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R. Rossi (*)

RING-OPENING REACTIONS OF STRAINED ALICYCLIC MOLECULES BY TRANSITION METAL COMPOUNDS OF GROUP VIII

Summary — Ring-opening reactions of strained saturated and unsaturated alicyclic derivatives by transition metal compounds of group VIII are reviewed. The emphasis will be on the mechanistic aspects of these catalytic or stoichiometric reactions. However, a quite relevant amount of information on the reactions which provide useful synthetic routes to known or new compounds is included. In this connection, the selectivity and stereospecificity of some ring-opening reactions will be illustrated.

The present review is devoted to describe and, where it is possible, to comment upon the various types of ring-opening reactions of saturated or unsaturated alicyclic strained derivatives by transition metal compounds of group VIII.

While scattered reports on this argument are found in the early literature, numerous reports have appeared since 1969. These more systematic investigations coincide with the relevant progress of transition metal catalysed organic reactions.

We have attempted to review the catalytic ring-opening reactions by transition metal compounds and the ring-opening reactions leading to isolable organometallic complexes under three aspects:

- to illustrate the unusual reactivity of some σ carbon-carbon bonds;
- to underline that the pathway of these reactions is intimately related to the nature of the transition metal used, to the type of the ligands attached to the metal, and to the structural features of the organic substrate;

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— to focuse on the potential synthetic utility of these reactions which, sometimes, show very high selectivity and stereospecificity.

This Article is divided in the following Sections:

1) Metal-catalysed rearrangements
2) Ring-opening-reactions yielding isolable transition metal complexes.

In this class of reactions, are included also those which give heterocyclic compounds deriving from insertion of the transition metal on a σ carbon-carbon bond of the strained organic substrate.

Another not less interesting field, that of the ring-opening polymerizations by transition metal compounds is not considered.

Various aspects of the subject here surveyed are dealt with more fully in recent articles or reviews. In particular, a paper of MANGO and SCHACHTSNEIDER [1971] deals with the metal catalysed valence isomerizations. Oxidative addition reactions of transition metal complexes are discussed by HALPERN [1970]. Furthermore, silver (I) catalysed rearrangements of strained bonds, which sometimes can be related to reactions included in the Section 1 of this Article, are discussed by PAQUETTE [1971].

As far as the coverage of the literature is concernend, we have searched Chemical Abstracts from 1965 to 1971 and a number of leading journals for the years 1970 and 1971. Work prior to 1965 has been cited only sporadically.

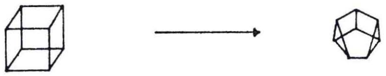
1) METAL CATALYSED REARRANGEMENTS

Many three- and four-membered rings undergo bond cleavage in the presence of transition metal complexes (Table 1-5). In such a way, thermodynamically unstable organic compounds are converted into more stable isomers.

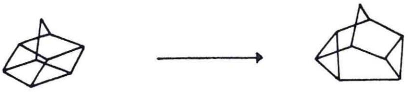
These carbon skeletal rearrangements, in the absence of metal catalysts, according to the Woodward-Hoffmann rules of orbital symmetry conservation (WOODWARD and HOFFMANN [1970], MILLER [1968], PEARSON [1970], GILL [1968]) are frequently thermally forbidden. Thus, the transformations (2)-(3) and (1)-(4) may be classified as disalloved [σ 2a + σ 2a] and [σ 2s + σ2s] reactions, respect-

(1) 

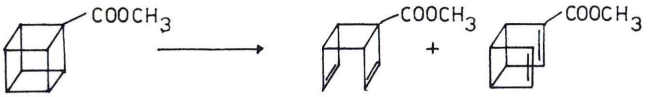
XXVI XXVII

(2) 

XVIIa XIX

(3) 

LXI III

(4) 

XVII b XVIII b LXII

ively. However, it appears that these and other similar processes can be facilitated under mild conditions by the presence of transition metal catalysts. Thus, XXVI is isomerized quantitatively to XXVII by a catalytic amount of rhodium dicarbonyl chloride dimer in chloroform solution at 65° (Table 2) (EATON and CEREFICE [1970]. XXVI appears to be the first compound unsubstituted at the bridgehead positions in the *cis, syn, cys*-tricyclo[5.3.0.0^{2,6}]decane derivatives series.

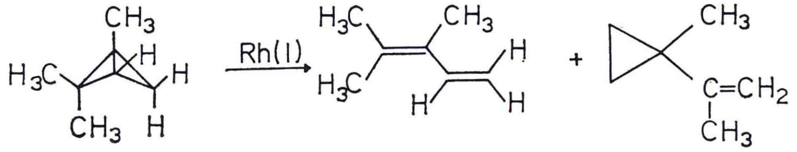
On the other hand, cubane (XVIIa) is quantitatively rearranged to cuneane (XIX) (equation 2) by palladium (II) complexes (CASSAR et Al. [1970b] (Table 2). Cuneane represents the second of the saturated $(CH)_8$ isomers so far synthesized, the first being cubane.

Another striking example of a selective and stereospecific metal-promoted isomerization is that of the reaction of *cis*-bicyclo [4.1.0] nona-2,4,6-triene (X) with rhodium dicarbonyl chloride dimer (Table 1). XI is quantitatively converted at 35° in 2 hr into *cis*-8,9-dihydroindene (GRIGG et Al. [1971b]). On the contrary, thermal rearrangement of XI affords a 9:1 mixture of *cis*- and *trans*-8,9-dihydroindene (VOGEL et Al. [1963]).

Thermally allowed reactions, such as the conversion of bicyclo [1.1.0]butanes into buta-1,3-dienes, which may be considered as concerted [σ 2s + σ 2a] processes for which appear necessary temperatures of 200-300° to obtain a reasonably rate of isomerization, may also occur at room temperature in the presence of specific transition metal catalysts (Table 5). Nevertheless, in such a case, the reaction pathway differs from that in the thermal process.

Gassman and Williams [1970] demonstrated indeed that 1,2,2-trimethyl-bicyclo[1.1.0]butane (XLIV) is rapidly isomerized by rhodium dicarbonyl chloride dimer to a mixture of 3,4-dimethyl-penta-1,3-diene (L) and 1-methyl-1-(α-methylvinyl)cyclopropane (LI) (equation 5).

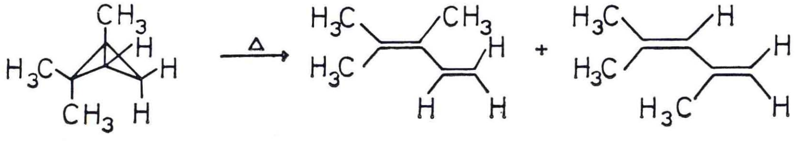
(5)



XLIV L (65.9 %) LI (34,1 %)

On the contrary, pyrolysis of XLIV at 300° gives a mixture of L and 2,4-dimethyl-penta-1,3-diene (LXIII) in the ratio of 53:47 (Skattebol [1970], Moore et Al. [1970]) (equation 6).

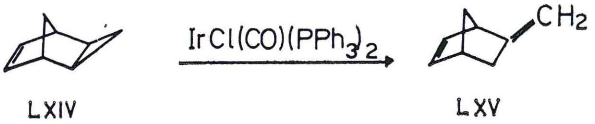
(6)



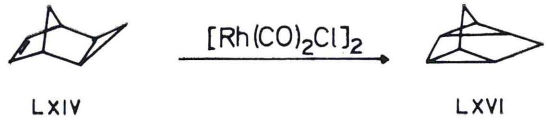
XLIV L LXIII

The nature of the transition metal catalyst or of the ligands attached to the transition metal exerts a relevant influence on the direction of isomerization. Thus, by reacting *exo*-tricyclo $[3.2.1.0^{2,4}]$ oct-6-ene (LXIV) with $IrCl(CO)(PPh_3)_2$, the only product of the very high selective isomerization is 5-methylenebicyclo [2.2.1] hept-2-ene (LXV) (equation 7) (Volger et Al. [1969b]). On the other hand, the reaction of LXIV with rhodium dicarbonyl chloride dimer gives selectively tetracyclo$[3.3.0.0.^{2,8}.\ 0^{4,6}]$octane (LXVI) (equation 8) (Katz and Cerefice [1969b]).

(7)



(8)



Many other examples are reported in Table 1-5.

GASSMAN et Al. [1971e], by analyzing the reaction products of XLIV with different palladium complexes, have clearly demonstrated the dependency of the mode of cleavage of highly strained polycyclic molecules on the nature of the ligand attached to the transition metal. When a chloroform solution of XLIV is reacted with dichloro-bis(benzonitrile) palladium (II) at 25° for 12 hr, a 1:13 mixture of LI:L is obtained. On the other hand, when di-μ-chloro-bis(π-allyl)palladium (II) is used as the catalyst, XLIV gives at 0° in 35 min (72% yield) a 3:46:41 mixture of 3,4-dimethyl-penta-1,3-diene, (E)-2-methyl-hexa-2,4-diene and (Z)-2-methyl-hexa-2,4-diene, respectively, in addition to a 3% yield of non characterized unsaturated cyclopropyl derivatives.

Transition metal catalysts, besides giving rise to «valence isomerization» (*) of polycyclic compounds, as exemplified in the equations (1)-(8), can produce skeletal rearrangements involving hydrogen shift also. Thus, LXIV, when heated at 90° with tris-(triphenylphosphine)-rodium chloride, is converted quantitatively into a mixture of 62% tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (LXVII), 32% tetracyclo [3.3.0.$0^{2,8}$.$0^{4,6}$]octane (LXVI) and 6% bicyclo[3.2.1]octa-2,6-diene (LXVIII) (equation 9) (KATZ and CEREFICE [1969b]).

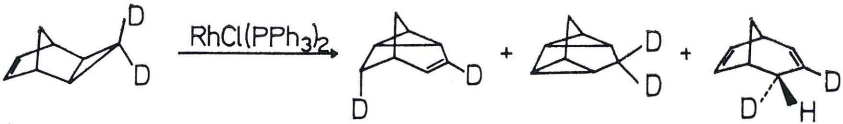
(*) Valence isomerizations are reactions accompanied by corresponding changes in the relative arrangement of σ- and π-bonds and only by small changes in interatomic distances and valence angles. This definition can be extensively applied to the isomerization showed in the equations (5) and (6).

Worthy of mention is that reactions of the type showed in the equations (7) and (8) are defined in literature (e.g. MANGO [1969]) «valence tautomerizations». However, this term seems uncorrect since «tautomerism» is observed only if the corresponding isomers are converted into each other under normal working conditions, the energy barrier to be overcome being relatively small.

(9) 

LXIV LXVII LXVI LXVIII

When LXIV is fully deuterium labelled in the position 3, the reaction gives stereospecifically *endo*-3,6-dideutero-tricyclo[$3.2.1.0^{2,7}$] oct-3-ene (LXX), 3,3-dideutero-tetracyclo [$3.3.0.0.^{2,8}.0^{4,6}$] octane (LXXI) and *endo*-3,4-dideutero-bicyclo[3.2.1]octa-2,6-diene (LXXII) (KATZ and CEREFICE [1971]) (equation 10).



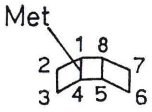
(10) LXIX LXX LXXI LXXII

On the basis of these results it has been possible to conclude that this isomerization involves the stereospecific transfer of a hydrogen atom across the face of the molecule which is coordinated to the rhodium atom (KATZ and CEREFICE [1971]).

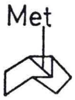
Very recently , rhodium (I) catalysed rearrangements of strained heterocycles have been also described (GRIGG et Al. [1971 a, b]). The few examples so far known are reported in Table 6.

With regard to the mechanism of the transition metal catalysed valence isomerizations, it has been proposed (MANGO [1969, 1971]; MANGO and SCHACHTSNEIDER [1971]) that thermally disallowed reactions may occur in the presence of suitable transition metal catalysts since the metal, by utilizing the appropriate d-orbitals, removes the symmetry restrictions exchanging electron pairs with the transforming ligands. Therefore, the concerted mechanism of this forbidden-to-allowed catalysis should be purely electronic (MANGO [1969]).

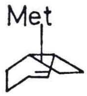
WRISTERS et Al. [1970] have also proposed a concerted mechanism for the catalysed rearrangements of strained saturated hydrocarbons. However, isomerizations should occur through three-centered metal-carbon bond interactions. Thus, *syn*-tricyclooctane (XX) should react with [norbornadiene-Rh-Cl]$_2$ forming a system analogous to LXXIII.



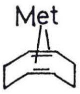
LXXIII



LXXIV



LXXV



LXXVI

In this system, which has not been considered to be an intermediate, concerted migration of carbon 6 to carbon 4 should lead to LXXIV. On the other hand, whereas concerted migration of carbon 6 to carbon 1 should give LXXV, concerted rearrangement of LXXIII could give metal-*cis, cis*-cycloocta-1,5-diene complex LXXVI.

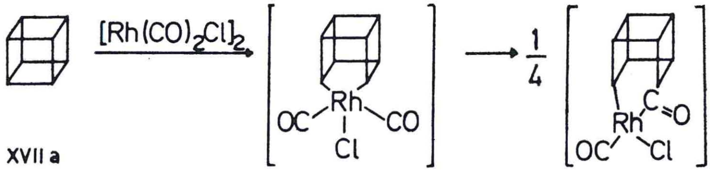
Extrusion of metal from LXXIV, LXXV, and LXXVI should therefore lead to the observed products which are bicyclo[4.2,0]-oct-2-ene (XXI), tetrahydrosemibullvalene (XXII) and *cis, cis*-cycloocta-1,5-diene (XXIII), respectively.

The system LXXIII, in dependence of the ligands of the metal may also proceed to fully inserted σ-bonded dialkyl metal complexes. Thus, the reaction between rhodium dicarbonyl chloride and *syn-* or *anti*-tricyclooctane, (XX) and (LXXVII), respectively, which yields acylrhodium complexes (WRISTERS et Al. [1970]), very probaly proceeeds via alkyrhodium intermediate complexes.

Recently, the concertdness of the transition metal-promoted valence isomerizations has received critical attention (KATZ and CEREFICE [1969 b, c; 1971], CASSAR et Al. [1970 a, b], BYRD et Al. [1971], KAIZER et Al. [1971], HALPERN [1970]).

KATZ and CEREFICE [1969 b, c; 1971] consider it likely that the rhodium (I) catalysed processes proceed through a non-concerted mechanism involving a σ-bonded metal complex. CASSAR et Al. [1970 a, b] have supported this view isolating, in some cases, acylrhodium compounds deriving from an oxidative-addition step similar to that reported in equation 11 (see also Section 2).

(11)

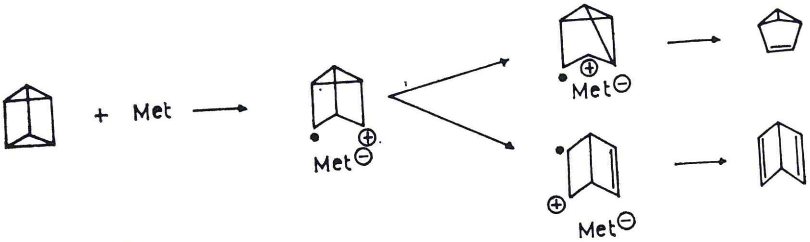


XVII a

However, some valence isomerizations summarized in Table 3 and 4, cannot even be interpreted in these terms. In fact rearrangement of tetracyclo [2.2.0.0^{2,6}.0^{3,5}]hexane derivatives (Table 3), tricyclo [4.1.0.0^{2,7}]heptane (XXXVI) and its 1-methyl derivatives (XXXVII) (Table 4) may also occur by weak Lewis acids which have not d-orbitals at readily accessible energies and for which an oxidative-addition mechanism can be ruled out (GASSMAN and ATKINS [1971 b, c]).

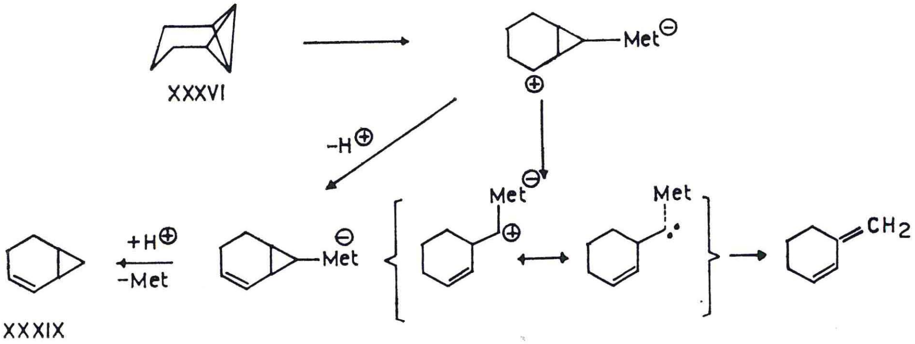
Concerning the carbon skeletal isomerization of prismane (Table 3), it has been suggested that the first step of this type of isomerization is the formation of a «very short-lived charge-transfer complex» between catalyst and prismane which gives a radical cation; a rapid rearrangement then should occur (KAIZER et Al. [1971]) (Scheme 1).

SCHEME 1

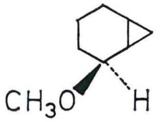


On the other hand, the formation of the products observed in the metal-promoted rearrangement of tricyclo [4.1.0.0^{2,7}]heptane (XXXVI) and its 1-methyl derivative (Table 4) has been interpreted in terms of the stepwise mechanism depicted in Scheme 2 (GASSMAN and ATKINS [1971 c]).

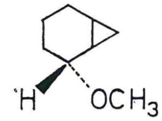
SCHEME 2



A confirmation that the reaction proceeds through intermediates similar to LXXVIII was obtained by reacting XXXVI with rhodium dicarbonyl chloride dimer in a nucleophilic solvent such as methanol. The reaction product consisted of a 4:1 mixture of LXXIX and LXXX (Gassman and Atkins [1971 c]).



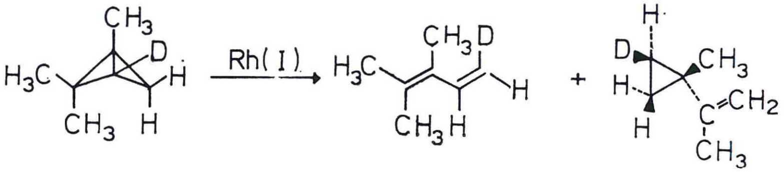
LXXIX



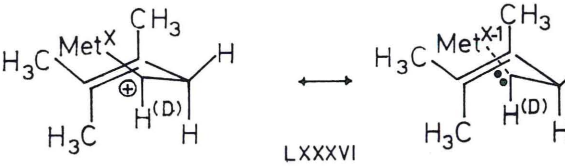
LXXX

Since this is the same ratio of isomer ethers as found in the reaction of XXXVI with methanol in the presence of sulfuric acid (Wiberg and Szeimies [1970]), this result indicates that transition metal carbonyl halides may react like Lewis acid catalysts with suitable substrates.

With regard to the mechanism of catalysed ring-opening reactions of bicyclo[1.1.0]butane derivatives (Table 5), Gassman and Williams [1970, 1972] by isotopic labelling experiments established that rhodium (I) catalysed ring-opening of XLIV involves a multistep process in which cleavage at the C1-C3 and C2-C3 bonds occurs. Thus, (Z)-1-deuterio-3,4-dimethyl-penta-1,3-diene (LXXXII), in addition to LXXXIII was stereospecifically obtained by reacting 1,2,2-trimethyl-3-deutero-bicyclo [1.1.0] butane (LXXXI) with rhodium dicarbonyl chloride dimer (equation 12).

(12) 

This result was interpreted (Gassman and Williams [1970], Gassman et Al. [1971 d] admitting that the catalysed rearrangement of XLIV or LXXXI proceeds via the intermediacy of the metal-bonded carbonium ion LXXXVI which may be also formulated as a hybrid to which a carbenoid species contributes.

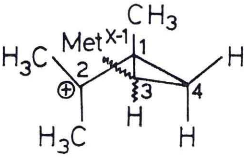


LXXXVI

Then, a 1,2 hydrogen shift in LXXXVI could account for the formation of LXXXII.

Sakai et Al. [1971 a] hypothesized an intermediate similar to LXXXVI in the palladium (II) catalysed rearrangement of other bicyclo [1.1.0] butane derivatives. Subsequently, this hypothesis was strongly supported by intramolecular trapping experiments, which established the carbenoid character of the intermediate of these reactions (Gassman and Nakai [1971 f].

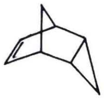
Capture of the carbonium ion LXXXVII by methanol in the rhodium (I) catalysed isomerization of XLIV, finally confirmed that the transition metal promoted rearrangement of simple bicyclo [1.1.0] butanes proceeds by a stepwise mechanism which involves initial cleavage of a side bond to yield the most stable ciclopropylcarbinyl carbonium ion (Gassman and Williams [1972]).



LXXXVII

Shifting of the C1-C3 bonding electrons in LXXXVII would produce the hybrid intermediate LXXXVI.

The suggestion that the possibility to effect valence isomerizations by transition metal catalysts is in general related to the bidentate character of the substrate, comes from the work of Volger et Al. [1969]. These Authors found that *endo*-tricyclo $[3.2.1.0^{2,4}]$ oct-6-ene (LLLVIII) in the presence of catalytic amounts of rhodium dicarbonyl chloride dimer fails to undergo a valence isomerization. The inability to coordinate as bidentate ligand to the transition metal may also explain the stability of *exo, endo*-tetracyclo $[3.3.1.0^{2,4}.0^{6,8}]$ octane (LXXXIX) to the catalysed rearrangement.



LXXXVIII

LXXXIX

This hypothesis is confirmed by the fact that *exo, exo*-tetracyclo [$3.3.1.0^{2,4}.0^{6,8}$] octane (IX) reacts with $IrCl(CO)(PPh_3)_2$ to yield *exo*-6-methylenetricyclo [$3.2.1.0^{2,4}$] octane (X) (Table 1) (VOLGER et Al. [1969]). IX, in fact, can act as a bidentate ligand.

However, as briefly outlined at the beginning of this Section, metal assisted valence isomerizations can easily occur if, in addition to a good bidentate character of both starting and product valence isomers, a «significant thermodynamic driving force for ligand transformation exists» (MANGO and SCHACHTSNEIDER [1971], KATZ [1969], KATZ and CEREFICE [1969 c]).

2) RING-OPENING REACTIONS YIELDING ISOLABLE TRANSITION METAL COMPLEXES

Reactions between alicyclic strained molecules and transition metal compounds may give rise to isolable transition metal complexes in which the organic moiety does not contain the original cycle any more. These reactions, we name «stoichiometric», may represents, at least in some cases, processes related to the transition metal catalysed isomerizations previously examined.

However, the «stoichiometric» reactions may result into complexes having different type of metal carbon bonds in dependence on the structure of the organic substrate, the nature of the transition metal and the type of ligands present in the transition metal compound in the reaction.

The driving force for the ring-opening reactions can be, sometimes, associated with the high reactivity of the transition metal toward oxidative-addition.

Oxidative-addition reactions which are expecially characteristic of low spin complexes such as those of rhodium(I), iridium(I), ruthenium (O), iron (O), and platinum (II), when performed on saturated alicyclic compounds, give rise generally to complexes in which the organic moiety is doubly σ-linked to the metal. However, at least in principle, a number of alicyclic unsaturated strained substrates can react with transition metal compounds such as those of rhodium (I), platinum (II) or iron (O) to give complexes in which the organic moiety is linked to the metal:

a) by a π-allyl and σ-bond;
b) by two σ-bonds;
c) by two π-allyl bonds.

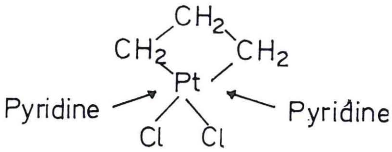
Unsaturated complexes of the class a), that is these containing a π-allyl and a σ-bond, can also originate transition metal compounds having a 1,3-diene system π-linked to the metal. In such a case, oxidative-addition represent only an intermediate step of the ring-opening process, the metal having at the end of the reaction with the organic substrate the same oxidation number as before the reaction.

Finally, it worth mentioning that ring-opening reactions of saturated or unsaturated alicyclic compounds by palladium (II) involve generally the formation of π-allyl complexes in which palladium preserves the oxidation number (II). Palladium (II), which has d^8 configuration, has in fact a low tendency to undergo oxidation to the d^6 configuration (HALPERN [1970]).

The relevant literature on the «stoichiometric» ring-opening reactions shall be examined considering also the different reaction paths to which some transition metal complexes, so formed, can be subjected:

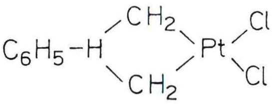
- chemical or thermal decomposition to ring-opened organic compounds;
- thermal conversion into isomeric complexes;
- chemical conversion into the original organic substrate or in a different cyclic compound;
- catalytic processes, such as the ring-opening reaction of the organic substrate.

The first example of opening of a carbon-carbon bond by insertion of a metal, in a simple alicyclic strained molecule, was described by TIPPER [1955]. This Author found that, when cyclopropane (XC) is reacted with a solution of chloroplatinic acid in acetic anhydride, a complex having composition $PtCl_2(C_3H_6)$ is obtained. The bis-pyridine derivative of this compound, on the basis of NMR (ADAMS [1961]) and X-ray data (BAILEY [1966]), was formulated as XCI.

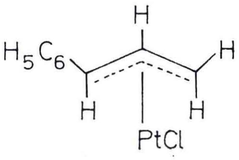


XCI

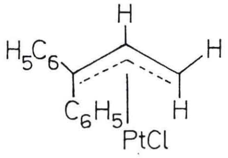
Phenyl-and hexyl-substituted cyclopropanes react with $PtCl_2(CH_2 = CH_2)_2$ in a similar manner (IRWIN and MCQUILLIN [1968]). However, the phenylcyclopropane-$PtCl_2$ complex of structure XCIII, when heated in CCl_4 solution, forms the π-allyl complex XCIII (IRWIN and MCQUILLIN [1968]). On the other hand, 1,1-diphenylcyclopropane (XCIV), when reacted with Zeise's dimer, gives the π-allyl complex XCV instead of the Pt-trimethylene derivative.



XCII



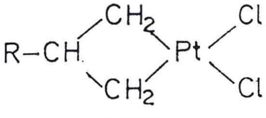
XCIII



XCV

BROWN [1970], by addition of cyclopropane to $HPtCl_3(CH_2{=}CH_2)$ in ethanol or to Zeise's dimer in ethanol, chloroform or dichloromethane, obtained the complex $PtCl_2(CH_3{-}CH{=}CH_2)_2$ which derived from the ring-opening of cyclopropane to propylene and the subsequent displacement of ethylene from the so formed olefin.

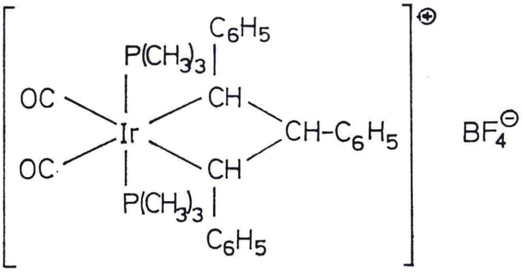
Finally, POWELL and MCQUILLIN [1917 a] demonstrated that the formation of complexes in the reaction between cyclopropane derivatives and Zeise's dimer parallels the electron density of the cyclopropane ring. In fact, the reaction does not occur if the substituent of the cyclopropane ring is electron withdrawing. However, for cyclopropanes having electron donor substituents (e.g. alkyl groups) the reaction occurs selectively, leading generally to heterocyclic compounds of formula XCVI.



XCVI

These compounds derive from insertion of platinum (II) on the least substituted carbon-carbon bond of the cyclopropane ring. Treatment of these complexes with KCN allows to recover the parent cyclopropane compound. On the contrary, *cis*-1,2-disubstituted cyclopropane compounds having electron donor groups do not give $PtCl_2$-trimethylene derivatives, but Pt-complexes yielding on decomposition by KCN olefinic compounds (POWELL and MCQUILLIN [1971 a]).

Reactions closely related to those occurring by platinum compounls are those between rhodium dicarbonyl chloride dimer and cyclopropanes (ROUNDHILL et Al. [1968], POWELL and MCQUILLIN [1971 b]), methylenecyclobutane (ROSSI et Al. [1971]) quadricyclene (CASSAR and HALPERN [1970]), and cubane (CASSAR et Al. [1970 a]), and that between triphenylcyclopropenium tetrafluoroborate (XVCII) and *trans*-IrCl(CO)) $(P(CH_3)_3)_2$ (TUGGLE and WEAVER [1970]). XCVI reacts with this complex to give XCVIII, which contains an unusual iridacyclobutane ring.

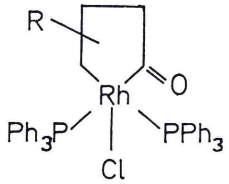


XCVIII

The interaction of rhodium dicarbonyl chloride dimer with cyclopropane (ROUNDHILL et Al. [1968]) or substituted cyclopropanes (POWELL and MCQUILLIN [1971 b]) produces complexes (Table 7) which involve rhodium (III) in five-membered ketonic heterocycles. Thus, a carbon-carbon bond of the cyclopropane ring formally opens inserting rhodium and a carbonyl group of rhodium dicarbonyl chloride.

As showed in Table 7, the fission of carbon-carbon bonds and, therefore the formation of 1-rhodiacyclopentane-2-one rings proçeeds with a large selectivity; for instance, benzyl- and phenylcyclopropane react at the less and the more substituted carbon-carbon bond of the cycle, respectively (Powell and McQuillin [1971 b]). After reaction, the recovered excess of cyclopropane contains olefinic products deriving from a very selective ring-opening reaction. n-Heylcyclopropane, which does not form a complex, however, gives 2-methyl-oct-1-ene and non-2-ene in the 3: 1 ratio.

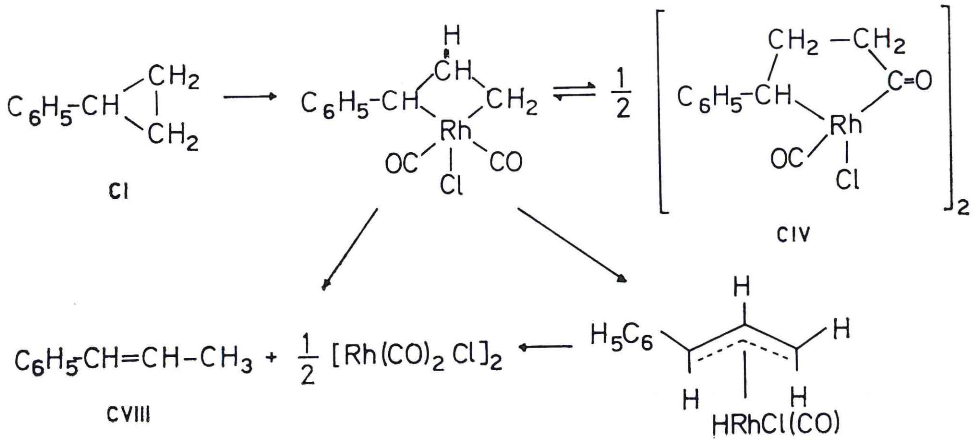
All the heterocyclic compounds reported in Table 7 undergo a stoichiometric reaction with triphenylphosphine eliminating carbon monoxide and yielding monomeric complexes of general formula XCIX (Roundhill et Al. [1968], Powell and McQuillin [1971 b]).



XCIX

However CIV deriving from phenylcyclopropane (CI), when heated with an excess of triphenylphosphine in chloroform solution, forms propenylbenzene (CVIII) and RhCl(CO) $PPh_3)_2$ (Powell and McQuillin [1971 b]). This result was interpreted on the basis of the reactions reported in Scheme 3.

SCHEME 3

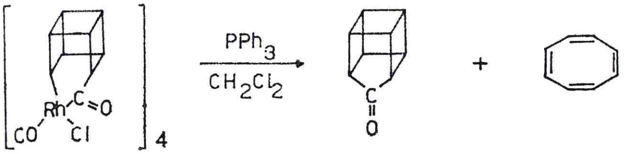


Thus, rhodium dicarbonyl chloride dimer should interact with cyclopropanes to form alkylrhodium (III) complexes prior to formation of the observed acylrhodium (III) derivatives.

This interpretation, suggested for the first time by Cassar et Al. [1970 a] for the reaction of cubane (XVIIa) with rhodium dicarbonyl chloride dimer, has been also applied to the reaction of other substrates with this rhodium compound (e.g. *syn* and *anti*-tricyclooctane (Wristers et Al. [1970]) and quadricyclene (Cassar and Halpern [1970]).

The acylrhodium compound CIX obtained from cubane (XVIIa), when treated with a stoichiometric amount of triphenylphosphine in dichloromethane solution, gives in 90% yield the cyclic ketone CX together with a small amount of cyclooctatetraene (CXI) (equation 13) (Cassar et Al. [1970 a]).

(13)

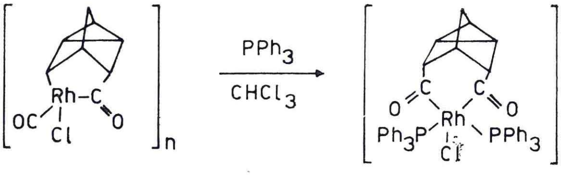


CIX CX CXI

Many other substituted acyl rhodium compounds deriving from cubane derivatives react similarly (Cassar et Al. [1970 a]).

On the contrary, the acylrhodium compound CXII prepared from quadricyclene reacts with a stoichiometric amount of triphenylphosphine in chloroform solution yielding CXIII (equation 14) (Cassar et Al. [1970]).

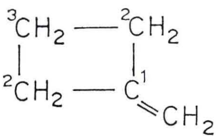
(14)



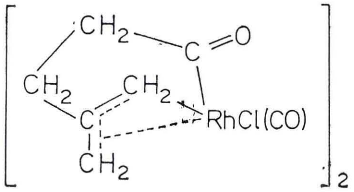
CXII CXIII

This apparently anomalous reaction results in insertion of a second carbonyl group on a carbon-rhodium bond.

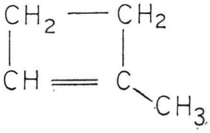
Actually, there is evidence that the formation of acylrhodium compounds starting from rhodium dicarbonyl chloride dimer and a strained alicyclic substrate is not limited to saturated compounds. In fact, methylenecyclobuthane (CXIV) reacts also to give a complex which, on the basis of IR and NMR data and reduction with sodium borohydride to 4-methyl-pentane-1-ol, has been formulated as CXV (Rossi et Al [1971]). This complex, deriving from ring-opening of CXIV at the C2-C3 bond, can also be prepared starting from 1-methylcyclobutane (CXVI) (Rossi et Al. [1972 a]).



CXIV



CXV



CXVI

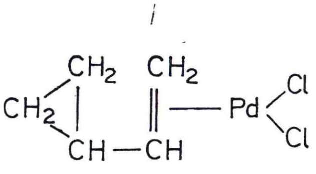
Concerning this point, it is interesting to notice that after reacting either CXIV or CXVI with rhodium dicarbonly chloride dimer, the recovered hydrocarbon is not isomerized. The reaction of CXV with a large excess of triphenylphosphine in chloroform solution at 65° for 48 hr gives methylenecyclobutane (CXIV), 1-methylcyclobutene (CXVI), $RhCl(CO)(PPh_3)_2$ and a new complex identified as CXVII (Rossi et Al. [1972 a]).

All these results may be rationalized according to what reported in Scheme 4 (Rossi et Al. [1972 a]).

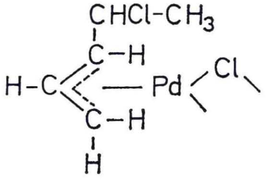
Cyclopropane and its mono- or polyalkyl derivatives, when treated at room temperature for 24 hr with di-μ-chloro-dichlorobis-(ethylene)dipalladium or bis(benzonitrile) palladium dichloride, do not give complexes. However, saturated compounds containing two cyclopropyl groups react to give π-allyl complexes (Ketley and Braatz [1968], Ketley et Al. [1970]). The structures of these complexes together with those of the starting materials are reported in Table 8.

Unsaturated cyclopropane derivatives react, on the other hand, with palladium dichloride to give π-allyl and, in particular cases, π-complexes. Vinylcyclopropane (CXXIX), when treated at 25° with di-μ-chloro-dichlorobis(ethylene)dipalladium, forms a π-complex with $PdCl_2$ through the olefinic bond (Ketley and Braatz [1967]).

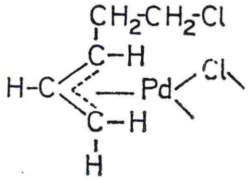
This complex, (CXXX), heated at 40° in benzene, gives a wine-red solution from which it has been possible to isolate a mixture of π-allyl complexes of structure CXXXI and CXXXII in a 5:3 molar ratio (Ketley and Braatz [1967]).



CXXX

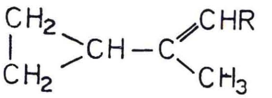


CXXXI

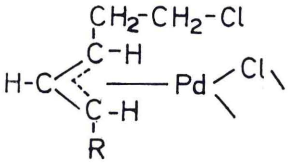


CXXXII

Vinylcyclopropane derivatives of general formula CXXXIII, by reaction with bis(benzonitrile)palladium dichloride in benzene at room temperature CXXXIII a, b, or at refluxing temperature, CXXXIII c, give π-allyl complexes of general formula CXXXIV (Shono et Al. [1968]).



CXXXIII a , $R = CH_3$
CXXXIII b , $R = C_6H_5$
CXXXIII c , $R = COOC_2H_5$

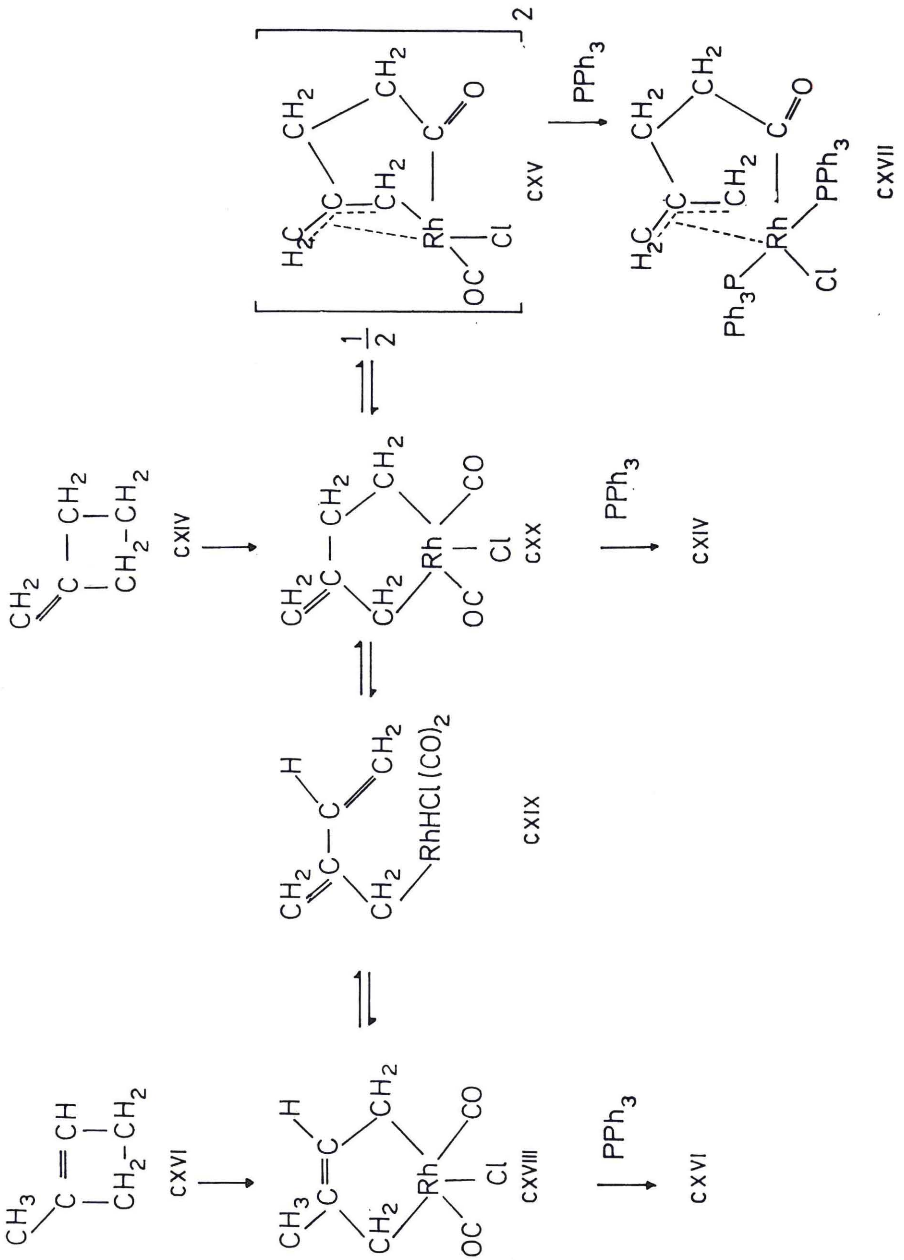


CXXXIV a , $R = CH_3$
CXXXIV b , $R = C_6H_5$
CXXXIV c , $R = COOC_2H_5$

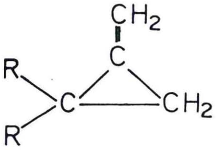
Methylenecyclopropanes, when reacted with bis (benzonitrile) palladium dichloride in benzene, are also converted into π-allyl complexes (Noyori and Takaya [1969]).

The direction of ring fission is markedly influenced by substitution of the cyclopropane ring. Thus, methylenecyclopropane (CXXX a), by ring-opening at the C1-C2 bond gives di-μ-chloro-bis (*syn*-2-chloro-1-methyl-π-allyl)dipalladium (CXXXVI). On the other hand, 2,2-diphenyl-cyclopropane (CXXXV b) by the C2-C3 cleavage

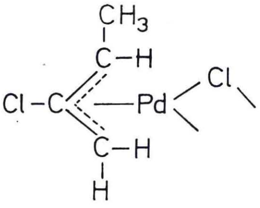
SCHEME 4



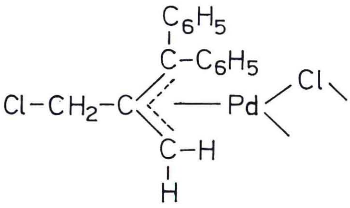
gives di-μ-chloro-bis (*syn*-2-chloromethyl-1,1-diphenyl-π-allyl)dipalladium (CXXXVII) (Noyori and Takaya [1969]).



CXXXV a, R = H
CXXXV b, R = C_6H_5

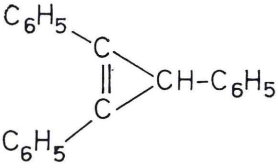


CXXXVI

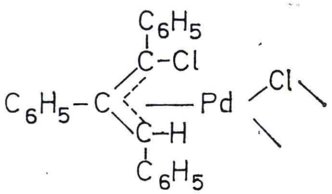


CXXXVII

1,2,3-triphenylcyclopropene (CXXXVIII) undergoes a similar reaction (Mushak and Battiste [1969]). Treatment of a solution of CXXXVIII in acetone, ethanol-methylene dichloride, or benzene with bis(benzonitrile)palladium dichloride at room temperature yields di-μ-chloro-bis(1-chloro-*syn, syn*-1,2,3-triphenyl-π-allyl)dipalladium (CXXXIX).



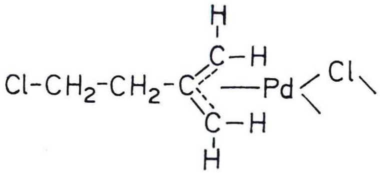
CXXXVIII



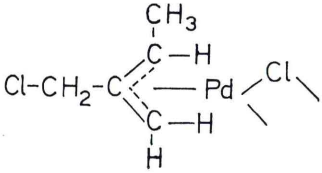
CXXXIX

Methylenecyclobutane (CXIV), reacts with palladium dichloride at 60° to give essentially two isomeric complexes, CXXVI and CXL, which derive from opening of CXIV at the carbon-carbon bond in β position with respect to the *exo*-methylene double bond (Rossi et Al. [1971]).

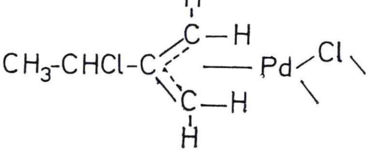
However, a third isomeric complex can be present, its presumable structure being CXLI (Rossi et Al. [1972 b], Citti [1972]). The cyclobutane ring would be opened through a cyclobutyl-homoallyl rearrangement, the cyclobutyl cation arising by donation of



CXXVI



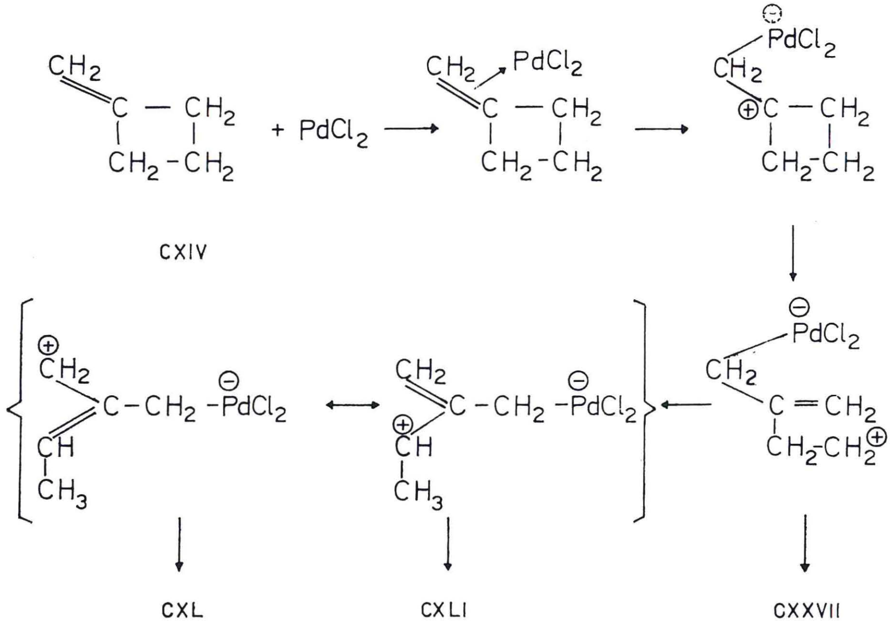
CXL



CXLI

an electron pair from the olefin to the palladium atom (Scheme 5) (Rossi et Al. [1972 b], Citti [1972]).

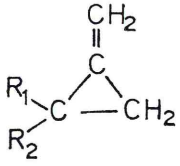
Scheme 5



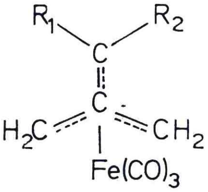
The same reaction at 65° using 1-methylcyclobutene (CXVI) does not give rise to π-allyl complexes. This can be related to the observed inability of CXVI to form initially a π-complex with $PdCl_2$, probably because of its steric requirements (Rossi et Al. [1972 b], Citti [1972]).

Ring-opening reactions reminiscent of those observed in the reactions between CXXX a, b and bis(benzonitrile)palladium dichloride, occur when phenyl substituted methylenecyclopropanes, CXLII a, b, c, are reacted with enneacarbonyldi-iron (NOYORI et Al. [1969]).

Tricarbonyl trimethylenemethane iron complexes of structure CXLIII a, b, c are obtained.



CXLII a ; $R_1 = H, R_2 = C_6H_5$
CXLII b ; $R_1 = CH_3, R_2 = C_6H_5$
CXLII c ; $R_1 = R_2 = C_6H_5$

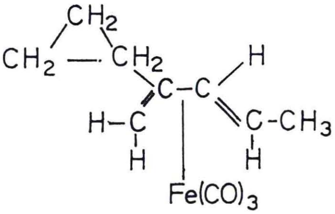


CXLIII a ; $R_1 = H, R_2 = C_6H_5$
CXLIII b ; $R_1 = CH_3, R_2 = C_6H_5$
CXLIII c ; $R_1 = R_2 = C_6H_5$

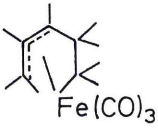
However, methylenecyclopropane itself, (CXXXV a), gives in low yield (ca. 2%) butadiene tricarbonyl iron (NOYORI et Al. [1969]).

The action of $Fe(CO)_5$ or $Fe_2(CO)_9$ on the vinylcyclopropanes CXLIV a, b, c (SAREL et Al. [1965]), on 1,1-dicyclopropylethylene (CXLV) (BEN-SHOSAN and SAREL [1969]), or on tricyclo [$3.3.2.0^{4,6}$] deca-2,7,9-triene (bullvalene) (CXLVI) (SCHRAUZER et Al. [1964, 1970]) furnishes also 1,3-diene-$Fe(CO)_3$ complexes (Table 9). However, when CXLV is reacted with $Fe(CO)_5$ for a long time (16 hr) in ethylcyclohexane at 140°, two metal carbonyl are formed. The first is identical in all the respects with that one, CL, obtained using a shorter reaction time (6 hr); the second, which is 3-(1'-propenyl)-cyclohex-2-enone tricarbonyl iron (CLIII) (BEN-SHOSHAN and SAREL [1969]), derives from a carbon monoxide insertion reaction coupled with a double cyclopropane ring-opening.

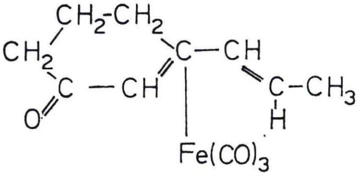
The formation of such 1,3-diene-$Fe(CO)_3$ complexes, starting from compounds containing a vinylcyclopropane group, has been interpreted as proceeding through an intermediate complex, CLIV, in which the organic moiety is π-allyl and σ-linked to the $Fe(CO)_3$ group (SAREL et Al. [1965]).



CL

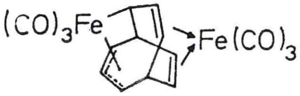


CLIV

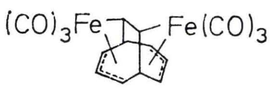


CLIII

Two similar stable complexes, CLV and CLVI, respectively, have been isolated from the reaction mixture deriving from the interaction between bullvalene (CXLVI) and $Fe_2(CO)_9$ (AUMANN [1971 a, b]).

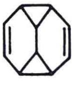


CLV

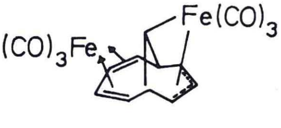


CLVI

CLVI, formally derives from tetracyclo $[4.4.0^{5,7}.0^{2,10}]$ deca-3,8-diene (CLVII) wich has been postulated as an intermediate in the thermal conversion of CXLVI into naphtalene (SCHRÖDER [1964]).



CLVII



CLVIII

CLVI, when heated at 120°, gives by thermally induced skeletal rearrangement, CLVIII in which a six-membered ring is coordinated to a $Fe(CO)_3$ group through a π-allyl system and a two center bond (AUMANN [1971 c]).

TABLE 1

Metal-Promoted Isomerizations of Polycyclic Cyclopropane Derivatives.

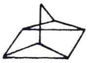
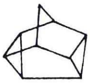
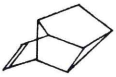
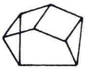
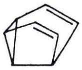
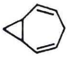
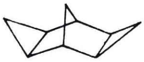
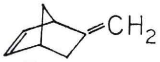
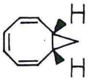
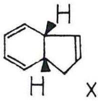
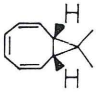
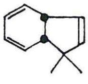
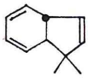
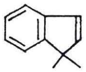
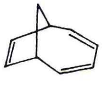
Substrate	Catalyst System	Products	References
 I	$[(C_2H_4)_2RhCl]_2$ $[1,5\text{-}C_8H_{12}PdCl_2]$ $[\text{norbornadiene-}PtCl_2]$ $[\text{norbornadiene-}RhCl]_2$	 II	Hogeveen and Volger [1967a]
 III	$[Rh(CO)_2Cl]_2$	 IV	Katz and Cerefice [1969c]
 V	$[\text{norbornadiene-}RhCl]_2$	 VI	Cassar et Al. [1970b]
 VII	$[(C_6H_5CN)_2PdCl_2]$	 VIII	Vedejis [1968]
 IX	$[Ir(CO)Cl(PPh_3)_2]$	 X	Volger et Al. [1969b]
 XI	$[Rh(CO)_2Cl]_2$	 XII	Grigg et Al. [1971b]
 XIII	$[Rh(CO)_2Cl]_2$	 +  XIV (80%) XV (2%) +  XVI (2%)	Grigg et Al. [1971b]
 LXXXIV	$[Rh(CO)_2Cl]_2$	 LXXXV	Katz and Cerefice [1969a]

TABLE 2

Metal-Promoted Isomerizations of Polycyclic Cyclobutane Derivatives.

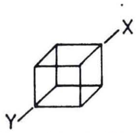
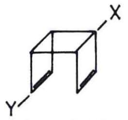
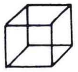
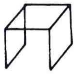
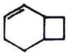
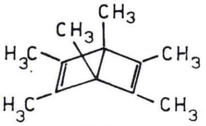
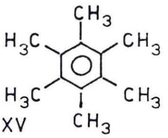
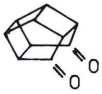
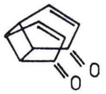
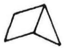
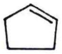
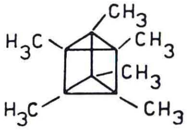
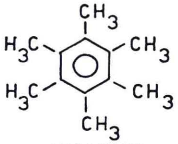
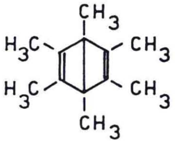
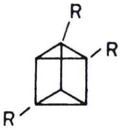
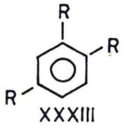
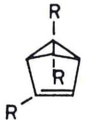
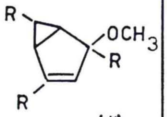
Substrate	Catalyst System	Products	References
 XVII a ($X=Y=H$) XVII b ($X=Y=COOCH_3$) XVII c ($X=COOCH_3$; $Y=H$)	$[\text{norbornadiene-RhCl}]_2$ $[1{,}5\text{-}C_8H_{12}\text{-RhCl}]_2$ $[\text{syn-tricyclooctadiene-RhCl}]_2$	 XVIII a ($X=Y=H$) XVIII b ($X=Y=COOCH_3$) XVIII c ($X=COOCH_3$; $Y=H$)	Cassar et Al. [1970a]
 XVIIa	$[(C_6H_5CN)_2PdCl_2]$	 XIX	Cassar et Al. [1970b]
 XX	$[\text{norbornadiene-RhCl}]_2$	 +  + XXI XXII  XXIII	Wristers et Al. [1970]
 XXIV	$[(\text{hexamethyl-Dewar-benzene-RhCl}]_2$	 XXV	Volger and Hogeveen [1967]
 XXVI	$[Rh(CO)_2Cl]_2$ $[\text{norbornadiene-RhCl}]_2$	 XXVII	Eaton and Cerefice [1970]
 XXVIII	$[Rh(CO)_2Cl]_2$	 XXIX	Gassman et Al. [1971a]

TABLE 3

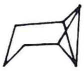
Valence Isomerizations of Prismane Derivatives.

Substrate	Catalyst System	Products	References
 XXX	[(hexamethyl-Dewar-benzene)-RhCl]$_2$	 XXV (5%)  XXXI (95%)	Hogeveen and Volger [1967b]
 XXXII (R = t-Bu)	[Na_2PdCl_4] [$Rh(CO)_2Cl]_2$ [$Ru_3(CO)_{12}$] [1,5-C_8H_{12}-RhCl]$_2$ [$C_5(CH_3)_5RhCl]_2$ [$C_5(CH_3)_5Rh(OAc)_2]_2$ [$Co(acac)_3$]	 + XXXIII  + XXXIV  XXXV(*) (R = t-Bu)	Kaizer et Al. [1971]

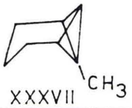
(*) These reactions were carried out in CH_3OH solution.

TABLE 4

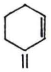
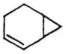
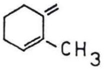
Metal-Promoted Isomerizations of
Tricyclo[4.1.0.0^{2,7}]heptane and Its 1-Methyl Derivative.



XXXVI



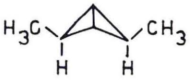
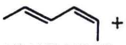
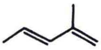
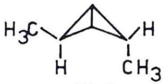
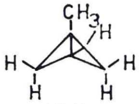
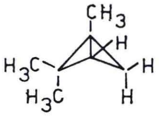
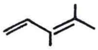
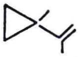
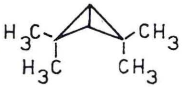
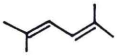
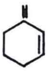
XXXVII

Substrate	Catalyst System	Products(*)	References
XXXVI	$[Rh(CO)_2Cl]_2$	 XXXVIII (98%)	Gassman et Al. [1971b,c]
XXXVI	$[RhCl(CO)(PPh_3)_2]$	XXXVIII (92%) +  XXXIX (5%)	Gassman et Al. [1971 b,c]
XXXVI	PtO_2	XXXVIII(24%) + XXXIX(62%)	Gassman et Al. [1971 b,c]
XXXVI	$[(\pi\text{-}C_3H_5)PdCl]_2$	XXXVIII (94%)	Gassman et Al. [1971 c]
XXXVI	$[Ru(CO)_3Cl_2]_2$	XXXVIII (44%) + XXXIX (12%)	〃
XXXVI	$[(C_6H_5CN)_2PdCl_2]$	XXXVIII (69%)	〃
XXXVI	$[Ir(CO)_3Cl]_2$	XXXVIII (91%)	〃
XXXVII	$[Rh(CO)_2Cl]_2$	 XL (96%)	〃
XXXVII	$[Ir(CO)_3Cl]_2$	XL (93%)	〃
XXXVII	$[(\pi\text{-}C_3H_5)PdCl]_2$	XL (93%)	〃

(*) The percentage yields are represented in parenthesis.

TABLE 5

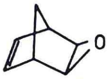
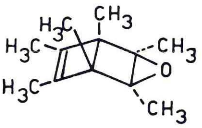
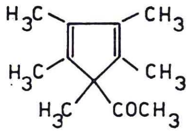
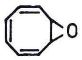
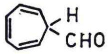
Catalysed Rearrangements of Bicyclo [1.1.0]butanes.

Substrate	Catalyst System	Products(*)	References
 XLI	$[(C_6H_5CN)_2PdCl_2]$	 +  + XLVII (37%) XLVIII (16%) +  XLIX (47%)	Sakai et Al. [1971 a]
XLI	$[Rh(CO)_2Cl]_2$	XLVII (75%) + XLVIII (3%) + + XLIX (22%)	Sakai et Al. [1971a]
 XLII	$[(C_6H_5CN)_2PdCl_2]$	XLVII (51%) + XLVIII (24%) + + XLIX (24%)	Sakai et Al. [1971 a]
XLII	$[Rh(CO)_2Cl]_2$	XLVII (60%) + XLVIII (8%) + + XLIX (32%)	Sakai et Al. [1971 a]
 XLIII	$[(C_6H_5CN)_2PdCl_2]$	XLIX (100%)	Sakai et Al. [1971a]
 XLIV	$[Rh(CO)_2Cl]_2$	 +  L (65,9%) LI (34,1%)	Gassman and Williams [1970]
 XLV	$[(C_6H_5CN)_2PdCl_2]$	 LII (100%)	Sakai et Al. [1971 b]
 XLVI	$[(C_6H_5CN)_2PdCl_2]$	 XXXVIII (100%)	Sakai et Al. [1971a]

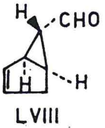
(*) The percentage yields are represented in parenthesis.

TABLE 6

Rearrangements of Strained Heterocycles by Rhodium Dicarbonyl Chloride Dimer.

Substrate	Products	References
 LIII(*)	 LV(*) LVII(*)	Grigg et Al. [1971 a]
 LIV	 LIX	Grigg et Al. [1971 a]
 LV	 LX	Grigg et Al. [1971 b]

(*) After heating the mixture of LVI and LVII with $[Rh(CO)_2Cl]_2$ at 100° for 15 min, the epimeric aldehyde LVIII can be isolated.



LVIII

TABLE 7

Reactions of Cyclopropane Derivatives with Rhodium Dicarbonyl Chloride Dimer.

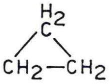
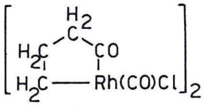
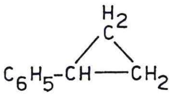
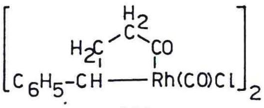
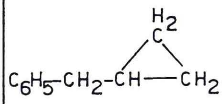
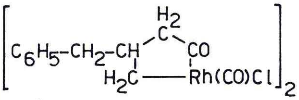
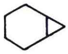
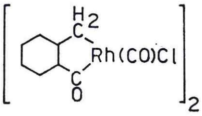
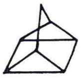
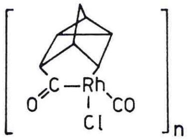
Substrate	Products	References
 XC	 C	Roundhill et Al. [1968]
 CI	 CIV	Powell and McQuillin [1971 b]
 CII	 CV	Powell and McQuillin [1971 b]
 CIII	 CVI	Powell and McQuillin [1971 b]
 I	 CVII	Cassar and Halpern [1970]

TABLE 8

π-Allylic Complexes of Pd(II) Deriving from Saturated Cyclopropane Derivatives and Di-μ-chloro-dichlorobis (alkene) dipalladium.

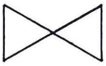
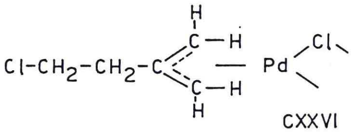
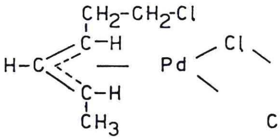
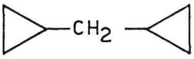
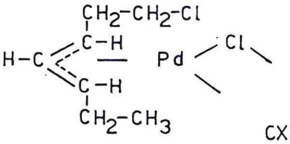
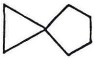
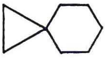
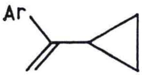
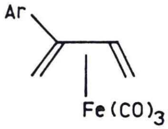
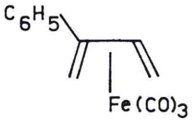
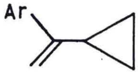
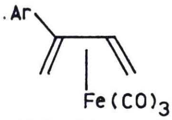
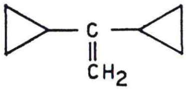
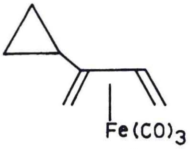
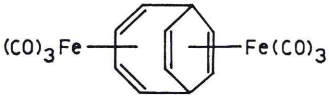
Cyclopropane Derivative	π-Allylic Complex	References
 CXXI	 CXXVI	Ketley and Braatz [1968]
 CXXII	 CXXVII	Ketley et Al. [1970]
 CXXIII,	 CXXVIII	Ketley et Al. [1970]
 CXXIV	—	Ketley et Al. [1970]
 CXXV	—	Ketley et Al. [1970]

TABLE 9

1,3-Diene-Fe(CO)$_3$ Complexes Prepared from Vinylcyclopropanes.

Substrate	π-Complex	References
 CXLIV a (Ar=p-CH_3O-C_6H_4)	 CXLVII (Ar=p-CH_3O-C_6H_4)	Sarel et Al.[1965]
 CXLIV b (Ar=C_6H_5)	 CXLVIII	Sarel et Al.[1965]
 CXLIV c (Ar=p-Cl-C_6H_4)	 CXLIX (Ar=p-Cl-C_6H_4)	Sarel et Al.[1965]
 CXLV	 CL	Ben-Shoshan and Sarel [1969]
 CXLVI	 CLII	Schrauzer et Al. [1964,1970]

CONCLUSIONS

The primary objective of the researches here surveyed is to predict either the propensity of a strained compound for the ring-opening or which reaction pathway will be followed. However, our understanding of these catalytic or stoichiometric processes is still rather inadequate and does not allow generally these predictions. Several competing factors, such as the nature of the transition metal, the structural features of the organic substrate and therefore the electronic energy levels of both the organic substrate and the metal can intervene.

Another cause for the difficulty in the full rationalization of the result can be that the observed overall product distribution can not reflect the true distribution obtained in the bond cleavage of the strained system. Extensive rearrangement, in fact, may rapidly follow the initial bond cleavage. Therefore a more detailed understanding of these reactions must await further study.

It is neverthless clear the value of these reactions. For instance, through «stoichiometric» ring-opening reactions have been obtained new classes of heterocyclic compounds in which the heteroatom is a transition metal. Many other unusual transition metal complexes have been prepared in this way.

On the other hand, the vast potential utility of the catalytic reactions has already found direct application in the synthesis of known or new alicyclic compounds. With regards to this, it also worthy mentioning that metal-promoted rearrangement of strained compounds not only may be good alternatives to thermal processes, but often represent the only way to rearrange alicyclic compounds into less strained isomers.

Finally, it must be pointed outh that mechanisms of some catalytic reactions have been related to these reactions (CASSAR et Al. [1970 a], ROSSI et Al. [1972 c]).

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