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Theoretical study of isomerism in phenoxyimine-based precursors of coordinative olefin polymerization catalysts

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ABSTRACT

Precursors of post-metallocene olefin polymerization catalysts, unlike their predecessors, are usually octahedral transition metal complexes with multidentate ligands. Such ligands may wrap around the central atom in many ways, thus yielding several isomeric species. For a wide range of phenoxyimine (FI) ligands with different substituents, all the theoretically predicted diastereomers of group 4 and 5 complexes are available synthetically. However, only one of the isomers is usually preferred, and this is determined by the nature of the substituents in the FI ligand. The origin and mechanism of such preference has not been completely elucidated. We attempted to describe it quantitatively on the basis of density functional theory and our calculations indicate that the main factor contributing to the stability of a particular isomer of the complex is the molar volume of the substituent at the nitrogen atom in the FI ligand.

1. Introduction

More than two decades after the spectacular discovery of metallocene-based catalysts in coordinative olefin polymerization, the research efforts have concentrated on other classes of compounds as prospective precursors of coordinative polymerization catalysts, for instance the complexes of chelating [ON]- and [ONNO]-type ligands. Of special interest are the group 4 complexes with phenoxyimine (FI) [1], salen, salan or salalen ligands [2–4], yielding the catalysts whose activities rival those of metallocenes.

Simultaneously with the on-going experimental works in the field of post-metallocene catalysts, theoretical research is carried out in order to understand the factors that influence the properties of the catalytic systems, and eventually design new catalysts *in silico*. The problem of isomerism, inherent in the octahedral complexes, must be taken into account when the theoretical study of the polymerization process is designed. For the most complicated case, when a hexakis–heteroleptic octahedral complex [Mabcdef], is involved, the number of possible isomers equals 30. Reducing the variety of ligands, and introducing the bidentate ones, limits this number to a certain extent. However, it is still absolutely necessary to consider all the possible isomers, and discuss their role in the polymerization process. This holds true not only in the case of propylene, which is a prochiral monomer and can distinguish between the individual enantiomeric active sites in the consecutive insertion events, but also for ethylene, where the relative energies of diastereomers (and possibly transition states derived from them) influence the course of the reaction in a similar way.

It was long before the era of the widespread computational techniques, when the efficient algorithms for enumerating the isomers of octahedral complexes were developed. It is claimed [5] that one of the most elegant and successful schemes was suggested by Bailar [6]. In this method, one isomer of a complex containing six different monodentate ligands is represented by three pairs of letters (a–f) denoting the ligands. The letters put side by side in a pair indicate the ligands located *trans* to each other and the first pair marks the vertical axis of the molecule. Then the letters are interchanged with the first pair left intact, which gives two additional isomers. Next, one ligand on the vertical axis is replaced and the interchange is performed again. In total, there are five iterations to this process, yielding 15 diastereomers with the corresponding enantiomers (which are not predicted within the Bailar scheme). Finally, if the complex contains some identical or multidentate ligands, the number of isomers is reduced either by symmetry or by the constraint allowing the chelate group to span only *cis* positions [6].

This procedure turned out to be especially amenable to the computer implementation. The original code, developed by Bennett [7], lacked the visualizer, which we added for the purpose of this and future studies (see Section 2). It should be mentioned that the Bailar method has already been applied by us in determining the number of relevant isomers in modeling the polymerization process over the $MgCl_2$-supported catalyst modified by a bidentate Lewis base [8], although without the programs mentioned above.

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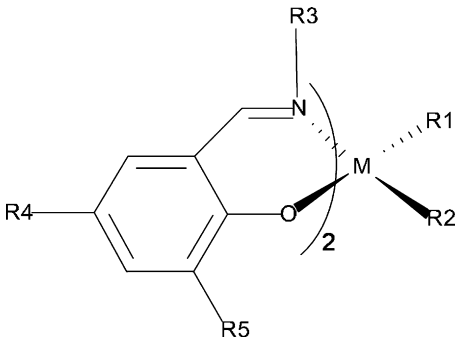

Fig. 1. Bis(FI) group 4 complex.

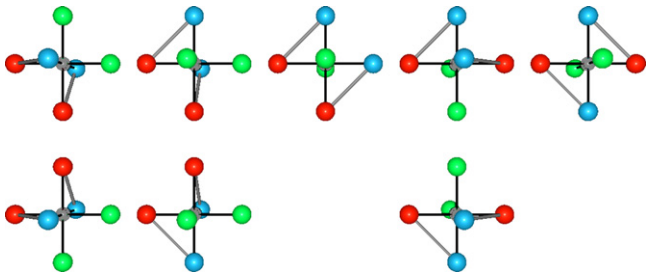

Fig. 2. Eight isomers of a bis(FI) complex. Chlorine atoms are green; oxygen—red and nitrogen—blue.

We listed and depicted all eight isomers of a bis(FI) octahedral complex, whose formula is given in Fig. 1. For the simplicity of this discussion, it is assumed that R1 = R2 = Cl and R3 = R4 = R5 = H. There are three pairs of enantiomers and two separate diastereomers (see Fig. 2). Only the species that have the chlorine atoms in the *cis* arrangement may be the potential precursors of α-olefin polymerization catalysts [1,2,9–12]. Taking this fact into account we get three diastereomers: N,N-*cis*-O,O-*trans*, N,N-*trans*-O,O-*cis* (both of the C_2 symmetry), N,N-*cis*-O,O-*cis* (C_1 symmetry) and their

Table 1
The N,N-*cis*-O,O-*trans* isomers of group 4 bis(FI) complexes.

No.	Metal	R1, R2	R3	R4	R5	Reference
1	Ti	Cl	Phenyl	H	H	[22]
2		*iso*-Propoxyl	Phenyl	H	H	[21,23]
3		Cl	Phenyl	H	*tert*-Butyl	[13,14]
4		Cl	Phenyl	Methyl	*tert*-Butyl	[24]
5		Cl	Phenyl	*tert*-Butyl	*tert*-Butyl	[25]
6		Cl	Phenyl	H	Phenyl	[26]
7		μ-O [a]	Phenyl	H	H	[23]
8		Cl	2,6-Difluorophenyl	H	*tert*-Butyl	[15]
9		Cl	2,6-Difluorophenyl	I	I	[27]
10		Cl	3,5-Difluorophenyl	*tert*-Butyl	*tert*-Butyl	[20]
11		Cl	Pentafluorophenyl	H	H	[28]
12		*iso*-Propoxyl	Pentafluorophenyl	H	H	[21]
13		Cl	Pentafluorophenyl	H	*tert*-Butyl	[15,29]
14		Methyl	Pentafluorophenyl	H	*tert*-Butyl	[30]
15		Cl	Pentafluorophenyl	*tert*-Butyl	*tert*-Butyl	[31]
16		Cl	Pentafluorophenyl	H	Trimethylsilyl	[32,28]
17		Cl	4-Trifluoromethylphenyl	*tert*-Butyl	*tert*-Butyl	[33]
18		Cl	2,4,6-Trimethylphenyl	H	*tert*-Butyl	[34]
19		N-Ethyl-salicylaldiminato-O	Ethyl	H	H	[35]
20		Cl	Benzyl	H	*tert*-Butyl	[18]
21		*iso*-Propoxyl	1-Phenylethyl	H	H	[21]
22		*iso*-Propoxyl	1-Phenylethyl	Methoxy	H	[36]
23		Cl	Allyl	H	Phenyl	[37]
24		*iso*-Propoxyl	NH_2	H	H	[38]
25		*iso*-Propoxyl	NH_2	*tert*-Butyl	H	[38]
26	Zr	Cl	Phenyl	H	*tert*-Butyl	[39,1,9]
27		Cl	Phenyl	Methyl	*iso*-Propyl	[40]
28		Cl	Phenyl	Methyl	*tert*-Butyl	[40,24]
29		Cl	Phenyl	Methyl	1-Adamantyl	[1,41]
30		Cl	Phenyl	H	Allyl	[42]
31		Cl	Pentafluorophenyl	H	Methyl	[43]
32		Cl	2,4,6-Trimethylphenyl	H	*tert*-Butyl	[34]
33		Cl	4-Allyloxyphenyl	H	*tert*-Butyl	[44]
34		Cl	Methyl	H	H	[45]
35		*iso*-Propoxyl	1-Phenylethyl	H	H	[36]
36		*iso*-Propoxyl	1-Phenylethyl	Methyl	H	[36]
37		Dimethylamino	Isopropyl	H	H	[22]
38		Cl	Cyclobutyl	Methyl	*tert*-Butyl	[46]
39		Dimethylamino	Cyclohexyl	H	H	[22]
40		Cl	Cyclohexyl	H	*tert*-Butyl	[46]
41		Cl	Cyclohexyl	Phenyl	1-Adamantyl	[46]
42		Cl	2-Methylcyclohexyl	Phenyl	1-Adamantyl	[46]
43		Cl	Allyl	H	*tert*-Butyl	[37]
44		Cl	Allyl	*tert*-Butyl	H	[37]
45		Cl	Ferrocenyl	H	*tert*-Butyl	[47]
46		Cl, Cyclopentadienyl	Ferrocenyl	H	*tert*-Butyl	[47]
47	Hf	Benzyl	Pentafluorophenyl	H	*tert*-Butyl	[48]
48		Benzyl	Pentafluorophenyl	1-Methyl-1-phenylethyl	1-Methyl-1-phenylethyl	[48]
49		Benzyl	Benzyl	1-Methyl-1-phenylethyl	1-Methyl-1-phenylethyl	[48]

[a] Dinuclear complex.

respective enantiomers which can be classified using the Δ/ Λ notation. The discussion of these enantiomers is usually omitted in theoretical and experimental works.

The review of the literature on the subject clearly reveals that the vast majority of the bis(FI) group 4 complexes occur as the N,N-*cis*-O,O-*trans* isomers in the solid state—see Tables 1–3. Relatively few examples of such complexes have been studied by DFT. The Fujita group reported the calculated structures of the complex No. 3 from Table 1 in Refs. [13,14]; items Nos. 8 and 13 in Ref. [15] and item No. 26 in Refs. [1,9,10]. Also, the complexes Nos. 4, 5 and 28 are discussed by other group in Ref. [16], together with another two species having R3 = cyclohexyl or *n*-butyl, whose structures have not been determined experimentally. Please note that all of these complexes exhibit the N,N-*cis*-O,O-*trans* arrangement of ligands. Additionally, certain N,N-*trans*-O,O-*cis* species, including items Nos. 50 and 51 from Table 2 were also studied theoretically [17,18].

It is worth mentioning that late transition metal ions, such as Ni^{2+}, form mono(FI) complexes, which are also of great importance in olefin polymerization. Such systems have been studied by Ziegler—see e.g. Ref. [19]. However, they are beyond the scope of our study, since their geometry is planar rather than octahedral.

NMR experiments also provide relatively large amount of information on the structure of isomeric bis(FI) complexes. Using this technique, it was possible to distinguish not only between the C_1- and C_2-symmetric species [20], but also between the two C_2-symmetric complexes, as deshielding of the protons in different R1 and R2 ligands by aromatic rings was observed [21]. However, the number of experiments, in which the isomers of these complexes were studied, is rather low. In addition to that, it was found that the mixture of the isomers may exist in solution [13,20], and their ratio depends on the temperature and the solvent applied [18].

Taking all these findings into account, we have engaged in a systematic study of the effect of substituents in the FI ligand on the structure of the complex, and attempted to elucidate what factors might be responsible for the different stability of particular isomers of the FI complexes.

2. Computational details

While it is relatively straightforward to determine the number of isomeric species for the complexes having only monodentate ligands without the aid of the computer, the presence of multidentate ligands makes the analysis much more difficult. For the efficient modeling of isomeric complexes, we have built the graphical interface that displays the results of calculations using the Bailar method. As a starting point, the code written in FORTRAN by Bennett [7] was adapted, and the custom graphical subroutine was added to it subsequently. Within the program, the variables that carry the information about the existing isomers are transferred from the original part of the code to the graphical procedure that handles the ligand colors and the positions of octahedra; finally the Persistence of Vision Raytracer (POV-Ray) [51] input file is automatically generated and processed by the POV-Ray. All 30 isomers are predefined in the form of octahedra consisting of seven spheres representing the metal and ligand atoms as well as six cylinders representing coordinative bonds. Additionally, another 12 cylinders are also defined to link the donor atoms belonging to bidentate ligands, if necessary. The numbering of spheres and their colors are defined within the FORTRAN subroutine, selected dynamically depending on the user choice of ligands (e.g. oxygen is red, nitrogen—blue and chlorine—green). The consecutive octahedra are obtained by translating the previous ones along the *x*-axis (for the species displayed in one row) or *y*-axis (one column). Since the absolute position of particular isomers depends on their number, it has to be calculated for each program run independently; the same applies to the coordinates of the camera and the source of light.

The program was compiled using the g77 compiler (GCC version 3.3.5), and the POV-Ray version 3.6.1 was applied to create the images.

The DFT calculations were carried out with the Gaussian 03 package [52]. The B3LYP density functional [53,54] was applied with the 6-311G(d,p) basis set on the C, H, N, O, F and Cl atoms [55–59], whereas the LANL2TZ basis set [60] obtained from the EMSL Basis Set Library [61,62] was applied for the transition metal atoms.

Substituent molar volume calculations were carried out for the respective hydrocarbons, i.e. benzene for the phenyl substituent, with the *Tight* option selected. The volume of molecular hydrogen was divided by half, and finally this value was subtracted from the volumes of hydrocarbons in order to obtain the values for substituents.

3. Results and discussion

3.1. Complexes of unsubstituted FI ligands

We were motivated to pursue this study when we accidentally found an apparent discrepancy with the literature data. While preparing the models for the insertion and termination transition states in order to investigate the olefin polymerization reaction catalyzed by bis(FI) complexes (this is why our model structures have R1 = R2 = CH_3), we discovered that the most stable isomer of the titanium bis(FI) complex having R3 = R4 = R5 = H is the N,N-*trans*-O,O-*cis*. This result is unexpected, because the other isomer, N,N-*cis*-O,O-*trans* is by far the most frequently encountered species in the X-ray experiments (*vide infra*). The rearrangement to the less abundant N,N-*trans*-O,O-*cis* isomer can be forced by increasing the steric bulk of the R3 substituent [21]. However, in our case, the N,N-*trans*-O,O-*cis* structure is preferred for R3 = H, despite its least sterically demanding nature, and independently of the kind of the transition metal atom (Zr, Hf and V were tested, see Table 4). Unfortunately, our finding could not be verified experimentally, because the imines with no substituent at the N atom are unstable, and the structure of the complex bearing such an unsubstituted ligand has not been published so far.

3.2. Complexes of N-substituted bis(FI) ligands

Attaching aliphatic or aromatic substituents, which are commonly used in precursors of polymerization catalysts, to the imine nitrogen atom changes the situation dramatically. Now, the N,N-*cis*-O,O-*trans* isomer becomes clearly preferred, until the steric hindrance at the nitrogen atom reaches certain point, i.e. at least the 2,6-dimethylphenyl substituent is selected—see Table 5. At this moment, again the N,N-*trans*-O,O-*cis* structure becomes slightly favored; however the difference in energy falls within the error of the computational method. Further increase in the steric bulk and introduction of the 2,6-diisopropylphenyl group slightly increases this effect. This result is in good agreement with the experimental data [17,21,22,49]. We also noticed that one of the Ti–N bonds in the now-non-preferred N,N-*cis*-O,O-*trans* isomer elongates as the bulk of the R3 substituent becomes larger. Attaching the extremely bulky 2,4,6-triphenylphenyl substituent causes further elongation of the Ti–N bond in this isomer, rendering the FI ligand monodentate. Similar effect was observed experimentally [21], though we also managed to optimize the geometry of the N,N-*trans*-O,O-*cis* structure.

Table 2
The N,N-*trans*-O,O-*cis* isomers of group 4 bis(FI) complexes.

No.	Metal	R1, R2	R3	R4	R5	Reference
50	Ti	Cl	2,6-Dimethylphenyl	H	H	[17]
51	Ti	Cl	2,6-Diisopropylphenyl	H	H	[22]
52	Ti	*iso*-Propoxyl	2,6-Diisopropylphenyl	H	H	[21]
53	Ti	Cl	2,6-Diisopropylphenyl	NO_2	H	[49]
54	Zr	Cl	2,6-Diisopropylphenyl	H	H	[22]

Table 3
The N,N-*cis*-O,O-*cis* isomers of group 4 bis(FI) complexes.

No.	Metal	R1, R2	R3	R4	R5	Reference
55	Ti	Cl	3,5-Difluorophenyl	Dimethylbenzyl	Dimethylbenzyl	[20]
56	Zr	Cl	-Ph-(3-PO-(3,5-CF_3Ph)$_2$)	H	*tert*-Butyl	[50]

Table 4
Relative energies of the three isomers of unsubstituted bis(FI) complexes (R3 = R4 = R5 = H), with respect to the most stable isomer, kcal/mol.

Metal	N,N-*trans*-O,O-*cis*	N,N-*cis*-O,O-*cis*	N,N-*cis*-O,O-*trans*
Ti	0.0	2.1	4.1
Zr	0.0	2.1	2.7
Hf	0.0	1.7	2.7
V	0.4	0.0	3.4

Table 5
Relative energies of the isomers of N-substituted bis(FI) complexes (R4 = R5 = H), with respect to the most stable isomer, kcal/mol.

R3	N,N-*trans*-O,O-*cis*	N,N-*cis*-O,O-*cis*	N,N-*cis*-O,O-*trans*
Methyl	2.7	2.3	0.0
Trifluoromethyl	9.5	4.6	0.0
tert-Butyl	7.9	[a]	0.0
Cyclohexyl	2.0	3.0	0.0
1-Adamantyl	14.2	[a]	0.0
Phenyl	3.2	2.4	0.0
Pentafluorophenyl	3.4	4.7	0.0
Naphthyl	2.3	2.3	0.0
2,6-Dimethylphenyl	0.0	3.2	0.2
2,6-Diisopropylphenyl	0.0	2.5	0.9
2,4,6-Triphenylphenyl		[a]	[a]

[a] One of the Ti–N bonds gets broken due to excessive steric hindrance.

It is particularly interesting to note that the electronic properties of the substituents have very little or no effect on the preference of any particular isomer. No matter what kind of substituent—aliphatic or aromatic—is attached to the nitrogen atom, the N,N-*cis*-O,O-*trans* isomer is the most stable, unless sterically demanding substituents are selected. To describe this behavior quantitatively, we decided to correlate the molar volume of the substituent with the Ti–N bond length in the N,N-*trans*-O,O-*cis* isomer. First, we ordered the substituents used in this study with respect to the calculated molar volume—see Fig. 3. Then we divided the substituents into two groups: aromatic and aliphatic.

For the aromatic substituents, we managed to perform a linear regression—see Fig. 4, obtaining the following formula:

$$r = 8.1000 \times 10^{-4} V + 2.2254 \quad (1)$$

with R^2 equal 0.8405, where r is the Ti–N bond length, and V is the molar volume of the substituent expressed in cm^3/mol.

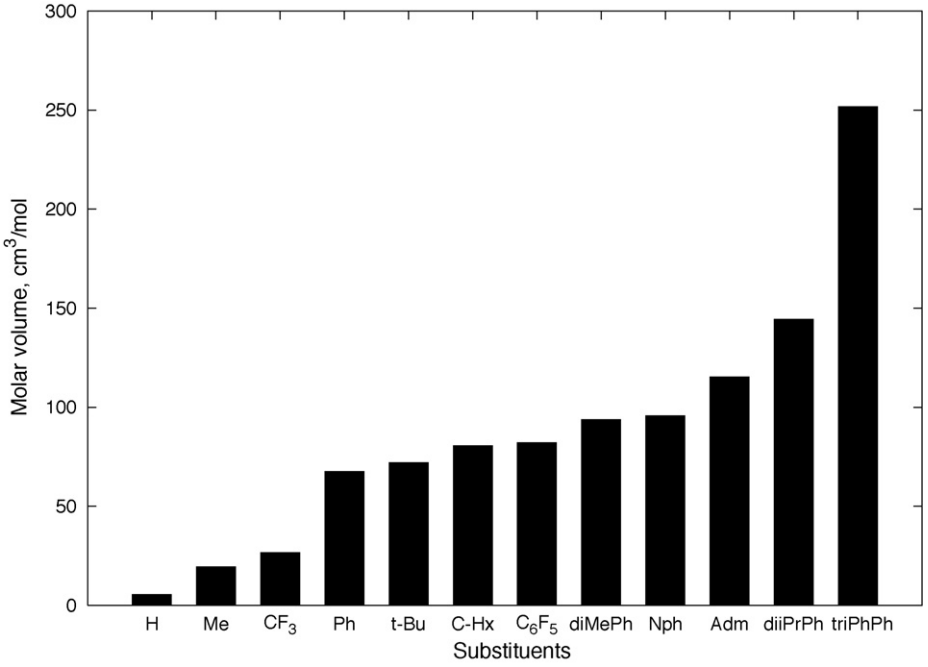

Fig. 3. The molar volume of the substituents analyzed in this study.

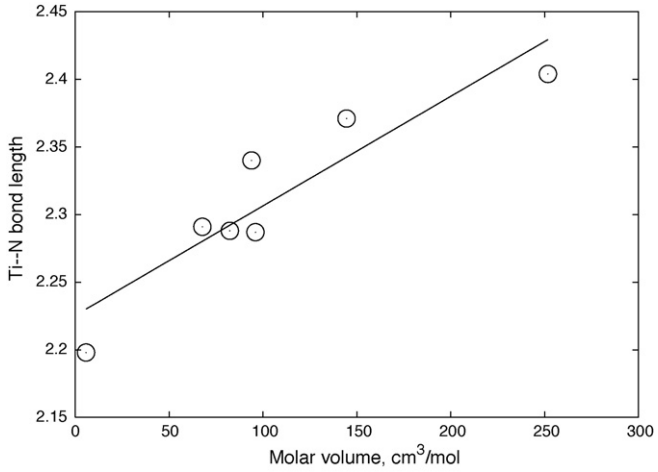

Fig. 4. The Ti–N bond length as a function of molar volume of the aromatic substituents in the N,N-*trans*-O,O-*cis* isomer.

We believe that the results of this regression are influenced by the electronic properties of the substituents. Additionally, it was impossible to find a reasonable linear fit for the aliphatic substituents, where R^2 was only 0.3924. Instead, the logarithmic dependence was found, but the points on the graph were still scattered:

$$r = 5.110 \times 10^{-2} \ln(V) + 2.12044. \quad (2)$$

This is probably due to the fact that the steric hindrance of these substituents is not always the function of their molar volume. For instance, the *tert*-butyl group, unlike the cyclohexyl substituent, exerts similar steric hindrance in all directions.

However, independently of the nature of the substituents, both formulae describe monotonically increasing functions. Thus the increase in the molar volume of the R3 substituent should lead to the significant elongation of the Ti–N bond.

The complexes discussed exhibit a pronounced *trans* influence clearly detectable in all species, no matter what substituents are attached to the nitrogen atom. For example, the N,N-*cis*-O,O-*trans* species has the neutral imine nitrogen atoms located opposite the methyl groups, which are stronger electron donors. Therefore the nitrogen atoms undergo labilizations accompanied by the elongation of the corresponding Ti–N bonds. For instance, according to our calculations, the Ti–N distance in the N,N-*cis*-O,O-*trans* isomer of the complex with the phenyl substituent at the nitrogen atom reaches 2.50 Å, compared to only 2.29 Å in the N,N-*trans*-O,O-*cis* species, which has the nitrogen atoms opposite to each other. Simultaneously, the elongation of the Ti–N bond is compensated by a slight shortening of the Ti–O distance.

As already mentioned, attaching any substituent to the nitrogen atom elongates the Ti–N bond due to steric repulsion—see Eqs. (1) and (2). This action clearly counteracts the lack of the strong *trans* influence directed toward the nitrogen atoms in the N,N-*trans*-O,O-*cis* isomer, which makes the Ti–N bond shorter. These conflicting phenomena raise the energy of this species and lead to the stabilization of the other isomer (N,N-*cis*-O,O-*trans*), until the most sterically demanding substituents that cannot be accommodated around the central atom even in this isomer are selected. Then the trend is reversed again.

Unusual stability of the N,N-*trans*-O,O-*cis* isomer for R3 = H may also be explained by the fact that the Ti–N bond is relatively short (see Table 6). We suspect that this prevents excessive deformation of the six-membered ring formed by the bidentate ligand attached to the metal atom, accompanied by the compression of the C=N bond in the phenoxyimine moiety, which was found in the N,N-*cis*-O,O-*trans* species.

Table 6
Calculated Ti–N bond length, Å.

R1, R2	R3	N,N-*trans*-O,O-*cis*	N,N-*cis*-O,O-*trans*
Methyl	H	2.20	2.31 (2.34 [a])
Cl		2.16	2.19
Methyl	Phenyl	2.29	2.50 (2.51 [a])
Cl		2.22	2.29
Methyl	2,6-Diisopropylphenyl	2.37	2.53 (3.14 [a])
Cl		2.28	2.39
Methyl	*tert*-Butyl	2.39	2.78 (3.03 [a])
Cl		2.31	2.42

[a] Two Ti–N bonds differ in length.

3.3. Influence of non-phenoxyimine ligands attached to the transition metal atom

Non-phenoxyimine ligands, denoted as R1 and R2 in the current work, are limited to chloride, alkyl, alkoxy and substituted amine groups in the experimental studies (see Tables 1–3). Their varied electronic properties modify the Ti–N bond length over a wide range through the *trans* influence discussed above. To examine whether the isomeric preferences in the bis(FI) complexes can be controled by non-phenoxyimine ligands, we repeated the DFT calculations for the selected species with R1 = R2 = Cl instead of the methyl group (see Table 6).

The presence of chloride, whose trans influence is weaker that that of the methyl group, leads to shortening of the Ti–N bonds in all the dichloro complexes discussed, comparing with the respective dimethyl species. However, the Ti–N bonds in the N,N-*cis*-O,O-*trans* isomers are still markedly longer than those in their N,N-*trans*-O,O-*cis* counterparts, which means that the *trans* influence is stronger for the chloride than the neutral phenoxyimine nitrogen atom and cannot be neglected in the case of the former.

Weaker trans influence of the R1 and R2 ligands being Cl rather than methyl results in the limited capabilities of accepting large R3 substituents. The opposing interactions discussed in the previous section (weaker trans influence shortens the Ti–N bond, whereas the bulky R3 substituent counteracts), especially important in the N,N-*cis*-O,O-*trans* isomer, become even more pronounced. The results shown in Table 7 indicate that for R3 = *tert-butyl*, the relative energy of both isomers is almost equal, which is not the case for the dimethyl complex (R1 = R2 = methyl; see Table 5). Additionally, for the more bulky 2,6-diisopropylphenyl group, the N,N-*trans*-O,O-*cis* isomer of the dichloro species is preferred by almost 10 kcal/mol over its counterpart; in the case of R1 = R2 = methyl, this preference is more subtle (cf. Table 5).

3.4. Complexes of FI ligands substituted at the phenolate ring

The experimental results presented in Tables 1–3 indicate that the isomerism of transition metal bis(FI) complexes is determined mainly by the substituents at the imine nitrogen atom; however, there is also larger diversity of R3 substituents, comparing with R1 and R2 or R4 and R5. On the other hand, the performance of

Table 7
Relative energies of the dichloro species (R1 = R2 = Cl), with respect to the most stable isomer, kcal/mol.

R3	N,N-*trans*-O,O-*cis*	N,N-*cis*-O,O-*trans*
H	0.0	2.2
Phenyl	3.9	0.0
tert-Butyl	0.0	0.4
2,6-Diisopropylphenyl	0.0	9.9

Table 8
Relative energies of the isomers of substituted bis(FI) complexes with respect to the most stable isomer, kcal/mol.

R4, R5	N,N-*trans*-O,O-*cis*	N,N-*cis*-O,O-*trans*
H	3.2	0.0
Methyl	4.9	0.0
Trichloromethyl	1.8	0.0
tert-Butyl	0.6	0.0
Phenyl	2.5	0.0
Adamantyl [a]	1.1	0.0
F	1.7	0.0
4F [b]	1.2	0.0

R3 = Phenyl.
[a] One adamantyl substituent in the *ortho* position with respect to the imine group.
[b] All four hydrogen atoms in the phenoxy ring are substituted with fluorine atoms.

the olefin polymerization catalyst can be adjusted in a wide range by the modification of the R3 [1,10,18], as well as the R4 and R5 substituents [1,10,63].

Our theoretical calculations demonstrate that miscellaneous substituents at the phenolate ring have little effect on the energetic differences between the isomers. No matter what substituents we selected, the N,N-*cis*-O,O-*trans* structure was always preferred, and the energy differences between the other isomer fell within much smaller range than those for varying substituents at the nitrogen atom—see Table 8.

4. Concluding remarks

We have theoretically demonstrated that the isomeric preferences in the bis(FI) group 4 complexes may be tuned by careful selection of the FI ligands. These preferences are determined solely by the nature of the substituent at the imine nitrogen atom, especially by its steric hindrance. Although one of the isomers, namely the N,N-*cis*-O,O-*trans*, is favored in most of the cases, there are notable exceptions where the substituents at the imine nitrogen atom are selected from the upper and lower extremes of the steric hindrance range. Gradual change in the isomeric preferences—from the N,N-*trans*-O,O-*cis* structure, through a very large zone of the N,N-*cis*-O,O-*trans* isomer, back to the N,N-*trans*-O,O-*cis* species—can be observed as the molar volume of the substituent increases. This behavior can be influenced to a certain extent by the non-phenoxyimine ligands attached directly to the transition metal atom.

Phenoxyimine ligands are considered as being electronically flexible [12]; hence we believe that the changes in the electron withdrawing or donating properties of the substituents attached to the FI frame are damped and minimized by the whole ligand. Thus electronic effects of these substituents do not play any major role in determining the isomeric preferences of the complexes.

The results presented in this work will serve for the future detailed study devoted to the olefin polymerization catalyzed by bis(FI) complexes, which is now in progress.

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