_{\text{Pt-P}}=996$ Hz.)
-59.0 ppm ($J_{\text{Pt-P}}=1098$ Hz.)

Study of this new complex by ^{195}Pt NMR spectroscopy, Figure 185, revealed that the resonance attributable to the new complex appeared as a triplet, or a doublet of doublets where the coupling constants were nearly equal. Its chemical shift was observed to be very much in the platinum(IV) region of the spectrum suggesting a weaker donation of electrons into the metal center. The ^{13}C NMR spectrum, Figure 186, is consistent with those observed for other phosphorus ligand substituted platinacyclopentanes. In addition, the ^{31}P NMR spectrum, Figure 187, is also consistent with bis-phosphorus substitution on the metal.

Reductive-elimination could not be induced from this molecule suggesting that the chelation effect does not allow for the dissociation of a phosphorus forming the required five coordinate species.

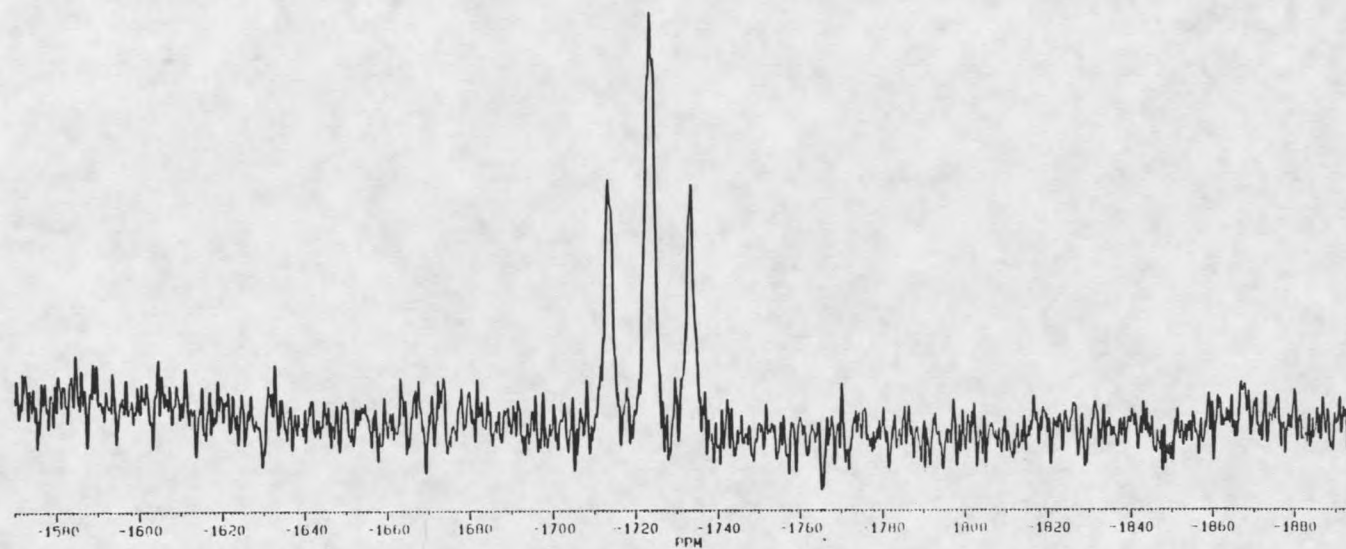


Figure 185. ^{195}Pt NMR Spectrum of Complex 130.

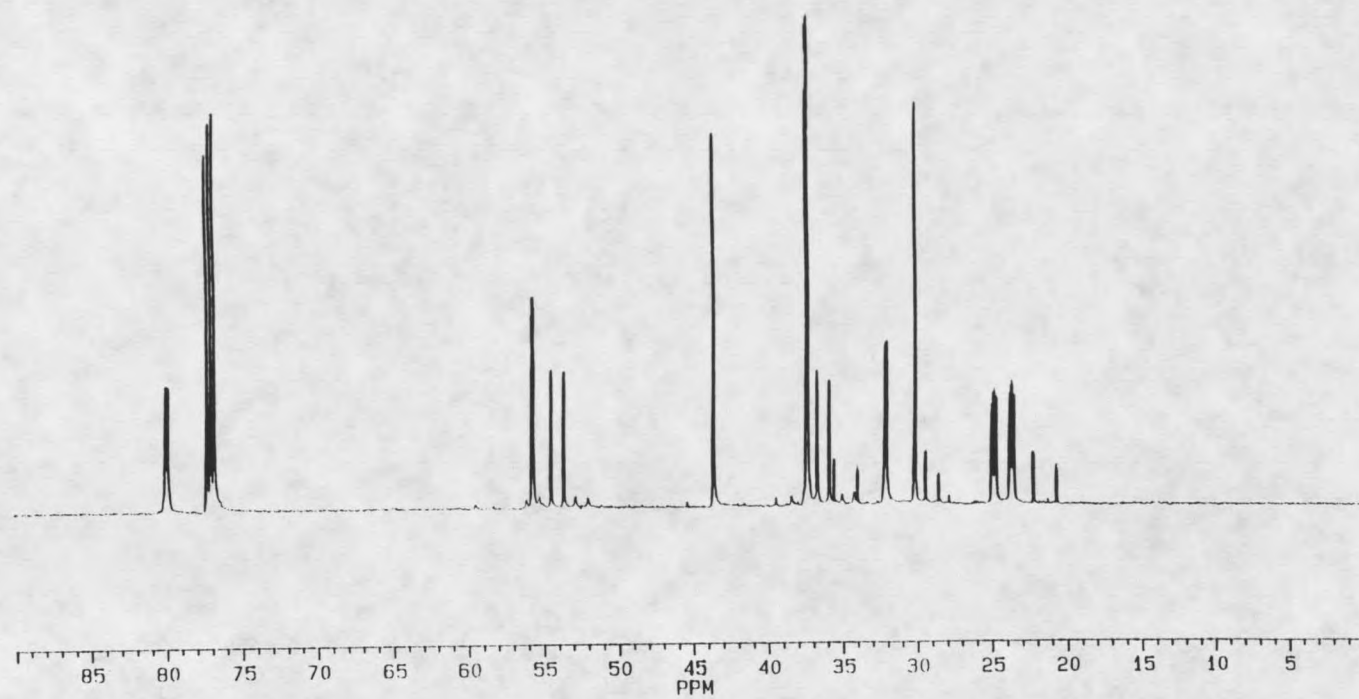


Figure 186. ^{13}C NMR Spectrum of Complex 130.

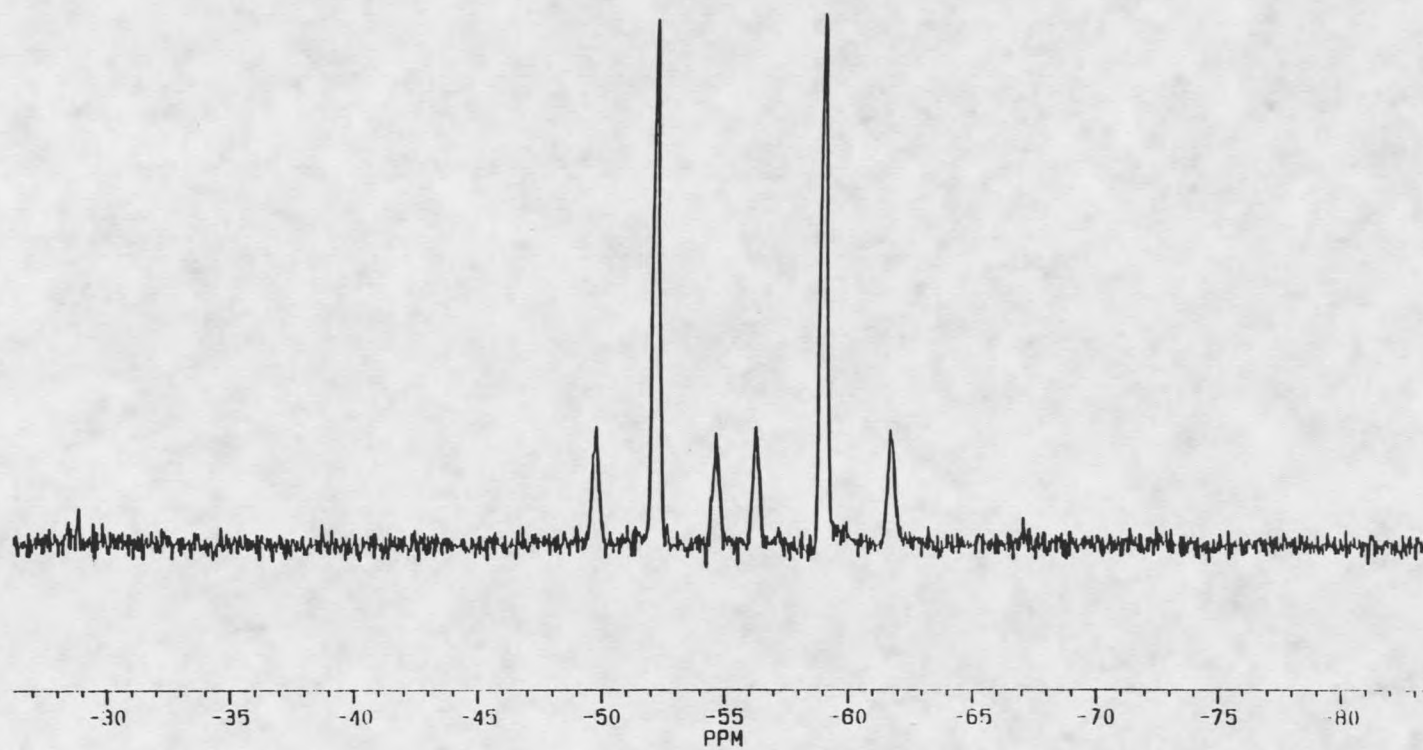


Figure 187. ^{31}P NMR Spectrum of Complex 130.

EXPERIMENTAL

General

All reagents were obtained from commercial sources unless otherwise noted. Diethyl ether was distilled from sodium and benzophenone and used immediately after distillation. Tetrahydrofuran was also distilled from sodium and benzophenone and used immediately. Methanol was HPLC grade and was used with no further purification. Pentane was distilled from lithium aluminum hydride prior to use. CDCl_3 was acquired from Cambridge Laboratories and was used without purification. NMR spectra were collected on either a Bruker AM500, WM250 or AC300. ^1H NMR spectra were collected at either 500 MHz, 300 MHz, or 250 MHz, in CDCl_3 unless otherwise noted. These spectra were referenced to the residual proton content in CDCl_3 located at 7.24 ppm (δ). ^{13}C NMR spectra were obtained at 125.5 MHz and at 75.5 MHz and were referenced to CDCl_3 (77 ppm). ^{31}P NMR spectra were obtained at 202.6 MHz. and referenced to external 1M H_3PO_4 . ^{195}Pt NMR spectra were obtained at 107.2 MHz and were referenced to external K_2PtCl_6 and are reported with respect to K_2PtCl_6 and $\text{Na}_2\text{Pt}(\text{CN})_4$. All coupling constants are measured in Hertz unless otherwise noted. Mass spectral data were acquired on a Varian MM-16F spectrometer or on a VG 7070 mass spectrometer. High resolution mass spectral analyses were performed on the VG

7070 mass spectrometer. Infrared spectral data were obtained on a Nicolet 5DX FT-IR spectrometer. X-ray crystallographic studies were performed using a Nicolet R3ME automated diffractometer and structural refinements were made using SHELXTL software. Zeise's dimer was synthesized by the method of Littlecott⁸³.

Synthesis of Complexes 21, 22, 23, 24, and 61. These complexes were synthesized by the method of Neilsen⁸⁵.

Reaction of Complex 22 with Lithium Aluminum Hydride to give 56. Added to a solution of 10 mL of tetrahydrofuran and 100 mg (0.18 mmol) of complex 22 was 4 equivalents (0.68 mmol) of LiAlH_4 . The solution rapidly developed a black precipitate. After 10 minutes of stirring at room temperature, the solution was filtered and excess solvent was removed giving a pale yellow pungent oil, 56, in 80% yield by ^1H NMR. ^1H NMR (CDCl_3) ppm 3.42 (m, 1H), 2.23 (brs, 1H), 2.01 (brs, 1H), 1.46 (m, 1H), 1.34 (brs, 1H), 1.21 (d, 3H), 1.11 (m, 1H), 1.0-1.4 (overlapping multiplets, 6H). ^{13}C NMR (CDCl_3) ppm 22.5, 71.7, 50.8, 34.5, 39.4, 28.6, 30.5, 36.6, 36.1. Nominal MS $m/e=140 \text{ M}^+$.

Reaction of Complex 22 with Sodium Borohydride to give 56. Added to a solution of 10 mL of methanol and 100 mg (0.18 mmol) of complex 22 was 4 equivalents (0.68 mmol) of NaBH_4 . The solution rapidly developed a black precipitate. After 10 minutes of stirring at room temperature, the solution was filtered and then mixed with 30 mL of water. This solution was then extracted with chloroform three times. Combination of the chloroform washings and subsequent removal of solvent gave compound 56 in 82% isolated yield. Purity was determined by ^1H NMR.

Reaction of Complex 22 with Sodium Borodeuteride to give 59. This experiment was performed in an analogous manner to the NaBH_4 example. Positioning of deuterium was accomplished by observed signal depletion in the ^1H NMR spectrum.

Reaction of Complex 22 with Bipyridine to give 60. To a 20 mL CHCl_3 solution of 100 mg (0.18 mmol) of complex 22 was added one equivalent (28 mg) bipyridine. The solution was stirred at room temperature for 20 hours upon which the solvent was reduced to one mL. Subsequent trituration with pentane gave a yellow solid in 94% yield. ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 22.2 (547), 75.2, 53.9, 43.8 (536), 43.6, 30.9, 28.7, 37.0, 37.2. ^1H NMR (CDCl_3) ppm 4.55 (dd, 1H), 3.75 (dd, 1H), 3.65 (dd, 1H), 2.87 (dd, 1H), 2.61 (brs, 1H), 2.33 (brs, 1H), 1.86 (dd, 1H), 1.4-1.7 (overlapping multiplets, 3H), 1.1-1.3 (overlapping multiplets, 3H)

Reaction of Complex 60 with NaBH_4 . Added to a solution of 10 mL of methanol and 100 mg (0.18 mmol) of complex 60 was 4 equivalents (0.68 mmol) of NaBH_4 . The color of the solution deepened slightly. After 10 minutes of stirring at room temperature, the solution was filtered and then mixed with 30 mL of water. This solution was then extracted with chloroform three times. Combination of the chloroform washings and subsequent removal of solvent gave no detectable amounts of 56.

Reaction of Complex 55 with NaBH_4 to give 62. Added to a solution of 10 mL of methanol and 100 mg (0.18 mmol) of complex 61 was 4 equivalents (0.68 mmol) of NaBH_4 . The solution rapidly developed a black precipitate. After 10 minutes of stirring at room temperature, the solution was filtered and then mixed with 30 mL of water. This solution was then extracted with chloroform three times. Combination of the

chloroform washings and subsequent removal of solvent gave compound **62**, an oil, in 87% yield by ^1H NMR spectroscopy. ^{13}C NMR (CDCl_3) ppm 17.6, 80.7, 49.0, 35.0, 36.6, 28.9, 30.5, 39.1, 36.8, 56.3.

Reaction of Complex **22** with Hydrogen Gas to give **56**. To a solution of 2 mL of CDCl_3 was added 100 mg (0.17 mmol) of complex **22**. The resulting solution was placed in a high pressure reactor (Parr Instrumental Bomb #4702 type T304 SS with a glass insert) and was pressurized to 730 psi with hydrogen gas followed by stirring at room temperature for 66 hours. Analysis of products was made by reducing the solvent volume to 0.5 mL and studied by ^1H NMR spectroscopy. Compound **56** was formed in 73% yield by ^1H NMR spectroscopy.

Reaction of Complex **22** with Sodium Acetate. To 20 mL of methanol was added 100 mg of complex **22** (0.18 mmol). To this was added 7 equivalents (102 mg, 1.26 mmol) of sodium acetate and the resulting solution was stirred at reflux for 24 hours. The solution was added to a 250 mL separatory funnel followed by 50 mL of water. The product was isolated by extraction of the aqueous solution with three 10 mL portions of chloroform. The solvent from the combined washes was removed and the residue was dissolved in CDCl_3 and studied by ^1H NMR spectroscopy. Observed was only complex **22**.

Reaction of Complex **22** with Sodium Azide to give Complexes **63** and **64**. To 20 mL of methanol was added 100 mg of complex **22** (0.18 mmol). To this was added 7 equivalents (81 mg, 1.26 mmol) of sodium azide and the resulting solution was stirred at reflux for 3, 11, and 23 hours. The solution was added to a 250 mL separatory

funnel followed by 50 mL of water. The product was isolated by extraction of the aqueous solution with three 10 mL portions of chloroform. The volume of the combined washes was reduced to 0.5 mL followed by trituration with pentane to give a yellow solid, mixtures of **63** and **64**. **63** ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 30.3 (606), 76.4 (55), 54.9, 42.5 (555), 42.4, 30.4, 30.5, 36.1, 37.5. **64** ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 31.5 (644), 77.6 (61), 53.9, 45.1 (598), 42.5, 30.2, 30.3, 36.3, 37.4. After 3 Hours at reflux **63** 31%, **64** 0%, **22** 69%. After 11 hours at reflux **63** 67%, **64** 19%, **22** 14%. After 23 hours at reflux **63** 33%, **64** 67%, **22** 0%.

Reaction of Complex **21** with Sodium Azide to give Complexes **65** and **66**. To 20 mL of methanol was added 100 mg of complex **21** (0.18 mmol). To this was added 7 equivalents (81 mg, 1.26 mmol) of sodium azide and the resulting solution was stirred at room temperature. The solution was added to a 250 mL separatory funnel followed by 50 mL of water. The product was isolated by extraction of the aqueous solution with three 10 mL portions of chloroform. The volume of the combined washes was reduced to 0.5 mL followed by trituration with pentane to give a yellow solid in 88 to 92% yield, mixtures of **65** and **66**. **65** ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 2.4 (392), 55.7 (101), 11.0 (421), 37.9, 28.5, 28.6, 38.0, 36.4, 62.6 (22). **66** ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 1.7 (424), 53.3 (109), 10.6 (451), 38.0, 28.7, 28.8, 38.3, 36.5, 62.5 (27)

Reaction of **65/66** with Trimethylphosphite. A 100 mg mixture of complexes **65** and **66** were placed in a 25 mL round bottom flask with 5 mL CHCl_3 and was treated with 40 μL (0.34 mmol) of trimethylphosphite by syringe. The mixture was allowed to stir at room temperature for 24 hours. Subsequent removal of solvent by

rotoevaporation and dissolution of the residue in CDCl_3 afforded, by ^1H NMR spectroscopy, only the syn-hydroxymethyl norbornyl cyclopropane. This determination was made by comparison to an authentic sample synthesized by the method of Neilsen.

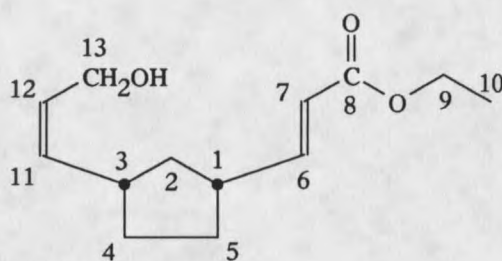
Reaction of 21 with Potassium Iodide to give 67. A solution containing 100 mg (0.18 mmol) of complex 21 and 20 mL of methanol was placed in a 50 mL round bottom flask. To this was added seven equivalents (207 mg) of potassium iodide. The resulting solution was stirred for 20 hours at room temperature. The original golden solution became orange tinted and cloudy. Filtration revealed an orange filtrate and a yellow precipitate. The filtrate was placed into a 250 mL separatory funnel and treated with 50 mL of water followed by extraction with three 10 mL portions of CHCl_3 . The combined washes were then reduced in volume to 0.5 mL upon which the residue was triturated with pentane. The pentane from the pentane washes was removed by rotary-evaporation to give a pale yellow oil, 67, in 71 yield. ^{13}C NMR (CDCl_3) ppm 202.3, 51.1, 41.2, 35.3, 36.1, 29.8, 28.7, 36.8, 38.0. GCMS Nominal $m/z=138 \text{ M}^+$.

Reaction of 21 with Potassium Thiocyanate. A solution containing 100 mg (0.18 mmol) of complex 21 and 20 mL of methanol was placed in a 50 mL round bottom flask. To this was added seven equivalents (121 mg) of potassium thiocyanate. The resulting solution was stirred for 20 hours at room temperature. The solution was placed into a 250 mL separatory funnel and treated with 50 mL of water followed by extraction with three 10 mL portions of CHCl_3 . The combined washes were then reduced in volume to 0.5 mL upon which the residue was triturated with pentane. The pentane from the pentane washes was removed by rotary-evaporation to give only the syn-

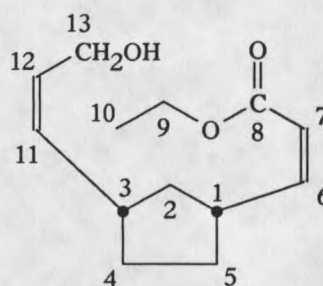
hydroxymethyl norbornyl cyclopropane.

Reaction of 21 and 23 with Ethyl Diazoacetate to give 131e, 131z and 132e,

132z. This procedure is provided as a modification to the original procedure performed by Neilsen². To a solution of 0.15g (0.27 mmol) of either 21 or 23 and 2 mL of chloroform was added 10 eq (308 mg) of Ethyl Diazoacetate gradually over 20 min. The solution was then stirred at room temperature for an additional 30 minutes. Chromatography of the resulting solution on silica gel using a 60% pentane-ether solution as the eluent afforded the products in 79% (131e and 131z)(E/Z=0.7) and 76% (132e and 132z)(E/Z=1.5) yield.



131e

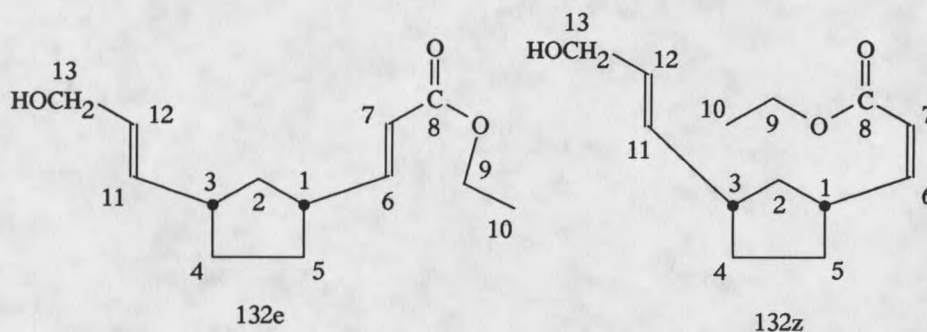


131z

131e ¹H NMR (CDCl₃) ppm H1 2.76 (m, 1H), H3 2.68 (m, 1H), H6 6.88 (dd, 1H), H7 5.74 (d, 1H), H9 4.22 (q, 2H), H10 1.28 (t, 3H), H11 H12 4.9-5.1 (overlapping multiplets, 2H), H13 4.20 (d, 2H), H2 H4 H5 1.0-1.5 (overlapping multiplets, 3H) 1.8-2.1 (overlapping multiplets, 3H). ¹³C NMR (CDCl₃) ppm C1 38.5, C2 40.3, C3 38.3, C4 32.4, C5 32.7, C6 152.5, C7 119.7, C8 166.8, C9 60.8, C10 14.0, C11 124.0, C12 139.4, C13 67.0.

131z ¹H NMR (CDCl₃) ppm H1 3.81 (m, 1H), H3 2.68 (m, 1H), H6 6.06 (dd, 1H), H7

5.64 (d, 1H), H9 4.22 (q, 1H), H10 1.28 (t, 1H), H11 H12 4.9-5.1 (overlapping multiplets, 2H), H13 4.19 (d, 2H), H2 H4 H5 1.0-1.5 (overlapping multiplets, 3H) 1.8-2.1 (overlapping multiplets, 3H). ^{13}C NMR (CDCl_3) ppm C1 42.8, C2 41.4, C3 39.1, C4 31.3, C5 32.2, C6 154.2, C7 118.4, C8 166.4, C9 60.8, C10 14.0, C11 123.6, C12 139.1, C13 66.9

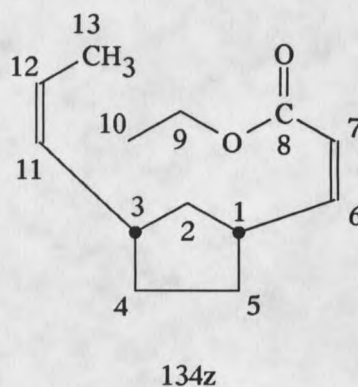
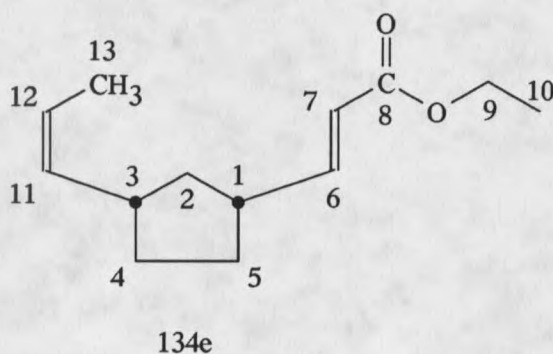


132e ^1H NMR (CDCl_3) ppm H1 2.63 (m, 1H), H3 2.61 (m, 1H), H6 6.87 (dd, 1H), H7 5.72 (d, 1H), H9 4.18 (q, 2H), H10 1.25 (t, 3H), H11 H12 5.45-5.7 (overlapping multiplets, 2H), H13 4.20 (d, 2H), H2 H4 H5 1.0-1.5 (overlapping multiplets, 3H) 1.7-2.1 (overlapping multiplets, 3H). ^{13}C NMR (CDCl_3) ppm C1 42.9, C2 40.0, C3 35.7, C4 29.9, C5 32.4, C6 152.7, C7 119.6, C8 166.4, C9 63.2, C10 14.0, C11 123.9, C12 139.2, C13 68.2. Exact Mass Calculated for $\text{C}_{13}\text{H}_{20}\text{O}_2$ 224.1412, Found 224.1404.

132z ^1H NMR (CDCl_3) ppm H1 3.74 (m, 1H), H3 2.61 (m, 1H), H6 6.05 (dd, 1H), H7 5.62 (d, 1H), H9 4.18 (q, 2H), H10 1.25 (t, 3H), H11 H12 5.45-5.7 (overlapping multiplets, 2H), H13 4.25 (d, 2H), H2 H4 H5 1.0-1.5 (overlapping multiplets, 3H) 1.7-2.1 (overlapping multiplets, 3H). ^{13}C NMR (CDCl_3) ppm C1 42.5, C2 41.0, C3 39.4, C4 29.8, C5 32.7, C6 154.5, C7 118.3, C8 166.3, C9 63.2, C10 14.0, C11 123.6, C12

139.6, C13 68.4. Exact Mass Calculated for $C_{13}H_{20}O_2$ 224.1412, Found 224.1404.

Reaction of Complex 133 with Ethyl Diazoacetate to give 134e and 134z. This procedure is provided as a modification to the original work of Neilsen. To a solution of 0.15g (0.26 mmol) of complex 133 and 2 mL of chloroform was added 10 eq (297 mg) of Ethyl Diazoacetate gradually over 20 min. The solution was then stirred at room temperature for an additional 30 minutes. Chromatography of the resulting solution on silica gel using a 60% pentane-ether solution as the eluent afforded the products, 134e and 134z, in 91% yield (E/Z=1.5).



134e 1H NMR ($CDCl_3$) ppm H1 2.65 (m, 1H), H3 2.83 (m, 1H), H6 6.88 (dd, 1H), H7 5.72 (d, 1H), H9 4.24 (q, 2H), H10 1.28 (t, 3H), H11 H12 5.2-5.4 (om, 2H), H13 1.56 (d, 3H), H2 H4 H5 1.1-1.4 (om, 3H) 1.8-2.1 (om, 3H). ^{13}C NMR ($CDCl_3$) ppm C1 42.7, C2 40.2, C3 37.8, C4 31.3, C5 32.2, C6 153.0, C7 119.4, C8 166.8, C9 60.5, C10 14.0, C11 135.1, C12 122.9, C13 14.8. Exact Mass Calculated for $C_{13}H_{20}O_3$ 208.1463, Found 208.1446.

134z 1H NMR ($CDCl_3$) ppm H1 3.79 (m, 1H), H3 2.83 (m, 1H), H6 6.10 (dd, 1H), H7

5.62 (d, 1H), H9 4.74 (q, 2H), H10 1.28 (t, 3H), H11 H12 5.2-5.4 (om, 2H), H13 1.56 (d, 3H), H2 H4 H5 1.1-1.4 (om, 3H) 1.8-2.1 (om, 3H). ^{13}C NMR (CDCl_3) ppm C1 39.1, C2 41.3, C3 37.9, C4 32.3, C5 32.6, C6 154.8, C7 118.1, C8 166.5, C9 60.5, C10 14.0, C11 135.3, C12 123.0, C13 15.0. Exact Mass Calculated for $\text{C}_{13}\text{H}_{20}\text{O}_3$ 208.1463, Found 208.1462.

Reaction of Complex 48 with Ethyl Diazoacetate to give 70 and 71. To a solution of 0.15g (0.28 mmol) of complex 48 and 2 mL of chloroform was added 10 eq (319 mg) of Ethyl Diazoacetate gradually over 20 min. The solution was then stirred at room temperature for an additional 30 minutes. Chromatography of the resulting solution on silica gel using a 60% pentane-ether solution as the eluent afforded the products, 70 and 71, in 93% yield. (70/71=1.4) 70 ^1H NMR (CDCl_3) ppm 2.65 (m, 1H), 2.56 (m, 1H), 6.87 (dd, 1H), 5.77 (d, 1H), 4.17 (q, 2H), 1.30 (t, 3H), 5.69 (m, 1H), 4.86 (d, 1H), 4.90 (d, 1H), 1.1-1.4 (om, 3H), 1.9-2.1 (om, 3H). ^{13}C NMR (CDCl_3) ppm 44.2, 39.5, 42.6, 31.2, 31.6, 152.9, 119.5, 166.9, 60.1, 14.0, 142.5, 112.9. Exact mass calculated for $\text{C}_{12}\text{H}_{18}\text{O}_2$ 194.13068, Found 194.13063. 71 ^1H NMR (CDCl_3) ppm 3.66 (m, 1H), 2.56 (m, 1H), 6.04 (dd, 1H), 5.63 (d, 1H), 4.17 (q, 2H), 1.30 (t, 3H), 5.69 (m, 1H), 4.86 (d, 1H), 4.90 (d, 1H), 1.1-1.4 (om, 3H), 1.9-2.1 (om, 3H). ^{13}C NMR (CDCl_3) ppm 44.4, 40.6, 38.9, 31.8, 32.1, 154.7, 118.2, 166.5, 59.8, 14.0, 142.7, 112.7. Exact mass calculated for $\text{C}_{12}\text{H}_{18}\text{O}_2$ 194.13068, Found 194.13202.

Synthesis of 77 and 78. Compounds 11a and 11b were synthesized by methylation of the analogous alcohols. The methylation was achieved by treating the mixture of the alcohols (3 g, 0.022 mol) with 2.2 eq. (1.16 g) of Sodium Hydride and

1.0 eq. Methyl Iodide (3.12 g) in dry tetrahydrofuran. This solution was stirred at room temperature for 36 hrs. upon which time the reaction was quenched by addition of water. This was followed by extraction with diethyl ether three times. The combined washings were then rotoevaporated to remove the ether and then the residue was vacuum distilled (55°C, 8 mmHg) to give a mixture of **77** and **78** as a colorless oil (2.1 g) in 63% yield. Anti to syn ratio = 2.2 **77** ^{13}C NMR (CDCl_3) ppm 16.6, 21.4, 30.6, 29.9, 36.0, 70.7, 58.1. Exact mass determination calculated for $\text{C}_{10}\text{H}_{16}\text{O}$ 152.1201, found 152.1193. **78** ^{13}C NMR (CDCl_3) ppm 13.6, 20.9, 28.5, 29.5, 35.7, 75.7, 58.3. Exact mass determination calculated for $\text{C}_{10}\text{H}_{16}\text{O}$ 152.1201, found 152.1196.

Reaction of **77** with Platinum(II) to give Complex **79**. To 3.2 eq (0.25g, 1.63 mmol) of the epimeric mixture in a 50mL round bottom flask was added 20 mL of diethyl ether. Subsequently one equivalent of Zeise's dimer (0.15g, 0.26 mmol), equal to the amount of the syn isomer, was added and the solution was stirred for 20 min. at room temperature to ensure complete reaction. All but 1 mL. of the solvent was then removed followed by trituration of the precipitate using three 20 mL. portions of pentane. The pentane washings were then collected to yield pure **78**. The remaining precipitate was then dried under a stream of dry N_2 . To this precipitate was then added 20 mL. of diethyl ether and 2 eq. of pyridine. The solution was stirred at room temperature for 15 min. followed by trituration with pentane yielding a yellow solid, **79**, in 80% yield. ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 0.5 (373), 57.5 (97), 13.7 (394), 38.3, 29.1, 28.8, 37.6, 40.5, 73.5 (15), 58.0.

Reaction of Complex 79 with Ethyl Diazoacetate to give 80 and 81. To a solution of 0.15g (0.28 mmol) of complex 79 and 2 mL of chloroform was added 10 eq (319 mg) of Ethyl Diazoacetate gradually over 20 min. The solution was then stirred at room temperature for an additional 30 minutes. Chromatography of the resulting solution on silica gel using a 60% pentane-ether solution as the eluent afforded the products, 80 and 81, in 88% yield. 80/81=1.7 ^1H NMR (CDCl_3) ppm H1 2.64 (m, 1H), H3 2.83 (m, 1H), H6 6.87 (dd, 1H), H7 5.73 (d, 1H), H9 4.15 (q, 2H), H10 1.25 (t, 3H), H11 H12 5.35-5.5 (om, 2H), H13 4.00 (d, 1H), H14 3.26 (s, 3H), 1.1-1.4 (om, 3H) 1.7-2.1 (om, 3H). ^{13}C NMR (CDCl_3) ppm C1 42.7, C2 41.4, C3 38.4, C4 31.3, C5 32.7, C6 154.3, C7 118.4, C8 166.7, C9 60.5, C10 14.1, C11 125.0, C12 137.8, C13 68.1, C14 57.7. Exact Mass calculated for $\text{C}_{14}\text{H}_{22}\text{O}_3$ 238.1569, Found 238.1572. 81 ^1H NMR (CDCl_3) ppm H1 3.79 (m, 1H), H3 2.83 (m, 1H), H6 6.05 (dd, 1H), H7 5.63 (d, 1H), H9 4.15 (q, 2H), H10 1.25 (t, 3H), H11 H12 5.35-5.5 (om, 2H), H13 3.92 (d, 2H), H14 3.26 (s, 3H), H2 H4 H5 1.1-1.4 (om, 3H), 1.7-2.1 (om, 2H). ^{13}C NMR (CDCl_3) ppm C1 39.1, C2 40.4, C3 38.5, C4 32.2, C5 32.5, C6 152.5, C7 119.6, C8 166.4, C9 60.5, C10 14.1, C11 125.1, C12 138.0, C13 68.2, C14 57.7. Exact Mass calculated for $\text{C}_{14}\text{H}_{22}\text{O}_3$ 238.1569, Found 238.1572.

Synthesis of 85. Compound 85 was synthesized by the method of Wittig⁷⁸ using o-bromofluorobenzene and 2,5-dimethylfuran. The product, an oil, was chromatographed on silica gel using hexane and diethyl ether in 40% yield. Purity was verified by ^1H NMR spectroscopy. ^1H NMR ppm (CDCl_3) 6.77 (s, 2H), 1.89 (s, 6H), 6.97 (d, 2H), 7.13 (dd, 2H). ^{13}C NMR ppm (CDCl_3) 15.2, 88.5, 118.2, 124.6, 146.7,

152.7.

Cyclopropanation of 85 to give 86. Compound 85 was cyclopropanated by the method of Kottwitz⁷⁹ using 5 eq. of diazomethane and palladium(II) chloride as the catalyst. Upon removal of solvent, the product was chromatographed on silica using hexane to remove impurities followed by diethyl ether to obtain compound 86 as a solid in 81% yield. Capillary GC revealed only one compound. MP Range 53.1-54.4 °C. ¹H NMR (CDCl₃) 0.84 (dd, 1H), 1.59 (dd, 2H), 1.24 (dd, 1H), 1.74 (s, 6H), 7.1-7.3 (om, 4H). ¹³C NMR ppm (CDCl₃) 13.8, 26.6, 83.6, 15.4, 151.0, 125.7, 117.7. Exact Mass. Calculated for C₁₃H₁₄O 186.1044 Found 186.1041.

Synthesis of 87. In a 25mL round bottom was placed 94 mg (0.51 mmol) of compound 86. To this was added 2 mL of diethyl ether and 150 mg (0.51 mmol) of Zeise's dimer. This solution was allowed to reflux for 5 hrs, at which time 5 ml of pyridine was added and the resultant mixture was stirred at room temperature for 30 minutes. Removal of solvents and trituration of the residue three times with pentane afforded 87 as a yellow solid in 78% yield. ¹H NMR (CDCl₃) ppm (J_{Pt-H} in Hz) 2.51 (dd, 1H) (85.1), 3.47 (dd, 1H) (83.3), 2.66 (m, 1H), 2.81 (d, 1H) (96.5), 1.75 (s, 3H), 1.66 (s, 1H), 7.0-7.2 (m, 4H). ¹³C NMR (CDCl₃) ppm (J_{Pt-C} in Hz) -8.63 (361), 58.0 (94), 13.7 (444), 86.2 (17), 147.7, 148.4, 86.8, 13.0, 15.6, 117.7, 126.2, 126.1, 117.2.

Reaction of Complex 87 with N₂CH₂ to give Compounds 88 and 89.

Diazomethane, generated from the reaction between Diazald and potassium hydroxide in a sidearm testtube, was delivered via a stream of nitrogen into a 10 dram vial containing complex 87 stirred in chloroform at room temperature for one hour. Twenty

equivalents of diazomethane were required to ensure complete reaction. Chromatography of the resultant chloroform solution using silica and diethyl ether afforded compound **88** in 15% yield and complex **89** in 30% yield and compound **86** in 55% yield. **88** ^1H NMR (CDCl_3) ppm 1.71 s 1H, 5.01 d 1H (10.3), 5.19 d 1H (17.1), 6.08 dd 1H (10.3, 17.1), 7.0-7.2 overlapping multiplet 4H. **89** ^1H NMR (CDCl_3) ppm ($J_{\text{P-H}}$ in Hz) 2.65 (38.7) (t, 2H), 2.46 (m, 1H), 1.93 (m, 1H), 3.61 (41.1) (m, 1H), 4.34 (56.9) (d, 1H), 6.83 (d, 1H), 7.05-7.2 (om, 3H), 1.15 (s, 3H), 1.70 (s, 1H). ^{13}C NMR (CDCl_3) ppm ($J_{\text{P-C}}$ in Hz) 21.7 (494), 36.1 (14.5), 51.5 (23.4), 45.5 (639), 88.4 (11.2), 152.9, 153.8, 84.9, 14.9, 16.3 (10.9), 118.2, 126.0, 126.3, 118.2.

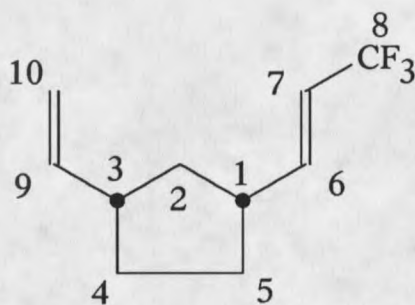
Reaction of Complex **87** with ^{13}C labelled Diazomethane. Experimental procedures were identical to the unlabelled experiment except ^{13}C labelled Diazald was employed.

Reaction of Complex **87** with $\text{N}_2\text{CHCO}_2\text{Et}$ to give Compounds **90**, **91**, and **92**.

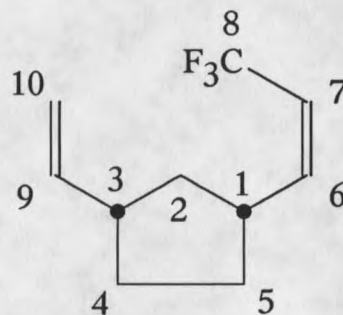
To a solution of 0.15g (0.25 mmol) of complex **87** and 2 mL of chloroform was added 10 eq (282 mg) of Ethyl Diazoacetate gradually over 20 min. The solution was then stirred at room temperature for an additional 30 minutes. Chromatography of the resulting solution on silica gel using a 60% pentane-ether solution as the eluent afforded the product **90** in 15% yield and complexes **91** and **92** in 30% yield. The remainder was compound **86**. **90** ^1H NMR (CDCl_3) ppm 1.30 t, 3H, 1.61 s, 3H, 1.63 s, 3H, 4.20 q, 2H, 5.02 d, 1H, 5.15 d, 1H, 5.98 d, 1H (15.5), 6.06 dd, 1H, 7.09 d, 1H (15.5), 7.0-7.3 overlapping multiplets, 4H. ^{13}C NMR (CDCl_3) ppm 14.0, 15.1, 15.3, 60.8, 83.8, 85.9, 112.9, 115.5, 117.6, 118.3, 118.7, 121.7, 122.2, 142.7, 143.3, 151.3, 166.9. **91** ^{13}C NMR

(CDCl₃) ppm (*J*_{Pt-C}) 30.8 (536), 36.5, 51.1 (28.9), 48.6 (604), 88.7, 118.2, 126.4, 123.7, 123.7, 125.4, 116.0, 84.8, 14.7, 16.1, 178.7 (36.9), 62.3, 13.5. ⁹² ¹³C NMR (CDCl₃) ppm (*J*_{Pt-C}) 26.8 (530), 37.0, 50.6 (12.8), 48.1 (610), 88.4, 118.5, 126.3, 124.3, 124.3, 125.1, 115.6, 85.2, 14.6, 16.1, 175.9 (32.1), 62.0, 13.5.

Reaction of Complex 48 with 2,2,2-Trifluorodiazaoethane to give 93 and 94. To a solution of 150 mg (0.28 mmol) of complex 48 and 10 mL of chloroform was added 10 mL of a prepared cold etherial solution of 2,2,2-trifluorodiazaoethane. The solution of 2,2,2-trifluorodiazaoethane was prepared by the method of Gilman and Jones⁸¹. The resulting mixture was stirred for four hours at room temperature. Upon completion, the volume was reduced to near dryness and the residue was dissolved in a 1:1 mixture of pentane/diethyl ether and was chromatographed on a short column of alumina. The fractions were combined and the solvent was removed to give a colorless oil, 93 and 94, in 86% yield. 93/94 = 1.3.



93

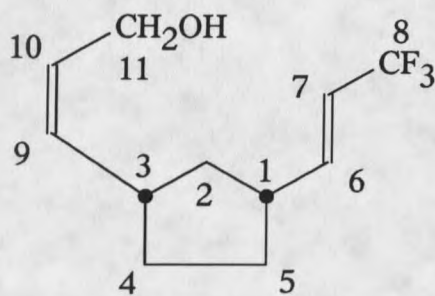


94

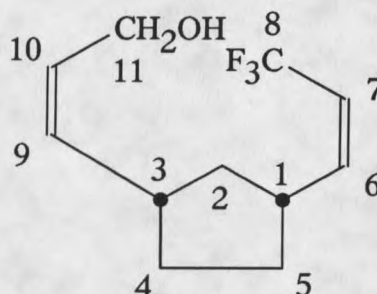
⁹³ ¹H NMR (CDCl₃) ppm H1 2.63 (m, 1H), H1 2.59 (m, 1H), H6 6.35 (dd, 1H), H7 5.57 (m, 1H), H9 5.79 (m, 1H), H10 4.91 (d, 1H) 5.00 (d, 1H), H2 H4 H5 1.0-1.7

(overlapping multiplets, 6H). ^{13}C NMR (CDCl_3) ppm ($J_{\text{F-C}}$) C1 41.9, C2 39.4, C3 44.1, C4 31.7, C5 31.5, C6 144.2 (6.5), C7 116.7 (32.7), C8 123.2 (269), C9 113.0, C10 142.3. Exact Mass Calculated for $\text{C}_{10}\text{H}_{13}\text{F}_3$ 190.0969, Found 190.0968. **94** ^1H NMR (CDCl_3) ppm H1 3.07 (m, 1H), H3 2.59 (m, 1H), H6 5.87 (dd, 1H), H7 5.50 (m, 1H), H9 5.79 (m, 1H), H10 4.91 (d, 1H) 5.00 (d, 1H), H2 H4 H5 1.0-1.7 (overlapping multiplets, 6H). ^{13}C NMR (CDCl_3) ppm ($J_{\text{F-C}}$) C1 38.9, C2 40.7, C3 44.3, C4 31.7, C5 32.2, C6 147.4 (5.5), C7 116.9 (33.8), C8 123.0 (269), C9 113.0, C10 142.3. Exact Mass Calculated for $\text{C}_{10}\text{H}_{13}\text{F}_3$ 190.0969, Found 190.0948.

Reaction of Complex 21 with 2,2,2-Trifluorodiazaoethane to give 95 and 96. To a solution of 150 mg (0.28 mmol) of complex 21 and 10 mL of chloroform was added 10 mL of a prepared cold etherial solution of 2,2,2-trifluorodiazaoethane. The solution of 2,2,2-trifluorodiazaoethane was prepared by the method of Gilman and Jones⁸¹. The resulting mixture was stirred for four hours at room temperature. Upon completion, the volume was reduced to near dryness and the residue was dissolved in CDCl_3 and analyzed by ^1H and ^{13}C NMR spectroscopy. Compounds 95 and 96 were formed in 91% yield by ^1H NMR. 95/96 = 1.5.



95



96

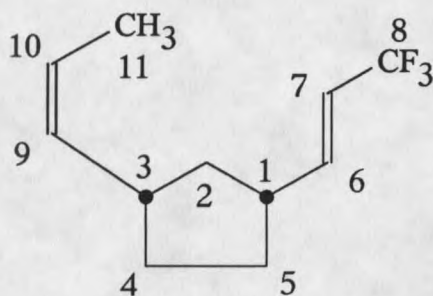
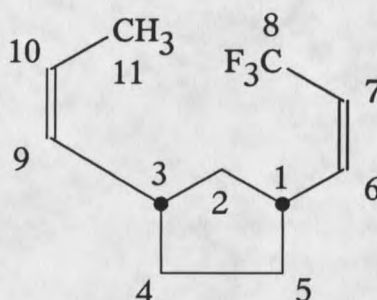
95 ^1H NMR (CDCl_3) ppm H1 2.63 (m, 1H), H3 2.86 (m, 1H), H6 6.81 (dd, 1H), H11 4.21 (d, 2H), H2 1.8-2.1 (overlapping multiplets, 2H), H4 H5 1.1-1.6 (overlapping multiplets, 4H), H7 H9 H10 (overlapping multiplets, 3H). ^{13}C NMR (CDCl_3) ppm ($J_{\text{F-C}}$) Hz. C1 41.2, C2 42.5, C3 40.2, C4 34.0, C5 34.5, C6 146.1 (6), C7 118.7 (32.7), C8 123.4 (268), C9 126.7, C10 134.9, C11 63.0.

96 ^1H NMR (CDCl_3) ppm H1 3.16 (m, 1H), H3 2.86 (m, 1H), H6 5.86 (dd, 1H), H11 4.21 (d, 2H), H2 1.8-2.1 (overlapping multiplets, 2H), H4 H5 1.1-1.6 (overlapping multiplets, 4H), H7 H9 H10 (overlapping multiplets, 3H). ^{13}C NMR (CDCl_3) ppm ($J_{\text{F-C}}$) Hz. C1 44.2, C2 43.8, C3 40.5, C4 32.7, C5 34.8, C6 149.1 (6), C7 119.1 (33.8), C8 123.1 (268), C9 125.3, C10 134.2, C11 63.0.

Reaction of Complex 133 with 2,2,2-Trifluorodiazaoethane to give 135e and 135z.

To a solution of 150 mg (0.28 mmol) of complex **21** and 10 mL of chloroform was added 10 mL of a prepared cold etherial solution of 2,2,2-trifluorodiazaoethane. The solution of 2,2,2-trifluorodiazaoethane was prepared by the method of Gilman and Jones⁸¹. The resulting mixture of complex **133** and the diazo-derivative was stirred for

four hours at room temperature. Upon completion, the volume was reduced to near dryness and the residue was dissolved in CDCl_3 and analyzed by ^1H and ^{13}C NMR spectroscopy. Compounds **135e** and **135z** were formed in 84% yield by ^1H NMR. Product ratio : **135e**/**135z** = 1.5.

**135e****135z**

135e ^{13}C NMR (CDCl_3) ppm ($J_{\text{F-C}}$) C1 42.1, C2 40.2, C3 37.7, C4 29.7, C5 32.3, C6 147.6 (5.5), C7 116.6 (32.7), C8 122.9 (270), C9 123.6, C10 135.0, C11 12.9.

135z ^{13}C NMR (CDCl_3) ppm ($J_{\text{F-C}}$) C1 39.1, C2 41.4, C3 37.9, C4 31.3, C5 32.5, C6 144.5 (6.5), C7 116.8 (32.7), C8 122 (269), C9 123.6, C10 135.0, C11 12.9.

Synthesis of Complex 102. To 150 mg (0.27 mmol) of complex **21** in a 50 mL round bottom flask was added 10 mL of acetone and 5 mL of formic acid (88% aqueous solution). The resulting solution was stirred for 12 hours at room temperature upon which the solution was poured into a 250 mL separatory funnel and neutralized with saturated sodium bicarbonate. Extraction of the product was accomplished by combining three 10 mL CHCl_3 washes of the aqueous solution, reducing the volume to 1 mL, and repeated trituration with pentane. This procedure gave a tan solid residue,

102, in 75% yield. ^1H NMR (CDCl_3) ppm ($J_{\text{Pt-H}}$) 3.96 dd 1H (84.6), 2.34 dd 1H (104.1), 5.66 dd 1H, 1.95 t 1H, 3.30 dd 1H (85.3), 1.16 d 1H, 2.29 m 1H, 1.28 m 1H, 2.12 m 1H, 1.45 m 1H, 2.29 d 1H, 1.09 brs 1H, 1.09 m 1H, 7.99 s 1H. ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 18.7 (553), 77.7 (69.1), 52.7, 38.3, 29.3 (32.6), 30.5, 44.2, 36.6, 160.8.

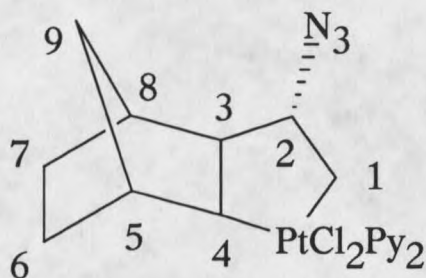
Synthesis of Complex 103. A 60 mg (0.11 mmol) sample of complex **22** was placed in a 50 mL round bottom flask and to this was added 5 mL of acetone and 1 mL of concentrated hydrochloric acid. The solution was stirred for 8 hours at room temperature upon which the solvent was removed and the residue was dissolved in CHCl_3 and washed three times with 5 mL portions of water. The CHCl_3 solution was then reduced in volume to 1 mL and triturated with pentane to give a tan solid, **103**, in 92% yield. This determination was made by comparison to data generated by Neilsen⁸².

Synthesis of Complex 105. To 100 mg (0.17 mmol) of complex **55** in a 25 mL round bottom flask was added 2 mL of CHCl_3 and 4 mL of freshly distilled n-butylamine. The resulting solution was stirred for 5.5 hours at room temperature. Removal of solvent and dissolution of the residue in CHCl_3 afforded complex **105** in quantitative yield by ^1H NMR spectroscopy. ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) 21.1 (555), 83.1 (59), 51.8, 40.6 (529), 44.2, 29.5 (30), 31.3, 37.2, 37.0, 57.2.

Synthesis of Complex 106. To 150 mg (0.27 mmol) of complex **21** in a 50 mL round bottom flask was added 10 mL of acetone and 5 mL of trifluoroacetic acid. The resulting solution was stirred for 12 hours at room temperature upon which the solution was poured into a 250 mL separatory funnel and neutralized with saturated sodium bicarbonate. Extraction of the product was accomplished by combining three 10 mL

CHCl_3 washes of the aqueous solution, reducing the volume to 1 mL, and repeated trituration with pentane. This procedure gave a tan residue, **106**, in 67% yield. ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) [$J_{\text{F-C}}$] 16.8 (557), 82.4 (75.5), 52.3, 40.7 (528), 44.1, 29.2 (32), 30.5, 37.9, 36.6, 156.7 [41.8], 114.1 [288].

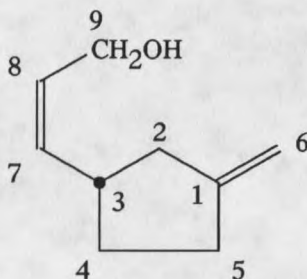
Synthesis of Complex 107. To 150 mg (0.25 mmol) of complex **106** in a 50 mL round bottom flask was added 25 mL of THF and 1.1 eq. (16 mg) of NaN_3 . The resulting solution was stirred at reflux for 15 hours upon which the solution was poured into a 250 mL separatory funnel. To this was added 50 mL of water and the resulting solution was washed three times with 10 mL portions of CHCl_3 . The collected CHCl_3 washes were combined and the volume was reduced to 1 mL on a rotary evaporator. The residue was then triturated with pentane to give a tan solid in quantitative yield by ^1H NMR spectroscopy.



^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) C1 19.0 (560), C2 65.4 (60), C3 54.3, C4 43.0 (534), C5 38.7, C6 29.1 (32), C7 30.8, C8 44.5, C9 36.7. ^1H NMR (CDCl_3) ppm H1 3.96 dd 1H, H2 2.34 dd 1H, H3 4.46 dd 1H, H4 1.79 dd 1H, H5 3.31 d 1H, H6 1.14 d 1H, H7 1.49 brs 1H, H8 1.27 brs 1H, H9 2.28 d 1H, H10 2.00 d 1H, H11 1.0-1.2 overlapping

multiplet 3H.

Synthesis of Compound 109. To 150 mg (0.27 mmol) of complex **22** was added 1 mL of CHCl_3 and 1 eq (42 mg) of bipyridine. The resulting solution was refluxed for 10 hours. An orange precipitate was observed and it was removed by filtration through a small silica gel column. The CHCl_3 filtrate was triturated with pentane and the pentane washings were collected. Removal of solvent gave compound **109** as an amber oil in 65% yield.

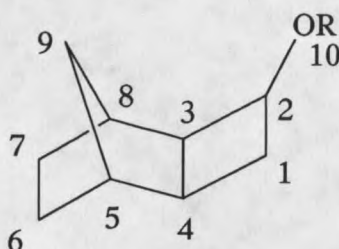


^1H NMR (CDCl_3) ppm H3 2.82 m 1H, H6 4.81 d 1H 4.82 d 1H, 5.44 dd 1H, 5.54 dd 1H, 4.20 d 2H, H2 H4 H6 0.9-1.5 overlapping multiplets 6H. ^{13}C NMR (CDCl_3) ppm C1 151.8, C2 29.8, C3 35.7, C4 28.7, C5 29.8, C6 105.4, C7 136.9, C8 127.9, C9 65.4. Nominal MS $M^+=138$.

Synthesis of Complexes 111, 113, 114, 115, and 117. A solution of 0.10g (0.189 mmol) of either **22** or **24** in 20 mL of chloroform was prepared and to it was added 5.0 eq (0.89 mmol, 0.046 mL) of trimethyl phosphite (Strem). This solution was allowed to stir for 1 hr. Characterizations were made in the presence of excess trimethyl phosphite. Products were observed in quantitative yield by ^1H NMR spectroscopy.

Synthesis of Compounds 112, 118, 119, 120, and 121. Removal of excess

trimethyl phosphite was achieved by co-distillation on a rotary evaporator using 100% ethanol. The residue was then dissolved in 10 mL of chloroform and refluxed for one hour. This chloroform was then rotoevaporated from this solution and the remainder was chromatographed on a long silica gel column using diethyl ether solution as the eluent. Removal of chromatographic solvent from the combined fractions afforded the products.



112 (79%) ^1H NMR CDCl_3 * H1 1.51 (m, 1H), 2.35 (m, 1H), H2 4.36 (dd, 1H), H3 2.34 (t, 1H), H4 1.21 (brs, 1H), H5 2.21 (brs, 1H), H6 1.01 (m, 1H), 1.43 (m, 1H), H7 1.02 (m, 1H), 1.44 (m, 1H), H8 2.02 (brs, 1H), H9 1.95 (dd, 1H), 2.00 (brs, 1H), H10 1.82 (brs, 1H). ^{13}C NMR ($J_{\text{C-H}}$ (Hz)) CDCl_3 C1 34.5 (134), C2 66.9 (148), C3 48.9 (141), C4 39.4 (143), C5 34.6, C6 28.0, C7 28.3, C8 35.4, C9 34.0. Exact Mass Calculated for $\text{C}_9\text{H}_{14}\text{O}\cdot\text{NH}_4$ 156.1388, Found 156.1383. 118 (88%) ^1H NMR CDCl_3 H1 1.50 (m, 1H), 2.20 (m, 1H), H2 3.86 (dd, 1H), H3 2.30 (t, 1H), H4 1.92 (dd, 1H), H5 1.95 (brs, 1H), H6 1.41 (m, 1H), 1.16 (m, 1H), H7 1.19 (m, 1H), 1.40 (m, 1H), H8 2.17 (brs, 1H), H9 2.05 (d, 1H), 0.95 (dd, 1H), H10 3.14 (s, 3H). ^{13}C NMR ($J_{\text{C-H}}$ (Hz)) CDCl_3 C1 31.1 (132), C2 74.6 (143), C3 47.2 (142), C4 39.4 (142), C5 35.0, C6 27.9, C7 28.2, C8 35.2,

C9 33.7, C10 55.9. Exact Mass Calculated for $C_{10}H_{16}O$ 152.1201, Found 152.1201. **119** (83%) ^{13}C NMR $CDCl_3$ C1 30.9, C2 69.1, C3 47.1, C4 39.3, C5 35.2, C6 27.5, C7 27.8, C8 36.4, C9 33.4, C10 160.1. Exact Mass Calculated for $C_{10}H_{14}O_2$ 166.0994, Found 166.1004. **120** (83%) ^{13}C NMR $CDCl_3$ C1 35.1, C2 69.9, C3 52.4, C4 37.9, C5 36.4, C6 26.8, C7 27.7, C8 37.2, C9 32.9. Exact Mass Calculated for $C_9H_{14}O \cdot NH_4$ 156.1388, Found 156.1389. **121** (85%) $CDCl_3$ C1 31.4, C2 78.0, C3 48.8, C4 37.1, C5 37.5, C6 26.9, C7 27.7, C8 38.0, C9 32.8, C10 54.7. Exact Mass Calculated for $C_{10}H_{16}O$ 152.1201, Found 152.1208.

Synthesis of Complex 122. A solution of 0.10g (0.17 mmol) of **107** in 20 mL of chloroform was prepared and to it was added 5.0 eq (0.80 mmol, 0.041 mL) of trimethyl phosphite (Strem). This solution was allowed to stir for 1 hr. Characterizations were made in the presence of excess trimethyl phosphite. Products were observed in quantitative yield by 1H NMR spectroscopy. ^{13}C NMR ($CDCl_3$) ppm (J_{P-C}) [J_{P-C}] 27.2 (361) [162] [5.8], 67.3 (41.3), [27.4] [6.3], 49.4, 49.8 (497) [159] [3.3], 44.4, 30.1 (23.4) [22.6] [<2], 30.8, 38.2, 36.6.

Synthesis of 123. Removal of excess trimethyl phosphite was achieved by co-distillation on a rotary evaporator using 100% ethanol. The residue was then dissolved in 10 mL of chloroform and refluxed for one hour. This chloroform was then rotoevaporated from this solution and the remainder was chromatographed on a long silica gel column using diethyl ether solution as the eluent. Removal of chromatographic solvent from the combined fractions afforded the product, 72%. ^{13}C NMR ($CDCl_3$) ppm C1 39.2, C2 55.8, C3 47.2, C4 37.1, C5 33.5, C6 27.7, C7 27.9, C8

35.7, C9 30.4.

Reaction of Complex 22 with Tri-n-butylphosphine to give 124. A solution of 0.10g (0.18 mmol) of 22 in 20 mL of chloroform was prepared and to it was added 5.0 eq (0.90 mmol, 182 mg) of tri-n-butylphosphine. This solution was allowed to stir for 1 hr. Characterizations were made in the presence of excess trimethyl phosphite. The product, 124, was observed in quantitative yield by ^1H NMR spectroscopy. ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) [$J_{\text{P-C}}$] 35.4 (427) [106] [<2], 77.8 (35) [19.3] [4.8], 54.3, 47.6 (403) [113] [<2], 37.0, 31.1 (<2) [14.5] [<2], 30.7, 43.0, 36.9.

Reaction of Complex 22 with Triphenylphosphite. A solution of 0.10g (0.18 mmol) of 22 in 20 mL of chloroform was prepared and to it was added 5.0 eq (0.90 mmol, 262 mg) of triphenylphosphite. This solution was allowed to stir for 1 hr. Analysis by ^1H NMR spectroscopy revealed only the presence of complex 22.

Reaction of Complex 22 with Triphenylphosphine. A solution of 0.10g (0.18 mmol) of 22 in 20 mL of chloroform was prepared and to it was added 5.0 eq (0.90 mmol, 236 mg) of triphenylphosphine. This solution was allowed to stir for 1 hr. The solvent was then removed by rotary evaporation and the residue was dissolved in CDCl_3 for analysis by NMR spectroscopy. Quantitative conversion to the products, 125 and 126, was observed by ^{195}Pt NMR spectroscopy. 125 ^{13}C NMR (CDCl_3) ppm ($J_{\text{Pt-C}}$) [$J_{\text{P-C}}$] 25.4 (529) [0], 80.3 (35) [19.4], 54.0, 60.9 (447) [105], 42.3, 31.2 (14.5) [13.7], 30.2, 37.1, 37.5. ^{195}Pt NMR (CDCl_3) ppm, referenced to K_2PtCl_6 ($J_{\text{P-Pt}}$) -2353 (770). 126 ^{195}Pt NMR (CDCl_3) ppm, referenced to K_2PtCl_6 ($J_{\text{P-Pt}}$) -2303 (860).

Decomposition of Complexes 125 and 126. Removal of excess

triphenylphosphine was accomplished by first reducing the solvent volume to approximately 0.5 mL and subsequent trituration of the sample five times with pentane. The residue was then dried under N_2 and dissolved in 10 mL of $CHCl_3$. The resulting solution was refluxed for twelve hours. The solvent was subsequently removed by rotary evaporation and the residue was dissolved in $CDCl_3$ for analysis by NMR spectroscopy. 1H NMR spectroscopy revealed the presence of both **22** and **112**. Observation of bis-triphenylphosphine platinum(II)dichloride was made by ^{195}Pt NMR spectroscopy.

Reaction of Complex **22** with Diphenylphosphinoethane (DPPE). A solution of 0.10g (0.18 mmol) of **22** in 20 mL of chloroform was prepared and to it was added 1.0 eq (0.18 mmol, 72 mg) of DPPE. This solution was allowed to stir for 1 hr upon which the solvent was reduced to approximately 0.5 mL and it was trituated three times with pentane. The residue, a tan solid, was dissolved in $CDCl_3$ and studied by NMR spectroscopy. The tan solid, complex **130**, was formed in 90% yield. ^{13}C NMR ($CDCl_3$) ppm (J_{Pt-C}) [J_{P-C}] 36.2 (405) [112.4], 79.9 [19.3], 55.6, 54.0 (405), 37.4, 32.0, 30.0, 43.6, 37.3. ^{195}Pt NMR ($CDCl_3$) ppm, referenced to K_2PtCl_6 (J_{Pt-P}) -1723 (996) (1098). ^{31}P NMR ($CDCl_3$) ppm (J_{P-Pt}) -52.3 (996), -59.0 (1098).

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APPENDICES

APPENDIX A
X-RAY DATA FOR COMPLEX 89

The unit cell is trigonal, space group R3. Rhombohedral cell dimensions (at 24 °C) are : $a=b=c=15.912$ (2) Å; $\alpha=\beta=\gamma=100.59$ (1)°; $Z=6$. Hexagonal cell dimensions are : $a=b=24.484$ (4) Å; $C=21.916$ (6) Å; $\alpha=\beta=90^\circ$; $\gamma=120^\circ$; $z=18$. The hexagonal cell was used for structure solution and refinement. Atom coordinates refer to the hexagonal cell. The structure was solved from a Patterson synthesis for the platinum position : 3173 observed data, $I>3\sigma(I)$; 287 least-squares parameters; $R=0.042$; $R_w=0.043$. Data were corrected for absorption by Gaussian integration : $\mu(M_oK\alpha)=58.4$ cm⁻¹; transmission factor range = 0.072 to 0.166.

Table 54. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$).

	x	y	z	U
Pt	5570 (1)	6677 (1)	8058 (1)	42 (1)
Cl(1)	6386 (1)	7268 (1)	8728 (1)	57 (1)
Cl(2)	4725 (1)	6104 (1)	7410 (1)	60 (1)
C(1)	5017 (4)	6183 (5)	8790 (4)	59 (5)
C(2)	5268 (5)	5794 (5)	9058 (4)	65 (6)
C(3)	5419 (5)	5463 (5)	8549 (4)	60 (5)
C(4)	5734 (4)	5920 (4)	7997 (4)	51 (5)
C(5)	6415 (4)	6000 (4)	8003 (4)	49 (4)
C(6)	6309 (4)	5374 (4)	7743 (4)	51 (5)
C(7)	6451 (5)	5211 (5)	7183 (4)	64 (6)
C(8)	6287 (5)	4585 (5)	7118 (5)	75 (6)
C(9)	5967 (6)	4149 (6)	7588 (5)	77 (7)
C(10)	5822 (5)	4306 (5)	8128 (5)	67 (6)
C(11)	5999 (5)	4927 (5)	8201 (4)	60 (5)
C(12)	5934 (5)	5306 (5)	8740 (4)	63 (5)
O	6506 (3)	5912 (3)	8654 (3)	56 (3)
C(13)	5914 (6)	5037 (5)	9367 (4)	83 (7)
C(14)	6993 (4)	6581 (4)	7765 (4)	57 (5)
N(1)	5304 (4)	7416 (4)	8112 (3)	50 (4)
C(15)	5362 (5)	7733 (5)	8626 (4)	59 (5)
C(16)	5263 (5)	8232 (5)	8668 (5)	67 (6)
C(17)	5087 (5)	8423 (5)	8154 (5)	69 (6)
C(18)	5030 (5)	8108 (5)	7628 (5)	69 (6)
C(19)	5140 (5)	7617 (5)	7620 (4)	64 (6)
N(2)	6144 (3)	7197 (3)	7270 (3)	45 (3)

Table 54. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$).

	x	y	z	U
C(20)	6519 (4)	7822 (4)	7286 (4)	48 (4)
C(21)	6863 (5)	8170 (4)	6793 (4)	60 (5)
C(22)	6844 (5)	7868 (5)	6267 (4)	64 (5)
C(23)	6467 (5)	7231 (5)	6244 (4)	64 (5)
C(24)	6118 (4)	6900 (4)	6743 (4)	47 (4)

Table 55. Bond Lengths ($\text{\AA}$).

Pt-Cl(1)	2.313 (2)	Pt-Cl(2)	2.317 (2)
Pt-C(1)	2.059 (8)	Pt-C(4)	2.089 (12)
Pt-N(1)	2.210 (10)	Pt-N(2)	2.188 (6)
C(1)-C(2)	1.486 (19)	C(2)-C(3)	1.529 (17)
C(3)-C(4)	1.565 (12)	C(3)-C(12)	1.549 (19)
C(4)-C(5)	1.578 (16)	C(5)-C(6)	1.531 (15)
C(5)-O	1.475 (10)	C(5)-C(14)	1.513 (11)
C(6)-C(7)	1.389 (15)	C(6)-C(11)	1.396 (13)
C(7)-C(8)	1.383 (18)	C(8)-C(9)	1.406 (16)
C(9)-C(10)	1.346 (18)	C(10)-C(11)	1.365 (17)
C(11)-C(12)	1.557 (16)	C(12)-O	1.456 (10)
C(12)-C(13)	1.514 (14)	N(1)-C(15)	1.334 (13)
N(1)-C(19)	1.329 (14)	C(15)-C(16)	1.362 (20)
C(16)-C(17)	1.371 (17)	C(17)-C(18)	1.354 (16)
C(18)-C(19)	1.357 (20)	N(2)-C(20)	1.333 (10)
N(2)-C(24)	1.348 (11)	C(20)-C(21)	1.374 (12)
C(21)-C(22)	1.358 (15)	C(22)-C(23)	1.358 (13)
C(23)-C(24)	1.376 (12)		

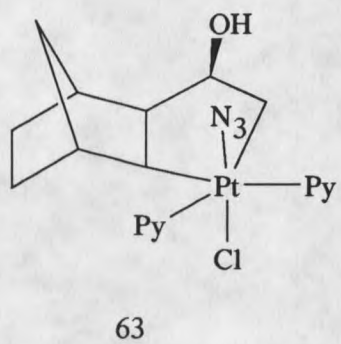
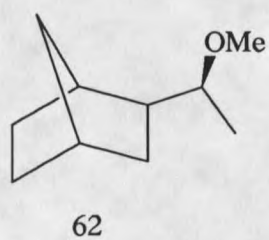
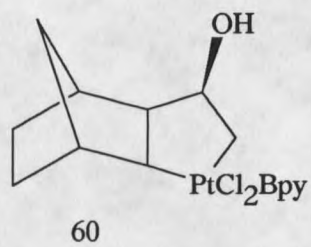
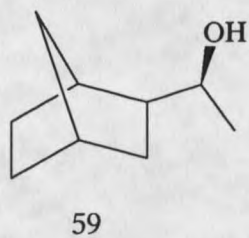
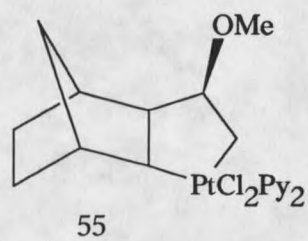
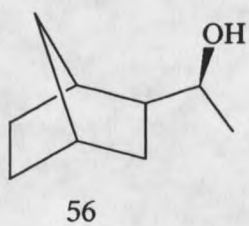
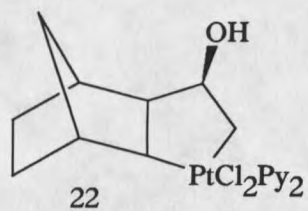
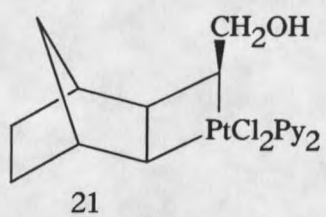
Table 56. Bond Angles (°).

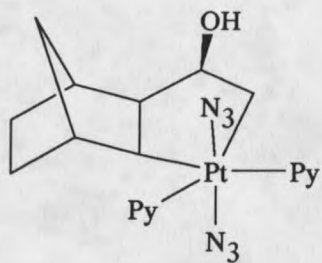
Cl(1)-Pt-Cl(2)	177.2 (1)	Cl(1)-Pt-C(1)	88.9 (2)
Cl(2)-Pt-C(1)	89.8 (2)	Cl(1)-Pt-C(4)	96.1 (3)
Cl(2)-Pt-C(4)	86.2 (3)	C(1)-Pt-C(4)	83.7 (4)
Cl(1)-Pt-N(1)	88.3 (2)	Cl(2)-Pt-N(1)	89.4 (2)
C(1)-Pt-N(1)	93.6 (4)	C(4)-Pt-N(1)	174.8 (3)
Cl(1)-Pt-N(2)	92.0 (2)	Cl(2)-Pt-N(2)	89.3 (2)
C(1)-Pt-N(2)	179.1 (3)	C(4)-Pt-N(2)	96.5 (3)
N(1)-Pt-N(2)	86.1 (3)	Pt-C(1)-C(2)	108.8 (7)
C(1)-C(2)-C(3)	109.8 (8)	C(2)-C(3)-C(4)	110.3 (9)
C(2)-C(3)-C(12)	112.2 (8)	C(4)-C(3)-C(12)	102.3 (8)
Pt-C(4)-C(3)	109.9 (8)	Pt-C(4)-C(5)	123.3 (5)
C(3)-C(4)-C(5)	101.3 (8)	C(4)-C(5)-C(6)	103.4 (7)
C(4)-C(5)-O	102.5 (7)	C(6)-C(5)-O	100.1 (8)
C(4)-C(5)-C(14)	123.2 (10)	C(6)-C(5)-C(14)	115.1 (9)
O-C(5)-C(14)	109.5 (6)	C(5)-C(6)-C(7)	132.5 (8)
C(5)-C(6)-C(11)	105.8 (8)	C(7)-C(6)-C(11)	121.7 (10)
C(6)-C(7)-C(8)	115.7 (9)	C(7)-C(8)-C(9)	120.6 (12)
C(8)-C(9)-C(10)	123.6 (12)	C(9)-C(10)-C(11)	116.0 (10)
C(6)-C(11)-C(10)	122.3 (10)	C(6)-C(11)-C(12)	104.8 (9)
C(10)-C(11)-C(12)	132.9 (9)	C(3)-C(12)-C(11)	106.3 (8)
C(3)-C(12)-O	101.5 (8)	C(11)-C(12)-O	100.2 (7)
C(3)-C(12)-C(13)	119.9 (10)	C(11)-C(12)-C(13)	114.9 (11)
O-C(12)-C(13)	111.4 (7)	C(5)-O-C(12)	97.8 (6)
Pt-N(1)-C(15)	122.2 (8)	Pt-N(1)-C(19)	121.9 (7)
C(15)-N(1)-C(19)	115.6 (11)	N(1)-C(15)-C(16)	124.4 (10)
C(15)-C(16)-C(17)	118.6 (10)	C(16)-C(17)-C(18)	117.7 (13)
C(17)-C(18)-C(19)	120.4 (11)	N(1)-C(19)-C(18)	123.4 (10)

Table 56. Bond Angles (°).

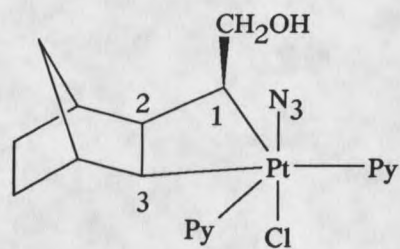
Pt-N(2)-C(20)	121.3 (6)	Pt-N(2)-C(24)	121.2 (5)
C(20)-N(2)-C(24)	117.5	N(2)-C(20)-C(21)	123.3 (8)
C(20)-C(21)-C(22)	119.0 (9)	C(21)-C(22)-C(23)	118.5 (9)
C(22)-C(23)-C(24)	120.8 (9)	N(2)-C(24)-C(23)	121.0 (8)

APPENDIX B
STRUCTURES

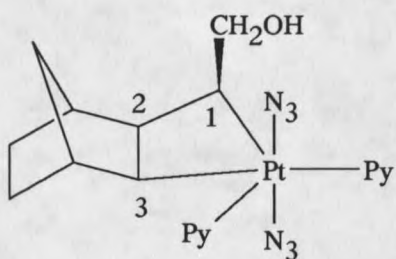




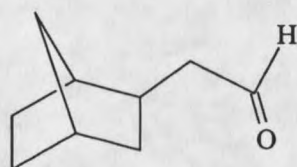
64



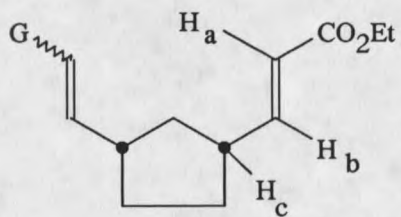
65



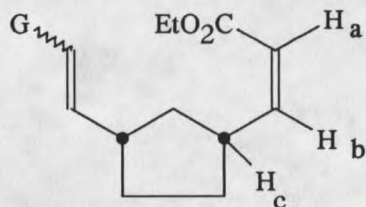
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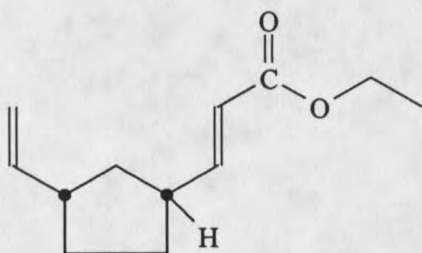
67



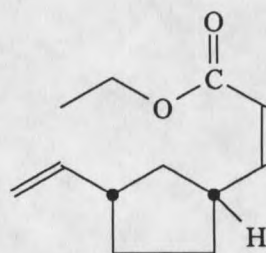
68



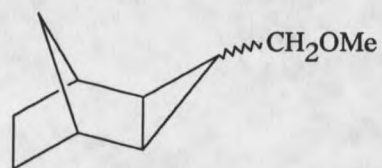
69



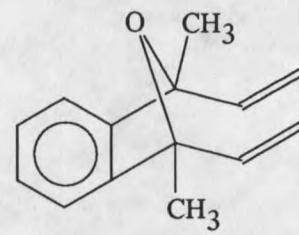
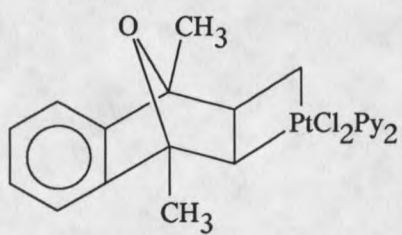
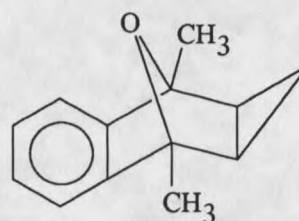
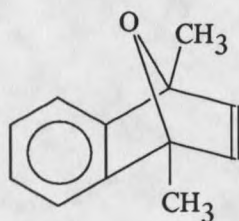
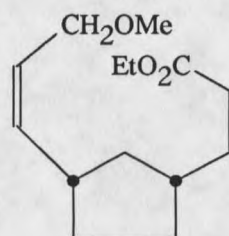
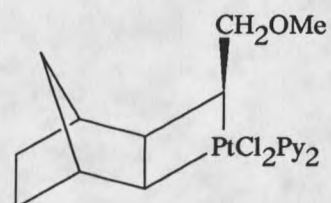
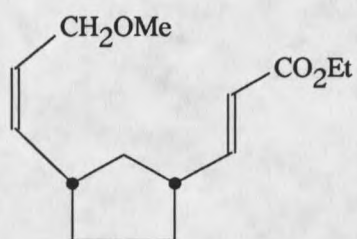
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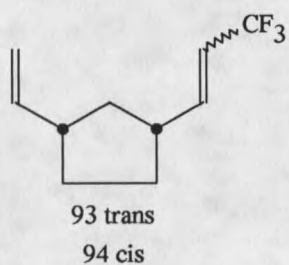
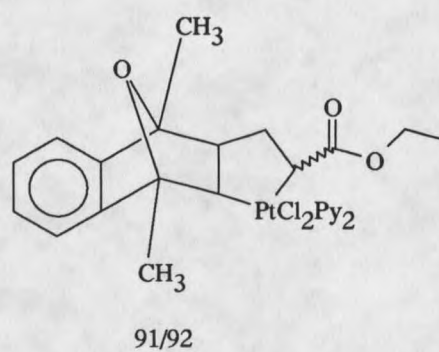
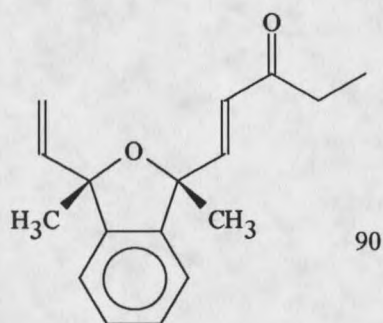
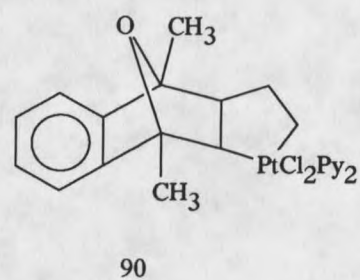
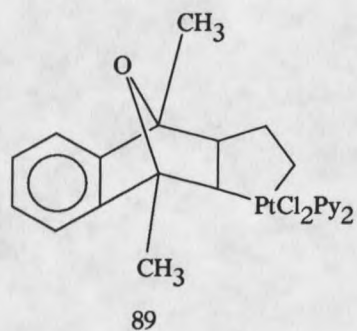


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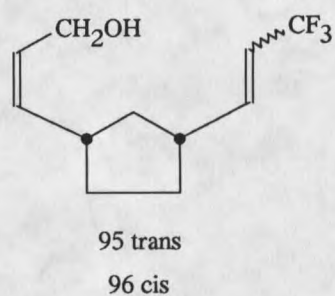


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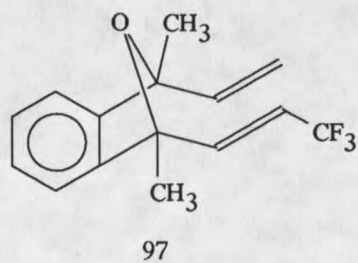


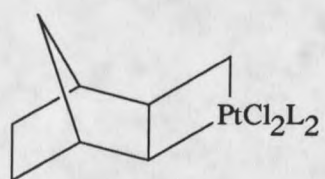


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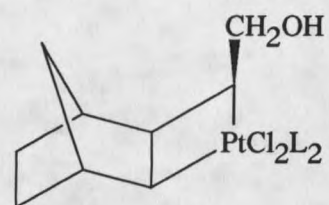


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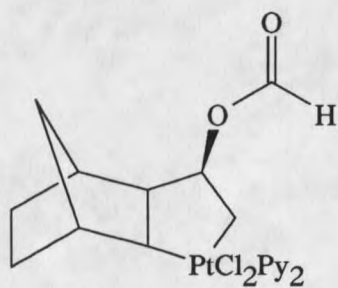




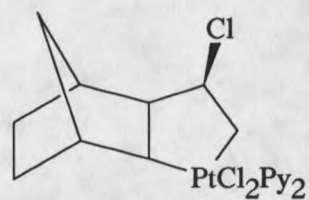
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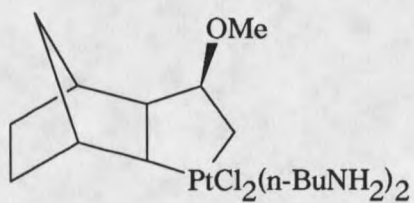
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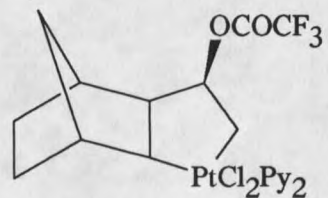
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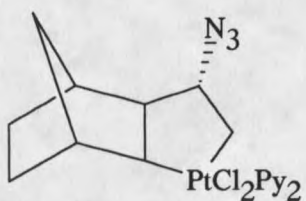
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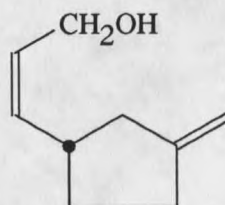
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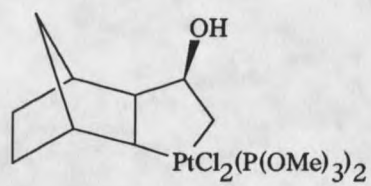
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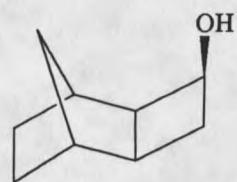
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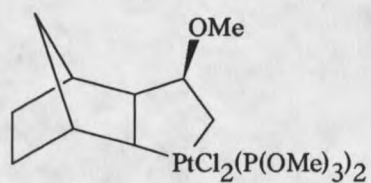
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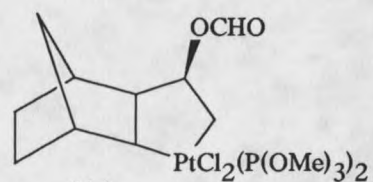
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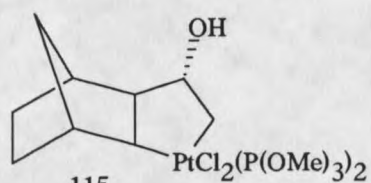
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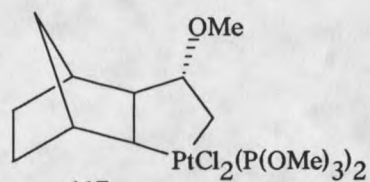
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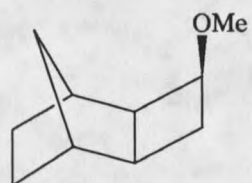
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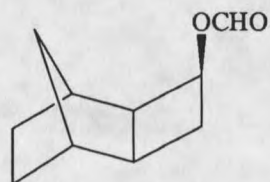
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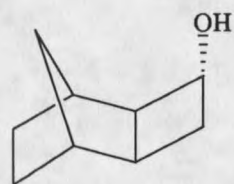
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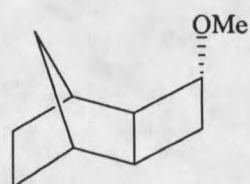
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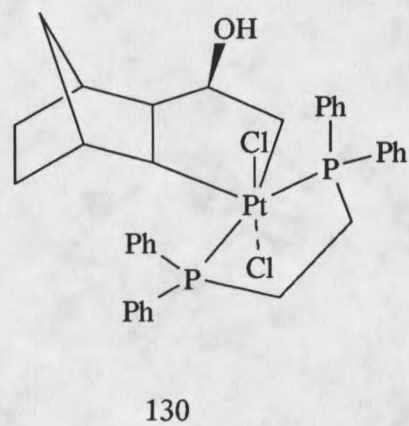
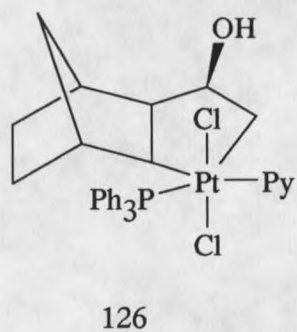
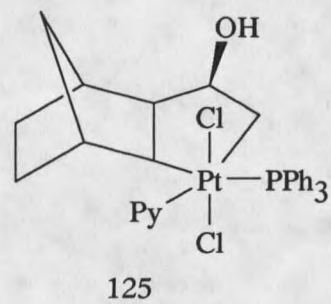
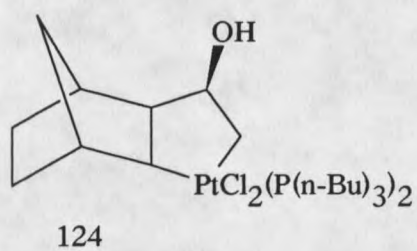
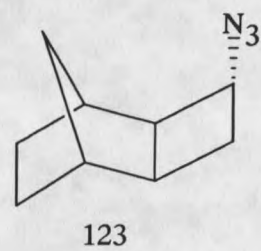
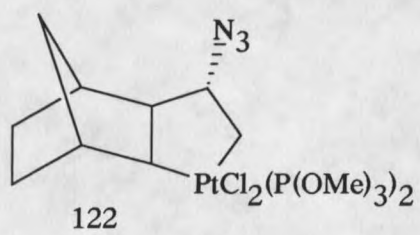
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