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Theoretical study on the structure of methyltitanium complexes: analysis by Paired Interacting Orbitals (PIO)

Akinobu Shiga*, **Junpei Kojima, Toshio Sasaki**
Chiba Research Laboratory, Sumitomo Chemical Co., Ltd., 5-1. Anesakikaigan, Ichihara 299-01 (Japan)

and Yasuo Kikuzono
Computer Center, Sumitomo Chemical Co., Ltd., 1-2-2, Nishimachi, Shinsenri, Toyonaka 565 (Japan)

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Abstract

The origin of the formation of a CH → Ti bond in a methyltitanium complex was studied by use of Paired Interacting Orbitals (PIO). Methyl group tilt is favoured when there is a ligand *trans* to the methyl. An electron-donating ligand axial to the tilting plane causes methyl to tilt into an agostic position. This methyl group tilt in the opposite direction is not favoured because of the overlap repulsion between the ligand orbital and orbitals of the methyl group. The PIO technique elucidates the properties such as structure, reactivity and stability of transition metal complexes.

Introduction

Many studies have been carried out recently on compounds having CH → M bonds. The formation of a CH → M bond is related to the formation of a metalcarbenoid which facilitates many catalytic reactions, such as olefin metathesis, olefin polymerization, cyclopropanation, and Fischer–Tropsch synthesis [1].

An X-ray diffraction study of [Ti(dmpe)(CH_3)(Cl)$_3$] revealed the presence of a CH → Ti bond [2]. They suggested that a deficiency of *d* electrons would be necessary for the formation of such a bond. The CH → Ti bond was around to be present in certain titanium complexes by use of the geometry optimization technique in ab initio calculations [3]. The conditions necessary for the formation of a CH → Ti bond were determined on the basis of fragment analysis [4].

A few years ago Fujimoto et al. [5] proposed a method for unequivocally determining which orbitals should play dominant roles in interactions between the systems **A** and **B**. They called the orbitals Paired Interacting Orbitals (PIO) and showed the usefulness of the PIO method to analyze the action of catalysts [6,7]. In

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this paper, the reason why there is a CH → Ti bond in methyltitanium complexes is studied by application of the PIO method.

Experimental

Octahedral (Oh) and tetrahedral (Td) models of complexes are as shown in Fig. 1. All angles at the center titanium atom are 90° in the octahedron and 109.5° in the tetrahedron. The tilting angle (α) of the methyl group is chosen to be tentatively 50, 109.5 and 170°. Bond lengths are given in the Appendix.

We divided a methyltitanium complex into a methyl group (fragment **B**) and a residual part (fragment **A**). 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 calculated by use of the extended Hückel method [8]. The extended Hückel parameters given in the Appendix are the same as those used by Eisenstein et al. [4]. Weighted H_{ij}'s were used. PIOs were obtained by use of the method by Fujimoto et al. [5]. All calculations were carried out by an ACACS system with NEAC ACOS 430 [9].

Results and discussion

Oh-[$CH_3Ti(H)_5$] and Td-[$CH_3Ti(H)_3$]

Figure 2 shows that whereas in the case of the Oh complex, the total energy is lowered when the methyl group is tilted, in the case of the Td complex it is not.

The overlap population of the PIO-1 is shown in Table 1. When the methyl group is tilted, the overlap population of the PIO-1 increases for the Oh complex, but decreases slightly for the Td complex. Let us first examine model **1**.

The representation of the PIO-1 in terms of the canonical MOs in model **1** is given in Fig. 3.

The constituent atomic orbitals of PIO-1 are listed in Table 2.

When the methyl group is not tilted, the PIO-1 of the fragment **A** is mainly composed of the canonical MOs ϕ_9 and ϕ_{12} both of which are unoccupied. They consist of the Ti d_{z^2} orbital, and the 1*s* orbital of the hydrogen located *trans* to the

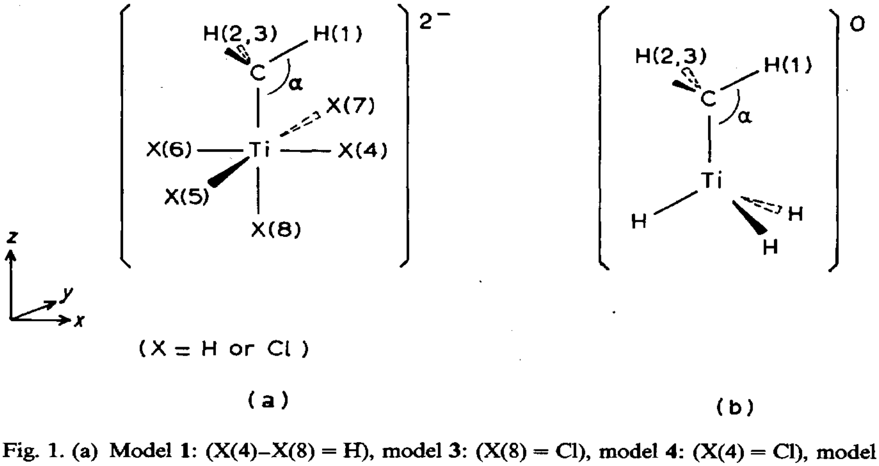


Fig. 1. (a) Model **1**: (X(4)–X(8) = H), model **3**: (X(8) = Cl), model **4**: (X(4) = Cl), model **5**: (X(5) = Cl), model **6**: (X(6) = Cl). (b) Model **2**.

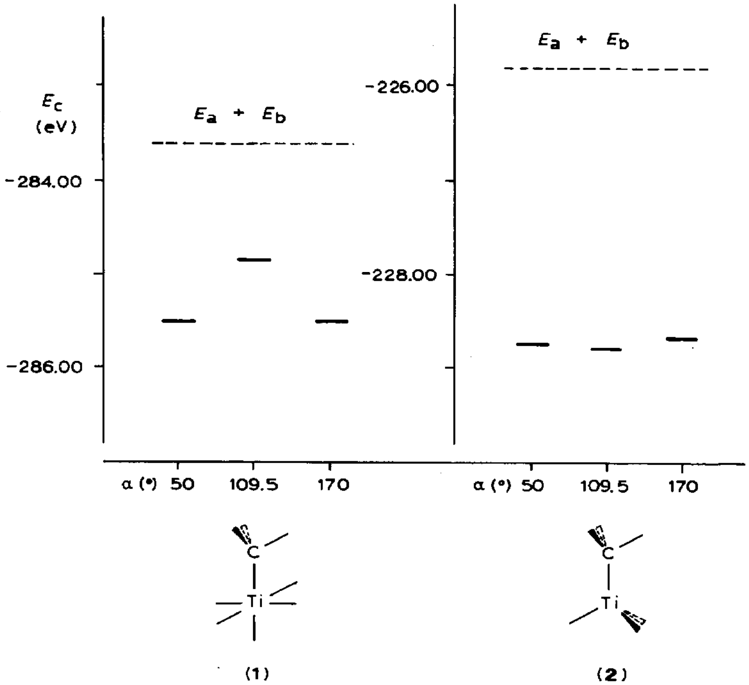


Fig. 2. Total energy of model **1** and model **2**.

Table 1

Overlap populations of PIO-1 in models **1** and **2**

Model	$\alpha = 50°$	$\alpha = 109.5°$	$\alpha = 170°$
1	0.319	0.245	0.283
2	0.323	0.334	0.305

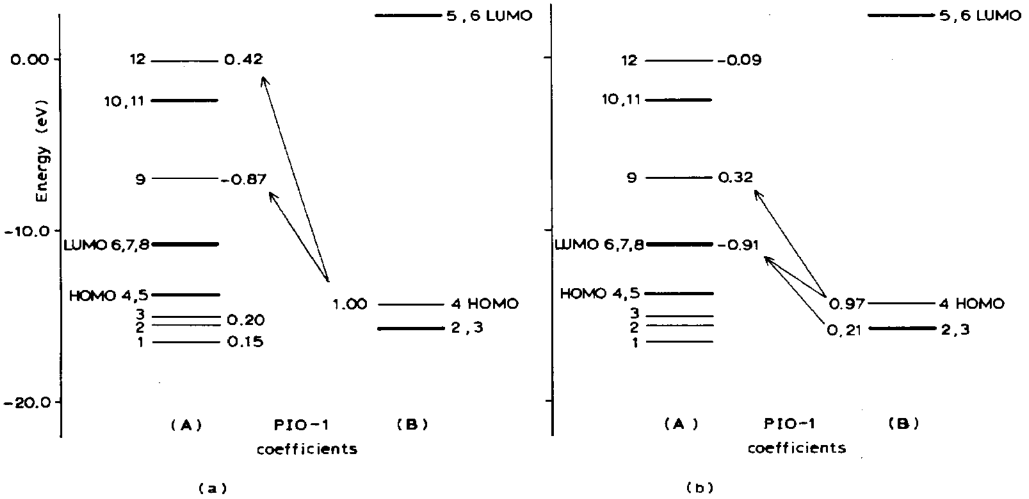


Fig. 3. Canonical MO representation of PIO-1 of model **1**; (a) $\alpha = 109.5°$, (b) $\alpha = 50°$.

Table 2

Localization ratio (%) of PIO-1 in models **1** and **2**

Model	α (°)	Fragment	
		A	**B**
1	109.5	Ti(d_{z^2}): 53.4, H(8): 45.6	C(p_z): 98.9
	50	Ti(d_{xz}): 97.8	C(p_x, p_z): 90.6 H(1): 8.7
	170	Ti(d_{xz}): 98.1	C(p_x, p_z): 93.2 H(2,3): 3.1
2	109.5	Ti(s, d_{z^2}): 98.3	C(p_z): 91.7 H(1,2,3): 2.8
	50	Ti(s, $d_{x^2-y^2}$, d_{x^2}, d_{xz}): 97.1	C(p_x, p_z): 92.1 H(1): 4.1,H(2,3): 1.9
	170	Ti(s, $d_{x^2-y^2}$, d_{z^2}, d_{xz}): 97.3	C(p_x, p_z): 92.6 H(1): 2.1,H(2,3): 2.7

Ti–C bond. The PIO-1 of the fragment **B** is the HOMO which consists of the p_z orbital of the methyl carbon. When the methyl group is tilted, the major compositions of the PIO-1 of the fragment **A** become the unoccupied canonical orbitals, ϕ_6, ϕ_7 and ϕ_8. These are degenerate nonbonding orbitals, composed of the Ti d_{xz}, d_{xy} and d_{yz} respectively.

Interestingly, the mixing of the *trans* hydrogen 1*s* orbital has disappeared. The composition of the PIO-1 has also changes slightly in fragment **B**. It now contains several hydrogen orbitals.

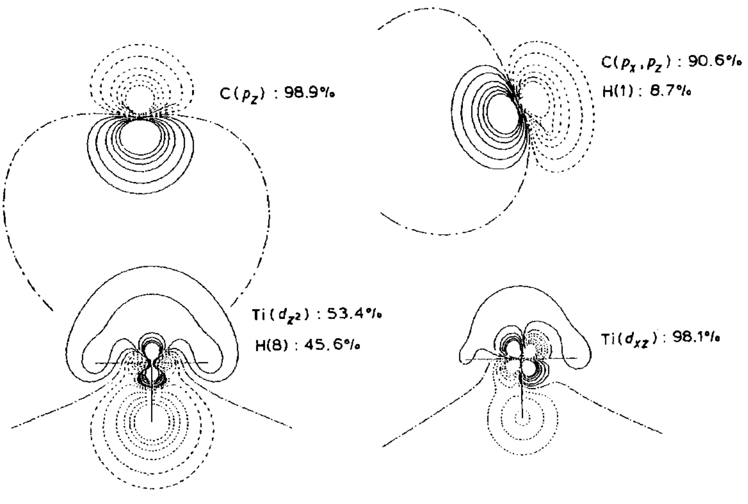
When the methyl group is not tilted, the occupied p_z orbital of the methyl group interacts with the unoccupied Ti d_{z^2} orbital which is destabilized by a σ-type overlap with the 1*s* orbital of the *trans* hydrogen. On the other hand, when the methyl group is tilted, the methyl orbital interacts primarily with the Ti d_{xz} orbital. This orbital is not influenced by the *trans* hydrogen and, therefore, lies lower than the d_{z^2} orbital. Consequently, the interaction between the occupied orbital of the methyl group and the unoccupied orbital of fragment A is strengthened by methyl tilting. This is why the overlap population of the PIO-1 in model **1** increased.

Thus a ligand is located in a position *trans* to the Ti–C bond, tilts the methyl group into the agostic position. These results are illustrated in the contour maps of the PIO-1 given in Fig. 4.

Now let us return to the Td complex, model **2**. The representation of the PIO-1 in terms of the canonical MOs and the extent of the localization of the PIO-1 on the AOs are given in Fig. 5 and in Table 2 respectively. They show that when the methyl group is tilted, the atomic orbital composition of the PIO-1 varies from Ti (d_{z^2}): 98% and C(p_z): 92% at $\alpha = 109.5°$ to Ti(d_{z^2}, d_{xz}): 97% and C(p_x,p_z): 92% at $\alpha = 50°$. The interaction between the orbital pairs initially is σ-type, but is replaced by a π-type interaction in the tilted structure. This is why the slight decrease in the overlap population of the PIO-1 in the Td complex (model **2**) when the methyl group tilts an effect which this complex undergoes only with difficulty.

Oh-[$CH_3Ti(Cl)(H)_4$] complexes

We now consider the influence of a chloride anion on the direction of the methyl group tilting. Model complexes are also shown in Fig. 1. Model **3** has a *trans*-chloro



(a) (b)

Fig. 4. Contour map of PIO-1 of model **1**; (a) $\alpha = 109.5°$; (b) $\alpha = 50°$.

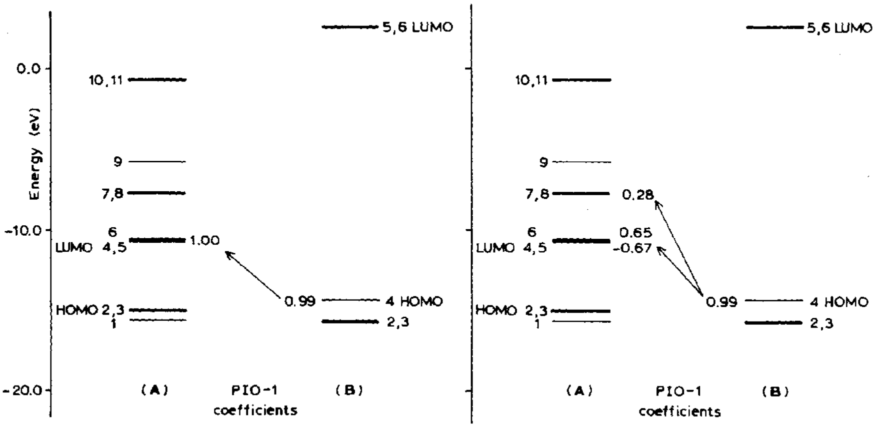
substituent whereas the others have ones that are *cis* chloro. Total energy of each model is shown in Fig. 6.

We first consider the case in which the methyl group is not tilted ($\alpha = 109.5°$), with the bonding energy of the methyl group defined as:

$$\Delta E = E_c - (E_a + E_b) \tag{1}$$

The bonding energy given in Table 3 shows that the bonding strength on the *trans*-isomer is larger than those of the *cis*-isomers. Overlap populations of the PIOs are also listed in Table 3.

The overlap populations of PIO-3 are negative in all of the *cis* isomers. This



(a) (b)

Fig. 5. Canonical MO representation of PIO-1 of model **2**; (a) $\alpha = 109.5°$; (b) $\alpha = 50°$.

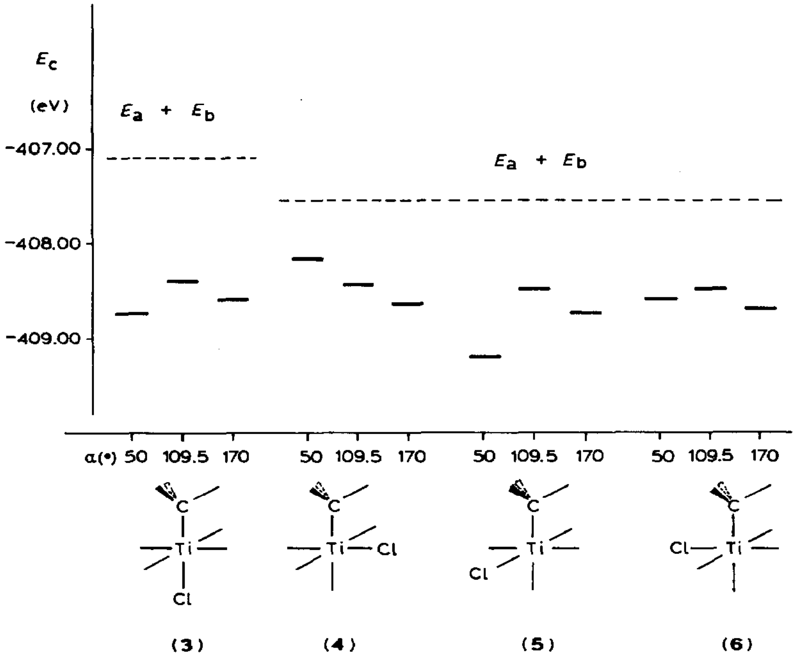


Fig. 6. Total energy of $[(CH_3)Ti(Cl)(H)_4]$ isomers.

implies that there is a decrease in the bonding energy in *cis* isomers. The extent of the localization of PIO-3 to atomic orbitals, and the representations of the MOs of these PIO-3 are given in Table 4.

In the *trans* isomer, the PIO-3 of fragment **A** is composed mainly of unoccupied canonical MOs, whereas in the *cis* isomers it is composed mainly of occupied MOs that contain the Cl $3s$ and $3p_z$ orbitals. As the PIO-3 of fragment **B** is composed of occupied orbitals, overlap repulsion is induced between the fragments **A** and **B** in the case of *cis* isomers. That is, the PIO-3 in the *cis* isomers represents the steric hindrance.

From Fig. 6, it can be seen that the total energy of model **5** is lowered markedly when the methyl group is tilted into the agostic position ($\alpha = 50^\circ$), and the overlap population of PIO-1 of model **5** increases at the same time. The composition of PIO-1 given in Table 5 shows that if a Cl atom is placed in the plane of the tilted methyl group (model **4**), the $3p$ and $3d$ orbitals of Cl participate in the orbital. The

Table 3

The methyl–Ti bonding energy (ΔE (eV)) and overlap populations of models **3**–**6** ($\alpha = 109.5^\circ$)

Model	ΔE	PIO			
		1	2	3	4
3	−1.32	0.225	0.042	0.041	−0.089
4	−0.90	0.262	0.069	−0.035	−0.091
5	−0.95	0.262	0.065	−0.023	−0.093
6	−0.99	0.262	0.068	−0.018	−0.095

Table 4

Localization ratio (%) and canonical MO(No) representation of PIO-3 of models **3–6** ($\alpha = 109.5°$)

Model	Localization ratio (%)		Canonical MO(No)	
	Fragment		Fragment	
	A	B	A	B
3	Ti(d_{xz}): 42.2 H(4): 16 Cl8(p_z): 29.6 H(8): 12	C(p_x): 46.8 H(1): 35.4	ϕocc 3,8 ϕunocc 10,11,15,16	ϕocc 2 ϕunocc –
4	Ti(d_{xz}): 26.2 H(6): 4.4 Cl4(s, p_z): 64.6 H(8): 4.6	C(p_x): 45.1 H(1): 54.4	ϕocc 1,4,5,6,7 ϕunocc 10,15	ϕocc 1,2 ϕunocc –
5	Ti(d_{yz}): 29.1 H(7): 5.4 Cl5(p_z, s): 59.3 H(8): 5.1	C(p_y): 42.0 H(2): 39.1 H(1,3): 9.4	ϕocc 1,4,5,6,7 ϕunocc 9,10,15	ϕocc 1,2,3 ϕunocc 7
6	Ti(d_{xz}): 29.1 H(4): 6.6 Cl6(p_z, s): 57.4 H(8): 5.7	C(p_x): 40.1 H(1): 11.2 H(2,3): 24.0	ϕocc 1,4,5,6,7 ϕunocc 10,15	ϕocc 1,2,3 ϕunocc 7

bonding between the Ti d_{xz} and the C p_x orbitals weakens and, overlap repulsion arises between the Cl and the CH_3 orbitals. In model **5**, on the other hand, tilting of the methyl group is facilitated by overlap between the Ti d_{xz} and the C p_x and p_z AOs.

Thus the results can be summarized as follows:

1. The existence of a ligand *trans* to the methyl group is necessary for methyl tilting.
2. Methyl tilting into an agostic position is promoted in those complexes having a ligand axial to the tilting plane.

Ligand effects

Finally we consider the influence of ligands on the methyl tilting into an agostic position. We examine the additional ligands, CN and OCH_3. Geometrical parameters are given in the Appendix.

ΔE is shown in Fig. 7.

Here we define the difference in energy as:

$$\Delta\Delta E(\alpha) = \Delta E(\alpha) - \Delta E(109.5°) \tag{2}$$

Table 5

Localization ratio (%) of PIO-1 of models **3–5** ($\alpha = 50°$)

Model	Fragment	
	A	B
3	Ti(d_{xz}, d_{z^2}, p_z): 73.8 Cl8(p_x, d_{xz}): 24.1	C(p_x, p_z): 91.8 H(1): 7.2
4	Ti(d_{xz}): 70.8 Cl4(p_z, d_{xz}): 28.7	C(p_x): 90.2 H(1): 8.4
5	Ti(d_{xz}): 96.0	C(p_x, p_z): 91.2 H(1): 7.8

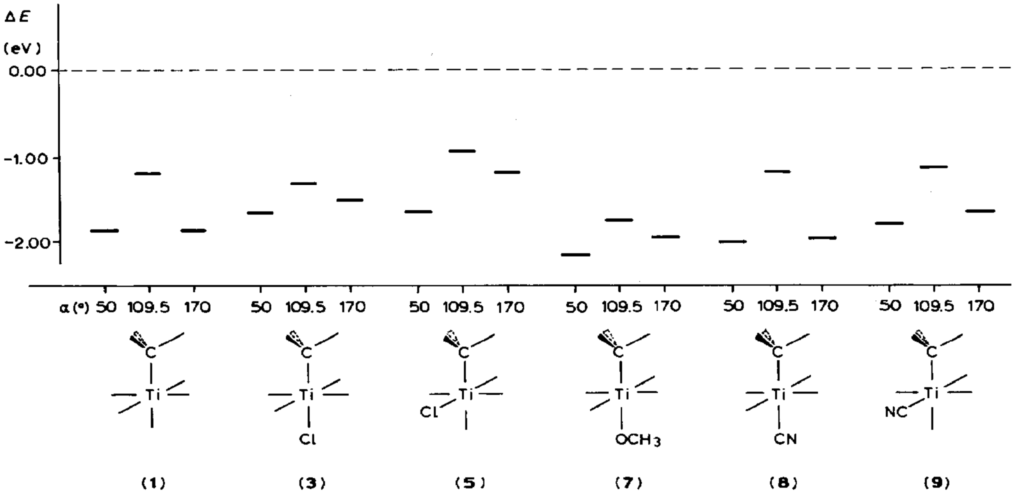


Fig. 7. Methyl–titanium bonding energies for various models.

The more negative the value of $\Delta\Delta E(50°)$, and the larger the difference between $\Delta\Delta E(50°)$ and $\Delta\Delta E(170°)$, the more favourable it is for the methyl group to be tilted into an agostic position. The values of $\Delta\Delta E$ are given in Table 6.

(a) trans-Ligand substituents. The stabilization due to tilting into the agostic position ($\Delta\Delta E(50°)$) decreases in the order: $CN > H > OCH_3 > Cl$. The differences in the overlap populations of PIO-1 between the models which show methyl tilting and those which do not, are given in Table 7, and are very similar to $\Delta\Delta E(50°)$ in value.

As already described, whether the methyl group tilts or not depends on the energy of unoccupied MOs which interact with the occupied MOs of the methyl group. The energy results from a π-overlap of a *trans*-ligand orbital with the Ti d_{xz} orbital. The compositions of PIO-1 (fragment A) and the energy of the unoccupied MOs are given in Table 8.

The unoccupied MOs contain mainly the Ti d_{xz} orbital. In the case of *trans*-CN, the energy of the unoccupied orbital is lower than the energy of d orbitals of atomic Ti because of the electron acceptability of the ligand. On the other hand, in the case

Table 6

Difference bonding energies of the tilted methyl group and of the untilted methyl ($\Delta\Delta E$ (eV)) and the difference between them in various models

Model	Ligand	$\Delta\Delta E(50°)$	$\Delta\Delta E(170°)$	$[\Delta\Delta E(50°)-\Delta\Delta E(170°)]$
8	*trans*-CN	−0.79	−0.77	−0.02
1	*trans*-H	−0.63	−0.64	+0.01
7	*trans*-OCH_3	−0.42	−0.20	−0.22
3	*trans*-Cl	−0.35	−0.20	−0.13
5	axial-Cl	−0.69	−0.26	−0.43
9	axial-CN	−0.62	−0.50	−0.12
1	axial-H	−0.63	−0.64	+0.01

Table 7

Overlap populations of PIO-1 ($\alpha = 50$, $109.5°$) and the difference between them in *trans*-ligand substituted models

Model	Ligand	$\alpha = 50°$	$\alpha = 109.5°$	Δ
8	*trans*-CN	0.311	0.221	0.090
1	*trans*-H	0.319	0.244	0.075
7	*trans*-OCH_3	0.296	0.277	0.021
3	*trans*-Cl	0.257	0.225	0.032

Table 8

Localization ratio (%) and the level of unoccupied canonical MOs of PIO-1 (fragment A) in *trans*-ligand substituted models ($\alpha = 50°$)

Model	Ligand	Localization ratio	ϕunocc level (eV)
8	*trans*-CN	Ti(d_{xz}): 84.0, N(p_x): 11.9	ϕ_{11}: −11.25
1	*trans*-H	Ti(d_{xz}): 97.8	ϕ_6: −10.81
7	*trans*-OCH_3	Ti(d_{xz},d_{z^2}): 93.9, O(p_x): 2.0	ϕ_{14}: −10.41
3	*trans*-Cl	Ti(d_{xz},d_{z^2}): 73.8, Cl(p_z): 24.1	ϕ_{10}: −10.65

of an electron-donating ligand, the energy is higher than the energy of *d* orbitals of atomic Ti. The energy of the unoccupied orbital determines the overlap population. An electron accepting ligand which is placed *trans* to the methyl enhances the tilting of the methyl group.

(b) Axial-ligand substituents. The differences between $\Delta\Delta E(50°)$ and $\Delta\Delta E(170°)$ given in Table 6, decrease in the order: Cl > CN > H. Overlap populations of PIO-1 and PIO-2 in $\alpha = 50°$ and $170°$, respectively, and the differences between them are given in Table 9. The overlap population of PIO-2 in $\alpha = 170°$ increases in the same order, whereas the others are less sensitive to the change in ligands. PIO-2 ($\alpha = 170°$) are made up of the orbitals Ti d_{yz}, the axial ligand p_z, the methyl C p_y and the methyl H 1*s* which is out of the tilting plane. As the axial ligand p_z and the orbitals of the methyl are filled, they induce an overlap repulsion between them. This repulsion decreases the overlap population of PIO-2 ($\alpha = 170°$).

The more readily the ligand donates electrons, the greater is the overlap repulsion, and thus, the easier it is to form an agostic methyl group. Thus when an electron-accepting ligand is *trans* to the methyl group and an electron-donating ligand is axial to the methyl, methyl group tilting to an agostic position is enhanced.

Table 9

Overlap populations of PIO-1 and PIO-2 and the difference between them in axial-ligand substituted models ($\alpha = 50$, $170°$)

Model	Ligand	PIO-1			PIO-2		
		$\alpha = 50°$	$\alpha = 170°$	Δ	$\alpha = 50°$	$\alpha = 170°$	Δ
5	axial-Cl	0.318	0.285	0.033	0.103	0.005	0.098
9	axial-CN	0.317	0.284	0.033	0.114	0.120	−0.006
1	axial-H	0.319	0.283	0.036	0.118	0.147	−0.029

Conclusion

Thus the formation of a C–H → Ti bond in methyltitanium complexes has been investigated by the PIO method. A ligand *trans* to the methyl group is necessary in order to tilt the methyl. The methyl tilting to an agostic position is favoured in the case of a complex having an electron-donating ligand axial to the tilting plane. These results are very similar to those reported previously [4]. When the structure, reactivity, stability and so on, of transition metal complexes are studied by fragment analysis, one should take account not only of HOMO and LUMO but also of other molecular orbitals. Energy levels of molecular orbitals are close together especially near the frontier orbitals in transition metal complexes.

PIO is induced by counting all molecular orbitals interactions between the fragments **A** and **B**. Use of the PIO method, clearly elucidates these interactions in terms of atomic orbitals and thus reveals contributions by each interaction component.

Acknowledgements

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Appendix

Geometrical parameters are assumed as follows: bond lengths (Å): Ti–C 2.15, Ti–H 1.60, C–H 1.09, Ti–Cl 2.15, Ti–O 2.10, Ti–C(CN) 1.90, O–C 1.42, C–N 1.15, bond angles (°): ∠HCH 109.5, ∠TiOC 113.0.

Coulomb integrals and orbital exponents are listed in Table 10.

Table 10

Extended Hückel parameters [a]

Orbital	H_{ij}(eV)	ζ_1	ζ_2	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			
N 2*s*	−26.0	1.950			
N 2*p*	−13.4	1.950			
O 2*s*	−32.3	2.275			
O 2*p*	−14.8	2.275			
Cl 3*s*	−30.0	2.033			
Cl 3*p*	−15.0	2.033			
Cl 3*d*	−9.00	2.033	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

[a] Contraction coefficients in the double- ζ expansion.

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