S$_N$2-Like Mechanism for the Ziegler−Natta Syndiospecific Catalysis at *ab Initio* Level

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The syndiospecific polymerization of propene has been known since the 1960s by means of homogeneous vanadium-based catalysts.[1]

In the 80s, the molecular mechanism of fluxional chiral complexes has been proposed.[2] The metallocenic revolution in iso- and syndiospecific polymerization[3] and, in the new century, the discovery of the octahedral postmetallocenic catalysts[4] have had important consequences to understand the catalytic cycle, and the fluxional mechanism has been revaluated.[5] The complexes give *chain-end controlled*[6] polymerization by means of secondary insertion of propene.

According to the chain-end control mechanism, the chirality of the last unit inserted in the chain controls the site's one, which acts as messenger, selecting the chirality of propene insertion. This mechanism is based on the fluxionality of the catalytic site, by means of the cleavage and restoring of a Ti−N bond, which gives a site configuration inversion, followed by monomeric insertion. This could explain the syndiospecificity.

In literature a transition state free energy barrier of about 15 kcal mol^{-1} has been proposed by theoretical models[6c] and comparison with analogous but neutral complexes.[7]

Here, we give insight about the syndiospecific bis(phenoxy−imine) Ti$^+$ catalyst, alkylated with a *sec*-propyl group.

Our calculations were performed with different catalyst models, starting with a really simple one, in which the substituent group of iminic N is −H (called NH), up to more complex ones, with substituents −F, −C$_6$H$_5$ and −C$_6$F$_5$ (respectively called NF, NPh, and NPhF), as in Chart 1. In all cases, the cocatalyst has not been included in the calculations.

The simpler models have led to information that, after analysis, has been used to find a compromise between complexity-realism and calculation resources.

DFT calculations were performed and models were studied at the B3P86/TZVP (or SVP, in some cases) level on the parallel platforms at CASPUR (*La Sapienza*, University of Rome), using the software GAUSSIAN03, and in our lab using GAUSSIAN09.

Minimum energy paths were computed scanning a selected leading coordinate and optimizing the energy with respect to all the remaining ones.

Our first target was the evaluation of a site fluxionality by means of a Ti−O, instead than a Ti−N, bond breaking. Calculations on NH and NF models showed a lower energy barrier for Ti−N bond cleavage (a difference of about 20 kcal mol^{-1}, at Ti−X = 4.0 Å), in accordance with literature models and the dative property of the Ti−N bond, as shown in Figure 1.

The second target was to study the effect of the substituent group of iminic N on the Ti−N bond breaking for the NF, NPh and NPhF models. Outcomes show similar values for the activation energy at 28.8 kcal mol^{-1}, more stable than NH model by
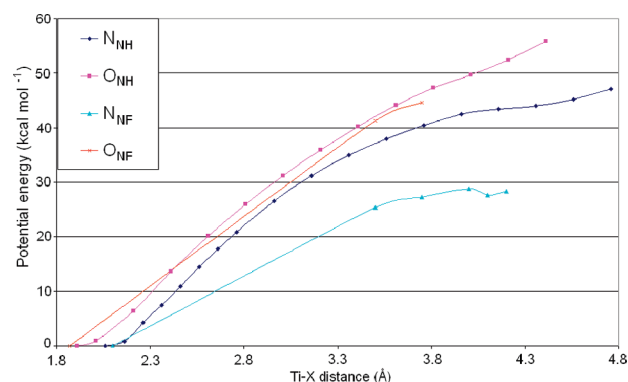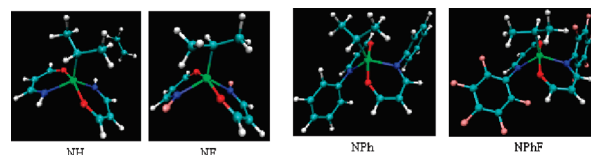
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Figure 1. Difference between Ti−O and Ti−N bond cleavage.

Chart 1. Optimized Structures of the Computed Models

NH   NF   NPh   NPhF

about 12 kcal mol^{-1} (Figure 2), in accordance to the electron-withdrawing nature of the substituents. The transition state corresponding to the maximum energy structure (for the NF model) has been confirmed by computing the vibrational frequencies: only one negative eigenvalue has been found. The free energy correction by means of normal-mode analysis has been performed, and $\Delta G^{\ddagger}$ = 26.9 kcal mol^{-1} has been computed.

The activation step of the catalytic cycle would correspond to the inversion process of the complex chirality. The Ti−N bond cleavage is correlated to the ligand isomerization by means of the torsion of Ti−O−C-C dihedral angle from 0 to 180°, which brings the reorientation of the chelating ring with inversion of the catalytic site.

In all models, the pentacoordinated initial structure corresponds to a bipyramidal complex with axial O's and equatorial N's.

At this point, we also considered the Berry pseudorotation[8] mechanism, which does not proceed by means of bond breaking-formation. This mechanism would bring the shift of the O−Ti−O configuration from axial to equatorial in a bipyramidal arrangement. However, the required equatorial configuration has not given a stable structure, so this mechanism has been put aside.

The role of the propene in the site chirality inversion has been taken into account. The NF model has been considered and the relative stabilization of the inversion step evaluated.

In Figure 3 is shown the barrier, of 21.9 kcal mol^{-1}, related to the activation−inversion process (a stabilization of about 7 kcal mol^{-1} with respect to the calculations without olefin). Again, the thermochemistry analysis gives a $\Delta G^{\ddagger}$ = 19.4 kcal mol^{-1}.

We observe a mechanism defined *S$_N$2-like*; in fact, the monomer coordination induces the breaking of the Ti−N bond *anti*, via a bipyramidal transition state with the bonded N and an O in axial positions (as shown in Scheme 1). The open iminic ring, like before, would invert the site chirality reforming the bond on the opposite orientation.

In order to evaluate the olefin insertion in the chain, we have considered the torsion[9] around the Ti-secondary C bond. In such a way, the olefin realizes the cyclic four-centers Cossee−Arlman
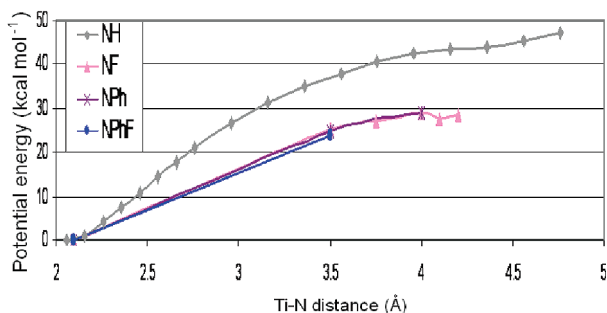
Figure 2. Different models for the Ti−N bond cleavage study.
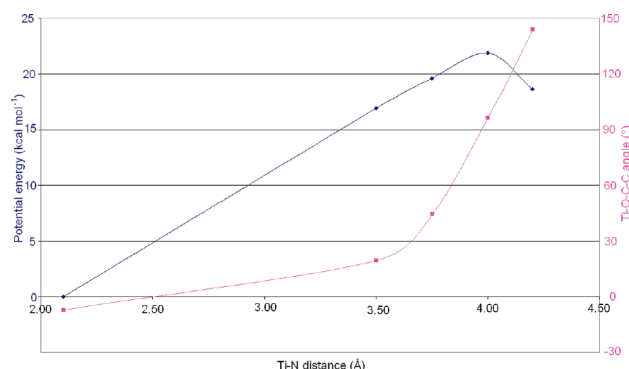
Figure 3. S_N2-like mechanism for the Ti−N bond cleavage.

Scheme 1. The S_N2-Like Mechanism
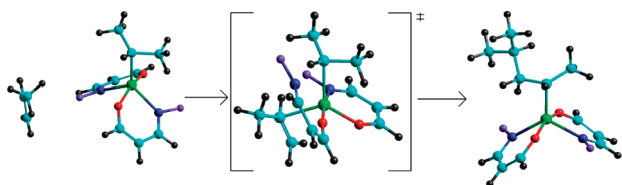
activated complex[10] Ti−C_α−C_I−C_{II}, and we observe spontaneous insertion in the chain after the transition state. An energy barrier of 7.2 kcal mol^{-1} was estimated for this kind of propene insertion.

The proposed S_N2-like mechanism modifies the literature catalytic scheme inversion−coordination−insertion to coordination−inversion−insertion.

We can summarize the outcome: the Ti−N bond cleavage is favored with respect to the Ti−O one (1); electron-withdrawing groups on N weaken its bond with Ti (2); the monomer-free structures are bipyramidal complexes (3); the olefin coordination induces the breaking of the Ti−N bond (4); the iminic ring-opening induces the isomerization of the ligand (5) and the inversion of the complex (6) via a bipyramidal transition state (7). So, the reaction mechanism can be schematized by means of computed structures, as in Scheme 1.

Following these results, it is possible to rewrite the whole scenario of the syndiospecific mechanism. We can highlight at least five steps, which will be repeated at every polymerization cycle: starting from the ionic couple catalyst−cocatalyst (1), the propene approaches the catalyst with the correct stereospecificity (2); the syndio- and regio- specific coordination takes place with an S_N2-like mechanism, with the olefin binding to the Ti and the

iminic N *anti* leaving it (3); the catalyst inverts its chirality (4); the monomer inserts, changing the chirality of the polymer chain's end carbon (5).

The reaction's transition state corresponds to the inversion step (3−4), according to the most recent literature.[6c]

If the wrong coordinations are not rejected, the syndiospecificity is lost. However, to take into account the experimental evidence of isolated errors in the chain,[4a,e,11] in our mechanism we could hypothesize that the selective steric hindrance raises the energy of the correct transition state so that the insertion takes place through an alternative high energy mechanism without inversion. In this way, in the next step the correct prochiral face can be accepted.

The proposed model seems to be a possible alternative to the literature one, in order to rationalize the sPP synthesis by means of postmetallocene homogeneous catalysts.

Supporting Information Available: A table of Cartesian coordinates of selected optimized structures corresponding to Figures 1−3. This material is available free of charge via the Internet at http://pubs.acs.org.

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