## SUPPORTING INFORMATION

## Expanding the Origin of Stereocontrol in Propene Polymerization Catalysis

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## 1. Details of computational methods

All the DFT static calculations have been performed at the GGA level with the Gaussian09 set of programs, ${ }^{1}$ using the B3LYP functional of Becke and Perdew. ${ }^{2}$ The electronic configuration has been described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for $\mathrm{H}, \mathrm{C}, \mathrm{N}$, and $\mathrm{O}(\mathrm{SVP})^{3}$ and with the SDD basis and pseudopotential ${ }^{4}$ at the metal (a f function with exponent 0.5 was added for Hf ). Stationary points were characterized using vibrational analysis, and this analysis has been also used to calculate zero-point energies and thermal (enthalpy and entropy) corrections ( $298.15 \mathrm{~K}, 1$ bar). Improved electronic energies, obtained from single-point energy calculations using a TZVP basis set ${ }^{5}$ on the main atoms, a solvation contribute (PCM model, ${ }^{6}$ toluene) and the dispersion corrections ${ }^{7}$ (EmpiricalDispersion=D3 in the Gaussian09 D. 01 package) are used in the paper and named as $\Delta E$. These energies added to the SVP-level thermal corrections are named $\Delta G$ in the remainder of the paper. The growing polymer chains have been simulated by iso-butyl groups and only the most stable TSs are reported. For each TS calculation, several chain conformations have been used in order to find the lower energetic path.

## 2. Scheme S1 of the "chiral growing chain orientation stereocontrol"



Scheme S1. Main features of Corradini model discussed in the text. In particular, in a) is reported the influence of $\alpha$-agostic interaction in the transition state (TS) of alkene insertion (here we used ethene) to select only two possible chain orientations (A and $\mathbf{A}^{\prime}$ ). The two chiral orientation of the growing chain were labeled as (-) and ( + ) growing chain according to the IUPAC recommendations for stereochemistry. In b) is shown the influence of chiral site (here a typical ansa-metallocene) to orient the growing polymer chain in $\mathbf{B}$ with respect to $\mathbf{B}^{\prime}$ to avoid the sterical interaction between chain and ligand. In $\mathbf{c}$ ) is reported the preferred orientation of the growing polymer chain which selects the propene enantioface (here re face, C ) in anti to the first $\mathrm{C}_{\alpha}-\mathrm{C}$ of the chain to avoid the sterical contact reported with an arrow (si face in $\mathrm{C}^{\prime}$ ). For the sake of readability in $\mathbf{b}$ ) the hydrogen atoms of the metallocene skeleton are omitted. With $\mathrm{P}=$ polymer chain.

## 3. Primary propene insertion TS into the methyl chain for the system Ia:



A


B

Figure S1. Primary propene insertion TS into the methyl chain for the system Ia at site 1 with the 1,2 si (A) and 1,2 re (B) enantioface. For both TSs the growing polymer chain does not assume a chiral conformation and the chain-monomer interactions are negligible. The energetic difference (free energies) of $3.5(2.0) \mathrm{kcal} / \mathrm{mol}$ are due to steric ligand-monomer interactions ( ${ }^{i} \mathrm{Pr}$ substituents on phenyl ring, see Chart 1) reported with a dashed red arrow in Figure $2(\mathbf{B})$. This interaction is also responsible of the larger $\mathrm{Hf}-\mathrm{N}-\mathrm{C}$ angle $\left(122.5^{\circ}\right)$ reported in $\mathbf{B}$ with respect to $\mathbf{A}\left(119.4^{\circ}\right) . \mathrm{H}$ atoms are omitted for clarity.

## 4. Regiochemistry of propene insertion promoted by system Ia



Figure S2. Secondary (or 2,1) propene insertion TS in the primary growing polymer chain at site 1 with the si (A) and re (B) enantioface. The lower energetic path leading to the structure $\mathbf{A}$ is due to steric ligand-monomer interaction reported with a dashed red arrow in $(\mathbf{B})$. H atoms are omitted for clarity. The preferred 2,1 insertion enantioface ( $\mathbf{A}$ ) is the same of the primary insertion reported in Figure 2 A, see text.

## 5. References

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