A Theoretical Analysis of Catalytic Roles by Paired Interacting Orbitals. Pd(II)-Catalyzed Nucleophilic Additions to C=C Bonds

Hiroshi Fujimoto* and Terumasa Yamasaki

Contribution from the Division of Molecular Engineering, Kyoto University, Kyoto 606, Japan. Received July 29, 1985

Abstract: By applying a certain pair of unitary transformations, the orbitals of the reagent and reactant are divided into two classes one being paired reactive and the other unpaired nonreactive for each given type of interaction. Roles of catalysts are demonstrated by using a few reactive orbitals that are obtained for the reacting system with and without the catalytic species. The addition of nucleophiles to a carbon–carbon double bond in the presence of palladium complexes is taken as a model to exemplify this simple analysis. The localizability of the orbitals and their electron populations change specifically reflecting the perturbation of the catalyst.

Though the roles of catalysts are evident from macroscopic observations, fine mechanisms of enhancing the reactivities of molecules and selectivities of chemical reactions still remain unrevealed in most cases. Small species, e.g., proton and other Lewis acids, often play crucial roles, but the influence of transition-metal complexes may be much more general and confusing. Transition-metal complexes are now within the reach of ab initio molecular orbital (MO) calculations. Detailed information on the reaction profiles, the activation energy, and also the transition-state structures is obtainable from theoretical calculations. The next aim is to generalize the conclusions derived for well-known systems to other more complicated systems.

What is important then is how to analyze the results of calculations. Simple devices to translate results of calculations into an intuitively accessible form would be very helpful. In this paper, we would show how the simple method of orbital transformations[1] can be utilized for that purpose. The addition of nucleophiles to olefin double bonds in the Wacker oxidation reaction[2] is taken as an example.

An important question concerning the Wacker process is the stereochemistry of addition. From kinetic studies of the reaction, Henry first proposed the mechanism which involved cis migration of a nucleophile from the metal to the coordinated olefin.[2b,c] On the other hand, stereochemistry of nucleophilic additions showed that external trans additions took place.[2j,l] In connection with this problem, a number of experiments have revealed that nucleophiles are divided into two classes: nucleophiles that undergo trans addition[3] and nucleophiles that undergo cis migration.[4] Theo-

retical calculations have also been carried out on transition-metal-catalyzed nucleophilic additions to carbon–carbon double bonds.[5] The factors that possibly govern the ease of external trans addition of nucleophiles as well as cis migration of coordinated nucleophiles have been discussed in terms of the frontier orbital scheme.[6] The following analysis will connect ab initio MO calculations closely with the simple orbital interaction concept and make the stereochemistry in hydroxypalladation clearer.

Method

We consider an interacting system A–B which consists of the reagent A and the reactant B. The catalyst is regarded here as a part of either A or B. The MO's Φ of the composite interacting system A–B are given by the linear combinations of the MO's of the fragment species A and B as[7]

$$\Phi_f = \sum_{i=1}^{m} c_{i,f}\phi_i + \sum_{j=1}^{M-m} c_{m+j,f}\phi_{m+j} + \sum_{k=1}^{n} d_{k,f}\psi_k + \sum_{l=1}^{N-n} d_{n+l,f}\psi_{n+l} \qquad (1)$$

where M and N denote the number of the basis functions of A and B, respectively. The occupied and unoccupied MO's of A are denoted by ϕ_i ($i = 1, 2, ..., m$) and ϕ_{m+j} ($j = 1, 2, ..., M - m$), respectively, and the occupied and unoccupied MO's of B are indicated by ψ_k ($k = 1, 2, ..., n$) and ψ_{n+l} ($l = 1, 2, ..., N-n$), respectively. The total number of electrons of the reacting system is $2m + 2n$. We define the intermolecular bond-order matrix $\mathbf{P}$ with respect to the MO's of A and the MO's of B.

$$\mathbf{P} = \begin{pmatrix} P_{i,k} & P_{i,n+l} \\ P_{m+j,k} & P_{m+j,n+l} \end{pmatrix} \begin{matrix} m \\ M-m \end{matrix} \qquad (2)$$
$$\qquad\quad n \qquad N-n$$

where

$$P_{i,k} = 2\sum_{f}^{m+n} c_{i,f}d_{k,f} \qquad (3)$$

We assume here without loss of generality that $M > N$.

We carry out a pair of unitary transformations of the MO's ϕ of A and ψ of B simultaneously within each fragment so that

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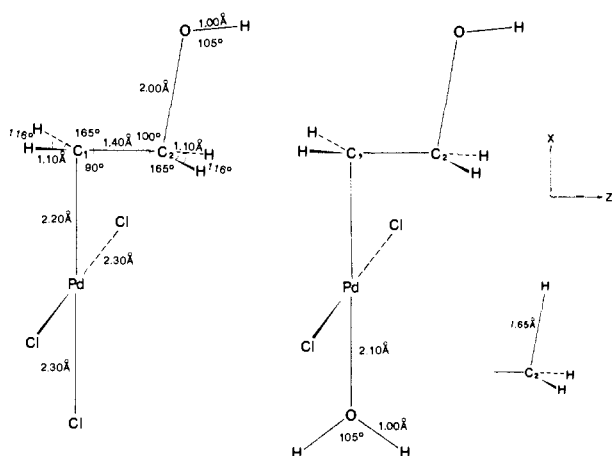
Figure 1. Reaction models for Pd(II)-catalyzed trans addition of OH⁻ and of H⁻ to an ethylene double bond.
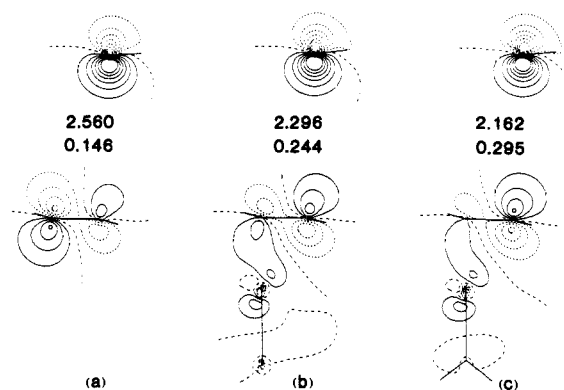

Figure 2. Principal pair of interacting orbitals of OH⁻ and ethylene–catalyst system. The numbers indicate the electron population (upper) and the overlap population (lower) for the pair of orbitals.

Table I. Contributions of Paired Interacting Orbitals to the Overlap Population between OH⁻ and C_2H_4

orbital pair (ϕ'_μ, ψ'_μ)	catalyst		
	none	$PdCl_3^-$	$Pd(H_2O)Cl_2$
$\mu =$			
1	0.146	0.244	0.295
2	−0.095	−0.082	−0.072
3	−0.012	−0.008	−0.007
4	0.002	0.002	0.002
5	−0.002	−0.001	−0.001
6	−0.002	−0.001	−0.001
7	−0.001	0.000	−0.001
8~11	0.000	0.000	0.000

nonzero values appear only on the diagonal elements of the bond-order matrix.[1]

$$P' = \begin{pmatrix} P'_{11} & 0 & 0 & \cdots & 0 \\ 0 & P'_{22} & 0 & \cdots & 0 \\ & & \cdots & & \\ 0 & 0 & 0 & \cdots & P'_{NN} \\ 0 & 0 & 0 & \cdots & 0 \\ & & \cdots & & \\ 0 & 0 & 0 & \cdots & 0 \end{pmatrix} \begin{matrix} \left.\vphantom{\begin{matrix}1\\1\\1\\1\end{matrix}}\right\} N \\ \\ \left.\vphantom{\begin{matrix}1\\1\\1\end{matrix}}\right\} M-N \end{matrix} \qquad (4)$$

By means of these coupled orbital transformations, the interaction between A and B is condensed into N pairs of reactive orbitals of the fragment species. In other words, the number of orbital pairs that are necessary to describe the interaction of A and B becomes dependent on the size of the smaller entity. The remaining $(M - N)$ orbitals of A are unpaired and, therefore, nonreactive. Some of the $P'_{i,i}$'s ($i = 1, 2, ..., N$) may also vanish.

In chemical reactions, the reagent molecule is often very small in the number of orbitals in comparison with the added catalytic species. Here, the paired orbital transformations gain ground. We can compare reactivities of a variety of reactants against a reagent by using the same number of similar reactive orbitals irrespective of the presence and size of catalysts. Incidentally, the interacting orbitals are also obtained for any subspace of P. The roles of the exchange repulsion and the delocalization interaction can be studied.

Results of Calculations

Trans Nucleophilic Additions. We first study the palladium-catalyzed trans additions of nucleophiles to an ethylene double bond. Special interest is devoted to clarify how palladium(II) complexes promote nucleophilic additions to olefins and how ligands modify such catalyses. In Figure 1 we show the reaction models. The structures of reacting systems were taken rather arbitrarily for the purpose of illustrating a basic trend.[8] The

Table II. Extent of Localization of the Principal Interacting Orbital of the Ethylene Fragment in OH⁻ Addition

orbital localizatn (%)	catalyst		
	none	$PdCl_3^-$	$Pd(H_2O)Cl_2$
on C(1)	72	23	10
on C(2)	15	48	65
on catalyst		20	21

Pd–C, Pd–Cl, and Pd–O bond lengths were taken from the literature.[9] A hydroxide ion and a hydride ion were chosen as the attacking nucleophiles for calculational simplicity. All the calculations were done by the GAUSSIAN 80 program,[10] taking the standard 3-21G basis set for hydrogen, carbon, and oxygen,[11] the MINI4 basis set for chlorine,[12a] and the MINI1 basis set for the core of Pd.[12b] The 4d, 5s, and 5p functions of Pd were taken from the recent work of Hay[13] and recontracted to double-ζ quality in use.

We first show the result of the calculation on the OH⁻ addition to ethylene. Except for the reaction under the strongly acidic condition, the attacking species is not the solvent molecule itself but most likely to be a hydroxide ion. In this case, the smaller species is the OH anion; it has eleven orbitals. Table I gives the overlap populations of eleven pairs of orbitals for the OH⁻ and the ethylene with and without a Pd complex. One sees that a pair of reactive orbitals (ϕ'_1, ψ'_1) explains substantially the interaction between the attacking nucleophile and the ethylene fragment. Figure 2 illustrates this principal orbital pair. In the absence of the palladium complex, the bonding lobe (indicated by solid lines) is not developed enough on the ethylene molecule to bind the attacking anion. A strongly antibonding region (shown by broken lines) on the adjacent carbon atom trespasses onto the reaction center C(2). The reason why nucleophilic additions are not facile is well-recognized.

When $PdCl_3^-$ is added to this system, the ethylene molecule is activated so that the bonding lobe on C(2) expands markedly and the antibonding lobe on the adjacent carbon C(1) becomes deflated. Table II presents some characteristics of these orbitals. The orbital of C_2H_4 that interacts with the OH⁻ orbital in the absence of the catalyst has a small population of only 15% on the C(2) atom.[14] In the presence of the palladium complex $PdCl_3^-$, the extent of localization of the orbital on C(2), however, increases

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(8) We assume here the reaction model in which the metal is only bonded to one carbon atom of olefin (see ref 5b). Studies of η^2 coordination are underway for other metal complexes.

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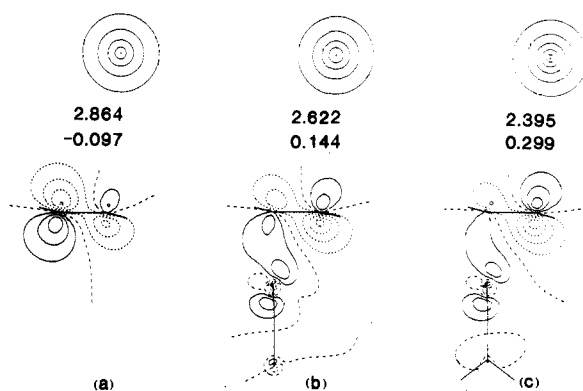
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Figure 3. Principal pair of interacting orbitals of H⁻ and ethylene–catalyst system.

Figure 4. Reaction models for Pd(II)-catalyzed cis addition of H⁻ and of OH⁻ to an ethylene double bond.

Figure 5. Two dominant pairs of interacting orbitals for OH⁻ migration in C_2H_4–Pd(OH)Cl_2^- system. The numbers indicate the electron populations (upper) and the overlap populations (lower) for the pairs of interacting orbitals.

to 48%. Unlike the frontier orbitals, the rehybridized interacting orbital is well-localized on the C_2H_4 moiety: the population of the orbital on the Pd complex is only 20%.

Substitution of the trans Cl ligand by a H_2O molecule leads to higher activation of ethylene. The interacting orbital of the complex acquires a population of 65% on C(2) of the ethylene molecule. The extent of the localization of the orbital on C(2), when it is compared within the C_2H_4 fragment, increases from 60% in the case of C_2H_4–$PdCl_3^-$ to 81% in the case of C_2H_4–$PdCl_2(H_2O)$. This trend in the orbitals is demonstrated clearly in the overlap populations between the pairs of interacting orbitals. When $PdCl_2(H_2O)$ is added to the system, the overlap population becomes about twice as large as that of the uncatalyzed system as shown in Figure 2. The paired counterpart of OH⁻ does not change much, but it tends to have a stronger p character as the ethylene molecule becomes more activated. This signifies that electron delocalization dominates the interaction, whereas the overlap repulsion almost fades away in catalyzed systems.

Figure 3 shows the orbitals for the addition of a hydride ion to an ethylene double bond. The overlap population is negative in the absence of the catalyst in this case, but the basic trend mentioned above is confirmed here again. Though the interaction models were chosen arbitrarily, one can see in Figure 3 that the interacting orbital of the ethylene fragment without any catalyst is almost the same as that for the OH⁻ addition. The two models compare roughly with each other. $PdCl_2(H_2O)$ activates the ethylene molecule more strongly than $PdCl_3^-$ does, but both of them are seen to be less effective in this case. The localization of the interacting orbital on C(2) of ethylene is weaker relative to the corresponding case of the OH⁻ addition. The stronger overlap repulsion between H⁻ and C_2H_4 than that between OH⁻ and C_2H_4 is not recovered efficiently by the catalyst.[15]

Another way of estimating the catalytic activities is simply to determine how many electrons occupy the pair of interacting orbitals. It is 2.56 in the absence of the catalyst in OH⁻ addition. This indicates the presence of strong closed-shell overlap repulsion. It is reduced to 2.30 by adding $PdCl_3^-$. By replacing the chloride ligand in the trans position to the coordinated ethylene molecule with a H_2O molecule, the number of electrons occupying the orbital pair is reduced further to 2.16. This value is sufficiently close to the optimum value of 2 to form an electron pair. A tight C–O bond is available now and, therefore, it is recognized that the addition is catalyzed by the $PdCl_2(H_2O)$ system. In the case of H⁻ addition, the number of electrons occupying the orbital pair is considerably larger in comparison with that in the OH⁻ addition. The hydride ion appears to be somewhat less suited for the trans additions.

The difference in the catalytic activities between $PdCl_3^-$ and $PdCl_2(H_2O)$ is easily explained. The calculation indicates that the activation of the ethylene molecule toward nucleophilic additions is ascribed mainly to two terms. One is the reduction of
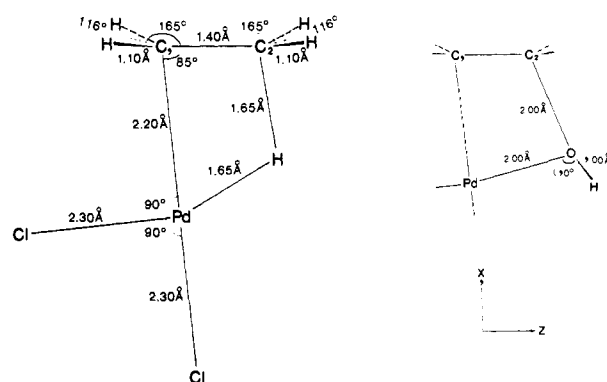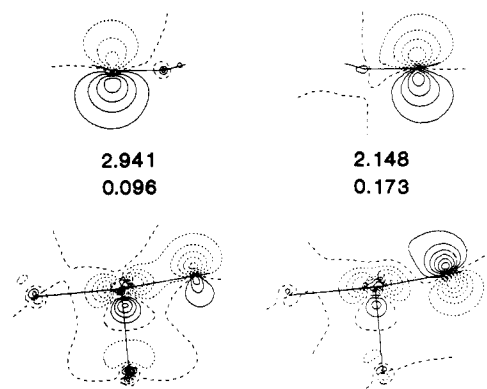
overlap repulsion, and the other is the enhancement of the ability to create the localized bonding orbital on the reaction center. It is necessary to remove some electron population from the π MO and place part of it in the π^* MO of the ethylene fragment and shift the rest into the catalyst orbitals.[16] The vacant 4d orbital of palladium is utilized for accepting electron population and for causing the intermixing of the π and π^* MO's. A fraction of electronic charge shifted from the C_2H_4 fragment is further distributed over the unpaired, nonreactive orbitals localized on the catalyst.

In the case of $PdCl_3^-$, the overlap interaction between the Cl ligand and Pd is very strong, as manifested in the large Pd–Cl overlap population (0.51), and, moreover, the Cl ligand has an excess electron. Accordingly, the relevant d orbital of palladium, i.e., $d_{x^2-y^2}$, is lifted so high due to the overlap and electrostatic effects of this ligand that the interaction with the π MO of ethylene cannot be effective. In the case of $PdCl_2(H_2O)$, the H_2O ligand is electronically neutral, and the overlap interaction between O and Pd is not strong. The Pd–O overlap population is as small as 0.13. The low-lying $d_{x^2-y^2}$ orbital is utilized effectively to remove electron population from the π MO and promote a part of the electron population to the π^* MO. The overlap repulsion between C_2H_4 and the attacking nucleophile is reduced efficiently, and the ethylene orbital gets to be localized well to interact strongly with the nucleophile. Experiments have proved the presence of an equilibrium for ligand interchange prior to addition. This indicates that the stronger activation of olefin double bonds by $PdCl_2(H_2O)$ favors the addition of nucleophiles.

Cis Migration of Nucleophiles. The intramolecular migration of a nucleophile to the coordinated olefin molecule is regarded as a [2 + 2] cyclic interaction. In order to study what orbitals actually participate in cis hydroxypalladation, we set up the reaction model shown in Figure 4. The reacting system was

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(15) The hydride orbital overlaps more strongly with the orbitals of the carbon atoms than the oxygen p orbital does. A direct comparison of overlap populations for the OH⁻ and H⁻ additions is not informative.

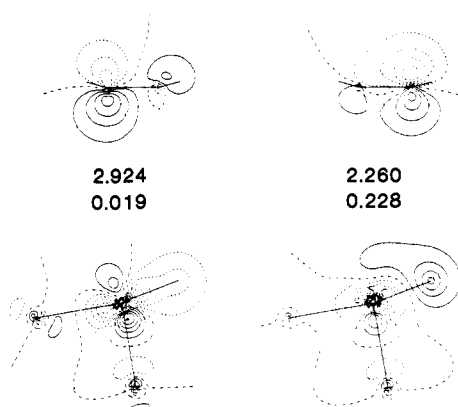(16) Fujimoto, H.; Inagaki, S. *J. Am. Chem. Soc.* **1977**, *99*, 7424.

Figure 6. Two dominant pairs of interacting orbitals for H⁻ migration in C_2H_4–Pd(H)Cl_2^- system.

partitioned into two fragments, i.e., C_2H_4 and $PdCl_2(OH)^-$. We compared this with the [2 + 2] interaction between C_2H_4 and $PdCl_2H^-$.

Two pairs of interacting orbitals are shown in Figure 5 for the OH⁻ migration. The ethylene orbitals are seen to be completely localized. However, the first pair of orbitals has an electron population of almost three, and, accordingly, this pair can hardly contribute to the bonding between the two fragments. A bonding interaction between the fragments is due to the second pair of orbitals. The lone-pair orbital of oxygen takes the main part in this pair and, therefore, the Pd–O bond is not weakened as the C(2)–O bond is formed. The migration of OH⁻ from palladium to C(2) of the coordinated olefin, retaining the C–Pd bond, seems to be unlikely.

Figure 6 illustrates two pairs of orbitals for the hydride migration. The first pair is only weakly bonding, and the interaction is governed virtually by the second pair of orbitals. The orbital of the $PdCl_2H^-$ fragment has an interesting shape, given by the in-phase mixing of the hydride 1s orbital and the $d_{x^2-y^2}$ and d_{xz} orbitals of Pd. One should note that the $d_{x^2-y^2}$ orbital has its extension in the direction nearly perpendicular to the Pd–H bond. This signifies that the migrating hydride is assisted by several d orbitals. As the hydride is bound to the C(2) atom, the $d_{x^2-y^2}$ orbital gets free, and it continues to form the bond with the C(1) atom. The cis migration of the hydride is more plausible by virtue of the neighboring d orbital participation.

In order to clarify this point, we carried out an analysis on the system illustrated in Figure 7. On the thermolysis pathway of *trans*-[PdEt$_2$(PR$_3$)$_2$], it was suggested experimentally that a phosphine ligand was removed, and then ethane and ethylene were liberated.[17] It is most likely that a hydride is eliminated from an ethyl ligand. This is just the reverse process of the cis-migration discussed above. The pairs of orbitals which play dominant roles are shown in Figure 7. They bear a close resemblance to the orbitals presented in Figure 6. This means that the orbital pairs shown in Figure 6, in particular the bonding pair on the right-hand side, are characteristic to this type of hydride migrations.[18]

In the case of olefin insertions into a Ti(IV)–Me bond, a four-membered cyclic transition state was located by a theoretical calculation.[18] We obtained two bonding pairs of interacting orbitals, one being localized more than 80% in the region of a newly formed Ti–C bond and the other well-localized in the Me–C bond
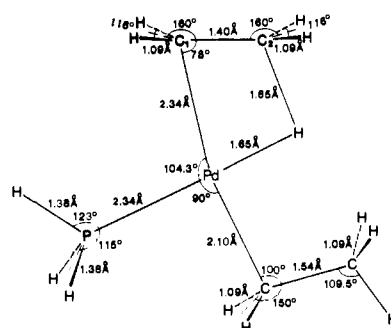

Figure 7. Reaction model and two dominant pairs of interacting orbitals for β-elimination reaction in Pd(PH$_3$)Et$_2$.

region. The interaction compared roughly with the electrophilic addition of BH$_3$ to an olefin double bond. In the present systems, however, the pair of orbitals are not localized well in the region between a specific pair of atoms. This indicates that tight four-membered cyclic interactions are not suited for these processes. The difference between the Ti(IV) and Pd(II) systems is ascribed mainly to the difference in the number of electrons populated in the four-membered cycle. For example, the electron populations of the orbital pairs are considerably larger than 2 in the present systems as shown in Figures 6 and 7. They were closer to 2 in the case of (CH$_3$TiCl$_2^+$–C$_2$H$_4$) and (HTiCl$_2^+$–C$_2$H$_4$) systems. The Pd(II)-catalyzed migratory addition of hydride will occur via a loosely bound four-membered cycle, if at all.

Conclusion

We have studied above Pd(II)-catalyzed nucleophilic additions to olefin double bonds. In the trans additions, the role of the catalyst is to modify the electronic structure of the reaction center. In contrast to this, Pd is involved in the reaction more directly in cis additions. The aspects of these interactions were demonstrated in the patterns of orbitals and interpreted by some simple quantities, e.g., localizability of orbitals, the number of electrons occupying the orbital pair, and so on. The calculations favor trans addition for hydroxide but cis migration for hydride in agreement with experiments and other theoretical calculations.[2j,l,4b,6] Thus, the analysis by the paired interacting orbitals makes it possible to connect the theoretical calculations closely with our empirical notions in chemistry by clarifying the local characteristics of chemical interactions.

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