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A theoretical study of the ligand effect of thiobisphenoxytitanium complex catalyst on the catalytic activity for ethylene polymerization

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Abstract

The effect of ortho-substituents (R = methyl, *tert*-butyl and triisopropylsilyl) of phenoxy groups in thiobisphenoxytitanium complex catalyst on the catalytic activity of ethylene polymerization was analyzed by applying ab initio molecular orbital theory and density functional theory. The calculation results revealed that the activation energy values of ethylene insertion reaction into a methyl–titanium bond of thiobisphenoxytitanium complexes with substituents on the ortho position of phenoxy ligands at the RHF level are in good correspondence with the tendency of ethylene polymerization activities. The activation energy values at the B3LYP/DZ, RHF/LANLL2DZ and B3LYP/LANL2DZ//RHF/DZ levels also show similar tendency. While the differences of the molecular weight of polyethylene prepared with these bisphenoxy complexes could not be explained from the activation energy values of β-H elimination reaction and the chain transfer reaction to monomer. The activation energy of ethylene insertion reaction is supposed to control the molecular weight of polyethylene.

Keywords: Quantum chemical calculation; Ethylene polymerization; Thiobisphenoxy; Titanium; Activity; Molecular weight

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1. Introduction

After the finding of the catalyst system of Cp_2ZrCl_2 and methylaluminoxane, many kinds of metallocene catalyst have been developed for the production of polypropylene, polyethylene and ethylene propylene diene rubber (EPDM) [1,2]. Recently, non-metallocene catalysts, which have no cyclopentadienyl ligand, are also attracted as the new generation catalyst [3]. Non-metallocene catalysts are expected to produce new polyolefin materials, which are not ever synthesized by using a solid Ziegler–Natta catalyst or a metallocene catalyst. In 1987, Miyatake and coworkers reported that titanium complexes with thiobisphenoxy ligand show a higher activity for olefin polymerization to give an amorphous polypropylene having extremely high molecular weight, and an ethylene–styrene alternative copolymer [4]. Such a catalyst system is one of the first examples of non-metallocene catalyst. Recently, they have reported that the catalytic activity of titanium complexes with chelating 2,2′-thiobis(4-methyl-6-R-phenoxy) (R = CH_3, ${}^tC_4H_9$, $({}^iC_3H_7)_3Si$) ligands became higher with the increase in the bulkiness of R group [5]. Molecular weight of polyethylene obtained with these catalysts also became higher with the increase in the bulkiness of R group. Further modification of this thiobisphenoxytitanium catalyst might be able to achieve a higher activity and higher performance as a new polyolefin.

In 1997, Morokuma and coworkers have calculated the activation energy of olefin insertion reaction to alkyl titanium complex with bisphenoxy ligands by the density functional method and have reported that a thiobisphenoxytitanium complex gives low activation energy in olefin insertion reaction [6]. The authors, however, discussed only about the insertion barriers for ethylene polymerization for the variety of simple Ti-chelating bridged alkoxide catalysts, and the effect of the ortho-substituents of this thiobisphenoxytitanium catalyst has not been analyzed yet. The quantitative understanding of the effect of substituent is important to

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find more effective transition metal complex catalyst quickly. In this paper, we analyzed the insertion reaction of ethylene into a Ti–C bond by quantum chemical method, and revealed the role of substituent from the point of both geometrical parameters of reaction intermediates and energy profile [7]. We also applied the computational method to the analyses of the β-H elimination reaction and the chain transfer reaction, which are key reactions to determine the molecular weight of polymer obtained.

2. Computational method

Geometries and energy values of the reactant, π-complex, transition state, and product (γ- and β-agostic) of ethylene insertion were obtained using restricted Hartree-Fock (RHF) method. The β-H elimination reaction and the chain transfer reaction were analyzed by the same way. Energy values were also calculated by the restricted second-order Møller–Plesset perturbation (RMP2) calculations [10] and the hybrid density functional theory (B3LYP) including electron correlation effect [11]. Two basis sets were used, one is the double zeta basis set (below denoted as DZ) which includes MIDI4 for titanium atom [12] and 3-21G basis set for other atoms, and another is the standard LANL2DZ. All calculations were performed by GAUSSIAN98 program [13]. When the substituent is methyl group, we also optimized the geometrical parameters and energy values at the B3LYP/LANL2DZ level and confirmed that the energy profile at the RHF/DZ level is in qualitative correspondence with that at the B3LYP/LANL2DZ level (Table 1). Thus, the data obtained at the RHF/DZ level were mainly adapted to the discussion of this paper.

3. Results and discussions

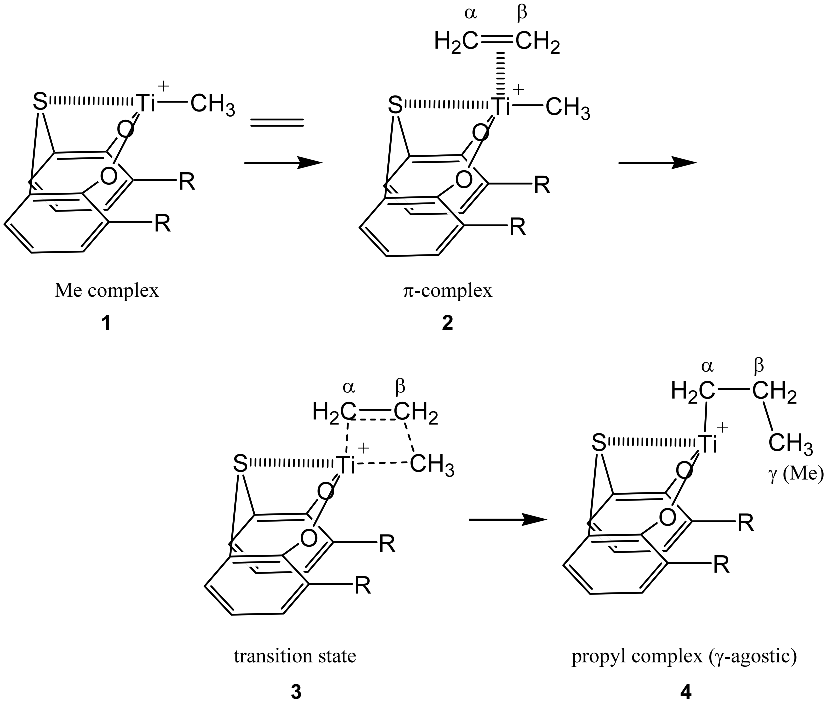
Many theoretical studies on an olefin insertion reaction into a metal–carbon bond have been reported [6,14]. Based on previous reports, four kinds of structure shown in Scheme 1, methyl complex (**1**), π-complex (**2**), transition state (**3**) and propyl complex (γ-H agostic structure) (**4**) were optimized at the RHF/DZ and RHF/LANL2DZ levels. Their main geometrical parameters are summarized in Table 2. Energy values calculated at the RHF level using these geometrical parameters are listed in Table 3. In addition, activation energy values calculated at other levels such as RMP2/DZ//RHF/DZ, B3LYP/DZ//RHF/DZ and B3LYP/LANL2DZ//RHF/LANL2DZ, are summarized in Table 4.

The reaction schemes of a β-H elimination and a chain transfer to monomer are shown in Scheme 2. The geometrical parameters of β-H agostic structure (**5**), transition state (**6**), propylene hydride complex (**7**), propyl ethylene complex (**8**), transition state (**9**), and ethyl propylene complex (**10**) were optimized at the RHF/DZ level. Their main geometrical parameters are summarized in Table 5. The structures **5**, **6** and **7** were also optimized at the RHF/LANL2DZ level. Energy values calculated using these geometrical parameters are summarized in Table 6.

Table 1
Geometrical parameters of optimized structures of ethylene insertion reaction of thiobisphenoxytitaniummethyl complexes at the RHF/DZ level

	Methyl complex	Ethylene π-complex	Transition state	Propyl complex (γ-agostic)	β-Agostic	Transition state	Propylene hydride complex
	1-Me	2-Me	3-Me	4-Me	5-Me	6-Me	7-Me
Ti–C(Me)	2.03(2.02)	2.05(2.03)	2.15(2.12)				
Ti–S	2.68(2.69)	2.97(3.18)	2.77(2.82)	2.68(2.70)	2.66(2.67)	2.77(2.85)	2.90(2.87)
Ti–O	1.74(1.78)	1.74(1.77)	1.77(1.79)	1.77(1.80)	1.77(1.80)	1.76(1.77)	1.74(1.77)
	1.74(1.78)	1.74(1.77)	1.77(1.79)	1.77(1.80)	1.77(1.80)	1.76(1.77)	1.74(1.77)
Ti–C(α)		2.66(2.59)	2.15(2.17)	2.00(2.00)	2.01(2.01)	2.23(2.29)	2.37(2.30)
Ti–C(β)		2.66(2.60)	2.53(2.51)		2.48(2.47)	2.61(2.71)	2.82(2.73)
C(α)–C(β)		1.34(1.37)	1.41(1.42)	1.57(1.57)	1.54(1.54)	1.39(1.39)	1.35(1.39)
C(Me)–C(β)			2.17(2.22)	1.59(1.60)	1.54(1.54)	1.51(1.50)	1.50(1.50)
Ti–H(β)					2.13(2.10)	1.73(1.67)	1.68(1.67)
C(β)–H(β)					1.14(1.14)	1.80(2.11)	2.50(2.16)
∠Ti–C(α)–C(β)					87.6(87.1)	89.4(91.5)	94.3(92.0)
Ti–H(γ)				2.58(2.38)			
				2.32(2.34)			
C(γ)–H(γ)				1.09(1.11)			
				1.10(1.11)			

Numbers in parentheses are optimized at the B3LYP/LANL2DZ level.



Scheme 1.

3.1. Insertion reaction

3.1.1. Geometry parameters of insertion reaction

3.1.1.1. Methyl complex. All structures of monomethyl complexes, 1-Me, 1-^{t}Bu and 1-^{i}Pr$_3$Si are optimized at the RHF/DZ level and shown in Fig. 1. Regardless the bulkiness of ortho-substituent, the bond lengths of Ti–C(Me) and the Ti–O of 1-Me, 1-^{t}Bu and 1-^{i}Pr$_3$Si, are almost the same at the RHF/DZ level. While, the distance between Ti and S of 1-Me is slightly different from others. The geometrical parameters obtained at the RHF/DZ level are almost the same as those of the titanium complex with no substituent in the phenoxy ligand calculated at the B3LYP/LANL2DZ level, which have been reported by Froese et al. [6b]. In using the LANL2DZ basis set, this distance is longer by 0.41 Å than that at the RHF/DZ level. Such a large elongation is not shown in other two models. Although we have not obtained a clear explanation yet, we think that the LANL2DZ basis set will give longer atomic distance than our DZ basis. The same tendencies are shown in the models of other reaction steps.

3.1.1.2. π-Complex. The structures of π-complexes, 2-Me, 2-^{t}Bu and 2-^{i}Pr$_3$Si optimized are shown in Fig. 2. In all cases, each methyl group occupies a trans position to sulphur atom and ethylene is in opposite site of phenoxy groups [15]. At the RHF/DZ level, there is little difference in comparison of the Ti–C(Me), Ti–O bond lengths and the distances between titanium and the each carbon of ethylene among these three structures. While, the distances between Ti and S are different by about 0.05 Å each other and 2-^{t}Bu shows the shortest distance. These geometrical parameters are not seriously different from those calculated at the RHF/LANL2DZ level.

The comparison of geometrical parameters between methyl complexes and π-complexes indicates that the Ti–C(Me) bond lengths and Ti–O ones are little different and the distances between Ti and S of π-complexes are longer by ca. 0.2 or 0.3 Å than those of methyl complexes in all cases.

3.1.1.3. Transition state. The structures of transition state, 3-Me, 3-^{t}Bu and 3-^{i}Pr$_3$Si, calculated at the RHF/DZ level are shown in Fig. 3. The four-centered metallacyclobutane structure obtained in every case are qualitatively similar to other complexes reported previously [6,14]. The computation of vibrational frequency of 3-Me indicated that the structure of 3-Me has only one imaginary frequency, which is the evidence that 3-Me is real transition state. Although the geometrical parameters obtained with DZ basis set are slightly different from those with LANL2DZ set, the kind of the basis set does not affect the parameters seriously in the case of these thiobisphenoxytitanium complexes.

In comparison among these three transition state models, the Ti–C(α) bond distances are equal and the distance between Ti and S is different by about 0.05 Å each other. The C–C bond distances of ethylene unit are longer by 0.07 Å than the standard length (1.34 Å) of

Table 2
Geometrical parameters of optimized structures of ethylene insertion reaction of thiobisphenoxytitaniummethyl complexes at the RHF/DZ level

	Methyl complex	Ethylene π-complex	Transition state	Propyl complex (γ-agostic)
	1-Me	2-Me	3-Me	4-Me
Ti–C(Me)	2.03(2.01)	2.05(2.03)	2.15(2.13)	
Ti–S	2.68(3.09)	2.97(3.18)	2.77(2.84)	2.68(2.71)
Ti–O	1.74(1.75)	1.74(1.77)	1.77(1.78)	1.77(1.78)
	1.74(1.76)	1.74(1.77)	1.77(1.78)	1.77(1.78)
Ti–C(α)		2.66(2.59)	2.15(2.12)	2.00(1.98)
Ti–C(β)		2.66(2.60)	2.53(2.53)	
C(α)–C(β)		1.34(1.37)	1.41(1.42)	1.57(1.56)
C(Me)–C(β)			2.17(2.19)	1.59(1.58)
Ti–H(γ)				2.58(2.41)
				2.32(2.38)
C(γ)–H(γ)				1.09(1.09)
				1.10(1.09)
	1-^{t}Bu	2-^{t}Bu	3-^{t}Bu	4-^{t}Bu
Ti–C(Me)	2.04(2.00)	2.05(2.02)	2.15(2.13)	
Ti–S	2.64(2.68)	2.87(2.95)	2.72(2.77)	2.64(2.66)
Ti–O	1.74(1.75)	1.75(1.75)	1.77(1.78)	1.76(1.78)
	1.74(1.75)	1.74(1.75)	1.76(1.77)	1.77(1.78)
Ti–C(α)		2.67(2.72)	2.15(2.12)	2.01(1.98)
Ti–C(β)		2.66(2.69)	2.53(2.53)	
C(α)–C(β)		1.34(1.35)	1.41(1.42)	1.57(1.56)
C(Me)–C(β)			2.18(2.19)	1.59(1.58)
Ti–H(γ)				2.39(2.40)
				2.42(2.41)
C(γ)–H(γ)				1.10(1.09)
				1.10(1.09)
	1-^{i}Pr$_3$Si	2-^{i}Pr$_3$Si	3-^{i}Pr$_3$Si	4-^{i}Pr$_3$Si
Ti–C(Me)	2.04(2.00)	2.05(2.02)	2.15(2.13)	
Ti–S	2.65(2.70)	2.92(3.00)	2.75(2.80)	2.66(2.69)
Ti–O	1.74(1.75)	1.75(1.75)	1.77(1.78)	1.77(1.78)
	1.74(1.76)	1.75(1.75)	1.77(1.78)	1.77(1.78)
Ti–C(α)		2.65(2.65)	2.15(2.12)	2.01(1.98)
Ti–C(β)		2.67(2.73)	2.53(2.53)	
C(α)–C(β)		1.34(1.35)	1.41(1.42)	1.57(1.56)
C(Me)–C(β)			2.18(2.18)	1.59(1.58)
Ti–H(γ)				2.57(2.44)
				2.32(2.39)
C(γ)–H(γ)				1.09(1.09)
				1.10(1.10)

Numbers in parentheses are calculated at the RHF/LANL2DZ level.

ethylene. In comparison with structures of π-complexes, the Ti–C(Me) bond distance of transition state is longer by 0.1 Å than that of π-complex in spite of the size of the ortho-substituent. While the distances between Ti and S of these transition state models become smaller than that of π-complex model by 0.15–0.2 Å.

Table 3
Total energy (in a.u.) for the reactants, and relative energies (in kcal mol^{-1}, relative to reactant plus ethylene) of the π-complex and the transition state for ethylene insertion reactions and β-H elimination reaction studied in this paper, calculated at the RHF/DZ level

	Insertion reaction				β-H elimination reaction		
Substituent	Reactants	π-Complex	Transition state	γ-Agostic	β-Agostic	Transition state	Propylene hydride complex
Me	−1965.474940	−26.7	−12.3	−29.0	−29.6	−12.9	−15.3
^{t}Bu	−2198.387875	−22.1	−8.4	−25.3	−29.2	−12.4	−14.4
^{i}Pr$_3$Si	−3163.775305	−25.9	−12.5	−29.4	−30.1	−13.2	−15.3

Table 4
Ethylene coordinattion energy (E_c) and activation energy(E_a) of ethylene insertion reaction into a Ti–C(Me) bond at the various levels (kcal mol^{-1})

	Me	^{t}Bu	^{i}Pr$_3$Si
E_c			
RHF/DZ	−26.7	−22.1	−25.9
RHF/LANL2DZ	−22.0	−17.5	−20.4
B3LYP/LANL2DZ//RHF/LANL2DZ	−20.4	−16.3	−18.8
E_a			
RHF/DZ	14.4	13.7	13.4
RMP2/DZ//RHF/DZ	9.3	8.5	8.9
B3LYP/DZ//RHF/DZ	5.1	4.1	3.8
RHF/LANL2DZ	17.1	16.2	16.1
B3LYP/LANL2DZ//RHF/LANL2DZ	6.5	6.3	6.2
Polym. Activity (kg-PE/mol-Ti/h) [5]	40	210	880

3.1.2. *Product (γ-H agostic interaction)*

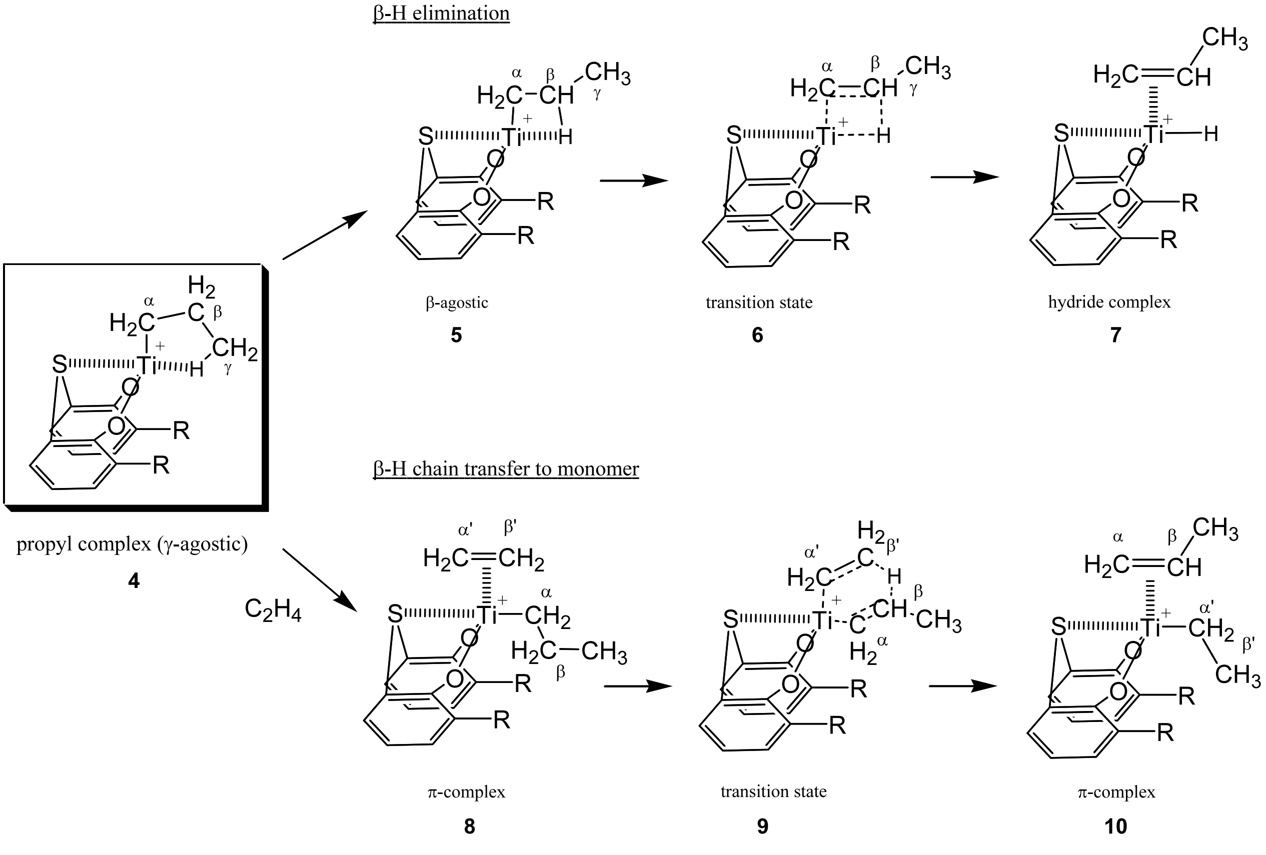
Fig. 4 shows the γ-H agostic structures 4-Me, 4-^{t}Bu and 4-^{i}Pr$_3$Si at the RHF/DZ level. As shown in Table 2, the Ti–O bond distances are almost equal, and Ti–C(α) bond distances are little different. The distances between Ti and S are slightly different by 0.04 Å. The bond distances of C(γ)–H(γ) of 1.09–1.10 Å are almost equal to the normal C–H bond length, suggesting the existence of very weak agostic interaction. The geometrical features obtained with the LANL2DZ basis set are not seriously changed from those with DZ basis set.

There are two structural differences of each propyl complexes (**4**) from the corresponding methyl complexes (**1**). One point is that Ti–O bond distances of propyl complexes (**4**) are longer by 0.02 or 0.03 Å, and another is that each Ti–C(α) bond of propyl complexes (**4**) is shorter by 0.03 Å than Ti–C(Me) of methyl complex.

These results indicate that the ortho-substituents of these phenoxy ligands do not affect the geometrical parameters of insertion reaction heavily. In other words, even bulky triisopropylsilyl group does not disturb the ethylene insertion. Actually, the structure of transition state 4-^{i}Pr$_3$Si shown in Fig. 5, shows the shortest distance between a hydrogen atom of ethylene and one of triisopropylsilyl group is more than 3.00 Å. Such a little influence of the bulkiness of substituent also seems to relate to the small differences among charges of these titanium atoms at each reaction step calculated using Mulliken population analysis by about 0.03.

3.1.3. *Energy profiles of insertion reaction and the comparison with an experimental activity*

The energy profiles are summarized in Tables 3 and 4. The stabilization energies by coordination of ethylene are 26.7, 22.1 and 25.9 kcal mol^{-1} to 2-Me, 2-^{t}Bu and 2-^{i}Pr$_3$Si models, respectively at the RHF/DZ level.



Scheme 2.

Table 5
Geometrical parameters (and degree) of optimized structures of β-H elimination reaction of thiobisphenoxytitaniummethyl complex

	β-H elimination			Chain transfer to monomer		
	β-Agostic	Transition state	Propylene hydride complex	Ethylene propyl complex	Transition state	Propylene ethyl complex
	5-Me	6-Me	7-Me	8-Me	9-Me	10-Me
Ti–S	2.66	2.77	2.90	3.03	2.98	3.01
Ti–O	1.77	1.76	1.74	1.75	1.76	1.75
	1.77	1.76	1.74	1.75	1.76	1.75
Ti–C(α?	2.01	2.23	2.37	2.04	2.12	2.46
Ti–C(β)	2.48	2.61	2.82	3.01	3.07	2.83
Ti–H(β)	2.13	1.73	1.68		2.93	
C(β)–H(β)	1.14	1.80	2.50	1.09	1.24	
C(α?–C(β)	1.54	1.39	1.35	1.54	1.50	1.35
C(β)–C(γ)	1.54	1.51	1.50			1.50
∠ Ti-C(α)–C(β)	87.6	89.4	94.3			
Ti–C(α′?				2.73	2.17	2.04
Ti–C(β′)				2.61		
C(α′)–C(β′)				1.34	1.48	1.55
C(β′)–H(β)					1.28	1.08
	5-^{t}Bu	6-^{t}Bu	7-^{t}Bu	8-^{t}Bu	9-^{t}Bu	10-^{t}Bu
Ti–S	2.62	2.72	2.81	2.91	2.88	2.86
Ti–O	1.77	1.76	1.74	1.75	1.76	1.76
	1.77	1.76	1.74	1.75	1.76	1.76
Ti–C(α?	2.01	2.23	2.38	2.04	2.13	2.51
Ti–C(β)	2.49	2.61	2.82	3.05	3.08	2.84
Ti–H(β)	2.13	1.73	1.69		2.96	
C(β)–H(β)	1.14	1.81	2.47	1.09	1.24	
C(α?–C(β)	1.54	1.39	1.36	1.54	1.50	1.34
C(β)–C(γ)	1.54	1.51	1.50			1.50
∠ Ti–C(α?–C(β)	87.9	89.3	93.7			
Ti–C(α′?				2.71	2.17	2.05
Ti–C(β′)				2.63		
C(α′?–C(β′)				1.34	1.48	1.55
C(β′)–H(β)					1.27	1.08
	5-^{i}Pr$_3$Si	6-^{i}Pr$_3$Si	7-^{i}Pr$_3$Si	8-^{i}Pr$_3$Si	9-^{i}Pr$_3$Si	10-^{i}Pr$_3$Si
Ti–S	2.65	2.75	2.85	2.94	2.93	2.87
Ti–O	1.77	1.76	1.74	1.75	1.76	1.76
	1.77	1.76	1.74	1.76	1.76	1.76
Ti–C(α?	2.01	2.23	2.38	2.04	2.12	2.51
Ti–C(β)	2.49	2.62	2.82	3.07	3.09	2.87
Ti–H(β)	2.13	1.73	1.68		2.96	
C(β)–H(β)	1.14	1.81	2.47	1.09	1.23	
C(α?–C(β)	1.54	1.39	1.35	1.54	1.50	1.34
C(β)–C(γ)	1.54	1.51	1.50			1.50
∠ Ti–C(α?–C(β)	88.0	89.4	94.1			
Ti–C(α′?				2.70	2.17	2.05
Ti–C(β′)				2.63		
C(α′?–C(β′)				1.34	1.48	1.55
C(β′)–H(β)					1.28	1.08

Based on these data, the order of stabilization energy seems not to relate to the bulkiness of substituent. Also, the coordination energy value of 2-Me decreases to 22.0 kcal mol^{-1} at the RHF/LANL2DZ level and to 20.4 kcal mol^{-1} at the B3LYP/LANL2DZ level. The coordination energy value seems to be more sensitive to the calculation method and the difference of energy values due to the kind of basis set is larger than that due to the electron correlation effect.

The activation energy value calculated from the energy difference between π-complex and transition state is decreasing with the increase in the bulkiness of substituents at the RHF/DZ level. It is noted that the order of activation energy values calculated at the RHF/

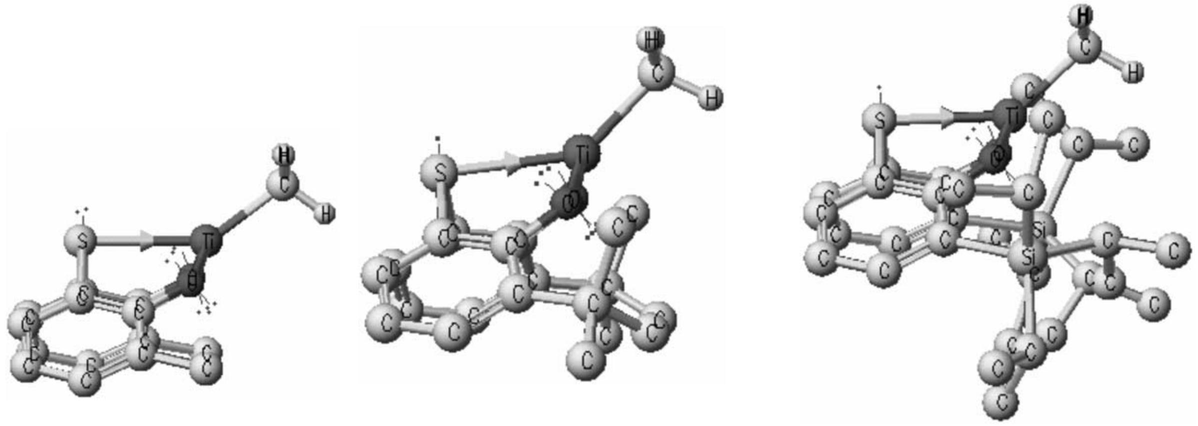
Table 6
Activation energy ($E_{a(\beta\text{-H})}$) of β-H elimination reaction and chain transfer to monomer at the various levels (kcal mol^{-1})

$E_{a(\beta\text{-H})}$	Me	^{t}Bu	^{i}Pr$_3$Si
β-H elimination reaction			
RHF/DZ	16.6	16.8	16.9
B3LYP/DZ//RHF/DZ	16.0	16.4	16.3
RHF/LANL2DZ	17.0	17.3	17.8
B3LYP/LANL2DZ//RHF/LANL2DZ	17.2	17.5	16.9
Chain transfer to monomer			
RHF/DZ	36.7	36.6	36.2
B3LYP/LANL2DZ//RHF/DZ	25.6	25.6	25.5
Molecular weight ($10^{-4} \times$ Mw)			
Cocatalyst			
MMAO	14	44	73
$(C_6F_5)_3B(C_6F_5)_4/Al(^iC_4H_9)_3$[5]	[a]	24	154

[a] Not available due to low yield of the polyethylene.

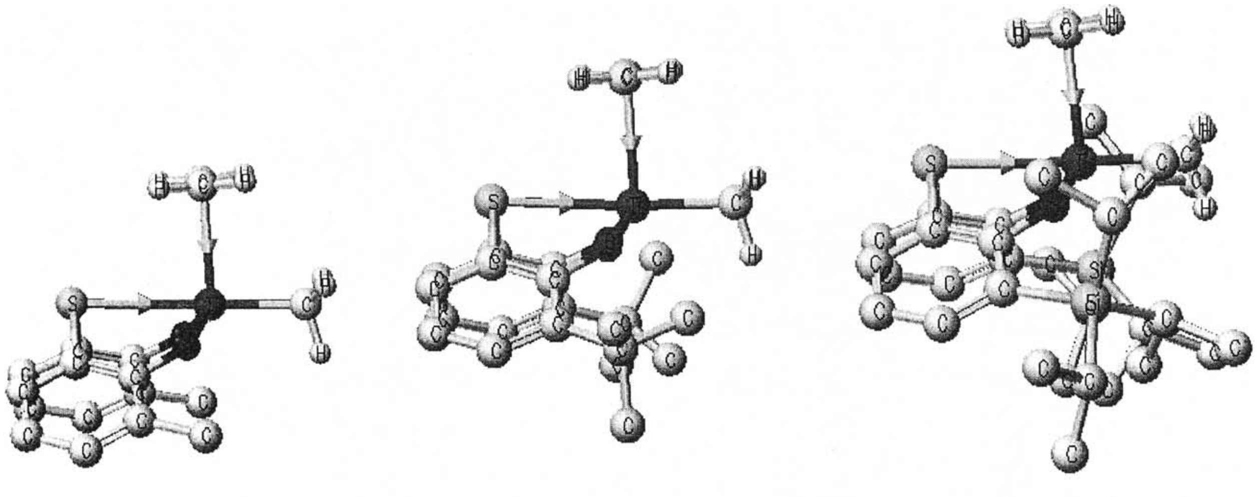
DZ level is in very good correspondence with the order of the polymerization activities obtained experimentally as shown in Table 4. The order of the values at the B3LYP/DZ level is also in good correspondence. However, those obtained at the RHF/LANL2DZ and B3LYP/LANL2DZ//RHF/LANL2DZ levels have only slight qualitative correlations, but that obtained at the RMP2/DZ//RHF/DZ level is not correlated with the tendency of polymerization activities. The reason of such inconsistency by the calculation method may be that the differences on geometrical parameters and interaction energy of intermediates is affected due to the difference of incorporation of electron correlation effect [16]. For example, one reason is that the π-complex structure determined at the RHF/DZ level is not a little different with that at the RMP2/DZ level. Other is the overestimation of electron correlation energy of RMP2 method.

The values of heat of formation of product (propyl complex) from π-complex calculated are shown in Table 3. The values of 2.3, 3.2, and 3.5 kcal mol^{-1} were obtained to 4-Me, 4-^{t}Bu, and 4-^{i}Pr$_3$Si, respectively at



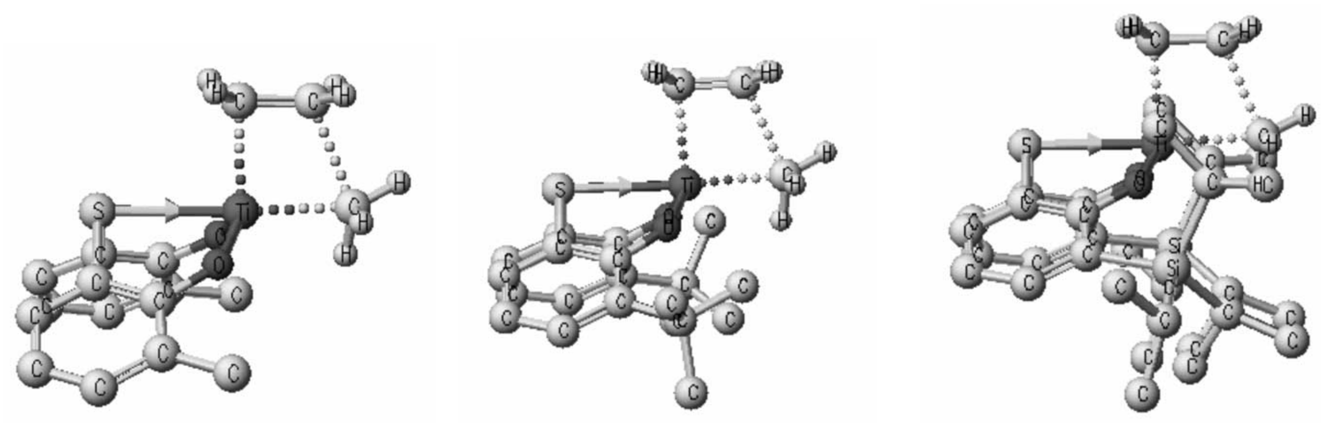
1-Me **1-tBu** **1-iPr$_3$ Si**

Fig. 1. Optimized structures of $S(C_6H_3RO)_2TiCH_3^+$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)



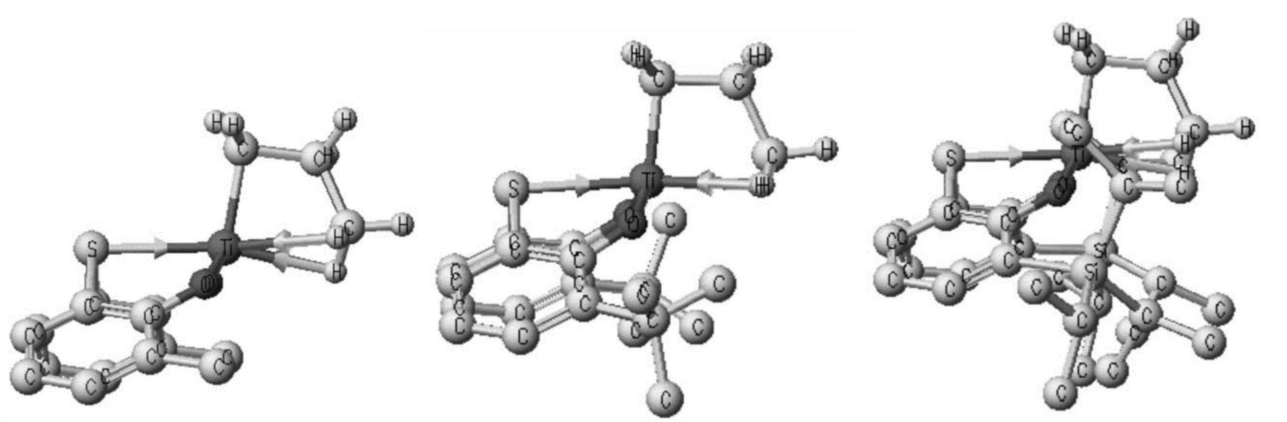
2-Me **2-tBu** **2-iPr$_3$Si**

Fig. 2. Optimized structures of $S(C_6H_3RO)_2TiCH_3^+(C_2H_4)$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)



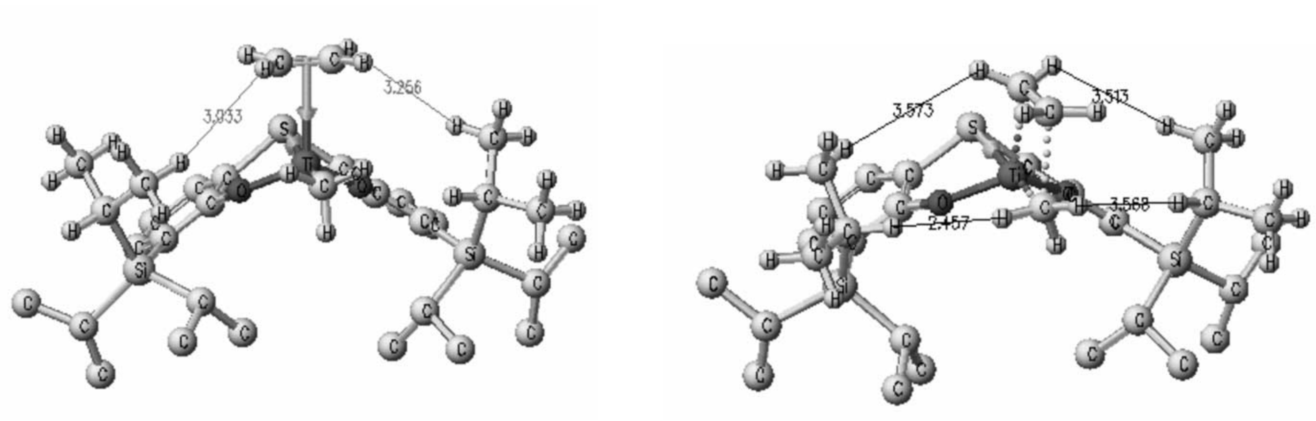
3-Me **3-tBu** **3-iPr$_3$Si**

Fig. 3. Transition state of $S(C_6H_3RO)_2TiCH_3^+(C_2H_4)$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)



4-Me **4-tBu** **4-iPr$_3$Si**

Fig. 4. Optimized γ-H agostic structures of $S(C_6H_3RO)_2TiC_3H_7^+$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)



π-complex transition state

Fig. 5. Side views of π-complex (2-^{i}Pr$_3$Si) and transition state (3-^{i}Pr$_3$Si) obtained at the RHF/DZ level.

the RHF/DZ level, indicating that the ethylene insertion reaction is exothermic and the value becomes larger as the increase of the bulkiness of substituents.

Morokuma and coworkers have supposed that the bulky substituent in bidentate non-cyclopentadienyl ligands makes olefin polymerization reaction accelerate on the basis of the IMOMM method [9,17]. They mentioned that the bulky substituent destabilizes the π-complex and does not affect the stability of transition state, and consequently activation energy becomes lower. If the acceleration of an olefin polymerization reaction due to the bulky substituent is a general rule [17], both of the ethylene complexation energy and the insertion barrier of ${}^{i}Pr_3Si$ model should be the smallest. Actually, the activation energy of 3-${}^{i}Pr_3Si$ is the smallest. However, the ethylene complexation energy of 2-${}^{i}Pr_3Si$ is not the smallest. In our calculation, the order of the ethylene complexation energy is not in agreement with the order of polymerization activity.

Thus, the activation energy profiles calculated at the RHF/DZ and B3LYP/DZ//RHF/DZ levels seem to be sufficient to account for the order of experimental polymerization activity of these chelating thiobisphenoxytitanium complexes, expected that the estimations of activation energy at these level may enable to predict the structure of new active catalyst for olefin polymerization.

3.2. Chain termination reaction

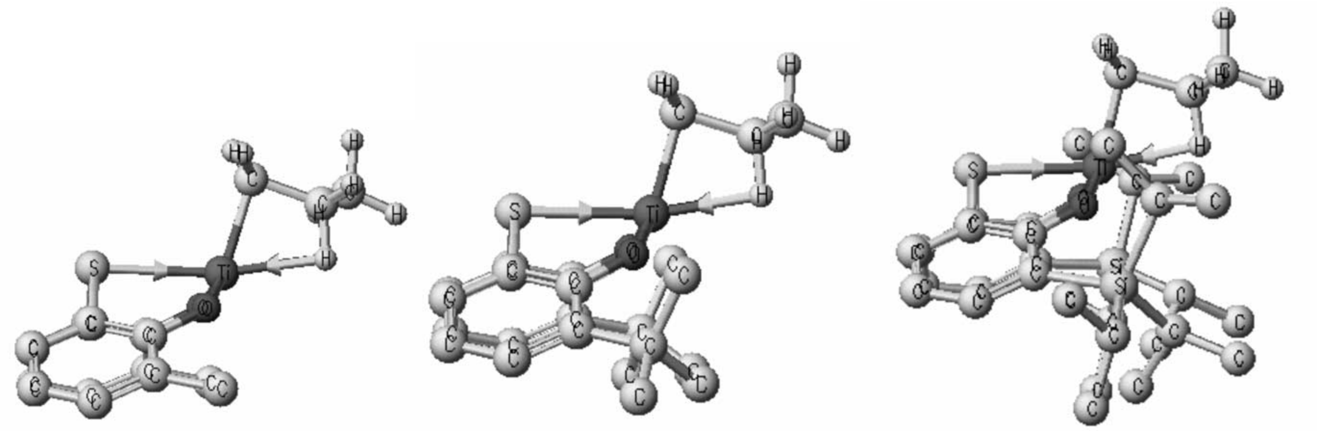
The molecular weight of polymer is one of the most important factors to influence the properties of a polymer material. Therefore, it is also important to understand the chain termination mechanism in detail to the design of catalyst for controlling the molecular weight polymer. Generally, the main chain termination reactions are considered to be the β-H elimination reaction and chain transfer reaction to monomer [17].

3.2.1. β-H elimination reaction

3.2.1.1. Propyl complex (β-H agostic interaction). Fig. 6 shows the β-H agostic structures, 5-Me, 5-${}^{t}Bu$ and 5-${}^{i}Pr_3Si$, determined at the RHF/DZ level. Geometrical parameters of these three structures are listed in Table 5. Bond distances are almost the same among these models, except for the distances between Ti and S, that is 5-${}^{t}Bu$ is shorter by 0.04 Å than that of 5-Me and by 0.03 Å than that of 5-${}^{i}Pr_3Si$. All angles of Ti–C(α)–C(β) in these models are smaller than 90° indicating the existence of a strong β-agostic interaction. The optimization of the structure of 5-Me with the restriction of the angle of Ti–C(α)–C(β) to normal tetrahedral angle 109.5° shows that the structure becomes less stable by 3.3 kcal mol^{-1}, indicating that this value shows the strength of agostic interaction of the thiobisphenoxytitanium complex.

3.2.1.2. Transition state of β-H elimination reaction. Fig. 7 shows the structures of the transition state of β-H elimination reaction of 6-Me, 6-${}^{t}Bu$ and 6-${}^{i}Pr_3Si$, obtained at the RHF/DZ level. In analogy with β-agostic structures, only the distances between Ti and S are slightly affected by the kind of the ortho-substituent of phenoxy ring. In comparison of these transition state structures with β-agostic ones, all Ti–C(α) bonds of transition state are longer by 0.22 Å than those of β-agostic one and the C(β)–H(β) bonds are elongated by 0.66 or 0.67 Å. While, all Ti–H(β) distances and all C(α)–C(β) bond lengths are shorter by 0.40 and 0.15 Å, respectively than those of β-agostic ones.

3.2.1.3. Propylene hydride complex from β-H elimination reaction. Fig. 8 shows the structures of propylene hydride complexes 7-Me, 7-${}^{t}Bu$ and 7-${}^{i}Pr_3Si$ resulted in the β-H elimination reaction. There is no large difference among the bond lengths and distances. The substituents of phenoxy ligands do not affect directly to the geometrical parameters of β-H elimination reaction. In comparison of each propylene hydride complex with the corresponding propyl complex (β-H agostic) and transition state, it is noted that the distance between Ti and S becomes longer by about 0.2 Å resulted in the elimination reaction which is close to the value of π-



5-Me **5-tBu** **5-iPr$_3$Si**

Fig. 6. Optimized β-H agostic structures of $S(C_6H_3RO)_2TiC_3H_7^+$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)

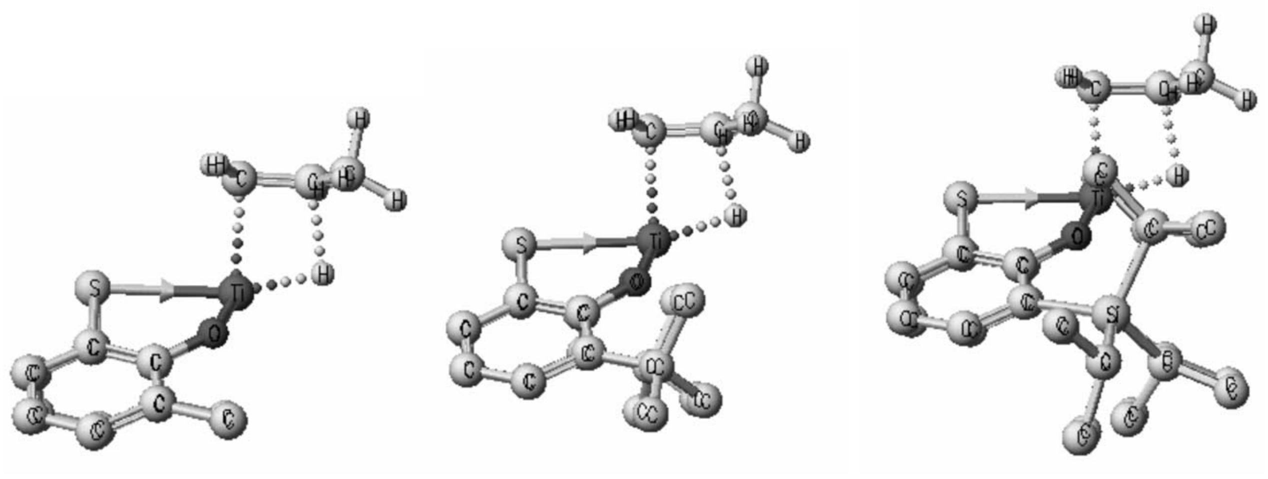


Fig. 7. Transition state of β-H elimination reaction of $S(C_6H_3RO)_2TiC_3H_7^+$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)

complex (**2**). Such mobility of the bridged S atom may be related to the characteristic polymerization capability of these thiobisphenoxytitanium complexes.

3.2.1.4. Energy profiles and comparison with experimental molecular weight. As shown in Table 3, the calculation results indicate that all β-H agostic propyl complexes are more stable by 0.6–3.9 kcal mol^{-1} than γ-agostic ones at the RHF/DZ level. The stability of β-agostic structure based on the γ-agostic one seems to be not dependent on the bulkiness of ortho-substituent, because the order of the energy values are not corresponding to the increase in the size of the substituent group.

The activation energy values of β-H elimination reaction and the molecular weight of polyethylene obtained experimentally are listed in Table 6. The values at the RHF levels increase from 16.6 to 16.9 kcal mol^{-1} with the increase in the bulkiness of substituents, and seem to be in good agreement with the order of the molecular weight. While, at the B3LYP/DZ//RHF/DZ level, the activation energy value of triisopropylsilyl substituted complex is less than that of tert-butyl group substituted one. The data at the B3LYP level should not be ignored completely, because the energy value at the B3LYP level includes electron correlation effect. Consequently, we could not conclude that the activation barrier of β-H elimination reaction is the principal factor to control the molecular weight of polyethylene with these thiobisphenoxytitanium complexes.

While, the propylene hydride complexes are less stable by 14.3–14.8 kcal mol^{-1} than β-agostic complexes and the values show that the β-H elimination reaction is endothermic. Similar instability profile has been re-

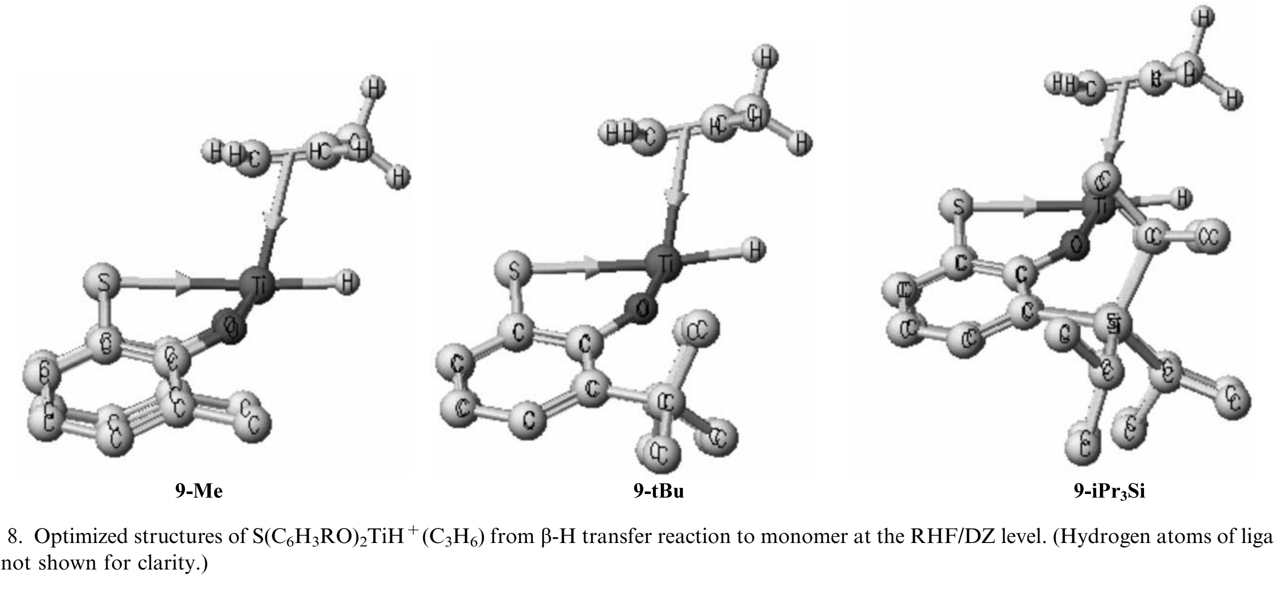
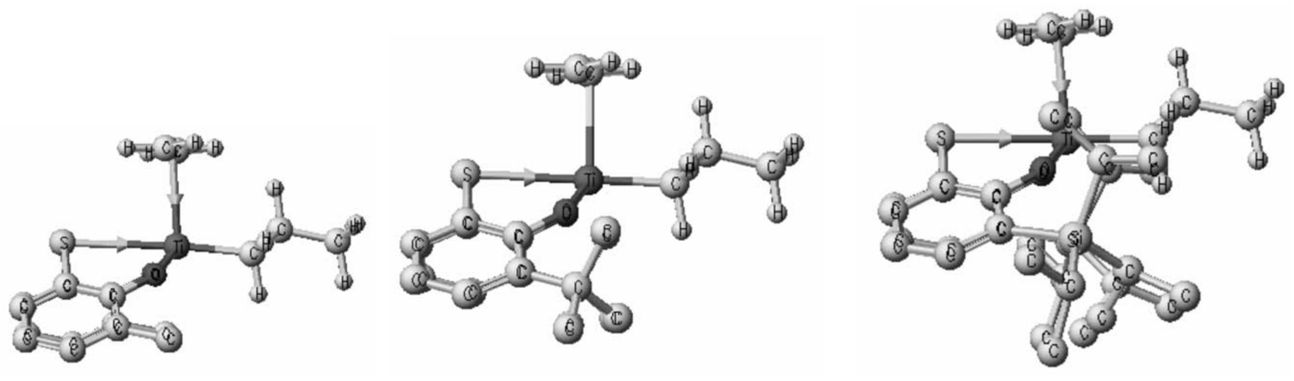


Fig. 8. Optimized structures of $S(C_6H_3RO)_2TiH^+(C_3H_6)$ from β-H transfer reaction to monomer at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)



8-Me **8-tBu** **8-iPr$_3$Si**

Fig. 9. Optimized structures of $S(C_6H_3RO)_2TiC_3H_7^+(C_2H_4)$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)

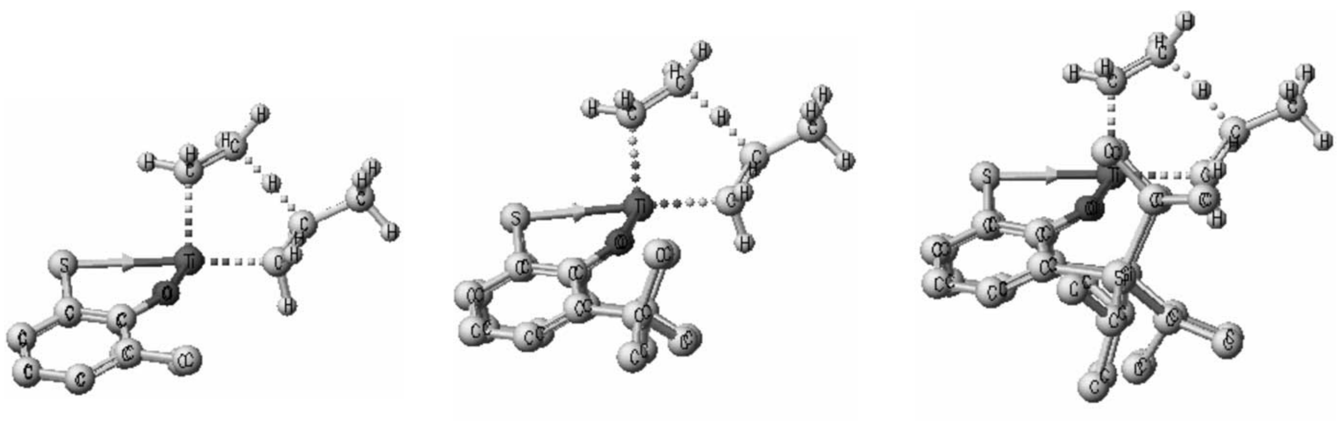
ported to the reaction of metallocene complexes previously [16]. As far as we know, olefin hydride titanium complexes have not be observed experimentally. Therefore, it is reasonable to think that the olefin hydride complex easily reacts with ethylene to make new ethyl complex.

3.2.2. *Chain transfer reaction to monomer from propyl ethylene π-complex*

Generally, chain transfer to monomer is another important reaction to determine the molecular weight of polyolefin [16]. The structures of 8-Me, 8-^{t}Bu and 8-^{i}Pr$_3$Si optimized at the RHF/DZ level are shown in Fig. 9. The optimized structures of transition state of chain transfer reaction; 9-Me, 9-^{t}Bu and 9-^{i}Pr$_3$Si are shown in Fig. 10. The structures of ethyl propylene complexes, 10-Me, 10-^{t}Bu and 10-^{i}Pr$_3$Si, are products of chain transfer reaction to monomer (Fig. 11). Their main geometrical parameters are summarized in Table 5.

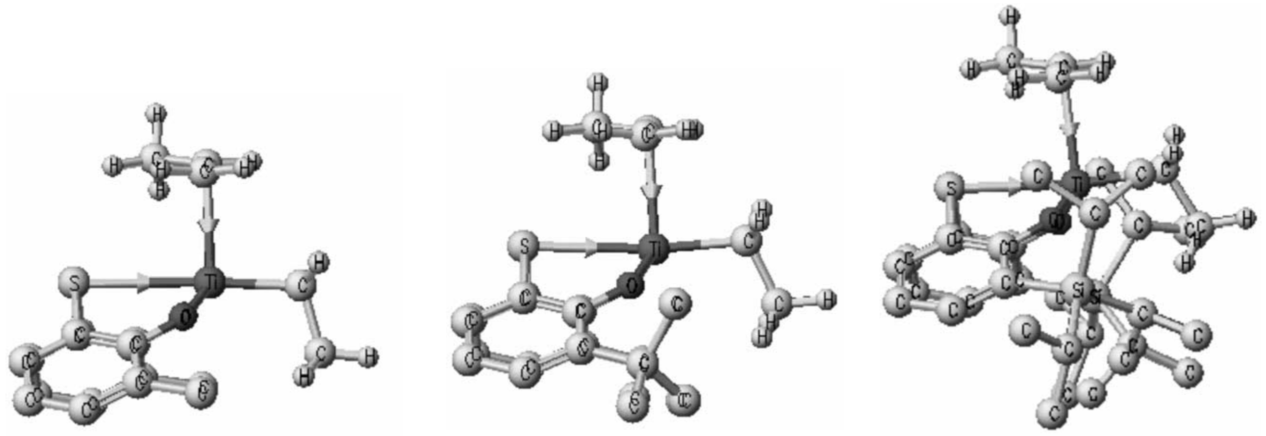
3.2.2.1. Propyl ethylene π-complex. There is no agostic interaction in these models, 8-Me, 8-^{t}Bu and 8-^{i}Pr$_3$Si. Also, the geometrical parameters of these models are not largely different from those of methyl ethylene π-complexes 2-Me, 2-^{t}Bu and 2-^{i}Pr$_3$Si. The ethylene coordination energy values based on propyl complexes (γ-H agostic) are 19–20 kcal mol^{-1} at the RHF/DZ level, and smaller by about 3–6 kcal mol^{-1} than those of methyl ethylene π-complexes. The energy differences seem to be due to the stabilization by the agostic interaction of propyl complex.

3.2.2.2. Transition state of chain transfer reaction. At the transition state, 9-Me, 9-^{t}Bu and 9-^{i}Pr$_3$Si show six-membered-ring structures. The distances between Ti and S of these models are slightly different by 0.05 Å among these three transition models. While, the C(α)–C(β) bond length is 1.50 Å in all cases and the C(α′)–C(β′) bond length is stretched to 1.48 Å compared with the normal CC double bond length, nearly equal to the standard CC single bond length, and longer than that in



9-Me **9-tBu** **9-iPr$_3$Si**

Fig. 10. Transition state structures of β-H transfer reaction to monomer of $S(C_6H_3RO)_2TiC_3H_7^+(C_2H_4)$ complex at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)



10-Me **10-tBu** **10-iPr$_3$Si**

Fig. 11. Optimized structures of $S(C_6H_3RO)_2TiC_2H_5^+(C_3H_6)$ from of β-H transfer reaction to monomer at the RHF/DZ level. (Hydrogen atoms of ligands are not shown for clarity.)

the case of the transition state of ethylene insertion into a Ti–C bond mentioned above.

3.2.2.3. Propylene ethyl π-complex. The agostic interaction between the ethyl group and titanium atom is not shown in all three models, 10-Me, 10-^{t}Bu and 10-^{i}Pr$_3$Si. The distance of Ti–C(α) is longer than that of Ti–C(β) in all cases. Such inclination of propylene coordinated structure has been obtained in propylene hydride complexes as mentioned above and has reported in the analysis on propylene methyltitaniumdichloride complex [18]. According to the report [18], the main reason about the inclination of propylene coordination seems to be due to electronic effect.

3.2.2.4. Energy profiles and comparison with experimental molecular weight. In all cases, activation energy value of chain transfer reaction to monomer is larger by about 22 kcal mol^{-1} than that of the insertion reaction and larger by about 20 kcal mol^{-1} than that of β-H elimination reaction at the RHF/DZ level as shown in Table 6. Such high activation energy value is sufficient to maintain high molecular weight of polymer. However, the order of these activation values is not in correspondence with the tendency of the experimental data. The activation energy values calculated at the B3LYP/LANL2DZ//RHF/DZ level also did not agree with the experimental data. Chain transfer reaction as well as β-H elimination reaction is not the major factor of controlling the molecular weight of polyethylene. Accordingly, we propose that the activation energy of olefin insertion reaction contributes to the determination of the molecular weight of polyethylene obtained with these thiobisphenoxytitanium complex. In other words, the low activation barrier of insertion reaction due to the substituents of thiobisphenoxytitanium complex leads to increasing the reaction rate of ethylene insertion and gives consequently higher molecular weight polyethylene.

4. Summary

The energy profiles of ethylene insertion reaction at the RHF/DZ and B3LYP/DZ//RHF/DZ levels were in good correspondence with the experimental activity data. Although the bulkiness of ortho-substituents of thiobisphenoxy ligand does not influence the geometrical parameters seriously, the bulky substituents induce the decrease of the activation energy of the olefin insertion reaction with these thiobisphenoxytitanium complex catalysts. While, the energy profiles of the β-H elimination reaction and that of the chain transfer reaction to monomer were not in correspondence with the tendency of experimental molecular data. From these results, it is concluded that the activation energy of insertion reaction affects not only the polymerization reaction but the molecular weight of polyethylene in the case of thiobisphenoxytitanium complex catalyst.

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