Journal of Organometallic Chemistry 718 (2012) 124–130

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Counter anion binding in the phenoxyimine, salan and metallocene olefin polymerization catalysts activated with perfluorophenylborate

Zygmunt Flisak [a,*], Akinobu Shiga [b]

[a] University of Opole, Faculty of Chemistry, Oleska 48, 45-052 Opole, Poland
[b] LUMMOX Research Lab. Takezono 2-18-4-302, Tsukuba 305-0032, Japan

ARTICLE INFO

*Article history:*
Received 30 March 2012
Received in revised form
30 July 2012
Accepted 1 August 2012

*Keywords:*
DFT
Paired interacting orbitals (PIO)
Phenoxyimine
FI catalyst
Olefin polymerization

ABSTRACT

Ion pair separation is a process that may influence the activity of homogeneous catalysts of olefin polymerization. We have studied the energy of separation for selected titanium and zirconium metallocene and post-metallocene catalytic ion pairs by means of DFT, dispersion-corrected DFT and Paired Interacting Orbitals method (PIO). Unusually weak cation–anion interactions in the bis(phenoxyimine) systems were attributed to strong electron-donating properties of the phenoxyimine ligands. Energy decomposition analysis (EDA) revealed that almost 70% of the counter ion binding energy results from electrostatic interactions. The PIO method made it possible to analyze the nature of the cation–anion binding and associate its strength with the total overlap population of PIOs.

## 1. Introduction

Research devoted to Ziegler–Natta catalysts still continues to produce unexpected results and breakthroughs, despite the fact that the objects of interest seem to be the best understood catalytic systems ever and thus this field of science might seem to be apparently exploited [1]. Modern design of olefin polymerization catalysts focuses mainly on two aspects: ligand modification and careful counter anion selection [2]. While the first approach yields unique systems, such as the phenoxyimine-based catalysts [3–8], the other one—equally important—adjusts their properties in a wide range. Apart from the selectivity and the molecular weight control—the catalytic activity appears to be one of the most prominent properties that is affected in this process [9–11].

Theoretical calculations assist in the explanation of mechanistic aspects of olefin polymerization. The inclusion of the complete ion pair in the theoretical model (rather than the isolated cation forming the active site), postulated for the first time more than a decade ago [12–15], is now possible for the vast majority of the catalytic systems. It turns out that cation–anion separation barriers can often be comparable with or even exceed insertion barriers [16–19]; thus weekly coordinating anions are the subject of intense quest. However, the binding strength of a counter anion is heavily influenced not only by its nature, but also by the ligands attached to the transition metal atom. Recently it was found that the catalysts obtained from bis(phenoxyimine) complexes demonstrate especially weak cation–anion interactions [19]. These compounds can exist in several isomeric forms, therefore it is important to perform calculations for the most stable species indicated by theory and experiment [20–23].

Eight representative metallocene and post-metallocene systems were chosen to compare the cation–anion interactions within the catalytic ion pair, namely indenyl, salan and two bis(phenoxyimine) titanium and zirconium complexes activated by perfluorophenylborate. The structures of the ligands and abbreviations used throughout this work are given in Fig. 1.

## 2. Computational details

### 2.1. DFT calculations

DFT calculations were carried out by using the ADF 2010.02 program [24–28]. The functional applied was made up of the exchange correction by Becke [29] and the correlation correction by Perdew [30] with the Vosko, Wilk and Nusair parametrization of the electron gas [31]. A valence triple-zeta Slater-type orbital basis set augmented with a single polarization function was applied to the titanium and zirconium atoms and double-zeta basis set with a single polarization function to the other atoms. The core

---

* Corresponding author. Tel.: +48 77 452 7141; fax: +48 77 452 7101.
*E-mail address:* zgf@uni.opole.pl (Z. Flisak).

0022-328X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2012.08.007

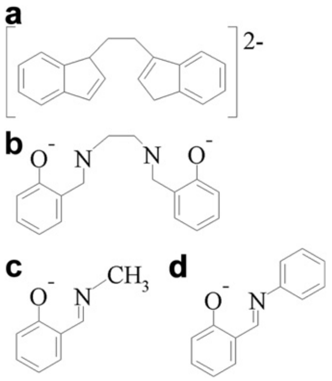

**Fig. 1.** Structures of the ligands: a) indenyl; b) salan; c) methyl substituted phenoxyimine (FI–Me); d) phenyl substituted phenoxyimine (FI–Ph).

definition used in the frozen core approximation extended up to 2p for Ti, 3d for Zr and 1s for B, C, N, O and F. The molecular density and the Coulomb and exchange potentials were fitted with an auxiliary s, p, d, f, and g set of Slater-type orbital functions [32] centered on each nucleus. First-order scalar relativistic corrections [33–35] were applied to all the systems studied. The geometry convergence criteria were $1.0 \times 10^{-4}$ au for energy and $1.0 \times 10^{-3}$ au Å$^{-1}$ for gradients. The integration parameter was set for 5.0. The charge distribution was analyzed by the Hirshfeld method [36,37]. Dispersion correction DFT-D3 [38] was added where indicated.

### 2.2. Paired interacting orbitals calculations

Paired interacting orbitals (PIO) calculation [39,40] is a method for unequivocal determination of the orbitals which play dominant roles in chemical interactions between two systems, [A] and [B], which construct a combined system [C]. The geometries of [A] and [B] are the same as those in the complex [C] ([A-B]≡[C]). In this method, first the extended Hückel MOs of [A], [B] and [C] are calculated. Then the PIOs are obtained according to the procedure proposed by Fujimoto et al. [39,40] and described in the Supporting Information. Finally, the N × M (N < M) orbital interactions in the complex [C] (M and N are the total numbers of the MOs of [A] and [B], respectively) are reduced to the interactions of N PIOs.

PIO calculation was carried out using the LUMMOX™ system [41,42], which has been successfully applied to both homogeneous and heterogeneous catalysts of olefin polymerization before [43–45].

## 3. Results and discussion

### 3.1. DFT calculations

The interactions between the cation and anion in the catalytic ion pair can be expressed in terms of ion pair separation energy [16]. Its value depends on the nature of both the precursor and the cocatalyst and may exceed 100 kcal/mol if calculated in the gas phase. For weakly coordinating anions, such as $B(C_6F_5)_4^-$, and $B(C_6F_5)_3Me^-$, it usually falls within a range of 55–75 kcal/mol and 75–95 kcal/mol, respectively [16]. The presence of the solvent reduces this value by ca. 30 kcal/mol.

The actual value of energy, which is required to partially separate the ions and facilitate the monomer coordination to the active site is even lower. The counter anion does not have to be brought to the infinity; instead it can be moved to the outer coordination sphere [46–48]. The barrier to this process (if ever existent) is much lower than that for the separation to the infinity [18,19].

**Table 1**
Cation–anion (M–C) distance and separation energies ($E_{sep}$) for the ion pairs investigated.

| Ligand | Metal M | M-C distance, Å | | $E_{sep}$, kcal/mol | |
|---|---|---|---|---|---|
| | | DFT | DFT-D3 | DFT | DFT-D3 |
| Indenyl | Ti | 2.438 | 2.368 | 70.98 | 97.74 |
| Salan | | 2.455 | 2.414 | 65.01 | 90.40 |
| FI–Ph | | 2.464 | 2.417 | 45.43 | 80.38 |
| FI–Me | | 2.485 | 2.451 | 50.36 | 76.37 |
| Indenyl | Zr | 2.534 | 2.463 | 78.79 | 103.30 |
| Salan | | 2.555 | 2.543 | 72.71 | 95.66 |
| FI–Ph | | 2.577 | 2.567 | 49.44 | 84.36 |
| FI–Me | | 2.570 | 2.594 | 59.30 | 82.97 |

The cation–anion bond length, expressed as a distance between the transition metal atom and a bridging methyl group bound to the perfluorophenylborate moiety (the M–C distance), can be a measure of the interaction energy [16]. It is clearly seen from Table 1 that the counter anion is the most strongly bound in the indenyl-based catalysts, which simultaneously exhibit the shortest Ti–C distances and the highest separation energies among all the systems investigated. On the other hand, the separation energies of 45–50 kcal/mol calculated for the bis(phenoxyimine) systems are the lowest among those reported in the literature [16,19]. It is not surprising that the comparison of the Ti–C distances is valid only for the species containing one transition metal atom: either titanium or zirconium. For the latter, the corresponding distances are longer due to larger metal ionic radius, but the separation energies are also higher than those for the titanium species.

The separation energies calculated using the newly-developed dispersion-corrected density functionals appear ca. 25–35 kcal/mol higher than the corresponding values calculated without this correction and the M–C distances become shorter in most of the cases. These significant differences can be attributed to the non-covalent interactions, such as London dispersion forces, which were shown to be substantial in ionic liquids and expected to increase with the size of the functional groups present in the cation and anion [49]. Nevertheless, the trends in energies and distances discussed in the previous paragraph also hold true in this case.

For the charge analysis, the fragment approach implemented in the ADF software was applied. The catalytic precursors $M(CH_3)_2L_1L_2$ and the ion pairs $MCH_3L_1L_2^+CH_3(C_6F_5)_3^-$ were divided into the $M^{4+}$, $CH_3^-$, $L_1^-$, $L_2^-$ and $CH_3(C_6F_5)_3^-$ fragments. In the case of indenyl and salan fragments bearing two negative charges, there is no $L_2^-$. The value of the sum of the charges on the $L_1^-$ and $L_2^-$ ligands $qL$ (see Table 2 and 3) obeys the following rule:

$$qL_{\text{indenyl}} > qL_{\text{salan}} > qL_{\text{FI-Ph}} > qL_{\text{FI-Me}} \quad (1)$$

At the same time, the charges on the transition metal atom $qM$ satisfy the following inequation:

**Table 2**
Charge analysis in the titanium catalysts calculated with no dispersion corrections.

| Ligand | $Ti^{4+}$ | $CH_3^-$ | $CH_3B(C_6F_5)_3^-$ [a] | $L_1^-$ | $L_2^-$ | $L_1^- + L_2^-$ |
|---|---|---|---|---|---|---|
| Precursor | | | | | | |
| Indenyl | 2.7481 | −0.7539 | −0.7522 | −1.2419 | – | −1.2419 |
| Salan | 2.9017 | −0.8033 | −0.8056 | −1.2928 | – | −1.2928 |
| FI–Ph | 2.9248 | −0.7764 | −0.7761 | −0.6858 | −0.6859 | −1.3717 |
| FI–Me | 2.9365 | −0.7584 | −0.7926 | −0.6980 | −0.6874 | −1.3854 |
| Ion pair | | | | | | |
| Indenyl | 2.6361 | −0.7420 | −0.8357 | −1.0576 | – | −1.0576 |
| Salan | 2.8052 | −0.7628 | −0.9035 | −1.1391 | – | −1.1391 |
| FI–Ph | 2.8520 | −0.7718 | −0.8822 | −0.5879 | −0.6085 | −1.1964 |
| FI–Me | 2.8491 | −0.7081 | −0.8993 | −0.6339 | −0.6076 | −1.2415 |

[a] $CH_3^-$ for the precursor.