# A Theoretical Study of Olefin Insertions into Ti–C and Ti–H Bonds. An Analysis by Paired Interacting Orbitals

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**Abstract:** Cyclic interactions between $C_2H_4$ and $CH_3TiCl_2^+$ and between $C_2H_4$ and $HTiCl_2^+$ have been examined by applying the method of interacting molecular orbitals with a view to studying reactivities of metal–carbon and metal–hydrogen bonds. Two sets of paired localized orbitals are shown to play dominant roles in each case, suggesting that the Ti–C bond and the C–C or H–C bond are likely to be formed concertedly. These systems are shown to resemble the electrophilic addition of $BH_3$ to an olefin double bond via a four-centered transition state from the interacting orbital viewpoint.

Molecular orbital theory has been shown to be very useful in elucidating the electronic structures of transition metal complexes and their roles in chemical reactions. Apart from a number of elaborate ab initio calculations, attempts have been made to derive some simple guides to understanding common trends in organometallic chemistry. For instance, the frontier orbitals were used to predict the similarity in the behavior of organic and inorganic molecules in chemical interactions.[2] However, in order to make an unambiguous comparison of reactivities among molecules of different sizes, devices are needed to find out the orbitals that participate virtually in chemical interactions. With a view to applying the lucid and useful concept of orbital interactions to ab initio MO calculations,[3] we proposed a method of unequivocally deriving the orbitals of reagent and reactant that play dominant roles in interactions.[4,5]

Insertions of olefin molecules into R–metal bonds in which R is a hydride, alkyl, vinyl, allyl, etc., are very familiar in organometallic chemistry, and this class of reactions can be related closely with the chain-growing or -terminating steps in olefin polymerization, particularly in the case in which metal is Ti.[6,7] Staley and collaborators have studied the gas-phase ion chemistry of $TiCl_4$.[8] $TiCl_3^+$ produced by electron-impact ionization of $TiCl_4$ gives rise to a cationic species $CH_3TiCl_2^+$, by chloride transfer from $CH_3TiCl_3$, that reacts with ethylene to yield $C_3H_5TiCl_2^+$. Though $H_2$ is eliminated finally, insertion of ethylene into the Ti–C bond has been suggested to take place in the process.

Steigerwald and Goddard very recently studied the reaction of $D_2$ with $HTiCl_2^+$ and $HTiCl_2$ by means of their generalized valence-bond theory and clarified that 2s + 2s additions would proceed with low activation energy when the metal–hydrogen bond was nonpolar and covalent.[9] Here, we report an analysis of a cyclic interaction of $CH_3TiCl_2^+$ and $HTiCl_2^+$ with $C_2H_4$, by applying the method of paired interacting orbitals.

## Method

The details of the theoretical treatment have already been described previously.[4] Here, we briefly mention the outline of the method. We consider an interacting system A–B that is composed of the reagent A and the reactant B. For the simplicity of discussion, we may assume that both A and B have closed-shell electronic structures. The modification that will be necessary in order to deal with interactions of open-shell systems is straightforward. The MOs $\Phi$ of the composite interacting system A–B can be expanded as linear combinations of the MOs of fragment species A and B frozen to the same structures as they have in A–B as:

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

where $M$ and $N$ are equal to the number of the MOs of A and B, respectively. The occupied MOs and the unoccupied MOs of A are denoted by $\phi_i$ ($i = 1, 2, \ldots, m$) and $\phi_{m+j}$ ($j = 1, 2, \ldots, M - m$) respectively, and the occupied MOs and the unoccupied MOs of B are indicated by $\psi_k$ ($k = 1, 2, \ldots, n$) and $\psi_{n+l}$ ($l = 1, 2, \ldots, N - n$), respectively. The coefficients, $c_{i,f}, d_{k,f}, \ldots$, can be calculated easily by solving simultaneous equations.[10]

We define the intermolecular bond-order matrix **P** with respect to the MOs of A and the MOs of B:

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

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

In general, the matrix **P** is rectangular of dimensions of $M \times N$. The product of **P** and its adjoint $\mathbf{P}^\dagger$ yields a symmetry matrix that can be diagonalized by a unitary transformation **U**:

$$\mathbf{P}^\dagger\mathbf{P}\mathbf{U} = \mathbf{U}\mathbf{\Gamma} \quad (4)$$

Then, by the use of eigenvectors **U** and eigenvalues $\mathbf{\Gamma}$, we may carry out transformations of orbitals within A and within B simultaneously, obtaining:[4,11]

$$P'_{\mu,\nu} = 0 \text{ for } \mu \neq \nu \quad (5)$$

where $P'_{\mu,\nu}$ represents the bond-order matrix for the new fragment orbitals $\phi'_\mu$ and $\psi'_\mu$. The interaction described by the various combinations of canonical MOs of the molecular species A and B is now represented by several sets of paired *fragment* MOs ($\phi'_\mu$, $\psi'_\mu$), $\mu = 1, 2, \ldots, s$, $s$ being the smaller of $M$ and $N$. The interacting orbitals are also obtained for any subspace of **P** in order to visualize what roles the various combinations of canonical MOs play in the course of chemical reactions.

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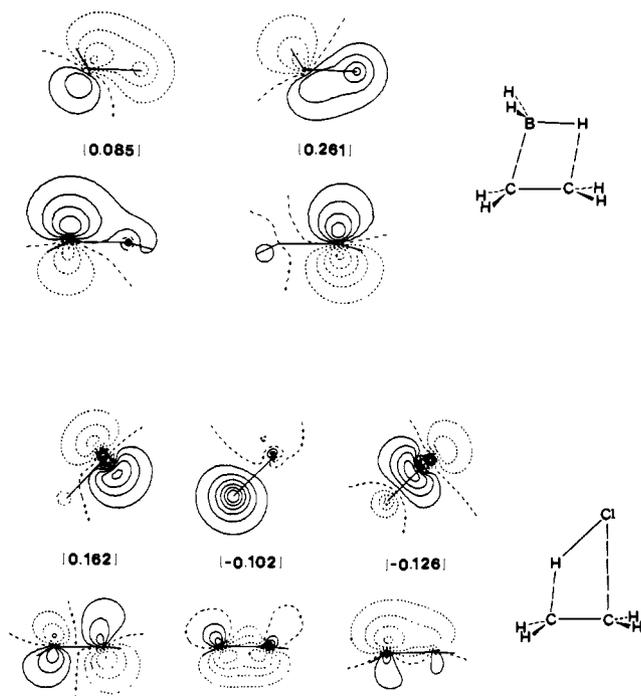
**Figure 1.** Pairs of orbitals participating in the interaction between $BH_3$ and $C_2H_4$ and in the interaction between HCl and $C_2H_4$. The values in brackets signify the overlap populations between the paired orbitals.

## Results of Calculations

Two good examples of reactions that take place via four-membered cyclic transition states were discussed by Morokuma, one being the addition of $BH_3$ to ethylene and the other the cis addition of HCl to ethylene.[12] The activation energy was reported to be 28 kJ mol$^{-1}$ for the former and 201 kJ mol$^{-1}$ for the latter. Addition of $BH_3$ to olefinic double bonds has often been argued as the key step in the hydroboration of olefins. On the contrary, the concerted addition of HCl to carbon–carbon unsaturated bonds is less familiar in organic chemistry. Figure 1 illustrates the dominant pairs of interacting orbitals for these two reacting systems at the transition states. The calculation was carried out with the standard 4-31G basis set.[13]

In these additions, two single bonds are formed between the reagent and the reactant and, therefore, each interaction should be described virtually by means of two bonding pairs of interacting orbitals, provided that the cyclic interaction is really a favorable process. In the case of the addition of HCl to ethylene, however, three orbital pairs were shown to participate significantly in the interaction. Among them, only the first pair of orbitals gives a bonding interaction. Other two pairs are strongly antibonding. This indicates that not only the electrons of the ethylene molecule that are relevant to the reaction but also the $\sigma$ electrons give rise to strong overlap repulsions with the electrons of H–Cl bond.

Overlap repulsion also exists in the addition of $BH_3$ to ethylene. The occupied MO of the B–H bond which is broken in the course of addition gives rise to a weak repulsive interaction by overlapping with the occupied $\pi$ MO of ethylene. This is manifested in the positive but relatively small overlap population for the first pair of interacting orbitals shown on the left-hand side in Figure 1. However, the repulsion is overcome by delocalization stabilization at the key stage of the reaction. Two pairs of interacting orbitals suffice for representing $BH_3$ addition.

A clearcut difference has been shown to exist in the orbital patterns between the two processes. In the case of $BH_3$ addition, the interaction is explained effectively by the two bonding pairs
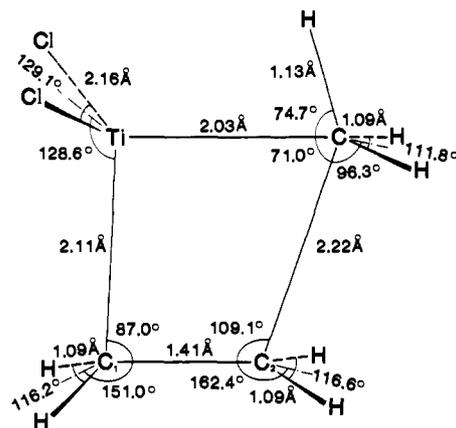


**Figure 2.** Reaction model for the $CH_2=CH_2$ insertion to $CH_3TiCl_2^+$.

of interacting orbitals. On the other hand, only a pair of orbitals shows a bonding interaction in the addition of HCl, and an additional pair of orbitals that is not relevant to the formation of new bonds gives rise to a strong antibonding interaction. The difference in the magnitude of activation energies between these two cases seems to be well reasoned. Thus, we may refer to the interacting orbitals for these typical systems to conjecture the ease of other cycloadditions through four-membered cyclic transition states.

The mechanism of olefin insertions is still not clear, particularly in the case of H–metal bonds. Though some stable ethyl complexes have been isolated,[14] reverse $\beta$ eliminations often take place. Cyclic interactions between R–metal or H–metal bonds and C–C double bonds have been assumed for the propagation step in olefin polymerization[15] and for $\beta$-hydride transfer associated with alkene elimination in transition metal complexes.[16] Thus, it may be worthwhile to examine whether or not the four-membered cyclic interaction is favorable in olefin insertion reactions. The system studied here is the interaction between $CH_3TiCl_2^+$ and $C_2H_4$. We first try to determine the transition state of the reacting system by adopting the minimal STO-3G basis functions for H, C, and Cl atoms and the double-$\zeta$ basis functions for Ti.[17] The structure obtained with these basis functions may not be so reliable. We will investigate the possibility of the four-membered cyclic transition state by means of comparing the patterns of interacting orbitals with those obtained for the $BH_3$ addition and for the HCl addition, after recalculating the electronic structure of the reacting system with the standard 4-31G basis set for H, C, and Cl atoms.

We applied the energy-gradient technique[18] to the $CH_3TiCl_2^+$ + $C_2H_4$ system and obtained the unstable equilibrium geometry shown in Figure 2 that seemed the most likely structure for the transition state of the insertion process.[19] The separation between Ti and $C_1$ was calculated to be 2.11 Å and the C(methyl)–$C_2$ bond length 2.22 Å. There may exist another equilibrium geometry that is produced by rotating the methyl group by 180° around its approximate $C_3$ axis. We did not obtain this structure, however, because the experiment showed that $H_2$ was eliminated in this process. The structure in Figure 2 indicates that the C–H bond in the $C_s$ symmetry plane is already stretched in comparison with other C–H bonds. As the methyl group is tilted to the position so that it has the C(methyl)–$C_2$ bond as its symmetry axis, this

(12) (a) Nagase, S.; Ray, N. K.; Morokuma, K. *J. Am. Chem. Soc.* **1980**, *102*, 4536. (b) Nagase, S.; Morokuma, K. *Ibid.* **1978**, *100*, 1666.
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(14) (a) Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* **1974**, *13*, 2213. (b) Schwarz, J. *Pure Appl. Chem.* **1980**, *52*, 733.
(15) Cossee, P. *J. Catal.* **1964**, *3*, 80.
(16) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. See, also: Sakaki, S.; Kato, H.; Kanai, H.; Tarama, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 813.
(17) Roos, B.; Veillard, A.; Vinot, G. *Theor. Chim. Acta* **1971**, *20*, 1.
(18) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.
(19) This system is too large to carry out the vibrational analysis, but one may imagine that there is no other realistic path for collapse of the complex. Hereafter, we assume this to be the transition state.

**Figure 3.** Three dominant pairs of interacting orbitals in the $CH_3TiCl_2^+$ – $C_2H_4$ system. The numbers indicate the extent of localization of orbitals on the reaction centers in percent.

hydrogen comes just in front of the empty Ti orbital and may be eliminated.

The $CH_3TiCl_2^+$ fragment is a transient species generated in the course of the reaction. The 4-31G calculation has actually shown that the isolated fragment state, if it exists, is located 106 kJ mol$^{-1}$ above the structure given in Figure 2. What is important here is that a loosely bound $\pi$ complex intervenes before reaching the four-centered unstable geometry. The complex is calculated to be 44 kJ mol$^{-1}$ below the transition state at the RHF 4-31G level. In the cationic Ti fragment, the site for ethylene coordination is empty from the outset, and therefore the ethylene molecule can slide in the coordination sphere of Ti without activation. The vertical distance between the Ti atom and the C–C bond in the complex is 2.41 Å. The interaction has been found to be explained effectively by a single pair of fragment orbitals, which shows that this complexation is purely due to electron donation from the $\pi$ MO of ethylene to the Ti orbital of relatively strong s character: 29% s, 15% p, and 56% d.

Figure 3 illustrates three pairs of interacting orbitals which participate dominantly in the interaction between $CH_3TiCl_2^+$ and $C_2H_4$ at the transition state. The overlap populations between these interacting orbitals were calculated to be positive, 0.300 for $(\phi'_1, \psi'_1)$ and 0.137 for $(\phi'_2, \psi'_2)$. The extent of localization of the orbitals around the reaction centers, i.e., Ti and C atoms, was estimated using the Mulliken population analysis[20] with respect to the orbitals of the first and the second bonding pairs. It is seen to be greater than 80% in the first pair. The Ti–C bond is already formed at this stage. The chlorine ligands are shown to be excluded from the reactive region, but they obviously serve as perturbers on the reaction center through the determination of the density matrix **P**. The localization of the orbitals in the second bonding pair $(\phi'_2, \psi'_2)$ is found to be somewhat less than that in $(\phi'_1, \psi'_1)$. The methyl group is not tilted enough and electron delocalization does not occur effectively in this pair. The third pair of orbitals represents an antibonding interaction between the C–H bonds of methyl and ethylene in this eclipsed conformation. However, the overlap repulsion is not strong enough to make this cyclic interaction unfavorable. The repulsion even makes the departure of one of the $C_2$ hydrogens easier. Thus, the interaction is recognized as a concerted process in terms of orbital patterns, though not fully synchronous.[21]

The energies and electron occupancies of these three pairs of fragment interacting orbitals are presented in Table I. The

(20) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833. This population analysis involves some arbitrariness, particularly when it is applied for such systems being studied here.

(21) The difference in the extent of localization of orbitals represents asynchroneity in the bond formation at the two reaction centers.

**Table I.** Energy and Electron Population of the Interacting Orbitals

| orbital | energy (au) | population | |
|---------|-------------|------------|---|
| $\phi'_1$ | −0.4941 | 0.925 | 2.389 |
| $\psi'_1$ | −0.2997 | 1.464 | |
| $\phi'_2$ | −0.6904 | 1.604 | 2.590 |
| $\psi'_2$ | −0.2699 | 0.986 | |
| $\phi'_3$ | −0.6580 | 1.802 | 3.367 |
| $\psi'_3$ | −0.5629 | 1.564 | |

**Table II.** Contributions of Interacting Orbitals to the Overlap Population between $CH_3TiCl_2^+$ and $C_2H_4$ Fragments

| orbital pair $(\phi'_\mu, \psi'_\mu)$ | overlap population | major constituents | |
|---|---|---|---|
| | | $CH_3TiCl_2^+$ MO | $C_2H_4$ MO |
| $\mu = 1$ | 0.300 | 21a′, 11a′, 22a′ | 6a′, 7a′ |
| 2 | 0.137 | 20a′, 18a′, 21a′ | 7a′, 4a′, 6a′ |
| 3 | −0.044 | 15a′, 16a′, 30a′ | 5a′, 4a′, 7a′ |
| 4 | −0.014 | | |
| 5 | −0.014 | | |
| 6 | 0.006 | | |
| 7 | 0.006 | | |
| 8 | −0.006 | | |
| 9 | −0.002 | | |
| 10 | −0.002 | | |
| 11 | −0.001 | | |
| 12 | 0.001 | | |
| 13 ~26 | 0.000 | | |

number of electrons populated in the orbital pair exceeds 2 both in $(\phi'_1, \psi'_1)$ and in $(\phi'_2, \psi'_2)$, indicating that the first and second pairs also include parts of overlap repulsion. Particularly a $\sigma$-type 4a′ MO mixes in $\psi'_2$ to increase the population of this hybrid orbital. The repulsive pair $(\phi'_3, \psi'_3)$ bears naturally a much greater electron population.

Table II shows the contributions of 26 orbital pairs to the overlap population between $C_2H_4$ and $CH_3TiCl_2^+$ fragments. The interaction is seen to be condensed efficiently into the first three pairs of interacting orbitals presented in Figure 3. The major constituent canonical MOs are also given for the first three pairs. On the $CH_3TiCl_2^+$ part, the lowest unoccupied 21a′ MO is the dominant constituent of the interacting orbital $\phi'_1$ that is responsible for the formation of Ti–$C_1$ bond, and the highest occupied 20a′ MO is the principal component of the interacting orbital $\phi'_2$ which participates in the formation of new C–$C_2$ bond. On the ethylene part, however, the highest occupied $\pi$-like MO (6a′) and the lowest unoccupied $\pi^*$-like MO (7a′) are mixed effectively both in $\psi'_1$ and $\psi'_2$ to yield the two localized interacting orbitals as shown in Figure 3. In the third pair $(\phi'_3, \psi'_3)$, the
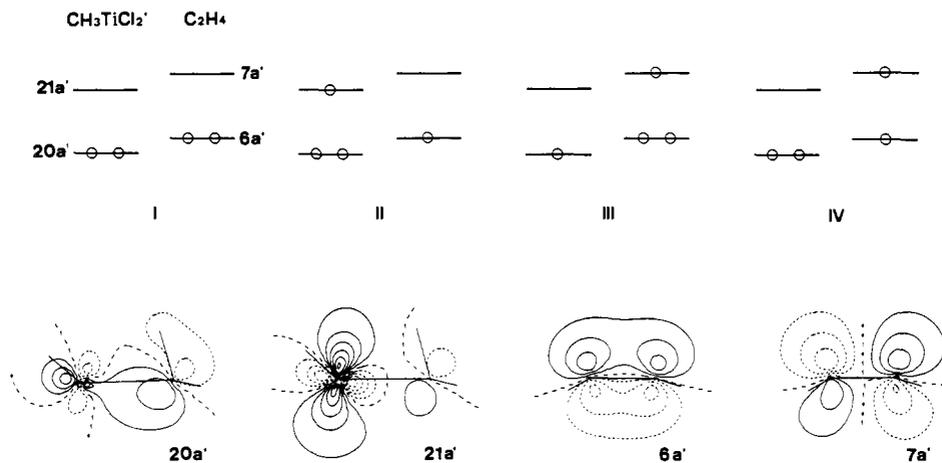
CH₃TiCl₂⁺   C₂H₄



Figure 4. A schematic illustration of important electron configurations in the $CH_3TiCl_2^+$ + $C_2H_4$ system.

CH₃TiCl₂⁺



unoccupied          occupied

C₂H₄



occupied          unoccupied

Figure 5. Interacting orbitals participating in the charge-transfer interactions between $CH_3TiCl_2^+$ and $C_2H_4$.

high-lying occupied MOs 15a' and 16a' of $CH_3TiCl_2^+$ overlap with the σ-type occupied MOs 4a' and 5a' of $C_2H_4$.[22]

The wave function of the ($CH_3TiCl_2^+$ + $CH_2$=$CH_2$) system can be expanded in terms of various electron configurations:

$$\Psi = \sum_p C_p \Psi_p \qquad (6)$$

The important electron configurations are illustrated schematically in Figure 4. The configuration analysis[10] shows that the coefficients $C_p$ for the configurations I, II, III, and IV are 0.4420, 0.2829, 0.1262, and −0.1064, respectively, in the present reaction model. The locally excited configuration IV of the ethylene fragment is induced efficiently. Electronic charges can thus migrate easily from methyl carbon to $C_2$, $C_2$ to $C_1$ within ethylene, and $C_1$ to Ti. The changes in the electron populations on going from the π complex to the transition state are −0.024 (decrease), −0.166, 0.223 (increase), and 0.019 for methyl carbon, $C_2$, $C_1$, and Ti, respectively.

Figure 5 illustrates the pairs of interacting orbitals which participate dominantly in the two directions of electron transfer, i.e., from $C_2H_4$ to $CH_3TiCl_2^+$ and from $CH_3TiCl_2^+$ to $C_2H_4$. In this case, the orbitals of the $C_2H_4$ fragment are seen to be delocalized over two carbons, looking very similar to the π and π* canonical MOs of the distorted ethylene molecule. On the other hand, the $CH_3TiCl_2^+$ unoccupied interacting orbitals consist of

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(22) It is possible to separate orbitals participating in overlap repulsion from those in delocalization interactions by carrying out orbital transformations for a subspace of **P**.





Figure 6. Pairs of orbitals participating in the interaction of $HTiCl_2^+$ with $C_2H_4$.

about 94% of the 21a' MO and 80% of the 20a' MO, respectively.

A comparison of the orbitals in Figure 3 with those in Figure 5 indicates clearly that the locally excited configuration IV of the ethylene plays a critical role in yielding the two sets of localized orbital pairs in the Ti–$C_1$ and C–$C_2$ bond regions. In fact, the Ti fragment is bent from the outset, and therefore the energy difference between the π complex and the transition state was attributed for the most part to the activation of the C–C double bond. The locally excited electron configuration is induced effectively in this case by virtue of the delocalization interaction,[23] taking advantage of simultaneous existence of the lowest unoccupied MO having a large amplitude on Ti and the highest occupied MO having a large amplitude on $CH_3$.

Figure 6 illustrates the two bonding pairs of orbitals for the $HTiCl_2^+$ and $C_2H_4$ systems. The geometry was chosen somewhat

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(23) Fujimoto, H.; Fukui, K. *Isr. J. Chem.* **1983**, *23*, 49.

arbitrarily in this case.[24] This system also gave the interacting orbitals of similar patterns to the $BH_3$ addition. In this case, overlap repulsion was found to be very weak compared with the bonding interactions. The coefficients of electron configurations corresponding to I, II, III, and IV in Figure 4 (the $HTiCl_2^+$ fragment orbitals are 16a' and 18a' instead of 20a' and 21a') were calculated to be 0.3473, 0.2487, 0.1580, and −0.1194, respectively. The interaction is stronger and the interacting orbitals are more localized in this system than in the $CH_3TiCl_2^+ + C_2H_4$ system studied above, but we see no significant difference in the trend. The spherical 1s orbital of hydrogen seems to be somewhat more suited for electron delocalization in comparison with the methyl group. This means, however, that the reverse elimination through the four-membered cyclic transition state can also take place more easily.

The systems studied here may be oxidized too strongly. In more general cases, the Ti center has six coordination in an octahedral arrangement,[6,7] and the Ti–R bond will be broken more easily than in the present systems. The formation of the R–C bond and, consequently, the formation of the Ti–C bond will take place more readily. It is time-consuming at present to carry out calculations on other systems, but the influence of ligands is included directly in the bond-order matrix and consequently in the interacting orbitals. The polarizability of olefins is also of importance and, in addition, the metal–R moiety should be moderately electron deficient in order to suppress the overlap repulsion.

## Conclusion

An application of the interacting orbital concept revealed some aspects of interactions in the insertion of $CH_2=CH_2$ to the C—Ti and H—Ti bonds. The concept of isolobal analogy appears to

be more plausible here than it was with the highest occupied and lowest unoccupied frontier orbitals.[25] Though it is difficult to conclude whether a cyclic interaction is concerted or not or whether it is synchronous or asynchronous even in simpler organic reactions,[26] we suggest here that the presence of the low-lying unoccupied orbital having a large amplitude on the d orbitals of metal, and the high-lying occupied orbital having a large amplitude on R, is the requisite to facilitate insertion reactions via four-centered transitions states. The most important stage in olefin insertion is the activation of the C–C bond, as has been indicated by the significant contribution of the locally excited configuration and by the localized interacting orbitals of the olefin fragment in the ground state of the composite reacting system. Thus, as for the significance of the vacant d orbitals in the metal, our conclusion is obviously in line with that of Thorn and Hoffmann[16] and of Steigerwald and Goddard.[9]

Since there are a variety of molecules involved in reactions and since only some particular structural units in molecules participate actively in chemical interactions, recognition of the similarity and dissimilarity in reactivities of molecules by means of patterns will be helpful. Thus, the simple orbital transformations to give the orbitals that are localized specifically in the reactive regions of molecules would be suited for elucidating common features of interactions for the reagent and reactant of various sizes by means of theoretical calculations.

(24) The H–C bond in the model is about 1.47 times longer than the normal C–H bond. This compares roughly with the C(methyl)–C₂ bond which is 1.44 times that of the normal C–C bond length.

(25) Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1.
(26) See, for example: Komornicki, A.; Goddard, J. D.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 1763. Hiberty, P. C.; Ohanessian, G.; Schlegel, H. B. *Ibid.* **1983**, *105*, 719.

# Line Shape of the Intervalence Transfer Band in Bridged Mixed-Valence Dimers: The Delocalized Case

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**Abstract:** An approximate method for the prediction of intervalence transfer (IT) band profiles for delocalized bridged mixed-valence dimers is given. The method is based on a three-site model, with the bridging ligand explicitly included. Potential energy surfaces along the totally symmetric vibrational sum coordinate are treated approximately as displaced harmonic oscillators. The force constants and displacements of the minima are obtained with second-order perturbation theory. We call this approximate procedure the second-order harmonic oscillator (SOHO) method. Transition intensities calculated from the SOHO method are in good agreement with those obtained numerically from the exact adiabatic potentials. The method is extended to include one coupled vibration on the bridging ligand. Simple expressions for the width of the IT absorption band at half-maximum are given. Implications for questions of electron delocalization in complexes of current interest in inorganic chemistry are discussed.

From the rich chemistry of bridged mixed-valence dimers and bridged metallic complexes, pioneered by Henry Taube and reviewed in volume 30 of *Progress in Inorganic Chemistry*,[1] there have emerged a number of interesting questions concerning electron delocalization in molecular electronic states. Considerable attention has been devoted recently to the questions of the extent and rate of spatial- and time-dependent delocalization of electrons

in these complexes, the shape of the corresponding intervalence transfer (IT) band, and the role of the bridging ligand in the electron-transfer process.

One particular mixed-valence complex, the Creutz–Taube ion, a pyrazine-bridged mixed-valence complex of ruthenium

$$\left[ (NH_3)_5RuN \bigcirc NRu(NH_3)_5 \right]^{5+}$$
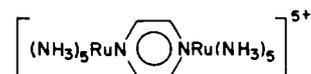
has been the focus of considerable attention and controversy.

(1) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1–73. (b) Haim, A. *Ibid.* 273–357. (c) Meyer, T. J. *Ibid.* 389–440. (d) Sutin, N. *Ibid.* 441–498.