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Site Chirality as a Messenger in Chain-End Stereocontrolled Propene Polymerization

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Recently, octahedral and C_2-symmetric Ti-bis(phenoxyimine) complexes[1] (see Scheme 1) were reported to afford highly syndiospecific chain-end controlled propene polymerization[2,3] through secondary monomer insertion.[4−6] The fact that C_2-symmetric precatalysts lead to syndiotactic polymers was rather unexpected, and the origin of the stereoselectivity for these catalysts still is rather unclear. In this communication, we propose a model which explains the observed experimental behavior.

As a remark, we recall that secondary and syndiospecific polymerization of propene has been known since the 1960's and was obtained with homogeneous V-based systems.[7] A molecular mechanics study indicated that the assumption of a fluxional octahedral chiral site (a C_2-symmetric V complex with two bidentate ligands, an active species with no experimental support) could rationalize the experimental syndiospecificity.[8] According to this model, the chirality of the last inserted monomer unit influences the chirality of the fluxional octahedral site which, in turn, dictates the chirality of propene insertion. The model we discuss here is strictly analogous and supports the theoretical proposal of an octahedral geometry for the active species in the V-based catalysts. Incidentally, the only mechanistic hypothesis proposed so far to explain the syndiospecificity of the new Ti-based catalysts also assumes a fluxionality of the catalyst.[2a]

The models we discuss here[9] include three elements of chirality: (i) the chirality of the fluxional octahedral site (Λ or Δ, see Scheme 1); (ii) the chirality of the coordinated propene molecule (*si* or *re*); and (iii) the chirality of the last tertiary C atom of the growing chain (labeled as *si*- or *re*-ending growing chains), which is determined by the chirality of monomer coordination in the last insertion step.[10]

Calculations on simplified model systems in which all of the bulky groups are omitted (see Scheme 2) indicated that whatever combination of the site chirality and orientation of a chiral secondary growing chain (modeled with the chiral $-CH(CH_3)CH_2CH(CH_3)_2$ group), there is no stereoselectivity in secondary propene insertion ($\Delta E^{\ddagger}$ between the two enantiofaces less than 0.2 kcal/mol), and thus a direct interaction between the prochiral monomer and the chiral growing chain can be excluded. In these transition states, the distance between the methyl group of the propene and the Cβ atoms of the growing chain is close to 4.5 Å, and this distance is well greater than the sum of the van der Waals radius of two C atoms or CH_3 groups (∼3.5−4.0 Å).

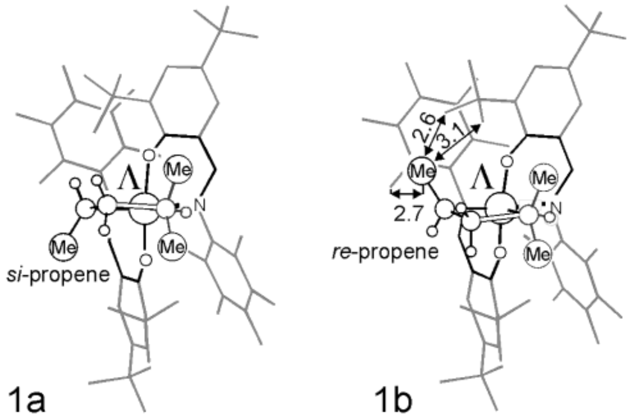
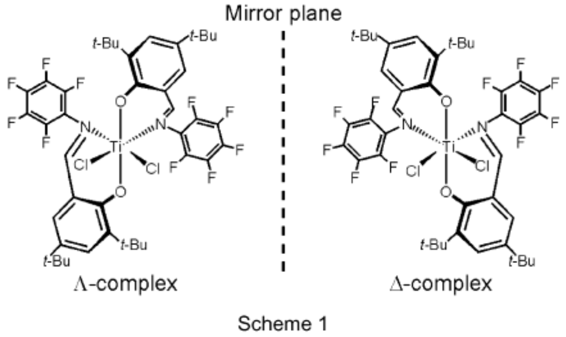
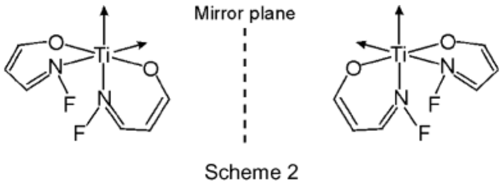


Figure 1. Transition states for *si* and *re* propene insertion on an achiral chain for a Λ site. Chirality elements in black; distances in Å.

Scheme 1



Scheme 2



Hereafter, we will show how the site chirality can act as a messenger between the chirality of the chain and the chirality of propene insertion. To investigate the influence of the chirality of the catalytic site on the chirality of 1-alkene insertion, we located the transition states for propene insertion on an achiral growing chain modeled with an isopropyl group. The diastereoisomeric QM/MM transition states for secondary insertion of a *si* and a *re* coordinated preopene of a Λ catalytic site are sketched in Figure 1.

Structure **1a** is favored relative to structure **1b** by 3.9 kcal/mol. This preference origins from steric interactions between the methyl group of the *re* coordinated propene and the nearby *t*-Bu and Ar groups (for a Δ site, the same preference is obtained for a *re* coordinated propene). Thus, according to our model, the chirality of the octahedral site dictates the chirality of secondary monomer insertion.

To investigate the influence of the chirality of the growing chain on the chirality of the catalytic site, we located the transition states for insertion of ethene on a *re*-ending growing chain (modeled with

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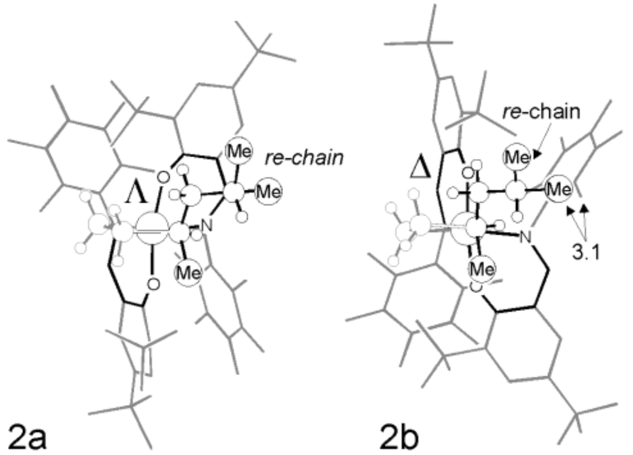

Figure 2. Transition states for ethene insertion on a *re*-chain for Λ (a) and Δ (b) sites. Chirality elements in black; distances in Å.

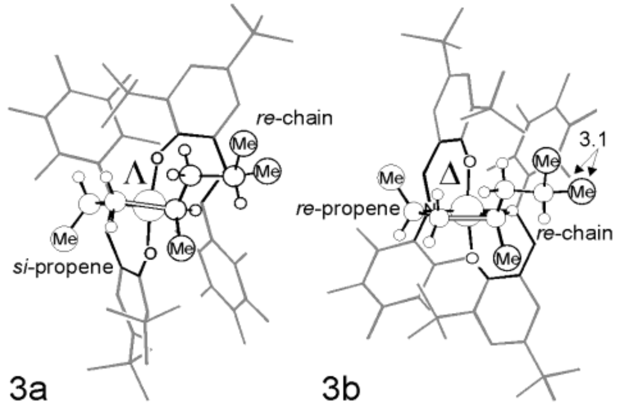

Figure 3. Transition states for (a) syndio and (b) isotactic propagation on a *re*-chain. Chirality elements in black; distances in Å.

the chiral $-CH(CH_3)CH_2CH(CH_3)_2$ group, see Figure 2) for the Λ (**2a**) and Δ (**2b**) chiralities at the catalytic site. Ethene was considered in place of propene to avoid the influence of the chirality of coordination of the propene molecule.

Structure **2a** is more stable than structure **2b** of 1.4 kcal/mol. This preference is mainly connected to steric repulsions between the substituents of the $C\gamma$ of the chain and the ortho substituents of the nearby Ar group. Thus, in the assumption of a fast $\Lambda-\Delta$ isomerization, our calculations indicate that a *re*-ending chain could induce a Λ chirality at the catalytic site (of course, a *si*-chain could induce a Δ chirality).

The transition states for insertion of a *si*- and *re*-propene on a *re*-ending chain for the Λ and Δ chiralities at the catalytic site are sketched in Figure 3. The high energy transition states with a *re* (*si*) propene on a Λ (Δ) site were not considered. Structure **3a** is favored relative to structure **3b** by 1.9 kcal/mol. Thus, our calculations indicate that a *re*-ending chain would favor the formation of a Λ complex which, in turn, dictates coordination and insertion of a *si*-propene and, consequently, the formation of a *si*-ending chain.

Therefore, in the assumption of a rapid fluxional equilibrium between the Λ and Δ chiralities before monomer insertion,[11] so that the energetically favored *re*-chain/Λ-site/*si*-propene or *si*-chain/Δ-site/*re*-propene isomers can be reached, our models explain the syndiospecificity of these catalysts.

Finally, we remark that for a given chirality at the catalytic site, we calculated a strong stereoselectivity in the propene insertion (~4 kcal/mol). This implies that these catalysts are expected to be highly isospecific if the insertion rate is much faster than the $\Lambda-\Delta$ isomerization.

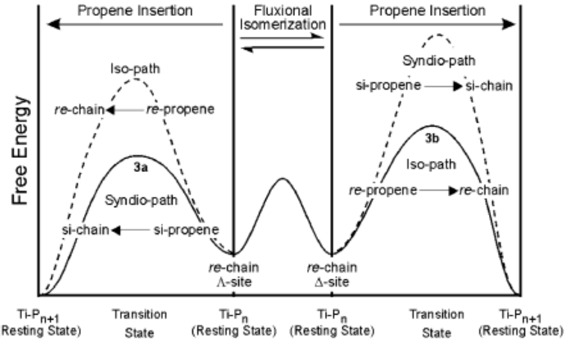

Figure 4. Hypothetical plot of the energy versus the reaction coordinate. The maxima **3a** and **3b** correspond to structures **3a** and **3b** of Figure 3.

Possible propagation paths for a *re*-ending chain are sketched in Figure 4. The lowest corresponds to insertion of a *si*-propene on a *re*-chain/Λ-site (full line, left side), which results in a syndiospecific enchainment. The competitive insertion of a *re*-propene occurs on a *re*-chain/Δ-site (full line, right side) and would lead to an isospecific enchainment. The syndio- and isospecific paths would be connected by a low energy isomerization between the *re*-chain/Λ-site and *re*-chain/Δ-site species. The insertion paths of a *re*-propene on a *re*-chain/Λ-site and of a *si*-propene on a *re*-chain/Δ-site (FISR-1999, dashed lines, left and right sides, respectively) which would lead to iso and syndiotactic enchainments, respectively, are predicted to be of higher energy.

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Supporting Information Available: Computational details, coordinates, and energies of all of the species reported (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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