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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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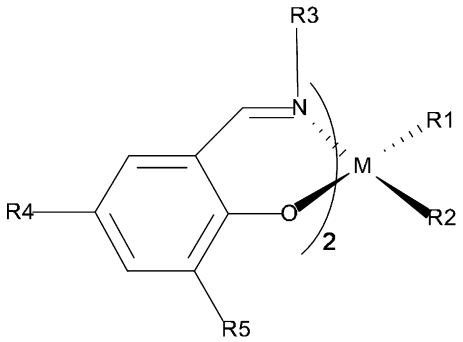

Fig. 1. Bis(FI) group 4 complex.

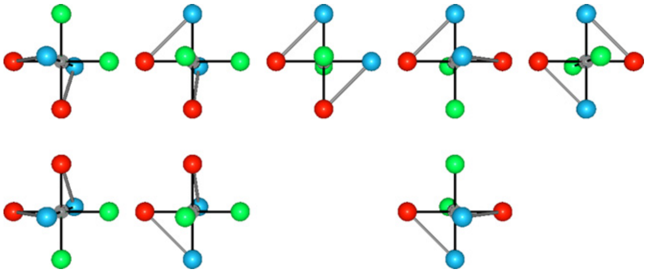

Fig. 2. Eight isomers of a bis(FI) complex. Chlorine atoms are green; oxygen—red and nitrogen—blue.

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.