Interactions of Rh(I) and Pd(II) with cyclopropanes in rigid systems : kinetics, product analyses and mechanisms
by Richard Bruce Taylor

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

Abstract:
The [(NBD)RhC1]2 catalyzed valence isomerization of quadricyclane (Q) and the reactions of (PhCN)2PdC12 with cyclopropane in a series of rigid systems were investigated. A detailed kinetic study of the Rh(I) catalyzed reaction of Q revealed that this was an unusually complex reaction. Two products were observed from this reaction, norborna-diene (NBD) and a bis(norbomadiene) (HCD). These products formed via parallel reactions from a common intermediate. Significant solvent effects on the rate constant were observed. In CDCl3, the reaction rate was inhibited by substrate at all temperatures, unaffected by NBD at 37°C and enhanced by NBD at low temperatures. Four different catalysts were shown to be operative in this system under different conditions. NBD exchange with [(NBD)RhC1]2 was shown to proceed by a dissociative mechanism. A reaction scheme was proposed and fitted by a computer modeling technique to accommodate the major features of this reaction. Activation parameters for this system were determined and compared for different reaction conditions in which different catalysts were operating. Evidence is presented which rule out the concerted and Lewis acid mechanisms. The “cheleotropic" mechanism is consistent with all results.

(PhCH)2 PdC12 was shown to effect facile rearrangements of a series of 4 substrates with exo- and/or endo-cyclopropanes in tri- and tetracyclic systems. A new Pd complex was characterized and stereochemistry determined. The hydrocarbon was readily displaced by Ph3P to produce a diene product. Stereospecific 1,3 chloropalladations and 1,2-H migrations were observed and a detailed mechanism was proposed. A correlation between the stability of 1,3-chloropalladation adducts and the stereochemistry of the Pd,Cl addition was observed and discussed. Cis-chloropalladation adducts appear to be generally unstable and to result in catalytic reactions whereas trans-adducts are generally stable and isolable.

INTERACTIONS OF Rh(I) AND Pd(II) WITH CYCLOPROPANES IN RIGID SYSTEMS: KINETICS, PRODUCT ANALYSES AND MECHANISMS

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Richard Bruce Taylor

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TABLE OF CONTENTS

TABLE OF CONTENTS—Continued

LIST OF TABLES

Tables

LIST OF FIGURES

Figures

ABSTRACT

The $[(\mathbf{NBD})RhCl]_2$ catalyzed valence isomerization of quadricyclane (**Q**) and the reactions of $(PhCN)_2PdCl_2$ with cyclopropane in a series of rigid systems were investigated. A detailed kinetic study of the Rh(I) catalyzed reaction of **Q** revealed that this was an unusually complex reaction. Two products were observed from this reaction, norbornadiene (**NBD**) and a bis(norbornadiene) (**HCD**). These products formed via parallel reactions from a common intermediate. Significant solvent effects on the rate constant were observed. In $CDCl_3$, the reaction rate was inhibited by substrate at all temperatures, unaffected by **NBD** at 37°C and enhanced by **NBD** at low temperatures. Four different catalysts were shown to be operative in this system under different conditions. **NBD** exchange with $[(\mathbf{NBD})RhCl]_2$ was shown to proceed by a dissociative mechanism. A reaction scheme was proposed and fitted by a computer modeling technique to accommodate the major features of this reaction. Activation parameters for this system were determined and compared for different reaction conditions in which different catalysts were operating. Evidence is presented which rule out the concerted and Lewis acid mechanisms. The "cheleotropic" mechanism is consistent with all results.

$(PhCH)_2PdCl_2$ was shown to effect facile rearrangements of a series of 4 substrates with *exo*- and/or *endo*-cyclopropanes in tri- and tetracyclic systems. A new Pd complex was characterized and stereochemistry determined. The hydrocarbon was readily displaced by Ph_3P to produce a diene product. Stereospecific 1,3 chloropalladations and 1,2-H migrations were observed and a detailed mechanism was proposed. A correlation between the stability of 1,3-chloropalladation adducts and the stereochemistry of the Pd,Cl addition was observed and discussed. Cis-chloropalladation adducts appear to be generally unstable and to result in catalytic reactions whereas trans-adducts are generally stable and isolable.

A PERSPECTIVE

The study of organometallic chemistry began with the isolation of the first organotransition metal complex in 1827 by Zeiss[1], $K^+ [(C_2H_4)PtCl_3]^-$. Over the next hundred years, this area of chemistry grew slowly. In the last 30 years, the study of organometallic chemistry has grown rapidly in scope and importance especially in the areas of heterogeneous and homogeneous catalysis. Most large scale industrial chemical processes today utilize catalysts to increase efficiency of production both in terms of increasing the product yield and in reducing energy costs due to the requirement of much less severe conditions for the catalyzed process. Homogeneous catalysts are used in about two dozen significant processes in the American chemical industry[2]. In 1982, the American Chemical Society began publication of a new journal, *Organometallics*, devoted solely to this area of chemistry. A historical review of the development of the study of organometallics has been published[3].

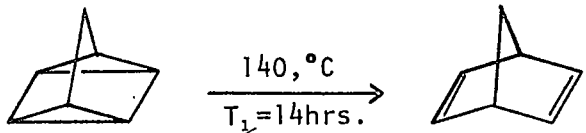
This thesis reports investigations of interactions between Rh(I) and Pd(II) organometallic complexes with cyclopropanes in rigid systems.

KINETICS OF THE Rh(I) CATALYZED VALENCE ISOMERIZATION OF QUADRICYCLANE

INTRODUCTION

Many thermally stable high energy carbocycles are known (Fig. 1). These molecules are orbital symmetry forbidden to valence isomerize by a concerted process, according to the Woodward-Hoffman rules for pericyclic reactions[4]. However, many of these strained small-ring compounds undergo a variety of facile rearrangements in the presence of a wide range of transition metal complexes. The first section of this thesis explores the interactions between one of these small strained carbocycles and a Rh(I) metal complex.

Quadricyclane (**Q**) is illustrative of the properties of these kinds of molecules. **Q** has a total strain energy[5] of 78.7 kcal mol^{-1} and a half life for thermal isomerization[6] to norbornadiene (**NBD**) of > 14 hours at 140°C (Eq. 1). The reaction is exothermic and yields



QUADRICYCLANE NORBORNADIENE (1)

26 kcal mol^{-1} of energy in the form of heat[7]. The stability of the molecule towards the ground state [σ2s + σ2s] cycloreversion process is a consequence of the requirement for conservation of orbital symmetry. In the presence of a variety of transition metals, however, these orbital symmetry restrictions are no longer the controlling factor and **Q** is known to isomerize to **NBD** rapidly even at low temperatures (Table 1). For instance, in the presence of a 2 mol % solution of [(**NBD**)RhCl]$_2$ (**5**), the half life for isomerization at -26°C is only 45 minutes[8].

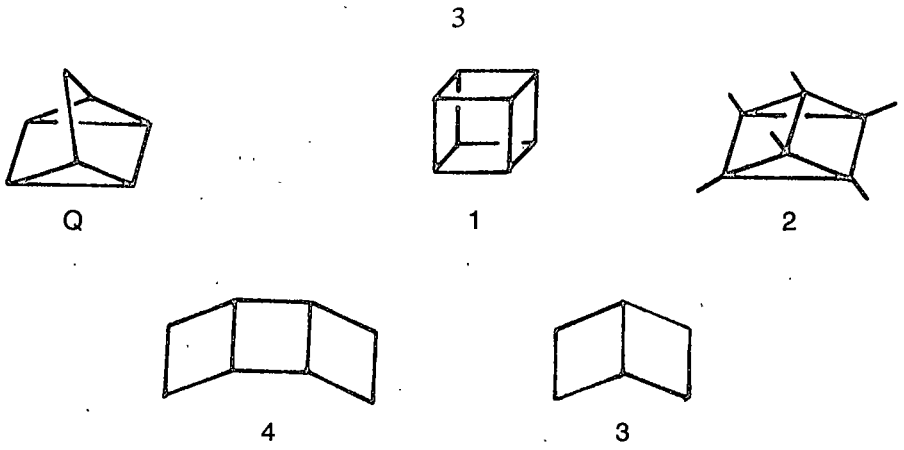


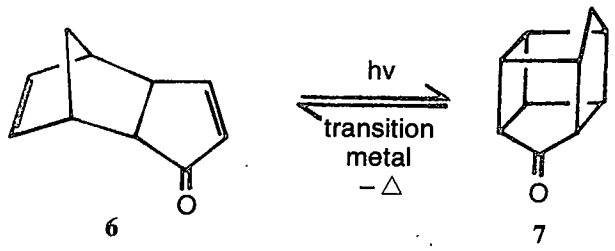
Figure 1. Several examples of thermally stable, strained carbocycles.

Table 1. A Partial List of Metal Complexes Known to Catalyze the Isomerization of Q.

[(**NBD**)RhCl]$_2$	[(**COD**)PdCl]$_2$
$(Et_2RhCl)_2$	[(π-methyallyl)PdCl]$_2$
[(**NBD**)Rh(OAc)]$_2$	$(PhCN)_2PdCl_2$
$Rh_2(CO)_4Cl_2$	CoTPP
$(Ph_3P)_3RhCl$	NiTPP
[(**NBD**)PtCl]$_2$	$Fe(CO)_5$
$(Et_2PtCl)_2$	Fe^{+2} (phthalocyanine)
$AgClO_4$, $AgNO_3$	$SnCl_2$

COD = cyclooctadiene; TPP = tetraphenylporphyrin.

Since many of these carbocycles are formed photochemically by allowed cycloaddition processes, these molecules are considered important as potential solar energy capture and storage devices. This, coupled with the ability to release the stored energy on demand by exposing the carbocycle to an appropriate transition metal catalyst, has led to a number of investigations into the feasibility of using these highly strained carbocycles as solar energy capture, storage and release systems[9]. Jones[9e] assessed the excitation energy storage capability of one such system, 6 → 7 (Eq. 2), and compared it to several substituted and unsubstituted quadricyclanes, prismane, cubanes and homocubanes.



6 7 (2)

The role that the metal plays in these rearrangements has generated a great deal of theoretical and experimental interest. The role of the metal must include provision of a low energy pathway for rearrangement that either alters the orbital symmetry of the substrate to make the concerted process allowed or provides a nonconcerted stepwise process. Three basic mechanisms have been proposed for the interaction of transition metals with strained carbocycles. These include the concerted or edgebound mechanism, the "cheleotropic" mechanism and the Lewis acid mechanism (Fig. 2).

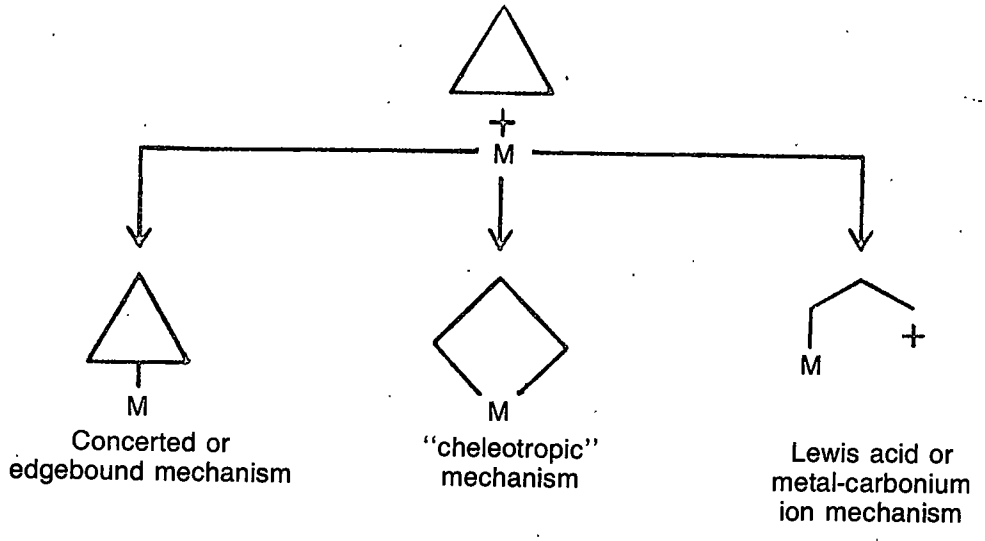


Figure 2. The three basic mechanisms proposed for metal catalyzed rearrangements of cyclopropanes.

The removal of orbital symmetry restrictions by coordination to a metal was proposed by Mango[10] in 1967. This mechanism involved an exchange of election pairs between the metal center and the transforming ligands. In 1970, Manassen[11] summarized

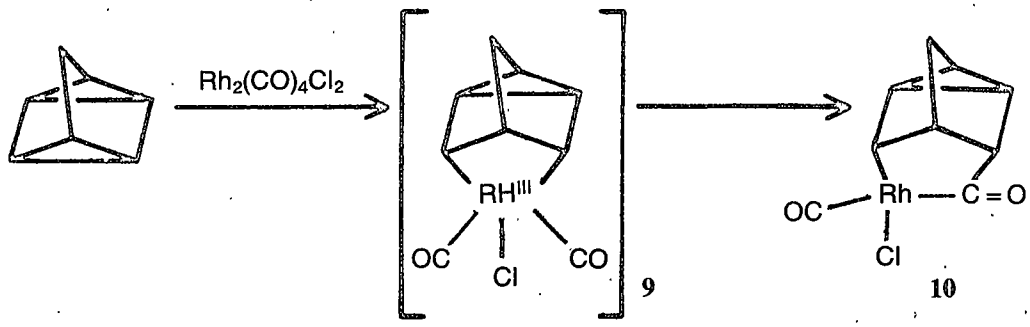
the selection rules that govern the energy of activation and Mango's explanation for the catalytic effect of a transition metal. Manassen investigated a variety of bivalent metal complexes of tetraphenylporphyrin or phthalocyanine for catalytic activity towards the isomerization of Q. He found that most of the d^6, d^7 and d^8 complexes were active while the d^9 and d^{10} complexes were not (Table 2). He also observed that square planarity of the complex appeared to be a necessary condition for catalytic activity. In 1971, Mango[12] discussed new symmetry restrictions based on ligand field effects. Little additional support for this mechanism has come more recently. Although this mechanism does account for the observed results in some cases, it is not generally thought to be a viable mechanism for metal catalyzed isomerizations today.

Table 2. Catalytic Activity for the Isomerization of **Q** to **NBD** for Square Planar Complexes of Bivalent Metal Ions by Manassen[11].

Ligand	Electron structure: Metal ion:	d^5 Mn^{2+}	d^6 Fe^{2+}	d^7 Co^{2+}	d^8 Ni^{2+}	d^8 Pt^{2+}	d^9 Cu^{2+}	d^9 Ag^{2+}	d^{10} Zn^{2+}
Phthalocyanine		–	+	+	–	+	–	–	–
Tetraphenylporphyrin				+	+		–	–	–
N,N′-Ethylene(salicylideneiminato)				+	–		–		–

The "cheleotropic" mechanism involves insertion of the metal into a C-C bond followed by cheleotropic extrusion of the metal. Support for this mechanism is largely derived from the isolation of stable carbonyl insertion products thought to arise from the metallacycle intermediates. Halpern[13] reported the isolation of such a carbonyl insertion product from the reaction of $Rh_2(CO)_4Cl_2$ (**8**) with **Q** in 1970 (Eq. 3). He proposed that **10** was produced by oxidative-addition of the metal to an edge bond of one of the cyclopropanes to form **9** followed by insertion of CO into one of the Rh-C bonds. Analogous rhodium carbonyl insertion products have been reported for cyclopropane[14], cubane[15] **3**, and **4**[16] (Fig. 3). Similar carbonyl insertion products from the reaction of $Fe(CO)_5$ with

quadricyclane and quadricyclanone have been reported by Aumann[17]. In addition, oxidative-addition intermediates were proposed by Noyori[18] in the Ni(0) catalyzed isomerization of Q based on the observation of 2,6-cycloaddition products when the reaction was run in the presence of a fivefold excess of acrylonitrile (Eq. 4).



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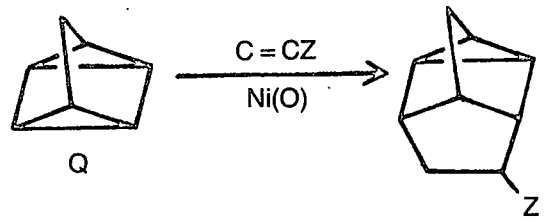
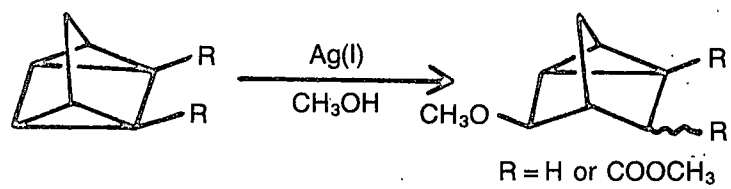


(4)

While these results give strong support for the "cheleotropic" mechanism, it should be noted that none of the metallacycle intermediates proposed for these systems have been isolated. Evidence for the concertedness of the metal extrusion is lacking as well, and it has not been generally established that extrusion of the metal from metallacycles results in C-C bond cleavage.

The Lewis acid mechanism involves electrophilic attack by the metal to form an intermediate metallacarbonium ion. Support for this mechanism comes from the trapping of intermediates with methanol in Ag(I) catalyzed reactions with quadricyclanes (Eq. 5) and observation of carbonium ion type rearrangement products for Ag(I) catalyzed reactions of homo-[19] and bishomocubanes[20] (Eqs. 6 and 7).



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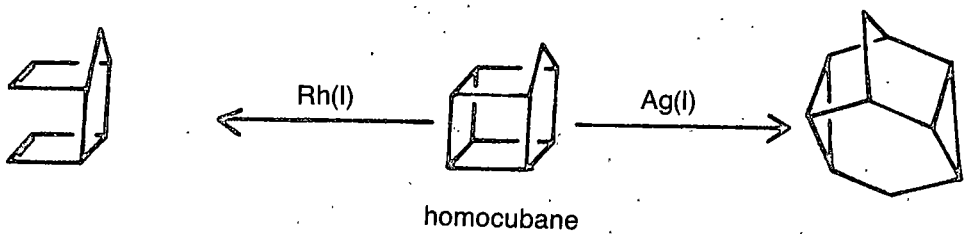

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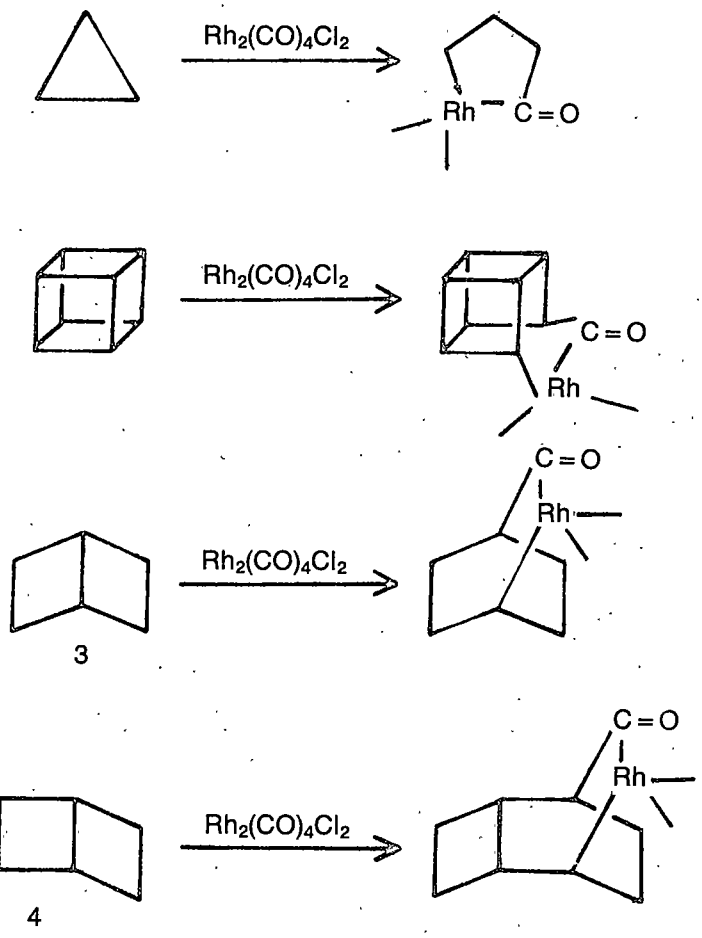
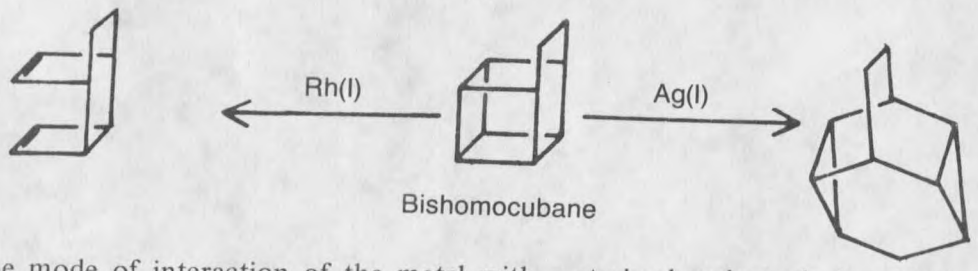
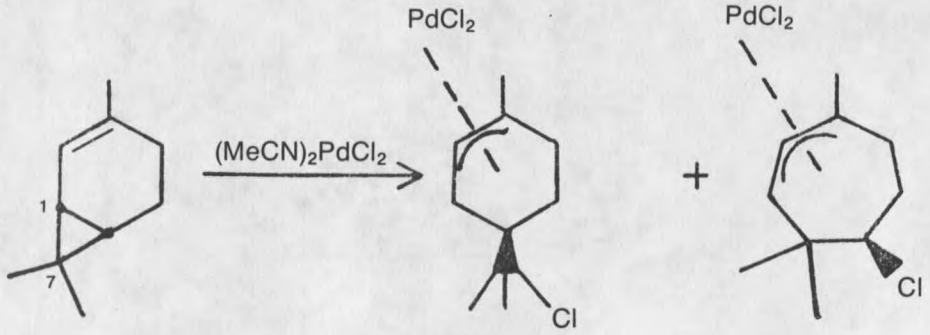


Figure 3. Known rhodium carbonyl insertion products from the reaction of $Rh_2(CO)_4Cl_2$ with small strained carbocycles.



(7)

The mode of interaction of the metal with a strained carbocycle is related to the metal's ability to donate electrons, its electron promotion energy, and the propensity of the metal to accept electrons, its electron affinity. A high electron promotion energy indicates that a metal will not donate electrons easily and a high electron affinity indicates that a metal strongly wants to accept electrons. Therefore, a metal like Ag(I) with a high electron promotion energy, 9.94 eV[21], and a moderate electron affinity, 7.59 eV[21], will favor the ionic or Lewis acid route. A metal like Rh(I) with low electron promotion energy and moderate electron affinity, 1.6 and 7.31 eV[21], respectively, will likely favor the oxidative-addition route. A metal like Pd(II) with a reasonably low electron promotion energy of 3.05 eV[21] and a high electron affinity of 18.56 eV[21] might be expected to interact by either the ionic or oxidative-addition route depending on ligands and on reaction conditions. Indeed, Bäckvall[22] recently proposed that both routes were operating in the reaction of $(MeCN)_2PDCl_2$ with (+)-car-2-ene (**11**) to account for the two products observed (Eq. 8).[a]



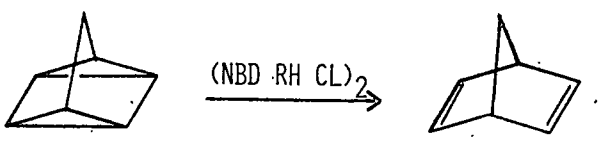
(8)

11 **56** **57**

[a]For an excellent review of metal catalyzed rearrangements of small ring organic molecules with 132 references up to 1976, see reference 23.

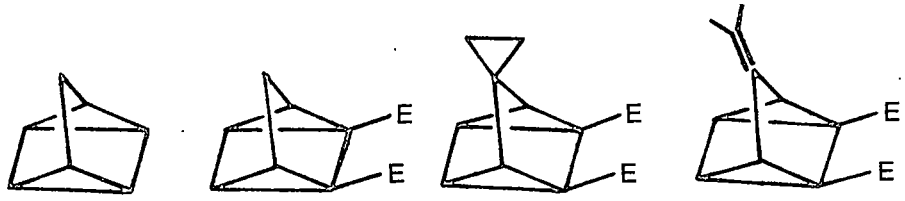
One of the major types of investigations of the mechanisms of chemical reactions has been the kinetic investigation. Kinetics alone are rarely able to determine a detailed mechanism but reaction mechanisms are rarely considered to be understood without a detailed kinetic analysis. Transition metal interactions with strained carbocycles are no exception and indeed most of the mechanistic investigations reported in this area rely, at least to some extent, on kinetics. It is perhaps not surprising for a relatively new area such as organometallics that, whereas many kinetic surveys have been done, very few detailed kinetic analyses have been reported. The remainder of this introduction will be devoted to a survey of some selected studies of metal catalyzed reactions of quadricyclanes that include kinetic investigations.

Since Volger[8] first reported on the metal catalyzed isomerization of quadricyclane in 1967, quadricyclanes have been the subject of a number of investigations. In 1970, Halpern[13] reported on the $[(\mathbf{NBD})RhCl]_2$ (**5**) catalyzed isomerization of **Q** (Eq. 9). He reported that **Q** was quantitatively converted to **NBD** in $CDCl_3$ and CCl_4. The kinetics obeyed the rate law $-d[\mathbf{Q}]/dt = k[\mathbf{5}]\ [\mathbf{Q}]$ with $k = 2.2$ and $1.8\ M^{-1}\ s^{-1}$ in $CDCl_3$ and CCl_4, respectively, at 40°C. He observed that the rate was unaffected by the addition of an excess of **NBD** and concluded that the reversible displacement of the **NBD** ligand from the catalyst by **Q** was not a feature of the mechanism. Halpern proposed that the mechanism of this reaction involved a rate determining oxidative-addition step on the basis of the isolation of the rhodium carbonyl insertion product **10** (Eq. 3), which was reported in the same paper, and by analogy to the Rh(I) catalyzed isomerization of cubane in which an oxidative-addition step was strongly implicated[15]. This was a very limited kinetic study and no experimental details were given.



(9)

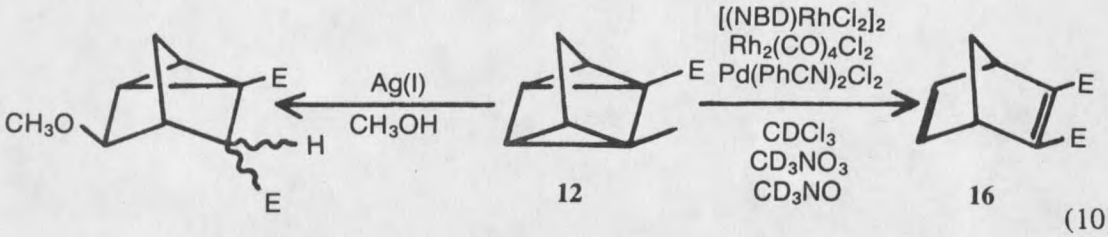
In 1973, Hogeveen[25] reported on the isomerization of a series of substituted quadricyclanes catalyzed by **5** (Fig. 4). He observed that all of these quadricyclanes were quantitatively converted to the corresponding NBD and suggested that the second order rate constants reported were composite rate constants which were the product of a pre-equilibrium and a rate determining step constant. Examination of the resulting rate constants suggested that substitution at the 7 position had little effect on the rate of reaction but that substitution at carbons 2 and 3 (or 5 and 6) which undergo C-C bond cleavage strongly affect the rates. For $-COOCH_3$ at positions 2 and 3, the rate is reduced by a factor of 5000. Again, this was a very limited kinetic study for which no experimental data was provided. Indeed, it is not obvious that the authors actually determined the reaction orders as no rate law was reported and note 9 cites the rate law determined by Halpern[13] for **Q** in reference to their reported rate constants.



	Q	12	13	14
$10^2k, M^{-1}s^{-1}$	5.5	0.6	0.4	0.6
Temp. °C	−26	45	38	60

Figure 4. Rate constants reported by Hogeveen[25] for the isomerization of the indicated quadricyclane catalyzed by **5** in $CDCl_3$. Each gave the corresponding **NBD**.

In 1974, Hogeveen again reported on the quadricyclane system concentrating on **12** and a comparison of Rh(I), Pd(II) and Ag(I) catalysts[26]. Each of these catalysts gave only the norbornadiene **16** in aprotic solvents but in methanol, $AgClO_4$ gave the isomeric mixture **15** (Eq. 10).



(10)

This implied that Ag(I) operates via an ionic mechanism whereas Rh(I) and Pd(II) do not. Second order rate constants were measured for each catalyst and it was found that [(**NBD**)RhCl]$_2$ exhibited pre-equilibrium kinetics while $Pd(PhCN)_2Cl_2$ obeyed a "real" second order rate law. The pre-equilibrium constant, K, in the rate law for Rh(I) was determined to be 0.3 M^{-1} at 60°C (Eq. 11). Three reaction schemes were proposed to account

$$\frac{-d[12]}{dt} = \frac{kK[12][Rh(I)]}{K[12]+1} \qquad (11)$$

for these results (Fig. 5). The pre-equilibrium observed for Rh(I) was thought to involve edgewise coordination of one cyclopropane to the metal followed by insertion. The scheme for Pd(II) was similar except that no pre-equilibrium was involved. The scheme for Ag(I) involved a rate determining oxidative-addition step followed by rapid evolution of a silver-carbonium ion intermediate. No experimental data was given in this report and the extent of the kinetic investigations is not clear.

Paquette argued strongly against complete insertion of Ag in the Ag(I) catalyzed isomerization of homo-[19] and bishomocubanes[20] on the basis of the rarity and high endothermicity of such complexes and by the demonstration of carbonium ion character in the activated complex. Paquette also demonstrated the rapid and reversible formation of homo- and bishomocubane-Ag^+ complexes prior to rearrangement. These papers are examples of excellent kinetic analyses accompanied by great mechanistic discussions.

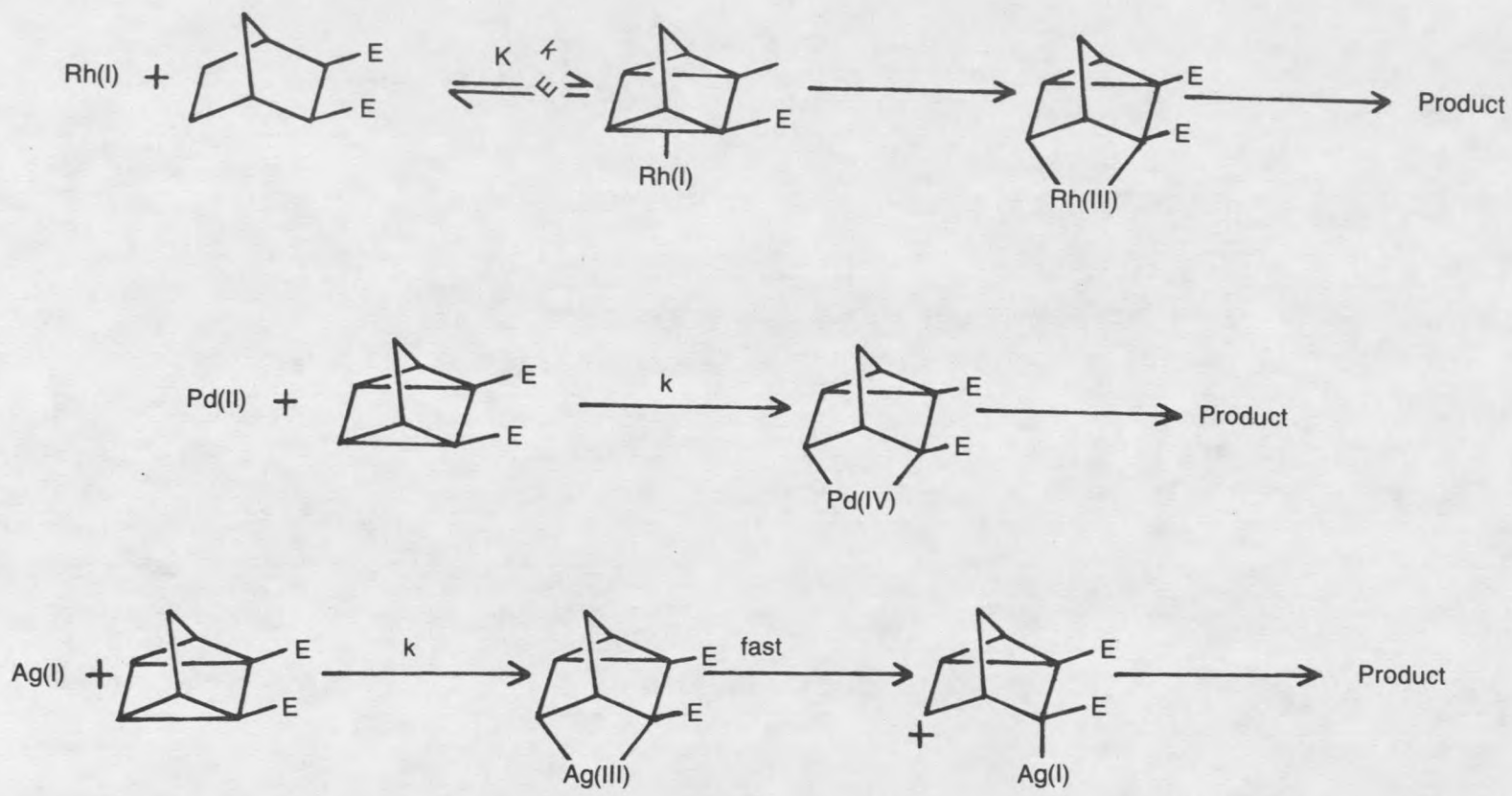


Figure 5. Mechanisms proposed by Hogeveen[26] for the interactions of Rh(I), Pd(II) and Ag(I) with quadricyclane, 2,5-dimethylester.

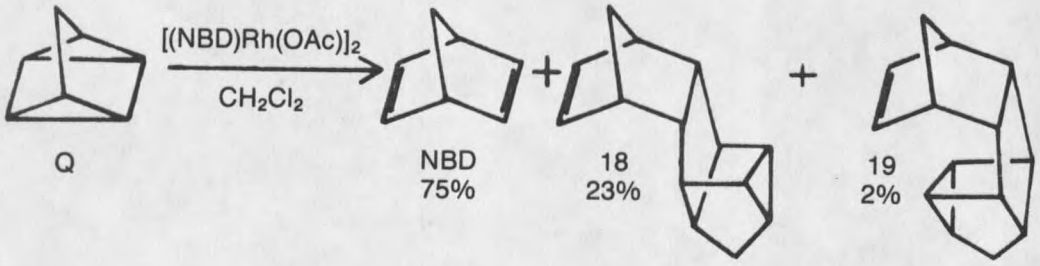
Noyori[18] reported on the bis(acrylonitrile) Ni(0) catalyzed isomerization of **Q** to **NBD** in 1975. Ni(0) is unique in that it catalyzes the $[2\sigma + 2\pi]$ cycloaddition of Q and acrylonitrile in addition to the isomerization to **NBD** (Eq. 4). The kinetics of this reaction were complicated by a reversible complexation of the product, **NBD**, with the Ni(0) catalyst resulting in product inhibition.

In 1976, Wilson and Rinker[27] reported on the isomerization of **Q** to **NBD** by cobalt tetraphenylporphyrin (**CoTPP**). The kinetics in this paper appear to be excellent. Temperature and solvent dependence for this reaction are shown in Table 3. The reaction was shown to be first order in **Q** in each solvent and first order in **CoTPP** in chloroform and carbon tetrachloride but, interestingly, second order in **CoTPP** in 1-chloronapthalene. However, no explanation was offered for the observed second order dependence of **CoTPP** or for the significant changes in activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, observed on changing the solvent from CCl_4 to $CHCl_3$ to 1-chloronapthalene. The increase in $\Delta H^{\ddagger}$ by almost 4 times and the concomitant decrease in $\Delta S^{\ddagger}$ by half on changing the solvent from CCl_4 to $CHCl_3$ indicate that the transition state and, therefore, the mechanism is changing with the solvent. The change in the form of the rate law in 1-chloronapthalene indicates that the reaction scheme, if not the mechanism, has changed in this solvent, as well.

Table 3. Thermal Parameters for **CoTPP** Catalyzed Isomerization of Q by Wilson and Rinker[27].

Solvent	k_o	$\Delta H^{\ddagger} \times 10^{-3}$ cal mol^{-1}	$\Delta S^{\ddagger}$ cal mol^{-1} K^{-1}
Carbon tetrachloride	$2.6 \pm 0.3 \times 10^3$ M^{-1} s^{-1}	1.73 ± 0.18	-42.8 ± 2.0
Chloroform	$1.75 \pm 0.25 \times 10^8$ M^{-1} s^{-1}	6.43 ± 1.2	-2.09 ± 3.0
1-Chloronapthalene	$3.48 \pm 0.15 \times 10^8$ M^{-2} s^{-1}	1.61 ± 0.15	-19.0 ± 1.0

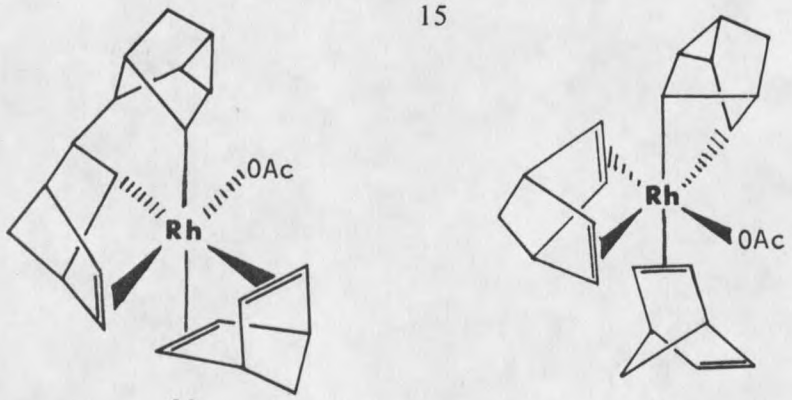
In 1979, Chen and Feder[28] reported on the [(**NBD**)RhAcO]$_2$ (**17**), catalyzed rearrangement of **Q** (Eq. 12). Several unique observations were made for this system. Quantitative conversion of **Q** to **NBD** was not observed for this Rh(I) complex. Two isomers of bis(norbornadiene) (**18**, **19**) were also produced by the reaction and accounted for 25% of the products. The product ratios were observed to be constant throughout the course of the reaction indicating that the products resulted from a common intermediate via parallel reactions. Kinetically, this system was unique, as well. In the presence of an excess of **NBD**, the rate law $-d[Q]/dt = 0.64\ s^{-1}\ [17]_0$ was obeyed. The reaction was first order in **17** and zero order in **Q**. At very low $[17]_0$, the reaction became first order in **Q**. When no



(12)

NBD was added to the reaction mixture, the rate was initially very slow but increased autocatalytically as product was produced until it reached the normal zero order rate. Of great mechanistic importance was the identification of a rhodiacyclohexane intermediate (**20**), (Fig. 6), produced at low temperature by the reaction, that was shown to proceed to products catalytically at higher temperatures. The Rh(III) complex **21** was proposed as a likely precursor intermediate which could either extrude **NBD** or rearrange to **20** which would yield the major bis(norbornadiene) product **18**. A detailed reaction sequence was proposed which accommodated the products, the intermediates and the observed rate law. The results of this investigation contrast strongly with the results for the analogous chlorine bridged catalyst described above (Eq. 9).

Finally, in 1982, Landis[29] reported on the valence isomerization of quadricyclane catalyzed by monomeric and polymer bound Sn(II) complexes. Quantitative conversion to



20 21

Figure 6. Intermediates from the 17 catalyzed isomerization of Q from reference 28.

NBD was observed. Although the kinetic study was quite limited, the authors reported that the reaction obeyed pseudo first order kinetics up to 50-70% conversion after which the rate decreased, suggesting poisoning of the catalyst by **NBD**. However, this feature of the reaction was not pursued further.

While the papers surveyed here were limited to investigation of a single type of substrate, the significant variations in mechanism and reaction kinetics observed as a result of what may appear to be minor changes in solvent, i.e., CCl_4 to $CDCl_3$, or catalyst, i.e., chlorine bridged to acetate bridged Rh(I), can be expected to occur in other substrate systems as well. In view of the significance of these variations, due caution must be exercised when drawing mechanistic conclusions or generalizing mechanisms between "similar" metal catalysts without the benefit of detailed analyses of each system.

Statement of the Problem

The $[(\mathbf{NBD})RhCl]_2$ catalyzed valence isomerization of quadricyclane was first reported in 1967 by Hogeveen and Volger[8] (Eq. 9). They observed the reaction at -26°C in $CDCl_3$ and reported that the isomerization to norbornadiene was quantitiative, that the reaction was first order in **Q** and "about first order in catalyst." "Apparent values" for the

activation parameters were reported as $\Delta H^{\ddagger} = 21 \pm 5$ kcal mole^{-1} and $\Delta S^{\ddagger} = 45 \pm 18$ eu. The large uncertainties given were attributed to "experimental difficulties."

In 1970, Halpern[13] reported rate constants for the same reaction in CCl_4 and $CDCl_3$ (40°C) of 1.8 and 2.2 M^{-1} sec^{-1}, respectively. He also reported that the rate was unaffected by the initial concentration of the product, **NBD**. This was particularly interesting because Volger[24] had previously reported that **5** was cleaved to a monomeric Rh complex by **NBD** in $CDCl_3$-CD_2Cl_2 solutions.

Although neither of these reports contained experimental sections, it appeared that this reaction obeyed simple, straightforward *pseudo* first order kinetics and had known rate constants. In addition, the substrate and catalyst were easily available. On this basis, coupled with an interest in the mechanisms of metal catalyzed rearrangements of strained ring systems, this reaction was chosen to be used as a test system on which to learn to do kinetics by NMR spectroscopy. Preliminary investigations of this system showed that this was not a simple straightforward system, as previously indicated, but that there were significant solvent effects on the rate constant, that there were at least two active catalysts or catalytic precursors in solution and that substrate inhibition was operative.

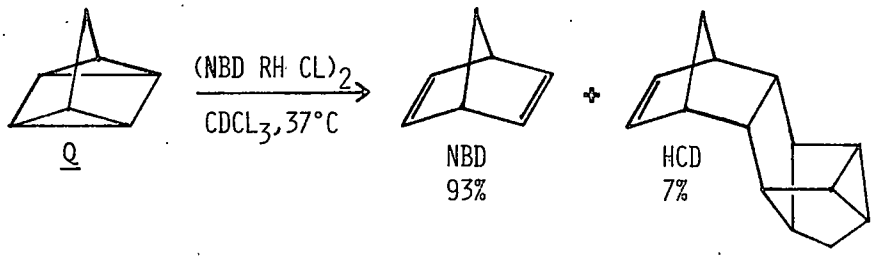
In view of the surprising results of our preliminary investigations and the general lack of detailed kinetic studies of these systems, it was concluded that a detailed kinetic analysis of the [(**NBD**)RhCl]$_2$ catalyzed valence isomerization of quadricyclane would be a timely contribution to the basic understanding of these types of systems. The analysis was performed and this section of this thesis is devoted to the results of that study.

RESULTS

Product Analysis

Product analyses of the [(**NBD**)$_2$RhCl]$_2$ catalyzed isomerization of **Q** were performed at 37°C by NMR spectroscopy in $CDCl_3$, CD_2Cl_2 and CCl_4. It was determined

that two products resulted from this reaction rather than the previously reported quantitative conversion to **NBD**[24] (Eq. 13). Along with the expected product, **NBD**, 3-7% of the known hydrocarbon dimer[30] **HCD** was observed and identified by its ^{1}H NMR spectrum (Fig. 7). In $CDCl_3$ and CD_2Cl_2, **HCD** comprised 7.0 and 6.7% of the product mixtures, respectively. In CCl_4, **HCD** comprised 3.5% of the products.



(13)

Two other observations in $CDCl_3$ and CCl_4 were made. First, the product distributions were constant at various **Q**:**5** ratios over the range 80:1 to 400:1, the significance of which will be discussed below. Second, the product distribution was constant throughout the course of the reaction (Table 4). This implies that the products are arising from a common intermediate via parallel reaction pathways. Any mechanistic scheme proposed for this reaction will have to account for these observations.

Solvent Effects on the Rate Constant

Rate constants for the Rh(I) catalyzed valence isomerization of **Q** (Eq. 13) were measured at 37°C in a variety of solvents by NMR spectroscopy. The solvents are divided into two general classes, non-polar and polar, and the result for each solvent is tabulated in Table 5. Errors for reported rate constants are within ±5% unless otherwise indicated.

In the non-polar solvents, CCl_4, benzene and chlorobenzene, the reaction obeyed *psuedo* first order kinetics and was well behaved. Plots of $\ln(I-I_\infty)$ vs time were linear over 7 half lives (Fig. 8). $[\mathbf{Q}]_0$ was varied 28 fold from 0.10-2.80 M and the $[5]_0$ was varied 8 fold from 0.5-4.0 $\times$ 10^{-3} M in CCl_4 and measured over the temperature range, -20 to 50°C. The reaction was found to be first order in both substrate and catalyst and to obey

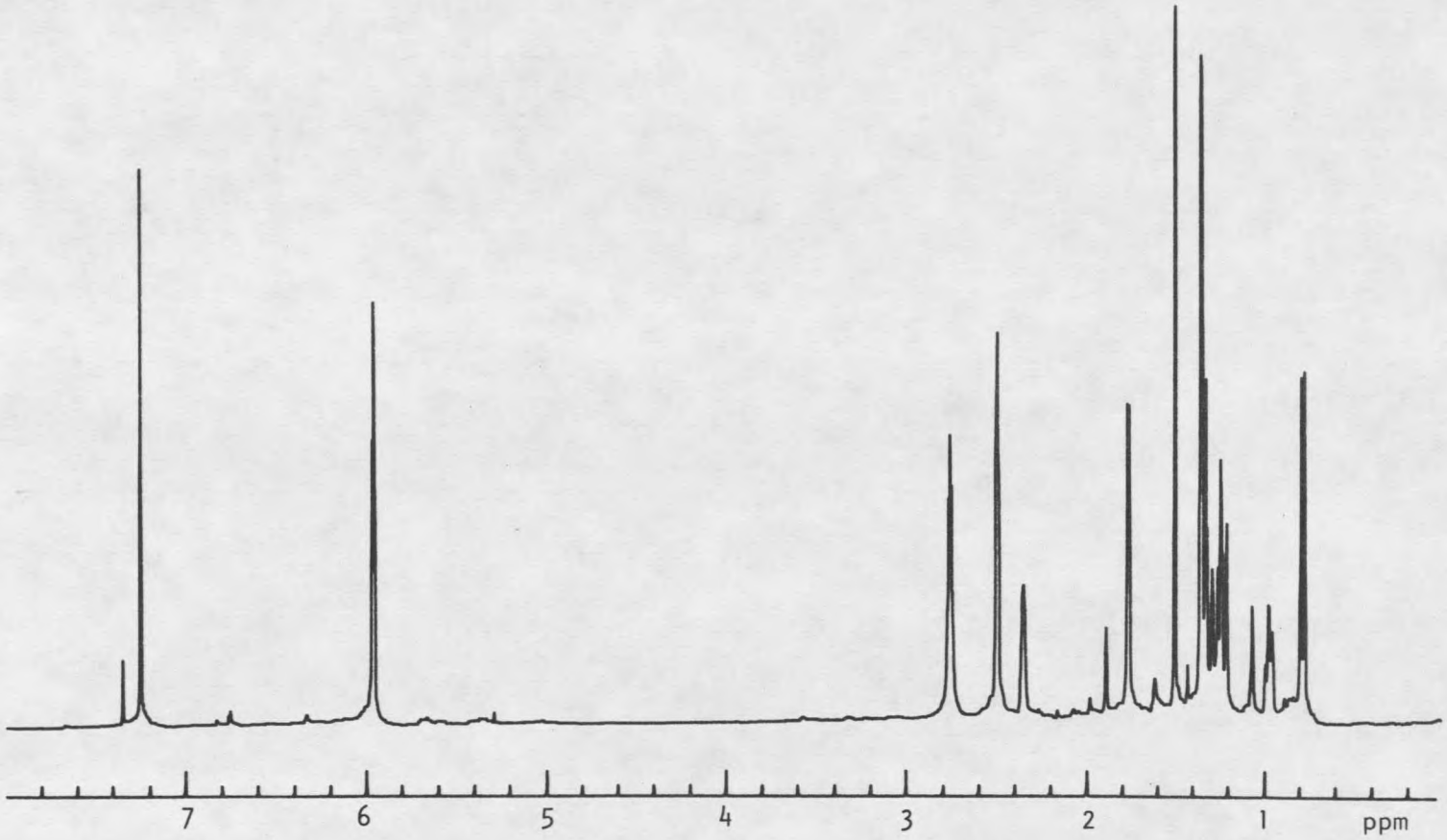


Figure 7. ^{1}H NMR spectrum of **HCD** (250 MHz, $CDCl_3$).

Table 4. Product Distributions for **5** Catalyzed Isomerization of **Q** During the Reaction.

Time, sec	[**Q**][a], mM	[**HCD**][b], mol %	Time, min	[**Q**][a], M	[**HCD**][b], mol %	Time, min	[**Q**][c], M	[**HCD**][b], mol %
0	100.0	—	0	0.40	—	0	0.40	—
16	85.2	8.4	1.5	0.238	5.24	2.0	0.286	5.30
46	51.3	5.36	3.5	0.175	6.14	2.5	0.268	4.35
76	30.5	5.64	5.5	0.152	6.13	3.0	0.250	5.16
106	17.9	6.05	7.5	0.141	6.41	4.0	0.206	4.21
136	11.4	7.20	9.5	0.135	6.55	5.0	0.172	4.21
166	6.67	6.26	17	0.110	8.19	6.5	0.130	5.01
196	4.11	7.00	19	0.092	7.23	7.5	0.109	4.65
226	3.41	6.59	21	0.081	7.04	9.0	0.089	5.25
256	2.26	6.32	23	0.070	6.87	10.0	0.076	4.87
600	0.0	6.87	25	0.062	6.97	11.5	0.060	5.32
1 hour	0.0	6.7	27	0.055	6.83	14.0	0.042	4.67
			45	0.0	7.04	16.5	0.034	4.68
			2 hours	0.0	7.0	1 day	0.0	3.5

[a] At 37°C, in $CDCl_3$, $[Rh]_0 = 1.0$ mM.
[b] Based on [**NBD**] + [**HCD**] − $[\mathbf{NBD}]_0$.
[c] At 37°C, in CCl_4, $[\mathbf{5}]_0 = 1.0$ mM.

Table 5. Rate Constants for the [(NBD)RhCl]$_2$ Catalyzed Isomerization of Quadricyclane in Various Solvents at 37°C.

Solvent	k, M^{-1} s^{-1}
CCl_4	2.9
Benzene	3.3
Chlorobenzene[b]	3.6
$CDCl_3$	26
CD_2Cl_2	23[a]
CD_3OD	> 500
Pyridine-d_5	0

[a] 23°C.
[b] This data by A. Hefenieder, NSF undergraduate research participant.

the rate law, d[NBD]/dt = k[Q][5], over the range of conditions investigated. The second order rate constants determined ranged from 2.9 M^{-1} s^{-1} in CCl_4 to 3.6 M^{-1} s^{-1} in chlorobenzene. The activation parameters in CCl_4 were determined and will be discussed later.

In more polar solvents, like $CDCl_3$, CD_2Cl_2, and CD_3OD, the rate constants for the reaction were increased dramatically to 26, 23 (30°C) and > 500 M^{-1} s^{-1}, respectively. These rates also obeyed *pseudo* first order kinetics and gave linear plots of $\ln(I-I_\infty)$ versus time over 5-6 half lives, in general (Fig. 8).

However, at intermediate $[Q]_0:[5]_0$, the plots show some biphasic character. The reason for this has not been ascertained and may be due to an experimental difficulty rather than to a true change in the reaction kinetics. Wherever this feature was observed, the rate for the reaction was determined from the initial portion of the plot. Pyridine completely inhibited the isomerization.

Rates were measured in several two solvent systems, as well. In these systems, CCl_4 was the major solvent with small amounts of a more polar solvent added. The solvents investigated included $CDCl_3$, CH_3CN, DMF, CH_3OH, CH_3COOH, and $CH_2ClCOOH$. Rates in these solvent systems obeyed *pseudo* first order kinetics and gave linear first order plots over at least 4 half lives. Second order rate constants are plotted versus the concentration

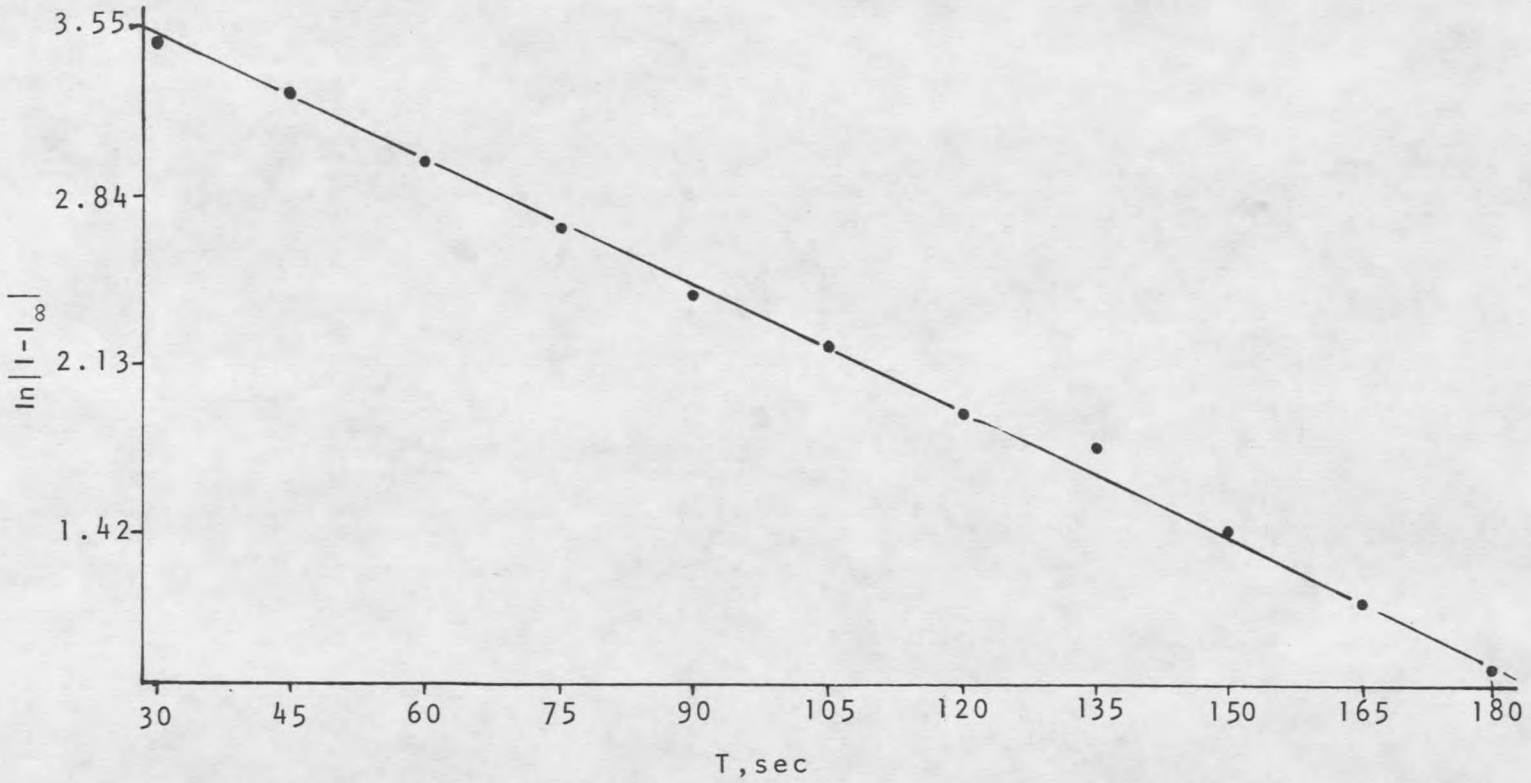


Figure 8. A *psuedo* first order plot of a typical kinetic run.

of the added polar solvent in Figure 9. The effectiveness of added solvents to increase the reaction rate follows the order: $CH_2ClCOOH \gg CH_3COOH > CH_3OH > DMF \gg CH_3CN > CDCl_3$.

Rate enhancements in polar solvents appear to be a general phenomenon. Of these solvents, $CDCl_3$ was chosen for detailed analysis. For the remainder of this chapter, the solvent referred to will be $CDCl_3$ unless otherwise noted.

Substrate Inhibition in Polar Solvents

Rates were measured in $CDCl_3$ over the substrate concentration range, $[Q]_0 = 0.04$-0.60 M; the catalyst concentration range, $[5]_0 = 0.43\text{-}2.5 \times 10^{-3}$ M; and over the temperature range, T = −23 to +37°C. A plot of the second order rate constant versus the initial substrate concentration at 37°C and $[5]_0 = 1.0 \times 10^{-3}$ M shows that the rate constant is dependent on the $[Q]_0$ and decreases as $[Q]_0$ is increased (Fig. 10). The rate constant for $CDCl_3$ reported in Table 5 is the ultimate rate constant determined by extrapolation to infinite dilution of Q. At $[Q]_0 > 0.4$ M the rate constant leveled out at 4.3 $M^{-1}\,sec^{-1}$.

This dependence on $[Q]_0$ is interpreted as substrate inhibition and is supported by the standard Lineweaver-Burke plot of $(velocity)^{-1}$ versus $[substrate]_0^{-1}$ for enzyme kinetics[31] in Figure 11. The leveling out of the rate constant at high $[Q]_0$:$[5]_0$ (Fig. 10) is interpreted as meaning that the active catalyst in solution is converted to a lower activity catalyst. Therefore, there are at least two active catalysts or catalytic precursors in solution in $CDCl_3$.

It is true that while the dependence of the rate constant on the $[Q]_0$ indicates substrate inhibition, this effect would be kinetically indistinguishable from the effect of a small impurity in the substrate that acted as a poison to the catalyst. In this case, the poison concentration would vary proportionately with the substrate concentration and would, therefore, demonstrate the same type of effect as substrate inhibition.

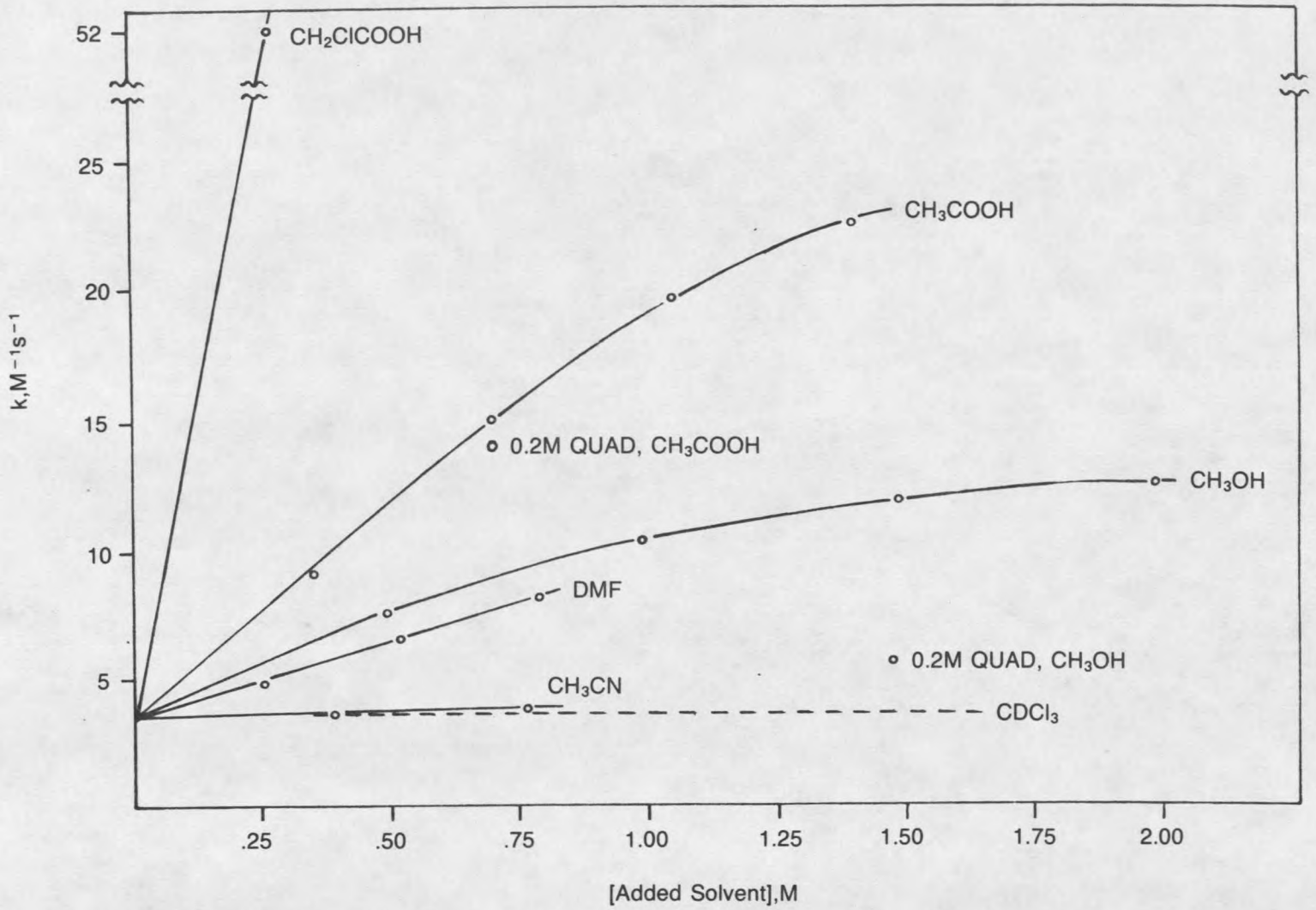


Figure 9. Rates for the reaction in Equation 9 in CCl_4 with small amounts of a more polar solvent added. $[Q]_0 = 0.1$ M, $[5]_0 = 1.0 \times 10^{-3}$ M at 37°C. $[5]_0 = 0.5 \times 10^{-3}$ M for CH_3OH and CH_3COOH.

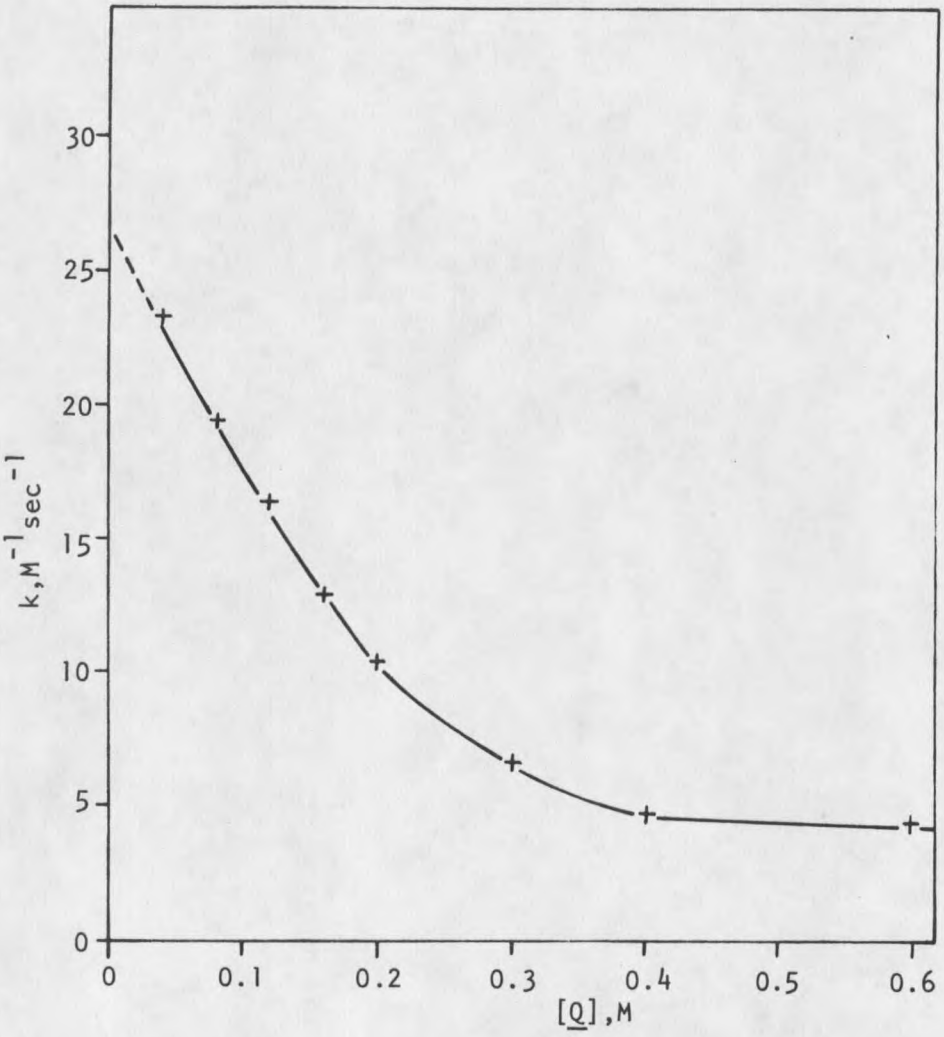


Figure 10. A plot of rate constant versus $[\mathbf{Q}]_0$ in $CDCl_3$ at 37°C for the reaction in Equation 9. $[\mathbf{5}]_0 = 1.0 \times 10^{-3}$ M.

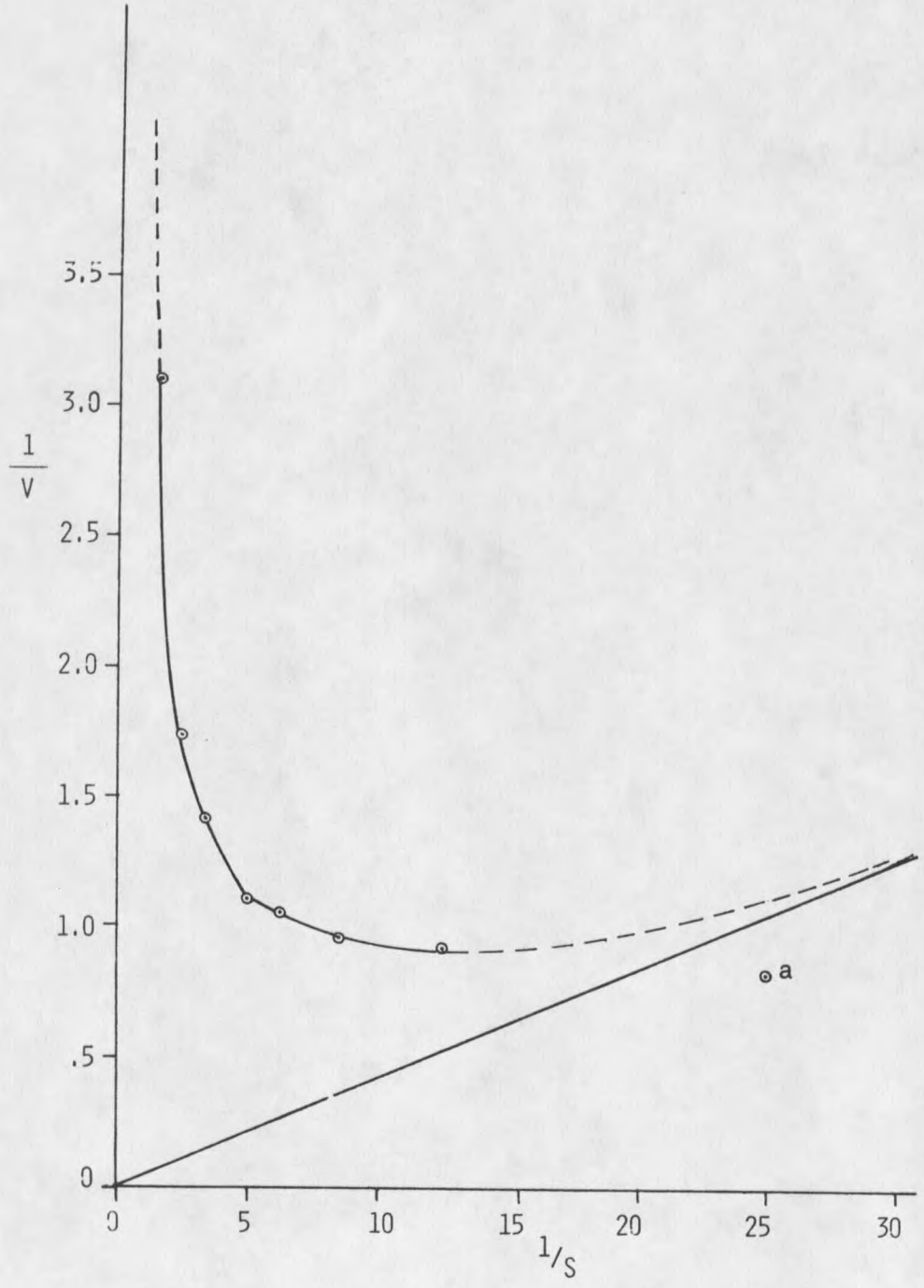


Figure 11. A Lineweaver-Burke plot for the isomerization of **Q** (Eq. 13) in $CDCl_3$ at 37°C. [**5**] = 1.0×10^{-3} M. [a]The rate was too fast to get a true initial rate for this point.

To test this hypothesis, rates were measured with crude preparations of quadricyclane and compared to rates for quadricyclane purified by: distillation on a 50 cm spinning band column; preparative gas chromatography; liquid chromatography on neutral, acidic and basic alumina, and silica gel; and treatment with $LiAlH_4$ or $KMnO_4$. In addition, quadricyclane prepared in this laboratory by the methods of Smith[32] and Mannasen[11] were compared to quadricyclane purchased from Aldrich. In each case, the rate constants determined were indistinguishable between relatively crude and highly purified quadricyclane within the limits of experimental error.

The following substances were added to the reaction mixture to test as potential poisons that might possibly survive the purification methods listed above: 90% technical grade cycloheptatriene, benzene, toluene, **NBD**, **HCD** and a crude product mixture. No effect on the rate constant was observed for any of these substances at 37°C. In view of the improbability of the concentration of an impurity in the quadricyclane remaining constant throughout the range of the methods of purification applied and the insensitivity of the reaction to the substances tested as poisons, it is concluded that the observed dependence of the rate constant on the $[Q]_0$ is due to substrate inhibition rather than to an impurity in the substrate.

Barnett[33] reported that for $(Ph_3P)_3$ RhCl or $(Ph_3P)_2$ Rh(CO)Cl, catalyzed ring opening of bicyclic cyclopropanes, the catalyst was poisoned by the HCl impurity in commercial $CDCl_3$. This is not the case for **5**, in which case, rates were observed to increase after addition of 1 μl HCl to the catalyst solution in $CDCl_3$ rather than to decrease. Barnett, also, showed that when O_2 was present the rates were 7 times faster than when O_2 was excluded. To test this effect for **5**, rates were measured for solutions with and without O_2 present. The measured rates were identical within experimental error. Thus, [(**NBD**)RhCl]$_2$ is not poisoned by small amounts of acid nor is it dependent on O_2 for activation.

The generality of substrate inhibition in polar solvents was tested in CD_2Cl_2, MeOH and CH_3COOH. Figure 12 is a plot of the second order rate constant versus the $[Q]_0$ at 30°C in CD_2Cl_2. The $[5]_0$ was 1.0×10^{-3} M. The rate constant in CD_2Cl_2 displays the same type of dependence on the substrate concentration as in $CDCl_3$. The ultimate rate constant is 23 $M^{-1}sec^{-1}$ by extrapolation to infinite dilution of substrate. Thus, the isomerization is slightly faster in CD_2Cl_2 than it is in $CDCl_3$ when the temperature difference is taken into account. It appears that the rate constant will level out at a slightly higher value as well.

Substrate inhibition in MeOH and CH_3COOH is demonstrated by the mixed solvent results which are shown in Figure 9. When the $[Q]_0$ was doubled from 0.10 to 0.20 M at 1.48 M MeOH and 0.70 M CH_3COOH the rate constants fell from 11.9 to 5.5 $M^{-1}s^{-1}$ and 15.0 to 13.7 $M^{-1}s^{-1}$, respectively. The inhibition process is so efficient in MeOH that the ultimate rate in methanol-d_4 could not be determined by the methods utilized. The highest rate constant measured was 512 $M^{-1}s^{-1}$ but the ultimate rate is probably much greater. The difficulty was that the inhibition process dominates the isomerization process at such low $[Q]_0:[5]_0$ ratios that, with rate constants greater than 500, the reaction is either almost over by the time the first point can be taken or it is completely inhibited. The inhibited rate constant in MeOH is 0.5 $M^{-1}s^{-1}$. The curvature in the plots for addition of CH_3COOH and MeOH to CCl_4 in the two solvent systems (Fig. 9) is attributed to the inhibition process becoming more effective than the isomerization process as the concentration of the polar solvent is increased at the $[Q]_0:[5]_0$ used.

Substrate inhibition was observed in $CDCl_3$ at low temperature and appeared to become more efficient relative to the isomerization process. At -0.4°C the rate constant leveled off at $\sim$0.20 M $[Q]_0$ (Fig. 13) rather than at $\sim$0.35 M $[Q]_0$ at 37°C.

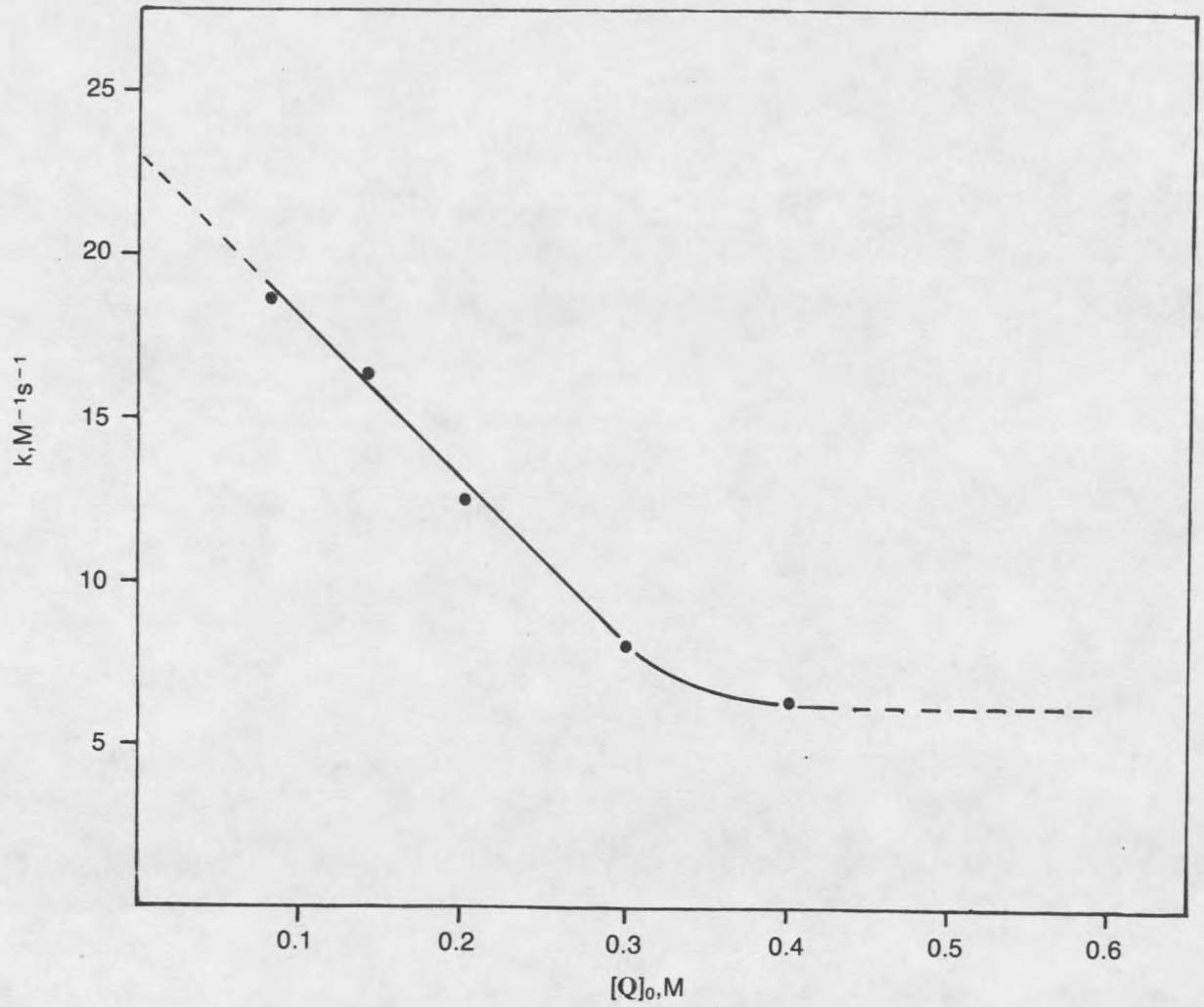


Figure 12. A plot of rate constant versus $[Q]_0$ at 30°C in CD_2Cl_2 for the reaction in Equation 13. $[5]_0 = 1.0 \times 10^{-3}$ M.

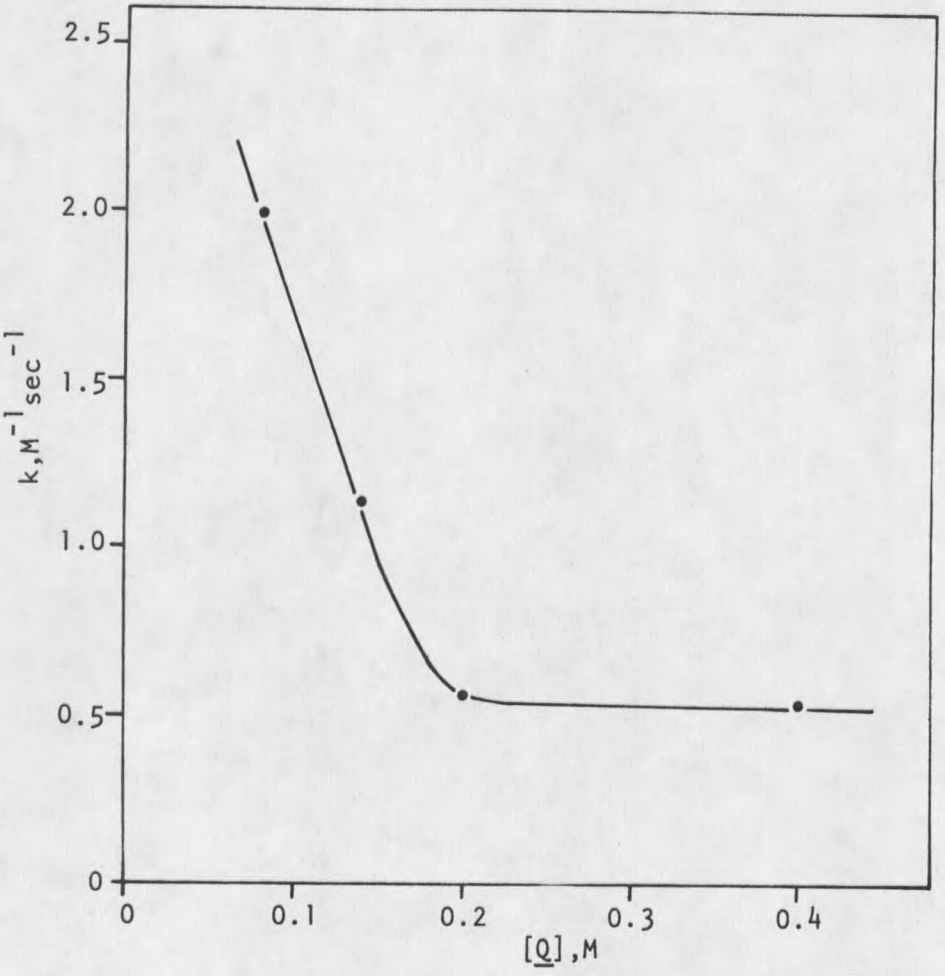
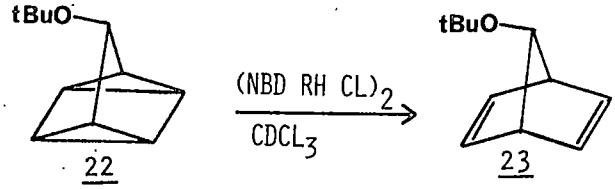


Figure 13. A plot of rate constant versus $[Q]_0$ at 0°C in $CDCl_3$ for the reaction in Equation 13. $[5]_0 = 1.0 \times 10^{-3}$ M.

Substrate Inhibition with 7-tert-butoxyquadricyclane

The 7-substituted quadricyclane, **22**, was prepared to check the generality of substrate inhibition in quadricyclanes substituted at remote sites and to further eliminate the possibility of the inhibition being due to an impurity in the substrate. A poison that would have the same retention time as **Q** in the gas chromatograph, for instance, would elute much sooner than **22** due to the difference in boiling point.

Rates were measured for the **5** catalyzed isomerization of **22** to **23** at 37°C in $CDCl_3$ (Eq. 14). This reaction obeyed *pseudo* first order kinetics with plots of $\ln(I-I_\infty)$ versus time being linear over 7 half lives. A plot of the second order rate constant versus the initial substrate concentration revealed that the rate constant exhibits the same type of dependence on $[22]_0$ as was observed for **Q** (Fig. 14). The ultimate rate constant for this reaction was 29 M^{-1} sec^{-1} which is slightly greater than for **Q**.



22 23 (14)

Activation Parameters For the Isomerization of Q in CCl_4 and $CDCl_3$

Activation parameters were determined for the valence isomerization of **Q** catalyzed by **5** in CCl_4 and $CDCl_3$ (Table 6). The activation parameters were calculated from the Eyring or activated complex theory[34] relation in Equation 15 with the transmission coefficient K taken as unity.

$$k = K \frac{RT}{Nh} \exp \frac{\Delta S^{\ddagger}}{R} \exp - \frac{\Delta H^{\ddagger}}{RT} \qquad (15)$$

The activation parameters for the reaction in CCl_4 were $\Delta H^{\ddagger} = 6.0 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -37.0 \pm 3.7$ kcal mol^{-1} K^{-1} based on rates measured at four temperatures from 37 to -20°C. Activation parameters were determined in $CDCl_3$ for $[Q]_0 = 0.12$ M and

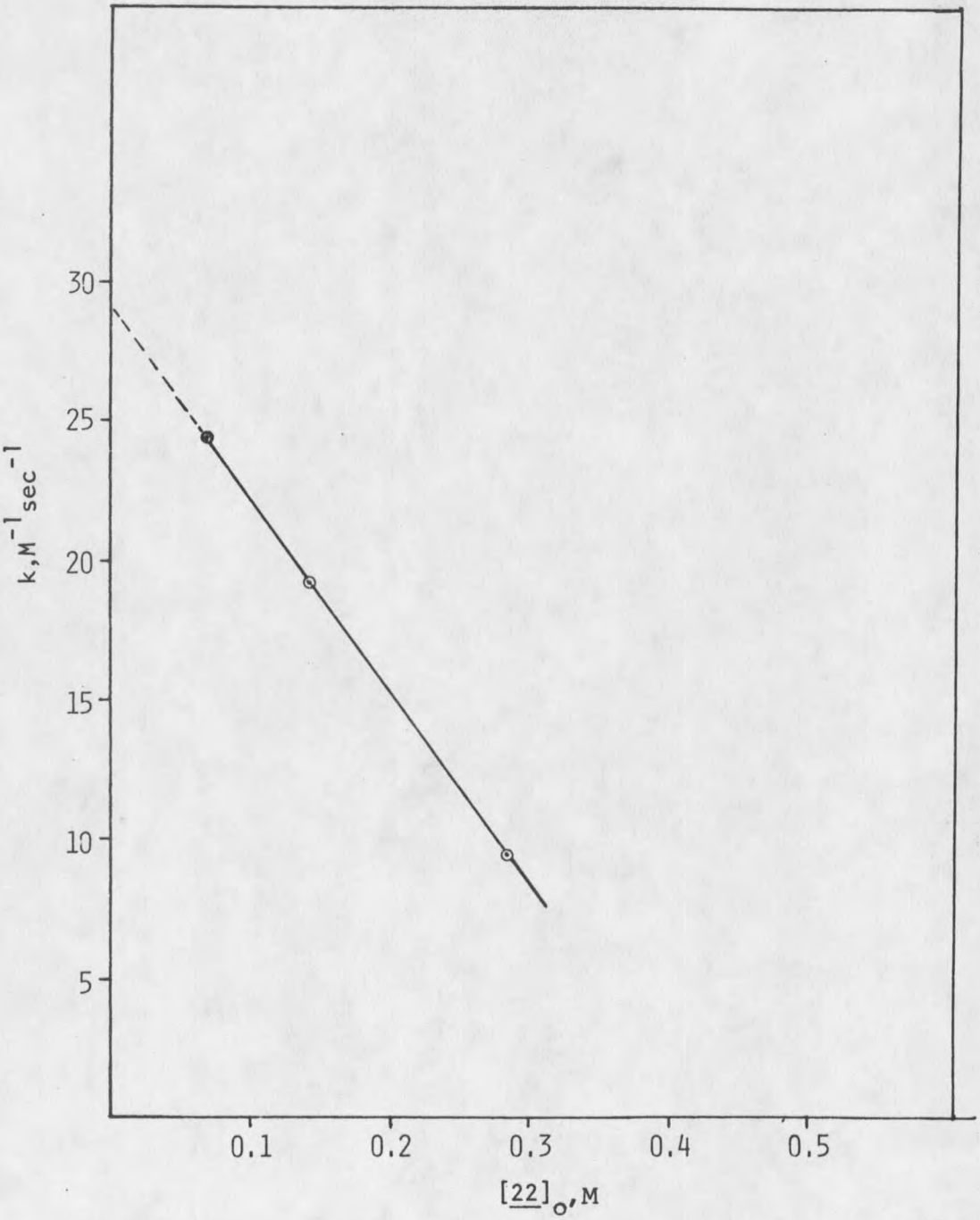


Figure 14. A plot of rate constant versus $[22]_0$ at 37°C in $CDCl_3$ for the reaction in Equation 14. $[5]_0 = 1.0 \times 10^{-3}$ M.

$[5]_0 = 1.0 \times 10^{-3}$ M based on rates at four temperatures from 37 to -23°C. $\Delta H^{\ddagger}$ was 13.0 ± 1 kcal mol^{-1} and $\Delta S^{\ddagger}$ was -12.1 ± 1 cal mol^{-1} K^{-1}. Activation parameters were also determined in $CDCl_3$ for $[Q]_0 = 0.40$ M and $[5]_0 = 1.0 \times 10^{-3}$ M based on rates at 37 and -0.4°C and found to be $\Delta H^{\ddagger} = 4.7 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -41 \pm 8$ cal mol^{-1} K^{-1}.

Table 6. Activation Parameters For the Rh(I) Catalyzed Isomerization of Quadricyclane.

Solvent	T, °K	k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$,[c] kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
CCl_4	310	2.9	6.0 ± 0.6	-37.0 ± 3.7
	285	1.1		
	273	0.80		
	252.5	0.26		
$CDCl_3$ [a]	310	16.3	13.0 ± 1	-12.1 ± 1
	296	5.7		
	272.6	1.4		
	250	0.073		
$CDCl_3$ [b]	310	4.3	4.7 ± 1	-41 ± 8
	272.6	0.52		

[a] $[Q]_0 = 0.120$ M, $[5]_0 = 1.0 \times 10^{-3}$ M.
[b] $[Q]_0 = 0.40$ M, $[5]_0 = 1.0 \times 10^{-3}$ M.
[c] Correlations for plots of ln k vs T^{-1} were > .99.

Effect of the Product, NBD, on $[(NBD)RhCl]_2$

Volger[24] showed that the rhodium dimer, **5**, was cleaved by **NBD** to a monomeric rhodium complex, **24**, in CD_2Cl_2-$CDCl_3$ (Eq. 16). Subsequently, Halpern[13] reported that

$$\underset{\mathbf{5}}{[(NBD)RhCl]_2} + 2NBD \rightleftharpoons \underset{\mathbf{24}}{2(NBD)_2RhCl} \qquad (16)$$

the reaction (Eq. 9) was not affected by the product, **NBD**, in agreement with our results above. Extrapolation of Volger's equilibrium data to 40°C revealed that the equilibrium constant for the rhodium dimer-monomer interchange was $K^{40°C} = 0.1$ M^{-1}.

The results reported in this section show that new equilibrium constants are warranted on the basis of revised NMR assignments for the rhodium monomer **24**. The new

equilibrium constants will be used to explain the lack of effect of the product on the reaction at 37°C and an enhanced rate constant at 1°C. Some of the results of this section have been published previously[35].

The characteristics of the rhodium complex were determined in CCl_4, $CDCl_3$, and benzene-d_6. Vapor phase osmometry (VPO) and NMR spectroscopy studies showed that **5** retained its dimeric structure in each solvent over the temperature range from the freezing point of the solvent to 25°C in the absence of **NBD** (Figs. 15(a), 16(a), and 17(a)). On addition of **NBD**, line broadening was observed in each solvent suggesting an exchange equilibrium between **NBD** and **5** (Figs. 15(b), 16(b) and 17(b)). For CCl_4 and benzene, **NBD** exchange was confirmed by NMR saturation-transfer experiments and shown to be in the slow exchange rate region at 25°C (Figs. 15(c) and 16(c)). In $CDCl_3$, the NMR spectrum was unresolved indicating that the exchange was in the intermediate exchange rate region at 25°C (Fig. 17(b)). Resolution of the spectrum at -55°C showed the presence of **NBD**, **5** and **24** (Fig. 17(c)).

The monomeric rhodium complex, **24a**, proposed by the earlier work[24], is shown in Figure 18. Protons Ha and Ha′ were thought to resonate at one frequency, 4.35 or 3.82 ppm, and protons Hb and Hb′ were thought to resonate at the other frequency. The resulting spectrum would have integrals in the ratio 3:3:2. Integration of our resolved spectrum yielded ratios of 2:1:1 for both the free **NBD** resonances (*) and the monomeric rhodium complex resonances (†) (Fig. 17(c)). This suggests that the olefinic, bridgehead and bridge protons of **NBD** bound in **24** are responsible for the resonances at 4.35, 3.82 and 1.17, respectively. These assignments were confirmed by NMR saturation transfer experiments (Fig. 19). Freezing point studies in $CDCl_3$ showed that **24** was, by far, the major rhodium containing species in the solution at -55°C.

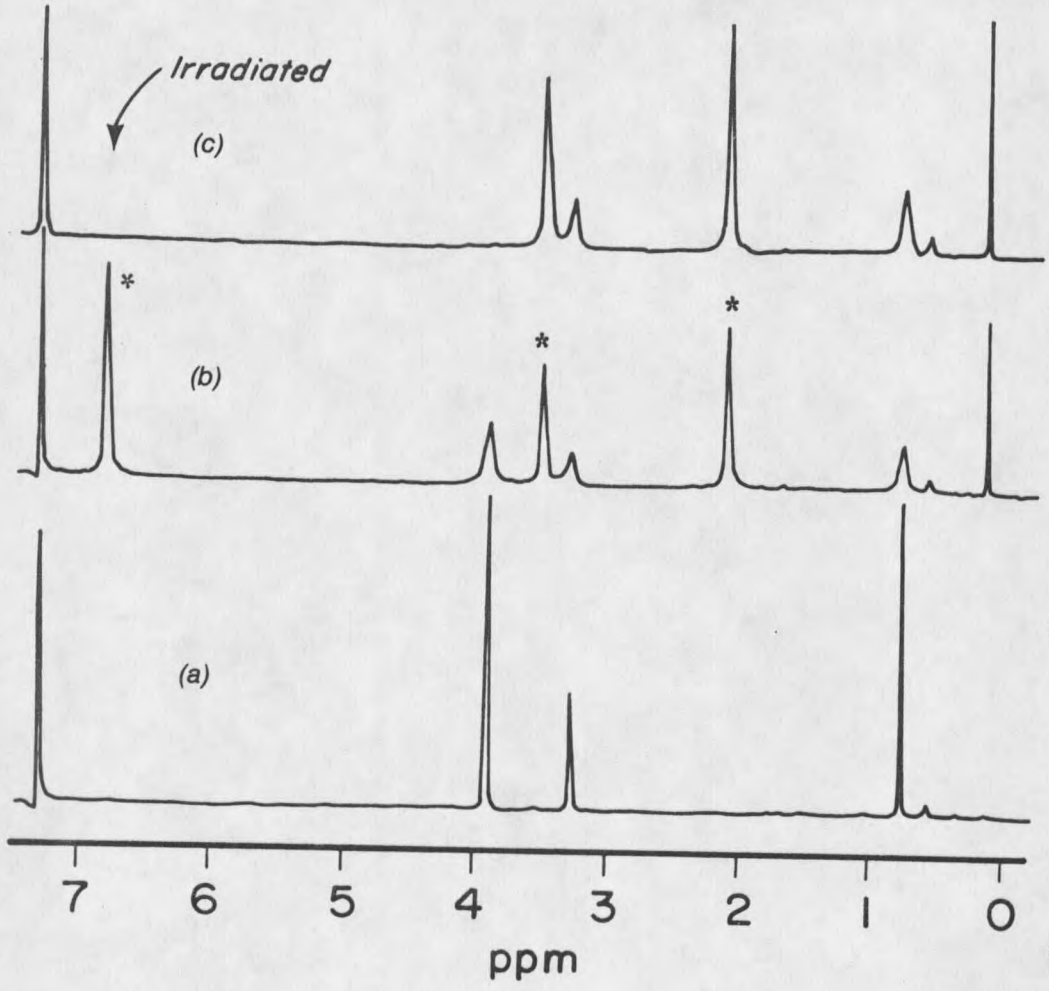


Figure 15. NMR spectra at 250 MHz of $[(\mathbf{NBD})RhCl]_2$ in benzene at 25°C: (a) rhodium complex alone; (b) rhodium complex and **NBD** (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed **NBD**; (*) resonances attributed to uncomplexed **NBD**.

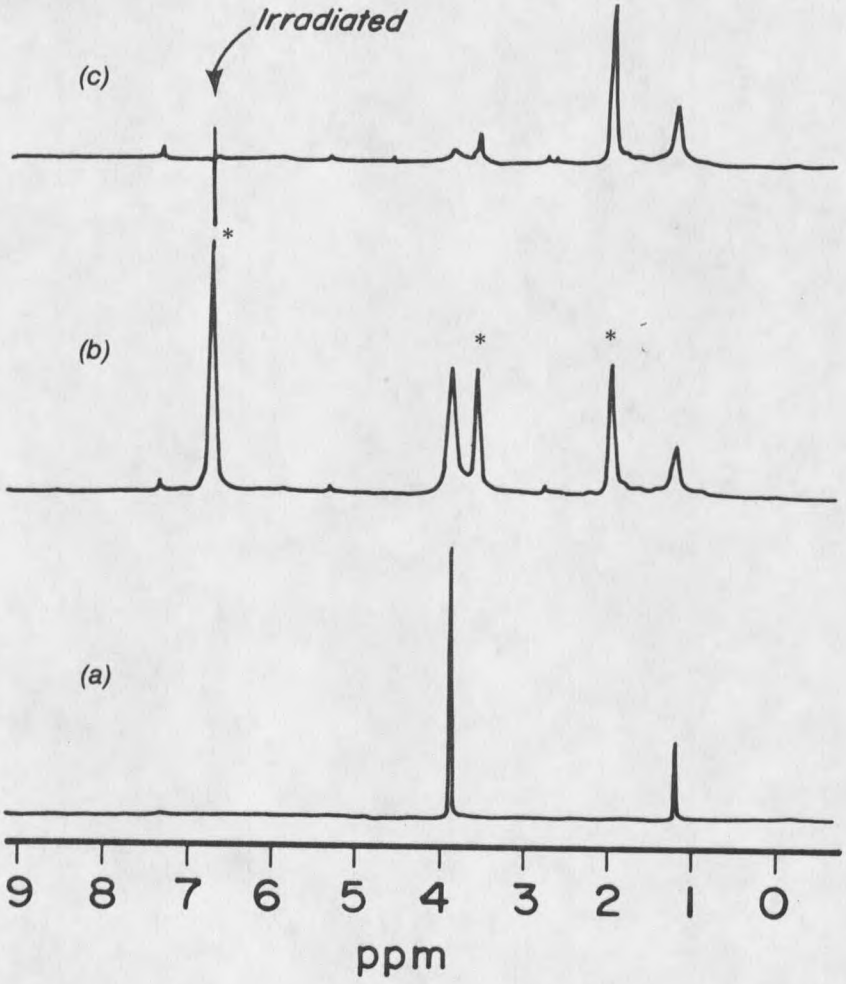


Figure 16. NMR spectra at 250 MHz of $[(\mathbf{NBD})RhCl]_2$ in CCl_4 at 25°C: (a) rhodium complex alone; (b) rhodium complex and **NBD** (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed **NBD**; (*) resonances attributed to uncomplexed **NBD**.

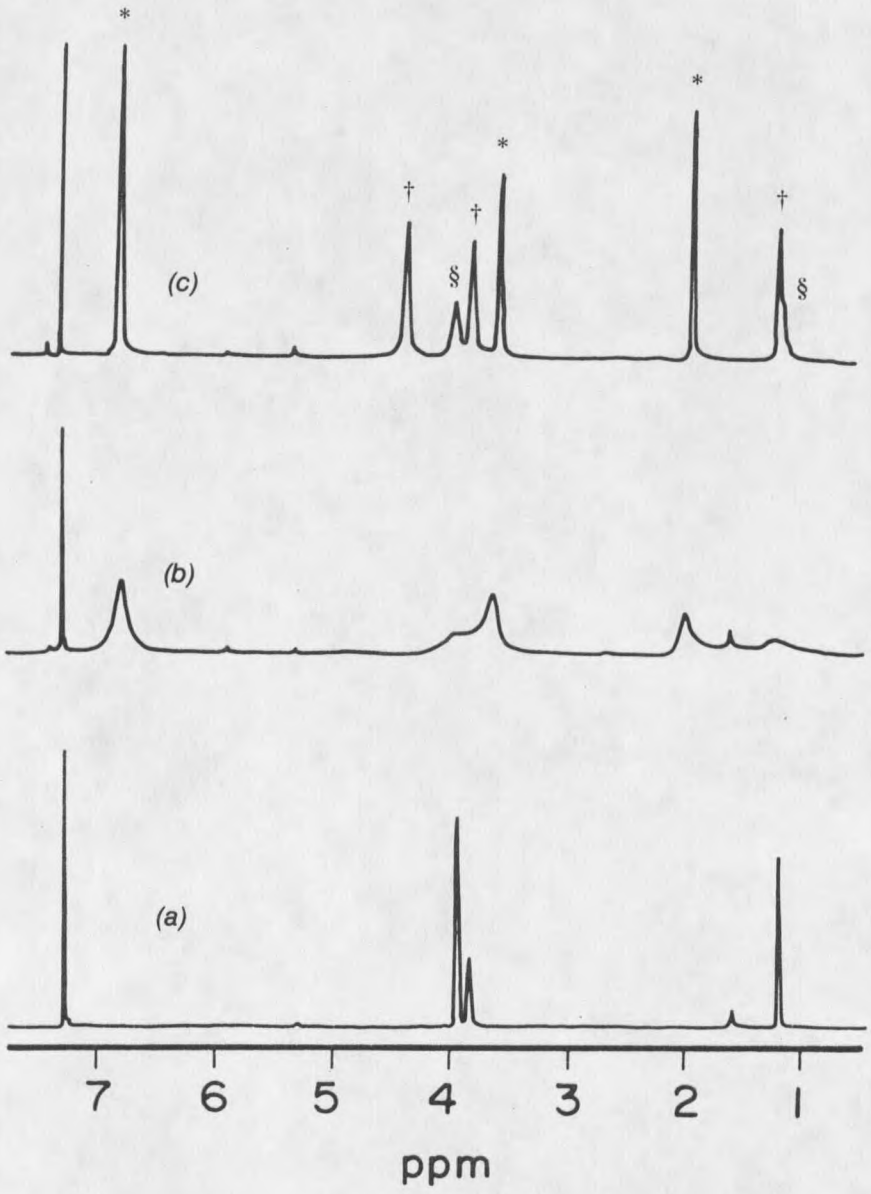
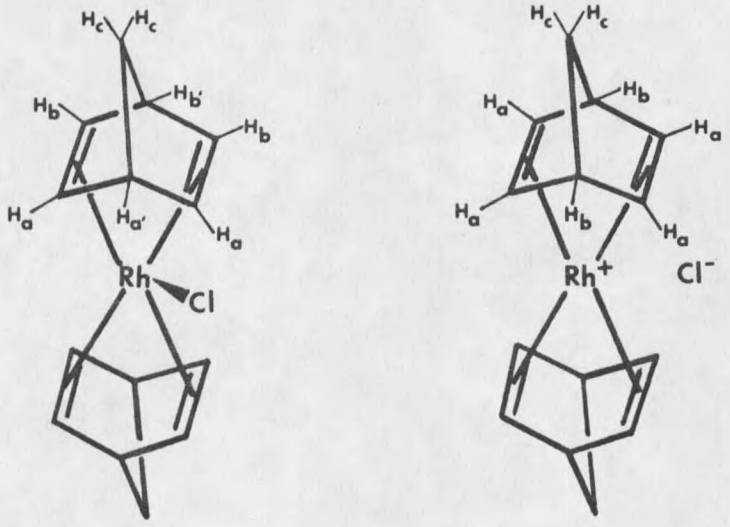


Figure 17. NMR spectra at 250 MHz of $[(\mathbf{NBD})RhCl]_2$ in $CDCl_3$ at 25°C: (a) rhodium complex alone; (b) rhodium complex and **NBD** (1:4 molar ratio); (c) same as part b but at -55°C; (*) resonances attributed to uncomplex **NBD**; (†) resonances of monomeric complex $(\mathbf{NBD})_2RhCl$; (§) resonances of the dimeric complex $[(\mathbf{NBD})RhCl]_2$.



24a **24b**

Figure 18. Proposed structures for the monomeric Rh complex **(NBD)$_2$**RhCl (**24**) and associated NMR proton equivalences; (**24**a) proposed by Hogeveen. (**24**b) intimate ion pair showing corrected NMR proton equivalences.

These new results impose the restriction that any proposed structure for **24** will have to account for the equivalence of the bridgehead protons. An intimate ion pair structure, **24**b, as shown in Figure 18, would meet the symmetry requirements imposed by the new assignments. The originally proposed structure cannot be ruled out completely, however, because at least two methods to accomplish the equivalence in the NMR spectrum are possible. First, the **NBD** exchange may be rapid enough to accomplish the task if the resonances for the protons *syn* and *anti* to the chlorine are very close together. Second, the Rh bound **NBD** moieties could be exhibiting fluxional behavior. Hence, it is apparent that the monomeric rhodium complex **24** has either a σ-bound chlorine or it is a very tight ion pair. The lack of a ^{35}Cl NMR spectrum suggests the σ-bound chlorine structure but is not conclusive.

In consideration of the new ^{1}H NMR assignments for **24**, new equilibrium constants for the reaction in Equation 16 were determined in $CDCl_3$ by NMR spectroscopy (Table 7).

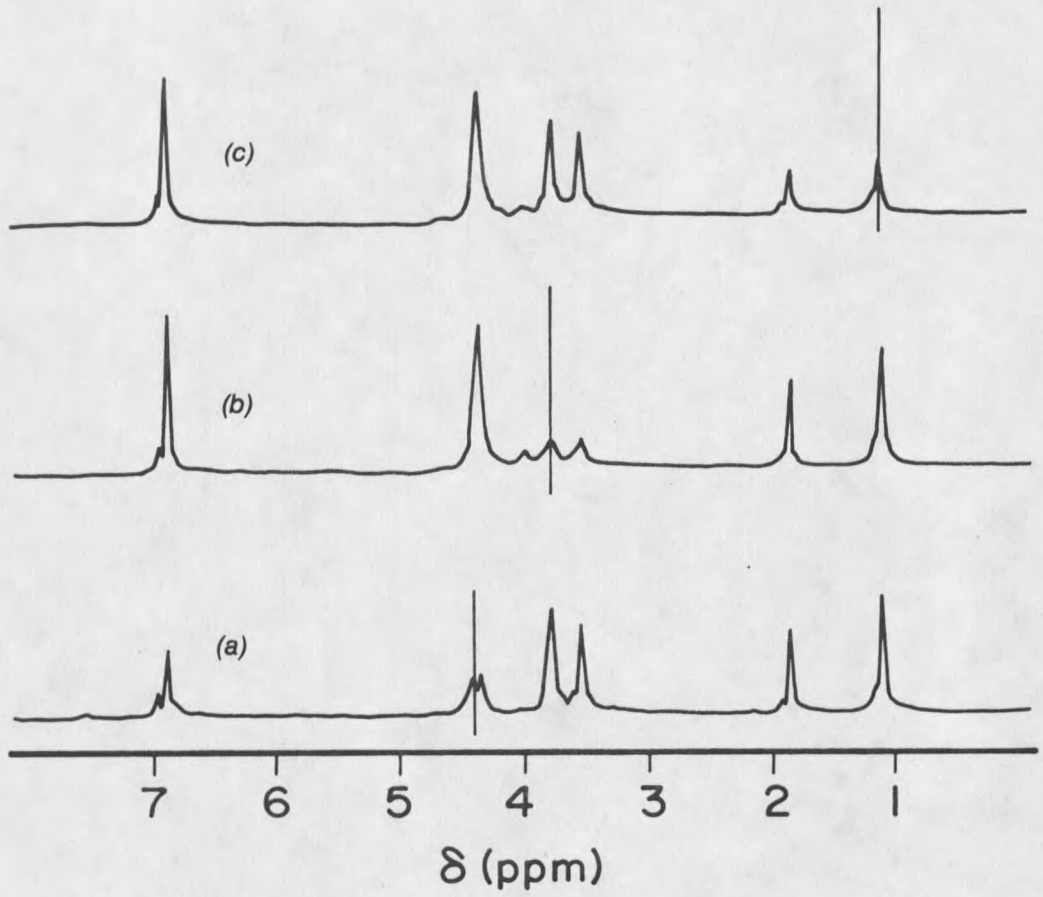


Figure 19. Saturation transfer NMR spectra at 300 MHz of the 4:1 mixture of **NBD** and **5** in $CDCl_3$ at -55°C: (a) irradiated at δ 4.38; (b) irradiated at δ 3.82; (c) irradiated at δ 1.17.

Equilibrium constants were determined at 7 temperatures in the range from 206.6 to 234.6°K. Extrapolation from these data points to 37°C via the expression log K versus T^{-1} (correlation coefficient = 0.99) gave an equilibrium constant of 4.5×10^{-6} M^{-1} ; 3.5×10^{-6} M^{-1} at 40°C. Thus, at the temperatures at which Halpern's and our rates were measured, an insignificant amount of the monomeric rhodium complex was present.

At lower temperatures, however, this equilibrium should have an observable effect on the kinetics when **NBD** is added to the reaction mixture. Rates were, therefore, measured at 0°C with and without **NBD** added (Table 8). In the reaction without added **NBD**, the

Table 7. Equilibrium Data for the 4:1 Mixture of **NBD** and $[(\mathbf{NBD})RhCl]_2$ in $CDCl_3$.[a]

T, °K	206.6	211.3	216.0	220.6	225.3	230.0	234.6
K_{eq}, M^{-1}	1.39	0.73	0.44	0.11	0.072	0.034	0.016

[a]Temperatures were determined using methanol. $\Delta H^0 = -15.8$ kcal.

pseudo first order plots were linear and gave an observed rate constant of 1.02×10^{-3} s^{-1}. In the reaction with two equivalents of **NBD** added, the plots were also linear and gave an observed rate constant of 2.3×10^{-3} s^{-1}. The observed rate constant was about 2.25 times greater with added **NBD** than without **NBD** added. The equilibrium concentrations of **5** and **24** at 0°C are 8.97×10^{-4} and 1.03×10^{-4} M, respectively, with two equivalents of **NBD** added. The individual rate constants for **5** and **24**, k_5 and k_{24}, were calculated assuming that k_{24} does not contribute to the observed rate significantly when no **NBD** is added to the reaction mixture. This assumption is valid given that the *pseudo* first order plots are linear. The individual rate constant k_5 is, then, equal to the observed rate constant with no **NBD** added divided by the concentration of **5** or $k_5 = 1.02$ $M^{-1}\,sec^{-1}$. The individual rate constant for **24** is calculated from the relation given in Equation 17 for the reaction with two equivalents of **NBD** added. Plugging in the appropriate values and solving

$$k_{obsd} = k_5\,[\mathbf{5}] + k_{24}\,[\mathbf{24}] \qquad (17)$$

for k_{24} yields a rate constant for **24** of 13.5 $M^{-1}\,sec^{-1}$, approximately 13 times greater than for **5**. Thus, in $CDCl_3$, it is apparent that there is another active catalyst or catalytic precursor stemming from **24** at low temperatures that is shown to be a more efficient catalyst for the valence isomerization of quadricyclane than **5**.

Table 8. Rate Data for Reactions in $CDCl_3$ at 0°C With and Without **NBD** added.[a]

$[Q]_0$, M	$[NBD]_0$, M	$[5]_0$, M	$[24]_0$, M	k_{obs}, s^{-1}	k_5, $M^{-1}\,s^{-1}$	k_{24}, $M^{-1}\,s^{-1}$
0.140	0	1×10^{-3}	0	1.02×10^{-3}	1.02	—
0.140	0.280	8.97×10^{-4}	1.03×10^{-4}	2.3×10^{-3}	1.02	13.5

[a]Resolved rate constants were calculated assuming $k_{obs} = k_5\,[\mathbf{5}] + k_{24}\,[\mathbf{24}]$.

This is not the case in CCl_4 or benzene. The equilibrium shown in Equation 16 is not observed over temperatures ranging from the freezing point of the solvent to 25°C. **NBD** exchanges with bound **NBD** in **5** which results in line broadening of the existing resonances only. To explore the possibility of this equilibrium being present at lower temperatures in non-polar solvents, a 4:1 molar ratio of **NBD:5** in toluene-d_8 was observed by NMR spectroscopy down to -90°C. In this experiment, the **NBD** exchange was again verified by NMR saturation transfer experiments but no evidence for **24** was gained at any temperature. The spectra were constant except that the linewidths narrowed at lower temperatures.

Two questions remain regarding the **NBD** exchange equilibrium with **5** and **24**. Does this exchange go by an associative or dissociative mechanism, and does **NBD** exchange directly with **24** as well as with **5**? The former question will be addressed later. The latter question was answered by utilization of the two dimensional Fourier transform NMR chemical exchange mapping technique (2DNOE).

The 2DNOE experiment produces a series of spectra which are related in two dimensions. When a stacked plot of these spectra is made it results in a map in which the normal one dimensional spectrum is contained in the horizontal spectrum at $F_1 = 0$ Hz (Fig. 20). The off $F_1 = 0$ Hz peaks are called cross peaks and they are a result of magnetization transfer by chemical exchange of protons from one environment to another. The cross peaks, therefore, correlate the resonances on $F_1 = 0$ Hz that are attributable to protons that are chemically exchanging between two different chemical environments. These correlations allow the chemical exchange processes to be mapped. In Figure 20, the cross peaks labeled A-B and B-A indicate that peaks A and B are due to protons that are chemically exchanging between two different chemical environments. Peak A at 6.75 δ is due to the olefinic protons on uncomplexed **NBD** and peak B at 4.35 δ is due to the olefinic protons of **NBD** bound to Rh in **24**. This correlation shows that uncomplexed **NBD** is exchanging directly with bound **NBD** in **24**.

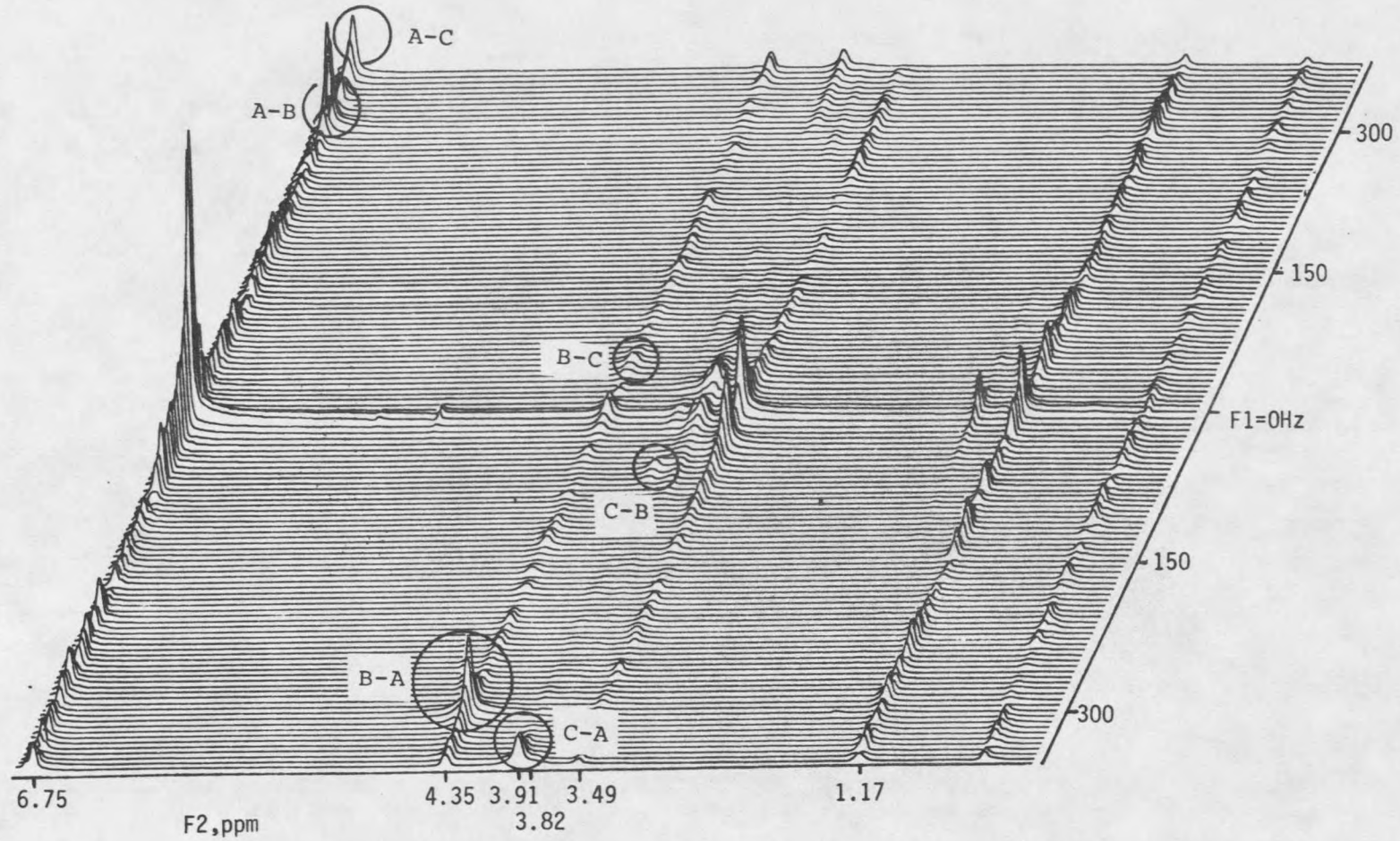
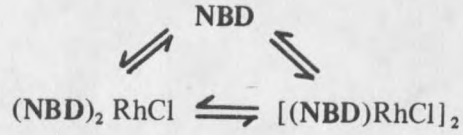


Figure 20. A stacked plot of the 2DNOE chemical exchange mapping experiment for the exchange equilibria in Equation 18.

Several other chemical exchange correlations are indicated in Figure 20. Cross peaks A-C and C-A show that **NBD** is exchanging with bound **NBD** in **5**. Cross peaks B-C and C-B demonstrate that **NBD** is exchanging directly between **24** and **5** as required by Equation 16. The final result is that **NBD** exchange occurs directly between uncomplexed **NBD** and each of the rhodium complexes, **5** and **24**, as well as directly between the two complexes (Eq. 18).

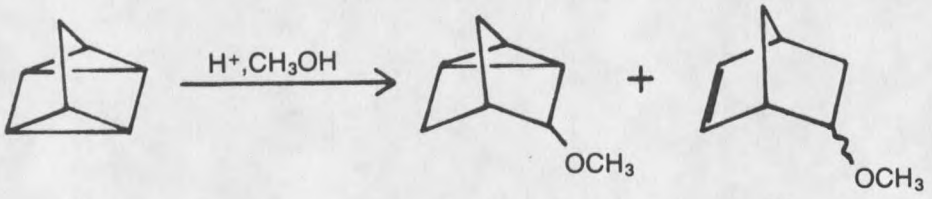


(18)

Test For Lewis Acid Mechanism in MeOH

It has been shown that, for Lewis acid catalyzed ring openings that are run in methanol, the carbonium ion intermediates can be trapped by solvent to yield methoxy addition products[26,36]. To test this possibility for the Rh(I) catalyzed isomerization of quadricyclane, products from the reaction run in MeOH were compared to products from the H^+ catalyzed reaction run in MeOH.

Sulfuric acid was utilized to effect the ring opening of quadricyclane in MeOH and yielded two methoxy capture products in the ratio 74:26 (Eq. 19).[a] They were identified as **25** and **26**, respectively, by their NMR and mass spectra. Reactions in MeOH catalyzed by either **5** or $Rh_2(CO)_4Cl_2$ yielded **NBD** as the major product with no methoxy



(19)

Q **25** **26**

[a]This reaction was reported in reference 36 but the product ratio reported was 23:77 for **25** and **26**, respectively, reversed from our result.

capture products formed at all. Therefore, no available carbonium ion intermediates are formed in the Rh(I) catalyzed valence isomerizations of quadricyclane reported herein and the Lewis acid mechanism is found unlikely to be responsible for the catalysis.

Test of H^+ Accelerator Hypothesis

Consideration of the dramatic rate enhancements observed for MeOH, CH_3COOH and $CH_2ClCOOH$ in the mixed solvent experiments (Fig. 19) led to the hypothesis that small amounts of H^+, either from the solvent or formed in the reaction, might be interacting directly with the catalyst and be responsible for the observed solvent effects rather than a change in the bulk solvent parameters. Experiments based on the addition of soluble organic bases to the reaction mixture in $CDCl_3$ were designed and carried out to test this hypothesis.

A suitable base would have to meet the following criteria: (1) be soluble in $CDCl_3$; (2) be easily protonated by weak acid in $CDCl_3$, i.e., CH_3COOH; (3) not affect the catalyst directly; and (4) not obscure the ^1H NMR resonances of the NBD vinyl protons. Pyridine, triethylamine (Et_3N) and tribenzylamine (TBA) were tested against these criteria. Pyridine was found unsuitable because it complexed strongly with **5** to the extent that a 5:1 mol ratio of pyridine:**5** stopped the NBD exchange equilibrium with **5** (Eq. 18). Pyridine by itself was also not protonated by CH_3COOH in $CDCl_3$. Et_3N, on the other hand, complexed with **5** in a labile fashion that did not inhibit the NBD exchange equilibrium. Et_3N was protonated by CH_3COOH in $CDCl_3$ and the protonated Et_3N did not complex with **5**. Rates measured in $CDCl_3$ with added Et_3N, however, showed that the unprotonated base acted as a competitive inhibitor of the reaction (Fig. 21). TBA proved to be soluble in $CDCl_3$, was easily protonated by CH_3COOH, did not affect the catalyst in an observable manner and did not obscure the product's proton spectrum. TBA was, therefore, the base found suitable to test the H^+ accelerator hypothesis.

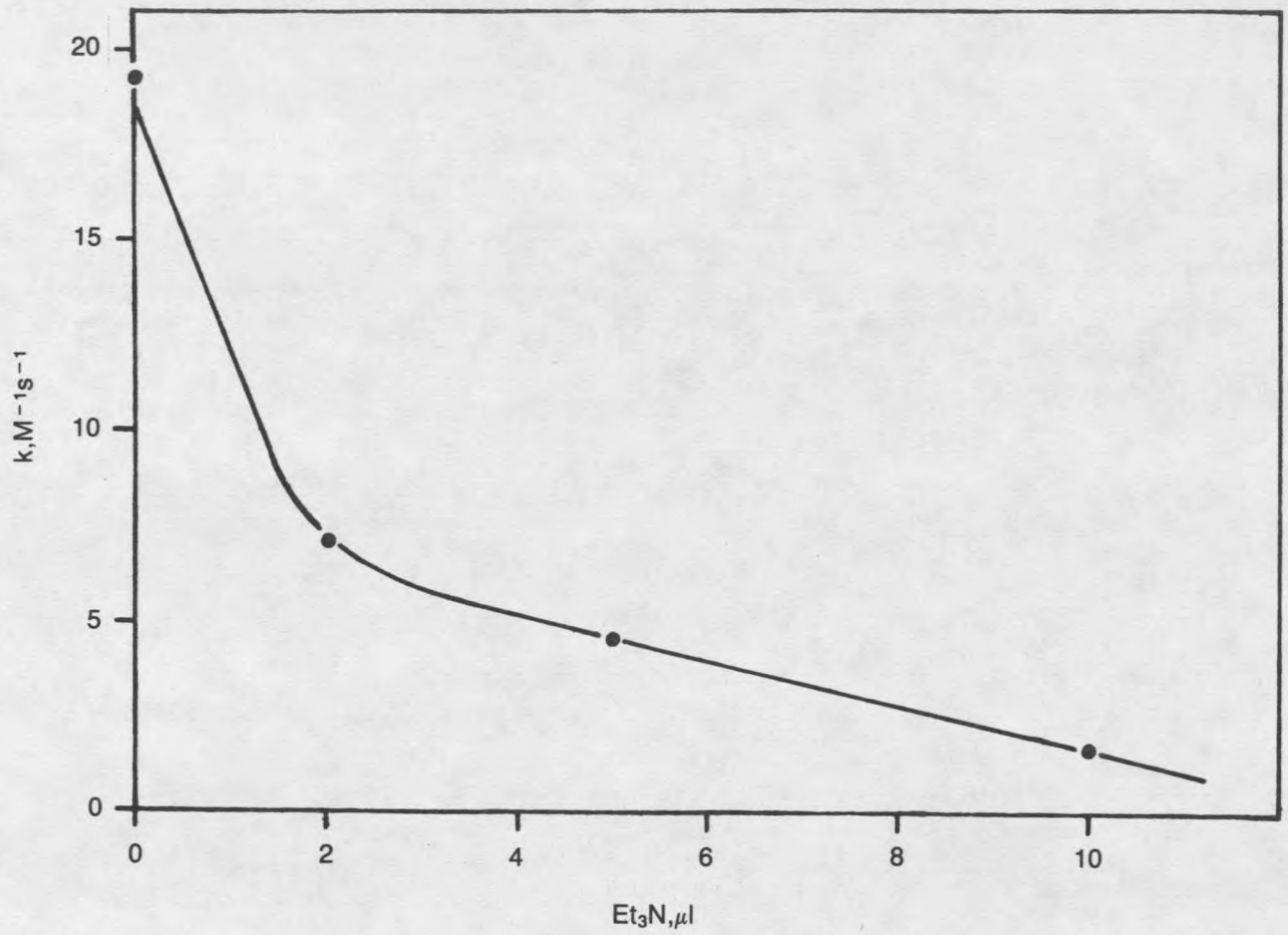


Figure 21. A plot of rate constant versus amount of Et_3N added to the reaction in Equation 13; 0.10 M Q, 0.001 M 5 in $CDCl_3$ at 37°C.

Rates measured for solutions of 0.10 M TBA, 0.10 M **Q** and 1.0×10^{-3} M **5** in $CDCl_3$ were compared to control solutions of the same composition minus the TBA. Second order rate constants for the two solutions were 12.0 and 12.8 $M^{-1} s^{-1}$, respectively. Thus, the reaction was shown not to be affected by the addition of TBA which was present in 100 fold excess over **5**. Therefore, the solvent effects on the rate constant observed in $CDCl_3$ are not attributable to acid from the solvent or acid produced by the reaction.

It would be well to note here that there were no observed effects on **5** in $CDCl_3$ by the addition of a 100 or 200 fold excess of acetic acid, as determined by NMR spectroscopy. This supports the idea that the effects on the rate constants observed for methanol and acetic acid, at least, are not due to H^+ effects on **5**. This inference must be tempered by the fact that the actual catalyst in solution is not known and may be affected differently than **5** which may be a catalytic precursor rather than the true catalyst.

Support for the "Cheleotropic" Mechanism: Observation of a New Rhodium Dicarbonyl Insertion Product

One of the key pieces of data supporting the "cheleotropic" mechanism for Rh interaction with cyclopropanes is the isolation of Rh carbonyl insertion products from $Rh_2(CO)_4Cl_2$ (**8**). Rh carbonyl insertion products have been observed for molecules such as quadricyclane[13] and cubane[15] which contain only cis-disubstituted C-C bonds in the ring and for cyclopropane which has only unsubstituted bonds. Halpern has reported[16] on a bi- and a tricyclobutane system which contain both cis-disubstituted and unsubstituted cyclobutane C-C bonds. In each case, only the cis-disubstituted bond was broken. The reaction of **8** with *exo,exo*-tetracyclo [3.3.1.0.^{2,4} 0^{6,8}] nonane (**27**), which contains both cis-disubstituted cyclopropyl bonds as well as monosubstituted cyclopropyl bonds, was investigated.

Reaction of an excess of **27** with **8** in $CDCl_3$ at room temperature for 3 hours followed by concentration and precipitation with pentane yielded a white powder presuma-

bly with the structure **29** in ~84% yield (Fig. 22). This complex had an IR spectrum (KBr) with strong absorbances at 2050 and 1725 cm^{-1} assigned to terminal and acyl carbonyls, respectively. This complex exhibited a rapid exchange equilibrium, believed to be interchange of the terminal and acyl carbonyl groups, as demonstrated by variable temperature NMR experiments. The facile exchange was not slowed enough at -65°C in $CDCl_3$ to fully resolve the NMR spectrum.

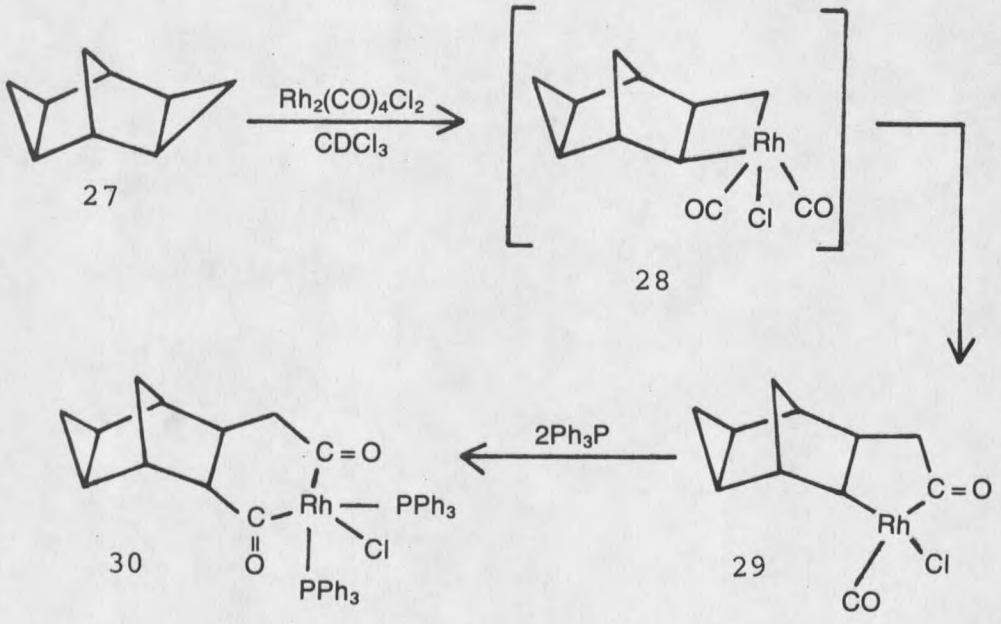


Figure 22. Reaction of **27** with $Rh_2(CO)_4Cl_2$.

In an attempt to stop the exchange by displacement of the terminal carbonyl with Ph_3P, 2.5 equivalents of Ph_3P was added to a solution of **29** in $CDCl_3$ and worked up as usual. A yellow powder (82%) was obtained and identified by IR and ^{13}C NMR spectroscopy. The carbonyl exchange was stopped but instead of the expected displacement and loss of the terminal carbonyl, the terminal carbonyl inserted into the remaining Rh-C bond to form the rhodiacyclohexadione **30**. The IR spectrum (KBr) contained absorbances at 1660 (m), 1620 (s), and 1590 cm^{-1} (w), similar to the IR data reported by Halpern for the analogous complex from quadricyclane[13]. The ^{13}C NMR spectra showed 2 C=0, 6 CH, and

3 CH_2 resonances which requires insertion into one of the side bonds of the cyclopropyl rings as opposed to attack of one of the cis-disubstituted cyclopropyl bonds from underneath.

This new Rh carbonyl insertion product is the first example of the insertion by Rh into the least substituted cyclopropyl bond when a cis-disubstituted cyclopropyl bond was available.

A Computer Simulated Kinetic Model

A reaction sequence was proposed which incorporated the major features of the experimentally observed kinetics in $CDCl_3$ at 37°C. These features include substrate inhibition and production of products from a common intermediate via parallel reaction paths. This scheme was then modeled by computer utilizing the HAVCHM program for integration of multistep rate equations written by Stabler and Chesick[37]. HAVCHM requires the input of each reaction step and its associated rate constant. HAVCHM then calculates and outputs the concentrations of each reactant, intermediate and product at requested time intervals. This output was treated identically to our experimental kinetic data. The resulting plots and rate constants were evaluated and compared to the experimental results. By an iterative process, the computer simulated kinetic model was refined to produce the reaction list in Table 9. The rhodium complexes are indicated by labels RH1 through RH5. The values of the rate constants for each step are listed to the right.

Table 9. Reaction List For the Kinetic Simulation Program HAVCHM.

1	RH1 + Q	$\xrightarrow{k_1}$	RH2	$k_1 = 24.0$	
2	RH2 + Q	$\xrightarrow{k_2}$	RH3	$k_2 = 24.0$	
3	RH3	$\xrightarrow{0.93k_3}$	RH2 + NBD	$k_3 = 41.0$	Parallel
4	RH3	$\xrightarrow{0.07k_3}$	RH1 + HCD		Reactions
5	RH3 + Q	$\xrightarrow{k_4}$	RH4	$k_4 = 5.0$	Inhibition step
6	RH4 + Q	$\xrightarrow{k_5}$	RH5	$k_5 = 5.0$	
7	RH5 + Q	$\xrightarrow{0.93k_6}$	RH5 + NBD	$k_6 = 4.75$	Parallel
8	RH5 + Q	$\xrightarrow{0.07k_6}$	RH4 + HCD		Reactions

Perhaps surprisingly, the proposed reaction sequence with the associated rate constants gives linear *pseudo* first order plots over 6 half lives at all **Q**:**5** ratios except at a narrow range of intermediate ratios where a slight biphasic character is observed which corresponds to the ratios at which a slight biphasic character was observed experimentally. A plot of the computer simulated rate constants versus the substrate concentrations inputed is compared to the experimental results for identical conditions in Figure 23. Agreement between the model and the observed results is excellent.

The Search for the Low Activity Rhodium Complex

Several attempts have been made to isolate and/or characterize the low activity rhodium complex believed to be responsible for the isomerization of quadricyclane at high $[Q]_0:[5]_0$ ratios in the polar solvents. As of this writing, the low activity Rh complex has not been identified.

Attempts to observe intermediate rhodium complexes by NMR spectroscopy were complicated by two factors. First, the facile exchange of **NBD** with the known rhodium complexes serves to broaden the spectrum of these complexes. Second, the high substrate to rhodium ratios required for production of the proposed low activity rhodium complex introduce dynamic range limitations which render the concentration of any rhodium complex too small to be seen with the available methods. Experiments were run in which the reaction mixture was made up at -60°C and contained an adequate amount of **5** to be easily seen by NMR spectroscopy. The reaction solution was placed in the probe of the WM250 spectrometer and slowly warmed while the reaction progress was monitored. Quadricyclane was observed to go directly to products and no intermediates were observed at any temperature.

Attempts to isolate the low activity rhodium complex were partially successful. Large scale reactions were run in which 50 mg of **5** was reacted with an excess of **Q** in $CDCl_3$

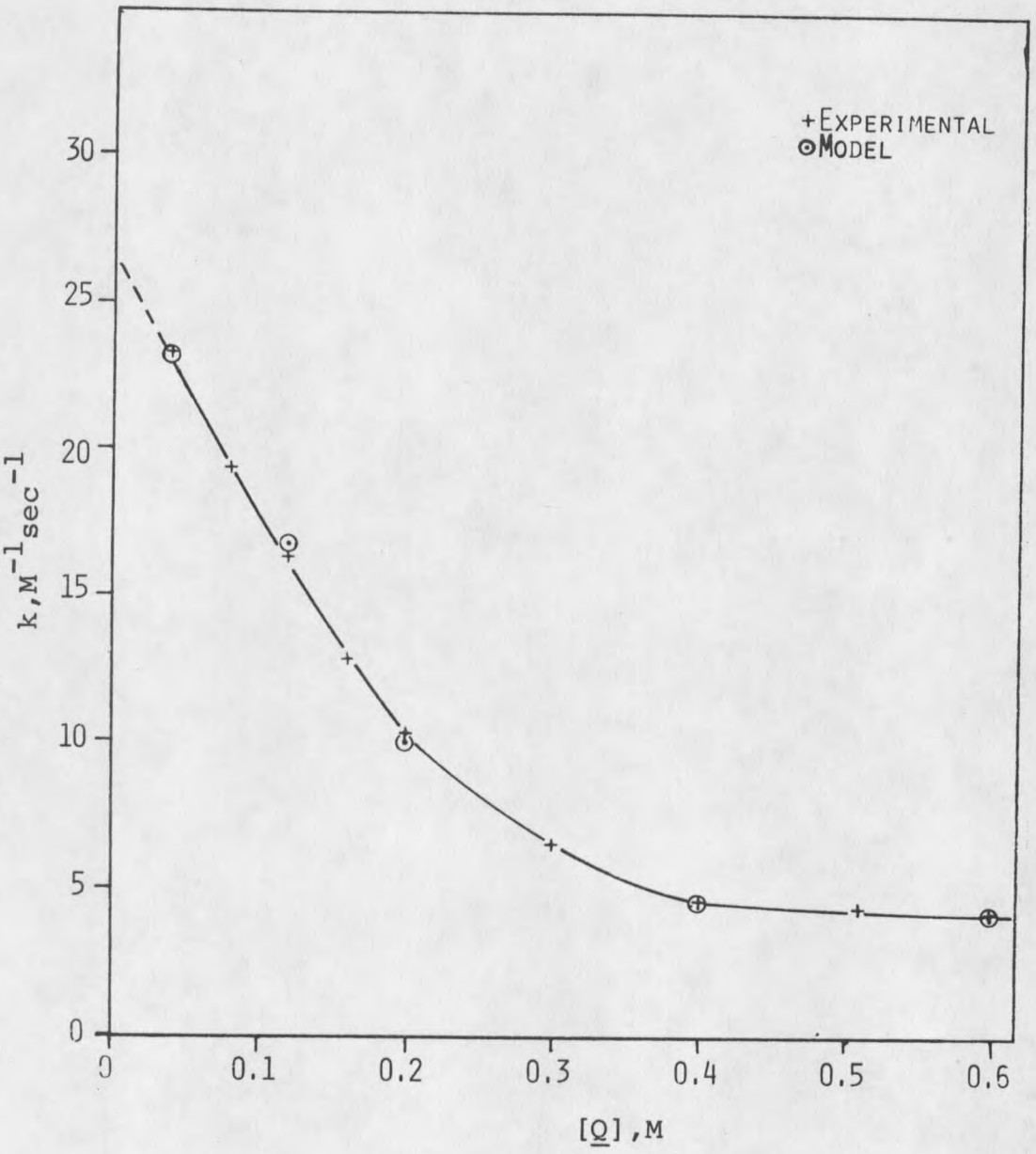


Figure 23. A comparison of experimental data (Fig. 10) versus results from the computer model for the reaction in Table 9.

under conditions that produce the low activity complex. The volatiles were removed by flash distillation and the rhodium products recovered. The recovered rhodium products demonstrated low catalytic activity toward quadricyclane isomerization but were not identified. The NMR spectrum of the rhodium products was broadened at room temperature (Fig. 24) and unresolved upon cooling to -65°C in $CDCl_3$ or -95°C in CD_2Cl_2. This spectrum contains resonances from 5.5 to 6.5 δ, indicative of olefins bound to Rh(III)[28]. The starting complex 5 is either buried, broadened or absent from this spectrum.

Although these results support the idea that the initial rhodium complex, **5**, is converted to another Rh complex or complexes during the isomerization reaction, the structure of that complex remains in doubt.

Attempts to isolate rhodium intermediates from the reaction in CCl_4 in a fashion similar to that reported above for $CDCl_3$ yielded only **5** (Fig. 24) and some unidentified insoluble material. The implications of these results will be considered in the discussion section.

DISCUSSION

Introduction

The foregoing results clearly show that the valence isomerization of quadricyclane catalyzed by $[(\mathbf{NBD})RhCl]_2$ is a reaction of unusual complexity rather than the simple, straightforward reaction previously indicated. This reaction is well behaved in non-polar solvents. It obeys *pseudo* first order kinetics and adheres to the rate law, $d[\mathbf{NBD}]/dt = k[\mathbf{Q}][\mathbf{5}]_0$, with rate constants on the order of 3 $M^{-1} s^{-1}$ at 37°C (Table 5). In polar solvents, however, the situation is quite different.

The rate constant shows unusual dependence on the solvent. Substrate inhibition but no product inhibition was generally observed in polar solvents. Rate enhancement dependent upon the product concentration at low temperatures and contributions from at least 3 catalysts or catalytic precursors were observed in $CDCl_3$. The product, **NBD**, was ob-

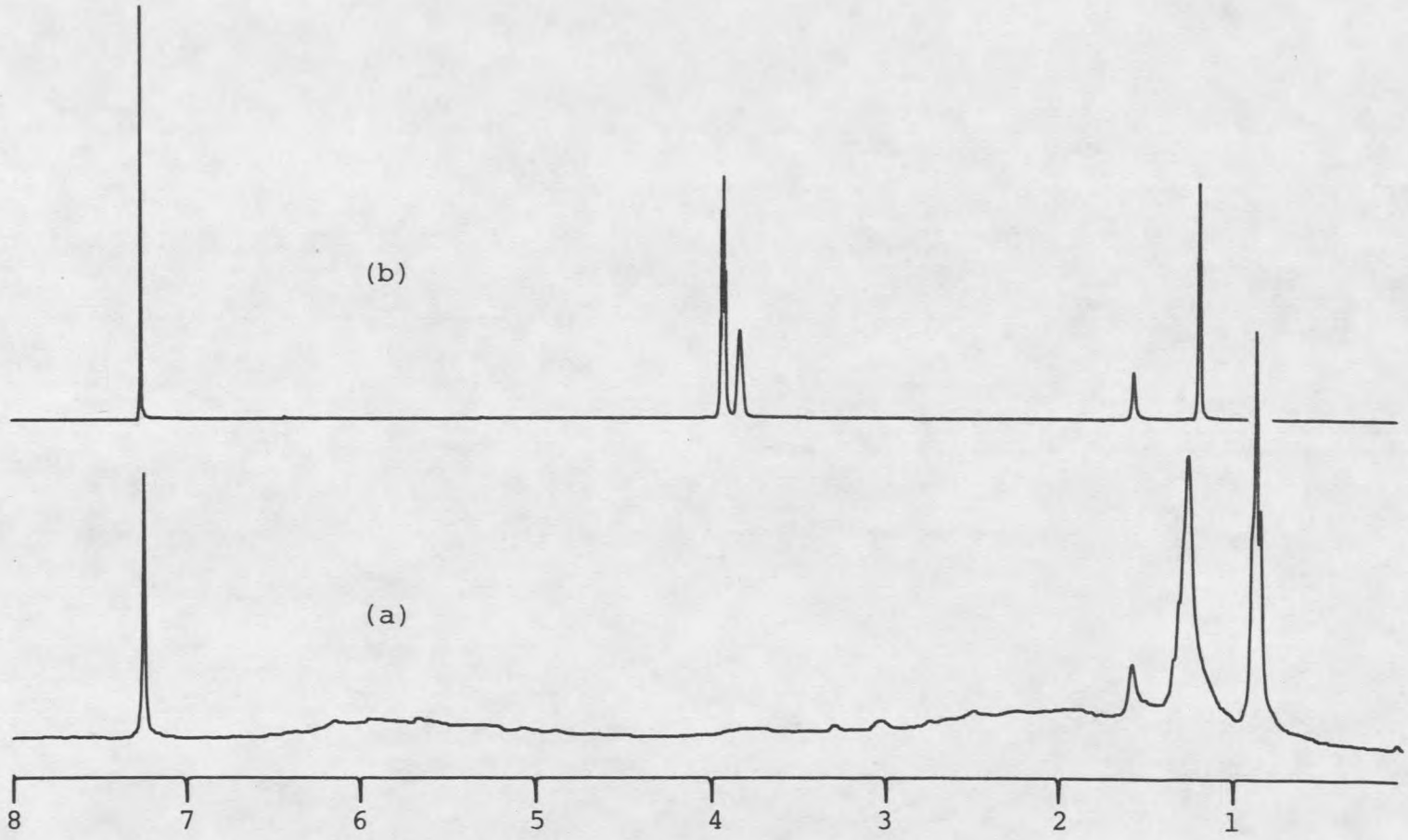


Figure 24. ^{1}H NMR spectra of Rh extracts from the **5** catalyzed isomerization of **Q**; (a) in $CDCl_3$ at high **Q**:Rh; (b) in CCl_4.

served to cleave the dimeric rhodium complex **5** to the monomeric rhodium complex **24** in the polar solvents but not in the non-polar solvents investigated. Finally, the observation of two products from this reaction with essentially constant ratios throughout the course of the reaction in both polar and non-polar solvents indicates that there are two effective parallel pathways proceeding from a common intermediate. These observations will be discussed in this section of the thesis.

Solvent Effects on the Rate Constant

While *pseudo* first order kinetics are observed for this reaction in polar solvents, unusual solvent effects are observed. Rate constants ranging from 26 to > 500 $M^{-1} s^{-1}$ at 37°C have been observed (Table 5). Rate enhancements for a series of polar solvents (Fig. 9) follow the order:

$$CH_2ClCOOH \gg CH_3COOH > MeOH > DMF \gg CH_3CN > CDCl_3.$$

The reason for this particular solvent order and magnitude of effect is not obvious. The observed rate enhancements do not correlate well with any single solvent parameter. A plot of rate constant versus Kosower Z values[38] gives a correlation coefficient of 0.75 for six solvents (Fig. 25). Similar plots for dielectric constant and for dipole moment gave poorer correlation coefficients of 0.66 and 0.61, respectively (Fig. 26). It is not surprising that no simple correlation exists between the rate constant for isomerization and a solvent parameter since there are at least two different and competing processes occurring simultaneously in this system and the solvent might be expected to affect these processes differently. Indeed, it has been shown that the inhibition process is more efficient relative to the isomerization process in CH_3OH than in CH_3COOH or $CDCl_3$ (Fig. 9).

Consideration of the protic solvents MeOH, CH_3COOH, and $ClCH_2COOH$ from the mixed solvent experiments (Fig. 9) suggests that the rate enhancements follow the order of the acidity of the solvent. A plot of the rate constants versus pk_a for these solvents,

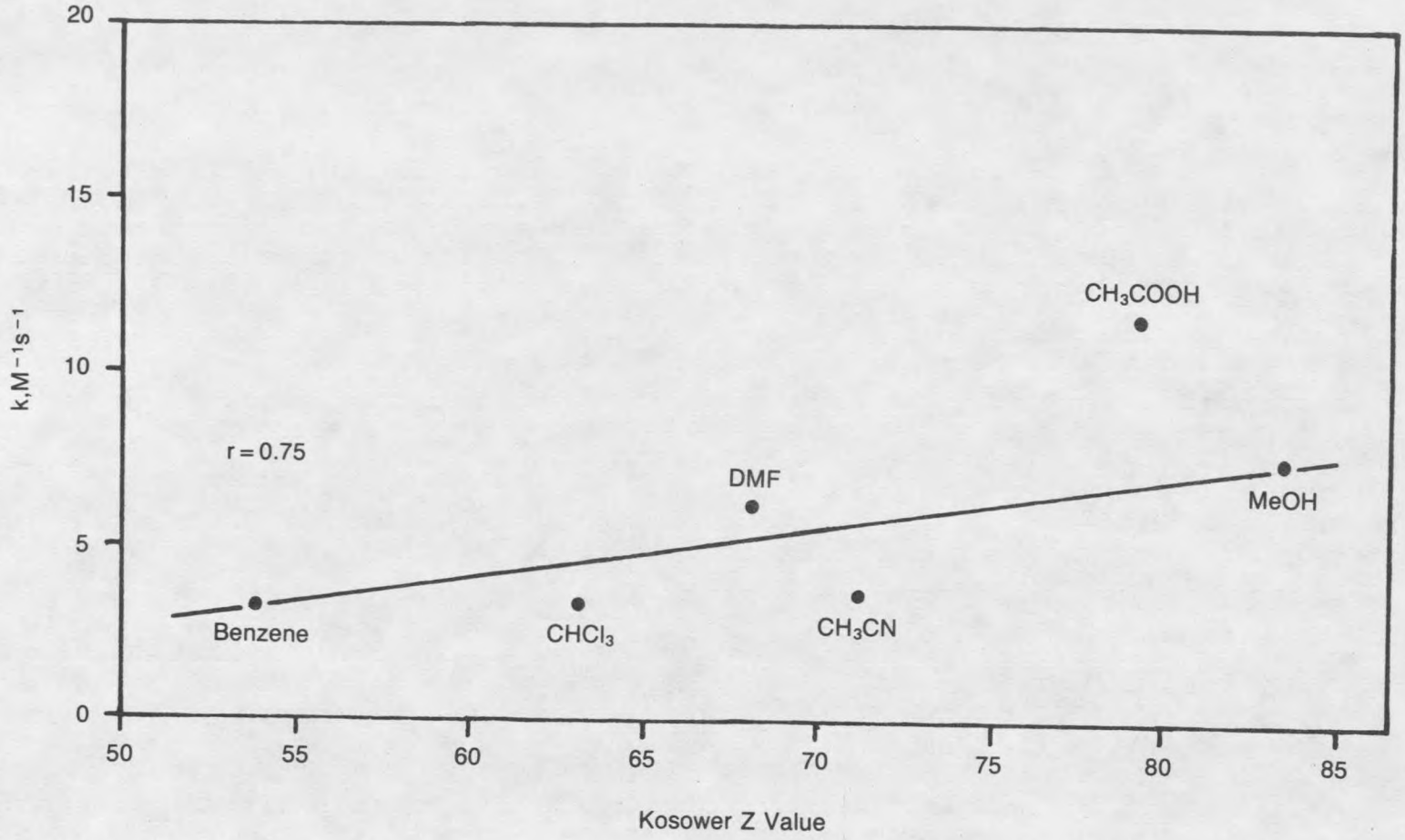
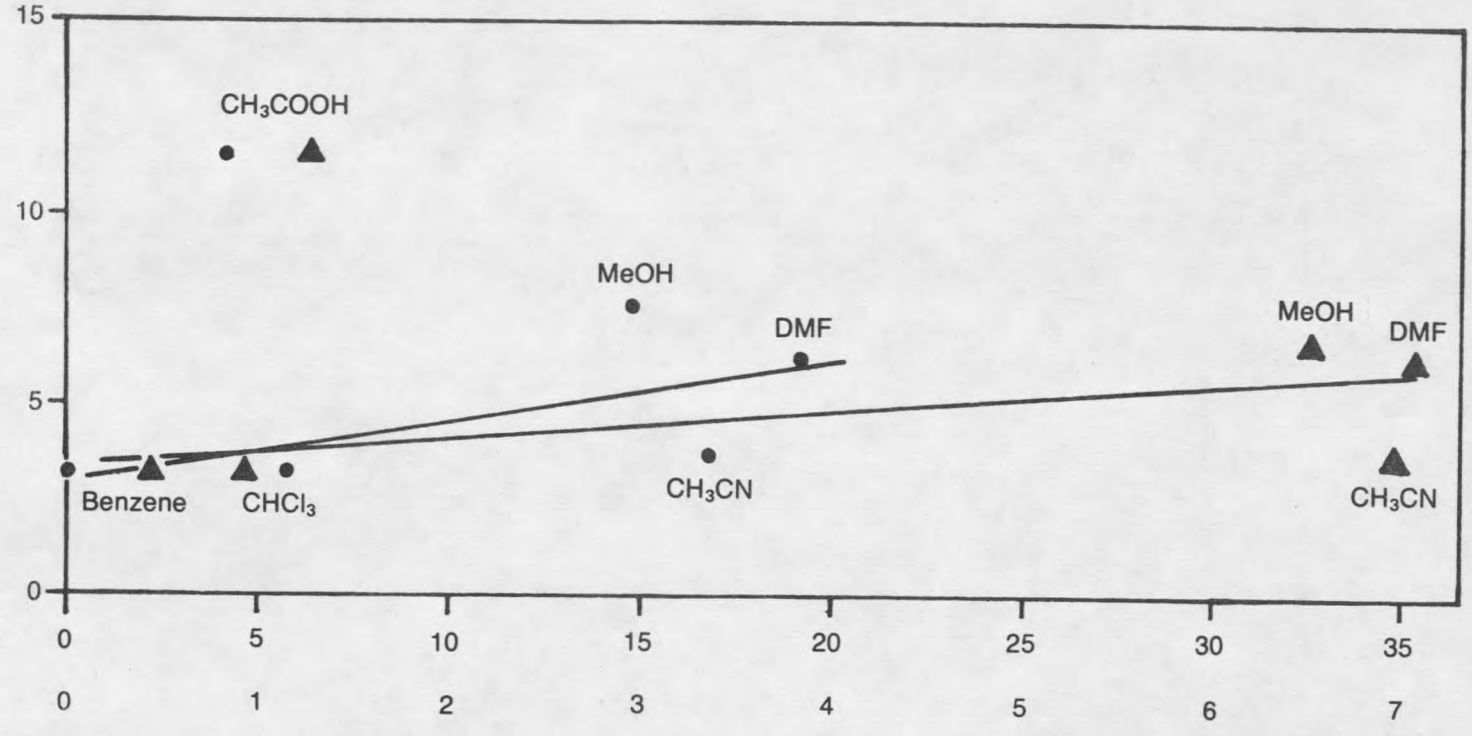


Figure 25. A plot of rate constant versus Kosower Z values for data points taken from the mixed solvent data (Fig. 9) at 0.5 M solvent added to CCl_4.



ıre 26. Plots of rate constant versus dielectric constant and dipole moment for data points from the mixed solvent data, Figure 9. The CH_3COOH points were omitted from the calculation of the correlation coefficients. ● = dipole moment; ▲ = dielectric constant.

however, does not give a significant correlation (Fig. 27). This was not considered conclusive because the relationship of the aqueous pk_a's for these acids to the pk_a's in CCl_4 is not known. To further test this possibility, rates were measured with the addition of an organic base, TBA, to the reaction mixture. $CHCl_3$ was chosen as the solvent to test the H^+ accelerator hypothesis since HCl is a common impurity in $CHCl_3$ and the observation of similar processes, particularly substrate inhibition, in each of these solvents suggests that the enhancement mechanism should be general. The use of $CHCl_3$ as solvent also avoids the complication of producing ion pairs from the reaction of the added acid with the base which would significantly alter the bulk solvent character. This study showed that the rate enhancements observed in polar solvents are not due to a simple dependence on H^+.

No simple correlation between rate constant and a solvent parameter has been observed. It seems apparent that any correlation that does not account for the inhibition process as well as the isomerization process will be unsuccessful in explaining the solvent effects on the rate constant. Such a correlation is beyond the scope of this work but could be made on the basis of ultimate rate constants determined by extrapolation to infinite dilution of the initial substrate concentration in a variety of polar solvents. Development of a new kinetic method capable of the determination of faster rates and the measurement of lower concentrations of substrate and product than available by the methods described herein would be required to determine ultimate rates over an adequate range of solvents.

Substrate Inhibition

The rate constant is dependent on the substrate to catalyst ratio in polar solvents. This dependence has been observed in $CDCl_3$, CD_2Cl_2, MeOH, and CH_3COOH (Figs. 9-13) and appears to be general for 7-substituted quadricyclanes as well (Fig. 14). This dependence has been shown to be due to substrate inhibition. The possibility of the inhibition being the result of impurity in the substrate was eliminated on the basis of experi-

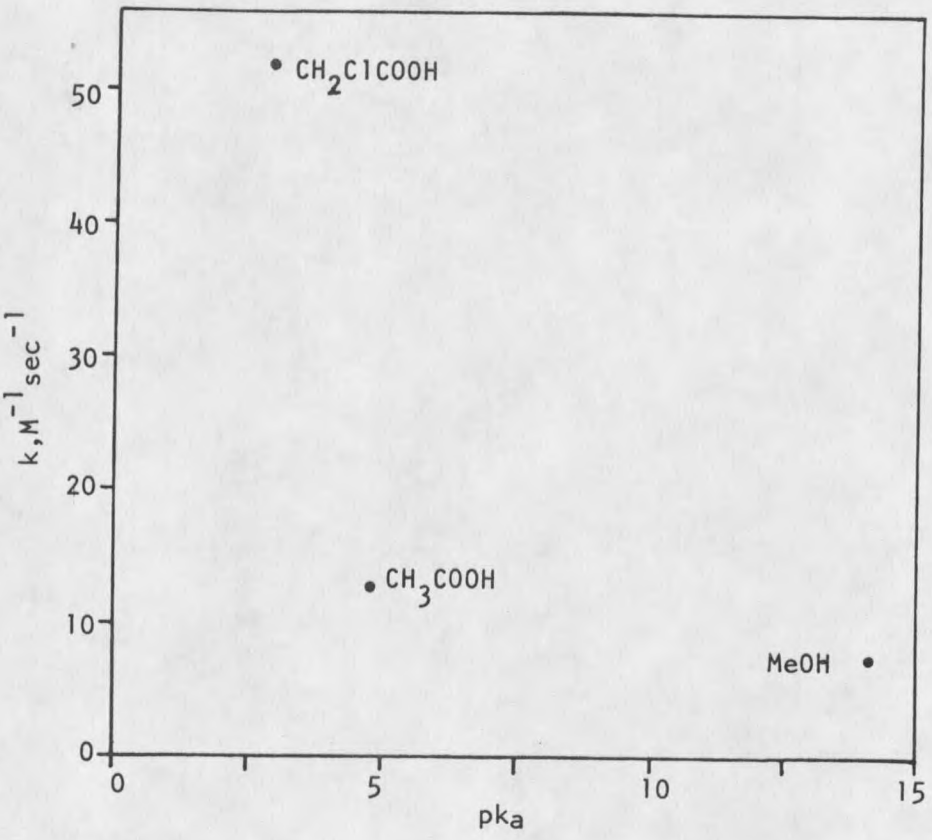


Figure 27. A plot of rate constant versus pk_a for MeOH, CH_3COOH and $CH_2ClCOOH$ taken from the mixed solvent results in Figure 9.

ments in which rates for crude preparations of substrate were compared to rates for substrate prepared by different methods and purified by a variety of techniques. The observed rate constants were unaffected by purification of the substrate. The reaction, also, proved to be quite insensitive to a variety of substances added to test for potential poisons. In addition, the 7-substituted quadricyclane **22** demonstrated the same type of dependence of the rate constant on the substrate concentration. It is beyond reasonable probability that any impurity could survive all of the above mentioned tests maintaining an identical ratio of itself to the substrate in all cases unless the inhibitor was the substrate. The observed substrate inhibition is proposed as the explanation for the difference in the rate constant reported by Halpern[13] for this reaction in $CDCl_3$ at 40°C and our rate constants at 37°C. Since the experimental conditions were not reported in Halpern's communication, it is reasonable to conclude that his reactions were run at high substrate to catalyst ratios resulting in the reported rate constant of 2.1 $M^{-1}\,sec^{-1}$ which is in good agreement with our rate constants at greater than 400:1 substrate to catalyst ratios, 4.3 $M^{-1}\,sec^{-1}$.

Having concluded that the inhibition is due to substrate, what is the nature of the inhibition reaction? Given that the inhibited rhodium complex (or complexes) has not been characterized, the inhibition process cannot be fully delineated but some inferences about the process can be made. First, it is apparent that the inhibition process involves a reaction of the substrate either with the catalyst or with some rhodium species that would otherwise become the catalyst. Second, the catalyst is not simply rendered inactive as a result of the inhibition reaction but is evidently converted to another catalytic species of lower activity. This is evident from the plot of the rate constant vs [substrate] for $CDCl_3$ (Fig. 10). At $[substrate]_0 > 0.40$ M, the rate constant became independent of the $[substrate]_0$, leveling out at $\sim 4.3\ M^{-1}\,sec^{-1}$. Third, consideration of the activation parameters for the reaction in $CDCl_3$ at low $[Q]_0:[5]_0$ versus high $[Q]_0:[5]_0$ indicates that the transition states arising from the high and low activity catalysts are substantially different. The

enthalpy of activation, $\Delta H^{\ddagger}$, for $[Q]_0:[5]_0 = 120$ was 13.0 kcal mol^{-1} compared to 4.7 kcal mol^{-1} for $[Q]_0:[5]_0 = 400$. The entropies of activation, $\Delta S^{\ddagger}$, were -12.1 and -41 cal mol^{-1} K^{-1} for $[Q]_0:[5]_0 = 120$ and 400, respectively (Table 6). The decrease in $\Delta H^{\ddagger}$ by almost two-thirds on going to high $[Q]_0:[5]_0$ indicates either that the bonds that must be lengthened or broken to achieve the transition state are substantially weaker for the low activity catalyst, or that there is a negative enthalpy process that is compensating. While this difference is probably significant, it is fairly difficult to draw structural conclusions from it. The difference in $\Delta S^{\ddagger}$, however, is more readily understood. Since this reaction is clearly bimolecular in each case, the increase in $\Delta S^{\ddagger}$ of greater than 3 times for the low activity catalyst must be due to increased orientational or steric requirements. This could be accounted for by the low activity catalyst having only a single available orientation which could react with a molecule of quadricyclane. This is probably a result of the rhodium complex acquiring an extra quadricyclane unit at high $[Q]_0:[5]_0$. Thus, the high activity catalyst might be a 3 or 4 coordinate rhodium (I) species and the low activity catalyst might be a hindered 5 coordinate Rh(I) species or a 6 coordinate Rh(III) that would require loss of a ligand to allow coordination of a quadricyclane molecule. If the low activity catalyst operated by a dissociative mechanism, however, it could not involve the loss of NBD in a reversible manner since the addition of NBD to the reaction mixture does not affect the kinetics. One could envision a mechanism in which a bidentate NBD might lose coordination to one olefin to become monodentate and open up a coordination sight. The transition state would, then, correspond to coordination of rhodium to a quadricyclane rather than oxidative addition of the quadricyclane to the rhodium complex. In this case, $\Delta H^{\ddagger}$ would be expected to decrease and $\Delta S^{\ddagger}$ would increase, as observed.

Evidence for a Third Catalyst at Low Temperatures in $CDCl_3$

Halpern[13] reported that the product, **NBD**, had no effect on the kinetics of the valence isomerization of quadricyclane catalyzed by **5** in $CDCl_3$ at 40°C. This result was unexpected on the basis of Volger's[24] observation that **5** was cleaved to the monomeric rhodium complex, **24**, in $CDCl_3$-CD_2Cl_2 solution (Eq. 16). Extrapolation of Volger's equilibrium constants to 40°C yielded $K_{eq}^{40°C} = 0.1\ M^{-1}$. At 40°C, this equilibrium should be significant and an observable effect on the kinetics would be expected. These investigations were repeated and it was found that **NBD** had no effect on the rate constant at 40°C but that Volger's ^1H NMR assignments were incorrect resulting in erroneous equilibrium constants. The redetermined constants are smaller and are listed in Table 7. Extrapolation of the new equilibrium constants to 40°C yields $K_{eq}^{40°C} = 3.5 \times 10^{-6}\ M^{-1}$. Thus, the equilibrium lies very far to the left at 40°C. On the basis of these new data, neither the amounts of **NBD** produced by the isomerization of **Q** during the reaction, nor the quantities of **NBD** added to the reaction in our investigations would decrease the concentration of **5** significantly. One would not, therefore, expect to see an effect of **NBD** on the rate constant at this temperature. However, at lower temperatures the monomeric rhodium complex is favored and one would predict a significant decrease in the concentration of **5** in the presence of **NBD**. In fact, the k_{obs} is 2.25 times larger at 0°C in the presence of **NBD** than in its absence (Table 8). Assuming the k_{obs} of $1.02 \times 10^{-3}\ s^{-1}$ is primarily due to **5**, then the rate constant for 0.001 M **5** is $1.02\ M^{-1}s^{-1}$ and the calculated rate constant for **24** would be $13.5\ M^{-1}s^{-1}$ or approximately 13 times larger. Therefore, not only is this equilibrium intimately related to the catalytic process but the monomeric rhodium complex **24** or a derivative thereof, is demonstrated to be a more efficient catalyst than **5** for the isomerization of quadricyclane.

Other Inhibition Processes

In addition to the equilibrium between **5** and **24** discussed in the previous section which resulted in rate enhancement at low temperatures, **NBD** is also involved in a direct exchange equilibrium with **NBD** bound to rhodium. Unlike the former equilibrium which does not occur in CCl_4 or benzene, the **NBD** exchange equilibrium was shown to be facile in CCl_4 and benzene, as well as in $CDCl_3$ and CD_2Cl_2 by NMR saturation transfer experiments. This equilibrium was observed in each solvent from the freezing point of the solvent up to 37°C. **NBD** exchange was demonstrated by 2DNOE chemical exchange mapping (Fig. 20) to take place directly between free **NBD** and **NBD** bound to both rhodium complexes formed in $CDCl_3$ (Eq. 18). The fact that this exchange does not apparently affect the reaction rate for quadricyclane isomerization indicates that the exchange and isomerization sites are different. This conclusion is supported by the results for the addition of Et_3N to the reaction in $CDCl_3$.

Et_3N was observed to bind weakly to **5** and was labile in $CDCl_3$. Although the exchange rates were not measured, the line broadening observed by NMR spectroscopy for free **NBD** with and without Et_3N added was qualitatively the same, indicating that **NBD** exchange was not inhibited by Et_3N. However, Et_3N was shown to competitively inhibit the isomerization of **Q** (Fig. 21). Since Et_3N inhibits the isomerization of **Q** but not the exchange of **NBD**, the exchange site for **NBD** must, therefore, be different than the isomerization site of **Q**.

Pyridine was observed to bind strongly to **5** but did not displace **NBD** in $CDCl_3$. A 5:1 mol ratio of pyridine:**5** in $CDCl_3$ stopped the **NBD** exchange and strongly inhibited the rate of isomerization, increasing the half life of the reaction from seconds to over an hour.

Since pyridine should coordinate to rhodium at the same site that Et_3N does and pyridine strongly inhibits both the isomerization and the exchange processes but Et_3N inhibits only isomerization, it is reasonable to conclude that the **NBD** exchange process proceeds by a dissociative mechanism. This suggests that pyridine affects the lability of **NBD** by increasing the strength of the Rh-**NBD** bonds. This is reasonable given that pyridine donates electron density to the metal but is incapable of significant π back bonding. The excess electron density on the metal can increase the π back bonding to **NBD** and therefore increase the strength of the Rh-**NBD** bonds. Et_3N, however, binds only weakly to **5** and although it should donate some electron density to the metal, apparently the interaction is not strong enough to affect the **NBD** exchange rate significantly. It is not reasonable to suggest that pyridine is blocking the site of **NBD** association because that would imply that the sites of exchange and isomerization are the same, in which case **NBD** would be a competitive inhibitor of the isomerization process and that is not observed.

Reaction Scheme

A reaction scheme that accommodates the major features of this reaction in $CDCl_3$ was developed and refined with the aid of a kinetic modeling program. One of the significant advantages of utilizing a computer modeling program is that one avoids the necessity of making the steady state approximation commonly used to reduce the rate law to manageable proportions[39]. In this case, the steady state approximation would clearly be invalid. The final reaction list is given in Table 9. This reaction scheme is abbreviated and contains the minimum steps considered necessary to model the experimental results.

RH1 is the complex **5**. The structures of the other rhodium complexes are not known, however, a structure for RH3 will be proposed. This list does not explicitly contain equilibria that would not materially affect the result of the model, i.e., the exchange of **NBD** with **NBD** bound to rhodium. This model is not intended, for instance, to discriminate

between RH3 being $Q_2(NBD)_2Rh_2Cl_2$ or the complex cleaved to Q_2(NBD)RhCl and (NBD)RhCl. In the latter case, (NBD)RhCl would rapidly dimerize to $[(NBD)RhCl]_2$, RH1, and the individual rate constants would have to be adjusted accordingly but the end result of the model would be the same.

Steps 3 and 4 are parallel reactions proceeding from a common intermediate, RH3, to yield the two products in constant ratio throughout the course of the reaction, as observed. Steps 1-4 correspond to isomerization by the high activity catalyst which is predominant at low $[Q]_0:[5]_0$ ratios. Step 5 is the inhibition step in which reaction of RH3 with Q yields a new rhodium species that then leads to isomerization by the low activity catalyst in steps 6-8. The inhibition step could involve any rhodium species produced by the reaction and is not limited to RH3. The inhibition step proposed acts as a siphon of rhodium from the high activity catalyst pathway into the low activity catalyst pathway. There is no proposed route for return to the high activity path. It is entirely possible that there could be a slow route back to the high activity path or a myriad of other paths that would not materially change the result of the model, i.e., a mechanism can always be more complicated. However, this model is intended to utilize the fewest steps that will accommodate the observed results.

Reaction steps 7 and 8 are parallel reactions to the two products of the low activity catalyst, analogous to the partition in steps 3 and 4. It is remarkable that the partition between products is apparently identical for both the high and low activity paths (Table 4), especially in light of the fact that the activation parameters suggest that two different mechanisms or transition states are involved for the isomerization by the two catalysts. It must be remembered, however, that the activation parameters relate only to the events occurring prior to and including the transition state of the rate determining step and that the product distribution most likely occurs after this.[a] It is, therefore, likely that the reac-

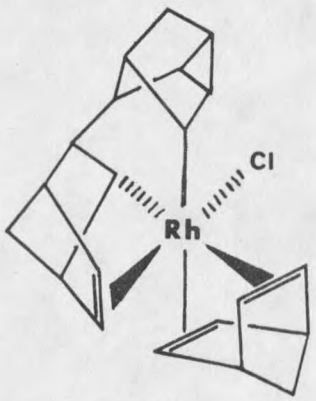
[a]Actually, any conclusion based on activated complex theory must be taken with a grain of salt because the theory itself may not be valid for a complex reaction.

tions leading to products after the rate determining step for each pathway are very similar. In any event, the identical product distributions for this reaction at high and low Q:5 ratios require that the free energy differences between the two paths to products be identical in each case.

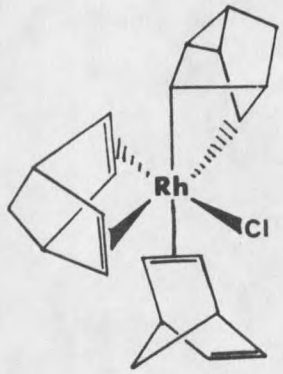
A comparison of results from the kinetic model to the experimentally observed results is given in Figure 23. Agreement is excellent. It should be noted here that agreement of a model does not constitute proof of a reaction scheme. However, a properly constructed model does demonstrate that the features contained in the model are able to account for the observed results. This has been demonstrated for the reaction scheme in Table 9.

A detailed discussion of the structures of the reaction intermediates will not be attempted owing to the lack of structural evidence for them. However, some discussion of the intermediate RH3 is warranted. RH3 in the proposed reaction scheme is a common intermediate leading to both products. It must, therefore, have at least two Q or **NBD** moieties associated to rhodium. Complex **31** is proposed as a reasonable structure for RH3 (Fig. 28). Complex **31** is a hexacoordinate Rh(III) species that could either extrude **NBD** or rearrange to **32** which could then produce **HCD**. This structure is given support by the identification of the analogous intermediate, **20**, from the [(**NBD**)Rh(OAc)]$_2$ (17) catalyzed isomerization of Q by Chen[28] (Fig. 6). Complex **20** is analogous to **32** with the difference that the Cl is replaced by OAc. Chen proposed that **20** was formed from **21** which is analogous to **31**.

Although Chen's system is identical to ours except that he used the acetate bridged rhodium complex rather than the chlorine bridged complex, the two systems are dramatically different kinetically. In the acetate bridged case, the rate was found to be dependent on [**NBD**]. At low [**NBD**]$_0$ this resulted in autocatalytic behavior until a sufficient excess of **NBD** was produced. In the presence of excess **NBD**, the rate was zero order in [Q] and



32



31

Figure 28. Proposed intermediate in the isomerization of Q catalyzed by $[(\mathbf{NBD})RhCl]_2$.

[**NBD**] and first order in **17**. At very high $[Q]_0:[17]_0$, rates were first order in **Q**. These observations are in direct contrast to the chlorine bridged system in which no dependence on **NBD** was observed, rates were first order in [**Q**], and substrate inhibition was observed. In addition, the dimeric rhodium complex was not cleaved to a monomeric rhodium complex by **NBD** in the acetate bridged case, however, **NBD** exchange was observed and thought to be an associative process involving $Rh_2(\mathbf{NBD})_3(AcO)_2$. The dramatic contrasts between these two very similar systems emphasizes the importance of detailed kinetic studies to the understanding of these systems and demonstrates, once again, the danger of generalization from one system to another without adequate investigation.

CCl_4 versus $CDCl_3$

Is the catalyst in CCl_4 the same as the low activity catalyst in $CDCl_3$? The reaction in CCl_4 looks very much like the reaction in $CDCl_3$ at high $[Q]_0:[5]_0$ ratios. The rate constant for CCl_4 was 2.9 versus 4.3 for $CDCl_3$. The reaction yielded the same products in each solvent. The product ratio was constant throughout the reaction in each solvent. The product distribution was 7.0% **HCD** in $CDCl_3$ and 3.5% **HCD** in CCl_4. The activation parameters for the reaction in $CDCl_3$ at high $[Q]_0:[5]_0$ were $\Delta H^{\ddagger} = 4.7 \pm 1$ kcal mol^{-1}

and $\Delta S^{\ddagger} = -41 \pm 8$ cal mol^{-1} K^{-1} compared to $\Delta H^{\ddagger} = 6.0 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 37.0 \pm 3.7$ cal mol^{-1} K^{-1} in CCl_4 (Table 6). The differences between the reactions in the two solvents are that the rate constant is 50% faster and the product distribution yields twice as much HCD in $CDCl_3$ than in CCl_4. These differences are of the size of solvent effects that might be expected upon changing the solvent from CCl_4 to $CDCl_3$ without changing the catalyst or mechanism. More significantly, the transition states should be similar if the catalyst is the same in the two solvents. In this case, the activation parameters are the same, allowing for experimental error. Therefore, since the reactants and the products are the same, the differences in rate constant and product distribution are of reasonable size and the activation parameters are the same, it would be reasonable to conclude that the catalyst in CCl_4 is very likely the same as the catalyst in $CDCl_3$ at high $[Q]_0:[5]_0$ ratios. This would imply that the reaction sequence for the isomerization in CCl_4 proceeds according to steps 5-8 of the reaction scheme in Table 9. If this is correct, it requires that conversion of **5** to the low activity catalyst must be very rapid in CCl_4 and occur within the time prior to the taking of the first data point. This requirement is necessary for the *pseudo* first order plots to be linear.

If the catalyst in CCl_4 is actually the same catalyst as at high $[Q]_0:[5]_0$ ratios in $CDCl_3$, then an extract of the rhodium containing portion of a reaction mixture in CCl_4 should be identical to an extract of a reaction mixture in $CDCl_3$ under conditions in which the low activity catalyst is produced. This was not observed. Isolation of the rhodium containing fraction of a large scale reaction in CCl_4 yielded only the initial rhodium complex **5**, whereas isolation of the rhodium fraction of a large scale reaction in $CDCl_3$ run at high $[Q]_0:[5]_0$ resulted in a complex product mixture in which **5** was not detected. This result implies that the true catalyst in CCl_4 is, or is derived directly from, **5** while the low activity catalyst in $CDCl_3$ is a quadricyclane addition adduct of some type.

If the catalysts are different, why are the activation parameters nearly identical? The molecular crystal structure of **5** has not been determined but consideration of a series of chlorine bridged Rh(I) compounds (Table 10) indicates that the dihedral angle between the two coordination planes for **5** should be close to 120° and that the metal-metal distance should be approximately 3.1 Å. A model of **5** constructed according to these parameters shows that the two metal atoms are effectively sterically shielded by the NBD ligands and the bridging chlorines. This would account for the larger negative $\Delta S^{\ddagger}$ for the reaction in CCl_4. In $CDCl_3$, one or both of the chlorine bridges in **5** are likely cleaved upon addition of **Q** to open up the complex which would relieve the steric interference resulting in the high activity catalyst. Addition of another molecule of quadricyclane at high $[Q]_0:[5]_0$ could then produce a sterically constrained rhodium complex of low catalytic activity.

Table 10. Dihedral Angles, ω, Between Coordination Planes and Metal-Metal Distances, d, For Chlorine Bridged Rh(I) Compounds[40].

Compound	ω deg	d, Å
$Rh_2(CO)_4Cl_2$	124	3.12
$[(C_2H_4)_2RhCl]_2$	115.8	3.02
$[(C_6H_{10})_2RhCl]_2$	115.8	3.09
$[RhCl(CO)(PMe_2Ph)]_2$	123.0	3.167
$(n\text{-}1,5\text{-}C_8H_{12})Rh_2Cl_2(P[OPh]_3)_2$	122.6	3.138

This type of solvent dependence has already been demonstrated for **5** with respect to bridge cleavage by **NBD**. In $CDCl_3$, **5** was cleaved to the monomeric complex **24** by **NBD** (Eq. 16). In CCl_4, the chlorine bridges in **5** remained intact upon addition of **NBD** to the solution. Therefore, it is reasonable to conclude that the catalyst in CCl_4 is derived directly from **5** and is not the same as the low activity catalyst in $CDCl_3$.

Mechanism of Rh(I) Interaction With Quadricyclane

Three basic mechanisms have been proposed for the interactions of transition metals with cyclopropanes (Fig. 2). These include: (1) the concerted mechanism which involves edgewise coordination of the metal to the cyclopropane to relieve orbital symmetry constraints and allow rearrangement in a concerted fashion, (2) the "cheleotropic" mechanism which involves insertion of the metal into a C-C bond followed by cheleotropic extrusion of the metal accompanied by bond reorganization, and (3) the Lewis acid mechanism which involves the formation of a metalla-carbonium ion intermediate commonly followed by carbonium ion rearrangements. The isomerization of quadricyclane has been proposed to occur by each of these mechanisms depending on the metal and the solvent used. Ag(I) is thought to interact via the Lewis acid mechanism. Rh(I) is generally thought to follow the oxidative-addition route but the concerted mechanism has been proposed on theoretical grounds, as well. Evidence for the Lewis acid mechanisms includes methoxy capture products for Ag(I) catalyzed rearrangements run in methanol[26,36]. Evidence for the oxidative-addition route includes isolation of Rh carbonyl insertion products from $Rh_2(CO)_4Cl_2$[13,16]. New evidence from this work rules out the concerted and Lewis acid mechanisms for the $[(NBD)RhCl]_2$ catalyzed isomerization of quadricyclane in favor of the oxidative-addition route.

Observation of two products from this reaction formed by parallel paths from a common intermediate requires that the mechanism must be stepwise unless a termolecular concerted process is to be invoked to explain the formation of **HCD**. One could argue that the kinetic results may be explained by two separate mechanisms that occur at constant relative rates and that the formation of **NBD** is a concerted process, but this does not solve the problem. This argument now requires that the metal interact with the substrate by a nonconcerted process as well as by a concerted process under identical conditions. While this

contention may not be ruled out, a priori, it is viewed as an unnecessary complication since there is no evidence to support it.

Support for the Lewis acid mechanism suffers from the complete lack of methoxy capture products from the Rh(I) catalyzed isomerization of **Q** in methanol. Methoxy capture products were the only products observed for the sulfuric acid catalyzed reaction in methanol (Eq. 19).

The "cheleotropic" mechanism is consistent with all of the observations in this report and it is considered the most likely mechanism for the Rh(I) catalyzed isomerization of **Q**. While no new evidence for this mechanism in this specific system is offered, support for the generality of the oxidative-addition route for Rh(I) interactions with cyclopropane in rigid systems is gained from the observation of the new rhodium dicarbonyl insertion product **30** from the reaction of **27** with $Rh_2(CO)_4Cl_2$ in $CDCl_3$ (Fig. 22). The monocarbonyl insertion product **29** is thought to arise via insertion of the metal into a side bond of one of the cyclopropyl rings to form the rhodiacyclobutane **28** followed by carbonyl insertion into one of the Rh-C bonds. On addition of Ph_3P, **30** is produced by insertion of the remaining CO into the remaining Rh-C bond.

It is interesting to note that this is the first case in which given a choice, rhodium inserted into the least substituted cyclopropyl bond. Insertion into the cyclopropyl side bond rather than from underneath, suggests that bidentate coordination of rhodium to both cyclopropyl rings is not important in this case. Mango[12] stressed that bidentate coordination of the substrate to the metal is an important feature of metal catalyzed valence isomerizations that proceed by a concerted process. The cyclopropyl rings in **27** are ideally situated for bidentate coordination to the metal, yet bidentate coordination appears to be unimportant in this favored case. If bidentate coordination is necessary for the concerted mechanism to be viable, this observation suggests that the concerted mechanism is proba-

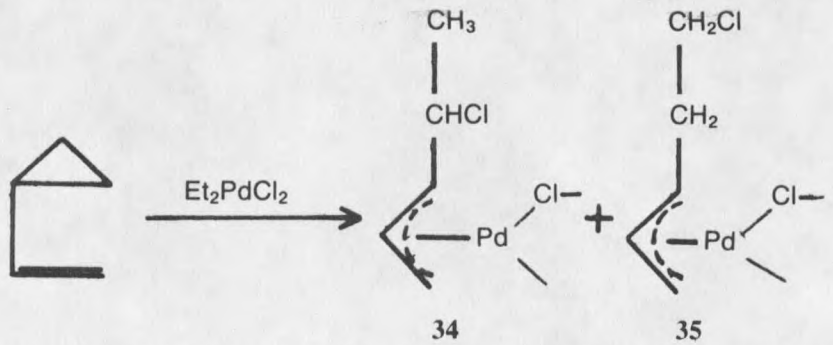
bly not a major pathway for metal catalyzed valence isomerizations of cyclopropanes in rigid systems.

INTERACTION OF Pd(II) WITH CYCLOPROPANES IN RIGID SYSTEMS

INTRODUCTION

The interactions of Pd(II) complexes with cyclopropane have received relatively minor attention when compared to other group VIII transition metals such as Pt(II) and Rh(I). Both Pt(II) and Rh(I)[41a] are commonly thought to interact with cyclopropanes via metal insertion into a C-C bond to form metallacycles. Although Pd(II) and Pt(II) have very similar electron promotion energies and electron affinities, 3.05 vs. 3.39 and 18.56 vs. 19.42 eV[21], respectively, their modes of interaction with cyclopropanes appear to be quite different. Pd(II) is generally thought to interact via ionic paths which result in halopalladation products rather than metallacycles. Two important questions concerning the mechanism of these halopalladation reactions are: (1) how is the ring activated by the metal and (2) what is the specific and overall stereochemistry of the reaction?

Palladium chloride complexes are known to form chloropalladation adducts with cyclopropanes. The first report of this type of product was by Ketley in 1967[42]. Vinyl cyclopropane was shown to react with bis(ethylene) palladium di-chloride, **33**, to give chlorine substituted π-allyl Pd complexes (Eq. 20). Two products, **34** and **35**, were reported



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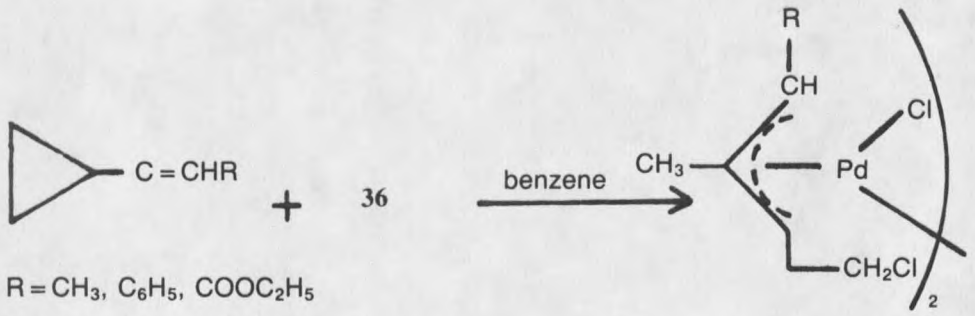
34 **35**

in 5:3 molar ratio for this reaction. The normal product for chloropalladations of cyclopropanes is **35** in which Pd and Cl are added across the cyclopropyl bond that is cleaved.

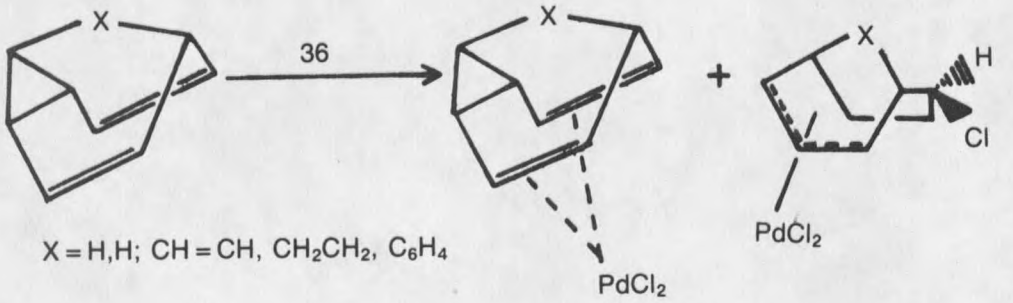
Complex **34** is unusual in that Cl is substituted on the cyclopropyl carbon that is not involved in the ring opening. This type of product is extremely rare for chloropalladations of cyclopropanes.

Shono[43] showed, in 1968, that the chloropalladation reaction was general for substituted vinyl cyclopropanes with $(PhCN)_2PdCl_2$, **36** (Eq. 21). In this case, only the normal products analogous to **35** were observed. Shono suggested that ring opening occurred via a cyclopropyl carbinyl-homoallyl rearrangement. In 1968 and 1970, Ketley reported on the



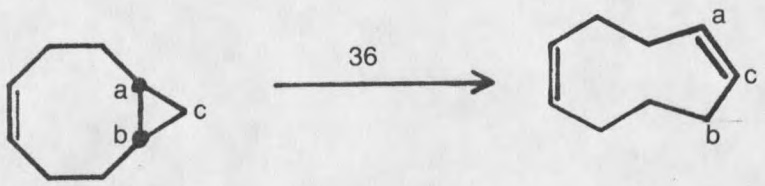
(21)

reactions of several bicyclopropanes with **33**. Spiropentane[44], dicyclopropyl[45] and dicyclopropylmethane[45] were each shown to yield a single chloropalladation product rapidly at 25°C in CH_2Cl_2. In 1973, Vedejs[46] reported the reactions of a number of homotropilidenes with **36** (Eq. 22). Two products were reported for each reaction. Along with bidentate coordination of the unrearranged diene to Pd, a Cl substituted π-allyl complex was observed for each substrate. None of these early reports offered mechanistic or stereochemical details regarding the ring opening by palladium.



(22)

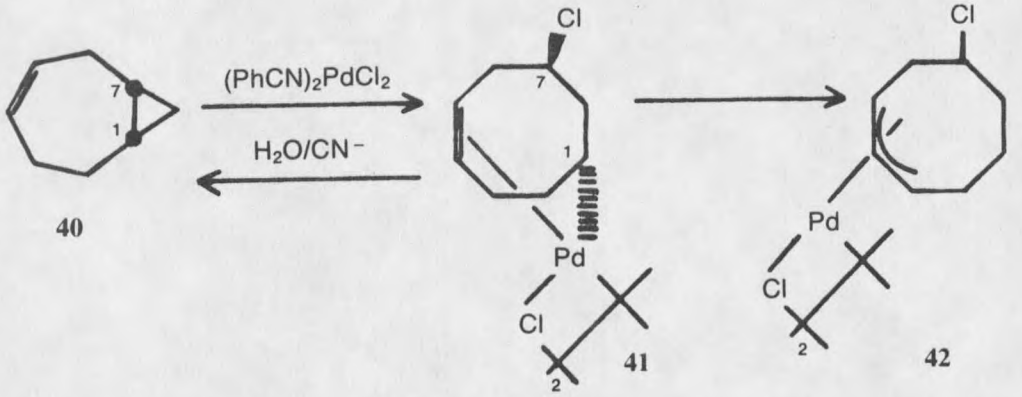
Rettig has been the most active researcher in the area of chloropalladations of cyclopropanes having published five full papers between 1972 and 1983. He has concentrated on bicyclic systems with cyclopropanes that are remote from C-C double bonds and are not subject to significant additional ring strain. Rettig[47] observed that cis-bicyclo [6.1.0]non-4-ene, **37**, was catalytically converted to cis,cis-1,5-cyclononadiene, **38**, in benzene at room temperature (Eq. 23). Pd was shown to initially coordinate to the olefin prior to rearrangement. Rettig concluded that this reaction proceeded by cis addition of Pd-Cl to the a-b bond followed by a 1,2 hydrogen migration and Pd-Cl elimination. Deuterium labeling studies showed that the hydrogen migration was stereospecific with migration only by the *endo*-**H**. When the reaction was quenched with aqueous CN^-, trans-bicyclo [6.1.0]non-4-ene, **39**, was produced. In this case, the Pd-Cl addition adduct was not isolated and the cis Pd-Cl addition was inferred from the labeling study and the observation of the trans hydrocarbon **39**.



37 **38** (23)

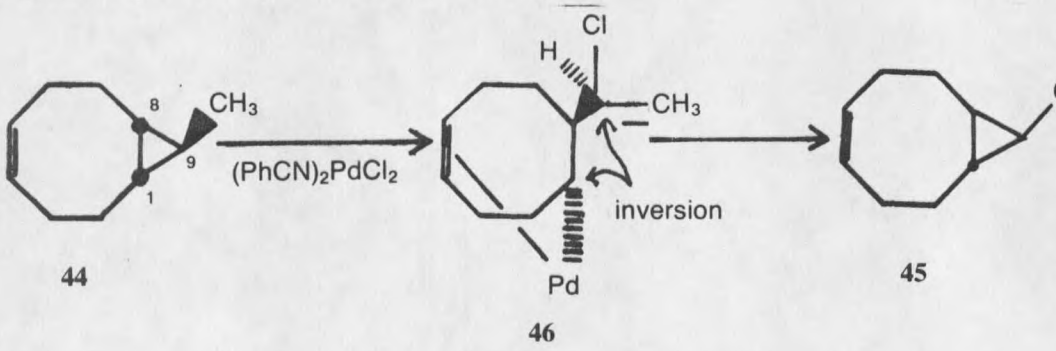
In 1975, Rettig[48] reported the reaction of bicyclo[5.1.0]oct-3-ene, **40**, with **36** (Eq. 24). The chloropalladation adduct, **41**, was formed in seconds at room temperature. Complex **41** was shown to be the result of trans addition of Pd-Cl across the cis disubstituted cyclopropyl bond with inversion at C_7. Treatment of **41** with aqueous CN^- resulted only in the starting hydrocarbon **40**. This is quite different than the reaction with **37** in which Pd-Cl was thought to add cis and reaction with CN^- produced the trans hydrocarbon **39**. Rettig suggested that the reaction in Equation 24 proceeds via an ionic mechanism with inversion of C_7 both upon attack by and elimination of Cl^-. He also observed that **41**

readily isomerized to **42** on sitting in $CDCl_3$ especially if some benzonitrile was left in the solution.



(24)

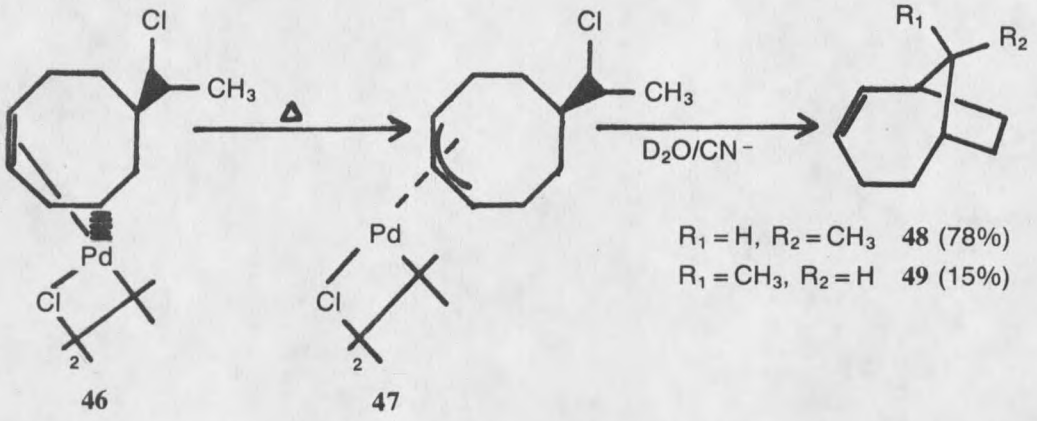
In 1981 and 1982, Rettig reported on the reactions of *endo*- and *exo*-9-methylbicyclo [6.1.0] non-4-ene, **43** and **44**, respectively. In the initial paper[49], **43** and **44** were shown to react with **36** to yield chloropalladation adducts in which Pd-Cl was added across the *exo*-cyclic cyclopropyl C-C bond. The stereochemistry of these adducts was not determined, however, they each reacted with CN^- to produce the new hydrocarbon 9-methyl-trans-bicyclo[6.1.0] non-4-ene, **45**. In the second paper[50], Rettig reported the crystal structure for **46**, the Pd-Cl adduct of **44**, which demonstrated that the ring opening proceeded solely with inversion of configuration at both newly formed asymmetric carbon centers (Eq. 25). Rettig concluded that this resulted from electrophilic corner-palladation at C_1 followed by attack by Cl^- at the activated C_9.



(25)

Most recently, Rettig reported[51] that **46** rearranged to the π-allyl palladium complex, **47**, upon refluxing in $CDCl_3$ (Eq. 26). The crystal structure of **47** was determined

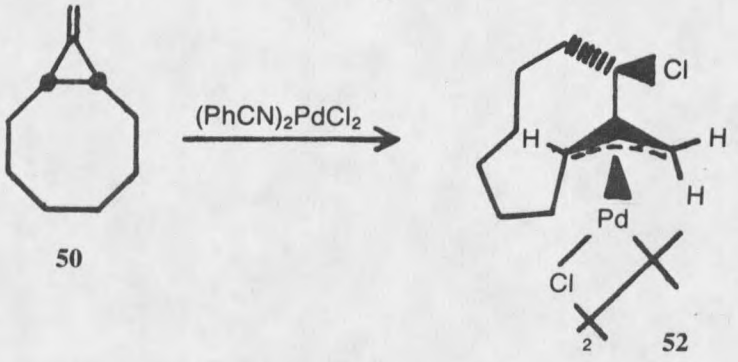
and showed that the rearrangement proceeded with retention of stereochemistry for Pd relative to the α-chloroethyl group (i.e., Pd and α-chloroethyl remain trans). A new and interesting type of product was reported for the CN^- induced dechloropalladation of **47**. Instead of the previously observed formation of a cyclopropyl ring via a 1,3-Pd,Cl elimination (vide infra), **47** gave two products, **48** and **49**, which resulted from a net 1,6-Pd,Cl elimination (Eq. 26). If this reaction is general, it may have considerable synthetic utility for this type of C-C bond formation.



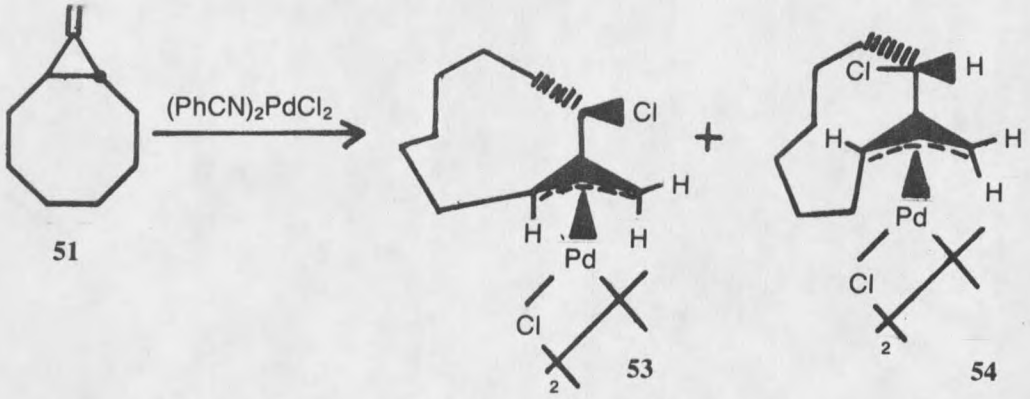
(26)

Hughes has reported 1,3 chloropalladations of alkyl-[52] and aryl methylenecyclopropanes[53] to yield η^3-allyl compounds. In 1981, Hughes[54] reported the chloropalladation of cis- and trans-9-methylenebicyclo[6.1.0]nonane, **50** and **51**. These reactions resulted in the cis chloropalladation products indicated in Equations 27 and 28. These reactions were viewed as orbital symmetry controlled electrocyclic ring opening processes (cyclopropyl cation → allyl cation) in which Pd coordinates to the methylene first. A disrotatory away (relative to Pd) opening scheme was presented. This scheme explained the 4:1 preference of **53** over **54** from the trans isomer **51** on the basis of the difference in steric hindrance at the two carbons subject to attack by Cl^- for the preferred disrotatory process.

Finally, Bäckvall[55] recently reported the reaction of (+)-car-2-ene, **55**, with $(MeCN)_2PdCl_2$ (Eq. 29). This reaction was shown to proceed with inversion of configuration at the site of palladium attack in **56** and overall trans stereochemistry for each prod-



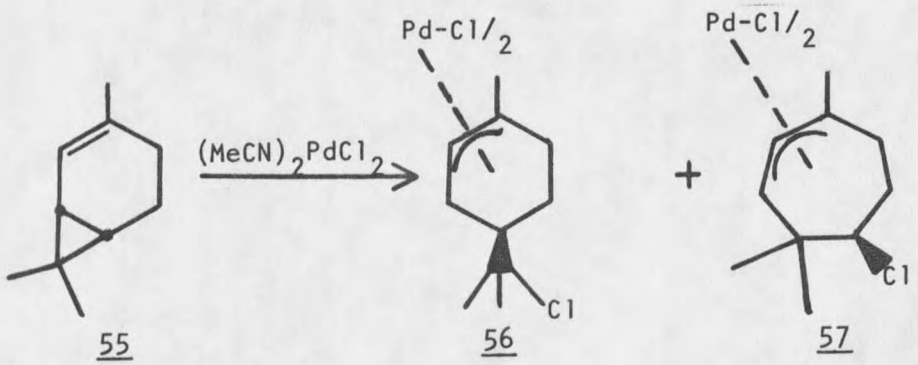
50 52 (27)



51 53 54 (28)

uct. A remarkable dependence of the product distribution on the reaction solvent was observed. Thus, the product ratio in $CHCl_3$ was 3:1, **56**:**57** whereas in benzene the product ratio was 1:6, respectively. This solvent dependence along with the two different types of products observed lead to the proposal in a subsequent paper by Bäckvall[22] that the two products were arising from two distinctly different mechanisms. He proposed that the ring expanded product **57** was the result of oxidative-addition of the 1,6 cyclopropyl bond to Pd to form a palladacyclobutane intermediate followed by Cl^- attack. The product **56** would result from ionic attack by Pd at C_1 followed by Cl^- attack at the activated C_7. The ionic path would be favored in $CHCl_3$. This is the first time, to the author's knowledge, that a metallacyclobutane intermediate has been proposed for palladium.

Clearly, this survey of the literature shows that the chemistry involved in chloropalladations of cyclopropanes is varied and not well understood. Table 10 summarizes the results for the chloropalladations surveyed herein with respect to the overall stereochemistry of the Pd-Cl addition and inversion of the carbon atoms attacked by Pd and Cl. Both



55 56 57 (29)

cis and trans stereochemistry has been observed along with inversion and retention of configuration at each carbon attacked. At least four mechanisms have been proposed to account for the observed results but much more work will be necessary before these reactions can be understood.

To help fill in this gap in our knowledge of these reactions, a survey of the reactions of $(PhCN)_2PdCl_2$, **36**, with a series of cis-disubstituted cyclopropanes in bridged tri- and tetracyclo-systems has been performed. The results of this investigation follow.

Table 11. Summary of the Known Stereochemistry of Chloropalladation Reactions.[a]

Compound	cis or trans Addition	Inversion at Pd-C	Inversion at Cl-C
37	cis		
40	trans	no	yes
44			
50	cis		
51	cis		
56	trans	yes	no
57	trans	no	yes

[a]References may be found in the text.

RESULTS

A series of four substrates containing *exo*- and/or *endo*-cyclopropane rings in rigid tri- or tetracyclic systems were prepared (Fig. 29). This series contained examples of both saturated and unsaturated substrates. Each of these compounds was reacted with stoichio-

metric amounts of $(PhCN)_2PdCl_2$, **36**, in $CDCl_3$ at room temperature.* The reactions were followed by NMR spectroscopy and allowed to react until no unreacted starting hydrocarbon was observable. The palladium complex **36** was weighed and dissolved in $CDCl_3$ resulting in a dark reddish solution. The substrate was then added and the solution lightened to a reddish yellow color as the reactions proceeded. Work up consisted of either flash distillation and concentration of the volatiles followed by preparative gas chromatography in the case of **58** or concentration of the reaction mixture followed by column chromatography on silica gel to isolate individual palladium complexes for the others. In general, these product mixtures were not clean necessitating column chromatography for isolation of the principle products. This had the unfortunate drawback that the product palladium complexes were seen to decompose on the column resulting in reduced yields. The yields reported are for isolated products unless otherwise indicated. Characterization of these products was based mainly on their ^1H and ^{13}C NMR spectra.

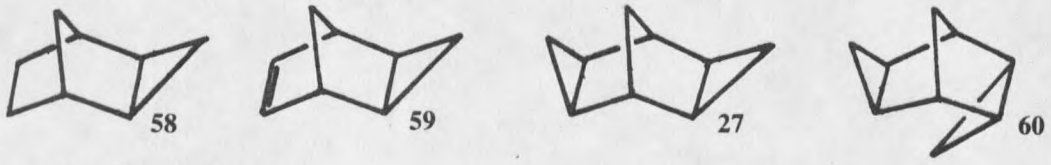
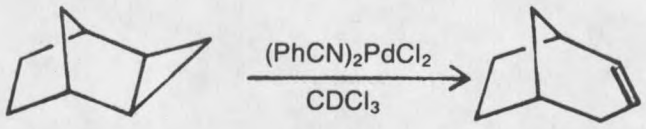


Figure 29. Four substrates.

Reaction of Tricyclic Compounds With **36**

A stoichiometric amount of the *exo*-tricyclic saturated compound **58** was shown to undergo a facile rearrangement with **36** in $CDCl_3$ at room temperature resulting in the formation of **62** in high yield (Eq. 30). This reaction yielded only the uncoordinated hydrocarbon which was identified by comparison of its ^1H NMR spectrum to that of the known compound[56]. No intermediate Pd complexes were isolated or identified.

*Preliminary work on reactions of **27** and **58** with **36** was performed by Scott Busse, MSU.



(30)

58 62

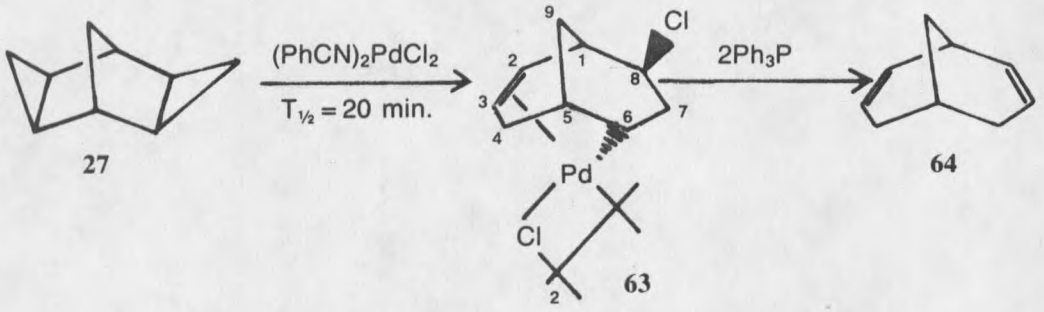
Stoichiometric amounts of the *exo*-tricyclic unsaturated compound **59** reacted very rapidly with **36** in $CDCl_3$ at room temperature. The half life for the disappearance of **59** was ~20 seconds with no **59** remaining after 2 minutes reaction time. This afforded a complex mixture of yellow palladium complexes. Examination of the olefinic region of the ^1H NMR spectrum, which contained ~8 olefinic resonances, indicated that there were at least three complexes present. Attempts to resolve this mixture by silica gel column chromatography were unsuccessful. The reaction components were mixed at 213°K and warmed slowly in the probe of the WM-250 NMR spectrometer in an attempt to observe reaction intermediates. No reaction was observed after 30 minutes at 223°K. At 243°K, products were observed to form slowly at the expense of the starting hydrocarbon. No new resonances attributable to reaction intermediates were observed indicating that there was not a significant energy well between reactants and the product complexes.

Treatment of these palladium complexes with 2 equivalents of Ph_3P in $CDCl_3$ resulted in the displacement of the hydrocarbon moiety from the palladium in less than two minutes at room temperature. Gas chromatography of the volatile portion of this reaction showed 4 or 5 small product peaks. This reaction was not pursued further.

Reaction of Tetracyclic Compounds With **36**

Reaction of stoichiometric amounts of the *exo,exo*-tetracyclic compound **27** with **36** in $CDCl_3$ at room temperature resulted in a complex reaction mixture as analyzed by ^1H NMR spectroscopy. All starting hydrocarbon **27** was consumed with a half life of 20 minutes at room temperature. Analysis of the volatile fraction yielded only benzonitrile which was displaced from **36**. Silica gel chromatography of the non-volatile fraction with

benzene yielded a yellow fraction which gave a fine yellow powder on concentration and precipitation with pentane. The yellow powder was analyzed and determined to be the 1,3 chloropalladation complex **63** (Eq. 31) which was isolated in 40% yield. The structure proof for **63** and the deuterated analog will be given in the next section. No other products were isolated or identified.



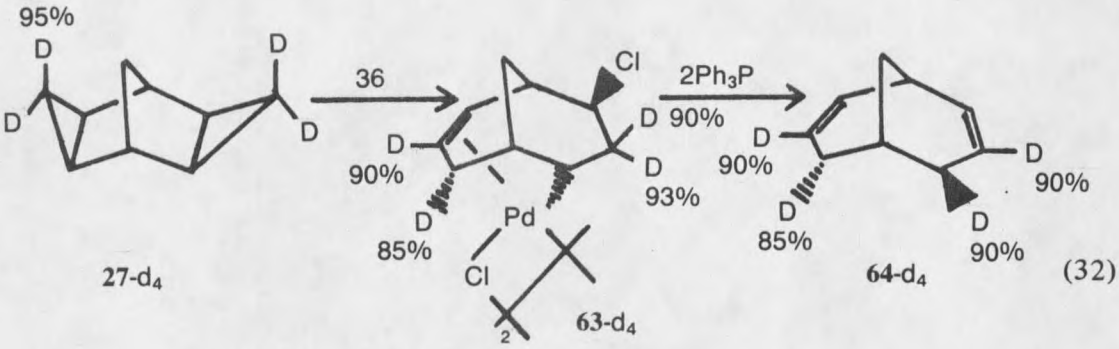
(31)

On addition of 2 equivalents of Ph_3P to a yellow solution of **63** in $CDCl_3$, a rapid reaction occurred. The solution turned light yellow within seconds followed by formation of yellow crystals of trans-$(Ph_3P)_2PdCl_2 \cdot CDCl_3$.[a] Work up and analysis of the volatile portion of this reaction revealed the *syn*-diene **64** in 95% conversion (Eq. 31). A minor product of < 5% of **64** was observed but not identified. The diene **64** was characterized from its ^1H and ^{13}C NMR and mass spectra. The ^{13}C NMR spectra contained 6 different resonances in the ratios 2:2:2:1:1:1 including 2 vinyl, 2 bridgehead and 2 bridge resonances required by the plane of symmetry through the 2 bridgehead and the C_9 bridge carbons. The *anti* isomer would have a center of inversion and would have only 5 non-equivalent carbon resonances, the bridgehead carbons now being equivalent. The accurate mass determination confirmed the molecular formula, C_9H_{12}. This diene was reported previously as a minor byproduct from the synthesis of asterane by Musso[57].

The labeled d_4-analog of **27** was prepared and was shown to have 95% label incorporation by ^1H NMR spectroscopy. The labeled compound **27**-d_4 was reacted with **36** under

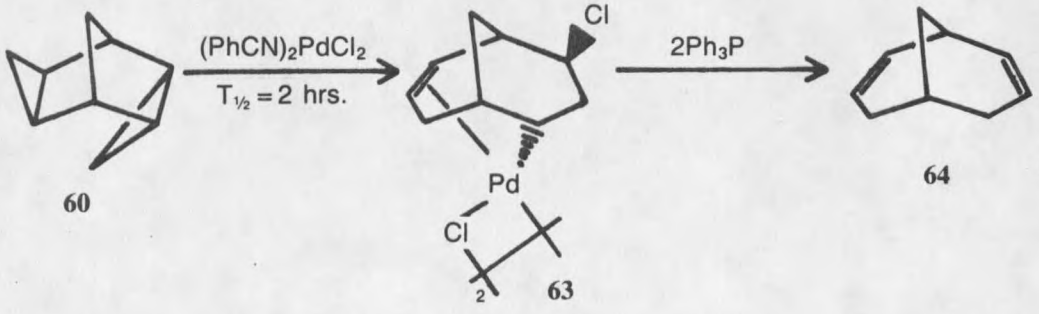
[a]The molecular crystal structure of this complex was determined by X-ray diffraction and will be published elsewhere.

identical conditions to those for **27** above (Eq. 32). Work up was the same, also. The labeled complex **63**-d_4 was isolated and analysis showed that a stereospecific 1,2 D-migration had taken place from one cyclopropyl bridge carbon to the *endo* position on C_4. The label in the other 3 positions remained essentially unchanged. When **63**-d_4 was treated with 2 equivalents of Ph_3P and worked up as before, the d_4-diene **64**-d_4 resulted. Again, a stereospecific 1,2 D-migration was observed but this time to the *exo* position on C_6. The other deuterium labels were unchanged.



27-d_4 **63**-d_4 **64**-d_4 (32)

The *exo,endo*-tetracyclic compound, **60**, was reacted with **36** under the standard conditions and worked up as for **27** (Eq. 33). A half life of 2 hours was observed at room temperature. This reaction was somewhat surprising in that it yielded only the 1,3 chloropalladation product **63**, the same product as from the reaction with the *exo,exo*-tetracyclic compound **27**. The ^1H and ^{13}C NMR spectra for the product from **60** were identical to that for **63** and this compound also produced the *syn*-diene **64** upon treatment with 2 equivalents of Ph_3P.



60 **63** **64** (33)

Characterization of the Chloropalladation Adducts **63** and **63**-d_4

The characterization of the chloropalladation adducts **63** and **63**-d_4 was principally based on NMR data. The ^1H NMR spectrum of **63** is shown in Figure 30. Quantitative ^1H, homonuclear selectively decoupled ^1H, and 2DFT homonuclear shift correlation (SECSY) NMR experiments were performed on **63**. Data from these experiments is correlated in Table 12 and all ^1H assignments are given. A stacked plot of the SECSY spectra is shown in Figure 31. ^1H coupled and decoupled ^{13}C NMR experiments were also performed. Chemical shifts, multiplicities and coupling constants from these experiments are given in the experimental section of this thesis. Elemental analysis of **63** is compatible with the molecular formula $(PdC_9H_{12}Cl_2)_2$. Although the molecular weight of this complex was not determined, it is expected that **63** is dimeric.

Table 12. Proton NMR Data for **63** From Homonuclear Decoupling and 2D SECSY Experiments.[a]

H[b]	δ, mult.	^1H-^1H Coupled Pairs (J)[c]
3	5.65, dd	3-2 (7 Hz), 3-4s (3 Hz), 3-4a (1.5 Hz)
2	5.22, t	2-3 (7 Hz), 2-1 (5 Hz), 2-4a or 9a (weak)
8	4.88, t	8-7s (7 Hz), 8-7a (7 Hz), 8-9s (med. weak)
6	3.50, br.t	6-7s (< 2 Hz), 6-7a (< 2 Hz), 6-5 (5 Hz)
7s	2.55, m	7s-8 (7 Hz), 7s-7a (14 Hz), 7s-6 (< 2 Hz)
1	2.55, m	1-2 (5 Hz)
4s	2.55, m	4s-3 (3 Hz), 4s-4a (11 Hz), 4s-5 (2-4 Hz)
4a	2.0 , m	4a-3 (1.5 Hz), 4a-4s (11 Hz), 4a-5 (2-3 Hz)
9a	2.0 , m	9a-9s (8-11 Hz), 9a-2 (weak)
9s	1.2 , m	9s-9a (8-11 Hz), 9s-8 (med.)
5	1.2 , m	5-6 (5 Hz), 5-4s (2-4 Hz), 5-4a (∼2 Hz), 5-7a (weak)
7a	0.75, qt	7a-8 (7 Hz), 7a-7s (14 Hz), 7a-6 (med.), 7a-5 (weak)

[a] 250 MHz, $CDCl_3$.
[b] s = *syn*, a = *anti* relative to bridge or olefin.
[c] Med. or weak refers to strength of off diagonal peaks in SECSY spectra, given only if the coupling constant is undetermined.

The ^{13}C NMR spectra of **63** contained 9 single carbon resonances. Two shielded olefinic carbons were observed at 104.8 and 91.8 δ indicating that they were π-bound to

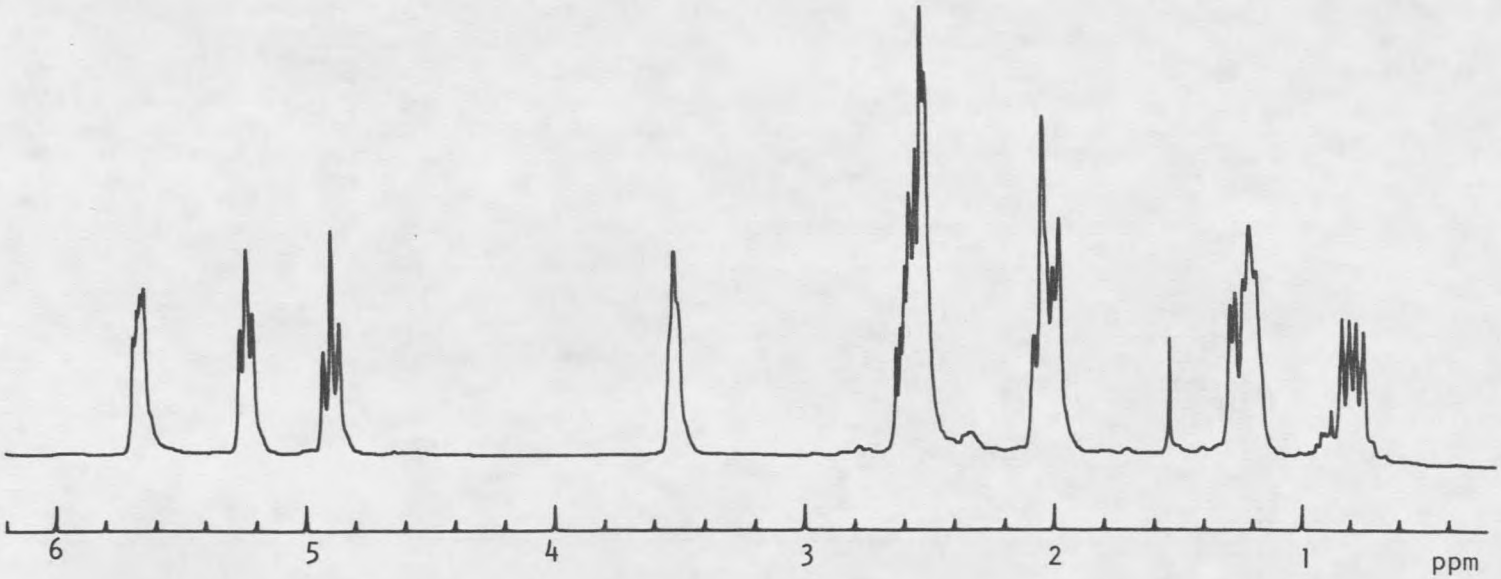


Figure 30. ^{1}H NMR spectrum of **63** (250 MHz, $CDCl_3$).

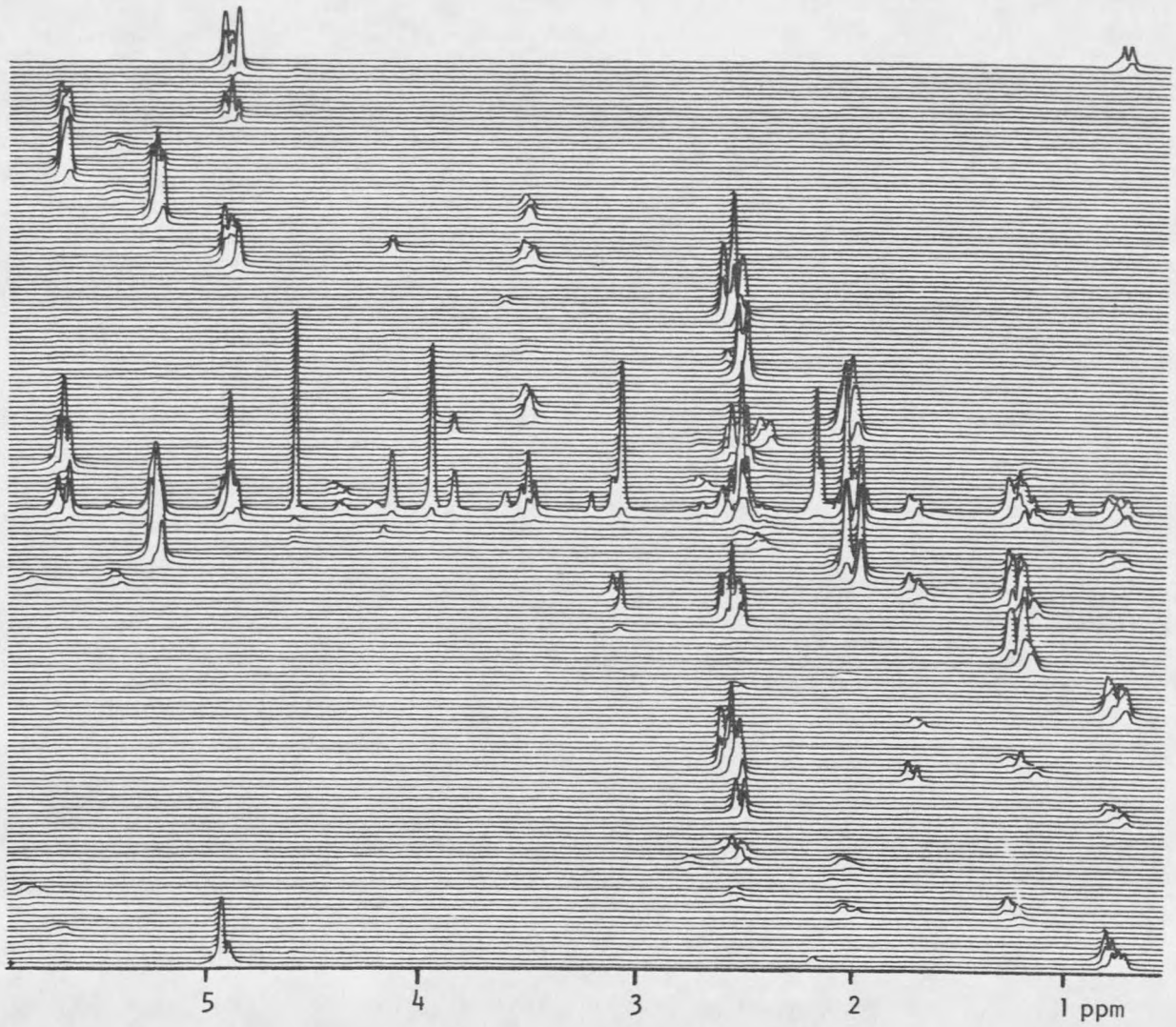


Figure 31. A stacked plot of the 2DFT SECSY experiment on **63**.

Pd[58]. Two deshielded methine carbons at 59.8 and 59.7 δ are assigned to the σ-bound Pd and Cl carbons. In addition, there were two methine and three methylene carbons between 39 and 25 δ assigned to the two bridgehead and three bridge methylene carbons, respectively.

The key to this structure is the ^1H-^1H coupling data. Once the assignments of Cl-C-H and Pd-C-H are made, one can make all the rest of the ^1H assignments by beginning with the vinyl ^1H's and following the couplings around the rings. The Cl-C-H and Pd-C-H assignments were made by comparison to the available range of model compounds including each palladium complex referenced in the introduction to this section and references within those papers. On the basis of 14 Pd complexes containing Cl-C-H, the range for these ^1H's was from 3.8-5.5 δ. On the basis of 7 complexes containing Pd-C-H, the range of reported values for these ^1H's was from 3.5-4.2 δ. Consequently, the resonance at 3.5 δ is assigned to the Pd-C-H, H_6, and the resonance at 4.88 δ is assigned to the Cl-C-H, H_8, in **63**.

Two basic questions remain. Is the Pd σ-bonded *syn* or *anti* to the double bond and what is the stereochemistry of the Pd and Cl? From the coupling data in Table 12 the vinyl ^1H resonance at 5.65 δ is coupled to the other vinyl ^1H and to two geminally coupled ^1H's at 2.55 and 2.0 δ. The vinyl resonance at 5.22 δ, on the other hand, is only significantly coupled to the methine ^1H at 2.55 δ in addition to the first vinyl ^1H. Thus, the vinyl ^1H's at 5.22 and 5.65 δ are assigned to H_2 and H_3, respectively. H_{4a} and H_{4s} are, then, assigned to the resonances at 2.0 and 2.55 δ on the basis of coupling to H_3. H_{4a} is assigned to 2.0 δ from the smaller coupling constant of 1.5 Hz to H_3 expected because the angle between H_3 and H_{4a} is close to 90°. A ^1H at 1.2 δ is coupled to both H_{4a} and H_{4s} and so is assigned to H_5. H_5 is coupled to the ^1H at 3.5 δ so this ^1H is assigned to H_6. Thus, Pd is σ-bound *anti* to the double bond. Continuing around the ring shows that

the Cl is attached at the 8 position, *syn* to the double bond and that the other assignments are as indicated in Table 12.

The Pd must be bound from underneath since it is both π- and σ-bound in **63** and the steric bulk of the bridge precludes the possibility of Pd binding from the top. This requires that H_6 is *exo* to the bridge. The coupling constant J_{H_5,H_6} = 5 Hz supports this conclusion. Generally, the coupling constant for an *exo* ^1H α to the bridgehead is on the order of 4-6 Hz while an *endo* ^1H α to the bridgehead is coupled to the bridgehead ^1H by 0-2 Hz[59]. In addition, the *endo* ^1H should be W coupled to the bridge proton *anti* to it by 1.5-2.5 Hz whereas the *exo* ^1H will not be coupled to either bridge ^1H.

The stereochemistry at position 8 is not so easily determined. H_8 is coupled by 7 Hz to a ^1H at 2.55 δ. However, the multiplet at 2.5 δ contains 3 ^1H resonances, two of which belong to ^1H's adjacent to H_8. If H_8 is coupled to the bridgehead ^1H, H_1, by 7 Hz, it would have to be *exo*. If H_8 is coupled to H_7, it would have to be *endo*. To distinguish between these two possibilities unambiguously, it was necessary to consider the labeled complex **63**-d_4. Since **27**-d_4 was labeled at the cyclopropyl bridges, both of the H_7 positions are deuterated in **63**-d_4. Therefore, if H_8 were *endo* and coupled to an H_7 proton by 7 Hz in **63**, this coupling should not be observed in **63**-d_4. Indeed, H_8 at 4.88 δ in the ^1H spectrum of **63**-d_4 is reduced to a singlet broadened by deuterium coupling. There is no apparent coupling to H_1. Therefore, H_8 must be *endo* to the bridge and the Cl *exo*. This conclusion is confirmed by the observation of a medium weak coupling between H_8 and H_{9s} in the SECSY spectra attributable to W coupling.

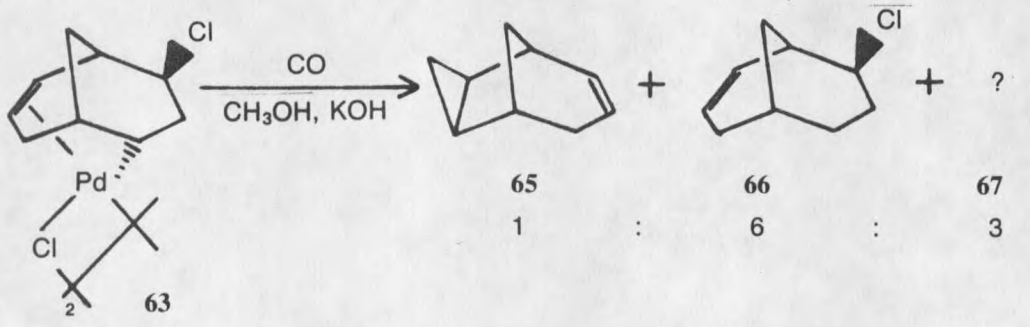
All of the ^1H assignments for **63** are firmly established. Analysis of **63**-d_4 was done by a direct comparison to **63**. The positions of deuterium label in **63**-d_4 were deduced from integration of each resonance combined with the evident losses of coupling. Thus, it was apparent that the 4a position had 85% deuterium and 15% hydrogen. The 3 position had 90% deuterium and the 7s and 7a positions had 93 and 90% deuterium label. No deu-

terium was detected in any of the other positions. Since label incorporation in **27**-d_4 was 95%, the net loss of deuterium in **63**-d_4 is less than 6% which is within the error of the analysis. Therefore, a stereospecific 1,2 H migration occurs from one of the cyclopropyl bridge protons to the 4 *endo* position on going from **27** to **63**.

The d_4-diene **64**-d_4 was characterized by quantitative comparison of its ^{1}H NMR spectrum to the spectrum of **64**. This spectrum was initially puzzling in that each resonance was present except for the 3 and 7 vinyl ^{1}H resonances due to the complete retention of label at these positions. Integration of this spectrum revealed that 0.85 and 0.90 equivalents of deuterium were present in the 4a,6a and 4s,6s positions, respectively. This, coupled with the observation that the geminal coupling between these *syn* and *anti* protons was missing, demonstrated that only the 4a and 6s positions were deuterated. Therefore, the 1,3 dechloropalladation of **63** is accompanied by a stereospecific 1,2 H-migration by one of the 7 hydrogens to the 6s position only.

Carbonylation of **63**

Several reports of carbonylation of σ-bonded palladium complexes with CO in basic methanol have been published[48,58,60]. In each case the Pd was replaced by $-COOCH_3$ with retention of stereochemistry. This reaction was attempted with **63** to further demonstrate its stereochemistry and to investigate the generality of this reaction to Pd complexes in rigid systems. The products of this reaction were not anticipated and are shown in Equation 34.



65 : **66** : **67**

1 : 6 : 3

(34)

The reaction was facile. Black Pd metal was precipitated immediately on addition of **63** to a stirred solution of CO in basic methanol. Upon work up 3 hydrocarbon products were isolated by preparative gas chromatography in the relative ratios of 1:6:3 for **65**, **66** and **67**, respectively. Products **65** and **66** were characterized by their ^{1}H NMR and mass spectra which are given in detail in the experimental section of this thesis. Product **65** had a parent ion at mass 120 and the characteristic base peak at mass 79 corresponding to $C_6H_7^+$. The ^{1}H NMR spectrum contained 2 vinyl ^{1}H's at 6.06 and 5.33 δ and characteristic cyclopropyl bridge ^{1}H's at 0.38 and 0.20 δ. Eight other protons were observed between 2.3 and 0.97 δ. The product **66** had peaks for a parent ion at mass 156 and an M^++2 ^{37}Cl isotope peak at mass 158 in the ratio of 3:1, respectively. Characteristic loss of Cl was observed in the mass spectrum at mass 121 together with the base peak at mass 79. The ^{1}H NMR spectrum contained 2 vinyl resonances at 5.90 and 5.72 δ and a Cl-C-H resonance at 4.19 δ. Ten aliphatic ^{1}H's were observed from 2.55-1.35 δ. The ^{13}C spectrum for **66** is given in the experimental section.

The product **67** was unidentified. It had spectra indicative of the expected methyl ester adduct except that the parent ion had a mass of 178 rather than the anticipated mass of 180 for $C_{11}H_{16}O_2$. The loss of 2 H's in this product could not be rationalized on the basis of the existing spectra and this structure was not pursued further.

DISCUSSION

Consideration of the structures of **63** and **63**-d_4 allow several conclusions about the chloropalladation of 27 to be drawn. Initial attack by Pd results in the cleavage of a cis-disubstituted cyclopropyl bond and formation of the C=C. It is reasonable to believe that this is the result of a 1,3 chloropalladation followed by Pd,Cl elimination as proposed by Rettig[47] for **37**. The labeled complex **63**-d_4 demonstrates that the Pd,Cl elimination involves a stereospecific 1,2 D migration to the *endo* position on C_4 with net inversion of configuration at C_4. Inversion at C_4 could result either from retention on addition and

inversion on elimination of Pd-Cl or by inversion on addition and retention on elimination of Pd-Cl.

The attack by Pd on the second cyclopropyl ring occurs from underneath resulting in a trans-1,3-Pd,Cl addition across the C_6-C_8 cyclopropyl bond with inversion of configuration at C_6 and retention at C_8. Elimination of Pd,Cl from **63**-d_4 on treatment with Ph_3P involves formation of the C=C at the chlorinated position C_8 rather than C_6 and another stereospecific 1,2 D migration to the *exo* position at C_6. This requires a second inversion of configuration at C_6.

It is evident from these observations that the mechanism of Pd interaction with the first cyclopropane is different than with the second cyclopropane. The first cyclopropane is opened with net inversion of configuration at the allylic position C_4 and the second ring is opened with net retention at the allylic position C_6. In addition to this, opening of the first ring proceeds with successive addition and elimination of Pd,Cl whereas opening of the second ring results in the formation of a stable Pd,Cl addition complex.

One obvious difference between these two reactions is that a remote double bond is present during the second ring opening process but not for the first. One might argue that the additional stabilization from π-bonding to the olefin could account for formation of the Pd,Cl adduct in the second ring opening. While this effect should have some influence on the course of the reaction, it is apparent that π-bonding to a remote olefin is not the sole determining factor in these systems. Rettig[47] has shown that in the case of the chloropalladation of **37** which contains a remote double bond, **37** was catalytically converted to the diene **38** and that no stable Pd,Cl adduct was formed. An alternative determining factor which is consistent with the current data may be the stereochemistry of the Pd,Cl addition.

The only known cases of stable σ,π-chloropalladition adducts involved trans addition of Pd,Cl (see Eqs. 24, 25; and 31). In the cases involving cis addition of Pd,Cl to cyclo-

propane, the reaction was either catalytic with no stable Pd adduct[47] or else a stable η^3,π-allyl Pd adduct was formed[54]. This suggests that cis-Pd,Cl adducts are reactive whereas trans-Pd,Cl adducts may be stable to further rearrangement. Consideration of the transition state proposed by Rettig[47] for rearrangement of a cis-chloropalladation adduct may give further insight into this difference in reactivity (Fig. 32).

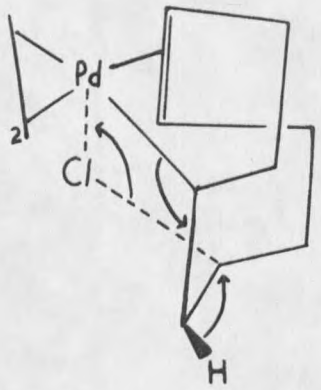


Figure 32. Rettig's proposed transition state for cis-Pd,Cl elimination, from reference 47.

In Figure 32, the Cl is aligned with the fifth coordination site of the Pd and the *endo*-H is trans with respect to the Cl. This arrangement is set up for a concerted Pd,Cl elimination with backside attack by the *endo*-H available to assist abstraction of the Cl by Pd which would account for a stereospecific 1,2-H migration. Conversely, the trans-Pd,Cl arrangement would not allow direct or concerted abstraction of Cl by Pd. In this case, an ionic or at least a stepwise mechanism is required.

A mechanism is proposed in Figure 33 for the Pd(II) mediated conversion of **27**-d_4 to **64**-d_4 which accommodates the observed ring openings, carbon configurations and stereospecific D migrations. Step A involves corner-palladation of one of the cyclopropanes followed by an *exo*,cis-1,3-chloropalladation of the cis-disubstituted cyclopropyl bond, step B. Step C entails a concerted Pd,Cl elimination accompanied by the stereospecific 1,2 D migration of the *endo*-D resulting in formation of the C_2,C_3 double bond and inversion of configuration at C_4. This is analogous to the mechanism proposed by Rettig (Fig. 32).

Step D is the isomerization of the π-bound Pd from the *exo* to the *endo* position necessary for *endo* attack required by **63**-d_4. This could be accomplished either by an intra- or an intermolecular process. Step E involves corner-palladation of the second cyclopropane followed by trans addition of Cl in step F to produce **63**-d_4 with inversion of configuration at C_6. Step G is a β-Pd-D elimination promoted by addition of Ph_3P to the metal resulting in an *endo* π-complex. This complex would isomerize to the *exo* π-complex[a] in step H followed by readdition of Pd-D with stereospecific deuterium transfer to the *exo* position of C_6. The last step is cis-Pd,Cl elimination to form the product **64**-d_4.

While this mechanism is not proven, it does account for the observed products and avoids some of the problems inherent in other potential paths. Three other stereochemistries are possible for the initial chloropalladation, cis-*endo*, trans with Pd *exo*, and trans with Pd *endo*. The cis-*endo*-chloropalladation would requires a cis or "front side" transfer of deuterium to yield the *endo*-D at C_4. This is unlikely. Either of the trans additions suffer from the apparent stability of this orientation to Pd,Cl elimination and would involve a stepwise loss of Cl^- which would increase the potential for deuterium scrambling. In the case of the Pd,Cl elimination from **63**-d_4, any mechanism that would form the double bond and perform the 1,2-D migration synchronously would require that Cl leave as Cl^+ and it is difficult to accept that Ph_3P is a strong enough nucleophile to accomplish this.

The reaction of the *exo*-tricyclic saturated compound **58** is the first example of Pd(II) catalyzed ring opening of a compound with only one cyclopropane and no unsaturation or significant additional ring strain in the molecule. The facile elimination of Pd,Cl from this molecule suggests that the ring opening proceeds by cis-1,3-chloropalladation followed by Pd,Cl elimination and a 1,2-H migration analogous to that proposed for **27**.

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[a]Equilibration of *exo* and *endo* isomers in Pd-π-allyl systems has been suggested by Collman and Hegedus, reference 41b.

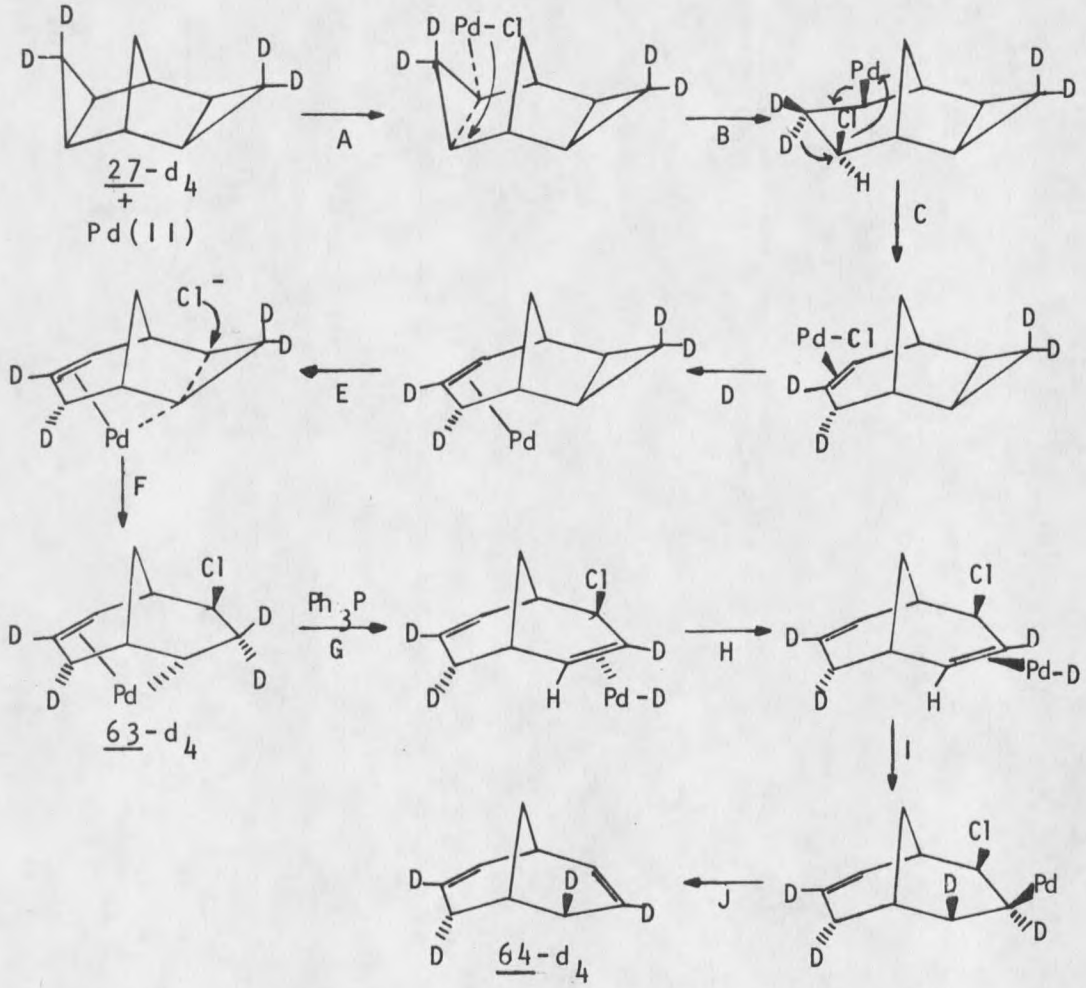

Figure 33. Proposed mechanism for the $(PhCN)_2PdCl_2$ interaction with 27.

The data is not sufficient to conclude whether the *exo* or *endo* cyclopropane in **60** is attacked first by Pd. It is however, tempting to suggest that the *endo*-cyclopropane is opened first resulting in formation of a C=C. This would, then, form the intermediate shown prior to step E in Figure 33 and the rest of the reaction would proceed identically. The decrease in reaction rate for **60** relative to **27**, $T_{1/2}$ = 2 hours versus 20 minutes, respectively, would be accommodated by this as well. Additionally, the reactions of **60** with Ir(I)[59] and Pt(II)[61] have been shown to occur preferentially with the *endo*-cyclopropane.

The relatively rapid reaction rate for **59**, $T_{1/2}$ = 20 seconds, demonstrates that the olefin has a significant role in activating the cyclopropyl ring towards chloropalladation. In the corner-palladation scheme, the olefin could help to stabilize the developing positive charge by a homoallylic donation of electron density and delocalization of the charge. This would result in a more facile reaction than in the saturated cases in which no stabilization of the transition state is possible.

SUMMARY

Two aspects of transition metal interactions with cyclopropanes in rigid systems have been explored. First, a detailed kinetic analysis of the Rh(I) catalyzed valence isomerization of quadricyclane was performed. Second, the reactions of Pd(II) with a series of cyclopropanes in tri- and tetracyclic systems were surveyed.

The [(NBD)RhCl]$_2$ catalyzed isomerization of quadricyclane was shown to be an unusually complex reaction. In addition to the previously reported product, norbornadiene, a second product, **HCD**, was observed in 7% yield. These products were formed by parallel reaction paths from a common intermediate. The hexacoordinate Rh(III) complex **31** (Fig. 28) was proposed as a likely candidate for this intermediate.

The rate constant for this reaction was dependent on the solvent in unexpected ways. In non-polar solvents, the reaction obeyed *psuedo* first order kinetics with rate constants on the order of 3 M^{-1} s^{-1} at 37°C. In polar solvents, the reaction also obeyed *pseudo* first order kinetics with rate constants measured ranging from 26 M^{-1} s^{-1} in $CDCl_3$ to > 500 M^{-1} s^{-1} in CD_3OD. However, substrate inhibition was a prominent feature of the reaction generally observed in polar solvents but not in non-polar solvents. Comparison of the activation energy parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, determined for this reaction in $CDCl_3$ and CCl_4 demonstrated that the active catalyst was different in each of these solvents. The catalyst in CCl_4 exhibited a relatively sterically hindered transition state and was thought to be, or to be derived directly from, [(NBD)RhCl]$_2$. The active catalyst in $CDCl_3$ is significantly less sterically hindered and likely results from cleavage of one or both of the chlorine bridges in [(NBD)RhCl]$_2$.

Two other active catalysts or catalytic precursors were demonstrated to be operative in polar solvents as well. First, in $CDCl_3$ at high substrate concentrations, the active catalyst, discussed above, was converted to a catalyst of low activity that was itself not subject to substrate inhibition. This low activity catalyst displayed a rate constant of 4.3 M^{-1} s^{-1} (at 37°C) and activation parameters that were very similar to the catalyst in CCl_4. This catalyst is likely a coordinatively saturated quadricyclane addition adduct of some Rh specie present in $CDCl_3$.

Second, a fourth catalyst derived from **(NBD)**$_2$ RhCl in $CDCl_3$ at low temperature was demonstrated to be 13 times as effective as the active catalyst derived from [**(NBD)**RhCl]$_2$. **(NBD)**$_2$ RhCl is produced in $CDCl_3$ by the product **NBD** in equilibrium with [**(NBD)**RhCl]$_2$ and is favored at low temperatures (Eq. 16 and Table 7).

A reaction scheme was presented in Table 9 which accommodates the major features of this reaction in $CDCl_3$ at 37°C. This scheme was refined with a kinetic modeling program to yield excellent agreement with the experimental data (Fig. 23).

Finally, evidence was presented which rendered the concerted and Lewis acid mechanisms unsupportable as explanations of the [**(NBD)**RhCl]$_2$ catalyzed isomerization of quadricyclane. The "cheleotropic" mechanism, on the other hand, was found to be completely consistent with the results of this investigation.

The reactions of $(PhCN)_2PdCl_2$ with a series of four compounds (Fig. 29) containing cyclopropanes in rigid systems were surveyed. This resulted in observation of the first example of ring opening by Pd(II) of a monocyclopropyl compound in which no unsaturation or significant additional ring strain was present in the molecule (Eq. 30). The new 1,3-chloropalladation adduct **63** was isolated and completely characterized (Eq. 31). This complex was shown to react with Ph_3P to yield the diene **64**. Deuterium labeling experiments provided the unambiguous elucidation of two stereospecific 1,2-D migrations (Eq.

32) and prompted proposal of the detailed reaction mechanism in Figure 33. This mechanism accounts for the stereochemistry, carbon configurations and products observed.

Finally, a correlation was drawn between the reactivity of chloropalladation adducts formed in these types of systems and the stereochemistry of the Pd,Cl addition. The available evidence, although still quite limited, indicates that trans-1,3-chloropalladation adducts are stable towards further reaction whereas cis-1,3-chloropalladation adducts are reactive and generally proceed catalytically to olefins via a synchronous 1,3-Pd,Cl elimination accompanied by a stereospecific 1,2-H migration.

EXPERIMENTAL

General

Instrumentation

All NMR spectra were acquired on the Bruker WM250 spectrometer operating at 250.132 MHz for ^{1}H and 62.83 MHz for ^{13}C. All spectra were run in $CDCl_3$ utilizing the solvent as an internal reference with $CHCl_3$ taken as 7.25 δ for ^{1}H and $CDCl_3$ taken as 77.0 δ for ^{13}C. Mass spectra were acquired utilizing VG Analytical, Inc. MM16F or 7070H spectrometers. Vapor-phase osmometry (VPO) experiments were performed with a Hewlett Packard Mechrolab 301 A instrument. The Honeywell CP-6 and VAX 11/780 computers were utilized for processing of kinetic data and kinetic modeling. Infra red spectra were obtained with the Beckman IR-20A spectrophotometer. Preparative GLC collections were performed utilizing an Aerograph Autoprep chromatograph series 2700 equipped with a 10 ft. X 3/8 in. column packed with 10% SE 30 on Chromsorb W or a 10 ft. X 1/2 in. column packed with 20% SE 30 on Chromsorb W.

Chemicals

$[(NBD)RhCl]_2$ was obtained from Strem Chemicals (lots no. 2064B, 2169B and 2546-B). Purity for each lot was determined by ^{1}H NMR and UV-vis spectroscopy. $(PhCN)_2PdCl_2$ and $Rh_2(CO)_4Cl_2$ were purchased from Strem Chemicals. $CDCl_3$, CD_3OD, pyridine-d_5, toluene-d_8, CD_3COOD, C_6D_6 and CD_2Cl_2 were obtained from Stohler Isotope Chemicals and used without further purification. 7-tert-butoxynorbornadiene was purchased from Frinton Laboratories and purified by chromatography on neutral alumina. NBD from Aldrich was purified by chromatography on neutral alumina and distilled prior

to use. Triethylamine from Baker was purified by the method of Swift[62]. Technical grade cycloheptatriene was obtained from Baker and used without purification. Other chemicals were purchased as reagent grade and used without further purification unless specified.

Synthesis of Substrates

Quadricyclane. For the early work, this compound was prepared by the method of Smith[32] and purified by distillation on a 50 cm spinning band column to better than 99.8% purity. Quadricyclane was later purchased from Aldrich which contained 2.12% NBD by ^{1}H NMR spectroscopy.

7-tert-butoxyquadricyclane. This compound was prepared by a modification of Gassman's procedure[63] in which 5 gr. of 7-t-butoxynorbornadiene was substituted for the 7-acetoxynorbornadiene. The reaction solution was irradiated for a total of 7 hours and worked up to yield 4.8 g (95%) of nearly pure 7-t-butoxyquadricyclane which was purified by preparative gas chromatography prior to use.

exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene, **59**; *exo,exo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane, **27**; *exo*-tricyclo[3.2.1.$0^{2,4}$]octane, **58**. These compounds were prepared by the method of Kottwitz[64]. For ^{1}H and ^{13}C NMR data of these compounds see reference 59.

endo,exo-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane, **60**. This compound was prepared by a variation of the method of Kottwitz[64] from *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene which was prepared by the method of Closs[65]. For ^{1}H and ^{13}C NMR data see reference 59.

exo,exo-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane-d_4, 27-d_4. This compound was prepared by the method of Campbell[59]. ^{1}H NMR showed that only the cyclopropyl bridge positions were deuterated and that label incorporation was 95%.

Kinetic Studies of Quadricyclane Isomerization

General Kinetic Method. All reactions were run in the probe of the Bruker WM-250 and measured by ^1H NMR spectroscopy. In a typical experiment, a 2-30 μl aliquot of substrate was added to an NMR tube along with sufficient solvent to bring the total volume to 490 μl. This tube was then placed in a thermostated bath and allowed to come to thermal equilibrium. Ten μl of a 0.050 M solution of $[(NBD)RhCl]_2$ in CCl_4 or $CDCl_3$ was then injected and the tube inverted twice to insure good mixing. The tube was replaced in the bath for $\sim$10 seconds to return to thermal equilibrium and removed, wiped dry and quickly lowered by a string into the NMR probe which was thermostated to the same temperature as the bath. This method allowed acquisition of the first data point in 20-30 seconds. Data points were taken at 30 second intervals to assure complete relaxation, until the reaction was finished. The reaction progress was followed by integration of the NBD vinyl ^1H resonance at 6.75 ppm. A spectrum was acquired with a single pulse, commonly, with a spectral width of 315 Hz and 1K data size. Lorentzian broadening of 1-3 Hz was applied before Fourier transformation to yield a smooth peak allowing reproducibility of digital integrals within 2%. Data were acquired locked or auto locked with the sample not spinning. Probe temperatures were calibrated using methanol as a temperature standard and regulated to within $\pm 0.5°C$.

Slopes were calculated by the method of least squares and all correlation coefficients were better than 0.99. Each rate constant reported is the average of at least 3 runs. Total errors were estimated to be within $\pm 5\%$.

Two variations of this method were used. Variation A involved the substitution of 50 μl of solvent with 50 μl of a 0.1 M solution of $Cr(acac)_3$ in the solvent to yield a 0.01 M solution of $Cr(acac)_3$ when diluted to 500 μl total volume. This variation allowed data points to be taken as often as 5 sec. Varation B was the same as variation A except that an in probe injection system was utilized as well. For variation B, the substrate and

sufficient solvent to total 150 μl were placed in the NMR tube, lowered into the NMR probe and allowed to come to thermal equilibrium. Three hundred and fifty μl of a solution of catalyst, $Cr(acac)_3$ and solvent were then injected from a thermostated syringe into the tube with sufficient force to assure good mixing. This method allowed the first point to be taken in as little as 2 seconds after mixing. Control experiments with $Cr(acac)_3$ are described below.

Exceptions to this method will be explained in the appropriate sections below.

Conditions for kinetic measurements in non-polar and polar solvents are given in Tables 13 and 14, respectively.

All comparative kinetic studies utilized the appropriate control reactions run on the current day with the current catalyst solution.

Table 13. Conditions for Kinetic Measurements in Non-Polar Solvents.

Solvent	$[Q]_0$ Range,M	$[cat]_0$ Range$\times 10^3$,M	T,°C	Kinetic Method
CCl_4	0.10-2.80	0.5-4.0	37.0	General
CCl_4	0.20	1.0	50.0	General
CCl_4	0.20	1.0,2.0	25.5	General
CCl_4	0.10	3.0	12.0	General
CCl_4	0.10	2.0,3.0,4.0	0.0	General[a]
CCl_4	0.10	10.0	-20.0	General[a]
Benzene	0.2	1.0,2.0	37.0	General[b]
Cl-benzene	0.2	2.0	37.0	General[b]

[a] After 20 points, the delay between points was increased to 60 seconds.
[b] Kinetics done on a Varian T-60 with analogue integration of Q cyclopropyl protons at 1.4 ppm.

Kinetic Measurements in Methanol-d_4. The general kinetic method was followed except as noted below. The $[(NBD)RhCl]_2$ was 0.050 M in $CDCl_3$. Five or 10 μl of a catalyst solution was added to either 4 or 8 μl solutions of Q in methanol-d_4 at 23.5°C. These experiments resulted in the reaction either being over before the first point could be

Table 14. Conditions for Kinetic Measurement in Polar Solvents.

Solvent	$[Q]_0$ Range,M	$[cat]_0$ Range$\times 10^3$,M	T,°C	Kinetic Method
$CDCl_3$	0.04-0.60	0.43-25	37.0	G,A,B[a]
$CDCl_3$	0.08-0.40	1.0	23.0	G
$CDCl_3$	0.08, 0.120	1.0	1.0	G
$CDCl_3$	0.08-0.40	1.0	-0.5	G[c]
$CDCl_3$	0.120	1.0	-23.0	G[b]
CD_2Cl_2	0.08-0.40	1.0	30.0	A

[a] G = General kinetic method, A = variation A, B = variation B.
[b] Two runs, data points taken every 4 minutes over ~3 hours.
[c] Delay between points was increased to 2 minutes after first 20 points.

taken or in the reaction being fully inhibited by the time the first point was taken. The inhibited rate was $\sim 0.5\ M^{-1}\ sec^{-1}$.

In an attempt to measure the reaction at an intermediate rate the following experiment was performed. Ten μl of the catalyst solution was added to a solution of 16 μl of **Q** in 400 μl methanol-d_4 and the rate observed as usual. The inhibited reaction mixture was removed from the probe after 10 minutes and another 10 μl of catalyst solution was injected and the rate again followed. This was repeated again after 11 minutes. The initial rate constants for the 3 injections of catalyst solution were 0.76, 21.4 and 520 $M^{-1}\ sec^{-1}$, respectively. The final rate constants were 0.25, 0.19 and 0.32 $M^{-1}\ sec^{-1}$ respectively based on total $[(NBD)RhCl]_2$ added. The initial rate constants were calculated on the basis of 0.001 M active catalyst for each injection.

Reaction of Q with $[(NBD)RhCl]_2$ in Pyridine-d_5. Ten μl of a 0.050 M solution of **5** in $CDCl_3$ was added to a solution containing 4 μl of Q in 486 μl pyridine-d_5 at 37°C. The isomerization did not occur and there was no change in the ^1H NMR spectrum after 1 hour time.

Kinetic Measurements in Mixed Solvents. These measurements were taken in CCl_4 by the general kinetic method previously described with the following exceptions. A portion of the CCl_4 was replaced by an equal volume of a more polar solvent so that the total volume remained at 0.5 ml in all cases. The $[5]_0$ was 1.0 mM except for the MeOH and HOAc rates for which the $[5]_0$ was 0.50 mM. The temperature was 37.0°C. The more polar solvents included $CDCl_3$, DMF, CH_3CN, MeOH-d_4, CH_3COOH, and $CH_2ClCOOH$ with concentrations indicated in Figure 9. Control solutions with CH_3COOH and CH_2CL-COOH were allowed to sit at 37°C for 1 hour prior to injection of the catalyst solution to assure that no acid catalyzed isomerization was taking place under the conditions used.

Kinetic Measurements with 7-tert-butoxyquadricyclane, 22. These measurements were made in $CDCl_3$ by variation A of the general kinetic method described above with the following changes. Reaction progress was determined by integration of the substrate methyl proton resonance at 1.32 ppm. $[5]_0$ was 0.5 mM and $[22]_0$ was varied from 0.08-0.36 M. 22 contained amounts of 23 varying from 2.1-36% at beginning of reaction.

Product Analysis of 5 Catalyzed Rearrangement of Q. Product analysis was performed on standard solutions of from 2-20 μl Q in 0.50 ml $CDCl_3$ with 1.0 mM 5 at completion of the reaction at 37 or 40°C and at 1 hour after. Products and product distributions were unchanged after 1 hour. Product distributions are given in Table 15. Two products were observed and identified by ^1H and ^{13}C NMR spectroscopy. The major product was NBD and constituted 93% of the products. The minor product was identified as HCD and constituted 7% of the product mixture. A third product was observed in < 1% yield but not identified.

Compound HCD[30]. ^1H NMR ($CDCl_3$): δ 5.95 (t,2H,J=1.9 Hz), δ 2.75 (m,2H), δ 2.49 (br s,2H), δ 2.34 (br s,1H), δ 1.76 (dd,2H,J=1 Hz), δ 1.35 (s,2H), δ 1.33 (dt,1H,J=6.7

and 1.8 Hz), δ 1.22 (d,1H,J=8.1 Hz), δ 0.97 (td,1H,J=4.8 and 1 Hz), δ 0.78 (d,2H,J=4.8 Hz); ^{13}C NMR ($CDCl_3$): δ 136.5 (d,J_{CH}=167 Hz), δ 52.5 (t,J_{CH}=133 Hz), δ 49.0 (d,J_{CH}=133.5), δ 45.8 (d,J_{CH}=139.6), δ 44.3 (d,J_{CH}=140 Hz), δ 36.9 (d,J_{CH}=152.8 Hz), δ 32.5 (t,J_{CH}=129.6 Hz), δ 18.2 (d,J_{CH}=174.4 Hz), δ 13.3 (d,J_{CH}=174.7 Hz); mass spectrum, m/e 184 (M^+).

Table 15. Product Distributions for **5** Catalyzed Isomerization of **Q**.[a]

		Product Distribution[b], mol %	
$[Q]_0$,M	$[NBD]_0$,mM[c]	NBD	HCD
0.040	1.26	92.5	7.50[d] (6.58)[e]
0.120	3.77	92.5	7.52 (7.01)
0.20	6.28	91.9	8.11 (7.38)
0.40	12.6	92.5	7.47 (7.54)
0.040	101.3	91.7	8.3 (5.45)
0.40	212.6	91.6	8.4 (6.77)

[a] At 40°C, in $CDCl_3$, $[5]_0$ = 1.0 mM.
[b] Based on [NBD] + [HCD] - $[NBD]_0$.
[c] **Q** contained 3.14% **NBD**.
[d] Analog integration.
[e] Digital integration.

Product Inhibition Studies on **Q** in $CDCl_3$. Rates were determined at 37.0°C by either the general kinetic method or by variation B described above except that the substrate solution contained one of the following: (1) 1, 2 or 3 equivalents of **NBD**; (2) 2 μl of **HCD**; or (3) 4 μl of a crude product extract prepared as described below. In cases 2 and 3, the $[Q]_0$ was 0.10 M (5 μl). The $[5]_0$ was 1.0 mM.

Preparation of Crude Product Extract. To a solution of 50 mg of **5** in 2 ml $CHCl_3$, 1 ml of **Q** was added in 50 μl aliquots with cooling. Upon completion of the reaction, the solution was put through a Waters Associates silica sep-pak and the sep-pak washed with 1 ml of $CHCl_3$. The colorless effluents were combined and concentrated by roto-evapora-

tion which removed the $CHCl_3$ but not **NBD**. NMR showed the major products to be **NBD** and **HCD**. All yellow Rh compounds were adsorbed on the silica sep-pak.

Preparation of **HCD**. **HCD** was isolated from the crude product mixture, above, by vacuum flash distillation of all more volatile products at 0.025 mmHg. The residual liquid was identified by comparison of its ^{1}H NMR spectrum to that of the known compound[30].

Comparison of the Kinetics of Crude and Purified **Q**. All measurements were taken following the general kinetic method described above. $[Q]_0$ was 0.20 M and $[5]_0$ was 1.0 mM in $CDCl_3$ at 37.0°C. Purification procedures included preparative gas chromatography at 70°C; chromatography on silica sep-pak; and stirring over either $LiAlH_4$ or $KMnO_4$ or neutral, basic, or acidic alumina.

Tests of Benzene, Toluene, **59** and 90% Technical Grade Cycloheptatriene as Inhibitors. Kinetic measurements were determined on solutions consisting of either 4 or 6 μl of **Q** with the addition of 4 μl of benzene, toluene, **59** or 90% technical grade cycloheptatriene and compared to rates of control solutions without any additive. All rates were determined in $CDCl_3$ at 37°C by the general kinetic method described above.

Interaction of Pyridine-d_5 with Isomerization Catalyst $[(NBD)RhCl]_2$ in $CDCl_3$. Forty μl of pyridine-d_5 was added to a solution of 5.3 mg of **5** in 0.4 ml $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. The Rh bound **NBD** resonances shifted from 3.91 → 3.88, 3.81 → 3.71 and 1.17 → 1.20 δ. On addition of an additional 40 μl of pyridine-d_5, the resonances shifted to 3.77, 3.60 and 1.09 ppm, respectively. Pyridine resonances appeared at 8.50, 7.55 and 7.16 in the first solution and shifted to 8.40, 7.44, 7.14 and 7.05 δ respectively upon addition of the second 40 μl of pyridine-d_5.

Twenty μl of **Q** was added to this solution and analyzed by ^{1}H NMR spectroscopy. **Q** was observed to isomerize to **NBD** with $\tau_{1/2}$ = 90 min. No change occurred in the Rh bound

NBD resonances. The product, **NBD**, spectrum showed well resolved fine coupling indicating very slow or no exchange was occurring.

Interactions of Acetic Acid-d_4 with **5** in $CDCl_3$. Ten μl CD_3COOD was added to a solution of 12.9 mg **5** in 0.5 ml $CDCl_3$ and analyzed by ^1H NMR. No change in the **5** resonances were observed. Forty μl (**Q**) was added to this solution at room temperature. The resulting reaction boiled the solution and isomerization was complete by the time the sample was placed in the spectrometer. All **NBD** resonances were broadened by exchange. Rh bound **NBD** resonances were not distinguishable. Upon addition of 5 μl pyridine-d_5 to the solution, all **NBD** peaks sharpened markedly and Rh bound **NBD** resonances reappeared. With the addition of 5 μl more pyridine-d_5, fine coupling was restored to the free **NBD** resonances. **HCD** resonances were also present and sharp under all conditions. Exchange was verified by saturation transfer experiments.

Interaction of HCl with **5** in $CDCl_3$. One μl of concentrated HCl was added to a solution of 9.7 mg **5** in 0.8 ml $CDCl_3$. This solution turned brown within 3 min. The Rh bound **NBD** peaks were broadened but not shifted. Addition of 10 μl **Q** resulted in rapid isomerization to the normal products. All **NBD** resonances were broad.

Interaction of Acetic Acid with Organic Bases in $CDCl_3$. Ten μl of pyridine-d_5 or Et_3N was added to a solution of 10 μl acetic acid in 0.5 ml $CDCl_3$ and compared to solutions of the base in $CDCl_3$ by NMR spectroscopy. Pyridine resonances showed no differences in the 2 spectra. Et_3N peaks were shifted downfield and slightly broadened with respect to the standard solution.

Ten μl of acetic acid was added to a 0.1 M solution of **TBA** in $CDCl_3$. The **TBA** NMR peaks were shifted downfield with respect to the original solution.

Interaction of **TBA** with **5** in $CDCl_3$. Five mg of **TBA** was added to a solution of 5 mg of **5** in 0.5 ml $CDCl_3$ and analyzed by ^1H NMR spectroscopy. The Rh bound **NBD** peaks were unchanged. Addition of 10 μl **Q** resulted in rapid isomerization of **Q** to the normal products. Rapid exchange of **NBD** was evident. Exchange was verified by NMR saturation transfer experiments.

Interaction of Et_3N with **5** in $CDCl_3$. Upon addition of 10 μl of Et_3N to a solution of 5 mg of **5** in $CDCl_3$ the color of the solution changed from light yellow to yellow orange. It was apparent from ^1H NMR analysis that Et_3N was coordinating weakly to **5**. This was evident from the appearance of 4 new peaks in the spectrum, attributed to **5**·Et_3N, in addition to the expected peaks for Et_3N. These peaks were broad and saturation transfer experiments demonstrated that ^1H's in these peaks were exchanging with ^1H's in both Et_3N and **5**. Addition of 10 μl **Q** to this solution resulted in the rapid isomerization of **Q** to the normal products. **NBD** exchange was shown to be facile in this solution without affecting **5**·Et_3N or the Et_3N exchange process. On addition of 20 μl of CH_3COOD to this solution, Et_3N was protonated and the peaks for **5**·Et_3N disappeared. The Et_3N peaks sharpened and moved slightly downfield. The Et_3N exchange process was stopped but **NBD** exchange was unaffected.

Kinetic Measurements in $CDCl_3$ with Organic Bases Added. Rates were measured by the general kinetic method in $CDCl_3$ with **TBA** or Et_3N added. Conditions for these measurements are given in Table 16.

^1H T_1 Measurements. Longitudinal relaxation times were measured for **Q** and **NBD** by the inversion recovery method[66]. Measurements were taken at 37°C in CCl_4 and $CDCl_3$ solutions containing 6 or 10 μl substrate (see Table 17).

Table 16. Conditions for Kinetic Measurements in $CDCl_3$ with Added TBA or Et_3N at 37°C and $[5]_0$ = 1.0 mM.

$[Q]_0$ Range,M	[TBA] Range,M	$[Et_3N]$ Range,M	Kinetic Method
0.10, 0.20	0	0.014-0.14	General[a]
0.10, 0.20	0.1	0	General[a]

[a]Total volume = 500 μl.

Table 17. ^1H T_1 Measurements.

Solvent	Substrate	$[Cr(acac)_3]$,M	T1 Range,sec
CCl_4	**NBD**	0	4.3-5.1
CCl_4	**Q**	0	4.0-4.7
CCl_4	**NBD**	0.01	< 0.22
$CDCl_3$	**Q**	0	< 4.5
$CDCl_3$	**NBD**	0	< 5.0
$CDCl_3$	**NBD**	0	12,25,35[a]
$CDCl_3$	**NBD & Q**	0.01	0.45-0.60

[a]O_2 excluded by N_2. T_1's for bridge, bridgehead and olefin protons, respectively.

Effect of O_2 on **Q** Isomerization. N_2 (passed through a drying column and BASF O_2 scrubber) was bubbled through $CDCl_3$ for 10 minutes prior to making up the reaction solution. NMR tubes were fitted with septums and flushed with purified N_2 prior to filling. Reaction solutions consisted of 10 μl of **Q**, 480 μl of $CDCl_3$, and 10 μl of 0.050 M **5** in $CDCl_3$. Kinetic determinations were made according to the general method at 25°C and compared to similar solutions with O_2 present. Resolved rate constants were 4.8 M^{-1} sec^{-1} for the O_2 excluded experiment and 4.1 M^{-1} sec^{-1} for the O_2 present experiment.

Effect of $Cr(acac)_3$ on Kinetics. Standard reaction mixtures were made according to variation A of the general kinetic method with 4 μl of **Q** in CCl_4 or 6 μl of **Q** in $CDCl_3$ and rates measured at 37°C. These rates were compared to control solutions made and measured according to the general kinetic method. Rate constants were 3.96 vs 4.0 M^{-1} sec^{-1} in CCl_4 and 17.1 vs 16.4 M^{-1} sec^{-1} in $CDCl_3$, respectively.

H^+ Catalyzed Rearrangement of **Q** in Methanol. Five hundred μl of **Q** was added dropwise to a solution of 5 drops of concentrated H_2SO_4 in 2.0 ml MeOH with cooling. Reaction was rapid and exothermic. Work up consisted of addition of 4 ml H_2O, neutralization with $NaHCO_3$, extracted 3 times with 5 ml ether, combined ether extracts and washed with H_2O, then dried over $MgSO_4$, filtered and concentrated. Analytical GC revealed 3 product peaks, **26**, **25** and unidentified in ratios 22:73:5 respectively by quantitative ^{13}C NMR.

Compound **26**. ^{13}C NMR ($CDCl_3$): δ 140.43 (d), δ 133.11 (d), δ 81.73 (d), δ 56.12 (q), δ 45.89 (d), δ 45.74 (t), δ 40.33 (d), δ 34.13 (t); mass spectrum: m/e 124 (M^+), 93 ($-OCH_3$).

Compound **25**. ^{13}C NMR ($CDCl_3$): δ 85.82 (d), δ 55.74 (q), δ 32.27 (d), δ 30.25 (t), δ 29.39 (t), δ 13.48 (d), δ 12.54 (d), δ 10.75 (d); mass spectrum: m/e 124 (M^+), 93 ($-OCH_3$).

Interaction of **NBD** with **5**

Equilibrium Measurements. A mixture containing 21.5 mg (0.050 mmole) of **5** and 18.75 μL (0.180 mmole) of **NBD** in 0.60 ml of $CDCl_3$ was placed in an NMR tube and analyzed in the WM-250 spectrometer at various temperatures. At each temperature, 4 NMR transients were taken with a delay time of 40 seconds. Sufficient resolution in the NMR spectra was achieved in the temperature range 206.6-234.6°K. The slope of log K vs 1/T gave $\Delta H = -15.8 \pm 1$ kcal, $r = 0.99$.

Saturation Transfer Experiments. $CDCl_3$: The saturation transfer solution consisted of 8.4 mg (18 mmole) of **5** and 7.4 μl (73 mmole) of **NBD** in 0.5 ml $CDCl_3$. The experiments were run at -55°C using 1.5 watts of decoupler power. CCl_4: The saturation transfer solution consisted of 7.6 mg (16 mmol) of **5** and 6.7 μl (66 mmol) of **NBD** in 0.5 ml CCl_4.

The experiments were run at 25°C using 1.5 watts of decoupler power. Benzene-d_6 : The saturation transfer solution consisted of 5.8 mg (13 mmol) of **5** and 5.1 μl (50 mmol) of **NBD** in 0.5 ml benzene-d_6 . The experiments were run at 25°C with 1.5 watts of decoupler power.

Vapor-Phase Osmometry. The data in Table 18 were collected at 37°C for mixtures containing 45.8 mg of **5** in 2.0 ml of solvent. Benzil was used for calibration.

Table 18. Vapor-Phase Osmometry on **5**.

		ΔR,Ω	
	Conc.,M	Benzene	$CHCl_3$
Benzil	0.05	29.5	28.47
Benzil	0.10	46.5	50.00
[(**NBD**)RhCl]$_2$	0.05	26.4	27.33

Freezing Point Depression Experiments (**FPD**). The **FPD** mixture consisted of 146.0 mg (0.320 mmol) of **5**, 97.0 μl (0.950 mmol) of **NBD**, and 7.443 g of $CDCl_3$. The **FPD** was 0.63±0.06°C below that of Stohler $CDCl_3$. The calculated **FPD** value for (**NBD**)$_2$ RhCl was 0.627°C. The calculated values for other possible complexes such as (**NBD**)RhCl and [(**NBD**)RhCl]$_2$ were 1.05 and 0.837, respectively.

Kinetic Measurements at 1°C. Measurements were made at 1.0±0.5°C by the general kinetic method described previously on 2 different solutions. The first solution consisted of 6 μl of **Q** in 484 μl of $CDCl_3$ and the second solution consisted of 6 μl of **Q** and 6 μl of **NBD** in 478 μl of $CDCl_3$. The observed rate constants $\times 10^3$ were 0.58±0.03 and 0.98±0.07 sec^{-1} , respectively.

^{1}H 2DFT Chemical Exchange Mapping Experiment. This experiment was performed on the Bruker WM-250 with the FTNMR2D program on a solution consisting of 5.8 mg

(12.6 mmol) of **5** and 4.6 μl (45.3 mmol) of **NBD** in 0.5 ml $CDCl_3$ at 213°K. Parameters: X1 = 128, X2 = 1024, NS = 4, N1 = 256, N2 = 2048; W1 = ±360.0 Hz, W2 = 1901 Hz, RD = 10 sec., ND = 3 sec. Acquisition time was 3.8 hours, transformed with Lorentz-Gauss (LB = -1.5, GB = 0.3) in t_1 and Lorentz-Gauss (LB = 0.3, GB = 0) in t_2.

Kinetic Modeling with HAVCHM. The experimentally observed kinetics for the **5** catalyzed isomerization of **Q** in $CDCl_3$ were modeled on the Honeywell L-66 and VAX 11/780 computers with the HAVCHM program written by R. N. Stabler and J. Chesick, Haverford College, May 1977[37]. HAVCHM is a program for integration of multistep rate equations using the Gear integration method. It requires the input of the rate laws with rate constants, species involved and initial concentrations of reactants. HAVCHM then calculates and outputs the concentrations of each reactant, intermediate and product at specified time intervals. This output may be compared to experimental data and the proposed mechanistic scheme evaluated and refined.

Several mechanistic schemes for the **5** catalyzed **Q** isomerization were proposed, tested and refined by an iterative process utilizing HAVCHM. For the final reaction list and a comparison with the experimental data, see Table 9 and Figure 23. Parameters utilized by the program: Error test constant for DIFSUB = 1×10^{-8}; min. step size = 1×10^{-12}; max. step size = 20; max. time for integration = 600 sec; NEQT = 1; NWRPLO = 1; MF = 1; NLARGE = 0; output requested for each species every 5 sec.

Reaction of **8** with **27** in $CDCl_3$. One hundred thirteen point five mg (0.292 mmol) of **8** was dissolved in 3 ml $CDCl_3$ and stirred magnetically at room temperature. One hundred μl (0.750 mmol) of **27** was added to this solution and allowed to stir for 3 hours. The solution was then concentrated and precipitated in pentane, centrifuged, washed and triturated in pentane and centrifuged again to yield 152.2 mg (∿84%) of a white powder, **29**, presumed to be a Rh insertion product analogous to **10**. This compound was shown to

exhibit a dynamic exchange process by variable temperature NMR spectroscopy which could not be stopped by cooling to -60°C in $CDCl_3$. IR(KBr): 2050 cm^{-1} (terminal C=O), 1725 cm^{-1} (acyl C=O); M.P.: 190-200°C decomp.

Reaction of Rh Insertion Product with Ph_3P. One hundred twenty-five point zero mg (0.477 mmole) of Ph_3P was added to a solution of 65.0 (0.207 mmol) of the Rh insertion product, **29**, in 3 ml $CDCl_3$ at room temperature and stirred for 10 minutes. The solution was worked up as reported above for the Rh insertion product to yield 142.2 mg (82%) of a yellow powder identified as **30** and an unidentified minor product present in ~4% abundance. ^{13}C NMR ($CDCl_3$): δ 247.70 (d,C=O,J_{Rh-C}=28.5 Hz), δ 226.21 (d,C=O,J_{Rh-C}=35.6 Hz), δ 135.15 (d,Ph_3P,J_{CP}=8.6 Hz), δ 130.19 (s,Ph_3P), δ 128.10 (d,Ph_3P,J_{CP}=12.8 Hz), δ 66.33 (d,J_{CH}=136 Hz), δ 51.19 (t,J_{CH}=137 Hz), δ 41.22 (d,J_{CH}=142 Hz), δ 40.47 (d,J_{CH}=153 Hz), δ 40.28 (d,J_{CH}=132 Hz), δ 23.12 (t,J_{CH}=134.5 Hz), δ 14.41 (d,J_{CH}=171 Hz), δ 13.12 (d,J_{CH}=165 Hz), δ 2.15 (t,J_{CH}=159 Hz); IR (KBr): 1660 cm^{-1} (m), 1620 cm^{-1} (s), 1590 cm^{-1} (w); mp = 190°C decomp.

Reactions of Tri and Tetracyclic Substrates with $(PhCN)_2PdCl_2$

General Procedure. All reactions were run at room temperature in $CDCl_3$ with stoichiometric quantities of substrate and **36**. No attempt was made to exclude oxygen. Reactions were followed by ^1H NMR and allowed to react until no starting substrate was left. Usual work up involved concentration of the reaction mixture by roto-evaporation at reduced pressure followed by silica gel column chromatography. Columns consisted of ~30:1, silica gel by weight and were packed in hexane. Products were eluted first with hexane to remove any uncomplexed hydrocarbons (colorless) and second with either benzene or $CHCl_3$ which eluted a yellow fraction containing the Pd complexes reported. An orange band of unknown composition could be eluted with ethyl acetate leaving behind a dark brown or black band on the column. The yellow product fraction was

concentrated by roto-evaporation and precipitated in pentane to yield a white or yellow powder. The powder suspension was centrifuged and the supernatant was concentrated and precipitated again to recover any remaining product. The powder was triturated and washed twice in pentane and then dried overnight in a vacuum desiccator at 0.025-0.05 mmHg. Reported yields are for isolated products unless otherwise noted. Products were identified by ^{1}H and ^{13}C NMR.

Reaction of **27** with **36**. The reaction mixture consisted of 1.00 g (2.61 mmol) of **36** and 0.317 g (2.64 mmol) of **27** in 20 ml of $CHCl_3$. The mixture was stirred magnetically for 4 hours and worked up in the usual fashion to yield 316 mg (40%) of a fine yellow powder identified as **63**: $^{1}H,^{1}H$ homonuclear decoupling and ^{1}H 2DFT SECSY results are correlated in Table 12; ^{13}C NMR ($CDCl_3$): δ 104.85 (C_3, J_{CH}=163.2 Hz), δ 91.82 (C_2, J_{CH}=157.1 Hz), δ 59.82 (C_8, J_{CH}=155±5 Hz), δ 59.72 (C_6, J_{CH}=155±5 Hz), δ 38.54 (1C, t, J_{CH}=134.9 Hz), δ 38.07 (1C, d, J_{CH}=140 Hz), δ 38.06 (1C, t, J_{CH}=132 Hz), δ 31.71 (1C, d, J_{CH}=140 Hz), δ 24.99 (1C, t, J_{CH}=129 Hz); M.P. = 160-170°C decomp. Anal. Calcd for $PdC_9H_{12}Cl_2$: C, 36.34; H, 4.07. Found: C, 36.52; H, 4.20.

2DFT SECSY on **63**. The 2D SECSY experiment was run in $CDCl_3$ on a 0.2 M solution of **63** on the WM-250 utilizing the FTNMR2D program. Parameters: X1 = 256, X2 = 1024, NS = 16, N1 = 512, N2 = 2048; W1 = ±520 Hz, W2 = ±1351 Hz, recycle delay = 2.7 sec; acquisition time = 4.5 hours; transformed with sine-bell apodization in both domains.

Reaction of **27**-d_4. The reaction mixture consisted of 109.0 mg (0.8790 mmol) of **27**-d_4 and 348.0 mg (0.9086 mmol) of **36** in 5 ml of $CDCl_3$. The reaction mixture was allowed to sit for 6 hours then worked up by the usual method to yield 179.1 mg (70%) of a fine yellow powder identified as **63**-d_4: ^{1}H NMR ($CDCl_3$), δ 5.65 (m, 90% D), δ 5.23

(1H,d,J=5.1 Hz), δ 4.88 (1H,br s), δ 3.49 (1H,d,J=5.4 Hz), δ 2.52 (2.1H,brt,J=5 Hz), δ 2.03 (1.15H,m), δ 1.21 (2H,m), δ 0.84 (m,93% D).

Reaction of **58**. The reaction mixture consisted of 210.1 mg (1.945 mmol) of **58** and 745.8 mg (1.947 mmol) of **36** in 15 ml of $CDCl_3$ and was allowed to sit overnight at room temperature. The solution was flash distilled and the volatiles were concentrated and the product collected by preparative gas chromatography. Conversion was > 95% by NMR spectroscopy to a single product identified as **62** by comparison of its ^{1}H NMR spectrum to that of the known compound[56]. ^{1}H NMR ($CDCl_3$): δ 5.8 (m,1H), δ 5.35 (m,1H), δ 2.3 (m,2H), δ 1.2 to 1.9 (m,8H); mass spectrum (70 eV), m/e 108 (M^+).

Reaction of **59**. The reaction mixture consisted of 317.3 mg (0.828 mmol) of **36** and 90.0 mg (0.849 mmol) of **59** in 5 ml $CDCl_3$. No starting material remained by NMR spectroscopy after 2 minutes. Work up by the usual method or flash distillation and analysis of volatiles and non-volatiles yielded a complex product mixture which was not resolved. No products were isolated or identified after treatment with Ph_3P. No intermediates were observed when the reaction was run in the NMR spectrometer at low temperatures ranging from 213-273°K.

Reaction of **60**. The reaction mixture consisted of 506.0 mg (1.321 mmole) of **36** and 159.4 mg (1.328 mmole) **60** in 10 ml $CDCl_3$. The mixture was allowed to sit overnight and worked up in the usual fashion to yield 139.8 mg (36%) of a fine yellow powder identified as **63**. ^{1}H and ^{13}C NMR spectra were identical to those for **63** prepared from **27**.

Reactions of Pd Complexes

Reaction of **63** with Ph_3P. Two equivalents of Ph_3P were added to a solution of 159 mg of **63** in 5 ml $CDCl_3$. The reaction was over in minutes and indicated by precipitation of yellow needles of $(Ph_3P)_2PdCl_2$. ^{1}H NMR showed > 95% conversion to product and

formation of an unidentified minor product, < 5%. The product mixture was worked up by silica gel chromatography to remove any residual Pd complexes in solution followed by concentration on a vacuum jacketed, solvent removal column and isolation by preparative GC to yield pure **64**[57]: ^{1}H NMR ($CDCl_3$), δ 5.98 (m,2H), δ 5.62 (dt,2H), δ 2.67 (br s, 1H), δ 2.49 (br d,2H), δ 2.37 (m,1H), δ 1.92 (d,2H), δ 1.69 (t,2H); ^{13}C NMR ($CDCl_3$), δ 132.7 (2C,d,J_{CH}=160 Hz), δ 126.4 (2C,d,J_{CH}=165 Hz), δ 34.75 (2C,t,J_{CH}=123 Hz), δ 29.68 (1C,d,J_{CH}=134 Hz), δ 28.95 (1C,t,J_{CH}=123 Hz), δ 25.20 (1C,d,J_{CH}=127 Hz); exact mass for C_9H_{12}, m/e 120.0938 (M^+,10 ppm), m/e 121.0972 (M^++1,-3.4 ppm).

Reaction of **63**-d_4 with Ph_3P. Two equivalents of Ph_3P was added to a solution of 179.1 mg of **63**-d_4 in 5 ml $CDCl_3$. The reaction was over in minutes as indicated by precipitation of yellow needles of $(Ph_3P)_2PdCl_2$. ^{1}H NMR showed > 95% conversion to **64**-d_4 and an unidentified minor product, < 5%. The product solution was worked up as described above for **64**. Product was isolated by preparative GC for analysis and identified as **64**-d_4: ^{1}H NMR ($CDCl_3$), δ 5.98 (br d,2H), δ 5.62 (dd,89% D), δ 2.67 (br m,1H), δ 2.43 (m,37% D), δ 2.37 (m,1H), δ 1.90 (m,43% D), δ 1.69 (t,2H); the ^{13}C NMR spectrum ($CDCl_3$) is similar to that of **64** except that the carbons at 126.4 and 34.3 δ are reduced in intensity and show deuterium coupling.

Carbonylation of **63** in Methanol. CO was bubbled through a solution of 50 mg KOH in 12 ml of dry methanol for 5 minutes prior to the addition of 315 mg (1.063 mmole) of **63**. Bubbling of CO was continued for 10 minutes longer and the solution was stirred magnetically. A black and grey precipitate began to form immediately. The solution was filtered to remove the precipitate and the filtrate was worked up by adding 20 ml H_2O, extracting twice with 25 ml ether, washing the ether portion with H_2O, drying over $MgSO_4$, filtering and concentrating by fractional distillation. This yielded 49.4 mg (39%) of a colorless solution containing 3 products in the ratio of 1:6:3 by NMR. The products

were isolated by preparative GC and determined by NMR and mass spectroscopy to be **65**, **66** and unidentified, respectively. The precipitate was grey upon drying rather than the anticipated black of Pd metal or Pd oxides. $CDCl_3$ was added to the precipitate and allowed to stand for a day in which time a green solution was formed. NMR spectroscopy of this solution revealed unreacted starting material along with some other unidentified ^1H resonances. The low yield was apparently due to an incomplete reaction.

Compound **65**. ^1H NMR ($CDCl_3$), δ 6.06 (m,vinyl), δ 5.33 (m,vinyl), δ 2.3 (dm,1H), δ 2.24 (m,2H), δ 1.97 (br d,1H), δ 1.43 (m,1H), δ 1.27 (br t,2H), δ 0.97 (1H,m), δ 0.38 (m,1H,cyclopropyl), δ 0.20 (m,1H,cyclopropyl); mass spectrum (70 eV), m/e (relative intensity), 120 (M^+,20), 105 (14), 91 (25), 79 (base,100).

Compound **66**. ^1H NMR ($CDCl_3$), δ 5.90 (dt,1H,vinyl), δ 5.72 (br t,1H,vinyl), δ 4.19 (br s,1H,H-CCl), δ 1.35-2.55 (m,10H); ^{13}C NMR ($CDCl_3$), δ 132.59 (1C,vinyl), δ 129.90 (1C,vinyl), δ 61.08 (1C,CHCl), δ 37.03 (1C), δ 32.44 (1C), δ 28.01 (1C), δ 26.37 (2C), δ 25.05 (1C); mass spectrum (70 eV), m/e (relative intensity), 156 (M^+,16), 158 (M^++2,5), 121 (loss of Cl,18), 79 (base,100).

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