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Akinobu Shiga[a]
[a] Tsutuba Research laboratory, Sumitomo Chemical Co., Ltd., Tsukuba, Japan

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THEORETICAL STUDY ON REACTIVITIES OF Ti-METHYL BONDS IN d^0 METHYLTITANIUM COMPLEXES FOR INSERTION OF ETHYLENE: ANALYSIS BY "PAIRED INTERACTING ORBITALS" (PIO)

Akinobu Shiga
Tsutuba Research laboratory
Sumitomo Chemical Co., Ltd.
6 Kitahara, Tsukuba 300-32, Japan

ABSTRACT

An effect of ligands on the reactivities of ethylene insertion in d^0 methyltitanium complexes/ethylene systems is studied by using PIO analysis, and local electrophilicity and nucleophilicity calculation based on extended Huckel MOs. Ligands are indispensable in order to guide an ethylene molecule into the right place for the insertion, however it is unavoidable that the insertion is weakened by the ligands because of mixing between the orbitals of the ligands and the Ti d orbitals and Cm p orbitals of the methyltitaniaum complexes. A ligand placed *trans* to the incoming ethylene has a strong negative effect on the insertion. Ligands placed out of the reaction plane do not have a large effect on the insertion. The reactivities of the insertion of the models are predicted.

INTRODUCTION

Highly active catalysts have modernized the manufacturing process of polyolefin. As the manufacturing processes become more efficient, more sophisticated catalysts by which we are able to control molecular weight and its distribution, copolymerization ratio, regio-and stereo- selectivities and so on, are requested to produce the polymers with desired physical and chemical properties. Being stimulated by the discovery of highly active homogeneous metallocene catalysts by Kaminsky *et al.*, much interest has been focused on homogeneous catalysts.

In order to develop such sophisticated catalysts it is indispensable to clarify the relationship between the structure of the active site and the catalyst performance on the basis of the precise and quantitative understanding of polymerization mechanism. Kawamura *et al.* [1] have reported the potential-energy profile of the orefin insertion process, which is a key step in the catalytic cycle in the Cossee polymerization mechanism. In spite of these elaborate calculations *ab initio* MO methods are not easy to apply to large and complicated catalytic systems used in industry from a practical point of view. Fujimoto *et al.* [2] proposed a method of determining unequivocally the orbitals which should play dominant roles in chemical interactions between two systems. The interaction between the catalytic species and an orefin in the Ziegler-Natta polymerization process was represented compactly in terms of a few pairs of localized orbitals. They called those orbitals "paired interactio~ orbitals" (PIO). By applying the PIO analysis on orefin insertion into the methyl-titanium bond of methyltitanium complexes, it is clarified that electron delocalization from orefin to the methyltitanium complexes and that from the methyltitanium to orefin play a crucial role in orefin insertion.[3]. Fujimoto *et al.* [4] also proposed the way of estimating the electrophilicity and the nucleophilicity of reaction site based on electron delocalization.

It is a very important matter for designing of novel polymerization catalyst to know the electrophilicity or Lewis acidic strength of the methyltitanium complex quantitatively. Here we describe the effect of ligands on the reactivities of ethylene insertion by calculating the electrophilicity and the nucleophilicity of the methyltitanium complexes according to the procedure proposed by Fujimoto *et al.* [4] This study is composed of three parts: (1) determination of the most simple ethylene insertion system and the geometrical structure of it's ethylene coordinated state by referring the results of *ab initio* calculation; (2) determination of the reference orbitals of the system by PIO analysis, and (3) calculation of the electrophilicity and the nucleophilicity of the methyltitanium complexes.

Models

The Cossee mechanism has been accepted for the mechanisum of orefin insertion as the most plausible one. An active site is alkyltitanium complex. Olefin coordinates to the titanium atom with its double bond parallel to the alkyl-titanium

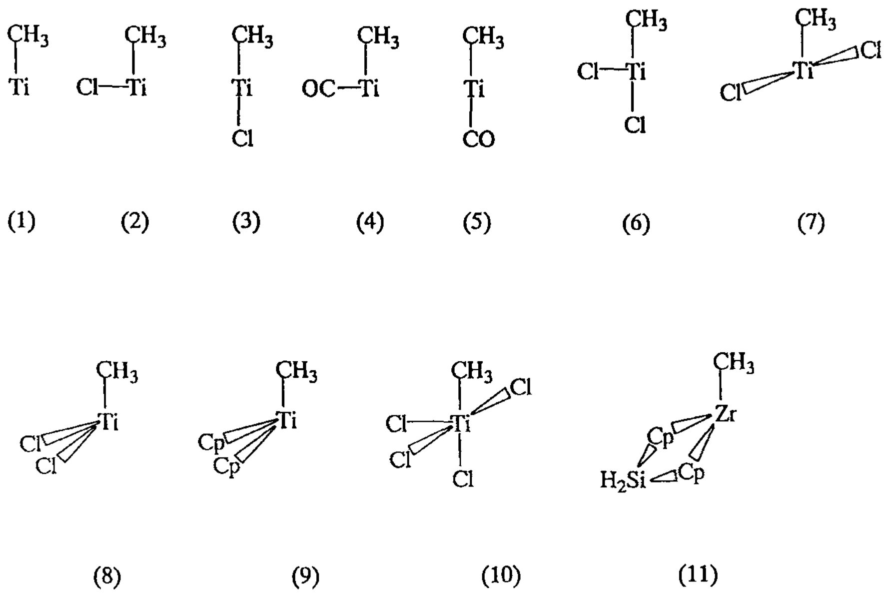

Figure 1. A Schematic illustration of model d^0 methyltitanium complexes.

bond. A four center~ reaction plane, which is composed of the titanium atom, the carbon atom of the alkyd group, and double bonded two carbon atoms of orefin, is formed at the orefin coordinated state and then *cis* opening of the double bond of orefin and a migration of the alkyl group to the ß-carbon of orefin take place concertedly to move to the transition state. H. Kawamura-Kuribayashi *et al.* [1] confirmed this procedure with *ab initio* MO calculation.

[Methyltitanium]$^{+3}$/ethylene is the most simple model of orefin insertion system. We can understand the effect of ligands on ethylene insertion by adding ligands to the methyltitanium. Models employed here are shown in Figure 1. Complex (2) has one Cl anion *cis* to the methyl group in the reaction plane and complex (3) has one Cl anion *trans* to the methyl group in the reaction plane. These Cl anions are replaced by carbon monoxide molecule in complex (4) and (5), respectively. Complex (6) has two Cl anions *cis* and *trans* to the methyl group in the reaction plane and complex (7) has two Cl anions perpendicular to the reaction place. The carbon atom of the methyl group, the Ti atom and the two Cl anion form a trigonal pyramid in complex (8). In complex (9) these two Cl anions are replaced by two cyclopentadienyl (Cp) anions. Complex (10) has four Cl anions, two of them placed *cis* and *trans* to the methyl group in the reaction plane and another two

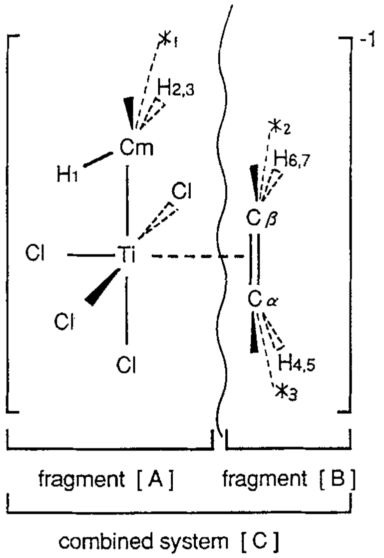

Figure 2. The combined system and fragment [A] and [B].

of them placed perpendicular to the reaction plane. Complex (11) is methylzirconocene, in which two Cp rings are bridged with H_2Si group.

We examined an ethylene coordinated state of each models. We assumed the geometrical structures of the models by referring to the reported structure [1, 5]. Details of the geometry of these models are given in the Appendix.

METHOD

PIO's Calculation

We divided a model system into a methyltitanium complex portion (fragment A) and an ethylene molecule (fragment B), as shown Figure 2. The geometries of [A] and [B] were taken to be the same as those in the original complex ([A + B] ≡ [C]).

The molecular orbitals of [A], [B] and [C] were calculated by applying the extended Hückel method. The extended Hückel parameters used are listed in the Appendix. Then, PIO's were obtained by applying the procedure that was proposed by Fujimoto *et al.* [2]. It is summarized as follows:

We expand first the MO's of a complex in terms of the MO's of two fragment species, by determining the expansion coefficients $c_{i,f}$,$c_{m+j,f}$ and $d_{k,f}$,$d_{n+l,f}$ in Equation 1.

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

$$f = 1, 2, \ldots, m+n$$

where Φf's are the MO's of the complex [C], ϕ and ψ are the MO's of the fragment [A] and [B] respectively, m and n indicate the number of occupied MO's of A and of B, respectively, and M and N represent the number of basis functions of A and of B, respectively.

We construct an interaction matrix P which represents the interaction between the MOs of the fragment [A] and the MOs of the fragment [B]

$$\mathcal{P} = \begin{pmatrix} P_{i,k} & P_{i,n+l} \\ P_{m+j,k} & P_{m+j,n+l} \end{pmatrix} \tag{2}$$

in which

$$P_{i,k} = 2\sum_{f=1}^{m+n} c_{i,f}d_{k,f} \qquad i = 1 \sim m,\ k = 1 \sim n$$

$$P_{i,n+l} = 2\sum_{f=1}^{m+n} c_{i,f}d_{n+l,f} \qquad i = 1 \sim m,\ l = 1 \sim N-n$$

$$P_{m+j,k} = 2\sum_{f=1}^{m+n} c_{m+j,f}d_{k,f} \qquad j = 1 \sim M-m,\ k = 1 \sim 1-n$$

$$P_{m+j,n+l} = 2\sum_{f=1}^{m+n} c_{m+j,f}d_{n+l,f} \qquad j = 1 \sim M-m,\ l = 1 \sim N-n$$

(3) We get transformation matrices U^A (for A) and U^B (for B) by:

$$\mathcal{P}^{\dagger}\mathcal{P}\mathcal{U}^{A} = \mathcal{U}^{A}\gamma \tag{3}$$

$$\mathcal{U}^{B}_{s,v} = (\gamma_v)^{-1/2}\sum_r^N P_{r,s}\mathcal{U}^{A}_{r,v} \quad (v = 1, 2\ldots N) \tag{4}$$

(4) We obtain the PIO's by applying the transformations defined by Equations 3 and 4:

$$\phi'_v = \sum_r^N U^A_{r,v}\phi_r \quad \text{(for A)} \tag{5}$$

$$\psi'_v = \sum_s^N U^B_{s,v}\psi_s \quad \text{(for B)} \tag{6}$$

The N x M (N $\leq$ M) orbital interactions in the complex C can thus be reduced to the interactions of N PIO's, N indicating the smaller of the numbers of MO's of the two fragments, A and B.

The PIO calculations were carried out on an LUMMOX system with NEC PC-9801RA[6].

Calculation of Electrophilicity and Nucleophilicity of Active Site

Electrophilicity (Lewis acidic strength) and nucleophilicity (Lewis basic strength) were calculated according to the procedure proposed by Fujimoto *et al.* [4]. The reference orbital, which is determined by PIO analysis, denoted here by δ_r can be expanded in terms of the occupied MO's ϕ_i and the unoccupied MO's ϕ_j of a methyltitanium complex (A).

$$\delta_r = \sum_{i}^{oc} d_{i,r}\phi_i + \sum_{j}^{uoc} d_{j,r}\phi_j \tag{7}$$

Then, the occupied and the unoccupied orbital that are the closest to δ_r are defined by Equations 8 and 9, respectively.

$$\phi_{oc}(\delta_r) = (\sum_{i}^{oc} d_{i,r}\phi_i)/(\sum_{j}^{oc} d_{i,r}^2)^{1/2} \tag{8}$$

$$\phi_{uoc}(\delta_r) = (\sum_{j}^{unoc} d_{j,r}\phi_j)/(\sum_{j}^{unoc} d_{j,r}^2)^{1/2} \tag{9}$$

These orbitals are given by a linear combination of the occupied and the unoccupied canomical MO's, respectively, and, therefore, the electron-donating or -accepting strength is evaluated by Equations 10 and 11,

$$\lambda_{oc}(\delta_r) = (\sum_{i}^{oc} d_{j,r}^2\epsilon_i)/(\sum_{i}^{oc} d_{j,r}^2) \tag{10}$$

$$\lambda_{unoc}(\delta_r) = (\sum_{j}^{unoc} d_{j,r}^2\epsilon_j)/(\sum_{j}^{unoc} d_{j,r}^2) \tag{11}$$

where ε_i or ε_j is the orbital energy of the component MO ϕ_i or ϕ_j. Using the same procedure described above, we can obtain the electron-donating and-accepting strength of the ethylene molecule (B). Then, a reactivity index (RI) is defined by Equation 12.

$$RI = 1/(\lambda_{Aunoc} - \lambda_{Boc}) + 1/(\lambda_{Bunoc} - \lambda_{Aoc}) \tag{12}$$

TABLE 1. Eigenvalues of PIOs of the Ethylene Coordinated State of the Model Complexes

complex	PIO-1	PIO-2	PIO-3	PIO-4	PIO-5	PIO-6	···	PIO-12
(1)	0.278	0.092	0.026	0.015	0.015	0.010	···	0.000
(2)	0.134	0.084	0.027	0.022	0.015	0.013	···	0.000
(3)	0.295	0.163	0.049	0.028	0.013	0.010	···	0.000
(4)	0.149	0.095	0.027	0.027	0.015	0.014	···	0.000
(5)	0.289	0.210	0.040	0.027	0.020	0.017	···	0.000
(6)	0.170	0.126	0.054	0.024	0.017	0.013	···	0.000
(7)	0.275	0.093	0.037	0.035	0.014	0.010	···	0.000
(8)	0.228	0.099	0.024	0.018	0.014	0.010	···	0.000
(9)	0.194	0.130	0.051	0.031	0.018	0.013	···	0.000
(10)	0.177	0.139	0.052	0.036	0.019	0.010	···	0.000
(11)	0.271	0.133	0.056	0.029	0.015	0.010	···	0.000

The first term on the right-hand side estimates the magnitude of electron delocalization from ethylene molecule (B) to the methyltitanium complex (A) and the second term estimates that from A to B.

RESULTS AND DISCUSSION

Eigenvalues of PIOs for the ethylene coordinated state in the model systems, the representation of the PIO-1 and the PIO-2 with linear combination of canomical MO's and the representation of the PIO-1 and the PIO-2 with linear combination of the AO's of the component atoms are summarized in Tables 1, 2, and 3, respectively.

PIO Analysis on $[CH_3Ti]^{+3}/C_2H_4$ System

We obtained twelve PIOs, PIO-1 to PIO-12. Eigenvalues shown in Table 1

TABLE 2. LLCMO Representation of PIO-1 and PIO-2 of Methyltitanium Complexes

complex	PIO-1
(1)	$0.880\phi_{5}(\text{LUMO})+0.315\phi_{8}+0.329\phi_{9}+\cdots$
(2)	$-0.689\phi_{8}(\text{HOMO})-0.417\phi_{13}+0.287\phi_{10}(\text{LUMO+1})-0.265\phi_{5}+0.190\phi_{3}$
(3)	$-0.858\phi_{9}(\text{LUMO})+0.467\phi_{11}-0.108\phi_{1}-0.106\phi_{13}$
(4)	$-0.543\phi_{11}(\text{LUMO+1})-0.457\phi_{9}(\text{HOMO})-0.426\phi_{16}-0.331\phi_{8}-0.214\phi_{2}$
(5)	$0.663\phi_{13}(\text{LUMO+3})+0.508\phi_{11}(\text{LUMO+1})-0.519\phi_{14}+\cdots$
(6)	$-0.874\phi_{12}(\text{HOMO})-0.277\phi_{4}-0.173\phi_{3}-0.175\phi_{17}$
(7)	$0.931\phi_{13}(\text{LUMO})+0.313\phi_{14}+\cdots$
(8)	$-0.970\phi_{13}(\text{LUMO})-0.126\phi_{18}+\cdots$
(9)	$0.636\phi_{31}(\text{LUMO})-0.662\phi_{32}-0.192\phi_{35}-0.144\phi_{40}+0.143\phi_{29}+\cdots$
(10)	$-0.842\phi_{20}(\text{HOMO})-0.233\phi_{6}-0.222\phi_{24}-0.219\phi_{14}+0.174\phi_{5}+0.147\phi_{1}+\cdots$
(11)	$0.839\phi_{33}(\text{LUMO})-0.494\phi_{34}+0.119\phi_{46}-0.103\phi_{39}+\cdots$

complex	PIO-2
(1)	$-0.895\phi_{4}(\text{HOMO})-0.353\phi_{3}-0.237\phi_{1}+\cdots$
(2)	$0.578\phi_{8}(\text{HOMO})-0.529\phi_{13}+0.475\phi_{10}(\text{LUMO+1})-0.224\phi_{12}+\cdots$
(3)	$-0.826\phi_{8}(\text{HOMO})+0.399\phi_{4}+0.281\phi_{7}+\cdots$
(4)	$-0.761\phi_{9}(\text{HOMO})+0.441\phi_{11}(\text{LUMO+1})+0.315\phi_{16}+0.212\phi_{4}-0.196\phi_{7}+\cdots$
(5)	$0.942\phi_{9}(\text{HOMO})+0.222\phi_{5}-0.165\phi_{3}+\cdots$
(6)	$0.524\phi_{10}-0.476\phi_{17}-0.425\phi_{1}-0.351\phi_{13}(\text{LUMO})+0.276\phi_{22}+\cdots$
(7)	$-0.862\phi_{12}(\text{HOMO})+0.530\phi_{5}-0.221\phi_{3}+\cdots$
(8)	$-0.894\phi_{12}(\text{HOMO})-0.288\phi_{5}-0.220\phi_{3}+\cdots$
(9)	$-0.656\phi_{29}(\text{HOMO-1})+0.585\phi_{26}+0.218\phi_{31}(\text{LUMO})-0.204\phi_{14}+\cdots$
(10)	$-0.468\phi_{1}+0.384\phi_{14}-0.373\phi_{13}+0.369\phi_{24}-0.269\phi_{28}-0.265\phi_{16}-0.204\phi_{6}-0.203\phi_{20}(\text{HOMO})+\cdots$
(11)	$0.649\phi_{26}-0.592\phi_{31}(\text{HOMO-1})-0.201\phi_{27}+0.183\phi_{16}+0.114\phi_{29}-0.106\phi_{33}(\text{LUMO})+\cdots$

TABLE 3. LCAO Representation of PIO-1 and PIO-2 of Methyltitanium Complexes

complex	PIO-1
(1)	$-0.836\ \mathrm{Ti}d_{x^2-y^2} + 0.425\ \mathrm{Ti}d_{z^2} - 0.280\ \mathrm{Ti}4s + \cdots$
(2)	$-0.497\ \mathrm{Cl}_6p_x - 0.416\mathrm{Cm}p_x - 0.400\ \mathrm{Ti}d_{z^2} + 0.395\ \mathrm{Ti}d_{x^2-y^2} - 0.322\ \mathrm{Cl}_63s - 0.317\ \mathrm{Ti}d_{xz} + \cdots$
(3)	$0.823\ \mathrm{Ti}d_{x^2-y^2} - 0.474\ \mathrm{Ti}d_{z^2} + 0.230\ \mathrm{Ti}4s + \cdots$
(4)	$0.515\ \mathrm{Ti}d_{x^2-y^2} - 0.472\ \mathrm{C}_62s - 0.456\ \mathrm{Ti}d_{xz} - 0.429\ \mathrm{C}_6p_x - 0.311\ \mathrm{Ti}d_{z^2} + 0.212\ \mathrm{C}_6p_z + \cdots$
(5)	$-0.809\ \mathrm{Ti}d_{x^2-y^2} + 0.455\ \mathrm{Ti}d_{z^2} - 0.239\ \mathrm{Ti}4s - 0.213\ \mathrm{Cm}p_x + \cdots$
(6)	$0.527\ \mathrm{Cm}p_z - 0.520\ \mathrm{Cm}p_x + 0.258\ \mathrm{Cl}_7p_z - 0.250\ \mathrm{Ti}d_{z^2} + 0.226\ \mathrm{Ti}d_{xz} - 0.203\ \mathrm{Cl}_6p_x + \cdots$
(7)	$0.829\ \mathrm{Ti}d_{x^2-y^2} - 0.446\ \mathrm{Ti}d_{z^2} + 0.259\ \mathrm{Ti}4s + \cdots$
(8)	$-0.803\ \mathrm{Ti}d_{x^2-y^2} + 0.421\ \mathrm{Ti}d_{z^2} - 0.301\ \mathrm{Cl}_6p_x - 0.301\ \mathrm{Cl}_7p_x - 0.227\ \mathrm{Ti}4s + \cdots$
(9)	$-0.739\ \mathrm{Ti}d_{x^2-y^2} + 0.383\ \mathrm{Ti}d_{z^2} - 0.288\ \mathrm{C}_{18}p_y + 0.225\ \mathrm{Ti}d_{xz} + 0.212\ \mathrm{C}_7p_y + 0.206\ \mathrm{C}_{16}p_y + \cdots$
(10)	$0.517\ \mathrm{Cm}p_x - 0.500\ \mathrm{Cm}p_z + 0.282\ \mathrm{Cl}_7p_x + 0.250\ \mathrm{Ti}d_{z^2} - 0.237\ \mathrm{Cl}_9p_z + 0.223\ \mathrm{Ti}d_{xz} + 0.183\ \mathrm{Cl}_73s + \cdots$
(11)	$0.725\ \mathrm{Zr}4d_{x^2-y^2} + 0.380\ \mathrm{Zr}5s - 0.356\ \mathrm{Zr}4d_{z^2} + 0.304\ \mathrm{Zr}5px - 0.158\ \mathrm{Zr}4d_{xz} + \cdots$

complex	PIO-2
(1)	$-0.502\ \mathrm{Cm}p_x + 0.447\ \mathrm{Cm}p_z - 0.407\ \mathrm{Ti}d_{z^2} - 0.277\ \mathrm{Ti}d_{xz} + \cdots$
(2)	$0.709\ \mathrm{Ti}d_{x^2-y^2} - 0.408\ \mathrm{Cm}p_z + 0.370\ \mathrm{Cm}p_x - 0.294\ \mathrm{Cl}_63s - 0.281\ \mathrm{Cl}_6p_x + 0.218\ \mathrm{Cm}2s + \cdots$
(3)	$-0.548\ \mathrm{Cm}p_z + 0.437\ \mathrm{Cm}p_z - 0.330\ \mathrm{Cl}_6p_x - 0.262\ \mathrm{Cl}_6p_z + 0.238\ \mathrm{Ti}d_{xz} + 0.208\ \mathrm{Cm}2s + \cdots$
(4)	$-0.502\ \mathrm{Cm}p_x - 0.480\ \mathrm{Ti}d_{x^2-y^2} + 0.453\ \mathrm{Cm}p_z + 0.232\ \mathrm{H}_1s - 0.218\ \mathrm{Cm}2s - 0.190\ \mathrm{Ti}d_{z^2} + \cdots$
(5)	$0.568\ \mathrm{Cm}p_z - 0.421\ \mathrm{Cm}p_x - 0.281\ \mathrm{Ti}d_{xz} + 0.278\ \mathrm{C}_6p_z + 0.250\ \mathrm{C}_62s - 0.204\ \mathrm{Cm}2s + \cdots$
(6)	$-0.576\ \mathrm{Cl}_6p_x + 0.515\ \mathrm{Ti}d_{x^2-y^2} - 0.491\ \mathrm{Cl}_7p_x - 0.398\ \mathrm{Cl}_63s - 0.331\ \mathrm{Ti}d_{z^2} - 0.193\ \mathrm{Cm}p_z + \cdots$
(7)	$0.508\ \mathrm{Cm}p_x - 0.454\ \mathrm{Cm}p_z + 0.333\ \mathrm{Ti}d_2 - 0.247\ \mathrm{H}_1s + 0.199\ \mathrm{Cm}2s + \cdots$
(8)	$0.535\ \mathrm{Cm}p_x - 0.474\ \mathrm{Cm}p_z + 0.322\ \mathrm{Ti}d_{z^2} - 0.251\ \mathrm{H}_1s + 0.207\ \mathrm{Cm}2s + 0.184\ \mathrm{Ti}d_{xz} + \cdots$
(9)	$-0.558\ \mathrm{Cm}p_x + 0.476\ \mathrm{Cm}p_z - 0.266\ \mathrm{Ti}d_{x^2-y^2} + 0.221\ \mathrm{H}_1s - 0.190\ \mathrm{Cm}2s - 0.137\ \mathrm{Ti}d_{z^2} + \cdots$
(10)	$-0.499\ \mathrm{Cl}_7p_x - 0.496\ \mathrm{Cl}_9p_x + 0.353\ \mathrm{Ti}d_{x^2-y^2} - 0.325\ \mathrm{Cl}_73s - 0.277\ \mathrm{Cm}p_z - 0.226\ \mathrm{Ti}d_{z^2} + \cdots$
(11)	$-0.498\ \mathrm{Cm}p_x + 0.417\ \mathrm{Cm}p_z + 0.223\ \mathrm{H}_1s - 0.185\ \mathrm{Zr}5p_z - 0.175\ \mathrm{Cm}2s \pm 0.159\ \mathrm{C}_{10}, \mathrm{C}_{22}p_y - 0.153\ \mathrm{Zr}5d_{z^2} + \cdots$

tell us that PIO-1 and PIO-2 have much larger contribution to the insertion than the ten other orbital pairs. The representation of the PIO-1 and the PIO-2 with linear combination of canomical MO's are given in Equations 13 and 14 for the methyl titanium fragment, and in Equations 15 and 16 for ethylene molecule. $[CH_3Ti]^{+3}$;

$$\mathrm{PIO}-1:\phi_1' = 0.880\phi_5(\mathrm{LUMO}) + 0.315\phi_8 + 0.329\phi_9 + \cdots \tag{13}$$

$$\mathrm{PIO}-2:\phi_2' = -0.895\phi_4(\mathrm{HOMO}) - 0.533\phi_3 - 0.237\phi_1 + \cdots \tag{14}$$

C_2H_4 part;

$$\mathrm{PIO}-1:\psi_1' = 0.978\psi_6(\mathrm{HOMO}) + 0.195\psi_5 + \cdots \tag{15}$$

$$\mathrm{PIO}-2:\psi_2' = 0.747\psi_7(\mathrm{LUMO}) - 0.537\psi_2 + 0.328\psi_5 \cdots \tag{16}$$

Equations 13 ~ 16) are expanded in terms of the AOs of the component atoms as shown in Equations 17 ~ 20, respectively.

$[CH_3Ti]^3$ part;

$$\mathrm{PIO}-1:\phi_1' = -0.836\mathrm{Tid}_{x^2-y^2} + 0.425\mathrm{Tid}_{z^2} - 0.280\mathrm{Ti4s} + \cdots \tag{17}$$

$$\mathrm{PIO}-2:\phi_2' = -0.502\mathrm{Cmp}_x + 0.447\mathrm{Cmp}_z - 0.407\mathrm{Tid}_{z^2} - 0.227\mathrm{Tid}_{xz} + \cdots \tag{18}$$

$[C_2H_4]$ part;

$$\mathrm{PIO}-1:\psi_1' = 0.649\mathrm{C}_\alpha\mathrm{p}_x + 0.595\mathrm{C}_\beta\mathrm{p}_x + \cdots \tag{19}$$

$$\mathrm{PIO}-2:\psi_2' = -0.602\mathrm{C}_\alpha\mathrm{p}_x + 0.618\mathrm{C}_\beta\mathrm{p}_x + 0.283\mathrm{C}_\beta\mathrm{p}_z + \cdots \tag{20}$$

Contour maps of PIO-1 and PIO-2 of the methyltitanium/ethylene system are given in Figure 3(a). Scince electron density must accumulate in the regions between Cm and C_β and between Ti and C_α in order for two new bonds to be formed during the insertion procedure, it is preferable for ethylene insertion that PIOs overlap in-phase in these bond regions. We can see this in-phase overlap in Figure 3(a).

From these results, it is shown that electron delocalization from π orbital of the ethylene to unoccupied orbitals of the methyltitanium, which are mainly composed of $3d_{x}2-{}_{y}2$ and $3d_{z}2$ orbitals of the Ti atom, and electron delocalization from occupied orbitals of the methyltitanium, which are mainly composed of $2p_x$

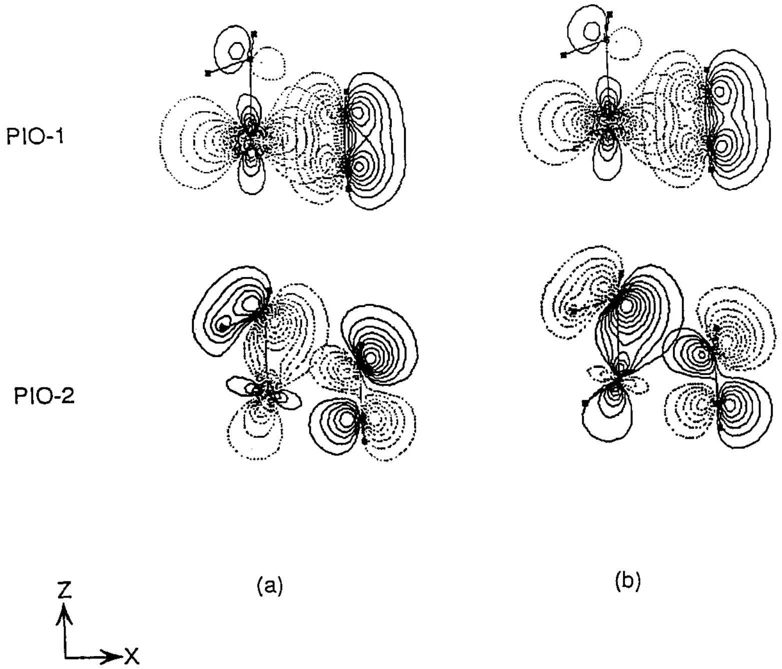

Figure 3. Contour maps of PIO-1 and PIO-2 of the ethylene coordinated state; (a) Complex (1) and (b) Complex (8).

and $2p_z$ orbitals of the methyl carbon atom and $3d_{z^2}$: orbitals of the Ti atom, to π^* orbital of the ethylene are essential for ethylene insertion.

A Ligand Effect

The electron delocalization takes place in the four center reaction plane. Therefore, it is suggested that ligands located in the reaction plane have a stronger effect on the electron delocalozation than other ligands located out of the reaction plane. A ligand effect on the electron delocalization is qualitatively understood by examining the contour maps of PIO-1 and PIO-2 of each model system shown in Figure 3(b) ~ Figure 5. Figure 4(a), PIO-1 of complex (2) which has a Cl anion *trans* to the incoming ethylene, shows strong out of phase overlap in the region between Cm and Cß and tells us that the electron delocalization is inconvenient. Figure 4(b) tells us that a Cl anion bans to the methyl group has little influence on the electron delocalozation. As shown in Figure 3(b) and in Figure 5(b), ligands located out of the reaction plane has little influence on the eloctron delocalization

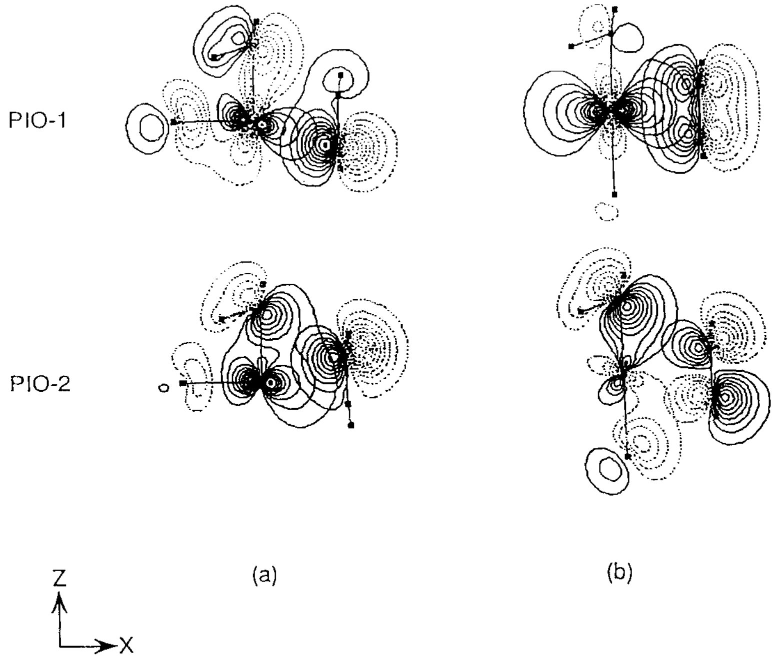

Figure 4. Contour maps of PIO-1 and PIO-2 of the ethylene coordinated state; (a) Complex (2) and (b) Complex (3).

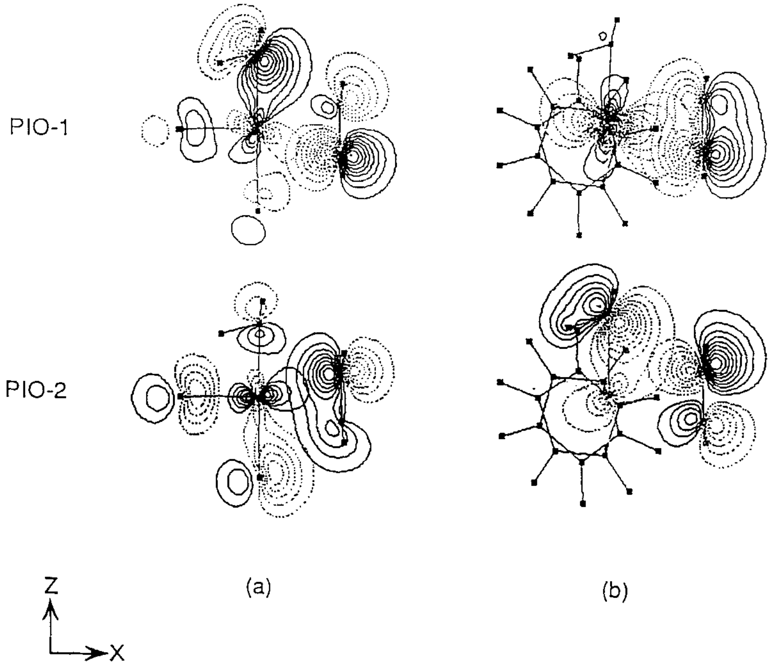

Figure 5. Contour maps of PIO-1 and PIO-2 of the ethylene coordinated state; (a) Complex (10) and Complex (9).

even in the case of the large C_p anion. From Figure 5(a), we can see that when a number of ligands increases, the electrophilicity of the methyltitanium complexes decreases.

Reactivity Index (RI) of the Model Systems

From the PIO analysis on the Complex(1)/ethylene system described above, it is deduced that the origin of electrophilicity of Complex (1) is mainly derived from $d_{x^2-y^2}$ and d_{z^2} orbitals of the Ti atom and that of nucleophilicity is mainly derived from p_x and p_z orbitals of the methyl carbon atom, and d_{z^2} and d_{xz} orbitals of the Ti atom. We determine a reference orbital δ_r as following Equations:

for unoc space of methyltitanium complexes,

$$(\delta_r)_{\mathrm{Aunoc}} = -0.8\mathrm{Tid}_{x^2-y^2} + 0.4\mathrm{Tid}_{z^2} \tag{21}$$

for oc space of methyltitanium complex,

$$(\delta_r)_{\mathrm{Aoc}} = -0.5\mathrm{Cmp}_x + 0.45\mathrm{Cmp}_z - 0.4\mathrm{Tid}_{z^2} - 0.3\mathrm{Tid}_{xz} \tag{22}$$

for oc space of the ethylene molecule,

$$(\delta_r)_{\mathrm{Boc}} = 0.65\mathrm{C}_\alpha\mathrm{p}_x + 0.6\mathrm{C}_\beta\mathrm{p}_x \tag{23}$$

for unoc space of the ethylene molecule,

$$(\delta_r)_{\mathrm{Bunoc}} = -0.6\mathrm{C}_\alpha\mathrm{p}_x + 0.6\mathrm{C}_\beta\mathrm{p}_x + 0.3\mathrm{C}_\beta\mathrm{p}_z \tag{24}$$

Nucleophilicity (λoc) and electrophilicity (λnuoc) of the methyltitanium complexes and the ethylene molecule, and reactivity index (RI) for the ethylene insertion are summarized in Table 4. The upper is a level of λnuoc, the weaker is an electrophilicity of a molecule, while the lower is a level of λoc, the weaker is a nucleophilicity of a molecule. The values of the λnuoc of Complexes (2, 4, 6, and 10) shows that a ligand located *trans* to the ethylene has a strong negative effect on the electrophilicity of them. Comparing the λunoc value of Complex (2) with that of Complex (4), and the λunoc value of Complex (3) with that of Complex (5), we can see that the smaller is an electronegativity of the ligand, the more favorable is the insertion. Kawamura-Kuribayashi *et al.* [1, 5] have reported the activation energies of the ethylene insertion in the Complex (8)/ethylene system and in the Complex

TABLE 4. Nucleophilicity (λ_{oc}) and Electrophilicty (λ_{unoc}) of Methyltitanium Complexes and Reactivity Index (RI) for Ethylene Insertion

complex	$\lambda_{Aunoc}(eV)$	$\lambda_{Aoc}(eV)$	RI
(1)	-10.40	-13.32	0.577
(2)	-5.90	-13.40	0.353
(3)	-9.94	-13.59	0.515
(4)	-6.65	-13.44	0.367
(5)	-10.09	-13.55	0.532
(6)	-4.90	-13.73	0.322
(7)	-8.58	-13.38	0.433
(8)	-9.00	-13.38	0.455
(9)	-6.94	-13.47	0.372
(10)	-0.23	-13.84	0.274
(11)	-9.11	-13.59	0.452
ethylene	-8.76	-13.19	

(11)/ethylene system with RMP2 level of *ab initio* calculation, 5.8Kcal/mol and 6.0Kcal/mol, respectively. RI of these systems, 0.455 and 0.452, respectively shows good correlation with the activation energies. According to the value of λoc and λunoc or RI we can quantitatively estimate a ligand effect on the ethylene insertion.

CONCLUSION

The ethylene insertion takes place in a four center reaction plane composed of the Ti atom, the carbon atom of the methyl group, and C_α and C_β of the ethylene molecule. PIO analysis clarified that two orbital interactions, between the unoccupied Ti d(tg) orbitals of methyltitanium complexes and the π orbital of the ethylene, and between the occupied Cm p orbitals, Ti d_{z^2}, d_{xz} orbitals of the

TABLE 5. Bond Lengths and Bond Angles of the Models

Bond lengths(Å)		Bond angle(dgrees)		
Ti-Cm	2.03	∠CmTiCl	in Complex(2),(7)	90.0
Zr-Cm	2.28		in complex(3)	180.0
Ti-Cl	2.22		in complex(8)	105.3
Ti-C	2.20	∠ClTiCl	in complex(6),(10)	90.0
Ti-C_α	2.51		in complex(8)	123.6
Ti-C_p	2.22	∠C_pTiC_p		123.6
Zr-C_p	2.23	∠C_pZrC_p		122.4
Zr-Si	3.42	∠CmTiC_p		105.3
C_α-C_β	1.35	∠CmZrC_p		110.6
C-C(C_p)	1.43	∠CmZrSi		136.8
C-H_1	1.10	∠CmTiC_α		104.8
C-H	1.09	∠Ti$C_\alpha C_\beta$		74.4
C-H(C_P)	1.08	∠TiCmH(1)		74.7
Si-H	1.42	∠*(1)CmH(1)		120.0
Si-C	1.88	∠*(2)$C_\alpha C_\beta$		173.4
		∠*(3)$C_\alpha C_\beta$		173.4
		∠HC_αH		120.0
		∠HC_βH		120.0
		∠HSiH		114.7

complexes and the π* orbital of the ethylene, are essential for the insertion. Ligands are indispensable in order to guide ethylene molecule into the right place for the insertion, however it is unavoidable that the insertion is weakened by the ligands because of the mixing between the ligands orbitals and the Ti d orbitals and Cm p

TABLE 6. Extended Hückel Parameters

Orbital	Hii(ev)	$\zeta 1$	$\zeta 2$	$C1$	$C2$
H1s	-13.60	1.30			
C2s	-21.40	1.625			
C2p	-11.40	1.625			
O2s	-32.30	2.275			
O2p	-14.80	2.275			
Cl3s	-30.00	2.033			
Cl3p	-15.00	2.033			
Si3s	-17.30	1.383			
Si3p	-9.20	1.383			
Si3d	-6.00	1.383			
Ti4s	-8.97	1.075			
Ti4p	-5.44	0.675			
Ti4d	-10.81	4.553	1.40	0.4206	0.7839
Zr5s	-9.87	1.817			
Zr5p	-6.76	1.776			
Zr4d	-11.18	3.835	1.505	0.6211	0.5796

orbitals of the complexes. A ligand placed *trans* to the incoming ethylene has a strong negative effect on the insertion. Ligands placed out of the reaction plane do not have a large effect on the insertion. The ligand effects on these two orbital interactions are quantitatively estimated and the reactivities of the ethylene insertion into the Ti-methyl bond is predicted by the local electro-and nucleophilicity of the complexes proposed Fujimoto *et al.* [4] The reactivities of ethylene insertion in these model complexes are predicted as a following order:

Complex (1) > (5) > (3) > (8) > (11) > (7) > (9) > (4) > (2) > (6) > (10).

APPENDIX

Geometric parameters of the models are given in Table 5. Coulomb integrals and orbital exponents are listed in Table 6.

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