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Role of the Metal Center in the Ethylene Polymerization Promoted by Group 4 Complexes Supported by a Tetradentate [OSSO]-Type Bis(phenolato) Ligand

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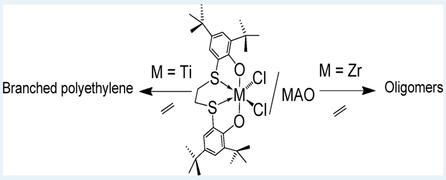
S *Supporting Information*



ABSTRACT: The mechanism responsible for the production of branched polyethylene from ethylene feed during its polymerization promoted by dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenoxy)}titanium complex **1** activated by methylalumoxane (MAO) was investigated by using a density functional theory (DFT) approach. The following processes, chain propagation (CP) reaction, beta hydrogen elimination (βHE, hydrogen elimination from an alkyl chain to the metal in the absence of a coordinated alkene) and transfer (βHT, hydrogen transfer from the alkyl chain to a coordinated alkene) were considered to individuate the possible competing reactions responsible for the production of ethylene oligomers. The latter two processes are generally ascribed as termination reactions for the chain propagation. We found that βHT is the more plausible termination pathway leading to the formation of oligomers that can be reinserted in the growing chain, and thus giving the branched polyethylene. Furthermore, by comparing the energetic profile of CP and βHT for the analogue zirconium compound **2** we found that βHT is 50 times more competitive with CP than for the Ti-based compound. As a matter of fact, the MAO activated zirconium complex exclusively produces oligomers with even number of carbon atoms, thus confirming fairly well the calculations that indicated the possibility of tuning the catalytic activity and selectivity of this class of compounds simply by changing the nature of the metal center.

KEYWORDS: ethylene oligomerization, titanium, zirconium, postmetallocene, DFT calculations

1. INTRODUCTION

During the past few years, the development of catalysts for the selective oligomerization of ethylene to 1-alkenes has been the objective of many studies in both industrial and academic contexts because of the use of these species in a variety of industrial processes like the synthesis of plasticizers, lubricants, detergents, and as comonomers in the synthesis of linear low density polyethylene (LLDPE). Presently, they are obtained by processes based on nickel catalysts containing P,O ligands (SHOP process), which give rise to a Schulz−Flory distribution of linear 1-alkenes.[1,2] However, such distributions do not closely match the market demand due, inter alia, to the growing importance of 1-hexene and 1-octene as comonomers in the production of polyethylene. Thus, intensive efforts have been devoted to the development of new catalytic systems to find more selective routes to desired 1-alkenes.[3,4] So far, the research in this field has however been mainly focused on late transition metals (Ni, Fe, Co, Cr) supported by a wide range of ligands, comprising bidentate and tridentate molecules incorporating O, S, P, and N as donor atoms.[5−10] Conversely, the use of group 4 metallocenes as oligomerization catalysts has yet to receive the attention deserved for their high catalytic activity displayed in the polymerization of ethylene. For istance, Bazan developed boratabenzene zirconium complexes that, activated by methylalumoxane (MAO), promote the oligomerization of ethylene giving rise to a Schulz−Flory distribution of 1-alkenes.[11] Also, Teuben reported half-sandwich titanium complexes very active and selective in the trimerization of ethylene.[12] Besides, the development of catalytic systems for the polymerization of ethylene based on group 4 metals bearing non cyclopentadienyl ligands has recently mushroomed;[13−15] this notwithstanding, the use of such complexes as oligomerization catalyst, after a proper tuning of the electronic and steric properties of the ligands, has been relatively less explored.[16−19]

Lately, the synthesis of a new group 4 based compound characterized by a tetradentate ligand with two phenoxo units linked by a 1−4 dithiabutanediyl bridge, so-called [OSSO]-type ligand, has been reported (Scheme 1). Interestingly, the titanium complex dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenoxy)}titanium complex **1**, once activated by MAO, promoted the stereoregular polymerization of various olefins (e.g., styrene to isotactic polystyrene)[20−29] and, in presence of ethylene feed, produced with high activity branched polyethylene

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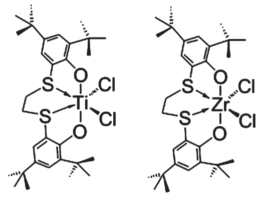
Scheme 1



1 2

characterized by branches with even number of carbon atoms.[30] In this respect, the presence of an unsaturated chain-end strongly suggested a mechanism involving the in situ formation of α-olefins by β-hydride elimination, while the reinsertion of these α-olefins during the polyinsertion process allowed the formation of branched polyethylene.

To gain more information about the mechanism responsible for the formation of branched polyethylene and to tailor group 4 based catalysts for eventually forcing the production of α-olefins, we decided to study the role played by different metal centers (e.g., Ti or Zr) and by the substituent on the ligand moieties (hydrogen or *tert*-butyl group) with respect to the mechanism involved in the formation of oligomers. In fact, it has been reported that in case of *meso ansa*-metallocenes the presence of different metal centers can influence the formation of branches in the homopolymerization of ethylene.[31] To this end, we used a double pronged approach involving both a theoretical study and further experimental work. In details, we used a DFT approach where we compared the transition state (TS) of the chain propagation (CP) reaction, the beta hydrogen elimination (βHE, hydrogen transfer from an alkyl chain to the metal), and the beta hydrogen transfer (βHT, hydrogen transfer from the alkyl chain to a coordinated alkene). To support and complete the information obtained from our calculations, a few polymerization reactions were performed in the presence of ethylene and of the zirconium-based system analogue to **1** (complex **2**), with the products of each reaction being studied in detail and the catalytic behavior as oligomer producer of **1** and **2** activated by MAO compared with respect to their capacity to propagate the polymerization.

2. EXPERIMENTAL PART

2.1. Materials. All air- and moisture-sensitive manipulations were performed under nitrogen atmosphere using standard Schlenk techniques and a MBraun drybox. All reagents and solvents were purchased from Aldrich. Dry solvents were dried by standard methods and distilled before use.

The ligand 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenol) was prepared according to the literature procedure.[20] MAO was purchased from Aldrich as 10% solution in toluene. Before use, the volatile components were removed in vacuum, and the resulting white powder was washed twice with dry hexane to remove the "free" $Al(CH_3)_3$. Polymerization grade ethylene was purchased from SON and further purified by bubbling through a 5 mol % xylene solution of Al^tBu_3.

2.2. Ethylene Olygomerization. The oligomerization reactions were carried out in a 100 mL glass flask equipped with a magnetic stirrer. In a typical procedure, toluene (20 mL) and powder MAO (Al/Zr mol = 1000) were added sequentially in nitrogen atmosphere, the flask was thermostatted at the desired temperature, evacuated and filled with 1 atm of ethylene. Finally, 5.6 μmol of catalyst precursor were added. Ethylene was fed continuously to keep the pressure constant.

The polymerization at 6 bar of ethylene pressure was carried out in a 250 mL, stirred glass autoclave thermostatted at 50 °C and then charged with a toluene solution (50 mL) containing the catalyst precursor (5.6 μmol) and dried MAO (Al/Zr mol = 1000). Ethylene was fed continuously to keep constant the pressure.

The mixtures were poured into acidified ethanol. The oligomers were recovered by washing the solution with acidified water and then with water until neutrality, and drying the organic layer in vacuum.

The ethylene composition in the liquid phase was calculated by Lewis and Luke's equation and using the fugacity function chart.[32]

2.3. Characterization. NMR spectra were recorded on Bruker Avance 400 or on Bruker Avance 300 spectrometers at 25 °C, unless otherwise stated. Chemical shifts (δ) are listed as parts per million. ^1H NMR spectra are referenced using the residual solvent peak at δ 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 77.23 for $CDCl_3$.

Gas chromatographic measurements of the mixture of oligomers were performed on a GC Thermo Electron Corporation equipped with a flame ionization detector operating at 250 °C and with Famewax column (crossbond PEG, 30 m, 0.32 mm ID).

As a further aid to signal assignment, ^1H and ^{13}C chemical shifts for 1-octene, 3-ethyl 1-octene and 2-octene have been computed at the BP86/6-311+G(2d,2p) level of theory. The numerical results for these calculations are shown in the Supporting Information. Apart from a global shift downfield of the signal by 0.20−0.30 ppm, the theoretical data match the assignment indicated in Figure 5 and fully support the presence of linear and 2-branched 1-alkenes, as well as of 2-alkenes.

2.4. Synthesis of 2. To a stirred solution of 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenol) (0.92 g, 1.9 mmol) in 20 mL of toluene was added a suspension of zirconium tetrachloride (0.36 g, 1.9 mmol) in 10 mL of toluene at room temperature. A yellow solid is formed immediately, and the mixture was stirred for further 2 h. The solvent was removed under reduced pressure, and the solid was washed twice with fresh hexane (2 × 5 mL) to give [OSSO]$ZrCl_2$ (**2**) (1.12. g, 1.68 mmol, 89%) as a yellow powder. Elemental Analysis(calc.): C: 54.58 (54.35); H: 6.83 (6.69); S 9.86 (9.67).

^{1}H NMR (300 MHz, ppm, $CDCl_3$): 1.28 (s, 18H, $C(CH_3)_3$), 1.47 (s, 18H, $C(CH_3)_3$), 2.56 ($^2J_{HH}$ = 9.7 Hz, 2 H, SCH_2), 3.13 ($^2J_{HH}$ = 9.7 Hz, 2 H, SCH_2), 7.17 ($^4J_{HH}$ = 1.3 Hz, 2H, ArH), 7.38 ($^4J_{HH}$ = 1.3 Hz, 2H, ArH).

^{13}C NMR (300 MHz, ppm, $CDCl_3$): 29.9 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 35.9 ($C(CH_3)_3$), 39.6 (CH_2S), 118.6 (arom.), 127.0 (arom.), 127.8 (arom.), 138.6 (arom.), 145.3 (arom.), 164.5 (arom.).

2.5. Computational Details. Gas phase electronic structure calculations were carried out using the Gaussian09[33] suites of codes, employing BP86 density functional theory (DFT) with the local exchange−correlation potential by Vosko et al.,[34] augmented in a self-consistent manner with Becke's exchange-gradient correction[35] and Perdew's correlation-gradient correction.[36]

The basis set employed was the LANL2DZ[37,38] with associate effective core potentials for second and third row atoms and the SVP[39] for the first row ones.

Geometries for all species (i.e., olefins, cation, olefin complexes, transition states (TSs), and final products) were fully

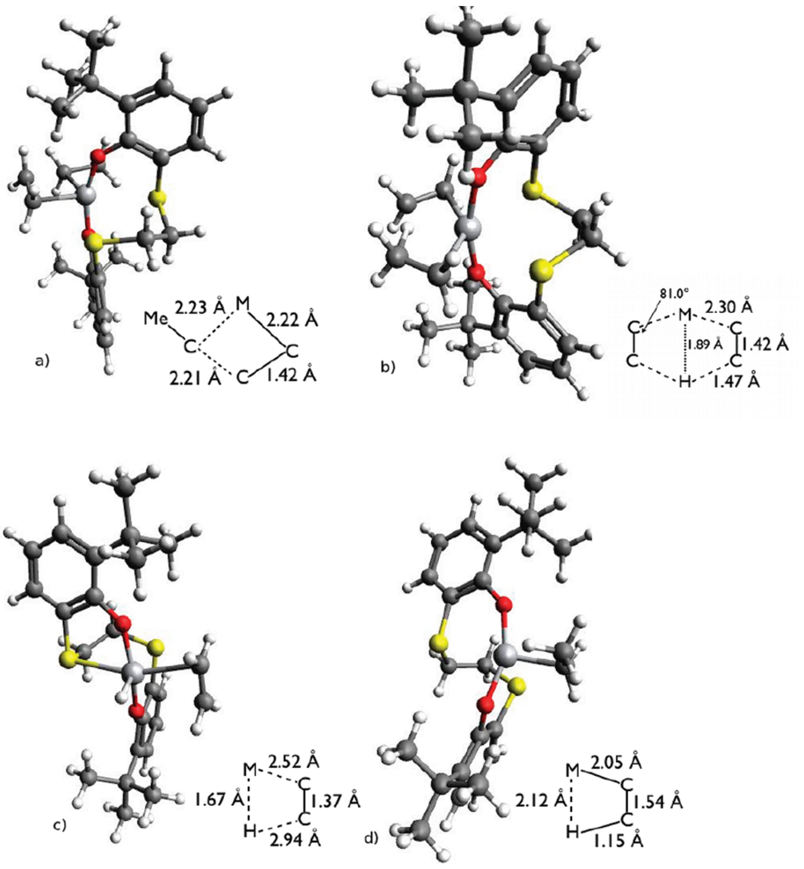


Figure 1. Transition state structures for the chain propagation (CP; a), beta-hydrogen transfer (βHT; b) and beta-hydrogen elimination (βHE; c) for Ti-[OSSO]-type Bis(phenolato) catalysts. Also, structure of the akyl-bearing cation (d) considered as the most active catalytic species in ethylene polymerization. The "stick and symbol" sketches provide structural details of the reactive metal−carbon−hydrogen moieties involved in CP, βHT, βHE, and of the stabilizing agostic interaction in the alkyl-bearing cation.

optimized and the stationary points found were characterized by means of frequency calculations. Often, putative structures for the chain propagation (CP) and beta-hydrogen transfer (βHT) TSs were built using literature data[40] by means of geometrical relaxation keeping constrained the "active" part (e.g., the distances between metal and carbon atoms in the four center TS for chain propagation, CP). The only difference with the latter procedure is related to the optimization of the TS for beta-hydrogen elimination (βHE), which was obtained by means of a constrained scan starting from the hydride plus ethylene adduct.

NMR chemical shifts for carbon and hydrogen in the olefins were computed at the BP86/6-311+G(2d,2p)[41] level of theory in the gas phase with the gauge independent atomic orbitals (GIAO)[42] using analytical derivatives.

3. RESULTS AND DISCUSSION

To model the possible reaction at the metal center, we opted for representing both the growing chain and the coordinated olefin mainly as two-carbon atom moieties (i.e., ethyl residue and ethylene, respectively). Given the uncluttered active center in the complex, we expect the difference with longer growing chains due to steric hindrance to be minor; similarly, electronic effects due to longer growing chains are expected to be weak (a limited set of tests supporting this idea is reported in the Supporting Information, Table 2). Conversely, we have explicitly investigated the role played by alkyl substituent in *ortho* position with respect to the phenolic oxidril by computing the energy barrier for the processes using either hydrogen or *tert*-butyl as substituents, as well as the effect due to the olefin chain length by substituting ethylene with propylene. The latter calculations have been carried out for the Ti complex to explore the competition between different olefins in the chain propagation process.

To investigate the possible competing processes, we begun studying the standard chain propagation (CP) reaction (characterized by a four-center transition state, TS) together with beta hydrogen elimination (βHE, i.e. from an alkyl chain to the metal in the absence of a coordinated alkene) and transfer (βHT, from the alkyl chain to a coordinated alkene) using an ethyl for the growing chain and ethylene as olefin. The optimized structures for the TS of such processes are shown in Figures 1 and 2 for species containing Ti and Zr, respectively.

These figures show also some of the geometrical parameters of the reactive part for the species containing the *tert*-butyl groups. As for the latter features, they appear to be scarcely remarkable, the main differences present between Ti and Zr species being due to a different ionic coordination radius. At the level of finer details, one may perhaps highlight a longer H−C_β distance (~0.01 Å) and a more acute metal−C_α−C_β angle in the Zr TS for βHT than in the Ti one. Since a similar difference between Zr and Ti species is also found in species where the metal atom bears only the growing alkyl chain, one may interpret such feature as due to β-agostic interaction, which should be more apparent in

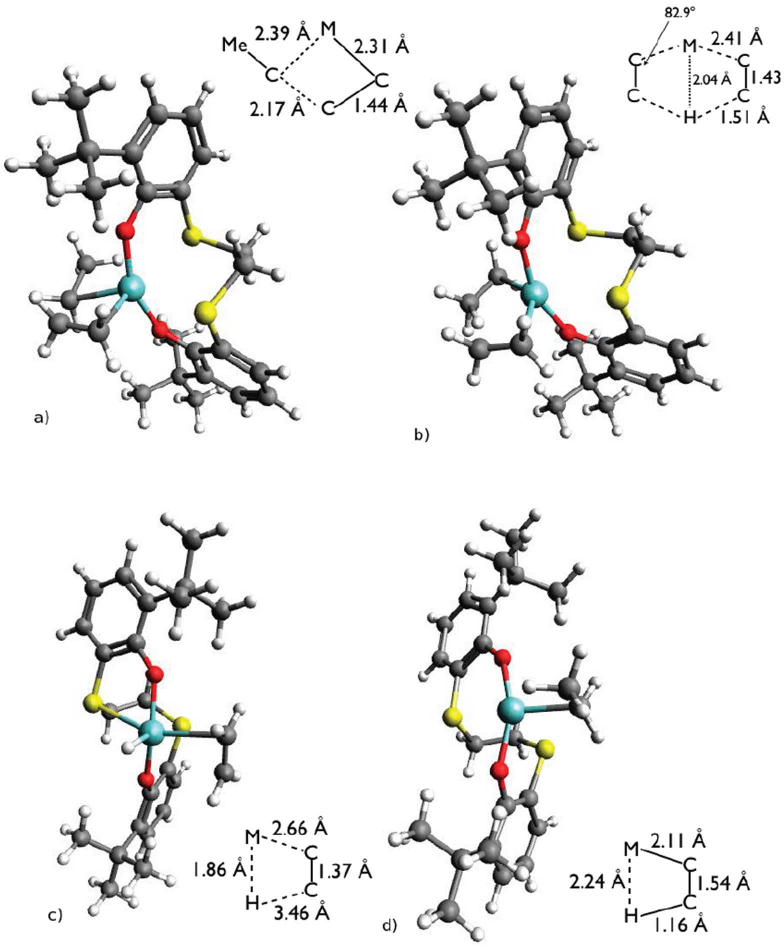


Figure 2. Transition state structures for the chain propagation (CP; a), beta-hydrogen transfer (βHT; b), and beta-hydrogen elimination (βHE; c) for Zr-[OSSO]-type Bis(phenolato) catalysts. Also, structure of the akyl-bearing cation (d) considered as the most active catalytic species in ethylene polymerization. The "stick and symbol" sketches provide structural details of the reactive metal—carbon—hydrogen moieties involved in CP, βHT, βHE, and of the stabilizing agostic interaction in the alkyl-bearing cation.

Table 1. $\Delta E_{act} = E_{act}(\beta\text{HT}) - E_{act}(\text{CP})$ for Different Metal Centers and Ortho-Substituents for Chain Propagation and Beta-Hydrogen-Transfer during Ethylene Polymerization[a]

metal/substituents	ΔE_{act} (kcal/mol)	ΔE_{act}[ZPE] (kcal/mol)
Ti/H	4.7	2.1
Zr/H	2.8	0.1
Ti/*tert*-butyl	4.9	2.3
Zr/*tert*-butyl	3.1	0.4

[a] Results obtained by difference between BP86/LANL2Z stationary point energies including (ΔE_{act}[ZPE]) or not including (ΔE_{act}) zero point energy corrections.

Zr complexes thanks to an expected more negative C_α.[43] Since the reactant species for both βHT and CP processes are either the same (i.e., the olefin-coordinated alkyl complexes) or two conformers of the latter, it is possible to discuss their relative propensity (or competition) simply comparing the TS energies. Thus, Table 1 gives $\Delta E_{act} = E_{act}(\beta\text{HT}) - E_{act}(\text{CP})$ in kcal/mol for both Ti and Zr species, with or without correction for zero point energies (ZPE) computed using harmonic frequencies for the hydrogen and *tert*-butyl substituted ligands.

As first comment, one may notice that the effect of the *ortho* substituents is minimal on both the absolute and the relative barrier heights when ethylene is used as monomer. In other words, this indicates that the preferential formation of isotactic polystyrene highlighted in the introduction ought to be due to the "bulkier" nature of the latter molecule, which provides the ingredient for an excluded volume interaction with the *tert*-butyl substituents. More relevant for the thrust of this study, the data in Table 1 and in Figure 3 indicate a more competitive βHT process for Zr-containing species than for Ti-containing ones. All other things being equal, the exponential dependence of the rate constant on the barrier height would suggest βHT to be roughly 50 times more competitive with CP when using zirconium-based catalysts that when using Ti-based ones if one excludes ZPE energy contributions. One, however, would also expect that this factor might be somewhat modified by the more constrained nature of the βHT TS, a six-center structure, with respect to the CP one and by the fact that βHT involves the transfer of a light hydrogen atom. To account for both these effects, we corrected the potential energy differences including ZPE contributions (see Table 1), which, however, only slightly modified the difference between Ti and Zr in the βHT/CP competition. Instead, the ZPE corrections had the net outcome of suggesting an even

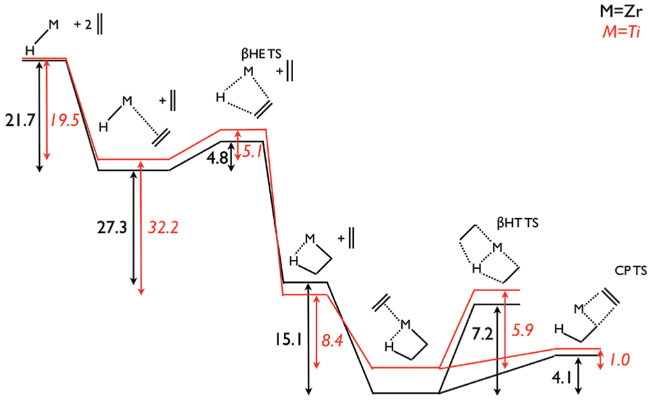


Figure 3. Potential energy surface for the reaction studied in this work. The zero of the energy scale is set as the energy of two free ethylene molecules (involved in later stages of the processes) plus the energy of the hydride cation previously suggested as the active species in Ti-based catalysts. Italic numbers and red lines refer to Ti-containing complexes; energies in kcal/mol. In the graph, we have omitted the final products of the CP process to avoid cluttering; the latter are, however, at least 15 kcal/mol lower in energy than their precursors.

more competitive βHT process with respect to CP for *both* metals.

As far as the competition between chain termination processes, the energetic diagram in Figure 3 also indicate that βHT should be expected to be the preferential chain termination reaction thanks to a substantially lower transition state barrier than the βHE one. ZPE corrections for the βHE process are found to change the barriers only slightly for both metals (E_{act}[ZPE] is 4.0 and 3.8 kcal/mol for Ti and Zr, respectively), therefore leaving this conclusion unmodified.

In this respect, it should be remarked that to meaningfully compare these two termination reactions one ought to place all transition states on the same free energy scale instead of the energy one as done by Talarico and Budzelaar,[44] which employed an effective shift of 16.8 kcal/mol capable of changing the character of the leading termination reaction for Cp ligand containing catalysts. This necessity is related to the fact that the molecularity of the systems involved in the two termination processes is different, so that one would need to account at least for different system entropies. In our cases, such correction would not change substantially the interpretation for both Ti- and Zr-based catalysts since it would predict, respectively, a βHE free energy barrier of roughly 15 and 12 kcal/mol; the latter values were estimated including ZPE energy corrections for the βHE TS and the catalyst bearing only the appropriate ethyl substituent. Needless to say, the value of the best effective shift for our catalysts could be somewhat different from the one suggested by Talarico and Budzelaar with the possible effect of modifying our conclusions. Unfortunately, we do not have enough experimental data to provide a more adequate estimate for such correction. Nevertheless, the substantial difference between βHT and βHE barriers as estimated in this work suggests the conclusion drawn above to be sufficiently robust.

The lower ΔE_{act} between βHT and CP processes afforded by Zr-based catalyst and the consequent enhanced competition between CP and βHT has a clear bearing on the behavior of Zr- or Ti-based catalyst. In particular, this finding indicates that Ti-OSSO catalysts should be expected to be more active in producing long polymeric chains than equivalent Zr species thanks to the low insertion barrier and the sufficiently high energy (5.9 kcal/mol) requested to activate βHT. This not withstanding, the βHT process is predicted to be sufficiently active in Ti-OSSO catalysts to provide a means by which ethyl or longer branches may appear along the carbon chains.[30] In fact, we feel justified to invoke the same growing chain swap based on βHT put forward for the formation of linear low density poly ethylene (LLDPE) with ethyl branches.[40] The same mechanism based on βHT appears to be also able to explain the presence of longer ramification containing even number of carbon atoms, previously addressed postulating an active βHE process. From our calculations the latter seems instead not able to compete. In this respect, it is important to call attention to the fact that the energy required to dissociate the linear alkene obtained via βHT from the complex should be quite low (roughly 8.4 kcal/mol for ethylene; vide infra for propylene) for Ti active species. In turn, this indicates that releasing linear alkenes in the reaction medium should be facile enough, thus providing a route for the reinsertion of this species into a chain growing onto a distinct reactive center.

Table 2. Transition State Barrier $E_{act} = E_{act}$(CP) for the Chain Propagation on the Ti-Complex with ortho *tert*-Butyl Substituents Using Ethylene or Propylene As Monomer[a]

metal/olefin/regiochemistry	E_{act} (kcal/mol)	E_{act} [ZPE] (kcal/mol)
Ti/ethylene/none	1.0	1.8
Ti/propylene/primary	3.6	4.7
Ti/propylene/secondary	5.8	6.7

[a] Results obtained as difference between BP86/LANL2Z stationary point energies with ([ZPE]) and without zero point energy corrections.

To investigate the competition in the CP process between ethylene and longer alkenes that can be released in the reaction environment following βHT, we also computed the CP barrier height for the propylene insertion into an ethyl-Ti bond on a complex bearing ortho *tert*-butyl substituents. We opted to investigate only Ti-based species because of their expected higher acidity. Table 2 provides the quantitative results of our calculations for both primary and secondary insertion, as well as for ethylene.

From these, one evinces that insertion of propylene is somewhat less favored than for ethylene; besides, a primary insertion of propylene appears to be easier than a secondary one, in good agreement with the general experience with early transition metal-based catalysts.[45] Despite the different CP barrier height for the two alkenes (roughly 2.6 kcal/mol for the less demanding primary insertion), the higher energetics requirement for propylene insertion appears to be sufficiently small to allow competition between the two monomers. This becomes even more evident considering that our calculations suggest a somewhat larger dissociation energy (roughly 12.4 kcal/mol) to detach propylene from the Ti-coordination site than for ethylene (vide supra, 8.4 kcal/mol), a datum that seems to imply a higher complexation constant for the former alkene.

Returning to the discussion on the CP/βHT competition and flipping the presented reasoning on its head, the lower ΔE_{act} between βHT and CP, that is, a much easier chain termination (or swap), for Zr-related catalyst indicates that the latter ought to be more prone to generating the α-olefins needed for the formation of the polymer branches seen in the case of Ti-based catalysts. These results are consistent with what was found by Caporaso et al.[40] for a few ansa-zirconocenes able to produce a substantial amount of ethyl branches and LLDPE while the

Scheme 2. Formation of Linear (A) and Branched (B) Olefins

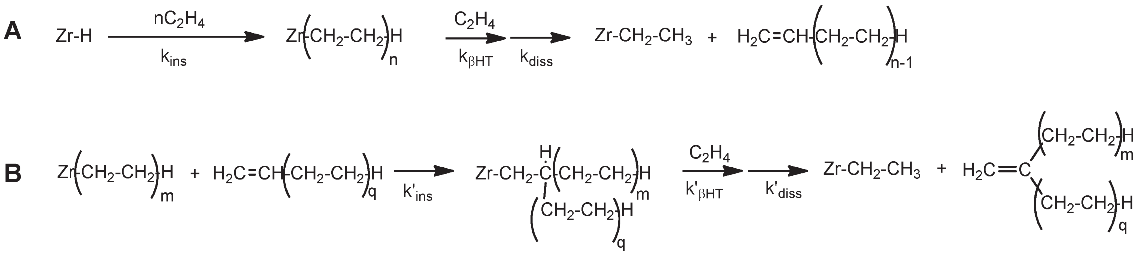


Table 3. Ethylene Oligomerization in Presence of 2/MAO

run[a]	T (°C)	$P_{\mathrm{E(feed)}}$ (atm)	$[\mathrm{E}]_{\mathrm{feed}}$ (mol L^{-1})	TOF ($\times 10^{-3}$, h^{-1})	1-alkenes (%)	2-alkyl-1-alkene[b] (%)
1	50	6	1.1	3.57	82	18
2	50	1	0.16	2.64	59	41
3	20	1	0.25	2.41	47	53
4	0	1	0.35	1.30	76	24

[a] Reaction conditions: toluene 20 or 50 mL, catalyst precursor 5.6 μmol,MAO/Zr (mol) = 1000, time =2 h. [b] ^{13}C NMR also reveals the presence, in traces, of 3-alkyl-1-alkenes because of the occasional reinsertion with 2,1 regiochemistry of the olefins produced.

equivalent Ti compounds generated only high density polyethylene.[31] Given the more competitive nature of βHT in Zr-based catalysts with respect Ti ones, one may even expect that after the formation of ethyl branch in position 2 from the metal, the alkyl chain could transfer another hydrogen to a newly coordinate ethylene generating 2-ethyl-1-alkenes in a way that is reminiscent of the formation mechanism for ethyl double branches in LLDPE. The 2-ethyl-1-alkenes may successively detach from the active site and be retrieved among linear 1-olefins. A similar process can also happen if it is a longer alkene coordinating to the metal center and acting as acceptor for the hydrogen transfer instead of ethylene, thus producing 2-ethyl-1-alkenes with longer substituent alkyl chains than ethyl in position 2 (vide infra, Scheme 2).

Given the indications obtained from the DFT calculations, we thus speculated that the zirconium complex characterized by a 2,2′-sulfur-bridged bis(phenolato) ligand (complex **2**) could produce an even more branched polyethylene and/or a sizable amount of oligomers by homopolymerization of ethylene. Since we found the *ortho* substituents influence on the energetic barriers was minimal, we synthesized the ligand 1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenol) from which the zirconium-based compound **2** was obtained by reaction with $ZrCl_4$ in toluene at room temperature. The ^{1}H NMR characterization of complex **2** showed the typical AB spin pattern for the CH_2 units in the bridge, confirming a molecular C_2-symmetry similarly to the Ti-based complex.[20] This fact clearly indicated that complexes **1** and **2** just differ from each other for the nature of the metal center.

We performed some ethylene polymerizations in presence of complex **2** activated by MAO at different experimental conditions as reported in Table 3.

The first interesting observation was that the zirconium system did not produce any solid polymer; however, a few oligomers were extracted from the reaction mixtures and fully characterized by ^{1}H, ^{13}C NMR, and GC-MS techniques. In Figure 4 the GC trace shows the oligomeric mixture coming from the reaction carried out at 50 °C. Generally, all the GC obtained were characterized by a Schulz−Flory distribution of C_{2n} unsaturated products, where n is the number of monomer molecules in the resulting olefins. From the observation of these distributions, it was evident that the prevailing active species was a Zr−H or Zr−C_{2n} compound since the insertion into the Zr-CH_3 bond should have been evidenced by the presence of unsaturated molecules with odd number of carbon atoms. The formation of olefins with an even number of carbon atoms in presence of the Zr-OSSO based catalyst is similar of what was reported for the corresponding Ti-OSSO one.

A deeper insight of the GC-MS analyses revealed a family of at least four isomers for each C_{2n} peak. To investigate the composition of such a family, we compared the GC profiles of mixtures with and without 1-dodecene as standard. This allowed recognizing the linear α-olefin among the hexamers, while the presence of 2-alkyl-1-alkenes, 1-alkenes, and 2-alkenes, the latter as trace, was evidenced by ^{1}H and ^{13}C NMR[46] analyses (Figure 5). The presence of such olefins was further confirmed by the results coming from computed ^{1}H and ^{13}C NMR data whose patterns agreed fairly well with the experimental results apart from a global shift of 0.20−0.30 ppm downfield.

While the traces of inner olefins could be explained considering the isomerization of linear 1-alkenes, the presence of vinylidenic alkenes is likely due to the incorporation of the lower molecular mass olefins (1-butene, 1-hexene), formed by means of βHT process, into the propagating chain (see Scheme 2). The mechanism invoked here is similar to the one proposed for the formation of branched polyethylene in presence of Ti-OSSO catalysts with the difference that in the case of the zirconium complex the competition between the CP and βHT processes is more pronounced as formerly predicted by calculations, and consequently the probability of producing lower molecular mass chains is higher.

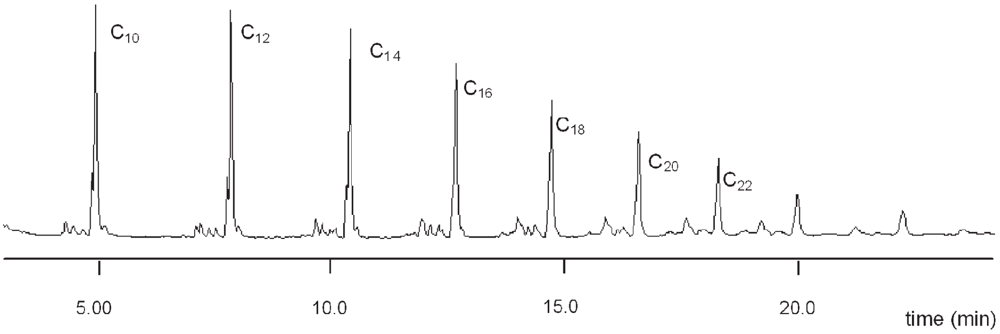


Figure 4. GC profile of the oligomeric mixture obtained at 50 °C and 1.1 mol L^{-1} of ethylene in the feed. (Table 3, run 1).

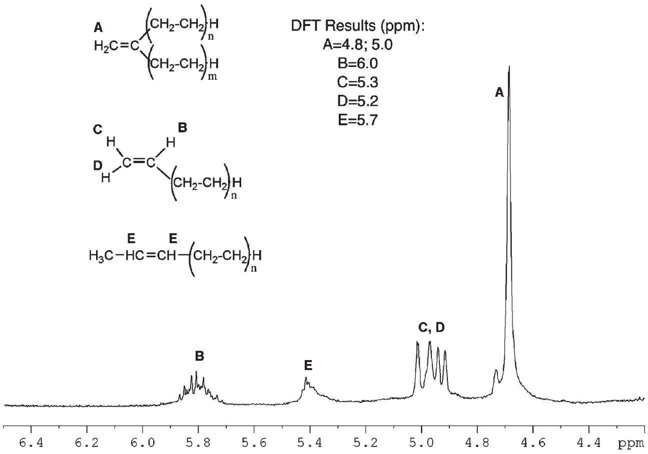


Figure 5. ^1H NMR of oligomeric mixture obtained at 50 °C and 0.16 mol L^{-1} of ethylene in the feed (Table 3, run 2) and chemical shift prediction from DFT calculations.

Furthermore, as reported above and as invoked for the formation of double ethyl branches in polyethylene obtained in presence of some *meso ansa*-zirconocenes characterized by competitive CP and βHT reactions, after the formation of an ethyl branch in position 2 from the metal, the alkyl chain could transfer another hydrogen to a coordinated ethylene generating the 2-ethyl-1-alkyl group that, in this case, can form the correspondent olefin for a further βHT and successively detach from the metal.[40,47]

The experimental data collected in presence of the Zr-OSSO based catalyst gave also an idea of the importance of the competition between the CP and βHT processes for Zr and Ti metal centers. In fact, the longest chain produced by the zirconium complex at 20 °C, as revealed by GC, had a molecular weight MW < 340 Da (12 ethylene units) while the more abundant olefins were C10−C12 (MW = 140−170 Da). Conversely, the molecular mass of polyethylene produced by the Ti-OSSO catalyst in the same experimental condition was $M_w = 9.5 \times 10^4$ Da (<3400 ethylene units).[30] These experimental findings are perfectly in line with the theoretical prediction for a reduced capability of Zr-based catalyst toward the chain propagation.

A further important observation is about the relative amount of linear and branched isomers belonging to each C_{2n} family. In fact, the ratio between 1-alkene and 2-alkyl-1-alkene increased with ethylene feed composition as reported in Figure 6. In particular, the zirconium-based system was able to produce more than the 80% of linear olefins at 1.1 mol L^{-1} of ethylene concentration. In these experimental conditions, the probability of inserting ethylene in the Zr-carbon bond rather than butene or higher molecular mass olefins seems to be favored. Such an aspect is of relevance since it indicates that the production of mainly linear olefins can be reached by modulating the experimental conditions.

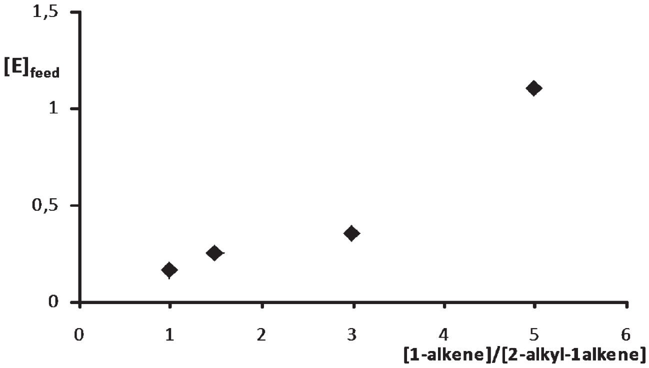


Figure 6. [1-alkene]/[2-alkyl-1-alkene] ratio with respect to the ethylene feed.

Summarizing the main results, we reiterate that, led by a computational exploration, we experimentally demonstrated the ability of the metal center in OSSO group 4-based catalysts to dramatically change the reaction products. In particular, the zirconium complex activated by MAO does not produce solid polymer, giving, instead, exclusively a mixture of oligomers; conversely, the titanium based catalyst produces solid polyethylene. These behaviors were well explained considering that the βHT process is much more competitive with respect to the CP in the zirconium complex rather than in the titanium one. However, both the catalysts showed the ability of inserting α-olefins into the metal−carbon bond to give branched oligomers or polymers respectively.

4. CONCLUSIONS

In this paper we reported a theoretical and experimental study on the [OSSO]-type group 4 based catalysts in the polymerization of ethylene. DFT calculations allowed predicting that, in the case of Zr-based compound, the mechanism of β-hydrogen transfer producing olefins can be strongly favored by the electronic characteristics of the metal rather than by steric hindrance of the groups on the ligand moieties. As a matter of fact, we found that the β-hydride transfer becomes 50 time more competitive with respect to the chain propagation by just changing the metal center from Ti to Zr. Experiments well support the latter calculations. In fact, they show that, in the presence of ethylene, the zirconium complex **2** activated by MAO produces exclusively oligomers. This is at variance with the titanium analogue **1** producing polymers. Intriguingly, the relative amount of 1-alkenes and 2-alkyl-1-alkenes was tuned by changing the reaction conditions. The production of 2-alkyl-1-alkenes among the others shows the tendency of this system to reincorporate α-olefins.

These results show that is possible to design a group 4 metal oligomerization catalysts taking into account the delicate balance between electronic effects of the [OSSO]-type ligand and the choice of the metal center. Although the activity of zirconium-based system reported in this study is not very high, the composition of oligomeric mixture appears interesting when it comes to design a system capable of producing different isomers of unsaturated molecules. Further experiments are in progress to enhance the catalytic activity and the selectivity of the zirconium complex **2** by modification of the ligand sphere.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Text and tables living details of the calculation methods and Cartesian coordinates and energies of all the structures. ^{13}C NMR of an oligomeric mixture (run 2, Table 3) and plot of ln(mole % olefin) versus carbon number for C_{10} through C_{26} fractions. This material is available free of charge via the Internet at http://pubs.acs.org.

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