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Influence of the ligand structure of hafnocene polymerization catalysts: A theoretical study on chain termination reactions in ethene polymerization

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ABSTRACT

Ligand effects on chain termination reactions in hafnocene-catalyzed ethene polymerization process have been systematically studied by quantum chemical methods. β-hydrogen transfer to metal, β-hydrogen transfer to monomer and hydrogenolysis were studied for 27 hafnocenes, initiating the chain termination reactions after insertion of the second ethene monomer. The results of the calculations were studied as a function of the ligand structure, focusing on the effects of various ancillary ligands, ligand substituents and bridging units. The ligand effects on chain termination reactions are strongly affected by combined effects of various structural units, in particular, in the cases of β-hydrogen transfer to monomer and hydrogenolysis. The results are expected to aid in design and development of new hafnocene polymerization catalysts.

1. Introduction

Group 4 metallocenes are ubiquitous pre-catalysts in the polymerization of α-olefins. Once activated with the appropriate cocatalyst the single-site nature of these catalytically active systems basically enables rational tailoring of the polymer product. A considerable number of properties of the produced polymers are a function the length of the polymer chain, which is determined by relative rates of olefin insertion and chain termination reactions. Concerning polymerization of ethene, there are four main chain termination processes: (1) β-hydrogen transfer to metal, (2) β-hydrogen transfer to monomer, (3) hydrogenolysis and (4) chain transfer to aluminum [1].

Amongst the group 4 metallocenes, zirconocenes stand out as the most studied species. Nevertheless, hafnocenes hold the promise in further catalyst development, particularly since they have been shown to produce higher molecular weight polymers than their corresponding zirconocene analogues [2]. Zirconocenes and hafnocenes are structurally nearly equal, which is due to the same size of the atom radii [3]. Hence, the reasons behind the different behaviors of the two catalyst families are not evident, however it has been postulated to originate from stronger metal–ligand bonds in hafnocenes [4]. From the point of view of reaction mechanisms, little is known about chain termination reactions in hafnocene-catalyzed olefin polymerization, with previous theoretical studies focusing on zirconocenes. The main emphasis of these studies been on the β-hydrogen transfer [5], hydrogenolysis [6], the latter commonly used in industry to control the molecular weight of the polymer product, having received much less attention (see Scheme 1). Studies on the fourth chain termination process, chain transfer to aluminum, are complicated by the difficult theoretical treatment of trimethylaluminium [7] together with the unknown structure of methylaluminoxane (MAO) cocatalyst, which therefore has been excluded from the optimizations and also no scavenger agent has been considered [8].

In the theoretical study reported herein, the focus is on the influence of the ligand structure of hafnocene catalysts on chain termination reactions in polymerization of ethene. The feasibility of three chain termination processes, namely β-hydrogen transfer to metal, β-hydrogen transfer to monomer and hydrogenolysis, is studied for altogether 27 hafnocenes. The effects of structural modifications are systematically analyzed as functions of ancillary ligands, ligand substituents and bridging units between the ancillary ligands, to clarify the role of the ligand structure on chain termination reactions.

2. Computational methods

All calculations were performed by the hybrid density functional B3LYP method [9]. The method has been shown to perform well for zirconocenes in studies of chain growth and termination

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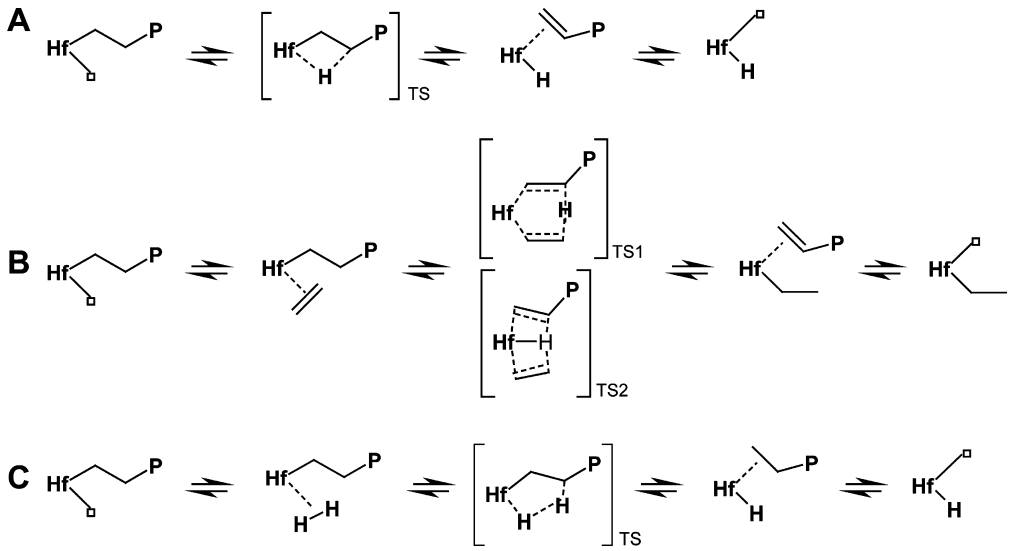

Scheme 1. Three reaction mechanisms for chain termination: (A) β-hydrogen transfer to metal, (B) β-hydrogen transfer to monomer and (C) hydrogenolysis.

reactions [5h]. For hafnium, Los Alamos ECP [10] (LANL2DZ) was employed, while the standard 6-31G* basis set was employed for all other elements. The B3LYP/LANL2DZ 6-31G* level of theory has been previously demonstrated to produce reliable structures for hafnocenes [11]. All hafnocenes were fully optimized without any constraints. Harmonic frequencies [12] were calculated for all structures to obtain zero-point energy corrections to the electronic energies, and to verify the correctness of the transition states. The calculations were carried out with the GAUSSIAN 03 program package [13].

3. Results and discussion

3.1. Choice of the hafnocenes

The studied dataset of catalysts, from herein referred to as the "Hf-set", contains altogether 27 hafnocenes. The "Hf-set" fulfills the following structural criteria: (a) exactly one Hf atom, (b) two monoionic "cyclopentadienyl" ligands (c) two chlorines as leaving groups and (d) no other transition metals than Hf. The "Hf-set" is comprised of two groups of hafnocenes: (1) crystallographically characterized hafnocenes (D1–D12 in Fig. 1) [11], which include a variety of structural units typical for metallocenes, and (2) additional hafnocenes (H1–H15 in Fig. 1), for which crystal structures are not available. Inclusion of the additional set enables direct comparison between a variety of structural modifications. The "Hf-set" includes a variety of catalyst complexes with widely different steric and electronic properties due to the ligand framework, thereby being useful for a comparative study reported below. The members of the "Hf-set" have been included in previous studies on the energetics of activation and chain propagation steps [14].

3.2. Catalytic intermediates along the chain termination paths

The studied termination processes, β-hydrogen transfer to metal (BHTme), β-hydrogen transfer to monomer (BHTmo) and hydrogenolysis (HG), were considered to start from a chain propagation product with a β-agostic polymeryl chain (pentyl, Fig. 2a), a conformation which is generally considered the most stable [15]. The BHTme takes place through a direct transfer of the β-hydrogen of the growing polymer chain to the metal center [5]. The transition state for BHTme is shown in Fig. 2b, and the product in Fig. 2c. After the reaction has taken place, the product (2c) may go through ejection of the vinylene. In the case of pentene, the ejection is highly endothermic, in average by 63.9 kJ/mol for the "Hf-set", which has been also noted in previous theoretical studies on zirconocenes [5f,g]. The resulting "naked" hydride is unstable, in average lying 54 kJ/mol higher than the preceding transition state, and is likely to not exist as such in the real polymerization process. Furthermore, isomerization of the polymer chain and reaction with another monomer to produce *trans*-vinylene has also been considered as a possibility [5f,16]. The subsequent reactions are not considered in this context.

Concerning BHTmo, a π-complex (Fig. 2d) is formed prior to the transition state. We have studied two transition states. The transition state reported by Talarico et al. for the case of propene polymerization (Fig. 2e) [17], requires less space around the metal than the typically investigated one (Fig. 2f) [5c–i]. Since the steric requirements are much lower for ethene polymerization than for polymerization of higher α-olefins, the latter transition state (2f) is favored in this context, by 13.8 kJ/mol in average for the "Hf-set". There are two exceptions, namely catalysts D11 and H7, favoring the transition state (2e), which is supported by the conclusions of Talarico and Budzelaar for hafnocenes with crowded center [18]. The termination product (2g) has an ethyl chain together with pentene attached to the metal. No agostic interactions are present in this stage. After ejection of pentene from the catalyst, β-agostic interaction from the remaining ethyl chain stabilizes the cation. This makes ejection of pentene usually endothermic, in average by 19.2 kJ/mol for the "Hf-set". The resulting ethyl product from which the pentene has been ejected, lies in average 69 kJ/mol below the preceding transition state. Note that the product of BHTme, the "naked" hydride lies 54 kJ/mol above the preceding transition state. The difference in the stability of the products (naked hydride for BHTme and ethyl product for BHTmo) is largely due to stabilizing agostic interactions from the ethyl chain.

The HG mechanism has been previously studied for zirconocenes [6], with the backside approach mechanism turning out to be the preferred mechanism. Coordination of H_2 to the metal center, with β-agostic interaction from the alkyl chain (Fig. 2h), is followed by a β-agostic transition state (Fig. 2i). The α-agostic transition state, which is formed from the front side insertion, was also considered for two hafnocenes, D1 and D12, β being favored over α by 22.1 and 11.1 kJ/mol, respectively. The product

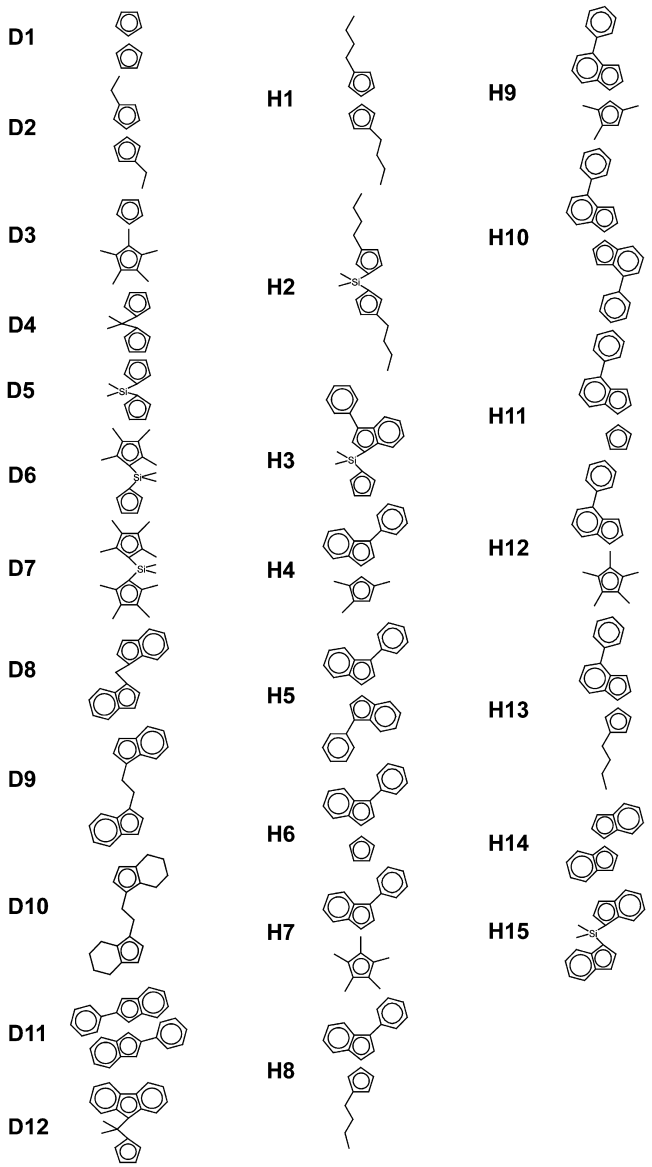

Fig. 1. Schematic ligand structures of the studied hafnocenes.

of HG (Fig. 2j) shows Hf–H interactions between the metal center and the pentane product. Ejection of pentane is usually endothermic, on average by 19.3 kJ/mol. The relative energy of the resulting "naked" hydride is in average 44 kJ/mol lower than for the preceding TS.

The energetics along the chain termination reaction pathways (Fig. 2a–j) are listed in Table 1 for the "Hf-set", from which the main features have been summarized to Table 2. Relative energies (ΔE) reported in the tables represent energy differences from the catalytic complexes to the sum of the energies of the free catalyst with β-agostic pentyl chain and free H_2, ethene, pentene and pentane molecules. In this context, the hafnocene D1 with β-agostic pentyl chain is set as a reference structure ($\Delta E = 0$) for the other ligand structures to be compared with.

3.3. Comparison of the hafnocenes

The ligand effects of hafnocenes for activation and propagation steps have been studied and analyzed for the "Hf-set" in preceding papers [14]. In Fig. 3, a detailed comparison of the three termination processes is shown for four catalysts as an example. These are D1, H14, D2 and D5 (see Fig. 1), which are select to be able to directly compare the structural modifications of changing the ancillary cyclopentadienyl (Cp) ligand to indenyl (Ind) (D1 versus H14), adding an alkyl substituent to the Cp ligand (D1 versus D2), and adding a $SiMe_2$ bridge (D1 versus D5). The comparison of each termination process begins from the β-agostic pentyl complex (a in Fig. 2). The left column in Fig. 3 shows the relative energies for the reaction pathway of BHTme, the middle column for BHTmo, and the right column for HG.

The starting point, β-agostic pentyl complex (a), is stabilized by large aromatic ligands and electron donating substituents. Hence, H14 with indenyl ligand lies lowest in energy. Moving to the transition state for BHTme (b), the energy differences get slightly smaller. The order of relative stabilities stays the same, the activation barrier is marginally higher for catalysts with bulkier ligands, which is due to steric hindrance, the activation energies increasing in the order D1 < D5 < D2 < H14. The products of BHTme (c) follow the same trends.

Concerning BHTmo, the feasibility for the formation of the π-complex (d) is improved by addition of a $SiMe_2$ bridge (D5), whereas the effect of adding ligand substituent (D2) or changing Cp to indenyl (H14) is reverse. On one hand, this is due to increased steric crowding in D2 and H14, and on the other hand, due to the wider Cp–Cp plane angle of D5, induced by the bridge. The relative stability of transition state is almost the same for D1, D2, and D5, while clearly higher for H14. The height of the activation barrier (f) is not influenced by change in ligand or ligand substituent. Instead, addition of a bridge increases the barrier due to the high relative stability of the preceding π-complex. The relative stabilities of the products (g) are in line with the relative stabilities of the transition states.

Comparison between BHTme and BHTmo reveals that, in each case, the relative energies are lower for the BHTmo than the BHTme transition state, by 1.1–14.8 kJ/mol. With respect to the plain Cp ligand (D1), the BHTmo TS is hindered by addition of a ligand substituent (D2) or by changing the ligand to indenyl (H14), both catalysts having almost the same relative stabilities in the transition states, whereas addition of a bridge (D5) facilitates the BHTmo TS.

With respect to the unsubstituted Cp complex (D1), coordination of H_2 in HG (h) is slightly hindered by addition of a substituent to the Cp ligand (D2) or by changing Cp to Ind (H14), which is apparently due to steric effects. Addition of a bridge (D5) has practically no influence. The relative energy is highest for D5 in the TS, reversing the order of the catalysts in the hydrogenolysis. D2 and H14 have increased energies relative to the unsubstituted Cp (D1). The relative stabilities of the products (j) are in line with the relative stabilities of the transition states.

The chain termination reactions studied for the "Hf-set" enable a similar comparison for a larger number of structural variables. In the following, the behaviors of the catalysts are analyzed to single out the effects of various bridging units, ancillary Cp ligands and ligand substituents. The analysis is based on the data given in Table 1. Graphical illustrations of the energetics along the chain termination pathways, like the one shown in Fig. 3, are given in Appendix 1 for each comparison.

3.3.1. The effect of bridge

The influence of adding a bridge between the ancillary Cp′ ligands can be clarified by comparing D1 to D4 and D5, H14 to D8, D9 and H15, H1 to H2, and H6 to H3. Bridges with Cp ligands slightly increase the relative energy of TS in BHTme. In BHTmo, the formation of π-complex is facilitated by addition of a bridge. The effects is strongest with short bridges due to opening of the Cp′–Cp′ plane angle. Addition of a bridge usually increases the

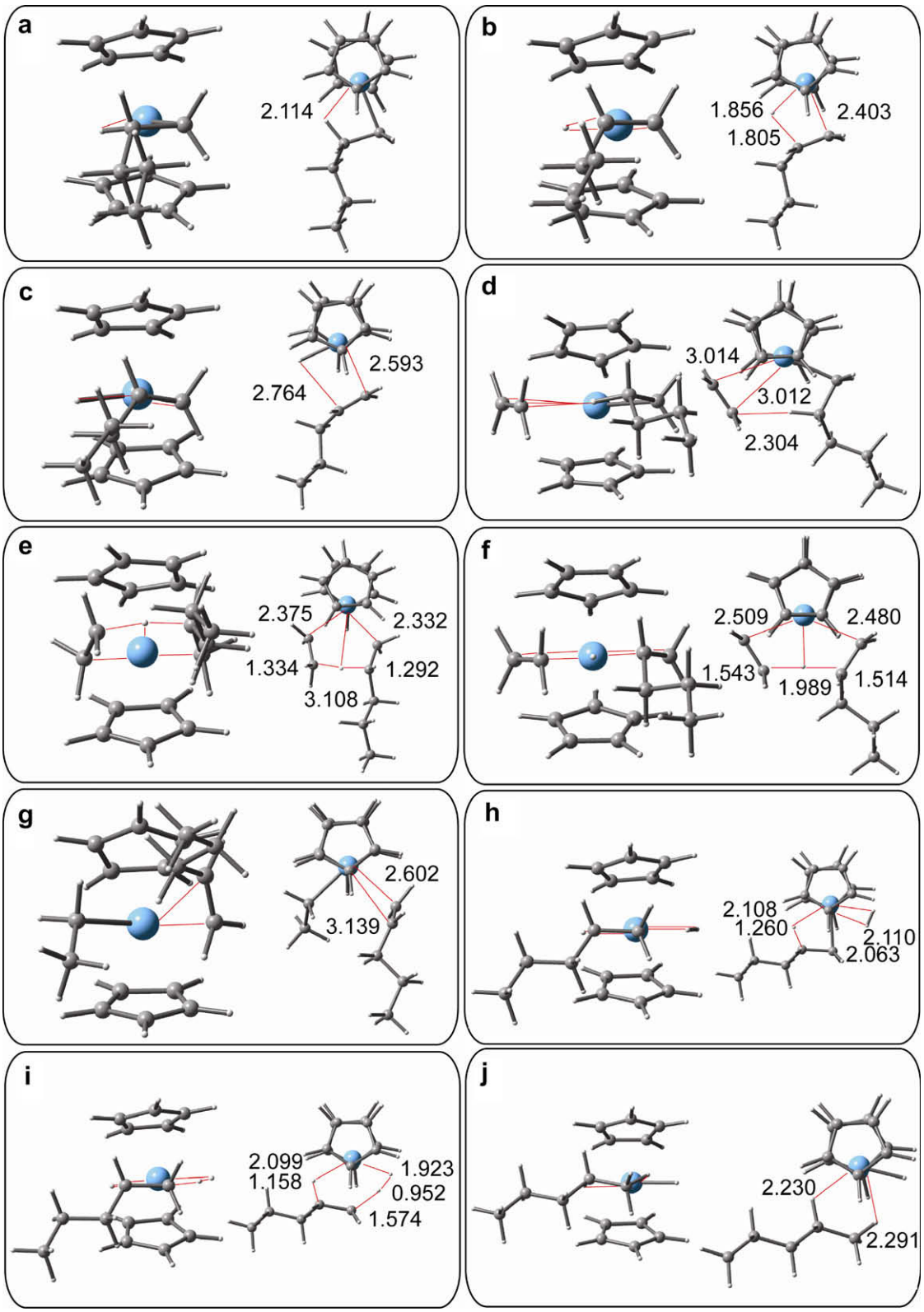

Fig. 2. Front and top views of the studied models of TS and products for catalyst D1 (see Figure ure1): (a) β-agostic pentyl product, (b) transition state for BHTme, (c) product of BHTme, (d) π-complex for BHTmo, (e) transition state 1 for BHTmo, (f) transition state 2 for product of BHTmo, (g) coordinated H_2 for HG, (h) β-agostic transition state for HG and (i) product of HG. The bond lengths are reported in Ångströms.

height of the activation barrier for BHTmo. This is with the exception of electron donating substituents (H2 and H3) which decrease the activation barrier, and also lower the relative energy of TS. Nevertheless, the changes in energies are small.

Comparing BHTme and BHTmo, the transition state of BHTmo is more stable for all bridged catalysts compared to BHTme. The addition of a bridge, a short one in particular, favors the formation of BHTmo TS, which is due to the more open reaction center.

Table 1
Relative energies (kJ/mol)[a] for the catalytic intermediates along the chain termination paths for the "Hf-set".

Hafnocene	β-agostic pentyl product (a)	β-H transfer to metal TS (b)	β-H transfer to metal product (c)	β-H transfer to monomer π-complex (d)	β-H transfer to monomer TS (e)	β-H transfer to monomer TS (f)	β-H transfer to monomer product (g)	Hydrogenolysis π-complex (h)	Hydrogenolysis TS (i)	Hydrogenolysis product (j)
D1	0.0	32.5	20.2	−19.1	46.5	22.8	−61.9	2.3	9.5	−50.4
D2	−14.1	23.1	11.9	−21.6	41.9	20.6	−66.1	−7.4	5.1	−57.6
D3	−20.5	19.6	12.7	−16.0	49.7	36.5	−60.5	−10.6	5.6	−61.3
D4	14.0	48.4	32.2	−23.9	51.4	25.1	−61.0	9.7	24.1	−39.9
D5	−1.9	34.7	23.1	−29.6	43.9	20.0	−63.7	−1.2	11.5	−49.4
D6	−10.7	29.1	17.6	−23.7	49.2	25.7	−61.3	−5.3	8.0	−53.8
D7	−12.7	30.4	15.4	−10.0	50.6	37.9	−41.4	1.3	13.2	−55.4
D8	−11.1	28.7	12.8	−37.7	31.7	8.1	−61.7	7.6	21.2	−49.4
D9	−34.6	6.4	−3.9	−44.9	20.2	6.0	−82.1	−2.8	6.7	−72.0
D10	−16.2	25.9	15.1	−10.4	47.6	38.3	−40.5	−6.7	5.8	−58.9
D11	−76.8	−27.4	−30.9	−54.1	−2.4	0.6	−96.0	−46.4	−32.3	−93.2
D12	−21.5	17.7	7.9	−41.4	25.5	11.4	−82.9	−0.4	13.5	−59.7
H1	−18.7	18.4	10.9	−27.7	40.8	28.6	−64.8	−10.8	−1.6	−62.3
H2	−14.0	26.1	14.9	−30.8	42.7	10.2	−67.1	−10.8	2.3	−58.1
H3	−24.8	16.1	7.8	−42.1	26.6	4.4	−80.7	−12.3	−0.3	−60.2
H4	−33.1	5.7	−4.7	−10.1	40.1	33.9	−51.5	−17.4	−7.2	−69.2
H5	−42.0	2.2	−5.2	−35.2	23.8	12.7	−66.4	−19.6	−0.5	−67.0
H6	−23.4	11.2	2.2	−22.3	38.9	27.3	−74.6	−4.3	5.2	−52.0
H7	−31.5	12.4	−4.1	−17.5	34.2	36.6	−49.8	−2.6	2.6	−69.6
H8	−27.0	10.3	2.4	−24.0	36.9	36.6	−75.8	−8.3	4.2	−51.6
H9	−41.4	−0.6	−8.0	−9.6	30.0	17.9	−62.7	−29.6	−9.5	−62.2
H10	−50.7	−14.0	−25.6	−42.4	4.5	2.4	−101.1	−50.8	−27.9	−87.9
H11	−27.9	7.6	−1.2	−23.9	37.2	29.2	−73.6	−9.2	−1.2	−60.1
H12	−33.6	11.9	−3.4	−31.5	30.5	25.9	−53.6	−1.4	5.4	−66.2
H13	−39.7	−1.8	−6.8	−36.7	38.7	20.2	−77.2	−31.8	−13.3	−63.8
H14	−39.8	1.5	−8.3	−44.0	11.4	0.4	−87.7	−35.2	−20.5	−76.8
H15	−33.4	8.4	−0.7	−46.9	20.3	0.9	−84.7	−12.4	0.9	−68.1

[a] Relative energies (ΔE + ZPE) are energy differences from the catalytic intermediates to the sum of the energies of the free catalyst with β-agostic pentyl chain and free H_2, ethene, pentene and pentane molecules. The β-agostic pentyl complex of hafnocene D1 is set as a reference structure ($\Delta E = 0$).

Table 2
Summary of the chain terminations for the "Hf-set".[a]

	ΔE_{avg}	ΔE_{min}	ΔE_{max}
Formation of π-complex is favored in BHTmo	−3.3	−37.9	31.8
Formation of π-complex is unfavored in HG	13.7	−4.3	32.2
Coordination of ethene (BHTmo) is stronger than coordination of H_2 (HG)	−17.1	−45.3	20.1
Relative stability of BHTme TS	14.2	−27.4	48.4
Activation barrier for BHTme	39.7	32.5	49.9
Relative stability of BHTmo TS (e)	33.8	−2.4	51.4
Activation barrier for BHTmo (e)	62.6	39.6	75.4
Relative stability of BHTmo TS (f)	20.0	0.4	38.3
Activation barrier for BHTmo (f)	48.8	27.4	60.6
Relative stability of HG TS	1.1	−32.3	24.1
Activation barrier for HG	12.8	5.2	22.9
The (f) TS in BHTmo is favored over (e)	−13.8	−32.5	2.9
The BHTme TS lies lower in energy than the BHTmo TS	−5.6	−28.2	23.3
Activation barrier is lower for BHTme than for BHTmo	−9.1	−23.3	13.4
The HG TS lies lower in energy than the BHTmo TS	−18.9	−41.1	13.2
The β-agostic pentyl product is favored over BHTme products	−29.3	−45.9	−18.2
The BHTmo product is favored over β-agostic pentyl product	−43.1	−75.0	−18.3
The HG product is favored over β-agostic pentyl product	−36.6	−53.9	−16.4

[a] Relative energies are given in kJ/mol.

In HG, coordination of H_2 is complicated when a bridge is added to a hafnocene with indenyl ligands. Addition of a bridge between plain Cp ligands has practically no effect. A bridge between plain Cp-rings somewhat increase, while a bridge between indenyls somewhat decrease, the activation barrier for HG. Overall, the changes are small.

3.3.2. The effect of Cp ligand

The influence of the ancillary Cp′ ligand (Cp′ = any cyclopentadienyl-based ligand) is compared for cyclopentadienyl (Cp), indenyl (Ind), tetrahydroindenyl (H_4-Ind) and cyclopentadienyl-fluorenyl (CpFlu). The effect of changing Cp to the more electron-rich Ind can be figured out by comparing D1 with H14 and D5 with H15. The β-agostic pentyl complex is greatly stabilized by the indenyl ligand. Activation barrier for BHTme increases, when Cp is changed to Ind, and the relative energy of the TS is lower for the Ind. In BHTmo, the formation of the π-complex is more exothermic for Cp than for Ind. The barriers for activation, however, are practically equal. Relative to BHTme, the transition state for BHTmo lies lower in energy, the difference being smaller for Ind than for Cp.

Combined effects of ligands and bridges are evident, somewhat complicating the interpretation of the effect of structural

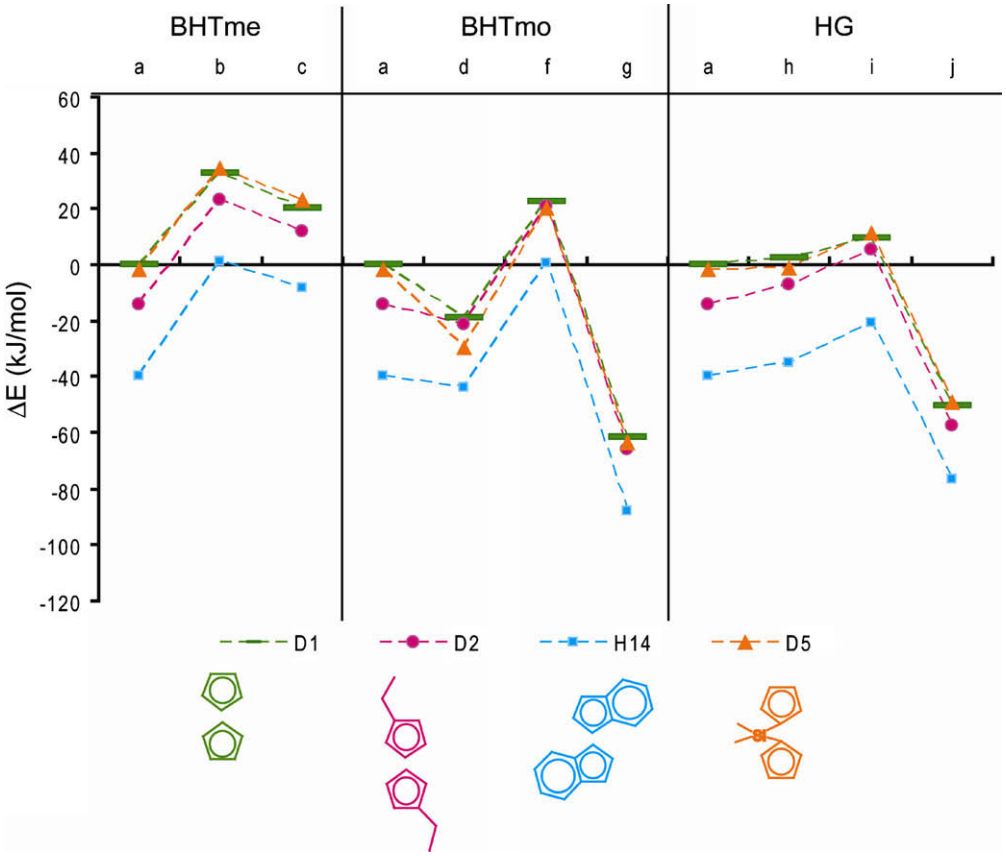

Fig. 3. Chain termination pathways in ethene polymerization by selected hafnocenes. (a) β-agostic pentyl product, (b) transition state for BHTme, (c) product of BHTme, (d) π-complex for BHTmo, (f) transition state for product of BHTmo, (g) coordinated H_2 for HG, (h) β-agostic transition state for HG, and (i) product of HG.

variations. Concerning HG, changing from Cp to Ind complicates the coordination of H_2 for bridged systems, but has practically no effect for unbridged systems. The relative energy of the TS is lower for Ind. The combined effects of ligands and bridges are also present in Cp to CpFlu comparison (D4 versus D12), making H_2 coordination more difficult for CpFlu. Generally, the trends between Cp versus Ind are the same as with Cp versus CpFlu.

The effect of changing Ind to H_4-Ind can be seen by comparing D9 to D10. The stability of the β-agostic pentyl complex is higher for Ind, while the activation barriers for BHTme are practically equal. In BHTmo, the π-coordination is more exothermic for Ind, contributing to the lower activation energy for H_4-Ind. Comparison between BHTme and BHTmo mechanisms reveals that for H_4-Ind, the BHTme TS lies lower in energy than BHTmo TS, whereas the relative energies of the two transition states are about the same for Ind. In HG, the main difference between the two ligands is easier coordination of H_2 in the case of H_4-Ind, while the relative energies of the TS are equal.

3.3.3. The effect of ligand substituent

The influence of adding 3, 4, 5 or 8 of methyl groups to the two Cp ligands can be analyzed by comparing D1 to D3, D5 to D6 and D7, H6 to H4 and H7, H11 to H9 and H12. The combined effects of structural units playing a role, the influences of methyl groups are best seen in D1 versus D3 comparison, which has no interfering structural variables. Addition of methyls increases the activation barrier for BHTme, resulting in decreased energy difference at the transition state. The presence of methyl groups also hinders the formation of π-complex in BHTmo, also leading to higher activation barrier. Therefore, the TS of D3 lies higher in energy, changing the stability order with respect to the initiation of the chain termination reaction from the β-agostic pentyl chain. Comparing BHTme and BHTmo for the D1 versus D3 pair, the relative energy is clearly higher for the BHTme TS in the case of D1. With the addition of methyl substituents, the difference between the two transition states becomes smaller, and in the case of D3, the BHTmo becoming even higher in relative energy. In HG, the coordination of H_2 is more easier, and also the activation barrier lower, with the plain Cp (D1) in comparison to the pentamethyl-substituted D3.

While the comparison D1 versus D3 shows the general trends in the effects of methyl substituents, the combined effects of structural units give rise to certain deviations from that behavior. Concerning alkyl substituents in general, the main deviations from the behavior of D1 versus D3 pair are reported in the following for the studied dataset.

For the comparison D5 versus D6 versus D7, all with $Si(CH_3)_2$ bridges, addition of methyl groups does not affect the activation barrier for BHTmo, while with plain Cp, the activation barrier increases. In HG, addition of methyl groups for the bridged Cp does not increase the activation barrier, as it did with the unbridged Cp.

Concerning the 3-PhIndCp (H6 versus H4,H7) and 4-PhIndCp (H11 versus H9,H12) hafnocenes, the presence of methyls hinders the formation of π-complex, as it also did with the plain Cp (D1 versus D3). Interestingly, however, the effect is stronger with just three methyls (H4,H9) rather than with five (H7,H12). The subsequent activation barrier is affected as well, trimethylated Cp decreasing the barrier, while pentamethylated Cp increases it. The effect is the strongest for the trimethylated 4-PhIndCp (H9), three methyl groups decreasing the activation barrier from 53 kJ/mol to 27 kJ/mol. Furthermore, methyl groups destabilize the BHTmo TS with respect to the BHTme TS in the case of 3-PhIndCp (H4,H7), but stabilize it in the case of 4-PhIndCp (H9,H12).

Table 3
Summary of the effects of ligand modifications of hafnocenes on β-hydrogen transfer and hydrogenolysis.

	Typically increased by	Typically decreased by	Maximum[a]	Minimum[a]
Relative stabilities of the β-agostic pentyl products	Large aromatic Cp′ ligands, electron donating substituents	Short bridges	D11	D4
Formation of π-complex in BHTmo	Bridges	Large aromatic Cp′ ligands, electron donating substituents	D4	H9
Coordination of H_2 in HG	Bridges with Cp ligands	Large aromatic Cp′ ligands, bridges with Ind ligands	D4	H12
Relative stability of TS for BHTme	Large aromatic Cp′ ligands, electron donating substituents	Bridge	D11	D4
Activation energy for BHTme	Large aromatic Cp′ ligands, electron donating substituents	Plain Cp ligand	D11	D1
Relative stability of TS for BHTmo	Large aromatic Cp′ ligands	(No clear trends)	D11	D10
Activation energy for BHTmo	(No clear trends)	(No clear trends)	H8	H9
Relative stability of TS for HG	Large aromatic Cp′ ligands, electron donating substituents	Bridge	D11	D4
Activation energy for HG	Bridges with Cp ligands	Bridges with Ind ligands	H10	H7

[a] Complexes (see Fig. 1) with maximum and minimum values within the "Hf-set".

Destabilizing effect is the strongest with three methyls (H4), whereas stabilizing effect is the strongest with five methyls (H12). Again in HG, three methyls give rise to unusual behavior, facilitating the coordination of H_2, but increasing the activation barrier.

Addition of one or two alkyl substituents larger than methyl can be analyzed by comparing D1 to D2 and H1, H6 to H8, and H11 to H13. The effects of larger alkyls are typically the same as with methyls.

The influences of phenyl substituents attached to the indenyl ligand can be elucidated by comparing H14 to D11, H5 and H10. However, the effect of the addition of phenyl substituents is not straightforward, the position of the phenyl substituent having a substantial influence. Concerning BHTmo, phenyl substituents generally hinder the formation of π-complex and increase the activation barrier, probably due to steric effects. In the case of BHTme, the phenyl substituents have no effect on the relative energy of the transition state. For BHTmo, however, the phenyl substituents destabilize the transition state with respect to the unsubstituted case. Comparison between BHTme and BHTmo shows that, with unsubstituted ligand, the BHTmo TS has same relative energy than the BHTme TS, whereas with phenyl substituents, the relative energies of the transition states are lower for BHTme.

The effects of the position of phenyl substituents can be illustrated by comparing D11 to H5 and H10, H6 to H11, H4 to H9, H7 to H12, and H8 to H13. The effects are dependent on the ligand framework, being strongest for the case of indenyl ligands (D11 versus H5 versus H10). Focusing on the phenyl-substituted indenyl ligands, the activation barrier for BHTme increase in the order 4-phenyl < 3-phenyl < 2-phenyl. In BHTmo, the 2-phenyl substituent hinders the formation of π-complex the most. The activation barrier for BHTmo increases in the order 4-phenyl < 3-phenyl < 2-phenyl. Comparing BHTme and BHTmo, the relative energies of the transition states are lower for BHTme. In HG, the coordination of H_2 is more hindered with 2-phenyl and 3-phenyl substituents compared to 4-phenyl substituent. The activation barriers decrease in the order 4-phenyl > 3-phenyl > 2-phenyl.

3.4. Summary of the ligand effects

Here we have considered the chain termination processes to start after insertion of the second ethene monomer, making the β-agostic pentyl product the starting point for the investigations. The effects that stabilize the β-agostic pentyl complex are of high relevance, as their influence is present all the way through the chain termination processes. The effects stabilizing the β-agostic pentyl complex, together with other catalytic intermediates along the ethene insertion and chain propagation pathway, have been studied previously [14]. In short, the catalytic intermediates are stabilized by large aromatic ligands and electron donating ligand substituents.

Typical effects of ligand modifications on the chain termination processes are summarized in Table 3. It should be noted that the influences of ligand modifications are not straightforward due to combined effects of various structural units. Large aromatic Cp′ ligands and ligand substituents typically stabilize, whereas bridges destabilize, the TS for BHTme. In BHTmo, there are no clear trends, the combined effects of the structural units playing a significant role. Nevertheless, the formation of the π-complex preceding BHTmo is facilitated by the presence of bridges and complicated by large aromatic Cp′ ligands and ligand substituents.

Marlg et al have calculated the termination barriers for BHTme and BHTmo for the corresponding D1 hafnocene and zirconocene, the barriers being 36 and 43 kJ/mol for hafnocene, and 30 and 45 kJ/mol for zirconocene [5h]. In this work, the barriers for the hafnocene are about the same, 33 kJ/mol and 42 kJ/mol, respectively. Another study on zirconocenes [5f] suggests that the addition of methyl substituents leads to higher relative energy of TS in BHTme and BHTmo, which is in line with the present study, and also in line with the experimental finding that catalysts with bulky ligand substituents produce high molecular weight polyethene [2]. Unfortunately, the availability of experimental data for hafnocenes over a set range of conditions is too limited for more throughout conclusions between theory and experiments. We are currently working to obtain more experimental data for the calculations involving the activation, propagation and termination steps to be compared with.

Experimental studies of HG mainly conclude that the molecular weight is easily decreased by adding small amounts of hydrogen [19]. Concerning present calculations of HG, steric effects are likely small due to the small size of H_2. Instead, HG seems to be affected by electronic effects, increased electrophilicity of the metal center increasing the binding energy of H_2. The electrophilicity is altered by electron donating character of the ligand framework. The effect of bridging units appears to be particularly strong. This is hardly surprising as the bridging units alters the Cp′–Hf–Cp bond angles Cp′–Cp plane angles, and thereby the ring slippage angle and electron donating capability of the ancillary ligand [20]. For comparison, in and experimental work on zirconocenes, addition of a silyl bridge between the Cp ligands has been shown to increase the electrophilicity of the metal center, thereby increasing hydrogen sensitivity [21].

4. Conclusions

Chain termination reactions for hafnocene-catalyzed ethene polymerization processes were studied by the hybrid density functional B3LYP method. The focus of the study was on the effect of ligand modifications on the termination reactions. To compare the influences of ligands a data set of 27 hafnocenes was systematically studied. The data set included both synthesized and hypothetical catalysts, the purpose of the latter being to enable direct comparison of a variety of structural modifications. Three chain termination reactions were studied: β-hydrogen transfer to metal, β-hydrogen transfer to monomer and hydrogenolysis. The chain terminations were initiated after insertion of the second ethene monomer, and altogether 13 catalyst intermediates along the chain termination pathways were studied for each hafnocene.

Analysis of the calculations focused on the effects of various ancillary Cp′ ligands, ligand substituents and bridging units. Large aromatic Cp′ ligands and electron donating substituents decrease, while a bridge increase, the relative energy of the transition state for β-hydrogen transfer to metal. Furthermore, large aromatic Cp′ ligands and electron donating substituents complicate the formation of the ethene π-complex for β-hydrogen transfer to monomer, while the presence of bridges facilitate its formation. In hydrogenolysis, the relative energy of the transition state is decrease by large aromatic Cp′ ligands and electron donating substituents. Overall, the influences of ligand modifications are not straightforward, which is due to combined effects of various structural units. The obtained trends provide new insight into the ligand effects on chain termination reactions, and are expected to aid in further catalyst development.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.070.

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