



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

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Abstract:

The [(NBD)RhCl]₂ catalyzed valence isomerization of quadricyclane (Q) and the reactions of (PhCN)₂PdCl₂ 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)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 "cheletropic" mechanism is consistent with all results.

(PhCH)₂ PdCl₂ 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.

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Bozeman, Montana

February 1984

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APPROVAL

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Richard Bruce Taylor

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ABSTRACT

The $[(\text{NBD})\text{RhCl}]_2$ catalyzed valence isomerization of quadricyclane (**Q**) and the reactions of $(\text{PhCN})_2\text{PdCl}_2$ 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 $[(\text{NBD})\text{RhCl}]_2$ 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 "cheletropic" mechanism is consistent with all results.

$(\text{PhCH})_2\text{PdCl}_2$ 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 organo-transition metal complex in 1827 by Zeiss¹, $K^+ [(C_2H_4)PtCl_3]^-$. 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 industry². 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 published³.

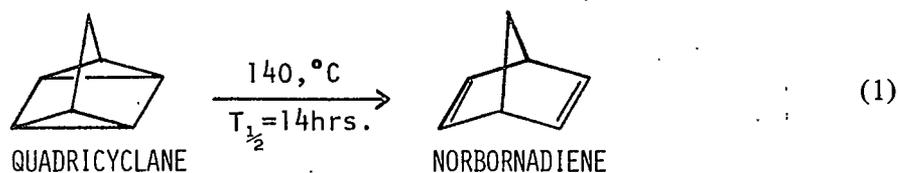
This thesis reports investigations of interactions between Rh(I) and Pd(II) organometallic complexes with cyclopropanes in rigid systems.

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 reactions⁴. 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 energy⁵ of 78.7 kcal mol⁻¹ and a half life for thermal isomerization⁶ to norbornadiene (**NBD**) of > 14 hours at 140°C (Eq. 1). The reaction is exothermic and yields



26 kcal mol⁻¹ of energy in the form of heat⁷. The stability of the molecule towards the ground state [$\sigma 2s + \sigma 2s$] 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 minutes⁸.

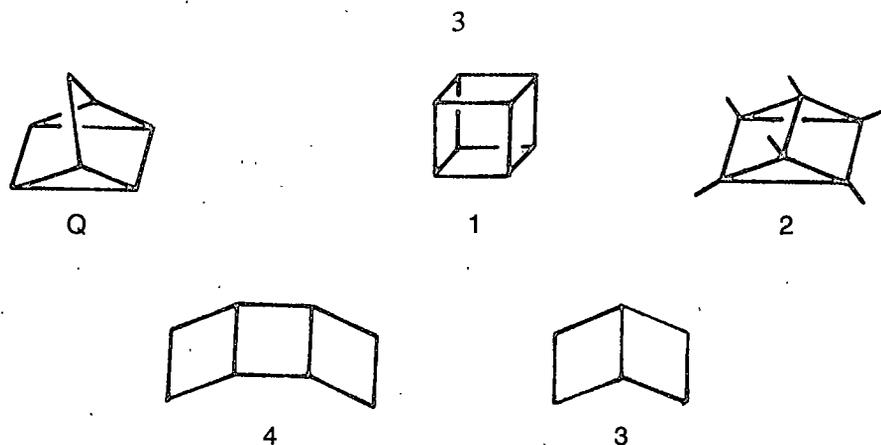


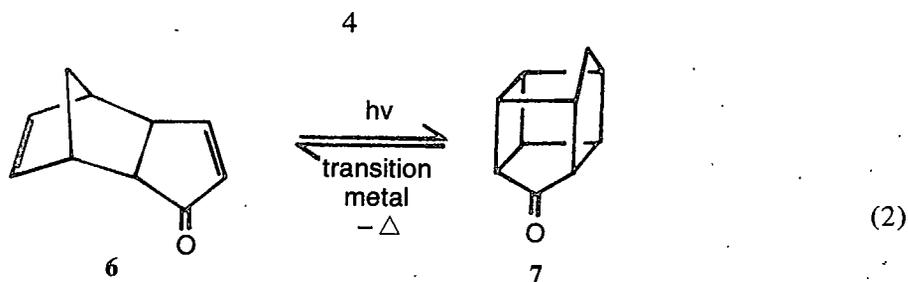
Figure 1. Several examples of thermally stable, strained carbocycles.

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

$[(\text{NBD})\text{RhCl}]_2$	$[(\text{COD})\text{PdCl}]_2$
$(\text{Et}_2\text{RhCl})_2$	$[(\pi\text{-methylallyl})\text{PdCl}]_2$
$[(\text{NBD})\text{Rh}(\text{OAc})]_2$	$(\text{PhCN})_2\text{PdCl}_2$
$\text{Rh}_2(\text{CO})_4\text{Cl}_2$	CoTPP
$(\text{Ph}_3\text{P})_3\text{RhCl}$	NiTPP
$[(\text{NBD})\text{PtCl}]_2$	$\text{Fe}(\text{CO})_5$
$(\text{Et}_2\text{PtCl})_2$	$\text{Fe}^{+2}(\text{phthalocyanine})$
$\text{AgClO}_4, \text{AgNO}_3$	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 systems⁹. 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.



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 “cheletropic” mechanism and the Lewis acid mechanism (Fig. 2).

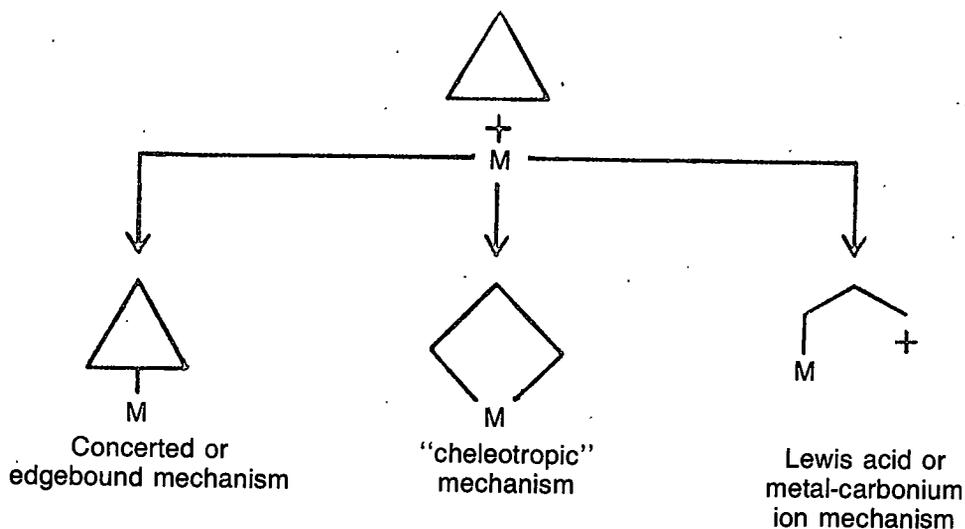


Figure 2. The three basic mechanisms proposed for metal catalyzed rearrangements of cyclopropanes.

The removal of orbital symmetry restrictions by coordination to a metal was proposed by Mango¹⁰ in 1967. This mechanism involved an exchange of electron pairs between the metal center and the transforming ligands. In 1970, Manassen¹¹ summarized

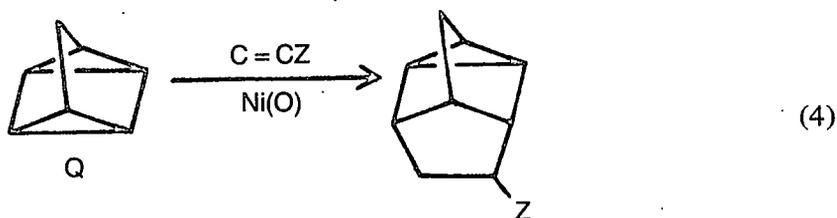
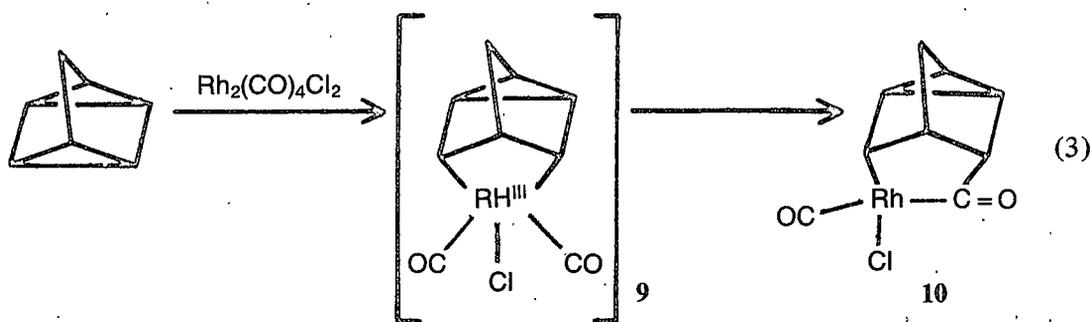
the selection rules that govern the energy of activation and Mango's explanation for the catalytic effect of a transition metal. Manassen investigated a variety of bivalent metal complexes of tetraphenylporphyrin or phthalocyanine for catalytic activity towards the isomerization of **Q**. He found that 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, Mango¹² 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 Manassen¹¹.

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

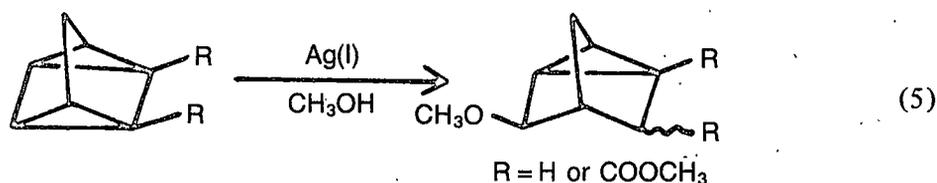
The "cheletropic" mechanism involves insertion of the metal into a C-C bond followed by cheletropic extrusion of the metal. Support for this mechanism is largely derived from the isolation of stable carbonyl insertion products thought to arise from the metallacycle intermediates. Halpern¹³ reported the isolation of such a carbonyl insertion product from the reaction of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (**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 cyclopropane¹⁴, cubane¹⁵ **3**, and **4**¹⁶ (Fig. 3). Similar carbonyl insertion products from the reaction of $\text{Fe}(\text{CO})_5$ with

quadricyclane and quadricyclanone have been reported by Aumann¹⁷. In addition, oxidative-addition intermediates were proposed by Noyori¹⁸ 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).



While these results give strong support for the "cheletropic" 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 metallacarbenium 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 bishomocubanes²⁰ (Eqs. 6 and 7).



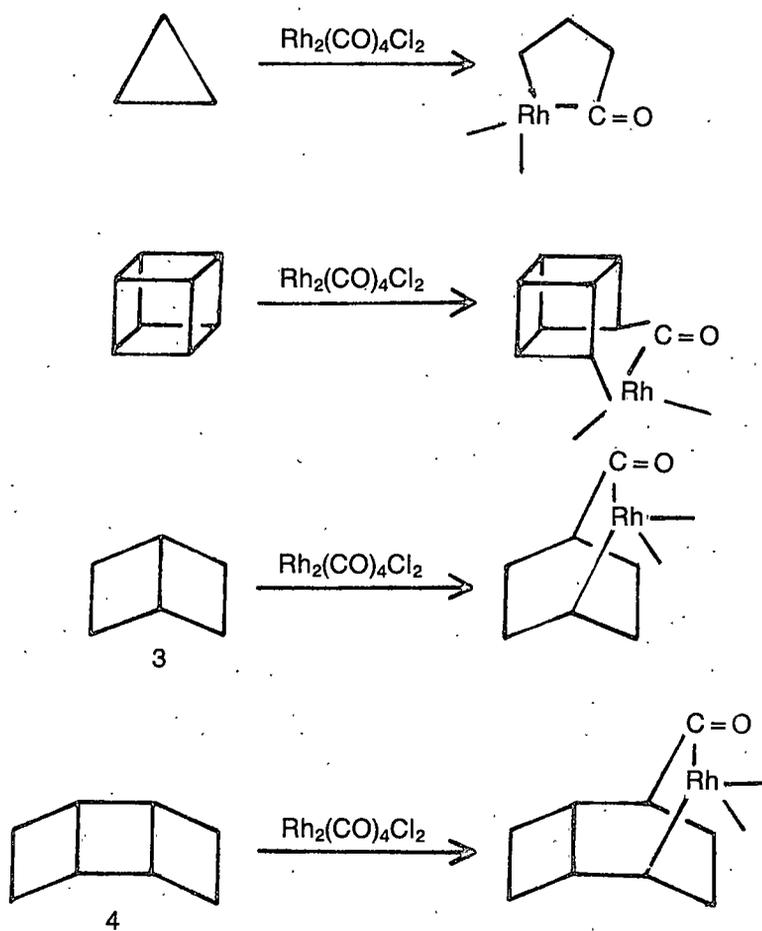
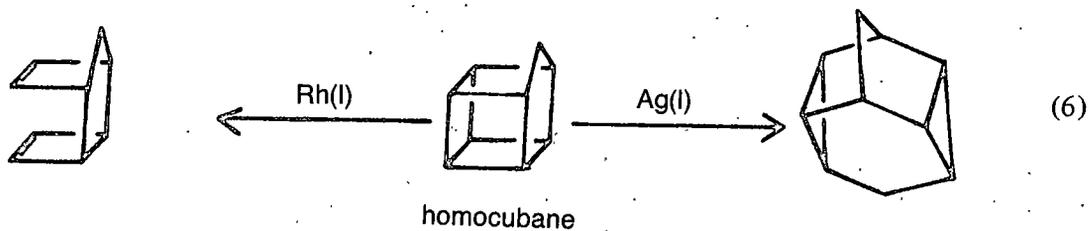
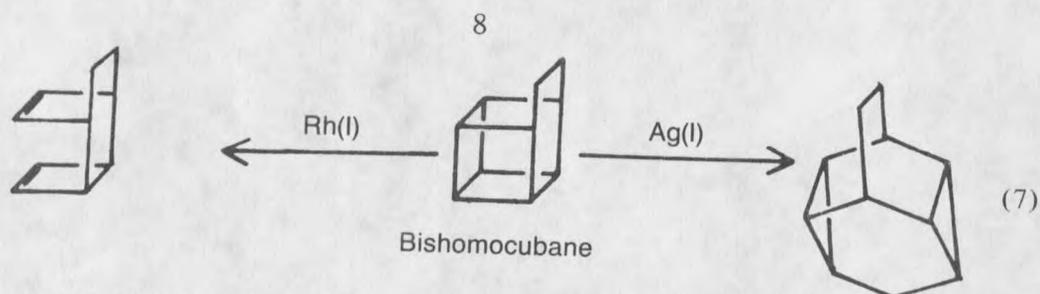
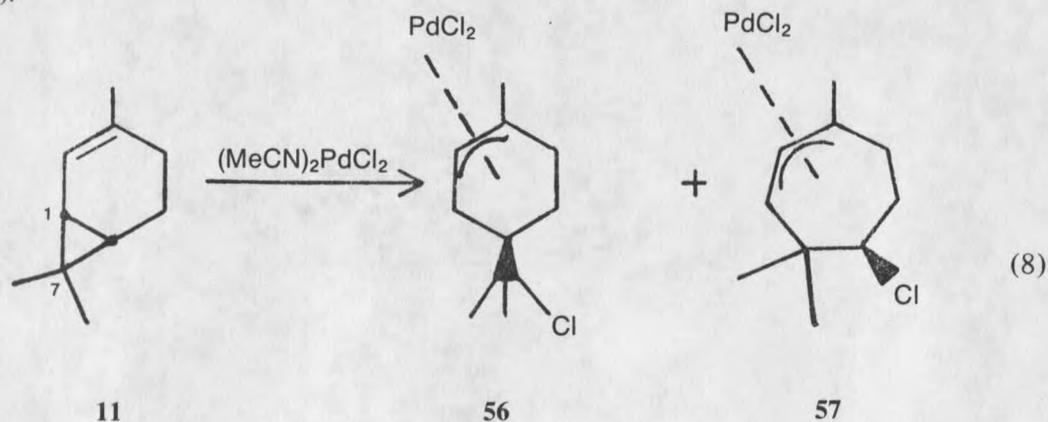


Figure 3. Known rhodium carbonyl insertion products from the reaction of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ with small strained carbocycles.



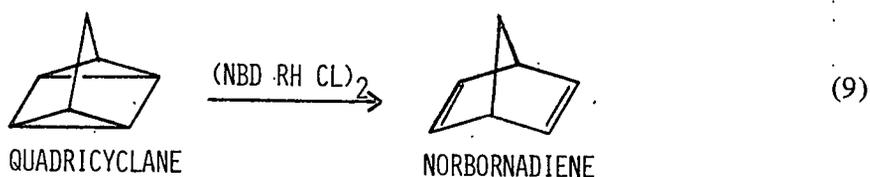
The mode of interaction of the metal with a strained carbocycle is related to the metal's ability to donate electrons, its electron promotion energy, and the propensity of the metal to accept electrons, its electron affinity. A high electron promotion energy indicates that a metal will not donate electrons 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 eV²¹, and a moderate electron affinity, 7.59 eV²¹, 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 eV²¹, respectively, will likely favor the oxidative-addition route. A metal like Pd(II) with a reasonably low electron promotion energy of 3.05 eV²¹ and a high electron affinity of 18.56 eV²¹ might be expected to interact by either the ionic or oxidative-addition route depending on ligands and on reaction conditions. Indeed, Bäckvall²² recently proposed that both routes were operating in the reaction of (MeCN)₂PdCl₂ with (+)-car-2-ene (11) to account for the two products observed (Eq. 8).^a



^aFor 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 Volger⁸ first reported on the metal catalyzed isomerization of quadricyclane in 1967, quadricyclanes have been the subject of a number of investigations. In 1970, Halpern¹³ reported on the [(NBD)RhCl]₂ (5) catalyzed isomerization of Q (Eq. 9). He reported that Q was quantitatively converted to NBD in CDCl₃ and CCl₄. The kinetics obeyed the rate law $-d[Q]/dt = k[5][Q]$ with $k = 2.2$ and $1.8 \text{ M}^{-1} \text{ s}^{-1}$ in CDCl₃ and CCl₄, 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 implicated¹⁵. This was a very limited kinetic study and no experimental details were given.



In 1973, Hogeveen²⁵ 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 $-\text{COOCH}_3$ 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 Halpern¹³ for **Q** in reference to their reported rate constants.

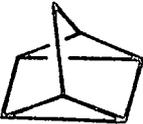
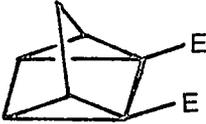
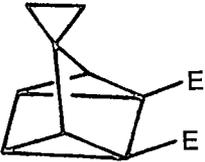
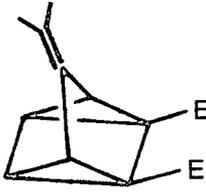
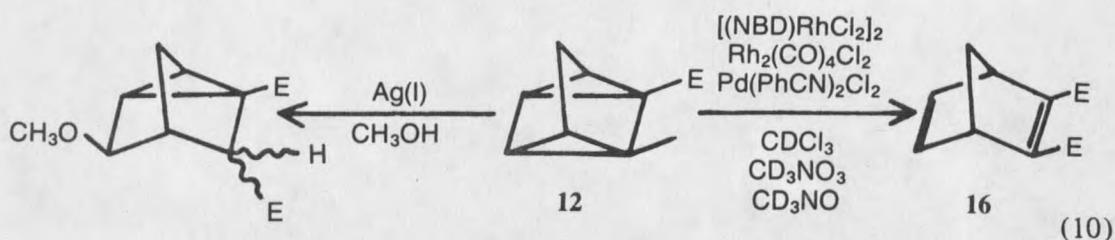
				
	Q	12	13	14
$10^2 k, \text{M}^{-1} \text{s}^{-1}$	5.5	0.6	0.4	0.6
Temp. °C	-26	45	38	60

Figure 4. Rate constants reported by Hogeveen²⁵ 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) catalysts²⁶. Each of these catalysts gave only the norbornadiene **16** in aprotic solvents but in methanol, AgClO_4 gave the isomeric mixture **15** (Eq. 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 $[(\text{NBD})\text{RhCl}_2]_2$ exhibited pre-equilibrium kinetics while $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ 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

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

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 bishomocubanes²⁰ 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.

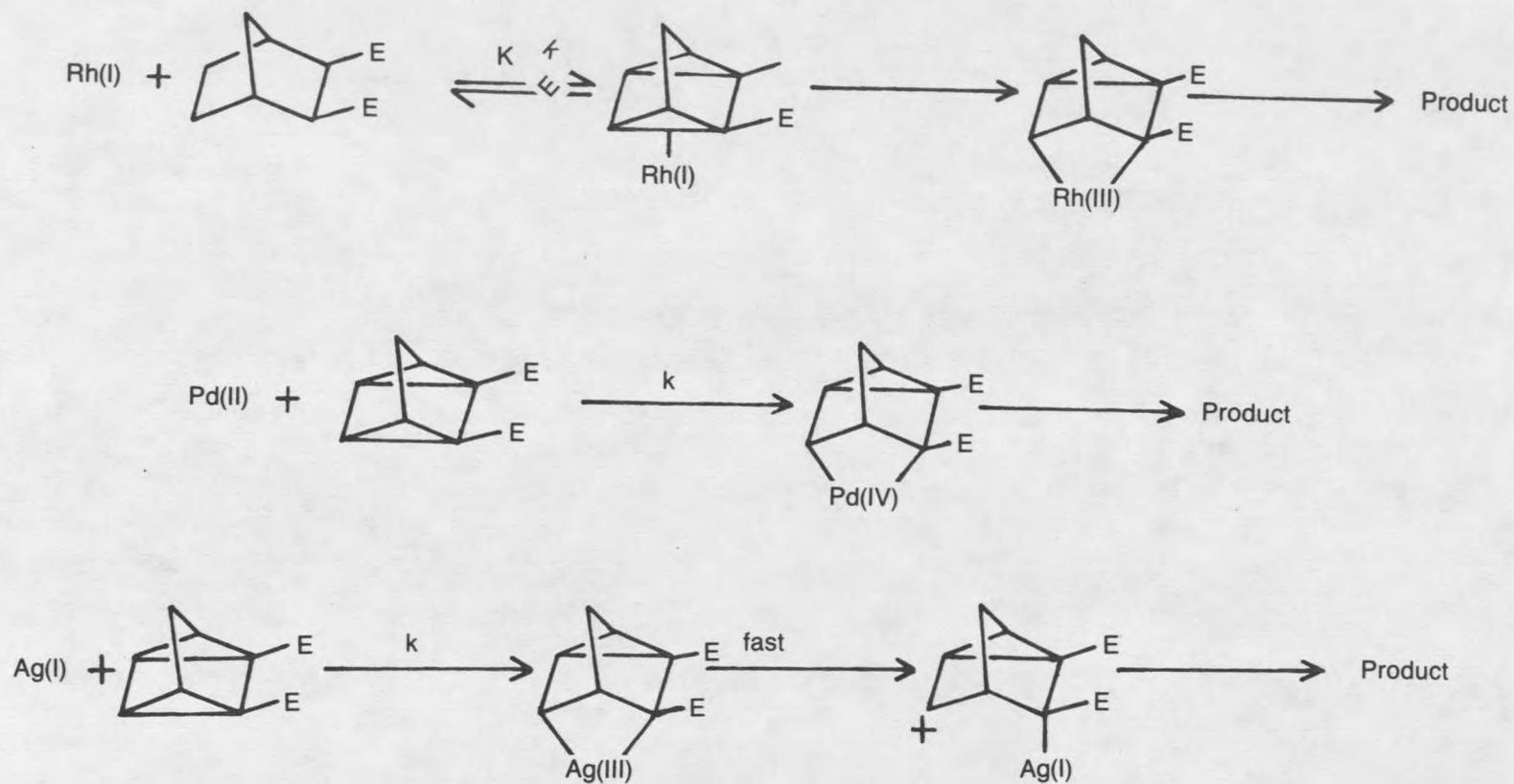


Figure 5. Mechanisms proposed by Hogeveen²⁶ for the interactions of Rh(I), Pd(II) and Ag(I) with quadricyclane, 2,5-dimethylester.

Noyori¹⁸ 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 Rinker²⁷ 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-chloronaphthalene. However, no explanation was offered for the observed second order dependence of **CoTPP** or for the significant changes in activation parameters, ΔH^\ddagger and ΔS^\ddagger , observed on changing the solvent from CCl_4 to CHCl_3 to 1-chloronaphthalene. The increase in ΔH^\ddagger by almost 4 times and the concomitant decrease in ΔS^\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-chloronaphthalene 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 Rinker²⁷.

Solvent	k_0	$\Delta H^\ddagger \times 10^{-3}$ cal mol ⁻¹	ΔS^\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-Chloronaphthalene	$3.48 \pm 0.15 \times 10^8$ M ⁻² s ⁻¹	1.61 ± 0.15	-19.0 ± 1.0

