Role of orbital symmetry in transition metal promoted ring opening reactions of methylenecyclopropanes and cyclobutenes

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Abstract. Transition metals catalyse a variety of organic reactions, of which the ring opening of strained ring organic molecules generated a lot of interest. Theoreticians predicted a metal orbital catalysed pathway, which involved concerted bond breaking and bond forming. On the other hand experimentalists were able to show that the reaction was not proceeding through a concerted pathway by intercepting the intermediates involved. There remained, however, two ring systems methylenecyclopropanes and cyclobutenes—whose reactions with metal complexes seemed to be of a concerted nature. An analysis of the reactions of different metal complexes with these ring systems and the theoretical predictions provide a rationale for understanding these reactions.

Keywords. Metal orbital catalysis; methylenecyclopropanes; cyclobutenes; ring opening reactions; orbital symmetry; transition metal.

1. Introduction

Several organic molecules with severely strained ring systems owe their stability to symmetry constraints present in the reaction pathways available to them. These symmetry constraints essentially form the walls of a potential energy well in which the molecule is encaged. Ever since the presence of these energy barriers were expounded (Woodward and Hoffman 1971), there have been repeated attempts to find ways and means of overcoming these constraints. Although the use of photochemical energy has been successful in many cases, often it brings about undesirable results. Transition metal complexes have also been quite useful in bringing about certain transformations. It is the intent of this article to review the role played by orbital symmetry in the transition metal catalysed reactions involving methylenecyclopropanes and cyclobutenes and to present some of our recent results in this field.

2. Mechanisms of ring opening reactions

2.1 *Theoretical models*

As early as in 1965, the role of transition metal complexes in rendering accessible these formally forbidden reaction pathways, was analysed theoretically (Mango and Schachtschneider 1965). This treatment predicted that the symmetry constraints of most forbidden reactions would be removed if they occurred in the coordination sphere of the transition metal complex.

This theoretical treatment was followed by several others (Fukui and Inagaki 1975; Pearson 1976; Pettit *et al* 1969; Dewar 1971). In a very interesting article on the origin of

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symmetry rules and their theoretical basis, Dewar (1971) has concluded that, just as antiaromatic molecules like cyclobutadiene are stabilized by transition metal complexes, anti-aromatic transition states will also be stabilized by transition metal complexes. This explanation completely ignores the role of supportive ligands and their symmetry. However, it has been shown (Mango and Schachtschneider 1971) that the presence of certain ligand geometries can result in a "restrictive ligand field" preventing the stabilization of the transition state.

Another view of the mode of action was (Pettit *et al* 1969) that the symmetry requirements were not necessarily removed. However there was a drastic reduction in the energy barrier, since the transfer of electrons in the transition state now took place from the HOMO to the LUMO of the metal complex. These were invariably *d*-orbitals of the metal and hence the difference was much lower than the difference between the HOMO and LUMO of the free ligand. The difference in the *d*-orbital energies however depended on the ligands and their symmetry and hence this view readily accommodates the role of "restrictive ligand fields".

Although these theoretical treatments arrived at the general conclusion that the activation energy of forbidden concerted reactions would be lowered in the coordination sphere of a transition metal complex, proof that these reactions were indeed concerted had to come from experiments. Pathways involving metallacycles, metallocarbenes and zwitterionic intermediates had to be eliminated.

2.2 *Preliminary experimental results*

The conversion of quadricyclane to norbornadiene was catalyzed by Rh(1) complexes. This process a $\sigma_2 S + \sigma_2 S$ cycloreversion was thought to occur in the coordination sphere of rhodium and hence an example of metal orbital catalysis. However the detailed investigation of the mechanism (Cassar and Halpern 1971) showed that the reaction proceeded through distinct intermediates (figure 1) such as 2. These could be trapped in the presence of carbon monoxide to give 3, before it ring-opened to give norbornadiene.

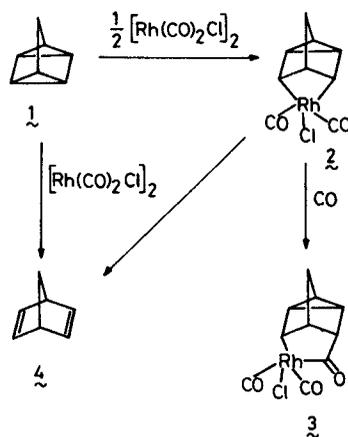The discovery of metallocycles as intermediates was followed by the discovery of

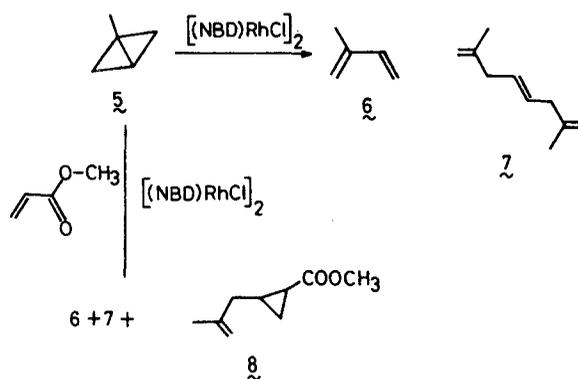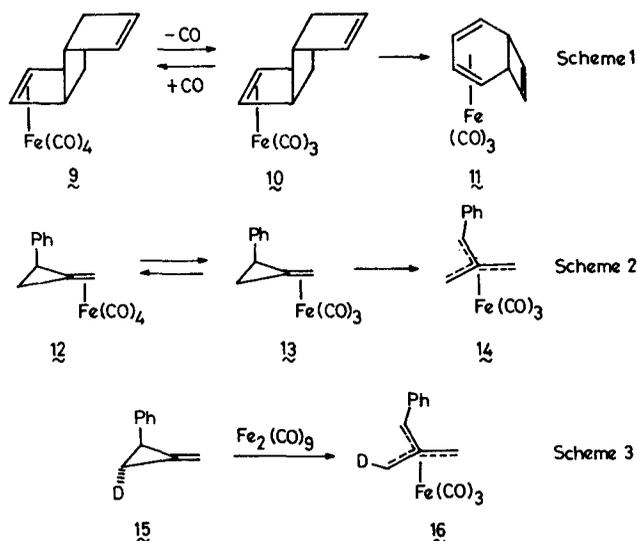**Figure 1.**   Rhodium(1)-catalyzed transformation of quadricyclane to norbornadiene.

Figure 2. Carbene intermediates in metal-assisted ring opening of bicyclobutenes.

metallocarbenes (Gassman and Reitz 1973). An example of a ring opening reaction which was thought to proceed in a concerted fashion but is in reality a carbene-mediated process is shown in figure 2. The intermediate carbene could actually be trapped in the presence of a trapping agent.

In spite of these reactions which had disappointed theoretical chemists, interest in these fields continued unabated. Slegir *et al* (1974) reported the ring opening of an Fe(CO)$_4$ complex of anti-tricyclo $|4,2,0,0^{2,5}|$ octa -3-7-diene 9 to give an iron tricarbonyl complex 11. The first step in the reaction sequence seemed to be a reversible dissociative step where the complex lost 'CO' to form a 16-electron complex 10. This coordinatively unsaturated intermediate then ring opened to give 11 (scheme 1).

According to the Woodward and Hoffman rules, cyclobutenes can only ring open in a conrotatory fashion when thermally excited. However, if the fused ring cyclobutene in 9 opened in a conrotatory-allowed pathway it would end up with a trans double bond.

In the absence of the metal the disrotatory pathway observed in the complex is forbidden and does not occur in refluxing hexane. So the metal seems to have lowered the energy of activation for this unfavourable process. In the absence of any evidence for metal stabilised reactive intermediates it was concluded that this was a concerted reaction occurring in the coordination sphere of the transition metal complex.

Another example of such a process came from the methylenecyclopropane ring system. Noyori *et al* (1969) reported the formation of a trimethylenemethane complex of $Fe(CO)_3$ from phenylmethylenecyclopropane and $Fe_2(CO)_9$ (scheme 2). Here, as in the reaction of cyclobutenes, a 16-electron intermediate seemed to have formed which then had ring-opened to give the final product. In this case, the ring opening of methylenecyclopropanes in the absence of the metal does not occur, since trimethylene-methane is an unstable biradical. However the mode of ring opening could be either disrotatory or conrotatory. The favoured mode of ring opening could be obtained from a theoretical calculation. In the interest of clarity it is best to examine the experimental results from these two ring systems separately.

3. ˙ Methylenecyclopropane ring opening reactions

The application of symmetry considerations to the ring opening of methylenecyclo-propanes to give trimethylenemethane complexes was done by Pinhas and Carpenter (1980a). They distinguished three modes of ring opening, a disrotatory towards the metal pathway, a disrotatory away from the metal pathway, and a conrotatory pathway in which both components of the breaking bond turn in the same direction. Using extended Huckel calculations they found that the disrotatory away from the metal pathway was the most favourable pathway.

To check this prediction they also synthesized trans-2-phenylmethylenecyclo-propane-3-d_1 4 and reacted it with $Fe_2(CO)_9$. This yielded a single product 15 (Pinhas and Carpenter 1980b). If one made the reasonable assumption that the phenyl group was anti to the coordinated $Fe(CO)_4$ in the initial complex, then the reaction had proceeded in the predicted mode (scheme 3). The stereospecificity with which the reaction had proceeded ruled out the intermediacy of a ring-opened zwitterionic species which had been implicated earlier (Billups *et al* 1972). It was also difficult to see how a metallacyclobutane intermediate could lead to a stereospecific product. Although this preliminary result was quite encouraging, the interaction of methylenecyclopropane with metal complexes is quite complex and leads to a variety of products depending on the metal and ligand. Even with the same metal and ligand system $Fe(CO)_n$ one can obtain as many as four products depending on the substituent on the ring carbons (table 1).

In the case of phenylmethylenecyclopropane itself two products were formed both stereospecifically (Pinhas 1980; Pinhas *et al* 1981). In view of this complexity, a more detailed study of the reaction was in order before making definitive claims about the mechanism (figure 3) of the reaction. The need for such a study was more obvious when two other research groups working on palladium and molybdenum came up with a cyclopropylcation mechanism for explaining the stereospecificity in their reactions.

Methylenecyclopropanes can be cleaved by palladium complexes to yield a variety of complexes (Noyori and Takaya 1969; Green and Hughes 1976). However the cleavage of the 2–3 bond of the methylenecyclopropane was investigated by Hughes *et al* (1979).

Table 1. Relative percentages of different products isolated and characterised from the reaction of methylenecyclopropanes and $Fe_2(CO)_9$.

Methylenecyclopropane	Intermediate olefin-$Fe(CO)_4$ complex*	Trimethylene-methane complex	Butadiene complex	Dinuclear complex
Methylenecyclopropane	—	—	100	—
2-Phenylmethylenecyclopropane	—	55	45	—
2,2-Diphenylmethylenecyclopropane	40	100	—	—
2,3-Trans-Dicarbomethoxy methylenecyclopropane	88	—	78	3
2,3-Cis-Dicarbomethoxy-methylenecyclopropane	65	—	88	1·5

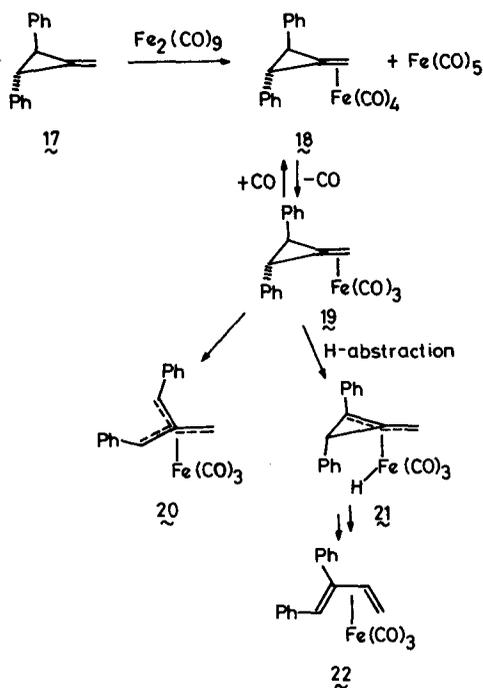* Percentage of intermediate with reference to starting material isolated at short reaction times.

Figure 3. Carpenter–Pinhas mechanism for the formation of butadiene and trimethylenemethane from 2,2-diphenylmethylenecyclopropane and iron carbonyl.
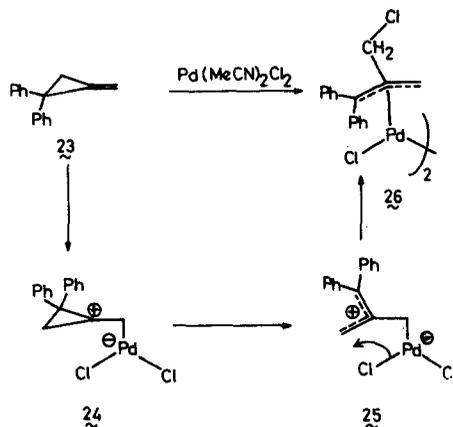
Figure 4. Zwitterionic intermediates in Pd(II)-promoted ring opening of 2,2-diphenylmethylene-cyclopropane.

Their results showed that the metal initially attacked the olefinic centre. The olefin complex then polarised to form a zwitterion with a cyclopropyl cation and an anionic metal centre. Cyclopropyl cations are known (Skell and Sandler 1958) to ring open very rapidly in a disrotatory fashion. Hence this zwitterion would undergo a ring opening reaction (figure 4) and then transfer a chloride ion to form the final product.

This mechanism seems to suggest that cleavage of the 2–3 bond of the methylene-cyclopropane is the result of the positive charge on the central atom. Such a reaction sequence has been implicated in the formation of the cationic trimethylenemethane complex of $|Cp \, Mo(CO)|^+$ (Barnes and Green 1980). It is supposed that $|Cp \, Mo(CO)_3|^+$ coordinated to the olefin and formed a zwitterionic species. This subsequently underwent a disrotatory ring opening, which was followed by loss of carbon monoxide. The metal then slipped into place forming the trimethylenemethane complex.

Although the Carpenter–Pinhas mechanism accounts very well for the stereo-specificity in the formation of the two products, trimethylenemethane and butadiene complexes, the formation of the trimethylenemethane complex could be equally well accounted for, by a zwitterionic mechanism. If this be the case the $Fe(CO)_4$ olefin complex partitions to give the zwitterionic intermediate and the $Fe(CO)_3$ complex. The $Fe(CO)_3$ complex would then be responsible for the formation of the butadiene complex but the zwitterion could ring open in a fast step and then lose a 'CO' to form the trimethylenemethane complex as shown in figure 5.

To distinguish between these two mechanisms, one had to prove that the 16-electron olefin complex was the intermediate which partitioned between the trimethylene-methane and butadiene complexes. Evidence suggesting that the 16-electron $Fe(CO)_3$ complex was indeed an intermediate in the pathway leading to the trimethylene-methane complex came when the olefin $Fe(CO)_4$ complex was isolated (Pinhas *et al* 1981) and characterised by x-ray crystallography. They then showed that careful treatment of this complex with trimethylamine-N-oxide a decarbonylating agent (Shvo and Hazum 1975) would lead to the formation of the trimethylenemethane complex. Another piece of evidence was that benzylidene acetone $Fe(CO)_3$ and "$Fe(CO)_3$" transfer reagent (Scholes *et al* 1974; Graham *et al* 1977) brought about the conversion of phenylmethylenecyclopropane to the butadiene and trimethylenemethane com-plexes observed in its reaction with $Fe_2(CO)_9$. When stereospecifically labelled methylenecyclopropane was used in the reaction with $Fe(CO)_3$ transfer reagent it led to the same stereospecific products in the same ratio. This strongly suggested that the $Fe(CO)_3$ olefin complex was a common intermediate for the formation of the butadiene and trimethylenemethane complexes.

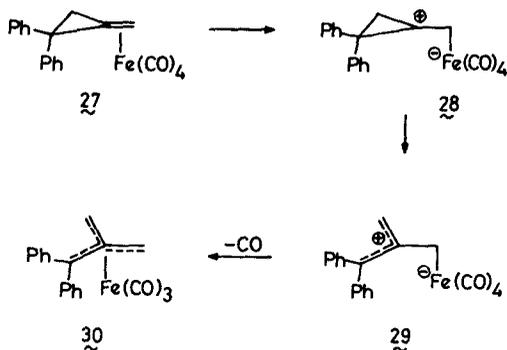However the final and conclusive evidence came from the observation of an induced

Figure 5. Zwitterionic mechanism applied to iron carbonyl-assisted ring opening of 2,2-diphenylmethylenecyclopropane.
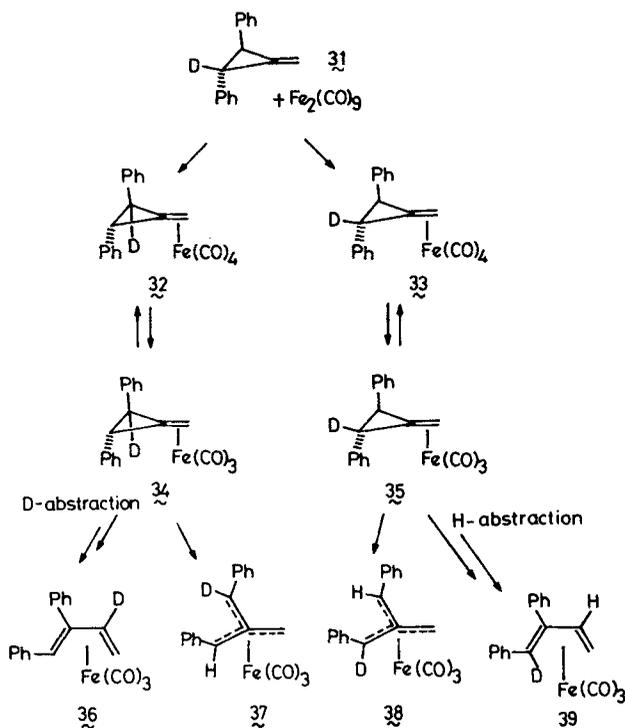
Figure 6. The induced kinetic isotope effect illustrated in the reaction of trans-2,3-diphenylmethylenecyclopropane-2-d_1 with $Fe_2(CO)_9$.

kinetic isotope effect (IKIE) (Samuelson and Carpenter 1981). This showed that the 16-electron olefin complex was partitioning between the butadiene and trimethylene-methane complexes as illustrated in figure 6. The IKIE arises from the fact that complexes 34 and 35 would be formed in equal proportions since they are identical except for the position of the isotope which is far removed from the reaction centre *i.e.* the olefin. However when 34 and 35 partition to give the butadiene and trimethylene-methane complexes, 34 gives more of the trimethylenemethane complex. This happens because D-abstraction is involved in the formation of the butadiene complex which makes the intermediate 34 to funnel into the easier pathway. However, there is no such favouring of one compound over the other in the reaction of 35. This leads to a ratio of 37/38 > 1·0. Since there was no direct isotope effect leading to this observation and since it was induced by an isotope effect in parallel pathway it has been termed the induced kinetic isotope effect.

If the cyclopropyl cation mechanism were operating, the difference in the ratio of 37/38 could not arise except as a result of a steric isotope effect as illustrated in figure 7. This effect is due to a difference in the C–H and C–D bond lengths and it would lead to a ratio of 37/38 > 1·0. The absence of steric isotope effect was confirmed by the reaction of 3-deuterio-2,2-diphenylmethylenecyclopropane. In this case there cannot be any induced kinetic isotope effect because the $Fe(CO)_3$ complex forms only the tri-methylenemethane complex but the possibility of a steric isotope effect would still exist.
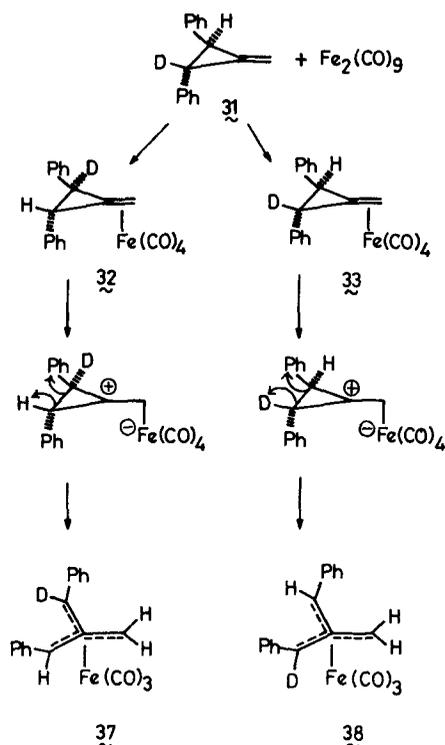
Figure 7. The steric isotope effect illustrated for the formation of trimethylenemethane complexes from trans-2,3-diphenylmethylenecyclopropane-2-d_1 and $Fe_2(CO)_9$.

Thus the evidence strongly points to a metal orbital catalyzed reaction pathway for the formation of trimethylenemethane complexes from methylenecyclopropanes and ironcarbonyls.

4. Cyclobutene ring opening reactions

The initial results obtained by (Slegir *et al* 1974) showed that the iron carbonyls were capable of promoting a disrotatory ring opening of the cyclobutene. The extended Huckel calculation done by Pinhas and Carpenter (1980a) also indicated that the disrotatory mode of ring opening, where the breaking bond moved towards the metal, was the lowest energy pathway. The other disrotatory mode of ring opening where the breaking bond moved away from the metal, was the highest energy pathway with the conrotatory mode falling in between.

Although these calculations fell in line with the known results, the available experimental data was not a good test for theory. The parent cyclobutene does not ring open to give the butadiene complex with iron carbonyls. A possible reason for this might be inferred from the substituent effect observed in the ring opening reactions of methylenecyclopropanes. The absence of any substituent on C-2 and C-3 of the methylenecyclopropane leads to H-abstraction reaction only. When one phenyl group is present on the ring carbon it leads to both H-abstraction and ring opened products.

When two phenyl groups are present only the ring-opened product is formed. Thus there seems to be a bond weakening effect associated with the presence of phenyl groups. However this simple substituent effect is not borne out in the reactions of substituted cyclobutenes (Samuelson 1983). 3-Phenyl cyclobutene isomerises to 1-phenylcyclobutene on reaction with $Fe_2(CO)_9$ possibly through a hydride intermediate as shown in figure 8. This seems to indicate that one is competing with a H-abstraction pathway.

One way to overcome this hurdle would be to lower the energy of activation for the ring opening reaction by increasing the number of substituents on the ring or suitably changing them. The other is to nullify the effect of H-abstraction by judicious substitution (Samuelson 1983). The latter approach has the added advantage that it is possible to judge the minimum substitution necessary to bring about the ring opening process. Both 3,3-diphenylcyclobutene and 1,3-diphenylcyclobutene failed to ring open on reaction with iron carbonyls. The former had the added advantage of a doubly weakened C-3–C-4 bond.

Thus simple cyclobutenes seem to be quite resistant to the ring opening reaction. This is quite surprising, considering the fact that bicyclocyclobutenes ring open in such a facile reaction.

What is more disconcerting is that some bicyclic cyclobutenes ring open in a disrotatory—away from the metal mode. This pathway is predicted to be the highest energy pathway according to the calculations (Pinhas and Carpenter 1980a). One example is the ring opening of the $Fe(CO)_4$ complex shown in scheme 4, to give the ring opened $Fe(CO)_3$ complex of O-p-dibenzene (Grimme and Schneider 1977). The other
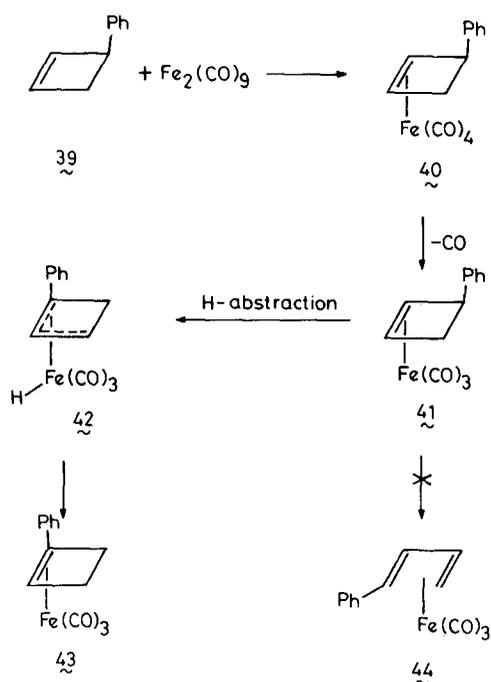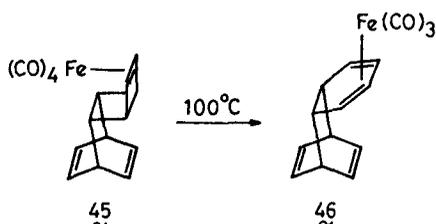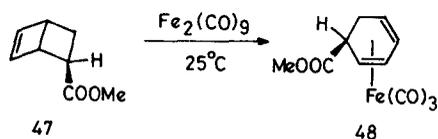

Figure 8. Isomerisation of 3-phenylcyclobutene.

Scheme 4   Scheme 5

example is the ring opening of a bicyclic adduct formed from the reaction of cyclobutadiene and methyl acrylate with $Fe_2(CO)_9$ (Samuelson 1983) as shown in scheme 5.

Apparently the iron coordinated *syn* to the carbomethoxy group as expected (Whitesides *et al* 1974). However contrary to the prediction made by theory the ring opened in a facile disrotatory—away from the metal mode!

In none of these reactions the presence of a metallacycle or other intermediates seems to be involved. Thus a metal orbital catalysed reaction seems to be the pathway chosen by the complex. However the predictions based on theory fall through.

5. Conclusion

Compared to the phenomenal success the Woodward and Hoffman rules have had in organic chemistry, the application of symmetry considerations to organotransition metal chemistry has yielded very little fruit. This is not to say that symmetry has no role in these reactions. What it does reveal is that the presence of the transition metal complex opens up a host of new pathways that were previously inaccessible to the free ligand.

This may involve a transition metal stabilised zwitterion, a metallacycle or a metallocarbene or even a metal orbital catalysed reaction pathway. For the simple reason that there are so many pathways available and at times not very different in energies—there does not seem to be a single factor determining the course of the reaction. The capability of the metal to form M–C bonds, C–C bond strength, steric encumbrances, and strain energy seem to play a role in determining the course of the reaction.

In the case of methylenecyclopropanes the choice of a metal in a higher oxidation state, as in the case of the molybdenum or the palladium complex, may lead to the formation of zwitterionic intermediates. The ability to form good M–C bonds could have also made this reaction pathway more favourable. The use of a first period transition metal in a low oxidation state favours the reaction proceeding through a metal orbital catalyzed pathway. The close correspondence between theory and experiment seems to indicate that symmetry plays a vital role in determining the mode of ring opening.

It is unfortunate however that none of the simple cyclobutenes ring open to form butadiene complexes. The fact that bicyclic cyclobutenes ring open, but in a mode different from that predicted by theory, is disturbing indeed. There are several possible explanations for this behaviour. The first is that the reaction is not really a concerted

orbital symmetry-controlled pathway. It is possible that this reaction is proceeding through a distinct intermediate as in the case of the Rh(1) catalyzed reaction of quadricyclane. The other explanation is that the structure assigned to the diene $Fe(CO)_3$ complexes in schemes 4 and 5 are incorrect. If the iron was coordinated on the other side of the diene unit in both cases, the ring opening has proceeded in complete accord with theory! An x-ray crystal structure determination of these complexes would resolve the question. Till now no such work has been done.

Further work has to be done in the cyclobutene ring system to determine the reaction mechanism. The predictions made by theory certainly had the effect of promoting research in this field and it will continue to do so till all questions regarding these reactions are solved satisfactorily.

Acknowledgements

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