

SUPPORTING INFORMATION

Ligand coordination driven by monomer and polymer chain: the intriguing case of salalen-Ti catalyst for propene polymerization

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1. Computational details

All DFT static calculations have been performed with the Gaussian09 set of programs,¹ using the B₃LYP functional of Becke and Perdew.² The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, O and Cl (SVP).³ Stationary points were characterized using vibrational analyses, and these analyses were also used to calculate zero-point energies and thermal (enthalpy and entropy) corrections (298.15 K, 1 bar). Improved electronic energies were obtained from single-point calculations using a TZVP basis set⁴ (SDD basis and pseudopotential⁵ at the metal and Br, I), and the SVP-level enthalpy and entropy corrections, solvation (CPCM model,⁶ toluene) and dispersion corrections⁷ (EmpiricalDispersion=D3 in the Gaussian09 D.01 package). The growing polymer chains were simulated by iso-butyl groups and only the most stable TSs were reported for the insertion reactions. The points in space defining the steric map were located with the SambVca package.⁸ The program analyses the first coordination sphere around the metal, which is the place where catalysis occurs. It is normally used to calculate the buried volume of a given ligand, a number that quantifies the amount of the first coordination sphere of the metal occupied by this ligand. For further details and for the maps reporting the 2D isocontour representation of the interaction surface for olefin polymerization see reference 9. For the *fac-mer* (FM) species we found two conformations mode reported in Figure S1; this implies that all TSs reported in the paper are calculated with both conformations and the lower energies (free energies) are reported in Table 1 and Table 2.

2. Conformations of FM species:

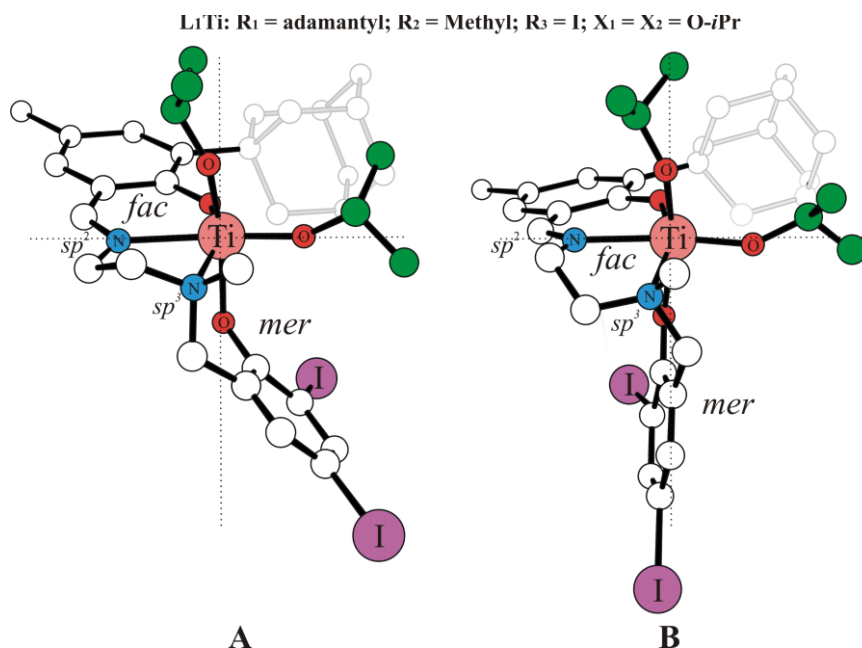


FIGURE S1. Calculated geometries for the precursor complex **L1** with X₁ and X₂ = O-*i*Pr (see Chart 1). The structure **A** agrees with the single crystal reported in literature.¹⁰ The structure **A** shows lower energy (free energy) only after adding dispersion correction⁷ to the DFT methods (see computational detail). H atoms omitted for clarity. For other ligands we found a preference for structures of type **B**.

3. %VBur analysis of FF and FM precursors L_1TiCl_2 :

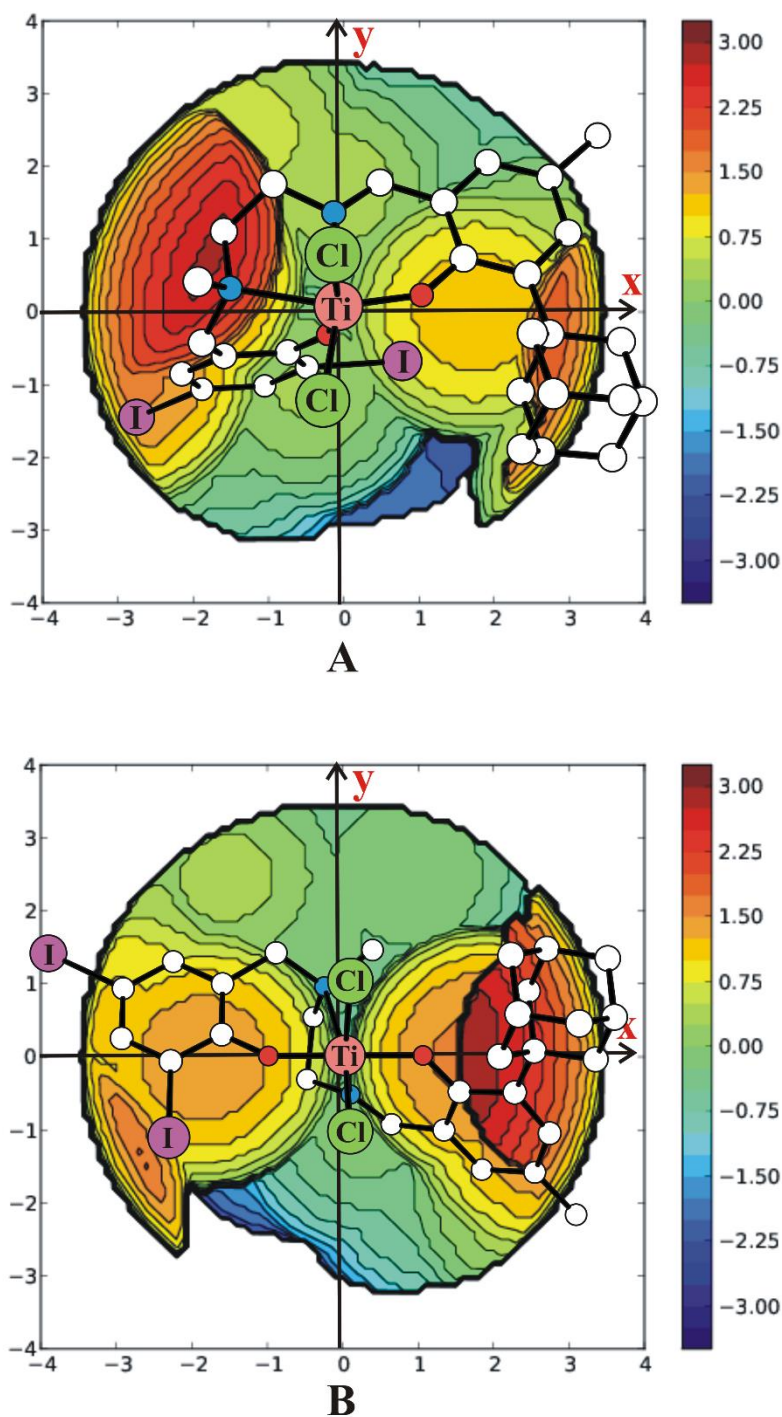


FIGURE S2. Comparison of dichloride precursors steric maps for the system L_1 coordinated with the FM (A) and FF (B) modes. The systems are oriented placing the metal center at the origin of the sphere, as indicated in the DFT calculated structures. The whole VBur% occupy space is similar in the two cases (from **60.8** %, see A to **61.8** %, see B, respectively).^{8,9} It is worth to note that for the FM specie (A) part of the space around the metal is occupied by the methyl group attached to the sp^3 N atom (see red region in A) whereas the I atoms are far from the two diastereotopic positions occupied by the chlorine atoms oriented along the z axis.

4. FM vs. FF equilibrium with probe molecules:

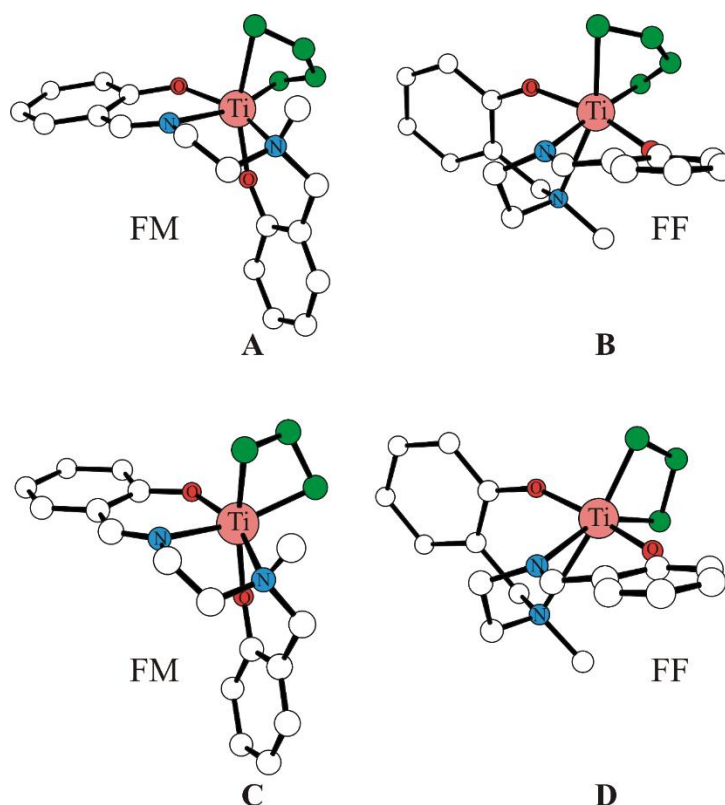


Figure S3. Coordination modes *fac-mer* (FM) and *fac-fac* (FF) for **Le** precursor with a $-\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2-$ (see **A** and **B** structures) and with $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (see **C** and **D** structures), respectively. H atoms omitted for clarity. The calculated electronic energy (free energy) preference (kcal/mol) for FM over FF coordination are 1.5 (2.1) kcal/mol and -1.6 (-2.7) kcal/mol, respectively, see text.

5. Propene insertion TS into $\text{LiTi}(\text{iBu})^+$ FM at site 1 and site 2:

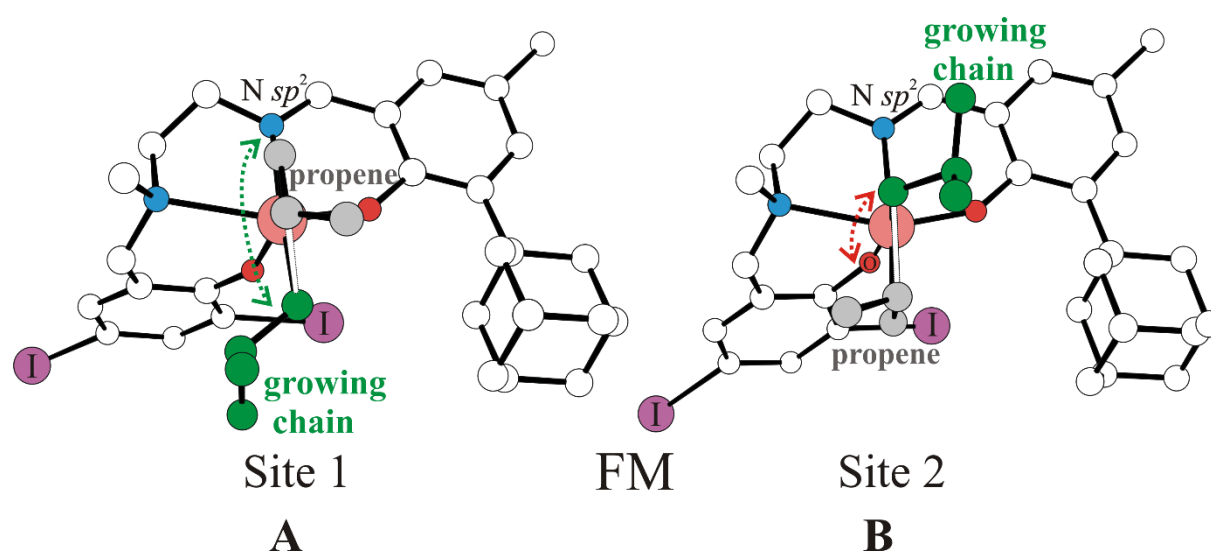


Figure S4. Propene insertion TSs into $\text{LiTi}(\text{iBu})^+$ with FM coordination mode at the site 1 (**A**) and the site 2 (**B**). The structures show the growing polymer chain *trans* to the $\text{N } sp^2$ imine (**A**) and to the phenoxy group (**B**). H atoms omitted for clarity.

6. Stereoselectivity for propene insertion TSs into $\text{LiTi}(\text{iBu})^+ \text{FF}$

site 2:

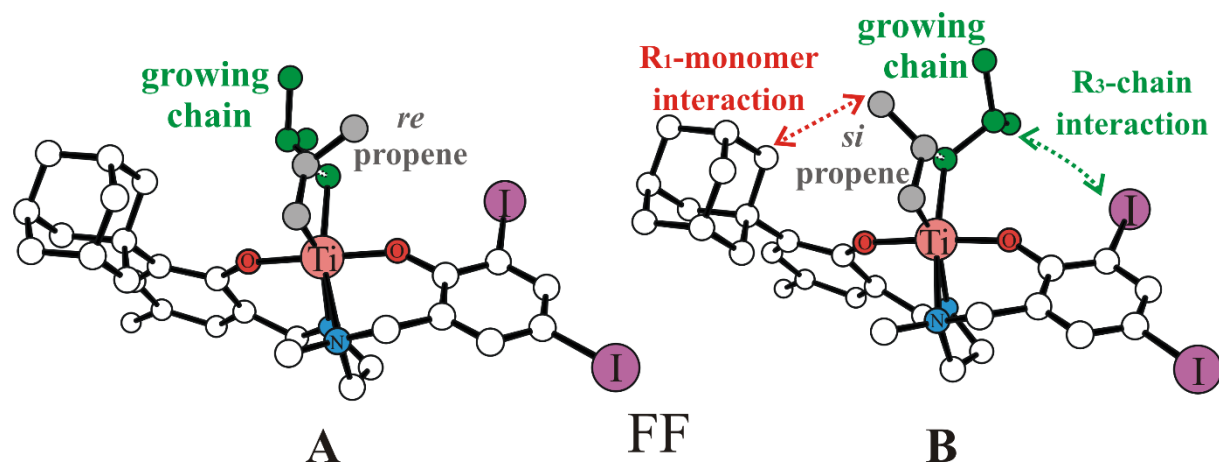


Figure S5. Propene TS for the right insertion (A) and for stereo-errors into FF $\text{LiTi}(\text{iBu})^+$ due to chain misorientation (B). The stereoselectivity calculated at the site 2 is 5.8 (7.1) kcal/mol (see Table S1). R₁ and R₃ (here Ad and I, respectively) both act sterically in B (with arrows) to increase the TS energies with respect to the right insertion (A). H atoms omitted for clarity.

7. Stereoselectivity for propene insertion TSs into FF and FM

$L_4Ti(iBu)^+$ complexes with $R_3=H$:

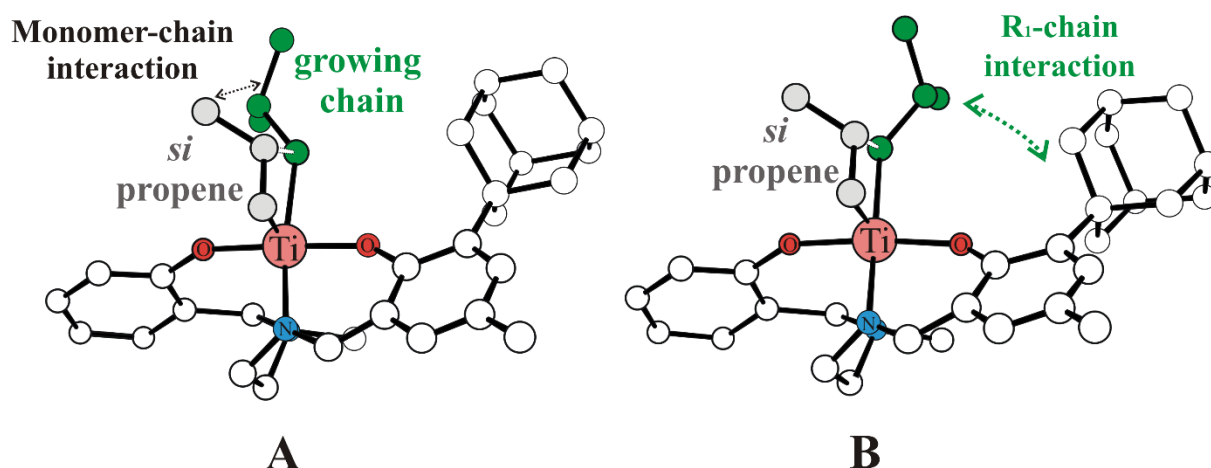


Figure S6. Propene TS stereo-errors into FF $L_4Ti(iBu)^+$ with $R_3 = H$ due to monomer misorientation relative to the chain (A) and chain misorientation (B). The TS energy (free energy) of A is 0.1 (0.2) kcal/mol lower than B. In this case the R_3 synergic effect (see Figure 4 of the text) is lost and the stereoselectivity value we calculated by comparing A and/or B energies with respect to the right insertion (not reported here) is 2.0 kcal/mol. H atoms omitted for clarity.

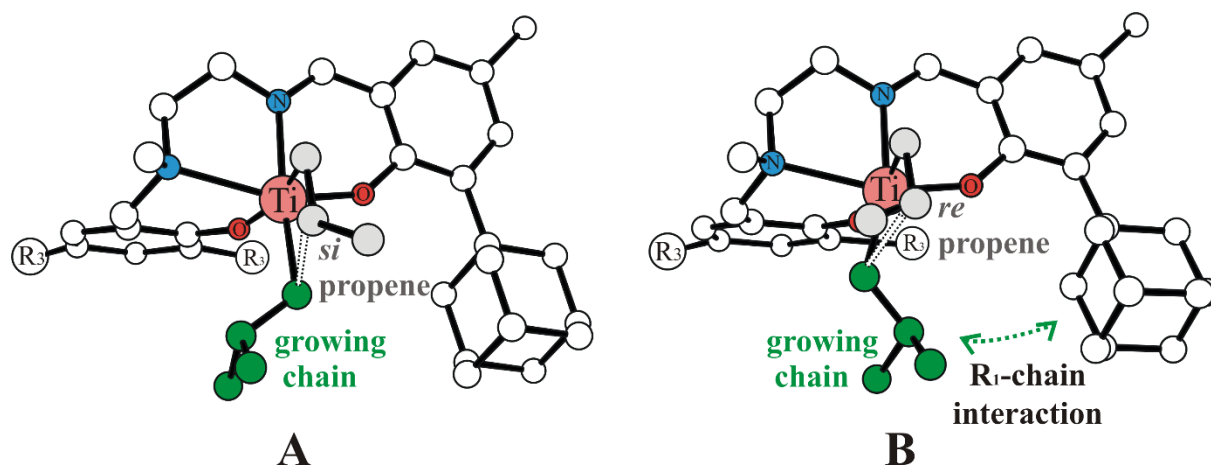


Figure S7. Propene insertion TSs into $L_4Ti(iBu)^+$ with FM coordination mode at the site 1 with the right (A) and wrong (B) propene enantioface. By replacing I with H for R_3 substituent, the stereoselectivity value is unchanged because R_3 is far from the active pocket in the FM coordination mode. H atoms omitted for clarity.

5. References

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- (10) CCDC 802925 contain the supplementary crystallographic data for the structure **L1** discussed in this paper and in the reference 5 of the text. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.