



Theoretical studies on the role of bridging group of CGC type ligands for the Ziegler–Natta catalysis

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ABSTRACT

The potential energy surfaces of the initial reactions of ethylene polymerization with the Ziegler–Natta catalysis related to the constrained geometric catalysts (CGCs) were studied by the B3LYP density functional method. Three metals (Ti, Zr, and Hf) in the Ziegler–Natta catalysis and eight bridging groups (BH, CH₂, NH, O, AlH, SiH₂, PH, and S) between cyclopentadienyl (Cp) and NH ligands were treated. The reaction occurs through two steps as that of Kaminsky type: the first step produces the complex without a barrier and the second is the insertion of ethylene into the metal–carbon bond through the transition state. The complex formation energy for each metal system correlates linearly to the electronegativity of the bridging atom for each row atom of the periodic table except for those of the BH-bridging systems. The energies of the reactions for the BH-bridging systems could be explained with the through-bond model as the reactions of ansa-metallocenes and the π back-donation of B=N double bond.

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1. Introduction

The Ziegler–Natta catalysis polymerization is one of the most important industrial polymerization reactions, and many experimental studies have been reported. Since Kaminsky and co-workers [1,2] discovered metallocenes bridging with Si atom between ligands as cyclopentadienyl (Cp) for the catalysis of polymerization in 1980, ansa-metallocenes of the early transition metals have attracted attention for homogeneous catalysis. Recently, the reactivity and the structures of ansa-metallocenes with several bridging atoms or groups were studied experimentally [3–14]. In our previous paper [15], the structures and the energies of the initial reaction of ethylene polymerization for the Ziegler–Natta catalysis with eight bridging groups of Cp ligands were studied by an ab initio MO and a density functional method. We pointed out two effects of the bridging groups for the energy of the reaction: one is the geometrical hindrance as the tilt angle and the other is the bond interaction. The former can be also explained with the electronegativity of the bridging group or atom. The latter comes from the orbital interaction through bonds as shown in the BH-bridging system.

On the other hand, Canich [16] proposed new type Ziegler–Natta catalysis, constrained geometric catalysis (CGC), which is changed one ligand as Cp for Kaminsky type catalysis to amino group. It is well known that the CGC produces a good stereo specific polymerization. Namely the space of one side of ligands becomes free.

It is important to find the role of the bridging group of ligands for the reaction of the CGC type of the Ziegler–Natta catalysis.

In this, the potential energies and geometrical characters for the initial reaction of ethylene polymerization of the CGC type including Ti, Zr, and Hf atoms and eight bridging groups have been reported systematically.

2. Calculation methods

All equilibrium- and transition state geometries were determined by the analytically calculated energy gradients with the B3LYP density functional method [17,18]. The stationary points were identified as the equilibrium or the saddle point by examining the calculated normal vibrational frequencies. The force-constant matrix that is, the vibrational frequencies were calculated by analytical second derivative procedures [19,20]. The basis sets of CEP-121G [21–23] for transition metal atoms and 6-31G(d,p) [24–33] for other atoms were used. The density functional calculations were carried out by GAUSSIAN 03 program package [34].

3. Results and discussion

3.1. Geometry of catalysis

The compounds of [XCp(NH)MCH₃]⁺ were used as a catalysis model of the CGC: M = Ti, Zr, and Hf; X = BH, CH₂, NH, O, AlH, SiH₂, PH, and S. Two type structures were obtained for [XCp(NH)MCH₃]⁺. The structures can be distinguished between

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linear- and bent-type for X–M–CH₃ angle as shown in Fig. 1. The X–M–CH₃ angles of the linear- and bent-type structures and the energy difference between two structures are listed in Table 1. The value of $\Delta E(L-B)$ in the table indicates the energy difference between the linear- and the bent-type structures, and the positive value means the bent-type structure is more stable than the linear-type one. Although the bent-type structures of the CGC of Ti-metal are almost equal energetically to the linear-types for each bridging system, the bent-type structures of Zr-metal are more stable in energy than the linear-types. For the CGC including Hf atom, only bent-type structures were found. The stable bent-type structures of the CGC including Zr and Hf atoms probably comes from the hybridization of d, s and p orbitals of the metals, because the difference between d and s or p orbital energy levels of Ti atom is larger than those of Zr and Hf atoms. The CGC of three metals (Ti, Zr and Hf) with BH-bridging group were found in only bent-type structure. For AlH-bridging systems, the linear-type structure was found in only for Ti-metal system and not for Zr- and Hf-metal systems. This probably corresponds to the electronegativity of the bridging atom, because the hybridization depends on the intensity of the potential field by ligands.

3.2. Potential energy

The relative energies at the stationary points of the reaction of ethylene and the CGC are listed in Table 2. To compute the relative energies from the stationary points of the reactions, the energies of the reactants of the bent-type structures for Zr- and Hf-metal systems were used, and the bent-type structures for the second-row bridging systems of Ti-metal system and the linear-type structures for the first-row bridging systems with Ti-metal were also used. The “Barrier” in the table indicates the energy barrier height at the transition state from the complex. The reaction occurs through two steps. The first step is the complex formation without an energy barrier, and the second is the ethylene insertion into the M–CH₃ bond through a transition state. The activation energy at the transition state is a negative value. The complex formation energies against to the electronegativity of the bridging atoms are shown in Fig. 2. The complex formation energies for Hf-metal systems are more stable than those for Ti- and Zr-metal systems. This is similar to the complex formation energies for ansa-metallocenes. The complex formation energies relate linearly to the electronegativity of the bridging atoms for the first- and the second-row bridging systems of each transition metal atom, except for the BH-bridging systems. The deviation from the linear relation between the complex formation energy and the electronegativity of the bridging atom for the BH-bridging systems probably can be explained from two reasons. One is the orbital interaction

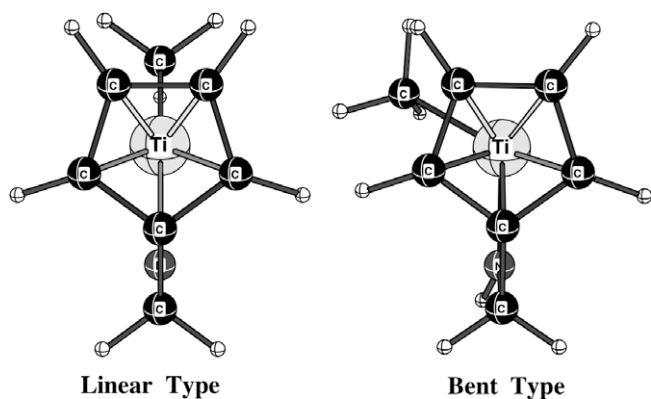


Fig. 1. Structure of the reactants.

Table 1

The angle of $\angle X-M-CH_3$ and the energy difference between linear- and bent-type for $[XCp(NH)MCH_3]^+$.

Metal (M)	Bridge (X)	$\angle X-M-CH_3$		$\Delta E(L-B)$
		Linear	Bent	
Ti	BH	–	110.4	–
	CH ₂	180.0	109.9	0.21
	NH	172.0	111.2	–0.85
	O	180.0	108.6	–0.03
	AlH	178.5	–	–
	SiH ₂	151.6	–	–
	PH	175.7	115.0	0.00
	S	174.3	–	–
Zr	BH	–	106.1	–
	CH ₂	180.0	103.2	2.82
	NH	172.0	106.0	2.10
	O	180.0	102.7	2.68
	AlH	–	104.6	–
	SiH ₂	163.7	103.8	2.96
	PH	167.4	105.5	3.07
	S	177.1	103.3	1.86
Hf	BH	–	107.7	–
	CH ₂	–	108.0	–
	NH	–	109.9	–
	O	–	107.3	–
	AlH	–	108.6	–
	SiH ₂	–	108.2	–
	PH	–	109.0	–
	S	–	108.8	–

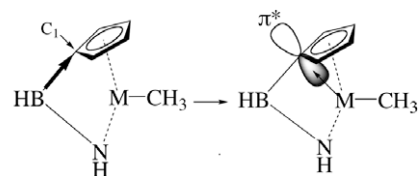
The units of $\angle X-M-CH_3$ and $\Delta E(L-B)$ are degree and kcal/mol, respectively.

Table 2

The relative energies of the reactions (kcal/mol).

Metal	Bridge	Complex	TS	Product	Barrier
Ti	BH	–27.35	–19.58	–35.33	7.77
	CH ₂	–25.96	–17.98	–32.91	7.98
	NH	–27.09	–18.86	–33.22	8.23
	O	–27.66	–19.44	–34.11	8.22
	AlH	–24.40	–16.88	–31.15	7.53
	SiH ₂	–25.44	–17.31	–32.16	8.14
	PH	–26.61	–17.98	–33.02	8.63
	S	–26.80	–17.65	–32.54	9.15
Zr	BH	–27.10	–16.59	–30.98	10.51
	CH ₂	–25.26	–15.97	–31.05	9.30
	NH	–25.94	–16.42	–30.30	9.51
	O	–26.48	–17.18	–30.92	9.26
	AlH	–25.88	–15.92	–29.60	9.97
	SiH ₂	–26.13	–16.20	–32.88	9.93
	PH	–26.26	–16.18	–30.09	10.08
	S	–27.04	–16.54	–31.52	10.50
Hf	BH	–30.03	–17.99	–30.33	12.04
	CH ₂	–28.23	–16.32	–30.18	11.91
	NH	–29.21	–16.75	–30.86	12.47
	O	–29.81	–17.69	–31.53	12.15
	AlH	–28.51	–16.66	–31.13	11.85
	SiH ₂	–28.86	–16.84	–32.15	12.03
	PH	–29.19	–16.34	–30.80	12.85
	S	–30.27	–16.69	–30.73	13.58

through the B–C bond as shown in the previous paper for ansa-metallocenes.



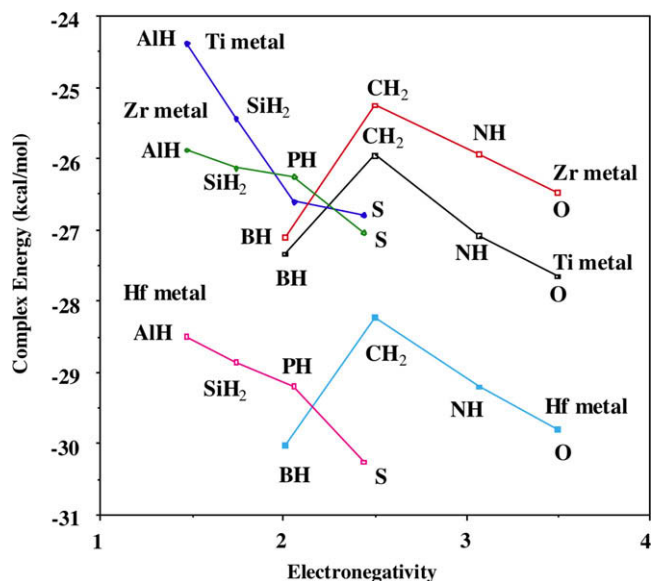


Fig. 2. The relation between complex formation energy and electronegativity of the bridging atoms.

Namely a boron atom has lower electronegativity than a carbon atom, and the electrons of B–C₁ (σ_{B-C}) bond in above model polarize to C₁ atom, C₁ (negative) and B (positive). Accordingly, the potential of C₁ (σ orbital) is more negative than other carbon atoms of Cp, and the π^* (p π) unoccupied orbital of Cp ligand expands much on C₁ atom. The expanded π^* (p π) orbital on C₁ atom interacts with d orbital of metal, because C₁ atom is the nearest one in Cp ligand from the metal atom. As the results, the orbital energy of unoccupied d orbital of metal becomes stable. The other reason is the double bond character between B and N atoms. Namely the lone pair orbital of N atom causes π back-donation to the vacant p π orbital of B atom. Then the π back-donation probably causes the electron movement from the metal atom.

The activation energies from the catalysis model plus ethylene for the electronegativity of the bridging atoms are also shown in Fig. 3. For each transition metal system, the activation energies

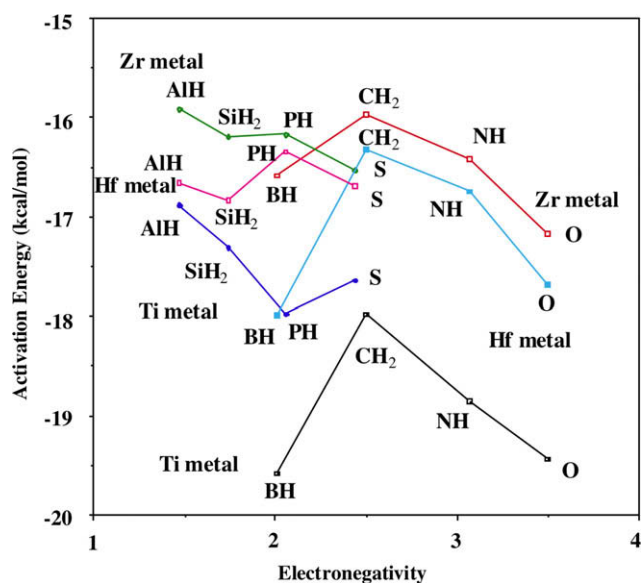


Fig. 3. The relation between activation energies and the electronegativity of the bridging atoms.

do not much change for the bridging systems of the second-row atoms. For the bridging systems of the first-row atoms, the energies correspond linearly to the electronegativity of the bridging atoms, except for the BH-bridging systems. This is similar to the relation of the complex formation energies and the electronegativity of the bridging atoms. Although the complex formation energies of Hf-metal systems are the lowest in the three metal systems for each bridging atom, the activation energies of Ti-metal systems are the lowest. The relation between the energy barriers and the electronegativity of the bridging atoms is shown in Fig. 4. For the bridging systems of the second-row atoms, the good linear relation between the energy barriers and the electronegativity can be obtained. For the bridging systems of the first-row atoms, the energy barriers are almost constant except for the BH-bridging system of Zr-metal. This means probably that the reaction with the lower complex formation energy occurs more favorable for the bridging systems of the first-row atoms.

3.3. Geometrical hindrance

To study the relation between the geometrical parameters of the reactants and the reactivity, some geometrical parameters of $[XCp(NH)MCH_3]^+$ were obtained. Although, the tilt angle for ansa-metalloenes was defined that for the CGC is not defined. Therefore, the tilt angle for the CGC is defined here as shown in Fig. 5. In the first, the crossing point between the line from the center (Y) of Cp ring along the plane of Cp and the line of the half divided angle for N–M–Y is defined as a point A. Then the angle of N–A–Y is called as the tilt angle for the CGC. The tilt angle was used for the following discussion of the reactivity and/or the complex stabilization of the catalysis. The relation between the tilt angles and the electronegativity of the bridging atoms is shown in Fig. 6. The tilt angles correlate to the electronegativity of the first- and the second-row bridging atoms for each transition metal, except for the BH-bridging systems. This indicates that the BH-bridging systems are not considered as the same type influence to the steric hindrance by the electronegativity in the case of other bridging systems. For the BH-bridging systems, the B–N bond became shorter than the usual single bond of B–N by the π back-donation. Consequently the tilt angles of the BH systems are calculated as narrow. The relation between the complex formation energies

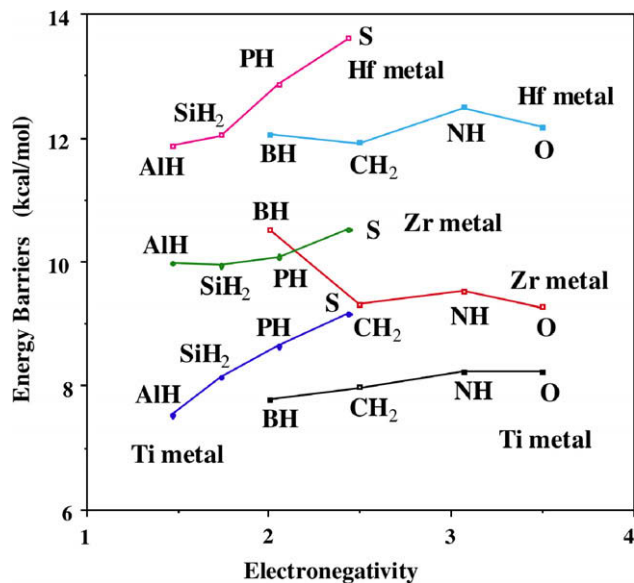


Fig. 4. The relation between the energy barriers and electronegativity of the bridging atoms.

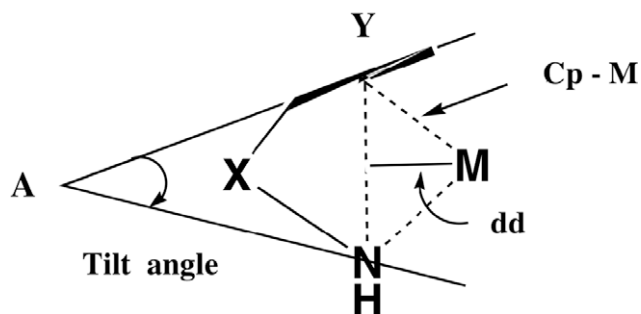


Fig. 5. Structural parameters of the CGC model.

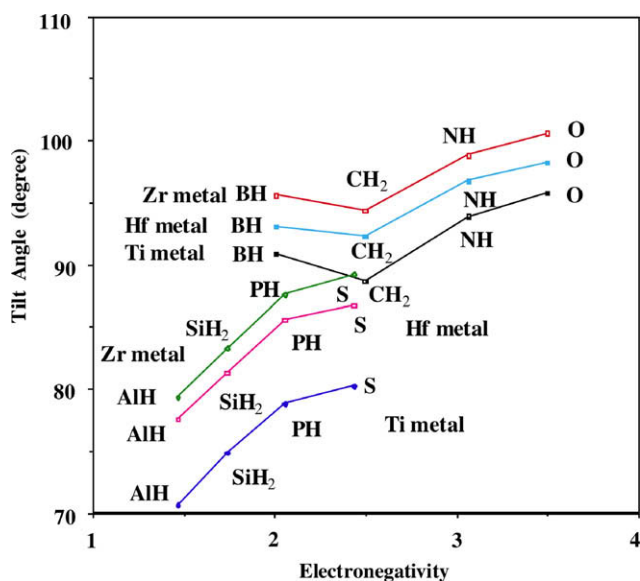


Fig. 6. The relation between the tilt angles and the electronegativity of the bridging atoms.

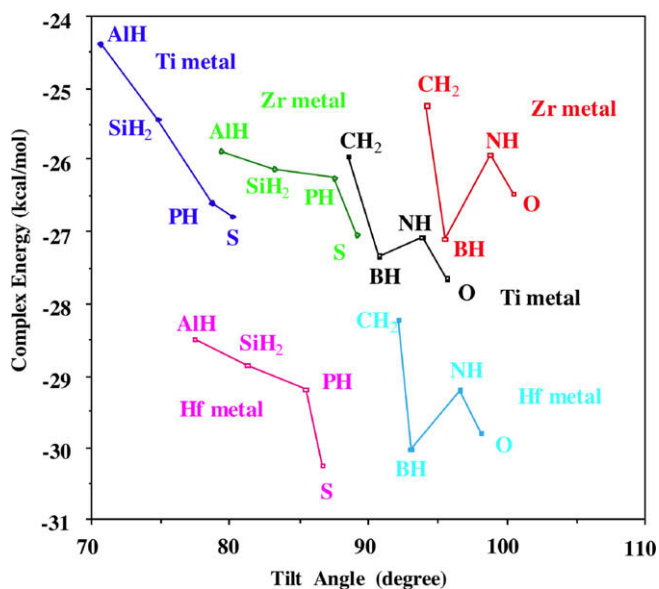


Fig. 7. The relation between the complex formation energies and the tilt angles.

and the tilt angles is shown in Fig. 7. The complex formation energies for each metal system correlate to the tilt angles for the

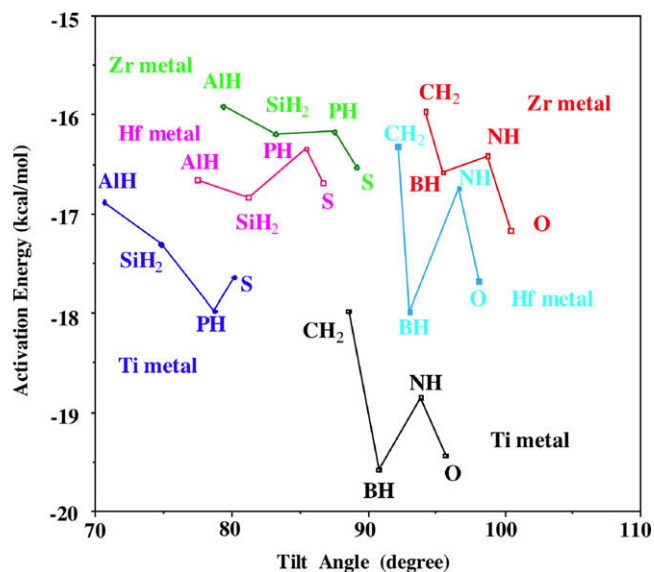


Fig. 8. The relation between the activation energies and the tilt angles.

bridging systems of the first- and the second-row atoms, except for the BH-bridging systems. The linearity of the relation is much poor than that of ansa-metalloenes in the previous paper [15]. The relation between the activation energies and the tilt angles is also shown in Fig. 8. For the bridging systems of the second-row atoms, the difference of the activation energies is not much. For the bridging systems of the first-row atoms, the linear relation between the activation energies and the tilt angles can be seen, except for the BH-bridging systems. The relation between the complex formation energies and the tilt angles (dose not show in here). The tilt angle and dd are the steric hindrance for the insertion of ethylene to the space of the complex. From above results, the stabilization of the complex and the reactivity for the BH-bridging systems does not relate to the steric hindrance, and probably comes from the electronic effects as described in the previous section. Namely the “through-bond model” for the B-bridging systems indicates the stabilization of unoccupied d orbitals of metal through the interaction of the expanded $\pi^*(p\pi)$ orbital on C₁ atom and d orbital of metal. Also the π back-donation from N atom to B atom probably cause the more positive charge on the metal atoms, although we did not show the electronic charge because of the basis sets dependency. The lowest unoccupied molecular orbital (LUMO) energy and the C₁-M distances of the reactants catalysis are listed in Table 3. The LUMO energies of the BH-bridging systems of each metal system are the lowest in the bridging systems of the first-row atoms. The C₁-M distances of the BH-bridging systems are the shortest in those of each metal system. These correspond to the through-bond model, and can be explained the

Table 3
The LUMO energy (a.u.) and C₁-M distance (Å).

Bridge	LUMO (a.u.)			C ₁ -M (Å)		
	Ti	Zr	Hf	Ti	Zr	Hf
BH	-0.280	-0.263	-0.269	2.205	2.365	2.350
CH ₂	-0.269	-0.250	-0.258	2.258	2.401	2.389
NH	-0.268	-0.251	-0.260	2.233	2.379	2.366
O	-0.276	-0.257	-0.267	2.228	2.374	2.365
AIH	-0.281	-0.255	-0.261	2.312	2.458	2.441
SiH ₂	-0.286	-0.258	-0.264	2.302	2.442	2.427
PH	-0.288	-0.257	-0.264	2.295	2.414	2.400
S	-0.287	-0.251	-0.267	2.334	2.423	2.412

deviation of the BH-bridging systems from the linear relations of the complex formation energies or the activation energies against the electronegativity of the bridging atoms or geometrical parameters.

From above results, the reactivity as the complex formation energy and/or the activation energies could be explained by two effects: the electronegativity of the bridging atoms and the orbital interaction between C_1 atom of Cp and d orbital of metal atom.

4. Conclusion

The initial reaction mechanisms of ethylene polymerization with the CGC model by incorporation of bridging atom or group for the Ziegler–Natta catalysis were studied by the B3LYP density functional method. The potential energies and the geometrical parameters of the stationary points of the insertion reaction of ethylene with the CGC type Ziegler–Natta catalysis including eight bridging atoms between Cp and NH ligands were calculated. For the reactants of the catalytic model, two-type structures, linear- and bent-type, for $X-M-CH_3$ were found. The linear-type structures for Ti-metal systems are almost equal in energy to the bent-type structures. For Zr-metal systems, the bent-type systems are more stable than the linear-type for each bridging system. The linear-type for Hf-metal system could not be found. These structures come from the hybridization of d, s and p orbital of metal atom. Although the complex formation energies of the bridging systems of the first-row atoms are larger than those of the bridging systems of the second-row atoms for ansa-metallocenes, the complex formation energies for the CGC type are almost the same for the bridging systems of the first- and the second-row atoms. The formation energies of the complex between ethylene and the CGC model by incorporation of bridging of oxygen and boron atoms are much stable in energy for each metal catalysis. The energy barriers at the transition states from the reactants indicate negative values for all systems.

For geometrical hindrance, the tilt angle of the reactant relates linearly to the complex formation energy for each transition metal, except for the BH-bridging systems. For the BH-bridging systems, the complex formation energies can be explained by the orbital interaction of C_1 and d orbital of metal atom through the polarization of the C_1-B σ bond. This orbital interaction effect is similar to that of ansa-metallocenes. The deviation of the relationship between the energies and electronegativity for the BH-bridging systems can be also explained by the π back-donation from N atom to B atom.

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