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A theoretical study of the insertion of olefins into Ti–methyl bonds by "Paired Interacting Orbitals"

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Abstract

Insertion of ethylene into the methyl–Ti bond of ($[CH_3Ti(Cl)_4/C_2H_4]^n$, $n = -1$ or -3) Oh-d^0, -d^2 and $[CH_3Ti(Cl)_2/C_2H_4]^n$, $n = +1$ or -1) Td-d^0, -d^2 methyltitanium complexes has been studied by applying Paired Interacting Orbitals (PIO). It is important for the insertion that the PIOs are in-phase between the methyl carbon and the ethylene C_β, and between the Ti and the ethylene C_α. This condition is satisfied in d^0 complexes. In d^2 complexes the orbital pair in the PIO-1, which consists mainly of the occupied Ti d_{xz} and the unoccupied ethylene π^* MO, overlap out-of-phase between the methyl carbon and the ethylene C_β. We can predict that, whereas the ethylene insertion is facile in d^0 methyltitanium complexes, it is not in d^2 complexes.

Introduction

More than thirty years have passed since the discovery of Ziegler polymerization of olefins. Although a number of studies on polymerization mechanisms have appeared, the Cossee mechanism [1] is widely accepted as the most plausible even if it is qualitative.

Novaro et al. [2] first studied the ethylene insertion process in the Cossee mechanism by means of ab initio restricted Hartree–Fock calculations. By optimizing the relative positions of the ethylene and the methyl group, they discovered the concerted motion that had been proposed by Armstrong et al. [3]. They estimated the activation energy to be the order of 15 kcal/mole. Insertion of olefins into transition metal–alkyl bonds was shown to be a key step in the Cossee mechanism. A few years ago, Fujimoto et al. [4] proposed a method for determining unequivocally the orbitals which should play dominant roles in interactions between the two systems. The interaction was best represented as a few pairs of localized orbitals. In each orbital pair, one orbital belongs to one fragment species and the other orbital to the other fragment species. They called these orbitals "paired interacting orbitals" (PIO). They used the method to study the insertion of ethylene into the Ti–C bond in methyltitanium dichloride [5]. They used an ab initio calculation to obtain the canonical molecular orbitals. We found that this approach was very useful for analyzing the extended Hueckel calculations [6], as it is difficult to carry out ab initio calculations for large molecular systems.

Thus, this method can be useful as a conventional way to gaining insight into reaction mechanisms without invoking time-consuming calculations. In this paper we report an analysis of ethylene insertion into the Ti–C bond in methyltitanium chlorides.

Method

The models employed here are Oh-type $[CH_3Ti(Cl)_4/C_2H_4]^n$ (where n is -1 or -3) and Td-type $[CH_3Ti(Cl)_2/C_2H_4]^n$ (where n is $+1$ or -1).

We examined the ethylene-coordinated state and the transition state, on the basis of the Cossee insertion mechanism. The model complexes are shown in Fig. 1.

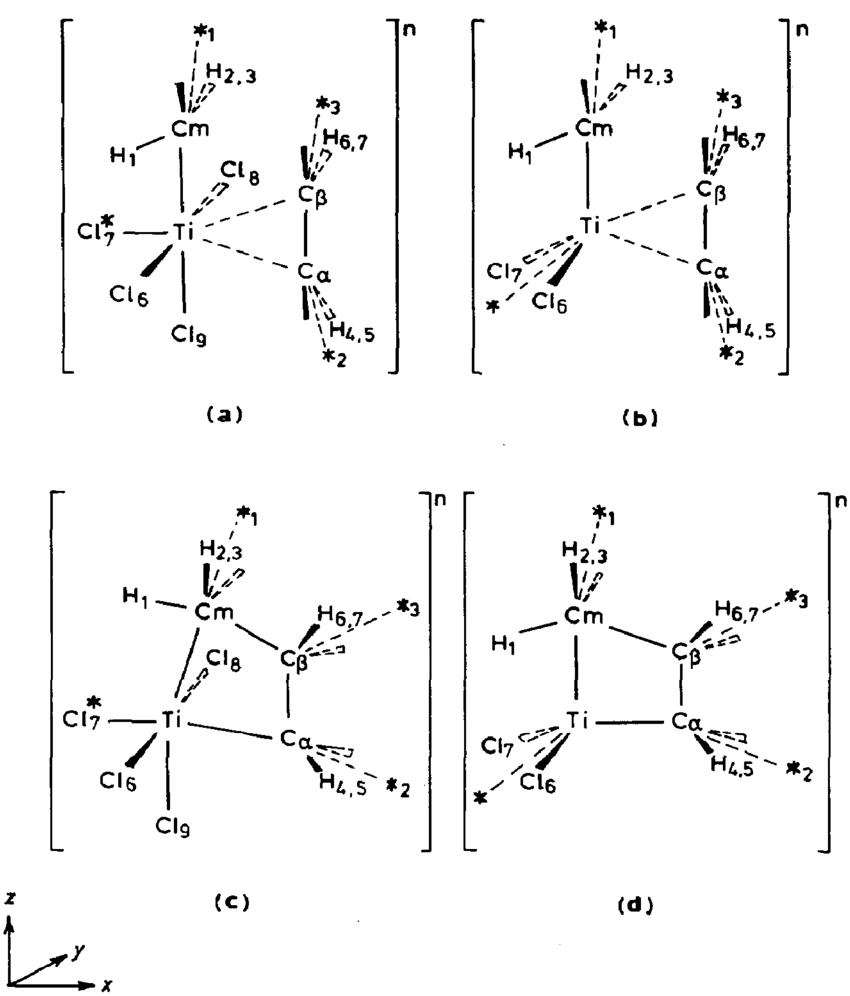
The geometry optimization technique was not adopted for determining the ethylene-coordinated state. We assumed their structures. The structure of the transition state of the Oh-type complex was determined by means of ab initio, restricted Hartree–Fock calculations [7]. We employed STO-3G basis functions for all atoms. The structure of the transition state of the Td-type complex has been previously reported by Fujimoto et al. [5]. Details of the geometry of the reaction models are given in the Appendix.

We divided a model complex into a methyltitanium chloride part (fragment **A**) and an ethylene molecule (fragment **B**). The geometries of [**A**] and [**B**] were the same as those in the original complex ([**A**–**B**] ≡ [**C**]). Molecular orbitals of [**A**], [**B**] and [**C**] were calculate by the extended Hueckel method [8]. The extended Hueckel parameters are given in the Appendix. PIOs were obtained by use of the procedure that was proposed by Fujimoto et al. [4]. All the calculations were carried out on an ACACS system with NEAC ACOS 430 [9].

Results and discussion

We obtained twelve PIOs (PIO-1–PIO-12). Of these, we consider two, PIO-1 and PIO-2 which have much larger contributions to the interaction than the other ten orbital pairs. This corresponds with the fact that two bonds, Ti–C_α and C_m–C_β, are formed in the transition state.

An ethylene-coordinated state is formed before the transition state. If the coordinated state is too stable the reaction cannot proceed to the transition state. Since electron density has to be accumulated in the region of the Ti–C_α and C_m–C_β bonds in the transition state, it is preferable that the PIOs are already in in-phase overlap in these bond regions in the ethylene-coordinated state. This, and the interactions at the transition state, should be useful for estimation of the activation barrier and which catalytic systems are favorable.



(a) (b)

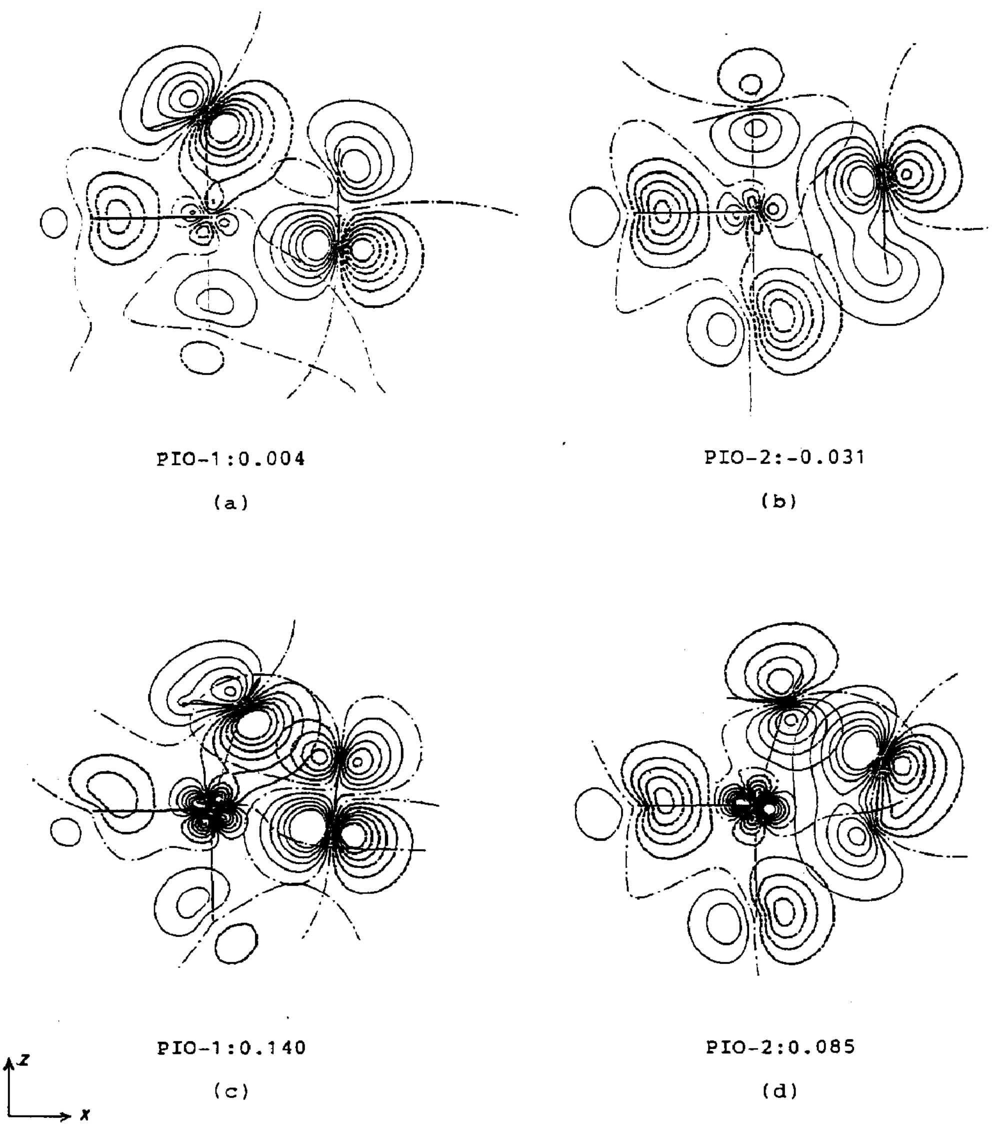
(c) (d)

Fig. 1. An illustration of models: (a) ethylene coordinated state of Oh-type complexes, (b) ethylene coordinated state of Td-type complexes, (c) transition state of Oh-type complexes, (d) transition state of Td-type complexes.

Oh-type $[CH_3Ti(Cl)_4/C_2H_4]$

(a) d^0 *complex.* Contour maps of PIO-1 and PIO-2 of the ethylene-coordinated state and the transition state and their overlap populations are given in Fig. 2.

As shown in Table 1, the components of PIO-1 of the methyltitanium chloride complex (fragment A) are the Ti *d* orbitals and the methyl C_m *p* orbitals, and those of the paired orbital of the ethylene part are the C_α,C_β *p* orbitals and the H(6), H(7) 1*s* orbitals. The orbital pair in PIO-1 shows in-phase overlap between the titanium and the ethylene C_α. Though the PIO-1 is also in-phase in the region between the methyl C_m and the ethylene C_β, an out-of-phase interaction is observed between the methyl C_m and the ethylene hydrogens. This antibonding interaction causes a decrease in the overlap populations of the PIO-1. As the CH bonds in ethylene bend more strongly with the slipping of ethylene into the transition state geometry, this antibonding interaction is expected to become weakened. Actually, the repulsive interaction disappears in the PIO-1 of the transition state.



PIO-1 :0.004

(a)

PIO-2:-0.031

(b)

PIO-1 :0.140

(c)

PIO-2:0.085

(d)

Fig. 2. Contour maps and overlap populations of PIO-1 and PIO-2 of the ethylene coordinated state [(a),(b)] and the transition state [(c),(d)] in Oh-d^0 complex.

The PIO-2 is composed of the occupied orbitals of the ethylene and the unoccupied Ti d_{xz}, the methyl C_m p_z and the occupied Cl(9) p orbitals. Overlap repulsion is found between Cl(9) and the ethylene C_α, H(4) and H(5), and as the insertion progresses, this repulsion is reduced; as is demonstrated in the PIO-2 of the transition state.

Clearly the interaction is in-phase between Ti and C_α and between C_m and C_β, in the PIO-1 and PIO-2 at the transition state and thus the insertion will be facilitated.

(b) d^2 complex. Figure 3 shows contour maps and overlap populations of PIO-1 and PIO-2 of the ethylene-coordinated state and the transition state.

Components of the PIO-1 of the ethylene-coordinated state are mainly the occupied Ti d_{xz} orbital and the unoccupied ethylene π^* MO. The PIO-1 has a large

Table 1

Main components (%) of PIO-1 and PIO-2 of Oh-type models

Model	PIO-1		PIO-2	
	fragment A	fragment B	fragment A	fragment B
Oh-d^0 complex ethylene coordinated state	Ti(d_{z^2},d_{xz}): 16.5 C_m(p_x,p_z): 63.0 Cl(7)(s,p_x): 9.7 Cl(9)(p_z): 4.0	C_α(p_x): 65.2 C_β(s,p_x,p_z): 11.1 H(6,7): 11.6	Ti($d_{x^2-y^2},d_{z^2},d_{xz}$): 16.7 C_m(p_z): 7.2 Cl(7)(s,p_x): 24.4 Cl(9)(s,p_x): 38.2	C_α(s): 15.4 C_β(p_x): 55.0 H(4,5): 14.5
transition state	Ti(d_{z^2},d_{xz}): 32.5 C_m(p_x,p_z): 54.0 Cl(7)(p_x): 4.8	C_α(p_x): 62.5 C_β(p_x): 18.2 H(6,7): 9.1	Ti($d_{x^2-y^2},d_{z^2}$): 21.3 C_m(p_x,p_z): 19.5 Cl(7)(s,p_x): 18.6 Cl(9)(s,p_x,p_z): 20.3	C_α(s,p_x,p_z): 22.8 C_β(s,p_x): 63.4 H(4,5): 6.3
Oh-d^2 complex ethylene coordinated state	Ti(d_{xz}): 80.7 C_m(p_x): 5.4 Cl(7)(p_z): 5.5 Cl(9)(p_x): 6.7	C_α(p_x): 49.5 C_β(p_x): 50.1	Ti($s,d_{x^2-y^2},d_{z^2}$): 20.2 C_m(p_x): 8.3 Cl(7)(s,p_x): 34.5 Cl(9)(s,p_x): 18.1	C_α(s,p_x): 36.6 C_β(s,p_x): 35.0 H(4,5): 8.0 H(6,7): 6.2
transition state	same as the value of Oh-d^0 complex [a]			

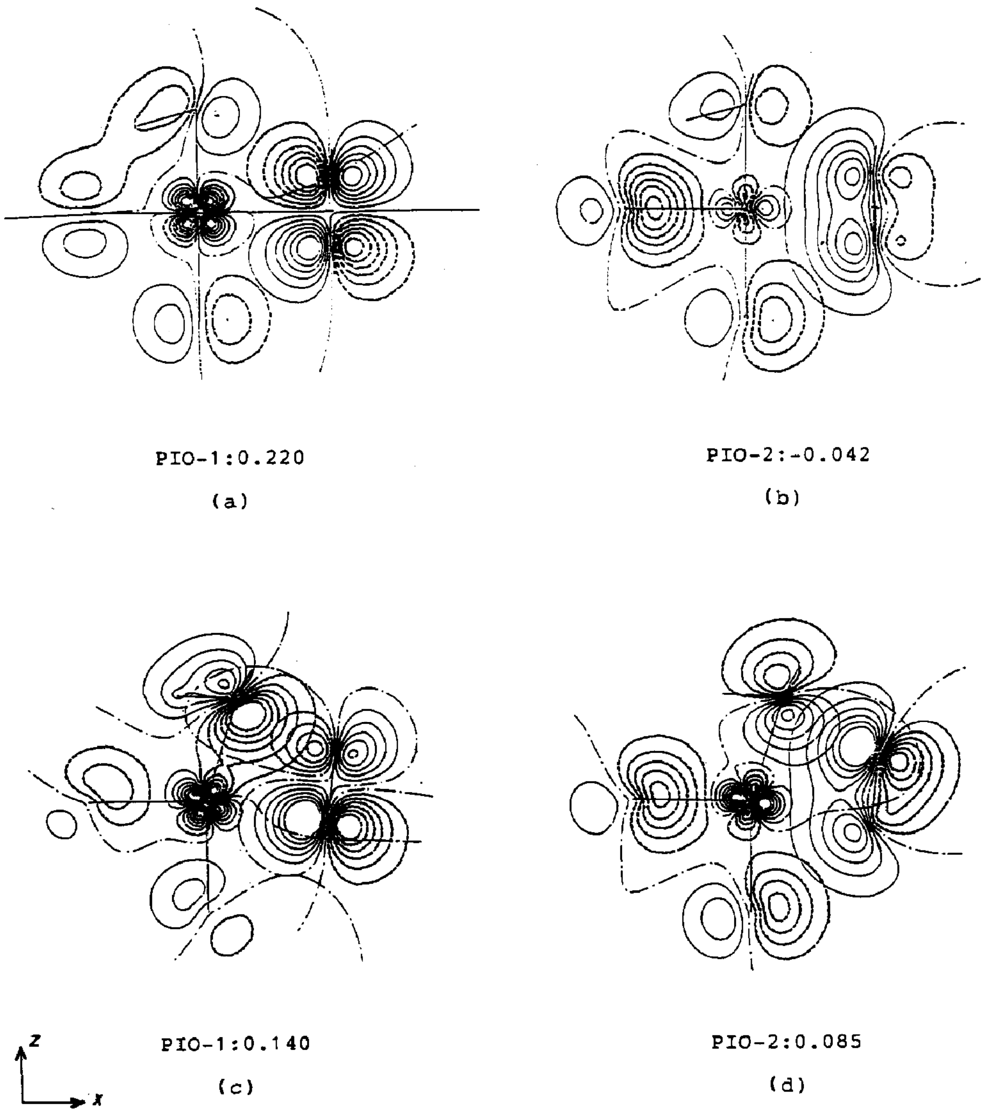
[a] The HOMO of the d^2-complex is composed of the Ti d_{xy} and d_{yz} orbitals in the transition state and hence the PIO-1 and PIO-2 are the same for d^0 and d^2 complexes. The d^2-complexes have the PIO-5 and -7 which show slightly stronger repulsive interactions than those in the d^0 complex in the transition state structure.

overlap population which suggests a significant stabilization of the complex in the ethylene-coordinated state. The contribution of the HOMO to the PIO-1 is large in the ethylene-coordinated state, whereas in the transition state, the HOMO is composed of the Ti d_{xy} and d_{yz} orbitals and hence it does not contribute to the

Table 2

Main components (%) of PIO-1 and PIO-2 of Td-type models

Model	PIO-1		PIO-2	
	fragment A	fragment B	fragment A	fragment B
Td-d^0 complex ethylene coordinated state	Ti($d_{x^2-y^2},d_{z^2}$): 77.8 C_m(p_x): 3.2 Cl(6,7)(p_x): 9.1	C_α(p_x): 57.6 C_β(p_x): 41.8	Ti(d_{z^2},d_{xz}): 20.5 C_m(p_x,p_z): 68.5 H(1): 6.6	C_α(p_x): 22.6 C_β(p_x,p_z): 46.9 H(6,7): 14.0
transition state	Ti($d_{x^2-y^2},d_{z^2}$): 80.9 C_m(s,p_x): 4.2 Cl(6,7)(p_x): 3.7	C_α(p_x): 84.4 C_β(p_x): 3.9 H(6,7): 4.0	Ti($d_{x^2-y^2},d_{xz}$): 23.4 C_m(p_x,p_z): 67.2 H(1): 6.3	C_α(p_z): 5.0 C_β(p_x): 71.6 H(6,7): 8.1
Td-d^2 complex ethylene coordinated state	Ti(d_{xz}): 89.2 C_m(p_x): 4.0	C_α(p_x): 47.2 C_β(p_x): 50.3	Ti($d_{x^2-y^2},d_{z^2}$): 76.6 C_m(p_x): 4.4 Cl(6,7)(p_x): 9.0	C_α(p_x): 50.7 C_β(p_x): 48.8
transition state	Ti($d_{x^2-y^2},d_{z^2},d_{xz}$): 91.8 C_m(s,p_z): 5.2	C_α(p_x): 49.4 C_β(p_x): 28.0 H(4,5): 8.9 H(6,7): 3.2	Ti($d_{x^2-y^2},d_{z^2},d_{xz}$): 80.5 C_m(p_z): 2.5 H(2,3): 4.0 Cl(6,7)(p_x): 4.6	C_α(p_x): 42.5 C_β(p_x): 56.8



PIO-1:0.220
(a)

PIO-2:-0.042
(b)

PIO-1:0.140
(c)

PIO-2:0.085
(d)

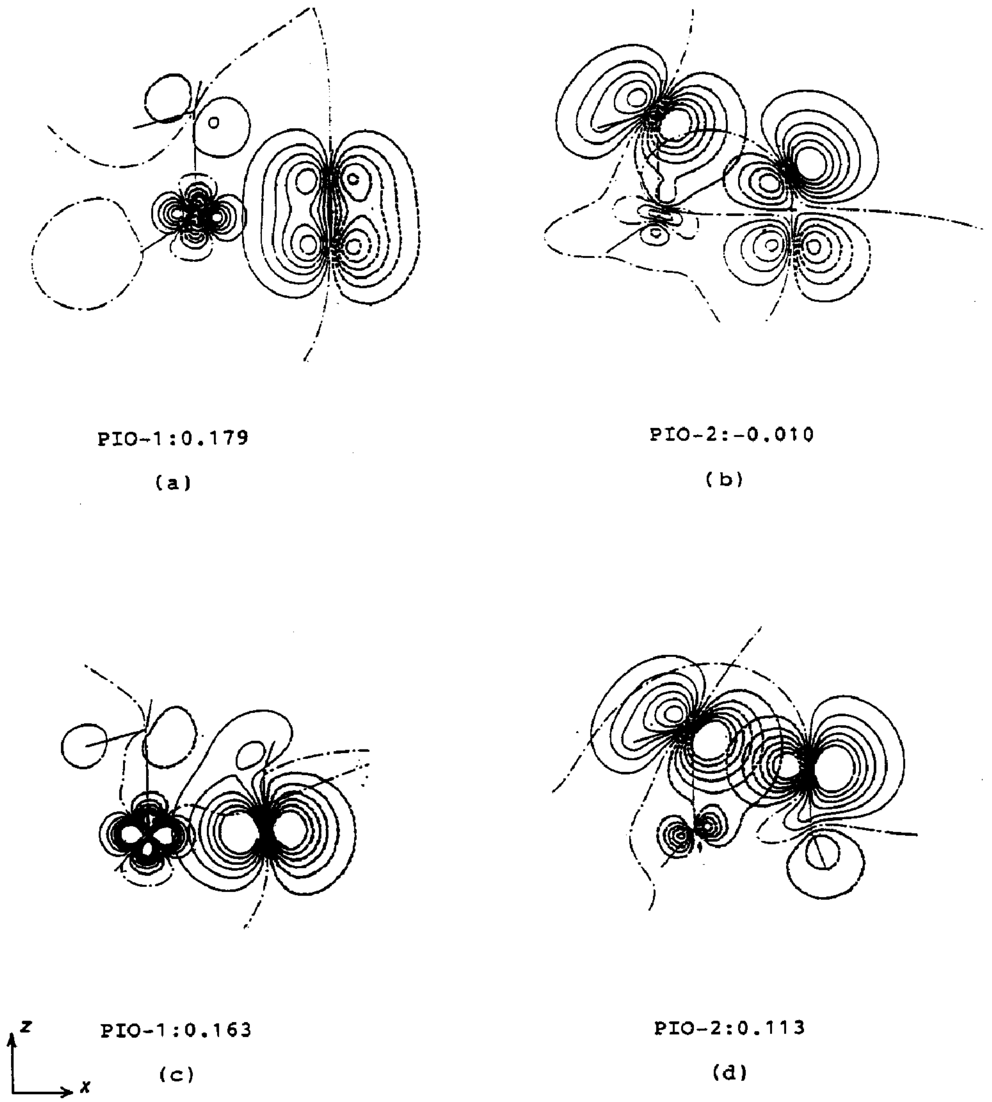
Fig. 3. Contour maps and overlap populations of PIO-1 and PIO-2 of the ethylene coordinated state [(a),(b)] and the transition state [(c),(d)] in Oh-d^2 complex.

PIO-1 by symmetry. The ethylene-coordinated state of the Oh-type d^2 complex is suggested to be stabilized much more strongly than that of the d^0 complex.

The methyl C_m component is very small in PIO-1 (see Table 1) and interacts out-of-phase with the ethylene C_β orbitals. The PIO-2 is also out-of-phase in this bond region. It is obvious that these out-of-phase interactions are not favorable for the insertion reaction. Thus, we predict that the ethylene insertion should not be facile in the Oh-type d^2 complex.

Td-type [$CH_3Ti(Cl)_2/C_2H_4$]

(a) d^0 complex. Contour maps and overlap populations of PIO-1 and PIO-2 are shown in Fig. 4.



PIO-1 :0.179

(a)

PIO-2:-0.010

(b)

PIO-1 :0.163

(c)

PIO-2:0.113

(d)

Fig. 4. Contour maps and overlap populations of PIO-1 and PIO-2 of the ethylene coordinated state [(a),(b)] and the transition state [(c),(d)] in Td-d^0 complex.

The PIO-1 of the ethylene-coordinated state is made of the occupied MO's of the ethylene fragment and the unoccupied Ti *d* orbitals. The PIO-1 is in-phase in the region between Ti and C_α and between C_m and C_β. The PIO-2 is also in-phase in these bond regions. Though an antibonding interaction appears between the methyl C_m and the ethylene hydrogens as shown in Figure 4(b), it is weakened at the transition state owing to the bending of the ethylene hydrogens (Figure 4(d)).

The PIO-1 and PIO-2, both of which are localized well between the titanium and the ethylene C_α and between the methyl C_m and the ethylene C_β respectively at the transition state, overlap in-phase in the region of bonds to be formed and, thus insertion is favored in this Td-type d^0 complex.

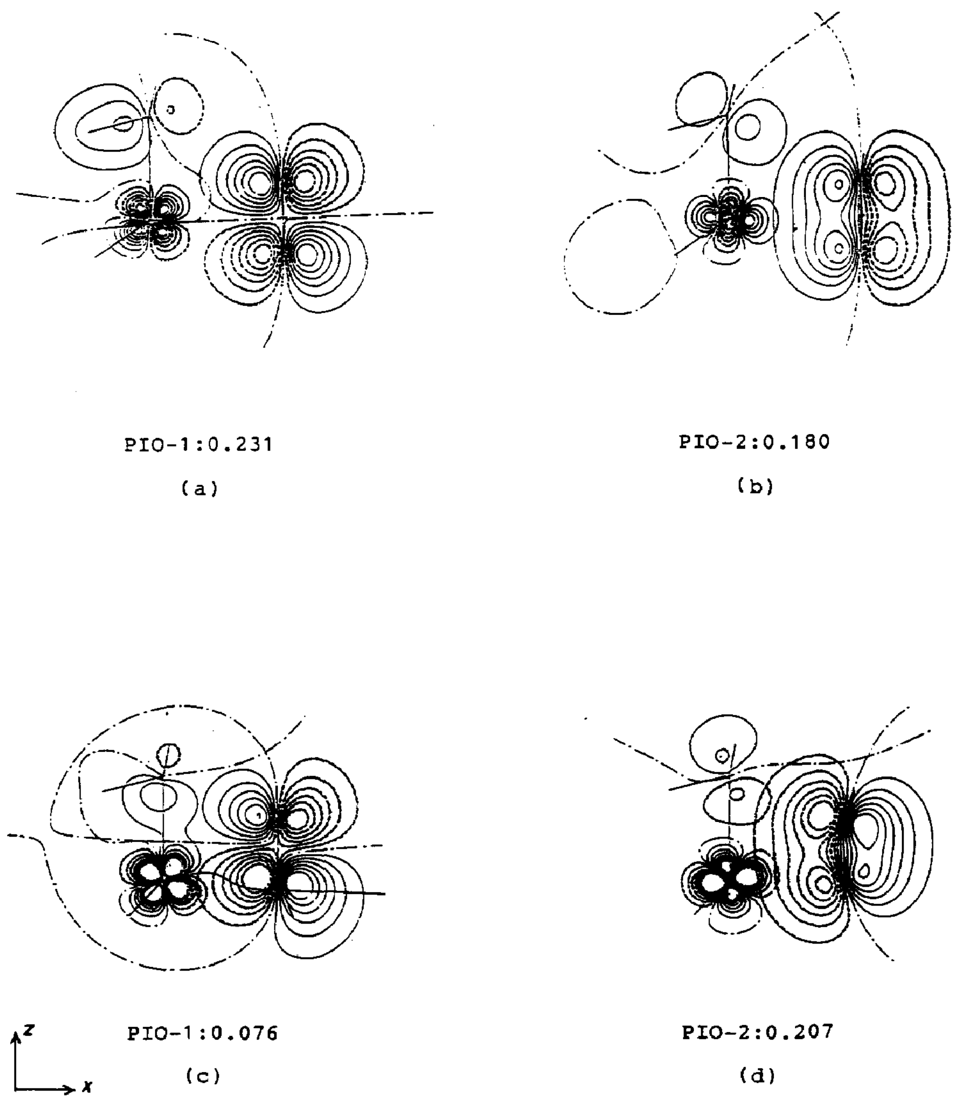


Fig. 5. Contour maps and overlap populations of PIO-1 and PIO-2 of the ethylene coordinated state [(a),(b)] and the transition state [(c(,(d)] in Td-d^2 complex.

(b) d^2 complex. Figure 5 shows contour maps and overlap populations of PIO-1 and PIO-2. The PIO-1 of the ethylene-coordinated state shows that two electrons fill the titanium d_{xz} orbital which interacts strongly with the ethylene unoccupied π^* MO. The overlap population of the PIO-1 is large and it shows that the complex is strongly stabilized. In the transition state, as shown in Table 2, the PIO-1 is composed of not only Ti d_{xz} and the ethylene π^*, but also of the Ti $d_{x^2-y^2}$, d_{z^2} and the hydrogen orbitals of ethylene. Some of these atomic orbitals overlap in-phase, but some overlap out-of-phase and therefore, the overlap population is smaller than that of the ethylene-coordinated state. The transition state of the d^2 complex is suggested to be not as well stabilized as that of the d^0 complex. It is predicted that the ethylene insertion would not be facile in the Td-type d^2 complex.

Table 3

Hueckel total energy (eV) of the ethylene-coordinated state and the transition state in various models and their differences

Model	Ethylene coordinated state	Transition state	ΔE
Oh-d^0 complex	-960.466	-960.686	-0.22
Oh-d^2 complex	-978.440	-976.308	$+2.13$
Td-d^0 complex	-660.611	-659.348	$+1.26$
Td-d^2 complex	-680.287	-677.085	$+3.20$

Finally, we can mention the energy of these models. The Hueckel energy of the ethylene-coordinated state and the transition state of the models employed in the present study are given in Table 3. One can see that the energy difference between the two states is large in d^2 complexes, in agreement with the discussion given above.

Conclusion

For the insertion of ethylene into the methyl–titanium bond it is important that delocalization of electrons occurs effectively from the occupied MO's of the ethylene to the unoccupied MO's of the methyltitanium complex, and from the occupied MO's of the methyltitanium complex to the unoccupied MO's of the ethylene. The PIOs which represent these interactions should be in-phase between the methyl C_m and the ethylene C_β and between the titanium and the ethylene C_α to favor the four-centered transition state.

The more stable is the transition state, the more facile is the insertion. On the other hand it is important for the facile insertion via four-centered transition state, that the ethylene-coordinated state which appears prior to the transition state on the reaction coordinate, is stabilized moderately. If it is stabilized too strongly, the activation energy of the insertion would become very large.

These conditions are fulfilled in the case of d^0 methyltitanium complexes. In d^2 complexes, on the other hand, two electrons occupy the Ti d_{xz} orbital in the ethylene-coordinated state which interacts strongly with the unoccupied ethylene π^* orbital. The π-complex is too strongly stabilized and can not readily decompose to give the addition product through the four-centered transition state. Ethylene insertion into the methyl–titanium bond is difficult in the d^2 complexes.

In the case of the d^1 complexes, the insertion will not be as facile as in the case of d^0 complexes, but is easier than in the case of d^2 complexes.

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Appendix

Geometrical parameters of the models are given in Table 4. Coulomb integrals and orbital exponents are listed on Table 5.

Table 4

Bond lengths (Å) and bond angles (°) of models

	Ethylene-coordinated state		Transition state	
	Oh-complex	Td-complex	Oh-complex	Td-complex
Bond length (Å)				
Ti–C_m	2.03	2.03	2.10	2.03
Ti–Cl	2.16	2.16	2.16	2.16
Ti–C_α	2.51	2.51	2.24	2.11
C_α–C_β	1.35	1.35	1.37	1.41
C_m–C_β	2.75	2.75	2.10	2.22
C–H(1)	1.19	1.10	1.10	1.13
C–H	1.10	1.10	1.08	1.09
Bond angle (°)				
∠ClTiCl	90	109.5	90.0	129.1
∠C_mTiCl*	90	109.5	105.7	138.5
∠C_mTiC_α	105.6	105.6	85.6	92.9
∠Ti$C_\alpha C_\beta$	74.4	74.4	85.3	87.0
∠Ti$C_m C_\beta$	52.6	52.6	74.1	71.0
∠TiC_mH(1)	74.7	74.7	77.6	74.7
∠*(1)C_mH(1)	120	120	105.0	118.0
∠HC_mH	109.5	109.5	107.8	111.8
∠*(2)$C_\alpha C_\beta$	173.4	173.4	150.8	151.0
∠*(3)$C_\beta C_\alpha$	173.4	173.4	164.1	162.4
∠HC_αH	120	120	116.0	116.2
∠HC_βH	120	120	115.2	116.6

Table 5

Extended Hueckel parameters

Orbital	*H*ii(ev)	ζ1	ζ2	*C*1	*C*2
H 1*s*	−13.6	1.30			
C 2*s*	−21.4	1.625			
C 2*p*	−11.4	1.625			
Cl 3*s*	−30.0	2.033			
Cl 3*p*	−15.0	2.033			
Ti 4*s*	−8.97	1.075			
Ti 4*p*	−5.44	0.675			
Ti 3*d*	−10.81	4.55	1.40	0.4206	0.7839

* Contraction coefficients in the double-ζ expansion.

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