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Molecular Modeling of the Regiochemistry of Olefin Insertion with Single-Site Polymerization Catalysts[1]

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Abstract—The regiochemistry of propene insertion promoted by metallocene and postmetallocene Column 4 metal catalysts is investigated with quantum mechanics techniques. It is shown that steric effects dominate the regiochemistry of monomer insertion with classical metallocene-based catalysts, whereas both electronic and steric effects contribute to the regiochemistry of propene insertion with postmetallocene catalysts.

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INTRODUCTION

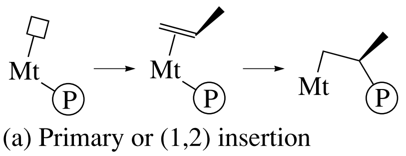
It goes without saying that enchainment of 1-alkenes into metal–carbon (Mt–C) bonds promoted by catalysts based on early transition metals occurs predominantly through primary (or 1,2) insertion (see scheme). Secondary (or 2,1) propene insertion, commonly referred to as regioirregular insertion or regiomistake, is a sporadic event which usually corresponds to less than 1% of the enchainments [1].

This regiochemistry holds for the classical heterogeneous catalysts based on $TiCl_3$ or $TiCl_4$ supported on $MgCl_2$ [2–4], for the homogeneous group 4 pseudotetrahedral metallocene catalysts as Cp_2MtCl_2, $C_2H_4(1\text{-Ind})_2MtCl_2$ or $Me_2C(Cp)(9\text{-Flu})MtCl_2$, for the so-called constrained geometry catalysts (CGC), and for the recently discovered octahedral stereorigid C_2-symmetric Zr complexes with tetradentate bridged bis(phenoxyamine) ligands [1].

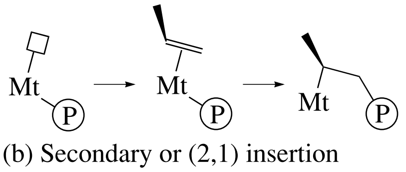
Despite the clear preference for primary enchainment shown by a overwhelming number of catalysts, secondary propene insertion into the Mt–alkyl bond has been known since the 1960s, when homogenous V-based catalytic systems were shown to polymerize propene through prevailingly secondary enchainments [5–9]. These systems were probably considered the exception that confirmed the rule. However, the discovery that bis(phenoxyimine)$TiCl_2$ precursors, despite the strong similarity with the bis(phenoxyamine) analogs [10, 11], work through secondary enchainments was rather surprising [12–14].

It is worth recalling that the presence of regiodefects along the polymer chain have a strong effect in lowering the crystallinity and melting point of the resulting polypropylenes. At the same time, there is also a close correlation between catalyst regioselectivity, on the one hand, and catalyst activity and polymer molecular weight, on the other hand, due to the lower monomer insertion rate at a secondary growing chain end and the competing β-H transfer to the monomer after a secondary insertion unit. Because of these two aspects, understanding the factors controlling the regioselectivity of the monomer insertion is important for an efficient catalyst design. The lower reactivity of a secondary growing chain with respect to a primary growing chain has been confirmed in three ways: by studying the activating effect of hydrogen, by copolymerization with ethylene [15, 16], and by end group analysis [17, 18].

For propene polymerization promoted by isotactic metallocene systems, ^{13}C NMR analysis has shown that the 2,1 units are always isolated between two isotactic blocks and, depending on the enantioselectivity of the following primary insertion on the secondary growing chain end, give rise to 2,1 erythro (e) and 2,1 threo (t) sequences, and to the formation of tetramethylene sequences (3,1 units), arising from the unimolecular isomerization of the secondary unit. A sequence of two secondary insertions has never been detected. Thus, in



(a) Primary or (1,2) insertion



(b) Secondary or (2,1) insertion

Scheme.

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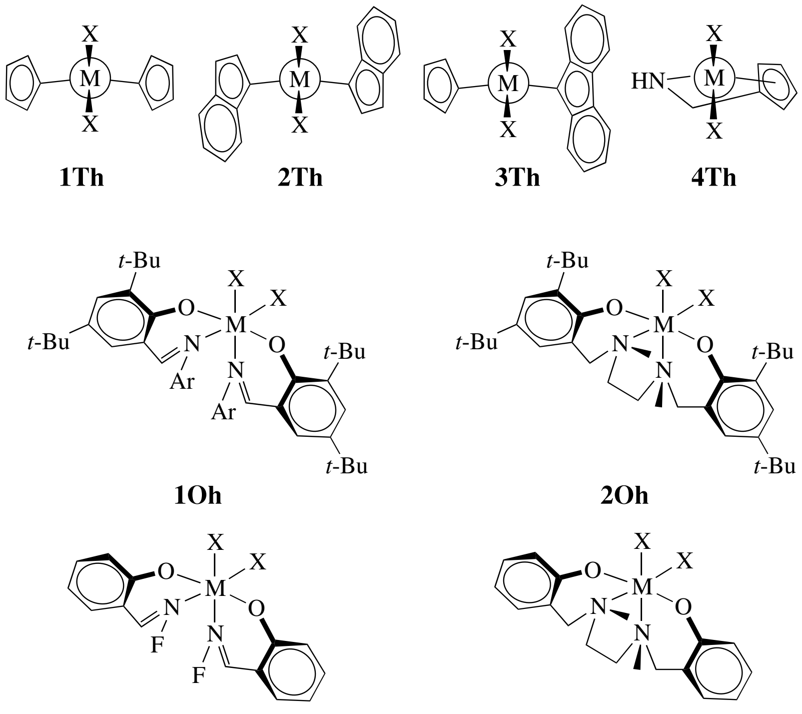


Chart

terms of regiochemistry, three propagation reactions occur, i.e., primary on primary chain end, secondary on primary chain end, and primary on secondary chain end.

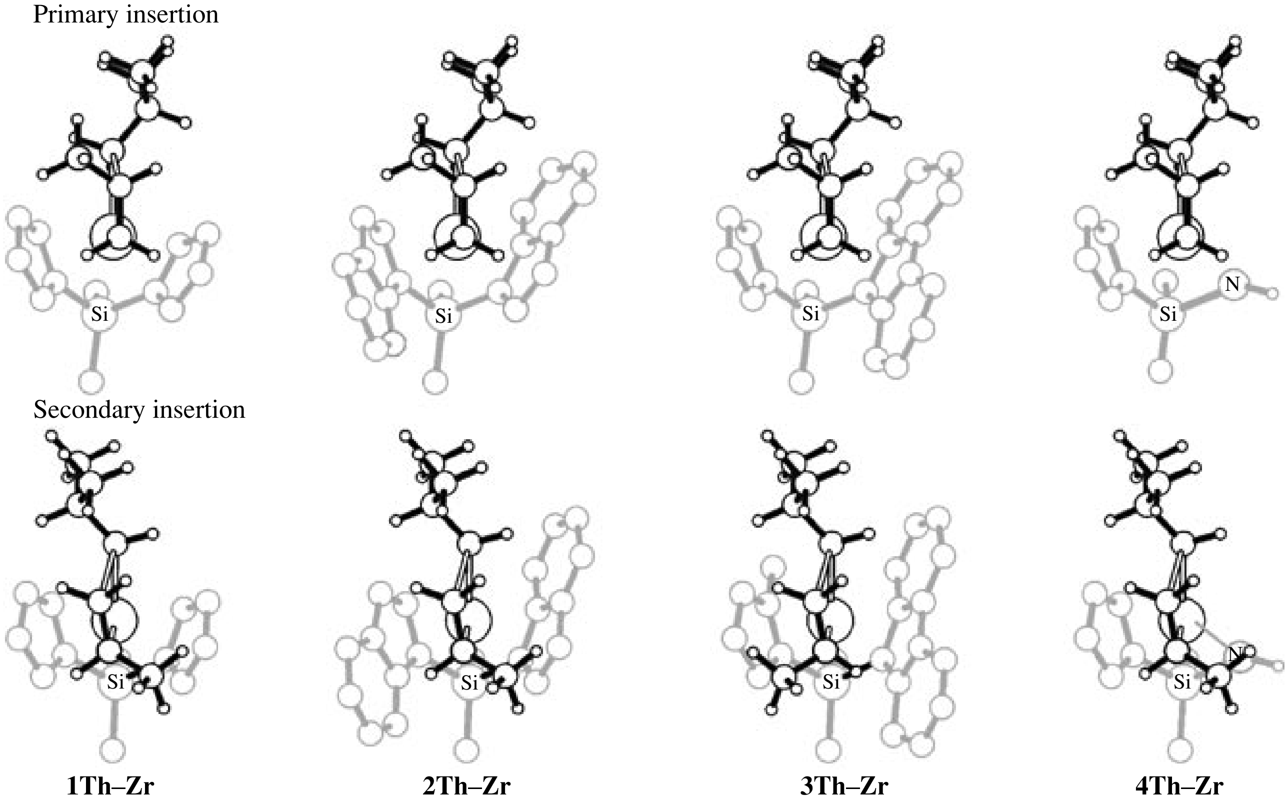
Previous calculations performed with molecular mechanics by some of us have shown that, in the case of metallocenes, the origin of regiochemistry of propene insertion is mostly steric in nature [19, 20]. Instead, in the case of octahedral postmetallocene catalysts, like unbridged bis(phenoxyimine) or bridged bis(phenoxyamine) precursors, it has been shown that electronic effects have a remarkable role [21]. However, a systematic comparison of the regiochemistry of propene insertion promoted by metallocene and postmetallocene catalyst systems has never been performed. In this manuscript, we try to fulfill this lack.

To this end, we will compare the regiochemistry of three typical metallocenes and of a CGC (see structures **1Th–4Th** reported in Chart), as well as the regiochemistry of structure **1Oh–4Oh**. For all these systems, we will consider primary and secondary insertion of the two enantiofaces of propene into the Mt–Me bond, for a total of four structures for each complex. Furthermore, for system **1Th** and **1Oh**, we will also investigate the regiochemistry of propene insertion into the Mt–isobutyl and Mt–isopropyl bonds. These two cases can be considered as models for propene insertion into a primary and secondary growing chain, respectively.

COMPUTATIONAL DETAILS

Stationary points on the potential energy surface were calculated with the Amsterdam Density Functional (ADF) program [22]. The electronic configurations of the molecular systems were described by a triple-ζ basis set on Ti (3*s*, 3*p*, 3*d*, 4*s*, and 4*p*) and Zr (4*s*, 4*p*, 4*d*, 5*s*, and 5*p*) [23]. Double-ζ STO basis sets were used for F, O, N and C (2*s*, 2*p*) and H(1*s*), augmented with a single 3*d* polarization function except for H, where a 2*p* function was used. The $1s^22s^22p^6$ configuration on Ti, the $1s^22s^22p^63s^23p^63d^{10}$ configuration on Zr, and the $1s^2$ shell on C, N, O, and F were assigned to the core and treated within the frozen core approximation. Energy differences were calculated at the GGA level, using Becke's [24] exchange corrections and Perdew's [25, 26] correlation correction.

The ADF program was modified by one of us [27] to include standard molecular mechanics force fields in such a way that the QM and MM parts are coupled self-consistently [28–30]. The simple model QM systems and the full QM/MM and QM systems are displayed in the figure. The partitioning of the systems into QM and MM parts only involves the skeleton of the postmetallocene **3Oh** and **4Oh** ligands. As for the connection between the QM and MM parts, this occurs by means of so-called "capping" dummy atoms, which are replaced in the real system by the corresponding "linking" atom [27, 30]. In order to reflect better the different electronic properties of the $-C_6H_5$ and $-C_6F_5$ rings, we used H and F atoms as capping atoms in **3Oh** and **4Oh**, respectively.



Transition states for primary and secondary insertion into the Zr–*i*-Bu bond of the **1Th–Zr**, **2Th–Zr**, **3Th–Zr**, and **4Th–Zr** metallocenes of Chart.

In the QM/MM optimizations, the ratio between the C–C bonds crossing the QM/MM border and the corresponding optimized C–H and C–F distances was fixed at 1.30 and 1.06, respectively. Further comments on the methodology can be found in previous papers [27, 31, 32]. The AMBER95 force field [33] was used for the MM potentials, except for Ti and Zr, which were treated with the UFF force field [34]. To eliminate spurious stabilizations from the long-range attractive part of the Lennard-Jones potential, we used an exponential expression fitted to the repulsive part of the Lennard-Jones potential [19, 31].

Table 1. Energy differences between the transition states for 2,1 and 1,2 propene insertion ($\Delta E^{\neq}_{\text{regio}}$) for the metallocenes and the CGC system of Chart

Model	Alkyl	$\Delta E^{\neq}_{\text{regio}}$, kcal/mol
1Th–Ti	Isobutyl	2.9
1Th–Zr	Methyl	3.9
1Th–Zr	Isobutyl	2.6
1Th–Zr	Isopropyl	0.9
2Th–Zr	Isobutyl	2.5
3Th–Zr	Isobutyl	2.8
4Th–Ti	Isobutyl	0.9

All the following structures are stationary points on the QM or combined QM/MM potential surface. The regioselectivity of each system, $\Delta E^{\neq}_{\text{regio}}$, was calculated as the energy difference between the transition states leading to secondary and primary insertion of the monomer. Within this choice, a positive value of $\Delta E^{\neq}_{\text{regio}}$ means that primary insertion is favored.

RESULTS

Catalysts with Tetrahedral Geometry of Coordination

The $\Delta E^{\neq}_{\text{regio}}$ calculated for metallocenes and for the CGC system of Chart 1 are reported in Table 1.

Tetrahedral systems: ligand effect. To address this point, we calculated the $\Delta E^{\neq}_{\text{regio}}$ for propene insertion into the Zr–*i*-Bu bond of the three metallocenes as well as into the Ti–*i*-Bu bond of the CGC systems of Chart. Independently of the regiochemistry of insertion, the transition states we obtained (illustrated in the figure) correspond to the classical Cossee-like four-center geometries and are stabilized by a strong α-agostic interaction. In all the cases, the growing chain is placed in an open part of space to reduce steric interactions with the ligand. For the iso- and syndiospecific **2Th–Zr** and **3Th–Zr** systems, this means that the growing chain develops away from the nearby six-member aromatic ring of the ligand, in agreement with the mechanism of the chiral orientation of the growing chain.

For the same reason, in the CGC system, the growing chain develops on the less crowded side, which is the side of the N-amido atom. Additionally, in the case of primary propene insertion, the methyl group of the propene is oriented anti (i.e., away from) relative to the growing chain, whereas in the case of secondary propene insertion the methyl group of the monomer is oriented away from the nearby six-membered ring of the ligand in **2Th–Zr** and **3Th–Zr**, and away from the cyclopentadienyl ring in **4Th–Ti**. These features, which minimize steric interactions between different groups, were shown to be at the origin of the stereoselectivity in both the primary and the secondary insertion [1].

The $\Delta E^{\neq}_{\text{regio}}$ reported in Table 1 for the **1Th–Zr**, **2Th–Zr**, and **3Th–Zr** metallocenes (close to 2.5 kcal/mol) show that primary insertion is always favored, and they are rather similar to the molecular mechanics $\Delta E^{\neq}_{\text{regio}}$ previously reported by Guerra and coworkers [19, 20]. Considering that the molecular mechanics calculations only include steric interactions, the similarity between the quantum mechanics and the molecular mechanics $\Delta E^{\neq}_{\text{regio}}$ clearly indicates that the driving force for primary propene insertion with metallocene-based catalysts is steric in nature. As already indicated, the clear preference for primary insertion can be ascribed to steric interactions between the methyl group of the secondary inserting propene and the ligand framework [19, 20]. The value of $\Delta E^{\neq}_{\text{regio}}$ for the CGC system is small, but this is a consequence of the small bulkiness associated to the H atom attached to the nitrogen. These findings further support the idea that steric effects play a key role in the regiospecificity of tetrahedral systems.

Tetrahedral systems: growing chain effect. To understand the effect of the growing chain on the regiochemistry of propene insertion, we calculated the $\Delta E^{\neq}_{\text{regio}}$ for propene insertion into the Zr–R bond (R = methyl, isopropyl, and isobutyl) of the **1Th–Zr** system of Chart. R = isopropyl and isobutyl are models of secondary and primary growing chains, respectively, in the case of propene homopolymerizations. The $\Delta E^{\neq}_{\text{regio}}$ reported in Table 1 for propene insertion into the Zr–Me bond is roughly 1 kcal/mol higher than the $\Delta E^{\neq}_{\text{regio}}$ for insertion into the Zr–isobutyl bond and roughly 3 kcal/mol higher that the $\Delta E^{\neq}_{\text{regio}}$ for insertion into the Zr–isopropyl bond. These numbers clearly indicate that the bulkiness of the growing chain has a strong effect on the regioselectivity of propene insertion. This behavior can be mainly ascribed to steric interactions between the chain and the methyl group of the primary inserting propene. Some of these interactions are already present in the case of insertion into the Zr–isobutyl bond and are much more relevant for propene insertion into the Zr–isopropyl bond. This conclusion is general, since it is a consequence of direct interaction between the monomer and the chain and is independent of the catalyst ligand framework.

Table 2. Energy differences between the transition states for 2,1 and 1,2 propene insertion ($\Delta E^{\neq}_{\text{regio}}$) for the octahedral systems of Chart

Entry	Model	Alkyl	$\Delta E^{\neq}_{\text{regio}}$, kcal/mol
1	**1Oh–Ti**	Isobutyl	0.3
2	**1Oh–Ti**	Isopropyl	–2.0
3	**1Oh–Zr**	Isobutyl	0.9
4	**1Oh–Zr**	Isopropyl	–1.4
5	**2Oh–Ti**	Isobutyl	4.4
6	**2Oh–Ti**	Isopropyl	2.4
7	**2Oh–Zr**	Isobutyl	3.6
8	**2Oh–Zr**	Isopropyl	1.4
9	**3Oh–Ti**	Isobutyl	0.1
10	**3Oh–Ti**	Isopropyl	–3.0
11	**3Oh–Zr**	Isobutyl	1.0
12	**3Oh–Zr**	Isopropyl	–1.3
13	**4Oh–Ti**	Isobutyl	4.3
14	**4Oh–Ti**	Isopropyl	1.7
15	**4Oh–Zr**	Isobutyl	4.0
16	**4Oh–Zr**	Isopropyl	1.1

Catalysts with Octahedral Geometry of Coordination

The $\Delta E^{\neq}_{\text{regio}}$ calculated for the octahedral models of Chart are reported in Table 2.

Octahedral-systems: ligand effect. In a first step, we explored the role of the interaction of the monomer with the *t*-Bu and Ar substituents on the **1Oh** systems and with the *t*-Bu substituents on the **2Oh** system. To this end, we compare the $\Delta E^{\neq}_{\text{regio}}$ values for the full systems **1Oh** and **2Oh** (entries 1–8 in Table 2) with the corresponding systems **3Oh** and **4Oh** (entries 9–16 in Table 2), in which the *t*-Bu are replaced by H atoms and the Ar group is replaced by a single F atom. Independent of the specific alkyl group bonded to the metal atom, the small changes in the $\Delta E^{\neq}_{\text{regio}}$ values of corresponding systems clearly indicate that the *t*-Bu, Ar, and Me substituents are not relevant for the regiochemistry.

In this respect, even the $\Delta E^{\neq}_{\text{regio}}$ of the bare model **3Oh** (entry 9) is reasonably close to the $\Delta E^{\neq}_{\text{regio}}$ of the corresponding full system **1Oh** (entry 1).

This finding clearly indicates that, differently from the tetrahedral systems, the regiochemistry of propene insertion with the octahedral systems is strongly influenced by the electronic properties of the metal atom, while steric effects, although present, play a minor role. The values in Table 2 indicate that the $\Delta E^{\neq}_{\text{regio}}$ calculated for the **1Oh** system is roughly 3.5 kcal/mol lower than that calculated for the corresponding **2Oh** system (compare entries 1–4 with entries 5–8, respectively). A similar difference is obtained when comparing the $\Delta E^{\neq}_{\text{regio}}$ calculated for the reduced **3Oh** system with the corresponding reduced systems **4Oh** (compare entries 9–12 with entries 13–16, respectively). This indicates that catalysts with the bis(phenoxyamine) ligand induce primary insertion more effectively than those with the bis(phenoxyimine) ligand. This is an intrinsic feature of the ligands, since it is independent of the metal atom and of the growing chain.

Analysis of the molecular orbitals (MO) at the transition states revealed the existence of an antibonding interaction between the MO corresponding to the incipient Mt–C bond and the MO corresponding to the lone pair of the N atom opposite to it. This trans influence is stronger for bis(phenoxyamine) systems because the lone pair of the amine N atom is higher in energy (i.e., more electron donating) than the corresponding lone pair of the imine N atom in the bis(phenoxyimine) systems. Secondary propene insertion increases this destabilization owing to the donating effect of the methyl group on the electron density of the incipient M–C bond [21].

The main message that stems from this section is that the regiochemistry of propene insertion with octahedral systems can be finely tuned with a suitable choice of electron properties of the heteroatoms coordinated to the metal. Ligands that increase electron density at the metal favor primary insertion, while ligands that make the metal more electron deficient favor secondary insertion.

Octahedral-systems: growing chain effect. In analogy with what we found for tetrahedral systems of Table 1, the $\Delta E^{\neq}_{\text{regio}}$ values calculated for primary insertion on a secondary chain are always 2–3 kcal/mol smaller than the $\Delta E^{\neq}_{\text{regio}}$ values calculated for the primary insertion on a primary chain. Since in a few cases, for instance, **1Oh**, the regiochemistry of 1,2 propene insertion on an primary chain is only slightly preferred, it implies that secondary propene insertion on a secondary chain is favored. This means that the secondary propagation becomes the predominant propagation mode in the bis(phenoxyimine) Ti based systems after occasional 2,1 insertion. These findings are in good qualitative agreement with the experimental results [12–14].

CONCLUSIONS

In this paper, we have compared the regiochemistry of propene insertion into the metal–alkyl bond, where isobutyl and isopropyl alkyl groups were used to simulate a primary and a secondary growing chain, respectively. In particular, we investigated propene insertion with three typical metallocenes and one constrained geometry catalyst showing a tetrahedral geometry of coordination at the metal atom. Moreover, we also considered four octahedral systems, containing both bis(phenoxyimine) and bis(phenoxyamine) ligands.

The main conclusions of the present study are as follows. In the case of metallocene-based catalysts, the regiochemistry of monomer insertion is essentially dominated by steric effects. Similar effects are also present in the case of the constrained geometry catalyst, where our calculations suggest that the bulkiness of the group bound to the N atoms plays a remarkable role.

As regards the role of the growing chain, primary propene insertion on a secondary growing chain is disfavored by steric interactions between the methyl group of the propene and the growing chain itself. This interaction strongly reduces the preference for primary insertion.

In the case of the octahedral systems, the regiochemistry of monomer insertion is instead a balance between steric and electronic effects. In the case of the bis(phenoxyimine) Ti based catalysts, primary propene insertion on an isobutyl group is only slightly favored. This implies that, in the case of an isopropyl group, secondary propene insertion is favored. Conversely, in the case of the bis(phenoxyamine)-based catalysts, primary insertion on an isobutyl group is strongly favored, and thus, also in the case of propene insertion on an isopropyl group, primary insertion is favored.

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