



Reaction of iridium with cyclopropanes contained in rigid ring systems
by William Henry Campbell Jr

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:

The reaction of $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ (Vaska's catalyst) with cyclopropane moieties contained within rigid ring systems was investigated. A variety of substrates were investigated, and several were labeled with deuterium. The results show that exocyclic methylene products predominate in most cases, but a diversity of other products was also obtained. Analysis of products demonstrates a great deal of regioselectivity of reaction. Further, mechanistic pathways leading to products are varied and highly dependent on the electronic and steric environment provided by the substrate. Endo-cyclopropane compounds seem to be more reactive (when chloroform is used as the reaction solvent) than their exo-counterparts. Catalytic reaction is enhanced in the presence of oxygen and when chloroform is used as the reaction solvent, but regioselectivity of reaction is somewhat decreased. Olefin products and substrates are capable of reaction with Vaska's catalyst and have been shown to establish a dynamic equilibrium in some cases.

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

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ABSTRACT

The reaction of $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ (Vaska's catalyst) with cyclopropane moieties contained within rigid ring systems was investigated. A variety of substrates were investigated, and several were labeled with deuterium. The results show that exocyclic methylene products predominate in most cases, but a diversity of other products was also obtained. Analysis of products demonstrates a great deal of regioselectivity of reaction. Further, mechanistic pathways leading to products are varied and highly dependent on the electronic and steric environment provided by the substrate. Endo-cyclopropane compounds seem to be more reactive (when chloroform is used as the reaction solvent) than their exo-counterparts. Catalytic reaction is enhanced in the presence of oxygen and when chloroform is used as the reaction solvent, but regioselectivity of reaction is somewhat decreased. Olefin products and substrates are capable of reaction with Vaska's catalyst and have been shown to establish a dynamic equilibrium in some cases.

INTRODUCTION

The field of organometallics is a rapidly growing area of chemistry. Much theoretically and synthetically useful knowledge has come about by the extensive research in organometallics. However, the mechanistic transformations that occur upon reaction of transition metal complexes with organic molecules, as well as electronic effects, stereochemistry, regioselectivity, synthetic applications and more are still at a relatively young age of understanding. One area of organometallics that has created considerable interest is the reaction of cyclopropane containing compounds with transition metals. These reactions range from stoichiometric reactions, yielding isolatable organometallic complexes to catalytic processes. A variety of metal complexes have been isolated or implicated as intermediates in the reactions of cyclopropanes with low valent transition metals. The list includes metallocyclobutanes (1), π -allyl-metal hydrides (2), olefin-metalcarbenes (3) and others (Figure 1). As isolated products, any of these may have potential use for synthetic transformations, and all have been postulated as prominent intermediates in catalytic processes.

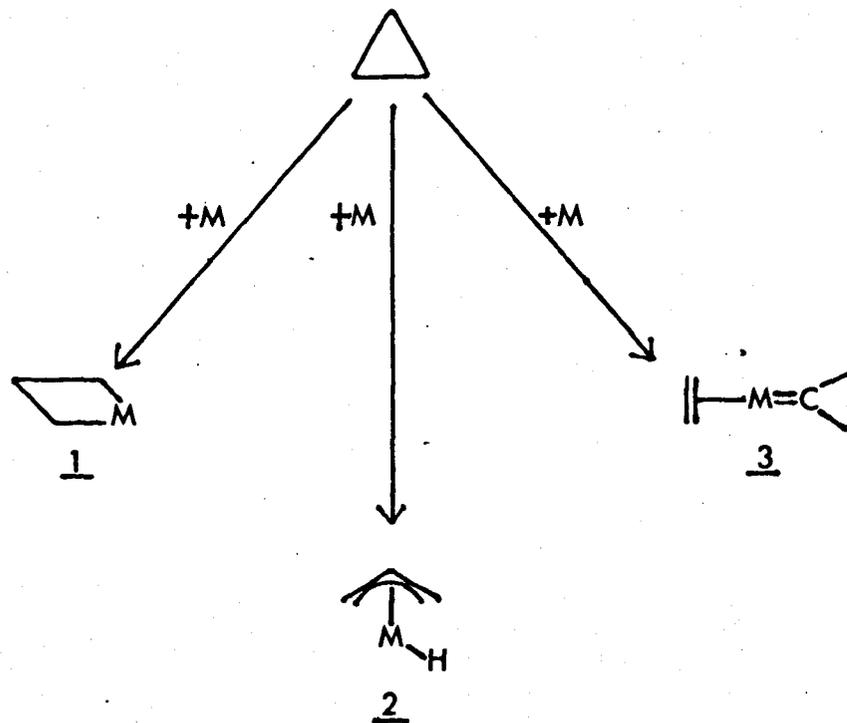


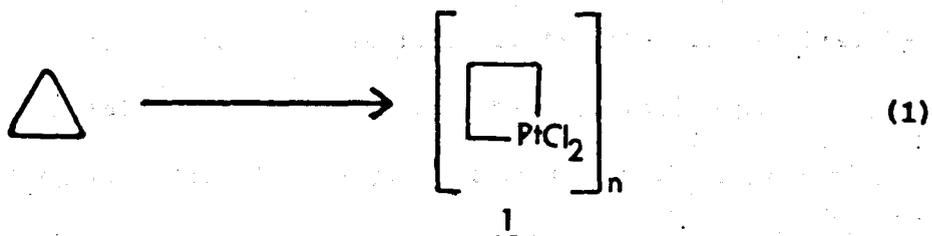
Figure 1. Postulated Intermediates and Isolated Product types from the Reaction of Cyclopropanes with Transition Metal Complexes.

The emphasis of this thesis is on the reaction of $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ (Vaska's catalyst) with cyclopropanes contained within rigid ring systems. The reactions studied involved catalytic isomerization of cyclopropanes to olefins and other cyclopropane products. As will be discussed shortly, Vaska's catalyst is somewhat novel with respect to its reaction with cyclopropane containing substrates, but the reactions of iridium have not been as extensively studied with the same detail as the reactions of other transition metal complexes. The intent of this research was to explore the reactions of Vaska's catalyst with a variety of substrates, which in some cases have been labeled with deuterium. Neither kinetic analysis nor characterization of iridium intermediates was achieved, but consistent mechanistic schemes will be proposed by considering both literature and the data obtained in this research. The proposed mechanistic schemes and the results obtained are intended to provide insight for further investigation.

Before a discussion of the results of this research is presented, an overview of literature dealing with the reactions of cyclopropanes with transition metals will be given. This overview will include a discussion of relative bonding interactions, intermediates of possible importance in catalytic reactions and work that has direct relevance to this investigation. The majority of available references on the reactions of cyclopropanes with transition metals deal with platinum complexes. Platinum complexes do not give facile catalytic reactions with cyclopropanes, but do

give good stoichiometric reactions to yield stable organometallic complexes. Proper treatment of these cyclopropane derived platinum complexes give organic products that are analogous or identical to products obtained from catalytic processes. It therefore seems reasonable that similar structures are produced as intermediates in catalytic processes.

In 1955 the first organometallic complex derived from the reaction of a transition metal with cyclopropane was reported.¹ In this article, Tipper reported on the reaction of cyclopropane with hexachloroplatinic (IV) acid to give, what was later shown by Chatt² to be, platinacyclobutane 1 (equation 1).



Before the structure of 1 was elucidated, it was postulated that cyclopropane-metal bonding was similar to olefin-metal bonding.¹ Analogous bonding interactions may still be of importance in transition states leading to metallocyclobutanes. In the Dewar-Chatt^{3,4} model for metal-olefin bonding the π -HOMO of the olefin donates electron density into an unfilled d-orbital of the metal to form a σ bond, further bonding, called backbonding can arise through donation of electron density from a filled d-orbital of the metal to the π -LUMO of the olefin. Backbonding interactions generate olefin-

metal π -bonds. Analogous bonding for cyclopropanes is achieved with the σ -HOMO's (4 and 5) and σ^* (6) of the cyclopropanes (Figure 2). These orbitals, according to the Walsh model⁵, have a considerable amount of π character. Interaction of 4 with an unfilled d-orbital (7) and interaction of 6 with a filled d-orbital (8) are also illustrated in Figure 2. The interaction illustrated as structure 7 is considered more important for bonding in transition states leading to metal insertion into a cyclopropane, but does not describe the bonding in metallocyclobutanes.^{6,7} Since the σ^* orbital (6) is relatively inaccessible for backbonding, backbonding is deemed less important for initial bonding interactions. The bonding illustrated as structure 8, however, is more indicative of the bonding in metallocyclobutanes. Thus, the transition state interactions leading to formation of metallocyclobutanes should be most facile when electron donating substituents are present on the cyclopropane ring. McQuillin,^{8,9} using cyclopropane substrates with para substituted phenyl substituents has shown that insertion of platinum into cyclopropane rings was more facile when the para substituents were electron donating. In some cases, strongly electron withdrawing substituents completely inhibited reaction. Electron donor ability of the cyclopropane is considered more important for primary interactions in or leading to the transition state, but backbonding from the metal to the cyclopropane σ^* orbital is a prerequisite for metallocyclopropane formation. Insertion of the metal into a cyclopropane bond is an example of oxidative addition to

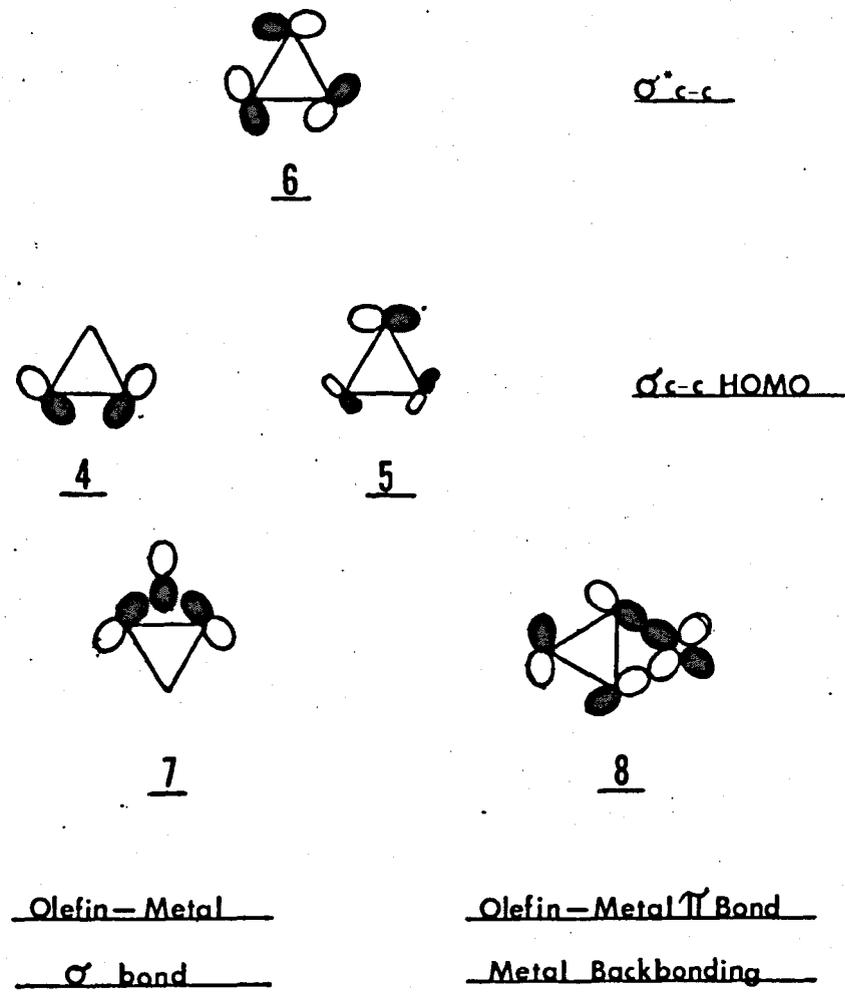
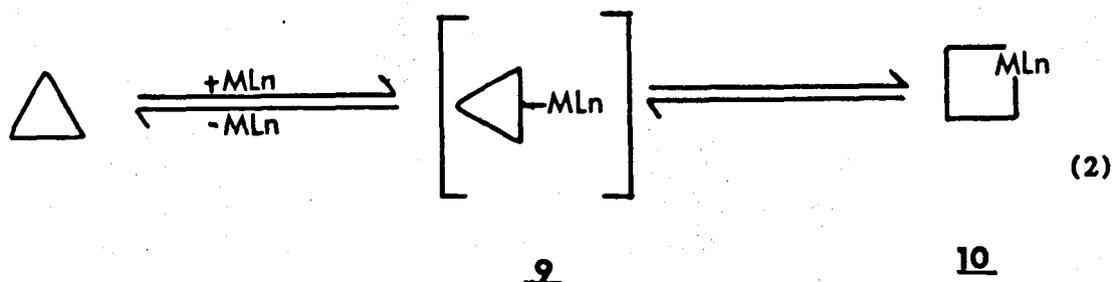


Figure 2. Molecular Orbitals for Cyclopropane and Cyclopropane-Metal Bonding.

the metal. Oxidative addition in these reactions results in a two electron oxidation of the metal.¹⁰ The overall sequence is shown in equation 2.



Structures such as 7 and 9 are termed edge complexes and have been implicated as intermediates. Volger^{11,12} reported that exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (11) and exo, exo-tetracyclo[3.3.1.0^{2,4}0^{6,8}]nonane (12) gave catalytic reaction upon treatment with Vaska's catalyst and other transition metal complexes, however endo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (13), exo, endo-tetracyclo[3.3.1.0^{2,4}0^{6,8}]nonane (14) and 6-methylene-tricyclo[3.2.1.0^{2,4}]octane (15) were unreactive with the same metal complexes. From these results Volger suggested that endo-bidentate edge complexes such as 16 and 17 were required intermediates for reaction (Figure 3). Subsequent work with Vaska's catalyst has show facile reaction to occur with 13 and other substrates that are incapable of achieving an endo-bidentate configuration.¹³ Waddington and Jennings^{14,15} have further elucidated the structures of platina cyclobutanes 18, 19 and 20 (Figure 4) which are not necessarily obtained from endo-bidentate edge complexes. Several other examples

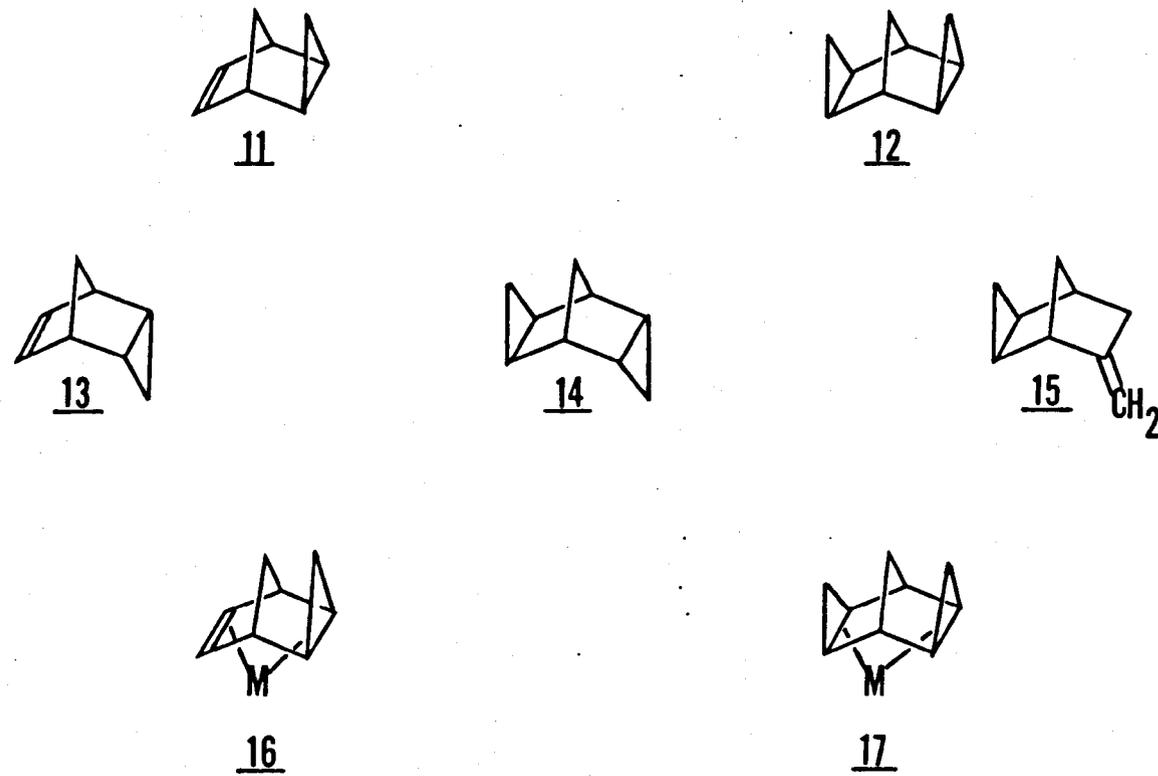


Figure 3. Substrates and Suggested Intermediates Investigated by Volger.

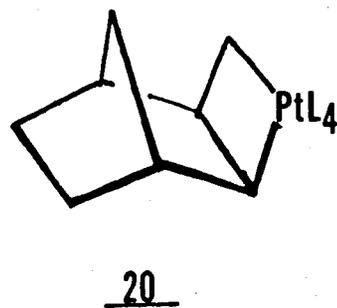
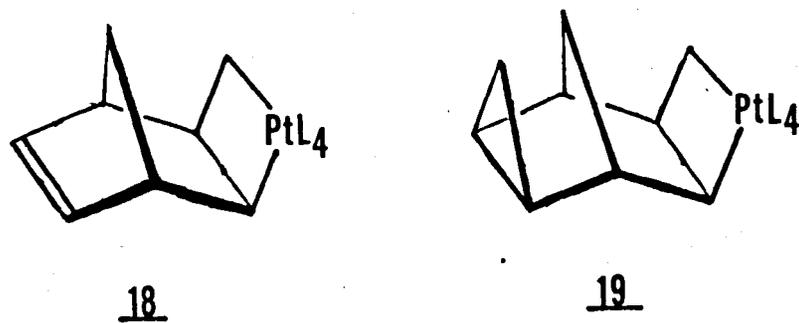
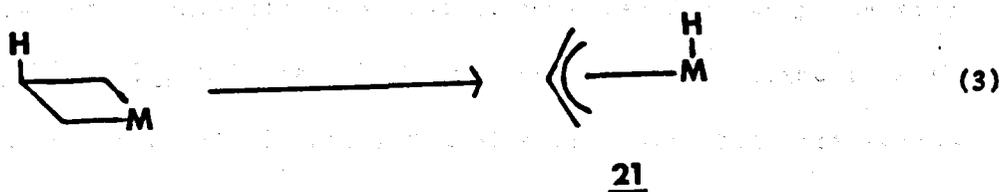


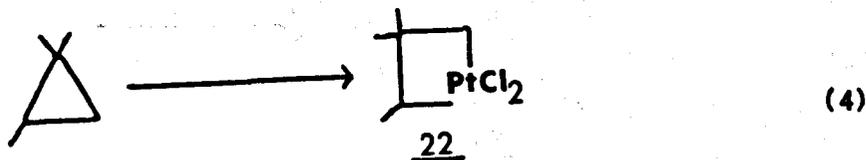
Figure 4. Platinum Complexes Characterized by Jennings and Waddington.

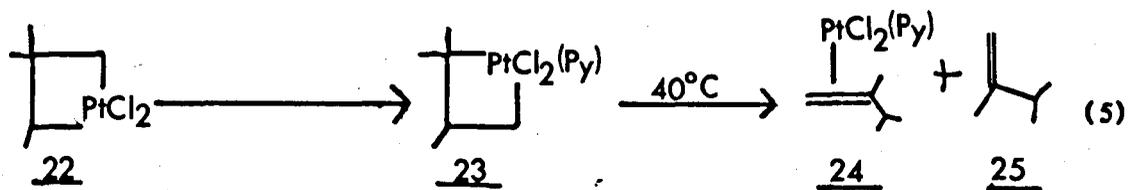
of platinacyclobutanes can be found in a review article by Puddephatt,⁶ and Ibers¹⁶ has published X-ray crystal data on some examples. No such intermediates have been isolated for iridium.

In both catalytic and stoichiometric reactions, metallocyclobutanes can go on to yield olefins as organic products. One major mechanistic pathway that has been implicated in the formation of olefins is β -hydride elimination. A hydrogen β to the metal in metallocyclobutane can be abstracted by the metal to give a π -allyl metal hydride (21) (equation 3).



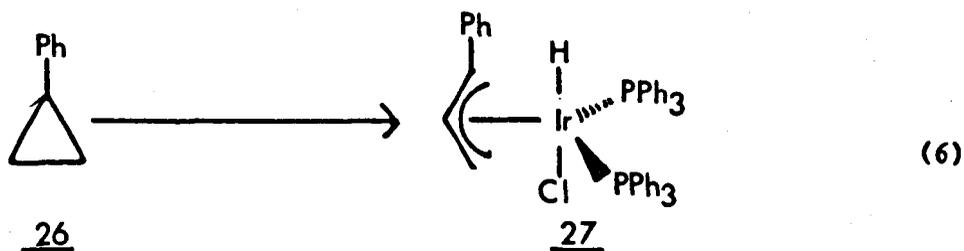
Cushman and Brown¹⁷ obtained dichloro-2,3,3-trimethyl-1-platinacyclobutane (22) from the reaction between 1,1,2-trimethylcyclopropane and Zeise's dimer (equation 4). Treatment of 22 with pyridine gave the rearranged platinacyclobutane 23 which upon heating to 40°C gave a mixture of olefin-platinum complex 24 and olefin product 25 (equation 5).





A more detailed investigation by Johnson and Cheng¹⁸ resolved the mechanism of this reaction to be consistent with β-hydride elimination from 23 to yield presumably a π-allyl platinum hydride which subsequently undergoes a reductive elimination to give 25. This mechanistic conclusion was reached by observing the production of 25a, 25b and 25c (Figure 5). Some β-hydride elimination from the hydrogens on the α-methyl groups was also observed, but abstraction of the ring hydrogens was preferred.

Although π-allyl metal hydrides have been implicated by several researchers as catalytic intermediates,^{7,10,19} no such intermediate had ever been characterized as a product from a β-hydride elimination reaction until 1979 when Ibers and Tulip²⁰ reported on the isolation of a π-allyl iridium hydride complex (27) from the reaction of phenyl cyclopropane (26) with IrCl(N₂)(Ph₃P)₂ (equation 6).



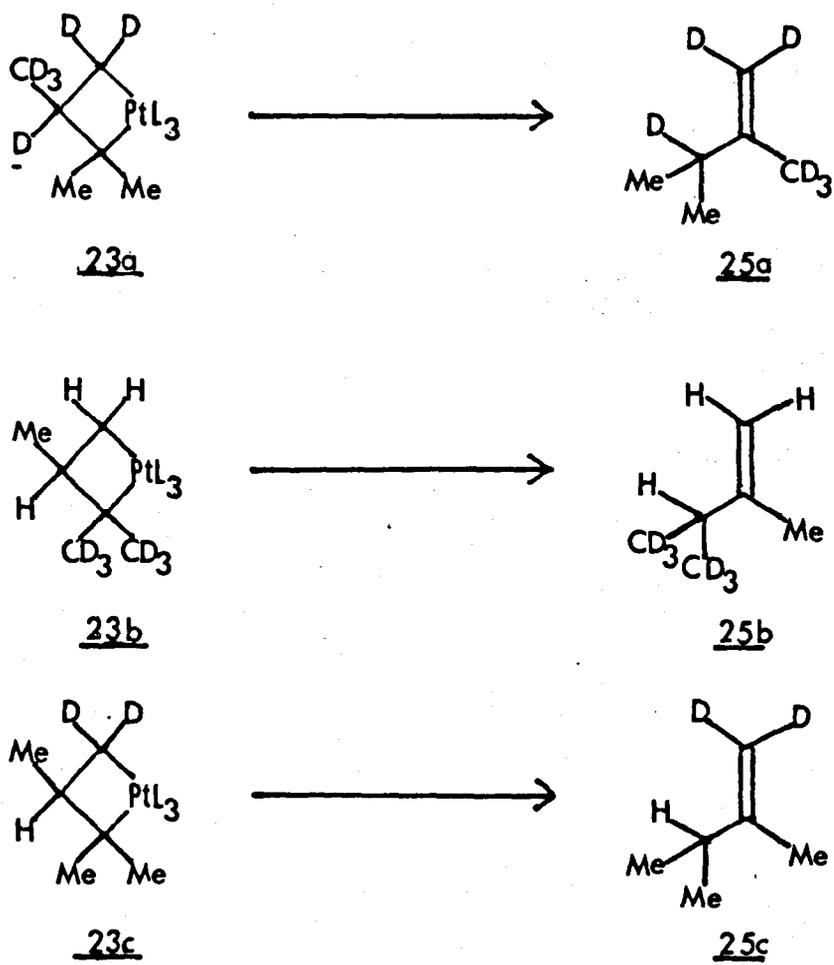


Figure 5. Production of Olefin Products from Deuterium Labeled 2,2,3-trimethyl-1-platinacyclobutane.

Product 27 was also obtained by the reaction of trans- β -methyl styrene and allyl benzene with the same iridium complex. The structure of 27 was confirmed by X-ray crystal data. Ibers attributes the isolation of 27 to its exceptional stability since attempts to obtain analogous complexes from cyclopropane and a number of simple olefins only gave organic products. Treatment of 27 with heat, CO or PF₃ gave β -methyl styrene as the only product.

The overall mechanism is depicted in Figure 6. Several points relative to the present research are demonstrated by this work of Ibers. First of course, β -hydride elimination is a viable decomposition pathway available to the iridacyclobutane 28. An equilibrium exists between the olefin product 30 and π -allyl hydride 27. In catalytic reactions the equilibrium lies furthest toward the free olefin, and in stoichiometric reactions the equilibrium favors metal complexes such as 27, 28 or 29. The position of equilibrium is suggested to be related to the thermodynamic stability of the iridium complex in question. Furthermore, the decomposition of 27 to 30 is regioselective. This regioselectivity is primarily due to the thermodynamic stability of the olefin. Starting materials are isomerized to the thermodynamically favored olefins, such as the isomerization of allyl benzene (31) to β -methyl styrene (30). One last point to consider in β -hydride eliminations is that the β -hydrogen and the metal must achieve a syn-periplanar configuration for β -hydride elimination to occur.^{10,20}

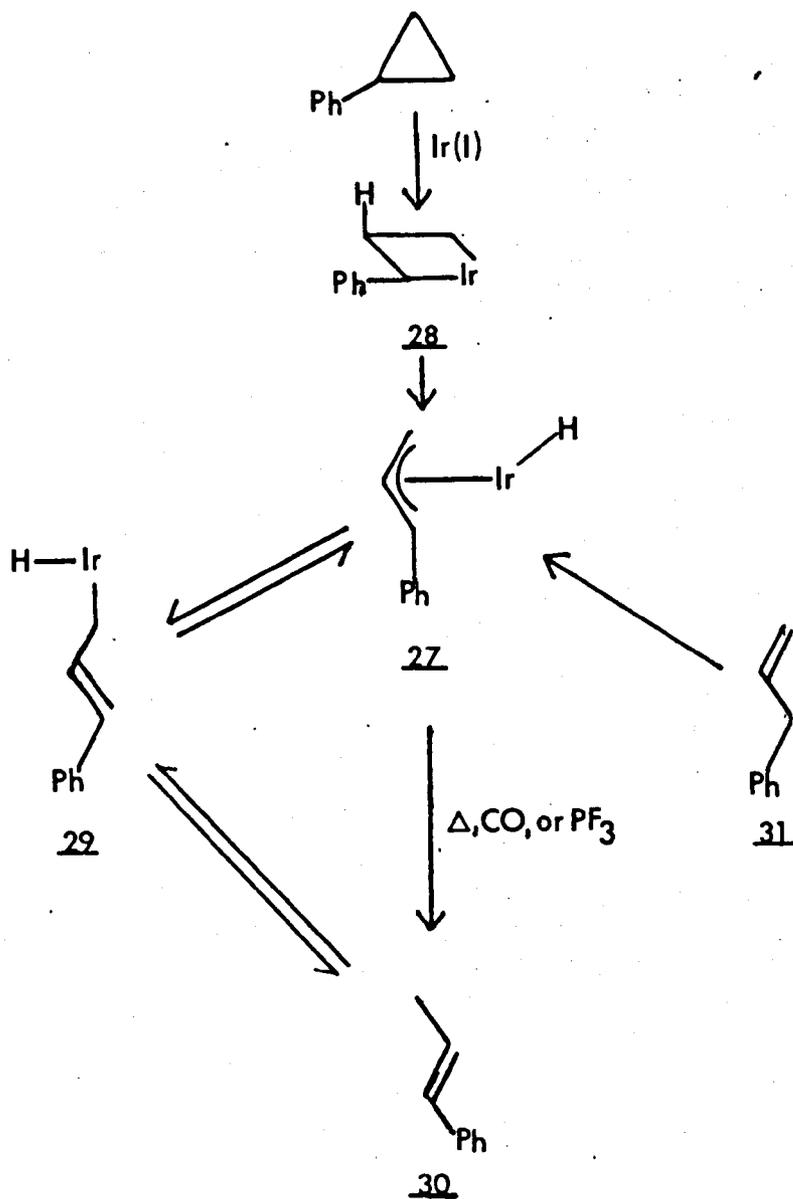
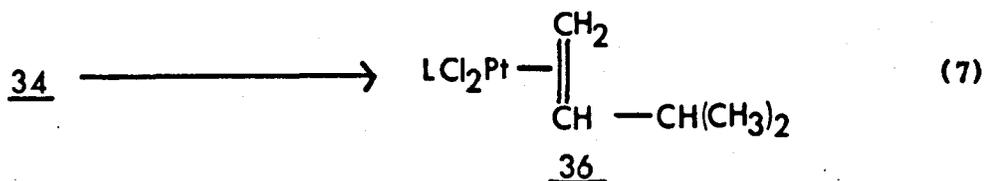


Figure 6. Reaction of Phenylcyclopropane with $\text{IrCl}(\text{N}_2)(\text{Ph}_3\text{P})_2$.

Other modes of decomposition are also possible for metallocyclobutanes and are related to the present investigation. Small structural differences in substrates can cause effects that make β -hydride elimination unfavorable. Geometric or steric constraints in which the proper geometric conformation for β -hydride elimination cannot be adopted, and electronic restrictions may alter the mode of decomposition to α -elimination. Puddephatt²¹ reported on a reaction involving a 1,3-hydride shift that was platinum mediated (Figure 7). In the mechanism proposed by Puddephatt, the platinacyclobutane 32 underwent loss of a ligand followed by abstraction of an α -hydride or deuterium to form 33 (note that depending on the position of platinum insertion, both possibilities result). The deuteride in 33 is then transferred to the next carbon via a reductive elimination resulting in platinum-carbon bond cleavage to give ylide 34. This ylide is then trapped by a ligand to give either 35 or 35a depending on the precursor platinacyclobutane. A similar mechanism in the same article explains the formation of olefin product 36. This product is obtained by a 1,2-hydride shift between 34 and 36 (equation 7).



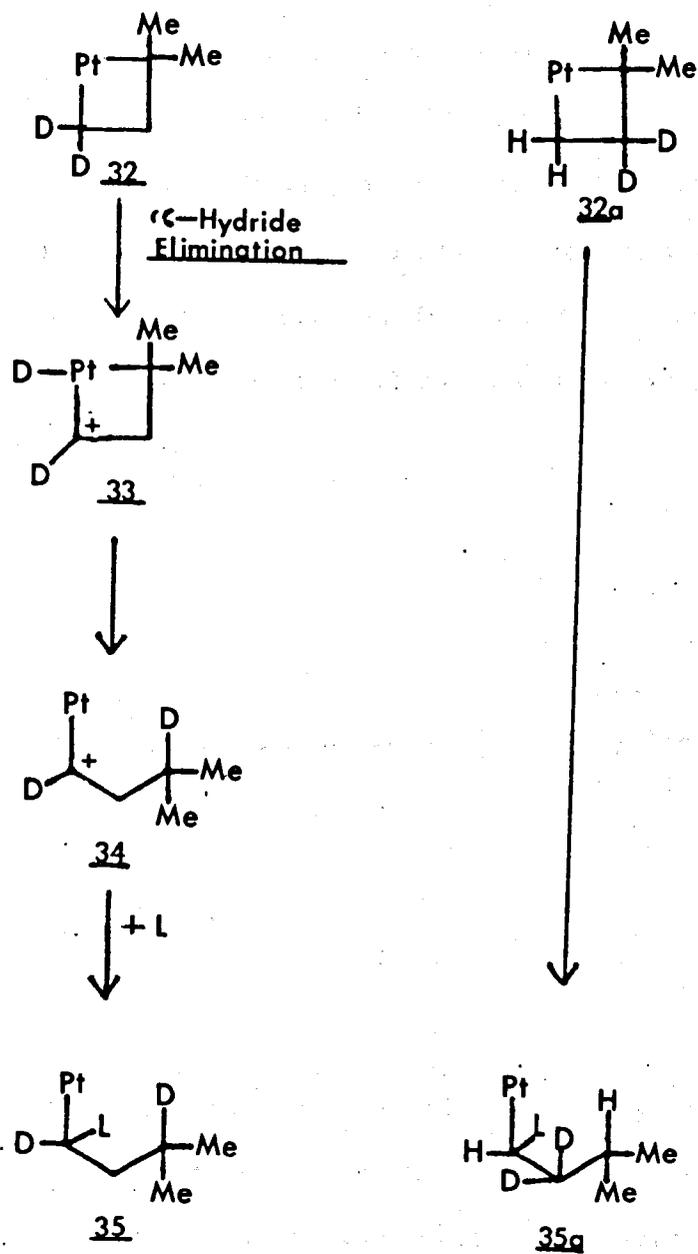
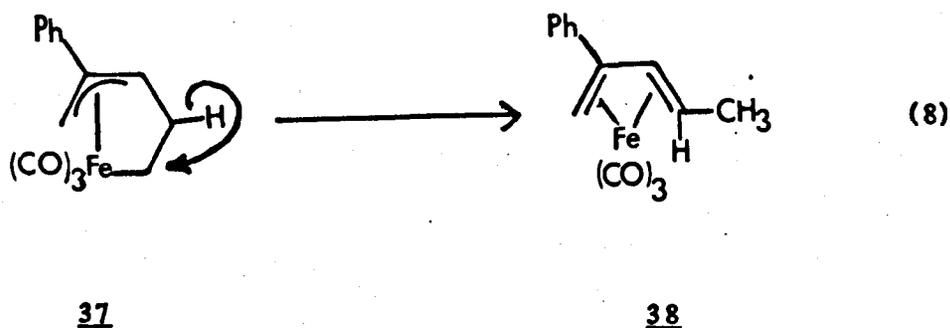


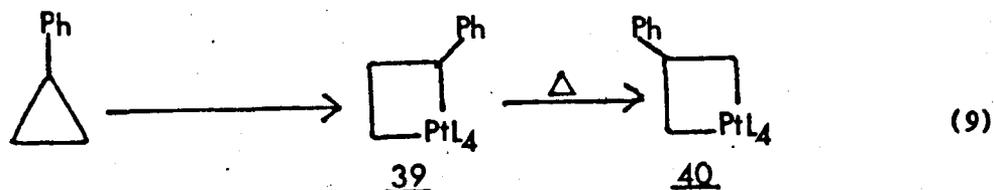
Figure 7. α -Hydride Elimination from a Platinacyclobutane.

A 1,2-hydride shift to displace a metal from a carbon in an Sn2 fashion is not commonly suggested as a mechanistic possibility. Katz²² did consider such a possibility in the rhodium catalyzed isomerization of 11, but subsequently demonstrated another mechanistic scheme to be more likely. The work by Katz will be discussed shortly, but an Sn2 displacement of iridium by a 1,2-hydride shift is consistent with some results obtained in this investigation. A related example was demonstrated by Sarel²³ in which iron complex 37 underwent a 1,2-hydride shift to give the η^4 -Fe complex 38 (equation 8.)

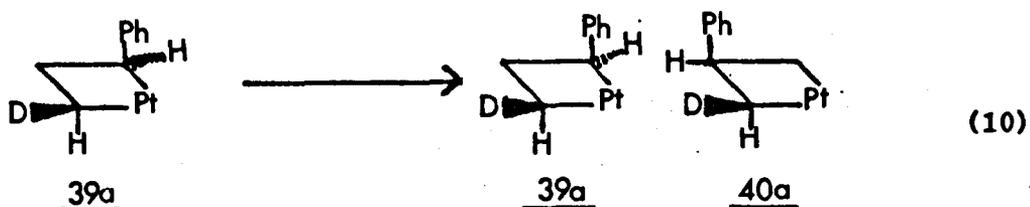


Metallocyclobutanes are known to yield starting cyclopropane as thermolysis products⁶ (see equation 2). This shows that oxidative addition of a cyclopropane to a metal center is reversible. On a similar note, Puddephatt²⁴ found that the platinacyclobutane 39, obtained from the reaction of Ziese's dimer with phenylcyclopropane, isomerized to 40 upon heating at 50°C for 45 minutes in chloroform.

A 1:2.3 ratio of 39 to 40 was obtained (equation 9).



Crossover experiments done by Casey²⁵ with *p*-tolylcyclopropane showed this isomerization to be intramolecular since no (*p*-tolyl)-platinacyclobutanes were recovered as products. Further, deuterium labeling experiments showed retention of stereochemistry in the products (equation 10) indicating that disrotatory ring opening to a free olefin and a metal carbene is not likely since loss of stereochemistry would be expected.



Three mechanisms were postulated to explain these results and are illustrated in Figure 8. The Puddephatt²⁴ mechanism suggests a concerted process in which the dashed lines in structure 41 indicate bond reorganization. Casey²⁵ proposed the other two mechanisms. The

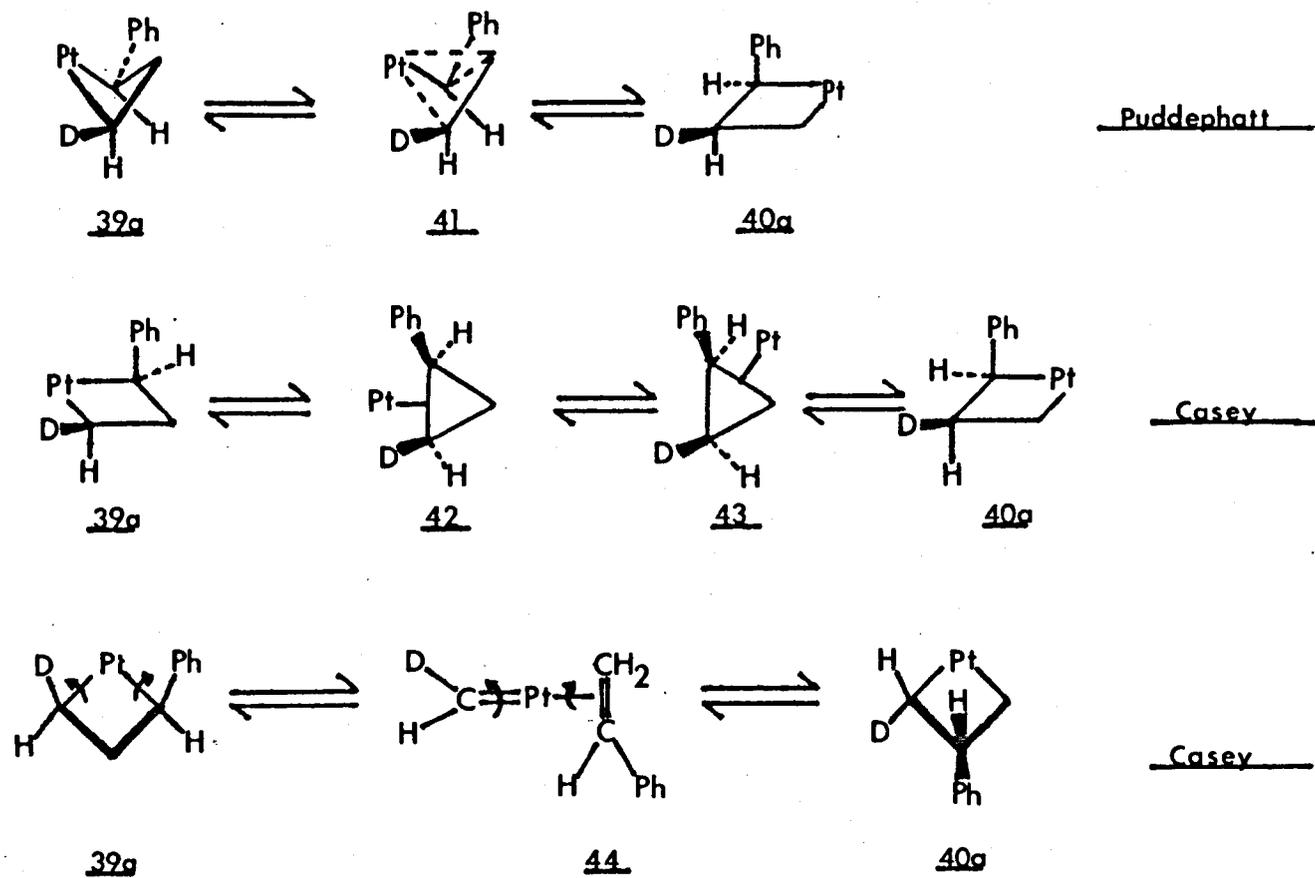
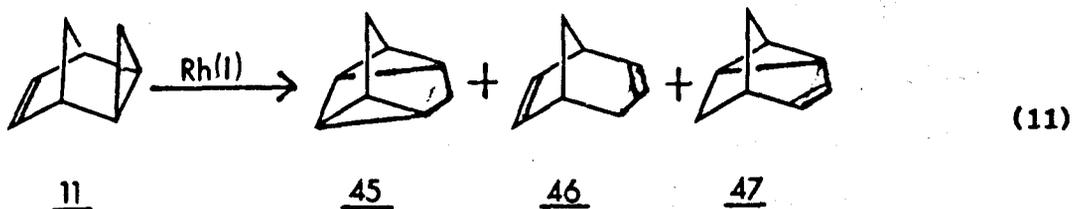


Figure 8. Postulated Mechanisms for the Isomerization of (Phenyl)-Platinacyclobutanes

first involves deinsertion of the metal to give the edge complex 42 which undergoes an edge to edge isomerization to 43 followed by reinsertion to give 40a. The second mechanism involves a disrotatory ring opening of 39a to give metalcarbene-olefin complex 44. The olefin and carbene are coplanar and perpendicular. A concerted rotation of the two ligands either gives 39a or 40a. As to which of these three mechanisms is most correct is not known. As will become clear later, isomerizations such as these may be implicated in the discussion of iridium catalysis. Future reference to this sort of isomerization will simply be referred to as a 1,2-metallo shift.

Cyclopropanes contained within rigid ring systems also undergo valence isomerization upon treatment with transition metal complexes; but reaction with these types of substrates have not been as heavily investigated. The only metal complexes that have been isolated and characterized from rigid ring cyclopropane substrates are those reported by Jennings and Waddington^{14,15} illustrated in Figure 3. In addition to the work by Volger, which has already been mentioned, several other examples of these reactions appear in the literature.⁷ Of particular interest to this research is the work reported by Katz^{22,26,27,28} on the rhodium catalyzed isomerization of 11. Katz found that reaction of 11 with $\text{RhCl}(\text{Ph}_3\text{P})_3$ gave three products as summarized in equation 11.



The mechanism of this reaction was pursued using deuterium labeled 11a and the overall mechanism shown in Figure 9 was postulated by Katz to account for the observed results.²⁸ No kinetic deuterium isotope effect was noted since in a mixture of 11 and 11a both substrates were consumed at an equal rate. However, the relative ratio of tetracyclo[3.2.1.0^{2,7}.0^{4,6}]octane (45) in the product mixture increased when 11a was the starting substrate. Product 45 showed no deuterium migration, whereas bicyclo[3.2.1]octa-2,6-diene (46) and tricyclo[3.2.1.0^{2,7}]oct-3-ene (47) showed deuterium migration each into an endo position in the product. The rate determining step was deduced to be oxidative addition of the cyclopropane onto the rhodium, but the product determining steps ostensibly came after the metal insertion. The deuterium isotope effect was a result of a competition between β -hydride elimination and complexation of rhodium with the distill olefin bond in structure 48. Complexation of the olefin with rhodium in 48, followed by reductive elimination of the metal leads to 45, whereas when a similar pathway after β -hydride elimination occurs, 47 is obtained. Product 46 shows an overall 1,2-hydride shift which is mediated by a β -hydride elimination to form π -allyl hydride 49 from rhodacyclobutane 48. Intermediate 49 then rearranges to give the η^1 -allyl complex 51 which upon reductive elimination yields 46.

The products obtained from the reaction of rhodium or platinum²⁹ with cyclopropanes in rigid ring matrices typically show a net cleavage of the cyclopropane ring juncture carbon-carbon bond.

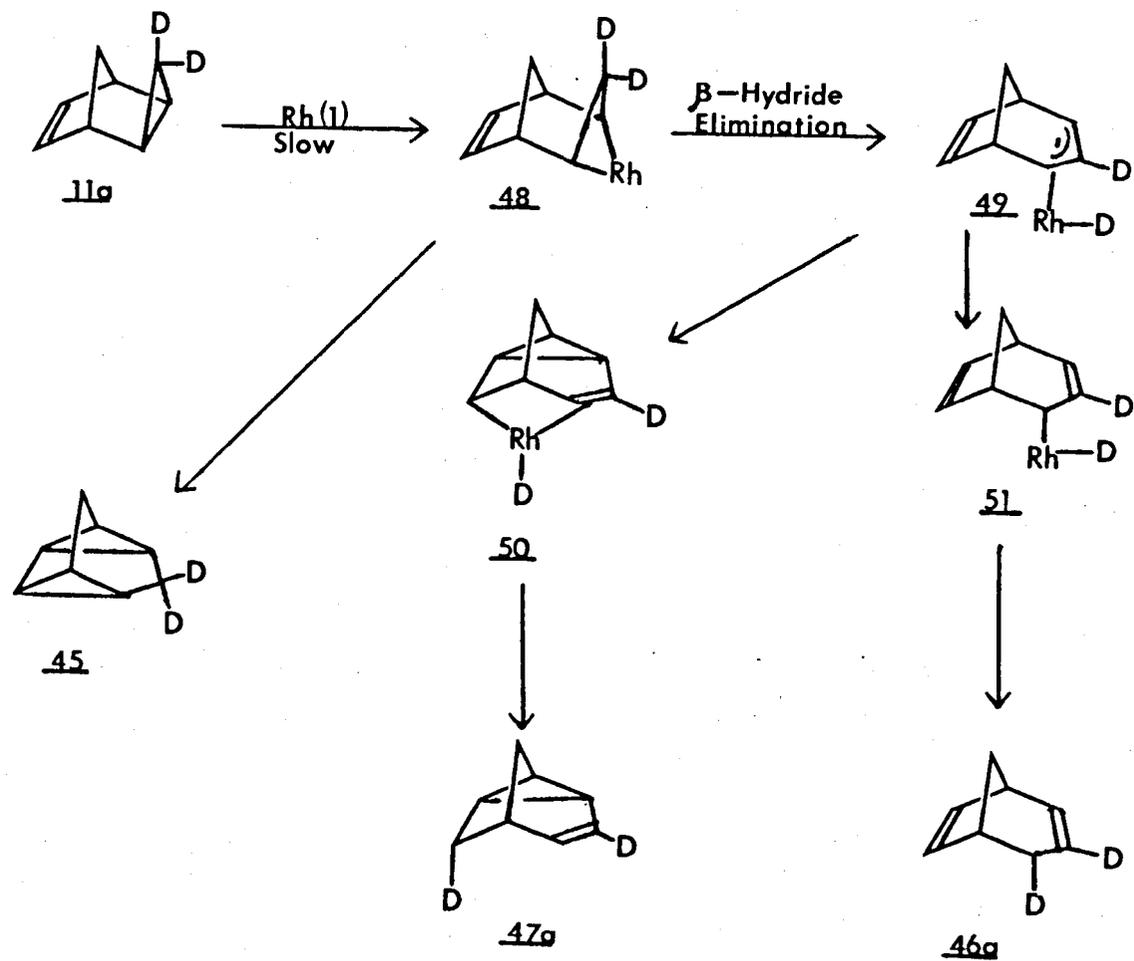


Figure 9. Mechanism for the Rhodium Catalyzed Valence Isomerization of **11**.

Furthermore, platinum is stoichiometric rather than catalytic in these reactions.¹⁴ Iridium, on the other hand, is catalytic and shows a preference for the formation of exocyclic methylene products which equate to the net cleavage of the cyclopropane bonds opposite to those cleaved in platinum and rhodium reactions. Other than the reactions reported by Volger, no research has been reported on the reactions of iridium catalysts with cyclopropanes contained in rigid polycyclic ring systems. The variety of tricyclic and tetracyclic cyclopropane containing compounds used as substrates for transition metal reactions is also limited, and much information may be gleaned from a greater variety of these sorts of substrates. As has been suggested by several researchers in this field, small structural changes in organic substrates can alter reaction pathways significantly. Finally, changes in reaction conditions could possibly yield reaction of substrates that were previously reported to be unreactive.

The work reported in this thesis was undertaken primarily as an exploratory investigation. By the use of deuterium labeling and various structural modifications of the substrates used, it was hoped to gain insight into the reaction of Vaska's catalyst with substrates containing cyclopropane moieties within a rigid polycyclic framework. Considering the available literature in combination with the results obtained in this research, consistent mechanistic schemes will be proposed. This work is considered to be a broad basis for further investigation rather than a detailed mechanistic investigation. A

more detailed investigation would require kinetic data, which was not obtained in the course of this research, as well as far greater insight into the nature of the active catalyst or catalysts. No serious attempts were made to investigate the inorganic aspects of these catalytic reactions, and the structure of the actual catalytic species is still unknown. It is assumed that the active catalyst is a low valent, coordinately unsaturated complex. For purposes of discussion and schematic representation, it will simply be referred to as Ir(1).

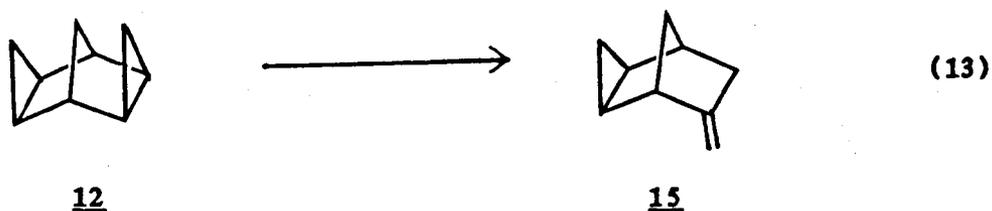
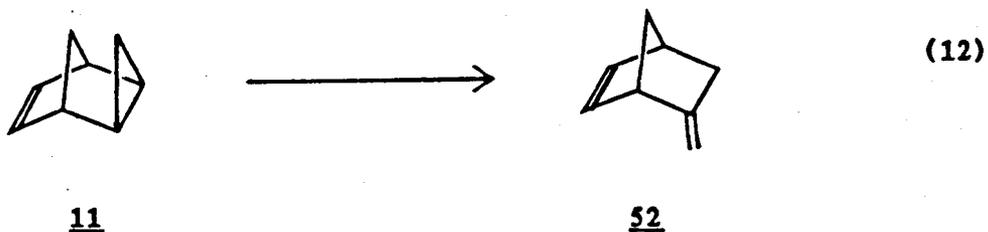
DISCUSSION

Section I

Reactions with Non-Deuterated Substrates

Preliminary Investigation

Volger,^{11,12} in 1969, reported on the reactions of 11 and 12 with Vaska's catalyst. At 130°C and using benzene as the reaction solvent, substrates 11 and 12 were quantitatively converted to 5-methylenebicyclo[2.2.1]hept-2-ene (52) and 15 respectively (equations 12 and 13).

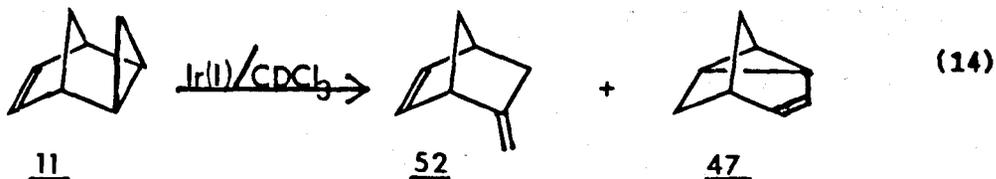


In attempting to reproduce Volger's work, reaction mixtures of 11 and 12 were placed in glass vessels, degassed by several successive freeze-thaw cycles under vacuum and finally sealed under vacuum. Analysis of the reaction mixtures showed that no reaction

had taken place after heating at 130°C for 2 hours. The experiments were repeated with heating for 32 hours, and still no observable reaction was obtained.

The reactions were then performed without N₂ purging or degassing prior to sealing the reaction vessels. Both reactions were successful upon heating for 2 hours, but the yields were not as high as expected. Reaction of 11 produced a 34% yield of 52 as the only product, and about 60% of 11 was recovered. Reaction of 12 gave a better yield of product, in that 15 was recovered, as the only product, in 60% yield. Repeated experiments gave consistent results. The results of these experiments demonstrated a definite need for oxygen as a reaction component, however the reason is not clear. The need for oxygen in these reactions will be addressed further in the conclusion of this thesis.

At this point it was decided to attempt the reaction of 11 in deuteriochloroform (CDCl₃). This was done to facilitate the analysis of reaction mixtures by ¹H NMR spectroscopy while using a less expensive deuterated solvent. The reaction proceeded smoothly to afford two products in an overall higher yield than when benzene was used as the reaction solvent. Compound 52 was produced in 33% yield and 47 was produced in 28% yield. Equation 14 illustrates these results and gives relative product yields. Relative yields will henceforth be reported. Absolute yields, relative to an internal standard, will be found in the experimental portion of this thesis.



The use of CDCl₃ as the reaction solvent caused two effects. First, the reaction went further toward completion, and second, two products were obtained rather than one. The nature of the effect of chloroform remains unknown, but certain possible aspects of the reaction were investigated. A thermal process to yield 47 was considered since 47 had been reported as a thermal isomerization product of 11 at higher reaction temperatures.³⁰ Also the possibilities of a radical or an acid catalyzed process were considered. All three possibilities were ruled out by performing control experiments. Substrate 11 was subjected to identical reaction conditions, excluding catalyst, and only 11 was recovered after 2 hours. The possibility of acid catalysis was eliminated by an experiment in which Na₂CO₃ was added along with all of the other reaction components. A radical process was ruled out by running the reaction with all of the reaction components and 10% (V/V) cumene as a radical inhibitor. Both the Na₂CO₃ and the cumene reactions produced results similar to those obtained in the standard reaction. Thus, it appears that 47 is a product of iridium catalysis.

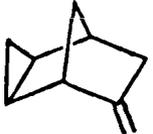
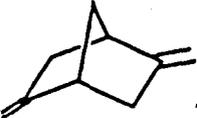
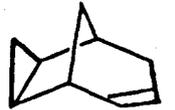
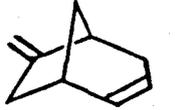
The reaction of 11 was also carried out using identical conditions except for the solvent used. Tetrahydrofuran, methanol and dichloromethane were independently used in place of chloroform. The catalyst failed to dissolve in any of these solvents, even at elevated temperatures, and no reaction ensued.

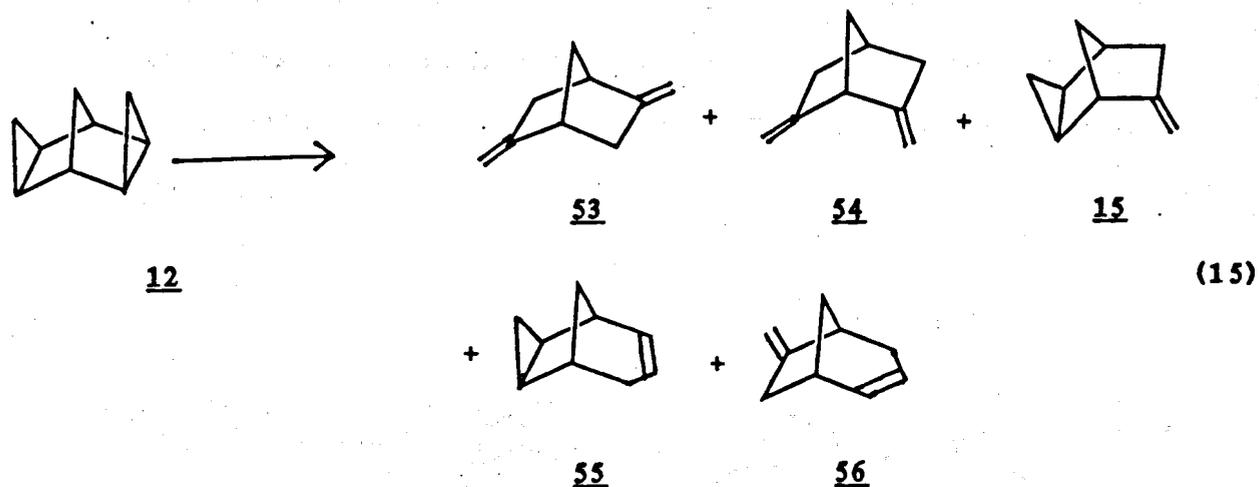
The role of chloroform in this reaction is obscure and has not been pursued. One possible explanation for the chloroform effect is that the polarity of this solvent may be stabilizing a polarized, if not charged, transition state or intermediate in or near the rate determining step. As will be seen later, carbocation intermediates are implicated in the reaction of some substrates. Transition state charge separation in all of these reactions is a reasonable hypothesis.

Reaction of 12 with Vaska's Catalyst in CDCl_3

When 12 was reacted with Vaska's catalyst in benzene, 15 was the only product obtained. The second cyclopropane ring did not undergo reaction. In light of the results obtained for the reaction of 11 in CDCl_3 , it seemed reasonable that the reaction of 12 might also be made to go beyond the reaction of one cyclopropane ring. A three hour reaction with iridium in CDCl_3 at 130°C gave five products. The product structures are given in equation 15. The relative yields of the products in equation 15 are presented in Table 1 along with data obtained from product mixtures resulting from longer reaction times.

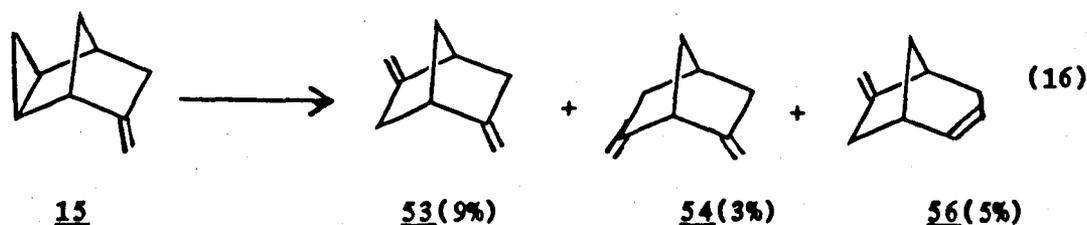
Table 1. Relative Product Yields from the Reaction of 12 with Vaska's Catalyst Relative to Time.

Product	% Yield Relative to Time		
	3 hours	6 hours	9 hours
 <u>15</u>	79	71	60
 <u>53</u>	9	17	23
 <u>54</u>	2	5	8
 <u>55</u>	2	—	—
 <u>56</u>	3	7	9
 <u>12</u>	5	—	—



The reaction of 12 was run for longer periods of time in an attempt to drive the reaction further toward completion. As can be seen from the data in Table 1, 15 was the predominant product even after 9 hours. Only 5% 12 was present after 3 hours and neither 12 nor exo-tricyclo[3.3.1.0^{2,4}]non-6-ene (55) were observable after 6 hours. It should be further noted that the percent change from 3 to 6 hours is similar to the change from 6 to 9 hours for products 15, 2,5-dimethylenebicyclo[2.2.1]heptane (53), 2,6-dimethylenebicyclo[2.2.1]heptane (54), and 6-methylenebicyclo[3.2.1]oct-2-ene (56). The indication is that the rate of formation of 53, 54 and 56 remain fairly constant between 3 and 9 hours and that the rate of reaction of 15 is also constant between 3 and 9 hours. It appears that 15 reacts at a much slower rate than 12 since 12 is virtually consumed after 3 hours. Product 15, on the other hand, is present in a relatively large amount even after 9 hours. Two possibilities exist

to explain this observation. First, catalytic activity of the iridium decreases with time, or second, 15 is less reactive than 12. As a test, 15 was isolated from a reaction mixture and subjected to identical reaction conditions for 3 hours. The results are presented in equation 16.



Production of 53, 54 and 56 paralleled the percent changes for 3 hour increments in the reactions using 12 as the starting substrate. Thus 15 reacts at a slower rate than does 12. Homoconjugation of the exocyclic methylene with the cyclopropane might cause electronic effects, in the cyclopropane, that retard iridium complexation or subsequent steps in the reaction mechanism. Using a frontier molecular orbital approach, one can envision electron donation from the HOMO of the cyclopropane to the LUMO of the olefin (see Figure 10). If it is assumed that in cyclopropane-iridium reactions the primary bonding interactions are between an empty d orbital of the metal and a HOMO of the cyclopropane, then this analysis might be at least partially valid.³ Substrates with strongly electron withdrawing groups in conjugation with a cyclopropane ring do not give catalytic reaction. Reaction was attempted with three substrates

containing a carbonyl functionality. They were bicyclo-[4.1.0^{1,6}]hept-2-one (57), bicyclo[3.1.0^{1,5}]hex-2-one (58) and exo-tricyclo[3.2.1.0^{2,4}]oct-6-one (59). None of these three substrates afforded catalytic reaction (equation 17).

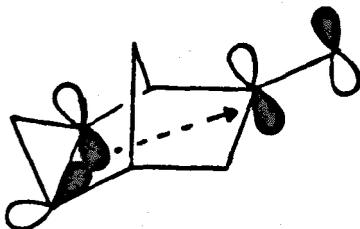
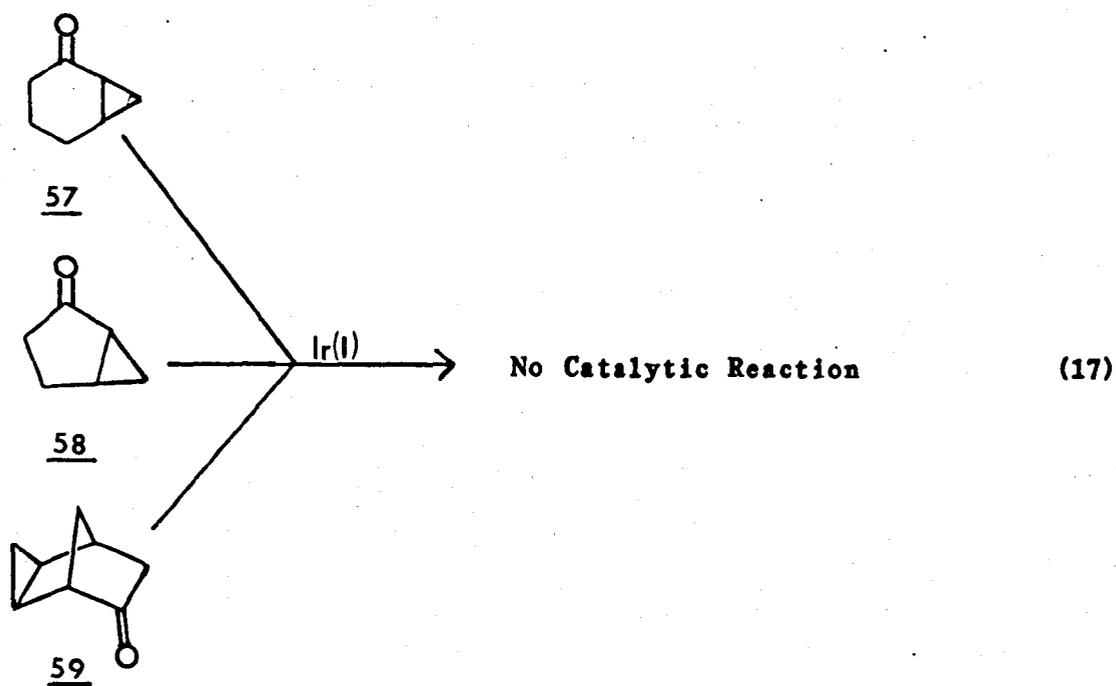


Figure 10. Through Space Electron Donation from a Cyclopropane HOMO to the Olefin LUMO in Compound 15.

Another possible explanation is that the exocyclic methylene might effectively compete with the cyclopropane for available bonding sites on the iridium. Kinetic analysis would be useful to discriminate such a competitive process from other effects, but reaction of 15 is inordinately slow to be attributed solely to product inhibition.

Reactions of substrates 11 and 12 with iridium demonstrates a fair amount of regioselectivity. Exocyclic methylenes are favored products from both substrates. Reaction of 15 also shows a great deal of regioselectivity in that 53 is preferred over 54 by about 4 to 1. More discussion of regioselectivity will be given after more examples are provided.

One topic that has not been mentioned is the identification of products. Product identification relied heavily on ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Corroboration of structure was obtained, whenever possible, with elemental analysis or mass spectroscopy. Since ^1H NMR was very important to this work for both structure elucidation and specific proton assignment (for deuterium labeling studies), a fairly detailed discussion of ^1H and ^{13}C NMR data will be presented in Section II of this discussion. Suffice it to say for now that products 15 and 55 have been previously reported in the literature^{12,29} and products 53, 54 and 56 have not been previously reported.

Preliminary Mechanisms

It might be helpful at this point, and useful for further discussion, to outline the mechanistic schemes that were being considered as working models early in this investigation. The mechanisms in Figure 11 show the initially proposed pathways to products. All steps have ample literature precedence. The initial step for both paths A and B is insertion of iridium into a carbon-carbon bond of the cyclopropane to give exo-iridacyclobutane 60 or endo-iridacyclobutane 64. Insertion is thought to be the slow step in similar reactions with other metals.²⁸ Once formed, the metallocyclobutanes could conceivably isomerize in a fashion as described by either Casey or Puddephatt.^{24,25} Using this logic, insertion of the metal might be exclusive to give, for instance, only 64 which subsequently rearranges to 60. Such a rearrangement will, henceforth, be termed a 1,2-metallo shift. The next step would be β -hydride elimination to give the iridium hydride complexes 62 or 66. Evidence exists for the intermediacy of π -allyl iridium hydride complexes, such as 61 or 65, in the formation of 62 and 66.¹⁶ Finally, reductive elimination of iridium from 62 and 66 gives products 63 and 67. For the sake of simplicity, products such as 63 will be termed exocyclic methylenes and products such as 67 will be termed ring expanded olefins.

Reaction of the Saturated Analogues of 11 and 13

One way to pursue this chemistry was to see the effects of substrate structural modifications on the products obtained by

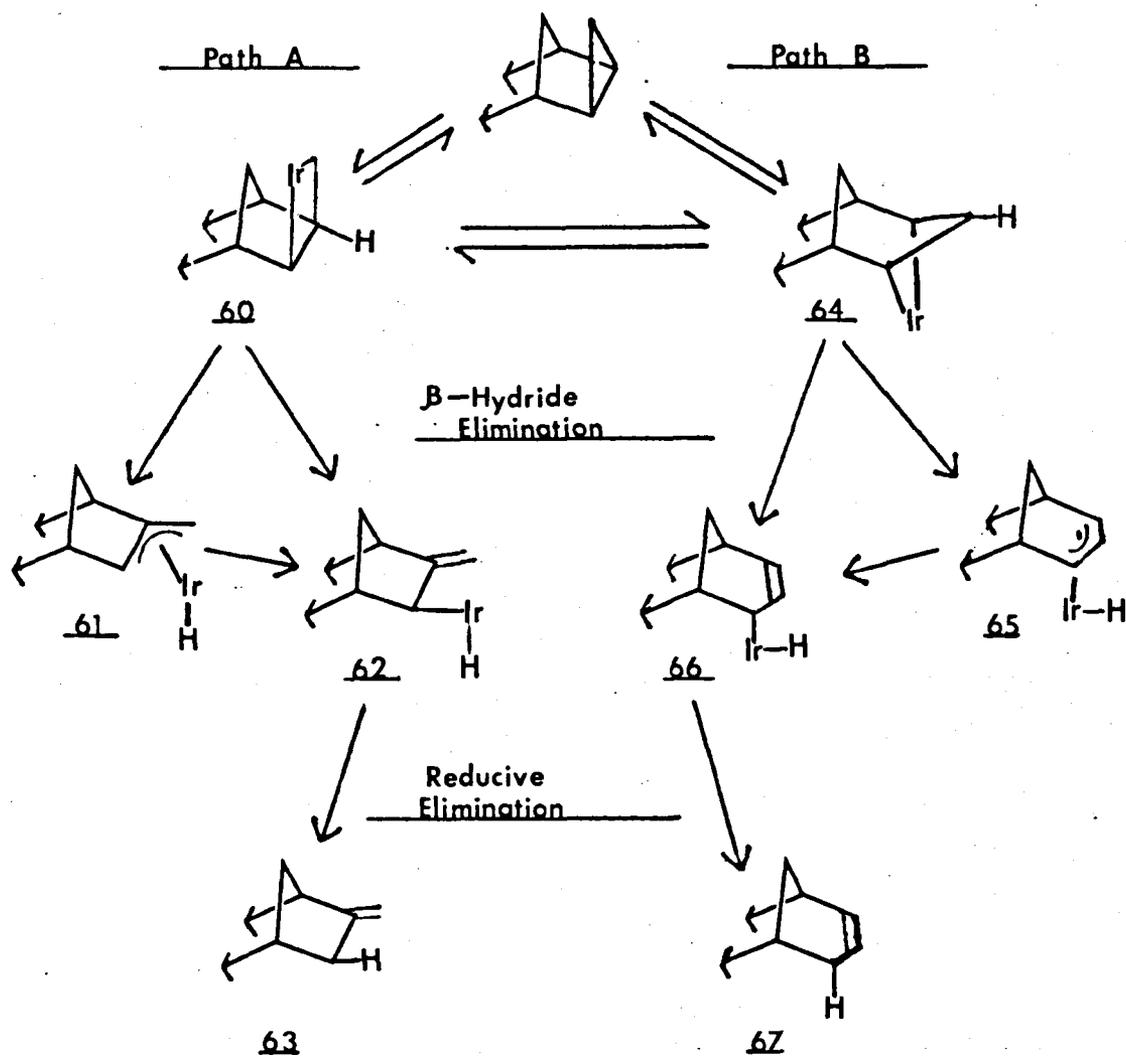
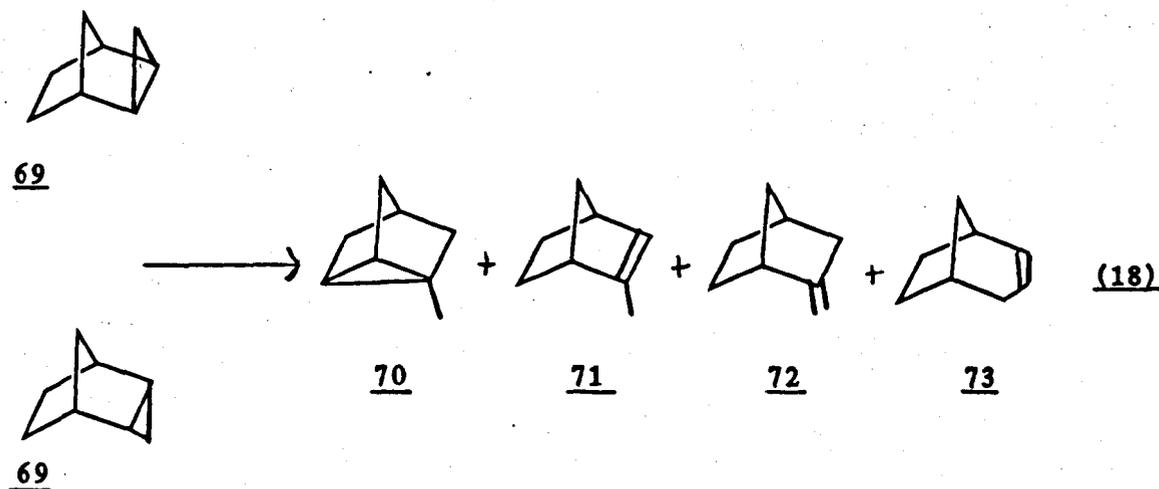


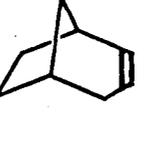
Figure 11. Preliminary Mechanistic Scheme for the Formation of Exocyclic Methylene and Ring Expanded Products.

iridium mediated reaction. To that end, and since reaction is more facile when CDCl_3 is used as the reaction solvent, it was decided to attempt reactions in CDCl_3 with substrates that were unreactive in benzene. The saturated analogues of 11 and 13, exo-tricyclo[3.2.1.0^{2,4}]octane (68) and endo-tricyclo[3.2.1.0^{2,4}]octane (69) respectively, gave no catalytic reaction when benzene was used as the reaction solvent. When reaction of 68 and 69 were run using CDCl_3 as the solvent, both gave good product yields. The results of these two reactions are summarized in equation 18 and in Table 2.



Both 68 and 69 gave 2-methylene bicyclo [2.2.1]heptane (72) as the major product. Compound 72, 2-methylbicyclo[2.2.1]hept-2-ene (71) and bicyclo[3.2.1]oct-2-ene (73) are known compounds (see experimental portion of this thesis). 2-methyltricyclo-[2.2.1.0^{2,6}]heptane (70) has no precedence in the literature and its structure has not been unambiguously proven in this research.

Table 2. Relative Product Yields from the Reaction of 68 and 69 with Vaska's Catalyst in CDCl_3 at 130°C .

Product	Relative percent from Substrate (Reaction Time)		
	68 (3 hours)	68 (4 hours)	69 (3 hours)
 <u>70</u>	—	3.5	—
 <u>71</u>	6	9.5	6
 <u>72</u>	47	78.5	61
 <u>73</u>	3	4.5	27
 <u>68</u>	43	4	—
 <u>69</u>	—	—	6

However, ^1H NMR data is consistent with the assigned structure (also see experimental portion of this thesis).

Products 72 and 73 are consistent with the mechanistic schemes in Figure 11. The isolation of 71 from these reaction mixtures adds another dimension to the proposed mechanism. Formation of 71, relative to the mechanism in Figure 11, can be explained as depicted in Figure 12. It is interesting to note that the ratio of 71 to 72 is fairly constant in all three product mixtures.

Path A (of Figure 12) is fundamentally identical to the mechanism proposed in Figure 11 up to the formation of the exocyclic methylene. Subsequent complexation of the iridium with the exocyclic methylene olefin followed by β -hydride elimination will yield the π -allyl complex 61. Complex 61 could also be formed directly from decomposition of the iridacyclobutane by β -hydride elimination (Path C). Once formed, 61 undergoes bond reorganization to yield iridium hydride 75 which, upon reductive elimination, gives the observed olefin methyl product 71. Path B describes another route for the decomposition of the iridacyclobutane yielding, again, intermediate 75. The formation of 71 from 69 can be perceived as occurring through analogous pathways.

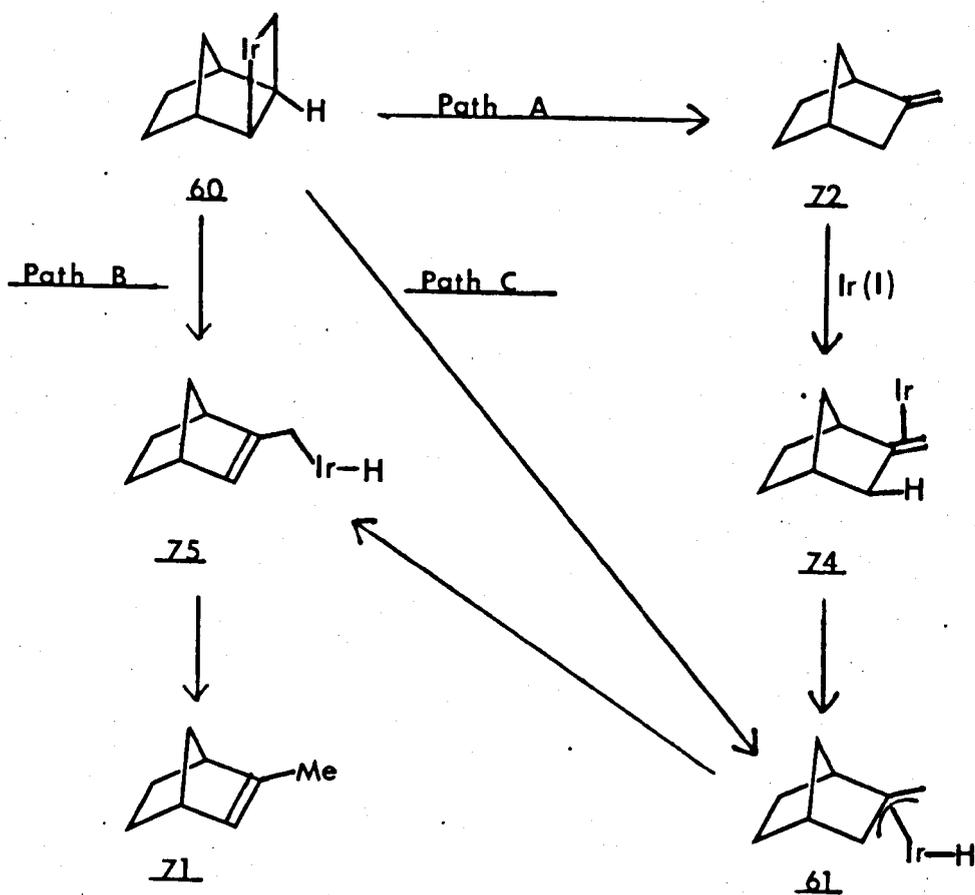


Figure 12. Possible Mechanistic Pathways to 71 from Substrates 68 or 69.

Product 70 is most likely formed in a fashion similar to 47 and will be discussed along with other similar products. Product 70 is not observable until late in the reaction and is most likely a product of the reaction of 71 with iridium.

It is also interesting to note the relative yields of 73 with respect to starting substrate. Product 73 represents a much larger proportion of the product mixture from the reaction of 69 than from 68. Considering the mechanism already proposed, the two intermediate iridacyclobutanes leading to 73 from 68 and 69 are 76 and 77 respectively (Figure 13).

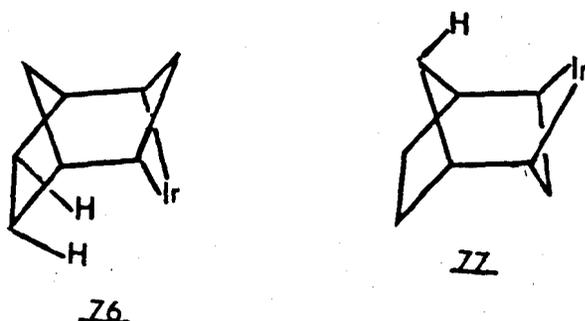


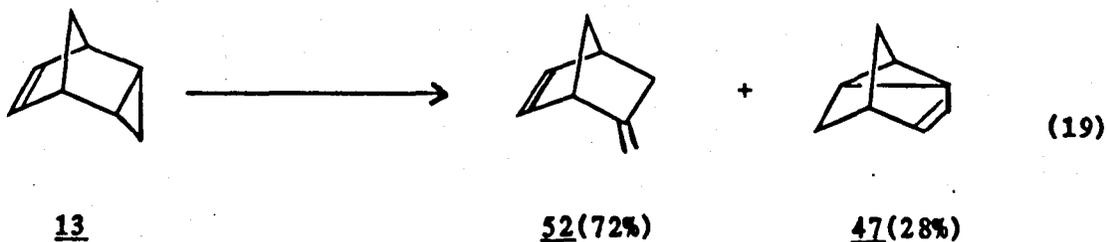
Figure 13. Iridacyclobutane Intermediates from Substrates 68 and 69.

The formation of 76 by direct attack of iridium from the endo side of the cyclopropane of 68 would be more sterically hindered than formation of 77 by direct attack of iridium from the exo side of the cyclopropane in 69. The endo protons on C₆ and C₇ shield the endo-cyclopropane bond of 68 to a greater extent than the bridge proton of 69 shields the exo-cyclopropane bond. The steric interactions between the ligands on iridium and the neighboring atoms on the carbocycle are difficult to assess. No analogous iridium

complex has ever been isolated, much less characterized.

The Reaction of Substrate 13 and 85

Substrate 13 was reported to be unreactive with Vaska's catalyst in a benzene solution.^{11,12} In CDCl_3 the reaction of 13 goes virtually to completion in three hours to give 52 and surprisingly, 47. The results of this reaction are summarized in equation 19. The same control experiments that were run with 11 were also run with 13, and the results were analogous. The products, 52 and 47, are a result of iridium catalysis.



Product 52 can be rationalized as coming about via a scheme analogous to that proposed in Figure 11 (Path A). However, 47 does not fit the mechanistic scheme proposed as Path B in Figure 11. The equivalent of an inversion of configuration must take place at either C_2 or C_4 of 13 to form 47. Two different mechanistic schemes to account for the observed results are considered in Figures 14 and 15.

The Puddephatt rearrangements²⁴ nicely accommodate a 1,2-metallo shift equilibrium between 78 and 79, but 47 is not easily obtained from either of these intermediates. So, a 1,3-metallo shift was

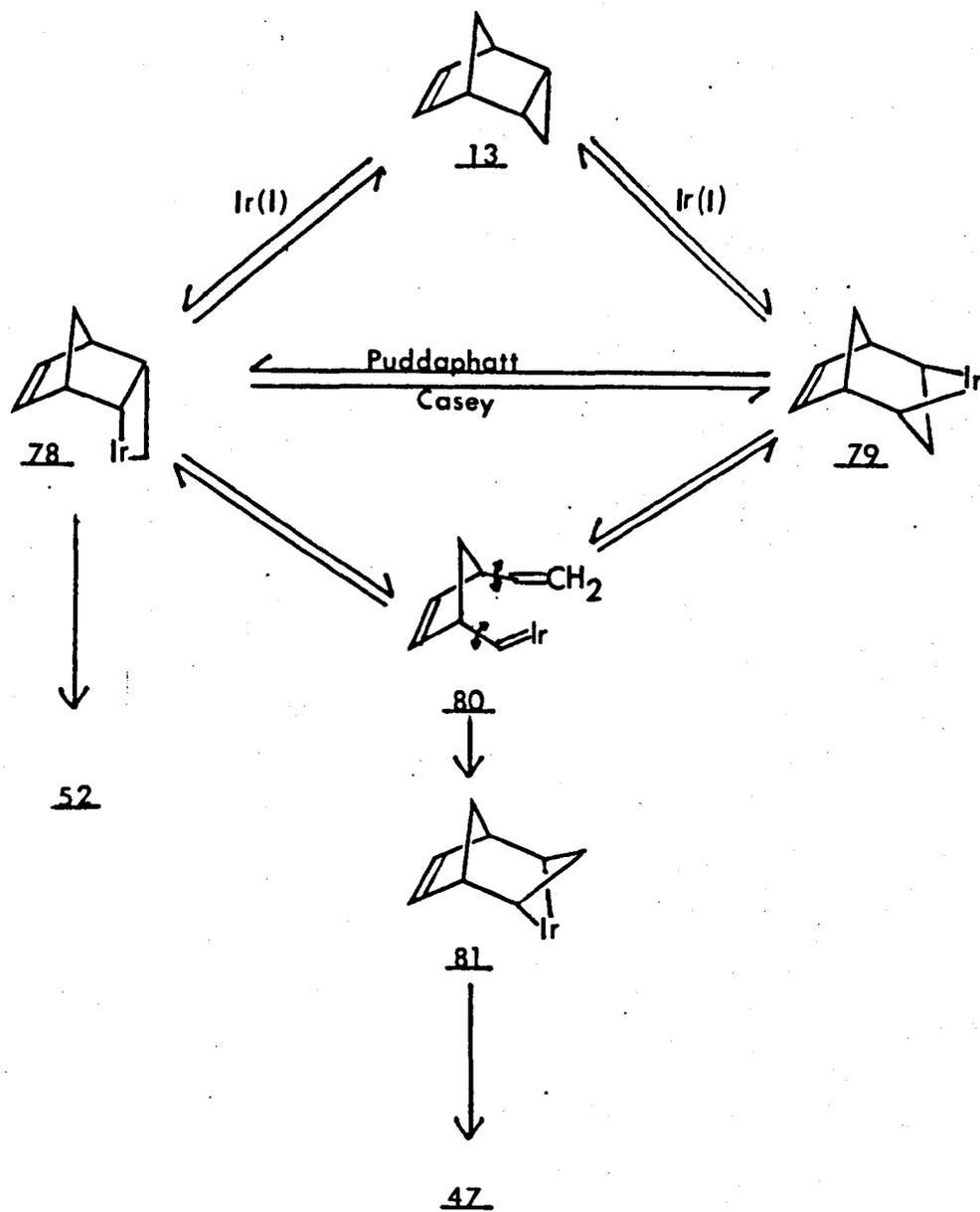


Figure 14. Production of 47 Through a 1,3-Metallo Shift Mechanism.

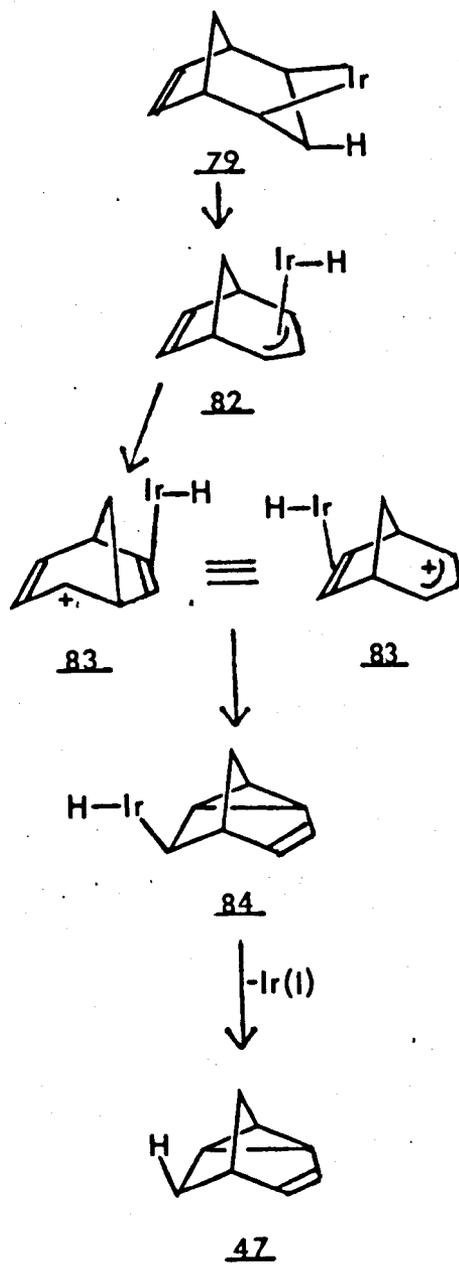


Figure 15. Production of 47 Through a 1,2-Bridgehead Shift Mechanism.

considered as a possible route to the product. A 1,3-metallo shift would yield an intermediate 81 identical to that proposed in Figure 11 (Path B). Subsequent mechanistic steps as described by Katz²⁸ (see Figure 9 on page 22) would yield the observed product. The alternative pathway to the Puddephatt rearrangement, is that which was proposed by Casey²⁵ for a platinacyclobutane system which rearranged at 52°C. Applying the Casey mechanism to this system, either intermediate 78 or 79 undergoes a 2 + 2 cycloreversion to form metallocarbene-olefin intermediate 80. Taking the Casey mechanism one step further, the reaction temperature of 130°C might be rigorous enough for dissociation of the iridium from olefin coordination to occur. This would allow the opportunity for free rotation of the sigma bonds of the carbene or olefin carbons. Thus, after proper rotation and recoordination, a 1,3-metallo shift could be envisioned to produce 80 from either 78 or 79. Although the intermediates used in Figure 14 have many precedents in the literature, a 1,3-metallo shift is a new idea.

Figure 15 depicts another pathway that was deemed feasible. In this mechanism, iridacyclobutane 79 decomposes to the π -allyl iridium hydride complex 82 upon β -hydride abstraction. Intermediate 82 then rearranges via a 1,2-bridge shift to give π -allyl carbocation/olefin-iridium hydride complex 83. Subsequent bond reorganization steps and, finally, reductive elimination of iridium provides product 47. The overall scheme in Figure 15 is unprecedented in the literature and was initially considered the less likely of the two proposed

possibilities. It should be easier to disprove the mechanism in Figure 15 than that in Figure 14 by labeling experiments since a skeletal rearrangement is implicit in this mechanism. Therefore, a labeling experiment was performed in which one of the bridgehead hydrogens of 13 was replaced by a methyl group.

Reaction of 1-methyl-endo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (85) could potentially give four ring expanded products: 4-methyltricyclo[3.2.1.0^{2,7}]oct-3-ene (86), 2-methyltricyclo[3.2.1.0^{2,7}]oct-3-ene (87), 1-methyltricyclo[3.2.1.0^{2,7}]oct-3-ene (88) and 5-methyltricyclo[3.2.1.0^{2,7}]oct-3-ene (89). All four products could be expected to result from a 1,2-bridge shift, whereas only 88 and 89 would be expected from the 1,3-metallo shift mechanism (Figure 16).

Upon reaction of 85 with iridium, only one product was obtained and that in 90% yield. ¹H and ¹³C NMR spectral data as well as elemental analysis confirm the structure 86 to be that product. A discussion of the structure proof will be given in Section II. A check for thermal rearrangement was performed showing that 85 is thermally stable under the reaction conditions used.

Reaction of 85 shows remarkable regioselectivity of iridium insertion and regioselectivity of the subsequent rearrangement and cyclopropane formation. The presumed, rearranged intermediate (90) is illustrated in Figure 17. The carbocation is not only allylic but is also tertiary and thus regioselectivity is not surprising. More insight, however, was gained with a deuterium labeling experiment

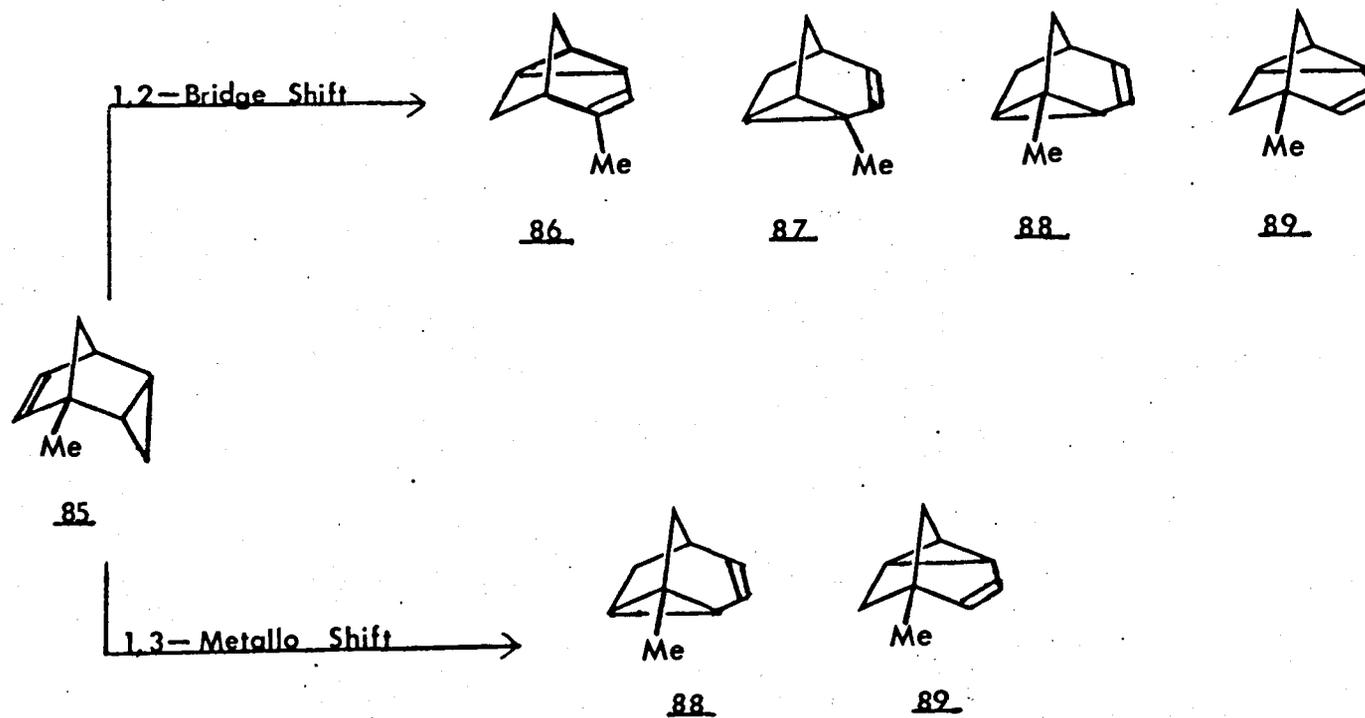


Figure 16. Possible Products from the Alternate Mechanisms of Reaction of **85** with Vaska's Catalyst.

which will be discussed shortly.

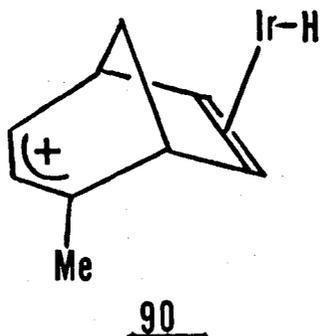


Figure 17. Proposed Intermediate in the Reaction of 85 with IR(1).

Even though 85 is thermally stable under the conditions used, the absolute regioselectivity of this reaction makes 85 suspicious as a good model for the reaction of 13 with iridium. Thus, it was decided to label 13 with deuterium to avoid the electronic or steric effects that might be active with the methyl label. Substrate 13a was synthesized and was found to contain 47% deuterium at each of the cyclopropane bridgehead carbons (this of course assumes equal distribution for the two positions). Reaction of 13a with iridium gave the results summarized in equation 20 and Table 3.

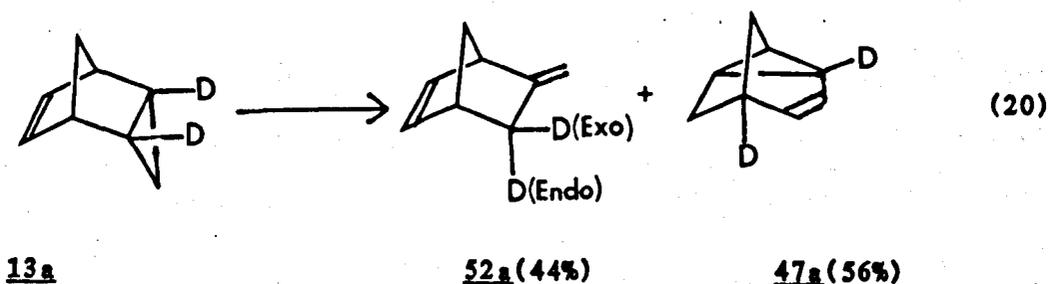
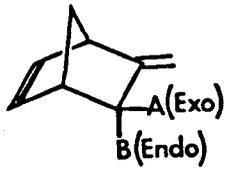
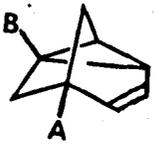


Table 3. Deuterium Contents of Products from 13a.

Position	% Deuterium of Products ^a	
		
A	50%	43%
B	5%	52%

a) % Deuterium is expressed as percent reduction of the equivalent of a one proton integral in the ^1H NMR spectrum.

The proton assignments of the ^1H NMR spectrum will be discussed separately in Section II of this discussion. Suffice it for now to say that deuterium was found only in the positions indicated. Product 52a is also out of the realm of the present discussion and will be presented again in more detail in Section III along with the possible relationship between 47 and 52 which will be used to explain regioselectivity and product deuterium isotope effects.

Had the formation of 47 occurred via a 1,3-metallo shift, the deuteriums would have been found on C_4 and in the endo position of C_6 instead of being found on C_1 and C_5 . However, an intermediate such as 90 in Figure 17 is not corroborated by the formation of 47a. A 1,2-bridge shift has occurred, but the product is derived from an

unsymmetrical intermediate. Consider Figure 18. An intermediate such as 91 would give both 47a and 47b as products. Also note that a deuterium isotope effect of 1.3 is present in favor of bridge migration to a non-deuterated carbon. A positive secondary isotope effect is consistent with a change in hybridization of the deuterium bearing carbon from sp^3 to sp^2 in the transition state. A revised mechanism that better explains the data is given in Figure 19.

The iridacyclobutane 79a is proposed, in this revised mechanism, to undergo carbon-iridium sigma bond cleavage rather than β -hydride elimination yielding carbocation 92. Bridge migration occurs, forming the more stable allylic carbocation 93. Loss of iridium with concomitant bond reorganization gives product 47a. An analogous mechanistic scheme can be envisioned for the reaction of 85 with iridium. The regioselectivity is greater with 85 due, most likely, to the additional driving force for the formation of an allylic-tertiary carbocation 94 (Figure 20).

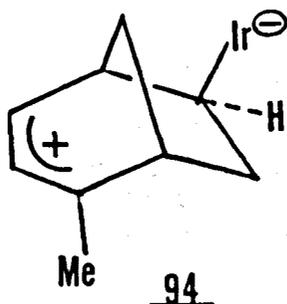


Figure 20. Proposed Intermediate from Reaction of 85 with Vaska's Catalyst-Revised Mechanism.

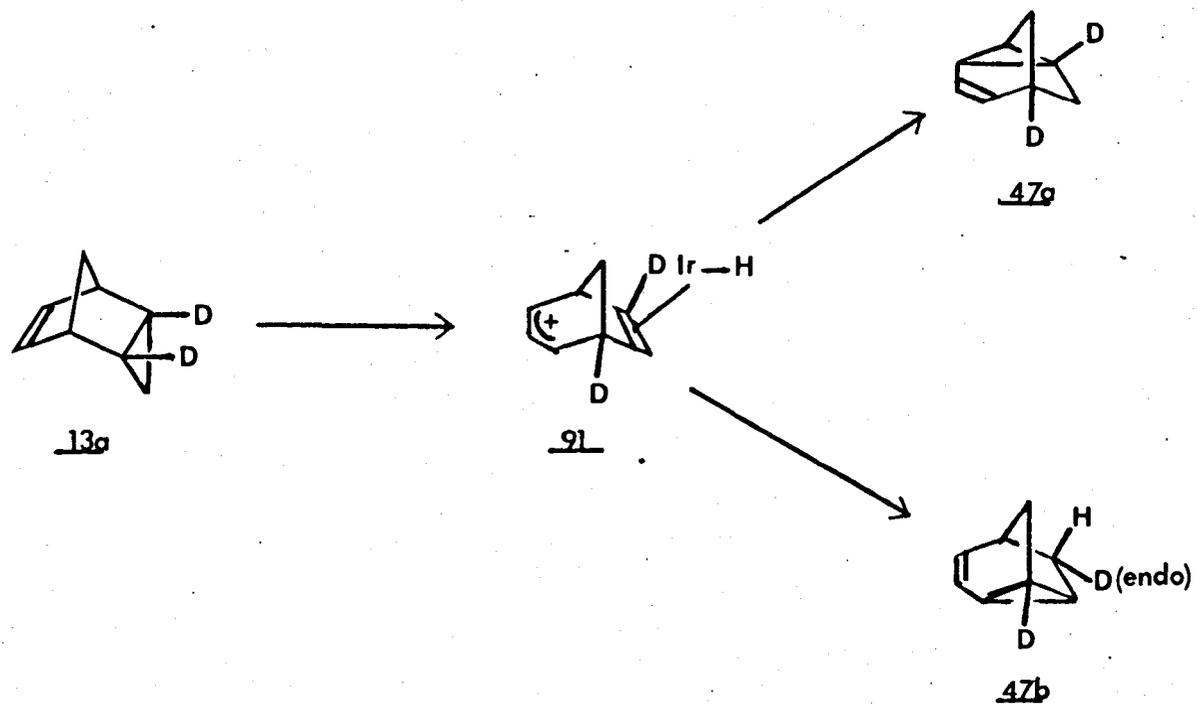


Figure 18. Scheme for the Expected Products from a Symmetrical Intermediate from 13a Via a 1,2-Bridge Shift.

