Synthesis, characterization and chemistry of platinum complexes derived from cyclopropanes with electron donors
by Mark Thomas Dimke

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

Abstract:
It has long been known that Zeise's Dimer inserts into cyclopropanes to form platinacyclobutanes. However, not all platinacyclobutanes are stable, and several have been shown to form novel organic products. It has also been shown that pi electron donors on the cyclopropane will stabilize the incipient carboncation formed by the platinacyclobutane. Various tactics can then be used to further direct the chemistry.

The first thrust of this research utilized strained ring systems to affect the chemistry about the platinacyclobutane. In the first example, 2,7,7-trimethyltircyclo[4.1.1.0^2,4]octane forms a platinacyclobutane in the presence of Zeise's Dimer which subsequently undergoes a carbocation mediated bond migration to form l,7,7-trimethyl-2-methylideyl-endo-6-chlorobicyclo[2.2.1]heptane. In the second case, cis tricyclo[5.1.0.0^2,4]octane undergoes a novel transformation upon treatment with Zeise's Dimer and triphenyl phospine to form 3-(chloromethyl)-6-methylidenyl-1 -cyclohexene. This is thought to be due to the proximity of the second cyclopropane to the first cyclopropane.

A second method utilized in the stabilization of the incipient carbocation generated by a platinacyclobutane is the use of an olefin alpha to the cyclopropane. Platinacyclobutanes from these systems undergo a rearrangement to form methylene tethered pi allylic complexes which have the unique ability to undergo a variety of regio and stereo-selective nucleophilic additions without decomposition of the complex. These complexes can then be decomposed utilizing a variety of methods yielding a plethora of interesting organic products based on the original diene that the cyclopropane was generated from.

A third method used to direct the chemistry resulting from platinacyclobutanes is the use of the lone pair of electrons on a heteroatom, in this case sulfur and nitrogen.

Both demonstrate the ability of a hetero atom to direct the chemistry of platinacyclobutanes. However in the case of amino cyclopropane, the nitrogen complexes to one platinum atom before a second inserts and thereby prevents chemistry alpha to the amine. In the case of phenyl cyclopropyl sulfide, the addition of Zeise's Dimer yields a rearrangement of the cyclopropane to a propenyl moiety.

In all cases, it was shown that the nature of the platinum carbon bond polarization in a platina(IV)cyclobutane is platinum minus carbon plus. Also, this thesis helps define how pi donating substituents on cyclopropanes direct the subsequent chemistry of platinacyclobutanes formed from these cyclopropanes.

SYNTHESIS, CHARACTERIZATION AND CHEMISTRY OF PLATINUM COMPLEXES DERIVED FROM CYCLOPROPANES WITH ELECTRON DONORS

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Mark Thomas Dimke

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

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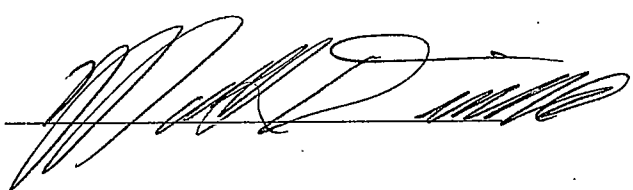
Signature 

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ABSTRACT

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INTRODUCTION

Historical Preface

The history of organometallic chemistry is quite rich and older than might be expected originating in 1827 with a compound discovered by a Danish pharmacist Zeise, commonly known as Zeise's salt, **1**.[1] The true nature of this salt was not understood unambiguously until Wunderlich and Mellor reported the first X-ray crystal structure in 1954 (See Figure 1).[2] Zeise's salt **1** launched a branch of chemistry, and even though this branch is nearly two centuries old, the chemistry has not seen its utility exhausted.

Indeed this thesis relies entirely on the novel chemistry that a closely related complex, Zeise's dimer, **2,** (see Figure 10) exhibits when it is allowed to interact with cyclopropanes to form platinacyclobutanes. Platinacyclobutanes were initially discovered in the fifties and received a good deal of attention at the time. However, by the late sixties it appeared that interest had waned. In the early eighties, interest in this area was revitalized by Jennings for its mechanistic and synthetic potential. His work with platinacyclobutanes took a general course. First, an olefin is cyclopropanated using standard organic methods. Second, Zeise's dimer **2** is reacted with the cyclopropane to form a platinacyclobutane. Third, the platinacyclobutane is treated with a series of reagents to effect the release of the organic substrate, yielding an organic product. When one examines the overall effect of this method, a ubiquitous olefin undergoes a novel

organic transformation while yielding mechanistic insights into all of organometallic chemistry. This thesis further examines the chemistry of platinacyclobutanes which have an electron donor in the α position. Before launching into a discussion of that chemistry, it would be useful to the reader to present an overview of bonding, common mechanistic pathways, and structure elucidation in the organometallic/organoplatinum arena.

Bonding

π Bonding in Organoplatinum Complexes

In the preface to this thesis, it was mentioned that Zeise's salt **1** was the first organometallic complex to be described. In addition, it was the first complex known to exhibit transition metal π bonding to an olefin. In this case, the π bonding is between platinum and ethylene (Figure 1).

Carbon monoxide and other related ligands such as nitrosyl and the isocyanides are probably the most common π bonding ligands. However, since π bound olefins are important to the chemistry discussed in this thesis, the discussion will center on this ligand.

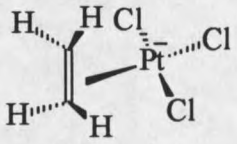

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Figure 1. Zeise's Salt 1.

The first thing that should be noted in the bonding of ethylene or any other olefin to a transition metal is that the carbon-carbon bond of the olefin is most often perpendicular to the plane of square planar complexes. The predominate factor influencing the orientation of the olefin is the steric effect from the other ligands.[3] However, one rare example where the olefin (styrene) is coplanar to the other ligands is a compound described by Miki et al.[4] Before engaging in further discussion of the π backbonding, an overview of the general orbital interactions of π bonding to metals would be useful.

The orbital picture for organometallic π bonds goes back to the Chatt, Duncanson, and Dewar model.[5,6] This involves two interactions, the first of which is a σ type interaction where the electrons in the π bond of the olefin are donated into the empty d_{sp}^2 hybrid orbital on the metal as shown in Figure 2.

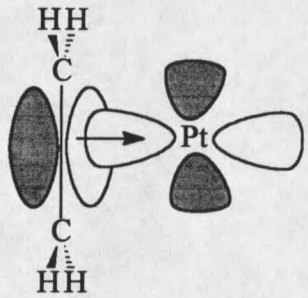


Figure 2. The Olefin Orbital Electron Donation to an Unfilled d_{sp}^2 hybrid Orbital.

The second interaction is the back donation of the filled d_{yz}, d_{xz} or d_{xy} orbital on the metal to the π^* orbital on the olefin as shown in Figure 3.

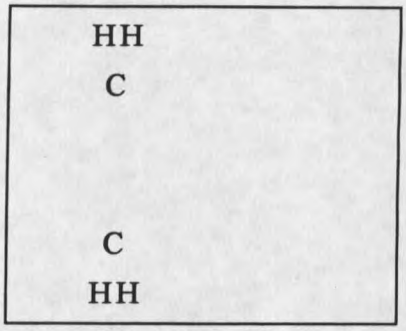


Figure 3. Donation of d Electrons Into π* Orbital.

In Figure 4, we see the combined interaction of this type of bonding to give a complete picture of a typical π bond to a metal.

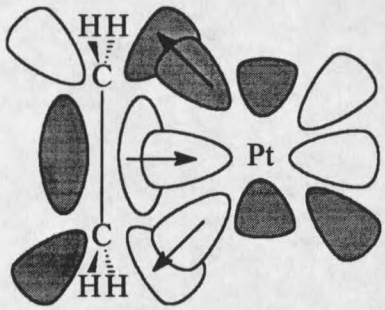


Figure 4. Combined Bonding Interaction.

In Figure 5, we see a depiction of both extremes of the Chatt, Duncanson, and Dewar model. In the first case, no back bonding occurs and the olefin is free to adopt any orientation that would be least sterically hindered. This extreme would also be theoretically marked by a completely planar ethylene ligand, as it is the backbonding that adds sp^3 character to the olefinic carbons. In the other extreme case, the backbonding is complete and formal bonds exist between the metal and the two carbons of the olefin forming a metallacyclopropane. This would give rise to hybridization approaching sp^3 at

both carbons and hence the protons would be bent away from the metal. Additionally, the carbon-carbon bond is lengthened as back bonding increases. The neutron diffraction structure of Zeise's salt **1** exhibits an intermediate case on the continuum between these two extremes.[7]

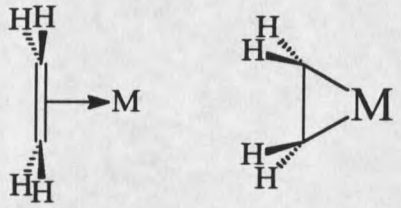


Figure 5. Bonding Extremes.

Bonding of π Allylic Metal Systems

Closely related to olefins are π allylic ligands. Formally, the π allylic moiety is a singly charged, η^3, four electron donor to the metal. Two representations of allylic ligands have been presented, one as two resonance structures, the other as a truly delocalized π system (Figure 6).

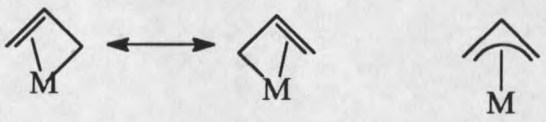


Figure 6. π Allyl Resonance Structures.

The suggestion from the two resonance structures is that there are σ bound and π bound ligands to the metal. This view is illustrative for accounting purposes. However, in x-ray structures, the carbon-carbon bonds of the η^3 form are the same length.[8]

Additionally, the reactivity of the terminal carbons is the same, but considerably different from the central carbon. This is in stark contrast to what would be predicted using the resonance structures.

Another good example of the differentiation between these two models is nucleophilic attack of a π allyl complex. Nucleophilic attack of π allyls occurs at the terminal carbons as opposed to the central carbon, with a few notable exceptions. If the frontier molecular orbitals of this type of system are examined, the three molecular orbitals of the allyl moiety, as well as the two molecular orbitals on the metal that interact with it first must be taken into account. In Figure 7, the five molecular orbitals of the allyl moiety and the metal that interact with it are illustrated. Ψ_1 is the bonding orbital for the allyl and can interact with the d_σ orbital on the metal. Ψ_2 is a nonbonding orbital and interacts with the $d_{\pi yz}$ metal orbital and Ψ_3 is the allylic antibonding orbital.

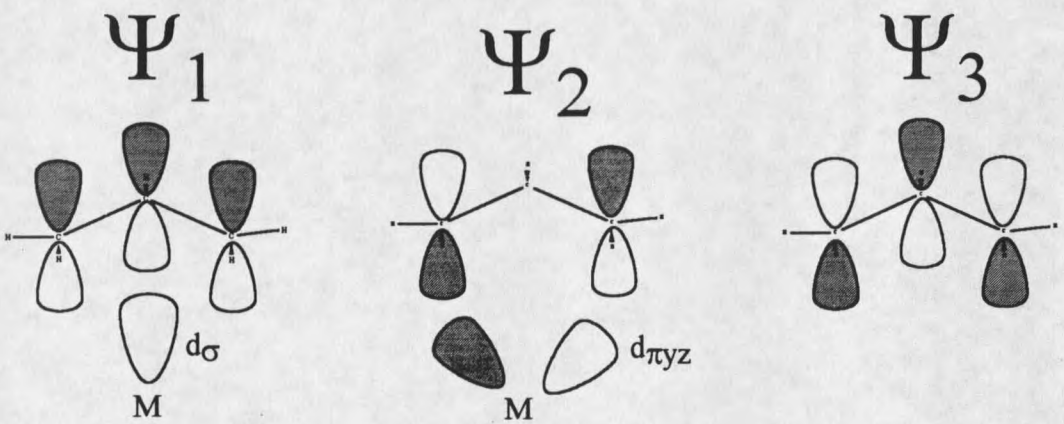


Figure 7. π Allyl Orbital Interactions.

π Allylic Complexes

Reaction of Metal π Allylic Systems

Examination of the frontier molecular orbitals (FMO) leads to the important observation that Ψ_2 is the lowest unoccupied molecular orbital (LUMO) when the metal is electron deficient, therefore when complexes of this type are attacked by the electrons of a nucleophilic reagent, the attack occurs on Ψ_2, i.e. the terminal carbons. Also, this attack occurs most often from the face opposite the metal. The electron deficiency of the complex which makes it susceptible to nucleophilic attack generally occurs for one of two reasons: either it has a high oxidation state or the metal has other electron deficient ligands. In either case, the end product of such an attack is typically a π bound olefin as shown in Figure 8.[9] This type of nucleophilic attack is by far and away the most useful and exploited chemistry of metal π allylic systems. In cases where the metal is electron rich, Ψ_3 is the LUMO. Therefore, when nucleophilic attack occurs it happens at the central carbon.

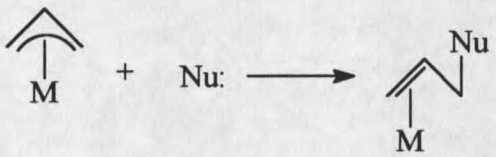
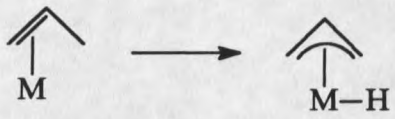


Figure 8. Nucleophilic Attack of a π Allylic Complex.

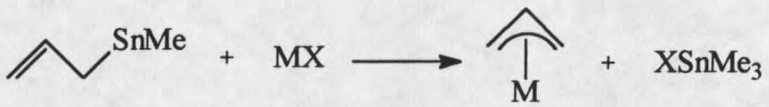
Formation of π Allylic Complexes

Pi allylic complexes can be generated by a number of methods. Three of the most common are illustrated in the following list.[10]

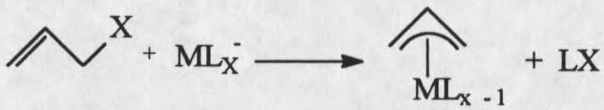
1. From alkenes by hydride elimination.[11]



2. From allylic compounds by nucleophilic attack on the metal.[12]



3. From an allyl compounds by electrophilic attack of the metal by the ligand.[13]



Oxidative Addition and Reductive Elimination

It would be well beyond the scope of this introduction to have a comprehensive and detailed discussion of the oxidative addition or reductive elimination topics since major chapters of organometallic textbooks are dedicated to these subjects.[14,15] Rather, this introduction will concentrate on the most important one of the four mechanisms of oxidative addition. As it is the chemistry of this pathway that is germane to this thesis. The mechanism that will be discussed is referred to as the three-center addition and is illustrated in Figure 9. Interestingly, when the concept of microscopic reversibility is

applied, it is this mechanism that is invoked for reductive eliminations which yield organic products.[16]

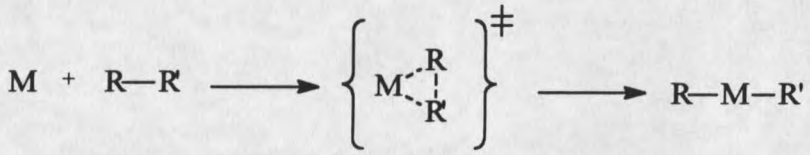
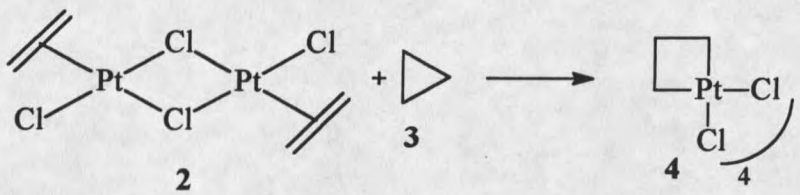


Figure 9. Three Center Oxidative Addition.

While Figure 9 is a cartoon example of a three center addition, it illustrates the salient features of all oxidative additions. The metal has undergone a formal oxidation in which the oxidation state, electron count and coordination number have all increased by two. In general, three center additions are the type of oxidative addition which require a nonpolar bond (most commonly hydrogen gas or hydrogen silicon) in which to insert. Less commonly, the metal may insert into carbon hydrogen or strained carbon-bonds. Among the important aspects of a three centered addition are that the initial addition is cis, and that the polarity of the solvent is generally unimportant.

Formation of Platinacyclobutanes via Oxidative Addition

A good example of this type of addition is McQuillin's modification of Tipper's method in which platinum (II) (Zeise's dimer **2**) inserts into a cyclopropane to yield a platinacyclobutane as shown Figure 10.[17,18]



2 3 4 4

Figure 10. Example of Oxidative Addition.

This reaction demonstrates all of the aforementioned features of a three center oxidative addition. The platinum has gone from a platinum(II) to a platinum (IV), from 16 to 18 electron complex, and the coordination number has gone from four to six. Although only the four charged ligands are shown in the platinacyclobutane, note that it is a tetramer and the remaining coordination sites are filled as a result of the chlorides bridging. The strained carbon ring has added cis to the metal and, unlike other additions which could rearrange, in this case must remain cis due to the methylene tether. While the oxidative addition of cyclopropanes is not the only case of a metal inserting into a strained ring[19], it is quite uncommon for metals to insert into other sized rings.[20] The other common example of this type of reaction is the oxidative addition of epoxides. However these reactions proceed via a different reaction mechanism and therefore should not be considered in the same light as the oxidative addition of cyclopropanes.[21]

Platinacyclobutane Complexes

Discovery and Structure Elucidation of Platinacyclobutanes

The first platinacyclobutane was prepared by Tipper in 1955 using cyclopropane gas **3** and hexachloroplatinic acid in acetic anhydride. Tipper did not realize however, what he had produced.[22] The structure that he proposed for the product was a neutral interaction like a π bound olefin, based on the Walsh type orbitals of cyclopropane. This assumption is not entirely unreasonable given the data that Tipper had collected. Cyclopropanes were known to behave and react in a manner similar to olefins. This led Walsh to propose the sp^2 hybridized orbital set shown in Figure 11.[23,24,25]

As can be seen in Figure 11, the combination of $\pi 1$ and $\pi 3$ orbitals or $\pi 2$ and $\pi 3$ orbitals appear as if they would be able to form a π type bond with metals as ethylene does. This may in fact be the reason that an edge bound metal complex was suggested as the first step in the platinum insertion into a cyclopropane.[26]

It had been suggested by Chatt and coworkers that the solid product that falls out of the ethereal solution, the initially precipitated complex (IPC), was either an oligomer or a polymer. Subsequently Fast Atom Bombardment (FAB) analysis by Gillard et al. indicated that the IPC is actually a tetramer as shown in Figure 12.[27] It was not until 1960 that Chatt and coworkers demonstrated by infrared and nuclear magnetic resonance (NMR) spectroscopy that the cyclopropane had oxidatively added to yield a platinacyclobutane.[28,29] One of the key discoveries that allowed the NMR work to be

performed was the observation that upon the addition of a strong ligand, such as an amine to the IPC, a monomeric species was formed and increased the solubility to a point that NMR analysis was possible (Figure 13). This observation was later confirmed by Gillard et al. in their 1966 x-ray structure of the pyridine monomer.[30]

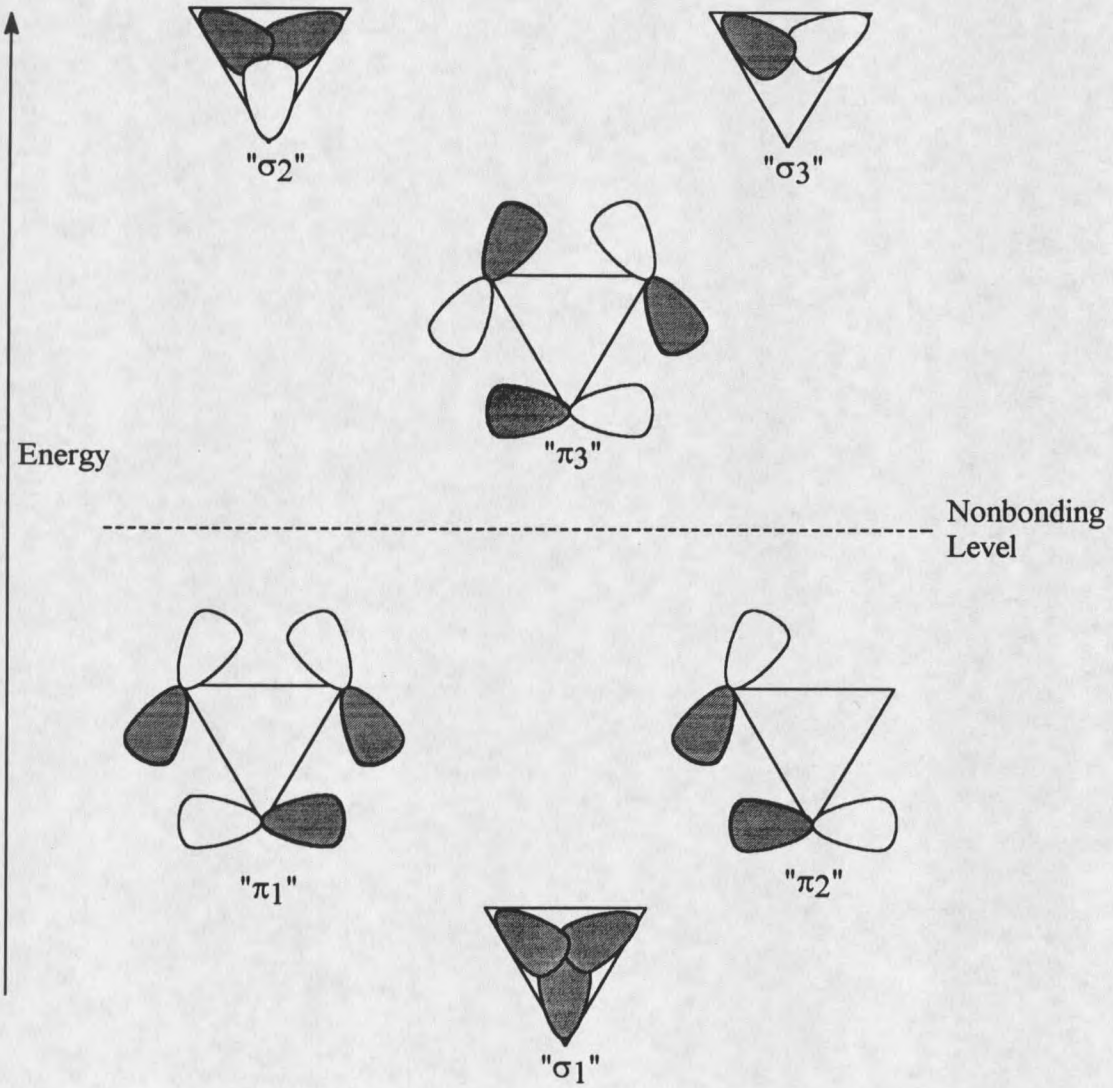


Figure 11. Walsh Orbitals for Cyclopropane.

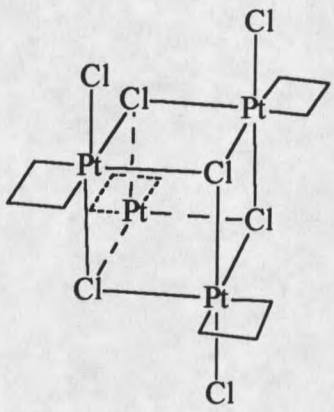


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Figure 12. Suggested Tetrameric Structure (IPC) for Platinacyclobutanes.

McQuillin's Method of Platinacyclobutane Formation

While Tipper's methodology of adding cyclopropane to hexachloroplatinic acid in acetic anhydride yielded the first example of a platinacyclobutane, it could not be generalized to substituted cyclopropanes.[31,32] However, McQuillin et al. demonstrated that Zeise's dimer **2** would react with a variety of cyclopropanes to form platinacyclobutanes.[33,34,35,36] Given that the tetrameric nature of these solids makes them extremely difficult to characterize, the teteramers are typically treated with two equivalents of a suitable neutral ligand, such as pyridine, acetonitrile, or tetrahydrofuran (THF) to form the monomers as shown in Figure 13. It is these monomeric species that have received nearly all of the efforts of characterization by nearly all techniques, including NMR work which will be discussed later in this introduction.

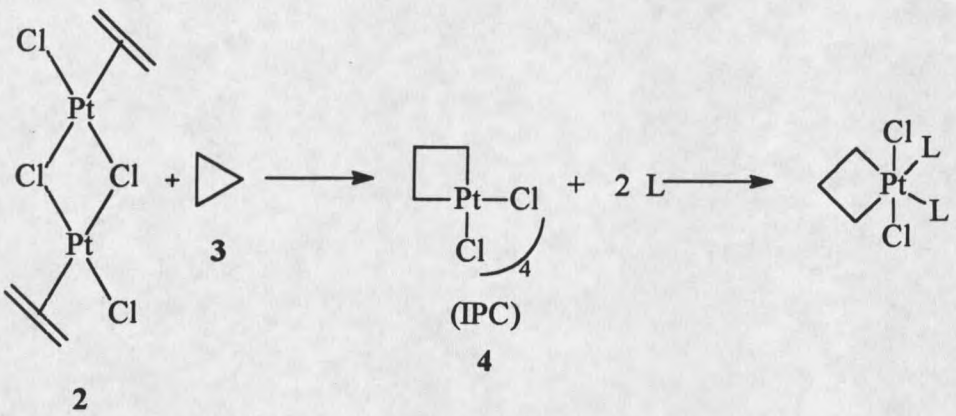
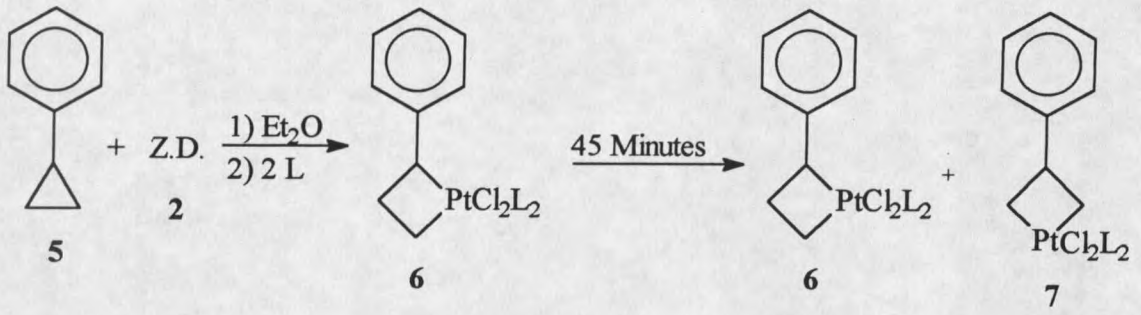


Figure 13. Oxidative Addition and Monomer Formation.

Puddephatt Rearrangement

In a 1976 paper, Puddephatt et al. demonstrated a rearrangement of platinacyclobutanes that now bears his name and is paramount to understanding all further chemistry of these complexes.[37] When a platinum (II) source (Zeise's dimer **2**) interacts with an unsymmetrically substituted cyclopropane, the platinum may insert into a specific bond. However, it can then undergo a rearrangement from this bond to either of the other two carbon-carbon bonds that make up the cyclopropane to form the other possible platinacyclobutanes. This is illustrated in the initial rearrangement that Puddephatt discovered. When phenyl cyclopropane **5** was allowed to react with Zeise's dimer **2,** only one platinacyclobutane **6** was initially observed by NMR, utilizing the addition of pyridine as a ligand. However, when this mixture was allowed to sit in chloroform, within 45 minutes at 50 °C the product isomerized into the mixture of products shown in Figure 14. It is of note that the mixture was roughly a 2 to 1 ratio in which the initial platinacyclobutane **6** observed was now the minor isomer.



5 6 6 7

Figure 14. Puddephatt Rearrangement.

Further studies of the Puddephatt rearrangement have shown that the rearrangement was not due to alkyl shifts and that all stereo- and regio-chemistry about the cyclopropane was preserved.[38,39,40] An additional observation is that any further chemistry from a platinacyclobutane need not come from the isomer of the platinacyclobutane that was observed. Perhaps one of the best examples of this comes from Williams' formation of phenalene **10** as shown in Figure 15.[41] In this case, the exclusive product of the platinacyclobutane **9** after reflux in benzene was the olefinic product phenalene **10**. This product was proposed to arise from the platinacyclobutane in which the platinum had inserted into the central bond, but interestingly enough this platinacyclobutane was never directly observed.

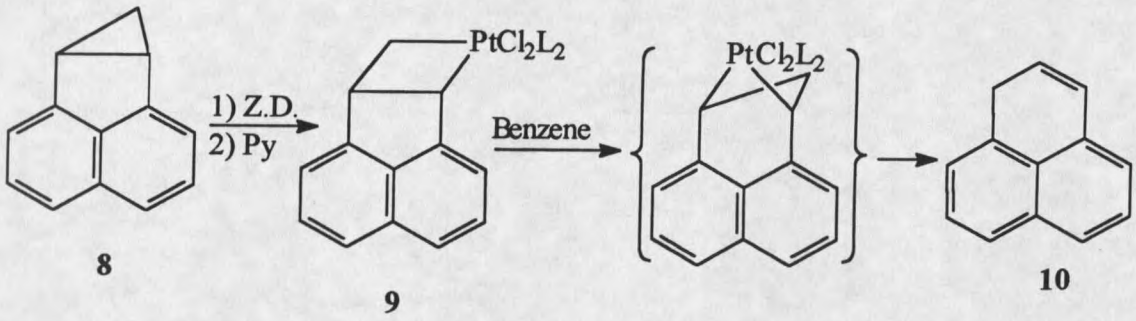


Figure 15. Formation of Phenalene 10.

Diversity and Limitations of Platinacyclobutane Formation

The versatility of McQuillin's methodology allows for the formation of an extremely wide variety of platinacyclobutanes. In a review article by Jennings and Johnson, greater than 70 platinacyclobutanes generated using McQuillin's method were summarized. Despite this number, there are still limitations to the methodology.[42] First, Zeise's dimer **2** will not typically insert into a cyclopropane that possesses any electron withdrawing group. Hoberg was able to overcome this limitation for cyclopropanes with α ketones.[43] The ketone was first transformed to the ketal. Then upon treatment of Zeise's dimer with the cyclopropane the platinacyclobutane formed. Finally deprotection of the ketal yielded the ketone substituted platinacyclobutane as shown in Figure 16.[44] Second, the more substituted the cyclopropane, the less likely it will be that Zeise's dimer **2** will insert.

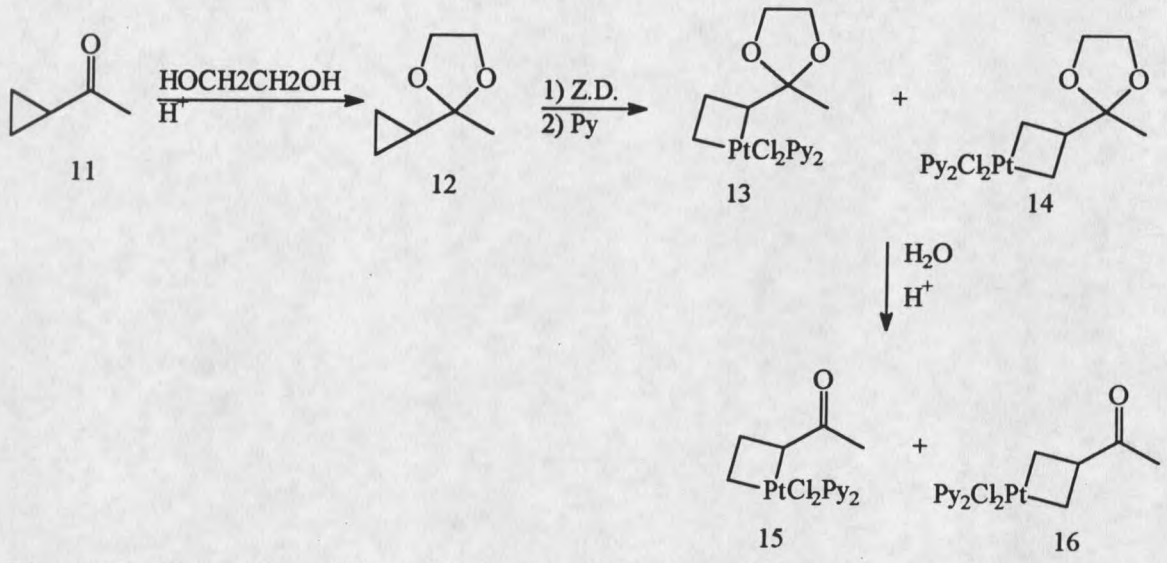


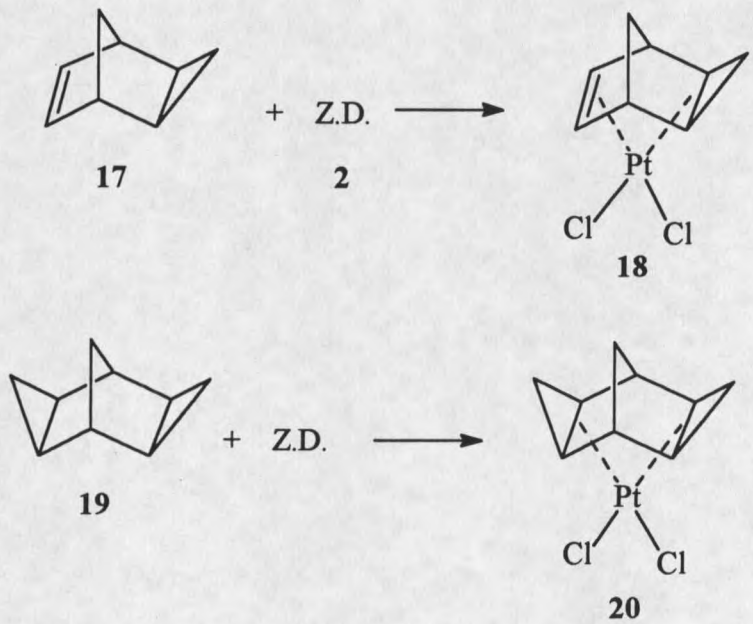
Figure 16. Formation of Acetyl Substituted Platinacyclobutanes.

Other than the restriction of no electron withdrawing groups on the cyclopropane, there seems to be little limitation on the insertion of Zeise's dimer into monosubstituted cyclopropanes as evidenced by the wide variety of alkyl and aryl monosubstituted platinacyclobutanes listed in Johnson's review article.[45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60] Geminally disubstituted alkyl and aryl cyclopropanes also reacted with Zeise's dimer **2** to form platinacyclobutanes. While only five of these cyclopropanes have been demonstrated to undergo this reaction, this is most likely a reflection of the lack of variety of starting materials rather than a lack of generality of the method.[61,62,63,64,65,66,67,68] In a similar fashion, a small series of alkyl and aryl trans-1,2 disubstituted cyclopropanes inserted platinum (II) to form stable platinacyclobutanes.[69,70,71,72,73,74,75,76]

Cis-1,2-Disubstutited Platinacyclobutanes

Given the versatility of this reaction, it might be assumed that nearly any alkyl or aryl substituted cyclopropane would react with Zeise's dimer **2** to yield a platinacyclobutane. However, initial attempts at formation of platinacyclobutanes from cis-1,2 disubstituted cyclopropanes led only to the observation of starting materials or decomposition of the platinacyclobutanes to form olefins.[77,78,79,80]

In a 1969 communication, Volger et al. reported that the interaction of Zeise's dimer **2** with both *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene **17** and *exo, exo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane **19** gave edge bound complexes as shown in Figure 17.[81]



17 **2** **18**

19 **20**

Figure 17. Volger's Proposed Structures.

However, in his 1980 review article, Puddephatt called these structures into question. Puddephatt never suggested that these structures were platinacyclobutanes, perhaps due

to the initial reports that cis substituted cyclopropanes were not stable! However, he expressed doubt as to whether these were edge bound complexes.[82] Shortly after Puddephatt's review, Jennings and Waddington reexamined Volger's work. Based on NMR analysis of the reaction products it was concluded that Vogler's postulates were in error and that the platinum had indeed undergone an oxidative insertion. The actual structures were the platinacyclobutanes shown in Figure 18.[83]

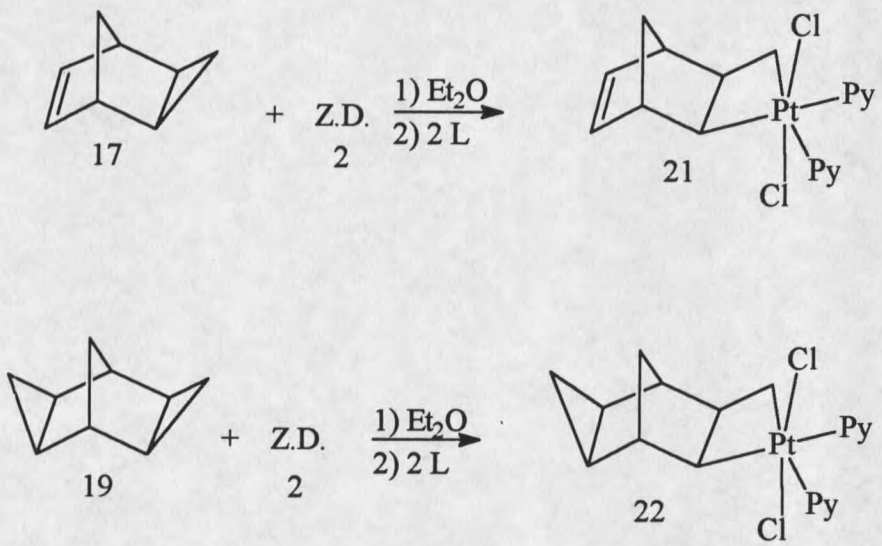
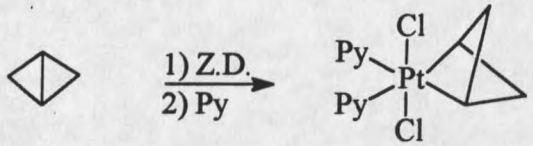


Figure 18. Insertions into Norbornyl Cyclopropanes.

These two norbornyl structures and one reported by Takaya et al. (Figure 19), represent the first observed cis-1,2 disubstituted platinacyclobutanes.[84]



23 **24**

Figure 19. Stable Cis Disubstituted Platinacyclobutane.

After these seminal discoveries, Jennings and coworkers produced a few bicyclic platinacyclobutanes (Figure 20),[85,86,87,88,89] as well as a whole host of tricylic platinacyclobutanes to which Wiberg et al. added one.[90] (Table 1)

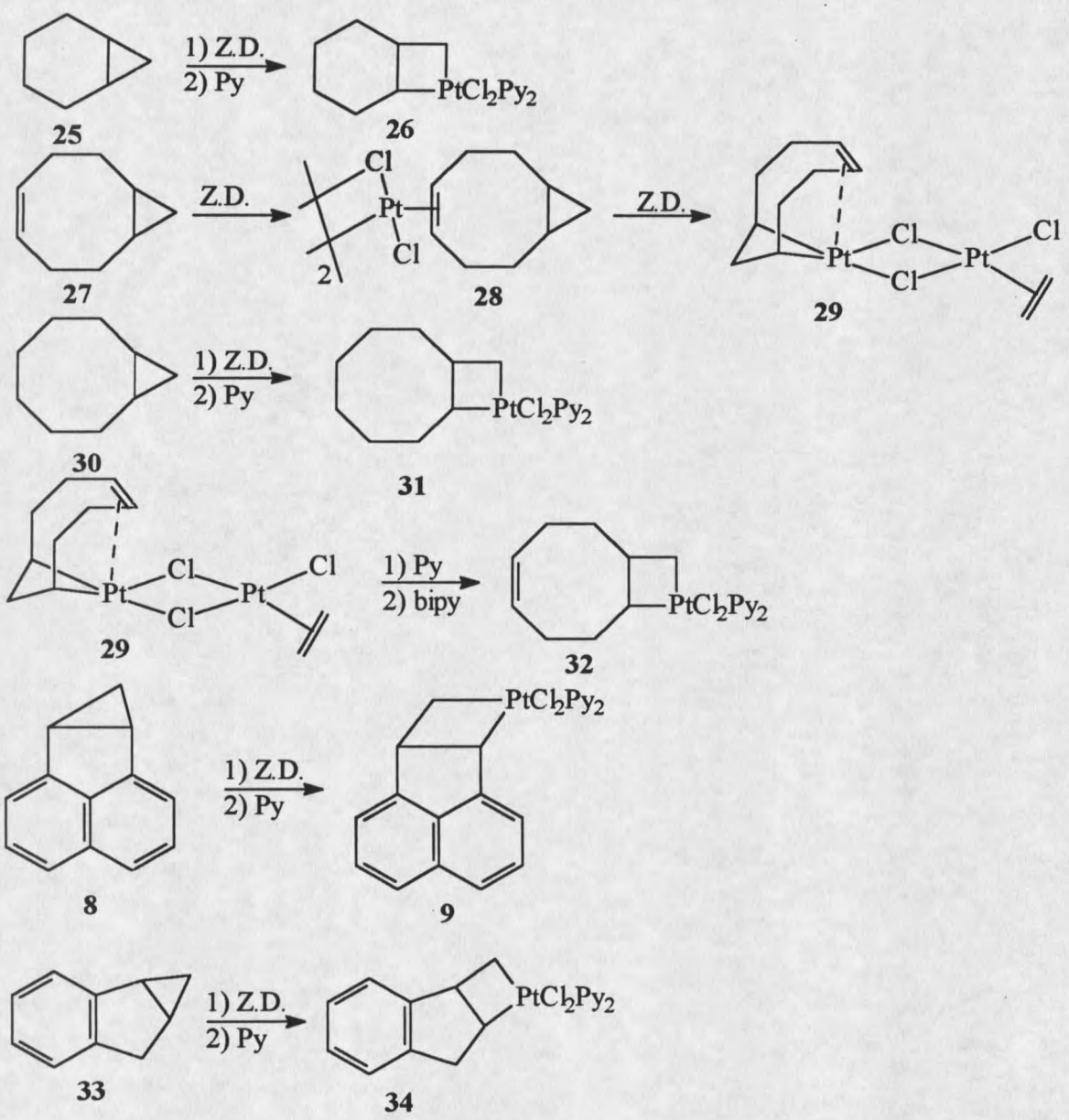
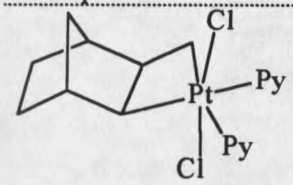
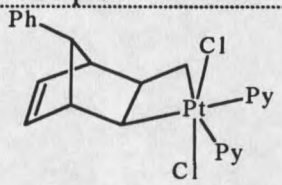
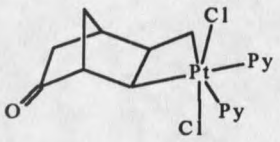
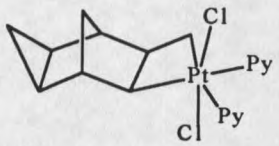
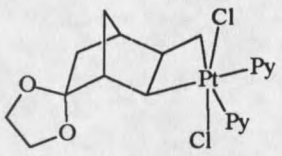
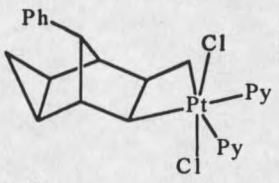
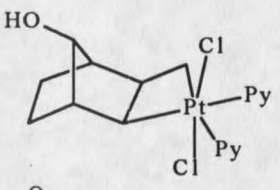
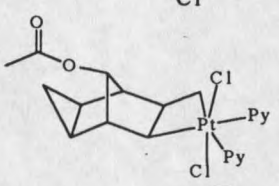
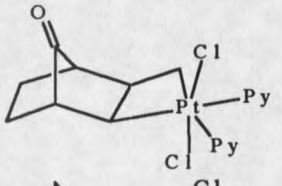
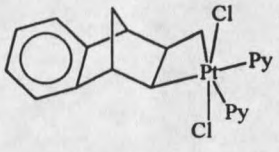
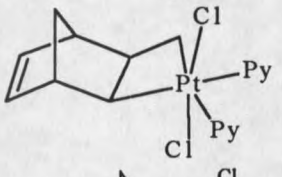
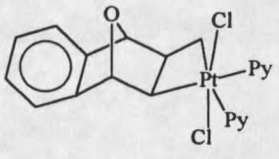
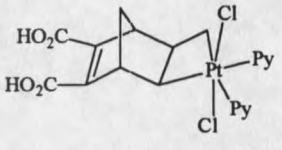
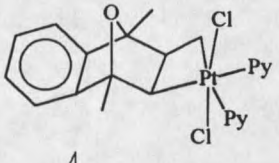
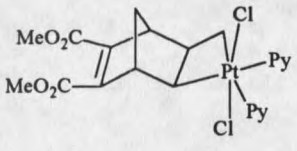
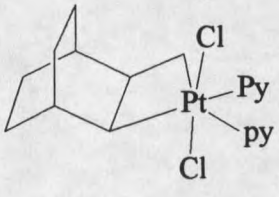
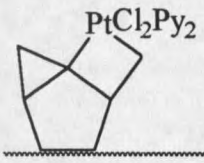


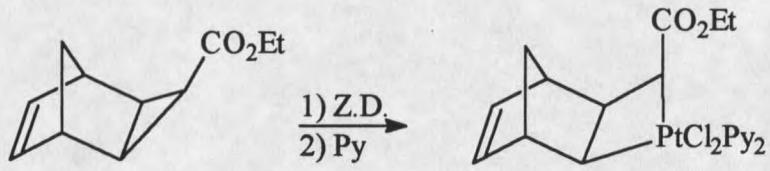
Figure 20. Bicyclic Platinacyclobutanes.

Table 1. Tricyclic Platinacyclobutanes

Complex	#	Reference	Complex	#	Reference
	**35**	91		**36**	92
	**37**	93		**22**	94
	**38**	95		**39**	96
	**40**	97		**41**	98
	**42**	99		**43**	100
	**21**	101		**44**	102
	**45**	103		**46**	104
	**47**	105		**48**	106
	**49**	107			

Trisubstituted Platinacyclobutanes

After the success that the Jennings group had synthesizing and exploring the chemistry of the cis disubstituted tricyclic platinacyclobutanes, the question arose whether the trisubstituted cyclopropanes might react with Zeise's dimer **2** if the trisubstituted cyclopropane incorporated the stabilizing feature of a norbornyl system. In a wide variety of cases, the norbornyl system causes the cyclopropane to be susceptible to electrophillic attack by the platinum giving stable platinacyclobutanes as illustrated in Table 2. The success of this method presumably relied on the fact that the insertion eliminated some ring strain. This methodology proved so powerful that, even with an electron withdrawing group such as an ester as one substituent, the insertion will occur if the norbornyl system has an olefin in the homoallylic position. (See Figure 21)

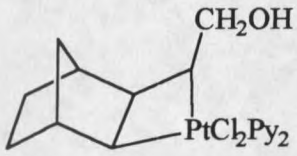
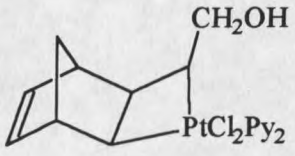
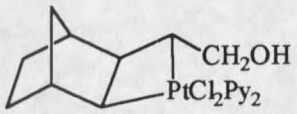
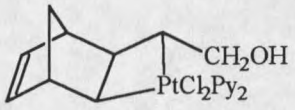
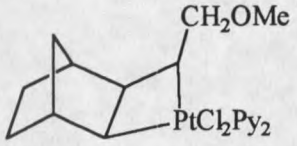
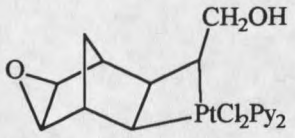
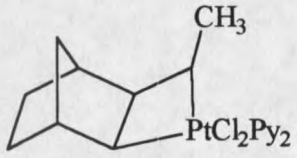
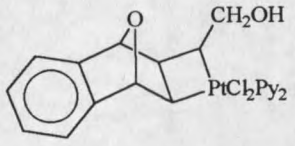
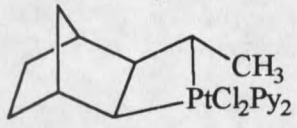
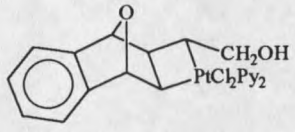
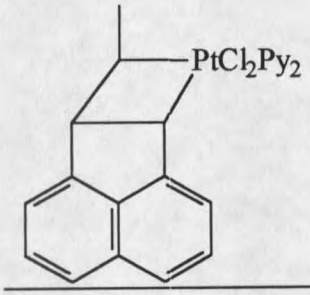
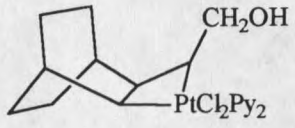


50 51

Figure 21. Insertion of Z.D. 2 into a Cyclopropane with an Electron Withdrawing Group.

The presence of the transannular olefin is thought to have two effects which allow the insertion to occure. First, it adds to the ring strain of the system. Additionally, it is presumed that the olefin has the ability to donate some of its electron density to the electron deficient cyclopropane, thereby rendering the cyclopropane less electron deficient and more subject to elecrophilic attack by platinum. [108]

Table 2. Trisubstituted Platinacylcobutanes.

Complex	#	Reference	Complex	#	Reference
	**52**	[109]		**53**	[110]
	**54**	[111]		**55**	[112]
	**56**	[113]		**57**	[114]
	**58**	[115]		**59**	[116]
	**60**	[117]		**61**	[118]
	**65**	[119]		**63**	[120]

NMR Spectroscopy of Organoplatinum Complexes

While the contributions of IR spectroscopy and X-ray crystallography have contributed greatly to the field of organoplatinum chemistry, NMR spectroscopy has become the generally preferred tool of the organometallic chemist as it has become more powerful and accessible over the last three decades. While X-ray crystallography is still the definitive elucidation technique in organometallics, it has the drawback of requiring a single crystal. For some classes of unstable compounds, the formation of suitable crystals is nearly impossible. Fortunately, over the last decade and a half, the power and ease of use of NMR spectroscopy has increased immeasurably, making the elucidation of at least the organic portion of organometallics generally achievable.

Organoplatinum chemists have a unique advantage when using NMR spectroscopy over the vast majority of the organometallic community, due to the fact that ^{195}Pt has a spin ½ and has a relatively large magnetogyric ratio of $5.75\gamma/10^7$ rad T^{-1} s^{-1}. In addition, ^{195}Pt has short T1 and T2 relaxation times, and a natural abundance of 33.7%.[121] While many elements have some of these characteristics, few if any metals have the combination of these that makes platinum and platinum-containing compounds so easy to observe directly using NMR spectroscopy. More importantly to the organoplatinum chemist, the ease of observation of platinum coupling in the ^1H and ^{13}C NMR spectroscopy facilitates structure elucidation.[122]

However, if the complex has a number of protons with similar chemical shifts and the protons have a great deal of coupling to one another, the spectral complexity increases

to the point that they becomes difficult to interpret. Add ^{195}Pt coupling to these complex proton spectra and they often become so cumbersome that the spectra are of diminished value. Fortunately in many cases, ^{13}C NMR spectroscopy with its wide chemical shift range, lack of carbon-carbon coupling, platinum-carbon coupling and platinum induced shift effects often yield sufficient information to overcome the ambiguities generated by the proton spectral complexity. More specifically, the presence of platinum tends to shift the resonance position for carbons directly bonded to it upfield. Since only 33.7% of the platinum is ^{195}Pt, carbon NMR signals tend to look like triplets, with the peaks in a 1:4:1 area ratio. These couplings tend to be quite large for $^{1}J_{Pt\text{-}C}$. For example, in the case of π bound olefins, the platinum induced upfield shift typically brings olefins into the 70 to 85 ppm range with approximately 250 Hz platinum coupling.[123] For σ bound carbons, the upfield shift is quite pronounced. In general, platinum bound methylenes tend to resonate in the range from -20 ppm to 60 ppm, with most resonating in the -15 to 20 ppm range. The coupling also varies greatly, but the range is generally 300 to 700 Hz. Carbons which are two bonds away from the platinum tend not to have their shifts affected and often have relatively small $^{2}J_{Pt\text{-}C}$ couplings. In general, these couplings run from 0 to 50 Hz for nonplatinacyclobutanes and 30 to 120 Hz for the ring carbons that are ^{2}J disposed in platinacyclobutanes. The $^{3}J_{Pt\text{-}C}$ bond couplings are often greater than that of ^{2}J couplings, ranging from 50 to 100 Hz. Given this type of shift and coupling information together with Distortionless Enhancement by Polarization Transfer (DEPT) information, it is then generally quite easy to elucidate the carbon skeleton of an organoplatinum complex.

Reactions of Organoplatinum Complexes

Addition of Hydrogen Gas Liberating the Organic Moiety

The addition of hydrogen gas has long been considered a mild, yet powerful method for releasing the organic moiety of organometallic complexes. In fact, it was in McQuillin's first paper on platinacyclobutanes in 1968 that he reported on the hydrogenation of several organoplatinum complexes. [124] These reactions gave rise to a number of alkyl products as shown in Figure 22. In addition, this method is often used to probe the carbon skeleton which was the case in McQuillin's original paper. Before the structure of platinacyclobutanes was well understood, the liberation of the organic moiety by the addition of hydrogen gas added credence to the hypothesis that the complexes isolated were indeed platinacyclobutanes. This was done by showing that the addition of Zeise's dimer **2** to a cyclopropane followed by the addition of hydrogen gas had broken a carbon-carbon bond in the cyclopropane bond.

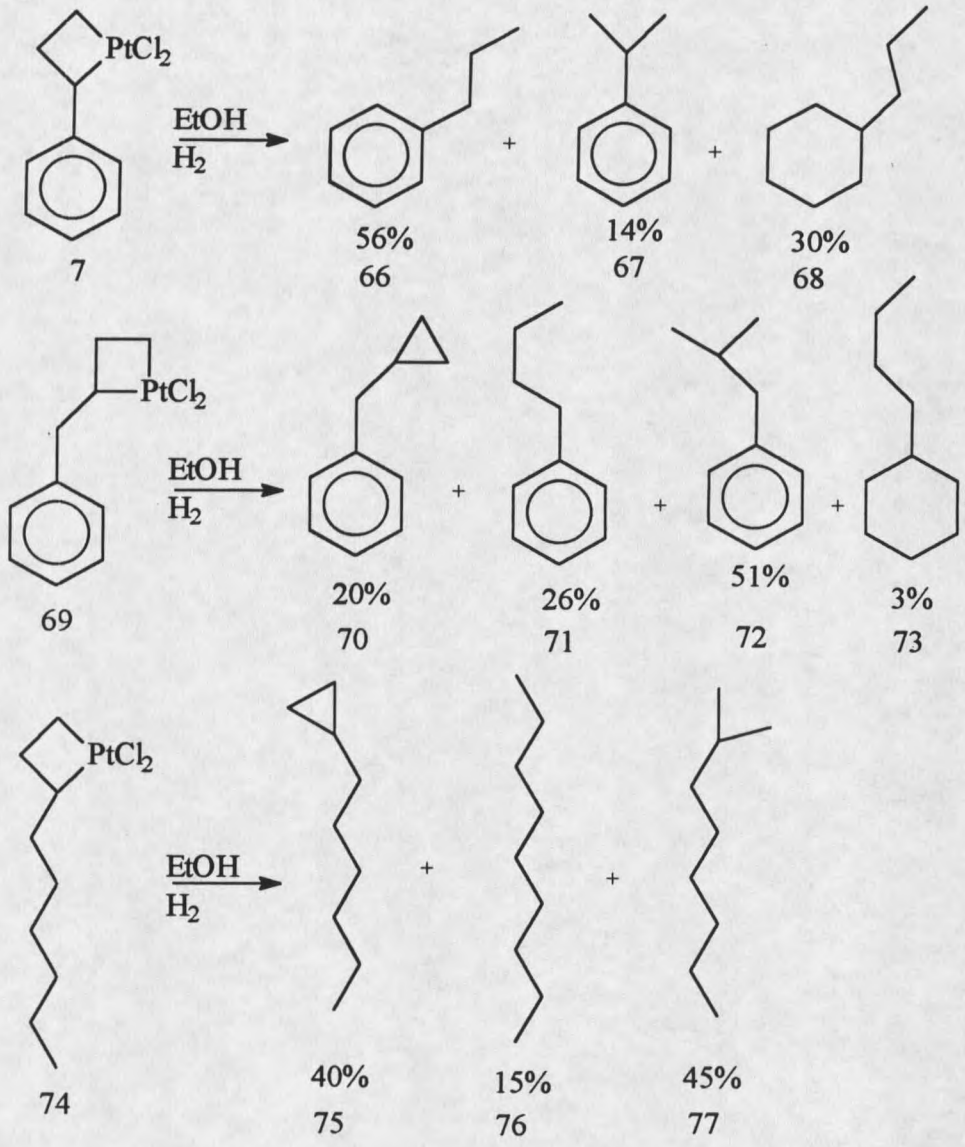


Figure 22. Results of Hydrogenation.

Olefin Products from Platinacyclobutanes
The Unstable Nature of Cis-1,2 disubstituted Platinacyclobutanes

In the early works of both Brown and McQuillin, they suggest that cis-1,2-disubstituted cyclopropanes when allowed to react with Zeise's dimer **2** form unstable platinacyclobutanes which spontaneously rearrange to form π allyls; these π allyls often decompose to olefins especially if treated with potassium cyanide.[125,126] The classic example of the decomposition of an IPC via potassium cyanide is the platinacyclobutane derived from norcarane. This reaction was discovered by McQuillin who observed olefinic products upon treatment of the IPC(derived from norcarane **25**) with aqueous potassium cyanide. This reaction was investigated further by Parsons and Jennings who were able to isolate and elucidate the structure of the monomeric platinacyclobutane derived from norcarane and describe additional olefinic products from the treatment of the IPC with aqueous potassium cyanide. (Figure 23).[127,128]

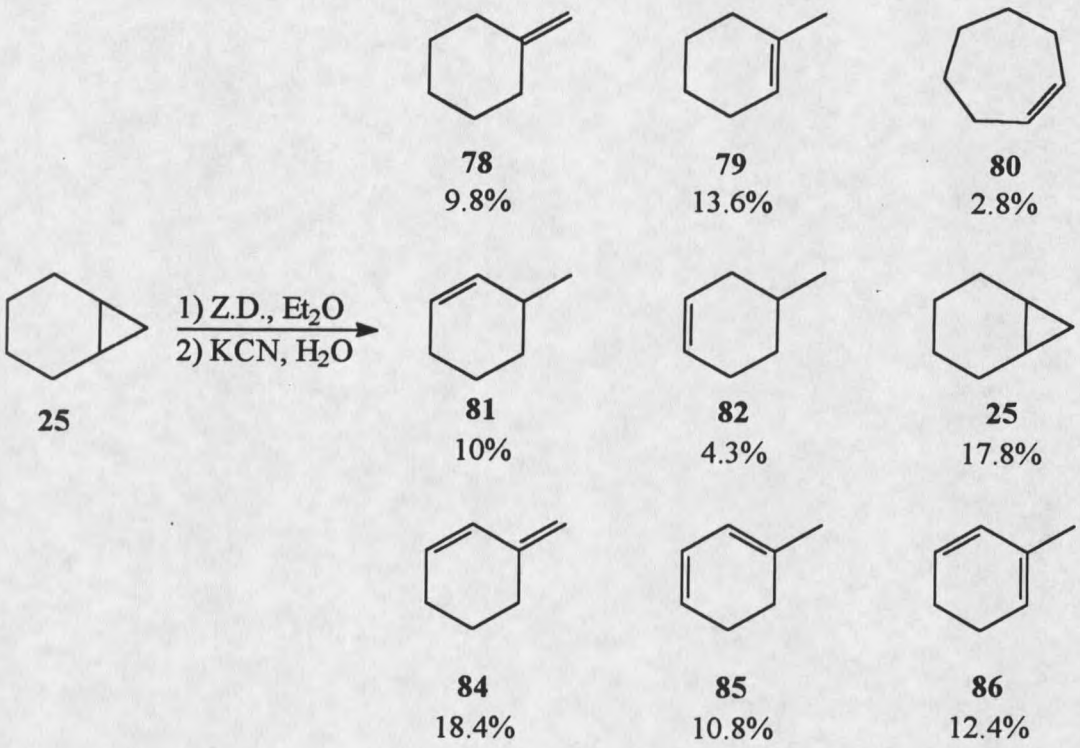
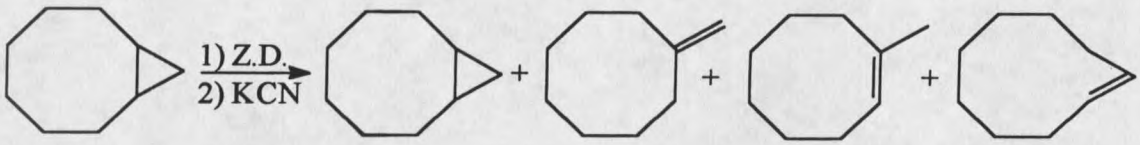


Figure 23. Formation of Olefinic Products from Norcarane.

This reaction, while yielding a plethora of products, illustrates that cyclopropanes and Zeise's dimer **2** have the potential to be valuable in organic transformations if these processes can be directed and controlled.

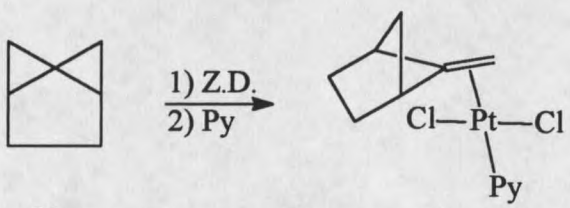
In a similar fashion, bicyclo[6.1.0]nonane **30** was treated with Zeise's dimer and then with aqueous potassium cyanide, again yielding a variety of olefinic products along with some starting material as shown in Figure 24. [129]



30 **30** **87** **88** **89**

Figure 24. Formation of Olefinic Products from Bicyclo[6.1.0]nonane.

Another interesting example of this type of reaction involves a report by Wiberg et al. in which spirane **90** undergoes a skeletal rearrangement upon treatment with Zeise's dimer **2** and then pyridine (Figure 25).[130]

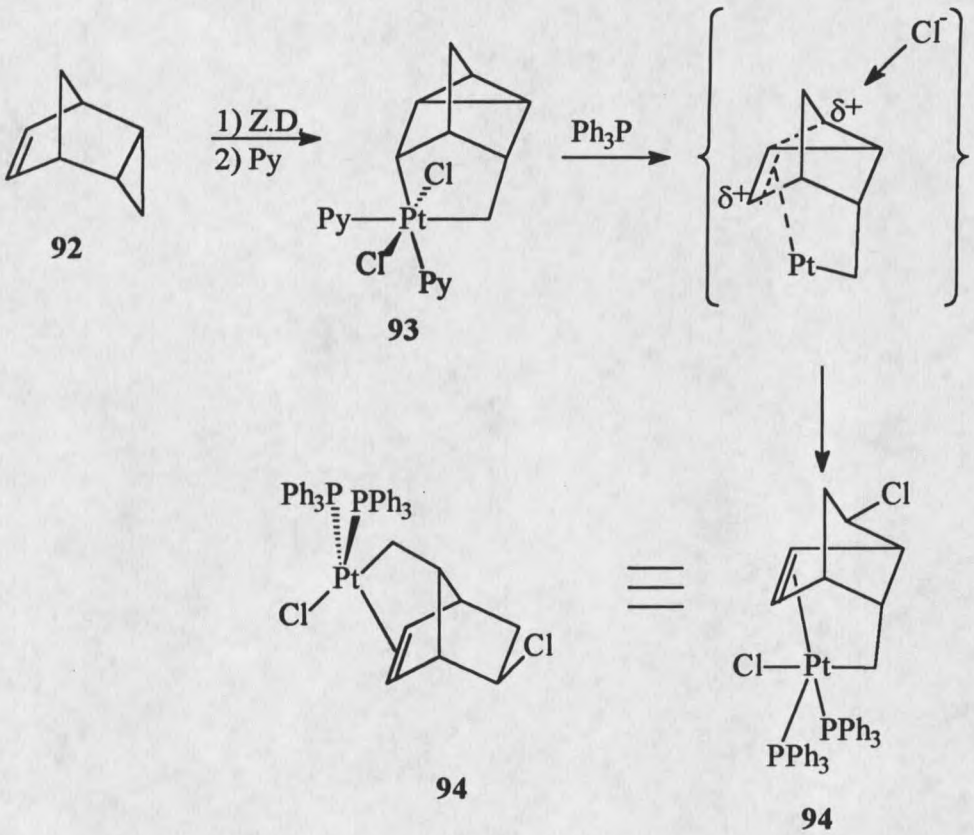


90 **91**

Figure 25. Wiberg's Skeletal Rearrangement.

This reaction not only demonstrates that disubstituted cyclopropanes can form olefins, but also demonstrates that skeletal rearrangement can be a driving force in the reaction.

Another intriguing example of a skeletal rearrangement has been demonstrated by Jennings and coworkers where *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene **92** was reacted with Zeise's dimer **2,** followed by triphenylphosphine, to form complex **94** as shown in Figure 26.[131]



92 93 94 94

Figure 26. Jennings' Norbornyl Rearrangement.

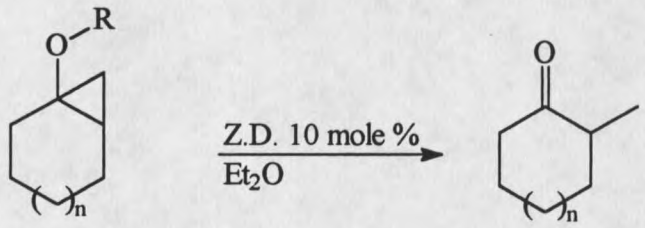
This reaction demonstrated that the reduction of ring strain can be a driving force in the transformations of cis-disubstituted cyclopropanes. It is also worth noting that this reaction prior to the addition of triphenylphosphine gave rise to a platinacyclopentane, **93.** Several interesting and important things occur when the triphenylphosphine is added. First, a proposed nonclassical carbocation stabilized by platinum complex is attacked by a chloride, which initially had to be bound to the Zeise's dimer **2**. Second, it is worth noting that it cannot be determined whether the chloride was free of the platinum when it acted as a nucleophile or was still coordinated to a separate platinum; however, it does act as a nucleophile and is not delivered via reductive elimination. Finally, this reaction

demonstrates that olefins which are part of the product make good ligands for the platinum.

Platinum Complexes Derived from Cyclopropanes with Electron Donors

Cyclopropanes with Oxygen Based Electron Donors

Hoberg demonstrated that an oxygen substituent can be used to direct the chemistry of a platinacyclobutane to form a series of ketones as shown in Figure 27.[132]

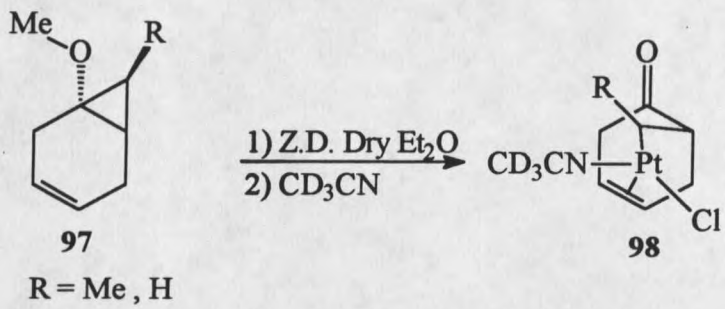


n	R
0	Et
1	Et
1	Me
1	H
3	Et

95 **96**

Figure 27. Zeise's Dimer 2 Catalyzed Ketone Formation.

It was proposed that in this case the lone pair of electrons on the oxygen could be used to stabilize a carbocation intermediate formed when the platinum dissociated from the oxygen bound carbon, thereby giving rise to the 2-methylcyclohexanone **96** selectively. In an effort to stabilize and perhaps trap the intermediate, an olefin was placed in the ring to act as a ligand for the tethered platinum, giving rise to a new complex shown in Figure 28.[133]



97

R = Me , H

98

Figure 28. Stabilization of the Platinum Intermediate Forming 98.

This reaction shed a great deal of light on the reaction in Figure 27, presuming that they share a similar reaction mechanism, to the point where the platinum is bound by the olefin as shown in Figure 29.

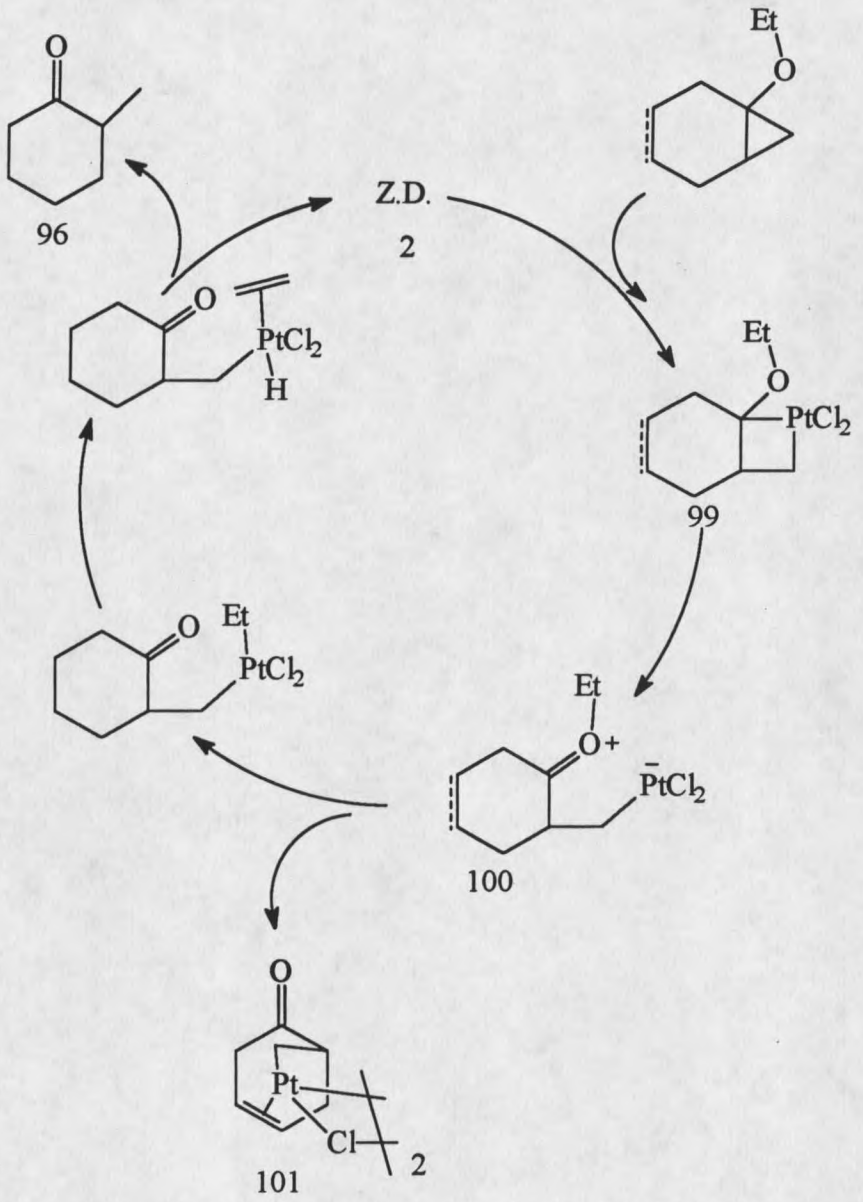


Figure 29. Mechanism for the Catalytic Synthesis of 1-Methylcyclohexanone 96.

Olefin Stabilized Platinacyclobutanes / Metallacyclobutanes

The formation of complex **98** leads to the interesting question of whether olefins might be able to redirect the reactions of other platinacyclobutanes. Stabilization of

reaction intermediates is useful for gaining insight into reaction mechanisms, and perhaps more importantly for a way to control and manipulate the outcome of organometallic reactions in general. The use of vinyl cyclopropanes in organometallic chemistry has had some investigation outside the arena of organoplatinum chemistry. The work utilizing vinyl cyclopropanes was pioneered by Aumann, when he interacted three different vinyl cyclopropanes with $Fe_2(CO)_9$ **103** to yield two η^4-complexed dienes. These reactions presumably proceed via π allyls which are also σ bound to the substrate as shown in Figure 30.[134] Three important aspects of this work foreshadow the interactions of Zeise's dimer **2** and vinylcyclopropanes. First, the cyclopropane bond that the iron inserts into is vicinal to the olefin. Second, the proposed metallocyclobutane decomposes to form a π allyl in which the metal has a σ bound tether. And lastly, the final product is a π bound olefin.