



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

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

Montana State University

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Abstract:

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

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

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

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

SYNTHESIS, CHARACTERIZATION AND CHEMISTRY OF
PLATINUM COMPLEXES DERIVED FROM
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by

John Ole Hoberg

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in

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APPROVAL

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John Ole Hoberg

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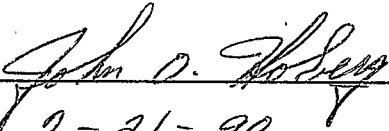
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ABSTRACT

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

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INTRODUCTION

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

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

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

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

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

Platinum Carbonyl Complexes

Structure and Bonding

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

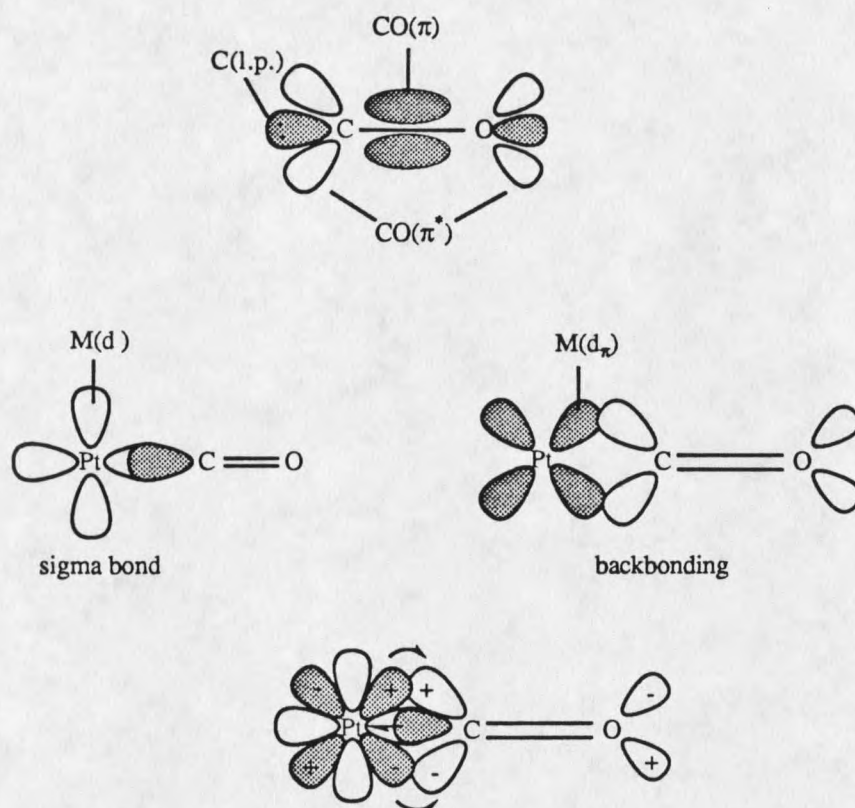


Figure 1. Pt-CO Bonding Scheme (bottom). The shading represents occupied orbitals and the plus and minus signs the phasing. Only one of the two π orbitals is shown in the structure of CO (top).

Formation and Characterization of Pt-Carbonyl Complexes

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

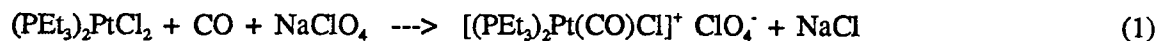
The electronic effects that ligands in Pt complexes have on $^1J_{\text{Pt,C}}$ and ^{13}CO NMR chemical shifts have also been studied. Changes in both the cis and trans ligands relative to the CO can have a marked affect on the chemical shift and Pt-C coupling. For complexes

such as trans-[PtX(CO)L₃]BF₄ (X = H, C₆H₄Cl, CH₂Ph, NCS, NO₃, Cl, Br or I) ¹³C measurements have been made. If X has a high trans influence, the platinum carbon (CO) coupling is between 960-990 Hz but if X has a low trans influence, the range is between 1660 and 1820 Hz¹⁰.

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

	Cl	Br	I
cis-[Pt(CO)X ₃]	2132	2112	2088
[PtX ₂ (CO) ₂]	2152	2130	2112
[Pt(bipy)(CO)X]	2145	2132	2120
cis-[(PEt ₃)PtX ₂ (CO)]	2100	2094	2085

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



Reactions Involving Pt-Carbonyls

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

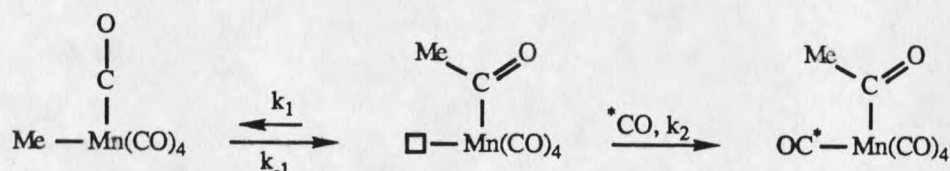


Figure 2. Migratory Insertion Mechanism (squares indicate vacant sites).

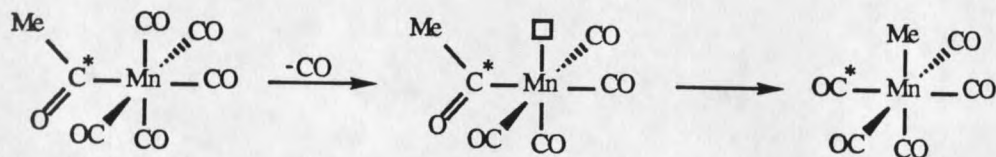
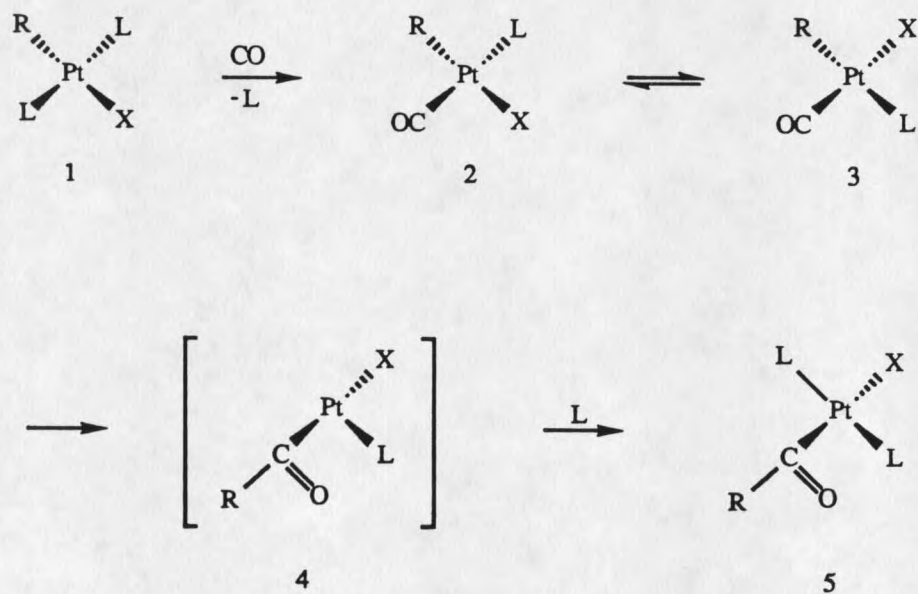


Figure 3. Reversible CO Insertion.

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

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



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

be made catalytic. As can be seen in Figure 4¹¹ metal-acyl groups can be carbonylated to esters in the presence of alcohols, to amides with amines, acids with water and aldehydes with H₂ present. When Pd is the metal, a tertiary amine is necessary to absorb the HX. Figure 5 outlines how the reaction is thought to proceed. Exactly what the mechanism is after CO insertion is as yet unclear. The three prevalent ideas for decomposition are as follows:

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

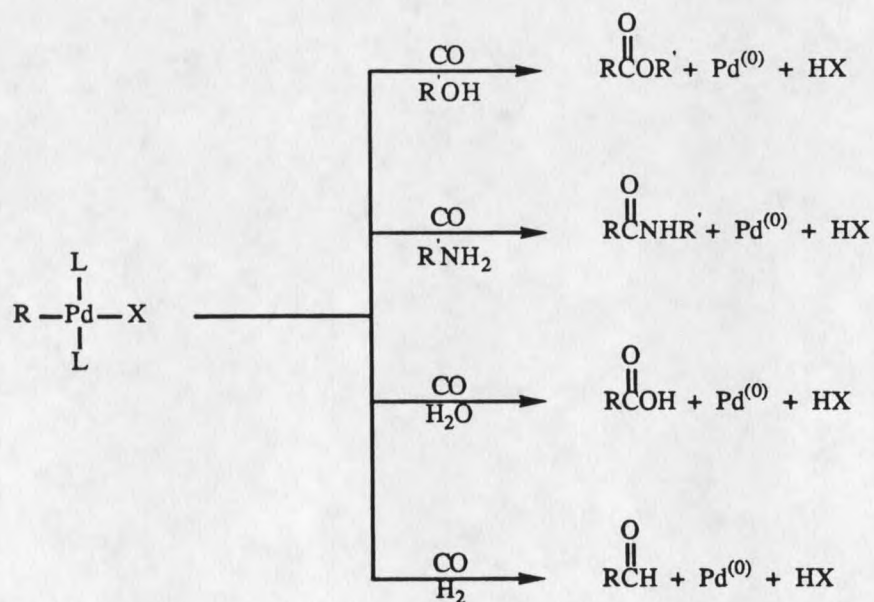


Figure 4. Palladium Catalyzed Reaction Pathways.

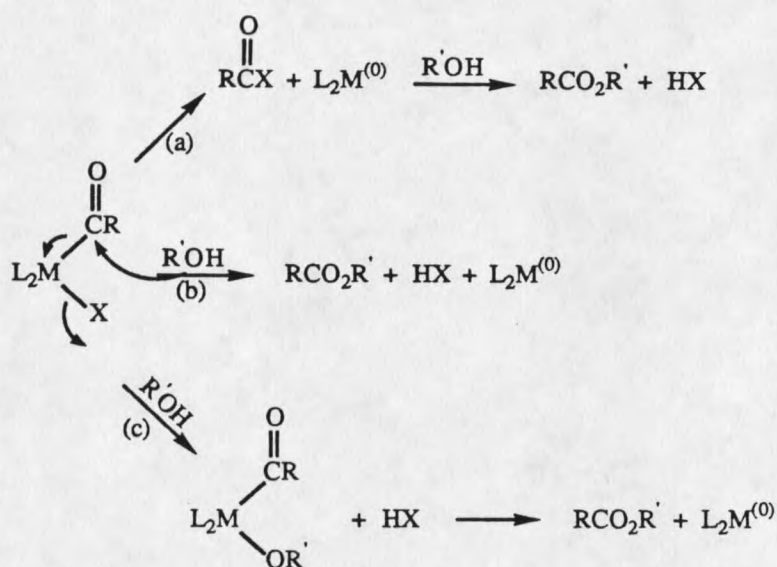


Figure 5. Proposed Pathways to Ester Formation.

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

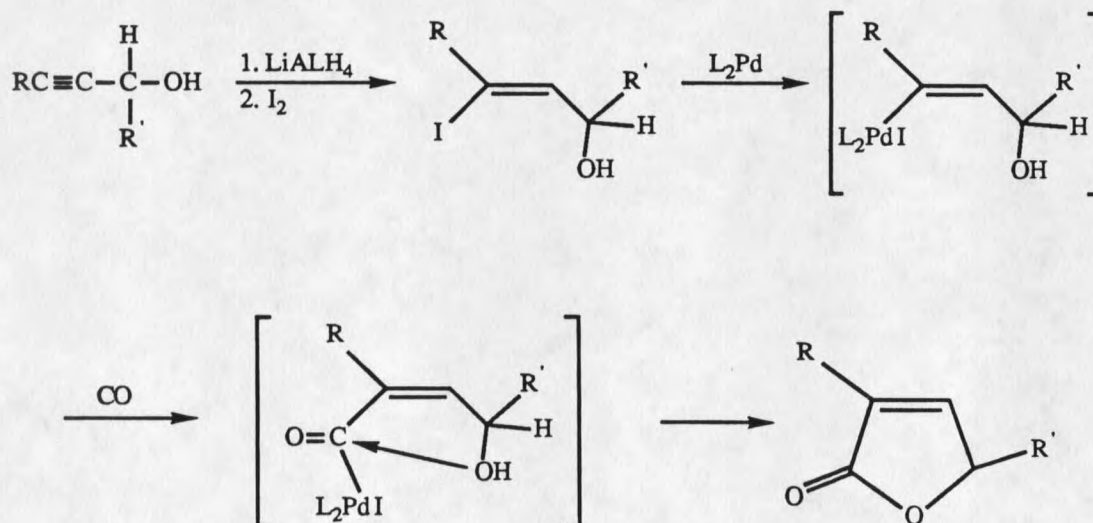


Figure 6. Palladium Catalyzed Lactone Formation.

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

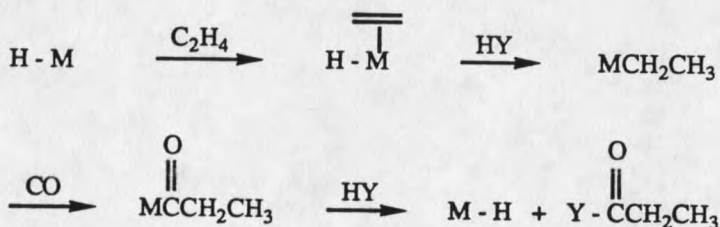
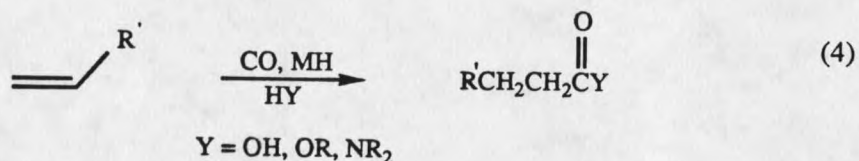


Figure 7. Carboalkoxylation of Ethylene

Platinum-Olefin Complexes

Structure and Bonding

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

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

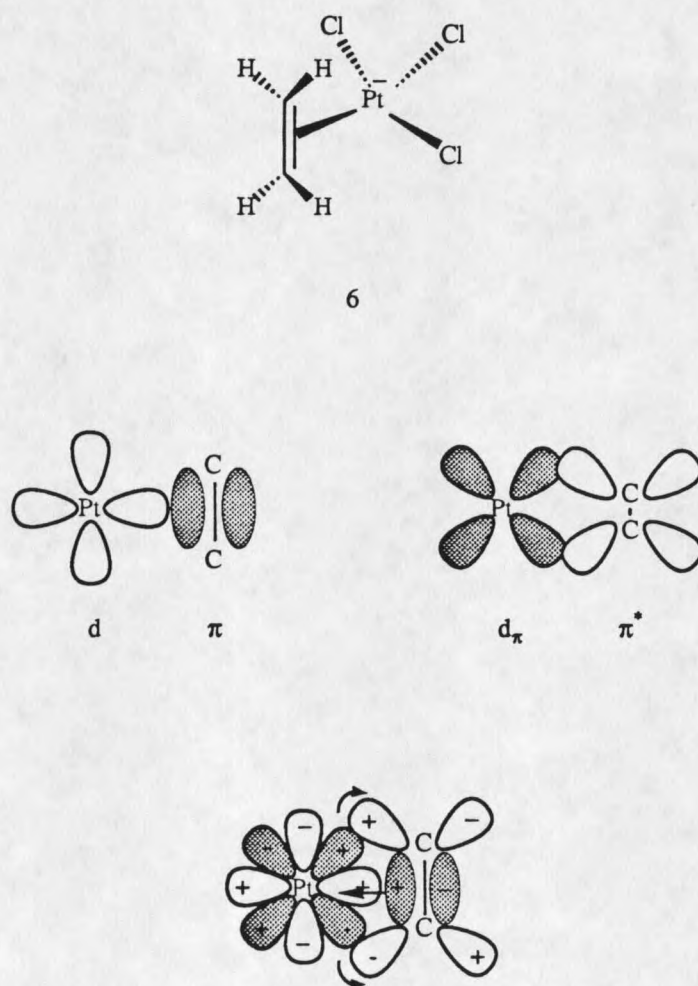


Figure 8. Bonding Scheme between Platinum and an Olefin. The shading represents occupied orbitals and the plus and minus signs the symmetry.

Olefins that bind to metals undergo lengthening of the C=C bond. The formation of the metal-alkene σ bond weakens the C=C bond by depleting the carbon π orbitals, thereby inducing elongation. The degree of back bonding from the metal also determines the amount of C=C bond lengthening. By filling the π^* orbital the C-C bond order can be reduced almost to a single bond. Zeise's salt, for example, is predominantly σ and its C-C length is 1.375Å, compared to free alkene (1.337Å). This would then be drawn as complex 7 which is the extreme of minimal back bonding. The other extreme is shown in complex 8 where back donation from the metal is very large. Pt(PPh₃)₂(C₂H₄)¹⁵ has a C-C distance of (1.43Å) inducing the substituents on the carbons to bend back away from the metal. When electron withdrawing groups are present on the olefin back donation is enhanced even more, such as Pt(PPh₃)₂(C₂(CN)₄), which has a C-C bond distance of 1.49Å¹⁶.



Characterization of Pt-Olefins

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

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

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

Table 3. Pt-Olefin Stretching Frequencies.

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

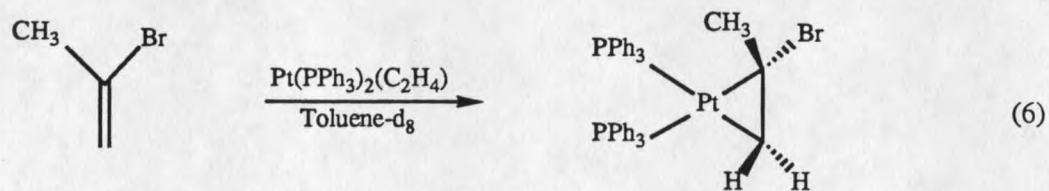
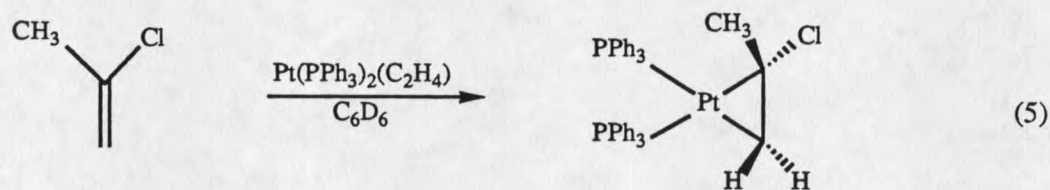
As was mentioned, ¹H and ¹³C NMR spectroscopy can be used to determine the difference between complexes such as 7 and 8. The vinyl protons and carbons shift significantly upfield depending on the amount of back donation from the metal. Carbon-13 resonances of platinum bound olefins will usually appear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

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

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

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

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



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

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

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

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

Reactions of Pt(II)-Olefins

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

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

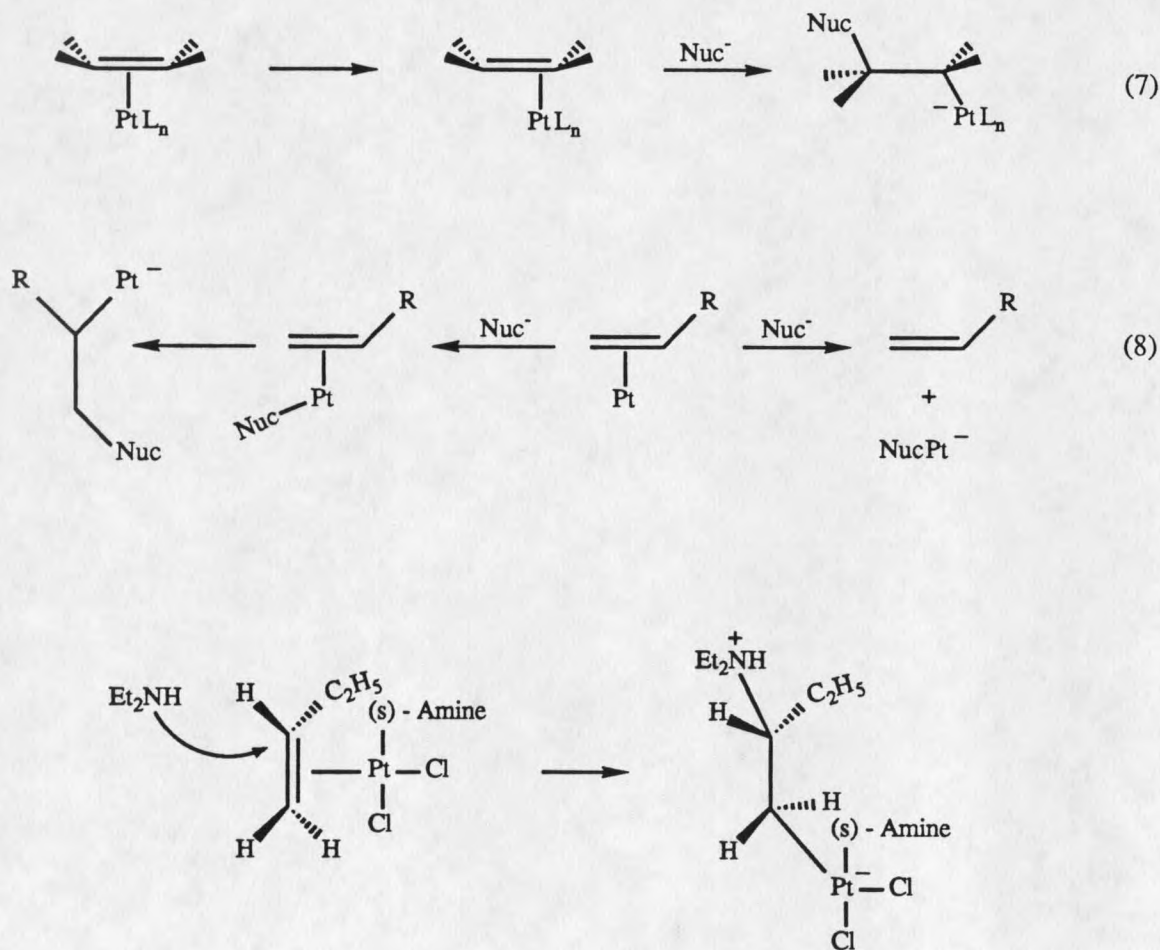


Figure 9. Amine Attack on a Pt(II)-Olefin

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

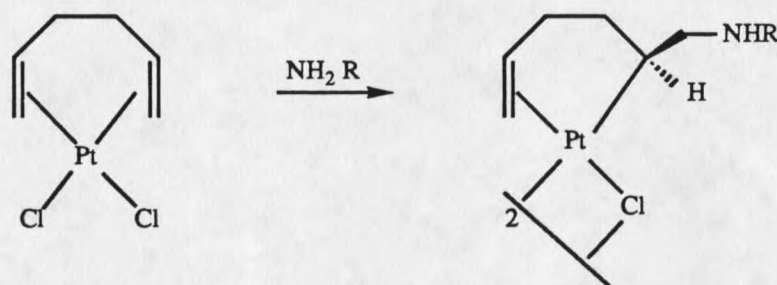
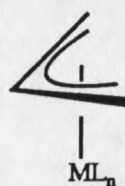


Figure 10. Nucleophilic Attack on a Platinum-chelated Olefin.

Platinum π -Allyls

Structure and Bonding

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



9

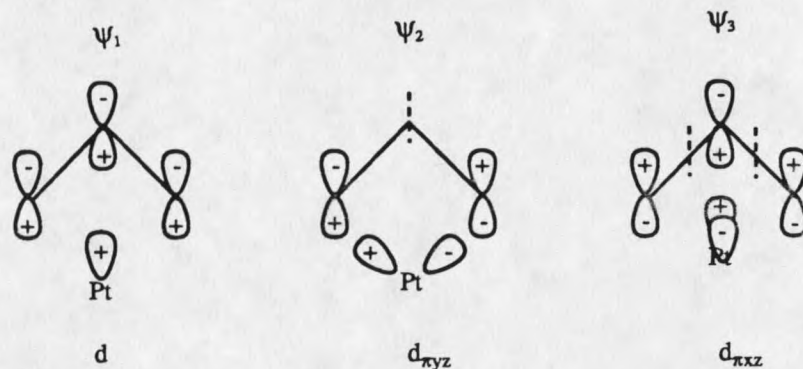


Figure 11. Pt- π -allyl Bonding Scheme. Nodes are shown as dotted lines.

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

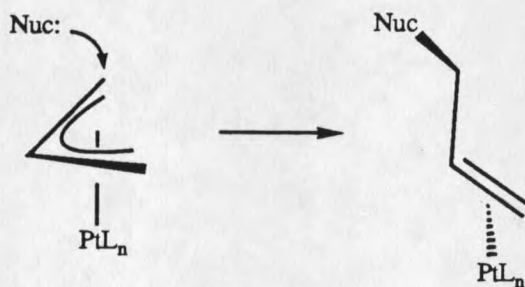


Figure 12. Nucleophilic Attack on Pt- η^3 -allyl.

Formation and Reaction

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

1. From an alkene³¹:
 $ML_2(\text{propene}) \rightarrow ML_2(\text{allyl})H$
2. From an allyl compound by nucleophilic attack on the metal³²:
 $CH_2=CHCH_2SnMe_3 + ML_nX \rightarrow (\eta^3-CH_2CHCH_2)ML_n + XSnMe_3$
3. From an allyl compound by electrophilic attack^{33,34}:
 $CH_2=CHCH_2Cl + ML_5^- \rightarrow (\eta^1-CH_2=CHCH_2)ML_5 \rightarrow (\eta^3-CH_2CHCH_2)ML_4$

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

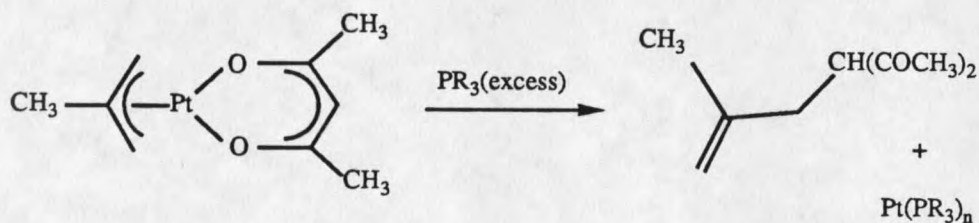


Figure 13. C-C Coupling Reaction of Methallyl and Acetylacetonate Ligands.

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

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

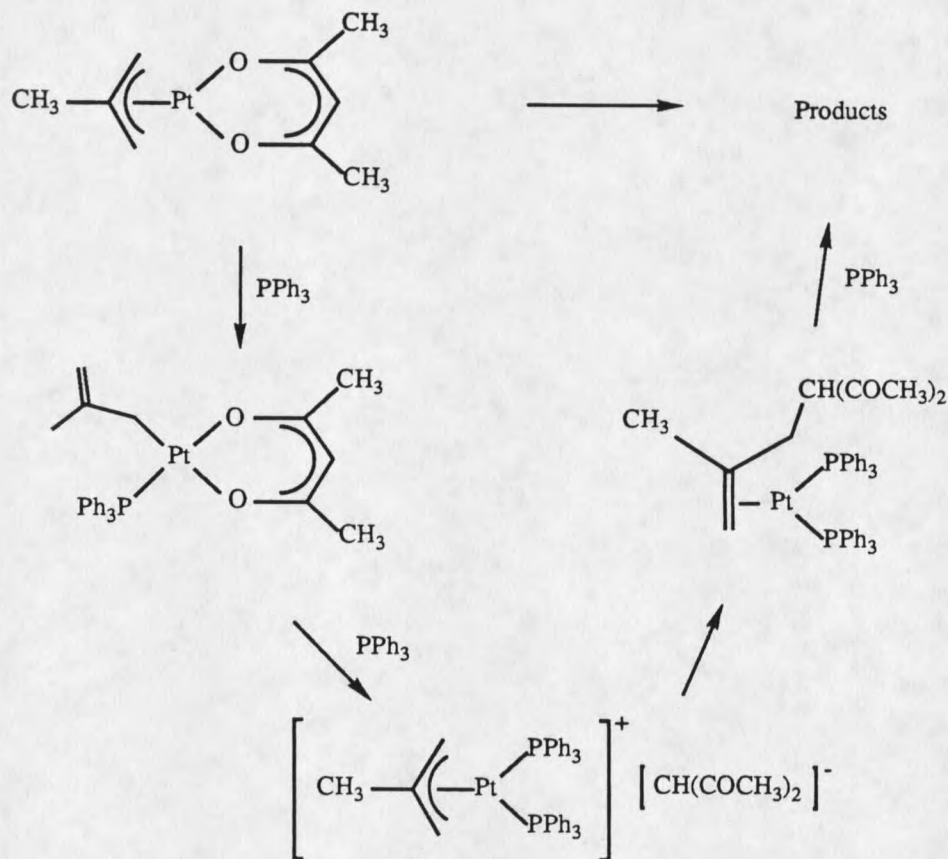


Figure 14. Mechanism of C-C Coupling

Platinum Olefin Isomerization

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

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

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

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

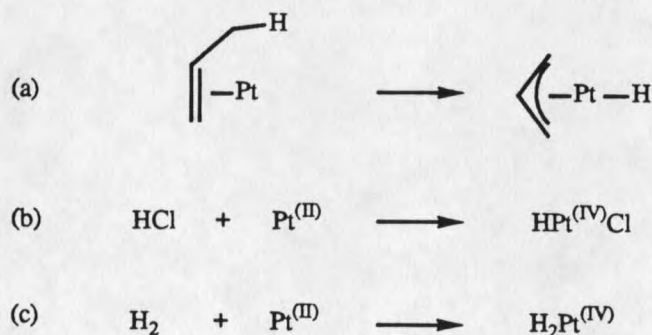


Figure 16. Hydride-Generating Reactions.

Alkene Hydrogenation

Hydrogenation catalysts add molecular hydrogen to olefins to give alkanes. Figure 17 depicts a proposed mechanism⁴⁶ of hydrogenation while Equations 10-12 show three modes of hydrogen activation⁴⁷. The first step in hydrogenation is oxidative addition of H₂ followed by olefin complexation. After alkene insertion, the metal alkyl reductively eliminates to give the alkane. Both Equations 10 and 11 exhibit oxidative addition of hydrogen. In Equation 11, the metal loses HX after the oxidative addition step. Equation 12 shows heterolytic hydrogen activation but it could also be an oxidative addition followed by deprotonation.

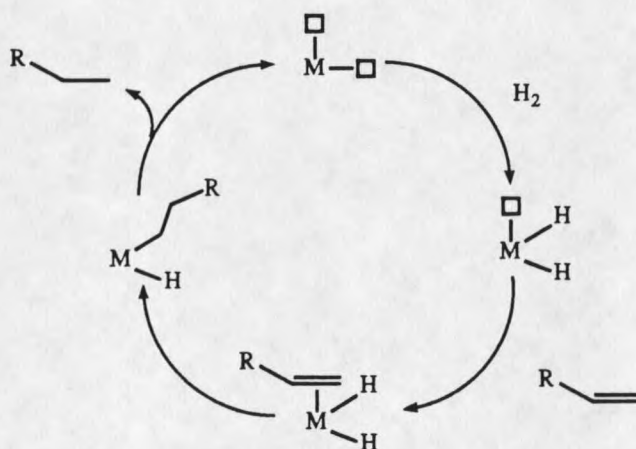
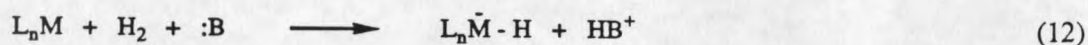
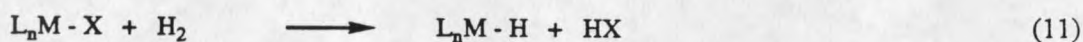
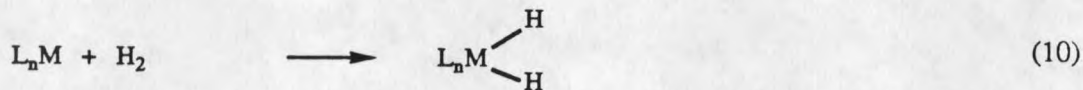


Figure 17. Hydrogenation Mechanism of an Alkene by Oxidative Addition of H₂ (squares represent an open site or labile ligand).



Platina(IV)cyclobutane Complexes

Structure and Bonding

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

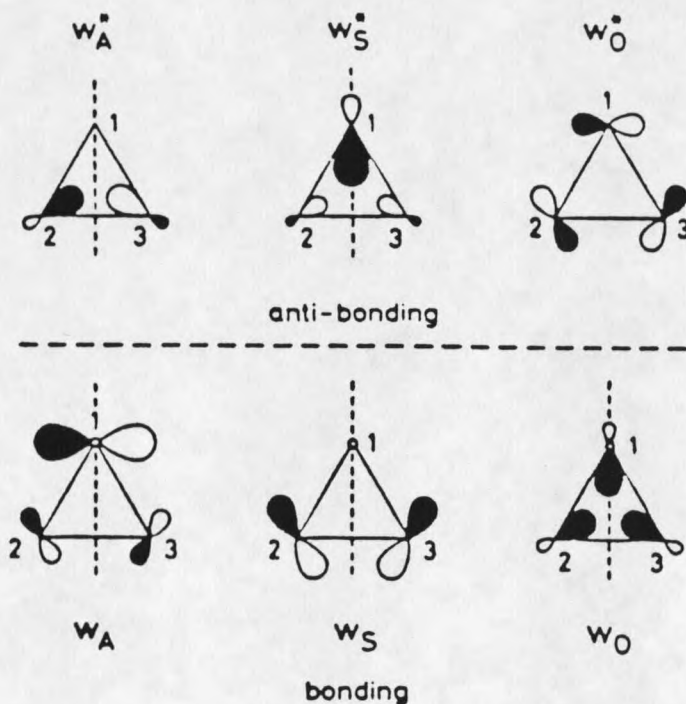


Figure 18. The Walsh-basis.

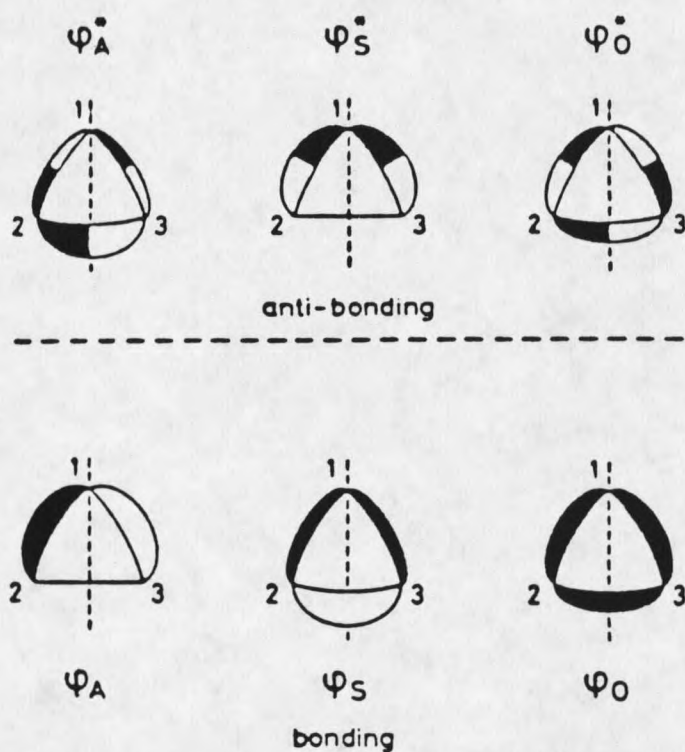
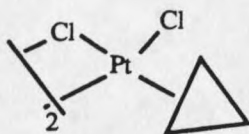
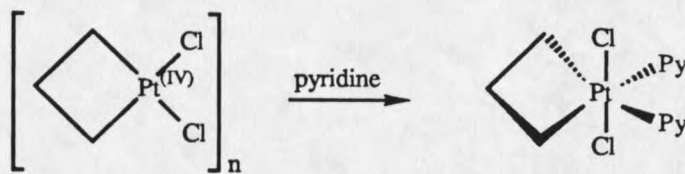


Figure 19. The (F.C.M.)-basis.

Tipper⁵⁶, using the analogy that transition metals complex with ethylene, reacted cyclopropane with hexachloroplatinic(IV) acid H_2PtCl_6 in acetic anhydride. Tipper's conclusion was that the dimeric cyclopropane complex **10** had formed. He compared this to Zeise's Dimer. Some years later Chat⁵⁷, using more sophisticated techniques, deduced that the cyclopropane had opened to give the platinacyclic derivative **11**. Reaction of this with pyridine would be expected to give the octahedral complex **12**, which was later confirmed by Gillard⁵⁸ using x-ray analysis.



10



11

12

The bonding scheme of platinum to cyclopropane is of much interest but is still in question. The simplest model would involve anionic ligand $C_3H_6^{2-}$ (where the carbon atoms are sp^3 -hybridized) and a d^6 platinum (d^2sp^3 -hybridized). The platinum and three carbon atoms form four two-center, two-electron σ bonds. This has the value of simplicity but does not describe the chemistry or differences in geometry in various molecules. Looking for a better model, McGinety⁵⁹ postulated four-center molecular orbitals comprised from the carbon atoms in the sp^2 -hybridized state (much like the Walsh cyclopropane) and a dsp^3 platinum. This would give σ orbitals in a trigonal bipyramidal array with a d-orbital in the equatorial plane. Figure 20 depicts the four occupied orbitals comprised from the eight bonding electrons. McGinety lists several advantages of his model but the shortcoming is that the MO's lead to no net platinum-cyclopropane bonding interaction. The picture he draws for us though is that there is the probability of bent bonds in platinacyclobutanes.

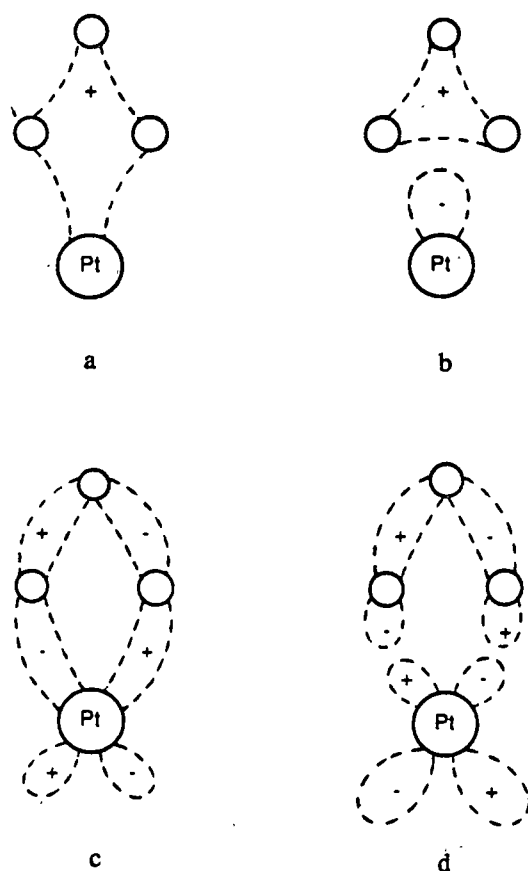


Figure 20. McGinney Platinacyclobutane Bonding Scheme. (a) and (b) are constructed from available σ -orbitals while (c) and (d) are from the metal d-orbital and p-orbitals of the carbon atoms.

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

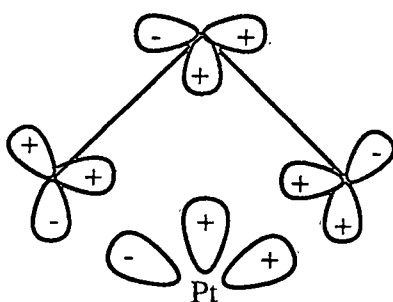


Figure 21. McQuillin Platinacyclobutane Orbital Model

Characterization of Platinacyclic Compounds

Insertion of platinum into cyclopropanes usually results in an insoluble precipitate (initially precipitated complex-IPC). Three methods have been employed in the characterization of this solid: mass spectrum, infrared and solid state (CP/MAS) NMR. The mass spectrum of $[(PtCl_2C_3H_6)_n]$ has been taken⁶¹, and the observation of a peak at m/e 1232 is believed to be the parent ion which corresponds to the tetramer **13**. The IR spectrum of these solids also displayed the presence of bridging and terminal chlorines. Comparison of the polymeric $\{[PtY_2(CH_2CH_2CH_2)]_n\}$ and the proposed tetramer show similar stretching frequencies. IR spectroscopy also identified the C_3H_6 unit as a platinacyclobutane. Table 6⁶² gives the stretching frequencies of two complexes in comparison to cyclopropane, indicating opening of the ring.

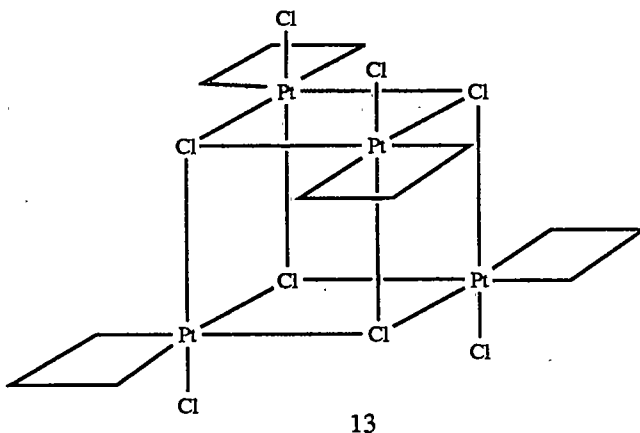


Table 6. Stretching Frequencies for Platinacyclobutanes.

C ₃ H ₆ unit	Pt(C ₃ H ₆)Cl ₂ Py ₂	[Pt(C ₃ H ₆)Cl ₂] ₄	C ₃ H ₆
C-H	2992	3025	3103
	2938	2954	
	2917	2948	
CH ₂ wag	1238	1255	
		1237	
CH ₂ deformation	1437	1414	1442
CH ₂ twist	1217	1165	
ring deformation	1134	1149	
	1087	1125	
CH ₂ rock	1038	1087	1029
		1022	
ring deformation	980	981	
CH ₂ rock	976	948	869
	892	890	
		663	
Pt-C ring deformation		563	

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

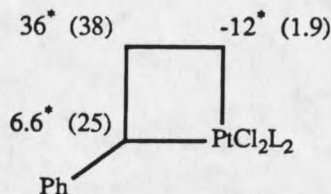
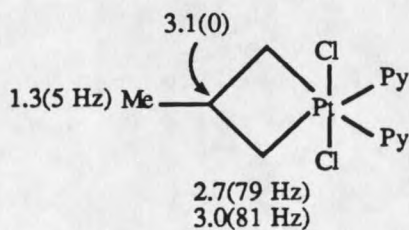


Figure 22. CP/MAS Resonances of a Platinacyclobutane (numbers in parentheses). The * Numbers are Solution ^{13}C Resonances.

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

^1H NMR spectra of simple cyclobutanes such as **14**⁵⁷ ($J_{\text{Pt,H}}$ in parentheses) are relatively simple to interpret. Platinum proton coupling has a range of 60-110 Hz for $^2J_{\text{Pt,H}}$, 0-50 Hz for $^3J_{\text{Pt,H}}$ and 0-10 Hz for $^4J_{\text{Pt,H}}$ ⁶⁵⁻⁶⁶. This is usually a good model for simple and complex platinacycles. Complex molecules have the problem of overlapping signals which make assignments difficult, but with today's high field NMR spectrometers and sophisticated techniques, proton NMR data is extremely useful in characterization. Moving from 60 or 100 MHz to a 500 MHz magnet has the advantage of spreading out what was once a cluttered spectrum.



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



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

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

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

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

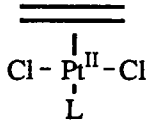
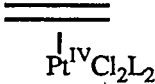
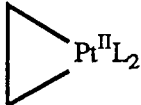
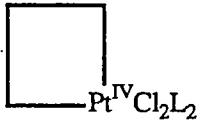
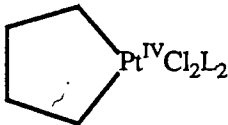
COMPLEX	in PPM	$^1J_{\text{Pt,C}}$ in Hertz	Ref.
	70 - 110	50 - 200	71, 72
	120	94	71
	40 - 65	not reported	20
	(-20) - 20	335 - 460	65, 66, 69, 70
	15 - 45	490 - 560	73, 74
$\text{L}_2\text{Pt}^{\text{IV}}(\text{Alkyl})_4$	(-5) - 20	660 - 730	74

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






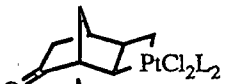
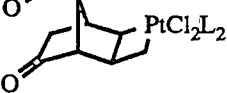


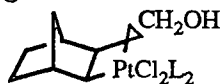
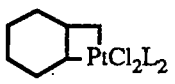
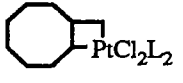

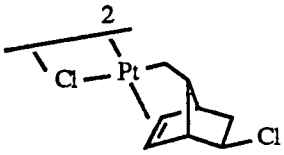
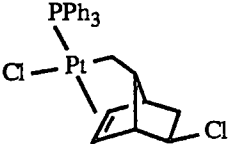
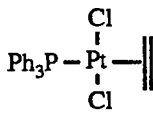
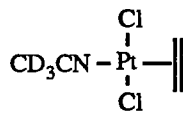
COMPLEX	LIGAND	SOVENT	SOLVENT (ppm)
	Py	CDCl ₃	3317
	Py	CDCl ₃	3308
	Py	CDCl ₃	3350
	THF	THF	3278
	THF	THF	3365
	Py	CDCl ₃	3368
	Py	CDCl ₃	3390
	Py	CDCl ₃	3333
	Py	CDCl ₃	3322
	Py	CDCl ₃	3334
	Py	Py - d ₅	3315
	Py	Py - d ₅	3300

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

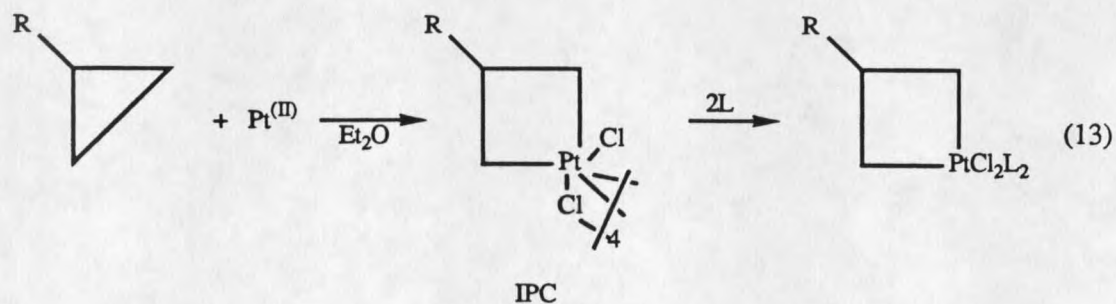
COMPLEX	SOLVENT	SHIFT (ppm)
	DMSO	1635
	CDCl ₃	723
	CDCl ₃	732
	CDCl ₃	687
	CD ₃ CN	1726

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

Formation of Platinacycles

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

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



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

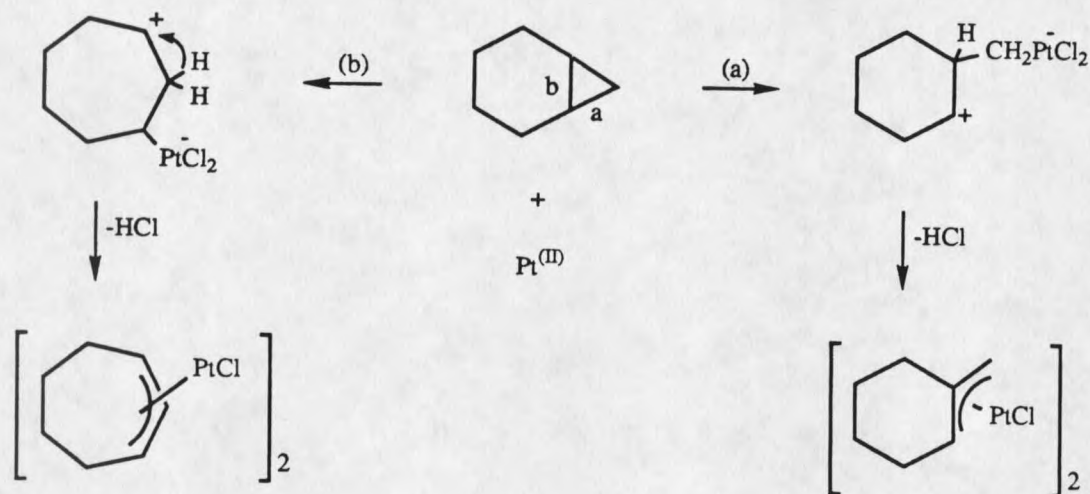
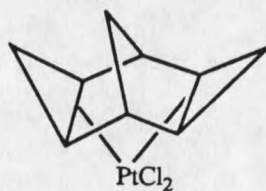


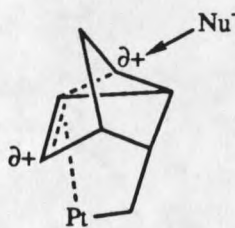
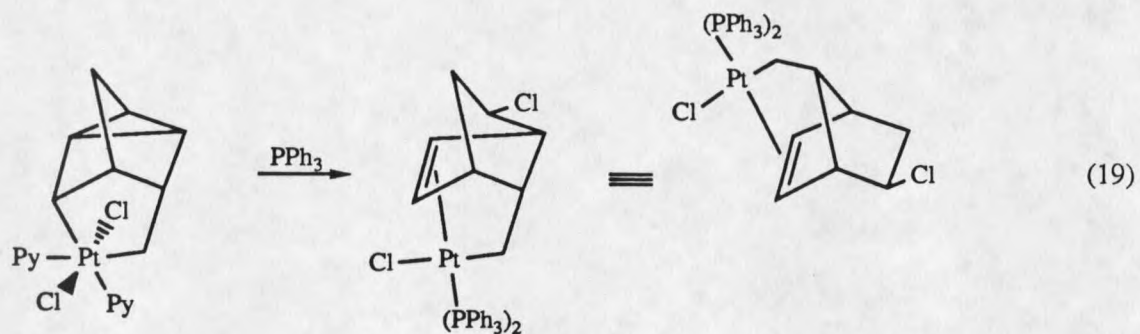
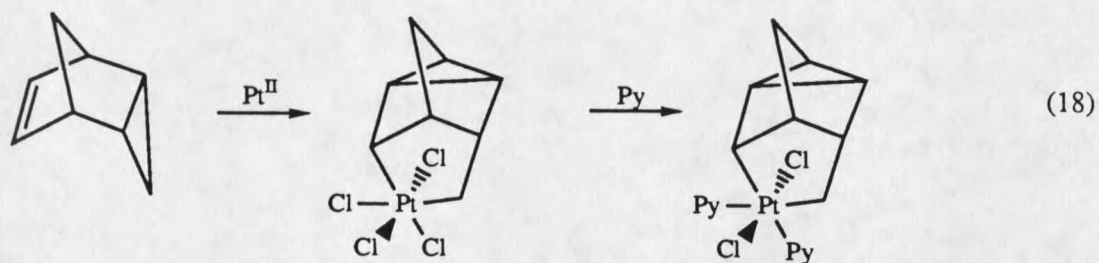
Figure 24. π -Allyl Formation from Norcarane and Pt(II).



15

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

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



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

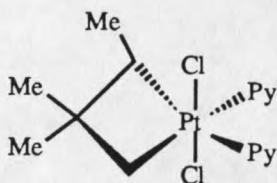


Figure 25. 2,3,3-Trisubstituted Platinacyclobutane.

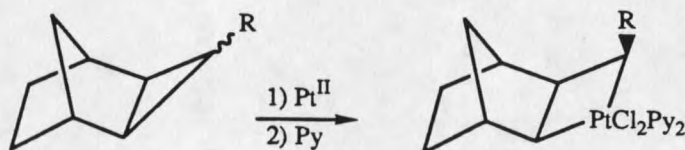


Figure 26. 2,3,4-Trisubstituted Platinacyclobutane.

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



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

