"Living" Propene Polymerization with Bis(phenoxyimine) Group 4 Metal Catalysts: New Strategies and Old Concepts

Giovanni Talarico,*,† Vincenzo Busico,† and Luigi Cavallo‡

Dipartimento di Chimica, Università di Napoli "Federico II", Via Cintia, 80126 Napoli, Italy, and Dipartimento di Chimica, Università di Salerno, Via Allende, 84081 Baronissi (SA), Italy

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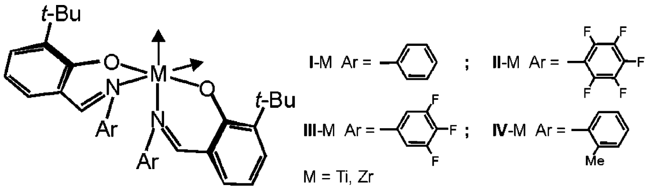
Bis(phenoxyimine)Ti catalysts with *ortho*-F-substituted phenyl rings on the N can be "living" propene polymerization catalysts. On the basis of DFT calculations, it has been proposed that the "living" behavior originates from an unprecedented *attractive* interaction between the said *ortho*-F atoms and a β-H of the growing polymer chain, which would render the latter less prone to be transferred to the metal (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 six-center transition structure for chain transfer to the monomer. A conceptually similar substituent effect has been reported before for several metallocene and non-metallocene catalysts; in the present case, though, this is partly *alleviated* by a weak *attractive* interaction between the *ortho*-F and a close-in-space α-H of the growing chain.

Introduction

The new class of C_2-symmetric group 4 metal catalysts bearing two phenoxyimine ligands[1−3] (Chart 1) has attracted much attention, inter alia, for the possibility to polymerize ethene and propene in a "living" manner.[4] This feature is highly unusual, in general, in Ziegler−Natta chemistry, because the growing polymer chains normally undergo comparatively fast β-H transfer. The impact of the said process, though, has been found to be negligible up to 25−50 °C for bis(phenoxyimine)Ti catalysts with an *ortho*-F-substituted phenyl ring on the N (e.g., **II**-Ti of Chart 1).[1−3]

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 be transferred to the metal and/or to the monomer.[2,5] This has been described as a new strategy for the control of catalyst behavior, as opposed to the "classical" one making use of *repulsive* nonbonded contacts in the coordination sphere of the transition metal.[6] Recent results of solution NMR studies on model compounds seemingly provide an independent validation to the concept.[7]

Chart 1



We have been intrigued by such a possibility, which would substantially expand the available tools in catalyst design. Therefore, we have carried out a combined experimental and theoretical investigation on some of the new catalysts. Herein we report on the main results obtained.

We decided to focus on propene polymerization, because the nature of the competing reaction paths is reasonably well-identified. In particular, a large body of experimental and theoretical results indicates that (i) propene insertion is the rate-limiting step in chain propagation (i.e., the insertion transition state is the highest point of the reaction path) and also that (ii) solvent and counterion effects, although undoubtedly important, are rather indiscriminate and do not largely affect the *relative* rates of the various possible insertion modes.[6,8,9] As a matter of fact, calculations that do not consider solvent and counterion explicitly, including those reported in previous papers by this laboratory on

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* To whom correspondence should be addressed. E-mail: talarico@chemistry.unina.it.

† Università di Napoli "Federico II".

‡ Università di Salerno.

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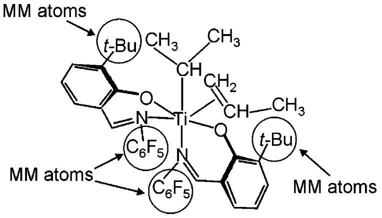

Figure 1. Partitioning between QM and MM treatment in the QM/MM approach for system **II**-Ti of Chart 1.

catalysts belonging to the very same class considered here,[10,11] are in very nice agreement with the experiments.

For ethene, instead, it is still unclear whether the rate-limiting step in chain propagation is monomer insertion or anion displacement from the active cation. Very recent calculations are actually more consistent with the latter hypothesis.[12,13]

Computational Strategy and Details

Stationary points on the potential energy surface were calculated with the Amsterdam Density Functional (ADF) program system,[14] developed by Baerends et al.[15,16] The electronic configuration of the molecular systems was 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 TZP). Double-ζ STO basis sets were used for fluorine, oxygen, nitrogen, and carbon (2s, 2p) and hydrogen (1s), augmented with a single 3d and 2p function, respectively (ADF basis set DZP).[14] 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.,[17] augmented in a self-consistent manner with Becke's[18] exchange gradient correction and Perdew's[19,20] correlation gradient correction.

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 quantum mechanics level. In a second approach, labeled as "QM/MM", the ^{t}Bu and Ar-on-N fragments were treated at the molecular mechanics level. As an example, the partitioning used in the QM/MM calculations for the specific case of **II**-Ti (Chart 1) is shown in Figure 1.

For the connection between the QM and MM part, we used "capping" dummy H atoms,[21,22] with the only exception of N−(C_6F_5) and N−($C_6H_2F_3$) bonds, for which we preferred to use F atoms to reflect the electron-withdrawing property of the aromatic fragment.

The ADF program was modified by one of us[21] to include standard molecular mechanics force fields in such a way that the QM and MM parts are coupled self-consistently.[22] 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 were fixed equal to 1.35 and 1.00, respectively, to reproduce the corresponding full-QM bond lengths. A more detailed description of the coupling scheme, as well as further comments on the methodology, can be found in previous papers.[21,23] The CHARMM force field[24] was used for the MM potentials, except for Ti and Zr, which were treated with the UFF force field.[25] To eliminate spurious stabilizations from the long-range attractive part of the Lennard-Jones potential,[23,26] we used an exponential expression fitted to the repulsive part of the Lennard-Jones potential.[23,27−29] Transition state geometries were approached by a linear-transit procedure, using the distance between the C(propene) and C(growing chain) atoms that are 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 that are 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.

Test calculations were also performed using a B3LYP functional,[30,31] obtaining similar trends.

Results and Discussion

Relevant reaction events in propene polymerization at a bis(phenoxyimine)M active species are shown in Scheme 1.

For Ziegler−Natta catalysts in general, β-H transfer *to the monomer* (Scheme 1, a−d) is normally much faster than that to the metal (Scheme 1, e,f).[6] We found experimentally that bis(phenoxyimine)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. As an example, in polypropylene samples obtained with **I**-$TiCl_2$/MAO at 20 °C we measured by ^{1}H NMR a content of terminal allyls of 1.1 mol % at $[C_3H_6] = 0.7$ M and of 1.4 mol % at $[C_3H_6] = 5.6$ M.[32]

As is well-known, the nature of M affects the regiochemistry of chain propagation. While M = Ti entails predominantly 2,1 (secondary) propene insertion into Ti−CH(CH_3)−CH_2−P (secondary chain, Scheme 1,

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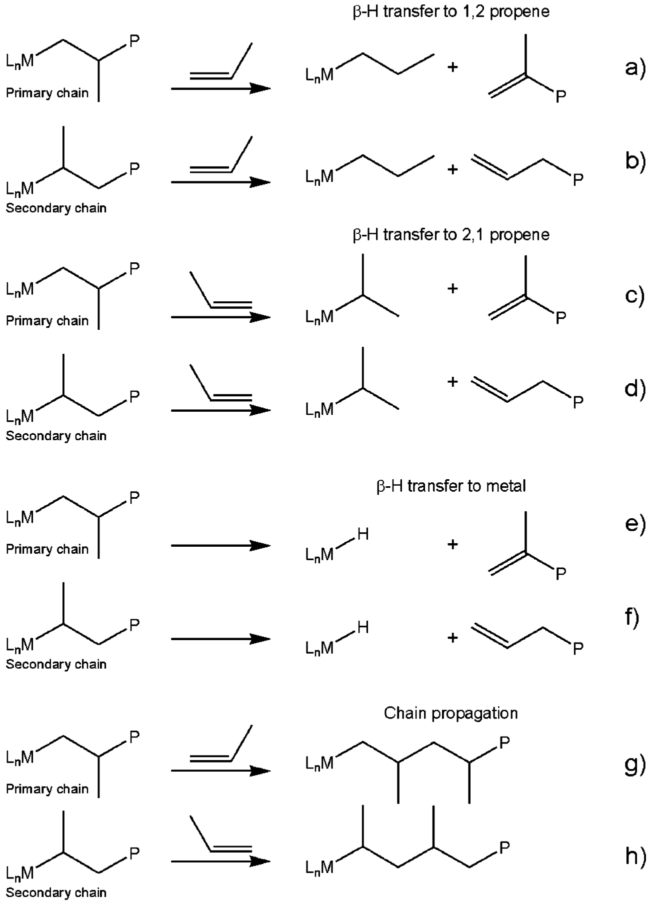
Scheme 1



h),[1,3,10,33,34] for M = Zr 1,2 (primary) insertion into Zr$-$CH$_2$$-$CH(CH$_3$)$-$P (primary chain) is favored (Scheme 1, g).[10,35]

On the other hand, our calculations indicate that the lowest energy pathway of β-H transfer to propene involves the latter in 1,2 orientation (Scheme 1, a,b).[36] This is fully consistent with (and at the same time explains) the experimental results of chain end-group analysis reported by Coates et al.[34] for non-*ortho*-F-substituted Ti-based catalysts and by Fujita et al.[35] 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 ($\Delta E^{\ddagger}_{\mathrm{T-P}}$) between the corresponding two transition states. In particular, the $\Delta E^{\ddagger}_{\mathrm{T-P}}$ values relevant to this investigation correspond to β-H transfer to 1,2 propene from a secondary chain (simulated with an isopropyl group) for M = Ti (Scheme 1, b) and from a primary chain (simulated with an isobutyl group) for M = Zr (Scheme 1, a). Such values are summarized in Table 1; for **II**-Zr, we also give the value corresponding to β-H transfer to 1,2 propene from a secondary chain.

Table 1. Calculated $\Delta E^{\ddagger}_{\mathrm{T-P}}$ (in kcal/mol) for the Systems of Chart 1 (see text)

system	alkyl chain	$\Delta E^{\ddagger}_{\mathrm{T-P}}$ (full-QM)	$\Delta E^{\ddagger}_{\mathrm{T-P}}$ (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

For a separate evaluation of electronic and steric contributions to $\Delta E^{\ddagger}_{\mathrm{T-P}}$, we compared the results of a full-QM analysis (Table 1, 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 1, column 4).

Let us now examine the data and in particular how $\Delta E^{\ddagger}_{\mathrm{T-P}}$ 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).[37] When M = Zr, $\Delta E^{\ddagger}_{\mathrm{T-P}}$ 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.[35]

The picture is remarkably different when M = Ti. Both for **I**-Ti and **II**-Ti, $\Delta E^{\ddagger}_{\mathrm{T-P}}$ is substantially larger than for the Zr homologues.[38] Importantly, however, the full-QM-calculated $\Delta E^{\ddagger}_{\mathrm{T-P}}$ 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,[3] whereas a "living" behavior is reported for catalysts based on **II**-Ti.[1-3]

To find a rationale for this, it is very instructive to compare the full-QM $\Delta E^{\ddagger}_{\mathrm{T-P}}$ 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 indeed that one of the said F atoms is at close nonbonded contact *with the monomer* in the transition states of both competing processes (Figure 2). Another, in turn, is at critically short distance *from the growing chain* in the transition state of β-H transfer to the monomer (Figure 2b), but *not* in that of monomer insertion (Figure 2a).

Remarkably, the remaining two *ortho*-F atoms, which point away from the active pocket, are by no means sterically irrelevant. In fact, their hindrance decreases the rotational freedom of the aromatic ring, which is in practice conformationally locked. As a matter of fact, if these two F's are removed,[1,39] according to our calculations the full-QM $\Delta E^{\ddagger}_{\mathrm{T-P}}$ value drops from 9 to 6 kcal/mol, that is, only 2 kcal/mol higher than for **I**-Ti. On the other hand, by replacing the remaining two *ortho*-

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(36) For each system, we calculated all possible TSs for monomer insertion and chain transfer to the monomer; in Table 1 we report the lowest $\Delta E^{\ddagger}_{\mathrm{T-P}}$ value.

(37) The calculated $\Delta E^{\ddagger}_{\mathrm{T-P}}$ values in Table 1 do not include ZPE, thermal corrections, and solvent and counterion effects; therefore, they cannot be expected to predict absolute average polymerization degrees. Instead, they can be used reliably to extract trends, because the aforementioned corrections and effects can be safely assumed to be similar when comparing similar reaction profiles.

(38) This effect is related in part to the nature of the metal, due to the stronger Zr−H bond compared to Ti−H. For homologous compounds in which Ar = H or F, using the same propagating chain, we found a difference between the Ti and Zr $\Delta E^{\ddagger}_{\mathrm{T-P}}$ values of ca. 4 kcal/mol.

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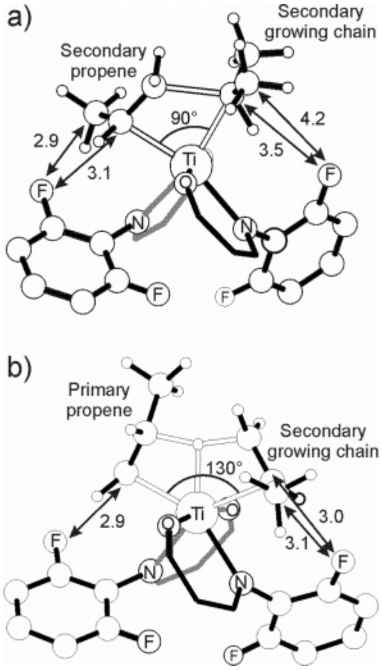

Figure 2. Transition states for 2,1 propene insertion (a) and β-H transfer to 1,2 propene (b) for **II**-Ti. For the sake of clarity, only the *ortho*-F atoms of the perfluorinated phenyl rings are shown, and the phenoxide rings are simply sketched in wire frame. Distances (in Å) between the *ortho*-F and the nearest-in-space C atoms of monomer and growing chain are given.

F's with two larger methyl groups (system **IV**-Ti), $\Delta E^{\ddagger}_{\mathrm{T-P}}$ increases again (last row of Table 1).[40] 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 $\Delta E^{\ddagger}_{\mathrm{T-P}}$ values.[1]

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* (Figure 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[41] aimed at estimating the extent of this H···F bonding interaction resulted in a bond order of 0.02 only, which roughly corresponds to a stabilizing interaction of about 1 kcal/mol.

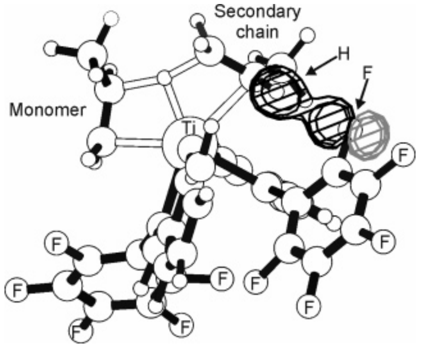

Figure 3. Transition state for β-H transfer to 1,2 propene at **II**-Ti, showing the attractive interaction of an *ortho*-F atom with an α-H atom of the growing chain. For clarity, only the MO portion that involves the H···F interaction (*ortho*-F···H distance, 2.1 Å) has been sketched.

It can be added that a similar weak intramolecular attractive H···F interaction has been detected experimentally in the aforementioned[7] solution NMR study on model (phenoxypyridine)Zr-benzyl species with a $-CF_3$ 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(phenoxyimine)-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 ca. 90°, can be accommodated in relatively small active pockets.[6,42,43] The latter instead has a bulkier six-center transition state spanning an angle of ca. 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 pseudo-tetrahedral 2,2′-substituted *rac*-bis(1-indenyl) *ansa*-metallocenes[44] and the square-planar Brookhart-type Ni and Pd catalysts[45] (Chart 2).

Whether or not this results in a "living" polymerization process is somewhat more complicated to foresee. It might be worth recalling at this point that any chain growth process with a fast initiation and a high ratio between the rates of propagation and transfer/termination begins with a transient "controlled" kinetic regime during which polymer molecular mass increases linearly with monomer conversion and M_w/M_n is 1 or slightly higher.[46] It can be licit to describe the whole process, at least in a first approximation, as "living" whenever the duration of the controlled regime compares with that of the polymerization experiment.[47] In turn, this is primarily related with the turnover frequency (TOF) of monomer insertion. For a limiting number average

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(40) An exceedingly low activity in propene polymerization has been found experimentally for catalyst system **IV**-$TiCl_2$/MAO (see: Furuyama, R.; Saito, J.; Ishii, S.-i.; Mitani, M.; Matsui, S.; Tohi, Y.; Makio, H.; Matsukawa, N.; Tanaka, H.; Fujita, T. *J. Mol. Catal. A: Chem.* **2003**, *200*, 31−42), probably due to the high steric congestion at the metal center.

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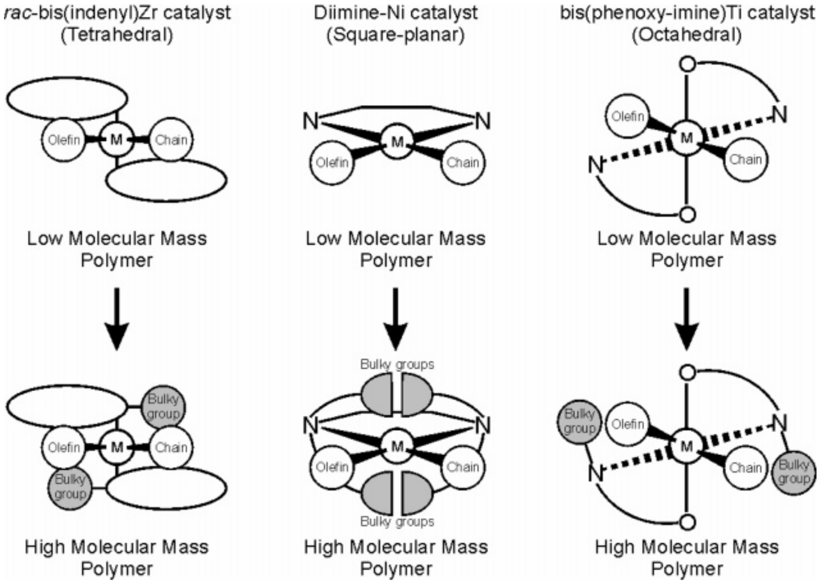
Chart 2



degree of polymerization of, indicatively, 1 × 10^4, the time interval during which the polymerization is “controlled” is 10 s for TOF = 1 ms^{-1} (which is typical of, for example, *ansa*-metallocenes[48]) and 3 h for TOF = 1 s^{-1} (which is instead representative of propene polymerization with **II**-Ti[49]).

Predicting the TOF of a specific catalyst is still—euphemistically—very difficult, because it depends on a high number of variables part of which, at present, cannot be modeled reliably. Therefore, just as an example, while we could calculate that **IV**-Ti gives polypropylene chains with a larger average molecular mass than **I**-Ti, we cannot provide a theoretical estimate of the average chain growth times.

One last remark concerns the possibility to extend the conclusions of this work to ethene polymerization. As we have already stressed in the Introduction, this is not immediate, as long as the complete kinetic model for this monomer is not clarified.[13] We simply note here that, under the same assumptions used for propene, our calculations provide a similar picture.[50] On the other hand, even if we limit the analysis to propene, the conclusions presented herein can already find important practical application, e.g., in the design of new stereoselective octahedral catalysts for controlled (“living”) isotactic propene polymerization, as has just been reported by some of us.[51]

Acknowledgment. We thank the CIMCF of the Università di Napoli “Federico II” for technical assistance. This work was supported by MIUR grants PRIN 2002 and FISR 1999 and by the Università di Salerno (grant Finanziamenti per Medie Apparecchiature 2003).

Supporting Information Available: Cartesian coordinates and energies of the structures discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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[47] How to apply a definition, of course, is partly subjective; for different viewpoints and results specifically in bis(phenoxyimine)Ti-catalyzed ethene polymerizations, it can be interesting to compare ref 5 and: Reinartz, S.; Mason, A. F.; Lobkovsky, E. B.; Coates, G. W. *Organometallics* **2003**, *22*, 2542−2544.

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[49] In our laboratory, for propene polymerization with **II**-Ti/MAO/2,6-di-^{t}Bu-phenol at 20 °C and [C_3H_6] = 5.9 M in toluene, we measured a TOF of 0.15 s^{-1}.

[50] As an example, for ethene polymerization we calculated a full-QM $\Delta E^{\ddagger}_{T-P}$ value of 6.6 kcal/mol (9.9 by QM/MM) for **I**-Ti and 9.2 kcal/mol (13.8 by QM/MM) for **II**-Ti, respectively.

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