



Decomposition of diazoalkanes by platinum(II) olefins
by Timothy Wayne Hanks

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:

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The platinum(II) olefin induced decomposition of ethyl diazoacetate in the presence of excess olefin also resulted in catalytic cyclopropane formation. This reaction was investigated with a variety of olefins and yields and stereochemical or regiochemical preferences reported.

Finally, it was observed that the platinum(II) olefins decomposed ethyl diazoacetate in the presence of alcohols, secondary amines and thiols to give products resulting from the insertion into the heteroatom-hydrogen bond.

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A thesis submitted in partial fulfillment
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Doctor of Philosophy

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

December 1986

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APPROVAL

of a thesis submitted by

Timothy Wayne Hanks

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ABSTRACT

Platinum(II) olefins decompose diazoalkanes under a variety of conditions to give important and varied products.

In the presence of pyridine, the diazoalkanes were stoichiometrically decomposed to form platinum(II) ylides. In one case, when the diazoalkane was ethyl diazoacetate, a low temperature NMR study was conducted. A trigonal bipyramidal ylide species, in which the olefin was still attached to the metal, was observed. It was also found with ethyl diazoacetate, that the square planar ylide product rearranged, with time, to form a platinum(II) alkane in which a chlorine had been transferred to the ylide carbon.

One exception to the synthetic scheme outlined above was noted in the case of diazofluorene, which formed a platinacyclobutane instead of an ylide under identical conditions. This platinacyclobutane incorporated the olefin moiety into the final product. Low temperature NMR experiments enabled observation of a unique "extended" ylide product in which the olefin had already inserted between the metal and the ylide center. The platinacyclobutane product was further shown to decompose on addition of DMSO to form a cyclopropane. When the olefin of the original metal complex was ethyl vinyl ether rather than ethylene, no intermediate platinacyclobutane was observed, and cyclopropane was formed directly. This reaction was later found to be catalytic.

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Finally, it was observed that the platinum(II) olefins decomposed ethyl diazoacetate in the presence of alcohols, secondary amines and thiols to give products resulting from the insertion into the heteroatom-hydrogen bond.

INTRODUCTION

The Role of Metals in Chemistry

Science and society are slowly evolving a better understanding of the place of the various elements in our biosphere. We are developing vast new sources of energy, but at the same time we are learning how to achieve our ends with less energy. One important application of this is in the science of materials development. We have found, for example, that inexpensive hydrocarbons can replace metals in structural and electrical applications. The result is better performance with less environmental impact. We are even beginning to appreciate our hydrocarbon sources as building blocks for industry rather than fuel for automobiles.

The role of the precious metals is also becoming understood. In the past, these materials were used almost exclusively as symbols of wealth, or as particularly useless forms of wealth. In the last two decades however, their true value has become apparent. There are two areas in which transition metals, including the rare second and third row metals, are unique. The first is the formation of compounds with unusual activity. Good examples of these are the platinum anti-cancer drugs and the gold anti-arthritis

agents. A second, and perhaps even more significant area is that of catalysts for hydrocarbon transformations.

Many of the recent advances made in the construction of new or less expensive materials are due to transition metal catalysts. The transition metals are uniquely suited to this role for several reasons. They can coordinate certain ligands, such as cyclopentadiene, in more than one mode. They can make and break very strong bonds at reasonable energies and finally, small amounts of catalyst can effect the transformation of large amounts of a substrate. Frequently, even this can be recovered.

The reason for this important and unique activity is the easy reversibility of the reactions. The metal is able to coordinate multiple substrates in close proximity, change their reactivity, and then release the product. The metal then, is a template on which reactions may occur. The fact that reactions take place within the coordination sphere of the metal also offers the opportunity to induce stereo- or enantiospecificity.

As with most chemical reactions, there are generally several ways of accomplishing a desired transformation. Finding the catalyst and conditions that provide the best selectivities and yields has often been a matter of luck. Of course, neither the trial and error method nor a reliance on serendipity is the best way to optimize a system. A theoretical understanding of the reactions and the catalysts is

essential for the advancement of the science. The development of new catalysts and new descriptions of their actions is one of the most important and exciting areas of chemistry today.

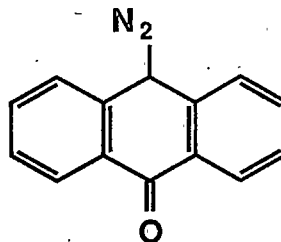
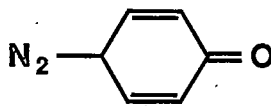
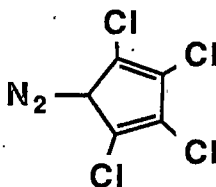
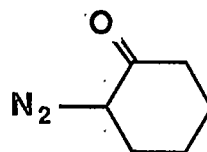
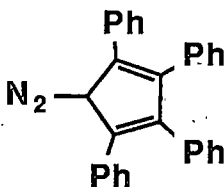
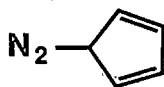
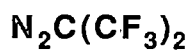
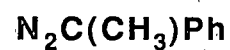
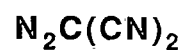
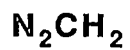
Diazoalkanes

The highly reactive family of compounds known as "diazoalkanes" were discovered more than a century ago by Curtius and von Pechmann¹. These complexes have the generic structure N_2CRR' , where R and R' can be nearly any organic moiety. During the past 100 years, literally hundreds of these compounds have been synthesized^{2,3}. They range in stability from those highly explosive under normal conditions, to those thermally stable to 60 °C or more.

Some of the more important diazoalkanes are shown in Table 1 on the following page. The most commonly used compounds of those listed are the diazoesters and diazomethane. In the very early work in this area, Curtius and later Buchner, used ethyl diazoacetate in reaction with various substrates⁴. Ethyl diazoacetate is a reasonably stable liquid, easily handled and relatively non-toxic. Today it can be purchased as is from several vendors, and is a favorite among researchers^{4,5}.

Diazomethane is also a very commonly used reagent. Unlike ethyl diazoacetate, diazomethane is a highly toxic, explosive gas. It is however, easily generated from Diazald

Table 1. Examples of Diazoalkanes.

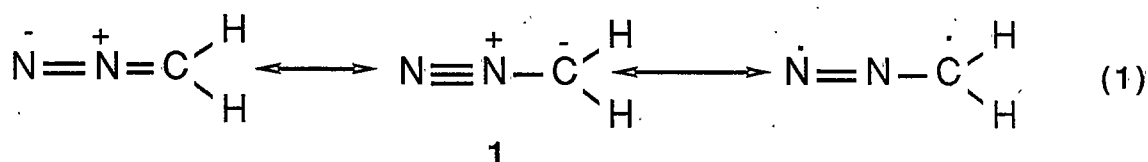


(N-methyl-N-nitroso-p-toluenesulfonamide) and base. This latter compound (Diazald) may be purchased directly along with special generating kits. Diazoethane is very similar to diazomethane and may be generated from 1-ethyl-3-nitro-1-nitrosoguanidine.

The preparation of other diazoalkanes varies, depending on the compound. The most common method of synthesis is by reducing the hydrazone made from the corresponding ketone or aldehyde⁶. This transformation permits the use of diazoalkane chemistry during the synthesis of complex molecules.

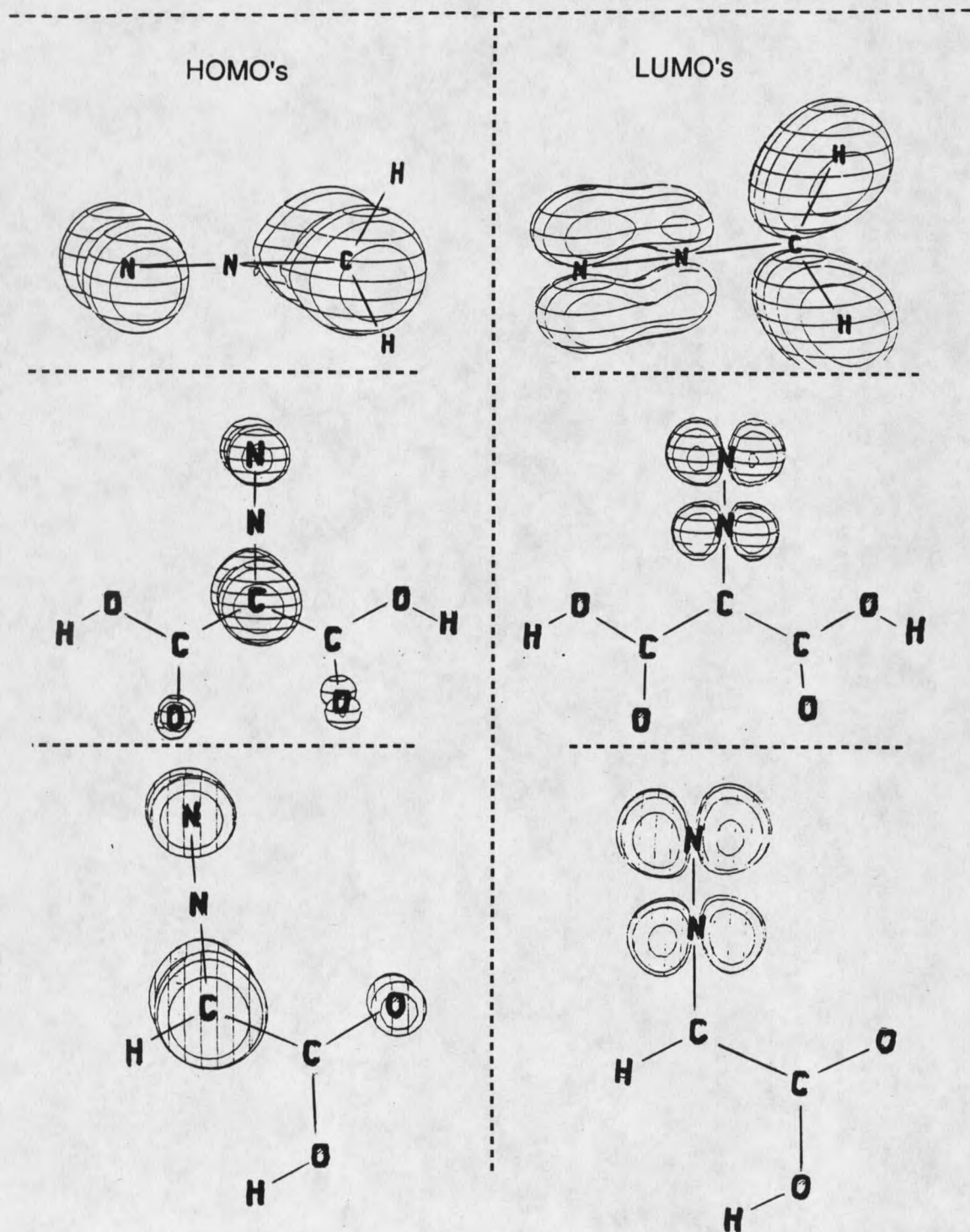
The Structure of Diazoalkanes

Electronically, diazoalkanes are unusual in that energetically favorable resonance structures involve charge separation. The bonding in diazomethane, for example is usually represented as in equation 1.



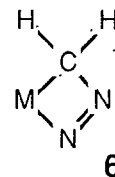
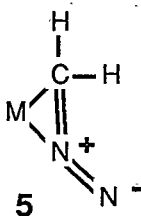
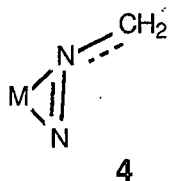
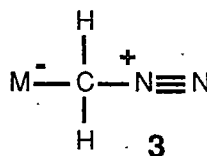
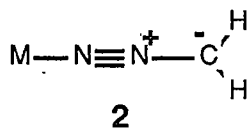
Albright and Freeman emphasize the importance of structure 1 in a paper comparing ¹³C and ¹⁵N NMR chemical shifts with INDO calculations⁷. More recent MNDO calculations corroborate the idea of a net excess of electron density on the carbon⁸. A more important result however, is the observation that the HOMO (Highest Occupied Molecular

Table 2. HOMO's and LUMO's for some Diazoalkanes as Predicted by MNDO.



Orbital) is located primarily on the carbon and terminal nitrogen, while the LUMO (Lowest Unoccupied Molecular Orbital) is centered on the N-N linkage. Table 2 depicts the HOMO and LUMO's of some diazoalkanes as predicted by MNDO. More sophisticated ab Initio treatments agree with this general description⁷.

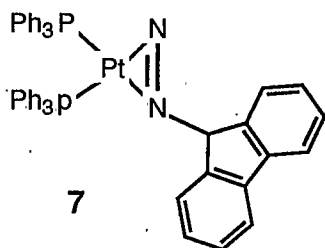
By FMO (Frontier Molecular Orbital) theory, diazoalkanes should attack electrophiles from either the terminal nitrogen or the carbon. Conversely, interactions with electron rich species should occur at the N-N linkage. An important application of this is the interaction of diazoalkanes with metals. The 5 realistic structures which may be drawn for this interaction are listed below.



Structures 2 and 3 are expected to be viable when the metal is behaving as an electrophile. Structure 3 would be expected to easily lose N₂ while structure 2 would not. Experimentally, examples of structure type 2 have been found and characterized by X-ray crystallography⁹, while no

examples of structure 3 are known. Compounds such as 2 do not lose N_2 easily and metals with the ability to form this type of structure show decreased ability to decompose diazocompounds. Complexes similar to structure 3 are frequently proposed as intermediates in the metal catalyzed decomposition of diazoalkanes. The facile loss of N_2 from this species would be expected to yield a "metal carbene". These "carbenoids" are of great current interest to organometallic chemists.

Structure type 4 is expected from interaction of diazoalkanes with electron rich metals. Several of these structures are known and have been characterized crystallographically, especially by Ibers^{10,11,12}. An example of this structural type is shown in the platinum(0) compound 7. As would be expected from this discussion, all known examples of this structural type are with metals in low oxidation states. These compounds also display a reduced ability to decompose to liberate N_2 .

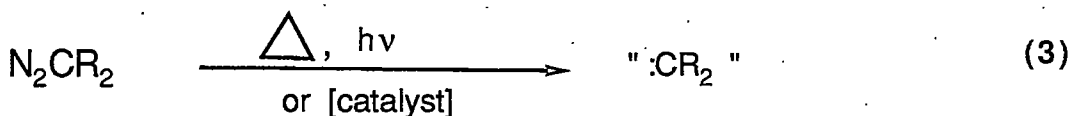
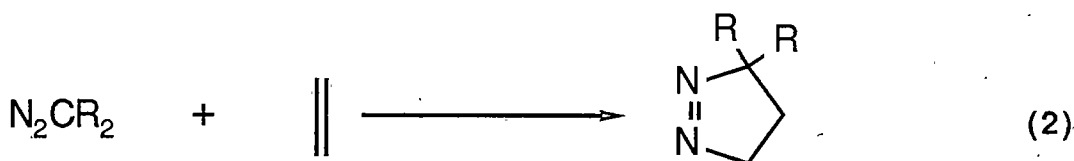


Molecules of structural type 5 would not be considered viable by the scheme presented here, and none are known¹.

Compounds of structural type 6 might be possible for electrophilic metals, but no examples have yet been observed.

The Decomposition of Diazoalkanes

Diazoalkanes display a variety of interesting activities. The two most important types are shown below in equations 2 and 3. Equation 2 is representative of a general class of reactions in which the N_2 moiety is retained. These reactions have been extensively reviewed^{1,3} and will not be discussed here.



A more important mode of reactivity is shown in equation 3. Diazocompounds can lose N_2 thermally, photochemically or chemically. The result is a carbene or carbenoid species. These highly reactive intermediates are responsible for the tremendous variety of processes for which diazoalkanes are best known. The exact reaction (or reactions) which will occur with a given substrate is highly dependent on the method of generation. This thesis is primarily concerned with the metal catalyzed decomposition

of diazoalkanes. This topic will be discussed in detail in later sections, while photochemical and thermal decomposition are considered briefly here.

The ground state of the carbene species generated from the diazoalkane may be either a singlet or a triplet. Which is the lowest energy species of a given carbene depends on the substituents on the carbene center. Frequently however, there is little difference between the two states and both may be present. The carbenes are so very reactive that several processes may occur with a single substrate, no matter how it is generated or which spin state it is in. This state of affairs led Doering to declare that methylene was "the most indiscriminate reagent in organic chemistry."¹⁴

Figure 1. Carbene Ground State Spin States.



Free carbenes have been observed to undergo the following reactions: addition to π systems, insertion into bonds (especially X-H bonds), carbene promoted rearrangements and 1,2-dipolarcycloadditions. Several comprehensive reviews concerning the chemistry of free carbenes exist,

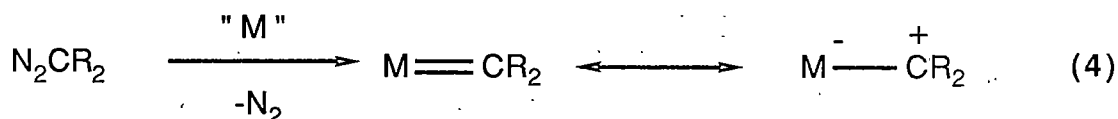
demonstrating the great interest this area holds^{2,3,4,5}. The ability to perform unique reactions however, is often of little use because of the indiscriminate nature of the reactant. Since the 1950's there has been an explosion of interest in the metal catalyzed decomposition of diazoalkanes to form "metal carbenoid" species. Not only are these complexes more selective than the free carbenes, but they offer the potential for stereo-, regio- and enantioselectivity as well.

Metal Carbenes

It was first observed, in the early part of this century, that metals could decompose diazoalkanes to form intermediates with vastly different reactivities than those generated by other methods^{1,5}. The nature of these species was not known and they were termed "carbenoids". The early metal catalysts were generally insoluble copper bronze or cupric sulfate amalgams. On occasion, other metals were found to cause similar reactions. Palladium¹⁶ and nickel^{17,18} were shown to catalyze the cyclopropanation of olefins, and nickel was shown to participate in some interesting stoichiometric reactions as well. Platinum also was shown to decompose diazomethane to polymethylene^{19,20}. Interestingly, platinum was the first of the nickel triad in which the decomposition of diazoalkanes was observed¹⁹, yet its possible utility as a catalyst has been almost

completely ignored to date. Indeed, until the 1970's no catalysts were known which offered any advantages over the inexpensive copper catalysts. These had to wait until a better theoretical understanding of the reaction developed.

In 1952, Yates suggested that metals decompose diazoalkanes to form electrophilic "metal-carbenes" (eq. 4). The metal-carbon π -bond was thought to be polarized, permitting nucleophilic attack on the carbene carbon²¹. This idea sparked considerable interest in the field after decades of relatively little attention.

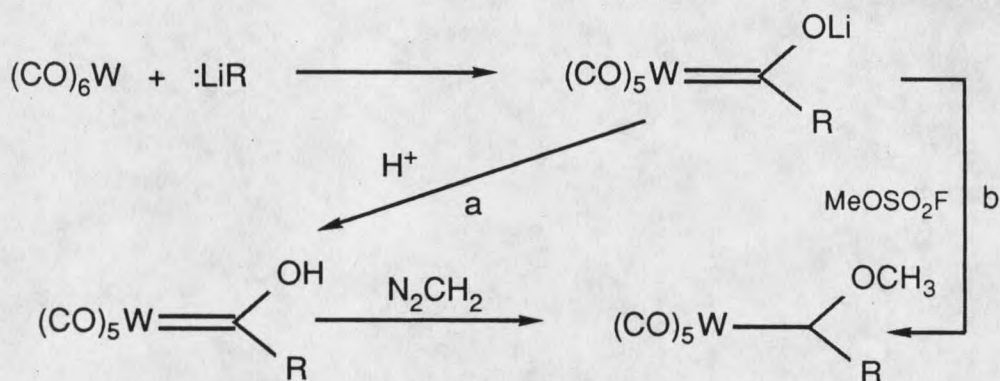


Twelve years after Yates proposed this structure, Fisher and Maasbol isolated and characterized the first metal-carbene²². This synthesis (Figure 2) defied the conventional wisdom of the time which suggested that metal-carbenes were too unstable to ever be isolated.

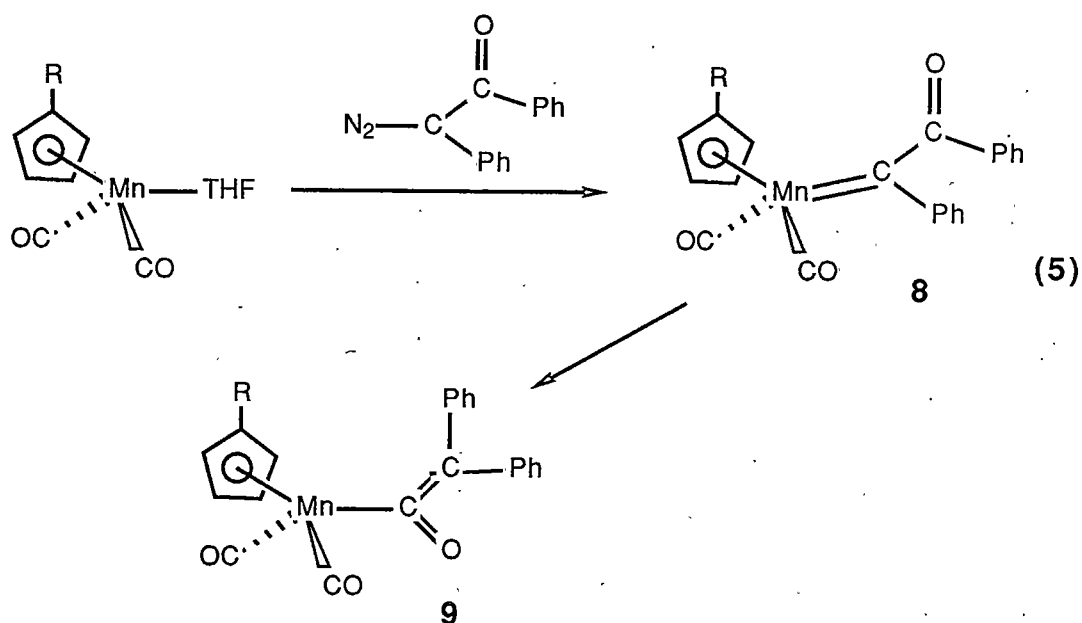
Fisher's original synthesis did involve diazomethane (path a), but not the metal catalyzed reaction under discussion. He also found routes to these complexes which did not involve diazoalkanes at all (path b). In later work, he was able to demonstrate that metal carbenes could stoichiometrically add to alkenes to form cyclopropanes²³. This supported the idea that metal-carbenes were involved in

all metal catalyzed decompositions of diazoalkanes. Until 1974 it was assumed that Fisher's work was the best evidence likely to be obtained in this matter. The only metal carbenes known were stabilized by heteroatoms α to the carbene carbon. Unfortunately, diazoalkanes with α heteroatom substituents are extremely unstable and cannot be isolated.

Figure 2. Synthesis of the First Isolated Metal Carbene.

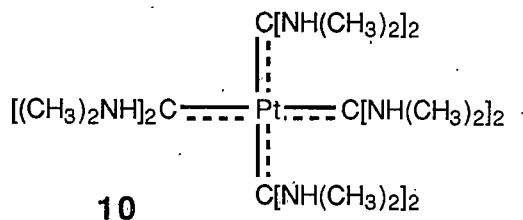


In a landmark paper, Herrmann was able to decompose a diazocompound and isolate the first non-hetero atom stabilized metal carbene²⁴. Equation 5 shows this reaction. A second interesting feature of this scheme is the stability of carbene 8 toward the Wolff rearrangement. In the free carbene there is a very facile migration of a phenyl group to form a ketene. The analogous reaction in the metal carbene (8 to 9) is only effected on irradiation with UV light. The isolation of 8 conclusively shows that this



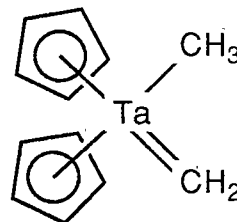
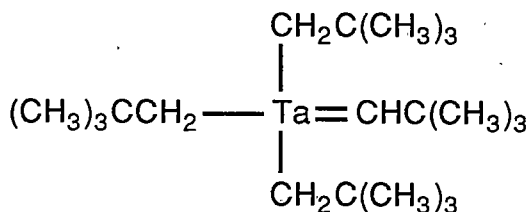
reaction is a metal catalyzed loss of N_2 , and not the attack of a free carbene on the manganese complex.

The formation of Fischer-type carbenes was soon extended to other transition metals, and hundreds are now known. Several platinum carbenes have also been reported²⁵, including a very intriguing tetra-carbene complex (10). This molecule was originally reported by Miller and Balch²⁶ and later characterized crystallographically²⁷.



A new family of nucleophilic metal carbenes was introduced about this time by Schrock²⁸. These complexes are

called "Schrock-type" carbenes or metal alkylidines to distinguish them from the electrophilic species found by Fisher. Schrock carbenes display a quite different reactivity than the Fisher carbenes. Instead of undergoing cyclopropanation and ylide formation, they participate in reactions such as Wittig-type alkylations, Lewis adduct formation, olefin metathesis and Ziegler-Natta polymerization. Some examples of these metal alkylidines are shown below²⁸.



Interest in metal-carbenes continues unabated. Current research includes investigations into their gas phases chemistry^{29,30}, the formation of new types of carbenes such as chiral carbenes^{31,32}, carbenes possessing α -hydrogens³³ and new types of non-heteroatom stabilized carbenes³⁴. Much of the emphasis of this work is on the search for models for catalytic reactions.

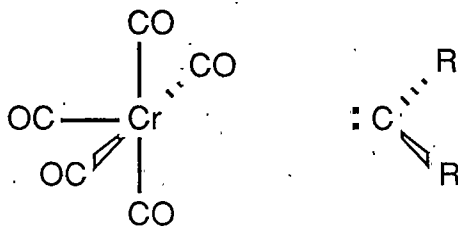
In addition to the stoichiometric work, Fisher's discovery spurred advances on the catalytic front. Nozaki³⁵ and Moser³⁶ introduced soluble copper catalysts. These were shown to give better yields in many cases. Salmon and Kochi demonstrated that diazocompounds reduced copper(II) cata-

lysts to copper(I) and that it was copper(I) that actually catalyzed the decomposition of the substrate³⁷. Finally, chiral copper catalysts were introduced, and it was proven that they could induce enantiospecificity³⁸. This was particularly significant, because it showed that the catalytic reactions must be taking place in the coordination sphere of the metal.

In the early '70's, Teyssie and co-workers demonstrated that other metals were viable alternatives to copper. Palladium³⁹ and rhodium⁴⁰ were shown to give excellent yields in the cyclopropanation of olefins. Rhodium, in particular has proven to be an outstanding catalyst for a variety of reactions involving diazoalkanes.

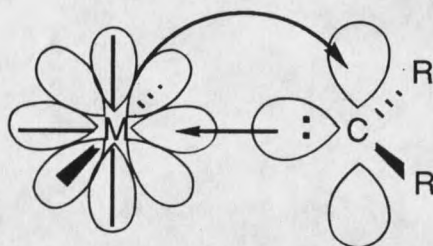
The Electronic Structure of Metal Carbenes

Interest in metal-carbenes by theoretical chemists has been increasing since the mid-1970's, yet the total number of studies completed to date is small. Most workers have found it convenient to describe metal carbenes as the interaction of a metal complex and a carbene. An example of this is the interaction of $\text{Cr}(\text{CO})_5$ with $:\text{CH}_2$, as shown below. This method of considering the orbitals makes clear



the relationship between the carbene and the rest of the complex.

Goddard has shown that Fisher-type carbenes are formed when a singlet carbene combines with a low-spin metal^{41,42}. The metal normally has closed-shell ligands such as CO or PR₃, which encourage the pairing of the d electrons. This pairing enables the complex to adopt the familiar donor/acceptor type bonding mode.



Singlet carbene formation is encouraged by the presence of a heteroatom α to the carbene center. The C-heteroatom bond is mostly p in character and the lone pair is able to donate electron density into the carbon p π -orbital⁴².

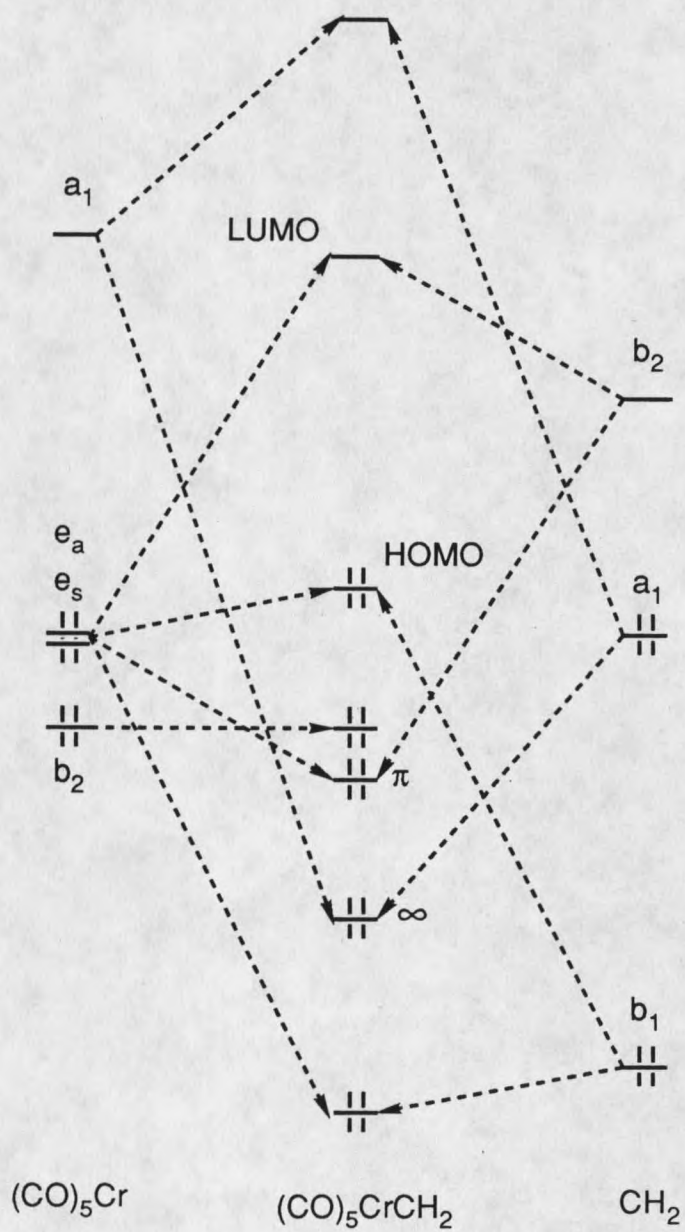
Figure 3 shows a qualitative molecular orbital diagram of the important orbitals for the formation of (CO)₅CrCH₂⁴³. It can easily be seen that the electron density for the metal-carbon σ bond lies mainly on the carbene carbon, while the π backbond is centered mainly on the metal. Also significant is the fact that the HOMO is centered on the metal while the LUMO is on the carbene carbon.

Electron density calculations reveal that the carbene carbon often carries an overall negative charge⁴⁴. This is contrary to the $M^- C^+$ polarization scheme usually drawn for these species. The localization of the LUMO on this carbon however, implies that this should be the site of nucleophilic attack. This is, of course, precisely what occurs.

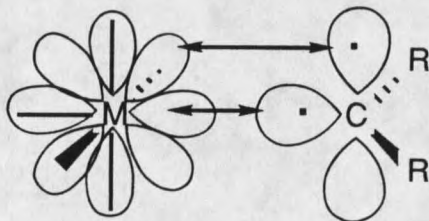
The extent of polarization of the π -backbond determines the reactivity of the metal-carbene complex. This is influenced by the metal, the metal ligands and the carbene substituents. The closer the metal e_g and the carbon b_2 orbitals are in energy, the better they overlap, and the higher the energy of the LUMO. A high energy LUMO is less susceptible to nucleophilic attack, and is necessarily less centered on the carbene moiety.

The lone pair electrons on the heteroatom compete with the metal e_g electrons for the carbene b_2 orbital. This results in a lengthening of the metal-carbene bond and a shortening of the metal heteroatom bond. The LUMO is concentrated even less on the metal and more on the carbene fragment. There it is dispersed onto the heteroatom as well as the carbene carbon. Overall, the presence of the heteroatom considerably stabilizes the complex.

Schrock type carbenes are formed from "high-valent" metal complexes and triplet carbenes⁴². Ionic ligand (halides, alkyl groups, etc.) prefer to bond to metal s electrons and tend to force the metal into a high-spin

Figure 3. A Qualitative MO Diagram of $(\text{CO})_5\text{CrCH}_2$.

configuration. The metal is then set up to bond to other orbitals occupied with a single electron.



A triplet carbene ground state is favored when the carbene substituents are not heteroatoms, but alkyl groups or hydrogen. A triplet ground state enables the carbene to form a "covalent" carbon-metal double bond. The electronic configuration of the resultant alkyldiene complex will not be discussed here, save to say that the carbene moiety behaves as a nucleophile rather than an electrophile.

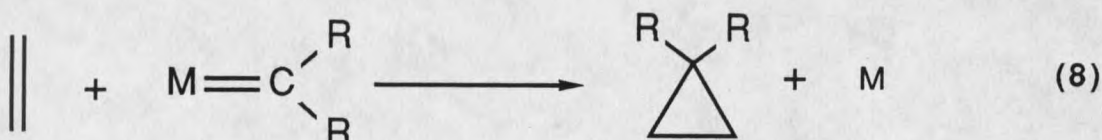
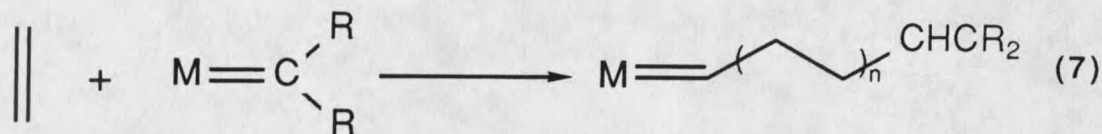
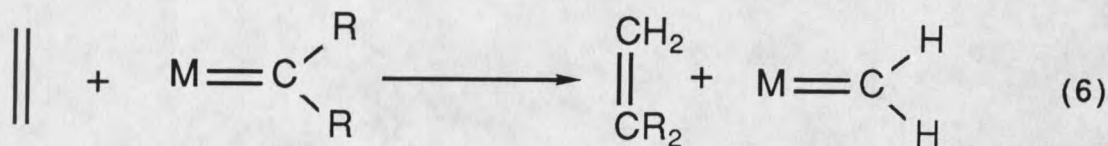
Goddard has suggested that, all other things being equal, the early transition metals should form alkyldiene complexes while the late should form Fischer carbenes. The situation becomes more complex though, with second and third row transition metals. Goddard says that other factors can easily determine which species is formed. Owing to the difference in reactivity between the two species, this becomes very significant in catalyst design with the heavier transition metals.

Catalysis

Metal-carbenes undergo a variety of reactions, both catalytic and stoichiometric. These are of great current interest, as recent reviews attest^{3, 24, 45, 46, 47, 48}. The sections that follow will focus on several catalytic and one stoichiometric reaction.

One of the most important reactions of metal-carbene chemistry is the interaction with π systems. There are three reactions which are thought to proceed along similar paths and through common intermediates. These are olefin metathesis, Ziegler-Natta polymerization and cyclopropanation (metathesis of alkynes may be similar to these as well, but this will not be discussed). Examples of these reactions are shown below in equations 6 through 8 respectively.

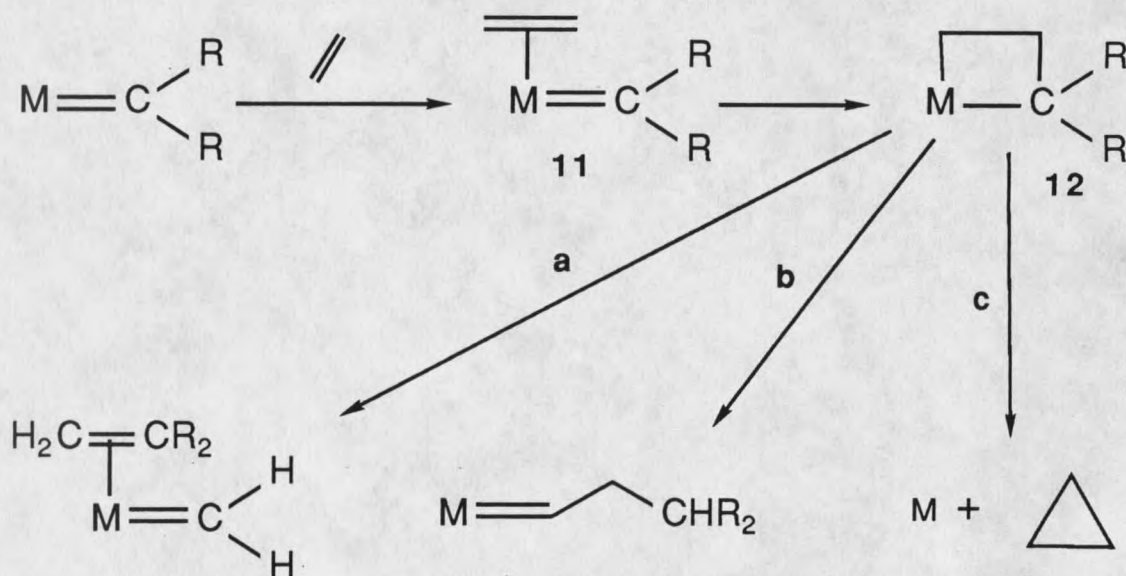
Olefin metathesis is the exchange of one half of an alkene with one half of another⁴⁹. This is an important industrial process and thought to involve Schrock-type alkyldiene intermediates. The Ziegler-Natta polymerization reaction is also important industrially and involves catalysts very similar to that of olefin metathesis^{50, 51}. Catalytic cyclopropanation of olefins is the only one of these processes that involves diazocompounds. It is not used on an industrial scale, but is very common in organic synthesis in the laboratory. This reaction is thought to involve Fisher-type carbenes⁵².



Starting from a metal carbene, each of these reactions has been proposed to associate an olefin (11) and then cyclize to form a metallacyclobutane (12). The metallacyclobutane can then decompose by three different routes to form the various products (Figure 4). Route a is essentially the reverse of the formation of the metallacycle and involves cleavage of two carbon-carbon bonds. The cleavage splits the metallacycle in the opposite direction however and a new metal-carbene and olefin result. The loss of an olefin here results in formation of a new metal-carbene, which can continue the reaction.

The Ziegler-Natta polymerization reaction (path b) involves the abstraction of an α hydrogen followed by reductive elimination of the hydride and the second metallacyclobutane carbon. This forms a new metal-carbene which can coordinate another olefin.

Figure 4. Proposed Mechanisms for Three Catalytic Reactions.



Cyclopropanation results from reductive elimination of the hydrocarbon moiety from the metallacycle and the formation of a new carbon-carbon bond. For catalysis to occur, a second equivalent of diazoalkane must be decomposed followed by coordination of a second equivalent of alkene.

Critical to this scheme is the metallacyclobutane, structure 12. Originally, these species were inferred to explain stereospecificity observed in the various reactions. Until recently however, the only known metallacyclobutanes were those of platinum. Even though platinum had not been reported to catalyze any of these reactions, the proposed role of metallacyclic intermediates promoted extensive study of platinacyclobutane chemistry⁵³.

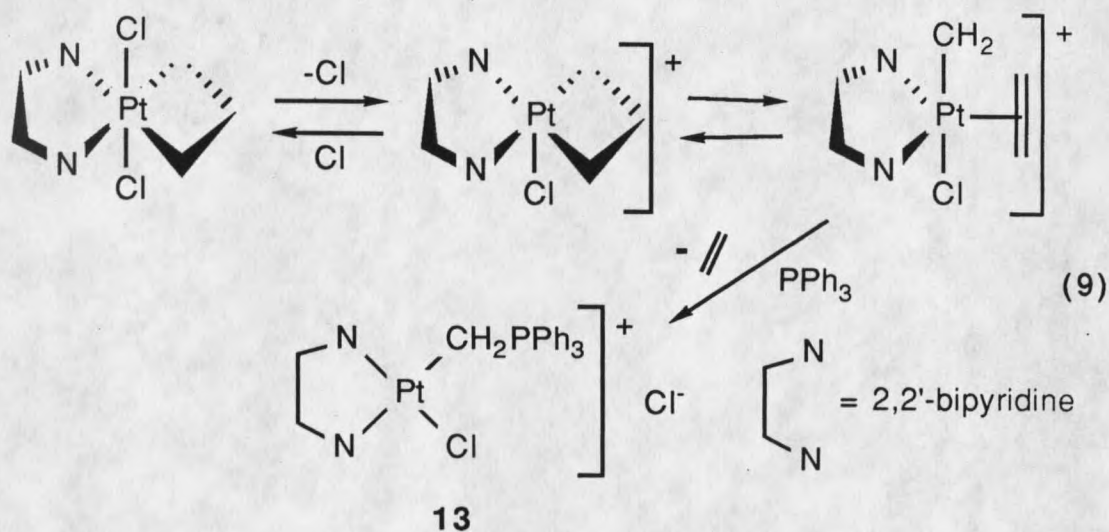
Platinacyclobutanes

Platinacyclobutanes were first synthesized in 1955 by Tipper³⁴. In 1960, Chatt proposed a metallacyclobutane structure for Tipper's compounds based on spectroscopic data and reactivities³⁵. Examples of both platinum(II) and platinum(IV) platinacyclobutanes can now be found in the literature. Prior to this work, only four synthetic routes to platinacyclobutanes were known (Table 3). By far the most common is Tipper's original method, which is the insertion of the metal into a cyclopropane. This method is effective with both platinum(0) and platinum(II). The other syntheses are relegated to one example. It should also be noted that none of these methodologies involve a metal-carbene and an olefin, even though platinum carbenes have been known for some years.²⁵

Platinacyclobutanes undergo a variety of reactions, including the three modes described in the preceding figure 33, 59, 60. The most common reaction is the reverse of Tipper's synthesis, i.e. reductive elimination to form cyclopropane. This can be induced thermally, photochemically or by reaction with strongly coordinating ligands such as phosphines.

Examples in which a metathesis-like cleavage of the ring occurs are less common, and the data less clear. Puddephatt has found that under certain conditions, unsubstituted platinacyclobutane eliminates large amounts of

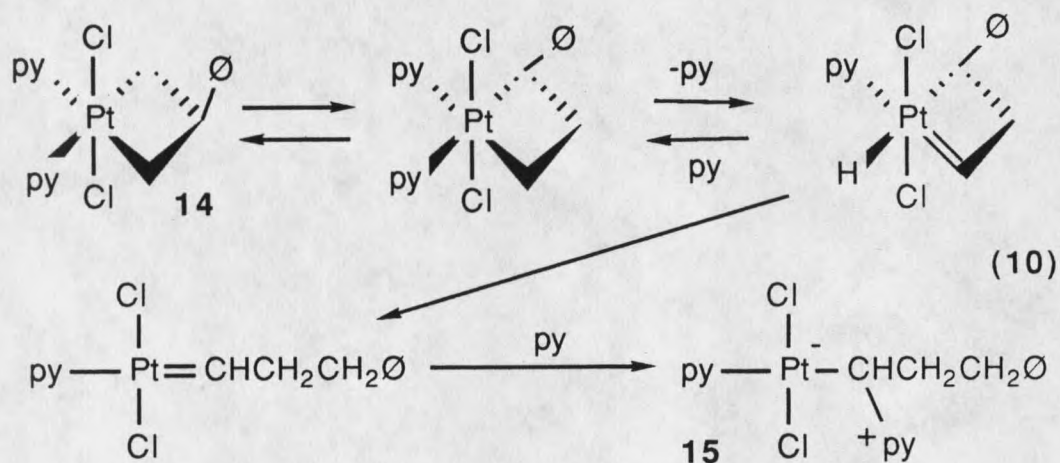
ethylene^{61,62}. This product presumably results from the mechanism shown in equation 9. Product 13 could not actually be isolated from the reaction mixture due to the large excess of phosphine used. This "ylide" species may be considered a "trapped" metal carbene. Other platinum ylides of the general structure $[\text{PtX}(\text{CH}_2\text{L})\text{L}_2]^+$ have been isolated and characterized as well⁶³. The relationship between ylides and metal-carbenes is discussed in more detail in a later section.



A titanacyclobutane was also reported to produce ethylene on decomposition. A mechanism similar to that shown above was proposed in this case as well⁶⁴.

Platinacyclobutanes have not been reported to form polymers on exposure to olefins nor have platinum carbenes been isolated from a Ziegler-Natta type ring opening (Figure 4, path b). Platinacyclobutanes will however, undergo a

ring opening to form platinum ylides on benzene reflux or exposure to bulky ligands. A proposed mechanism for this reaction is shown in equation 10⁶³. The first step is a reversible rearrangement known as the "Puddephatt" rearrangement⁶⁴. Formation of the more sterically hindered platinacyclobutane appears to be necessary before α -hydride abstraction can occur. The transfer of the α -hydrogen, as opposed to some other process, has been confirmed by deuterium labeling. Once the hypothetical platinum carbene is formed, it is trapped to form the platinum ylide complex 15. This demonstrates that the crucial decomposition step for Ziegler-Natta polymerization is possible with platinacyclobutanes.



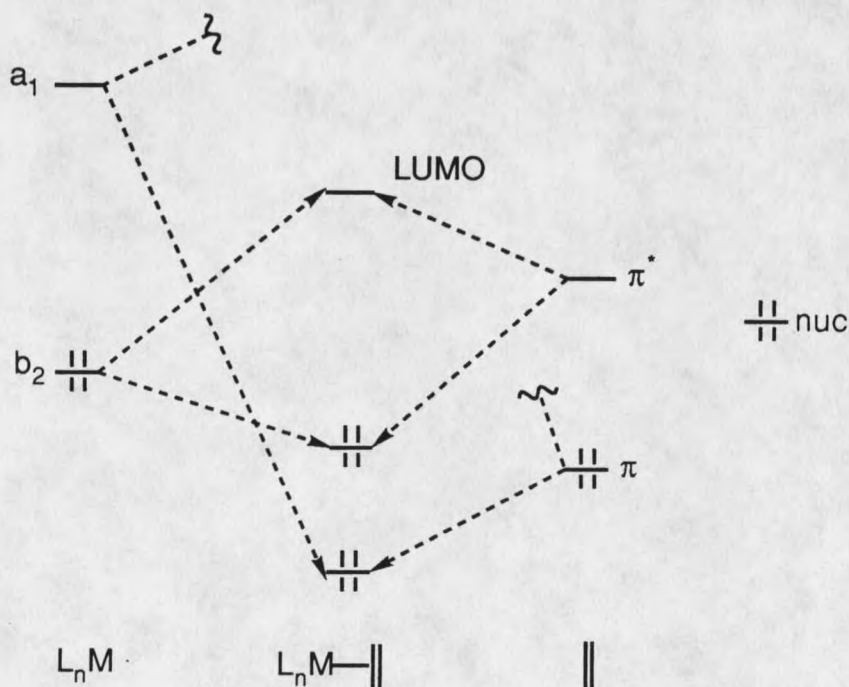
Metals and Olefins

The platinacyclobutane results show that metallacyclobutane can undergo the various decompositions necessary for the three catalytic cycles shown in Figure 4. Yet, the lack

of physical evidence for metallacyclobutanes in these catalytic reactions (with one notable exception), requires discussion on whether they are formed in the first place. Eisenstein and Hoffmann have addressed this question theoretically in several papers since 1980.

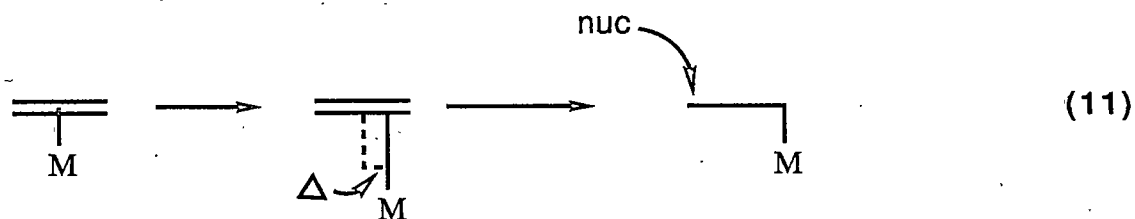
The complexation of olefins by metals results in greatly increased susceptibility to nucleophilic attack on the olefin moiety^{67,68}. According to Extended Huckel calculations however, this interaction should result in deactivation towards nucleophiles^{69,70}. Figure 5 shows how interaction of the olefin π^* orbital with the metal b_2 orbital results in an increase in the energy of the LUMO for

Figure 5. The Effect of Metal Coordination On Olefins.



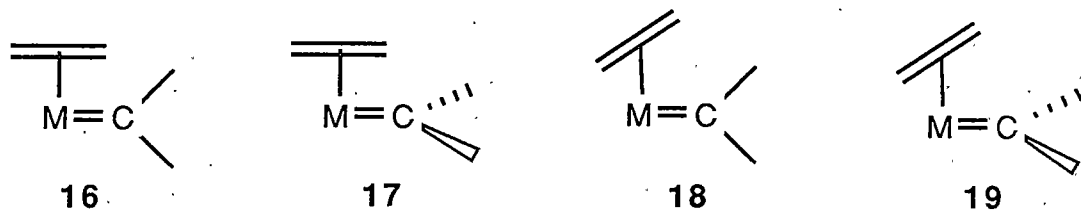
the olefin. This increase in energy decreases the orbital overlap with the incoming nucleophile, and thus the reaction is less favorable.

These results, of course, are not consistent with the observed facts. Eisenstein and Hoffmann explain this discrepancy by proposing that the olefin "slips" across the metal as shown in equation 11. Calculations show that this displacement increases the overlap with the incoming nucleophile until, at a certain point, it surpasses that found in the free olefin. The extent of activation is dependent on the metal, the coordination number and the oxidation state.

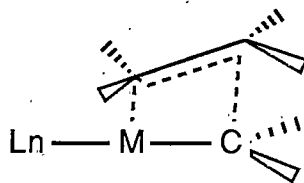


There is considerable difference between external attack by a nucleophile and the cyclization of a metal-carbene/olefin complex. This later reaction was also investigated by Eisenstein and Hoffmann^{7,1}. They found that certain geometrical features were required for the reaction to take place. Structure 17 should be able to cyclize, while 16, 18 and 19 should be prohibited from doing so. The factors determining the relative orientation of the carbene

and alkene moieties have also been discussed⁷². Once again these were found to be highly metal and ligand dependent.

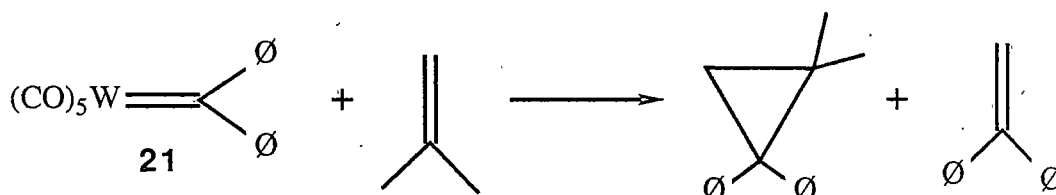


Eisenstein and Hoffmann's results also suggest that for some electron counts, specifically d^2 - d^6 species from the metal-carbene/olefin side, neither the carbene/olefin nor the metallacyclobutane are stable geometries. Instead, a non-classical structure such as 20 is predicted. For these species, the reductive elimination of a cyclopropane is a forbidden process. For electron counts greater than d^6 (from the metal-carbene/olefin side), metallacyclobutanes are predicted to be stable. Most of these results correlate well with experiment, although titanacyclobutanes are known which are quite stable. The results described here would predict a non-classical structure for such compounds.



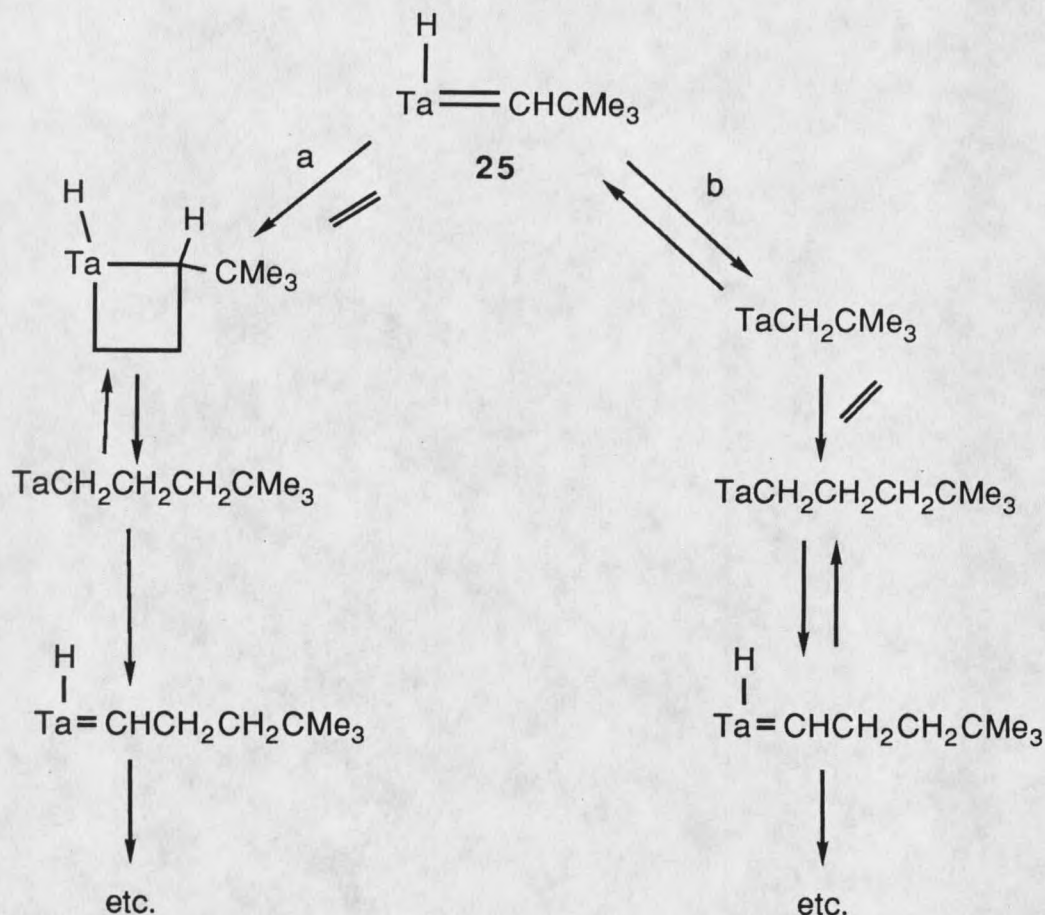
20

Recent experimental evidence has made the carbene to carbene/olefin to metallacyclobutane mechanism seem very probable for the three catalytic reactions shown in Figure 4. Casey has shown that compound 21 can stoichiometrically form both cyclopropanes and metathesis products in the presence of olefins⁷³.



Grubbs⁷⁴ has synthesized a titanacyclobutane which is a metathesis catalyst (compound 22). Later, he found that complex 23 also catalyzed metathesis⁷⁵, the first step being the formation of the titanacyclobutane 24. Compound 23 is simply a stabilized titanium carbene. $\text{Al}(\text{Me})_3\text{Cl}$ is presumably lost from the complex, followed by coordination of the olefin and cyclization to the metallacyclobutane. This system is especially interesting because it is a living polymer. In the presence of olefin the metathesis proceeds as normal, but when this is exhausted, the chain terminates in a stable titanium-carbene. The chain begins to grow again on addition of more olefin. Because of results like these, the mechanism under discussion has received wide acceptance for the metathesis reaction^{76, 77, 78}.

Figure 6. Possible Mechanisms for Ziegler-Natta Polymerization.



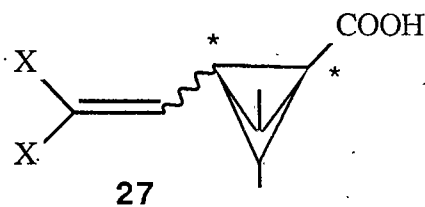
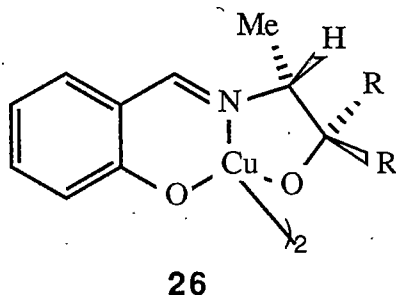
b. The resolution of this question must await further investigation.

The mechanism originally suggested in Figure 4 for cyclopropanation was very popular at one time, but has recently come under serious attack. The question will be treated in detail after a little background on the reaction and the catalysts currently in use.

Catalytic Cyclopropanation

Catalytic cyclopropanation of olefins is an extremely important synthetic methodology^{3,47,48}. A variety of metals have been shown to catalyze the reaction including Cu, Ag, Pd, Fe, Rh, Ru, Re, Co and Mo. The use of platinum in this role has not been reported to date. The catalyst providing the best activity for a given system is dependent on the substrate olefin and the diazoalkane employed, though the reasons for this are not well understood.

Insoluble copper catalysts were the first to be used, and still retain some popularity⁸². Several workers have reported increased yields with soluble catalysts, and these have largely replaced the insoluble species⁸³. Specialty catalysts, such as compound 26, have been introduced which are capable of special selectivity. Compound 26 was used to generate 27 with a high degree of regio-, stereo- and



X = CH₃ or Cl

* = Chiral

enantioselectivity. This is highly significant, as 25 is an important intermediate in the synthesis of certain insecticides^{84,85}.

Laidler and Milner have studied other copper(II) Schiff complexes similar to 26 with a variety of olefins. The degree of optical induction was found to be highly olefin dependent in this system⁸⁶. Other chiral copper catalysts have been developed as well. Marlin and co-workers have described copper complexes of 3-trifluoroacetyl-(+)-camphor and derivatives which exhibit enantiomeric excess of up to 100:1⁸⁷ with certain substrates. The construction of chiral catalysts for optical induction is an important step in the development of this area.

Copper catalysts are subject to low yields and limited scope⁸⁸. This has prompted the search for new catalysts with unique activity. Palladium, particularly as palladium(II) acetate has found widespread use. It is the catalyst of choice for the cyclopropanation of terminal olefins⁸⁹ and α, β -unsaturated olefins⁹⁰. Diazomethane has been found to work very well with palladium, perhaps better than with any other catalyst. Palladium's use with ethyl diazoacetate has been much less successful. With this diazoalkane and unstrained olefins such as cyclohexene, only polymer is produced⁹¹.

Another important metal in this reaction is rhodium. There are a number of different rhodium catalysts, the most

common being rhodium(I) acetate dimer. This species is the most versatile of the known catalysts, giving excellent results with a variety of substrates^{48,92}. Another rhodium catalyst of interest is a rhodium-porphyrin complex introduced by Callot. This complex shows excellent stereoselectivity, though at the expense of yields⁹³.

Other important catalysts have recently been introduced. Molybdenum hexacarbonyl has been shown to cyclopropanate α, β -unsaturated esters and nitriles in good yields⁹⁴. Nakamura and Otsuka have developed a chiral cobalt catalyst which will cyclopropanate certain olefins in good yields and in high ee⁹⁵. These workers have also reported on some mechanistic studies.

There is considerable effort being made to find catalysts which are stereoselective. The current generation of catalysts rarely provide selectivities greater than 4:1. The highly hindered catalysts such as the rhodium-porphyrin compound, which do offer special selectivities, suffer from limited scope and poor yields with all but a few substrates. Doyle has shown that stereoselectivities are highly dependent on the metal and to a much lesser degree on the ligands⁹⁶. He found that selectivities were linearly related by equation 12.

$$(\text{isomer ratio})^{\text{catalyst 1}} = S * (\text{isomer ratio})^{\text{catalyst 2}} \quad (12)$$

S, in equation 12, is the relative index of selectivity. It is equal to 1.7 for copper, 1.0 for rhodium and .59 for palladium. Copper complexes are the most selective catalysts, but also the least subject to ligand effects. Rhodium shows less selectivity, but yields are much superior and selectivity can be altered greatly by ligand substitution. Palladium displays a very different reactivity, even being selectively opposite the others on occasion. Doyle has suggested that stereoselectivity is directly related to the degree of polarization of the metal-carbene bond. The more highly polarized the carbene, the more reactive and the less selective it will be.

Regioselectivities are also quite poor and highly metal dependent. Explanations for this vary. Doyle again suggests that metal-carbene bond polarization is the cause with more highly polarized species going through "earlier" transition states⁹⁷. Other workers have suggested that two mechanisms may be operating, with the ability of the metal to coordinate olefins determining selectivity⁹⁸.

All cyclopropanation catalysts suffer from competing reactions to a greater or lesser degree. The most common of these reactions is dimerization of the carbene fragment. This can be minimized by keeping the diazoalkane concentration low as compared to the substrate⁹⁹, but it is still a problem, particularly with copper.

Insertion into carbon-hydrogen bonds is another potential problem¹⁰⁰, although there is some question as to whether this can compete with cyclopropanation. Some early reports of C-H insertion may have been due to rearrangements of originally formed cyclopropanes⁸⁸.

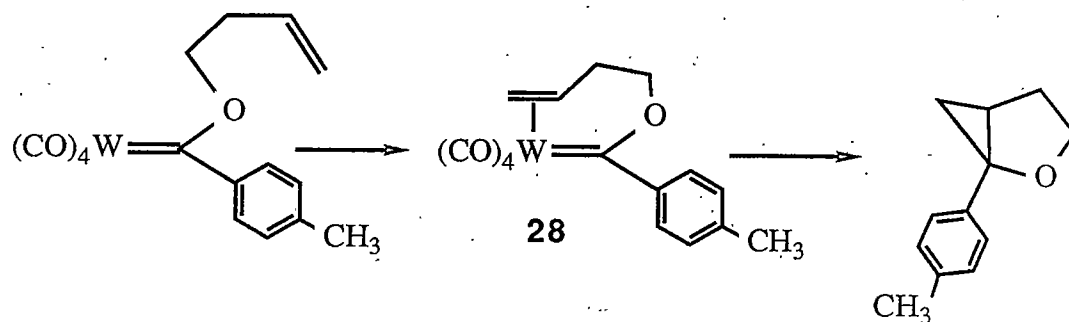
Other reactions which may cause difficulties are polymer formation, insertion into X-H bonds (X= O, S, N), rearrangements or reaction with substrates which deactivate the catalyst. Many of these difficulties, including poor regio- and stereoselectivities are metal dependent. As a greater understanding of this reaction grows, a host of new catalysts will be developed. These will be both ligand and metal specific for the problem at hand. Central to the construction of these species is the elucidation of the mechanism(s) involved.

The Mechanism of Catalytic Cyclopropanation

Metal-carbenes have not been observed to catalyze the cyclopropanation of olefins, nor have they been isolated from a catalytic system. Nevertheless, there is very little question that they are the primary intermediates in the process. Fisher discovered that metal-carbenes would stoichiometrically cyclopropanate olefins shortly after he isolated the carbenes themselves^{101, 102}. Currently there are several such species that are known to undergo this reaction^{103, 104, 105, 106}.

More convincing evidence for the intermediacy of metal-carbenes in the catalytic reaction comes from the transfer of optical activity from a catalyst to a cyclopropane. This requires that the reaction take place within the coordination sphere of the metal⁹⁵. Doyle has demonstrated a linear correlation between the stereoselectivities of the stoichiometric cyclopropanation reaction of a tungsten-carbene and the catalytic reaction of rhodium acetate¹⁰⁷. This strongly suggests a common mechanism between the two.

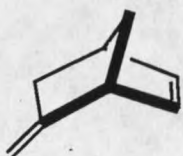
The next step in the carbene to carbene/olefin to metallacyclobutane mechanism presented in Figure 4 is the coordination of an olefin to the metal-carbene/olefin species. Very good evidence for this type of complex in the stoichiometric reaction has been found recently by Casey. He has been able to observe the tungsten-carbene/olefin complex 28 by NMR. This compound then collapses to form a cyclopropane¹⁰⁸. A similar structure (29) has been characterized by X-ray crystallography¹⁰⁹. The complex exists as two structures, 29a and 29b. At room temperature these rapidly interconvert. By the arguments of Eisenstein and Hoffmann,



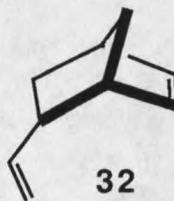
participating in reactions with this catalyst, yet it is perhaps the most effective cyclopropanating agent known.

Hubert, Noels and co-workers have suggested that two mechanisms may be operating^{9,1}. The first being the metal-carbene/olefin mechanism for palladium and other strongly olefin coordinating catalysts. Non-coordinating catalysts such as rhodium were proposed to follow a second mechanism. Copper catalysts were postulated to be intermediate, as some are known to coordinate olefins while others apparently do not. These workers also suggested that differences in regioselectivity could be attributed to the ability to coordinate olefins^{9,8}.

Doyle has disputed the idea that a metal-carbene/olefin intermediate is present in the palladium reaction^{11,1}. His investigation began with the observation that coordinated olefins are activated towards nucleophilic attack, while the metal-carbenes implicated as cyclopropanation catalysts are electrophiles. He has also demonstrated that olefins 31 and 32 form stable adducts with palladium(II). These adducts do not form cyclopropanes on addition of ethyl diazoacetate, nor does the addition of additional catalyst ($\text{PdCl}_2 \cdot 2\text{PhCN}$ or $\text{Rh}_2(\text{OAc})_4$) cause a reaction. If additional olefin is added



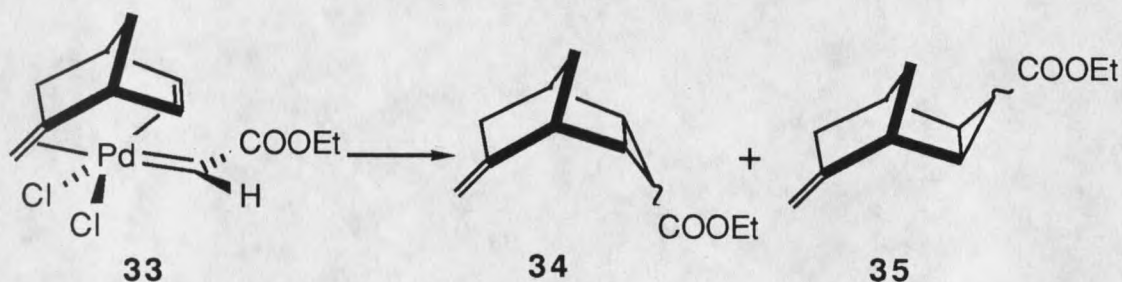
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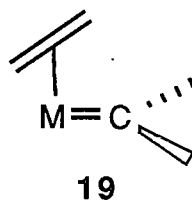
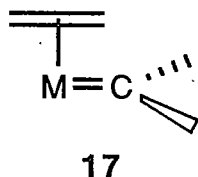
to the palladium adducts however, cyclopropanation rapidly occurs.

These results are inconsistent with the collapse of a metal-carbene/olefin complex or with electrophilic attack of a coordinated olefin on the diazoalkane. They are, however consistent with intermolecular attack of an uncoordinated olefin on an electrophilic metal-carbene. Additional evidence for this idea comes from the products formed from the cyclopropanation. Palladium prefers to attack the endocyclic double bond of compound 31. If the cyclopropanation were the result of the collapse of the metal-carbene/olefin species 33, only the endo cyclopropane, isomer 34 (formed via syn attack), should be formed. Doyle has found that the exo isomer, 35 (formed from anti attack), was preferentially formed in a 54:46 ratio with ethyl diazoacetate. When diphenyl diazomethane was used this ratio became an even greater 50:1¹¹¹.



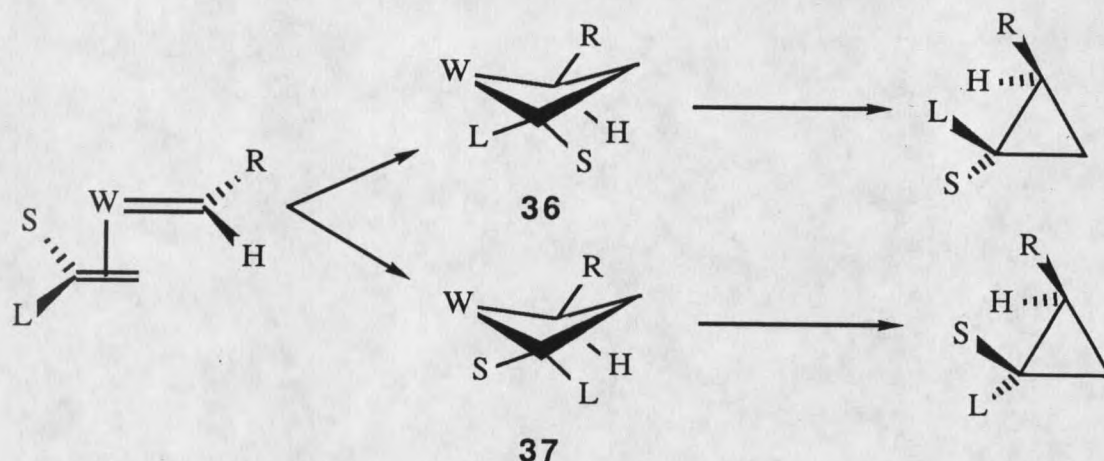
If these results are interpreted in light of Eisenstein and Hoffmann's results, it is clear that other factors not

considered by Doyle, might be at play here^{71,72}. It may be recalled that they showed that a geometry similar to 17 was required for the collapse of a metal-carbene/olefin to a metallacyclobutane. It is not known if the bidentate olefins 31 and 32 coordinate in a geometry similar to this or if they might be locked into a configuration more like that of 19. There are several metal-carbene/olefins known which have geometries similar to 19, or intermediate between that of 17 and 19. These compounds are not able to form cyclopropanes. Doyle's conclusions, therefore, may only be valid for the particular system studied.

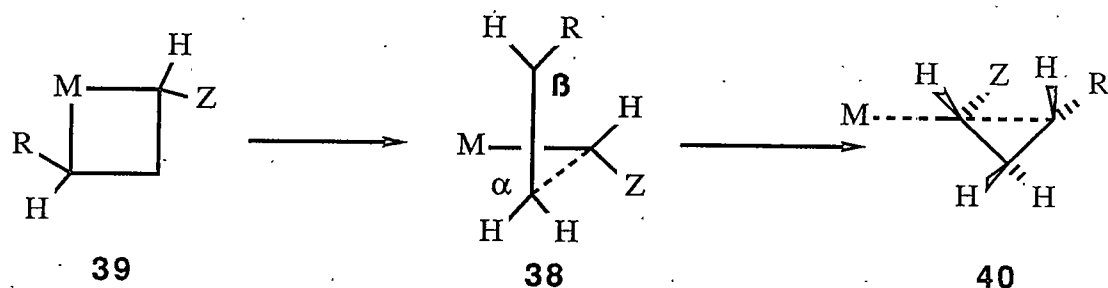


There are other challenges to the carbene/olefin to metallacycle mechanism. Casey and Polichnowski designed a series of experiments in which they hoped to elaborate on the idea that the stereoselectivities of the cyclopropanation reaction were determined at the metallacyclobutane stage¹¹². According to this hypothesis, a metal-carbene should react with cis olefins to form metallacyclobutanes as in structures 36 and 37. The puckering of the metallacyclobutane (in analogy with platinacyclobutanes) should make structure 36 more stable than 37. As the large group

L increases in size, the difference in energy should also increase. Since 36 yields syn cyclopropanes and 37 yields anti, the validity of this argument and the extent of ring puckering should be demonstrable.



Casey and Polichnowski did find a preference for the cis isomer, but this preference smoothly decreased with increasing size of L. In several related reactions, a preference for the less thermodynamically stable isomer was repeatedly observed. Brookhart proposed a new mechanism to account for these results³³. In this mechanism, the transition state 38 is the result of an association between the electrophilic metal-carbene and one carbon of the olefin. The carbon labeled β is the center best able to support the developing positive charge. The stereoselectivity results from the partitioning between the metallacyclobutane 39 and structure 40. As R becomes more bulky,



formation of 39 becomes energetically more favorable, and the amount of anti isomer increases.

Brookhart's mechanism explained Casey's results, but failed to account for the strong preference for anti products with diazocarbonyl compounds. Doyle has proposed a modification of this mechanism as shown in Figure 7¹⁰⁷. In this scheme, the metal-carbene forms a π -complex with the olefin. The formation of 41a is always preferred over 41b, but as the steric bulk of R increases, K_c becomes slower as compared to K_t . The result is a decrease in the syn to anti ratio with increasing size of R.

With ethyl diazoacetate, K_t is always preferred because the carbonyl stabilizes the developing plus charge (structure 42). Doyle predicts that increasing the nucleophilicity of the carbonyl will increase the stereo-preference for the anti isomer. The magnitude of this effect will depend on the ability of the group R to stabilize the developing charge. Ethyl vinyl ether, for example, should show little

Figure 7. Doyle's Mechanism for Catalytic Cyclopropanation.

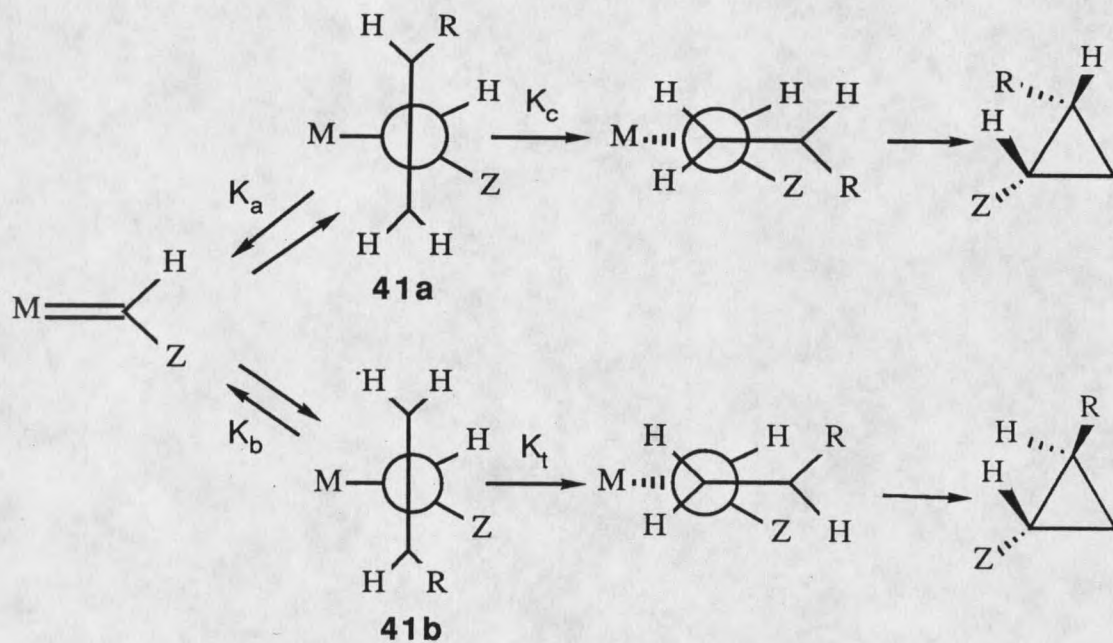
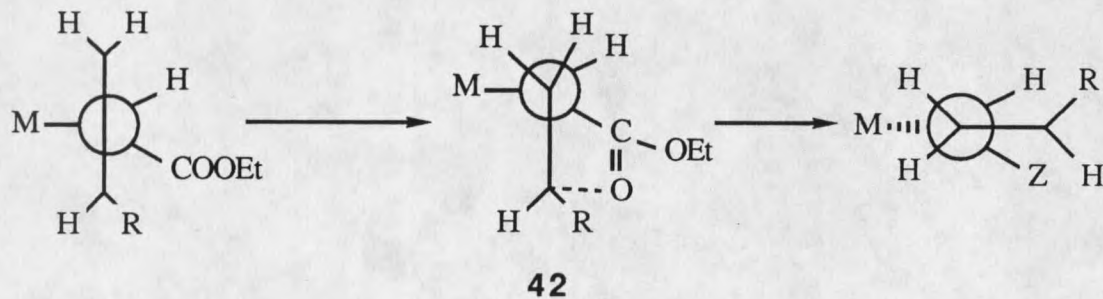


Figure 8. Catalytic Cyclopropanation with Ethyl Diazoacetate.



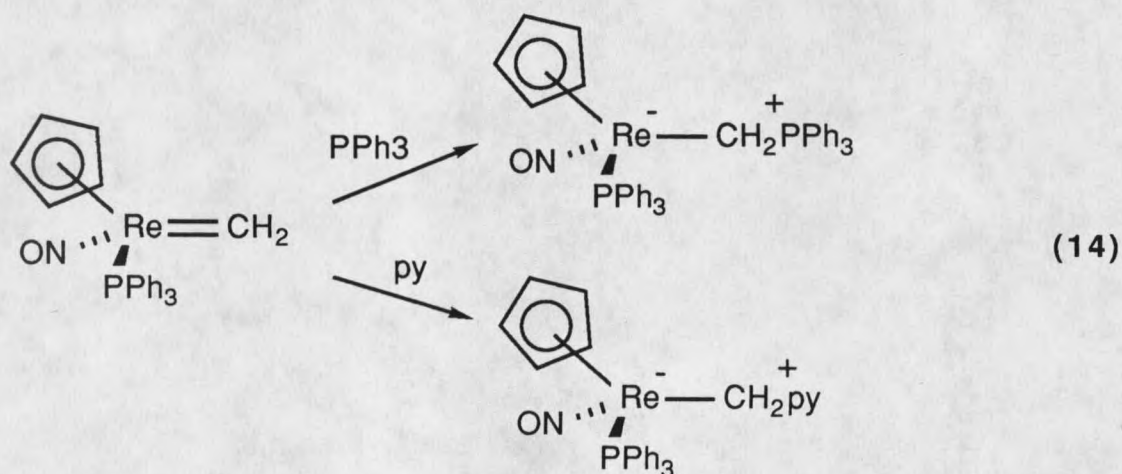
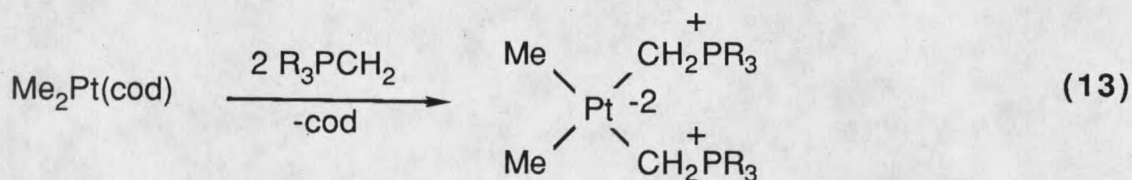
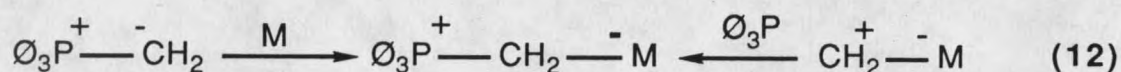
preference for the anti isomer, since the oxygen lone pair electrons are easily available for stabilization.

This latest mechanism is a far cry from that introduced in Figure 4. It includes neither a metal-carbene/olefin complex nor a metallacyclobutane. It does however, appear to be consistent with all published stereochemical and regiochemical data and offers a unified mechanism for all catalysts. Doyle has offered some testable ideas for the construction of new catalysts with high stereoselectivity. Additional work will determine the validity and applicability of this mechanism.

Ylides

The term "ylide" refers to species which contain a σ -bond between two atoms which bear opposite charges. Poor overlap between the concerned orbitals means that there is very little π character to the bond. Traditionally, these complexes have been of the type $R_n-X^+-C^-R_2$, where X is phosphorus, sulfur or less commonly, arsenic or nitrogen. These species have been known for some time and several reviews concerning their preparation and reactivity are available^{113, 114, 115, 116}. A particularly interesting use of these compounds has come to light recently. They are very unique ligands for transition metals. Reviews discussing this aspect of ylide chemistry have also appeared^{117, 118}.

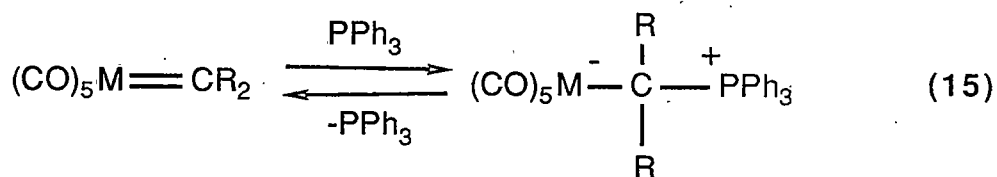
In their role as ligands for transition metals, metal ylides may also be considered stabilized or "trapped" metal carbenes. Equation 12 is more than just a way of visualizing ylides, it also represents two common methods of synthesizing them. Equations 13¹¹⁹ and 14¹²⁰ are examples of these synthetic methodologies.



Equation 14 is very exciting in light of the previous mechanistic discussions because it implies the ability to trap the metal carbene species suggested for so many processes. The presence of a trapping agent, such as triphenyl phosphine or pyridine, could be used to stop a catalytic

reaction by forming a stable ylide, and thus demonstrate the existence of a metal-carbene intermediate in a given system.

In one case (eq. 15), a metal-carbene can be reversibly converted to an ylide. The ease of removal of the phosphine is directly related to the electrophilicity of the carbene carbon center. For the examples given in equation 15, typical enthalpies of reaction lie in the -15 to -20 Kcal mol⁻¹ range^{118,121}.



M=Cr, W and rarely Mo

Platinum ylides have been prepared as well. Table 4 lists examples of the known synthetic routes to these complexes. The nucleophilic attack of an amine on a coordinated olefin, as shown in the third example in Table 4, forms a product which may stretch the definition of the term "ylide". A better description might be "extended" ylide. The fourth example was discussed earlier as a model for the metallacyclobutane decomposition in the Ziegler-Natta polymerization reaction. The reaction was originally discovered by Gillard and has been found to be a fairly general reaction for platinacyclobutanes. The last entry in

Table 4. Synthetic Routes to Platinum Ylides.

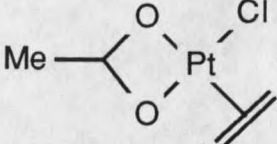
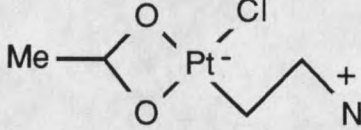
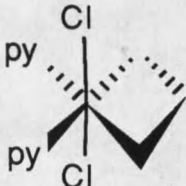
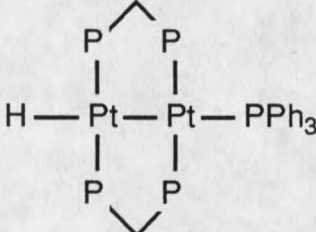
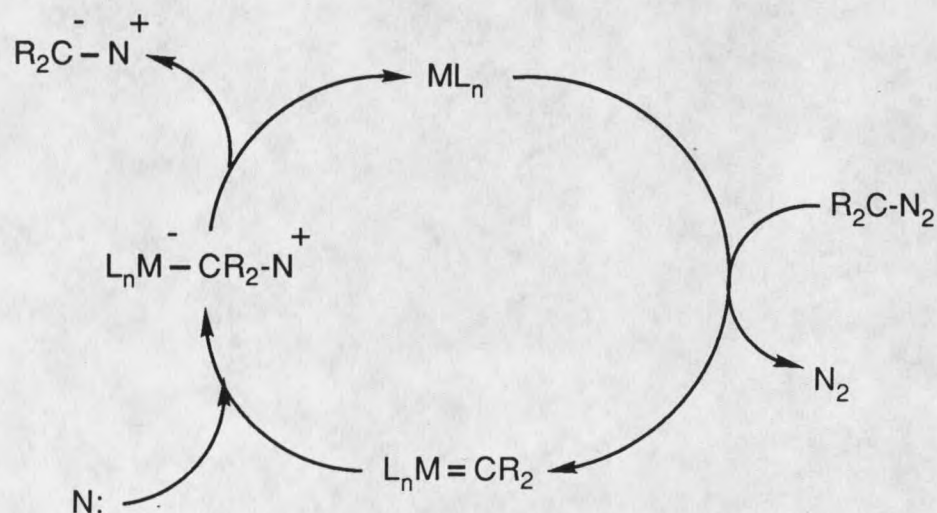
Exp.				Ref.
1	$\text{Me}_2\text{Pt}(\text{cod})$	$\xrightarrow[-\text{cod}]{2 \text{ R}_3\text{PCH}_2}$	$\begin{array}{c} \text{Me} \quad \quad \quad \text{CH}_2\text{PR}_3^+ \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{Pt}^{-2} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{Me} \quad \quad \quad \text{CH}_2\text{PR}_3^+ \end{array}$	119
2	$(\text{PPh}_3)_4\text{Pt} + \text{CH}_2\text{I}^+\text{I}^-$	\longrightarrow	$\left[\begin{array}{c} \text{Ph}_3\text{P} \quad \quad \quad \text{CH}_2\text{PR}_3^+ \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{Pt} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{Ph}_3\text{P} \quad \quad \quad \text{Cl} \end{array} \right] \text{I}^-$	122
3		$\xrightarrow{:N}$		123
4		\longrightarrow	$\begin{array}{c} \text{Cl} \quad \quad \quad \text{CH}(\text{py})\text{CH}_2\text{CH}_2\text{CH}_3 \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{Pt} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{py} \quad \quad \quad \text{Cl} \end{array}$	124
5		$\xrightarrow{\text{N}_2\text{CH}_2}$	$\text{CH}_3 - \begin{array}{c} \text{P} \quad \quad \quad \text{P} \\ \quad \quad \\ \text{Pt} \quad \quad \text{Pt} \\ \quad \quad \\ \text{P} \quad \quad \quad \text{P} \end{array} - \text{CH}_2\text{PPh}_3^+$	125

Table 4 is of particular interest because it involves the multiple decomposition of diazoalkanes to form metal-carbenes. These species then undergo several reactions within the same molecule. These are Pt-H bond insertion, bridged carbene formation and ylide formation.

Transition metal ylides are interesting from several stand points, particularly as reagents for organic synthesis^{117, 118}. They are, for example, involved in the metal catalyzed insertion of diazoalkanes into X-H bonds. Their most important use however, is the catalytic formation of non-metal ylides.

Several catalysts have been shown to decompose diazoalkanes in the presence of an appropriate nucleophile to form ylides. Rhodium is particularly effective and has been shown to catalytically form sulfonium, ammonium and halonium

Figure 9. Scheme for the Metal Catalyzed Formation of Ylides.

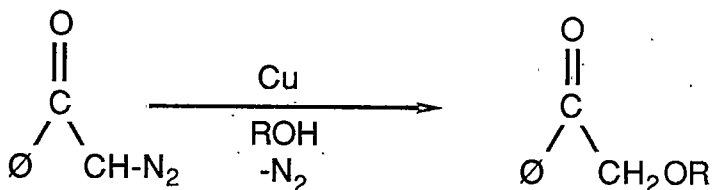


ylides¹²⁶. The method shown schematically in Figure 9 has proven to be a highly satisfactory route to these species.

The ability for a catalyst to form ylides has been shown to correlate linearly with its ability to cyclopropanate olefins¹²⁷. This supports the idea that metal-carbenes are formed in each reaction and that the degree of polarization of these intermediates is critical to the reactivity.

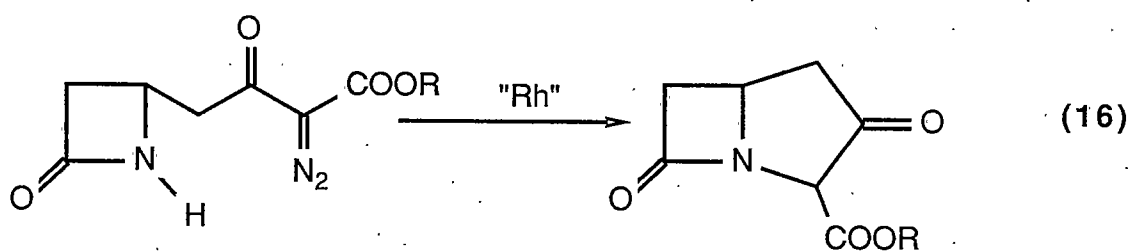
Catalytic Insertions into X-H Bonds

Free carbenes have long been known to insert into bonds between heteroatoms and hydrogen³. These reactions suffer from poor selectivity, often inserting into C-H or even C-C bonds competitively. The copper catalyzed decomposition of diazocompounds can also lead to X-H insertion products. This was first observed by Yates with alcohols in the early 1950's¹²⁸.



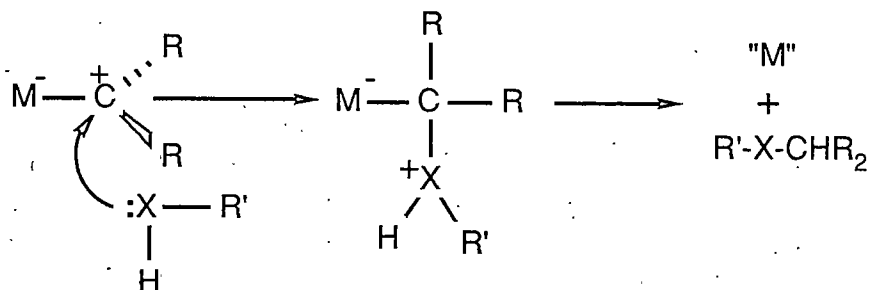
Other workers later found that copper also permitted insertion into S-H bonds¹²⁹. Interest in this area grew rapidly in the early 1970's when Teyssie reported that rhodium could catalyze the insertion of carbenes into the

O-H bond of alcohols, acids and even water¹³⁰. This led the use of the reaction in the synthesis of some natural products^{131,132}. Later, insertions into N-H bonds were observed. A key step in the Merck synthesis of carbapenams is shown in equation 16 and involves the intramolecular insertion of a metal carbene into the N-H bond¹³³.



Rhodium is probably the best catalyst for this reaction in terms of selectivity. The major limitation of the rhodium catalyzed reaction is with allylic species, or with other, more complex substrates which contain olefins¹³⁴. Cyclopropanation strongly competes under these conditions and may even become the major reaction pathway.

Mechanistically, this reaction is thought to be related to ylide formation. The nucleophilic substrate is thought to



attack the electropositive metal-carbene, followed by rearrangement and elimination¹³⁹.

Summary

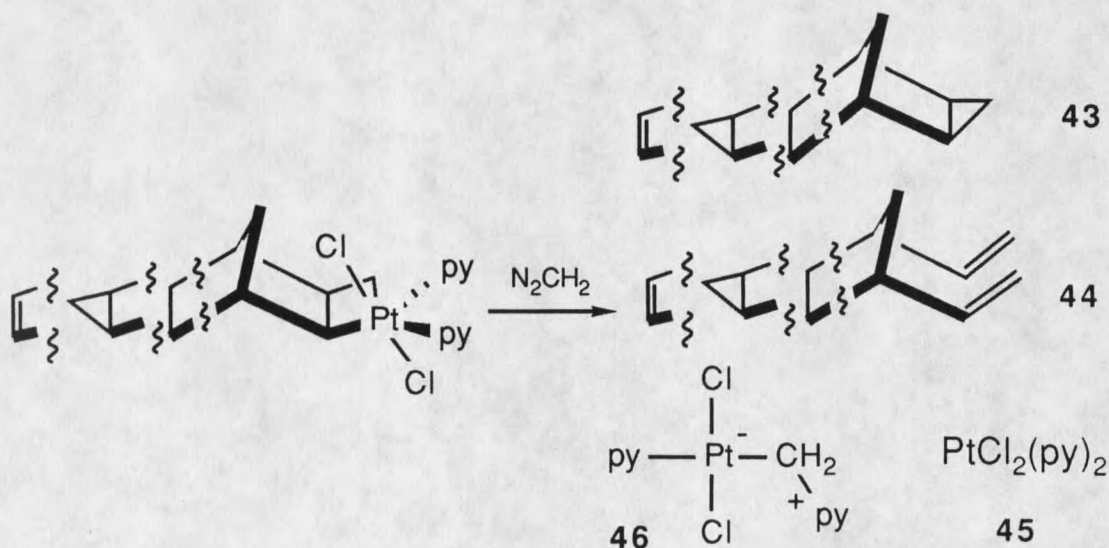
The interaction of diazoalkanes and metals represents a very important area of chemistry. Several important reactions, including cyclopropanation of olefins, ylide formation and insertion into X-H bonds are known. These reactions are important in both laboratory syntheses and industrially.

The factors influencing catalyst activity and selectivity are only now becoming understood. More work remains to be done before catalysts can be designed for specific applications. The areas of stereo-, regio- and enantio-selectivities are particularly important at this stage. Current catalysts are severely limited in both scope and selectivity. New modes of influencing selectivity must be found while retaining good yields. Perhaps even more important is the development of better descriptions of the known modes of influencing selectivity. These descriptions will arise from both improved computational methods and innovative experiments with new catalysts.

PLATINUM YLIDES

Introduction

Shortly before this work began, Ekeland discovered that platinum(IV) cyclobutanes of the norbornyl series would decompose diazomethane¹³⁶. The volatile products from this reaction were the cyclopropane from reductive elimination (43), and a di-olefin which results from the incorporation of CH₂ into the hydrocarbon (44). The non-volatile products found were bis(pyridine) platinum dichloride (45) and a platinum(II) ylide species (46). This latter product was characterized by NMR spectroscopy, X-ray photoelectron spectroscopy (XPS) and finally, by X-ray crystallography¹³⁶.



The Formation of an Ylide from a Platinacyclobutane

An investigation of another platinacyclobutane was undertaken to help in understanding the nature of this reaction. The platinacyclobutane from phenylcyclopropane (compound 14) was prepared by standard techniques^{3,4} and exposed to diazomethane under the same conditions as those used by Ekeland. The non-volatile products from this reaction were found to be the same as those observed previously. The volatile products were the cyclopropane and styrene. This latter product is the result of a net loss of CH₂ from the original hydrocarbon.

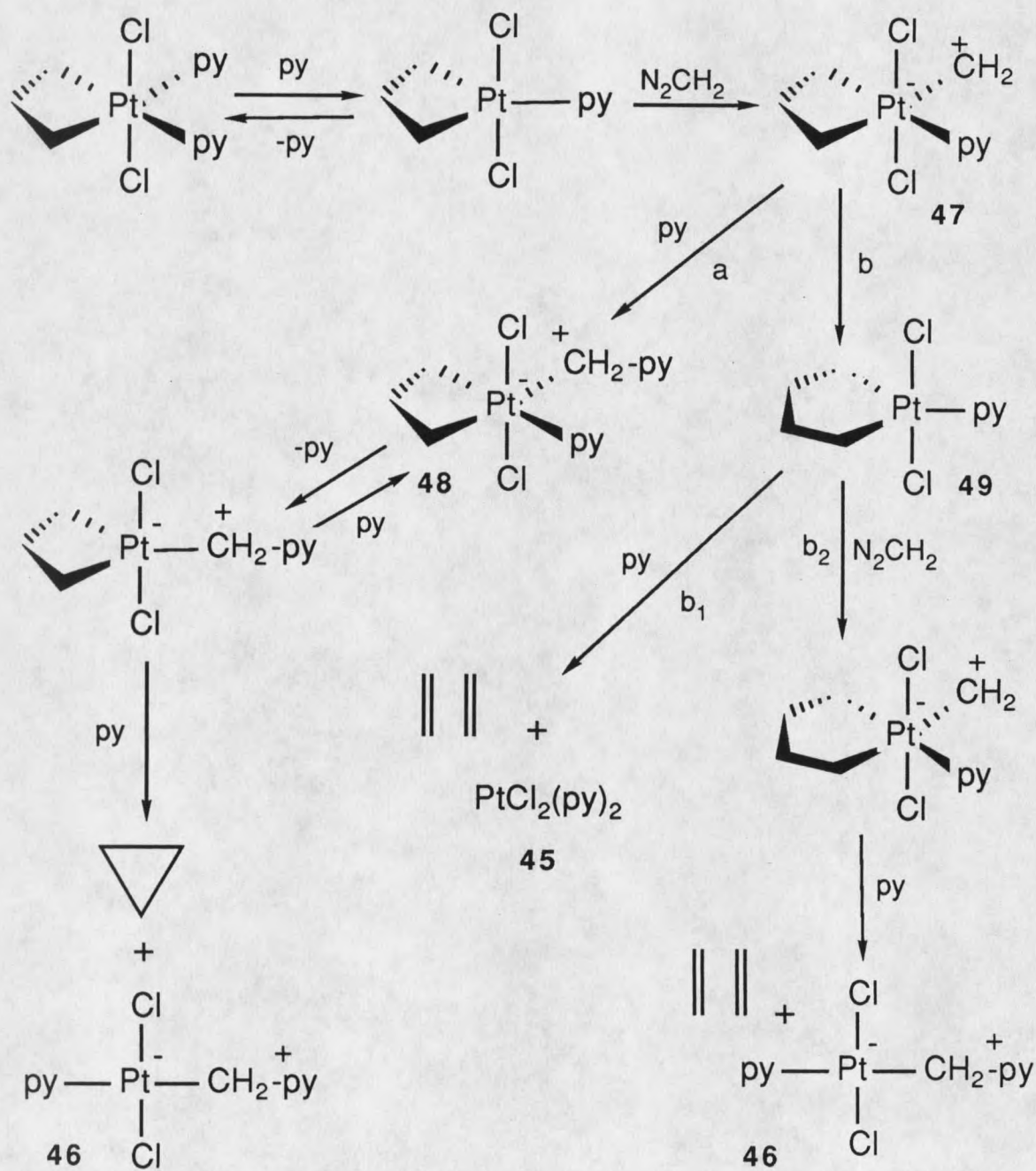
The effect of temperature on the reaction was investigated. It was found that the ratio of styrene to phenyl cyclopropane increased as the temperature was lowered from 20 °C to 0 °C (see Table 5). At very low temperatures, an unexpected preference for phenyl cyclopropane was observed.

Table 5. Ratio of Styrene to Phenylcyclopropane from the Decomposition of a Platinacyclobutane at Various Temperatures.

Temperature:	<u>20 °C</u>	<u>0 °C</u>	<u>-70 °C</u>
Ratio:	3:1	5:1	1:5

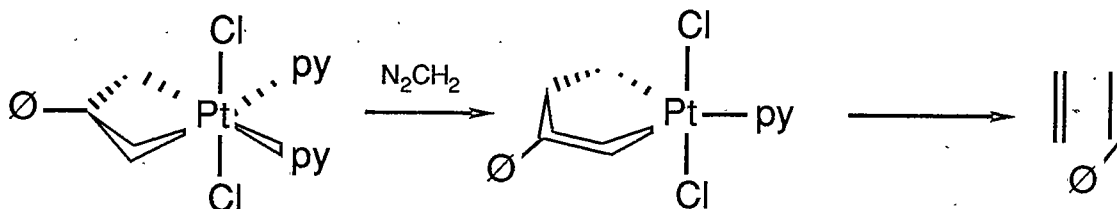
Figure 10 shows a proposed mechanism for the reaction which is a modification of a scheme originally proposed by Ekeland. The first step is the reversible loss of

Figure 10. A Proposed Mechanism for the Reaction of Diazo-methane with Platinacyclobutanes.



pyridine, a reaction known to be very facile in this system. It is thought that the first step in most reactions of octahedral platinum(IV) is such a loss of a ligand to open up a coordination site. The second step is the decomposition of the diazoalkane to form an electrophilic metal carbene (47). This reaction also has considerable precedence as discussed in the previous chapter. The highly reactive metal carbene is then proposed to undergo one of two competing reactions. The first, route a, is attack by a pyridine (either intra- or intermolecular) to form the platinum(IV) ylide 48. Other studies have found that the ylide moiety in these species is rather unreactive. Therefore, loss of the second pyridine from the metal, followed by reductive elimination is postulated. This results in formation of the observed ylide 46 and the cyclopropane product.

The second route (b) from platinacyclobutane/carbene complex 47 is the migration of one of the platinum-carbon metallacycle bonds to form platinacyclopentane species 49. Waddington has shown that platinacyclopentanes readily undergo a double reductive elimination reaction (path b₁) to form olefins¹³⁹. This process would lead to the formation of bis(pyridine) platinum dichloride and the diolefin 44 when the norbornyl system is being considered. The decomposition in the phenyl platinacyclobutane case leads to production of styrene and ethylene.



The partitioning between these pathways is expected to be dependent on the platinacyclobutane and temperature. This has indeed been found to be the case. It is reasonable to assume that migration of a metal-carbon bond is less temperature sensitive than the intermolecular attack of a pyridine. It is not at all clear what causes the inversion of the product ratio between 0 °C and -70 °C. One possibility is that the diazomethane is reacting in a different mode at this temperature. For example, it has previously been observed that diazoalkanes can reduce metals under certain conditions³⁷. Evidence will be presented later which indicates that platinum can form adducts with diazoalkanes at low temperature in ether in which the N_2 moiety is retained. A mechanism in which the diazoalkane remains intact while forcing elimination of phenyl cyclopropane is possible, and perhaps explains the product selection at low temperature.

If the platinacyclopentane 49 is particularly stable, another decomposition route (b₂) might occur. A second

equivalent of diazomethane may be decomposed followed by metallacycle decomposition and ylide formation. This step is necessary to explain the observation by Ekeland that the ylide production exceeded that of cyclopropane formation in one case.

A Direct Synthesis of Platinum(II) Ylides

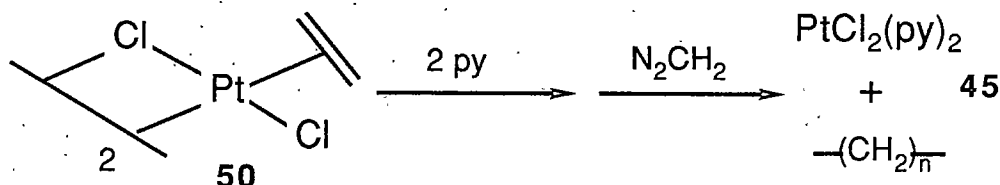
Ekeland's reaction was the first observation of platinum(IV) causing the decomposition of diazomethane. The isolation of an ylide was very good evidence for the intermediacy of platinum carbenes in the reaction. Platinum (II) ylides had been previously observed by other workers, but these contained only limited structural variation, and only rarely due to the decomposition of diazoalkanes.

Compound 46 was interesting both by virtue of its mode of formation, and for its potential reactivity as a "trapped" platinum carbene. It was desirable to investigate both aspects of this compound. Formation of this compound by the Ekeland method however, was a slow process that suffered from poor yields. Therefore, a new synthetic strategy was proposed in which the ylide could be formed directly.

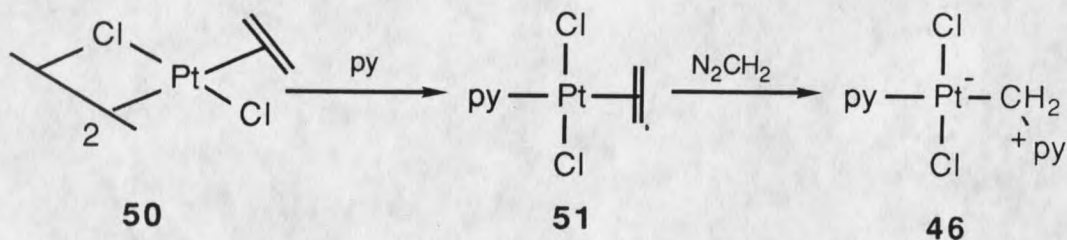
Synthesis of 46

An ether solution of 200 mgs of Zeise's dimer (compound 50) was placed in an ether solution containing 2 equivalents of pyridine. Two equivalents of diazomethane were generated and added to the solution with stirring. Analysis

of the reaction mixture revealed little or no formation of the desired product and almost exclusive formation of bis(pyridine) platinum dichloride. This latter species is known to be formed from the decomposition of Zeise's dimer in pyridine. The rate of this second reaction is dependent on the concentration of pyridine, but does occur on the time scale described here. It was also found that 45, unlike Zeise's dimer, did not decompose diazomethane.

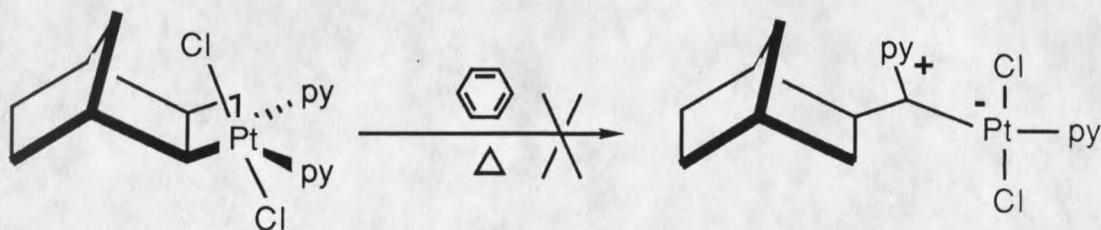


A revised reaction scheme was then attempted in order to minimize the formation of bis(pyridine) platinum dichloride. A single equivalent of pyridine was added to 200 mgs of Zeise's dimer in ether to form the pyridine monomer 51. This species is soluble in ether and catalyzes the decomposition of diazoalkanes at rates comparable to Zeise's dimer. A second ether solution was prepared containing roughly three equivalents of diazomethane and one equivalent of pyridine. The two solutions were then mixed with stirring to give the desired product. It was found that gentle heating resulted in shorter reaction times and better yields. Under optimized conditions, yields of greater than 90% of the ylide 46 were obtained.



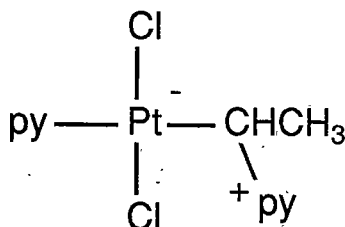
The product of this reaction was found to give spectral data identical to an authentic sample of 46 prepared independently. Spectroscopic details may be found in Appendix B.

This synthetic methodology has obvious advantages over the Ekeland method and the more commonly used Gillard reaction described in the first chapter¹²⁴. Both of these methods require the formation of a platinacyclobutane prior to the ylide forming step. The latter reaction is also limited to chains of three carbons containing only substituents which permit platinacyclobutane formation. Indeed, not all platinacyclobutanes will undergo the Gillard ring opening. The author has found, for example, that platinacyclobutanes from the norbornyl series will not form ylides by this method.



The Synthesis of Other Ylides

While the synthetic route described previously appears to have considerable potential, it was necessary to demonstrate this by reaction with other diazoalkanes. The next substrate used was diazoethane. The generation of this compound was somewhat more difficult than diazomethane and it was less soluble in ether, making it more difficult to manipulate the diazoalkane that was generated. These difficulties limited production of the desired ylide to a maximum yield of 80%.



52

Critical NMR data for ylide 52 include a quartet in the proton spectrum at 5.99 ppm which displays platinum coupling of 116 Hz. This is assigned to the proton β to the platinum. The α carbon is located at 38.6 ppm in the ^{13}C spectrum and is platinum coupled by 862 Hz. Complete spectral data for this compound can be found in Appendix B.

Two other ylides were prepared in a similar manner, except that chloroform was found to be a more suitable solvent. These were the ylides from the p-methyl- and

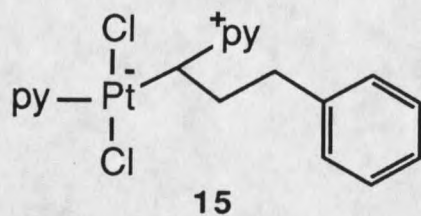
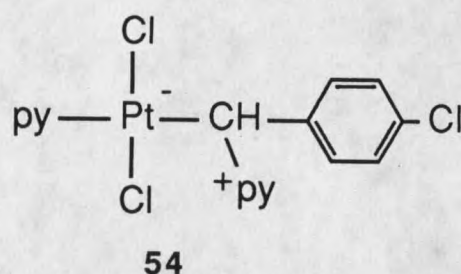
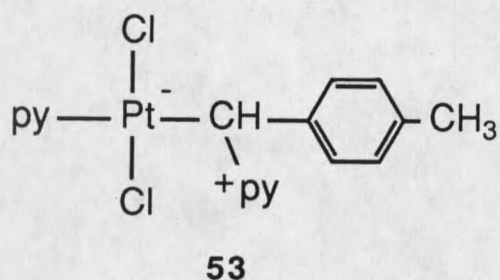


Table 6. Critical NMR Data for Compounds 46, 52, 53, 54 and 15.

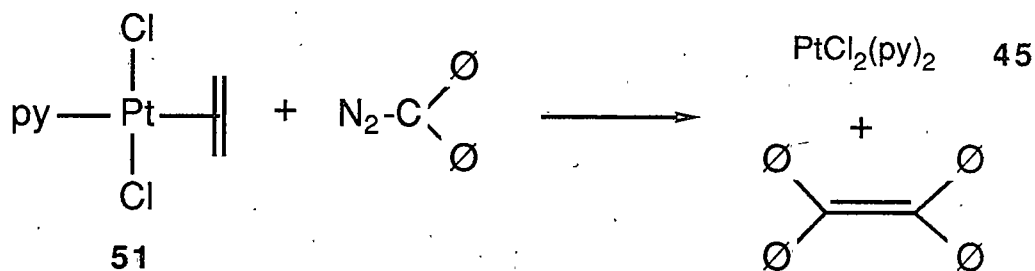
Compound Number:	<u>46</u>	<u>52</u>	<u>53</u>	<u>54</u>	<u>15</u>
α -Carbon (ppm):	30.1	38.6	49.5	48.9	43.9
$^1J_{Pt-C}$ (Hz):	751	862	690	714	790
β -Hydrogen (ppm):	5.45	5.99	7.00	7.25	5.83
$^2J_{Pt-H}$ (Hz):	100	116	90	110	109
Platinum (ppm):	1852	1839	1878	1886	----
Ref.	135	----	----	----	65

p-chlorophenyldiazomethanes, 53 and 54 respectively. Unlike the diazoethane and methane reactions, these did not require heat. The diazocompounds were found to react almost explosively at room temperature. The p-chloro derivative proved to be the easier to prepare, forming the desired ylide in 75% yield by NMR spectroscopy. The p-methyl derivative was only formed in 25% yield. These reactions were not optimized and, given their extreme reactivity at room temperature, it seems probable that better yields could be obtained at lower temperatures. Critical spectral data for all these ylides and another ylide (15) prepared by Gillard's method, are shown in Table 6.

The protons β to the platinum could not be cleanly observed for compounds 53 and 54 by ^1H NMR spectroscopy due to the fact that they are shifted into the aromatic region. The shift for this proton in compound 53 is reasonably certain, but the platinum coupling is obscured. The opposite is true for compound 54, where the small peaks due to platinum coupling can be resolved, but the main peak cannot. The α carbons for these compounds are normal for ylides and are doublets in the ^{13}C spectra, leaving no doubt as to the structures at this center.

To help determine the scope of the reaction, three other diazocompounds were reacted under the same conditions. These were ethyl diazoacetate, diazofluorene and diphenyl diazomethane. The first two compounds result in

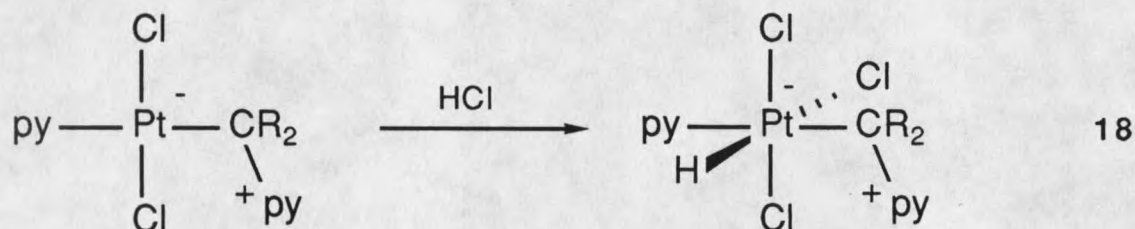
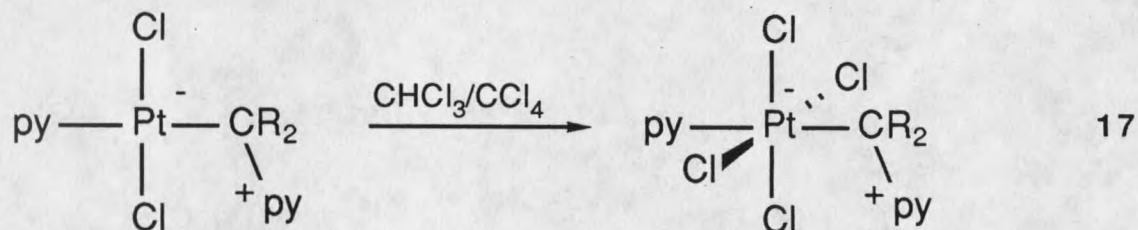
unusual products and are discussed later in detail. Diphenyl diazomethane did not yield stable ylides under these conditions; only tetraphenyl ethylene and bis(pyridine) platinum dichloride could be isolated from the reaction. This was not entirely unexpected due to the severe steric problems which should occur in the hypothetical ylide product. It was hoped that the aromatic rings might have stabilized the intermediate carbene species however, if such a stabilization did occur, it was not sufficient to form an isolatable product.



Ethyl Diazoacetate and Zeise's Pyridine Monomer

Under the conditions described previously, ethyl diazoacetate reacted within one minute to form a mixture of three products. The proton NMR spectrum showed peaks at 6.59, 5.62 and 4.90 ppm, each of which displayed platinum coupling of more than 100 Hz. The chemical shift and coupling of these peaks was similar to that of the platinum ylides previously described, suggesting that all of these products had an ylide type structure.

There were several structural possibilities for these products. For example, Puddephatt had reported that platinum (II) ylides could be oxidized to form platinum(IV) ylides in refluxing chloroform and carbon tetrachloride³⁸. It is also possible that a platinum(IV) ylide could be formed from the oxidative addition of HCl (a common impurity in chloroform) across the platinum of the ylide. Examples of these two reactions are shown in equations 17 and 18 respectively.



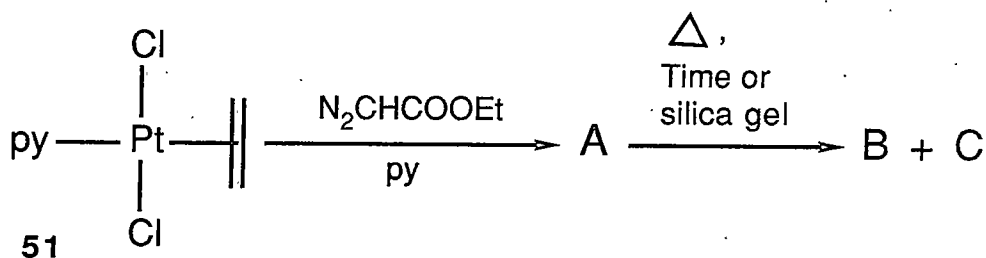
Under the conditions of the reaction, it is feasible that one or both of these processes might have been occurring. If the expected ylide product did have some unknown susceptibility towards oxidation to platinum(IV) species, this could be eliminated by running the reaction in benzene,

since this solvent should not contain HCl or be able to oxidatively add Cl₂.

The decomposition of the diazocompound in benzene proceeded at a rate similar to that in chloroform, to produce the same products (though in slightly different ratios). The overall yield of "ylide type" products in benzene was between 60 and 80% as opposed to optimized yields of better than 90% in chloroform. The side products from this reaction were the same as before, bis(pyridine) platinum dichloride and the maleate and fumarate esters from the dimerization of the carbene moiety.

This experiment effectively demonstrated that addition of Cl₂ or HCl to the ylide was not the cause of the extra products. Attempts were made to separate the three compounds by column chromatography with silica gel. These efforts resulted in changes in the ratios of products, but no real purification. It was observed that the product with a proton at 5.62 was converted to the other two products on silica gel or with time. These latter two products were always observed in a 3:1 ratio, with the product having a proton resonance at 6.59 ppm always in greater yields. The three products will be referred to as species A, B and C respectively.

Further investigation showed that species A was the kinetic product and could be formed exclusively when the reaction was run at 0 °C. Refluxing A in benzene converted



it to B and C in the familiar 3:1 ratio in good yields, though some decomposition to bis(pyridine) platinum dichloride was noted. Elemental analysis of a sample containing nearly pure A and a sample containing a mixture of B and C demonstrated that all of the products had empirical formulas equivalent to that of the expected ylide product (Table 7).

Table 7 Elemental Analysis for Products A, B and C.

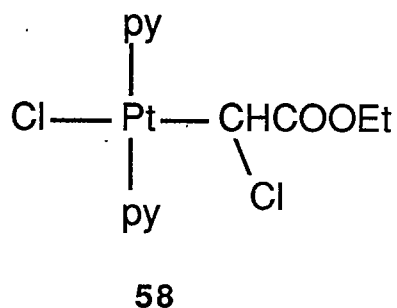
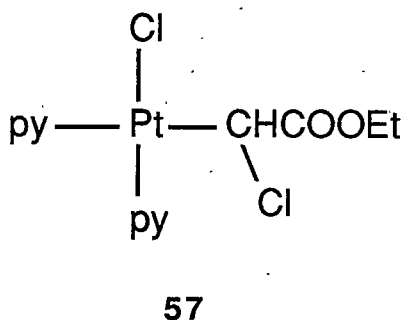
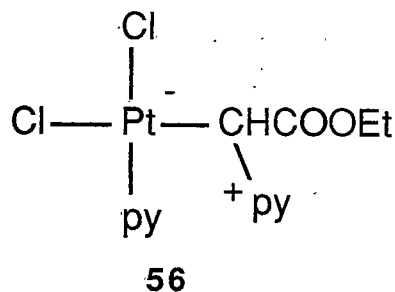
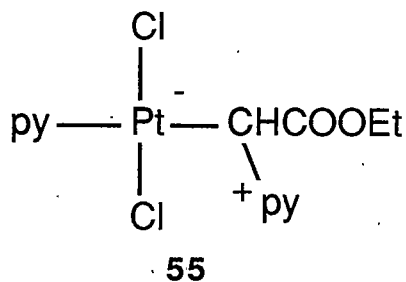
<u>Sample</u>	<u>% C</u>	<u>% H</u>	<u>% Cl</u>
Theoretical	32.94	3.14	13.92
Mostly A	32.64	3.27	14.13
Mix of B and C	32.99	3.24	13.59

Structural Assignments of Products A, B and C

The results shown in Table 7 confirm that oxidation products were not responsible for the additional peaks. It appeared instead that a structural isomerization was

occurring. Figure 11 shows the four most reasonable structural possibilities for products A, B and C. Structure 55 is the expected ylide and 56 is its cis isomer. Compounds 57 and 58 are not ylides at all, but rather platinum alkanes resulting from transfer of a chlorine from the metal to the α carbon.

Figure 11. Possible Structures for Products A, B and C.



In order to distinguish between the possible structures, additional NMR spectral data was acquired. Table 8 contains the data critical to this discussion, while Appendix B gives complete data for the compounds.

Table 8. Critical NMR Data for Products A, B, C and Compound 46.

Compound:	<u>A</u>	<u>B</u>	<u>C</u>	<u>46</u>
α -Carbon (ppm):	26.9	42.2	32.2	30.1
$^1J_{Pt-C}$ (Hz):	796	734	921	751
β -Hydrogen (ppm):	5.62	6.59	4.90	5.45
$^2J_{Pt-H}$ (Hz):	118	119	123	100
Platinum (ppm):	1817	1984	1966	1852
Ortho py ₁ (ppm):	8.86	8.86	8.86	8.92
Protons py ₂ (ppm):	8.52	9.05	8.86	9.05

The assignments for A, B and C are not obvious from Table 8, but they do follow from logic. Compound A, the kinetic product, is expected to have the structure 55 in analogy with the reactivities of other diazoalkanes. There is no reason to suppose that insertion into a Pt-Cl bond is preferred with this diazoalkane when it has not been observed in any other system, nor is there reason to assume a cis configuration as in structure 56. The chemical shift

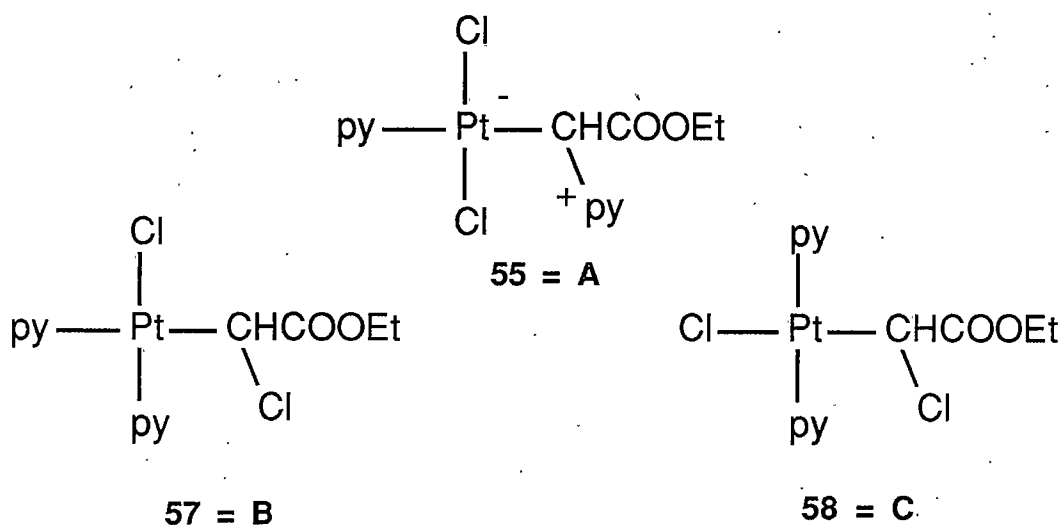
and coupling data for this species are all consistent with other platinum(II) ylides.

The most striking difference between the NMR spectra of compounds B and C and the previously observed ylides are the ^{195}Pt chemical shifts. These shifts are at least 80 ppm further downfield than any other ylide shift reported. This difference is greater than the entire known ^{195}Pt NMR shift range for ylides. It is also important to note that the thermodynamic products differ from each other in platinum chemical shift by less than 20 ppm, while they differ from the kinetic product by at least seven times that. Platinum chemical shifts are highly sensitive to ligand effects¹³⁸ and a shift of this magnitude suggests a difference in the ligand environment of the metal. It is reasonable to conclude from this that products B and C are the chloroalkanes 57 and 58.

Compound C can be assigned structure 58 on the basis of two pieces of data. The first is the observation that the protons in the ortho position on the pyridines are equivalent. This observation holds true for the ortho ^{13}C shifts as well (see Appendix B). In all of the ylide products reported in this thesis, there are two non-equivalent pyridine ortho protons. One of these resonances is always very close to 8.86 ppm while the other is offset by varying amounts. The resonances near 8.86 ppm frequently (but not always) show small platinum coupling, demonstrating that

this resonance is for the pyridine on the platinum. In product C, both resonances are located at 8.86. It was not possible to distinguish platinum coupling to this peak, since one of the resonances for compound B is also located at that position.

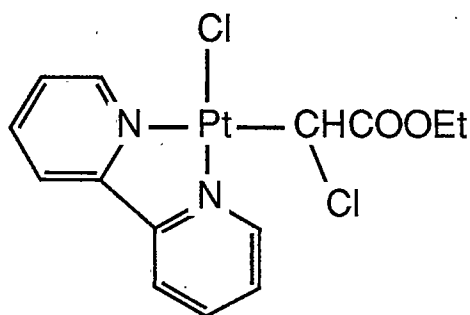
Another piece of supporting data is the large platinum-carbon (and to a lesser degree platinum-hydrogen) spin-spin coupling. This increase in coupling is likely due to a difference in the trans influence being seen by the α carbon. Platinum carbon coupling constants are known to be related to bond strength¹³⁸ and bonds trans to a chlorine are known to be shorter than bonds trans to a pyridine in platinum(II) systems. Together, these observations strongly support the assignment of structure 58 to compound C. Compound B is then assigned structure 57 by process of elimination.



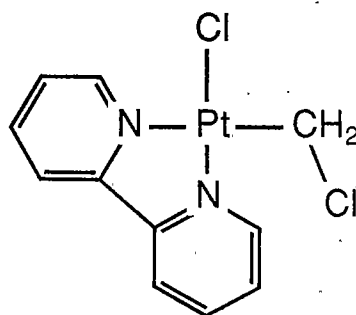
In order to help substantiate these assignments, a model of compound 57 (B) was prepared. One equivalent of 2,2'-bipyridine was added to a benzene solution containing a mixture of the three products from the previous reaction. The mixture was refluxed for four hours, the solvent rotoevaporated and the product purified by dissolution in chloroform and precipitation from pentane. Isolated yield of the product was 74%.

There was only one product isolated from this reaction. It is required to adopt structure 59 due to the bite size of the nitrogen ligand. A similar compound, structure 60, was prepared by reacting the methyldine ylide under the same conditions. Table 9 lists critical spectral data for 57, 59 and 60.

It can be seen from this data that the platinum and proton shifts of compounds 57 and 59 are essentially identical. The platinum shift is gratifying support of the idea that the chlorine transferred products are found significantly downfield from the platinum(II) ylides.



59



60

Table 9. Critical NMR Data for 57, 59 and 60.

Compound:	<u>57</u>	<u>59</u>	<u>60</u>
α -Carbon (ppm):	42.2	28.4	----
$^1J_{Pt-C}$ (Hz):	734	866	----
β -Hydrogen (ppm):	6.59	6.58	5.72
$^2J_{Pt-H}$ (Hz):	119	114	97
Platinum (ppm):	1984	1983	----

The ^{13}C shifts and $^1J_{Pt-C}$ couplings are very different for the two complexes. The author does not have a good explanation for this observation other than the fact that steric interactions in 57 must lead to a geometry different than that of 59. The pyridine ligands in 57 would be expected to twist out of the plane of the molecule, while the bipyridal ligand requires the aromatic rings to remain in the plane. The result of this may be that somewhat different orbital interactions are in effect in the two compounds. Similar large and unexpected changes in the ^{13}C shifts of these α -carbons were later observed with other

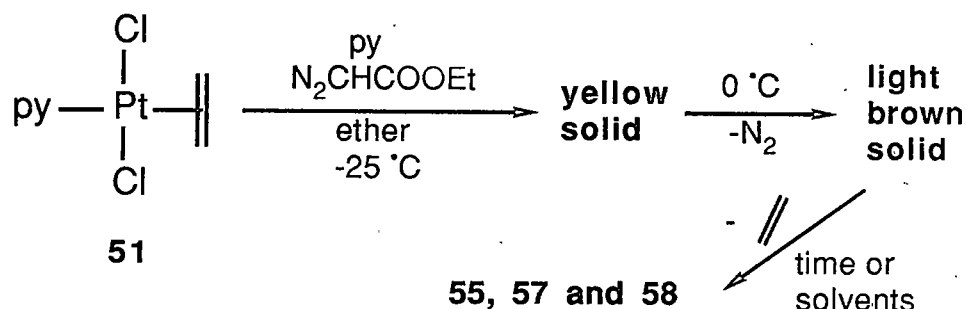
ylide systems. These are discussed in subsequent sections.

The difficulty in purification of these compounds and the resultant inability to obtain crystals for X-ray analysis was unfortunate. A logical interpretation of NMR data and the synthesis of a model compound however, enable satisfactory structural assignments. The scheme presented here is consistent both with the available data and with the reactivity of related systems. The propensity for compound 55 to rearrange to 57 and 58 is quite interesting and unique. Other ylide species were not observed to undergo this rearrangement, even on prolonged benzene reflux. This suggests that 55 should be particularly susceptible to nucleophilic attack and may display unique reactivity. This idea is addressed in a later section.

Variable Temperature Analysis of the Formation of 55

It had been observed that when the reaction of ethyl diazoacetate and Zeise's pyridine monomer was carried out in ether at low temperature, a solid was quickly formed with no evolution of gas. When the ether solution was warmed from $-25\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$, the solid evolved a gas and darkened slightly. The resulting solid slowly decomposed with time at room temperature under ether, and decomposed within 15 minutes in air. Attempts to dissolve this species in any suitable solvent (chloroform, methylene chloride, benzene, THF etc.) resulted in rapid loss of a second gas and

darkening of the solution. The resulting solution contained the product mixture described above.



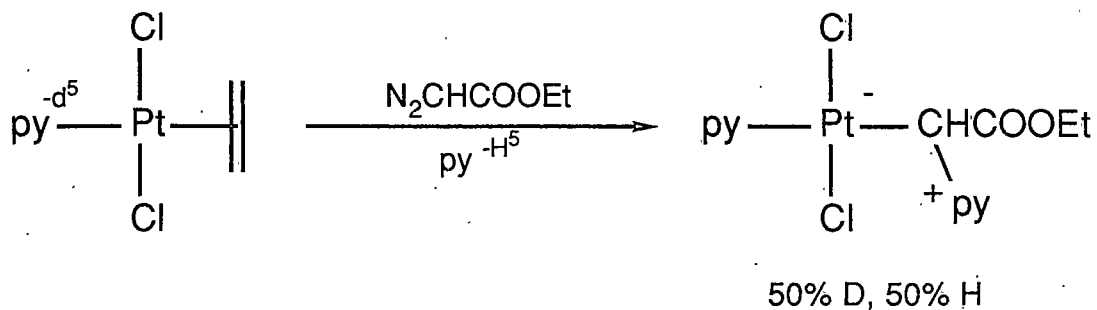
The original solid proved to be too unstable to analyze by available techniques. The second solid was also difficult to analyze, but IR data of rather dubious quality was obtained. This data provided no evidence of an N-N stretch, suggesting that the first gas to be given off was N_2 and the second was ethylene. This supposition was confirmed by bubbling the gas produced at each step through Br_2 . The first gas was unreactive while the second formed dibromoethane.

These intermediates were of interest, since they could potentially reveal the mode of initial diazoalkane coordination and mechanistic insights into its decomposition. The reaction was run in chloroform at depressed temperatures in the hopes of observing one or both of these species.

The pyridine monomer of Zeise's dimer was dissolved in d^1 -chloroform in a 10 mm NMR tube. The tube was lowered into

a multinuclear, variable temperature probe and cooled to -40 °C. The sample was permitted to equilibrate and the probe tuned. A second d^1 -chloroform solution containing one equivalent of pyridine and one equivalent of ethyl diazoacetate was prepared and cooled in a dry ice/chloroform bath. The original solution was quickly removed from the spectrometer, the two solutions mixed and the resulting mixture again lowered into the instrument. The NMR spectrometer was re-tuned and a proton spectra acquired. Average time from mixing to acquisition of the first proton spectra was two minutes.

The proton spectra revealed that no decomposition of the diazoalkane had occurred under the reaction conditions. The pyridine resonances were equivalent and shifted from either the platinum monomer or the free pyridine. This rapid exchange of pyridine, even at low temperature, was consistent with earlier observations. When H^3 -Zeise's pyridine monomer was reacted with ethyl diazoacetate and d^3 -pyridine, the pyridines were found to be scrambled in the products.

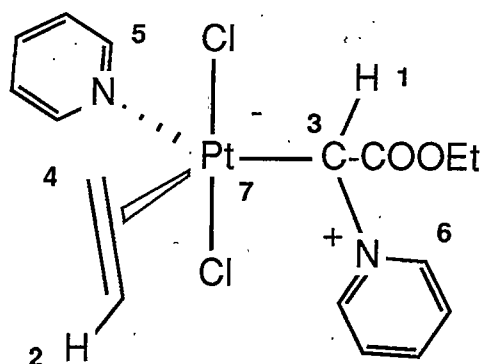


The diazoalkane is indefinitely stable at this temperature. It is possible that the diazocompound associates with the platinum in competition with the pyridines under these conditions. If this is the case, the amount of the associated product was too small to be observed. There was also no loss of ethylene from the platinum complex to form bis(pyridine) platinum dichloride.

On warming the mixture to 0°C, two intermediate species were formed. One of the products was in much higher concentration than the other throughout the course of the reaction. The data obtained for the minor isomer is somewhat questionable due to this low abundance. As time went on, the ylide 55 was formed. At maximum concentration, the two intermediates represented approximately 70% of the reaction mixture. When this point was reached, the mixture was again cooled to -60 °C and ^{13}C and ^{195}Pt data accumulated. It was found that the intermediate concentration remained constant over the several hours needed for acquisition of this data.

The major intermediate in this reaction mixture was assigned structure 61 based on the critical NMR data presented in Table 10. Complete data for this compound is found in Appendix B along with the available data for the minor intermediate.

From the data presented in Table 10, it is obvious that 61 is an ylide-type compound. The data also shows that the ethylene moiety is still coordinated to the



61.

Table 10. Critical NMR Data for 61.

 ^1H Spectrum

- 1) α -ylide proton, 5.39 ppm, 1 proton, platinum coupling cannot be resolved from the background.
- 2) ethylene protons, 4.65 ppm, 4 protons, $^2J_{\text{Pt-H}}=36$ Hz.

 ^{13}C Spectrum

- 3) α -ylide carbon, 43.9 ppm, doublet, $^1J_{\text{Pt-C}}=796$ Hz.
- 4) ethylene carbons, 91.0 ppm, triplet, platinum coupling cannot be resolved.
- 5) ortho pyridine carbon, β to platinum, 153 ppm, 2 carbons, doublet.
- 6) ortho pyridine carbons δ to platinum, 149 ppm, 2 carbons, doublet.

 ^{195}Pt Spectrum

- 7) 1792 ppm.

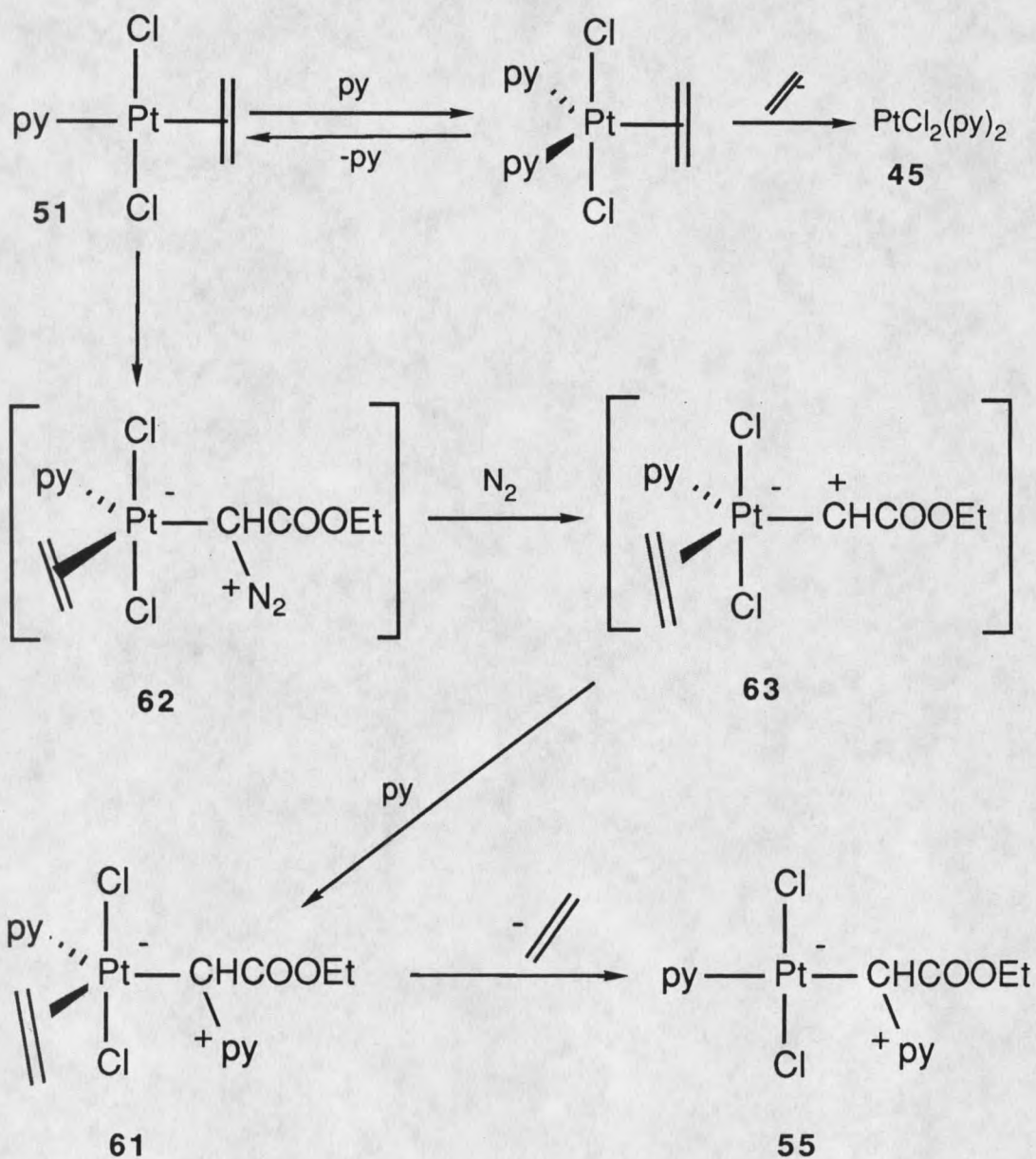
metal. This fact is clear, both because of the olefin chemical shifts and because of the platinum-carbon coupling to the olefin. This observation is consistent with the ether reaction, which indicated that N_2 was lost from the molecule prior to the loss of ethylene.

The minor isomer in this reaction displays resonances only subtly different from that of 61. It is not at all clear what this species is, but some of the possibilities are explored a little later in this thesis.

A mechanism consistent with the observed data and with the current theories presented in the literature is shown in Figure 12 (following page). The first step in this mechanism is the rapid exchange of pyridines via an associative mechanism. This is the classic attack of a nucleophile on the unoccupied p_z -type platinum orbital to form a trigonal bipyramidal species. This then loses pyridine to reform 51. This trigonal bipyramidal intermediate is also a source of bis(pyridine) platinum dichloride in this reaction via a loss of ethylene.

The diazoalkane can will compete with the pyridines for the fifth coordination site on the platinum. As was discussed in the introduction, the most probable site of coordination for a profitable interaction is via the carbon. Compound 62 can lose N_2 , either directly to form the platinum carbene 63, or by an S_N2 type process involving pyridine. Either of these two routes results in the

Figure 12. A Proposed Mechanistic Scheme for the Formation of 55 via 61.

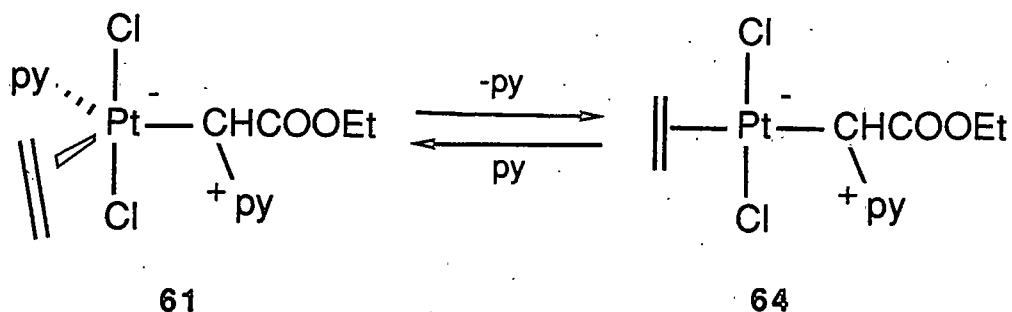


formation of the observed product 61. The next step is loss of ethylene to form ylide 55, a reaction which has precedence in the formation of bis(pyridine) platinum dichloride.

What then is the minor isomer? It certainly is not the platinum carbene 63. The ^{13}C shifts for this compound are expected to be very far downfield (300-350 ppm). If the carbene is formed at all it is probably only as a fleeting transition state.

Another possibility is that 61 is in equilibrium with a similar species which has lost pyridine (64). The large number of different pyridine resonances in the reaction mixture makes it difficult to use this information in a meaningful way. The initial equilibrium however, shows that this type of an equilibrium is a reasonable mode of action. If this is what is occurring, the fact that two distinct intermediate species are seen requires the exchange of pyridine to be slow on the NMR time scale, even at room temperature. This is in marked contrast with the initial equilibrium which is very rapid, even at $-40\text{ }^\circ\text{C}$. It seems more likely that the major intermediate observed in this reaction is actually the result of a rapid equilibration between 61 and 64, and that the minor isomer is something else entirely.

There are two other possibilities for the identity of the minor isomer. The first is that some structural isomer



of 61 is formed and is in equilibrium with that compound. This argument requires the same assumptions about the rate of isomerization as the pyridine exchange reaction. There is also no real reason to suppose such an equilibrium exists or is important if it does exist.

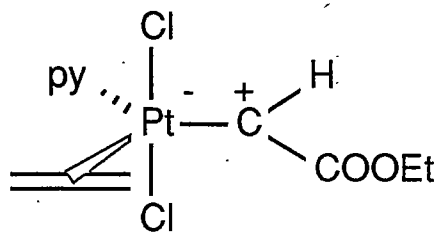
The final possibility, and the one preferred by the author is that the minor intermediate is structure 62. This would be consistent with the ether reaction in which a solid product is formed at low temperature which contains both the ethylene and pyridine moieties. Structures similar to 62 are frequently proposed as intermediates in the metal catalyzed decomposition of diazoalkanes, but they have never been observed. The NMR data for the minor intermediate is also consistent with a structure such as 62. It is an ylide very much like 61, but with the positive charge being stabilized by the N_2 moiety rather than the pyridine.

The Relationship between 61 and other Proposed Intermediates

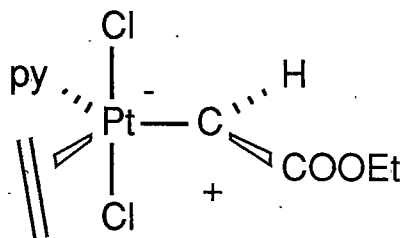
One particularly interesting feature of this investigation was the observation of at least one product (61) in

which the olefin and a "carbenoid" moiety (in the stabilized form of an ylide) were present on the metal simultaneously. These kinds of molecules are postulated as intermediates in various catalytic reactions such as olefin metathesis, Ziegler-Natta polymerization of olefins and cyclopropanation of olefins (see discussion in Chapter 1, pp 21-33). It seems rather unusual that these compounds do not cyclize to form metallacyclobutanes, especially since platinacyclobutanes are known and are often quite stable⁵³. It is possible that the pyridine competes with the olefin for the electrophilic center. It must be recalled however, that neither platinacyclobutanes or products which could be ascribed to the decomposition of platinacyclobutanes are observed in these systems, even when the reaction is run in the absence of the pyridine.

According to Eisenstien and Hoffmann^{71,72}, the relative geometries of the olefin and carbene moieties are critical to the cyclization reaction. That is, structure 65 should be able to cyclize, while 66 should not.



65

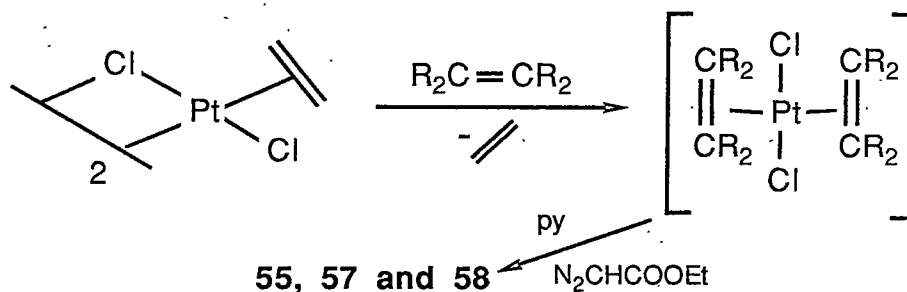


66

In a discussion with Eisenstein¹³⁹, she predicted that geometry 65 would be the more stable geometry, presuming that the carbene (or ylide) and the olefin were equatorial. She also predicted that 65 should easily cyclize to a platinacyclobutane. She did point out however, that other geometries, in which one or both of these moieties were equatorial, were easily accessible. In these geometries, the olefin and carbene moieties could very well be unable to cyclize. Thus, it is not clear theoretically why these reactions do not result in platinacyclobutane formation.

The Effect of Other Coordinated Olefins

Attempts were made to force cyclization by modification of the olefin. Zeise's dimer was dissolved in an excess of the new olefin. In some cases, heat was applied to drive off ethylene and force replacement with the new olefin. Pyridine was added to the solution and the excess olefin removed by rotoevaporation or column chromatography in the cases of less volatile olefins. The alkenes used in this experiment were ethyl vinyl ether, 1-octene, cyclohexene, styrene and cis-stilbene. In all cases, results identical to that of the platinum-ethylene compound were obtained. No evidence of platinacyclobutanes or products due to the decomposition of platinacyclobutanes could be identified. In most cases, good yields of the ylide-type products 55, 57 and 58 were obtained.



Reactions of Platinum Ylides

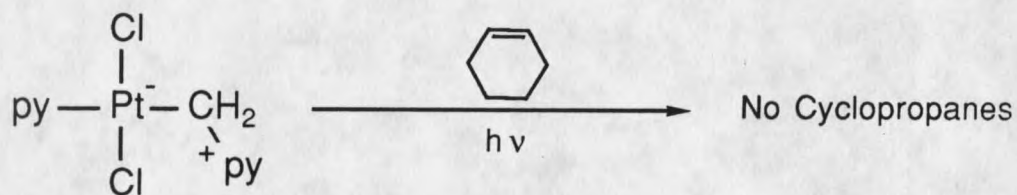
The synthesis of several new ylides provided impetus to search for new reactivity for these compounds. Recognizing that these species are simply stabilized or "protected" metal carbenes, attempts were made to force the ylides into reacting as a Fisher-type carbenes. The first attempted reaction was the formation of cyclopropanes.

Attempts to Form Cyclopropanes

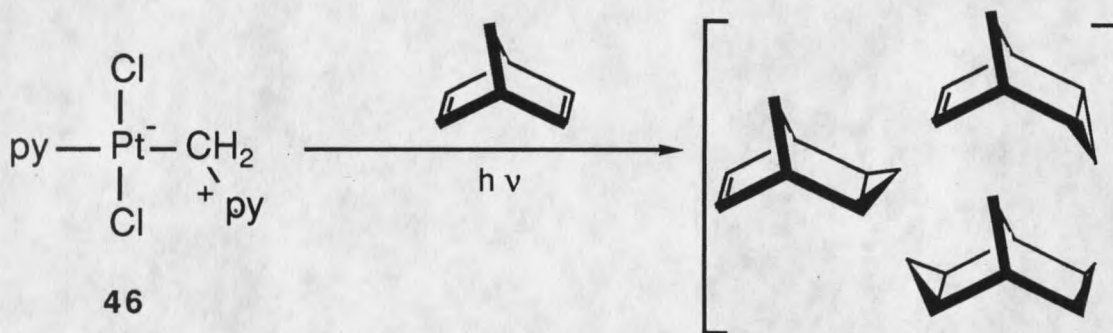
The ylides proved to be unreactive towards olefins at room temperature. Platinum(II) ylides have been reported to be quite stable thermally and this proved to be the case here as well. No evidence of cyclopropanation was found after refluxing ylides with alkenes under various conditions.

Next, photochemical generation of a reactive species was tried. The four different attempts which were made at this reaction are listed in Figure 13. The ylides were dissolved in ether or chloroform, placed in a quartz

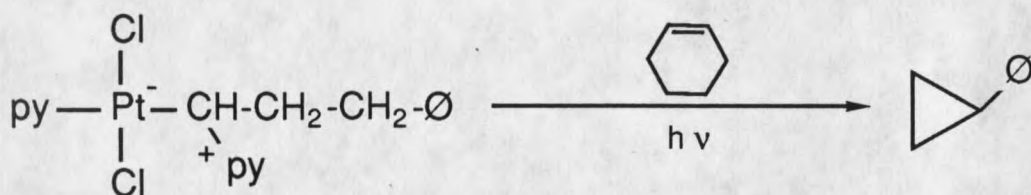
Figure 13. Photochemical Reactions with Platinum Ylides.



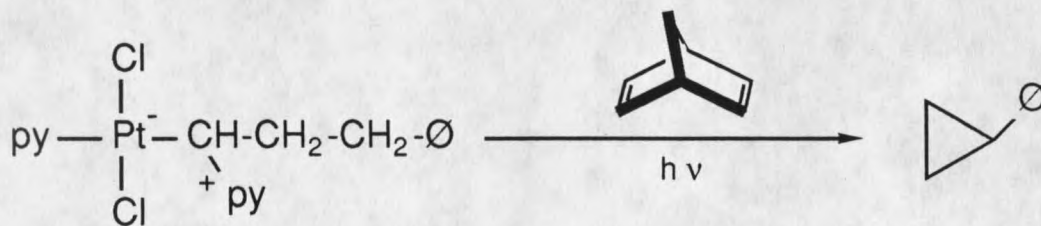
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46



15



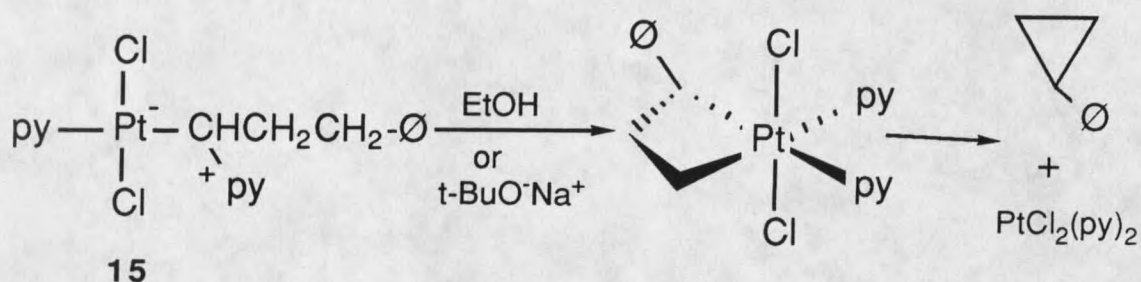
15

reaction vessel with a 10 fold excess of olefin and exposed to intense UV radiation.

In only one case were products formed in which coupling of the ylide and the olefin could be demonstrated. The reaction of the methylenide ylide 13 with norbornadiene gave 3 products by GC mass spectroscopic analysis. Two of these had masses which corresponded to addition of CH_2 and one which corresponded to addition of C_2H_4 . Yields of the first two products were very low and, yields of the third, were at the limits of detectability. These products could not be isolated, nor was additional data concerning their structure obtained. The other products arising from the reactions with the methylenide ylide were bis(pyridine) platinum dichloride and an intractable brown residue.

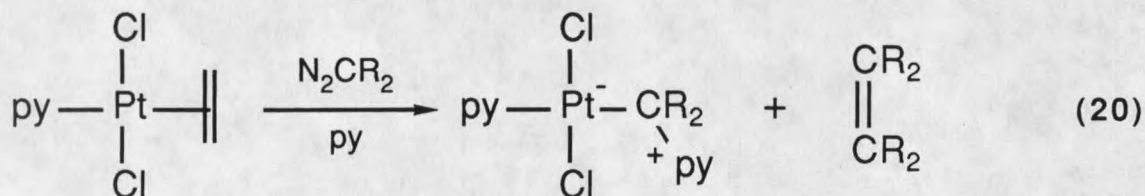
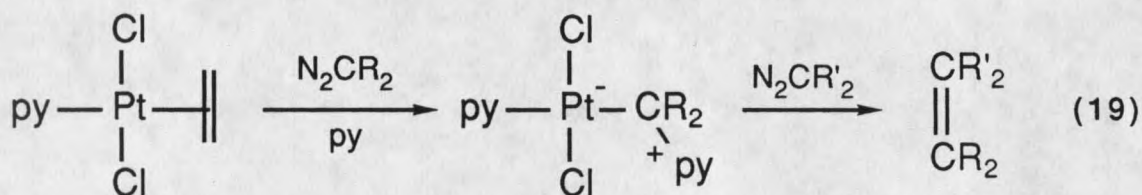
The photo-decomposition of ylide 15 did lead to a cyclopropane, but this did not include the incorporation of the olefin. Instead, it appears that the ylide cyclized to form a platinacyclobutane, which decomposed by reductive elimination to form bis(pyridine) platinum dichloride and phenyl cyclopropane.

This recyclization to form the platinacyclobutane from which it was generated, followed by decomposition, seemed to be a common reaction path for ylide 15. Attempts to displace the pyridine by reaction with base, or even ethanol resulted, once again, in the formation of phenyl cyclopropane.



Attempts to Form Alkenes

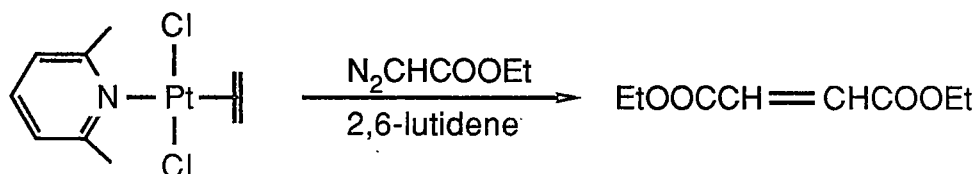
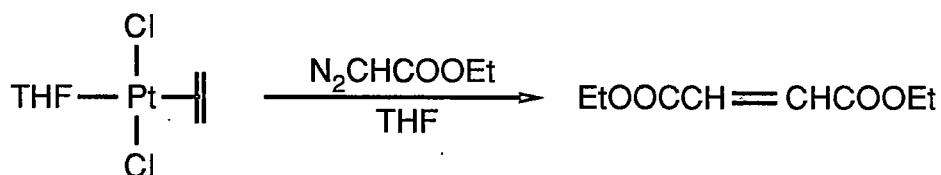
Another reaction which appeared to have potential was the formation of "mixed" alkenes from the reaction of ylides with diazoalkanes. Support for this scheme, outlined in equation 19, comes from the ready formation of dimers of the carbene moiety on reaction of platinum and diazoalkanes. The major competing side reaction in the formation of platinum(II) ylides is the formation of these dimers (equation 20).



Other Reactions

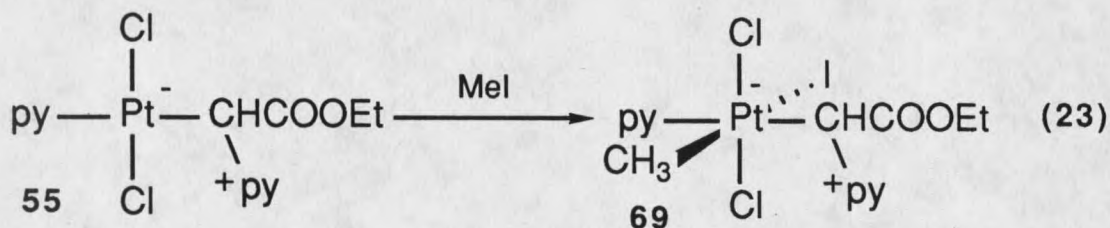
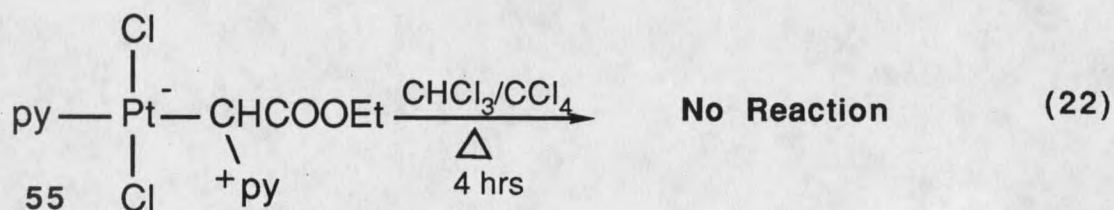
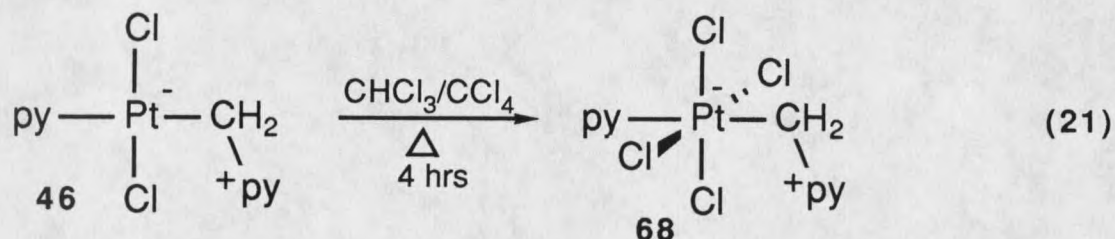
Other reactions attempted with these ylides include exposure to aldehydes, ketones and thiols. No products of interest were found with any of these substrates. Once again it was concluded that the pyridine ligands were bound too tightly to the carbon to afford reactivity at that site. This observation is consistent with a highly electrophilic species in which the metal-olefin π bond is highly polarized.

The best way to counteract the great electrophilicity of the ylide seemed to be by reducing the nucleophilicity of the "trapping" moiety. This was done by using THF and 2,6-lutidine instead of pyridine. Unfortunately, ylides could not be isolated from these reactions. Once again only $\text{PtCl}_2(\text{py})_2$ and the carbene dimers were observed.



The previous attempts at developing new reactions for the platinum ylides were largely unsuccessful. Oxidative

addition reactions of the metal to form platinum(IV) ylides could be made to occur however (see eq. 21-23). These reactions had been previously reported by Puddephatt with ylides generated by the Gillard method^{5,6}.



It can be seen that ylide 52 reacts as was previously reported in CHCl_3 and CCl_4 to form the platinum(IV) ylide 68. Ylide 55 would not react under these conditions however. This compound did react with methyl iodide to form a compound which was assigned the structure 69 based on previous work^{5,6}. As might be expected from previous discussions, other ylide type isomers were observed, presumably

from isomerization of 69. These compounds were not characterized. Available data for all characterized compounds can be found in Appendix B.

Summary

A new and facile synthesis of platinum(II) ylides has been discovered. This reaction has been used to produce several unique ylides, including one, 55 which undergoes an isomerization to two other platinum(II) alkyl species. Low temperature NMR studies of the formation of 55 show that the decomposition of ethyl diazoacetate involves the intermediacy of two species, each of which contains both the ylide moiety and the coordinated alkene. These compounds do not cyclize to form platinacyclobutanes under any of the conditions explored, in spite of predictions that they could.

Platinum carbenes have not been observed in these reactions and attempts to generate such species resulted in failure, as did attempts to form more reactive ylides. The heart of this difficulty seemed to be the great electrophilicity of the hypothetical platinum carbene species. Good electron donors become too tightly bonded to permit reaction, while poor donors do not stabilize the compound sufficiently to permit isolation.

These ylides were observed to react to give new products under conditions that had previously been reported

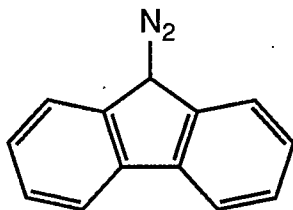
by other workers. Platinum(IV) ylides were shown to be formed via oxidative addition, similar to other such species. These reactions were not explored in detail, nor were the products well characterized.

PLATINUM(II) AND DIAZOFLUORENE

A Unique Synthesis of a Platinacyclobutane

The last chapter described the formation of several platinum(II) ylides. It was observed that phenyl diazomethane derivatives could undergo this reaction, but that diphenyl diazomethane reacted to form only $\text{PtCl}_2(\text{py})_2$ and tetraphenyl ethylene under the same conditions. This result was attributed to steric effects.

A diazoalkane similar to diphenyl diazomethane is diazofluorene (70). Though the molecular weight is nearly the same, it is less bulky than diphenyl diazomethane because the aromatic rings are constrained to a plane. This feature might also be expected to permit stabilization of a charge on the carbene carbon in a platinum-carbene type product.



70

As with other diazoalkanes, reaction of diazofluorene with Zeise's pyridine monomer in chloroform resulted in the

dimer of the carbene portion of the molecule. Nothing resembling a platinum carbene was observed, nor was a product seen which suggested incorporation of ethylene. When a second equivalent of pyridine was added under the standard ylide forming conditions described in the last chapter however, a bright red platinum containing product was formed. As with diazomethane and ethane, it was necessary to gently heat the reaction mixture to achieve reasonable rates. A summary of critical NMR data for this compound can be found in Table 11 and complete data found in Appendix B.

Table 11. Critical NMR Data for the Product from the Reaction of 70 with 51 and Pyridine.

¹H Spectrum

- 1) 3.17 ppm, singlet, 4 protons, platinum coupling of 88 Hz.
- 2) aromatic protons from 7 to 9 ppm, 18 protons.

¹³C Spectrum

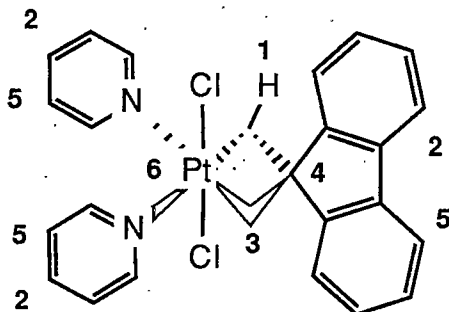
- 3) -4.65 ppm, triplet, 2 carbons, platinum coupling of 376 Hz.
- 4) 60.8 ppm, singlet, 1 carbon, platinum coupling of 95 Hz.
- 5) nine aromatic carbon resonances corresponding to 22 carbons, pyridine ligands are equivalent.

¹⁹⁵Pt Spectrum

- 6) 3350 ppm.

Characterization of 71

These data are clearly inconsistent with an ylide structure. In particular, there are 4 aliphatic protons and 2 aliphatic carbons and the platinum resonance is 1500 ppm downfield of a typical Platinum(II) ylide resonance. This shift is so dramatic, in fact, as to suggest a platinum(IV) species instead of a platinum(II). Based on these results, structure 71 was assigned to the product.



71

The aliphatic resonances clearly indicate incorporation of ethylene into the product. Furthermore, the equivalency of the two carbons and four protons indicates a symmetrical molecule. The platinum shift is within the 3200-3400 ppm range found in our laboratories¹⁴⁰ for platinacyclobutanes. The platinum-carbon and platinum-hydrogen couplings are also consistent with a platinum-carbon sigma bond as in the proposed platinacyclobutane structure^{136, 137, 140}.

Crystals of the product were obtained by diffusion of heptane into a chloroform solution of the platinacycle.

X-ray crystallographic analysis confirmed the postulated structure, but the bond angles and distances found for this structure are not published here due to the poor refinement obtained for the structure. The problems in refinement arose from the fact that there were four molecules per unit cell, giving a total of 120 unique, non-hydrogen atoms. This was very near the limit of the computer's ability to refine. A second difficulty was that the unit cell was nearly, but not quite symmetrical. It appeared that a slight disordering of the crystal prevented a two molecule unit cell from being formed. Attempts to freeze out this problem by acquiring a new data set at a low temperature failed when the crystal shattered on cooling. A diagram of the structure can be found in Figure 15.

The formation of complex 71 was rather surprising in view of the last chapter. It would appear that the metal carbenoid species formed from the decomposition of the diazoalkane is able to cyclize, unlike previous reactions. A mechanism based on the previous results and discussion is proposed in Figure 16.

Intermediate 72 is drawn as a platinum carbene rather than as an ylide to emphasize the steric problems of having a pyridine associated too closely with the carbenoid center. The formation of 73 is the result of cyclization of 72; the unique step in the diazofluorene reaction. Finally, 73 undergoes a Puddephatt-type⁴⁶ rearrangement to form 74

Figure 15. A Diagram of 71.

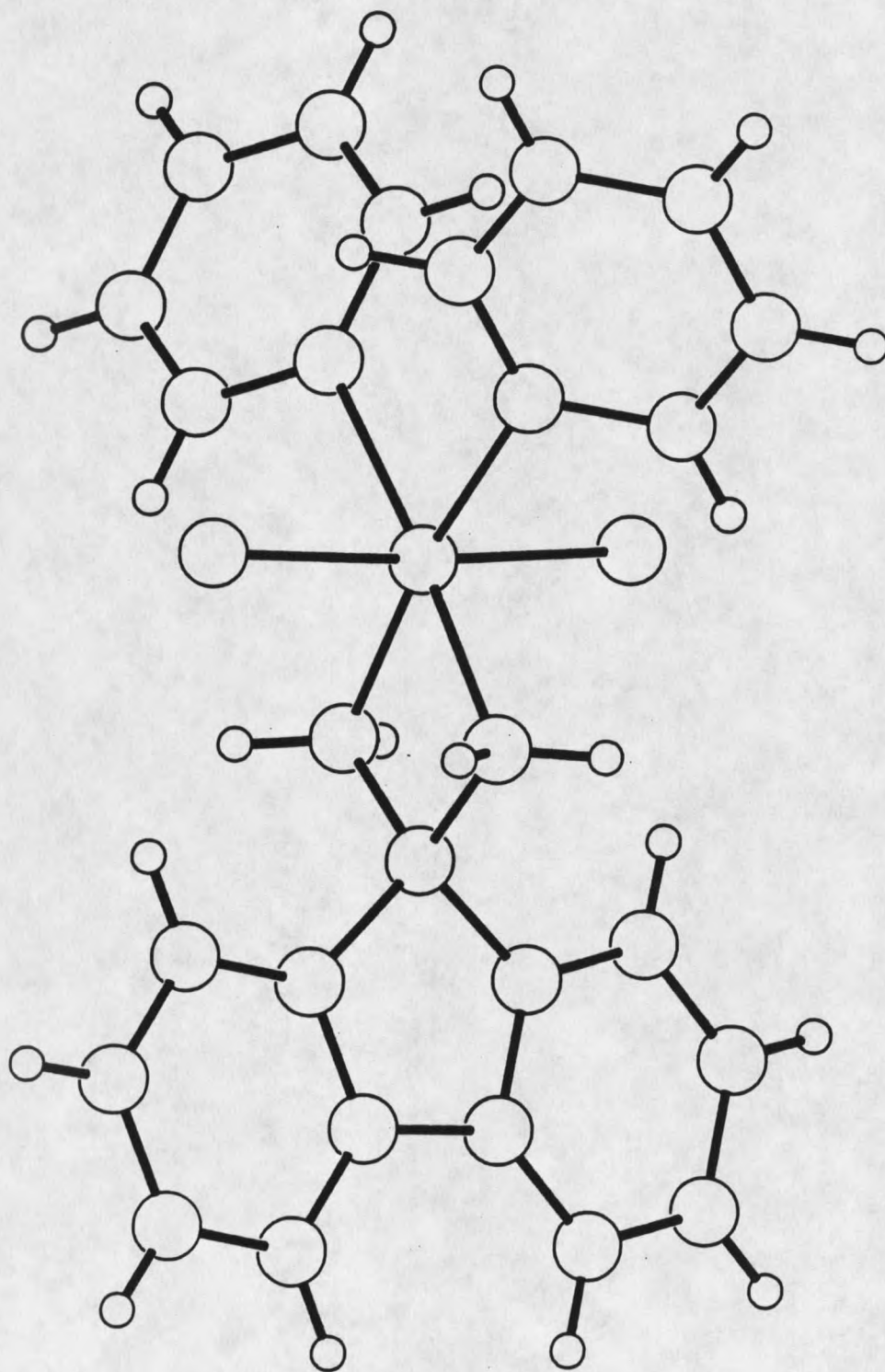
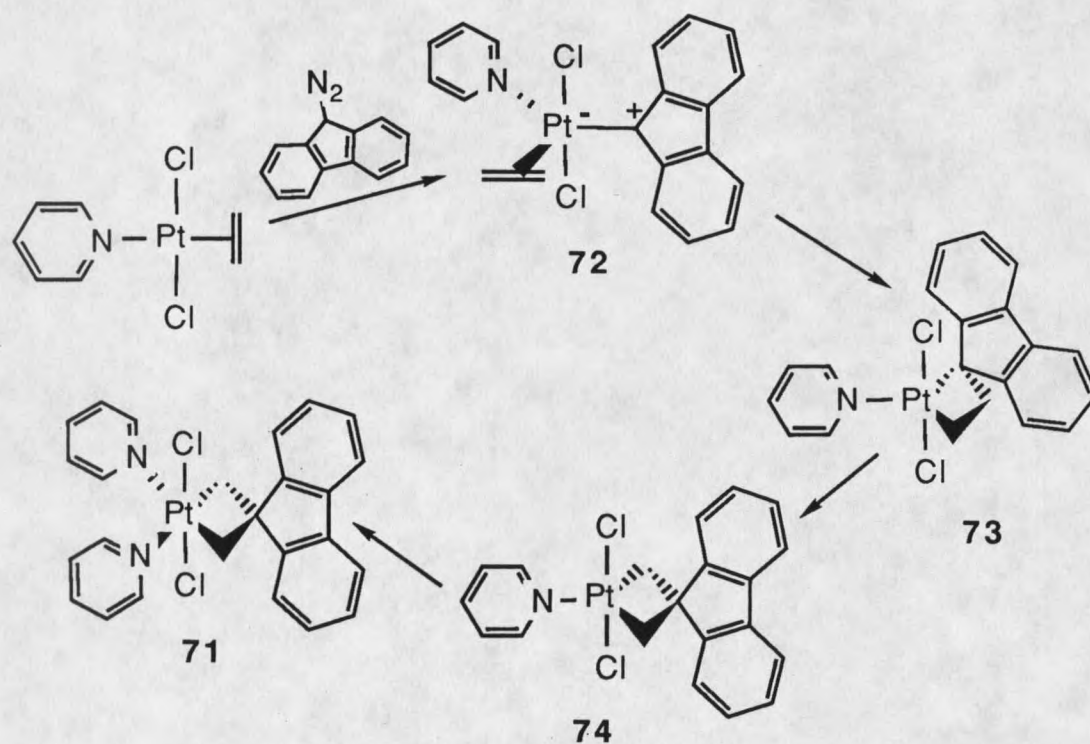


Figure 16. A Proposed Mechanism for the Formation of 71.



and then onto the observed product by coordination of the second pyridine. All of these steps are reasonable and have precedence (see Chapter 1). In order to support this mechanism, an NMR study was conducted.

Variable Temperature NMR Studies

A d^1 -chloroform solution of Zeise's pyridine monomer was placed in a 10 mm NMR tube and lowered into a heteronuclear, variable temperature probe. This solution was cooled to $-40\text{ }^\circ\text{C}$, allowed to stabilize and the instrument

tuned. A second d^1 -chloroform solution containing a second equivalent of pyridine and an equivalent amount of the diazofluorene was prepared. This solution was placed in a dry ice/chloroform bath and allowed to equilibrate. The original solution was quickly withdrawn from the NMR spectrometer, mixed with the second solution and replaced in the instrument. Proton spectra, taken within two minutes of mixing, showed that the pyridines were equivalent and that the diazoalkane had not decomposed. As with the ethyl diazoacetate studies, there was no evidence of coordination of the diazoalkane to the platinum at this temperature.

The mixture was carefully warmed to 30 °C while being monitored by proton NMR spectroscopy. An intermediate was observed to "grow in" followed by appearance of the product 71. When the intermediate had reached maximum concentration (about 60% of the reaction mixture), the solution was cooled to -40 °C to permit ^{13}C and ^{195}Pt NMR data to be collected. Table 12 shows the critical NMR data for this intermediate, while complete data can be found in Appendix B. Based on this data, structure 75 was assigned to this compound.

This data is clearly inconsistent with any of the structures proposed in Figure 16. The platinum chemical shift is that of a platinum(II) ylide, but the platinum-carbon coupling indicates that the central carbon of the fluorene moiety is not directly platinum bound. It is also obvious that there are two sp^3 carbons indicating that the

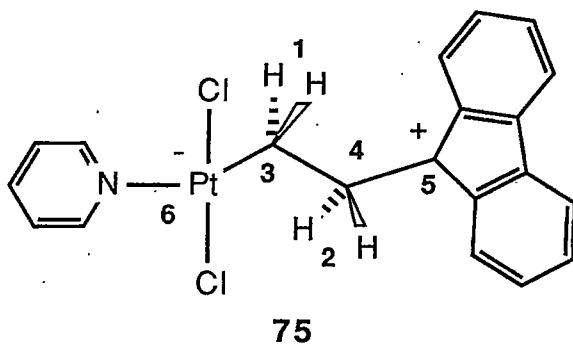


Table 12. Critical NMR Data for 75.

¹H Spectrum

- 1) 2.2 ppm, 2 protons, coupling to platinum cannot be resolved.
- 2) 2.8 ppm, 2 protons, coupling to platinum cannot be resolved.

¹³C Spectrum

- 3) -16.5 ppm, 1 carbon, triplet, $^1J_{Pt-C}$ - 655 Hz.
- 4) 38.8 ppm, 1 carbon, triplet.
- 5) 82.5 ppm, 1 carbon, singlet, coupling to platinum cannot be resolved.

¹⁹⁵Pt Spectrum

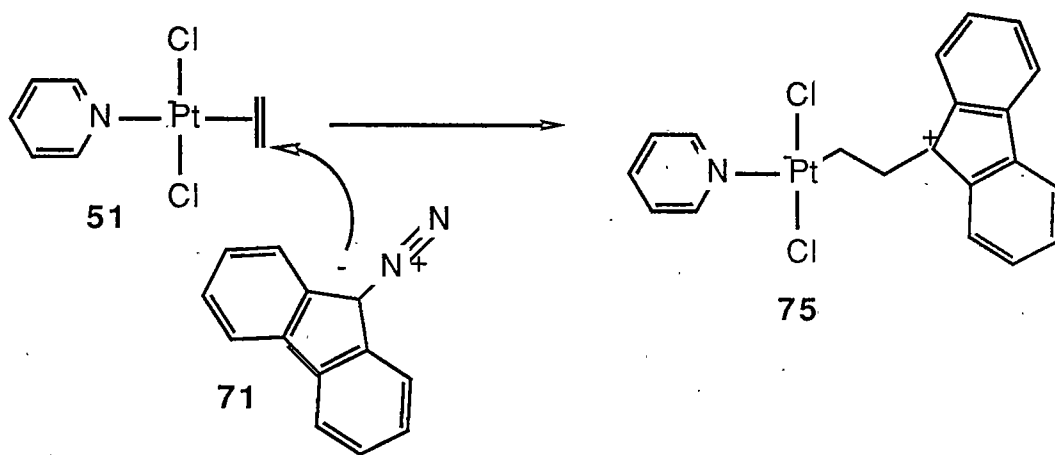
- 6) 1834 ppm.

ethylene has already been inserted between the platinum and the fluorene moiety.

It is not clear from the spectral data where the second equivalent of pyridine is located. The very large number of aromatic resonances in the spectra make assignments of any particular pyridine difficult. The fact that the "carbonium" center (labelled 5 in structure 75) is at a moderate shift of 82.5 ppm in the ^{13}C spectrum suggests that the pyridine is associated with this center, but this cannot be conclusively proven.

Mechanistic Implications

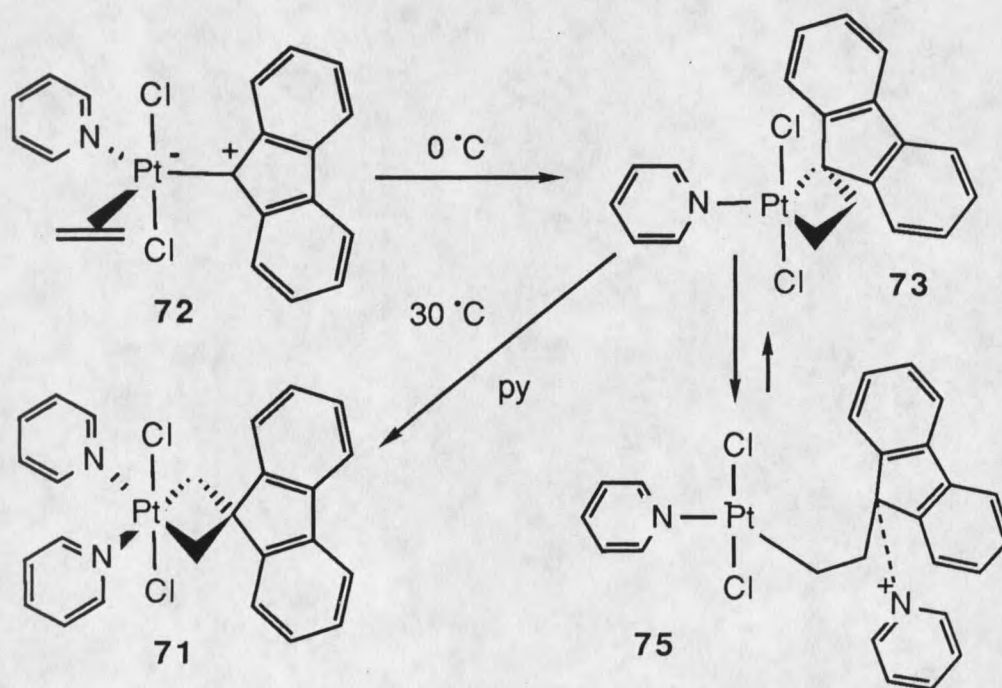
There are two reasonable routes to the formation of compound 75. The first possibility is nucleophilic attack by the diazoalkane on the coordinated olefin (eq. 24). This scheme, if true, is unprecedented. In one case, with palladium, it was shown that attack of a diazoalkane on a coordinated olefin could not occur¹¹¹. The possibility



remains however, that diazofluorene reacts very differently than other diazoalkanes, and that this is the mode of attack.

Another possibility is proposed in Figure 17. This scheme is a modification of the mechanism proposed in Figure 16. It is noted here that compounds 73 and 75 are very similar structurally, the only difference being the distance between the platinum and the central fluorene carbon. It seems possible that 73 is quickly formed at low temperature, but is unstable for steric reasons and opens to 75. When sufficient energy becomes available, the small equilibrium

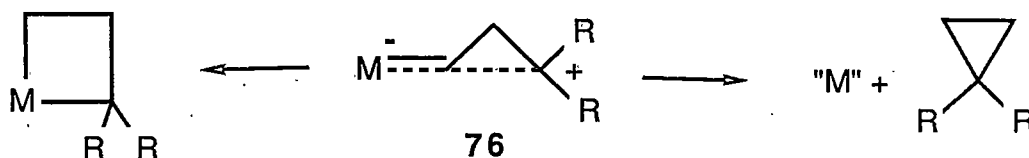
Figure 17. Proposed Mechanism for the Formation of 71 via 75.



concentration of 73 can undergo the Puddephatt rearrangement to the observed product, 71.

Relationship of 75 to Other Intermediates

Compound 75 is intriguing, not only by virtue of its intermediacy in the formation of platinacyclobutane 71, but also because of its resemblance to intermediates proposed by Brookhart and Doyle. Both workers proposed a structure similar to 76 to explain the stereo selectivity found in catalytic cyclopropanations. In Brookhart's mechanism, 76 can either cyclize to form a metallacyclobutane, or can cyclopropanate directly. Doyle's mechanism makes no provision for formation of the metallacyclobutane, but has 76 cyclize to form a cyclopropane.



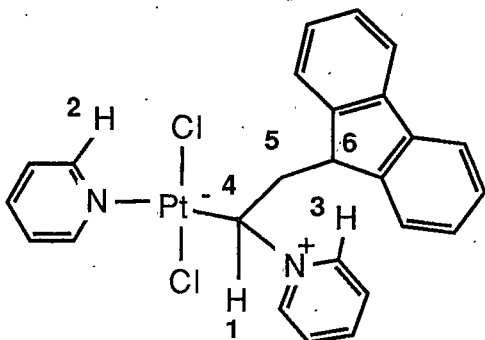
Compound 75, although formed differently than the proposed intermediates for catalytic cyclopropanation, never the less is a good model for them. It shows no

tendency to form a cyclopropane directly, preferring to cyclize to the metallacyclobutane exclusively. This is inconsistent with Doyle's mechanism, but strongly supportive of Brookhart's, as he predicted that metallacyclobutane formation should be encouraged by steric bulk on the "carbonium" center of 76.

Other Reactions

The Formation of 77

Additional support for a portion of the mechanism proposed in Figure 13 was obtained by refluxing platinum-cyclobutane 71 in benzene. This is the Gillard method of forming platinum ylides, and the product formed was assigned structure 77 on the basis of NMR spectral data. Critical data for this compound is found in Table 13 and complete data in Appendix B.



77

Table 13. Critical NMR Data for 77.

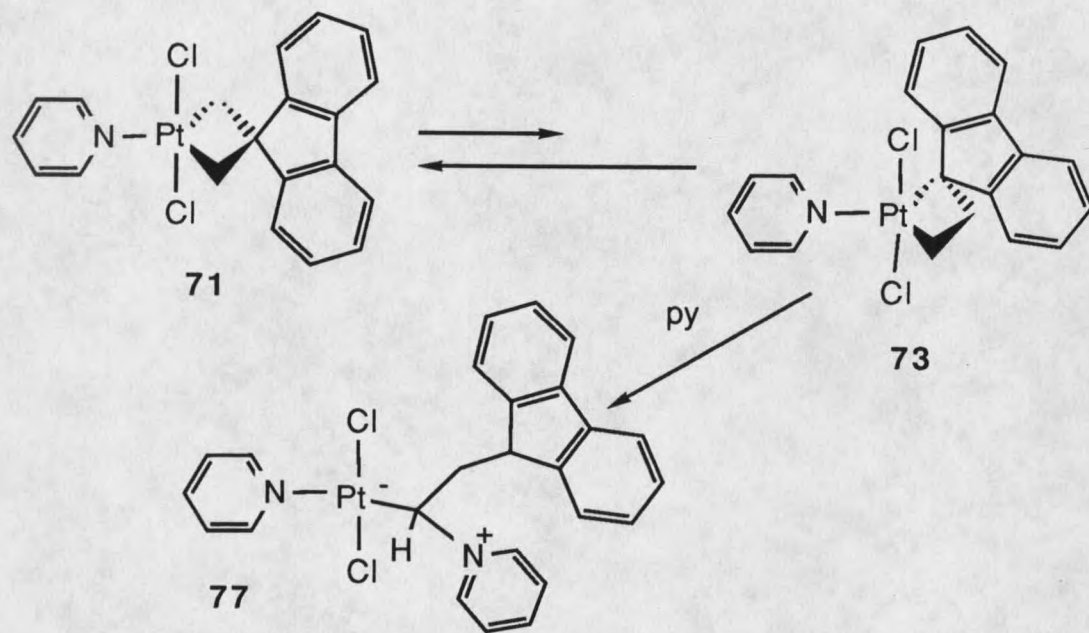
¹H Spectrum

- 1) 6.86 ppm, 1 proton, triplet, $^2J_{Pt-H}$ -104 Hz.
- 2) 8.89 ppm, 2 protons, doublet.
- 3) 8.61 ppm, 2 protons, doublet

¹³C Spectrum

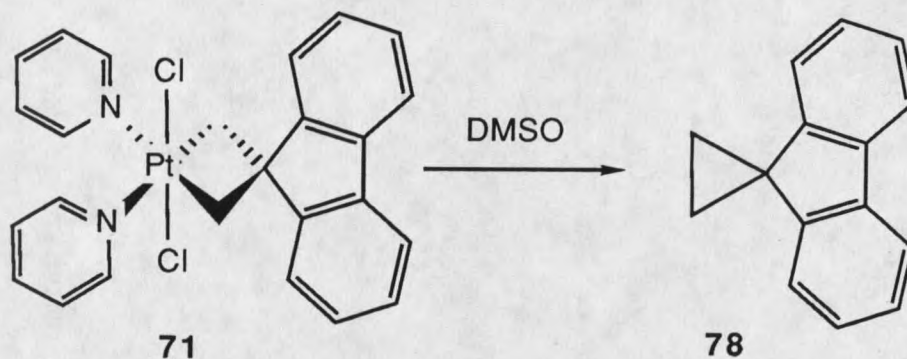
- 4) 41.4 ppm, 1 carbon, doublet, $^1J_{Pt-C}$ -810 Hz.
 - 5) 39.7 ppm, 1 carbon, triplet.
 - 6) 46.5 ppm, 1 carbon, doublet, $^3J_{Pt-C}$ -35 Hz.
-

Structure 77, not surprisingly, has NMR spectra quite similar to that of ylide 15. It is reasonable to conclude that both ylides are formed by the same mechanistic pathway, since they are both formed under identical conditions from platinacyclobutanes. In analogy with the mechanism described by Puddephatt⁶³, compound 77 is formed by equation 25. Once again, structure 73 is required as an intermediate. In the case of the phenyl platinacyclobutane, both isomers can be observed in solution. The greater steric bulk of the fluorene platinacyclobutane undoubtedly results in a shift of the equilibrium towards isomer 71. Even so the reactive isomer still seems to be the more hindered 73, as with other platinacyclobutanes.



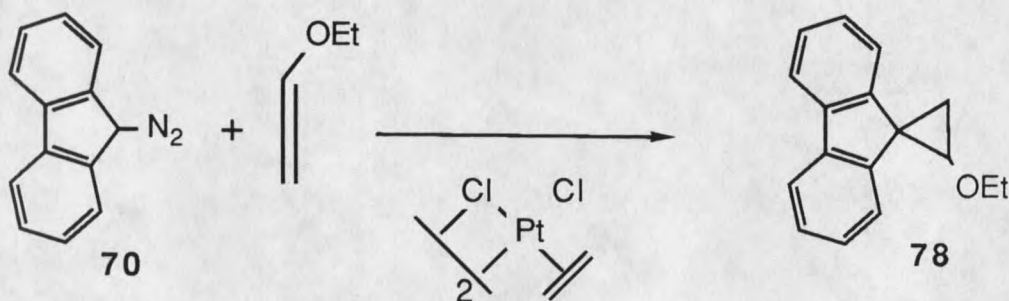
Reductive Elimination of 71

When compound 71 is treated with DMSO, the spirocyclopropane 78 is formed in good yield. Spectral data for this compound can be found in Appendix B. The formation of a cyclopropane from the decomposition of a platinacyclobutane is not a new reaction in itself, but the sequence of reactions from Zeise's pyridine monomer to the formation of a cyclopropane is the first report that platinum can perform this important reaction. It also reinforces the view that the mechanistic observations made in this work are applicable to the mechanism of the catalytic cyclopropanation reaction.



Other Platinum(II) Olefins

If the ethylene on Zeise's pyridine monomer is replaced by ethyl vinyl ether, a cyclopropane is formed directly from the reaction with diazofluorene. With this olefin, no intermediate platinacyclobutane can be isolated. The spiro cyclopropane product 79 was identified by the NMR spectroscopy and mass spectroscopy, this data is reported in Appendix B.



The failure to observe a platinacyclobutane from this reaction was not entirely surprising. There are few reports

of tri-substituted platinacyclobutanes and no published reports of platinacyclobutanes containing ether functionalities.

Attempts were made to extend this reaction to other olefins, but these were largely unsuccessful. Cyclohexene and cis-stilbene produced small amounts of products which corresponded to addition products in the mass spectrometer, but these could not be isolated. Cyclooctene and diethylmaleate did not react under these conditions. Styrene produced an unusual product in good yield that appeared to contain both the fluorene moiety and two equivalents of styrene. This product was not identified.

Summary

Diazofluorene displayed unique reactivity with Zeise's pyridine monomer in chloroform. A new spiro platinacyclobutane was synthesized and characterized. Variable temperature NMR studies of the formation of this compound resulted in observation of an unusual "extended" glide. This compound is remarkably similar to intermediates proposed by Brookhart and Doyle in the catalytic cyclopropanation of olefins. The cyclization of this compound to a platinacyclobutane is inconsistent with Doyle's mechanism, but consistent with that proposed by Brookhart.

Platinacyclobutane 71 was found to undergo reactions common to other platinacyclobutanes including ring opening

to an ylide via the Gillard method and reductive elimination of a cyclopropane. This last result represents the first reported cyclopropanation of an olefin by platinum mediated decomposition of a diazoalkane. This is also the first reported isolation of a metallacyclobutane during an olefin cyclopropanation reaction. This observation lends credence to some of the earlier mechanisms of cyclopropanation which have fallen into disfavor recently^{33,107}.

It was found that replacing the olefin on the metal had a great effect on the reaction. Ethyl vinyl ether was found to produce cyclopropanes directly while a sampling of 1,2-disubstituted olefins showed little or no propensity to react under these conditions. Styrene was found to produce good yields of a non-cyclopropane containing product, which was not identified.

CATALYTIC CYCLOPROPANATION

Introduction

One of the primary motivations for investigating the chemistry of organometallic compounds is the search for new catalysts. Furthermore, platinum complexes have long been used as models for intermediates in certain catalytic reactions, including reactions involving the metal catalyzed decomposition of diazoalkanes. The validity of these models became more apparent as metals such as rhodium and palladium became recognized as important catalysts in these systems.

As these catalysts were developed however, the possible utility of platinum to catalyze reactions such as cyclopropanation had been almost completely ignored^{1,41}. The results discussed in the last chapter however, prompted an investigation of possible catalytic activity on the part of platinum(II) olefins. The results of this investigation are reported here.

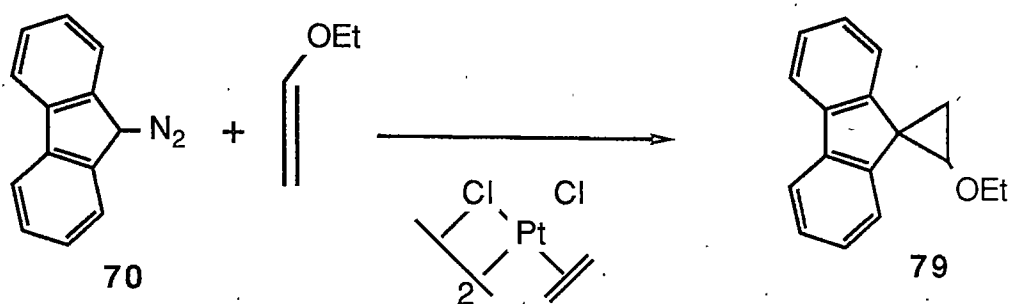
Platinum as a Cyclopropanation Catalyst

It had previously been observed that both Zeise's dimer and its pyridine monomer catalyzed the decomposition of diazoalkanes (chapter 1). Since pyridine had been previously shown to be a trapping agent for the platinum carbene

intermediate (i. e. ylide formation), it was anticipated that catalytic cyclopropanations could be carried out with Zeise's dimer.

The Reaction with Diazofluorene

The first reaction was an extension of the stoichiometric reaction between ethyl vinyl ether and diazofluorene. A chloroform solution of diazofluorene was added slowly with stirring to a chloroform solution containing a catalytic amount (20 mgs) of Zeise's dimer and a 5 fold excess of ethyl vinyl ether, based on diazofluorene. Evolution of N_2 was slow at room temperature, so gentle heating ($\approx 40^\circ C$) was begun. Formation of the expected spiro cyclopropane in a 50% yield based on diazoalkane was found. Other products from this reaction included the dimer of the carbene and other unidentified compounds.



This result demonstrated that platinum could cyclopropanate olefins in reasonable yields. It was important to establish that this reaction was a general one, since

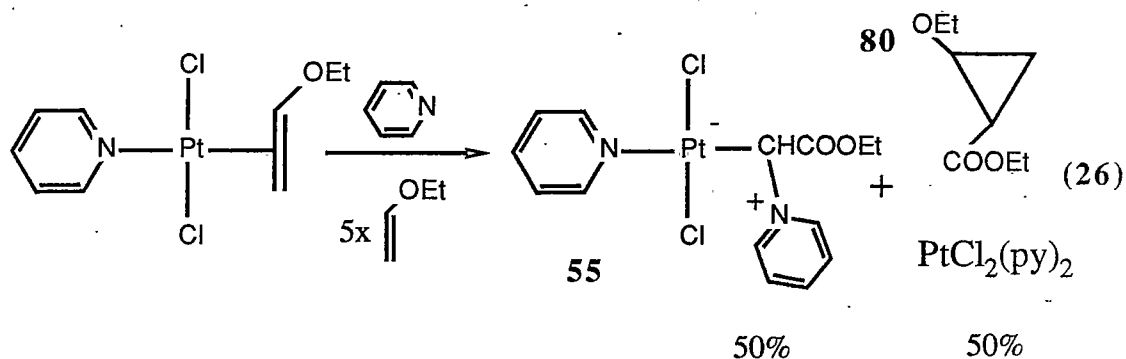
diazofluorene had previously been shown to react differently from other diazoalkanes. A logical choice for further investigation was ethyl diazoacetate. This compound is very easy to work with and large amounts of data exist on its reaction with olefins in the presence of various catalysts.

The Reaction with Ethyl Diazoacetate

It had previously been found that ethyl diazoacetate produce either maleate and fumarate esters or ylide type products (in the presence of pyridine) when decomposed by platinum(II) alkenes. If cyclization of a metal carbene/olefin species was required to form cyclopropanes, as had been previously postulated⁴⁷, then this reaction would not be possible. If, on the other hand, cyclopropanation was the result of electrophilic attack of the olefin on a metal carbene, as has been more recently proposed by Doyle and others^{33,107}, then the reaction should be possible in excess olefin.

This idea was tested first on a stoichiometric scale. Zeise's pyridine monomer was reacted with ethyl diazoacetate and pyridine in chloroform as previously described. The reaction was carried out in varying amounts of excess olefin. It was found that the formation of cyclopropane 80 was proportionally related to olefin concentration (eq. 26). When a five fold excess of diazoalkane was added to the solution, the ratio of ylide formation to cyclopropane formation was about 1:1. Compound 80 was

characterized by standard methods and compared to an authentic sample prepared by a literature procedure.



This experiment showed that cyclopropanation was possible with ethyl diazoacetate, as well as showing that nucleophilic attack of uncoordinated olefin on the metal-carbene was a viable route to cyclopropanes. When the reaction of Zeise's dimer, ethyl vinyl ether and ethyl diazoacetate was carried out under the catalytic conditions described earlier, 80 was formed catalytically in 30% yield.

Yield Optimization

At one time, yields of 30-50%, based on diazoalkane, were considered quite reasonable. Newer catalysts however, particularly rhodium based species, typically cyclopropanate olefins in yields of 90% or more. The formation of 80 in 30% yield therefore was disappointingly low. To remedy this situation, several attempts at improving yields were made.

Slow addition of the diazoalkane minimized the formation of the maleate and fumarate esters, but this increased the yield to only 40%. It was observed that other, unknown products were being formed and that the catalyst was being deactivated with time. Further investigation suggested that the unknown products were oligomeric in nature. These products not only reduced the yield, but made isolation of the cyclopropane products difficult.

Other workers have previously reported similar deactivation of palladium with ethyl diazoacetate⁹⁰. This has severely limited the utility of palladium catalysts with this diazoalkane. It seems probable that the deactivation of the catalyst and oligomer formation are related. One possibility is that the catalyst becomes coated with the high molecular weight compounds and additional diazoalkane is unable to reach the active sites.

Attempts were made to circumvent this possible problem by running the reaction in other solvents. Benzene and aliphatic hydrocarbon solvents gave product distributions essentially identical to chloroform. Ether and THF resulted in dramatic increases in the oligomer production while ethanol gave rise to a different reaction altogether. This latter phenomena is discussed more fully in the next chapter. Finally, strongly coordination solvents such as pyridine and DMSO resulted in formation of adducts which would not decompose the diazoalkane.

Other possibilities for improving yields are to modify the ligands on the platinum or by the use of other diazoalkanes. These ideas were not investigated, although it was observed by the author that Zeise's dimer could cyclopropanate cyclohexene with diazomethane in moderate yields ($\approx 50\%$ without optimization of conditions).

Stereoselectivity

The cyclopropanation reaction was extended to other olefins. Since the best results were obtained without the use of solvent, all of these reactions were run in neat olefin. Solutions of 25 mgs of Zeise's dimer in 2 ml of olefin were rapidly stirred as 0.5 ml of ethyl diazoacetate was added dropwise. Excess olefin was removed by rotoevaporation and the products dissolved directly in d^1 -chloroform. Ratios of syn and anti products were measured by integration of the carbonyl peak from an integratable ^{13}C NMR spectrum. Standards of all cyclopropane products were prepared by reaction with $\text{Rh}_2(\text{OAc})_4$ under identical conditions and by comparison to literature values¹⁰⁷.

The results of this study are presented in Table 14 along with the standard values for the $\text{Rh}_2(\text{OAc})_4$ and literature values for $\text{PdCl}_2 \cdot \text{PhCN}_2$ ⁴⁸. Values obtained for the rhodium catalyst were within experimental error of literature values in all cases.

Yields for the platinum catalyzed reaction varied from 0 to 40%, while palladium gave similar yields ranging from 5 to 40%. The yields for rhodium were uniformly greater than 85%.

Table 14 shows that the stereoselectivity of platinum is generally slightly better than that of palladium, but worse than that of rhodium. The exceptions to this are with styrene and ethyl vinyl ether. With styrene, only polymeric products were observed. Other olefins such as methyl

Table 14 Stereoselectivities for 3 Cyclopropanation Catalysts.

Ratios of Anti to Syn Cyclopropanes from
the Reaction of Ethyl Diazoacetate and
an olefin.

<u>Olefin</u>	<u>Rh₂OAc₄</u>	<u>Zeise's Dimer</u>	<u>PdCl₂·PhCN₂</u>
Ethyl Vinyl			
Ether:	1.7	10	1.5
Styrene:	1.7	--*	1.6
Cyclohexene:	3.6	2.8	2.2
Cyclooctene:	1.6	1.4	---**
1-Methyl-			
cyclohexene:	2.7	1.5	2.1
1-octene:	1.4	1.3	---**

*- Only trace amounts of cyclopropane formed.

** - Data not available.

acrylate and allyl ether gave similar results under these conditions. The exact nature of these polymers is unknown, but they seemed (by NMR) to be primarily based on the olefin.

Ethyl vinyl ether gave very high selectivity for the anti isomer. The exact ratio varied from run to run but averaged at least 10:1. This result is quite spectacular in light of Doyle's mechanism¹⁰⁷, where he predicted that vinyl ethers should be relatively inert to the electronic effects which were postulated to determine stereoselectivity (see Chapter 1). This selectivity is more than twice that of any other catalyst yet reported, including the new rhodium catalysts being developed by Doyle¹⁴². Two possibilities exist for this phenomenon. The first is that the platinum is rearranging the cyclopropanes to the anti isomer after the original reaction is complete¹⁰⁷. The second is that a previously unknown interaction between ethyl vinyl ether and the platinum catalyst is occurring. Details of this effect must await further investigation.

Regioselectivity

The catalytic reaction of Zeise's dimer and ethyl diazoacetate with two other substrates was also investigated in order to explore the regioselectivity of the catalyst. Again, standard reactions with $\text{Rh}_2(\text{OAc})_4$ were performed and found to be consistent with literature reports. These data,

along with literature values for the $\text{PdCl}_2 \cdot \text{PhCN}_2$ catalyst, are reported in Table 15.

Table 15. Regioselectivities for 3 Cyclopropanation Catalysts.

Ratio of Exocyclic to Endocyclic Cyclopropanes from the Reaction of Ethyl Diazoacetate and an Olefin.


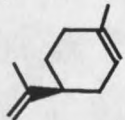
<u>Olefin</u>	<u>Rh_2OAc_4</u>	<u>Zeise's Dimer</u>	<u>$\text{PdCl}_2 \cdot \text{PhCN}_2$</u>
	2.8	2.8	0.16
	2.2	2.2	3.6

Table 15 shows that platinum has a regiochemical preference virtually identical to the rhodium catalyst and dramatically different from that of palladium. This suggests that the reaction with Zeise's dimer is mechanistically similar to the non-olefin coordinating rhodium species rather than the strongly olefin coordinating palladium. Once again, it appears, at least with ethyl diazoacetate, that the coordination of the olefin to the metal is unimportant to the reaction.

Summary

Both Zeise's dimer and its pyridine monomer have been found to catalyze the cyclopropanation of olefins. Yields

are generally poor, primarily due to the formation of oligomers and catalyst deactivation. Attempts at yield enhancement were only minimally successful, but other possibilities remain. These may yet result in the development of important platinum based cyclopropanation catalysts.

Stereoselectivities were found to be intermediate between those of palladium and rhodium. One dramatic exception to this is with ethyl diazoacetate in which a strong preference for the anti isomer is observed. The reason for this preference may be a platinum catalyzed isomerization of the cyclopropane product or a previously unknown interaction between the metal and the ether oxygen.

Regioselectivities were found to be virtually identical to that of the rhodium catalyst and quite different from the palladium species. This suggests that olefin coordination plays little or no role in the cyclopropane formation.

INSERTIONS INTO X-H BONDS

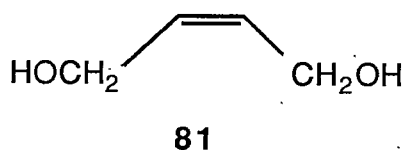
Introduction

Unlike catalytic cyclopropanation of olefins, platinum has been reported to insert into X-H bonds¹⁴¹. The Author is unaware however, of any systematic study of this reaction with platinum. This report briefly explores some of the scope and limitations of the insertion reaction.

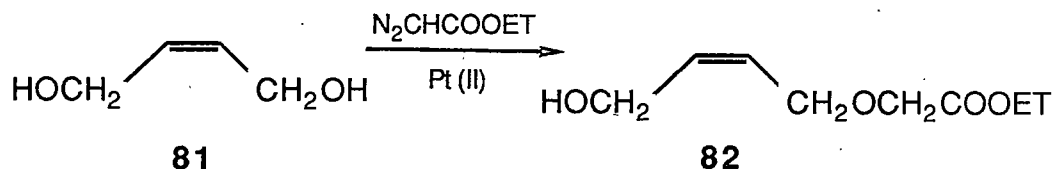
O-H Bonds

The current investigation was extended into this area because of some rather serendipitous results. An attempt was made to cyclopropanate compound 81 in the hopes that the high stereoselectivity observed with ethyl vinyl ether would be repeated. The substrate was reacted with ethyl diazoacetate and Zeise's dimer under the standard conditions described in the last chapter. The reaction proceeded unusually well, with no apparent loss of activity on the part of the catalyst. After addition of the diazoalkane was complete, the excess olefin was removed by rotoevaporation and the product analyzed by NMR and mass spectroscopies.

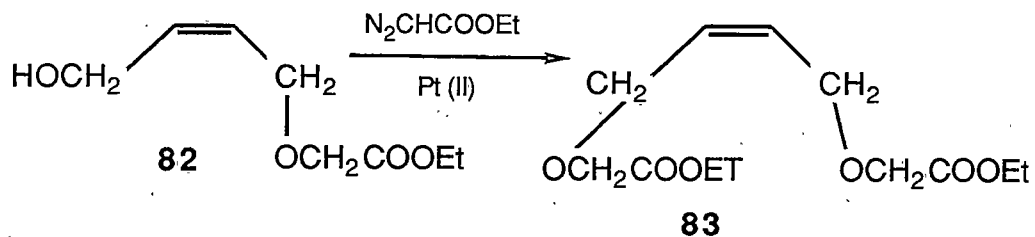
NMR data showed excellent yields (greater than 90%) of a single product. This species was obviously not a cyclopropane however, as two olefin peaks were observed in



both the ^1H and ^{13}C spectra. Complete spectral data for this compound is listed in Appendix B. This data is consistent with the insertion of the carbene moiety into one of the O-H bonds of the molecule to form product 82.



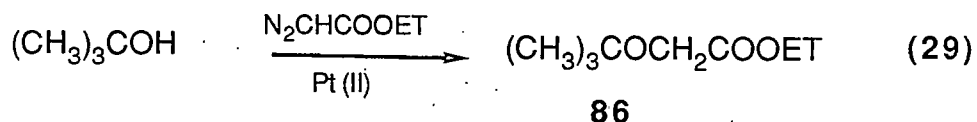
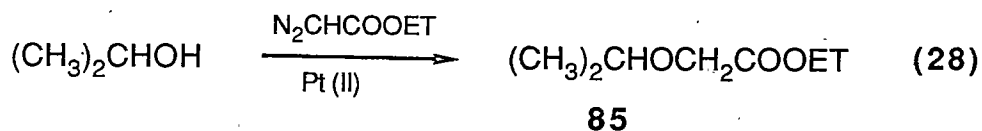
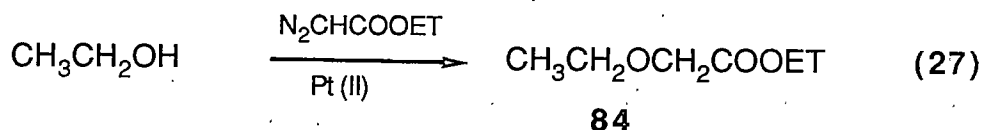
The other products from this reaction were the maleate and fumarate esters, present in very small amounts, and another product which was assigned structure 83. Spectral data for this compound can be found in Appendix B. Compound 82 could be subsequently converted to 83 in excellent yield by addition of additional ethyl diazoacetate in the presence of Zeise's dimer. Once again, there was no evidence of cyclopropane containing products or oligimeric species. Overall yield from 81 to 83 was 85% based on diazoalkane.



Other transition metals, especially rhodium and copper, are known to catalyze this reaction. Yields with these catalysts are often quite good, though much less so when the substrate also contains an olefin¹³⁴. The excellent yields observed for the reactions of 81 and 82 with ethyl diazoacetate are quite remarkable in this regard, however data for direct comparison between catalysts with this substrate was not available.

The reaction was repeated with ethyl, isopropyl and *t*-butyl alcohols (eq. 27-29) with even better results. Yields in all cases were better than 95%. The products from these reactions were identified on the basis of NMR and mass spectroscopies. Spectral data are reported in Appendix B.

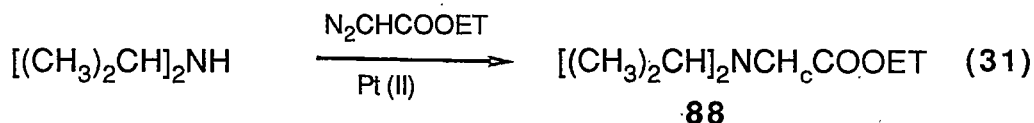
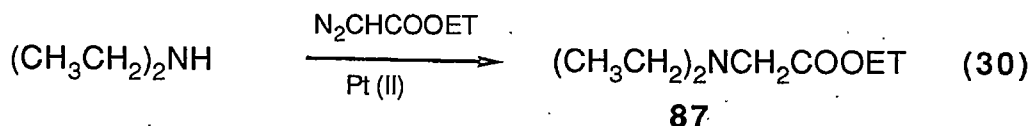
One rather interesting observation with this system is that increasing the steric bulk of the alcohol from ethyl to *t*-butyl has no adverse effect on yields. This is in marked contrast from results obtained with some other catalysts^{130, 134}.



N-H and S-H Bonds

It was of interest to extend this reaction to amines, as several important natural products have been synthesized using the insertion into an N-H bond¹³³. Primary amines rapidly formed unreactive, insoluble adducts under the reaction conditions. Presumably these species are analogous to bis(pyridine) platinum dichloride. The N-H insertion could be effected with secondary amines however, though in poorer yields than obtained with alcohols (80-85%). Side products other than the carbene dimers were observed to be formed in small yields, but were not identified. Equations 30 and 31 show the two examples of this reaction that were explored.

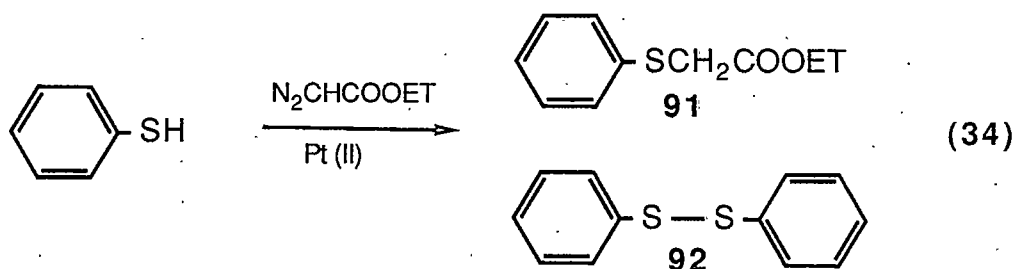
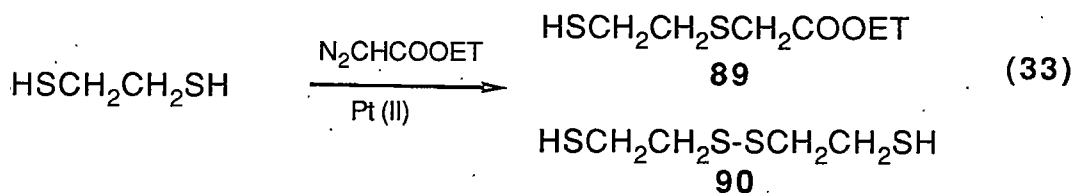
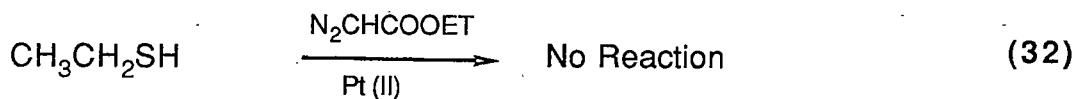
Products were characterized by the usual methods and data is again reported in Appendix B.



Three other substrates were reacted under the same conditions. These were ethanethiol, ethanedithiol and thiophenol (eq. 32-34). Yield of these reactions were less satisfactory than with amines and alcohols, 60 and 70% for the latter two respectively. Ethanethiol rapidly produced an unreactive, insoluble adduct, similar to the primary amines.

The products from the ethanedithiol and thiophenol were characterized as usual.

Significant amounts of side products were observed from the two successful reactions. In each case, it appeared that H_2 was lost, resulting in formation of an S-S bond. Products 90 and 92 could only be clearly seen by GC/MS, as their NMR resonances overlapped with the major products. The mode of formation of these interesting products is unknown.



The formation of X-H insertion product probably proceeds via the mechanism discussed on pages 53 and 54 of this thesis. The hetero atom donates a lone pair of electrons to the highly electrophilic metal-carbene. The platinum can then abstract the acidic proton and reductively eliminate the product.

Summary

Platinum(II) in the form of Zeise's dimer has proven to be an excellent catalyst for the insertion of carbenes, derived from diazoalkanes, into O-H bonds. It is also

effective at promoting insertions into N-H bonds and to a lesser degree into S-H bonds. This brief investigation has opened a very promising area of research.

EXPERIMENTAL

Equipment and Chemicals

The ^1H , ^{13}C and ^{195}Pt NMR spectra were obtained on a Bruker WM-250 NMR spectrometer. Infrared spectra were obtained on a Nicolet 5DX FT-IR spectrometer. Nominal mass spectra were obtained on a VG/MM16F (Vacuum Gas/Micro Mass) spectrometer interfaced to a Varian 1400 series gas chromatograph. Product mixtures were separated on a 15 meter SE-30 capillary column prior to mass spectral analysis. Accurate mass results were obtained on a VG 7070E mass spectrometer. Elemental analysis were performed by Galbraith laboratories.

ChemicalsSolvents:

The following reagent grade solvents were purchased from Baker and used without further purification: Benzene, ethyl acetate, DMSO, pyridine, CCl_4 , ethanol, pentane, hexane and heptane. Also from Baker were THF and diethyl ether which were distilled from CaH_2 before use and CHCl_3 which was run through a short column of basic alumina before use.

Pyridine d^5 , benzene d^6 and $CDCl_3$ were purchased from either Stohler/KOR Stable Isotopes or Norell Inc. and used without further purification.

Reagents:

The following were purchased from Aldrich and used without further purification: cyclopropyl benzene, Diazald, 1-ethyl-3-nitro-1-nitrosoguanidine, ethyl diazoacetate, 4-chlorobenzaldehyde, p-tolualdehyde, benzophenone hydrazone, 9-fluorenone, dipyridal, 2,6-lutidine, ethyl vinyl ether, cyclooctene, 1-methylcyclohexene, norbornadiene, 5-methyl norbornene, dipentene, 1-octene, methyl acrylate, allyl ethyl ether, 2-butene-1,4-diol, diethyl amine, diisopropyl amine, ethanethiol, ethanedithiol and thiophenol.

Cyclohexene, isopropanol, t-butyl alcohol and methyl iodine were purchased from Baker. Styrene was purchased from Eastman and diethyl maleate was purchased from Chem Services. All were used without further purification.

$Rh_2(OAc)_4$ was purchased from Strem Chemicals. K_2PtCl_4 was purchased from Strem Chemicals or obtained via the Johnson-Matthey Corporation precious metals loan program.

Synthesis of Substrates

Preparation of Platinacyclobutane 14

Compound 14 was prepared by the method of Al-Essa and Puddephatt¹⁴³. Physical data can be found in the literature^{143, 136}.

Preparation of p-Methylphenyl Diazomethane

p-Methylphenyl diazomethane was prepared from the corresponding aldehyde by the method of Closs and Moss⁶. The diazoalkane was stored in an amber bottle over dry ice until used.

Preparation of p-Chlorophenyl Diazomethane

p-Chlorophenyl diazomethane was prepared from the corresponding aldehyde by the method of Closs and Moss⁶. The diazoalkane was stored in an amber bottle over dry ice until used.

Preparation of diphenyl diazomethane

Diphenyl diazomethane was prepared from benzophenone hydrazone according to the procedure of Smith and Howard¹⁴⁴.

Preparation of Diazofluorene

A solution of 6 g of 9-fluorenone (0.033 mole) in 60 ml of ethanol was prepared. An equivalent of hydrazine hydrate was added slowly and the mixture heated for 20 minutes. The crystalline hydrazone was collected by filtration.

An ether solution containing 4 g of the hydrazone, 7 g of mercuric oxide and 2 g anhydrous sodium sulfate was prepared. To this, 0.5 ml of a saturated KOH/EtOH solution was added and the resulting mixture stirred for 1 hr. The solution was filtered and the solvent removed by rotoevaporation. The bright red product was recrystallized from ethanol/water and the product isolated in 88% yield.

^1H : 7.92(2H, d); 7.52(2H, d); 7.36(2H, t); 7.28(2H, t).
 ^{13}C : 132.8(2C, s); 131.3(2C, s); 126.2(2C, d); 124.4(2C, d); 120.8(2C, d); 119.1(2C, d).

Preparation of Ylides

Formation of 46 from 14

To a stirred solution of 14 in 15 ml of CDCl_3 at 0 °C, was bubbled a three fold excess of diazomethane (Diazald). The reaction mixture was stirred for an additional hour, and the volital products removed by vacuum distillation. Overall yield of products was 83%, with styrene and phenyl cyclopropane formed in a 5:1 ratio. The reaction was run at room temperature and at -70 °C by the same method. Products were formed in 80 and 75% yields respectively. The ration of styrene to phenyl cyclopropane was 3:1 and 1:5 respectively. Formation of 46 was between 20 and 40% under all conditions.

Formation of 46 and 52 from Zeise's Dimer

Zeise's dimer (200 mg, 0.68 mmole) was dissolved in 2 ml of ether by addition of 1 equivalent (54 μ l) of pyridine. This solution was quickly added to a solution containing a second equivalent of pyridine and a three fold excess of either N_2CH_2 or N_2CHCH_3 (2.04 mmole) in 15 ml of dry ether. The reaction was stirred for one hour and the solvent removed by evaporation. The product was dissolved in chloroform and purified by chloroform elution on a silica gel chromatography column. The product isolated in 95% yield for 46 and 80% yield for 52.

Formation of 49 and 54

Zeise's dimer (200 mg, 0.68 mmole) was dissolved in 2 ml of $CHCl_3$ by addition of one equivalent of pyridine (54 μ l) with stirring. A second solution containing one equivalent of pyridine and one equivalent of the diazoalkane (87 and 101 mg for p-methyl and p-chlorophenyl diazomethane respectively) dissolved in 2 ml of $CHCl_3$. The two solutions were mixed and vigorous gas evolution ensued. The reaction was complete in roughly 10 seconds. Products 53 and 54 were purified by chloroform elution on a silica gel column. Yields were 25 and 75% respectively.

Reaction of Diphenyl Diazomethane and Pt(II)

Diphenyl diazomethane was reacted with Zeise's dimer under the conditions described above. Only $PtCl_2(py)_2$ and

Formation of 61

A solution of 200 mg of Zeise's dimer and 54 μ l of pyridine in 1 ml of CDCl_3 was placed in a 10 mm NMR tube and lowered into a variable temperature, multi-nuclear NMR probe. The solution was then cooled to $-40\text{ }^\circ\text{C}$. A second solution containing 54 μ l of pyridine and 78 μ l of ethyl diazoacetate was dissolved in 300 μ l CDCl_3 and cooled on a dry ice/ CHCl_3 bath to approximately $-60\text{ }^\circ\text{C}$. When both solutions had equilibrated, the first was removed from the probe and the second added to it. The resulting solution was quickly reinserted into the probe and a proton spectrum acquired. The temperature of the probe was gradually raised to $-10\text{ }^\circ\text{C}$, with constant monitoring of the solution by ^1H NMR. The reaction was permitted to proceed until the concentration of 61 reached a maximum (after about 30 minutes). The solution was then cooled to $-40\text{ }^\circ\text{C}$ and ^{13}C and ^{195}Pt NMR spectra acquired.

Formation of 15

Ylide 15 was formed from platinacyclobutane 14 by the method of Gillard¹²⁴.

Formation of 68

Ylide 46 (100 mg, 0.23 mmoles) was dissolved in a solution of 5 ml CHCl_3 and 5 ml CCl_4 . The mixture was refluxed for 2 hours, the solvent removed by rotoevaporation and the mixture analyzed by NMR spectroscopy. Relative yield of 68 by NMR was 55%.

tetraphenyl ethylene could be isolated from the reaction mixture.

Formation of 55

Ethyl diazoacetate (78 μ l, 0.68 mmole) was reacted with Zeise's dimer under the conditions described above, except the reaction was run in an ice bath. The reaction was complete (evidenced by the cessation of gas evolution) in 15 minutes. The product was purified by precipitation from a rapidly stirred solution of pentane. Isolated yield was 91%.

Thermal Isomerization of 55 to 57 and 58

Ylide 55 (200 mgs, 0.39 mmoles) was dissolved in 5 ml of benzene and refluxed for 4 hours. The solvent volume was reduced to 2 ml by rotoevaporation and the product precipitated by pouring the solution into 6 ml of rapidly stirred pentane. Products 57 and 58 were isolated in a 3:1 ratio in 90% yield.

Formation of 59

A benzene solution containing 200 mg of a mixture of 55, 57 and 58 and 95 mg (0.60 mmoles) of 2,2'-bipyridal was refluxed for 4 hours. The product was purified by precipitation from pentane and isolated in 74% yield.

Formation of 60

Compound 60 was formed from a benzene solution of 46 reacted under the conditions described above. Isolated yield was 68%.

Formation of 69

Ylide 55 (200 mg, 0.39 mmole) is dissolved in 2 ml of methyl iodine at room temperature and permitted to stand for four hours. The methyl iodine was then removed by vacuum distillation. The product mixture was separated on silica gel by elution with pentane, benzene, CHCl_3 , CH_2Cl_2 and methanol. The benzene fraction contained three products which displayed only platinum coupled methyl groups in the ^1H NMR spectrum. The chloroform fraction contained one major product which was assigned structure 69, as well as several structural isomers in lesser yield. The methanol fraction contained several products of unknown composition as well as $\text{cis-PtCl}_2(\text{py})_2$ (stereochemistry confirmed by X-ray spectroscopy).

Reactions of YlidesThermal Decomposition; General

Attempts were made to decompose various ylides by refluxing them in benzene, or in various olefins, ketones or aldehydes. No products of interest were found under these conditions and the ylides were recovered in nearly quantitative yields.

Photochemical Decomposition; General

The ylide (200 mg) was dissolved in 20 ml of either cyclohexene or norbornadiene and placed in a water jacketed pyrex reaction vessel. A mercury vapor lamp was placed near

the vessel and the sample irradiated for 4 hours. The olefin was removed by rotoevaporation and the products analyzed by NMR spectroscopy and/or GC/MS.

Ylide 46 yielded only $\text{PtCl}_2(\text{py})_2$ and an intractable residue in cyclohexene. The same reaction in norbornadiene yielded trace amounts of three products. By GC/MS, two of these products showed parent ions of 106 indicating mono incorporation of CH_2 , while a third product showed a parent ion of 120, indicating di-incorporation of CH_2 .

Ylide 15 yielded $\text{PtCl}_2(\text{py})_2$ and cyclopropyl benzene in good yields. This latter compound was identified by GC/MS and NMR comparison with an authentic sample.

Chemical Decomposition of 15

Ylide 15 yielded cyclopropyl benzene on dissolution in EtOH in nearly quantitative yield.

Ylide 15 (100 mg) was dissolved in 2 ml of CHCl_3 and a 1 molar solution of KOH in water placed over the solution to form a biphasic mixture. This was stirred vigorously for 12 hours at room temperature. The water layer was removed, the chloroform solution dried with sodium sulfate and the solvent removed by rotoevaporation. Cyclopropyl benzene was again formed in nearly quantitative yield.

Crossed Alkene Formation; General

A three fold excess of a diazoalkane was added to a chloroform solution containing 100 mg of an ylide. When gas evolution ceased (typically within 10 minutes), the

chloroform was removed by rotoevaporation and the product mixture analyzed by GC/MS. In general, only dimers of the carbenes from the diazoalkane were formed. In the case of ylide 55 in reaction with diazofluorene, a small amount of a product assigned the structure 67 was observed.

The Formation and Decomposition of 71

Formation of 71

Diazofluorene was reacted with Zeise's dimer under the conditions preciously described for the formation of ylides 53 and 54, except that the chloroform solution was gently heated for 15 minutes. Compound 71 was isolated by precipitation from pentane in 94% yield. Crystals of 71 were grown by slow diffusion of heptane into a chloroform solution of 71.

Formation of 75

A CDCl_3 solution containing 200 mg of Zeise's dimer and 54 μl of pyridine was placed in a 10 mm NMR tube and lowered into a variable temperature, multi-nuclear NMR probe. The solution was cooled to $-40\text{ }^\circ\text{C}$ while a second CDCl_3 solution containing 54 μl of pyridine and 131 mg (0.68 mmoles) of diazofluorene was prepared. The latter solution was cooled on a dry ice/acetone bath to roughly $-60\text{ }^\circ\text{C}$ and permitted to equilibrate. The original solution was removed from the probe, the two solutions quickly mixed and then returned to the probe. A ^1H spectrum was obtained within two minutes of

mixing. The solution was warmed to 30 °C while being monitored by ^1H NMR spectroscopy. Intermediate 75 was observed to grow in. When it had reached maximum concentration (after about 30 minutes) the sample was cooled to -40 °C and ^{13}C and ^{195}Pt NMR spectral data obtained.

Formation of 77

Platinacycle 71 was converted to ylide 77 in refluxing benzene by the method of Gillard¹²⁴.

Formation of 78

Platinacycle 71 (100 g, 0.16 mmoles) was dissolved in 300 μl of DMSO and permitted to stir at room temperature for 6 hours. The resulting mixture was dissolved in 5 ml of chloroform and repeatedly extracted with water. The chloroform solution was dried over sodium sulfate, filtered and rotoevaporated. Compound 78 was isolated in 43% yield.

Cyclopropane Formation

Formation of 79

Zeise's dimer (200 mg) was dissolved in 500 μl of ethyl vinyl ether. After evolution of ethylene had ceased (about 5 minutes), 54 μl of pyridine was added to the mixture. The monomeric platinum olefin species was precipitated from 5 ml of rapidly stirred pentane, and redissolved in chloroform. To this solution, 54 μl of pyridine and 131 mg of diazofluorene were added with stirring and gentle heating. After evolution of N_2 had ceased (about 10 minutes), the product

was obtained by precipitating platinum containing products from pentane. Compound 79 was isolated from the pentane layer in 78% yield.

Formation of 80

The reaction was run as for the formation of 79 with the following modifications: A five fold excess of ethyl vinyl ether was added to the mixture, and no heat was applied. The reaction was completed (based on N_2 evolution) within 2 minutes. Cyclopropane 80 was isolated in 45% yield. If the second equivalent of pyridine was not added, the product could be isolated in 86% yield.

Catalytic Cyclopropanation

General

To a stirred solution of the olefin (3 ml), a catalytic amount (20 mg) of either Zeise's dimer or $Rh_2(OAc)_4$ was added. Ethyl diazoacetate (500 μ l) was added dropwise over 2 hours. The catalyst was removed by addition of 10 ml of pentane and filtering the precipitate. Excess olefin was removed by rotoevaporation or vacuum distillation with the higher boiling olefins. Product ratios were determined by comparing the carbonyl resonances of the two isomers from integratable ^{13}C NMR spectra or by measurement of the total ion current of a GC/MS trace. Regiochemical ratios were assigned by integration of the olefin peaks from integratable ^{13}C NMR spectra. Isomers were assigned on the bases of

literature reports¹⁰⁷. In all cases, ratios obtained by the standard cyclopropanation with the rhodium catalyst were satisfactorily close to published values.

Insertion Reactions

Formation of 82

Zeises dimer (20 mg) was dissolved in 3 ml of 2-butene-1,4-diol. Ethyl diazoacetate (500 μ l) was added dropwise with stirring over 2 hours. Platinum containing species were removed by precipitation with pentane and excess alcohol by rotoevaporation. Insertion product 82 was isolated in 95% yield.

Formation of 83

Zeises dimer (20 mg) was dissolved in 450 μ l of 82. Ethyl diazoacetate (200 μ l) was added dropwise with stirring over 1 hour. The product was isolated in the normal manner in 85% yield.

Insertion reactions: General

All additional insertion reactions were conducted as in the formation of 82. Products were analyzed by GC/MS, ¹H NMR and sometimes ¹³C NMR spectroscopy.

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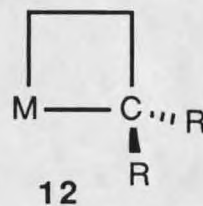
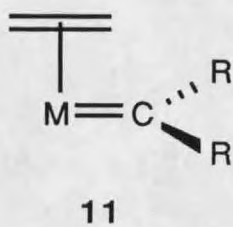
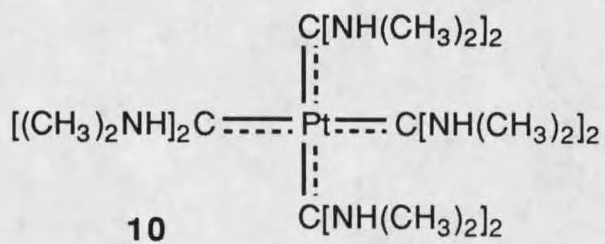
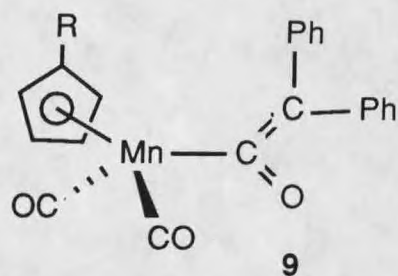
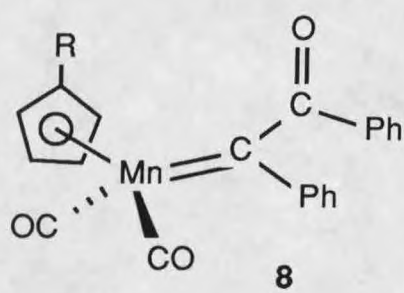
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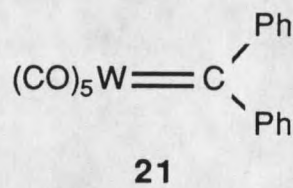
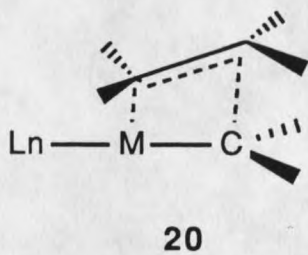
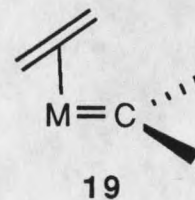
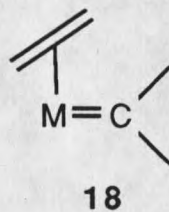
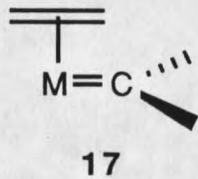
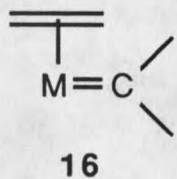
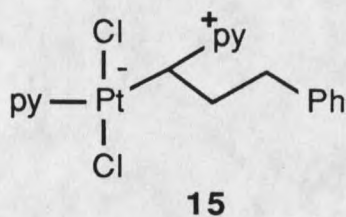
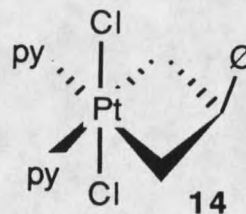
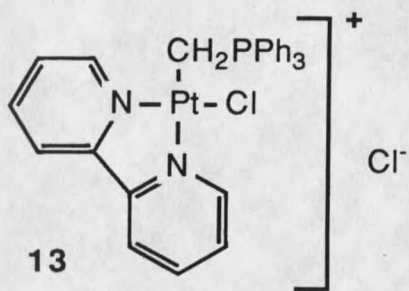
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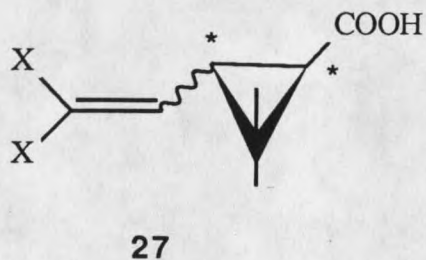
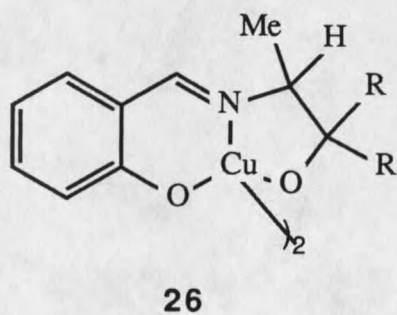
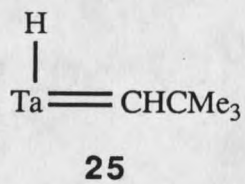
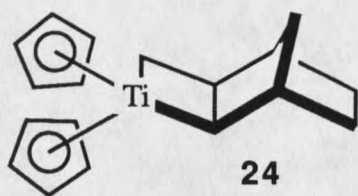
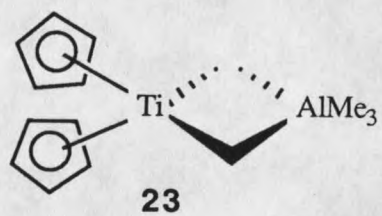
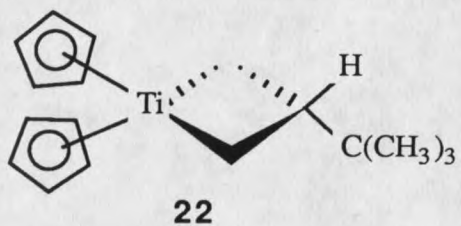
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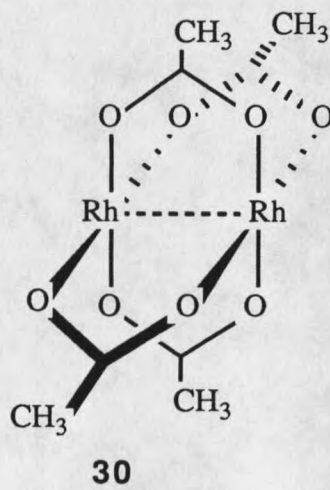
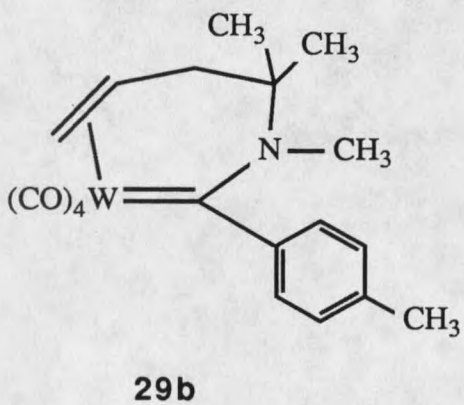
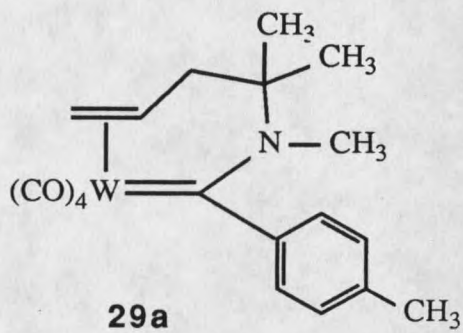
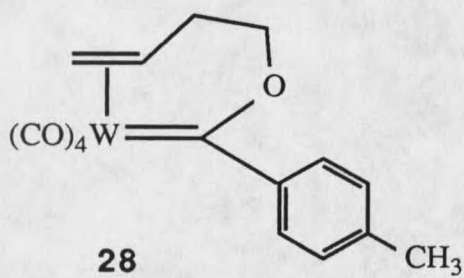
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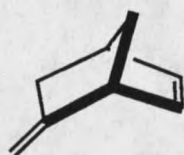
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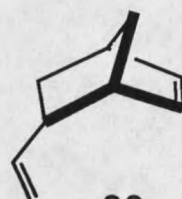




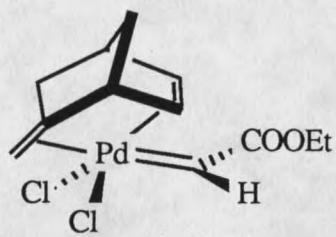




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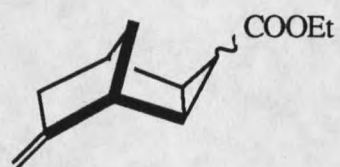
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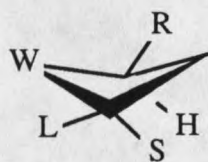
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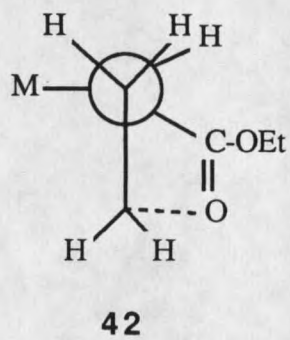
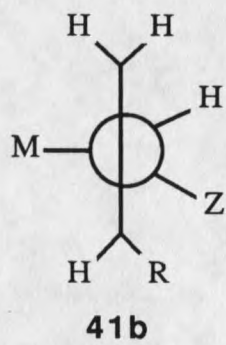
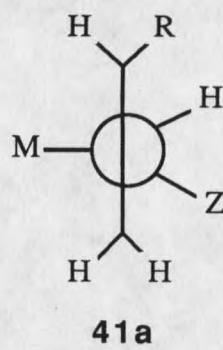
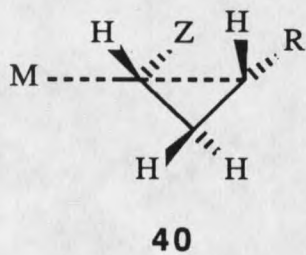
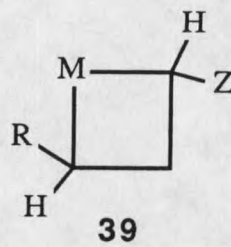
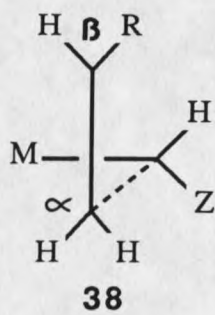
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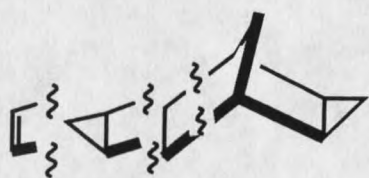


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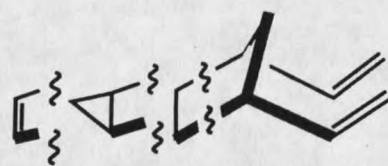


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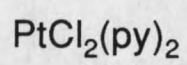




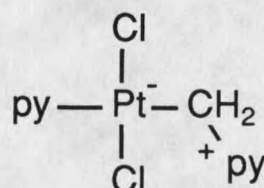
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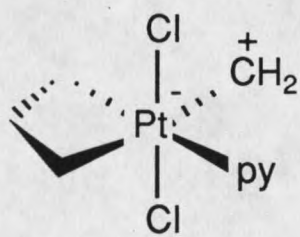
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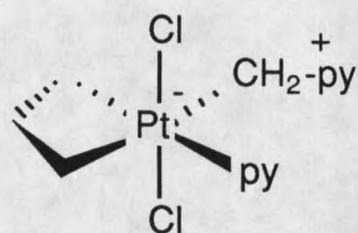
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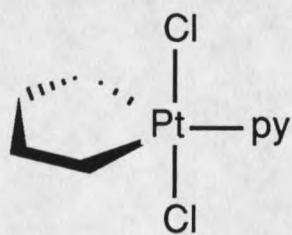
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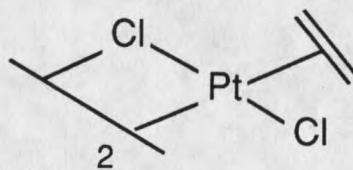
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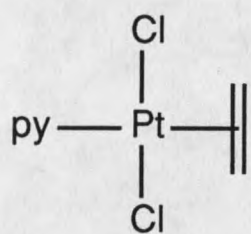
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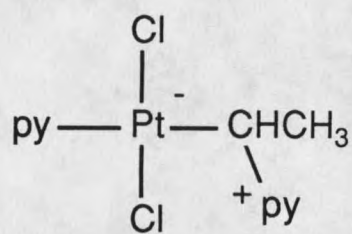
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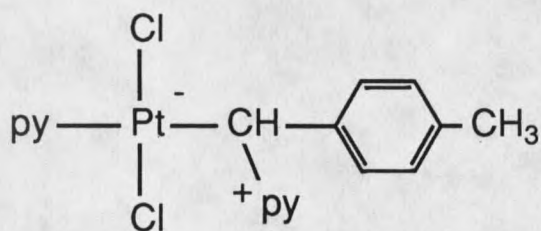
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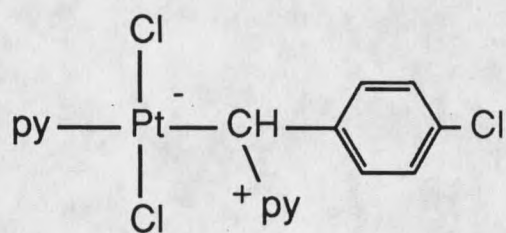
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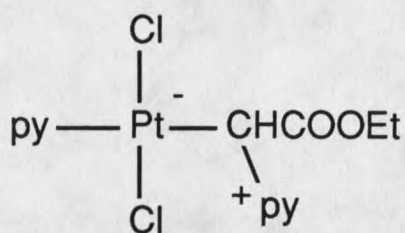
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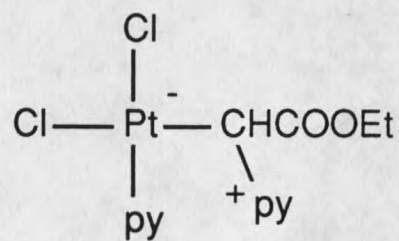
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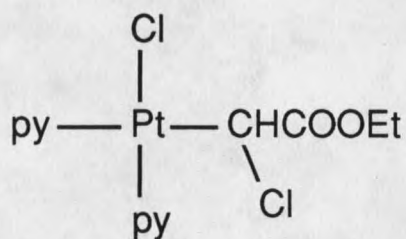
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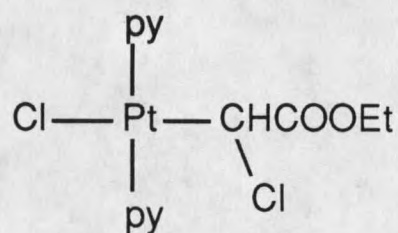
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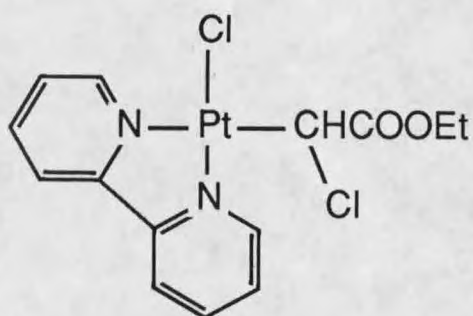
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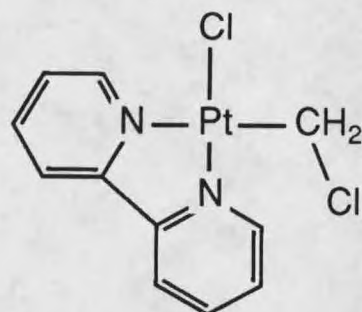
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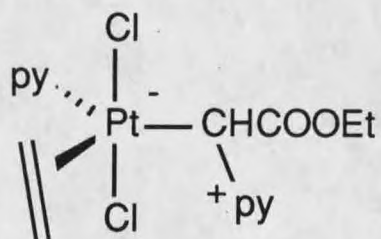
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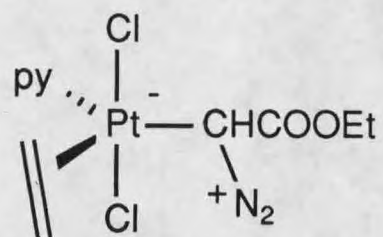
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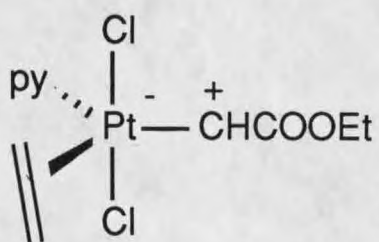
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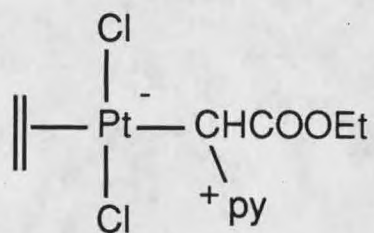
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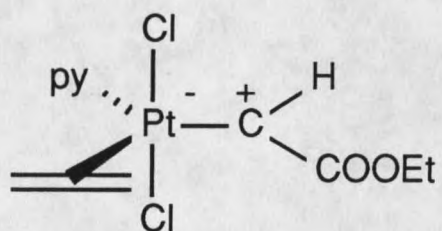
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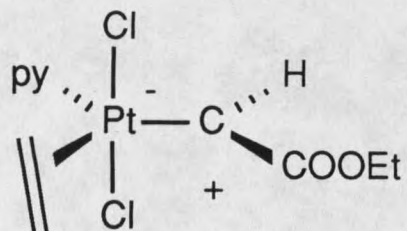
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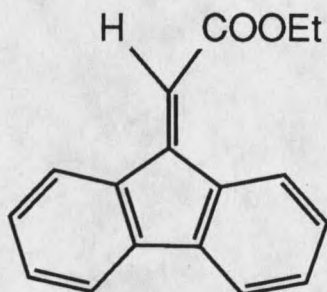
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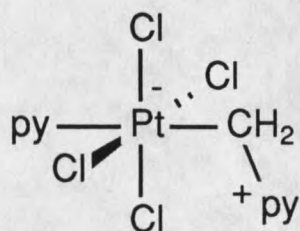
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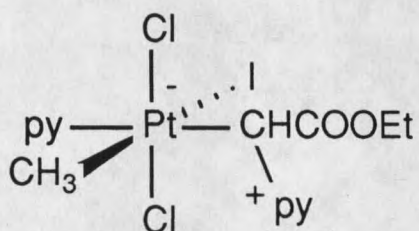
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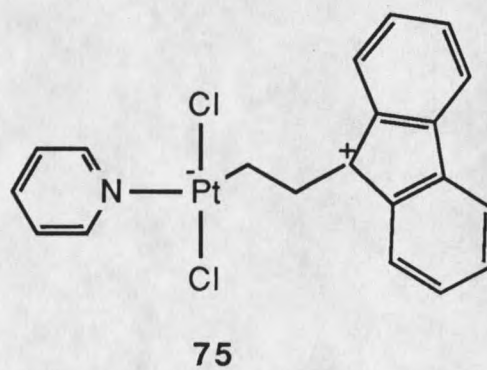
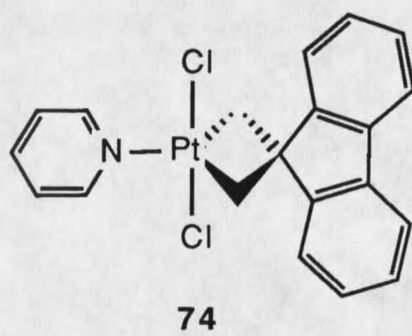
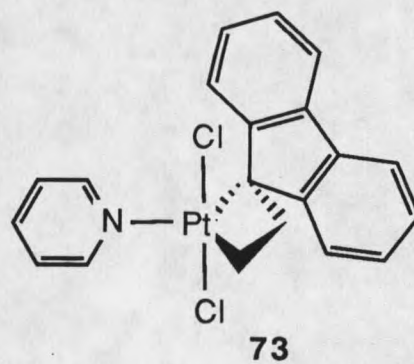
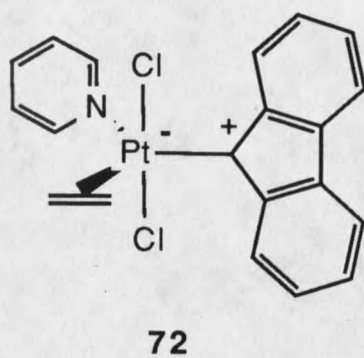
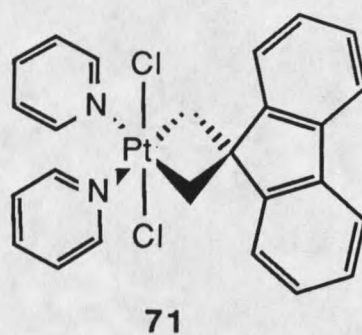
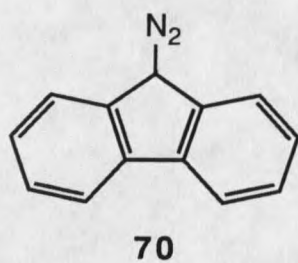
67

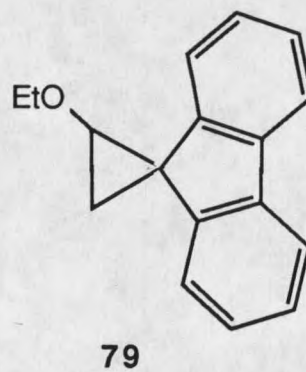
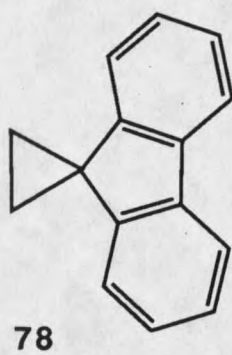
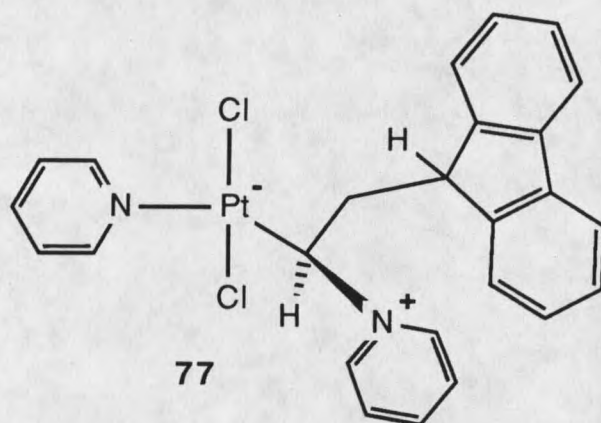
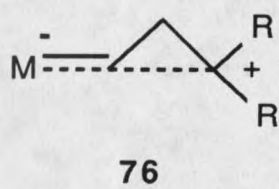


68



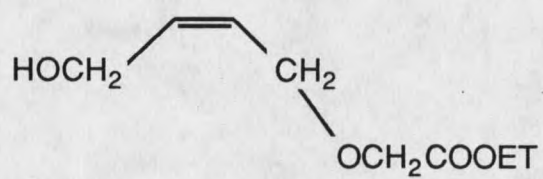
69



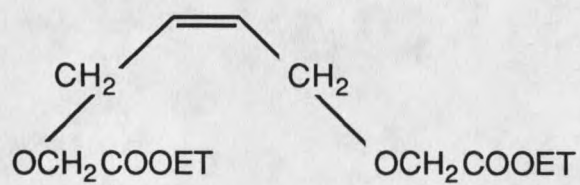




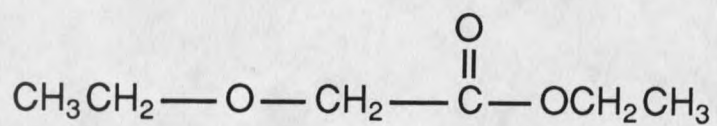
81



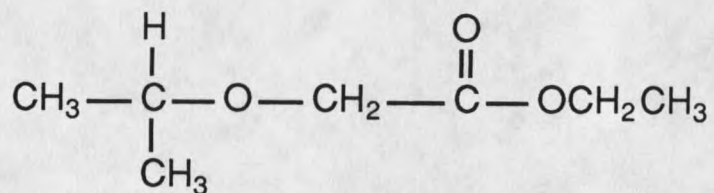
82



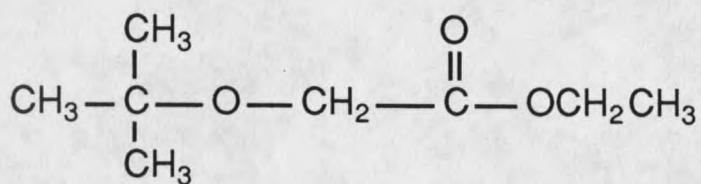
83



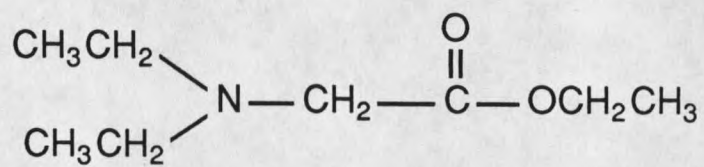
84



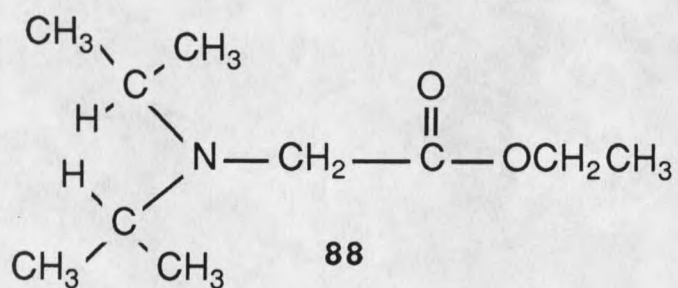
85



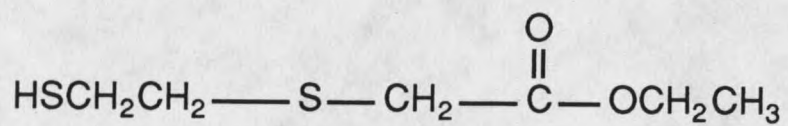
86



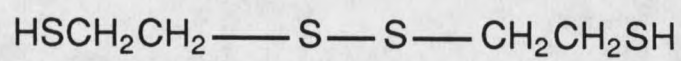
87



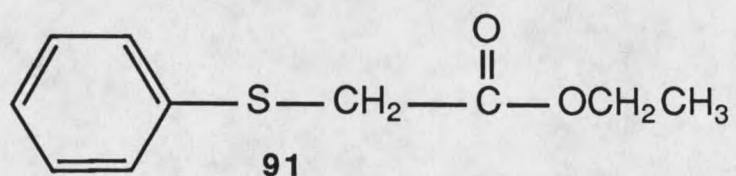
88



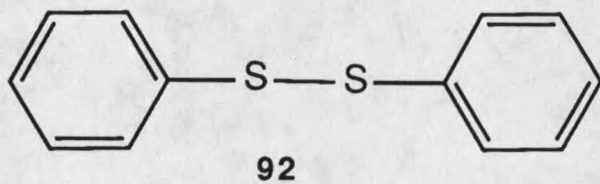
89



90



91



92

APPENDIX B

SPECTROSCOPIC DATA FOR SELECT COMPOUNDS

COMPOUND 46

 ^1H NMR (CDCl₃)

py-1: o-8.92(2H, d); m-7.25(2H, t); p-7.75(1H, t)

py-2: o-9.05(2H, d); m-7.62(2H, t); p-8.02(1H, t)

CH (ylide): 5.45(2H, s) $^2J_{\text{Pt-H}}=100$ Hz ^{13}C NMR (CDCl₃)

py-1: o-151.7(2C, d); m-126.6(2C, d); p-139.8(1C, d)

py-2: o-143.3(2C, d); m-124.6(2C, d); p-137.1(1C, d)

CH (ylide): 30.1(1C, t) $^1J_{\text{Pt-C}}=751$ Hz ^{195}Pt NMR (CDCl₃)*

1852

COMPOUND 52

 ^1H NMR (CDCl₃)

py-1: o-8.86(2H, d); m-7.15(2H, t); p-7.7-7.5(m)

py-2: o-8.91(2H, d); m-7.7-7.5(m); p-8.05(1H, t)

CH (ylide): 6.01(1H, q) $^2J_{\text{Pt-H}}=116$ HzCH₃: 1.80(3H, d) ^{13}C NMR (CDCl₃)

py-1: o-151.7(2C, d); m-126.0(2C, d); p-139.8(1C, d)

py-2: o-141.9(2C, d); m-124.5(2C, d); p-136.8(1C, d)

CH (ylide): 38.5(1C, d) $^1J_{\text{Pt-C}}=766$ HzCH₃: 23.9(1C, q) ^{195}Pt NMR (CDCl₃)*

1839

COMPOUND 53

 ^1H NMR (CDCl₃)

py-1: o-8.92(2H, d); m-7.12(2H, t); p-7.61(1H, t)

py-2: o-9.01(2H, d); m-7.69(2H, t); p-8.02(1H, t)

CH (ylide)**: 7.00(1H, s) $^2J_{\text{Pt-H}}=90$ Hz

phenyl ring: 7.2(4H, m)

 ^{13}C NMR (CDCl₃)

py-1: o-151.8(2C, d); m-125.5(2C, d); p-140.4(1C, d)

py-2: o-143.5(2C, d); m-124.5(2C, d); p-136.6(1C, d)

CH (ylide): 43.9(1C, d) $^1J_{\text{Pt-C}}=790$ Hzphenyl ring*: C1-136.6(1C, d), C2-130.6(2C, d), C3-C4-129.3
(3C, d and s) ^{195}Pt NMR (CDCl₃)*

1878

COMPOUND 54

 ^1H NMR (CDCl₃)

py-1: o-8.90(2H, d); m-7.20-7.32; p-7.60-7.72
 py-2: o-9.05(2H, d); m-7.72-7.60; p-8.05(1H, t)
 CH (ylide)**: 7.25(1H, s) $^2J_{\text{Pt-H}}=110$ Hz
 phenyl ring: 7.20-7.32

 ^{13}C NMR (CDCl₃)

py-1: o-153.5(2C, d); m-125.8(2C, d); p-140.9(1C, d)
 py-2: o-143.6(2C, d); m-124.5(2C, d); p-137.0(1C, d)
 CH (ylide): 48.9(1C, d) $^1J_{\text{Pt-C}}=714$ Hz
 phenyl ring** : C1-132.8(1C, s); C2-131.5(2C, d),
 C3-122.6(2C, d), C4-141.1(1C, s)

 ^{195}Pt NMR (CDCl₃)*

1886

COMPOUND 55

 ^1H NMR (CDCl₃)

py-1: o-8.86(2H, d); m-7.2-7.3; p-7.5-7.7
 py-2: o-8.52(2H, d); m-7.2-7.3; p-7.5-7.7
 CH (ylide): 5.62(1H, s) $^2J_{\text{Pt-H}}=118$ Hz
 CH₂: 3.89(2H, q)
 CH₃: 1.20(3H, t)

 ^{13}C NMR (CDCl₃)

py-1: o-153.3(2C, d); m-125.9(2C, d); p-137.9(1C, d)
 py-2: o-150.5(2C, d); m-125.5(2C, d); p-137.2(1C, d)
 CH (ylide): 26.9(1C, d) $^1J_{\text{Pt-C}}=796$ Hz
 CH₂: 60.2(1C, t)
 CH₃: 14.3(1C, q)
 C=O: 175.9(1C, s)

 ^{195}Pt NMR (CDCl₃)*

1817

ELEMENTAL ANALYSIS

Calculated for C₁₄H₁₆O₂N₂Cl₂Pt: C-32.94; H-3.14; Cl-13.92
 Observed: C-32.64; H-3.27; Cl-14.13

COMPOUND 57

 ^1H NMR (CDCl₃)

py-1: o-8.86(2H, d); m-7.2-7.3; p-7.5-7.7
 py-2: o-9.05(2H, d); m-7.5-7.7; p-8.04(1H, t)
 CH (ylide): 6.59(1H, s) $^2J_{\text{Pt-H}}=119$ Hz
 CH₂: 4.18(2H, dq, protons are not equivalent)
 CH₃: 1.26(3H, t)

COMPOUND 57 (cont.)

 ^{13}C NMR (CDCl₃)

py-1: o-153.6(2C, d); m-126.1(2C, d); p-138.6(1C, d)

py-2: o-151.9(2C, d); m-125.0(2C, d); p-137.1(1C, d)

CH (ylide): 42.2(1C, d) $^1J_{\text{Pt}-\text{C}}-734$ HzCH₂: 60.9(1C, t)CH₃: 14.5(1C, q)

C=O: 176.6

 ^{195}Pt NMR (CDCl₃) *

1984

COMPOUND 58

 ^1H NMR (CDCl₃)

py-1: o-8.86(2H, d); m-7.2-7.3; p-7.5-7.7

py-2: o-8.86(2H, d); m-7.2-7.3; p-7.5-7.7

CH (ylide): 4.90(2H, s) $^2J_{\text{Pt}-\text{H}}-123$ HzCH₂: 3.91(2H, dq; protons are not equivalent)CH₃: 1.34(3H, t) ^{13}C NMR (CDCl₃)

py-1: o-153.4(2C, d); m-124.6(2C, d); p-137.8(1C, d)

py-2: o-153.4(2C, d); m-124.6(2C, d); p-137.8(1C, d)

CH (ylide): 32.3(1C, d) $^1J_{\text{Pt}-\text{C}}-921$ HzCH₂: 60.4(1C, t)CH₃: 14.2(1C, q)

C=O: NA

 ^{195}Pt NMR (CDCl₃) *

1966

ELEMENTAL ANALYSIS (A 3:1 MIXTURE OF 2.14 AND 2.15)Calculated for C₁₄H₁₄O₂N₂Cl₂Pt: C-32.94; H-3.14; Cl-13.92

Observed: C-32.99; H-3.24; Cl-13.59

COMPOUND 59

 ^1H NMR (CDCl₃)

py-1: o-8.84(1H, d); m-7.32(2H, m); p-7.7-7.9

py-2: o-9.11(1H, d); m-7.7-7.9; p-8.13(1H, t)

CH (ylide): 6.58(1H, s) $^2J_{\text{Pt}-\text{H}}-114$ HzCH₂: 4.24(2H, dq, protons are not equivalent)CH₃: 1.34(3H, t)

COMPOUND 59 (cont.)

 ^{13}C NMR (CDCl₃)

py-1: NA

py-2: NA

CH (ylide): 28.4(1C, d) $^1J_{\text{Pt-C}}=866$ HzCH₂: 60.8(1C, t)CH₃: 14.3(1C, q)

C=O*: 173.2

 ^{195}Pt NMR (CDCl₃)*

1983

ELEMENTAL ANALYSISCalculated for C₁₄H₁₄O₂N₂Cl₂Pt: C-33.07; H-2.76; Cl-13.98

Observed: C-32.95; H-2.99; Cl-13.83

COMPOUND 60

 ^1H NMR (CDCl₃)

bipyridene*: 8.8(2H, d); 8.0-8.3(4H, m); 7.7(2H, m)

CH (ylide): 5.72(2H, s) $^2J_{\text{Pt-H}}=97$ Hz

COMPOUND 61

 ^1H NMR (CDCl₃)

py-1 & 2: o-8.65(4H, b); m-7.3(4H, b); p-7.8(2H, b)

ethylene: 4.65(4H, s) $^2J_{\text{Pt-H}}=36$ HzCH (ylide): 5.39(1H, s) $^2J_{\text{Pt-H}}=\text{NA}$ CH₂: 4.2(2H, b)CH₃: 1.2(3H, t) ^{13}C NMR (CDCl₃)

py-1: o-153(2C, d); m-128(2C, d); p-136(1C, d)

py-2: o-149(2C, d); m-125(2C, d); p-136(1C, d)

ethylene: 91(2C, t) $^1J_{\text{Pt-C}}=\text{NA}$ CH (ylide): 43.9(1C, d) $^1J_{\text{Pt-C}}=796$ HzCH₂: 61(1C, t)CH₃: 14(1C, q)

C=O: 174

 ^{195}Pt NMR (CDCl₃)*

1792

COMPOUND 62

 ^1H NMR (CDCl_3)

py-1: Not resolved, similar to 2.18
 ethylene: 4.58(4H, s) $^2J_{\text{Pt-H}}-36$ Hz
 CH (ylide): 5.39(1H, s) $^2J_{\text{Pt-H}}-\text{NA}$
 CH_2 : 4.2(2H, b)
 CH_3 : 1.3(3H, t)

 ^{13}C NMR (CDCl_3)

py-1: o-151(2C, d); m-128(2C, d); p-139(1C, d)
 ethylene: 88(1C, t) $^1J_{\text{Pt-C}}-\text{NA}$
 CH (ylide): 53.8(1C, d) $^1J_{\text{Pt-C}}-\text{NA}$
 CH_2 : 63(1C, t)
 CH_3 : 14(1C, q)
 C=O: 179

 ^{195}Pt NMR (CDCl_3) *

1797

COMPOUND 68

 ^1H NMR (CDCl_3)

py-1^{**}: o-8.92(2H, d); m-7.26(2H, d); p-7.65(1H, t)
 py-2^{**}: o-8.93(2H, d); m-7.28(2H, d); p-7.75(1H, t)
 CH_2 (ylide): 5.45(2H, s) $^2J_{\text{Pt-H}}-131$ Hz

COMPOUND 69

 ^1H NMR (CDCl_3)

py-1: o-8.77(2H, d); m-7.25-7.35; p-7.70-7.82
 py-2: o-9.03(2H, d); m-7.25-7.35; p-7.70-7.82
 CH (ylide): 5.88(1H, s) $^2J_{\text{Pt-H}}-105$ Hz
 CH_2 : 4.18(2H, q)
 CH_3 : 1.32(3H, t)
 Pt- CH_3 : 2.02(3H, s) $^2J_{\text{Pt-H}}-697$ Hz

COMPOUND 71

 ^1H NMR (CDCl_3)

py: o-8.92(4H, d); m-7.2-7.8; p-7.2-7.8
 fluorene: 2-8.38(2H, d); all others^{**}-7.2-7.8
 CH_2 : 3.17(4H, s) $^2J_{\text{Pt-H}}-88$ Hz

COMPOUND 71 (cont.)

 ^{13}C NMR (CDCl₃)

py: o-149.3(4C, d); m-125.1(4C, d); p-138.1(2C, d)
 fluorene: 1-152.3(2C, s); 2-153.4(2C, d); 3-119.7(2C, d);
 4-118.7(2C, d); 5-129.0(2C, d); 6-141.0(2C, s);
 spiral juncture: 60.8(1C, s) $^2J_{\text{Pt}-\text{C}}-95$ Hz
 CH₂: -4.65(2C, t) $^1J_{\text{Pt}-\text{C}}-376$ Hz

 ^{195}Pt NMR (CDCl₃)*

3350

ELEMENTAL ANALYSIS

Calculated for C₂₅H₂₂O₂N₂Cl₂Pt: C-48.70; H-3.57; Cl-11.53
 Observed: C-48.39; H-3.63; Cl-11.71

COMPOUND 75

 ^1H NMR (CDCl₃)

py-1: o-8.94(2H, d); m-7.0-8.5 ; p-7.0-8.5
 py-2: o-9.20(2H, d); m-7.0-8.5 ; p-7.0-8.5
 fluorene^{**}: all 7.0-8.5
 Pt-CH₂: 2.20(2H, d) $^2J_{\text{Pt}-\text{H}}-\text{NA}$
 Pt-CH₂-CH₂: 2.68(2H, d)

 ^{13}C NMR (CDCl₃)

py-1: o-150.4(2C, d); m-133.3(2C, d); p-144.3(1C, d)
 py-2: o-149.8(2C, d); m-133.3(2C, d); p-142.4(1C, d)
 fluorene^{**}: 1-144.3(2C, s); 2-130.1(2C, d); 3-127.2(2C, d);
 4-120.7(2C, d); 5-129.0(2C, d); 6-139.1(2C, s)
 Pt-CH₂: -16.5(1C, t) $^1J_{\text{Pt}-\text{C}}-655$ Hz
 Pt-CH₂-CH₂: 38.8(1C, t)
 spiral juncture: 82.5(1C, s)

 ^{195}Pt NMR (CDCl₃)*

1834

COMPOUND 77

 ^1H NMR (CDCl₃)

py-1: o-8.61(2H, d); m-7-8 ; p-7-8
 py-2: o-8.89(2H, d); m-7-8 ; p-7-8
 fluorene^{**}: all 7-8
 Pt-CH (ylide): 6.86(1H, t) $^2J_{\text{Pt}-\text{H}}-104$
 Pt-CH-CH₂: 2.51(2H, m)
 Pt-CH-CH₂-CHR₂: 4.68(1H, t)

COMPOUND 77 (cont.)

 ^{13}C NMR (CDCl₃)

py-1: o-153.7(2C, d); m** -127.3-124.4; p-139.8(1C, d)
 py-2: o-151.7(2C, d); m** -127.3-124.4; p-136.8(1C, d)
 fluorene¹ 1-148.0(1C, s); 1'-146.2(1C, s); 2-142.7(1C, d);
 2'-139.8(1C, d); all others** -124.4-127.3
 Pt-CH (ylide): 41.36(1C, d) $^1J_{\text{Pt}-\text{C}}$ -810 Hz
 Pt-CH-CH₂: 39.7(1C, t)
 Pt-CH-CH₂-CHR₂: 46.5(1C, d) $^3J_{\text{Pt}-\text{C}}$ -35 Hz

COMPOUND 78

 ^1H NMR (CDCl₃)

cyclopropane: 0.08(4H, s)
 fluorene: 2-8.40(2H, d); 3-7.35(2H, t); 4-7.22(2H, t);
 5-7.72(2H, d)

 ^{13}C NMR (CDCl₃)

fluorene: 1-141.1(2C, s); 2-129.0(2C, d); 3-128.0(2C, d);
 4-126.7(2C, d); 5-128.0(2C, d); 6-138.1(2C, s);
 spiral junction*: 78.0
 cyclopropane: 2.0(2C, t)

GC/MS

M⁺-192(100); 165(52)

COMPOUND 79

 ^1H NMR (CDCl₃)

cyclopropane: 4.13(1H, dd); 2.24(1H, dd); 1.98(1H, dd)
 fluorene: 2-8.38(2H, d); 3-7.28(2H, t); 4-7.18(2H, t);
 5-7.68(2H, d)
 CH₂: 4.36(1H, dq); 4.06(1H, dq)
 CH₃: 1.09(3H, t)

 ^{13}C NMR (CDCl₃)

fluorene: 1-144.3(2C, s); 2-134.5(2C, d); 3-124.1(2C, d);
 4-120.1(2C, d); 5-128.9(2C, d); 6-134.1(2C, s);
 spiral junction: 35.4(1C, S)
 cyclopropane: 67.2(1C, d); 23.5(1C, t)
 CH₂: 66.7(1C, t)
 CH₃: 14.5(1C, q)

GC/MS

M⁺-236(6.3); 207(20.0); 191(14.0); 179(100)

Accurate Mass

Calculated for C₁₇H₁₆O: 236.1207
 Observed Mass: 236.1204

COMPOUND 82

 ^1H NMR (CDCl_3)

olefins: 5.66(1H, dt); 5.51(1H, dt)
 CH_2OH : 4.02(2H, d)
 $\text{CH}_2\text{-OR}$: 4.04(2H, d)
 $\text{O-CH}_2\text{-COOEt}$: 3.93(2H, s)
 $\text{O-CH}_2\text{-CH}_3$: 4.05(2H, q)
 CH_3 : 1.15(3H, t)
 OH : 3.18(1H, b)

 ^{13}C NMR (CDCl_3)

olefins: 133.1(1C, d); 126.5(1C, d);
 CH_2OH : 57.9(1C, t)
 $\text{CH}_2\text{-OR}$: 60.6(1C, t)
 $\text{O-CH}_2\text{-COOEt}$: 66.4(1C, t)
 $\text{O-CH}_2\text{CH}_3$: 67.0(1C, t)
 CH_3 : 13.8(1C, q)

GC/MS

M^+ -174(0); 156(100); 143(4.5); 128(9.8)

COMPOUND 83

 ^1H NMR (CDCl_3)

olefins: 5.52(2H, t)
 $\text{CH}_2\text{-OR}$: 3.99(4H, d)
 $\text{O-CH}_2\text{-COOEt}$: 3.85(4H, s)
 $\text{O-CH}_2\text{-CH}_3$: 4.00(4H, q)
 CH_3 : 1.15(6H, t)

 ^{13}C NMR (CDCl_3)

olefins: 129.1(2C, d)
 $\text{CH}_2\text{-OR}$: 60.7(2C, t)
 $\text{O-CH}_2\text{-COOEt}$: 66.5(2C, t)
 $\text{O-CH}_2\text{CH}_3$: 67.1(2C, t)
 CH_3 : 13.8(2C, q)

GC/MS

NA

COMPOUND 84

 ^1H NMR (CDCl_3)

$\text{O-CH}_2\text{-COOEt}$: 3.76(2H, s)
 ester: CH_2 : 3.95(2H, q); CH_3 : 1.04(3H, t)
 ether: CH_2 : 3.26(2H, q); CH_3 : 1.04(3H, t)

GC/MS

M^+ -132(3); 103(38); 87(100);

COMPOUND 85

¹H NMR (CDCl₃)

O-CH₂-COOEt: 3.89(2H, s)
ester: CH₂: 4.04(2H, q); CH₃: 1.18(3H, t)
ether: CH: 3.53(1H, m); CH₃: 1.10(6H, d)

GC/MS

M⁺-146(8); 117(54); 87(100);

COMPOUND 86

¹H NMR (CDCl₃)

O-CH₂-COOEt: 3.79(2H, s)
ester: CH₂: 3.98(2H, q); CH₃: 1.06(3H, t)
ether: CH₃: 1.02(9H, t)

GC/MS

M⁺-160(0); 145(72); 117(12); 87(44); 57(100)

COMPOUND 87

¹H NMR (CDCl₃)

N-CH₂-COOEt: 4.05(2H, s)
ester: CH₂: 4.05(2H, q); CH₃: 1.13(3H, t)
amine: CH₂: 4.72(4H, m); CH₃: 1.13(6H, d)

GC/MS

M⁺-159(4); 144(10); 130(21); 115(100); 100(100)

COMPOUND 88

¹H NMR (CDCl₃)

N-CH₂-COOEt: 4.16(2H, s)
ester: CH₂: 4.15(2H, q); CH₃: 1.40(3H, t)
amine: CH: 4.72(2H, m); CH₃: 1.25(12H, s)

GC/MS

M⁺-187(5); 172(7); 143(3); 127(33); 114(54); 99(100)

COMPOUND 89

¹H NMR (CDCl₃)

S-CH₂-COOEt: 3.22(2H, s)
ester: CH₂: 4.19(2H, q); CH₃: 1.30(3H, t)
thiol^{**}: CH₂: 2.90(2H, dd); CH₂: 2.77(2H, dd)

COMPOUND 89 (cont.)

GC/MS

M⁺-180(2); 178(12); 152(43); 146(11); 134(8); 105(78);
45(100)

COMPOUND 90

GC/MS

M⁺-186(19); 184(100); 158(2); 156(4); 126(54); 124(73);
92(68); 64(69)

COMPOUND 91

¹H NMR (CDCl₃)

aromatics^{**}: 7.10-7.55
S-CH₂-COOEt: 3.65(2H, s)
ester: CH₂: 4.19(2H, q); CH₃: 1.15(3H, t)

¹³C NMR (CDCl₃)

aromatics^{**}: 137-125
S-CH₂-COOEt: 35.8(1C, t)
ester: C=O: 168.9(1C, s); CH₂: 60.8(1C, t); CH₃: 13.5(2C, q)

GC/MS

M⁺-196(100); 168(2); 151(3); 123(100); 109(32); 77(33)

COMPOUND 92

GC/MS

M⁺-218(100); 185(18); 154(22); 109(100)

* -¹⁹⁵Pt data is referenced to a standard solution of 1 molar K₂PtCN₄ in D₂O at 25 °C. This standard is used rather than the more commonly used Na₂PtCl₆, because it is less susceptible to temperature and it resonates at higher field than most organometallic compounds. This latter feature permits chemical shifts to be reported as positive values, as with other nuclei. The platinum chemical shifts reported in this thesis may be converted to the platinum hexachloride standard by subtracting 4736 ppm.

** - These values were not rigorously determined.

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