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An Orbital Interaction Rationale for the Role of Catalysts

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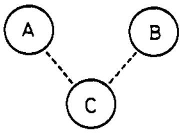
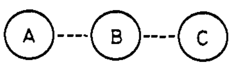
Abstract: The orbital interaction scheme having successfully been applied to interpreting the nature of two-molecule interactions is extended to three-body interactions involving catalytic actions of the third species influencing the two molecules to react with each other. The importance of the interactions among HOMO's and LUMO's of three species is stressed with some perturbation theoretical formulations to explain how the third species can assist an energetically or symmetrically disfavored process to take place. Several illustrative examples are given.

The molecular orbital (MO) perturbation theory based on the orbital interaction of molecules has played a significant role in developing the theory of chemical reactions.[1-4] The reactivity indices derived from such an approach defined in regard to the isolated reactant molecule concisely reflected various chemical data.[1] Recently elucidated, various stereoselective phenomena[5] were also treated in the same fashion.[1c] Theories of organic chemical reactions thus far developed have mostly been engaged in bimolecular interactions but few in three-body interactions.[3e] The marvellous activity of catalysts is essentially based on the role of a third species in two-molecule interactions. An abundance of experimental results has been accumulated and are now ready for our investigation of the detailed mechanism.

Consider a catalytic process in which the interaction between two reactants A and B is promoted in the presence of the third species C. The species C may interact with both A and B simultaneously (Scheme I) and may also interact only with one of them (Scheme II). In the present paper the perturbed energy and wave function are given by extending the theory for bimolecular interactions developed previously by the group of the present authors.[3a]



Scheme I



Scheme II

Theory

The ground-state wave function of the total interacting system Ψ_0 is represented by a linear combination of various configuration functions Ψ_K.

$$\Psi_0' = \sum_K C_K \Psi_K$$

The function Ψ_K is constructed by Slater determinants so as to be a spin eigenfunction, each determinant being composed of the MO's of isolated systems A, B, and C of the same geometry as in the interacting system. These MO's may be occupied or unoccupied in the initial states of each isolated molecule.

The interaction energy of the three systems, ΔW, is defined by the following equation

$$\Delta W = W - (W_{\mathrm{AO}} + W_{\mathrm{BO}} + W_{\mathrm{CO}}) \tag{1}$$

where W_{AO}, W_{BO}, and W_{CO} are the ground-state energies of each isolated system, and W is the lowest energy of the whole interacting system.

The secular determinant is represented by

$$\begin{vmatrix} H_{00} - E \ldots H_{0K} - S_{0K}E \ldots H_{0L} - S_{0L}E \ldots \\ H_{K0} - S_{K0}E \ldots H_{KK} - E \ldots H_{KL} - S_{KL}E \ldots \\ H_{L0} - S_{L0}E \ldots H_{LK} - S_{LK}E \ldots H_{LL} - E \ldots \end{vmatrix} = 0 \tag{2}$$

in which the subscripts stand for electronic configurations, H being the Hamiltonian operator of the combined system, and H_{IJ} and S_{IJ} are the integrals represented by

$$H_{IJ} = \int \Psi_I^* H \Psi_J \mathrm{d}\tau$$
$$S_{IJ} = \int \Psi_I^* \Psi_J \mathrm{d}\tau$$

On the assumption that H_{00} is the lowest of all diagonal elements, that no others are equal to H_{00}, and that S_{IJ} and H_{IJ} in the off-diagonal elements are small, the perturbed energy H_{00}' can be expanded in the following form

$$H_{00}' = H_{00} + \sum_K \frac{|H_{0K} - S_{0K}H_{00}|^2}{H_{00} - H_{KK}} + \sum_K \sum_{L(\neq K)} \frac{(H_{0K} - S_{0K}H_{00})(H_{L0} - S_{L0}H_{00})(H_{KL} - S_{KL}H_{00})}{(H_{00} - H_{KK})(H_{00} - H_{LL})} + \text{(small terms of higher than 3rd order)} \tag{3}$$

The subscripts K and L stand for configurations not equal to 0. The perturbed wave function Ψ_0' is given by

$$\Psi_0' = \left\{1 - \sum_K \frac{S_{K0}(H_{0K} - S_{0K}H_{00})}{H_{00} - H_{KK}} - \frac{1}{2}\sum_K \frac{|H_{0K} - S_{0K}H_{00}|^2}{(H_{00} - H_{KK})^2}\right\}\Psi_0 + \sum_K \left\{\frac{H_{K0} - S_{K0}H_{00}}{H_{00} - H_{KK}} + \sum_{L(\neq K)} \frac{(H_{L0} - S_{L0}H_{00})(H_{KL} - S_{KL}H_{00})}{(H_{00} - H_{KK})(H_{00} - H_{LL})}\right\}\Psi_K + \text{(small terms of higher than 2nd order)} \quad (4)$$

We will consider the case in which two reactant molecules (A and B) cannot effectively interact with each other until a third species or catalyst (C) intervenes between them (Scheme I). In this way one can assume that the MO overlapping between A and B, s_{ab}, is 0 while those between A and C and between B and C, denoted by s_{ac} and s_{bc}, respectively, have small nonzero values. If it is further assumed that the interaction is not so strong, and that H_{IJ} is nearly proportional to S_{IJ}, one can obtain the general relation of the order of magnitude between the off-diagonal elements and MO overlaps

$$H_{IJ} - S_{IJ}H_{00} \propto S_{IJ} = o(s_{ac}{}^{\mu}s_{bc}{}^{\nu})$$

in which μ and ν are the minimum numbers of electron transfer between A and C, and between B and C, respectively, required to shift the electron configuration from I to J.[3a]

We are now concerned with the effect of an intermediary C on the interaction between A and B. For this purpose, one can take out of account those terms in the right-hand sides of eq. 3 and 4 containing the configurations where electron rearrangements take place only either between A and C or between B and C. To be of present interest: (1) the electron configurations of the combined system involved in each term should contain at least one of the transferred or polarized configurations of molecule A and at least one of the transferred or polarized configurations of molecule B; (2) the order of magnitude of the term in Ψ_0' is not higher than the third order of MO overlap ($o(s_{ac}{}^{\mu}s_{bc}{}^{\nu})$, $\mu + \nu \leq 3$), and that in H_{00}' is not higher than the fourth order of MO overlap ($o(s_{ac}{}^{\mu}s_{bc}{}^{\nu})$, $\mu + \nu \leq 4$).

The terms appearing in Ψ_0' which involve occupied MO's of A and unoccupied MO's of B or the reverse are as follows:

$$\Psi_0': \quad \sum_{i}^{\substack{\text{A}\\ \text{occ}}} \sum_{l}^{\substack{\text{B}\\ \text{uno}}} \left[\left\{\frac{H_{0,i\to l} - S_{0,i\to l}H_{00}}{H_{00} - H_{i\to l,i\to l}} + \sum_{m}^{\substack{\text{C}\\ \text{occ}}} \frac{(H_{0,m\to l} - S_{0,m\to l}H_{00})(H_{m\to l,i\to l} - S_{m\to l,i\to l}H_{00})}{(H_{00} - H_{m\to l,m\to l})(H_{00} - H_{i\to l,i\to l})} + \sum_{n}^{\substack{\text{C}\\ \text{uno}}} \frac{(H_{0,i\to n} - S_{0,i\to n}H_{00})(H_{i\to n,i\to l} - S_{i\to n,i\to l}H_{00})}{(H_{00} - H_{i\to n,i\to n})(H_{00} - H_{i\to l,i\to l})}\right\}\Psi_{i\to l} + \sum_{n}^{\substack{\text{C}\\ \text{uno}}} \sum_{m}^{\substack{\text{C}\\ \text{occ}}} \left\{\frac{(H_{0,m\to l} - S_{0,m\to l}H_{00})(H_{m\to l,i\to n} - S_{m\to l,i\to n}H_{00})}{(H_{00} - H_{m\to l,m\to l})H_{00} - H_{i\to n,i\to n})}\Psi_{i\to n} + \frac{(H_{0,i\to n} - S_{0,i\to n}H_{00})(H_{i\to n,m\to l} - S_{i\to n,m\to l}H_{00})}{(H_{00} - H_{i\to n,i\to n})(H_{00} - H_{m\to l,m\to l})}\Psi_{m\to l}\right\} + \sum_{n}^{\substack{\text{C}\\ \text{uno}}} \sum_{m}^{\substack{\text{C}\\ \text{occ}}} \frac{H_{0,(i\to n,m\to l)} - S_{0,(i\to n,m\to l)}H_{00}}{H_{00} - H_{(i\to n,m\to l)(i\to n,m\to l)}} \times \Psi_{i\to n,m\to l}\right] + \sum_{j}^{\substack{\text{A}\\ \text{uno}}} \sum_{k}^{\substack{\text{B}\\ \text{occ}}} [\text{corresponding terms involving unoccupied MO's of A and occupied MO's of B}] \quad (5)$$

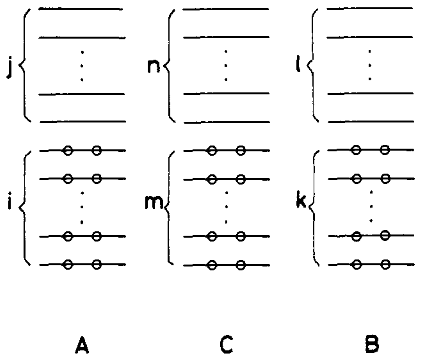


Figure 1.

The letters i, j, k, l, m, and n represent the occupied orbitals and the unoccupied orbitals of A, B, and C molecules (Figure 1). The arrow in the subscripts, e.g., $i \to l$, signifies the electron transfer from the ith occupied MO of A to the lth unoccupied MO of B. The last term of expression 5 includes all the corresponding terms originating from the mathematical equivalency of A and B.

The energy terms in H_{00}' are correspondingly given in the same order of expression 5.

H_{00}':

$$\sum_{i}^{\substack{\text{A}\\ \text{occ}}} \sum_{l}^{\substack{\text{B}\\ \text{uno}}} \left[\frac{|H_{0,i\to l} - S_{0,i\to l}H_{00}|^2}{H_{00} - H_{i\to l,i\to l}} + 2\sum_{n}^{\substack{\text{C}\\ \text{uno}}} \mathbf{R}\,\frac{(H_{0,i\to n} - S_{0,i\to n}H_{00}((H_{i\to l,0} - S_{i\to l,0}H_{00})(H_{i\to n,i\to l} - S_{i\to n,i\to l}\mathrm{H}_{00})}{(H_{00} - H_{i\to n,i\to n})(H_{00} - H_{i\to l,i\to l})} + 2\sum_{m}^{\substack{\text{C}\\ \text{occ}}} \mathbf{R}\,\frac{(H_{0,m\to l} - S_{0,m\to l}H_{00})(H_{i\to l,0} - S_{i\to l,0}H_{00})(H_{m\to l,i\to l} - S_{m\to l,i\to l}H_{00})}{(H_{00} - H_{m\to l,m\to l})(H_{00} - H_{i\to l,i\to l})} + 2\sum_{n}^{\substack{\text{C}\\ \text{uno}}} \sum_{m}^{\substack{\text{C}\\ \text{occ}}} \mathbf{R}\,\frac{(H_{0,i\to n} - S_{0,i\to n}H_{00})(H_{m\to l,0} - S_{m\to l,0})(H_{i\to n,m\to l} - S_{i\to n,m\to l}H_{00})}{(H_{00} - H_{i\to n,i\to n,})(H_{00} - H_{m\to l,m\to l})} + \sum_{n}^{\substack{\text{C}\\ \text{uno}}} \sum_{m}^{\substack{\text{C}\\ \text{occ}}} \frac{|H_{0,(i\to n,m\to l)} - S_{0,(i\to n,m\to l)}H_{00}|^2}{H_{00} - H_{(i\to n,m\to l),(i\to n,m\to l)}}\right] + \sum_{j}^{\substack{\text{A}\\ \text{uno}}} \sum_{k}^{\substack{\text{B}\\ \text{occ}}} [\text{corresponding terms involving unoccupied MO's of A and occupied MO's of B}] \quad (6)$$

Here **R** signifies the real part.

We look at the sign of the third-order perturbation energy term in eq 3. One can write one of the third-order perturbation terms as

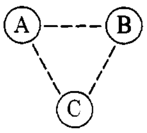
$$S_{0K}S_{KL}S_{L0} \times \frac{(H_{0K}/S_{0K}) - H_{00})((H_{KL}/S_{KL}) - H_{00})((H_{L0}/S_{L0}) - H_{00})}{(H_{00} - H_{KK})(H_{00} - H_{LL})}$$

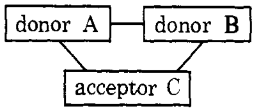
The term $((H_{IJ}/S_{IJ}) - H_{00})$ usually is negative if S_{IJ} is small. Accordingly, the condition that this term becomes negative is

$$S_{0K}S_{KL}S_{L0} > 0 \quad (7)$$

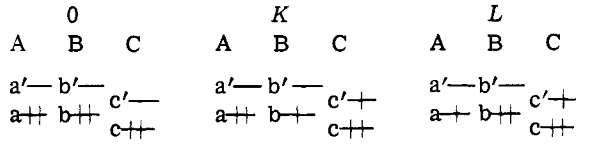
since the product of energy gaps in the denominator is of plus sign in the ground-state interaction. Suppose that we can choose, the only one, the most important combination of three configurations 0, K, and L from such third-order terms by considering the donor-acceptor relationship of the three interacting systems A, B, and C. The inequality in (7) plays a conspicuous role in determining the mode of favorable interaction of A, B, and C if one permits the direct interaction between the reactants A and B. This implies the consideration of a cyclic three-molecule interaction (Scheme III). For instance, consider the case of the following type of interaction:

Scheme III





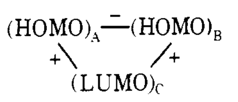
Then the most important combination of electron configurations is



where a, b, and c are HOMO's and a′, b′, and c′ are LUMO's, and obviously

$$S_{0K}S_{KL}S_{L0} \sim -s_{\mathrm{ab}}s_{\mathrm{ac'}}s_{\mathrm{bc'}} > 0$$

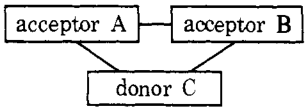
It is to be noted that the order of magnitude of these terms is of the third order of MO overlaps. The condition for stabilization is hence schematically represented by



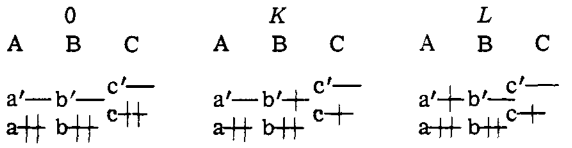
(7a)

where + and − denote in-phase and out-of-phase overlapping of MO's.

Similarly, the second important case is



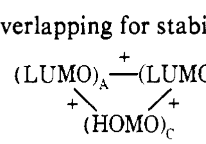
with the important combination of configurations



of the relation

$$S_{0K}S_{KL}S_{L0} \sim s_{\mathrm{a'b'}}s_{\mathrm{a'c}}s_{\mathrm{b'c}} > 0$$

The mode of MO overlapping for stabilization is evidently



(7b)

The use of these phase relationships is very convenient for discussing the mechanism of chemical reactions in general and will be discussed later with some applications to catalytic phenomena. Thus, it is to be noted that according to Scheme III the third-order terms with respect to MO overlapping come to be important.

Coming back to Scheme I again, it is significant here to investigate the physical reason for the mixing of configuration in the rearrangement of electronic structure of the interacting system. For instance, look at the three kinds of terms of $\Psi_{i\to l}$ in expression 5. The first one comes from the interaction between Ψ_0 and $\Psi_{i\to l}$ due to an indirect MO overlappings between A and B. The remaining two come from the mixing of delocalized configuration $i \to l$ induced by the delocalization $m \to l$, and by the one $i \to n$, respectively. The first three terms in H_{00}' of eq 6 can be understood similarly. The terms of $\Psi_{i\to n}$ and $\Psi_{m\to l}$ in Ψ_0' and the fouth in H_{00}' are interpreted to come from mutual induction between the delocalizations $i \to n$ and $m \to l$. The last terms given explicitly in Ψ_0' and H_{00}' signify a simultaneous delocalization from i to n and from m to l.

In this connection it is desired for practical uses to reduce expressions 5 and 6 into a form represented in terms of the MO's of isolated species A, B, and C. The first step is the reduction of the overlap integral S_{IJ} between two configurations I and J into the MO overlappings s_{ac} and s_{bc}. For instance, $S_{0,i\to l}$ in the first term of the coefficient of $\Psi_{i\to l}$ in eq 5 might have the order of magnitude of $2^{1/2}s_{il}$ $(=o(s_{\mathrm{ab}}))$ if a direct orbital overlapping between molecules A and B were allowed. Since we have assumed that $s_{\mathrm{ab}} = 0$, we have to be concerned with higher order terms, which are of the form $2^{1/2}s_{im}s_{ml} = o(s_{\mathrm{ac}}s_{\mathrm{bc}})$. It follows therefore that the order of magnitude of Ψ_0' is $o(s_{\mathrm{ac}}s_{\mathrm{bc}})$ and that of the corresponding term in H_{00}' is $o(s_{\mathrm{ac}}^2s_{\mathrm{bc}}^2)$.

Similarly, the order of magnitude of the remaining two terms of the coefficient of $\Psi_{i\to l}$ in eq 5 is also $o(s_{\mathrm{ac}}s_{\mathrm{bc}})$ and that of the corresponding term in H_{00}' is $o(s_{\mathrm{ac}}^2s_{\mathrm{bc}}^2)$.

In this way, one can derive expressions 5 and 6 represented in terms of each MO of the isolated species, A, B, and C. The procedure is similar to the derivation of eq 20 from eq 8b of ref 3a. The corresponding expressions are omitted here for brevity.

The remaining terms satisfying the conditions mentioned before, which appear in Ψ_0', are those which involve the interactions between occupied orbitals of A and B and unoccupied orbitals of C (eq 8 and 9). The first two terms of ex-

$$\Psi_0'\colon \sum_{i}^{\overset{\mathrm{A}}{\mathrm{occ}}} \sum_{k}^{\overset{\mathrm{B}}{\mathrm{occ}}} \sum_{n}^{\overset{\mathrm{C}}{\mathrm{uno}}} \sum_{n'}^{\overset{\mathrm{C}}{\mathrm{uno}}} \left[\left\{ \frac{(H_{0,k\to n'} - S_{0,k\to n'}H_{00})(H_{k\to n',i\to n} - S_{k\to n',i\to n}H_{00})}{(H_{00} - H_{i\to n,i\to n})(H_{00} - H_{k\to n',k\to n'})} \Psi_{i\to n} + \frac{(H_{0,i\to n} - S_{0,i\to n}H_{00})(H_{i\to n,k\to n'} - S_{i\to n,k\to n'}H_{00})}{(H_{00} - H_{i\to n,i\to n})(H_{00} - H_{k\to n',k\to n'})} \Psi_{k\to n'} \right\} + \frac{H_{0,(i\to n,k\to n')} - S_{0,(i\to n,k\to n')}H_{00}}{H_{00}' - H_{(i\to n,k\to n'),(i\to n,k\to n')}} \Psi_{i\to n,k\to n'} \right] \tag{8}$$

H_{00}':

$$\sum_{i}^{\overset{\mathrm{A}}{\mathrm{occ}}} \sum_{k}^{\overset{\mathrm{B}}{\mathrm{occ}}} \sum_{n}^{\overset{\mathrm{C}}{\mathrm{uno}}} \sum_{n'}^{\overset{\mathrm{C}}{\mathrm{uno}}} \left[2\mathrm{R} \frac{(H_{0,i\to n} - S_{0,i\to n}H_{00})(H_{k\to n',0} - S_{k\to n',0}H_{00})(H_{i\to n,k\to n'} - S_{i\to n,k\to n'}H_{00})}{(H_{00} - H_{i\to n,i\to n})(H_{00} - H_{k\to n',k\to n'})} + \frac{|H_{0(i\to n,k\to n')} - S_{0,(i\to n,k\to n')}H_{00}|^2}{H_{00} - H_{(i\to n,k\to n'),(i\to n,k\to n')}} \right] \tag{9}$$

pression 8 and the first one in 9 represent the mixing-in of one by way of the other of $i \to n$ and $k \to n'$ configurations, the orders of magnitude being ($o(s_{ac}s_{bc}^2)$ or $o(s_{ac}^2s_{bc})$ in Ψ_0', and $o(s_{ac}^2s_{bc}^2)$ in H_{00}'. The last terms in eq 8 and 9 result from the ditransferred configurations in which A and B act as donors and C as an acceptor (the orders of magnitude are $o(s_{ac}s_{bc})$ in Ψ_0' and $o(s_{ac}^2s_{bc}^2)$ in H_{00}').

Similarly, the terms involving the interaction between unoccupied orbitals of A and B and occupied orbitals of C are shown in eq 10 and 11. The criterion for picking up these terms was only the magnitude of the numerators. The second step is the discussion of the magnitude of denominators. The energy difference of two configurations can easily be approximated in terms of the difference between two MO energies. One can see the significance of the highest occupied (HO) MO and the lowest unoccupied (LU) MO of each isolated system in the summations in eq 8-11. Evidently, these particular MO's make the magnitude of corresponding denominators smallest. As well as in two-molecule interaction cases,[3] the conspicuous role of HOMO and LUMO can in this way apply to the present case.

Ψ_0':

$$\sum_{j}^{\overset{\mathrm{A}}{\underline{\mathrm{uno}}}} \sum_{l}^{\overset{\mathrm{B}}{\underline{\mathrm{uno}}}} \sum_{m}^{\overset{\mathrm{C}}{\underline{\mathrm{occ}}}} \sum_{m'}^{\overset{\mathrm{C}}{\underline{\mathrm{occ}}}} \left[\left\{ \frac{(H_{0,m'\to l} - S_{0,m'\to l}H_{00})(H_{m'\to l,m\to j} - S_{m'\to l,m\to j}H_{00})}{(H_{00} - H_{m'\to l,m'\to l})(H_{00} - H_{m\to j,m\to j})} \Psi_{m\to j} + \frac{(H_{0,m\to j} - S_{0,m\to j}H_{00})(H_{m\to j,m'\to l} - S_{m\to j,m'\to l}H_{00})}{(H_{00} - H_{m\to j,m\to j})(H_{00} - H_{m'\to l,m'\to l})} \Psi_{m'\to l} \right\} + \frac{H_{0,(m\to j,m'\to l)} - S_{0,(m\to j,m'\to l)}H_{00}}{H_{00} - H_{(m\to j,m'\to l),(m\to j,m'\to l)}} \Psi_{m\to j,m'\to l} \right] \quad (10)$$

H_{00}':

$$\sum_{j}^{\overset{\mathrm{A}}{\underline{\mathrm{uno}}}} \sum_{l}^{\overset{\mathrm{B}}{\underline{\mathrm{uno}}}} \sum_{m}^{\overset{\mathrm{C}}{\underline{\mathrm{occ}}}} \sum_{m'}^{\overset{\mathrm{C}}{\underline{\mathrm{occ}}}} \left[2\mathrm{R} \frac{(H_{0,m\to j} - S_{0,m\to j}H_{00})(H_{m'\to l,0} - S_{m'\to l,0}H_{00})(H_{m\to j,m'\to l} - S_{m\to j,m'\to l}H_{00})}{(H_{00} - H_{m\to j,m\to j})(H_{00} - H_{m'\to l,m'\to l})} + \frac{|H_{0,(m\to j,m'\to l)} - S_{0,(m\to j,m'\to l)}H_{00}|^2}{H_{00} - H_{(m\to j,m'\to l),(m\to j,m'\to l)}} \right] \quad (11)$$

Hence, the important orbital interactions for Scheme I which are of interest in the theory of catalysis may be

$$\begin{array}{ll} (\mathrm{HOMO})_{\mathrm{A}}\text{—}(\mathrm{LUMO})_{\mathrm{C}}\text{—}(\mathrm{LUMO})_{\mathrm{B}} & \\ & (12\mathrm{a}) \\ (\mathrm{HOMO})_{\mathrm{A}}\text{—}(\mathrm{HOMO})_{\mathrm{C}}\text{—}(\mathrm{LUMO})_{\mathrm{B}} & \\ (\mathrm{HOMO})_{\mathrm{A}}\text{—}(\mathrm{LUMO})_{\mathrm{C}}\text{—}(\mathrm{HOMO})_{\mathrm{B}} & \\ & (12\mathrm{b}) \\ (\mathrm{LUMO})_{\mathrm{A}}\text{—}(\mathrm{HOMO})_{\mathrm{C}}\text{—}(\mathrm{LUMO})_{\mathrm{B}} & \end{array}$$

The first two schemes follow from investigating expressions 5 and 6, and the remaining two come from eq 8-11.

It follows similarly that the corresponding ones for Scheme II are represented by

$$\begin{array}{ll} (\mathrm{HOMO})_{\mathrm{A}}\text{—}(\mathrm{HOMO})_{\mathrm{B}}\text{—}(\mathrm{LUMO})_{\mathrm{C}} & \\ & (12\mathrm{c}) \\ (\mathrm{LUMO})_{\mathrm{A}}\text{—}(\mathrm{LUMO})_{\mathrm{B}}\text{—}(\mathrm{HOMO})_{\mathrm{C}} & \end{array}$$

These particular orbital interaction schemes are derived from eq 5 and 6 by interchanging B and C.

The schemes 12a-c should be taken into account in addition to usual HOMO-LUMO interactions between two components of A, B, and C, when one considers the catalytic action of the third species on the other two.

Such a schematic presentation of particular orbital interactions is useful for a modification of the orbital symmetry rule;[5] that is, even if the overlap integral between $(\mathrm{HOMO})_{\mathrm{A}}$ and $(\mathrm{LUMO})_{\mathrm{B}}$ or $(\mathrm{LUMO})_{\mathrm{A}}$ and $(\mathrm{HOMO})_{\mathrm{B}}$ happens to be zero, an indirect $(\mathrm{HOMO})_{\mathrm{A}}$-$(\mathrm{LUMO})_{\mathrm{B}}$, $(\mathrm{LUMO})_{\mathrm{A}}$-$(\mathrm{HOMO})_{\mathrm{B}}$, $(\mathrm{HOMO})_{\mathrm{A}}$-$(\mathrm{HOMO})_{\mathrm{B}}$, or $(\mathrm{LUMO})_{\mathrm{A}}$-$(\mathrm{LUMO})_{\mathrm{B}}$ interaction through the intermediator C can assist the symmetry-disfavored process to take place.

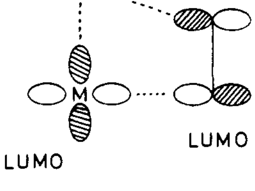
The present approach is easily extended to the excited state reactions, in the same fashion as in the two-species interaction case.

Discussion

Apparently complicated reactions catalyzed by transition metal complexes are composed of successive elementary processes: coordination of ligands on metal, reaction of ligands, and detachment of product ligands accompanied by regeneration of active catalytic species. Chemical transformations on metal are the present interest, which are classified into a variety of elementary processes: insertion of one ligand between metal and another, recombination of ligands, isomerization or rearrangement of coordinated molecules, and so on. We will discuss and examine the mechanism of such elementary processes in the light of the theoretical framework developed in the previous section.

Insertion Processes. The insertion reaction of coordinated unsaturated bonds into the metal-hydrogen or metal-carbon bond is one of the important elementary processes common to hydrogenation, hydroformylation, polymerization, etc.[6] It should be noted that in most of the insertion processes the ligands H^- or R^- attacking on the unsaturated bonds have occupied orbitals of low ionization potential and at the same time inserting species have unoccupied orbitals at low energy levels. One is tempted by these facts to conclude that the charge transfer from one to the other ligand through metal (scheme 12a) is rather more important than the electron delocalization from both ligands to metal or the reverse (scheme 12b). That is, the electron delocalization from the HOMO of the ligand A of which the bond with metal undergoes fission by insertion to the LUMO of inserting ligand B is in this way expected to play a predominant role. A similar view was proposed for metal-catalyzed polymerization by Furukawa, in which electrons of coordinated alkyl are partly delocalized to an unoccupied orbital of metal and subsequently to the π^* orbital of the monomer olefin.[7]

One can conveniently apply the picture mentioned above to the regioselectivity of insertion, if one considers a direct



interaction of $(\mathrm{HOMO})_A$ and $(\mathrm{LUMO})_B$, being led to Scheme III. The observed regioselectivity of the following reactions[8]

$$(\pi\text{-}C_5H_5)_2MoH_2 + CH_2{=}CHX \longrightarrow (\pi\text{-}C_5H_5)_2MoH\text{–}CHXCH_3$$

$$X = CN,\ CO_2CH_3$$

is consistent with the fact that LUMO's of the above olefins have the largest amplitude at the terminal carbon.

Metathesis and Dimerization of Olefins

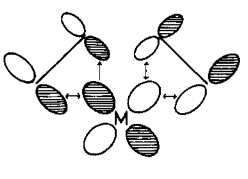
Facile disproportionation reactions of olefins on some transition metals have been observed,[9] i.e.,

$$R_1R_1C{=}CR_1R_1 + R_2R_2C{=}CR_2R_2 \rightarrow 2R_1R_1C{=}CR_2R_2$$

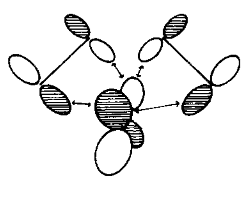
Some intermediates have been proposed: cyclobutane[10] or quasi-cyclobutane[11] intermediates, carbenoid complexes,[12] and five-membered metallocyclic structures.[13] A related reaction, the dimerization of olefins to cyclobutane derivatives, has also been known to take place in the presence of zero valent iron,[14] nickel,[15] and cobalt[16] catalysts.

Notwithstanding the thermal dimerization of ethylenes to form cyclobutane is a symmetry-disfavored process;[5] the metathesis and the dimerization of olefins occur readily in the presence of transition metal catalysts. Several theoretical chemists have paid attention to the orbital and state symmetry aspects and examined the relaxation effect of the metal d orbital on the symmetry restriction.[17]

We can find interesting terms in two pairs of formulas, eq 8 and 9 and 10 and 11, which may be likely to argue for suprafacial-suprafacial approach[5] of two olefins on the catalysts. One pair of these formulas implies the electron delocalization from ligands to metal. The term which involves the HOMO's of coordinated olefins and the LUMO of the catalyst is predicted on the basis of scheme 12b to be the most important. Of the other terms related to the delocalization from metal to ligands (expressions 10 and 11), the one which involves the LUMO's of both ligands and the HOMO of catalyst may be prominent. Here a symmetry restriction arises which does not appear if $n \neq n'$ in eq 8 and 9 or $m \neq m'$ in eq 10 and 11. In the case that n and n' are taken as the $(\mathrm{LUMO})_C$ and m and m' as the $(\mathrm{HOMO})_C$, the symmetry properties of $(\mathrm{HOMO})_A$ and $(\mathrm{HOMO})_B$, and those of $(\mathrm{LUMO})_A$ and $(\mathrm{LUMO})_B$, should be the same in order that A and B can approach favorably with a certain symmetry. The overlapping $S_{i\to n,k\to n}$ or $S_{m\to j,m\to l}$ is zero otherwise. As stated in the last section, this symmetry rule forms a striking contrast to that for the bimolecular system in which the $(\mathrm{HOMO})_A$-$(\mathrm{LUMO})_B$ interaction, or the symmetry property of $(\mathrm{HOMO})_A$ and $(\mathrm{LUMO})_B$ is significant. The $(\mathrm{HOMO})_A$-$(\mathrm{LUMO})_C$-$(\mathrm{HOMO})_B$ and $(\mathrm{LUMO})_A$-$(\mathrm{HOMO})_C$-$(\mathrm{LUMO})_B$ interactions among two olefin molecules and metal are favored by the same symmetries of HOMO's and of LUMO's in contrast to bimolecular interaction, as is illustrated below.



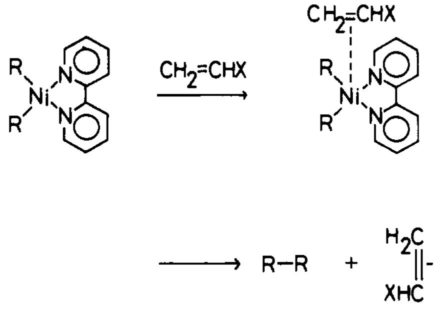
HOMO LUMO HOMO



LUMO HOMO LUMO

2 + 2 Cycloreversion. Cleavage of the cyclobutane ring to olefins is one of the most investigated reactions catalyzed by transition metal complexes; cubane to *syn*-tricyclooctadiene,[13a] quadricyclane to norbornadiene,[18] prismane to Dewar benzene,[19] and so forth. Recent studies of the conversions of cubane[20] and of quadricyclane[21] by the Rh complex have demonstrated the involvement of oxidative addition of the metal to the hydrocarbons through carbon–carbon bonds. Although these facts seem to show that the catalytic processes proceed by Scheme II (A-B-C), a possibility still remains that the transition state for the cycloreversion may be appropriately represented by Scheme I or by Scheme III, in which a relevant metal orbital interacts with both orbitals simultaneously. It is likely that the metal adduct intermediates may be located in a bypath not leading directly to the products and it may rearrange just prior to the cycloreversion process into such a symmetrical geometry as proposed for olefin dimerization. Interaction according to Scheme I or to Scheme III satisfies the condition $S_{0K}S_{KL}S_{L0} > 0$ in the same way as the interaction among two olefins and metal shown before.

Recombination of Ligands. It would be meaningful to refer to the recombination reactions of alkyl ligands in dialkyl(dipyridyl)nickel complex, promoted by coordination of electron-accepting olefins.[22] The activation energy $\Delta H^{\ddagger}$ is about 15.6 kcal/mol for R = ethyl in the presence of acrolein while it is 68 kcal/mol in the absence of the olefin. The ligand-ligand recombination reaction can be the object of our present interest when the ligands to be bonded are considered reactants A and B, and the combined system of the rest of the metal complex and the coordinated olefin is considered catalyst C. One can see that the terms of eq 8 and 9 involving the occupied orbitals of A and B and the unoccupied orbitals of C are more important than the terms of eq 10 and 11, since the reactants A and B are anionic ligands. The contribution of such a delocalization term increases as the ability of the catalyst system C to accept electrons increases, or as the LUMO of coordinating olefins is lowered. As a result the recombination of anionic ligands on metal takes place readily as the interaction between the HOMO's of the reactants by way of the LUMO of the intermediary catalyst is favored (eq 8 and 9). This conclusion is consistent with the order of electron-accepting ability of coordinated olefins.



The formulas derived in the theory section are applicable to another type of catalytic processes, in which catalyst C interacts preferentially with one of two reactants (B). One can obtain the appropriate terms for Scheme II by formally replacing the subscripts k, l, m, and n by m, n, k, and l in each term of Ψ_0' and H_{00}'. The terms originating from the electronic configurations which contain any zero configuration of A or B can be neglected as before. A further restriction may be taken into consideration from the point of view of a chemical aspect. The reactants A and B cannot be in an equivalent chemical situation in contrast to Scheme I. No

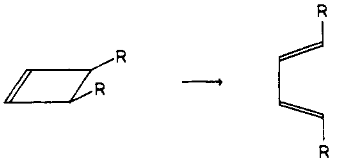
$$2 \sum_{i}^{\substack{\mathrm{A}\\ \mathrm{occ}}} \sum_{k}^{\substack{\mathrm{B}\\ \mathrm{occ}}} \sum_{n}^{\substack{\mathrm{C}\\ \mathrm{uno}}} \mathrm{R} \left\{ \frac{(H_{0,\, i\to n} - S_{0,\, i\to n}H_{00})(H_{k\to n,\, 0} - S_{k\to n,\, 0}H_{00})(H_{i\to n,\, k\to n} - S_{i\to n,\, k\to n}H_{00})}{(H_{00} - H_{i\to n,\, i\to n})(H_{00} - H_{k\to n,\, k\to n})} \right\} \qquad (13)$$

$$2 \sum_{j}^{\substack{\mathrm{A}\\ \mathrm{uno}}} \sum_{l}^{\substack{\mathrm{B}\\ \mathrm{uno}}} \sum_{m}^{\substack{\mathrm{C}\\ \mathrm{occ}}} \mathrm{R} \left\{ \frac{(H_{0,\, m\to j} - S_{0,\, m\to j}H_{00})(H_{m\to l,\, 0} - S_{m\to l,\, 0}H_{00})(H_{m\to j,\, m\to l} - S_{m\to j,\, m\to l}H_{00})}{(H_{00} - H_{m\to j,\, m\to j})(H_{00} - H_{m\to l,\, m\to l})} \right\} \qquad (14)$$

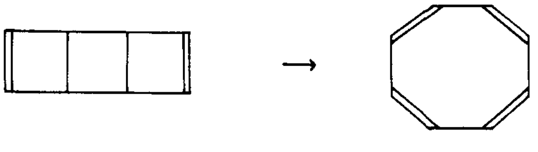
mechanisms are conceivable by which electron delocalizations from B to C ($k \to n$) and from C to B ($m \to l$) can promote those from B to A ($k' \to j$) and from A to B ($i \to l'$), respectively. Of the terms surviving such selections, the energy terms involving $i \to n$ and $k \to n$ (eq 13) or $m \to j$ and $m \to l$ (eq 14) are expected to contribute most seriously to catalytic action. The formulas 13 and 14 imply the importance of the interactions between the HOMO's and between the LUMO's of the reactants (12c) in case of electron-donating and -accepting catalysts, respectively.

Electrocyclic Reactions and Valence Isomerizations

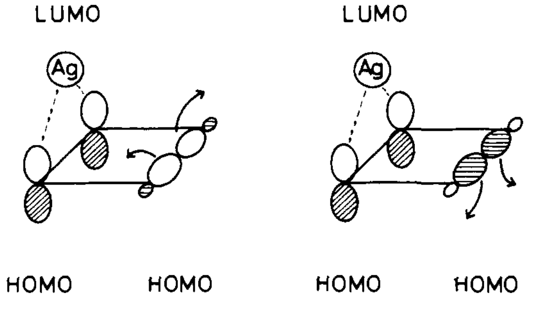
Disrotatory ring opening of cyclobutane to butadiene is unfavorable in the ground state reactions.[5]



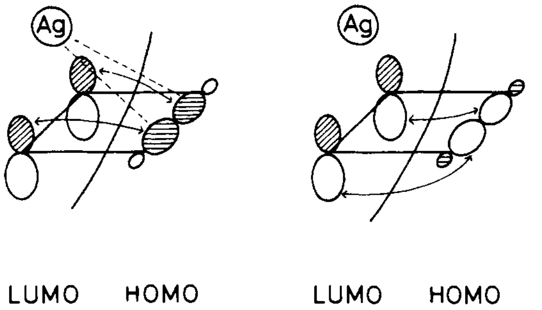
However, such chemical transformations have been observed to occur readily in the presence of certain catalysts. Isomerization of tricyclo[4.2.0.0^{2,5}]octa-3,7-diene to cyclooctatetraene is completed within 40 min in the presence of $AgBF_4$ but does not occur in 24 hr in the absence of catalysts.[23] An analogous phenomenon is observed in the Rh(I)-catalyzed valence isomerization of Dewar benzene to benzene.[19] We believe that the catalyzed electrocyclic reactions are initiated by the coordination of the cationic metal ion or complex on the π bond.



The important orbital interaction, $(\mathrm{HOMO})_A$–$(\mathrm{HOMO})_B$–$(\mathrm{LUMO})_C$, may be represented as follows. $S_{0k}S_{KL}S_{L0} = S_{0,i\to n}S_{i\to n,k\to n}S_{k\to n,0} \simeq s_{ik}{}^2s_{kn}{}^2 > 0$ (Scheme II). If direct interaction is allowed between A and C, $S_{0K}S_{KL}S_{L0} \simeq -s_{in}s_{kn}s_{ik}$ (Scheme III). In this case $S_{0K}S_{KL}S_{L0}$ cannot be positive.[24] There are two modes of disrotatory ring opening: in the directions syn and anti to the metal.

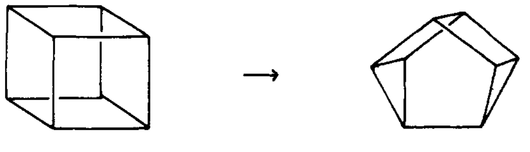


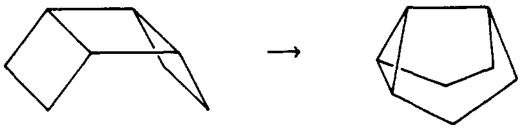
The discrimination between syn and anti disrotation is an unprecedented category. This stereochemical problem will be a significant subject of experiments in the near future. The preference of the anti-disrotation is predicted within our present knowledge. Suppose that the whole system is composed of two parts, the electron-accepting combined system of Ag^+ and C=C double bond, and the electron-donating σ bond to be cleaved, in order to appreciate the secondary effects of Ag^+. The preferential anti extension of the π orbital in the LUMO due to anti-bonding overlapping with the metal orbital may favor the interaction between the π orbital and the larger lobes of the original σ bond orbital in the direction anti to the metal. In addition the larger lobes of the σ bond orbital is compelled to be in an opposite sign relation with the metal orbital in case of syn disrotation. This secondary orbital interaction growing as the rotation proceeds may result in less stabilization. In anti disrotation there is no disadvantage of such a phase restriction in the secondary interaction.

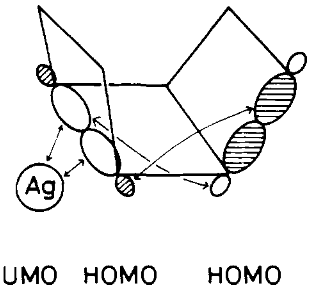


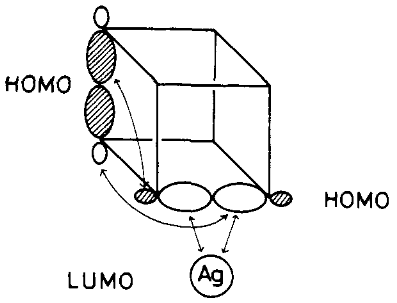
Another class of chemical reactions suggesting the importance of the $(\mathrm{HOMO})_A$–$(\mathrm{HOMO})_B$–$(\mathrm{LUMO})_C$ interaction is a valence isomerization of strained saturated compounds. The typical members of the reactions are the skeletal rearrangements of cubane, homocubane, and basketene to cuneane, norsnoutane, and snoutene, respectively,[25] and of *syn*-tricyclo[4.2.0.0^{2,5}]octane to tetrahydrosemibullvalene.[26] The occurrence of thermally "forbidden" [$2\sigma_a + 2\sigma_a$] transformations[5] is readily understood by the HOMO–HOMO interaction induced by the catalysts. The orbital interactions are illustrated below for cubane and tricyclooctane. The other possible way of assigning the phase relation between two σ orbitals is rejected on account of steric hindrance.

This interaction scheme is supported by the fact that the rate of isomerization of cubane derivatives decreases remarkably as the number of the electron-accepting carbomethoxy substituents increases; the ratio of the reaction rate for the parent structure and mono- and di-substituted cubanes is 17,000:310:1. The considerable changes may be attributed to the lowering of the HOMO energy level by the substitution, or to the increase in the absolute value of the denominator in eq 13. One can see a cause for no change of the *anti*-tricyclo[4.2.0.0^{2,5}]octane under the same condition in the geometrical restriction. Two modes of interaction are conceivable but sterically inaccessible.

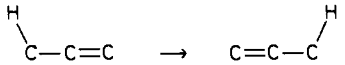


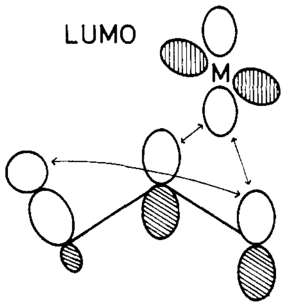






Sigmatropic Shift. A $[_{\pi}2_s + _{\sigma}2_s]$ sigmatropic hydrogen shift[5] was observed to take place in the presence of $Fe(CO)_5$ catalyst, in which the hydrogen transfer occurs in the same side as the coordinated olefin[27] (referred to as "syn" interaction hereafter). The isotope effect on the rate and the degree of deuterium incorporation in the $DCo(CO)_4$-catalyzed isomerization of 3-phenylpropene to 1-phenylpropene seem to indicate an internal 1,3-hydrogen shift via complex formation.[28] If the metal complexes are electron acceptors, one can draw the $(HOMO)_A$-$(HOMO)_B$-$(LUMO)_C$ interaction among the C—H bond, the C=C bond, and the metal. Although the "anti" interaction is also conceivable in the same sense as in the electrocyclic reactions, the mode of "syn" 1,3-sigmatropic shift is depicted here. The illustration clearly shows the possibility of 1,3-sigmatropic rearrangement in a suprafacial-suprafacial manner. The corresponding scheme $(LUMO)_A$-$(LUMO)_B$-$(HOMO)_C$ for electron-donating catalysts suggests the same conclusion on the steric course.[29]



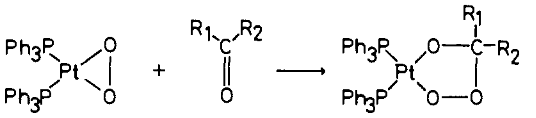


Activation of Molecular Oxygen

The activation and the reactions of the ground state $(^3\Sigma_g{}^-)$ oxygen molecule under the influence of catalysts have been one of the most interesting and important subjects in organic chemistry and also in biochemistry. We consider the following reactions as bimolecular ones of the substrate with activated oxygen which is coordinated to metal surrounded with ligands. The activation mechanism will be understood as a three-body interaction of Scheme I among the ligands (A), metal (C), and oxygen (B).

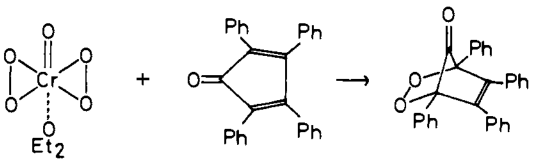
The frontier orbitals of $^3\Sigma_g{}^-$ O_2 are doubly degenerate singly occupied (SO) MO's. Generally SOMO can donate and accept electrons to unoccupied orbitals and from occupied orbitals of another molecule, respectively. The high electronegativity of oxygen suggests the importance of charge transfer from electron-donating ligands through metal, or of electron acceptance in one of SOMO's (eq 5 and 6). The other SOMO may take part in the reverse delocalization though to a less degree than the former transfer. The electron configuration of the activated oxygen depends on the balance between these two modes of electron delocalization. If electron acceptance of oxygen occurs exclusively, or the ligands are electron-releasing groups, the configuration of O_2 will resemble that of superoxide $O_2{}^-$. When the reverse electron transfer is comparably remarkable the activated oxygen may be endowed with such a property as $^1\Delta_g$ O_2 which is specified by the powerful electron acceptability as pointed out in theoretical investigation of the 2 + 2 cycloaddition mechanism.[30] The electronic structure of coordinated molecular oxygen is expected to be a mixed configuration within the range from $O_2{}^-$ to $O_2(^1\Delta_g)$ according to the nature of metal and ligands.

An addition reaction of carbonyl species with bis(triphenylphosphine)platinum oxide[31] may be classified into the superoxide-like reaction of oxygen activated by a powerful σ donor, triphenylphosphine, although the mechanism has not been clarified by experiment as yet. A parallel approach of an unsaturated bond to the coordinated O_2 is possible since the symmetry of the HOMO of electron-donating superoxide is the same as that of the LUMO of electron-accepting carbonyl species, that is, antisymmetric.



A similar activation mechanism has appeared for onium-catalyzed oxygenation of hydrocarbons.[32] Electron delocalization from the counteranion of sulfonium, phosphonium, and so on, through vacant d orbitals of the cationic center, has been considered to activate the ground state oxygen molecule. An experimental support for the involvement of the superoxide configuration was also provided by a certain enzymic reaction. Oxidative cleavage of tryptophan to the dicarbonyl compound catalyzed by tryptophan-2,3-dioxygenase with Fe^{2+} at the catalytic site is inhibited by superoxide dismutase.[33]

Subsequently another possibility that activated oxygen behaves as $^1\Delta_g$ molecular oxygen is exemplified by the oxygenation of electron-donating tetraphenylcyclopentadienone by diperoxychromium(VI) oxide etherate to 1,2,3,4-tetraphenyl-5,6-dioxabicyclo[2.2.1]hept-2-en-7-one.[34] The HOMO of the substrate and the LUMO of $^1\Delta_g$ molecular oxygen are both antisymmetric. Diels-Alder type reaction of superoxide cannot be favored by the symmetry of the frontier orbital, since the LUMO of the diene is symmetric while the HOMO of superoxide is antisymmetric. Hence, oxygen ligand in diperoxychromium oxide is expected to behave as a $^1\Delta_g$ type species. The difference in electronic structure of the oxygen ligand between bis(triphenylphos-



phine)platinum oxide and diperoxychromium oxide may be due to the electron acceptability of nonreacting ligands, i.e., electron-donating phosphine and electron-accepting oxygen.

References and Notes

(1) (a) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology", P.-O. Lowdin and B. Pullman, Ed., Academic Press, New York, N.Y., 1964, p 513; (b) K. Fukui, "Modern Quantum Chemistry", Vol. 1, O. Sinanoglu, Ed., Academic Press, New York, N.Y., 1965, p 49; (c) K. Fukui and H. Fujimoto, "Mechanism of Molecular Migrations", Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N.Y., 1969, p 118; K. Fukui, "Theory of Orientation and Stereoselection", Springer-Verlag, Heidelberg, 1970; *Acc. Chem. Res.*, **4**, 57 (1971).

(2) (a) J. N. Murrell, M. Randić, and D. R. Williams, *Proc. R. Soc. London, Ser. A*, **284**, 566 (1965); J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **46**, 1768 (1967); (b) R. Rein and M. Pollak, *ibid.*, **47**, 2039 (1967); (c) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968); (d) L. Salem, *ibid.*, **90**, 543, 553 (1968).

(3) (a) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968); (b) K. Fukui, *Int. Congr. Pure Appl. Chem. 23rd*, **1**, 65 (1971); (c) H. Fujimoto and K. Fukui, *Adv. Quantum Chem.*, 6, 177 (1972); (d) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **42**, 3399 (1969); H. Fujimoto and K. Fukui, *ibid.*, **44**, 2936 (1971); (e) H. Fujimoto, S. Kato, S. Yamabe, and K. Fukui, *ibid.*, **46**, 1071 (1973).

(4) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972); R. F. Hudson, *Angew. Chem.*, **85**, 63 (1973); J. D. Bradley and G. C. Gerrans, *J. Chem. Educ.*, **50**, 463 (1973).

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(6) A number of chemical species other than olefins and CO are known as inserting reagents. (a) N_2: M. E. Vol'pin, *Pure Appl. Chem.*, **30**, 607 (1972); M. E. Vol'pin, V. B. Shur, R. V. Kudrjavtsev, and V. B. Prodjako, *Chem. Commun.*, 1038 (1968); J. Chatt, G. A. Heath, and R. L. Richards, *ibid.*, 1010 (1972); J. Chatt, G. A. Heath, and G. J. Leigh, *ibid.*, **444** (1972). (b) CO_2: L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **90**, 3896 (1968); A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Commun.*, 98 (1968); S. Komiya and A. Yamamoto, *J. Organomet. Chem.*, **46**, C58 (1972); V. D. Blanco, S. Doronzo, and M. Rossi, *ibid.*, **35**, 337 (1972); A. Miyashita and A. Yamamoto, *ibid.*, **49**, C57 (1973); M. E. Vol'pin, *Pure Appl. Chem.*, **30**, 607 (1972). (c) CS_2: I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, **66**, 161 (1974). (d) SO_2: F. A. Hartman and A. Wojciki, *Inorg. Chem.*, 7, 1504 (1968).

(7) J. Furukawa, *Shokubai*, **13**, 107 (1971).

(8) A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, **94**, 1886 (1972).

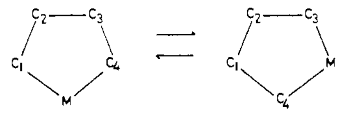
(9) For example, see N. Calderon, *Acc. Chem. Res.*, **5**, 127 (1972), and references cited therein.

(10) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968); E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *ibid.*, **92**, 528 (1970); W. B. Hughes, *ibid.*, **92**, 532 (1970).

(11) (a) C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, **7**, 269 (1967); (b) D. L. Crain, *ibid.*, **13**, 110 (1969); (c) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

(12) (a) G. S. Lewandos and R. Pettit, *J. Am. Chem. Soc.*, **93**, 7087 (1971); (b) G. Dall'asta, *Makromol. Chem.*, **154**, 1 (1972).

(13) (a) J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1970); (b) R. H. Grubbs and T. K. Brunck, *J. Am. Chem. Soc.*, **94**, 2538 (1972). The importance of the nuclear configuration which involves two coordinated olefins or tetramethylene-like structures on metal still remains, even if the metallocyclic species takes part in the disproportionation reactions. The interconversion of the metallocyclic species



is considered to occur through such a symmetrical transition state geometry as is illustrated in the text.

(14) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, 373 (1961); P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965).

(15) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind.* (*London*), 20 (1960); G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962).

(16) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(17) (a) F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.*, **89**, 2484 (1967); **91**, 1030 (1969); **93**, 1123 (1971); F. D. Mango, *Tetrahedron Lett.*, 4813 (1969); 505 (1971); 1509 (1973); (b) W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4788 (1967); R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); (c) W. Th. A. M. van der Lugt, *Tetrahedron Lett.*, 2281 (1970); (d) G. L. Caldow and R. A. MacGregor, *J. Chem. Soc. A*, 1654 (1971); (e) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970); ref 3e.

(18) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967).

(19) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967).

(20) L. Cassar, P. E. Eaton, and J. Halpern, *J. Am. Chem. Soc.*, **92**, 3515 (1970).

(21) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).

(22) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 (1971).

(23) W. Merk and R. Pettit, the former paper cited in Ref 17b.

(24) This conclusion originates from the spherical symmetry of the LUMO of Ag^+. If Rh(I) can provide a relevant d orbital for the interaction with substrate, the argument on 2 + 2 cycloreversion may be made on the basis of Scheme III.

(25) L. A. Paquette, *J. Am. Chem. Soc.*, **92**, 5765 (1970); *Acc. Chem. Res.*, **4**, 280 (1971).

(26) J. Wristers, L. Brener, and R. Pettit, *J. Am. Chem. Soc.*, **92**, 7499 (1970).

(27) F. G. Cowheard and J. L. von Rosenberg, *J. Am. Chem. Soc.*, **91**, 2157 (1969).

(28) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

(29) A cyclic interaction mechanism is also conceivable, which suggests a possibility of involvement of hydride shift to metal as an intermediate step.

(30) S. Inagaki, S. Yamabe, H. Fujimoto, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 3510 (1972); S. Inagaki and K. Fukui, submitted for publication.

(31) R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968).

(32) K. Fukui, K. Ohkubo, and T. Yamabe, *Bull. Chem. Soc. Jpn.*, **42**, 312 (1969); K. Ohkubo, T. Yamabe, and K. Fukui, *ibid.*, **42**, 2220 (1969); K. Ohkubo, *ibid.*, **47**, 557 (1974).

(33) F. Hirata and O. Hayaishi, *J. Biol. Chem.*, **246**, 7825 (1971).

(34) H. W. S. Chan, *Chem. Commun.*, 1550 (1970).