

Theoretical Chemistry Accounts

Flexional Bis(phenoxy-imine) Zr and Ti Catalysts for Polymerization

--Manuscript Draft--

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Abstract:	<p>Bis(phenoxy-imine) complexes of zirconium or titanium, a type of Fenokishi-Imin (FI) catalysts, allow the production of polyethylenes with well-defined bimodal molecular weight distributions. Interestingly, by substitution of phenyl rings in the bis(phenoxy-imine) ligands by perfluorinated phenyl rings, the polymerization reaches a desired unimodal behaviour. These catalysts have 3 isomers of similar energy that can be easily interconverted. It is likely that the bimodal behaviour is due to the coexistence of more than one isomer in the reaction vessel. Here, we perform static and dynamic DFT calculations to understand the isomerization of the catalytic active species. We analyze the relative Gibbs energies of the different isomers and the barriers for the isomerization processes. Further characterization of the isomers is obtained through stereo maps, aromaticity measures, and NCI plots. Our results show that by changing the phenyl group by a perfluorinated phenyl ring, one of the isomers is particularly stabilized, thus explaining the unimodal behaviour of the polyethylene production process.</p>	

Response to Reviewers:

Ref.:
Ms. No. TCAC-D-20-00507
"Flexional Bis(phenoxy-imine) Zr and Ti Catalysts for Polymerization"
Theoretical Chemistry Accounts

Dear Dr. Poater,

We have now received sufficient referee advice on your manuscript:

"Flexional Bis(phenoxy-imine) Zr and Ti Catalysts for Polymerization"

which you submitted to "Theoretical Chemistry Accounts".

Based on the comments of the reviewer(s), I would be pleased to reconsider for publication a manuscript incorporating minor revisions that address their points. Together with preparation of your revised manuscript, please assemble a list of responses to each point raised by the referee(s).

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With kind regards,

Dr. Ilaria Ciofini & Prof. Carlo Adamo
Editor-in-Chief
Theoretical Chemistry Accounts

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COMMENTS TO THE AUTHOR:

Reviewer #1: Poater et al. reported a theoretical work about the origin of multimodal or monomodal polyethylene (PE) from differently substituted Fenokishi-Imin (FI) type catalysts based on Ti or Zr. Based on their calculations, the authors came to the conclusion that, for catalysts with substitution patterns leading to multimodal distributions, this behavior arises from the coexistence of different isomers in the reaction system. When the phenyl groups were replaced by perfluorinated phenyl rings, the authors found that the unimodal behaviour of PE was due to the fact that a specific isomer was particularly stabilized. Overall, I believe that the conclusions of the authors make sense and that the authors did a good work in considering all the possible isomers involved in the process and in applying advanced theoretical approaches to gain understanding of the aromaticity of the perfluorinated phenyl rings. Additionally the manuscript is well written, systematic and understandable to readers without strong computational background. Therefore, I suggest acceptance of the article after few minor corrections.

a) In Scheme 1 the authors show the 5 possible isomers before catalyst activation and mention that after activation the number of isomers is reduced to just 3. Although the methylated isomers are sketched in Figure 1 it would be helpful to have the full structures included in Scheme 1.

OUR ANSWER: Maybe we were not clear enough in the discussion of the different possible isomers. The two isomers that disappear from Scheme 1 to Figure 1 are D and E, but they disappear as isomers, leading to transition states in Figure 1. Thus, we have added a comment to clarify this: "In fact, these two transition states have a similarity with the isomers D and E of Scheme 1, respectively."

b) Some sentences could be clearer; for instance at the beginning of Page 2 "5 Within the spectrum of solutions to obtain multimodal PEs, dual reactor cascades coexist with catalytic duality, and also of special relevance is to control the chosen pH.26,27,28,29,30" it is not very clear what is a "dual reactor (reaction?) cascade" and a "catalytic duality". Also, at the beginning of Page 4, in the sentence ". This increase for Ti is not accidental, since both bidentate ligands, removing the methyl ligand and the metal, amounts 64.8, 65.2 and 66.4% for Zr, and 70.9, 70.7, and 71.3% for Ti." it seems that something is missing and is not very clear at the moment.

OUR ANSWER: We have corrected these sentences to make them be clearer.

c) When the authors discuss the parameters that define the substituents aromaticity at Page 4 "the maximum aromaticity is achieved at a value of 1. From the electronic point of view, FLU gives values close to zero for aromatic and greater numbers for non-aromatic or antiaromatic rings, and PDI gives high positive values (close to those obtained for benzene 0.1030) as indicative of aromatic character, whereas small values correspond to non-aromatic species (FLU and PDI results in Figure 3 for A-C with Zr, and Tables S3 and S4 for others)." the authors mention in some cases "small" "large" "greater" values used to assign aromatic behavior, however this kind of terminology is quite unclear and it would be better to establish a range of values in each case.

OUR ANSWER: We have clarified this expressions "higher", "greater"...

Reviewer #2: Few things to say about manuscript ID TCAC-D-20-00507 by Poater and co-workers. I sincerely guess this is a very nice work that, surely, will be of interest for the TCA readership community. The computational methodology is rather adequate, as it is expected given the proven level of the PIs. The structural, energy (including Conceptual DFT), orbital, aromaticity, and NCI analysis are concise, clear, and direct. Just the appearance of a few typos, e.g., "contrast" instead of "contrasts" (page 4, line 59, left), authors should use bold typography for some letters as done for others (paragraph before Fig. 2), etc. (something that might be polished during proof stage). In opinion of this referee, the present communication should be accepted in TCA. I also guess that will be a great contribution to honour Prof Carbo in his 80th birthday.

OUR ANSWER: We thank the positive comments, and we corrected the text following the suggestions.

[Click here to view linked References](#)

Flexional Bis(phenoxy-imine) Zr and Ti Catalysts for Polymerization

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KEYWORDS: *Olefin Polymerization, Mechanism, FI catalysts, DFT, Isomerization, Multimodal Catalysis.*

Supporting Information Placeholder

ABSTRACT: Bis(phenoxy-imine) complexes of zirconium or titanium, a type of Fenokishi-Imine (FI) catalysts, allow the production of polyethylenes with well-defined bimodal molecular weight distributions. Interestingly, by substitution of phenyl rings in the bis(phenoxy-imine) ligands by perfluorinated phenyl rings, the polymerization reaches a desired unimodal behaviour. These catalysts have 3 isomers of similar energy that can be easily interconverted. It is likely that the bimodal behaviour is due to the coexistence of more than one isomer in the reaction vessel. Here, we perform static and dynamic DFT calculations to understand the isomerization of the catalytic active species. We analyze the relative Gibbs energies of the different isomers and the barriers for the isomerization processes. Further characterization of the isomers is obtained through stereo maps, aromaticity measures, and NCI plots. Our results show that by changing the phenyl group by a perfluorinated phenyl ring, one of the isomers is particularly stabilized, thus explaining the unimodal behaviour of the polyethylene production process.

INTRODUCTION

Obtaining new polyolefins, as well as characterizing them having well-defined structures, to move to new materials,^{1,2,3} has been attempted using homogeneous olefin polymerization catalysts.^{4,5,6,7,8} Among polyolefin family, polyethylene (PE) is known as the simplest and widely used plastic, which is produced worldwide as much as tens of millions of tons per year.^{9,10,11} PEs were discovered in the late nineteenth century and have ended up being the most common plastic, with one third of the world market.¹² This linear polymer is widely used in packaging. Chemically, PEs are distinguished by having an excellent combination of mechanical properties and processability, which is mostly achievable by homogeneous and heterogeneous catalysis,^{13,14,15} respectively.

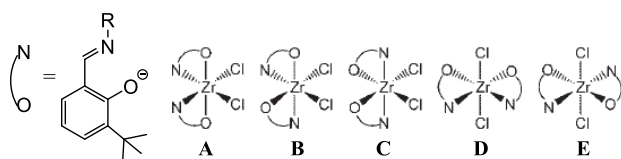
The great advance in the production of PE began with the development of catalysts that favoured the polymerization in mild conditions of temperature and pressure.¹⁶ From the first Phillips catalysts based on chromium trioxide,¹⁷ it passed to those of Ziegler, that is, a combination of titanium halides and organoaluminum compounds. Although the latter meant an improvement in reaction conditions,¹⁸ the former had much less production cost. However, both types are industrially suitable for the generation of high density polyethylene (HDPE). The inclusion of magnesium chloride improved the activity of Ziegler catalysts. Later, Kaminsky and Sinn gave a boost to the catalytic activity of metallocenes, thanks to the improvement of their solubility.^{19,20}

If we look at PEs, those that are of special interest possess well-defined and controlled multimodal molecular weight distributions. Multimodal PEs are already commercially available, but with difficulty in controlling the reaction conditions to avoid from the decomposition of the catalyst itself to differences in the chain transfer mechanism.^{9,10,22} In addition, it may have to coexist with a factor of multiple presence of catalytically active species, and this, in the end avoids the rigorous control over the molecular weight distributions.^{21,22,23,24,25} Within the spectrum of solutions to obtain multimodal PEs, dual reactor cascades coexist with catalytic duality. And also of special relevance is to control the chosen pH.^{26,27,28,29,30} In particular, catalysis by structural isomers according to the coordination of ligands around the metal center is feasible from a single precatalyst for bis(phenoxy-imine) early transition metals, also called FI catalysts for olefin polymerization.^{31,32} Next, once activated by methylaluminoxane (MAO), FI catalysts lead to PEs with highly controlled particle-size;^{33,34} ethylene-propylene copolymers with unique propylene distributions; highly thermally stable and with very high tacticity polypropylenes (PPs); highly regioirregular high molecular weight poly(1-hexene)s; and a wide array of unique block copolymers, unaffordable with other types of catalysts.^{35,36,37,38,39,40,41}

With the aim to understand the FI catalysis with early transition metal complexes for olefin polymerization,^{42,43,44} Fujita and coworkers demonstrated that bis(phenoxy-imine) Zr complexes are single precatalysts that can form bimodal PEs with very high activities.^{45,46} However, its activity is highly dependent on the nature of the substituent on the imine-nitrogen. Interestingly, when

the phenyl group attached to the imine-nitrogen is substituted by a pentafluorophenyl group, the catalyst generates unimodal PEs.

Five isomers (**A-E** in Scheme 1) of the bis(phenoxy-imine) zirconium or titanium based precatalysts can coexist. However, the catalytic activity does not occur with the neutral complexes, but with the cationic form where both chloride atoms are substituted with just a single methyl group. The pentacoordination leads to only three isomers (homologous to **A-C** bearing both phenoxy-imine ligands), *i.e.* *cis-N/trans-O* (**A**), *cis-N/cis-O* (**B**), and *trans-N/cis-O* (**C**). According to Density Functional Theory (DFT) calculations by Koga and Nagaoka *et al.*, isomer **A** *cis-N/trans-O* results as the most stable one with isomer **C** close in energy.⁴⁷ Bis(phenoxy-imine) modified ligands could tune the preference for unimodal polymerization instead of multimodal with the three isomers, and further calculations try to reach this goal.⁴⁸ Finding any clue to be able to go from multimodal to unimodal catalysis is an unresolved issue for FI catalysts.⁴⁹ Here we want to better characterize the isomerization among the multimodal polymerization species, for zirconium and titanium, by static and dynamic quantum calculations.



Scheme 1. Five possible isomers for a bis(phenoxy-imine) Zr complex with R = C₆H₅ or C₆F₅.

COMPUTATIONAL DETAILS

DFT calculations were performed with the Gaussian09 set of programs.⁵⁰ For geometry optimization, the GGA functional BP86 was used.^{51,52} Geometry optimizations were performed without symmetry constraints, while the located stationary points were characterized as minima or transition state by analytical frequency calculations. The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, and O (SVP keyword in Gaussian).⁵³ For Zr and Ti, we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set contracted (standard SDD keywords in Gaussian).^{54,55,56} Electronic energies were improved using the M06 functional⁵⁷ with the triple- ζ valence plus polarization basis set for main group atoms (TZVP keyword in Gaussian). The M06-PCM(DCM)/TZVP~SDD/BP86/SVP~SDD energies were corrected with zero point energies and thermal corrections calculated at the BP86/SVP~SDD level of theory to obtain the Gibbs energy in the gas-phase. To this energy, we added the solvation energy calculated with the polarizable continuous solvation model PCM using CH₂Cl₂ (DCM) as solvent.^{58,59}

AIMD simulations were performed using the Born-Oppenheimer scheme as implemented in the CP2K Quickstep code.^{60,61} The electronic structure calculations were done at the DFT level using the Perdew-Burke-Ernzerhof exchange and correlation functional.⁶² Within CP2K the Kohn-Sham molecular orbitals are described by a linear combination of Gaussian-type orbitals, whereas an auxiliary planewave basis set is employed to expand the electron density.⁶³ A double- ζ basis set with a polarization function,⁶⁴ in conjunction with the Goedecker-Teter-Hutter pseudopotentials,^{65,66} was used for all the atoms (standard DZVP-GTH in CP2K). The auxiliary planewave basis set was defined by a cubic box of 20 \times 20 \times 20 Å³ and by an energy cutoff of 300 Ry. The equations of motion were integrated using a time

step of 0.5 fs. The systems were first equilibrated at 300 K for 2 ps in the NVT ensemble and then were sampled for an additional 10 ps.^{67,68}

Moreover, aromaticity and non-covalent interactions (NCI) indices have been used for the characterization of the ligands. We choose the harmonic oscillator model of aromaticity (HOMA)⁶⁹ as a structural aromaticity index. We also computed two electronic indices, namely, the fluctuation index (FLU)⁷⁰ and the *para*-delocalization index (PDI),⁷¹ using AIMAll⁷² together with ESI-3D^{73,74} packages. As a magnetic indicator of aromaticity, we used the out-of-plane component of nucleus independent chemical shift (NICS_{zz}).⁷⁵ Finally, the NCIs were calculated using the NCIPLOT program developed by Contreras-García *et al.*^{76,77} All the above calculations were performed at the BP86/SVP~SDD level of theory.⁷⁸

RESULTS AND DISCUSSION

DFT calculations were carried out to describe the thermodynamics and the interconversion processes of the three isomers of the cationic catalysts, bearing a methyl group on the metal (either zirconium or titanium).⁷⁹ For the interconversion, there are two symmetric pathways: **A**→**B**→**C** and **A'**→**B'**→**C'**. And also **A**→**C'** and **B**→**B'** that link the previous ones. In fact, these two transition states have a similarity with the isomers **D** and **E** of Scheme 1, respectively. **X** and **X'** are enantiomers. Figure 1 summarizes all these steps, and Table 1 the relative energies. Next, the scheme has been repeated replacing the metal (Zr by Ti), and also replacing the hydrogen atoms on the phenyl rings by fluorides.

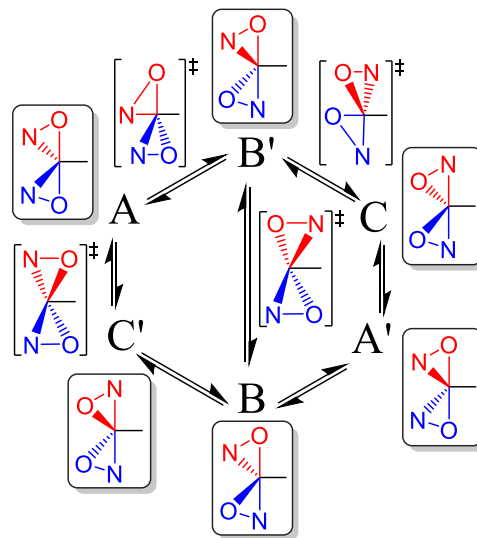


Figure 1. Isomerization paths between **A-C**. The structure of the bis(phenoxy-imine) is shown in Scheme 1.

Table 1. Relative Gibbs energies of isomers **A-C** and of the transition states of the possible interconversions (energies in kcal/mol).

	Zr (R=C ₆ H ₅)	Ti (R=C ₆ H ₅)	Ti (R=C ₆ F ₅)
A	0.0	0.0	0.0
TS(A→B')	9.9	9.4	9.9
B'	-1.4	-1.6	-2.7
TS(B'→C)	8.0	10.3	9.8
C	-1.2	-0.1	-0.5
TS(A→C')	4.8	10.4	12.1

TS(B→B')	6.6	11.6	11.6
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Table 1 gives the barriers for the interconversion among the different isomers studied. In the sequence from **A** to **C** passing through **B**, the two transition states involved (shown in Figure 2) require the motion of only one bidentate ligand in each of them. The **TS(A→C')** on the other hand, requires the synchronous concerted movement of the two bidentate ligands at the same time. The **TS(B→B')** is of a similar nature and both coincide with having angles close to 109° with the coordinating atoms of the bidentate ligands. As can be seen the barriers are not larger than 12 kcal/mol. This result indicates that the interconversion is facile and that the three isomers are in equilibria in the three studied cases. We have also analysed the rotation of the aryl groups in all isomers. The barriers obtained were found to be lower than 7.2 kcal/mol, indicating that at room temperature these aryl groups have free rotation.

The barriers of the processes **A→C'** and **B→B'** increase substantially when changing Zr by Ti. This result can be explained taking into account the shorter Ti-N bond distances with respect to the Zr-N ones by around 0.2 Å.

Results in Table 1 show that **B** isomer is favoured thermodynamically. This result contrasts with the calculations by Koga and Nagaoka et al.⁴⁷ that favour complex **A**. However, these calculations were performed using a different FI-catalyst, which proves that the stability of the different isomers is very dependent on the substitution of the aromatic rings. Our results show that despite **B** is the most stable for Zr (R = C₆H₅) catalyst, **C** differs by only 0.2 kcal/mol and, therefore, we have both isomers in substantial concentration. For Ti (R = C₆H₅), **B** is also the most stable and **C** and **A** coexist in significant proportions. Finally, for Ti (R = C₆F₅), **B** is by far the most stable and abundant, thus explaining why in this case we move from bimodal to unimodal molecular weight PE distribution.

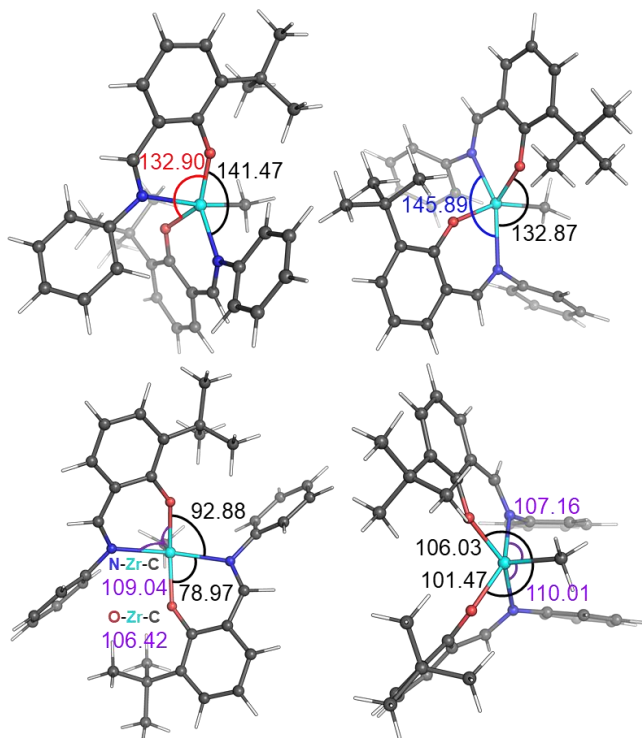


Figure 2. Geometry of the transition states for zirconium, **TS(A→B')** (top left), **TS(B'→C)** (top right), **TS(A→C')** (bottom

left), and **TS(B→B')** (bottom right), with hydrogen atoms on phenyl rings. Main angles in deg.

Conceptual DFT,^{80,81} by means of the chemical hardness, confirms a trend where **B** is the hardest isomer, while **C** is the softest one, with **A** in between for any of the three complexes analyzed (see Table S1). Thus, isomer **B** is the less prone to react.⁸² The per-fluorination means a decrease of the chemical hardness, and thus an increase of the reactivity for those catalysts. More interestingly, those fluorides break partially the equilibrium between the three isomers, favoring more strongly **B**, and this is also checked in the relative Gibbs energies in Table 1, by 2.7 kcal/mol. In addition, it is facile to conclude that the inclusion of Ti enlarges the energy barriers of the processes **A→C'** and **B→B'** that could be explained by the shorter Ti-N bond distances with respect to the Zr-N ones by around 0.2 Å.

Sterically, no significant difference is expected in the metal sphere for the three isomers **A-C**, since all ligands are identical. Numerically, the buried volume %V_{Bur},^{83,84,85,86} describing the sterical bulkiness on the methyl ligand amounts 51.9, 52.3, and 53.4%, respectively, for the Zr based structures, while 56.8, 56.2, and 59.0% for Ti ones. This increase for Ti is not accidental, since taking into account only both bidentate ligands, thus removing the methyl ligand and the metal, the %V_{Bur} amounts 64.8, 65.2 and 66.4% for Zr, and 70.9, 70.7, and 71.3% for Ti. Thus, the simple %V_{Bur} rationalizes in a facile way the better catalytic performance of Zr based catalysts.¹⁴ However, %V_{Bur} is not useful to differentiate between isomers **A-C**,^{87,88} in particular which of them is more significantly reactive towards entering olefins.

To characterize dynamically the isomerization among the three isomers (**A-C**) we performed an ab initio molecular dynamics simulation starting from species **A**. The most relevant structural fluctuations of the metal environment led that accidentally **A** is transformed to **B** and next **C** sequentially, overcoming the repulsive forces between bidentate ligands with the methyl ligand on zirconium⁸⁹ (see SI video for the whole dynamic sequence).⁹⁰ The CP2K energies for each extreme are in agreement with static Gaussian calculations, with **B** and **C**, placed 0.7 and 2.3 kcal/mol below **A**, respectively. More interestingly, the energy barriers for the interconversion **A→B'** and **B'→C** were found to be 13.7 and 11.0 kcal/mol, respectively.

At this point, we wanted to know the reason for the high stability of isomer **B** in the Zr (R = C₆F₅) catalyst. We checked first the aromaticity of the ligands in the Zr and Ti complexes by means of geometric, electronic and magnetic measures.⁹¹ In the particular case of the HOMA geometry index (see Figure 3 for **A-C** with Zr, and Table S2 for others), the maximum aromaticity is achieved at a value of 1. From the electronic point of view, FLU gives values close to zero for aromatic and larger numbers for non-aromatic or antiaromatic rings, and PDI gives high positive values (close to those obtained for benzene 0.1030) as indicative of aromatic character, whereas small values correspond to non-aromatic species (FLU and PDI results in Figure 3 for **A-C** with Zr, and Tables S3 and S4 for others). Finally, we have the magnetic NICS_{zz} measure, in this case we took the negative value of the out-of-plane component of the isotropic shielding at 1 Å in and out from the ring plane (NICS(in,out)_{iso,zz}). Here, negative values indicate the presence of diatropic currents associated to aromaticity and positive values indicate paratropic currents, corresponding to non-aromatic or antiaromatic compounds (see Figure 3 for **A-C** with Zr, and Table S5 for the rest of the systems).

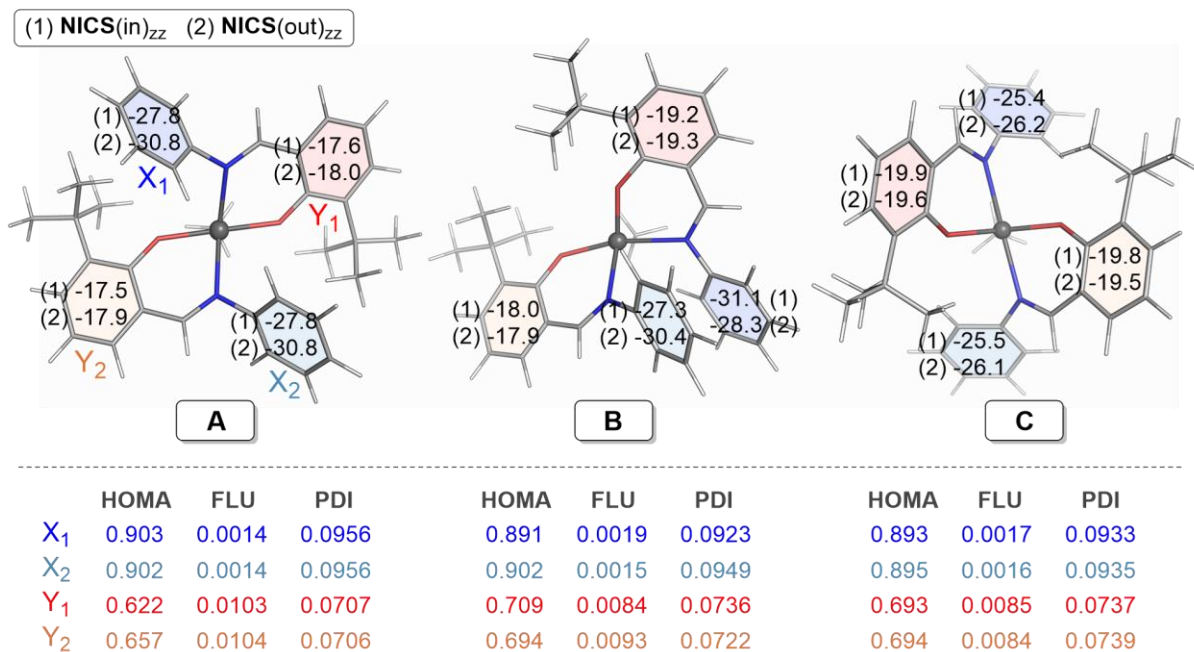


Figure 3. NICS_{zz}, HOMA, FLU and PDI aromaticity results of the aryl groups (X₁, X₂, Y₁ and Y₂) in isomers **A**, **B** and **C** for the Zr complex. In the case of NICS_{zz}, in (1) and out (2) measures correspond to those were the Bq is located pointing forward or back the paper plane, respectively.

The aromaticity of the ligands is maintained in all the isomers, since we observe really small changes in the values obtained. This might seem like an insubstantial result, but it is the confirmation that multimodal catalysis is not really influenced by the aryl groups of the catalyst, because of their aromaticity, but maybe the steric hindrance they produce. Knowing this, a possible idea for future investigations would be to try to make a difference, taking for instance groups with enough steric capacity to block isomerization. Nevertheless, there are tiny differences to be discussed here yet, since according to all aromaticity measures pentafluorobenzene (X₁ and X₂) and tetrafluorobenzene (Y₁ and Y₂) rings (Tables S2-S5) are the less aromatic ones, even though the potential H-bonds that fluorides might create.^{92,93} Therefore, the aromaticity is decreased with the substitution of H by F. Another remarkable difference among the set of isomers is that **B** has a significant increase in the NICS_{zz} (in positions pointing towards the other aryl group, (2) of X₁ and (1) of X₂, are ~3 ppm higher (more negative, *i.e.* more negative) than the external positions, in Figure 3),⁹⁴ due to the coupling of the magnetic fields in the π - π stacked pairs of rings,^{95,96} We also observe a quantitatively similar increase in the NICS(out)_{zz} values of rings X₁ and X₂ in isomer **A**, due to the interaction of the aryls with the tert-butyl groups. Those values mentioned above, could be contaminated by the overlap between aryl rings.⁹⁷ In this line, to further confirm the π - π stacking,^{98,99} NCI plots to better describe those interactions were carried out.¹⁰⁰ Figure 4 collects the plots for **B** with the Ti based catalyst. When perfluorating the aryl rings on nitrogen the interaction between rings seems to enlarge slightly. Actually, the distance among both aryl rings is 4.127 and 4.256 Å with and without fluorides, respectively, thus the fluorides favor this interaction (see Table S6 for further details).

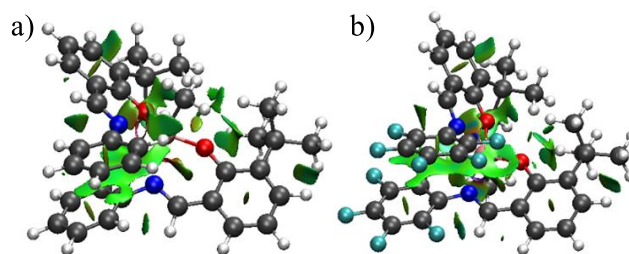


Figure 4. NCI plots of isomer **B** for Ti based catalyst with (a) hydrogen atoms on the aryl rings or (b) fluorides.

CONCLUSIONS

The analysis of the different isomers of bis(phenoxy-imine) zirconium and titanium complexes with a methyl ligand has allowed us to understand the change from bimodal to unimodal PE polymerization process when the H atoms of the phenyl group in the phenoxy-imine ligand are substituted by fluor atoms. Small energy differences between the three isomers in the zirconium complex allow their coexistence, thermodynamically speaking. From a kinetic point of view, the interconversion among the different isomers is facile. The replacement of zirconium by titanium did not change anything, as found experimentally. However, the perfluorination of the aryl rings of the phenoxy-imine ligand leads to an isomer **B** much favoured than isomers **A** and **C**, thus partially explaining the unimodal behaviour observed. The higher stability of the isomer **B** is not due to aromaticity but to better π - π stacking interactions, as confirmed computationally with the evaluation of the non-covalent interactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information provides the Cartesian coordinates, absolute energies, conceptual DFT, stereo maps, and

1 aromaticity results of all computed species discussed in this
2 work; and the simplified molecular dynamics simulation se-
3 quence.

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8 Notes

9 The authors declare no competing financial interests.

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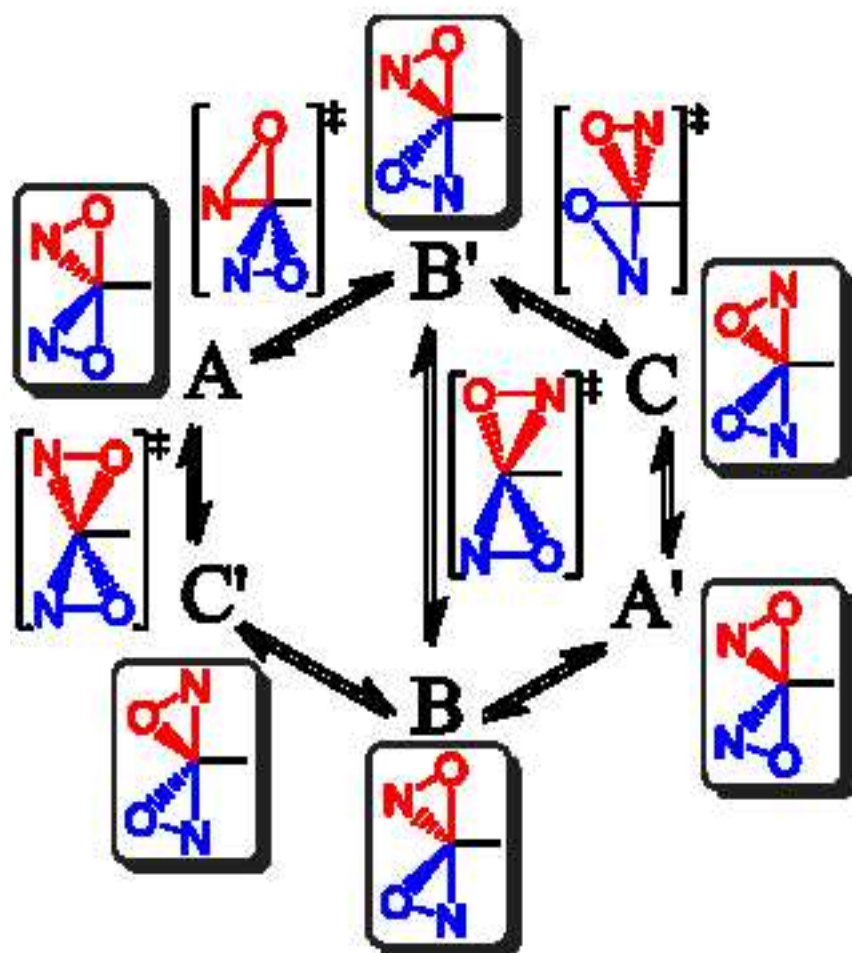
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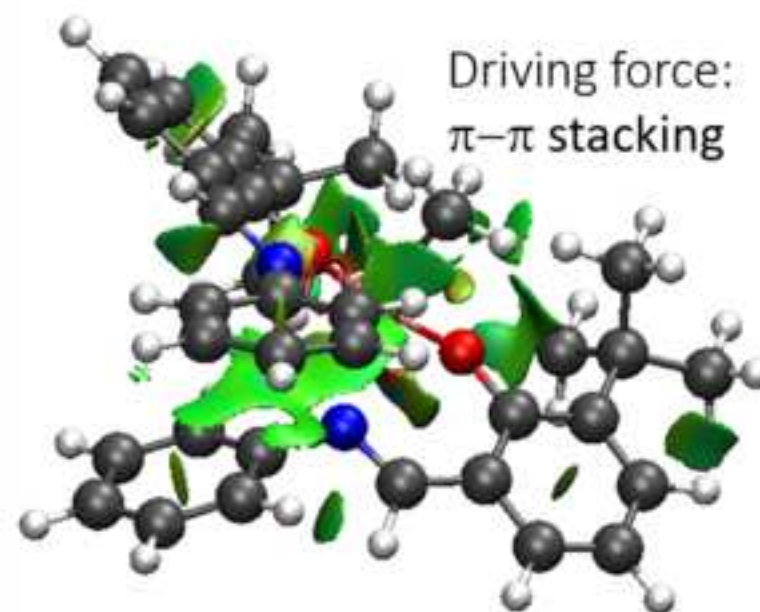
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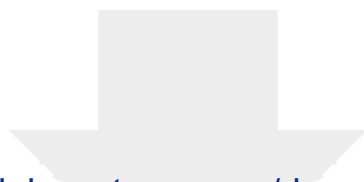
Unimodal or Multimodal Polymerization Catalysts?



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