Transition Metal Catalyzed Rearrangements of Small Ring Organic Molecules

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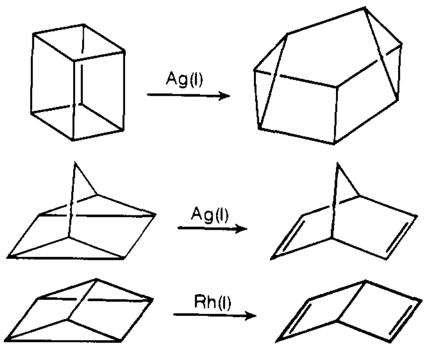
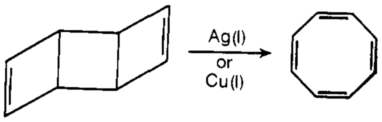
Contents

I. Introduction

Starting in 1967, a number of research groups began to report a variety of unexpected and unusual molecular rearrangements. In all of these reports, a highly strained organic molecule rearranged upon exposure to a transition metal complex.





In the first 3 years, over 70 reports appeared in the chemical literature. The field has continued this rapid growth to become one of the more exciting and controversial new areas of chemistry.

Partial reviews of this area have previously appeared.[2] However, no comprehensive review of the field has appeared. The purpose of this discussion is to critically survey the existing literature through January 1974 and selected later articles when completeness is served. It is limited to rearrangements catalyzed by transition metals in organic molecules possessing three- and four-membered rings. Though they are mentioned when appropriate, no attempt has been made to cover those reactions which lead stoichiometrically to stable organo-transition metal complexes.

II. Basic Principles of Organometallic Chemistry and Homogeneous Catalysis

A. Concepts of Metal–Olefin Bonding

To explain the mechanistic implications in this new field, it is necessary to review the basic concepts of organometallic chemistry in general, and homogeneous catalysis in particular.

The Dewar–Chatt–Duncanson[3,4] model of olefin binding in transition metal complexes is represented pictorially in Figure 1. A σ bond is formed through donation of the π orbital electrons of the olefin into an empty metal orbital of appropriate symmetry. The figure uses a p orbital for illustration. Electron density is thus transferred from the olefin (σ basicity) to the metal. This can be viewed as a simple Lewis acid–base interaction. The π^* orbital of the olefin, in contrast, is the recipient of electron density from a filled metal orbital (π acidity), forming a metal–olefin π bond. That is, the acid–base roles are reversed. This synergistic (literally "working together") effect makes the resulting bond stronger than either of the two individual bonds.

It is apparent that in all olefin–metal interactions there are two effects which must be considered. The first is the metal's inherent ability to accept electrons into the p orbital, and the second is its ability to donate electrons from its d_{xy} orbital. The former may be approximated by the electron affinity of the metal or metal ion and the latter by its promotion energy. Table I presents selected data for these values. A high promotion energy indicates the metal will be a poor electron donor. A large electron affinity indicates the metal is a good electron acceptor. From a consideration of these two properties, the character of the bonding in an olefin complex may be anticipated.

Thus, for platinum(0) complexes, donation of electrons from the metal into the π^* orbital of the olefin should be of paramount importance. This follows from both its low promotion energy and a low electron affinity. In the case of mercury(II), a stronger Lewis

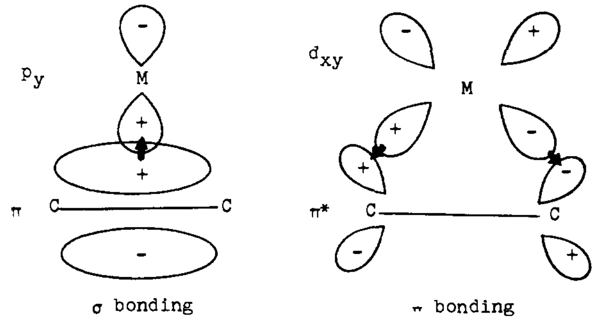


Figure 1. Dewar-Chatt-Duncanson model of olefin transition metal bonding.

TABLE I. Selected Data[a]

Atom or ion	Electronic confign	Promotion energy,[b] eV	Electron affinity, eV
Ni(0)	d^{10}	1.72	1.2
Pd(0)	d^{10}	4.23	1.3
Pt(0)	d^{10}	3.28	2.4
Rh(I)	d^8	1.6	7.31
Ir(I)	d^8	2.4	7.95
Pd(II)	d^8	3.05	18.56
Pt(II)	d^8	3.39	19.42
Cu(I)	d^{10}	8.25	7.72
Ag(I)	d^{10}	9.94	7.59
Zn(II)	d^{10}	17.1	17.96
Hg(II)	d^{10}	12.8	18.75
Cd(II)	d^{10}	16.6	16.9

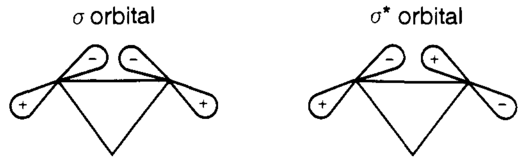
[a] Taken from R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961). [b] $nd^{10} \rightarrow nd^9(n+1)p$; $nd^8 \rightarrow nd^7(n+1)p$.

acid, the donation of electrons from the orbital of the olefin into the empty metal orbital will be the major facet of the bonding. This is because Hg(II) has a high promotion energy and a correspondingly large electron affinity. Metals intermediate between these extremes form relative strong metal–olefin bonds in which both types of bonding are important. A good example is palladium(II), whose large electron affinity makes it an efficient electron acceptor while its low promotion energy allows efficient back-donation to the olefin.

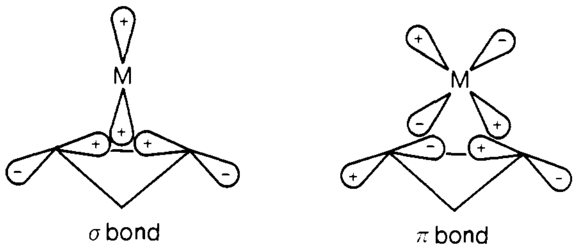
This description of transition metal–organic bonding has neglected the other ligands bound to the metal. Obviously they will modify the character of the metal–organic bond.[6] For example, carbon monoxide binds primarily by accepting electrons from the metal into its antibonding orbital. This shift of electron density causes a corresponding increase in the promotion energy and electron affinity of the metal. Conversely, amines bind to transition metals by donating their unpaired electrons into an empty metal orbital. This lowers the metal's electron affinity and promotion energy. Phosphines interact with the metal in a synergistic manner, donating nonbonding electrons in a σ fashion and accepting electrons in a π fashion. Substituents on the phosphine can alter the phosphine's, and hence the metal's, donating-accepting properties. As a general rule, ligands which increase electron density lower the electron affinity and the promotion energy of the metal; ligands which decrease electron density on the metal raise the promotion energy and the electron affinity.

B. Concepts of Metal Bonding to Carbon–Carbon σ Bonds

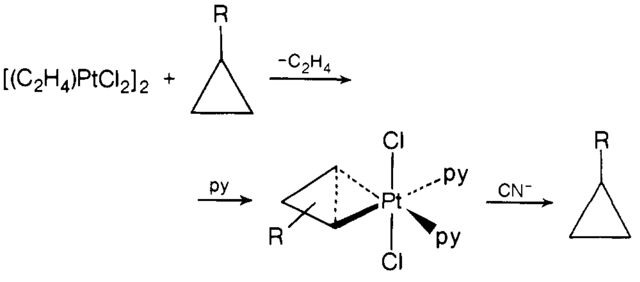
From these simple concepts of metal–olefin bonding a reasonable description can be developed of the interaction of three- and four-membered rings with transition metals. The Walsh[7] model of cyclopropane and a similar model of cyclobutane by Salem[8a] and by Hoffmann and Davidson[8b] describe the higher occupied molecular orbitals as largely p orbital in character. The analogy between the "banana-bond" in cyclopropane and the π bond in olefins is obvious. The comparison is further heightened by the recent isolation and characterization of a number of cyclopropane–transition metal complexes.[9]



The description of organometallic bonding to σ bonds possessing high p-orbital character is also composed of two parts.[9a,10] The σ bond is formed by electron donation from the carbon–carbon bond into an empty metal orbital. Again, the metal is capable of back-donation into a relatively low-lying σ* orbital of the hydrocarbon. However, because the σ* will generally be of higher energy than the analogous π* orbital, back-donation should be less important than in the olefinic case. Thus, the description of the interaction of three- and four-membered rings with transition metals follows closely the description of olefin–metal interaction. The major difference arises in the relative inaccessibility of the antibonding σ* orbital for back-donation from the metal. Thus, the electron-accepting capability of the metal will be more important in the binding of cyclopropane or cyclobutane.



Evidence for this mode of bonding comes primarily from the work of McQuillan and Powell.[9a] They studied the displacement of ethylene from $[(C_2H_4)PtCl_2]_2$ with various substituted cyclopropanes. The rate of reaction was found to depend markedly on the electron donor capacity of the cyclopropane ring. In fact, substitution of cyano, methylketo, or carbomethoxy on the ring completely suppressed the reaction. When electron-rich cyclopropyl compounds were employed, addition of pyridine yielded stable organo metal complexes. The cyclopropanes could be regenerated from these complexes by treatment with aqueous potassium cyanide. Thus, some cyclopropyl character remains in the complex. In these complexes, a steric effect was found which favored the metal complexing to the least hindered bond of the cyclopropane ring. However, when the substituent was *p*-methyltolyl, bonding occurred with the most hindered bond. Thus, there is a delicate balance between electronic and steric effects.



C. Coordinative Unsaturation, 18-Electron Rule, Oxidative Addition, and Insertion

To bind to an organic molecule a metal must first possess a vacant coordination site; i.e., it must be coordinatively unsatu-

SCHEME I

$$\underset{\mathbf{1}}{HCo(CO)_4} \underset{+CO}{\overset{-CO}{\rightleftharpoons}} \underset{\mathbf{2}}{HCo(CO)_3} \underset{-olefin}{\overset{+olefin}{\rightleftharpoons}} \underset{\mathbf{3}}{HCo(CO)_3(olefin)}$$

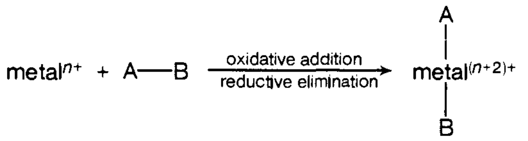
	1	**2**	**3**
Co(I)	8	8	8
H	2	2	2
(CO)	8	6	6
(Olefin)	0	0	2
Total valence electrons	18	16	18
Coordiatively:	Saturated	Unsaturated	Saturated

rated.[11] Transition metals possess nine valence orbitals (five *n*d orbitals, one ($n + 1$)s orbital and three ($n + 1$)p orbitals). By binding sufficient ligands to place 18 electrons in these valence orbitals they achieve an inert gas configuration. This is known as the 18-electron rule.[11,12] A metal with 18 electrons in its valence shell is *relatively* inert; a metal with less than 18 electrons is relatively reactive.

An example of this is provided by hydridocobalt tetracarbonyl, from which a carbon monoxide ligand must be dissociated before it can bind to an olefin[13] (see Scheme I). In this case olefin binding is suppressed in the presence of excess carbon monoxide. A further example is provided by the hydrogenation of Wilkinson's catalyst (**4**)[14] (see Scheme II). Here it is a phosphine which must dissociate to allow complexation of the olefin. As with carbon monoxide in the cobalt case, addition of excess phosphine can stop the hydrogenation.

Note that in the catalytic sequence of hydrogenation the original catalyst and all of the intermediates possess either 16 or 18 electrons. Dissociation occurs with the 18-electron species, addition with the 16-electron species. This illustrates the utility of the 18-electron rule.

Insertion of a transition metal into a two-electron bond of a substrate is called oxidative addition. In oxidative additions the metal is formally[11] oxidized by donation of two electrons to the substrate. Therefore, it is not unexpected that facility for oxidative addition has been related to promotion energy of the metal with some success.[15] The reverse of oxidative addition is reductive elimination.

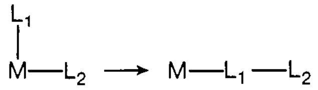


$$\text{metal}^{n+} + A\text{—}B \underset{\text{reductive elimination}}{\overset{\text{oxidative addition}}{\rightleftharpoons}} \text{metal}^{(n+2)+}(A)(B)$$

The generality of these processes is well documented[11,16] for a variety of metal complexes and substrates. Examples of both of these processes are found in the oxidative addition of hydrogen to tris(triphenylphosphine)chlororhodium(I) (**4**) to yield the dihydrido rhodium(III) species **5**, and in the reductive elimination of a carbon–hydrogen group from species **10** to return the original catalyst, **4**.

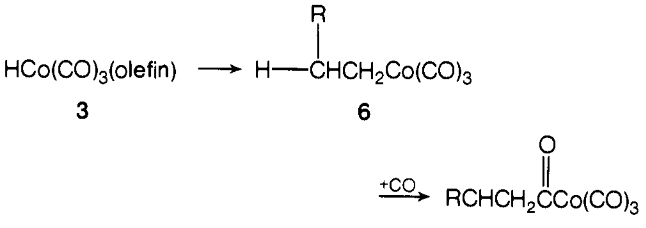
Further examples of oxidative addition are provided in Figure 2. The wide variety of substrates illustrated in this figure highlight the generality of the concept of oxidative addition. Notice that the active species are, in general, square-planar d^8 complexes in which the metal possesses 16 valence electrons.

"Insertion" of a ligand into the metal–ligand bond of another ligand bond to the same metal is also a well-recognized process.



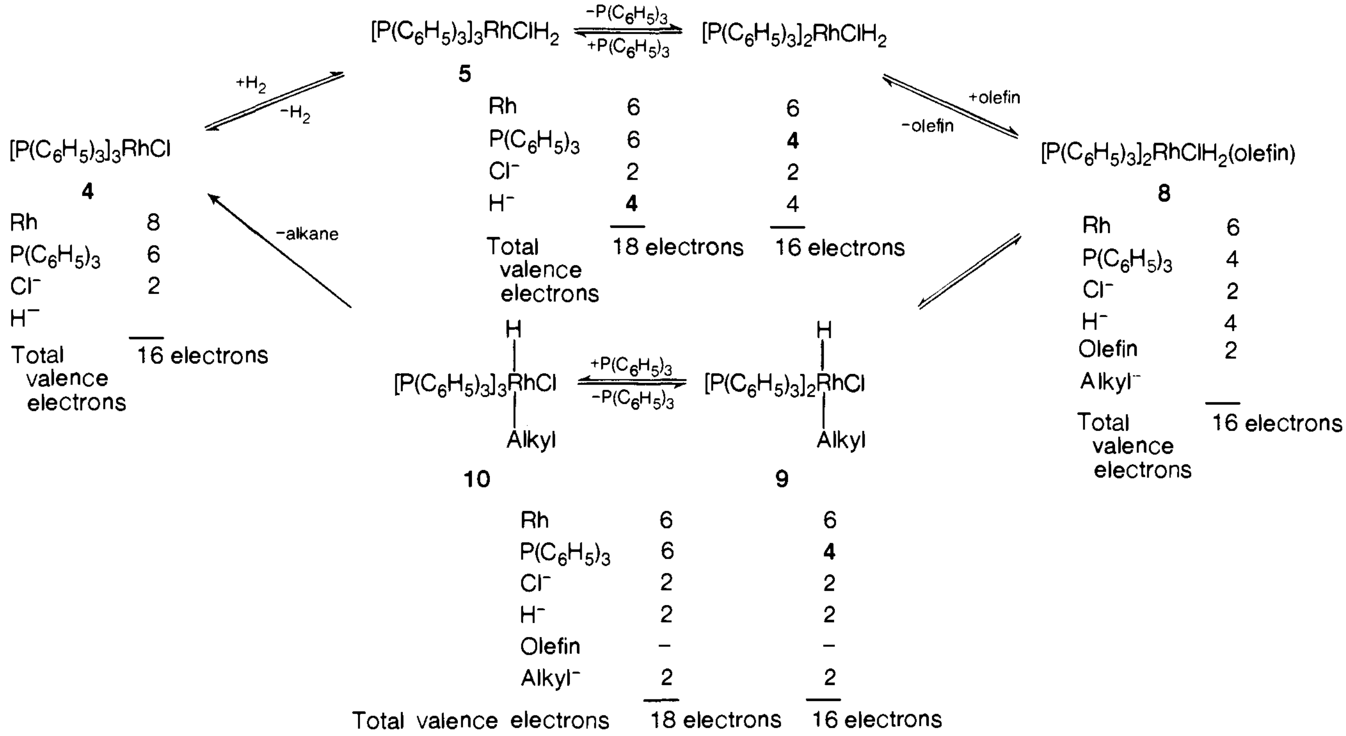
$$M(L_1)\text{—}L_2 \longrightarrow M\text{—}L_1\text{—}L_2$$

Reactions of this type provide the basis for most transition metal catalyzed polymerization reactions. Two examples can be found in the insertion of olefin into the hydrogen–cobalt bond of **3**. The subsequent insertion of carbon monoxide into the cobalt–carbon



$$\underset{\mathbf{3}}{HCo(CO)_3(olefin)} \longrightarrow \underset{\mathbf{6}}{H\text{—}CH(R)CH_2Co(CO)_3} \xrightarrow{+CO} \underset{\mathbf{7}}{RCHCH_2C(=O)Co(CO)_3}$$

SCHEME II. Mechanism of Olefin Hydrogenation with Wilkinson's Catalyst (**4**)



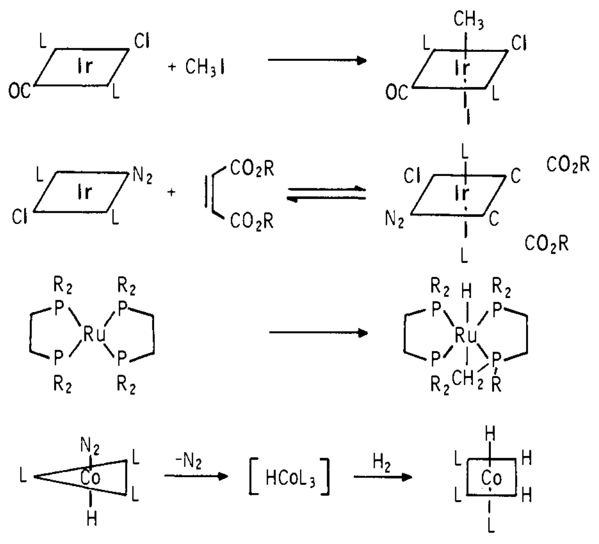


Figure 2. Examples of oxidative addition. Examples are taken from ref 11 and 16: $L = P(C_6H_5)_3$, R = Me

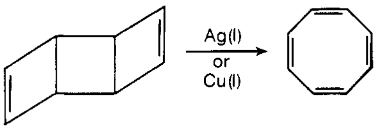
bond of **6** gives the metal acyl compound **7**. In the hydrogenation sequence for Wilkinson's catalyst, the same insertion reaction is seen for the conversion of **8** into **9**.

These basic concepts of organometallic bonding, coordinative unsaturation, oxidative addition, and insertion provide the basis with which to discuss the transition metal catalyzed rearrangements of three- and four-membered rings.

III. Unsaturated Four-Membered Ring Compounds

A. Cyclobutene to Butadiene

In 1967 Pettit and Mark[17] began to report compounds which underwent transition metal catalyzed ring opening of cyclobutene to butadiene. In the first reported example, *anti*-tricyclooctadiene (**11**) isomerized to cyclooctatetraene in the presence of silver tetrafluoroborate with a half-life of 5 min at 56 °C.



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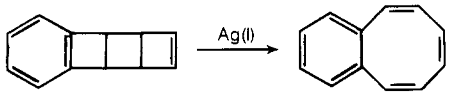
In similar examples, benzotricyclooctadiene (**12**) isomerized to benzocyclooctatetraene (**13**), and dibenzotricyclooctadiene (**14**) isomerized within 10 s into dibenzocyclooctatetraene.



12 13

The intermediacy of the *o*-xylylene derivative (**15**) was demonstrated by trapping it as its Diels–Alder addition product with maleic anhydride (see Figure 3).

The dramatic heightening of reactivity induced by the catalyst is obvious when the thermal stabilities of compounds **11** and **12** are considered. While the products are the same as in the Ag(I)-catalyzed rearrangements, **11** undergoes thermal isomerization[18a] with a half-life of 20 min at 140 °C and **12** is completely converted[18b] to **13** only after refluxing ca. 4 h at 180 °C. Clearly, the transition metal has sharply lowered the energy barrier for these transformations.

Further examples of the cyclobutene to butadiene rearrangement are provided in Figure 4. The rearrangements of *anti*-tricyclooctene (**16**) and benzotricyclooctane (**17**) clearly show that two unsaturated centers are not necessary for reaction.[20] Besides silver(I), nickel, copper, platinum, and palladium complexes were found by Pettit to be effective catalysts for these isomerizations.[21] Interestingly, a nickel(II) complex catalyzed the isomerization of **16** but not of **17**. Thus, nickel must complex with the olefin, rather than the aromatic ring. In a related example, a palladium(II) catalyst, isoelectronic with nickel(II), led to rearrangement of **12** into **19** rather than the Ag(I) product, benzocyclooctatetraene (**13**).[21a] This is also consistent with the metal binding to the olefin rather than the aromatic ring. An examination of the chemistry of these metals shows that Ag(I) complexes strongly with benzene, while no nickel aromatic complexes are known.[22] In contrast, Ni(II) and Pd(II) form strong metal-olefin bonds, while Ag(I) binds only weakly without the presence of electron-withdrawing substituents on the olefin.

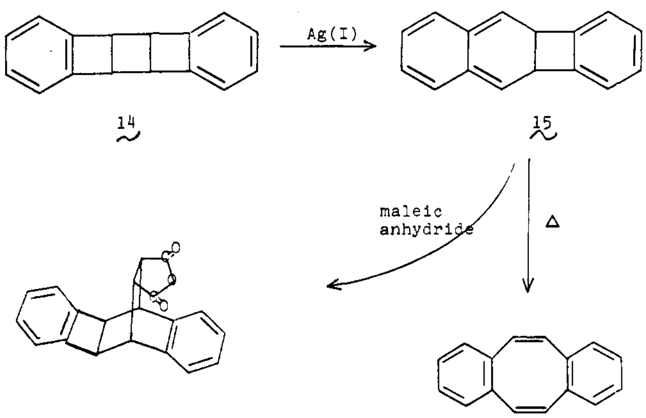


Figure 3. Trapping of the xylylene intermediate in the silver(I)-catalyzed rearrangement of dibenzotricyclooctadiene.

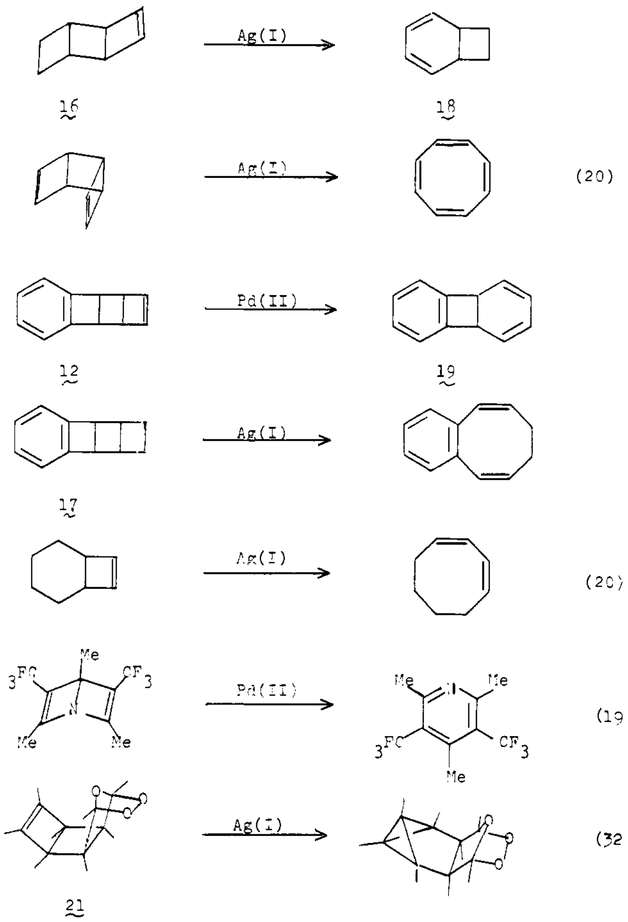
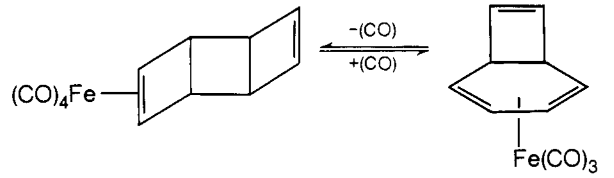


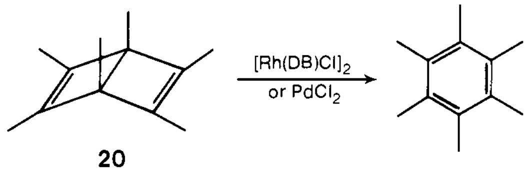
Figure 4. Other examples of the transition metal catalyzed "cyclobutene to butadiene" rearrangement. (References to rearrangements not covered in text are in parentheses.)

Recently, support for the intermediate complex was received, when Pettit, et al.[23] showed the rearrangement of a number of iron-complexed cyclobutenes to butadienes.



B. Dewar Benzene to Benzene

A transformation related to those discovered by Pettit is the rearrangement of hexamethyl(Dewar benzene) (**20**) into hexamethylbenzene. This rearrangement has been extensively studied by research groups of Maitlis[24] and Volger,[25,26] employing a variety of palladium and rhodium complexes. This conversion is extremely exothermic, since it leads to an aromatic product. In the rhodium(I)-catalyzed rearrangement, kinetic and NMR observations[26] suggest a complex series of equilibria in which two Dewar benzene molecules (DB) are complexed to a single rhodium atom complex **21**. The rate-determining step was postulated to be the rearrangement of this bis(Dewar benzene) complex.



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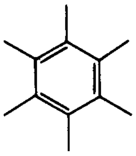
$$[\mathrm{Rh(DB)Cl}]_2 \rightleftharpoons \mathrm{Rh(DB)Cl} \underset{+\mathrm{DB}}{\overset{-\mathrm{DB}}{\rightleftharpoons}} \underset{\mathbf{21}}{\mathrm{Rh(DB)_2Cl}}$$

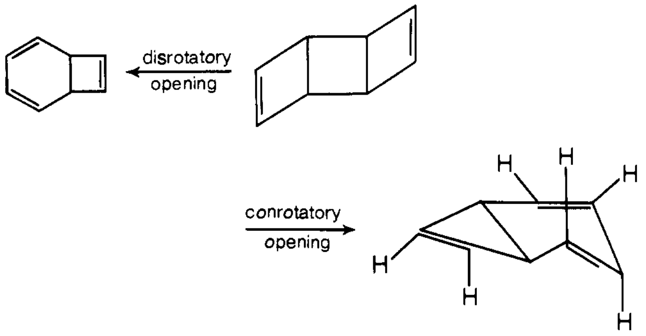
$$\longrightarrow {}^1\!/_2[\mathrm{Rh(DB)Cl}]_2 +$$

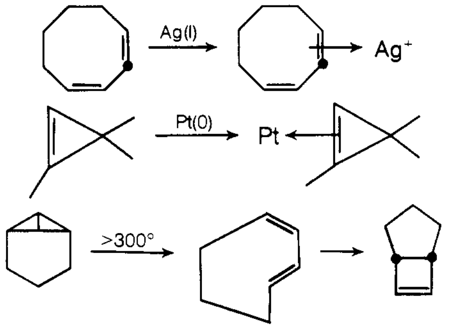


As before, the energy of activation for this rearrangement was found to be substantially lowered when compared to the thermal isomerization. A value of 31 kcal/mol was determined for the thermal rearrangement; this was lowered to 19 kcal/mol for the rhodium-catalyzed rearrangement.[26] The metal catalyst has opened a pathway of considerably lower energy for the isomerization.

C. Orbital Symmetry and Metal Catalysis

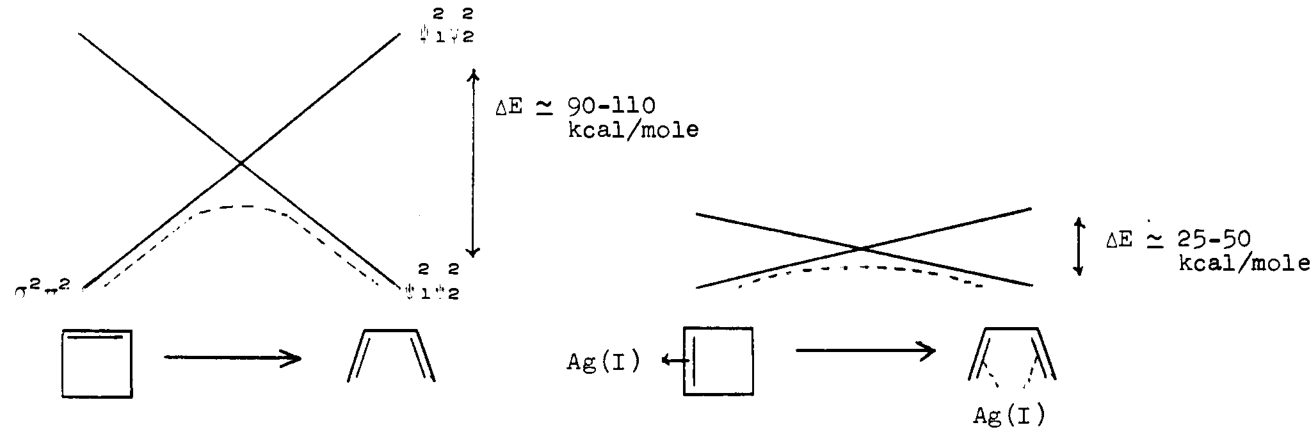
The reason for the high thermal stability of these extremely strained cyclobutene molecules is the well-known constraint of orbital symmetry.[27,28] In the Woodward–Hoffmann[27] formalism, disrotatory opening is symmetry forbidden, while in the bicyclic molecules conrotatory opening is inhibited since it leads to an even more highly strained product. In the example below, the symmetry-allowed product possesses a trans olefin in a six-membered ring. There are two ways in which the metal may interact to lower the energy barrier. The first possibility is that the symmetry-allowed pathway is followed and the transition metal somehow stabilizes the product. Arguing against this, Pettit has pointed out[21] that a strained trans double bond would lead to either a stable metal olefin complex[29] or to the starting olefin (via intramolecular closure[30]). Such reactions of highly strained trans olefins are well documented.





The second possibility is that the restraints of orbital symmetry of the organic moiety are removed or changed by complexation to a transition metal. Pettit[21] has shown that in the Woodward–Hoffmann sense complexation of cyclobutene to a transition metal leads to an "allowed" reaction if two electrons are shifted from p_yd_{yz} hybrid metal orbital into a p_xd_{xz} hybrid orbital. That is, the restraints of orbital symmetry are still operative, but different metal orbitals bind the product than bind the reactant. Since the energy difference between metal orbitals is postulated to be small, certainly smaller than that between the ground and excited state of butadiene, the barrier to conrotatory rearrangement will be lowered, if not removed. This is shown schematically in Scheme III.

SCHEME III



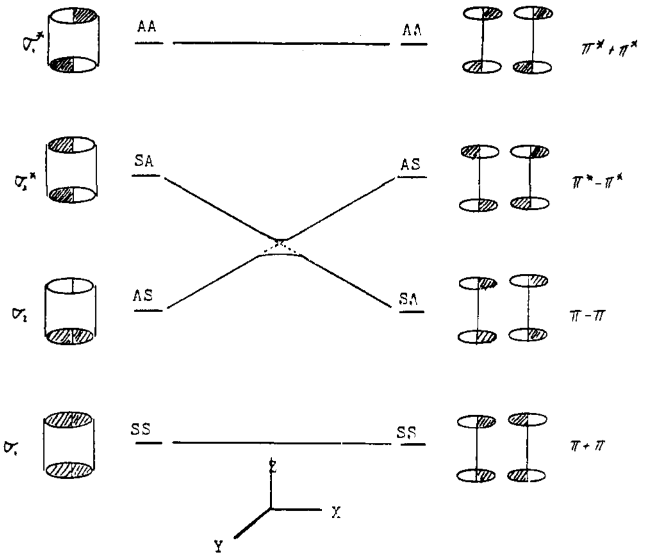
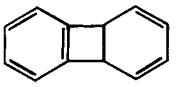


Figure 5. Orbital correlation diagram for the ethylene/cyclobutene transformation. Symmetry elements are the *xz* and *yz* mirror planes, respectively.

Similar arguments have been presented for the reaction of two ethylenes being converted into cyclobutane through the interaction of transition metals (vide infra). More recently Dewar[28] has stated that "transition metals may catalyze pericyclic reaction if, and only if, they involve an antiaromatic transition state", that is, only if they are symmetry forbidden. The underlying concept is that the low-lying "π^* orbitals" of the transition state will be stabilized by bonding to the transition metal. Such bonding produces the extreme stability of the transition metal complexes of antiaromatic molecules, such as cyclobutadiene.[31]

In agreement with this hypothesis, **18** fails to undergo further reaction in the presence of Ag(I) to give cyclooctatriene. Dewar points out that this also explains the failure of **19** to undergo further rearrangement to give benzocyclooctatetraene. Both of these rearrangements have "aromatic" [32] transition states which are not stabilized by complexation to metal complexes.



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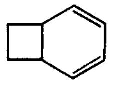


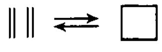
18

An interpretation similar to that of both Dewar and Pettit can be put to an experimental test. If it is assumed that the major function of complexation to the metal is to transfer electrons from the π orbital of the cyclobutene into the antibonding orbital, in a formal sense the reaction becomes "allowed". This is similar to the well-known photolytic inducement of unallowed reactions. Thus, those catalysts which can more efficiently backbond will enhance the reactivity of the bound substrate and/or stabilize the antiaromatic transition state. Thus, it may be possible through systematic variation of the metal and attached ligands of the catalyst to vary the energetics of the isomerization in a predictable manner. To date, no study has appeared to test this hypothesis.

IV. Saturated Four-Membered Ring Compounds

A. Cyclobutane to Ethylene and Orbital Symmetry

The changes in orbital symmetry induced by transition metals have received the most study in the case of the dimerization of ethylene. Not surprisingly, it is the reverse reaction which is normally observed. However, the dimerization of ethylene over a molybdenum catalyst has been observed by Pettit and coworkers in extremely low yield (0.1%).[33] Norbornadiene, however, has been shown to dimerize under catalysis by a variety of transition metals.[34]



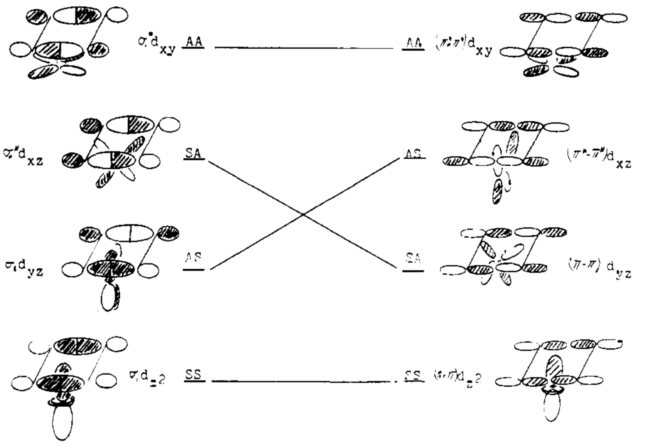


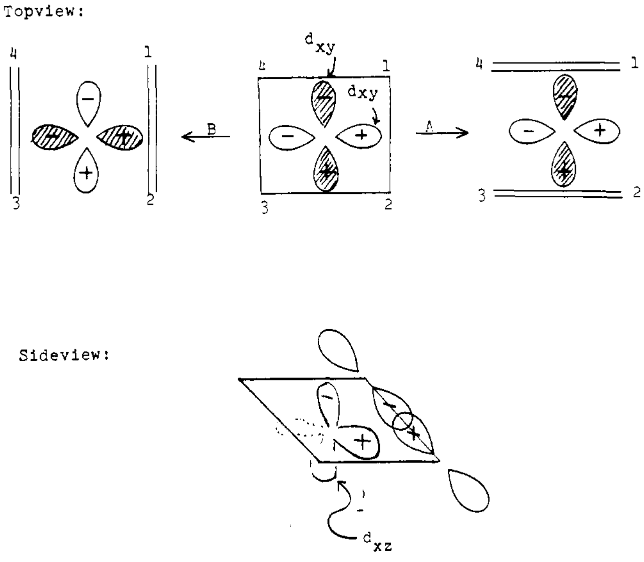
Figure 6. Orbital correlation diagram for the transition metal catalyzed ethylene/cyclobutane transformation. The symmetry elements used are the *yz* and *xz* mirror planes respectively.

Theoretical treatments of the dimerization of ethylene and the reverse reaction have been reported.[35,36] The correlation diagram for the suprafacial dimerization of ethylene is presented in Figure 5.[37] When a transition metal, e.g., of electronic configuration d^8, serves as a template for the reaction, the correlation diagram can be presented as in Figure 6.[35,36] The correlation diagram in Figure 6 is based on two assumptions: (1) the complex is square planar; and (2) the product remains symmetrically bonded throughout the reaction. It should be noted that, as in the Ag(I) (i.e., d^{10}) catalyzed rearrangement of cyclobutene to butadiene, it is the difference in the energies of the two crossing metal orbitals (in this case d_{xy} and d_{xz}) which determine the facility of the reaction. As Mango has pointed out,[35] the propensity for rearrangement will in large part depend upon the relative energies of the two interchanging orbitals.

While cases of olefin dimerization to form cyclobutanes remain relatively rare, the reverse reaction has become a well-recognized metal catalyzed process. Pettit has shown cyclobutane is transformed into ethylene in about 3% yield with the same molybdenum catalyst.[33]

Calculations by Mango and Schachtsneider show that in the reverse reaction the propensity for dissociation by the two paths,

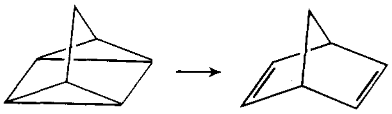
SCHEME IV



"A" and "B", are critically dependent upon the electron density in the d_{yz} and d_{xz} orbitals (see Scheme IV). This is understandable when one considers that the distribution of electron density between these orbitals will determine the carbon–carbon bond whose σ^* orbital will become populated through back-donation. For example, if the d_{xz} orbital is filled and the d_{yz} orbital is empty, path "A" would be followed. In this case the d_{xz} orbital donates electron density into the σ^* orbitals of the C_1–C_2 and C_3–C_4 bonds, lowering the bond strength of these bonds. Thus, substituents on the complex theoretically can dramatically influence the course of a reaction by changing the relative energies of d_{xz} and d_{yz}.

B. Quadricyclene to Norbornadiene

The first observation of this type of reaction was the metal catalyzed rearrangement of quadricyclene (**22**) to norbornadiene.[38,39] Hogeveen and Volger[38] found that at −26 °C this



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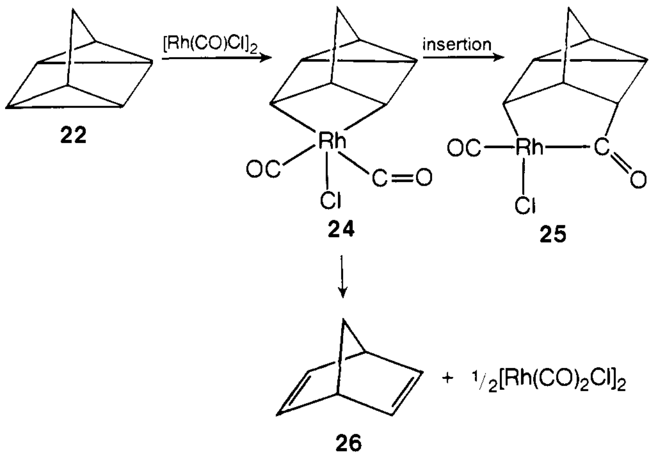
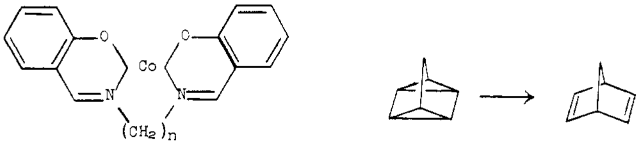
reaction proceeded readily using metal diene complexes of Rh(I), Pd(II), and Pt(II) as a catalyst. The half-life for isomerization was found to be 45 min when a 2 mol % solution of $[Rh(norbornadiene)_2Cl]_2$ was used as the catalyst. This is in contrast to the thermal, uncatalyzed rearrangement which has a half-life of 14 h at 140 °C.[40] They suggested that complexation was through the π character of the cyclopropane bonds. An NMR study of the catalyst in solution[42] indicated that the olefins are not readily dissociated from the catalyst at low temperature. Thus, while crude activation parameters were obtained ($\Delta H^{\ddagger} = 21 \pm 5$ kcal/mol, $\Delta S^{\ddagger} = 45 \pm 18$ eu), it was not possible to determine the actual catalytic species in solution.

Manassen[41] has studied the effect of both the number of metal valence electrons and geometry of the catalyst for this reaction. Using a series of square-planar macrocyclic ligands, including tetraphenylporphine and phthalocyanine, with a variety of metals, he found no obvious relationship between the number of valence electrons and catalytic activity. When **23** was used as the catalyst and the number of methylene groups was increased incrementally, he found that only the square-planar complexes, and not those with tetrahedral geometry would act as a catalyst for the isomerization. His results are shown in Figure 7.

Perhaps the most significant work on the rearrangement mechanism of quadracyclene to norbornadiene was the capture of a possible intermediate by carbon monoxide insertion when rhodium dicarbonyl chloride dimer was used as the catalyst.[43] The isolation of insertion product (**25**) suggests a mechanism in which Rh(I) underwent oxidative addition to the edge bond of





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$n =$	Magnetic Susceptibility	% Conversion
2	2.28≠	100
3	4.50	50
4	4.37	0
5	4.26	0
6	4.23	0
CH_2 replaced by two phenyls	4.34*	0

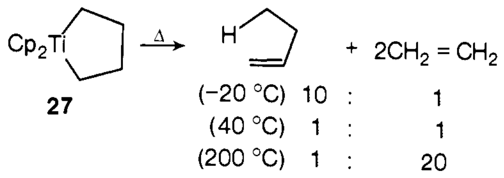
≠square planar *tetrahedral

Figure 7. The effect of geometry of the catalyst on the isomerization of quadracyclene to norbornadiene.

quadricyclene (**22**). The metallocyclopentane (**24**) thus formed could, depending upon the conditions, undergo insertion of carbon monoxide to give a stable acyl derivative (**25**), or decompose in a cheletropic[44] manner to yield norbornadiene (**26**).

If the species **24** is considered the metal-substrate complex, it is possible the formation of norbornadiene occurs in a concerted manner, though it is not the symmetrical intermediate of the published theory (vide supra). However, the intermediacy of **24** in the formation of norbornadiene has not been demonstrated experimentally.

Evidence that an intermediate such as **24** could lead to the observed products has recently been obtained. Whitesides et al. have recently shown[45a] that titanium metallocycles of structure **27** may decompose with carbon–carbon bond cleavage. Thus with titanium the possibility of a "cheletropic"

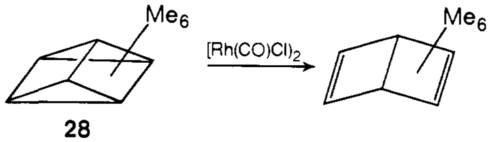


mechanism has been demonstrated. Unfortunately, similar experiments with platinum metallocycles failed to yield any products resulting from carbon–carbon bond cleavage.[45b]

More recently, kinetic evidence has led Hogeveen et al.[39] to propose that a different mechanism is operating for the case of catalysts comprised of different metals, such as Ag(I). Such mechanisms are in accord with those postulated for rearrangements of other small ring systems—particularly catalysts of a Lewis acid nature (vide infra). However, more detailed equilibrium and kinetic data are necessary to substantiate this proposal.

C. Prismane to Dewar Benzene

Hogeveen and Volger studied[46] a similar reaction in which hexamethylprismane (**28**) is arranged into hexamethyl(Dewar benzene). The thermal rearrangement of **28** leads primarily to



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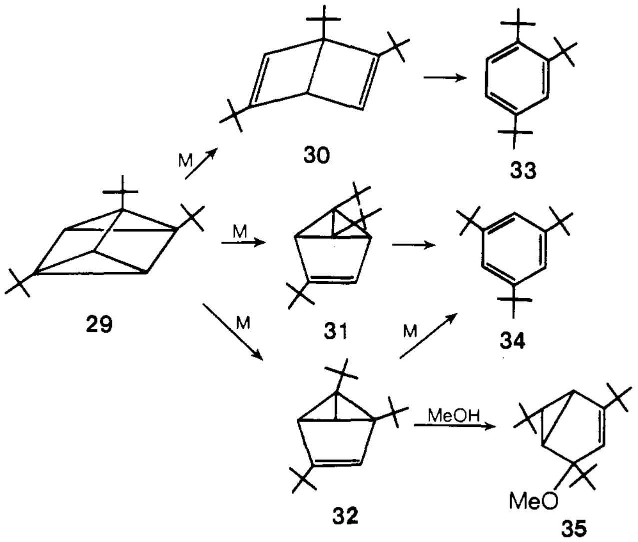
hexamethylbenzene with activation parameters of $\Delta H^{\ddagger} = 34$ kcal/mol and $\Delta S^{\ddagger} = 15$ eu. Surprisingly, in the Rh(I) catalyzed reaction less than 5% hexamethylbenzene is found. This is in strong contrast to Ag(I) (vide supra). When 5 mol %

TABLE II. Products from Catalyzed Decomposition of Tri-*tert*-butylprismane

Catalyst	Solvent	$t_{1/2}$, min	% 29	% 30	% 31	% 33	% 34	% 35
$HgCl_2$	MeOH	<1	0	90	10	0	0	0
$HgCl_2$	Pyridine	<1	0	87	13	0	0	0
$SnCl_2 \cdot 2H_2O$	MeOH	0.5	0	71	14	0	0	14
$SnCl_2 \cdot 2H_2O$	Pyridine	1320	50	42	8	0	0	0
$ZnCl_2$	MeOH	4	50	36	14	0	0	0
Na_2PdCl_4	MeOH	10	50	35	5	0	0	10
$[Rh(CO)_2Cl]_2$	MeOH	20	50	34	13	0	0	3
$[Pd(OAc)_2]_3$	MeOH	4	50	33	17	0	0	0
$[1,5\text{-}C_8H_{12}RhCl]_2$	MeOH	31	50	32	18	0	0	0
$[Cu(OAc)_2H_2O]_2$	MeOH	18	50	19	22	0	0	11
$Ru_3(CO)_{12}$	MeOH	12	50	20	26	0	0	4
$Pb(OAc)_2 \cdot 3H_2O$	MeOH	9	50	10	27	0	0	13
$[C_5Me_5RhCl_2]_2$	MeOH	120	50	6	27	1	0	16
$AgNO_3$	MeOH	<1	0	5	51	6	38	0
$AgNO_3$	Pyridine	5	50	2	22	4	22	0
$C_5Me_5Rh(OAc)_2H_2O$	MeOH	300	50	4	33	0	0	13
1,3,5-Trinitrobenzene	MeOH	460	50	2	28	2	8	10
$Co(acac)_3$	MeOH	13	50	2	26	0	0	21
HCl	MeOH	35	50	0	0	50	0	0
Thermal (110°)	Pyridine	18 hr	50	0	0	25	25	0

$[Rh(Me_6DB)Cl_2]_2$ was used as the catalyst, the isomerization had a half-life of 40 min at −30 °C. Treatment of **28** with HF–BF_3 led to ca. equal amounts of Dewar benzene and benzene. The acid-catalyzed reaction was found to be extremely rapid, even at −80 °C.

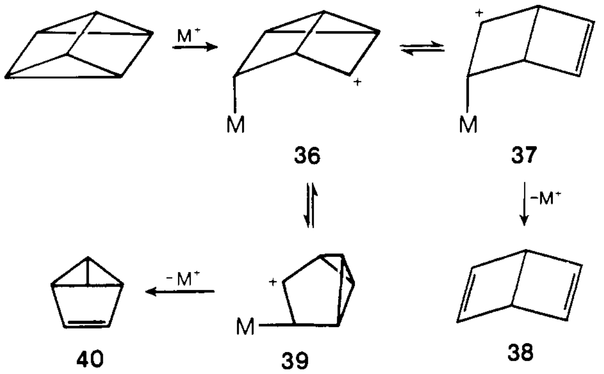
In a closely related study, Kaiser, Childs, and Maitlis[47] have studied the metal-catalyzed rearrangement of the highly hindered tri-*tert*-butylprismane (**29**). As in the rearrangement of hexamethylprismane (**28**), the tri-*tert*-butylprismane (**29**) also exhibits a dramatic rate enhancement in the presence of transition metals when compared to the thermal rearrangement. Depending upon the catalyst and solvent, different products were found (see Table II).



The presence of **31** led Maitlis to suggest a mechanism in which a charge transfer complex between the catalyst and substrate is formed which then partitions among the various products. A similar mechanism in which the metal functions primarily as Lewis acid and avoids a radical cation is presented in Scheme V.

The catalyst adds to the prismane in a Lewis acid fashion, generating a metallo carbonium ion, **36**. This carbonium ion then partitions among the two valence isomers **37** and **39**. Such isomerizations are well precedented by the well-known cyclopropylcarbinyl rearrangement.[48] Extrusion of the metal then leads to the products. That the **36** to **37** step is reversible is indicated from formation of a bicyclobutyl product when **21** (see Figure 4) was treated with Ag(I). Clearly in this case, the system of equilibrating ions has been reached from **38**. It should also be possible to enter this system of equilibrating ions via benzvalene, **40**.

SCHEME V

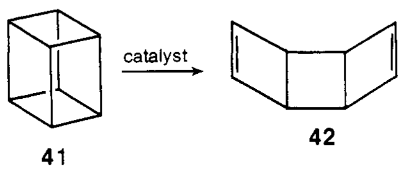


D. Cubane Rearrangements

1. Effect of the Catalyst and Solvent

For the compounds previously mentioned, no differentiation could be made between the three possible mechanisms. Only the isolation of the carbon monoxide insertion product, **24**, argues against a concerted mechanism. The metal-catalyzed rearrangements of cubane (**41**),[49,50] however, show a clear distinction between the cheletropic and carbonium ion mechanism. Depending upon the conditions and catalyst, cubane (**41**) rearranges in two distinct manners.

The product is either tricyclooctadiene (**42**) or the pentacyclic



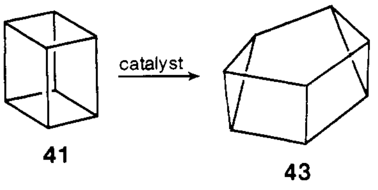


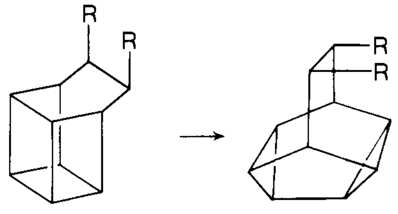
TABLE III. Products from Metal-Catalyzed Rearrangements of Dicarboethoxybasketane (44)[a]

Catalyst	Solvent	Temp, °C	Reaction time	% 45	% 46	% 47
$Ni(COD)_2P(C_6H_5)$[b]	Toluene	35	1.5 days	0	49	51
$Rh(Ph_3P)_3Cl$	$CDCl_3$	50–55	15 days	0	33	67
$Rh(Ph_3P)_2COCl$	$CDCl_3$	50–55	12 days	0	23	76
$Rh(Ph_3P)_2COBr$	$CDCl_3$	50–55	70 h	0	23	76
$Rh(Ph_3P)_2COI$	$CDCl_3$	50–55	41 h	0	23	76
$[Rh(NOR)Cl]_2$	$CDCl_3$	50–55	69 h	0	22	77
$PdCl_2(Ph_3P)_2$	$CDCl_3$	50–55	12 h	41	23	35.5
$PdI_2(Ph_3P)_2$	$CDCl_3$	50–55	7 days hl[c]	4	34	61
$PdCl_2(Ph_3As)_2$	$CDCl_3$	50–55	6 h	61.5	9.5	29
$PdI_2(Ph_3As)_2$	$CDCl_3$	50–55	60 h	6	39.5	54
$PdCl_2(Ph_3Sb)_2$	$CDCl_3$	50–55	8 days	100	0	0
$PdI_2(Ph_3Sb)_2$	$CDCl_3$	50–55	4 h	23	22.5	54
$PdCl_2[P(OCH_3)_3]_2$	$CDCl_3$	RT	28 days	67	8	24
$PdBr_2[P(OCH_3)_3]_2$	$CDCl_3$	50–55	46 h	25	25	50
$PdI_2[P(OCH_3)_3]_2$	$CDCl_3$	50–55	13 days hl[c]	11	32	56
$PdCl_2[P(OPh)_3]_2$	$CDCl_3$	50–55	4 h	94	2	4
$PdI_2[P(OPh)_3]_2$	$CDCl_3$	50–55	6 days	36.5	18	45.5
$PdCl_2(py)_2$	$CHCl_3$	Reflux	10 days hl[c]	100	0	0
$PdCl_2(NOR)$	$CDCl_3$	45–50	10 days	100	0	0
$PdI_2(NOR)$	$CDCl_3$	50–55	72 h	86	4	9
$PdCl_2(PhCN)_2$	$CDCl_3$	RT	28 days	100	0	0
$PdI_2(PhCN)_2$	$CDCl_3$	50–55	19 h	95	0	0
$PdCl_2$	Aq CH_3OH	RT		100	0	0
$AgNO_3$	Aq CH_3OH	RT		100	0	0

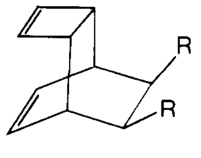
[a] Taken from ref 54. [b] H. Takaya, M. Yamakawa, and R. Noyori, *Chem. Lett.*, 781 (1973). [c] Half-life.

compound **43**, which has been named trivially cuneane.[51] Cuneane has been estimated[52] to be 30 to 40 kcal/mol more stable than cubane. A simple calculation[53] predicts tricyclooctadiene (**42**) to be 35 to 50 kcal/mol more stable than cubane. Thus both of these totally unexpected rearrangements are energetically favorable.

Dauben and Kielbania[54] have thoroughly investigated the effect of both ligand and solvent on the ratios of the two types of products. Their study of the effect of catalyst variation on products in the rearrangement of dicarbomethoxybishomocubane (**44**) to either **45, 46,** or **47** is presented in Table III.



44, R = CO_2CH_3 **45**



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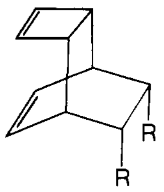

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Clearly, those catalysts which have high electron affinities and promotion energies, e.g., $AgNO_3$ and $PdCl_2$, lead to the cuneane-type product **45.** In contrast, those complexes which possess low electron affinities and promotion energies and efficiently back bond, e.g., Rh(I) catalysts, lead to the tricyclooctadiene products **46** and **47.** However, palladium(II), which falls between these extremes, gives a varying mixture of products depending upon the coordinated ligands. In the series $PdX_2[P(C_6H_5)_3]_2$, the percent of cuneane product decreases in the order Cl > Br > I. This is expected, based on the known electron-withdrawing power of these ligands. This effect is also seen in the nonhalogen ligands of the palladium catalysts. In the series $PdCl_2(L)_2$ the cuneane product (**45**) decreases in the order L = $P[O(C_6H_5)]_3$ > $P(OMe)_3$ > $P(C_6H_5)_3$. This follows exactly the ability of these ligands to remove electron density from the metal.

TABLE IV. Effect of Solvent

Solvent	% 45	% 46 and 47
$CDCl_3$	41	58
CH_2Cl_2	43	57
CH_3CN	55	44.5
CD_3COCD_3	56.5	44.5
CD_3SOCD_3	71	28.5
$HOCH_2CH_2OH$	85	15
CH_3OH	86	13.5

The effect of solvent is also dramatic, the percentage of the cuneane product (**45**) increasing with the polarity of the solvent (Table IV).

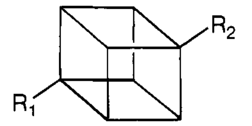
2. *Kinetic Studies*

A further differentiation between the catalysts Ag(I) and Rh(I) can be seen in the effect of substituents on the cubane rate of rearrangement.[50,51] The results of Cassar, Eaton, and Halpern are presented in Table V. It is apparent that Ag(I) is far more sensitive to substituent effects than Rh(I). Koser[55a] and later Paquette, et al., in great detail,[55c,e] using Taft σ^* polar substituent constants have found linear free energy relationships giving the value of ρ^* as ca. −1.5. Similar analyses of the Rh(I)-catalyzed reaction yield the value $\rho^* = -0.5$. Clearly, the rearrangement catalyzed by Ag(I) develops more carbonium ion character on the cubane moiety than does the Rh(I) catalyzed reaction.

Paquette et al.[55b] in their detailed kinetic analyses of bishomocubane rearrangements have demonstrated the presence of a preequilibrium between the catalyst and the substrate.

$$Ag^+ + S \rightleftharpoons [AgS]^+ \xrightarrow{k} Ag^+ + \text{products}$$

TABLE V. Cubane Kinetic Data[a]

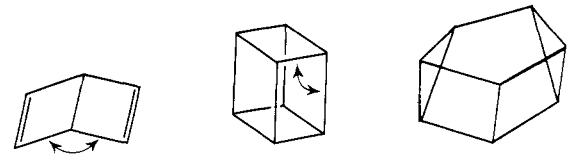


	$k_{Ag(I)}$[b]	$k_{Ag\ rel}$	$k_{Rh(I)}$[c]	$k_{Rh\ rel}$
$R_1 = R_2 = H$	3.0×10^{-1}	17 000	14	123
$R_1 = CH_2OAc$; $R_2 = H$	2.3×10^{-2}	1 300		
$R_1 = R_2 = CH_2$-OAc	1.5×10^{-2}	830		
$R_1 = CO_2Me$; $R_2 = H$	5.5×10^{-3}	310	8.8×10^{-1}	7.7
$R_1 = R_2 = CO_2$-Me	1.8×10^{-5}	1	11.4×10^{-2}	1

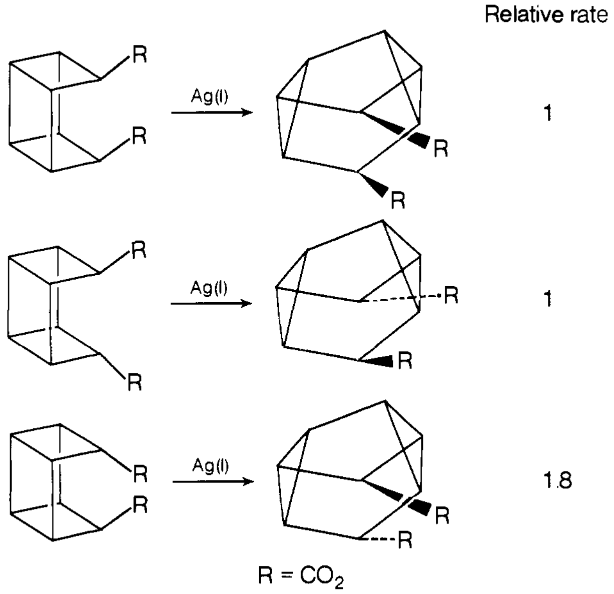
[a] Taken from L. Cassar, P. E. Eaton, and J. Halpern, *J. Am. Chem. Soc.*, **92**, 3515, 6366 (1970). [b] M^{-1} sec^{-1}, $AgClO_4$ in benzene. [c] M^{-1} sec^{-1}, $Rh(norbornadiene)_2Cl_2$ in chloroform.

However, it has not been demonstrated that the preequilibrium complex is an intermediate in the actual isomerization. This is exactly analogous to the rearrangements of bicyclobutane (vide infra).

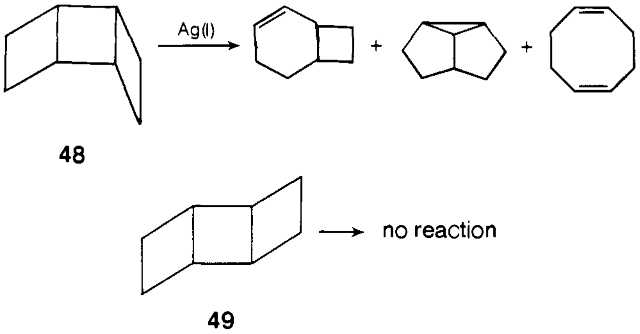
Dauben et al. have discussed the propensity for the rearrangement of cubane derivatives by Ag(I) in terms of relief of angular compression in the cuneane product.[56] In addition it has been demonstrated by Paquette and Westberg[57] that the rate of rearrangement in a series of secocubane derivatives depends only slightly on steric compression at a site remote from this angle. Thus, it may be postulated that compression of this angle has an effect other than raising the energy of the ground state. To definitively separate these effects, however, the energies of the reactants and products must be accurately determined for a series of cubyl derivatives. Unfortunately, such data are not currently available.



normal angle contracted angle cuneane (**43**)

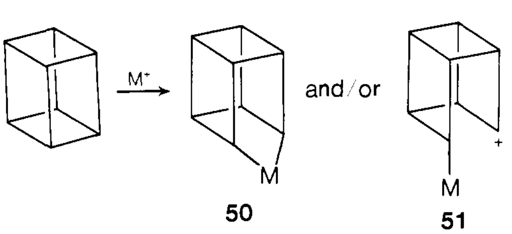


In a possibly related study Heilbronner et al.[58] have suggested from photoelectron spectra and MO calculations that differences in electron density of the central bonds in *syn*- and *anti*-tricyclooctanes **48** and **49**, rather than steric effects, determine their reactivity with Ag(I). Thus, the higher electron density in the *syn*-tricyclooctane (**48**) renders it more susceptible to electrophilic attack in comparison to the anti isomer (**49**).

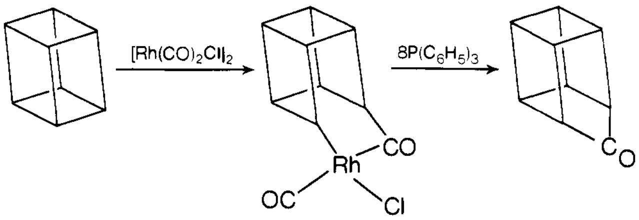


3. Mechanistic Discussion

All of these results can be accommodated by intermediate equilibrium between the oxidative addition product (**50**) and the metallo-carbonium ion **51**. A catalyst whose electron affinity and promotion energies are relatively low will favor **50** at equilibrium, while a catalyst whose electron affinity and promotion energies are high will favor **51**, localizing positive charge on the cubyl moiety. Increasing solvent polarity on such an equilibrium obviously favors the carbonium ion. The oxidative addition intermediate **50** leads to the tricyclooctadiene while the metallo carbonium ion **51** gives the cuneane product.



Tricyclooctadiene (**42**) is formed via a "cheletropic" mechanism analogous to that proposed for the metal-catalyzed rearrangement of quadricyclene to norbornadiene (vide supra). The secondary deuterium isotope effect for the trideuteriomethyl substituent in this rearrangement was determined to be essentially one when Rh(I) was the catalyst.[55e] This indicates little hybridization change in the rate-determining step of the rearrangement, a fact explicable in terms of an initial oxidative addition of the catalyst into a C–C bond to yield **50**. Evidence which supports the intermediacy of **50** in the rearrangement of cubane (**41**) to tricyclooctadiene (**42**) has been martialed by Eaton et al. When cubane (**41**) was treated with a stoichiometric amount of $[Rh(CO)_2Cl]_2$, it was possible to isolate **52** in greater than 90% yield.[51]



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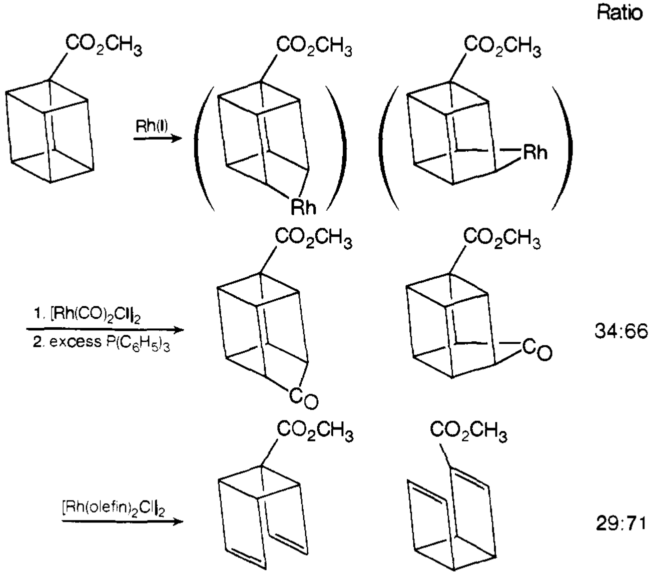
When carbomethoxycubane was isomerized,[50] evidence was obtained which strongly implicated the intermediacy of oxidative addition adduct in the formation of the diene product. The isolated carbon monoxide insertion products were obtained in approximately the same ratio as the corresponding diene products

SCHEME VI

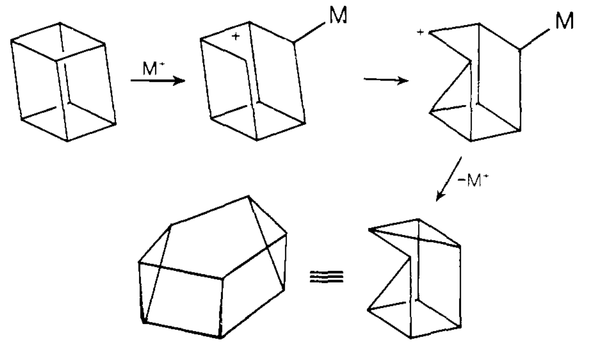


(Scheme VI). This suggests that both sets of products arise from a common set of intermediates.

In addition, the ratio of the rate of isomerization with $[Rh(NOR)Cl]_2$ (NOR = norbornadiene) to rate of insertion with $[Rh(CO)_2Cl]_2$ was found to be essentially constant ($4.1 \pm 0.5 \times 10^{-2}$ M^{-1} sec^{-1}) with the three substituted cubanes used in Table V. This strongly suggests the two divergent processes have a similar rate-determining step. However, it should be emphasized that the evidence is only circumstantial, and final confirmation of such an intermediate awaits further experimentation.

The other product formed in the metal-catalyzed rearrangement of cubane is cuneane (**43**). As shown, it is formed predominantly with catalysts which function as Lewis acids. A mechanism for its formation, similar to that advanced by Maitlis et al.[47] for the rearrangement of tri-*tert*-butylprismane, was suggested by Halpern et al.[59] The mechanism is presented in Scheme VII. As before, it is the facile rearrangement of the cyclopropyl carbinyl carbonium ion which is the fundamental process of the rearrangement.

SCHEME VII



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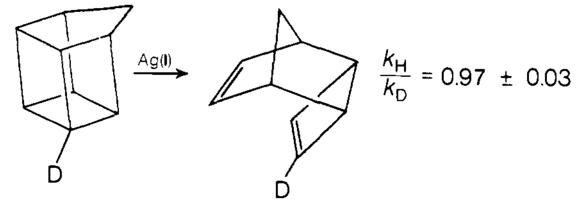
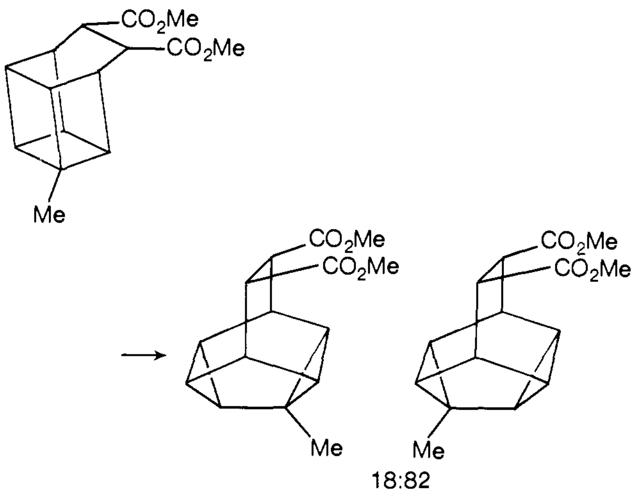
The evidence for this mode of reaction relies heavily on the kinetic, solvent effect, and catalyst variation discussed earlier. In addition, Paquette has recently thoroughly studied the Ag(I)-catalyzed rearrangement of substituted cubanes.



$$\frac{k_H}{k_D} = 0.97 \pm 0.03$$

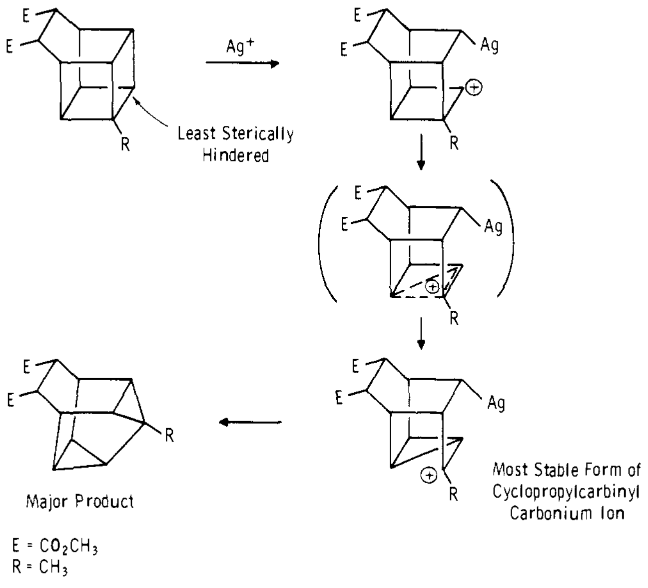
The observation[55d] of a small inverse isotope effect for 4-deuteriohomocubane does not add greatly to the understanding of the mechanism. The small magnitude may be due to observation of a preequilibrium followed by a rate-limiting step which thus obscures the actual magnitude of the isotope effect.

However, new insight was achieved when substituted 1,8-bishomocubanes were isomerized[60] in the presence of silver ion. Here, there is clearly a large selectivity for the distal isomer. The same effect was also observed with an acetoxymethyl substituent in the 4 position—again favoring the distal isomer.



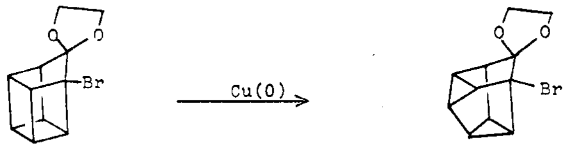
This bias for the distal product and the additional observation, also by Paquette et al.,[55c] that 5,6-disubstituted bishomocubanes are ca. ten times less reactive than expected (from $\Sigma\sigma^*$) leads to a more detailed picture of the mechanism (Scheme VIII). In this mechanism, the electrophilic attack by the silver ion takes place so as to (1) generate the most stable cyclopropylcarbinyl carbonium ion and (2) avoid steric hindrance from large substituents.

SCHEME VIII

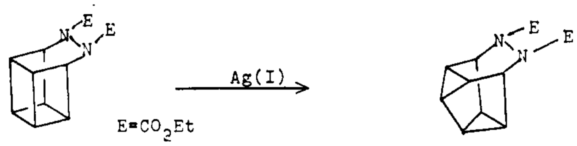


4. *Related Examples*

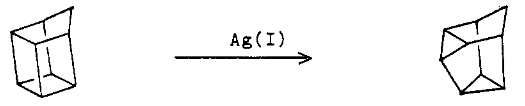
These two general mechanisms can be used to account for a number of similar rearrangements, such as quadricyclene to norbornadiene and prismane to benzene and benzvalene. Further examples of related rearrangements are provided below (references are given in parentheses):



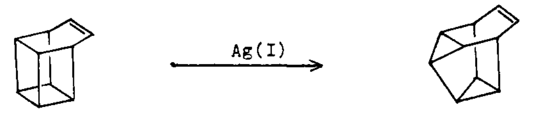
(61)



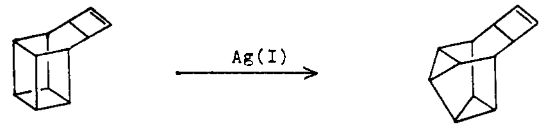
(62)



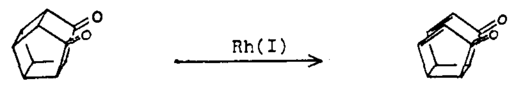
(56,63)



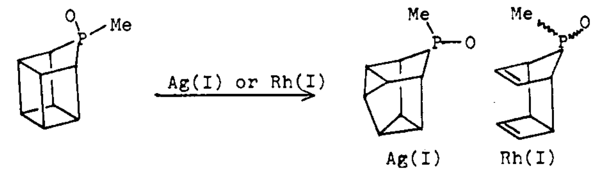
(56,63)



(64)



(65)



(66)

E. Summary

The evidence for the rearrangement of cyclobutenyl compounds thus falls basically into three types. The first is concerted ring opening of cyclobutyl complexes. While this possibility has been overly discussed from a theoretical viewpoint, little experimental evidence has evolved to support the concerted nature of these transformations.

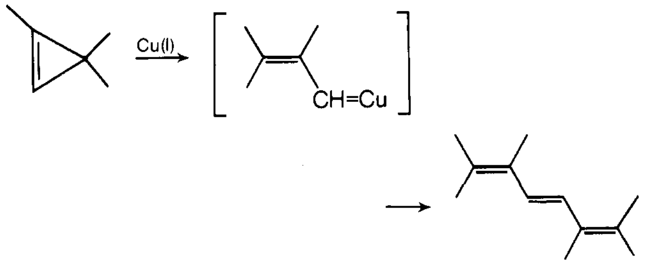
The second general mechanism, "the cheletropic mechanism", is initiated by oxidative addition to a cyclobutyl bond followed by a "cheletropic" cleavage to yield two olefins and regenerate the catalyst. Evidence for this reaction rests on (1) the trapping of the presumed intermediate as its carbon monoxide insertion product and (2) the demonstration that such a cheletropic decomposition is available for metallocycles. However, evidence is lacking which provides proof for the postulated intermediate and the nature of the "concertedness" of the metallocycle decomposition.

The third mechanism, the "Lewis acid mechanism", which entails a metallo-carbonium ion will be discussed in further detail in the following sections.

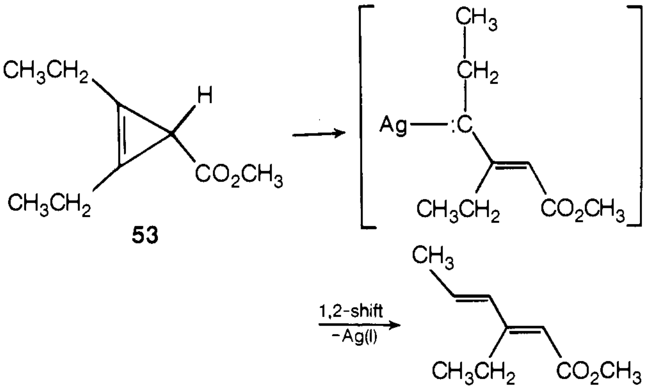
V. Unsaturated Compounds with Three-Membered Rings

A. Cyclopropene Isomerizations

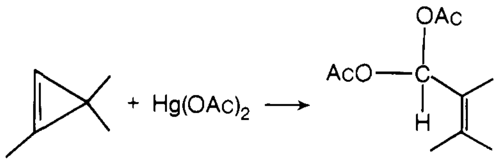
In 1964 Stechl[67] observed the copper(I)-catalyzed dimerization of tri- and tetramethylcyclopropene to an unexpected butadiene derivative. A metal-complexed carbene was postulated as an intermediate.



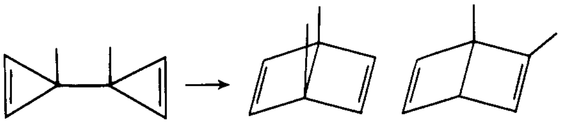
More recently, a series of cyclopropenes, e.g., **53**, were shown to be isomerized to a 1-carbomethoxybutadiene in the presence of Ag(I).[68] These authors also invoked a metal complexed carbene similar to those suggested for the dimerization of trimethylcyclopropene and the transition metal catalyzed rearrangement of bicyclo[1.1.0]butanes (vide infra), and implicated in the thallic acetate and mercuric acetate cleavage of 1,3,3-trimethylcyclopropene.[69]



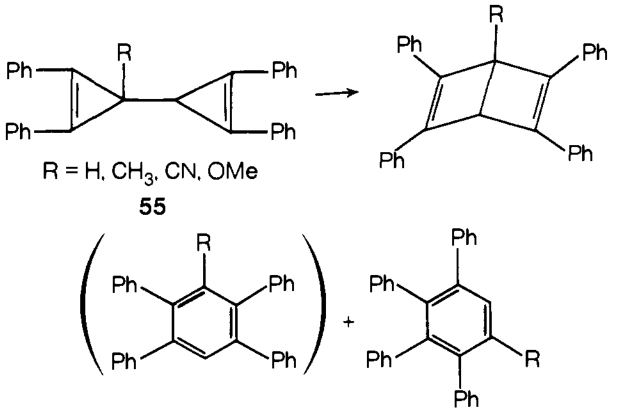
53



More thoroughly explored are a series of Ag(I)-catalyzed isomerizations of biscyclopropenyl compounds (**54** and **55**).[70-73]



54

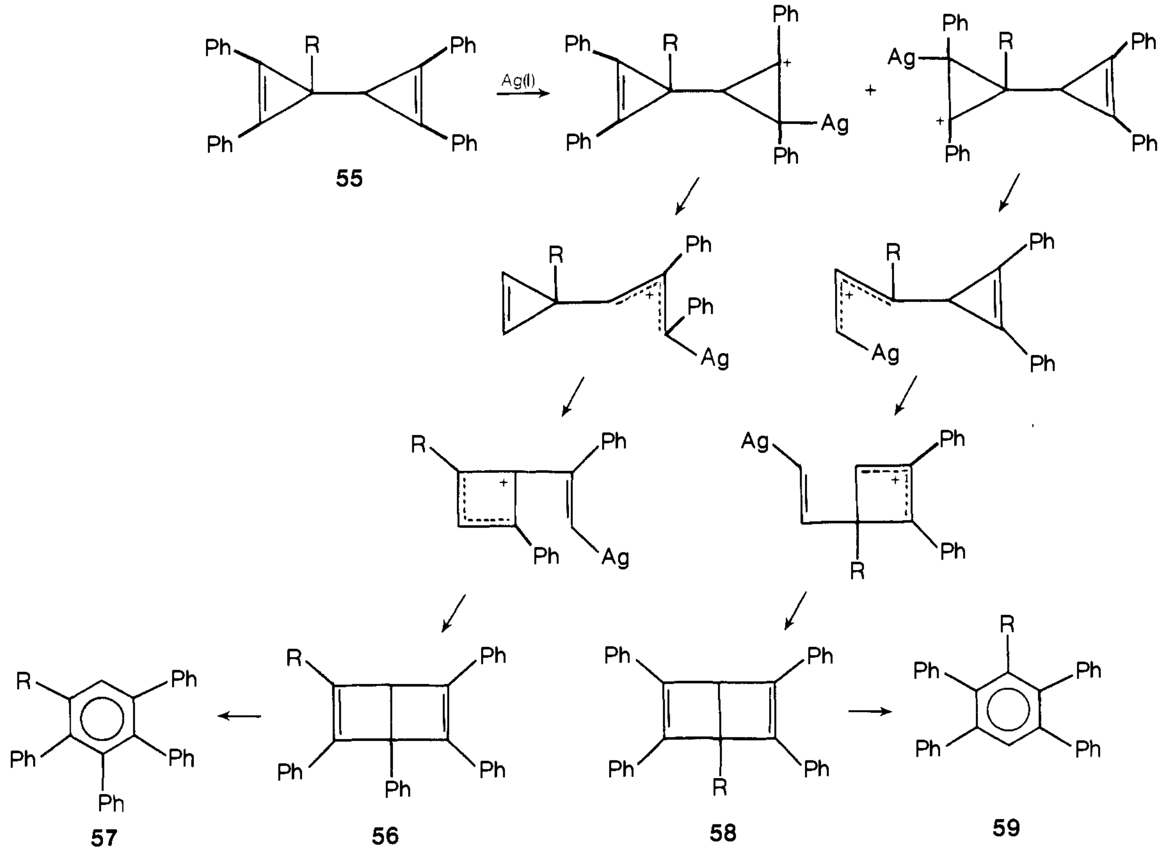


R = H, CH_3, CN, OMe

55

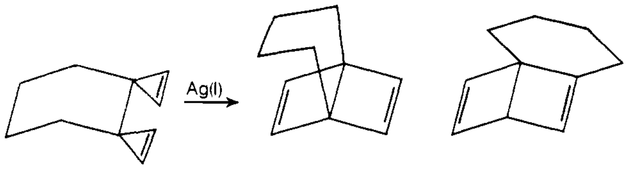
Andrae et al. have suggested the mechanism in Scheme IX for this unexpected transformation. When **55** was isomerized, **56** was found to rapidly isomerize to **57**, while **58** was more slowly isomerized to **59**, and therefore proved isolable. Support for the

SCHEME IX



proposed mechanism comes from (1) the isolation of both isomers in the rearrangement of **54** and (2) the effect upon the rearrangement of the substituent group "R". When R is hydrogen or methyl, the rearrangement proceeds smoothly at 50°; however, the introduction of a cyano substituent (R = CN) completely retards the reaction, even at 110°. As expected when R is a methoxy substituent, the rearrangement proceeds extremely rapidly at room temperature. As the mechanism predicts, in this case (R = OMe) the Ag(I) ion attacks exclusively on the substituted cyclopropene ring, generating the most stable allyl cation and leading only to products **58** and **59.**

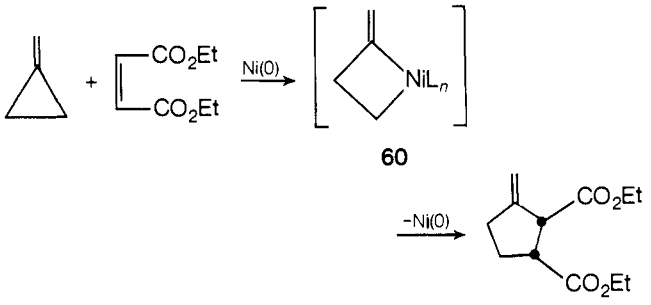
Landheer et al.[73] have demonstrated that this reaction also takes place when the cyclopropenes are cis-dispiro to a six-membered ring. Interestingly, the propelladiene product increased with increasing polarity of the solvent.



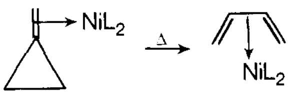
$CDCl_3$	0.20	1
DME	0.45	1
CD_3Cl	0.70	1
CH_3OH	0.78	1

B. Rearrangements of Methylenecyclopropane

Methylenecyclopropane has been shown[74] to rearrange in the presence of Ni(0) to butadiene. When olefinic ligands are present in solution, the intermediate **60** is trapped in a cycloaddition reaction.

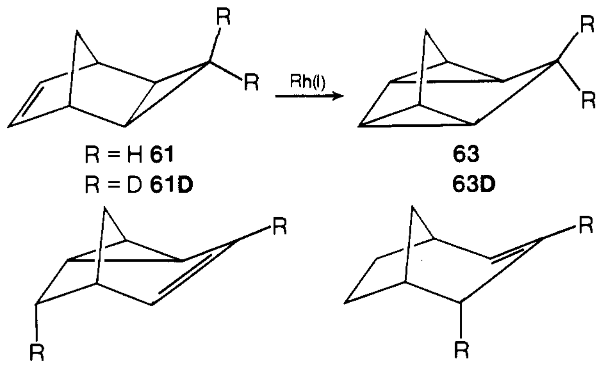


It may be assumed that Ni(0) first coordinates to the olefin before inserting into the σ bond. The rearrangement to butadiene has been shown by Wilke et al. to proceed through a metal–olefin complex.[74a]



C. Rearrangement of *exo*-Tricyclo[3.2.1.0^{2,4}] oct-6-ene

The transition metal catalyzed rearrangement of the tricyclooctene **61** has been studied by Volger and Hogeveen[75,76] and extensively by Katz and Cerefice.[77-80] In a series of communications, the latter investigators have carefully examined the mechanism of this rearrangement. Employing Rh(I) catalysts, different ratios of products were found depending upon the attached ligands. In addition, *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**62**) was found to be inert to metal catalysis. This is in striking contrast to the thermal rearrangement where **62** is rearranged approximately ten times more rapidly than the *exo*-tricyclooctene (**61**).[82]



R = H **61**
R = D **61D**

63
63D

64
64D

65
65D

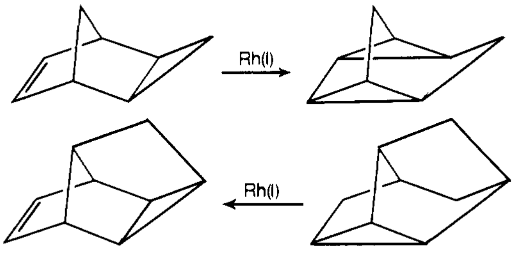
When a mixture of **61** and **61D** was treated with Wilkinson's catalyst (**4**), it was found[77] that both compounds were consumed at an identical rate. However, an examination of the products showed that **63D** was formed in larger amounts than **63** (the unlabeled isomer). This clearly demonstrates that an intermediate which is partitioned among the products is formed in the rate-determining step.

$$\begin{tikzcd} & & \mathbf{63} \\ \mathbf{61} + \mathrm{Rh(I)} \arrow[r, "k_{\text{rate det}}"] & [\mathrm{int}] \arrow[ur] \arrow[r] \arrow[dr] & \mathbf{64} \\ & & \mathbf{65} \end{tikzcd}$$

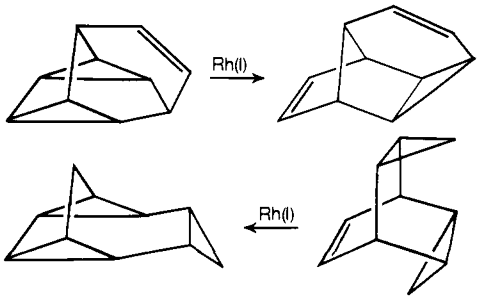
An NMR investigation[78,79] of the two remaining products showed the migrating deuterium was introduced only into the *endo* position in **64D** and **65D**. A mechanism[79b] which accounts for these observations is presented in Scheme X. The oxidative addition is rate determining. The product ratios are determined by the relative rate of hydrogen abstraction vs. olefin insertion. Product **65** is formed by a net 1,2-migration of the endo hydrogen via the intermediate allylrhodium hydride. The two other products, **63** and **64**, are the olefin insertion products from the oxidative addition intermediate (**66**) and the intermediate allylrhodium hydride (**67**). Such an allylrhodium hydride accounts for the endo stereochemistry of the migrated deuterium and is consistent with mechanistic conclusions reached in the metal-catalyzed rearrangement of bicyclo[2.1.0]pentane to cyclopentene (vide infra).

Katz and Cerefice[80] have also shown that there is a delicate balance of energetic factors which determine the facility of a compound toward rearrangement. It was found that with the introduction of a carbon bridge into **61**, the direction of the reaction was reversed; i.e., **68** now rearranged into **69**.

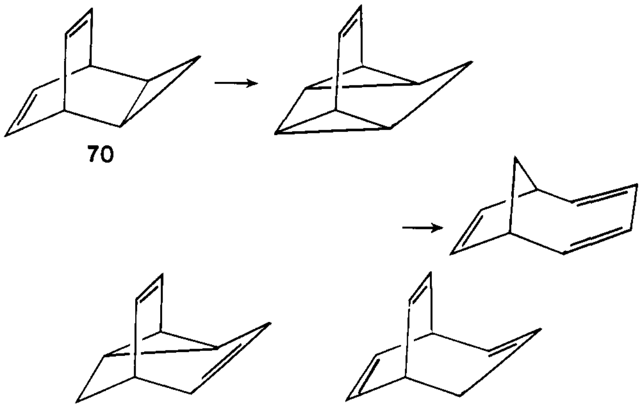
Other similar rearrangements have been observed by deMeijere and Meyer.[81] The first is analogous to the conversion of **68** to **69** observed by Katz,[80] the second to the conversion of **61** into **63**. Indeed, these rearrangements are delicately balanced by electronic and steric effect.



69 **68**



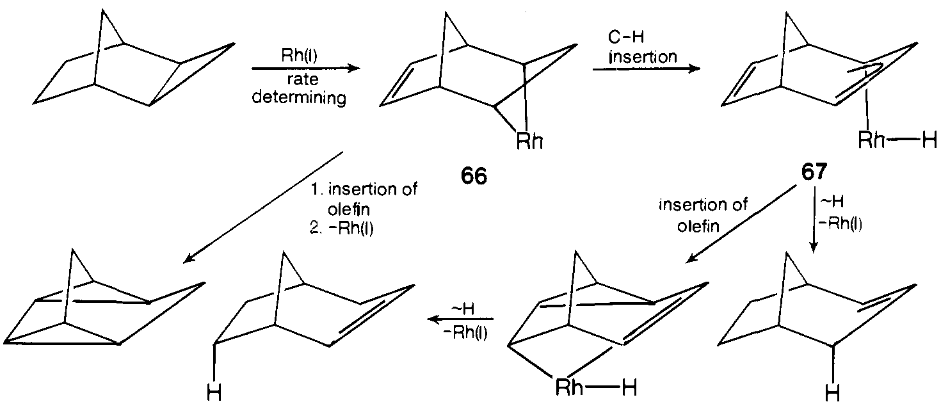
The Rh(I)-catalyzed rearrangement[79a] of **70** is, not unexpectedly, also closely related to that of **61**. The isolation of similar products suggests that this reaction proceeds via a mechanism very similar to that of **61**.



70

Volger and Hogeveen[75,76] have shown that treatment of **61** with Ir(I) leads to an entirely new product, **71**. Moreover, as in the case of Rh(I) complexes, they found that the endo analog (**62**) was inert to transition metal catalysis. This was also construed

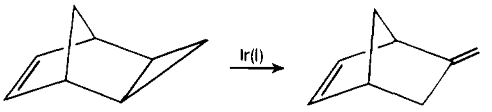
SCHEME X



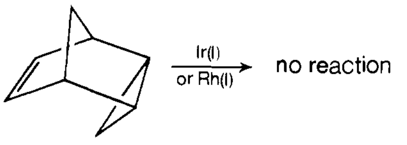
66
67

63 **64** **65**

as indicating the coordination of the catalyst was from the underside of the molecule. Thus, the cyclopropane bond is properly situated for metal binding only in **61**, but not in the endo compound **62**.

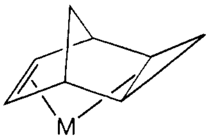


61 **71**



62

This view was enhanced by spectral identification and isolation, respectively, of a Rh(I) and Pt(II) complex of structure **72**. These complexes are analogous to the many transition metal complexes of norbornadiene.[83] In constrast, no complexation could be detected with **62**. It must be pointed out that the isolated complexes did not give further rearrangement.

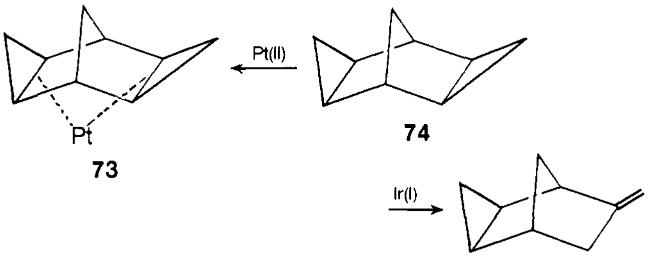


72

VI. Saturated Compounds with Three-Membered Rings

A. Tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane

A stable metal complex similar to **72** was also isolated[76] in a compound with no olefinic bonds. In this case, the complex **73** was formed by bonding to both *exo*-cyclopropanes of tetracyclononane **74**. As in the case of **61**, however, the complex failed to give further rearrangement.



73 **74**

Interestingly, **74** rearranged to a product analogous to the rearrangement product of **61** when Vaska's compound (IrCl(CO)[P(C$_6$H$_5$)$_3$]$_2$) was employed as the catalyst. Possibly, the high stability of the iridium-phosphorus bond to dissociation prevents the substrate from chelating, which in turn prevents insertion of the olefin (**61**) or cyclopropane (**74**) into the metal-carbon bond. For this reason the substrates react as isolated cyclopropane bonds.

B. Rearrangement of Bicyclo[2.1.0]pentane

Bicyclo[2.1.0]pentane (**75**) was shown by Gassman, Atkins and Lumb to rearrange[85] to cyclopentane when treated with [Rh(CO)$_2$Cl]$_2$. Wiberg and Bishop[86] have shown the rearrangement to be catalyzed by metals characterized by low electron affinities and promotion energies. In fact, while Rh(I) is an excellent catalyst at room temperature, soluble Ag(I) complexes fail as catalysts at 110°.

Further investigation has demonstrated that specifically labeled isomers of **75** rearrange to give product mixtures in which the label is scrambled. Gassman et al.[85] found that deuterium substituents were randomly distributed in the products. Also, addition of Rh(I) and **75** to a specifically labeled cyclopentene led to scrambling of the deuterium. In a control experiment, cyclopentene did not rearrange when **75** was withheld from the mixture.

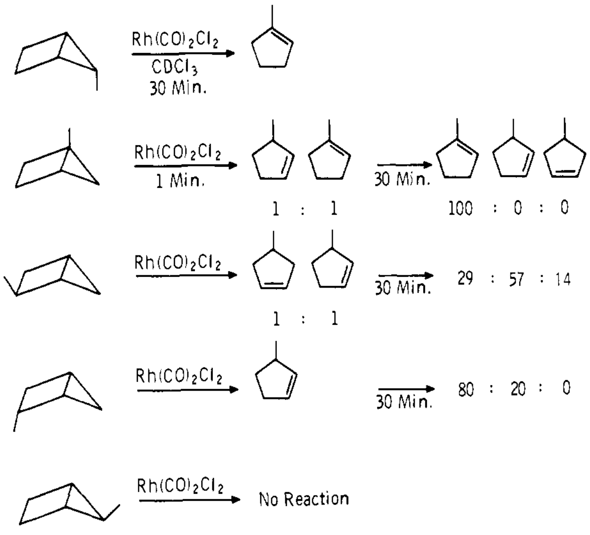
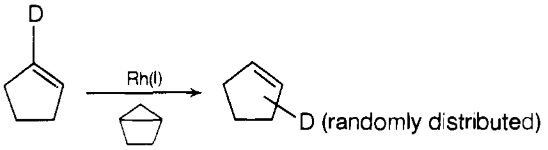


Figure 8. Products of the Rh(I)-catalyzed rearrangement of the monomethylbicyclo[2.1.0]pentanes.[84,86]

Wibert and Bishop[86] found that the employment of methanol-*O*-*d* as the solvent led to multiple deuterium incorporation into the product. Importantly, added olefins also incorporated deuterium.



The rearrangement of a number of substituted derivatives by Wiberg and Bishop led to an explanation of these results. Table VI presents the relative rates of Rh(I)-catalyzed isomerization of some substituted bicyclo[2.1.0]pentane derivatives. Aside from the electronic effect of an ester substituent, the most notable aspect is the lack of rearrangement with a 5-exo substituent.

The analysis of the products in the isomerization of the methyl derivatives offers further insight into the mode of rearrangement. The results are presented in Figure 8. The following experimental results have led to the hypothesis of an intermediate rhodium hydride and the reaction mechanism below.[86] This mechanism accounts for the lack of rearrangement with 5-exo-substituted derivatives. Abstraction of the 5-exo proton has been shown by deuterium labeling not to be rate limiting.[86] Therefore, as in the rearrangement of **61**, oxidative addition is presumed to be the rate-determining step. The stereochemistry of the addition has

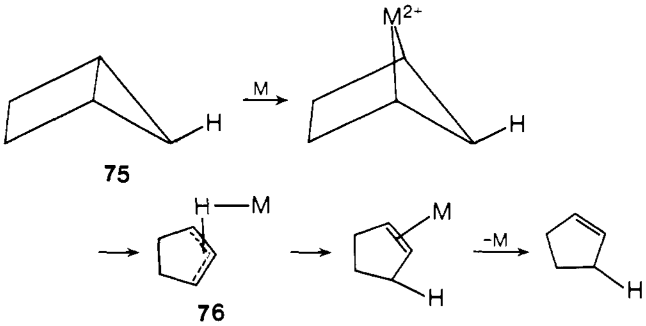
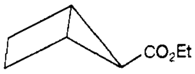
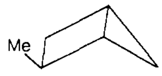
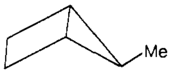
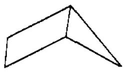
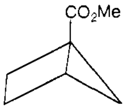
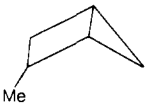
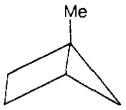
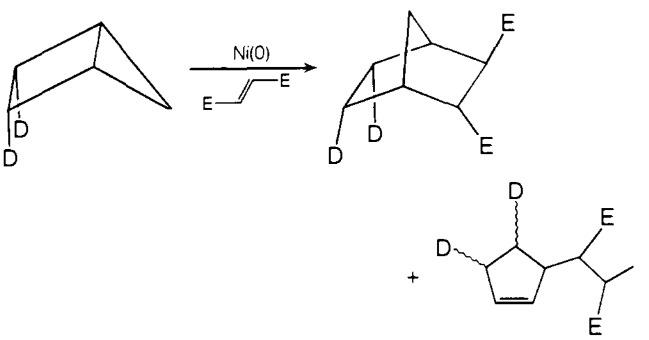


TABLE VI. Relative Rates of the Rh(I)-Catalyzed Rearrangement of Substituted Bicyclo[2.1.0] pentanes[86]

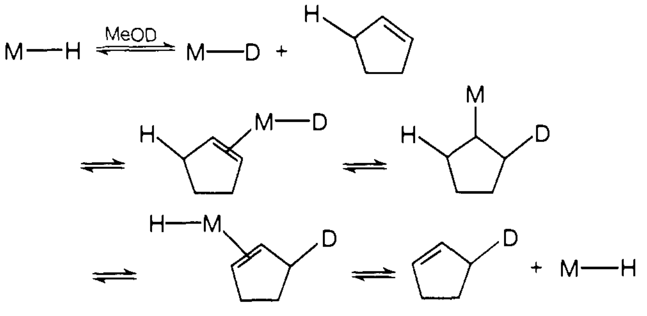
Compound	Rel rate	Compound	Rel rate
	No reaction		1.8
	No reaction		2.5
	Not > 0.025		3.3
	1.0		

received support from the laboratory of Professor Noyori.[87] Addition of activated olefins to bicyclopentane (**75**) has been shown to be predominantly on the exo face. The thermal addition has previously been shown to be predominantly from the endo face of the molecule.[88]

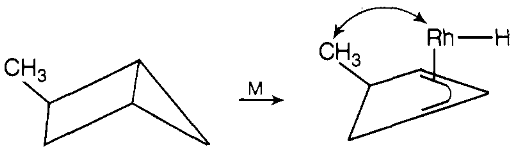


E = CO_2Me

Formation of **76** accounts for the further rearrangement of the product olefins, since metal hydrides are well known to catalyze olefin isomerizations.[89] In addition, these hydrides will exchange protons with methanol-*d*, yielding metal deuterides,[89] accounting for deuterium incorporation.

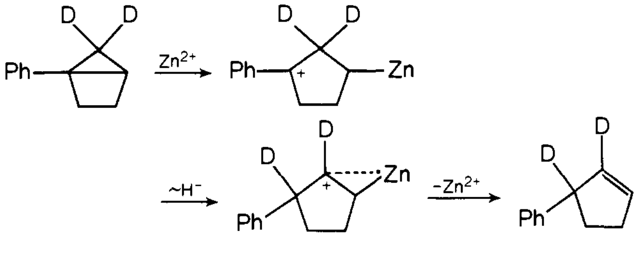


The small amount of isomerization in the rearrangement of *exo*-2-methylbicyclo[2.1.0]pentane (see Figure 8) is attributed to a methyl–metal steric interaction. Thus the short-lived **77** does not have the requisite stability for the multiple addition–eliminations which result in olefin scrambling. The other methyl derivatives yield metal hydrides of higher stability, therefore capable of further isomerizing the product olefins.

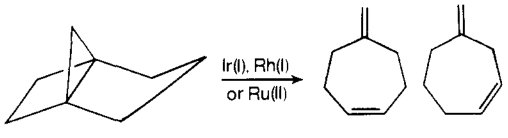


77

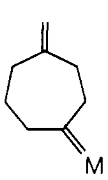
McKinney and Chou[90a] have provided an example of a Lewis acid catalyzed rearrangement of a bicyclopentane. They employed Zn(II) (very high promotion energy) with 5,5-dideuterio-1-phenylbicyclo[2.1.0]pentane.



Gassman and Armour[88] have shown that tricyclooctane (**78**) undergoes an entirely different reaction than **75**. The products from this rearrangement were explicable in terms of formation of the transition metal carbene complex **79**. Insertion of the carbene into each of the α hydrogens provides the observed products. Such metal-complexed carbenes have received much support in the transition metal catalyzed rearrangement of bicyclobutane and its derivatives (vide infra).



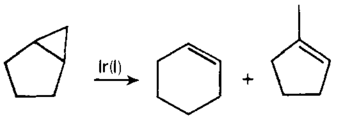
78



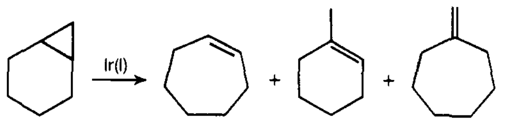
79

C. Related Examples

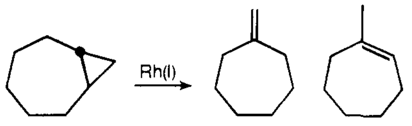
Other molecules possessing cyclopropyl moieties have been shown to undergo similar reactions. The results of these rearrangements suggest a mechanism similar to those of bicyclopentane (**75**) and tricyclooctane (**61**). The factors which deter-



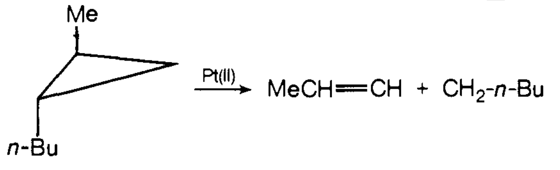
(84)



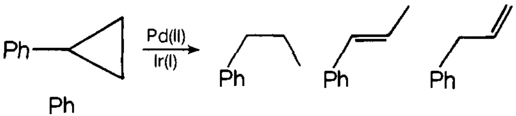
(84, 9a)



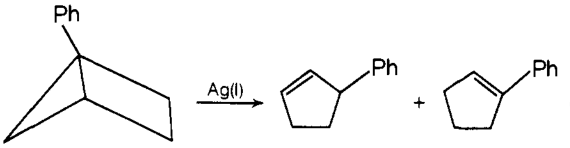
(84)



+ MeCH$_2$CH—CH-n-Bu (9a)



(84, 90b)



(90a)

mine the relative amounts of products and subsequent isomerization remain to be determined. It is clear, however, that ease of reactivity is related to the strain inherent in the substrate.[91]

D. Bicyclobutane Rearrangements

1. Introduction

No class of transition metal catalyzed rearrangements has been the subject of more controversy[92] than those of bicyclobutane. At the present time, it is possible to present only a general mechanistic picture which is consistent with the experimental facts. Therefore, in this section, a mechanism is put forth and then followed by the supporting facts. An attempt is also made to point out the possible pitfalls in the mechanistic scheme presented.

Moore's hydrocarbon tricyclo[4.1.0.0^{2,7}]heptane (**80**), is used as an illustrative example throughout this section. Simpler bicyclobutanes, primarily 1,2,2-trimethylbicyclo[1.1.0]butane (**84**) (see Figure 10) are also employed.

A mechanistic outline of the rearrangements undergone by bicyclobutanes in the presence of transition metals is presented in Figure 9. The nomenclature adopted is the anglicized version of that originally proposed by Paquette,[93] i.e. "paths A, B, C, D" as opposed to "paths α, β, γ, and δ". The products from these possible rearrangements are shown in Figure 10, where **84** is the substrate.

TABLE VII.[a] Effect of Catalyst on the Products of Moore's Hydrocarbon, 80

Catalyst	Mol % catalyst	Temp, °C, solvent	% 81	% 82	% 83
AgBF$_4$	0.45	40°, "minutes"	100		
ZnI$_2$	6.5	25°, Et$_2$O	88	11	
HgBr$_2$	9.0	50°, Et$_2$O	85	8	
[Rh(CO)$_2$Cl]$_2$	4.0	25°, CH$_3$-CN		98	
[Ir(CO)$_3$Cl]$_2$	5	25°, CHCl$_3$		91	
[π-CH$_2$=Ch-CH$_2$)$_2$PdCl]$_2$	1.2	25°, CHCl$_3$		94	
(PhCN)$_2$PdCl$_2$	5	25°, CH$_3$CN		69	
[C$_6$F$_5$Cu]$_4$	2	25°, CH$_3$Cl		74	
[(C$_6$H$_5$)]$_2$Rh-(Co)Cl	5	65°, CH$_3$CN		92	5
[Ru(Co)$_3$Cl$_2$]$_2$		25°, CH$_3$CN		44	12
PtO$_2$	5	65°, CH$_3$CN		62	24

[a] Taken from ref 96.

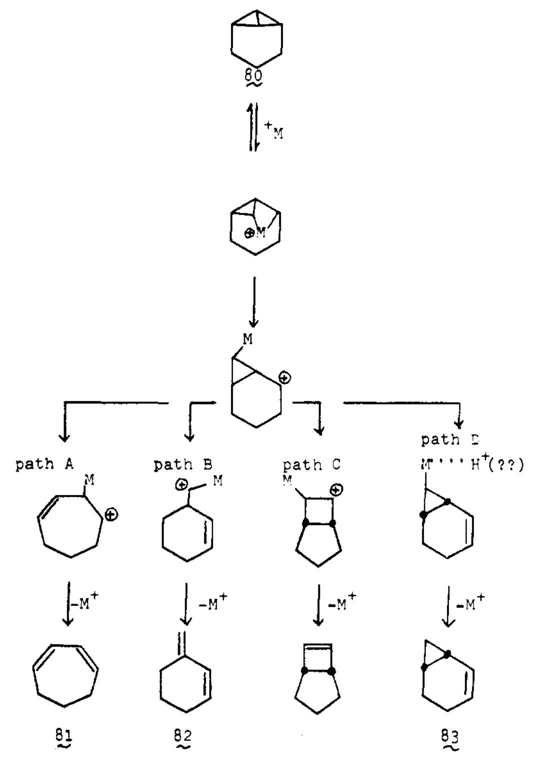


Figure 9. The general modes of the transition metal catalyzed rearrangement of Moore's hydrocarbon.

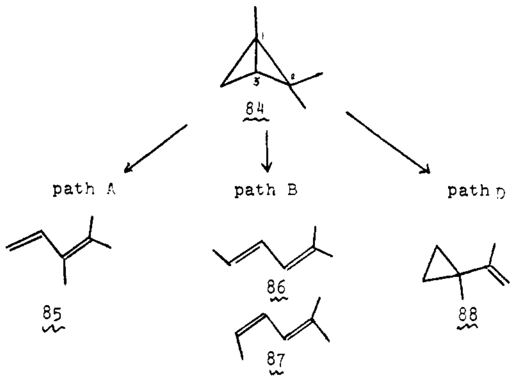


Figure 10. Rearrangement paths of 1,2,2-trimethylbicyclo[1.1.0]butane, assuming C2–C3 bond attack by the transition metal catalyst.

The estimated heats of reaction of the four modes of rearrangement find type A and type B greatly favored over type C and type D. Indeed, special conditions must be met for the type C rearrangement to take place (vide infra). To date, the type D rearrangement is relatively unexplored. Thus, the origin of products such as **83** remains unexplained, but an area requiring future study.

2. Effect of Catalyst and Reaction Conditions

The use of methanol as the solvent for the metal-catalyzed rearrangement of bicyclobutanes leads to methyl ether products.[94] It is now apparent that this is an acid-catalyzed addition of methanol to bicyclobutane. The source of this protonic acid is not well understood. However, it seems to be formed via at least two different processes.[95]

The effect of catalyst on the rearrangement products of Moore's hydrocarbon is presented in Table VII.[96] It must be cautioned that only general trends should be extrapolated from

TABLE VIII.[a] Products from the Transition Metal Catalyzed Rearrangement of 1,2,2-Trimethylbicyclobutane (84)

Catalyst	Mol % catalyst	% 85	% 86 and 87
$Rh(CO)[(C_6H_5)_3P]_2I$	3.0	100	
$PdCl_2(C_6H_5CN)_2$	0.2	20	80
$PdCl_2(C_6H_5CN)_2$	3.0	100	
$PdCl_2[(C_6H_5)_3P]_2$	0.3	60	40
$PdCl_2[(C_6H_5)_3P]_2$	3.0	100	
$PdCl_2[(C_6H_5)_3As]_2$	0.3	30	70
$PdCl_2[(C_6H_5)_3As]_2$	1.5	60	40
$PdCl_2[(C_6H_5)_3As)]_2$	3.0	100	
$PdCl_2[(C_6H_5)_3Sb)]_2$	0.3	15	85
$PdCl_2[(C_6H_5)_3Sb]_2$	3.0	35	65
$PdCl_2[(C_6H_5)_3Sb]_2$	6.0	100	
$PdCl_2(py)_2$	0.3	15	85
$PdCl_2(py)_2$	3.0	55	45
$PdCl_2(py)_2$	6.0	55	45
$AgBF_4$	3.0		100

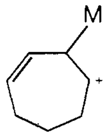
[a] W. G. Dauben, R. Gagosian, and A. J. Kielbania, Jr., unpublished results.

these data. This cautionary note is based on two facts: first, the systematic variation of catalyst and solvent is still lacking and, secondly, the product ratio varies with the concentration of catalyst (see Table VIII).

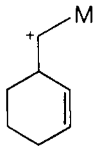
The latter complication has been neatly explained by Gassman, Meyer and Williams[97] who demonstrated that ligand exchange with the product leads to a new complex, exhibiting a different selectivity from that of the original complex. It would thus appear that in future experiments, successively larger mole percents of catalyst should be used until a constant ratio of products is obtained, e.g., $PdCl_2(py)_2$ in Table VIII. This will ensure as much as possible the integrity of the catalytic species.

The path of rearrangement is clearly dependent upon the catalyst, both metal and attached ligands. As seen with cubane isomerizations, Ag(I) and Rh(I) are at opposite ends of the spectrum, the former leading to path A and the latter to path B products.

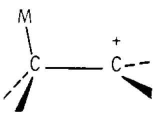
An examination of the two precursors leading to the type A, **89**, and type B, **90**, products yields a clue to the selectivity of the catalyst. In a metallocarbonium ion such as **89a**, stabilization of the carbonium ion must be via a three-center, two-electron bond as pictured in **91a**. In the molecular orbital formalism, **91a** is a resonance contributor to a metal-complexed olefin, **91b**.



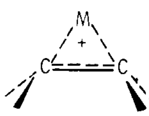
89



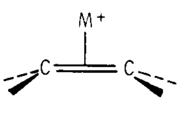
90



89a

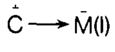


91a



91b

This, moreover, clearly requires movement of the metal to become symmetrically bonded. With an ion such as **92a**, this mode of stabilization is no longer possible. Rather, stabilization may be rendered via back-donation into the vacant p orbital of what

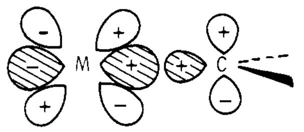


92a

92b

92c

is essentially a metal-complexed carbene. Such a scheme of bonding has been proposed by Noyori[98] and is pictured below.

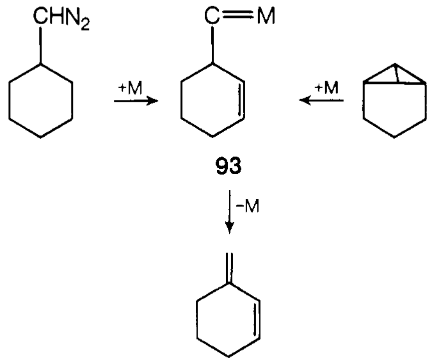


In his description, the lone pair electrons of the singlet carbene are donated to a vacant metal orbital of appropriate symmetry. Simultaneously, the metal donates electrons from a d orbital into the vacant p orbital of the carbene. Thus, the degree of donation–back-donation determines the ionic character of metal–carbene bond as portrayed in **92a** → **92c**.

The selectivity of the catalyst then is determined by the stabilities of **89a** and **92a**. The following rationale predicts the mode of reaction. If the catalyst has a low electron affinity, e.g., Pd(0), the form **92a** is favored over **89a**, for the metal can donate electrons (directly via the metal–carbon π bond) to the carbonium ion center. With catalysts of higher electron affinity which function as electron acceptors via the σ bond, the determining factor is the promotion energy of the catalyst. Those catalysts with large promotion energies are not capable of back-bonding and prefer to form the β-metallo carbonium ion in which the metal is insulated from the cationic site, and thus receives "more" electron density via σ donation.[99] In contrast, catalysts possessing large electron affinities, but low promotion energies, favor the metallo-carbonium ion **92**. Although in this case the metal is bound directly to what must be a very poor σ donor, the synergistic bonding leads to a relatively more stable metal–carbon (i.e., carbene) bond.

Evidence for the intermediacy of such metal complexed carbenes is extensive and quite convincing.

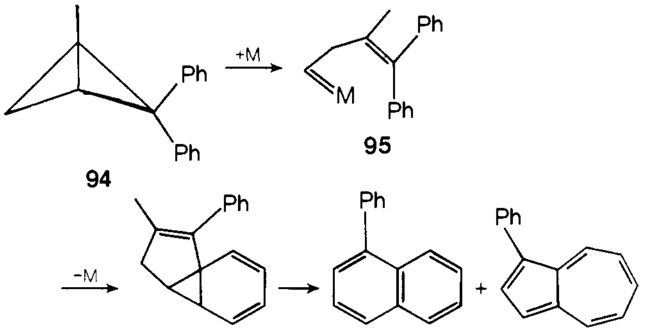
Masamune,[100] Gassman,[96,101] and Paquette[102] have shown that diazoalkanes decomposed by transition metals lead to the same products as found in the path B rearrangements of bicyclobutanes. Presumably, the product arises from the same intermediate, i.e., the metallocarbene **93**. However, in the Ag(I)-catalyzed decomposition of diazoalkanes, the path B product is still formed. This demonstrates that for this catalyst a pathway other than that followed in the rearrangement of bicyclobutanes is operating.



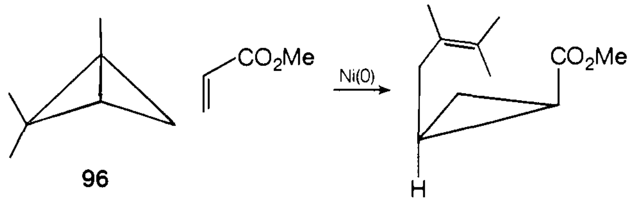
82

The most conclusive proof of metallo-carbenes comes from trapping experiments. Gassman et al.[103] found that decomposition of 1-methyl-2,2-diphenylbicyclobutane (**94**) led to products best described as originating via intramolecular attack of the intermediate metallo-carbene **95**.

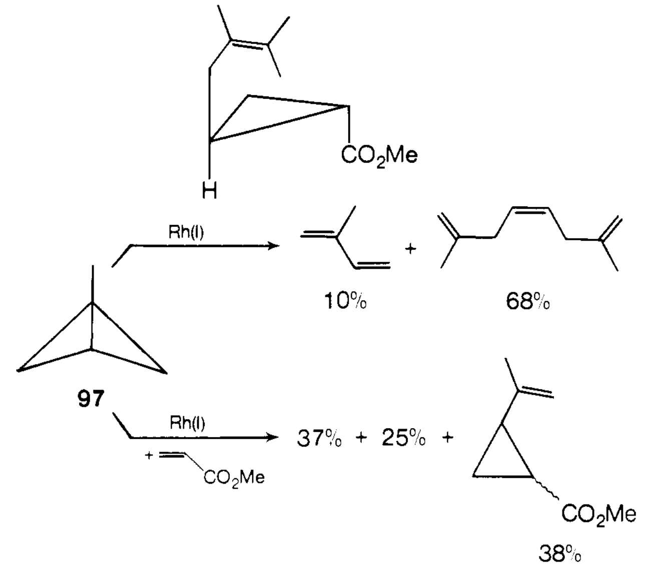
Noyori[104] has provided good evidence of intermolecular capture of an intermediate carbene in the decomposition of **96**. Similarly, Gassman and Reitz[105] have trapped the metal complexed carbene during the rearrangement of 1-methylbicyclobutane (**97**). In the absence of added olefin the major product is a dimer, similar to that observed by Stechl.[67] But, in the presence of methyl acrylate, carbene addition products are observed.



94 **95**

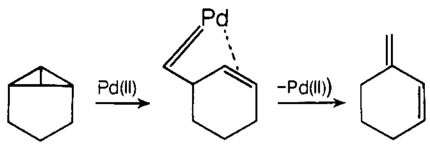


96



97

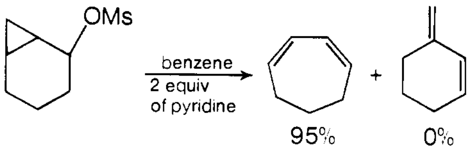
Finally, Dauben and Kielbania[106] have observed, by NMR, an intermediate which they believe to be the metallocarbene **98** in the palladium(II)-catalyzed rearrangement of Moore's hydrocarbon (**80**). This intermediate was shown to decompose to the normal path B product, methylenecyclohexene (**82**).



80 **98**

Thus, the hypothesis of an intermediate metallocarbene in the path B isomerization is well founded. Detection of a primary complex, which then partitions among the various paths, has not, however, been accomplished.

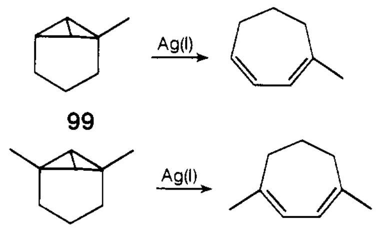
The intermediacy of a metallo carbonium ion in path A is supported by the work of Masamune et al.[107] Generation of the carbonium ion by solvolysis led to the expected type A product, with none of the type B product. In this case, the product is formed with extrusion of a proton instead of the metal ion expelled in the catalyzed rearrangement. Further evidence for a carbonium ion pathway has accumulated from the rearrangement of substituted bicyclobutanes (vide infra).



While solvent effects would be expected to offer valuable information on the intervention of a carbonium ion intermediate, no complete study has yet appeared. Paquette did accumulate some comparative rate data; however, it offered little insight into the mechanism (see section 6). An experiment employing a catalyst which yielded ca. equal amounts of path A and path B products in different solvents might prove very beneficial (as it did indeed in the cubane isomerization).

3. Effect of Substitution on Products of the Rearrangement of Moore's Hydrocarbon

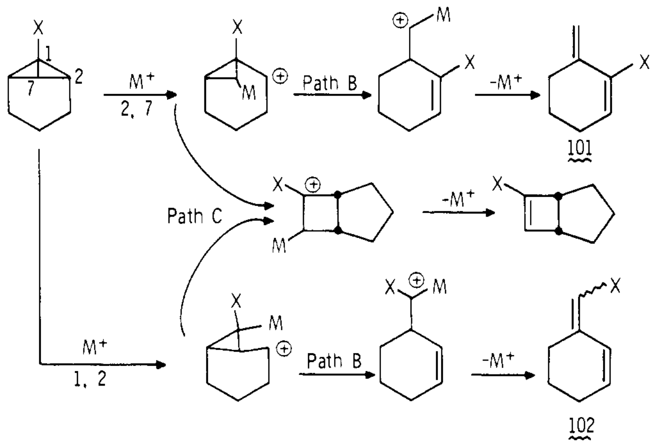
In the rearrangement of Moore's hydrocarbon to cycloheptadiene, the type A rearrangement, a carbonium ion is generated at carbons 2 and 6 of the original molecule. Clearly, substitution of a stabilizing group at these positions will enhance this reaction. Thus, both **99** and **100** lead only to type A products with Ag(I) as the catalyst. Indeed, the rate of isomerization is moderately accelerated (vide infra).



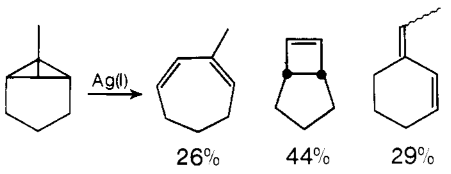
99

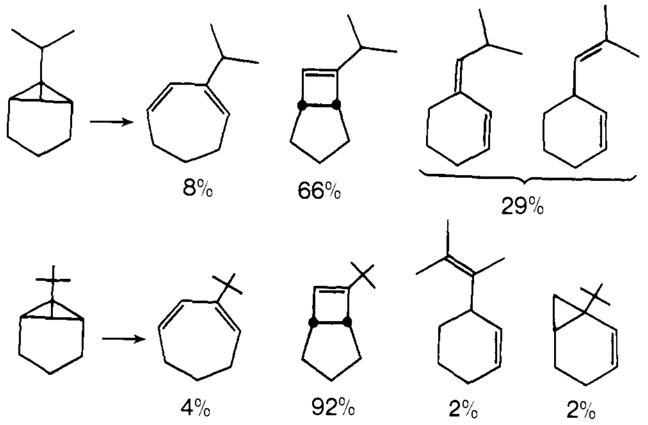
100

Substitution at the one position, however, leads to a more complicated scheme. Attack of the metal catalyst may now occur at either the 1,2 or 2,7 bond of the substrate. As seen below, these different directions of attack can lead to two different path B products **101** and **102** and the path C product. Ostensibly, the driving force for these pathways is formation of the tertiary carbonium ions. Thus, substitution at the one position favors type B and C products at the expense of the type A product.

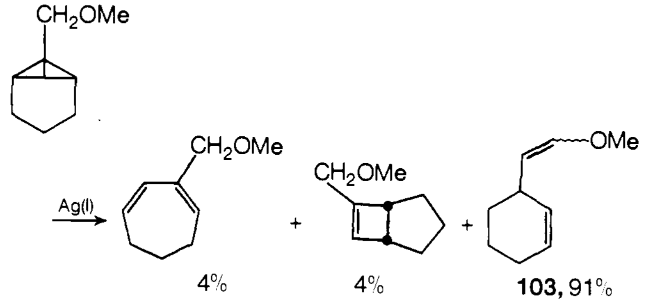


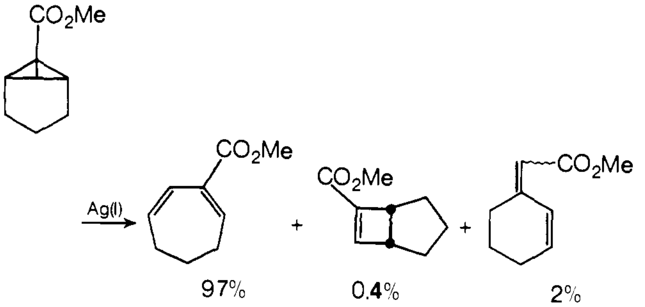
A steric effect appears to be operating as the substituent at the one position grows larger. This leads to more path C product with catalysts such as Ag(I), which possess large promotion energies and electron affinities. For example, Ag(I) leads to the following product distribution.[93]



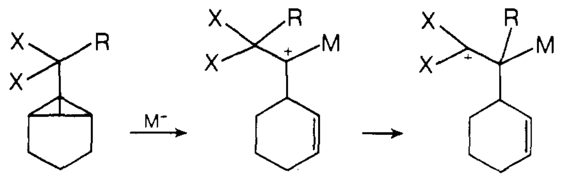


Other variations occur when the group at the 1 position can trap the carbonium ion, or is an electron-withdrawing group. In the former case, new products arise, while in the latter case the type A rearrangement becomes dominant.[93,108]





It is assumed that **103** arises through hydride shifts leading to the more stable carbonium ion. Since, isopropyl substitution also gives this type of product and since a methyl group migrates when the substituent is *tert*-butyl, this appears to be a general reaction whenever carbonium ion stabilization can be enhanced. Consequently, Paquette has designated this rearrangement type B.



Unfortunately, only a 1-methyl substituent has been employed with Rh(I) as the catalyst. In contrast to Ag(I), Rh(I), apparently less prone to attack the more electron-rich 1,2 bond, attacks the 2,7 bond which leads to only the "other" type B product, **101.** It is unfortunate that other investigators have not, as yet, systematically studied their catalysts as Paquette has done with Ag(I).

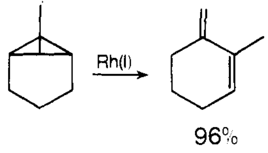
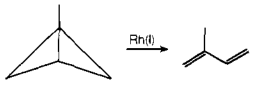
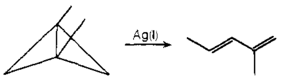
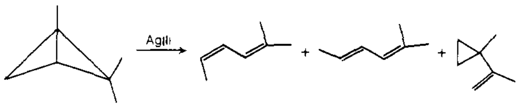
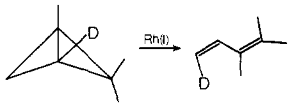
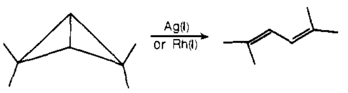
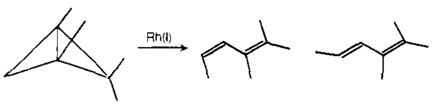
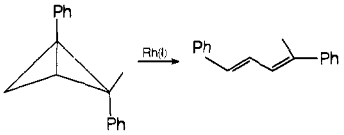


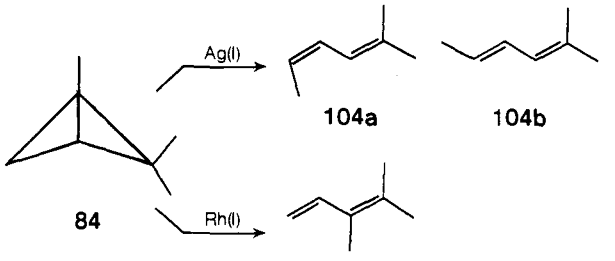
TABLE IX.[a] Transition Metal Catalyzed Isomerizations of Some Substituted Bicyclobutanes

	(84)
	(109)
	(109)
	(101)
	(109)
	(101)
	(109)

[a] Numbers in parentheses refer to references in the text.

4. Effect of Substitution on Other Bicyclo[1.1.0]butanes

Table IX shows the various rearrangement products of other substituted bicyclobutanes. Unfortunately, differentiating the possible modes of rearrangement is rarely possible without further labeling. For example, **84** gives different products with

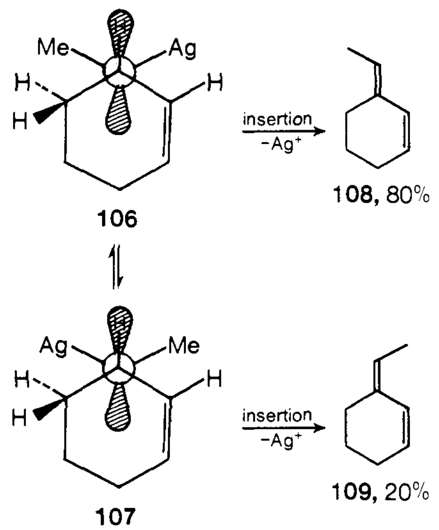


Ag(I) and Rh(I), **104** and **105,** respectively. But deuterium labeling[101] and intermediate trapping[105] studies were necessary to determine the path of the Rh(I) rearrangement. It is clear, however, that the products are those expected from the metallocarbene, and cyclopropylcarbinyl pathways as discussed for Moore's hydrocarbon.

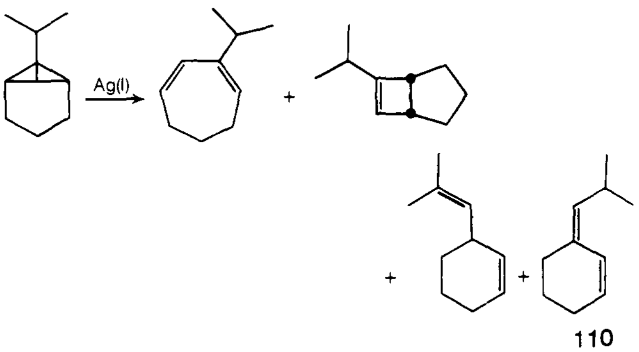
5. Stereospecificity in Bicyclobutane Rearrangements

The type A rearrangement of Moore's hydrocarbon cannot yield stereochemical information. However, the type B, C, and D rearrangements are suitable for stereochemical studies of the products.

In the type B rearrangement, the analysis must account for the ratios of syn and anti substituents in the product ethylidenecyclohexenes. With Ag(I), this may be ascribed to the relative populations of the two rotamers **106** and **107** which lead to the two products **108** and **109,** respectively. In this scheme the two rotamers exist in equilibrium, with **106** slightly favored. This rotamer may be favored because the steric interaction of

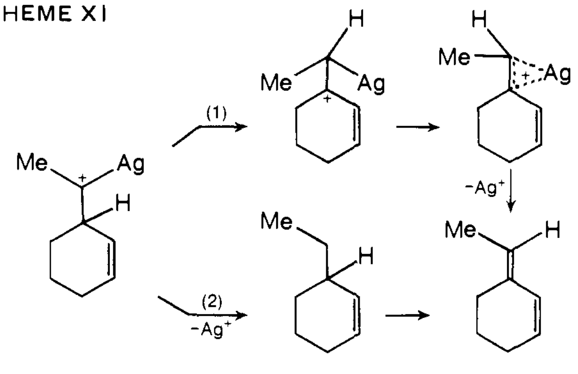


the silver atom with the syn-5 hydrogen is larger than that between the methyl group and the same syn-5 hydrogen. A clue that this is the case comes from Ag(I)-catalyzed isomerization of 1-isopropyltricyclo$[4.1.0.0^{2,7}]$heptane where the only type B product is **110.** In this case, the steric interaction between the silver atom and the syn-5 hydrogen is *less* than between the isopropyl group and the syn-5 hydrogen.

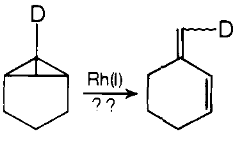


The insertion can be viewed as either (1) a hydride shift followed by metal decomplexation with olefin formation, or (2) by metal decomplexation to yield a free carbene, which then inserts to form the olefinic bond (Scheme XI). At the present time, it is not possible to distinguish between the two pathways.

SCHEME XI

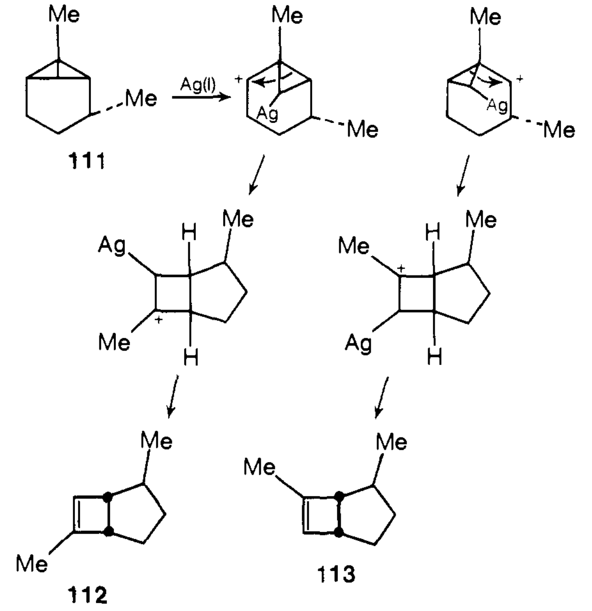


An interesting experiment which would shed further light on the intricacies of the type B rearrangement is pictured below.



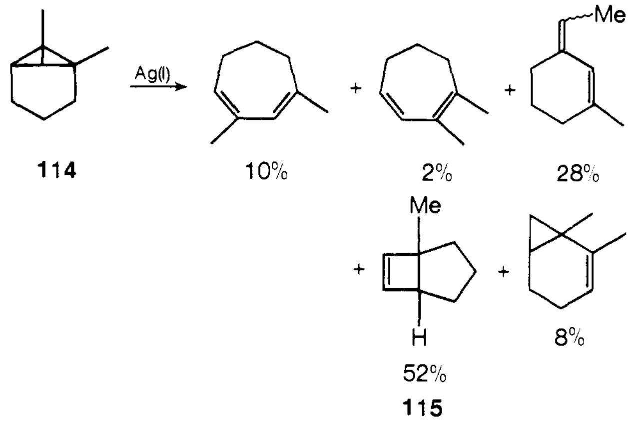
In such a case it would be expected that there would exist a preponderance of a single rotamer and thus lead to only one product. If, however, the intermediate carbene exists long enough for rotation to occur, a mixture of isomers would be expected. Such an experiment would give an important clue to the nature of the intermediate and its formation.

SCHEME XII



The type C rearrangement has proven rich in stereochemical detail. Paquette and Zon[110] have carefully investigated the effect of substitution upon this rearrangement. Their results are presented in Table X and are explicable in terms of the general mechanistic scheme shown earlier. The specific case of 1,3-*cis*-dimethyl Moore's hydrocarbon, **111**, is illustrated in Scheme XII.

The first important point is that the ratio of the products **112** to **113** is determined by the ratio of 2,7 to 6,7 bond attack by the Ag(I) electrophile. The ratio of these attacks depends primarily on the electron density in these bonds as modified by the 3-substituent, e.g., Me *vs.* OMe, and possibly a slight steric interaction. The steric interaction is best illustrated by the 1,2-dimethyl substituted Moore's hydrocarbon **114**, which leads only to the type C product **115** resulting from initial 6,7 bond cleavage.[111]



Attack at the 1,2 or 1,6 bonds leads to the expected type A and type B products.

In the simple bicyclobutanes, stereospecificity has been demonstrated by the groups of Paquette[109] and Masamune.[112] While the specificity is clear for Ag(I) catalysis, it appears diminished when Rh(I) and Pd(II) catalysts are employed.

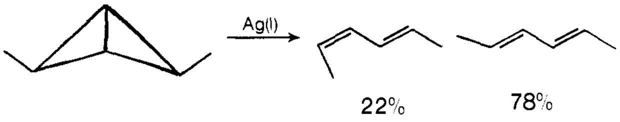
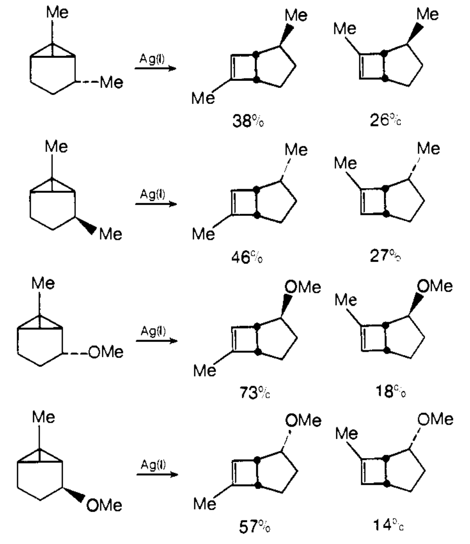
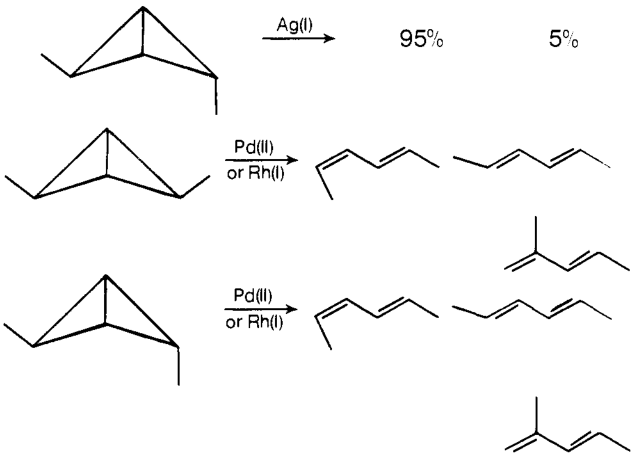


TABLE X.[a] Silver(I)-Catalyzed Type C Rearrangements of 2-Substituted-1-methyltricyclo[4.1.0.0^{2,7}]heptanes



[a] Taken from ref 110.

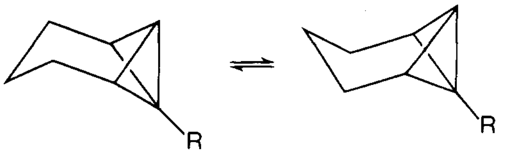


6. Kinetic and Isotopic Studies

Paquette and his colleagues have amassed a large body of kinetic data on the Ag(I)-catalyzed rearrangements of bicyclobutanes. Table XI is a compendium of much of their data.

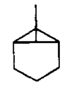
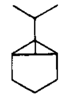
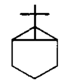
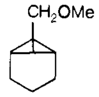
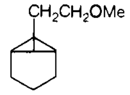
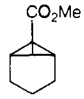
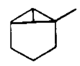
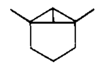
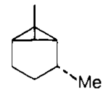
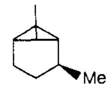
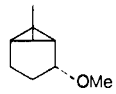
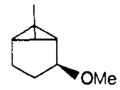
It is clear from a cursory analysis of Table XI that the results cannot be explained in only electronic terms. Indeed, an attempted analysis similar to those of cubane (vide supra) fails completely. A steric effect is operating, and indeed is equal in importance to the electronic effect of the substituent.

The magnitude of the steric effect is best evidenced by the series of 1-alkyl-substituted derivatives of Moore's hydrocarbon. Substitution of a methyl group leads to an increase in rate due to the group's electron-releasing properties relative to hydrogen. However, as the groups become larger, the rate decreases, falling off very dramatically for *tert*-butyl substitution. Paquette suggests this arises from hindrance induced by shifting the equilibrium **116A**/**116B** toward **116B**. This blocks attack of the catalyst not only at the 1,2 bond by the bulk of the substituent, but also attack at the 2,7 bond through the shifting of the equilibrium.



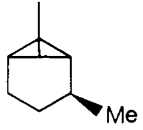
116A 116B

TABLE XI.[a] Rates of Isomerization of Substituted Bicyclobutanes

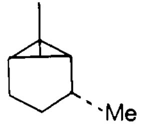
Compound	Initial rates of isomerization, k_{Ag}, M^{-1} sec^{-1}	Rel rate
	2.27 x 10^{-3}	1
	5.7 x 10^{-3}	2.51
	2.14 x 10^{-3}	0.94
	1.31 x 10^{-4}	2.96
	6.71 x 10^{-3}	2.96
	3.35 x 10^{-3}	1.48
	3.75 x 10^{-6}	0.0017
	2.26 x 10^{-2}	10
	5.56	2450
	7.25 x 10^{-3}	3.19
	3.31 x 10^{-3}	1.46
	5.12 x 10^{-4}	0.23
	2.30 x 10^{-4}	0.10

[a] Taken from ref 108 and 110.

The steric effect is also manifested in the rates of rearrangement of **117** and **118**. Here again, the hindrance to the opposite side of the molecule blocks 2,7 bond attack.

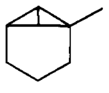


117

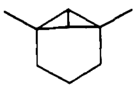


118

Electronic effects are most dramatically demonstrated with the carbomethoxy substituent. Here, the rate falls off dramatically as it does in the case of carbomethoxy substitution on molecules rearranged by transition metals (vide supra). Further support comes from rates of the 2-methyl- and 2,7-dimethyl-substituted derivatives **119** and **120** which exhibit acceleration of 10 and



119



120

2450, respectively, in their rates of isomerization. It is surprising that two methyl groups lead to a rate much greater than that expected from the monosubstituted derivative. This may indicate a change in the rate-determining step.

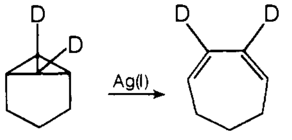
A possible explanation of this comes from Paquette's careful kinetic analysis of the rearrangement of Moore's hydrocarbon (**61**).[113] He has demonstrated than an equilibrium between catalyst and substrate (**80**) precedes the rate-determining step. The kinetics correspond to the scheme shown below, where k_2 is rate determining.

$$\mathrm{Ag^+ + substrate} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ag\text{-}substrate} \xrightarrow[-\mathrm{Ag^+}]{k_2} \mathrm{product}$$

The dimethyl substitution may have greatly increased both the amount of complex, as well as the absolute rate of k_2. It is in fact possible that the rate of complexation may become rate determining if the substitution has greatly lowered the rate of k_{-1}. In such a case, the reaction may approach a concerted rearrangement.

Paquette's group has also provided a wealth of kinetic deuterium isotope effects on the rate of isomerization. These studies are consistent with a mechanism initiated by edge bond attack.

Compound **121** isomerizes to cycloheptadiene with an inverse isotope effect of 0.847.[114] This is attributed[114] to the change from 40% s to 30% s character in the intermediate edge bound complex. Such an isotope effect is a general phenomenon whenever the rate of disappearance of starting bicyclobutane is considered. This is probably associated with the rate of attack to form the metal–substrate complex.

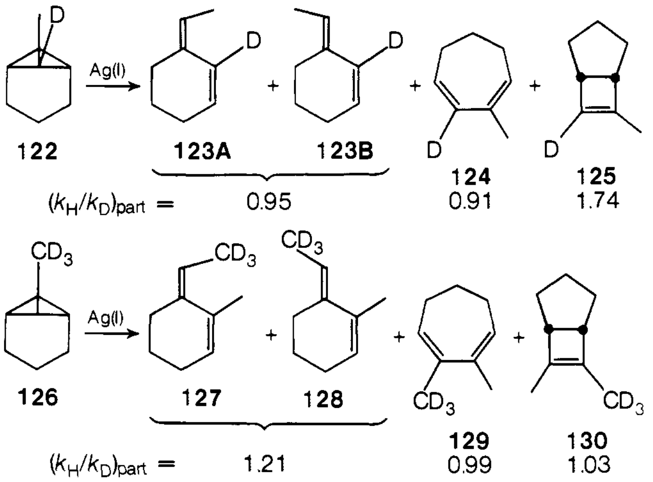


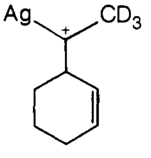
$k_H/k_D = 0.847$

121

The rearrangements of labeled 1-methylbicyclobutanes, **122** and **126**, are interesting when considered together (Scheme XIII). The effects must be viewed, however, as a product of both complexation (small and negative) and a partitioning effect, $(k_H/k_D)_{part}$, between the different products. This is similar to that observed by Katz in the rearrangement of tricyclooctanes **61** and **61D**. Again, there is an inverse isotope effect associated with complexation either at the C1–C2 bond or the C2–C7 bond. However, the *fractionation* to form the ethylidenecyclohexenes is affected noticeably. The trideuterio-substituted **126** shows a large positive partitioning effect, the result of a contribution from **131**. As expected, there is *little* deuterium induced perturbation for the formation **129, 130** from **126** or **123A, 123B** from **122.**

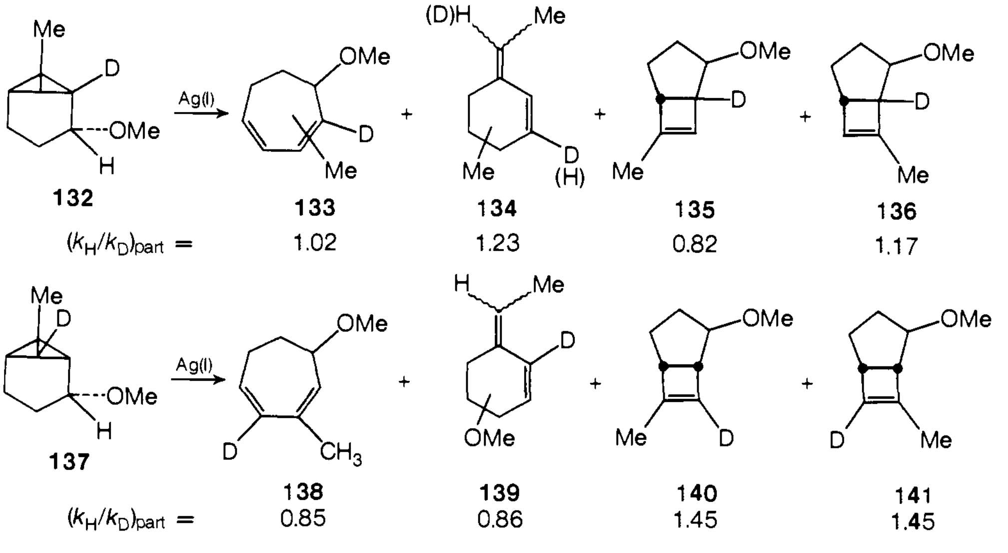
SCHEME XIII





131

The anomaly in these results is the large effect found in the formation of type C product, **125.** Insight into this effect can be gained from the isotopic studies performed on **132** and **137.**[108] The formation of type A (**133** and **138**) and type B (**134** and **139**) products is again consistent with edge bond attack followed by subsequent rearrangement. The formation of the type C rearrangement products also shows a large positive isotope effect when the deuterium is substituted on the bond which is attacked. In contrast, **135,** which is formed by attack at the C6–C7 bond of **132,** shows negative isotope effect. These results indicate an unusually large isotope effect is present when the type C rearrangement is induced by attack at a deuterium substituted bond. The exact nature of this large effect is not yet clear, but at the present remains a characteristic of the type C rearrangement.

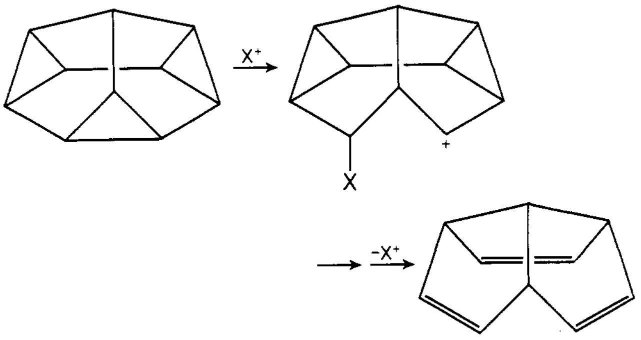


7. Summary

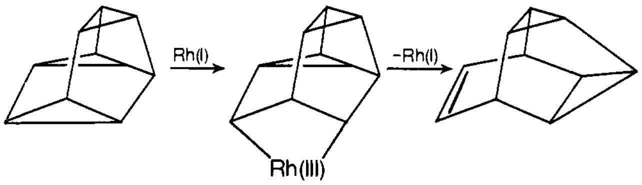
Thus, the rearrangement of bicyclobutanes can be viewed as presented in Figure 9. The relative rates and partitioning between the different paths depend heavily on the substitution present in the molecules.

E. Rearrangements of Diadamane

Diadamane, like cubane, undergoes two different rearrangements depending on the nature of the transition metal catalyst.[115] Both gaseous HCl and silver perchlorate in benzene lead to triquinacene via an acid mechanism. In fact, when employing silver(I) in methanol, a methyl ether was the product. In contrast Rh(I) catalyzes a rearrangement similar to that of quadracyclene and those described in section V.C.

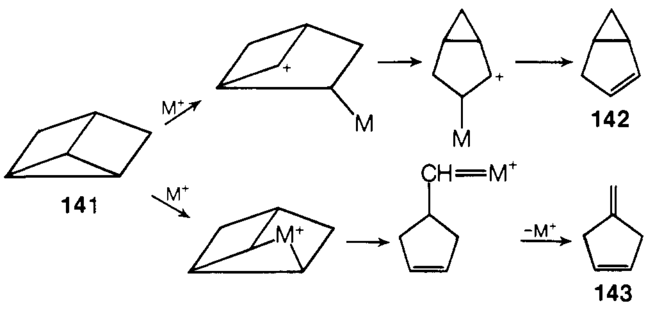


$X^+ = Ag^+$ or H^+



F. Rearrangement of Tricyclo$[2.2.0.0^{2,6}]$hexane

Roth and Katz[116] have demonstrated that the rearrangement of tricyclo$[2.2.0.0^{2,6}]$hexane (**141**) proceeds smoothly in the presence of transition metal catalysts. As in the rearrangements of bicyclobutane the products are explicable in terms of metallo carbonium ion and a metal-complexed carbene. As expected, Ag(I) favors formation of **142**, while Rh(I) leads predominantly to **143**.



G. Summary

Three general modes of transition metal catalyzed rearrangement have been demonstrated for cyclopropyl or cyclopropenyl compounds. The first, which is also an important mechanism for cyclobutyl compounds, is the "Lewis Acid" mechanism. It involves an intermediate metallo carbonium ion which undergoes further rearrangement to yield the final products. Evidence for such a mechanism comes primarily from solvent and substitution effects.

The second general mechanism is generation of a metallo carbene complex which inserts or dimerizes to yield the final products. This path is well established from the trapping and spectral identification of the intermediate carbene complex.

The third mechanism occurs with a net 1,2-migration of a hydrogen atom. An intermediate metal complex with the cyclopropane forms an allylmetal hydride complex by inserting into a carbon–hydrogen bond. This complex then decomposes to yield the product. Evidence for this mechanism comes from kinetic studies demonstrating an intermediate and substitution studies which are compelling for the intermediacy of a metal hydride.

A fourth mechanism, though less common, is also possible. In this mechanism, an oxidative addition intermediate is also formed. This intermediate then may insert an olefin or (as in the four-membered ring case) decompose cheletropically.

VII. Conclusion

The growth of this new field has been rapid. This review has sought, in a timely manner, to point out the generality of the mechanisms emerging in the transition metal catalyzed rearrangements of small ring hydrocarbons. Admittedly, there are many gaps remaining to be filled, but the outline of this emerging field has been set.

VIII. Addendum

The interaction of cyclopropane rings with transition metals is continuing to be investigated. Rettig et al.[117] have shown another case where a cyclopropane is bound to a metal and freed to again yield a cyclopropane. Notably, in this case a *cis*-cyclopropane was transformed into its *trans* analog. Ogoshi et al.[118] have isolated the addition products of Rh(I) anions to cyclopropanes containing electron-withdrawing groups. The rhodium(I) octaethylporphyrin also adds to a single cyclopropane in quadricyclene without further rearrangement. Aumann[119] has also trapped this initial intermediate by reacting iron pentacarbonyl with quadricyclene. The intermediate was trapped via insertion of a carbonyl group similar to that observed by Cassar and Halpern.[43]

Mango[120] has again reviewed his theory of orbital symmetry control via transition metal catalysts, but no new data have appeared to support this as an active reaction path.

Green[121] and Fitjer[122] have further explored the interaction of cyclopropylidenes with transition metals. Green, employing a palladium reactant, isolated a metal–carbene complex. Fitjer, using zinc iodide, found interesting cationic rearrangements with alkenylidene cyclopropanes.

Bickelhaupt et al.[123] have extended (see ref 73) the silver(I)-catalyzed rearrangements of *cis*-dispirocyclopropenyl compound to yield the highly strained tricyclo$[3.2.2.0^{1,4}]$nona-2,5-diene, a propelladiene. They also captured a carbonium ion intermediate and employed deuterium-labeling experiments to substantiate the proposed mechanism.

Paquette et al.[132] have again demonstrated the different paths of rearrangement of Rh(I) and Ag(I) catalysts. Their substrate was a complex tetracyclic diene which interestingly rearranged to the Rh(I) product when passed over alumina.

Kawanisi et al.[124] have demonstrated a new Ag(I)-catalyzed reaction of a bicyclo[2.1.0]pentane moiety in the transformation of dehydronoriceane to 2,4-ethenonoradamantane. The Solomons[125] have explored the mechanism of the rearrangement of vinylcyclopropanes. Their interesting paper indicates initial coordination of the catalyst [Rh(I)] with the olefin followed by insertion into the cyclopropane and a stereospecific cis β-hydride elimination.

Reactions of bicyclobutanes continue to elicit a good deal of interest. Recent publications[124–126] have shown a variety of substituted bicyclobutanes to undergo rearrangements expected from past results. In the rearrangement of *trans*-tricyclo$[5.1.0.0.^{2,4}]$octa-5-nonene boron trifluoride again leads to the type D product while Ag(I) goes to the type A product.

Two other developments which are of importance are the further exploration of the oxidation–reduction mechanism for small ring rearrangements and the determination of the heats of reactions of metal-catalyzed processes. In the former, Koser and Faircloth[130] have interpreted their result for Ag(I)-catalyzed rearrangement of quadricyclene to norbornadiene as consistent with a two-electron redox reaction. In the latter, Wiberg and Connon[131] have begun to give firm numbers for the heats of reactions. Benzvalene was isomerized to benzene with a $\Delta H_r = -66.7$ kcal/mol; quadricyclene to norbornadiene with a heat of reaction of $\Delta H_r = -26.2$ kcal/mol. Work is in progress for the paths taken by Moore's hydrocarbon (**80**). These and other developments are starting to add maturity to this relatively young field.

Acknowledgment. The author would like to thank Professors W. Dauben, R. Noyori, L. Paquette, and G. Whitesides for making available their results prior to publication. The helpful comments of Helen Connon, Dr. A. Kielbania, Dr. J. L. Roustan, and Professor K. B. Wiberg have all added to the clarity of this work.

IX. References and Notes

(1) See, for example, ref 17, 38, and 46.

(2) See ref 11 and 16a, as well as D. J. Cardin, B. Centinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 2, 99 (1973); L. A. Paquette, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, in press.

(3) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).

(4) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(5) For a more detailed description, see G. E. Coates, M. L. H. Greene, and K. Wade, "The Transition Elements", Methuen and Co., London, 1968, pp 13–19; R. Mason, *Chem. Soc. Rev.*, **1**, 431 (1972); F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", Wiley, New York, N.Y., 1968, Chapter 7.

(6) See, for example, P. M. Maitlis in The Organic Chemistry of Palladium, "Metal Complexes", Vol. 1, Academic Press, New York, N.Y., 1971; C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).

(7) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(8) (a) L. Salem and J. S. Wright, *J. Am. Chem. Soc.*, **91**, 5947 (1969); (b) R. Hoffmann and R. B. Davidson, *ibid.*, **93**, 5699 (1971).

(9) (a) F. J. McQuillan and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 2123 (1972); *Tetrahedron Lett.*, 3313 (1971); (b) C. F. H. Tipper, *J. Chem. Soc.*, 2045 (1955); (c) R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbron, and D. R. Russell, *J. Organomet. Chem.*, **33**, 247 (1971); (d) J. A. McGinnety, *ibid.*, in press; (e) M. Lenarda et al., *ibid.*, **46**, C29 (1972); (f) D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 1227 (1969).

(10) For a similar, but slightly different description of the metal–cyclopropane bond, see ref 9d.

(11) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968).

(12) (a) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972); (b) R. P. Mitchell and R. V. Parrish, *J. Chem. Educ.*, **46**, 811 (1969).

(13) See, for example, F. Basolo and R. G. Pearson, ref 5.

(14) S. Montelatiti, A. ven der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1054 (1968), and references cited therein.

(15) See L. Vaska, *Inorg. Chim. Acta*, **5**, 295 (1971), and references cited therein.

(16) (a) J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1970); (b) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, **7**, 54–94 (1968); (c) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).

(17) W. Mark and R. Pettit, *J. Am. Chem. Soc.*, 89, 4787 (1967).

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