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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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].

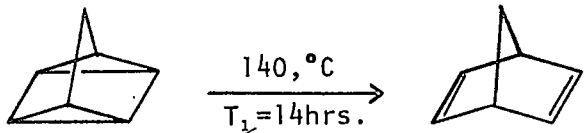
This thesis reports investigations of interactions between Rh(I) and Pd(II) organometallic complexes with cyclopropanes in rigid systems.

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].

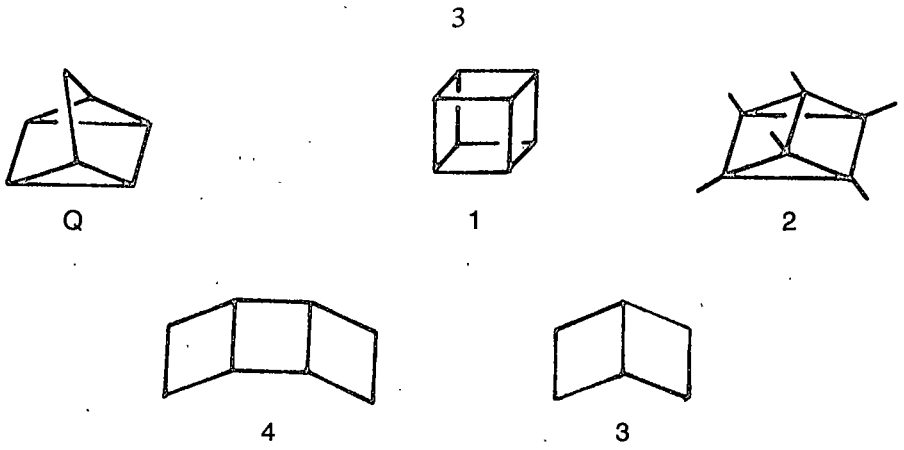


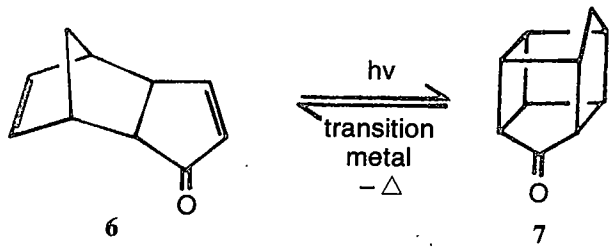
Figure 1. Several examples of thermally stable, strained carbocycles.

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).

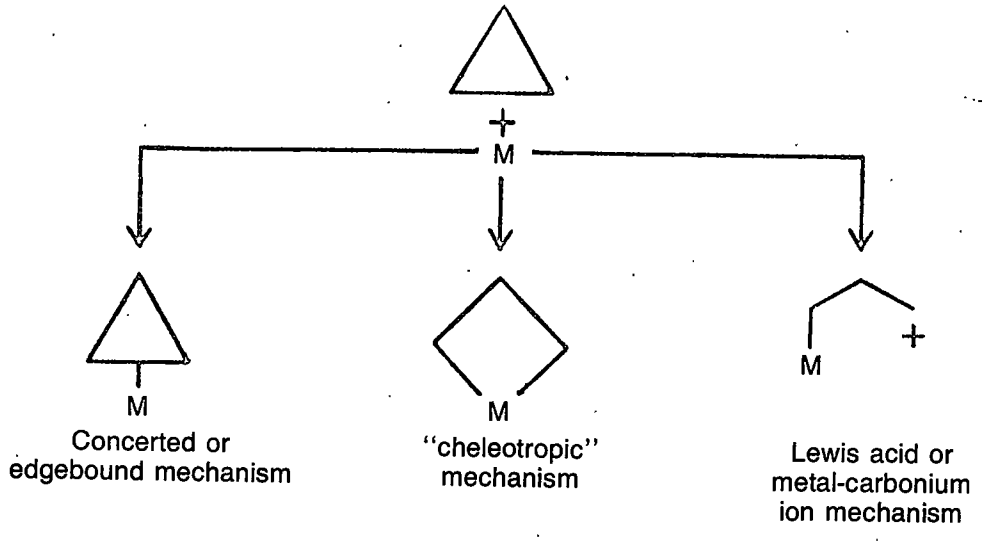


Figure 2. The three basic mechanisms proposed for metal catalyzed rearrangements of cyclopropanes.

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

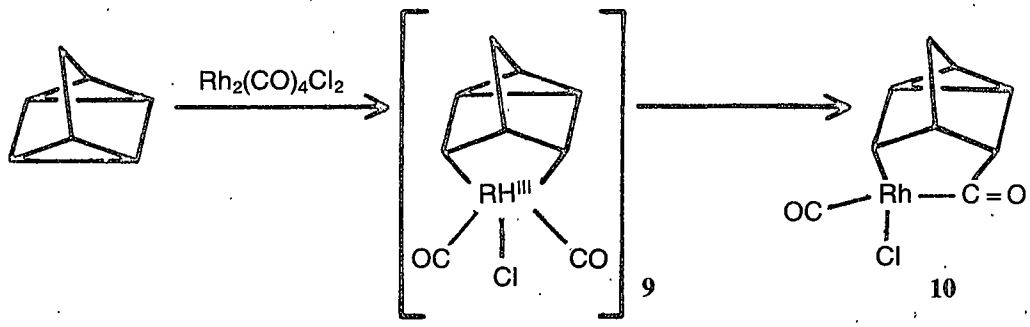
the selection rules that govern the energy of activation and Mango's explanation for the catalytic effect of a transition metal. Manassen investigated a variety of bivalent metal complexes of tetraphenylporphyrin or phthalocyanine for catalytic activity towards the isomerization of Q. He found that most 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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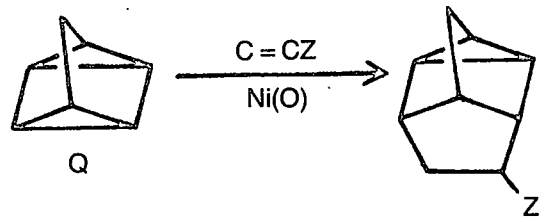
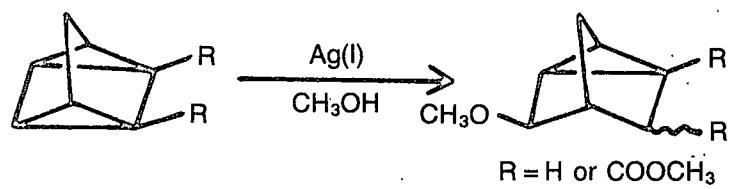


(4)

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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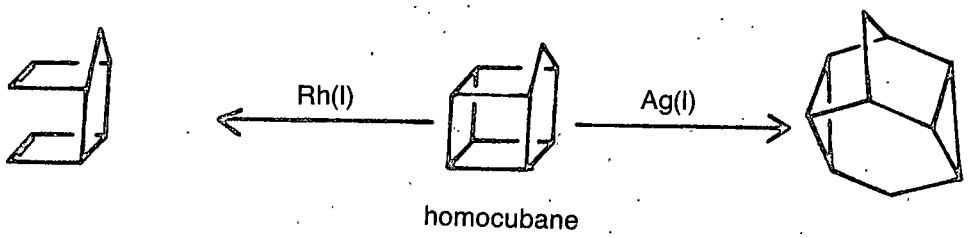

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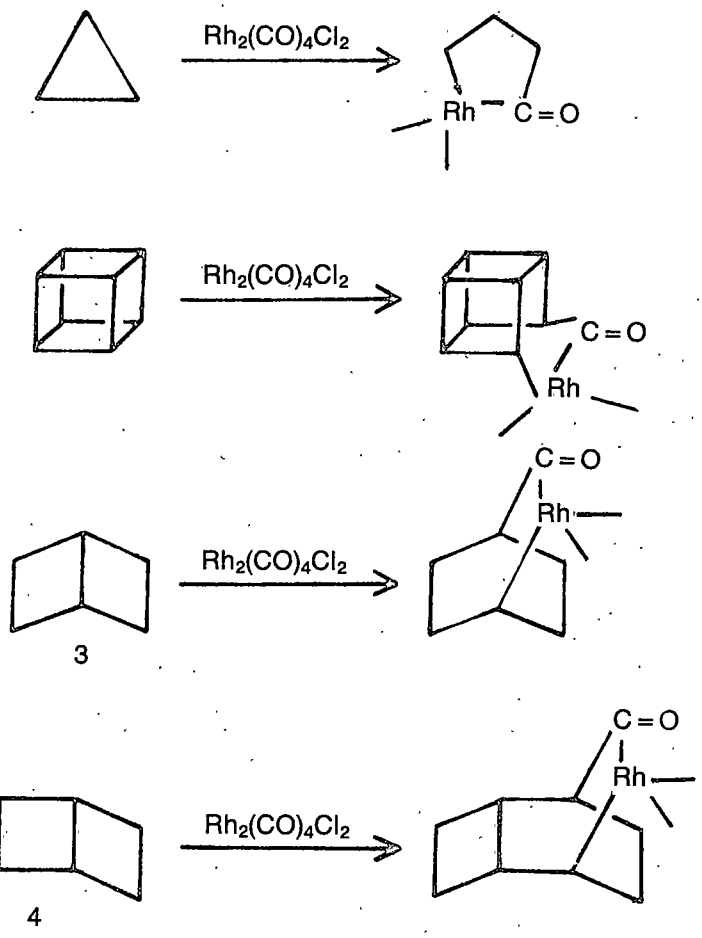
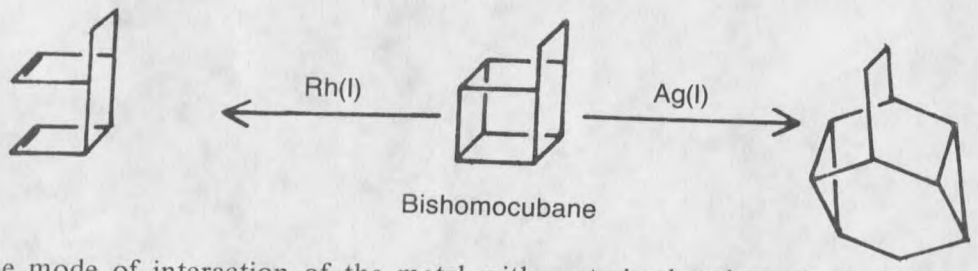
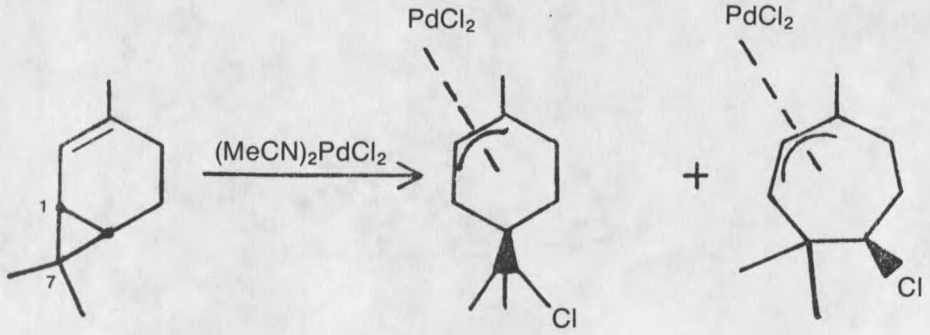


Figure 3. Known rhodium carbonyl insertion products from the reaction of $Rh_2(CO)_4Cl_2$ with small strained carbocycles.



(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]



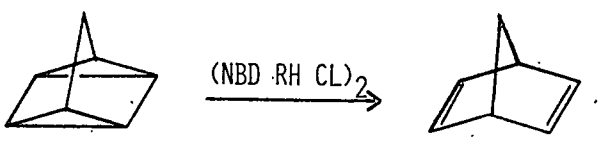
(8)

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.

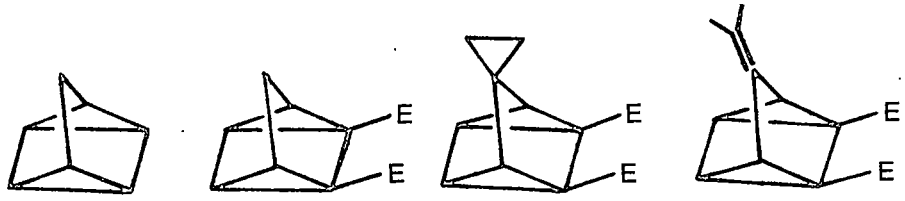
One of the major types of investigations of the mechanisms of chemical reactions has been the kinetic investigation. Kinetics alone are rarely able to determine a detailed mechanism but reaction mechanisms are rarely considered to be understood without a detailed kinetic analysis. Transition metal interactions 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)

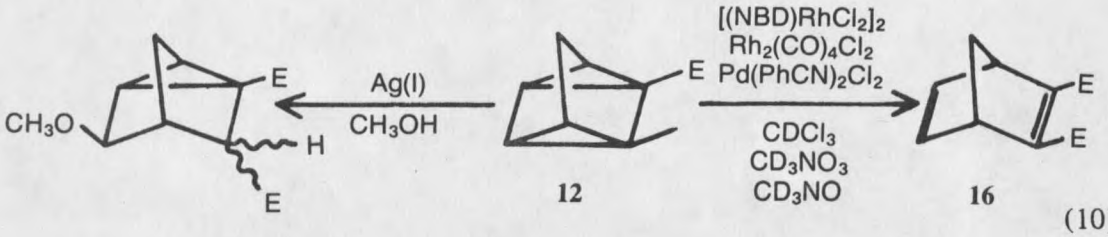
In 1973, Hogeveen[25] reported on the isomerization of a series of substituted quadricyclanes catalyzed by **5** (Fig. 4). He observed that all of these quadricyclanes were quantitatively converted to the corresponding NBD and suggested that the second order rate constants reported were composite rate 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.

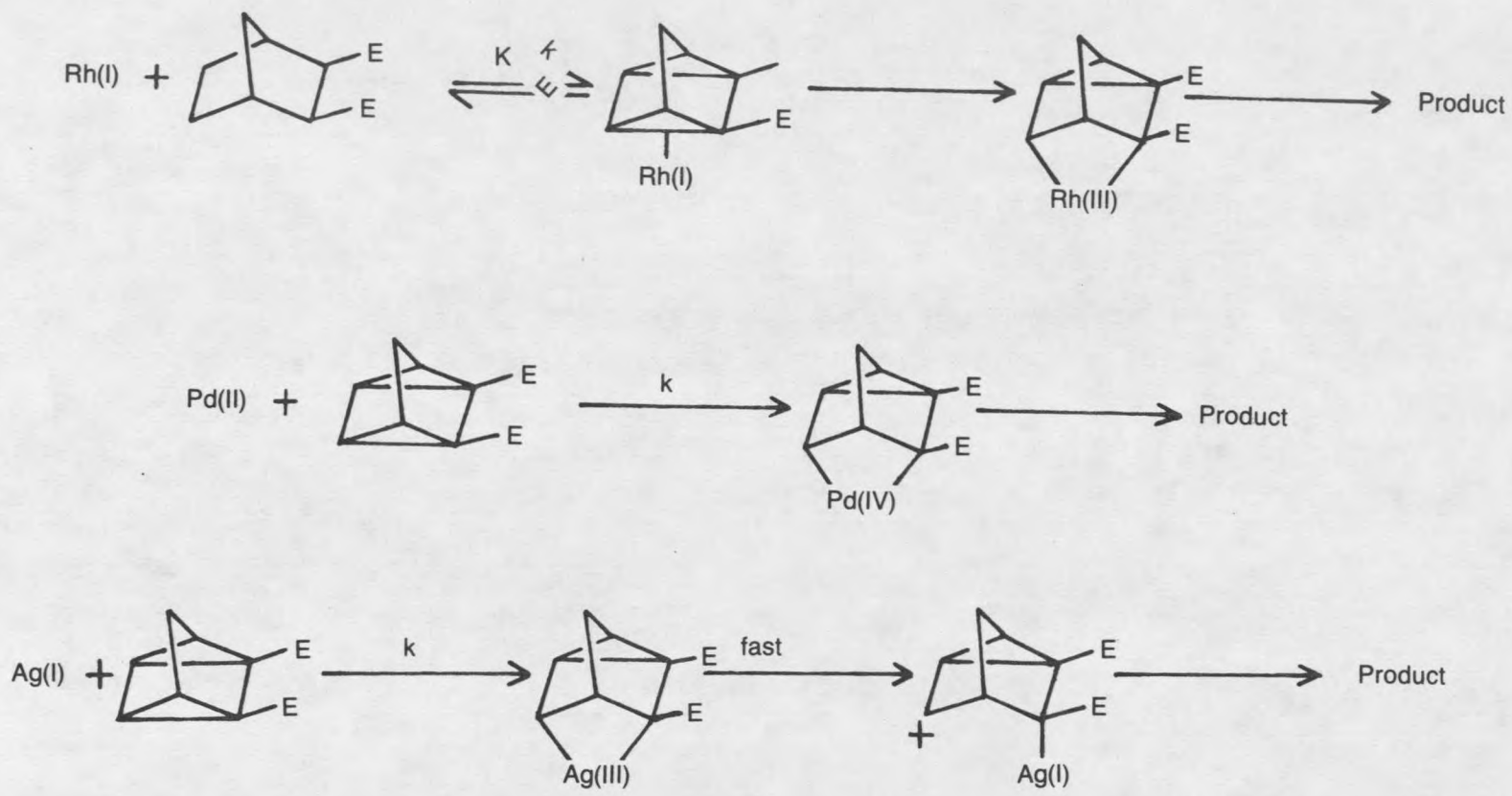


Figure 5. Mechanisms proposed by Hogeveen[26] for the interactions of Rh(I), Pd(II) and Ag(I) with quadricyclane, 2,5-dimethylester.

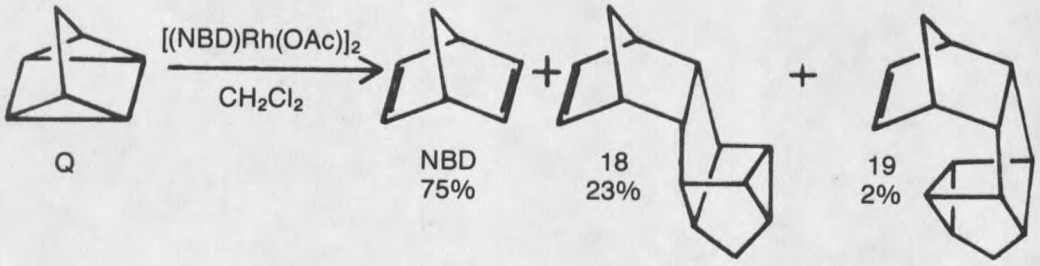
Noyori[18] reported on the bis(acrylonitrile) Ni(0) catalyzed isomerization of **Q** to **NBD** in 1975. Ni(0) is unique in that it catalyzes the $[2\sigma + 2\pi]$ cycloaddition of Q and acrylonitrile in addition to the isomerization to **NBD** (Eq. 4). The kinetics of this reaction were complicated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

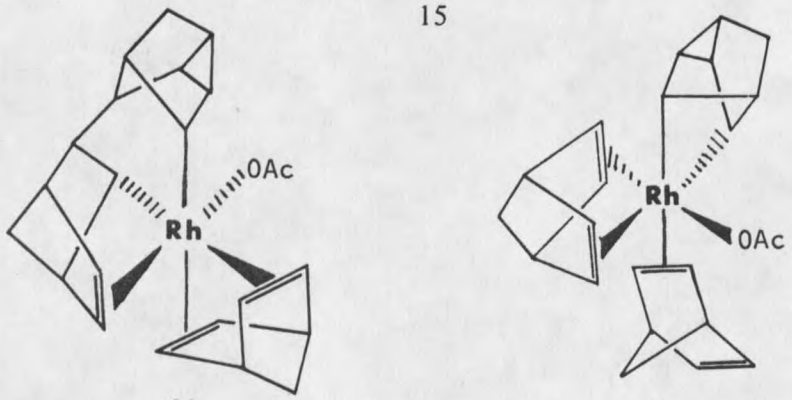
In 1979, Chen and Feder[28] reported on the [(**NBD**)RhAcO]$_2$ (**17**), catalyzed rearrangement of **Q** (Eq. 12). Several unique observations were made for this system. Quantitative conversion of **Q** to **NBD** was not observed for this Rh(I) complex. Two isomers of bis(norbornadiene) (**18**, **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.

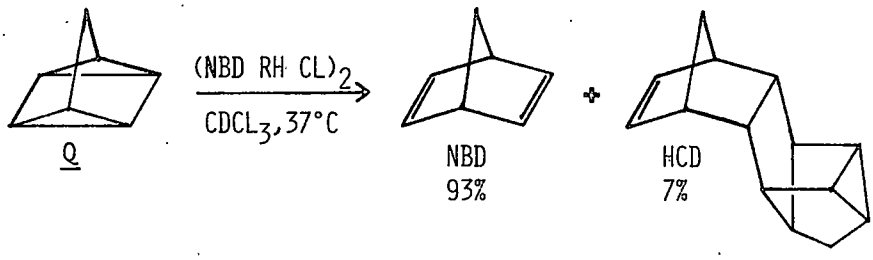
In view of the surprising results of our preliminary investigations and the general lack of detailed kinetic studies of these systems, it was concluded that a detailed kinetic analysis of the [(**NBD**)RhCl]$_2$ catalyzed valence isomerization of quadricyclane would be a timely contribution to the basic 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

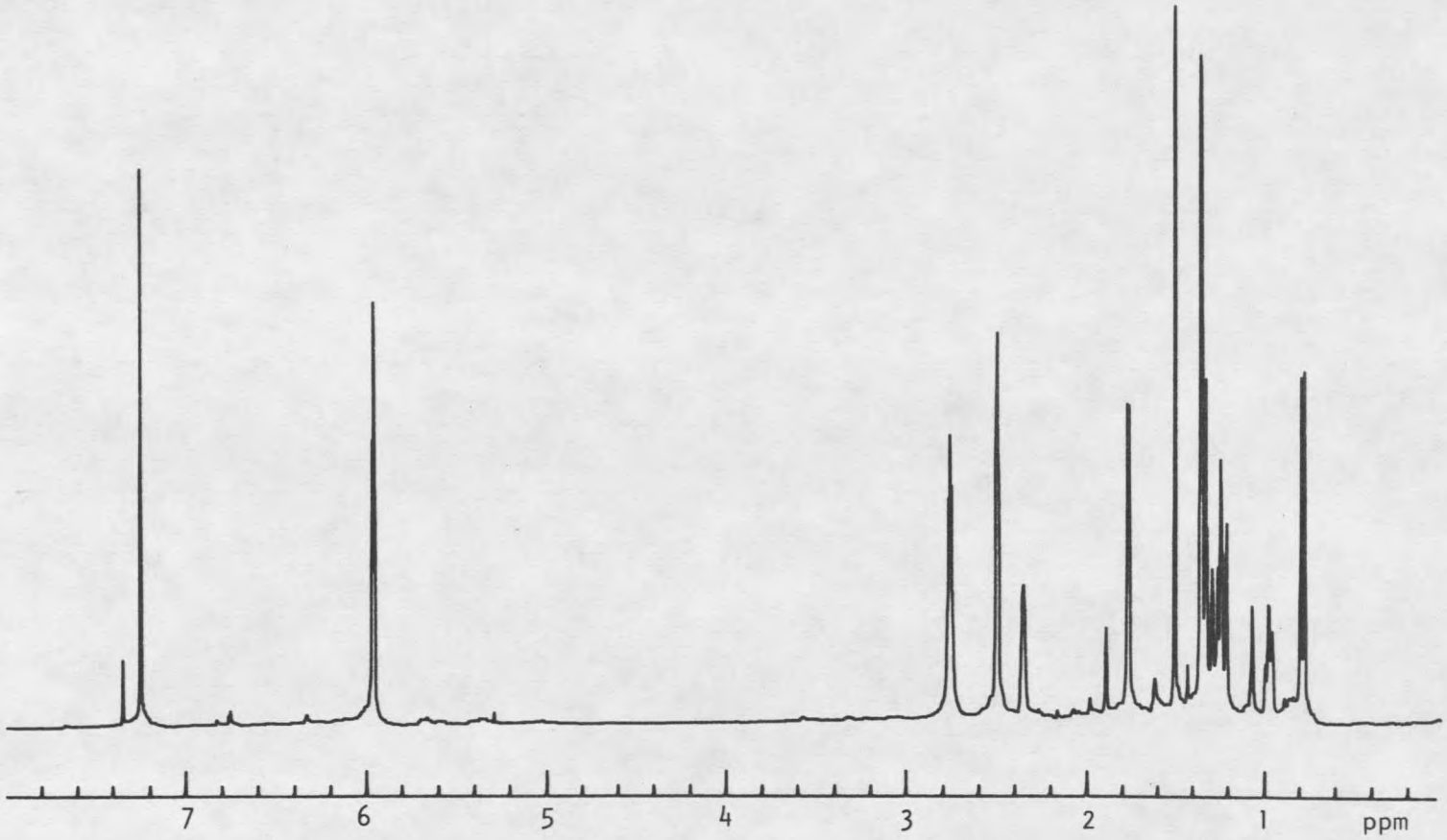


Figure 7. ^{1}H NMR spectrum of **HCD** (250 MHz, $CDCl_3$).

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

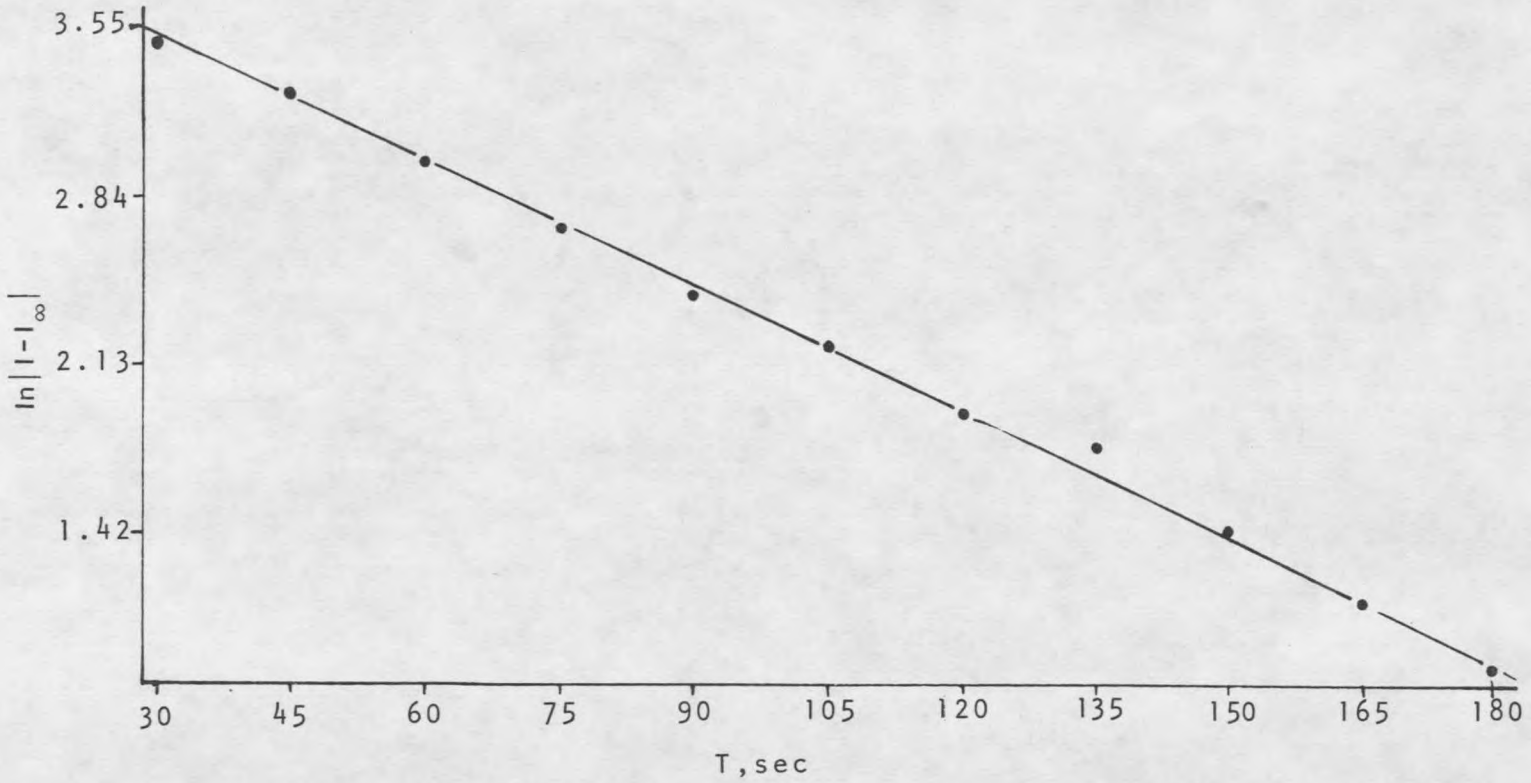


Figure 8. A *psuedo* first order plot of a typical kinetic run.

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.

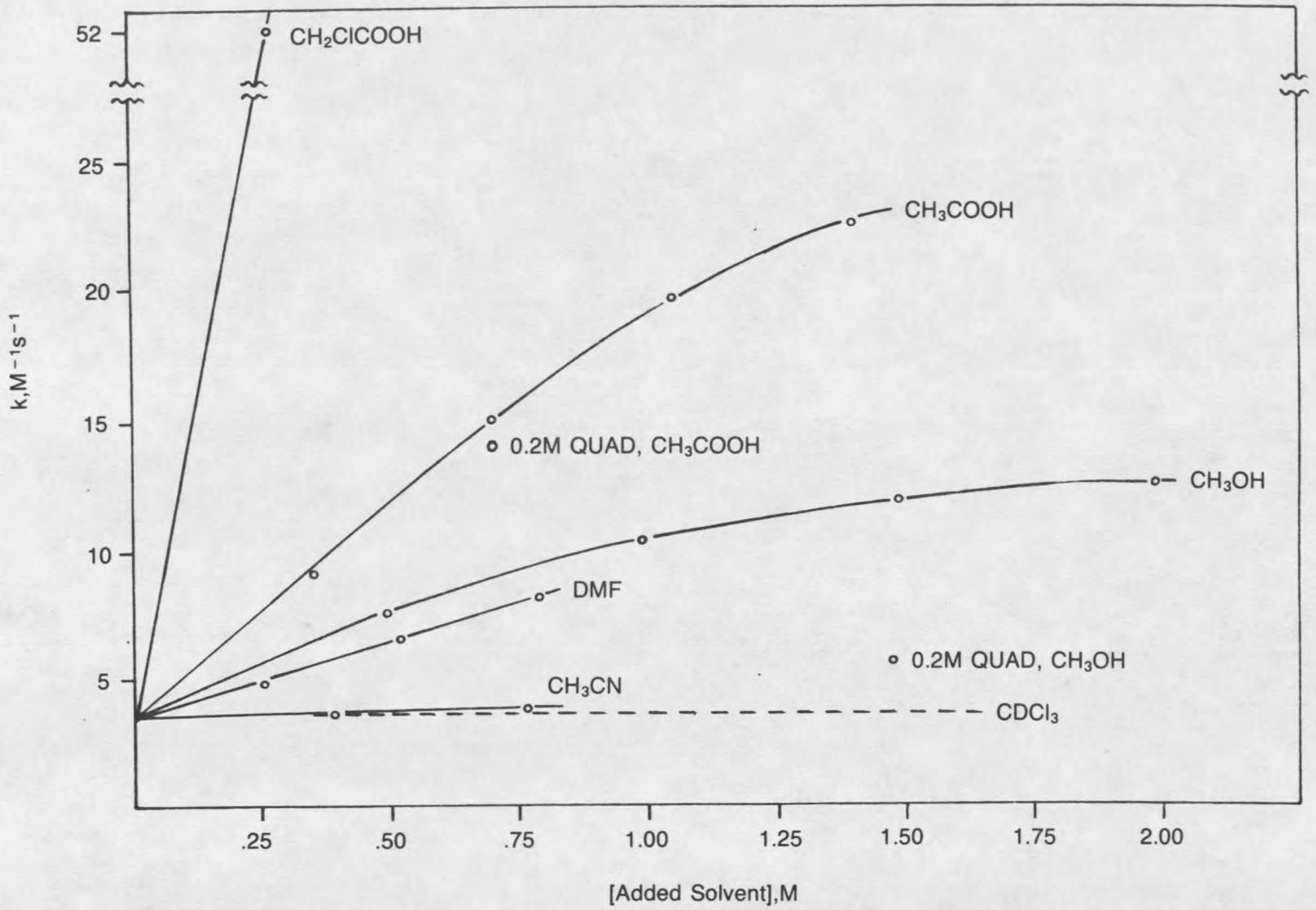


Figure 9. Rates for the reaction in Equation 9 in CCl_4 with small amounts of a more polar solvent added. $[Q]_0 = 0.1$ M, $[5]_0 = 1.0 \times 10^{-3}$ M at 37°C. $[5]_0 = 0.5 \times 10^{-3}$ M for CH_3OH and CH_3COOH.

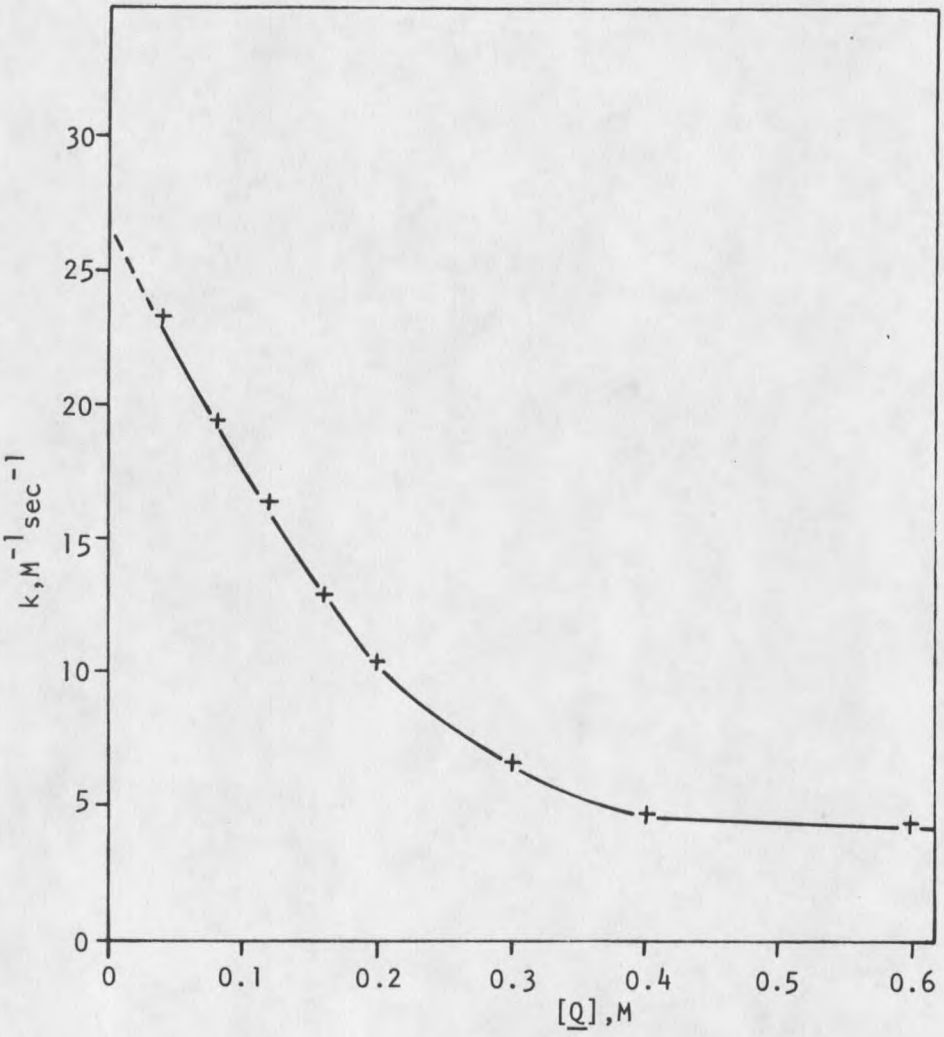


Figure 10. A plot of rate constant versus $[\mathbf{Q}]_0$ in $CDCl_3$ at 37°C for the reaction in Equation 9. $[\mathbf{5}]_0 = 1.0 \times 10^{-3}$ M.

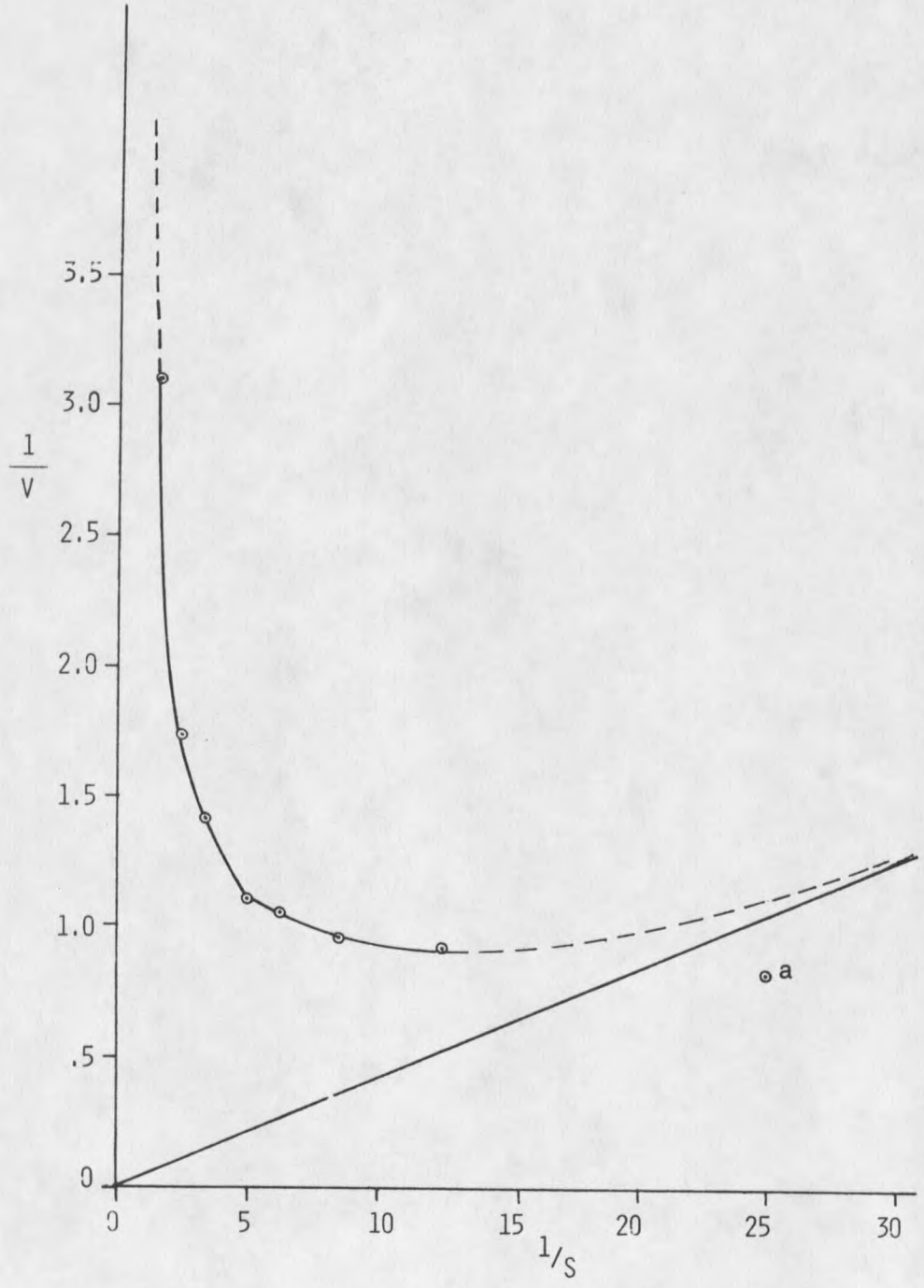


Figure 11. A Lineweaver-Burke plot for the isomerization of **Q** (Eq. 13) in $CDCl_3$ at 37°C. [**5**] = 1.0×10^{-3} M. [a]The rate was too fast to get a true initial rate for this point.

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.

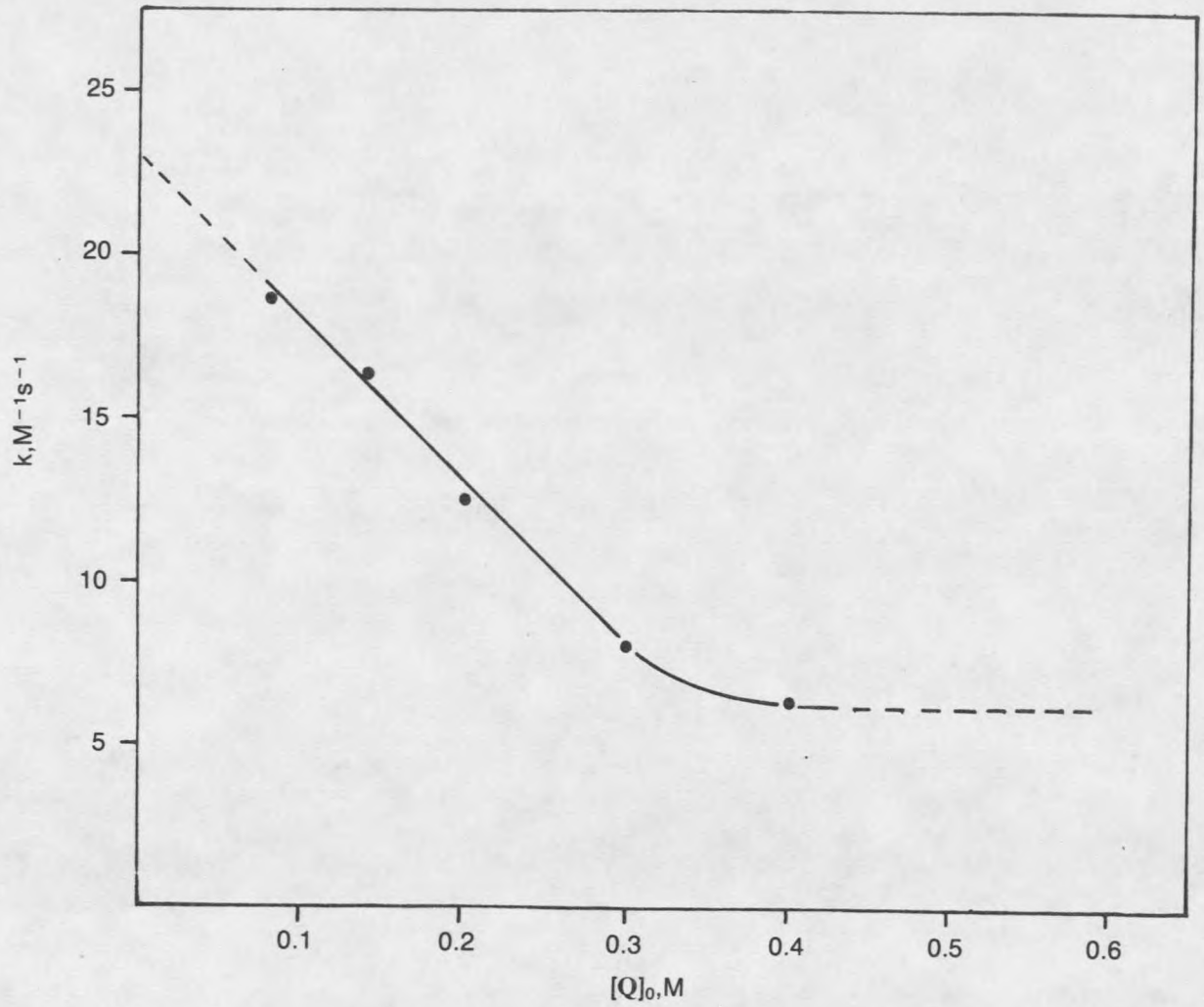


Figure 12. A plot of rate constant versus $[Q]_0$ at 30°C in CD_2Cl_2 for the reaction in Equation 13. $[5]_0 = 1.0 \times 10^{-3}$ M.

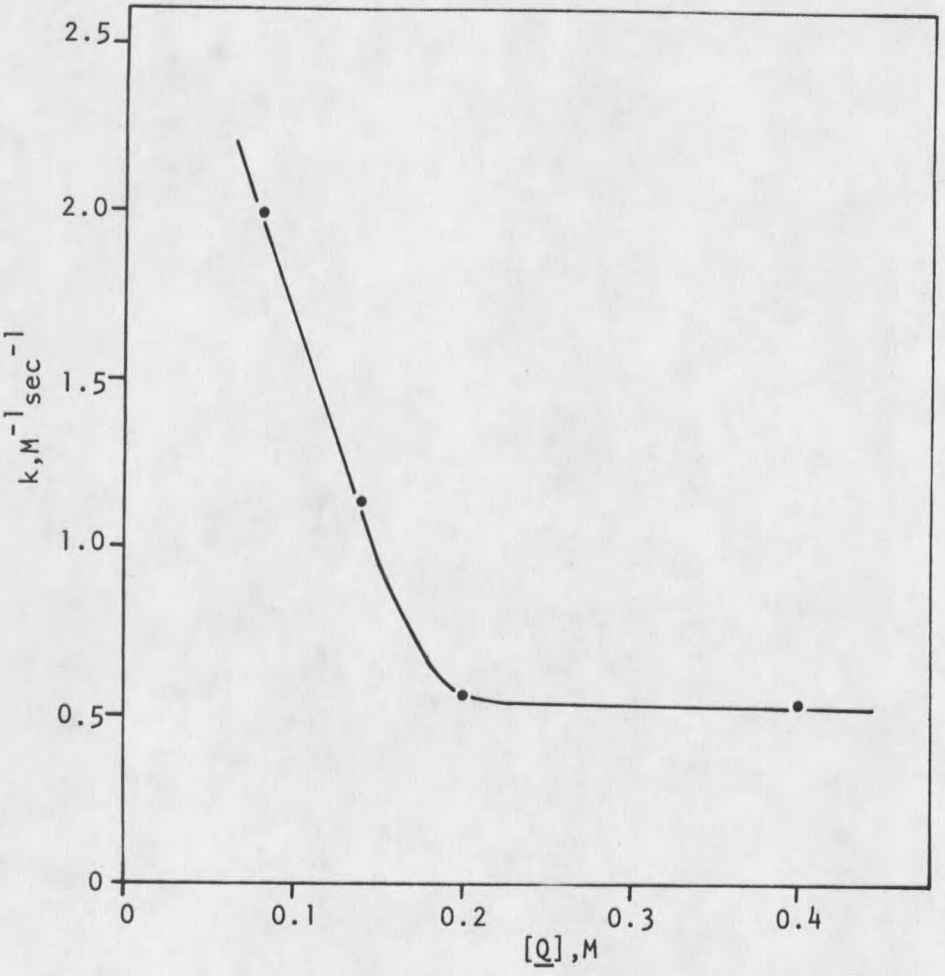
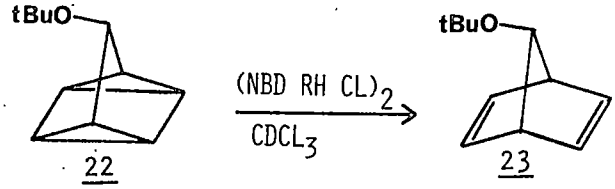


Figure 13. A plot of rate constant versus $[Q]_0$ at 0°C in $CDCl_3$ for the reaction in Equation 13. $[5]_0 = 1.0 \times 10^{-3}$ M.

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

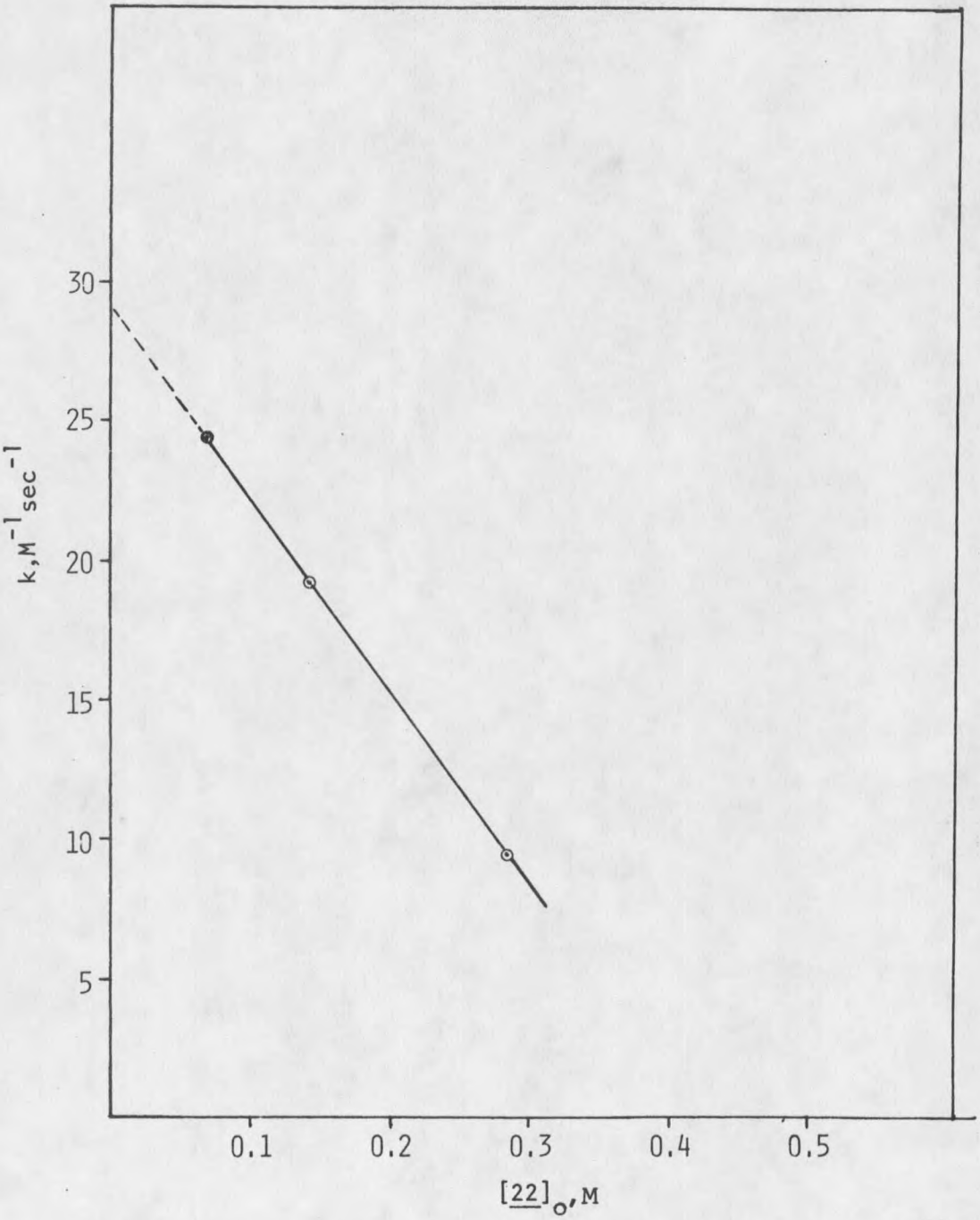


Figure 14. A plot of rate constant versus $[22]_0$ at 37°C in $CDCl_3$ for the reaction in Equation 14. $[5]_0 = 1.0 \times 10^{-3}$ M.

$[5]_0 = 1.0 \times 10^{-3}$ 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.

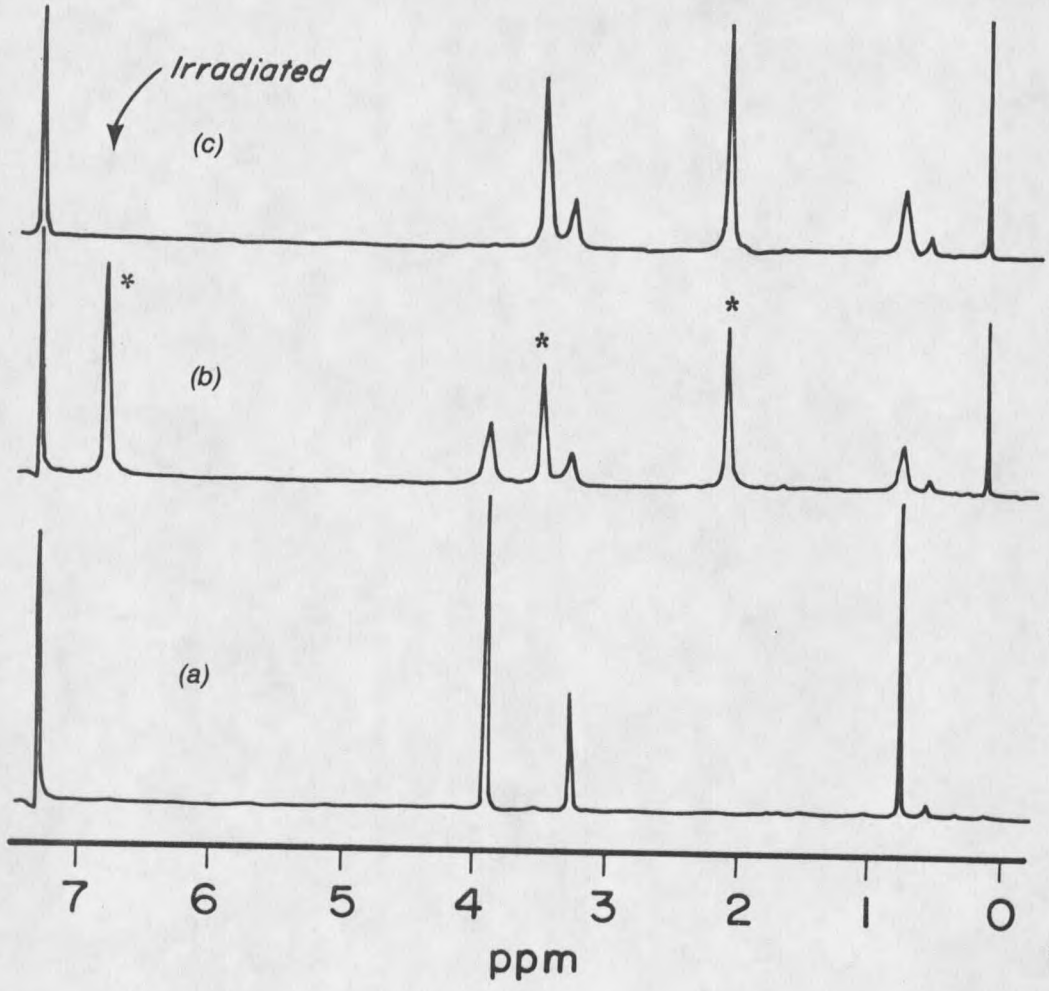


Figure 15. NMR spectra at 250 MHz of $[(\mathbf{NBD})RhCl]_2$ in benzene at 25°C: (a) rhodium complex alone; (b) rhodium complex and **NBD** (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed **NBD**; (*) resonances attributed to uncomplexed **NBD**.

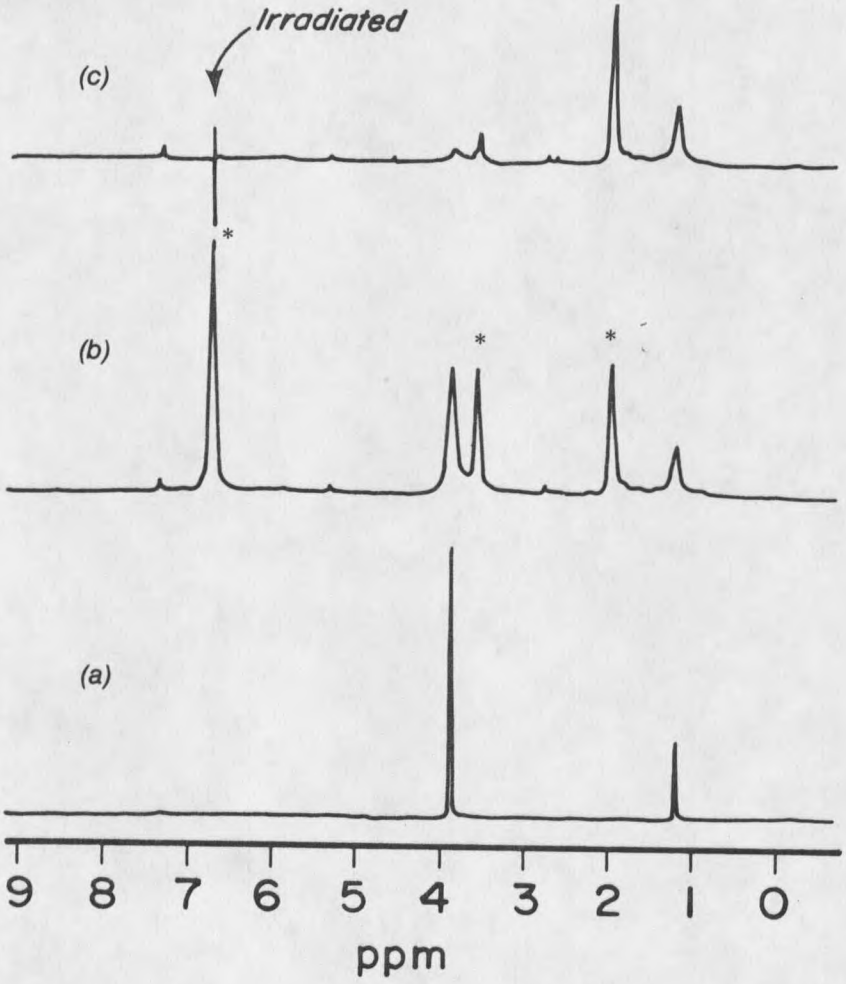


Figure 16. NMR spectra at 250 MHz of $[(\mathbf{NBD})RhCl]_2$ in CCl_4 at 25°C: (a) rhodium complex alone; (b) rhodium complex and **NBD** (1:4 molar ratio); (c) same as part b but decoupled at the olefinic resonance of uncomplexed **NBD**; (*) resonances attributed to uncomplexed **NBD**.

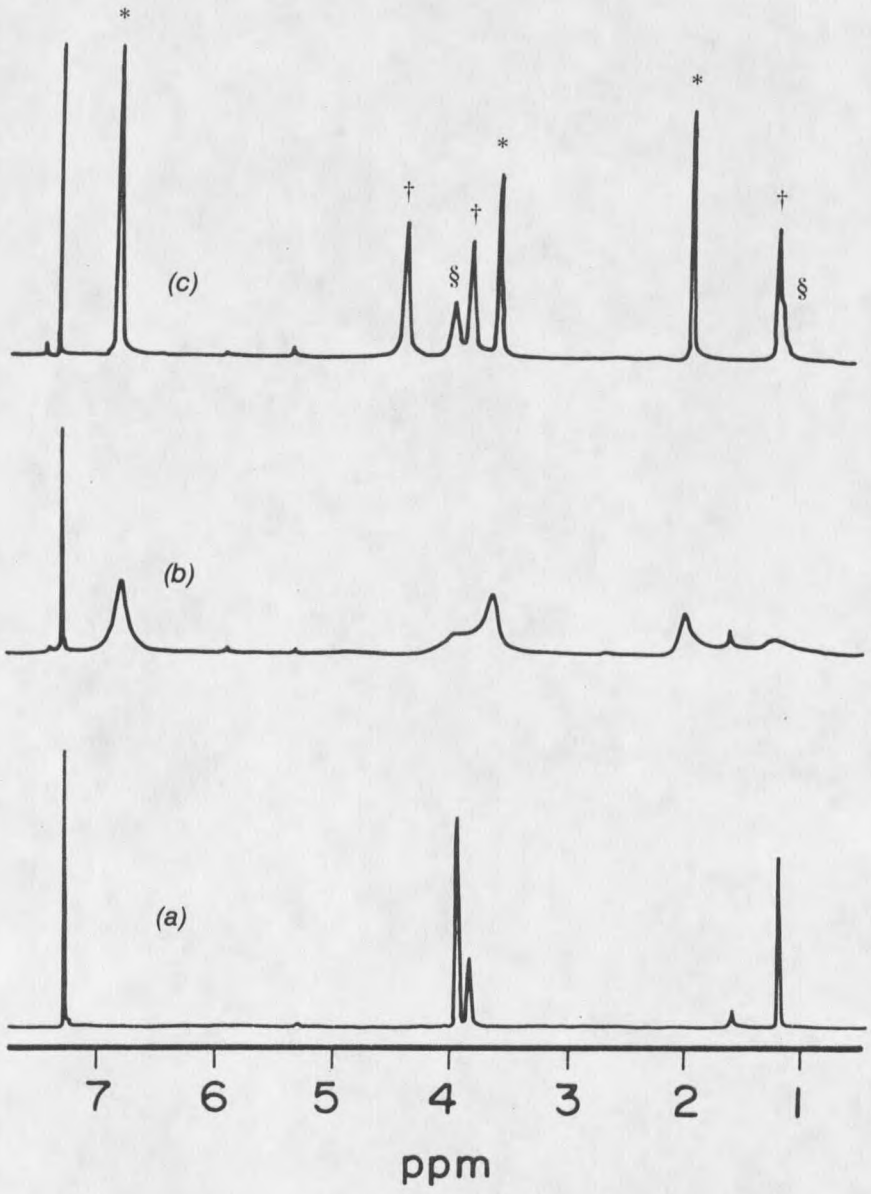
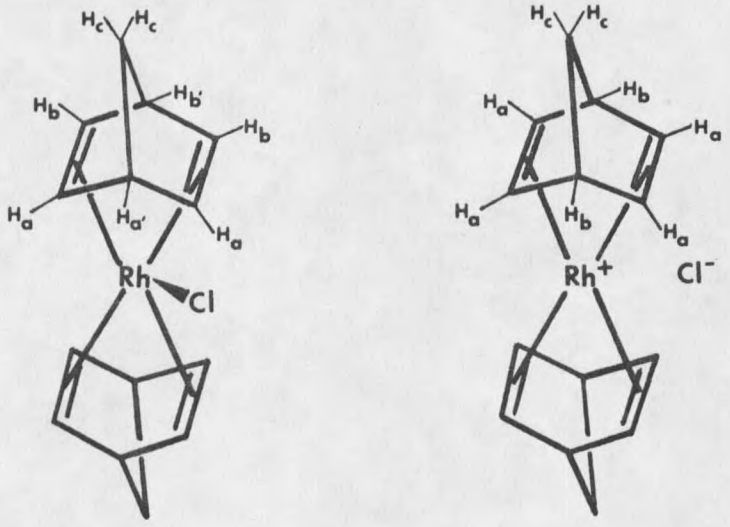


Figure 17. NMR spectra at 250 MHz of $[(\mathbf{NBD})RhCl]_2$ in $CDCl_3$ at 25°C: (a) rhodium complex alone; (b) rhodium complex and **NBD** (1:4 molar ratio); (c) same as part b but at -55°C; (*) resonances attributed to uncomplex **NBD**; (†) resonances of monomeric complex $(\mathbf{NBD})_2RhCl$;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

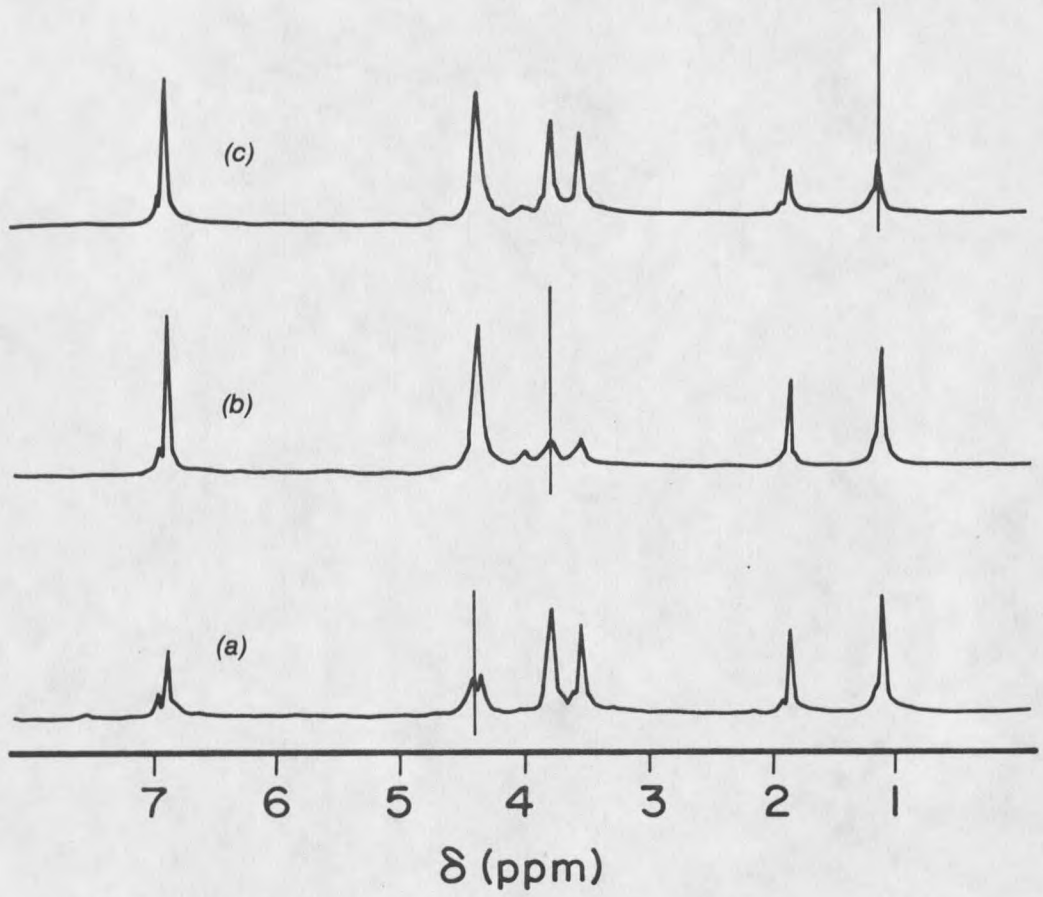


Figure 19. Saturation transfer NMR spectra at 300 MHz of the 4:1 mixture of **NBD** and **5** in $CDCl_3$ at -55°C: (a) irradiated at δ 4.38; (b) irradiated at δ 3.82; (c) irradiated at δ 1.17.

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**.

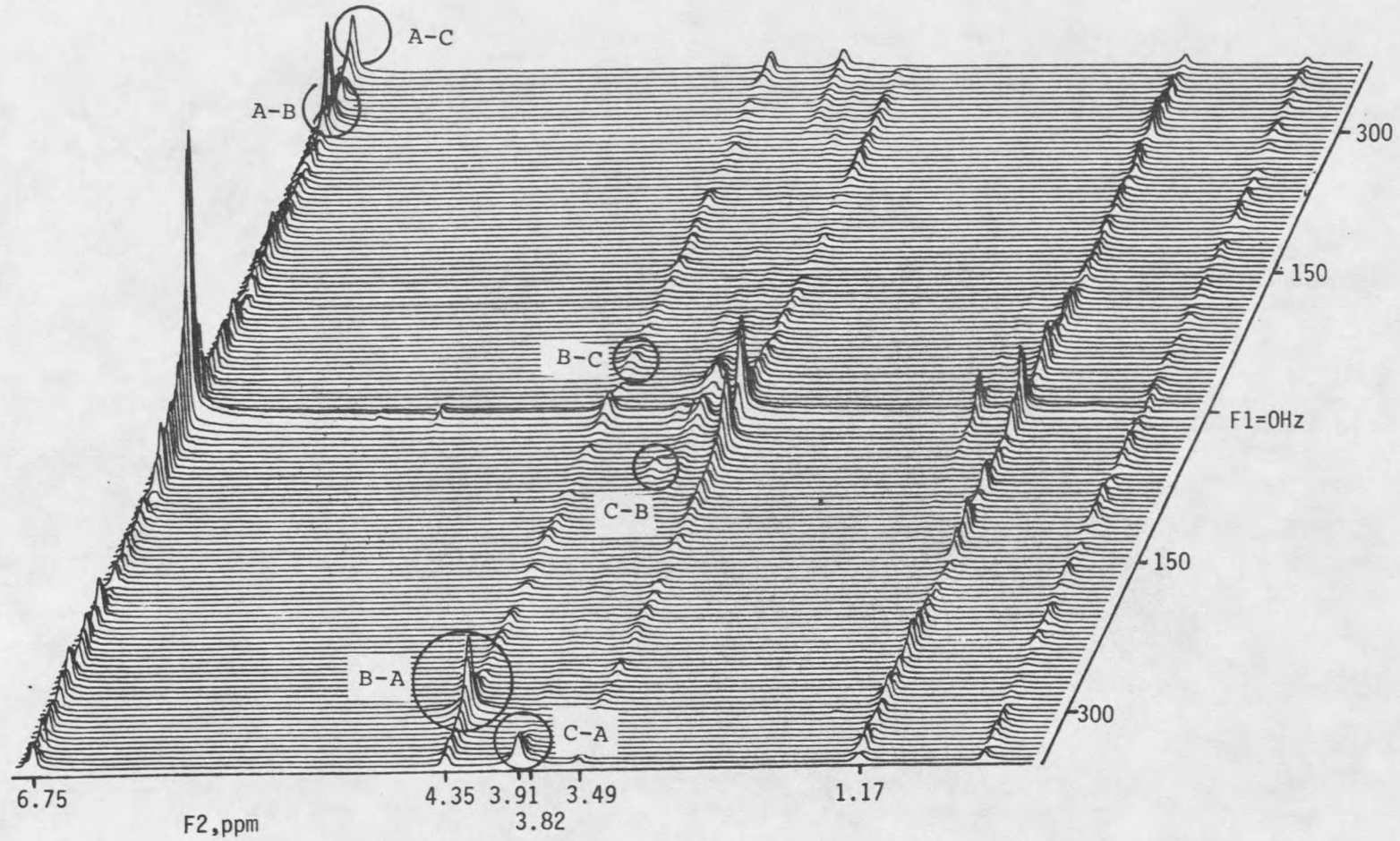
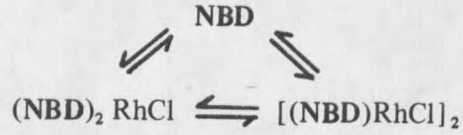


Figure 20. A stacked plot of the 2DNOE chemical exchange mapping experiment for the exchange equilibria in Equation 18.

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).

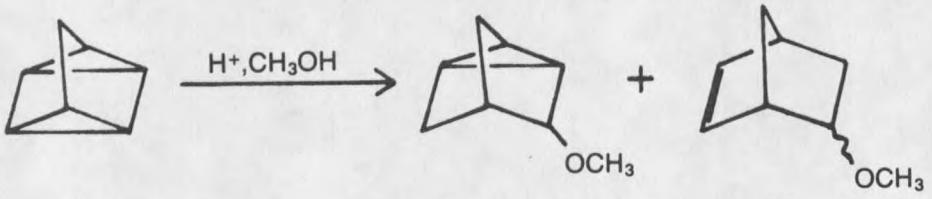


(18)

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.

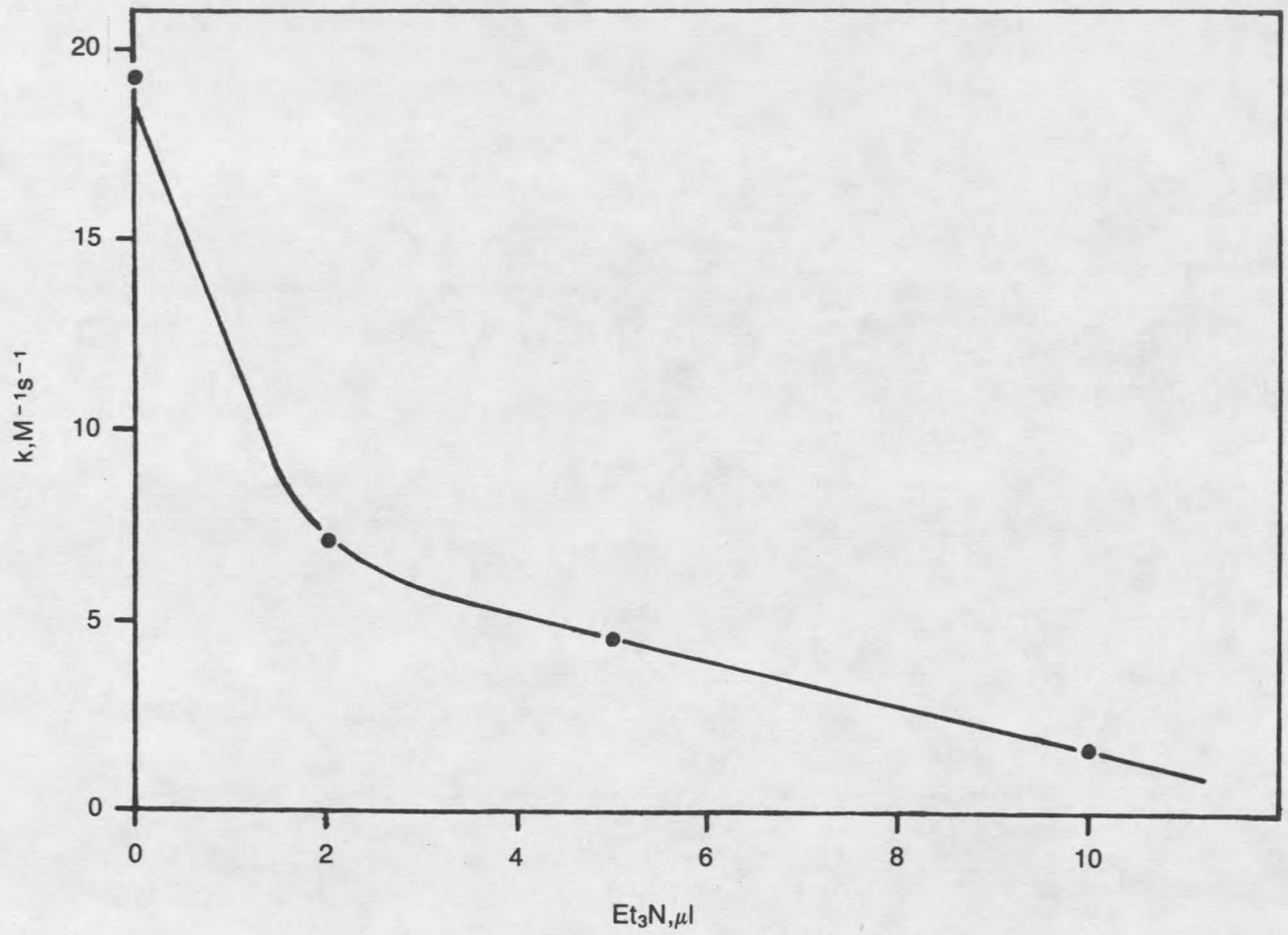


Figure 21. A plot of rate constant versus amount of Et_3N added to the reaction in Equation 13; 0.10 M Q, 0.001 M 5 in $CDCl_3$ at 37°C.

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.

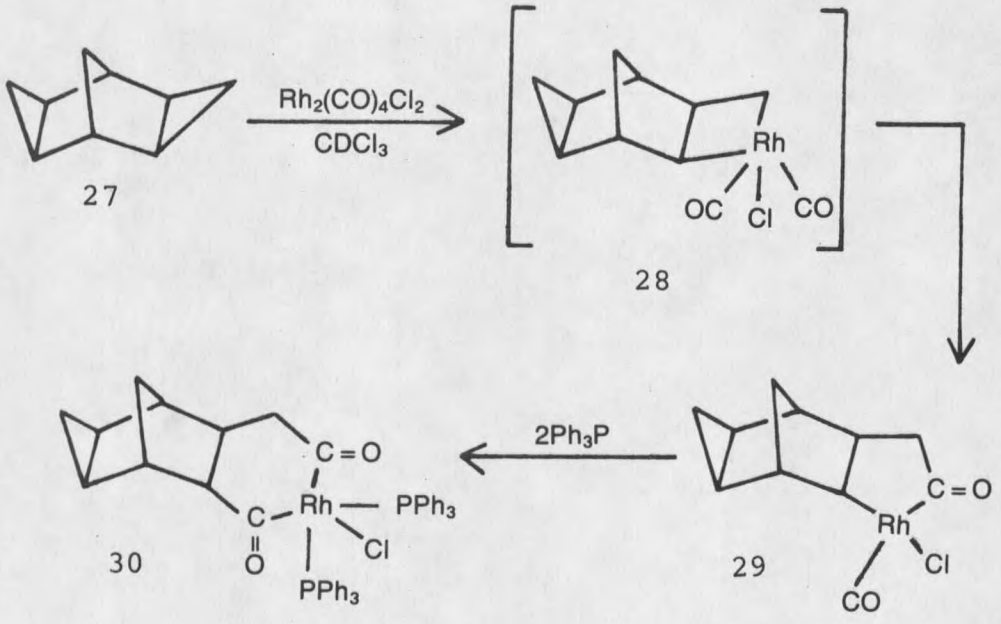


Figure 22. Reaction of **27** with $Rh_2(CO)_4Cl_2$.

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 $CDCl_3$

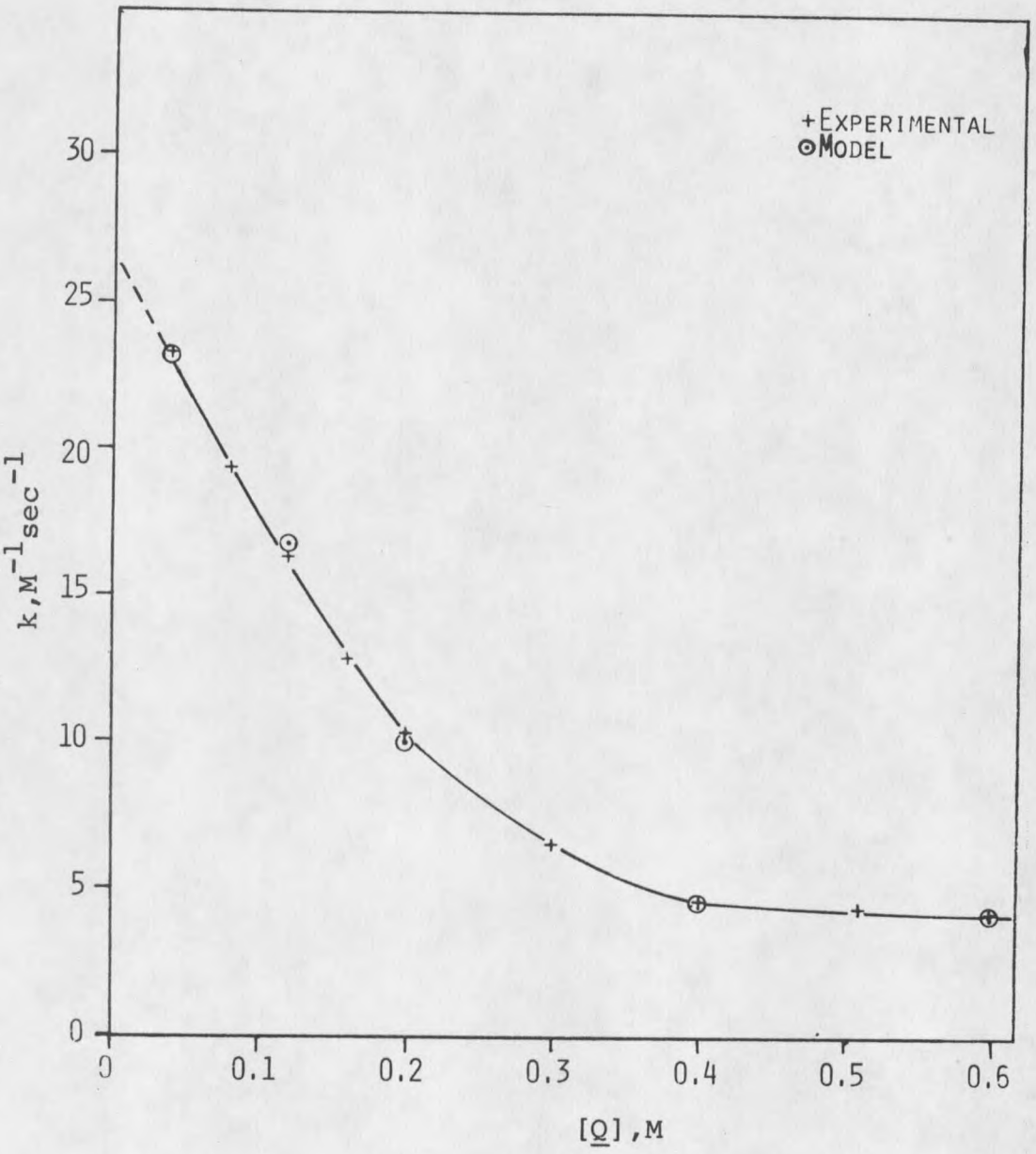


Figure 23. A comparison of experimental data (Fig. 10) versus results from the computer model for the reaction in Table 9.

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-

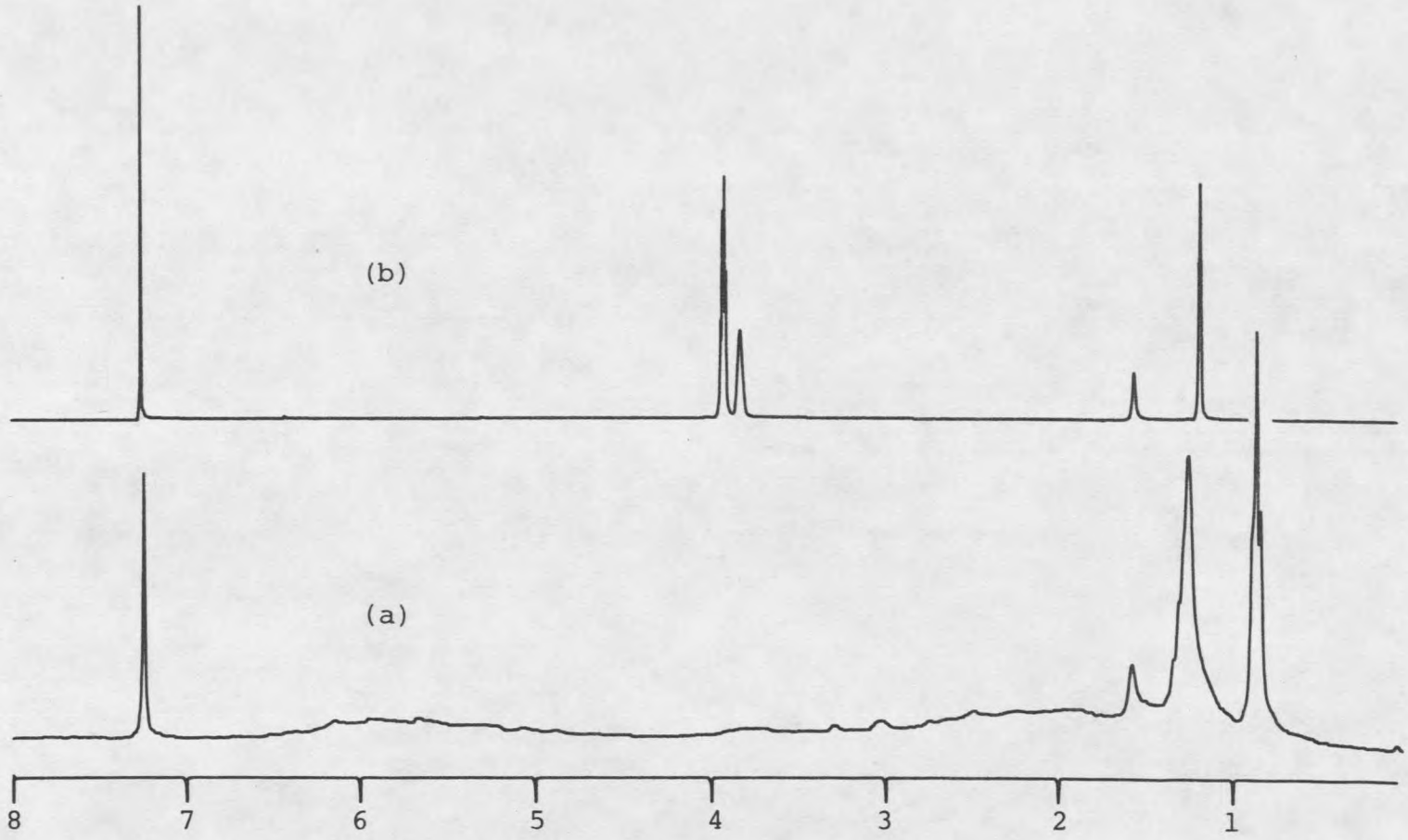


Figure 24. ^{1}H NMR spectra of Rh extracts from the **5** catalyzed isomerization of **Q**; (a) in $CDCl_3$ at high **Q**:Rh; (b) in CCl_4.

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,

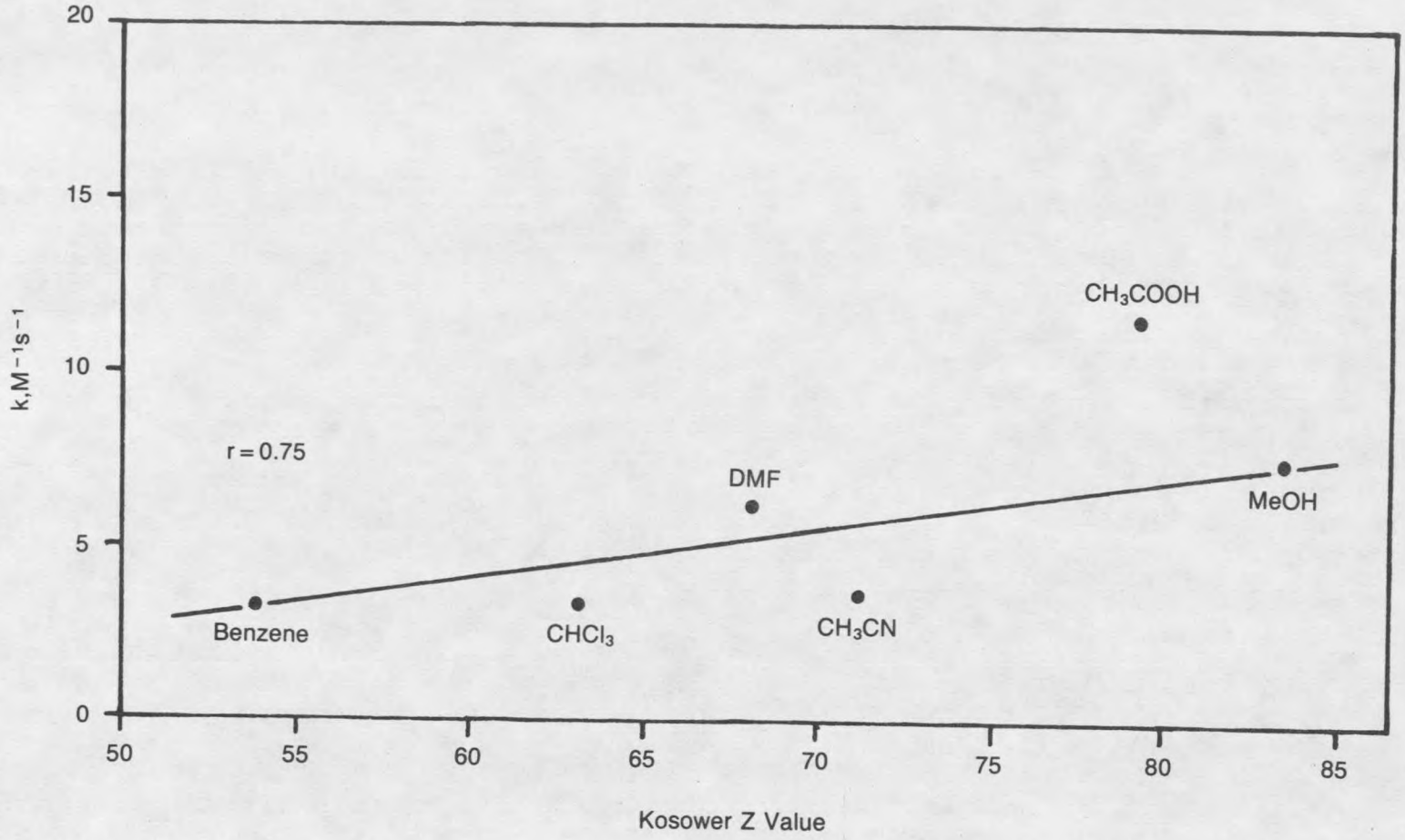
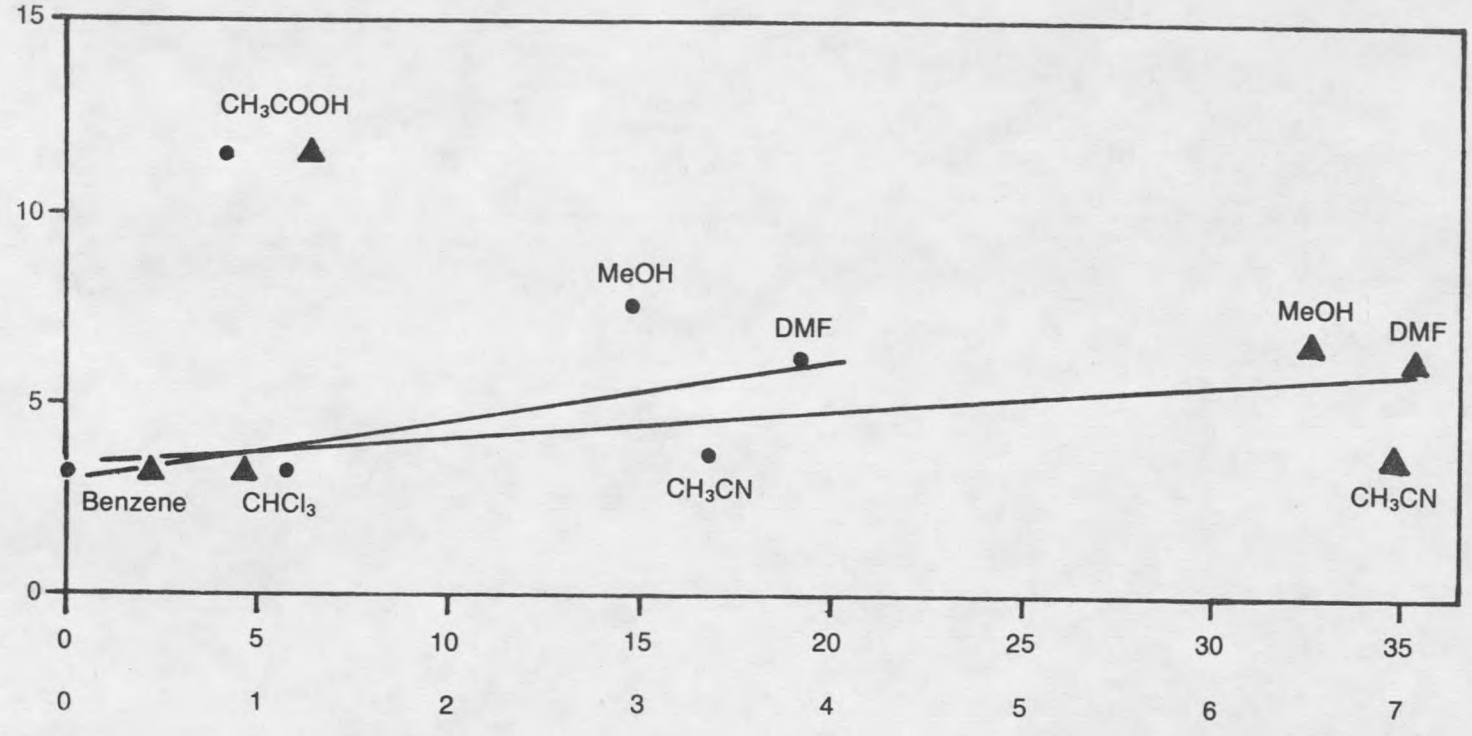


Figure 25. A plot of rate constant versus Kosower Z values for data points taken from the mixed solvent data (Fig. 9) at 0.5 M solvent added to CCl_4.



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-

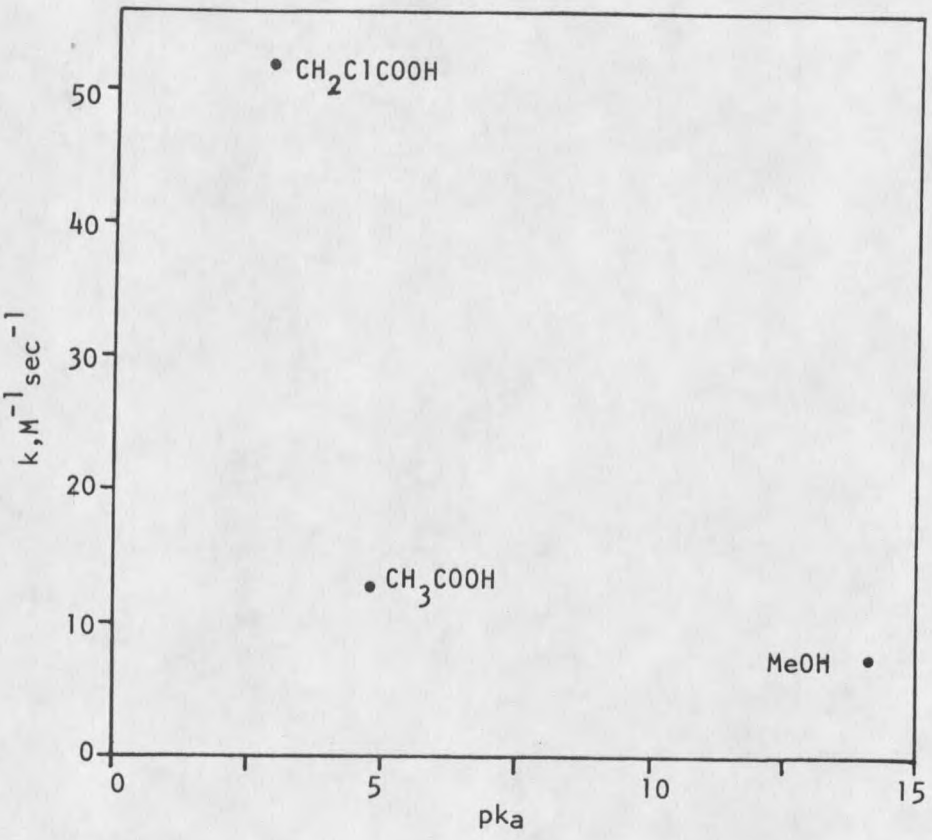


Figure 27. A plot of rate constant versus pk_a for MeOH, CH_3COOH and $CH_2ClCOOH$ taken from the mixed solvent results in Figure 9.

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-

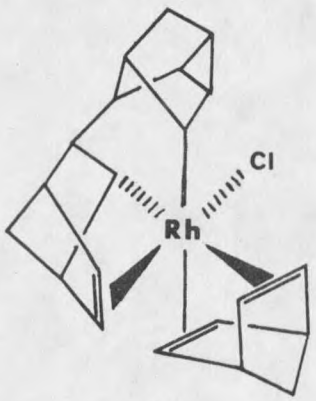
[a]Actually, any conclusion based on activated complex theory must be taken with a grain of salt because the theory itself may not be valid for a complex reaction.

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.

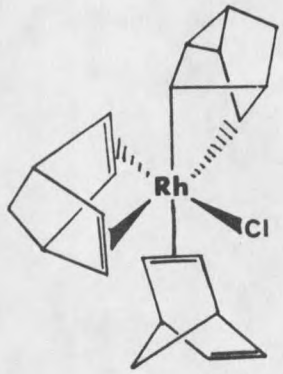
A comparison of results from the kinetic model to the experimentally observed results is given in Figure 23. Agreement is excellent. It should be noted here that agreement of a model does not constitute proof of a reaction scheme. However, a properly constructed model does demonstrate that the features 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-

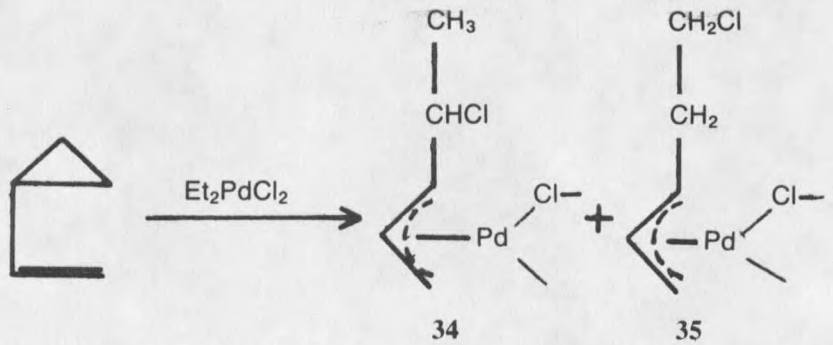
bly not a major pathway for metal catalyzed valence isomerizations of cyclopropanes in rigid systems.

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



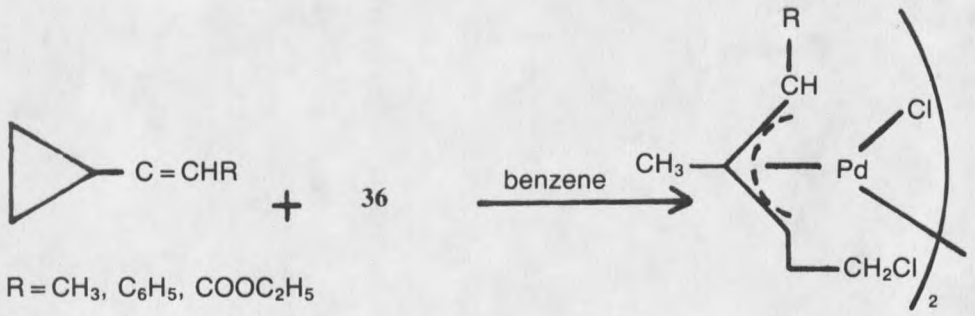
(20)

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.

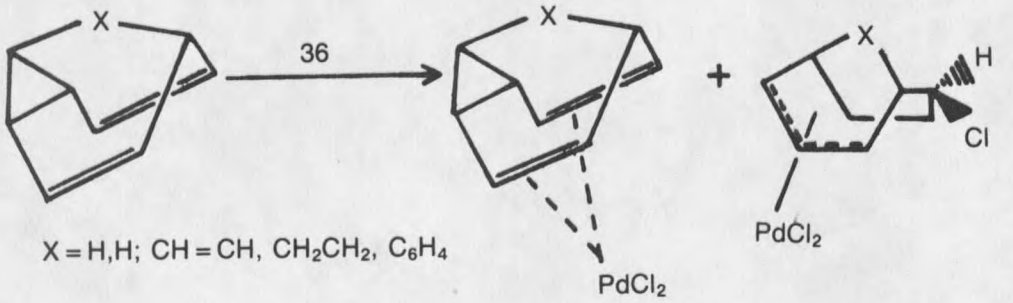
Complex **34** is unusual in that Cl is substituted on the cyclopropyl carbon that is not involved in the ring opening. This type of product is extremely rare for chloropalladations of cyclopropanes.

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



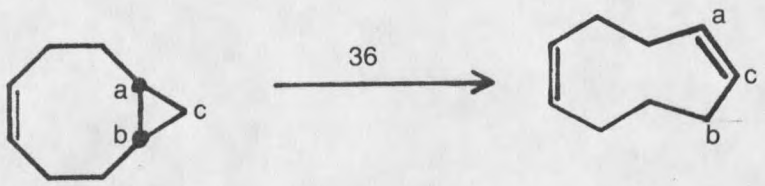
(21)

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)

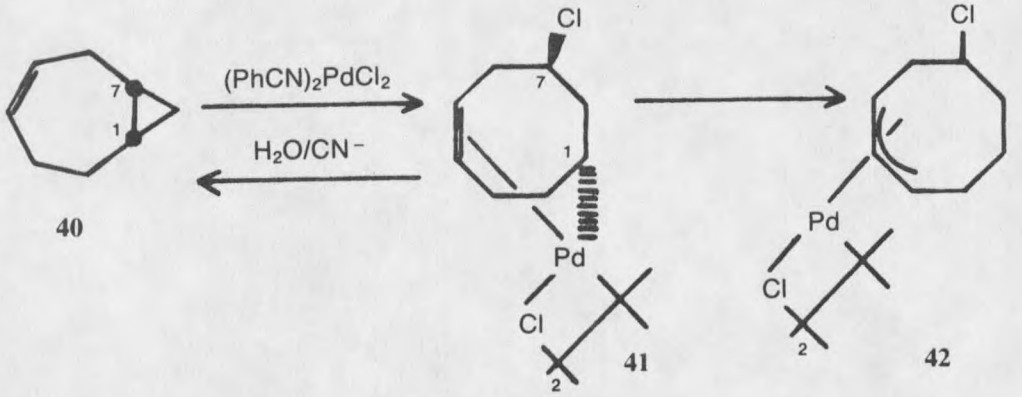
Rettig has been the most active researcher in the area of chloropalladations of cyclopropanes having published five full papers between 1972 and 1983. He has concentrated on bicyclic systems with cyclopropanes that are remote from C-C double bonds and are not subject to significant additional ring strain. 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)

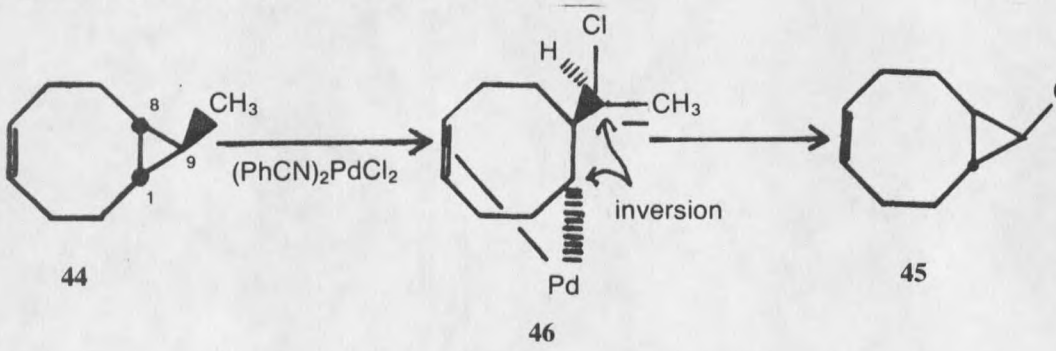
In 1975, Rettig[48] reported the reaction of bicyclo[5.1.0]oct-3-ene, **40**, with **36** (Eq. 24). The chloropalladation adduct, **41**, was formed in seconds at room temperature. Complex **41** was shown to be the result of trans addition of Pd-Cl across the cis disubstituted cyclopropyl bond with 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