

Living Propene Polymerization with Bis(phenoxy-imine) Group 4 Metal Catalysts: A Theoretical Study¹

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Abstract—Bis(phenoxy-imine)Ti catalysts with *ortho*-F-substituted phenyl rings on the N can promote living propene polymerization. On the basis of DFT calculations, it has been proposed that the “living” behavior originates from an unprecedented attractive interaction between the aforesaid *ortho*-F atoms and a β -H of the growing polymer chain, which would render the latter less prone to being transferred to the metal and/or to the monomer. In this paper, we report on a thorough full-QM and combined QM/MM investigation of representative model catalysts, demonstrating that the key factor is instead the repulsive nonbonded contact of the F-substituted rings with the growing polymer chain and an incoming propene molecule, which destabilizes the sterically demanding 6-center transition structure for chain transfer to the monomer. A conceptually similar substituent effect has been reported before for several metallocene and nonmetallocene catalysts.

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INTRODUCTION

Recent reports of living stereoselective polymerization of 1-alkenes with octahedral bis(phenoxy-imine)-based catalysts [1] (Chart 1) opened new routes to the discovery of new materials with precisely controlled molecular weights, narrow molecular weight distributions, end-functionalized polymers, and well-defined block copolymers [2]. However, within this large family of group 4 octahedral catalysts, only a limited number of systems show this particularly desirable behavior, because the active species of this class undergo comparatively fast transalkylation with AlMe_3 (in equilibrium with the methylalumoxane cocatalyst) and β -H transfer. The former process, however, can be effectively suppressed by removing or trapping [3] “free” AlMe_3 . The latter, in turn, has been found to be “negligible” up to 25–50°C for Ti-based catalysts with an *ortho*-F-substituted phenyl ring on the imine N. As a consequence, the system **II** of Chart 1 promotes living propene polymerization [2, 4, 5].

On the basis of DFT calculations, it has been proposed that the reason for such a remarkable and atypical behavior is an attractive interaction between the *ortho*-F and a β -H of the growing polymer chain, making the latter less prone to being transferred to the metal and/or to the monomer [2, 6]. Consequently, these attractive interactions were supposed to provide a conceptually new strategy to achieve living olefin polymerization [2] as opposed to the “classical” one making use of repul-

sive nonbonded contacts in the coordination sphere of the transition metal [7]. Recent results of solution NMR studies on model compounds seemingly provide an independent validation to the concept [8].

In this communication, we report on a thorough combined experimental and theoretical investigation of representative bis(phenoxy-imine)M catalysts (**I–IV** of Chart 1; M = Ti, Zr), aimed at identifying the factors presiding over the “living” behavior in propene polymerization.

COMPUTATIONAL STRATEGY AND DETAILS

Stationary points on the potential energy surface were calculated with the Amsterdam Density Functional (ADF) program system [9] developed by Baerends et al. [10, 11]. The electronic configuration of the molecular systems were described by a triple- ζ STO basis set on titanium for 3s, 3p, 3d, 4s, 4p and on zirconium for 4s, 4p, 4d, 5s, 5p (ADF basis set IV). Double- ζ STO basis sets were used for fluorine, oxygen, nitrogen, and carbon (2s, 2p) and hydrogen (1s), augmented with a single 3d, 3d, and 2p function, respectively (ADF basis set III) [9]. The inner shells on titanium (including 2p), zirconium (3d), fluorine, oxygen, nitrogen, and carbon (1s) were treated within the frozen core approximation. Energies and geometries were evaluated by using the local exchange-correlation potential by Vosko et al. [12] augmented in a self-consistent manner with Becke’s [13] exchange gradient correction and Perdew’s [14, 15] correlation gradient correction.

¹ The text was submitted by the authors in English.

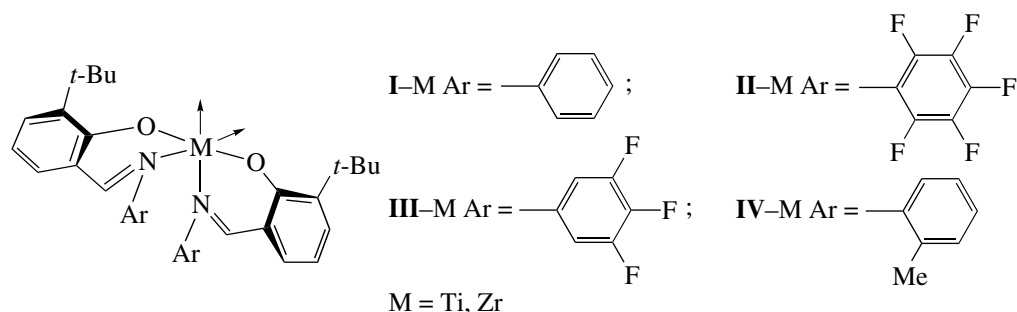


Chart 1.

For reasons that will become clear in the following section, two different computational approaches were used to model the systems of Chart 1. In a first approach, referred to as “full-QM” throughout the paper, all atoms were treated at a quantum mechanics level. In a second approach, labeled as “QM/MM,” the *t*-Bu and Ar-on-N fragments were treated at a molecular mechanics level. As an exemplification, the partitioning used in the QM/MM calculations for the specific case of **II**-Ti (Chart 1) is shown in Fig. 1.

For the connection between the QM and MM part, we used “capping” dummy H atoms [16, 17], with the only exception of N-(C₆F₅) and N-(C₆H₂F₃) bonds, for which we preferred to use F atoms to reflect the electron-drawing property of the aromatic fragment.

The ADF program was modified by one of us [16] to include standard molecular mechanics force fields in such a way that the QM and MM parts are coupled self-consistently [17]. A more detailed description of the coupling scheme, as well as further comments on the methodology, can be found in previous papers [16, 18]. The CHARMM force field [19] was used for the MM potentials, except for Ti and Zr, which were treated with the UFF force field [20]. Transition state geometries were approached by a linear-transit procedure, using the distance between the C(propene) and C(growing chain) atoms which were going to form the new C–C bond as reaction coordinate, while optimizing all

other degrees of freedom. Consistently, in the case of termination reaction, we used the distance between the C(propene) and H(growing chain) atoms which were going to form the new C–H bond. Full transition state searches were started from the geometries corresponding to maxima along the linear-transit curves.

RESULTS AND DISCUSSION

Relevant reaction events in propene polymerization at a bis(phenoxy-imine)M active species are shown in the scheme.

For Ziegler–Natta catalysts in general, β -H transfer to the monomer (Scheme 1a–1d) is normally preferred to β -H transfer to the metal (Scheme 1e, 1f) [7]. We found experimentally that bis(phenoxy-imine)M catalysts are no exception in this respect. In fact, the fraction of olefinic ends in the polypropylene chains turned out to be independent of propene concentration within the experimental uncertainty, which implies that chain propagation and β -H transfer have the same reaction order on the monomer. Just as an example, in polypropylene samples obtained with **I**-TiCl₂/MAO at 20°C, we measured by ¹H NMR a content of terminal allyls of 1.1 mol % at [C₃H₆] = 0.7 M and of 1.4 mol % at [C₃H₆] = 5.6 M.

As already reported experimentally [1, 4, 21, 22] and theoretically [23], the nature of M affects the regiochemistry of chain propagation. While M = Ti entails predominantly 2,1 (secondary) propene insertion into Ti–CH(CH₃)–CH₂–P (secondary chain—Scheme 1h) [21, 22], for M = Zr, 1,2 (primary) insertion into Zr–CH₂–CH(CH₃)–P (primary chain) is favored (Scheme 1g) [23, 24].

Interestingly, our calculations indicate that the lowest energy pathway of β -H transfer to propene involves the latter in 1,2 orientation (Scheme 1a, 1b).¹ This is fully consistent with (and at the same time explains) the

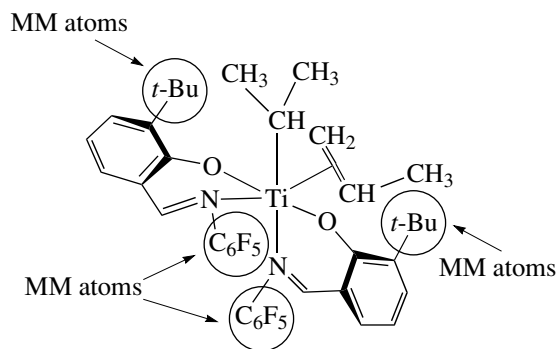
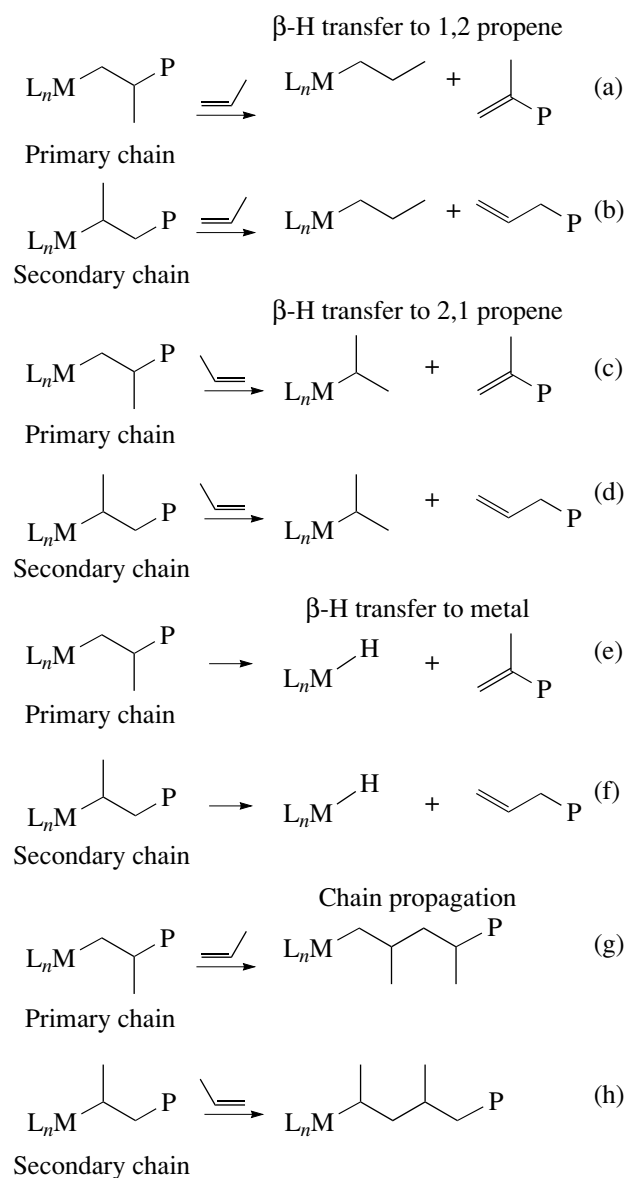


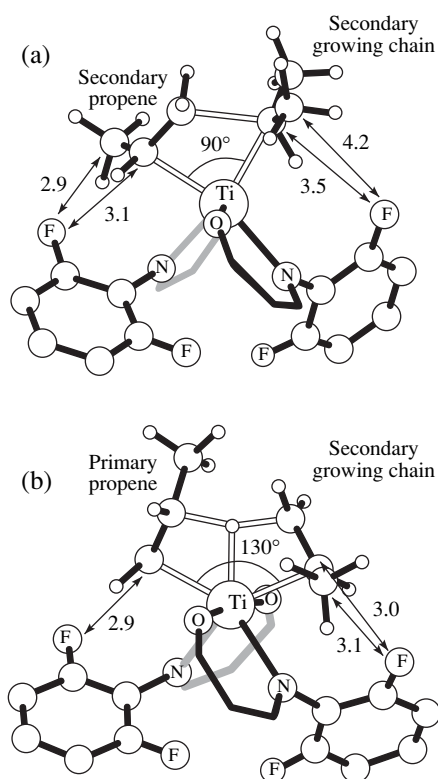
Fig. 1. Partitioning between QM and MM treatment in the QM/MM approach for system **II**-Ti of Chart 1.

¹ For each system, we calculated all possible TSs for monomer insertion; for chain transfer to the monomer, in the table we report the lowest ΔE_{T-P}^\ddagger value.

**Scheme 1.**

experimental results of chain end-group analysis reported by Coates et al. [22] for non-*ortho*-F-substituted Ti-based catalysts and by Fujita et al. [24] for Zr-based ones.

Assuming that the average polymer molecular mass is dictated by the competition between propene insertion and propene-induced chain transfer, we computed the internal energy difference (ΔE_{T-P}^\ddagger) between the corresponding two transition states. In particular, the ΔE_{T-P}^\ddagger values relevant to this investigation correspond to β -H transfer to 1,2 propene from a secondary chain (simulated with an *iso*-propyl group) for M = Ti (Scheme 1b) and from a primary chain (simulated with an *iso*-butyl group) for M = Zr (Scheme 1a). Such values are summarized in the table; for **II**-Zr, we also give

**Fig. 2.** Transition states for 2,1 propene insertion (a) and β -H transfer to 1,2 propene (b) for **II**-Ti.

the value corresponding to β -H transfer to 1,2 propene from a secondary chain.

For a separate evaluation of electronic and steric contributions to ΔE_{T-P}^\ddagger , we compared the results of a full-QM analysis (table, column 3) with those of QM/MM calculations (see previous section), in which the Ar substituents were treated at the MM level, thus considering their steric effects only (table, column 4).

Before discussing the results, we note that caution is mandatory when comparing QM/(MM) predictions

Calculated ΔE_{T-P}^\ddagger (in kcal/mol) for the systems of Chart 1 (see text)

System	Alkyl chain	ΔE_{T-P}^\ddagger (full-QM)	ΔE_{T-P}^\ddagger (QM/MM)
I -Ti	Secondary	4.0	4.8
I -Zr	Primary	-0.2	0.5
II -Ti	Secondary	8.8	9.9
II -Zr	Primary	0.4	1.6
II -Zr	Secondary	-1.0	1.0
III -Ti	Secondary	4.4	4.8
IV -Ti	Secondary	7.4	7.8

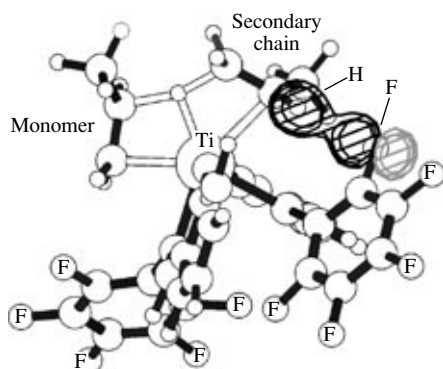


Fig. 3. Transition state for β -H transfer to 1,2 propene at **II**-Ti, showing the attractive interaction of an *ortho*-F atom with an α -H atom of the growing chain. For clarity, only the MO portion which involves the H...F interaction (*ortho*-F...H distance, 2.1 Å) has been sketched.

which refer to different processes, rather than to the same process with different regio- or stereochemistries. Therefore, the table should be used to extract trends, without attaching too much significance to the individual numbers.

That being said, let us now examine the data and, in particular, how ΔE_{T-P}^\ddagger is affected by the possible presence of *ortho*-F atoms on the Ar ring bound to the imine N (systems **I**-M and **II**-M). When $M = \text{Zr}$, ΔE_{T-P}^\ddagger is always close to 0, in line with the experimental finding that catalysts based on **I**-Zr and **II**-Zr are able—at most—to oligomerize propene [24].

The picture is remarkably different when $M = \text{Ti}$. For both **I**-Ti and **II**-Ti, ΔE_{T-P}^\ddagger is substantially larger than that for the Zr homologues. Importantly, however, the full-QM-calculated ΔE_{T-P}^\ddagger jumps from 4.0 kcal/mol for **I**-Ti to almost 9 kcal/mol for **II**-Ti. This is also in nice agreement with the experiments. Indeed, catalysts based on **I**-Ti afford propene polymers of relatively low average molecular mass [4], whereas a “living” behavior is reported for catalysts based on **II**-Ti [1, 2, 4].

In order to find a rationale for this, it is very instructive to compare the full-QM ΔE_{T-P}^\ddagger values with those resulting from the QM/MM approach. The fact that they are very similar indicates that the main effect of the *ortho*-F in **II**-Ti is steric.

A deeper examination of the relevant transition state geometries shows that one of the aforesaid F atoms is at close nonbonded contact with the monomer in the transition states of both competing processes (Fig. 2). Another, in turn, is at a critically short distance from the growing chain in the transition state of β -H transfer to the monomer (Fig. 2b), but not in that of monomer insertion (Fig. 2a). For the sake of clarity, only the *ortho*-F atoms of the perfluorinated phenyl rings are shown, and the phenoxide rings are simply sketched in wire frame. Distances (in Å) between the *ortho*-F and the nearest-in-space C atoms of monomer and growing chain are given.

On the other hand, by replacing the remaining two *ortho*-F atoms with two larger methyl groups

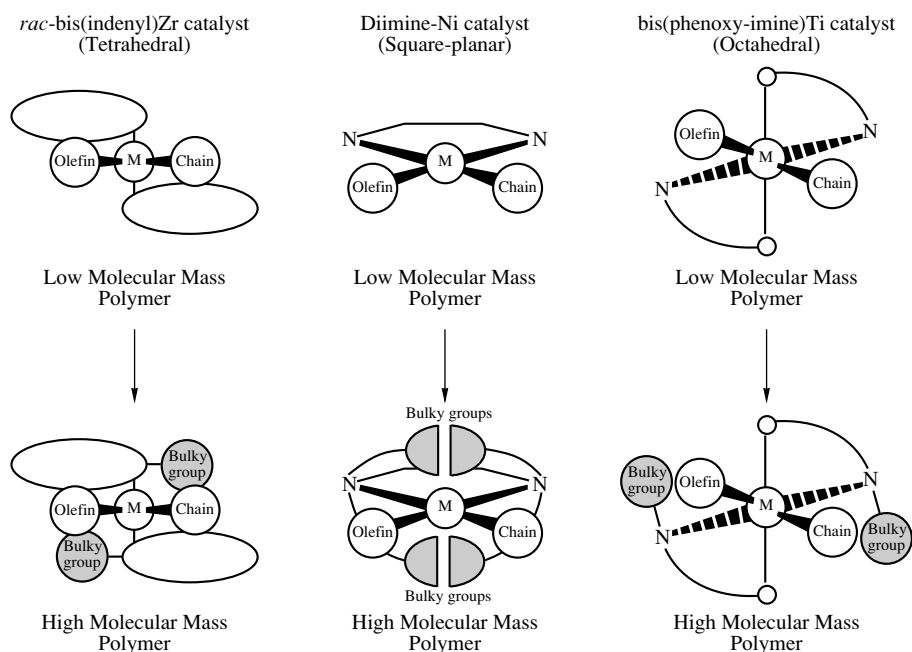


Chart 2.

(system **IV**-Ti), $\Delta E_{\text{T-P}}^\ddagger$ goes up again (last row of table). In our opinion, all this provides a consistent picture of the steric nature of the ortho effect.

How crucial the *ortho* substitution of Ar is on the balance between chain propagation and transfer is further indicated by the fact that **III**-Ti (with F atoms in *meta* and *para*, but not in *ortho*) and **I**-Ti have similar full-QM and QM/MM $\Delta E_{\text{T-P}}^\ddagger$ values.

Interestingly, though, we did find out that the *ortho*-F atoms on Ar in **II**-Ti are not completely innocent from the electronic standpoint. Molecular orbital analysis gave evidence for a partial attractive interaction between one of them and the nearest α -H atom of the chain in the transition state of β -H transfer to the monomer, which is therefore slightly stabilized (Fig. 3). This feature, on the other hand, turned out to be negligible in the (sterically more open) transition state of monomer insertion.

Natural bond order (NBO) analyses [25] aimed at estimating the extent of this H \cdots F bonding interaction gave a value of 0.02 only, which roughly corresponds to a stabilizing interaction of about 1 kcal/mol.

It can be added that a similar weak intramolecular attractive H \cdots F interaction has been detected experimentally in the aforementioned [8] solution NMR study on model (phenoxy-pyridine)Zr-benzyl species with a $-\text{CF}_3$ ligand fragment at close nonbonded contact with an α -(methylene)H of a benzyl group.

CONCLUSIONS

In conclusion, it appears that the “*ortho*-F effect” in propene polymerization promoted by bis(phenoxy-imine)Ti catalysts represents one more application of a general and consolidated concept, i.e., that chain propagation and chain transfer to the monomer have very different space requirements and therefore react differently to ancillary ligand substitution. The former process has a compact four-center transition state, and the reacting atoms, which span an angle of approximately 90° , can be accommodated in relatively small active pockets [7, 26, 27]. The latter instead has a bulkier six-center transition state spanning an angle of approximately 130° , which is more easily destabilized by the steric pressure of substituents suitably located in the ligand framework.

Previous cases of highly successful applications of the same concept are the pseudotetrahedral 2,2'-substituted *rac*-bis(1-indenyl) *ansa*-metallocenes [28] and the square-planar Brookhart-type Ni and Pd catalysts [29] (Chart 2).

Whether the result can be defined a “living” polymerization depends primarily on the TOF of monomer insertion. For a limiting number average degree of polymerization of, e.g., 1×10^5 , the time interval during which the polymerization is “controlled” is 100 s for TOF = 1 ms^{-1} (which is typically the case of *ansa*-met-

allocenes) and 1 day for TOF = 1 s^{-1} (which is instead representative of propene polymerization with **II**-Ti). How to apply a definition, as usual, is also a matter of common sense.

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